

Optical Second Harmonic Generation Studies of Electrochemical Interfaces

Shah Mohammad Abdul Baten

**Submitted to Imperial College London in partial fulfilment of the
degree of Doctor of Philosophy**

**Department of Chemistry
Imperial College London**

February 2012

Statement of Originality

I declare that the works described in this thesis are my own works, and to the best of my knowledge they do not include any materials previously published or written by another person except where referenced.

Shah Mohammad Abdul Baten

Abstract

Electrochemical oxidation of metal electrodes in aqueous media has been examined by *in situ* optical second harmonic generation (SHG), a nonlinear optical technique of second order.

Simultaneous SHG and cyclic voltammetry experiments were carried out on Cu electrodes in alkaline media. The SHG response was found to be sensitive as Cu was oxidised first to Cu_2O and then to CuO . The formation of Cu_2O causes resonant contribution to the SHG signals due to the band-gap of Cu_2O . As the upper layer, CuO is formed; it generates an electric-field induced second harmonic (EFISH) response. When the oxides layers are reduced, the SHG intensity changes markedly. The correlation of oxidation and reduction charge with the SHG signal intensity is found to be a useful method to investigate the oxide formation.

The oxidation of Au electrodes in acidic media has been investigated. The initial growth of the compact (or α -) oxide causes a decrease in SHG intensity which is suggested to be the effect of the oxide growth on surface plasmons originated from the d -electrons in Au. When the thicker hydrous (or β -) oxide layers are formed at constant potentials on top of the α -oxide, the reductions of them are accompanied by remarkable sharp peak in the SHG response that appear just before any reduction charges begin to pass. As the β -oxide layer gets thicker with longer oxidation time and then reduced, the initial peak evolves into two before merging to form one broad peak. The SHG peaks are suggested to be linked to an order-disorder transition phenomenon at the α -/ β -oxide interface; or it can also be due to the presence of the surface traps.

These investigations have shown that the SHG technique with its inherent submonolayer sensitivity can be a useful technique to study electrochemical oxidation of metal electrodes.

Acknowledgements

I would like to express my sincere gratitude to my supervisors, Dr. C. Paul Wilde and Dr. Alan G. Taylor for their invaluable guidance and support throughout my PhD studies. Many thanks for giving me an opportunity to work with you and for your encouragement and advices.

I am grateful to Dr. Marina Kuimova for her help with some initial stage laser set up and SHG measurements. I must thank Dr. Chris Barnett for his help in electronics and Stephen Atkins for his help in electrode preparation. I also thank Simon Bastian and Simon Turner for their support in instrumentation. Special thanks go to Professor Anthony Kucernak for the software routine in Lab View used for data acquisition. I must mention Chris, Nicho, Christos, Abdullah, Ehsan and Fabrice from Professor Kucernak research group and Dr. Gökhan Yahioğlu for their friendship. I thank Dr. Khurom Kiyani and Dr. Murshed Siddick for their friendship in Edinburgh and later on at Imperial. I am grateful to Dr. Tim Albrecht for co-ordinating the thesis submission and examination process.

I would like to express my profound respect, deep veneration and endless love for my father Shah Mohammad Abdul Jabbar, May he always be in good health; and I pray for my late mother Fatima Begum, May she be in peace, *Rabbir hamhuma kama rabbayani sageera*. Ameen! I remember my brothers- Chand, Tara, Bala, and Lala; sisters- Lucky and Ruby; nephews- Sumon, Salahuddin, Ananda, Siyam, Shihab and Rabbi; and my nieces- Lithi, Shanti, Tinni, Khushi and Labonno for their unconditional support. I also remember Ayah Legimin dan Ibu Ana, Sis Mina, Kak Udin, Naoemi and the adorable kids- Najla, Naurah and Ahmad from my other family at U/5 of Makassar.

Finally, I express my love and affection for my wife Wardha Ardhini to be with me through the good times and the bad. My hard and long journey with the PhD studies and finishing this thesis come to an end with good news; I and Wardha are elated with the birth of our baby son, Shah Hizqil Shaheedi. It gives us immense pleasure every time he smiles.

To

Wardha Ardhini

***who was born in Balikpapan
in the beautiful island of Borneo***

Contents

Title	1
Statement of Originality	2
Abstract	3
Acknowledgements	4
Contents	6
List of figures	11
List of tables	17
 Chapter 1 Introduction	 18
1.1 Introduction	18
1.2 Electrochemical interfaces	19
1.2.1 Introduction	19
1.2.2 Faradaic and non-faradaic processes	20
1.2.3 Theory of the electric double layer	21
1.2.4 The structure of the electric double layer	22
1.2.5 The Poisson-Boltzmann equation for the electric double layer	24
1.2.6 The Grahame equation: the relation between surface charge, σ and surface potential, ψ_0 at the electric double layer	26
1.2.7 Double layer capacitance	27
1.2.8 The Lippmann equation, electrocapillary curve and <i>the potential of zero charge</i> (PZC)	29
1.2.9 Total capacitance of the electric double layer	32
1.3 Cyclic voltammetry	33
1.3.1 Introduction	33
1.3.2 Reversible processes	34
1.3.3 Irreversible and quasi-reversible processes	37
1.3.4 Surface process- adsorption	39
1.3.5 Three electrode cell configuration	40
1.3.5.1 Working electrode	40
1.3.5.2 Counter electrode	41
1.3.5.3 Reference electrode	41

1.4	Epioptics- study of surfaces and interfaces by linear and nonlinear optical techniques	43
1.5	Linear optical techniques	44
1.5.1	Spectroscopic ellipsometry (SE)	44
1.5.2	Reflectance difference/anisotropy spectroscopy (RDS/RAS)	46
1.6	Nonlinear optical technique: second harmonic generation (SHG)	47
1.6.1	Introduction to nonlinear optics	47
1.6.2	Nonlinear polarisation	49
1.6.3	Optical second harmonic generation	50
1.6.4	Nonlinear susceptibility and symmetry consideration	51
1.6.5	SHG as a surface probe	53
1.6.6	Electric-field induced second harmonic (EFISH) generation	54
1.6.7	Nonlinear susceptibility at an interface- generation of SHG	56
1.7	SHG as a nonlinear optical technique for surface and interface studies	57
1.7.1	Introduction	57
1.7.2	Electrochemical and second harmonic generation (SHG) studies of Cu	58
1.7.3	Electrochemical and second harmonic generation (SHG) studies of Au	63
1.8	This Work	66
Chapter 2	Experimental	67
2.1	Introduction	67
2.2	Experimental set up	67
2.3	Optical components	69
2.3.1	Laser	69
2.3.2	Mirrors	69
2.3.3	Beam splitter	69
2.3.4	Long pass filter	70
2.3.5	Half wave plate	70
2.3.6	Polarizer	71
2.3.7	Lens	71
2.3.8	Dispersing prisms	71
2.3.9	Iris and beam tube	71
2.3.10	Blue pass filter	72
2.3.11	SH photon detector	72
2.4	SHG measurement protocol	73
2.4.1	Near-constant intensity of the laser beam	73
2.4.2	Optical alignment	74
2.4.3	Thermal stability in the laser lab	74

Chapter 3 Second harmonic generation studies of the oxidation of Cu 75

electrodes

3.1	Introduction	75
3.2	Cu structure	75
3.3	Cu electrochemistry	76
3.3.1	Introduction	76
3.3.2	Cyclic voltammetry of Cu in neutral and weakly alkaline solution	77
3.3.3	Pourbaix diagrams of Cu	78
3.3.4	Oxidation of Cu to the Cu(I) state and formation of Cu ₂ O	80
3.3.4.1	Oxidation mechanism	80
3.3.4.2	Thickness and structure of the electrochemically formed Cu ₂ O	81
3.3.5	Oxidation of Cu to the Cu(II) state and formation of CuO/Cu(OH) ₂	82
3.3.5.1	Cu to Cu(II) oxidation mechanism	83
3.3.5.2	Thickness and structure of the electrochemically formed CuO/Cu(OH) ₂ layer	84
3.4	Experimental	85
3.4.1	Spectroelectrochemical cell	85
3.4.2	Electrode preparation	86
3.4.3	Electrolyte	86
3.4.4	Pretreatment protocol	86
3.4.5	Data collection	87
3.5	Results and discussions	88
3.5.1	Cyclic voltammetry of Cu in borax buffer	88
3.5.2	Cyclic voltammetry of Cu at various scan rates	89
3.5.3	Cyclic voltammetry of Cu: “window opening” experiments	93
3.5.4	Test for nonlinear optical response from Cu	95
3.5.4.1	Power dependence of SHG intensity for Cu	95
3.5.4.2	Polarisation dependence of SHG intensity	96
3.5.5	Simultaneous SHG and cyclic voltammetry experiments on Cu	97
3.5.5.1	Introduction	97
3.5.5.2	SHG and cyclic voltammetry: potential reversed at the top of the first oxidation current peak, AI	98
3.5.5.2.1	Origins of SHG contributions	99
3.5.5.2.2	SHG in the forward scan	99
3.5.5.2.3	SHG is sensitive to surface layers	100
3.5.5.2.4	SHG response from semiconducting Cu ₂ O	100
3.5.5.3	SHG and complete cyclic voltammetry of Cu	101
3.5.5.3.1	Introduction	101
3.5.5.3.2	EFISH response from CuO between point “a” and “b”	103

3.5.5.3.3	SHG change at point “b”	106
3.5.5.3.4	SHG intensity change between point “c” and “d”	106
3.5.5.3.5	Full recovery of SHG signals at the end of the cyclic voltammogram	107
3.5.6	“Window opening” experiments: SHG and cyclic voltammetry of Cu	108
3.5.6.1	Introduction	108
3.5.6.2	Single SH signal peak, labelled “R” in Fig. 3.20	111
3.5.6.3	Development of two SH signal peaks, “r ₁ ” and “r ₂ ”	111
3.5.6.4	Disappearance of peak “r ₂ ” (trough)	111
3.5.7	SHG spectroscopy of Cu oxidation and reduction	112
3.5.7.1	Introduction	112
3.5.7.2	Data normalisation procedure	113
3.5.7.3	Resonance contributions to the SH intensity	114
3.5.7.4	EFISH: Field dependent SHG between 0.2 - 0.8 V	119
3.6	Conclusion	121
Chapter 4	Second harmonic generation studies of the compact and hydrous oxide growth at Au electrodes	122
4.1	Introduction	122
4.1.1	Overview	122
4.1.2	Importance of Au electrochemistry	122
4.1.3	The field of Au nanotechnology	123
4.2	Au electrochemistry	124
4.2.1	Au electric double layer	124
4.2.2	Au oxidation: Mechanism of Au α -oxide formation	125
4.2.3	Growth of Au α -oxide	127
4.2.4	Au β -oxide	128
4.2.5	Growth of Au β -oxide	129
4.3	Experimental	131
4.3.1	Spectroelectrochemical cell	131
4.3.2	Electrode preparation	132
4.3.3	Electrolyte	132
4.3.4	Pretreatment protocol	132
4.3.5	Data collection	133
4.4	Results and discussions	134
4.4.1	Au cyclic voltammetry in H ₂ SO ₄	134
4.4.2	Formation and reduction of Au β -oxide	138
4.4.3	SHG and cyclic voltammetry of Au: Formation of Au α -oxide	140
4.4.3.1	SHG response in the electric double layer region	142

4.4.3.2	Sharp decrease in SHG signal	142
4.4.3.3	Influence of surface plasmon on SHG response	143
4.4.3.4	SHG signals between 1.2 and 1.5 V and back to 0.4 V	144
4.4.3.5	Test of SHG response from Au β -oxide grown at 1.8 V vs SCE	144
4.4.3.6	Conclusion	146
4.4.4	SHG studies of Au β -oxide	147
4.4.4.1	Introduction	147
4.4.4.2	SHG response from Au β -oxide	147
4.4.4.3	A possible EFISH response from Au β -oxide	152
4.4.4.4	SHG due to interfacial order/disorder phenomenon	153
4.4.4.5	Au ₂ O ₃ .H ₂ O/Au ₂ O ₃ .2H ₂ O interface giving rise to second SHG peak, “a ₁ ”	154
4.4.4.6	SHG response from local defects and electron trapping	155
4.5	Conclusion	156
Chapter 5	Conclusion and future work	157
5.1	SHG studies of oxide formation and reduction at Cu Electrode	157
5.2	SHG Studies of Au compact and hydrous oxide	159
5.3	Future work	160
5.3.1	Apply SHG to investigate the onset of oxidation	160
5.3.2	SHG and electrochemical studies on Cu in acidic and alkaline media	160
5.3.3	SHG and mechanistic studies on Cu and Au electrodes	161
5.3.4	SHG studies on deposited Cu or Au films on Si substrate	161
References		162
Publications and conference paper		169

List of figures

Chapter 1

Figure 1.1	Schematic diagram of the (a) ion, (b) potential (ψ) and (c) charge (σ) distribution across the metal/electrolyte interface for weak specific adsorption. ψ^M , ψ^{IHP} , ψ^{OHP} and ψ^{sol} are the potentials at the metal, inner Helmholtz plane (<i>IHP</i>), outer Helmholtz plane (<i>OHP</i>), and bulk solution respectively. σ^M , σ^{IHP} and σ^{OHP} indicate the excess charge on the metal, inner plane, and at the start of the diffuse layer respectively. The layer between <i>IHP</i> and <i>OHP</i> is about 0.3 nm thick, which is called the <i>Stern layer</i> , and is tightly bonded with water molecules, solvated ions, and specifically bonded ions. [33, 41, 45]	23
Figure 1.2	A schematic diagram of a parallel plate capacitor comprised of two metal plates of opposite charges separated by a dielectric material (adapted from Ref. [46]).	28
Figure 1.3	Electrocapillary curve of surface tension vs potential for Hg in contact with 1.0 N HCl. The charge density on the electrode at a particular value of the potential difference, V is given by the slope of the electrocapillary curve at that potential [51].	30
Figure 1.4	Electrocapillary vs E curve. When the electrocapillary vs E curve (part 1.4a) is a perfect parabola, the electrode charge density varies linearly with potential difference (part 1.4b). A further differentiation gives a capacity that is potential independent (part 1.4c). However, experimental electrocapillary curves are not perfect parabolas [51].	31
Figure 1.5	Potential-time behaviour at the working electrode following the application of triangular waveform in cyclic voltammetry. E_2 is potential limit in the forward scan and E_1 and E_3 are in the reverse scan [53].	33
Figure 1.6	Diagram showing how current density increases with increasing scan rate where E_p^A is the potential of the anodic current peak [modified from Ref. [53]].	35
Figure 1.7	Cyclic voltammogram for a single electron transfer reaction showing the parameters of importance as diagnostic criteria. i_p^A and i_p^C are the anodic and cathodic peak current at the potential E_p^A and E_p^C respectively. It can be seen that $\frac{i_p^A}{i_p^C} = 1$ [53].	36
Figure 1.8	A plot of the dependence of the peak current on the square root of the potential sweep rate, showing the transition from reversible to irreversible behaviour of the reactions with increasing sweep rate [53].	38
Figure 1.9	An example of cyclic voltammogram for the reduction of adsorbed O and reoxidation of the product R where the electron transfer is reversible [60].	39
Figure 1.10	A schematic diagram of a three electrode electrochemical cell showing the Cu working electrode (WE), platinum counter electrode (CE) and reference electrode (RE).	41

Figure 1.11	Comparison of conventional and epioptic probes. For conventional surface probe UHV is required but epioptic probes are applicable in all pressure and temperature regimes [65].	43
Figure 1.12	A schematic diagram showing the incident, reflected, and transmitted light and the angles they make at the surface under study, θ_i , θ_r and θ_t with the normal direction respectively in an ellipsometry experiment.	45
Figure 1.13	A schematic diagram of ellipsometry experiment showing the conversion of polarisation state (linear) of incident beam to the polarisation state of (elliptical) reflected beam [adapted from Ref. [67]].	45
Figure 1.14	Relation between induced polarisation and the electric field that induces it, (a) in a linear dielectric and (b) in a crystal lacking inversion symmetry [79]	48
Figure 1.15	Schematic representation of the SHG process. Radiation of frequency ω generates a nonlinear polarisation in the material that has inherent nonlinear susceptibility and then re-radiate at a frequency of 2ω [88, 90].	51
Figure 1.16	The face centred cubic (fcc) crystal structure of NaCl with one Cl ⁻ ion sitting at (0,0,0) and one Na ⁺ ion sitting at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The crystal is centrosymmetric, since an inversion of any ion about the central Na ⁺ ion leaves the crystal structure unchanged [89]	52
Figure 1.17	Schematic representation of SHG experimental geometry on a sample with thickness, d and an infinitesimally thin sheet of polarisation at a distance of ξ from the surface from which all surface and interface dipole contributions to SH originate. Z is the distance measured normal to the surface.	54
Chapter 2		
Figure 2.1	Schematic diagram of the optical arrangement for the simultaneous cyclic voltammetry and SHG experiments. The diagram illustrates the optical components that are used for experimental set up.	68
Figure 2.2	Absorption spectra of long pass filters. The filter allows the transmission of electromagnetic radiation between 600 – 1000 nm. It is used to attenuate any residual photons of the pump beam at 532 nm.	70
Figure 2.3	Diagram of a Rochon prism. It shows how the extraordinary beam is deviated and the ordinary beam is propagated.	71
Figure 2.4	Absorption spectra of the blue pass filter. The filter allows the transmission of the electromagnetic radiation only between 350 – 550 nm and the wavelengths of the SH photons fall within this range.	72
Chapter 3		
Figure 3.1	Face centred cubic (fcc) lattice structure of Cu atom. The diagram shows that one Cu atom is at the centre of each side and one at the vertices. Every atom has 12 nearest neighbours which gives the highest packing density of 74%. For clarity the atoms have been drawn apart from each other.	76

Figure 3.2	Cyclic voltammogram of polycrystalline Cu in alkaline medium at scan rate 5 mV s^{-1} in 0.1 M borax buffer of pH 9.2.	78
Figure 3.3	Pourbaix (Potential-pH) diagram for Cu in H_2O or Na^+ containing solution showing the redox species of Cu that are stable or undergo dissolution or corrosion [178].	79
Figure 3.4	Schematic diagram showing Cu_2O thin film and Cu electrode surface as Cu is oxidised to grow Cu_2O in the Cu/electrolyte interface.	81
Figure 3.5	Crystal structure of Cu_2O . Orange balls represent oxygen atoms and white ones copper atoms. Cu_2O crystallises in the cuprite structure formed by a bcc array of oxygen atoms with metal inserted between two consecutive oxygen layers [182].	82
Figure 3.6	Schematic diagram of formation of CuO thin film where Cu^{2+} ions are driven to the interface by applied dc electric field [141].	83
Figure 3.7	Schematic representation of the flow cell used for the combined cyclic voltammetry and optical experiments. Working electrode (WE) is a rectangular Cu foil with surface area of 0.20 cm^2 , Counter electrode (CE) is a Pt wire, and Reference electrode (RE) is $\text{Hg}/\text{Hg}_2\text{Cl}_2$ in contact with saturated KCl solution.	85
Figure 3.8	Pretreatment protocol and limits of potential scan. It is shown that the electrode is pretreated at -1.70 V , voltammogram recording started at -0.80 V and stopped at 0.80 V with 1.00 and 0.90 V being the negative and positive potential limits respectively.	87
Figure 3.9	Current and voltage curve from a Cu electrode in 0.1 M borax buffer solution of pH 9.2 with scan rate 5 mV s^{-1} .	88
Figure 3.10	Anodic and cathodic polarisation curve of poly-Cu in 0.1 M borax buffer of pH 9.2 with various scan rates.	90
Figure 3.11	Scan rate dependence of potential position of the anodic and cathodic current peaks when Cu is oxidised in 0.1 M borax buffer solution of pH 9.2 at various scan rates.	91
Figure 3.12	Scan rate dependence of anodic and cathodic peak current densities when Cu is oxidised in 0.1 M borax buffer solution of pH 9.2 at various scan rates.	92
Figure 3.13	Cyclic voltammogram of Cu in 0.1 M borax buffer of pH 9.2 with various positive reversing potentials with sweep rate 5 mV s^{-1} .	93
Figure 3.14	Total anodic and cathodic charges, obtained from cyclic voltammogram in 0.1 M borax buffer of pH 9.2, dependence on the maximum positive scanning potential.	94
Figure 3.15	Optical SH intensity from the surface of Cu electrode as a function of power of incident beam. 780 nm illumination with $P_{\text{in}} - P_{\text{out}}$ laser geometry is used.	95
Figure 3.16	Polar plot of the input-polarisation angle dependence of the SHG signal intensity for Cu electrode held at -0.8 V in 0.1 M borax buffer of pH 9.2 under <i>p</i> -polarised laser illumination at 780 nm .	96
Figure 3.17	Cyclic voltammetry (CV) and SHG response for Cu in 0.1 M borax buffer of pH 9.2 at 5 mV s^{-1} . The <i>p</i> -polarised incident is at 780 nm . The scan was reversed at -0.02 V [3].	98

Figure 3.18	Cyclic voltammogram and SHG response for Cu in 0.1 M borax buffer solution of pH 9.2. Scan rate is 5 mV s ⁻¹ . The p-polarised incident laser beam of 780 nm from an amplified Ti: Sapphire oscillator is used [3].	102
Figure 3.19	SH intensity response vs applied potential in the vicinity of lowest SHG signals where the variation in the SH intensity is dominated by the third-order nonlinear susceptibility, χ^{dc} (EFISH). The parabolic fits demonstrate the quadratic dependence of the SH intensity on the applied field. Scan (a) is forward scan, and (b) is reverse scan.	104
Figure 3.20	Simultaneous cyclic voltammetry and SHG from a Cu electrode in 0.1 M borax buffer of pH 9.2 with reversing potential of -0.16 V at 5 mV s ⁻¹ under p- polarised illumination from 780 nm from a Ti-Sapphire oscillator. The potential scan was reversed at -0.15 V.	108
Figure 3.21	As for Fig. 3.20 except the reversing potential which is 0.05 V.	109
Figure 3.22	As for Fig. 3.20 except the reversing potential which is 0.15 V.	109
Figure 3.23	As for Fig. 3.20 except the reversing potential which is 0.5 V.	110
Figure 3.24	Simultaneous cyclic voltammetry and SHG from a Cu electrode in 0.1 M borax buffer of pH 9.2 with reversing potential of -0.16 V at 5 mV s ⁻¹ under p- polarised illumination from 780 nm from a Ti-Sapphire oscillator. The potential scan was reversed at 0.95 V.	110
Figure 3.25	Cyclic voltammogram and SHG response at poly-Cu 0.1 M borax buffer of pH 9.2 at 5 mV s ⁻¹ under <i>p</i> -polarised illumination from a Ti-Sapphire oscillator at 730 nm.	115
Figure 3.26	As for Fig. 3.25 except incident laser illumination at 755 nm.	115
Figure 3.27	As for Fig. 3.25 except the incident illumination is at 780 nm.	116
Figure 3.28	As for Fig. 3.25 except the incident beam used is of 810 nm.	116
Figure 3.29	As for Fig. 3.25 except the incident beam used is of 840 nm.	117
Figure 3.30	Cyclic voltammogram and SHG response at poly-Cu 0.1 M borax buffer of pH 9.2 at 5 mV s ⁻¹ under <i>p</i> -polarised illumination from a Ti-Sapphire oscillator at 880 nm.	117
Figure 3.31	Wavelength dependence of SHG intensity from poly-Cu electrode under illumination from Ti: Sapphire Oscillator with $p_{in} - p_{out}$ geometry. Wavelength dependent SHG data are normalised. Current data of cyclic voltammogram are not plotted here.	118
Figure 3.32	SH intensity response spectra vs. applied potential where the variation in the SH intensity is dominated by EFISH contribution. The parabolic fits of $I^{2\omega} = I_0^{2\omega} + (V - V_0)^2$ demonstrate the quadratic dependence of the SH intensity on the applied field in the forward direction of the scan. SHG data are normalised.	120
Figure 3.33	As for Fig. 3.32 except the SHG intensity data are taken from the reverse scan.	120

Chapter 4

Figure 4.1	Cyclic voltammogram of poly-Au electrode in 0.1 M H ₂ SO ₄ at 5 mV s ⁻¹ .	124
Figure 4.2	Schematic diagram of the post-electrochemical place exchange reaction in monolayer oxide formation. Surface metal atoms exchange position with oxygen species resulting reduction of repulsive electrostatic energy [from Ref. [153]].	126
Figure 4.3	Schematic diagram of formation of hydrous Au ₂ O ₃ on top of inner compact AuO where Au ⁺⁺ ions are driven to the top by applied dc electric field as shown by arrows in the figure.	129
Figure 4.4	Schematic representation of the flow cell used for the combined cyclic voltammetry and optical experiments. Working electrode (WE) is a Au disk insulated in PTFE with surface area of 0.20 cm ² , counter electrode (CE) is a Pt wire, and reference electrode (RE) is Hg/Hg ₂ Cl ₂ in contact with saturated KCl.	131
Figure 4.5	Cyclic voltammogram of polycrystalline Au electrode in 0.1 M H ₂ SO ₄ at 5 mV s ⁻¹ showing the double layer region, growth and reduction of Au α-oxide.	134
Figure 4.6	Cyclic voltammogram of polycrystalline Au electrode in 0.1 M H ₂ SO ₄ at scan rate 5 mV s ⁻¹ , where the potential is scanned well into the oxygen evolving regime.	135
Figure 4.7	Cyclic voltammogram of polycrystalline Au electrode in 0.1 M H ₂ SO ₄ at scan rate 5 mV s ⁻¹ with various positive potential limits.	136
Figure 4.8	Plot of cathodic peak potential vs limiting potential. Cathodic peak potentials shift as the potential scan is reversed at more positive going scanning potentials for the CV of poly-Au in 0.1 M H ₂ SO ₄ at 5 mV s ⁻¹ .	136
Figure 4.9	Reduction charge density (μC cm ⁻²) and number of monolayers grown as functions of positive going potential limits in the cyclic voltammetry experiments on of poly-Au in 0.1 M H ₂ SO ₄ at 5 mV s ⁻¹ .	137
Figure 4.10	The potential scanning sequence of Au β-oxide formation and reduction cyclic voltammetry experiment. The β-oxide was grown by holding the electrode at 1.9 V, then after degassing at 1.4 V the oxide was reduced.	138
Figure 4.11	Reduction profiles for oxide films grown at poly-Au electrode by holding the electrode at 1.9 V vs SCE for various lengths of time in 0.1 M H ₂ SO ₄ . The reduction was carried out at 5 mV s ⁻¹ [32].	139
Figure 4.12	Reduction peak potentials of Au α- and β-oxide film formed on a poly-Au electrode in 0.1 M H ₂ SO ₄ vs time of oxide growth at 1.9 V vs SCE.	139
Figure 4.13	Cyclic voltammogram and SHG response for the oxidation of a polycrystalline Au electrode under illumination at 780 nm from diode pumped Ti-Sapphire oscillator in 0.1 M H ₂ SO ₄ at 5 mV s ⁻¹ . The upper potential limit is 1.5 V vs SCE [32].	141
Figure 4.14	Potential vs current and SHG intensity at a poly-Au electrode in 0.1 M H ₂ SO ₄ with maximum scanning potential of 1.1 V and 1.2 V vs SCE. Scan rate is 5 mV s ⁻¹ [32]. A much lower average laser power (~40 mW before it incident at Au surface) of the fundamental beam was used in this experiment. Lower average laser power was used during alignment which was not switched to full average laser power, typically 300 mW.	141

Figure 4.15	Simultaneous cyclic voltammogram and SHG response from polycrystalline Au in 0.1 M H ₂ SO ₄ at 5 mV s ⁻¹ . The potential scan is reversed at 1.4 V vs SCE.	145
Figure 4.16	SHG response with the reduction profile of Au electrode in 0.1 M H ₂ SO ₄ which was held at 1.8 V vs SCE for 30 s.	145
Figure 4.17	Cyclic voltammogram and SHG response for the reduction of Au β-oxide grown on poly-Au in 0.1 M H ₂ SO ₄ at 1.9 V vs S.C.E. for 10 s. The scan rate was 5 mV s ⁻¹ .	148
Figure 4.18	Cyclic voltammogram and SHG response for the reduction of Au β-oxide grown on poly-Au in 0.1 M H ₂ SO ₄ at 1.9 V vs SCE for 90 s. The scan rate was 5 mV s ⁻¹ .	149
Figure 4.19	Cyclic voltammogram and SHG response for the reduction of Au β-oxide grown on poly-Au in 0.1 M H ₂ SO ₄ at 1.9 V vs SCE for 150 s. The scan rate was 5 mV s ⁻¹ .	149
Figure 4.20	Cyclic voltammogram and SHG response for the reduction of Au β-oxide grown on poly-Au in 0.1 M H ₂ SO ₄ at 1.9 V vs SCE for 270 s. The scan rate was 5 mV s ⁻¹ .	150
Figure 4.21	Cyclic voltammogram and SHG response for the reduction of Au β-oxide grown on poly-Au in 0.1 M H ₂ SO ₄ at 1.9 V vs SCE for 300 s. The scan rate was 5 mV s ⁻¹ .	150
Figure 4.22	Normalised SHG intensities as functions of the applied potential. The oxides were grown at 1.9 V vs SCE for variable durations and then reduced at the scan rate of 5 mV s ⁻¹ .	151
Figure 4.23	Schematic illustration of the interfaces between three-layer oxides. The outer Au β-oxide (Au ₂ O ₃ ·2H ₂ O) layer is more hydrated than the inner Au β-oxide (Au ₂ O ₃ ·H ₂ O) and the third layer is the Au α-oxide (AuO).	154
Chapter 5		
Figure 5.1	Simplified Pourbaix diagram of Cu in H ₂ O showing the corrosion, passivation and immunity domains of potential and pH [178].	160

List of tables

Chapter 3

Table 3.1	Oxidation charge (q+) and reduction charge (q-) and the percentage dissolution when variable scan rates are applied for cyclic voltammetry of Cu.	90
Table 3.2	Oxidation peak current density, i_p^A , reduction peak current density, i_p^C and the ratio of oxidation and reduction peak current densities as functions of scan rate in Cu cyclic .	91
Table 3.3	The energy of the fundamental photons and that of the SH photons.	113
Table 3.4	Sample data to show the normalisation procedure to compare the variable wavelength SHG data by spanning them between zero and 100 and to show them in one graph.	114

Chapter 4

Table 4.1	Data of window opening cyclic voltammetry experiments on poly-Au electrode in 0.1 M H ₂ SO ₄ . Total reduction charge, ($\mu\text{C cm}^{-2}$) and number of monolayers are tabulated as functions of scanning potential limits.	137
-----------	--	-----

Chapter 1

Introduction

1.1 Introduction

The work described in this thesis is concerned with the optical second harmonic generation (SHG) studies of electrochemical oxide formation and reduction at metal electrodes. SHG is a nonlinear optical technique which is ideally suitable for the study of the processes at the electrode/solution interface. In this technique, light of frequency, ω with electric field, $\mathbf{E}(\omega)$ induces a nonlinear polarisation in a sample on which it is incident. This nonlinear polarisation and the electric field strength are related to the property of the material called *the nonlinear susceptibility*, $\chi^{(2)}$. The theory of SHG will be covered in detail later in the chapter; but under a simple approximation, it is assumed that when a SHG is generated only from electric dipoles in centrosymmetric media, the nonlinear susceptibility, $\chi^{(2)}$ is zero. But at surfaces and interfaces this symmetry breaks down and SHG can be generated at the interface. Because of this surface sensitivity, SHG has been applied for the last two decades to study electrochemical interfaces. These studies have mainly focussed to the investigations of the surface film formation and ion adsorption at metals [1], the use of rotational anisotropy to investigate single crystals and to the study of surface reconstruction [2] driven by the potential, ionic adsorption, metal deposition or chemisorptions; but SHG has rarely been applied to the investigation of surface oxidation of electrodes [2, 3].

In this lab, a recent SHG study of anodic oxidation of Si showed that the chemical state of the Si surface, during surface oxidation, was reflected in changes in the SHG intensity [4]. This prompted the investigations reported here which were directed at establishing the factors that affect SHG from oxide surfaces, and the usefulness of SHG for the investigation of oxide formation and reduction. Oxide growth is a complex field that has been studied for many years, and different types of oxides can be grown at metal electrodes by electrochemical process. The oxidation of metal electrodes represents a system which goes through significant changes in surface properties. Therefore, it was decided to test if SHG is also useful for the characterisation of the oxides formed and reduced at metal electrodes.

In this project, two important electrochemical systems have been investigated. They were chosen for the technological interest and industrial applications but also because they feature systems where more than one oxide layer can be grown at electrode surface, and where there are separate current peaks in the cyclic voltammogram for either oxidation or reduction (or both). This separation of the current peaks allows the correlation of the electrochemical response with the SHG response. The first system chosen to examine is the oxidation of Cu. Under appropriate conditions (when pH is neutral to weakly alkaline) there are two

distinctive anodic and two separate cathodic current peaks, generally accepted to be representing the formation and reduction of Cu_2O and CuO or $\text{Cu}(\text{OH})_2$ [3, 5-17], and this makes Cu oxidation an ideal candidate to be investigated by SHG. The second system examined in this study is the oxide formation at Au electrode, which has been the focus of many investigations for several decades [18-32]. Because an understanding of the noble metal oxidation processes, such as oxidation process at Au, provides the foundation for the investigation of other industrially important metals [22]. Additionally, the formation of the initial compact (or α -) oxides, AuO at Au electrode surface is followed by the growth of the thicker hydrous (or β -) oxide, Au_2O_3 at higher potentials and these two oxides are reduced in separate current peaks [21, 25, 27, 28, 31] making this a unique system to study the oxide formation and removal by SHG technique.

1.2 Electrochemical interfaces

1.2.1 Introduction

As this thesis is about the SHG studies of the metal electrode/solution interfaces; this section presents a brief discussion of electrochemical interfaces. When two phases come in contact with each other an interface is formed and interfaces can be solid/liquid, liquid/liquid or solid/solid interfaces. An electrochemical interface can be produced by applying a potential to the electrode which is in contact with an electrolyte and then using a reference electrode. In an electrode/solution interface except at *the point of potential of zero charge* (pzc or ψ_{pzc}) an electrode carries a net charge of, σ^M and there is an equal but opposite charge, σ^S in the solution side [33]. When a potential is applied across the interface, charged species are attracted to the electrode and solvent molecules are repelled from the electrode into the electrolyte. Therefore, *the electrochemical interface* is made up of the electrode which has surface charge, an adjacent layer of counter ions, attracted by the electric field and then the electrolyte in the vicinity of the electrode but distant enough to maintain its bulk electrolyte character. These layers of surface charge and the adjacent layer of counter ions make the so called *the electric double layer* which will be discussed in detail later.

The electric double layer works like a capacitor. At all times charge on the electrode surface and charge in the solution are equal but of opposite sign [33],

$$\sigma^M = -\sigma^S \quad (1.1)$$

The charge on the metal, σ^M represents an excess or deficiency of electrons and they are distributed in a very thin layer on the electrode surface. On the other hand, the charge in the solution σ^S is made up of excess cations or anions close to the electrode surface. The *electric double layer* at a given potential is

characterised by the *double layer capacitance*. When σ is the charge (either electrons or ions) at the interface then the *double layer capacitance* is dependent on the potential difference, ψ across the interface, so the double layer capacitance can be expressed as [33],

$$C = \frac{d\sigma}{d\psi} \quad (1.2)$$

Before we discuss *the electric double layer* and *double layer capacitance*, a brief discussion of *faradaic* and *non-faradaic processes* is provided here.

1.2.2 Faradaic and non-faradaic processes

In faradaic process, charges are transferred across the metal-solution interface. This electron transfer causes oxidation or reduction of a species in solution or at the electrode itself (perhaps by dissolution to a soluble ion or by oxidation to form an insoluble oxide). The amount of chemical reactions at the electrode is proportional to the quantity of charge transferred. These reactions or processes are governed by *Faraday's law* hence they are called *Faradaic processes* [33]. The charge required to convert m moles of reactant material to product in an electrode reaction that involves the transfer of n electrons can be calculated by *Faraday's law* [34]

$$q = \int_0^t i dt = mnF \quad (1.3)$$

where F is Faraday constant which has the value of $96485.33 \text{ C mol}^{-1}$. The electric current associated with the reduction or oxidation of chemical substance is called the *Faradaic current*.

Under some conditions at a given electrode-solution interface, there is a range of potentials where no electron transfer takes place due to the fact that the charge transfer processes are not thermodynamically or kinetically favourable. But processes such as adsorption or desorption may take place through electrostatic interactions. These processes are called *non-faradaic processes* because no *Faradaic current* passes between the electrode and the solution [33]. Such processes do not involve the acceptance or giving up of electrons at the electrode/solution interface. When a potential is applied, electrons and oppositely charged ions from the solution are attracted by the electrode due to electrostatic forces. Such chemical processes in the electric double layer are the examples of non-faradaic processes.

1.2.3 Theory of the electric double layer

Structurally an *electric double layer* consists of two layers of charge. The *electric double layer* region is the area that starts at the electrode surface and extends into the electrolyte solution. The simplest structural model of the electric double layer was proposed by Helmholtz [35], who suggested that the excess charge of the metal is neutralised by a molecular layer of ions of equal and opposite charge to that on the metal phase. Although the model helps explain the basic features of charged surfaces, it does not explain an important property which is the *capacitance* of the electric double layer [36]. Complementing Helmholtz's concepts of the electrostatic model for the electric double layer as a metal-counter ion interaction, Gouy [37] and Chapman [38] also considered the thermal motion of the ions in the electrolyte solution. The attraction or repulsion of the ions by the charged electrode is balanced by the tendency of the ions to diffuse away into the electrolyte solution. This resulted in the formation of the theory of a diffuse layer that is extended beyond a molecular layer [36].

The distribution of the ions at the electrode surface can be described by means of *the Boltzmann equation* which can be combined with *the Poisson equation* to formulate a relation between the charge density and the potential, which is the so called *Boltzmann-Poisson equation*. Gouy and Chapman made use of the theory of electric double layer to planar surfaces [37, 38, 39] and derived an expression for the potential in the *diffuse layer*. The potential and ion distribution for the spherical surfaces can be quantified using *the Debye and Hückel theory* [36, 40].

The Gouy-Chapman model and *the Debye and Hückel theory* made significant improvement to the theory of electric double layer by introducing a diffuse layer away from the electrode surface in which the potential decreases exponentially. But the model fails to accommodate highly charged electric double layers as it ignores the finite size of the ions and treats the solvent as a medium of continuous charge distribution with a definite dielectric constant [41]. In order to resolve this problem of the Gouy-Chapman model, Stern [42] combined the ideas of Helmholtz for instance, ions being in contact with the electrode, with that of Gouy-Chapman of a diffuse layer with ions being scattered due to the thermal motion; and introduced an internal layer called *the Stern layer*. Stern suggested that due to their finite size, ions could not approach the electrode indefinitely closely beyond a plane of the closest approach and would stay put at a specific distance. Grahame [43] interpreted the theory of two planes of closest approach and they are called specifically adsorbed ions and non-specifically adsorbed ions. The planes at these specific distances in between the electrode surface and bulk of the solution side of the counter ions are defined as the inner Helmholtz plane and outer Helmholtz plane [36, 44] respectively. In the next section the structure of the electric double layer is discussed with a diagram.

Grahame [43] further contributed to the interpretation of the *electric double layer* model by relating surface charge, σ and surface potential, ψ_0 based on *the Gouy-Chapman theory* [44]. So finally, within the *electric double layer* we have two planes of closest approach; one is the metal electrode surface for

the specifically adsorbed ions and the other one is for non-specifically adsorbed solvated ions. In addition to the planes, electric double layer also has a diffuse layer which extends into the bulk solution.

1.2.4 The structure of the electric double layer

Before we discuss the structure of the electric double layer, we introduce the concept of *ideal polarised electrode* (IPE). Because the concept of ideal polarised electrode is important in describing the electric double layer. An ideal polarised electrode is an electrode at which no charge transfer takes place across the metal electrode/solution interface irrespective of an applied external potential [33]. No electrode has the characteristics of an ideal polarised electrode, but over certain limited potential range, some electrode/solution system such as, Hg electrode in contact with KCl solution approaches the behaviour of ideal polarizability [33].

As illustrated in Fig. 1.1, the electric double layer can be considered as a structure of an interface layer between a metal electrode and an electrolyte solution held at a potential difference, ψ . The interface can be divided into several distinct regions as shown in Fig. 1.1. First the metal layer, which is a thin two-dimensional layer of excess charges adjacent to the solution. The next layer is only one or two molecular diameter in thickness and mainly contains solvent molecules, dipole oriented neutral molecules and *specifically adsorbed ions* [45]. The specifically adsorbed ions are generally unsolvated ions, especially in the direction of metal. This layer or plane is called *the inner Helmholtz plane (IHP)* which is defined as the plane that passes through the centre of the specifically adsorbed species that are in contact with the metal electrode [46]. Then the third layer develops when a potential is applied. Due to the electrostatic force, ions can approach the electrode and form a counter layer close to the electrode surface to a distance given by their primary solvated shell. This layer of solvated counter ions which are non-specifically adsorbed, forms a plane, which is called *the outer Helmholtz plane (OHP)* and is defined as the plane that passes through the centre of electrostatically adsorbed ions at their closest approach to the electrode [45, 46]. The layer between the *IHP* and *OHP* is called *the Stern layer*.

The region which extends from the *OHP* out into the bulk of the solution is referred to as *the diffuse layer* and is characterised by a concentration gradient of solvated ions induced by the electric field, which extends from the electrode surface into the solution [46]. The diffuse layer is called the *Gouy-Chapman layer* and is consist of mobiles ions. These mobile ions follow the Poisson-Boltzmann statistics. The potential at the point where the bound *Stern layer* ends and the mobile Gouy-Chapman diffuse layer begins is called *the zeta potential (ζ -potential)* [36]. The concentration of potential-influenced ions where ζ -potential is zero is called *the isoelectric point (iep)* [47]. This should not be confused with the point of *potential of zero charge (pzc or ψ_{pzc})* where the surface charge is zero. The zeta potential, ζ refers to the hydrodynamic interface while the point of potential of zero charge, ψ_{pzc} refers to the surface charge for the solid/liquid interface [47].

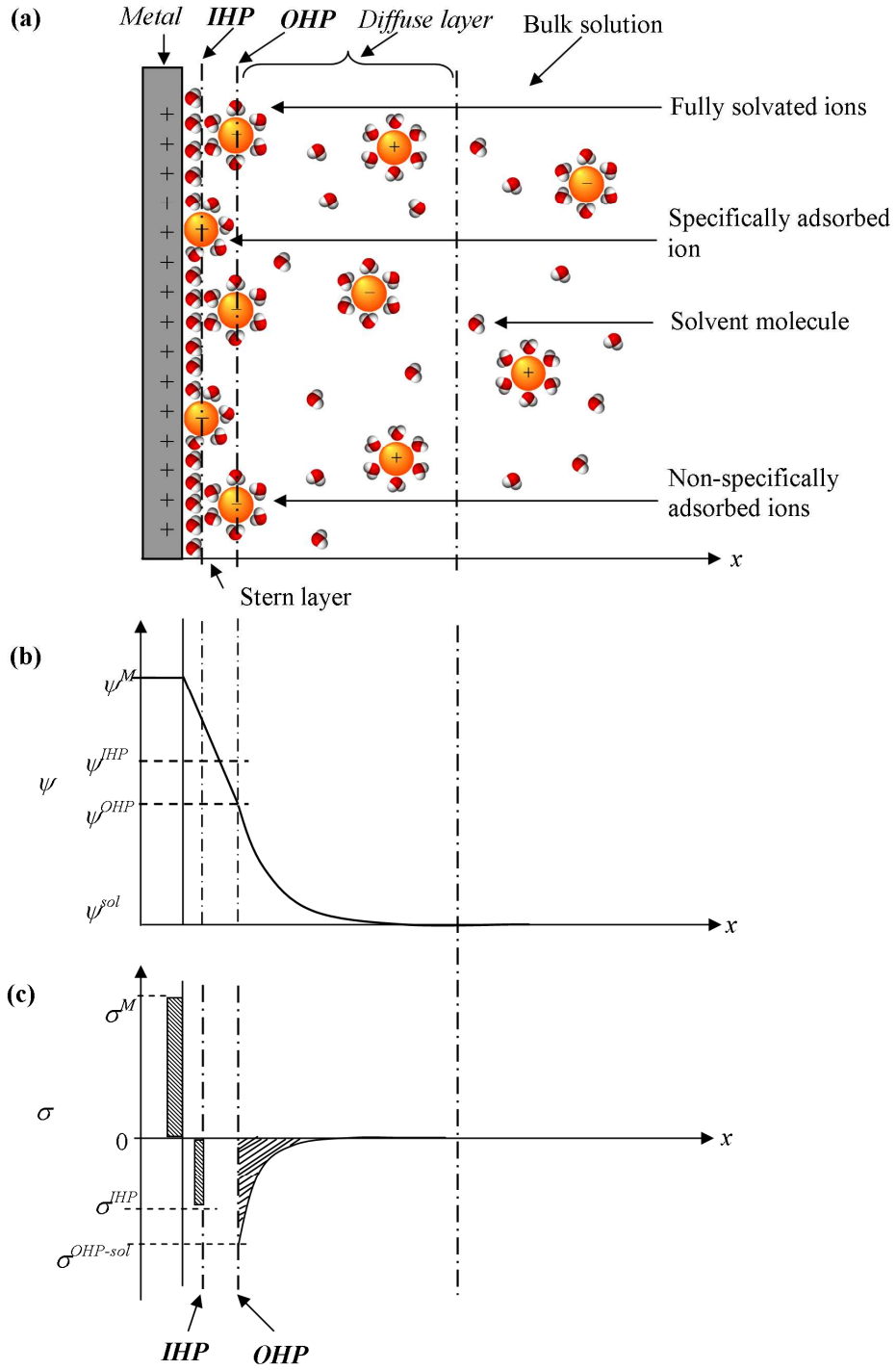


Figure 1.1 Schematic diagram of the (a) ion, (b) potential (ψ) and (c) charge distribution (σ) across the metal/electrolyte interface for weak specific adsorption. ψ^M , ψ^{IHP} , ψ^{OHP} and ψ^{sol} are the potentials at the metal, inner Helmholtz plane (IHP), outer Helmholtz plane (OHP), and the bulk solution respectively. σ^M , σ^{IHP} and σ^{OHP} indicate the excess charge on the metal, inner plane, and at the start of the diffuse layer respectively. The layer between IHP and OHP is about 0.3 nm thick which is called the *Stern layer*, and is tightly bonded with water molecules, solvated ions, and specifically bonded ions [33, 41, 45].

In the next section, we apply *the Poisson-Boltzmann equation* to the mobile ions in *the Gouy-Chapman diffuse layer* and relate the charge density to the potential of diffuse layer for metal electrode/electrolyte interface.

1.2.5 The Poisson-Boltzmann equation for the electric double layer

The charge density ρ and electric potential distribution $\psi(x, y, z)$ in the solution are related by the Poisson equation [36]-

$$\nabla^2 \psi = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = - \frac{\rho(x, y, z)}{\epsilon \epsilon_0} \quad (1.4)$$

where $\rho(x, y, z)$ is the local electric charge density and ϵ_0 is the permittivity of free space and ϵ is the relative dielectric permittivity of the medium. In the solution ions are mobile and their spatial distribution obeys Boltzmann statistics [36]. For simplicity, we assume the electrolyte to consist of anions and cations of the same charge number Z (here 'Z' should not be confused with lower case 'z' which is a component of the Cartesian coordinate) [48] and the local ion density is given by-

$$n_i = n_0 e^{\frac{ZW_i}{k_B T}} \quad (1.5)$$

where W_i is the electric work needed to bring a charged ion from solution to the electrode surface with potential difference ψ . The concentrations of anions and cations from Eq. (1.5) are $n_- = n_0 e^{\frac{Ze\psi}{k_B T}}$ and $n_+ = n_0 e^{-\frac{Ze\psi}{k_B T}}$ [48]. Here n_0 is the concentration of ions in the bulk electrolyte. So the charge density, $\rho(x, y, z)$ can be expressed as-

$$\rho(x, y, z) = Ze(n_+ + n_-) = Zn_0 e \left(e^{-\frac{e\psi(x, y, z)}{k_B T}} - e^{\frac{e\psi(x, y, z)}{k_B T}} \right) \quad (1.6)$$

Substituting the Eq. (1.6) into Eq. (1.4) we get

$$\nabla^2 \psi(x, y, z) = \frac{Zn_0 e}{\epsilon \epsilon_0} \left(e^{-\frac{e\psi(x, y, z)}{k_B T}} - e^{\frac{e\psi(x, y, z)}{k_B T}} \right) \quad (1.7)$$

This is *the Poisson-Boltzmann equation*, which is a second order partial differential equation. We will solve this equation analytically for a simple geometry such as planar surface.

We consider the symmetry for extended planar surface where the potential in the y and z directions is the same and we equate the differential coefficients with respect to y and z to zero [36]. The potential becomes a function of x only. Therefore we write the Poisson-Boltzmann equation in the following manner-

$$\frac{d^2\psi(x)}{dx^2} = \frac{Zn_0e}{\epsilon\epsilon_0} \left(e^{\frac{e\psi(x)}{k_B T}} - e^{-\frac{e\psi(x)}{k_B T}} \right) \quad (1.8)$$

For small potential such as $\psi \ll \frac{k_B T}{e}$ we can expand the exponential function into a series-

$$e^{\frac{e\psi(x)}{k_B T}} - e^{-\frac{e\psi(x)}{k_B T}} = 1 + \frac{e\psi(x)}{k_B T} - 1 + \frac{e\psi(x)}{k_B T} \pm \dots \quad (1.9)$$

and ignore all the terms but the first one and get the following *Poisson-Boltzmann equation*-

$$\frac{d^2\psi(x)}{dx^2} = \frac{2Z^2 n_0 e^2}{\epsilon\epsilon_0 k_B T} \psi(x) \quad (1.10)$$

the general solution of which is -

$$\psi(x) = C_1 e^{-\kappa x} + C_2 e^{\kappa x} \quad (1.11)$$

$$\text{with } \kappa = \sqrt{\frac{2Z^2 n_0 e^2}{\epsilon\epsilon_0 k_B T}}. \quad (1.12)$$

The constants, C_1 and C_2 can be defined by considering the surface potential $\psi(x=0) = \psi_0$ and the potential at points far away from the surface disappear i.e., $\psi(x \rightarrow \infty) = 0$. The second boundary condition ensures that for the distant points, the potential does not become infinity and therefore, $C_2 = 0$. Then from the first boundary condition we get $C_1 = \psi_0$. Therefore the solution of *the Poisson-Boltzmann* is given by [36]-

$$\psi(x) = \psi_0 e^{-\kappa x} \quad (1.13)$$

ψ_0 is the potential at the interface between the OHP and the diffuse layer. Fig. 1.1 and Eq. (1.13) show that the potential is a function of distance from the OHP into the diffuse layer and potential decreases exponentially with the distance and for a large distance the potential should disappear. The decay length, λ_D for the potential is given by the inverse of the quantity of κ , such that $\lambda_D = \kappa^{-1}$. This is called *the Debye length* [36]. When the concentration of an electrolyte solution increases then *the Debye length* decreases.

The potential drop across *the Stern layer* (the layer between IHP and OHP) has linear dependence with the distance from the metal electrode surface which ensures that there is a constant dielectric permittivity in *the Stern layer* [48].

1.2.6 The Grahame equation: the relation between surface charge, σ and surface potential, ψ_0 at the electric double layer

The US electrochemist D.C. Grahame [43] made significant contribution to the measurements of double layer capacitance using metal/solution interface. Based on the Gouy-Chapman theory Grahame derived an equation that relates surface charge, σ to the surface potential, ψ_0 . Therefore, when we know the surface

charge, $\sigma(\psi_0)$ for an electric double layer system, then we can calculate $\frac{d\sigma}{d\psi_0}$. In fact, $\frac{d\sigma}{d\psi_0}$ is the

expression for the *electric double layer capacitance*, which is measurable. The *Grahame equation* can be derived by equating the sum of the surface charge and the charge of the ions in the double layer to zero. From this electroneutrality condition of the electric double layer Grahame deduced the following equation [36]-

$$\sigma = \sqrt{8n_0 \epsilon \epsilon_0 k_B T} \cdot \sinh\left(\frac{Ze\psi_0}{2k_B T}\right) \quad (1.14)$$

This is the so called *Grahame equation* which gives the relation between the surface charge, σ and the surface potential, ψ_0 for the electric double layer, based on the Gouy-Chapman theory.

The Grahame equation can be simplified for low potential by expanding sinh series ($\sinh x = x + \frac{x^3}{3!} + \dots$) and ignoring all the terms except the first one which leads to the following simple equation that relates the surface charge with the surface potential and Debye length-

$$\sigma = \frac{\varepsilon\varepsilon_0\psi_0}{\lambda_D} \quad (1.15)$$

From the Eq. (1.15) we see that for a low potential, the surface charge density is proportional to the surface potential [36]. After *the Grahame equation* we discuss the double layer capacitance in the next section.

1.2.7 Double layer capacitance

Before discussing the electric double layer capacitance, we here briefly talk about the parallel plate capacitor as the electric double layer model can be described as a parallel plate capacitor similar to the model shown in Fig. 1.2 below. A simple capacitor is a parallel plate capacitor that consists of two parallel conducting plates with a charge, $+\sigma$ stored on one plate and an equal but opposite charge, $-\sigma$ stored on the other plate, and the plates are separated by a dielectric with relative permittivity, ε .

The capacitance of a given system depends only on the geometry of the plates and the properties of the dielectric between them. For a parallel plate capacitor, Eq. (1.2) can be written in the following way [33]-

$$C = \frac{\varepsilon\varepsilon_0 A}{d} \quad (1.16)$$

here ε_0 is the dielectric permittivity of the free space, ε is relative dielectric permittivity of the medium, A is the surface area of one of the metal plates, and d is the distance between the plates. Therefore the capacity per unit area,

$$C^A = \frac{\varepsilon\varepsilon_0}{d} \quad (1.17)$$

An analogy can easily be drawn between *the electric double layer* and *the parallel plate capacitor*, and suggest the presence of capacitance at the metal electrode/solutions interface. The metal electrode surface is one of the two plates of the capacitor, the solvated counter ions layer at OHP is equivalent to the other charged plate, and the layer of the specifically and non-specifically adsorbed species in the *Stern layer* is analogous to the dielectric material between the two plates [46].

Structurally, we have just seen that the electric double layer looks similar to parallel plate capacitor. Now we would like to see the similarity in the mathematical expressions for the capacitance for the two models.

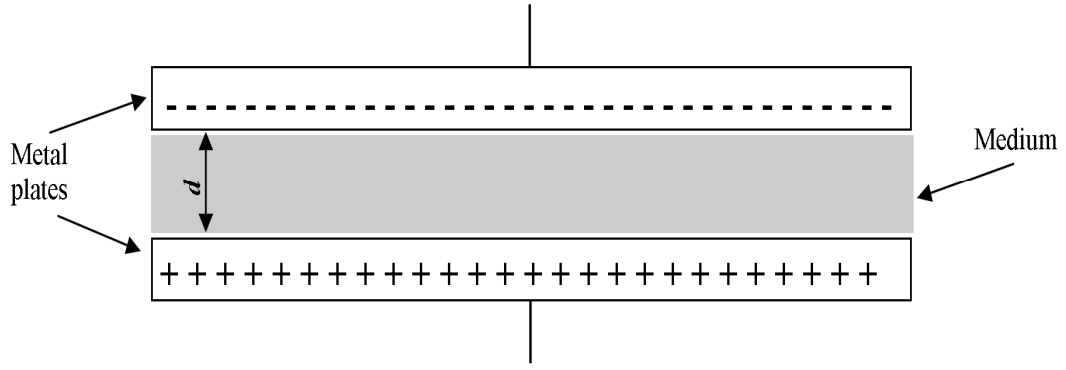


Figure 1.2 A schematic diagram of a parallel plate capacitor comprised of two metal plates of opposite charges separated by a dielectric material (adapted from Ref. [46]).

The differential capacitance per unit area, A between the regions separated by a specific distance can be defined as-

$$C^A = \frac{d\sigma}{d\psi} \quad (1.18)$$

We substitute the Eq. 1.14 (Grahame equation) for the electric double layer charge, σ into Eq. (1.18). Therefore the capacitance of the electric double layer per unit area, A is [36]

$$C^A = \frac{d\sigma}{d\psi_0} = \frac{d \left(\sqrt{8n_0 \epsilon \epsilon_0 k_B T} \cdot \sinh \left(\frac{Ze\psi_0}{2k_B T} \right) \right)}{d\psi_0} \quad (1.19)$$

$$\Rightarrow C^A = \sqrt{\frac{2Z^2 n_0 e^2 \epsilon \epsilon_0}{k_B T}} \cdot \cosh \left(\frac{Ze\psi_0}{2k_B T} \right) \quad (1.20)$$

Substituting Eq. (1.12) and the relation $\lambda_D = \kappa^{-1}$ we get

$$C^A = \frac{\epsilon \epsilon_0}{\lambda_D} \cdot \cosh \left(\frac{Ze\psi_0}{2k_B T} \right) \quad (1.21)$$

We expand cosh into a series as

$$\cosh x = 1 + \frac{x^2}{2!} + \frac{x^4}{4!} + \dots \text{ . We ignore all the terms except the first and get-}$$

$$C^A = \frac{\epsilon\epsilon_0}{\lambda_D} \quad (1.22)$$

Now we can compare the capacitance of the electric double layer in Eq. (1.22) with the capacitance of the parallel plate capacitor as illustrated in Fig. 1.2 above. We see that electric double layer, with its surface charge on the metal and the solvated counter ions at OHP, behaves like a parallel plate capacitor, in which the distance between the parallel plates is given by *the Debye length*, λ_D [36, 41]. When the electrolyte concentration increases, then the Debye length decreases, which in turn cause an increase in the electric double layer capacitance. Therefore, the electric double layer capacitance increases with increasing electrolyte concentration.

1.2.8 The Lippmann equation, electrocapillary curve and the potential of zero charge (PZC)

The Lippmann equation is concerned with the surface tension between *an ideal polarised electrode* and an electrolyte solution [49]. The thorough explanation of the surface tension as a function of the applied potential, and the electrocapillary equation are available in the literature [50, 51]. In short, if certain parameters are held constant, such as the chemical potential, μ_j of the adsorbing species, *the Lippmann equation* states that the ratio of the change in surface tension, $\partial\gamma$ over the change in the potential drop, ∂E across the interface gives the negative of the surface charge density, $-\sigma^M$. Therefore we write the Lippmann equation as follows [51]-

$$\left(\frac{\partial\gamma}{\partial E} \right)_{\mu_j} = -\sigma^M \quad (1.23)$$

$$\text{with condition,} \quad d\mu_j = 0 \quad (1.24)$$

where μ_j denotes the chemical potentials of the adsorbing species.

The interfacial tension is an entity which can be quantified and a typical electrocapillary curve can be obtained by plotting the surface tension as a function of applied potential using a *dropping mercury electrode (DME)* in contact with 1.0 N HCl as illustrated in Fig. 1.3. The curve is parabolic and passes through a maximum value, which is called *the electrocapillary maximum*. The maximum corresponds to the condition when the electrode has no excess charge and hence the slope of the curve is zero. That is-

$$\left(\frac{\partial \gamma}{\partial E}\right)_{\mu_j} = -\sigma^M = 0 \quad (1.25)$$

The potential at this point is *the potential of zero charge (PZC)* for the system and the relation for excess charge, $\sigma^M = \sigma^S = 0$ holds. At potentials more negative than the PZC, the electrode surface has a negative excess charge, and at more positive potentials, there is a net positive surface charge.

The separation of charge normal to the interface gives *the electric double layer* the characteristic of a parallel plate capacitor. But the relationship between charge and potential for this capacitor generally is not linear. As a result the capacity of the electric double layer may not remain constant. Therefore it is necessary to define a differential capacity, C in the following way [51, 52]-

$$C = \left(\frac{\partial \sigma^M}{\partial V}\right)_{\mu_j} = -\left(\frac{\partial^2 \gamma}{\partial V^2}\right)_{\mu_j} \quad (1.26)$$

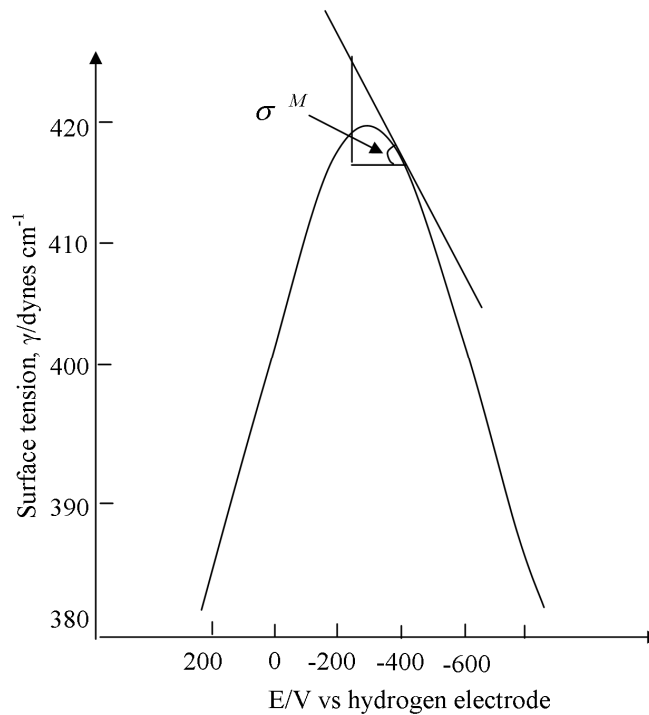


Figure 1.3 Electrocapillary curve of surface tension vs potential for Hg in contact with 1.0 N HCl. The charge density on the electrode at a particular potential difference, V is given by the slope of the electrocapillary curve at that potential [51].

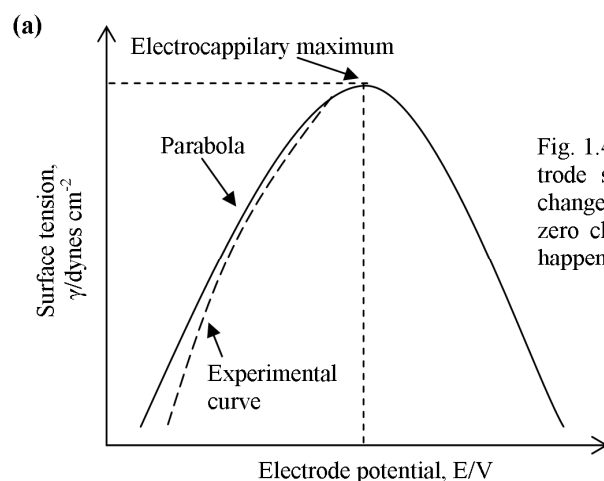
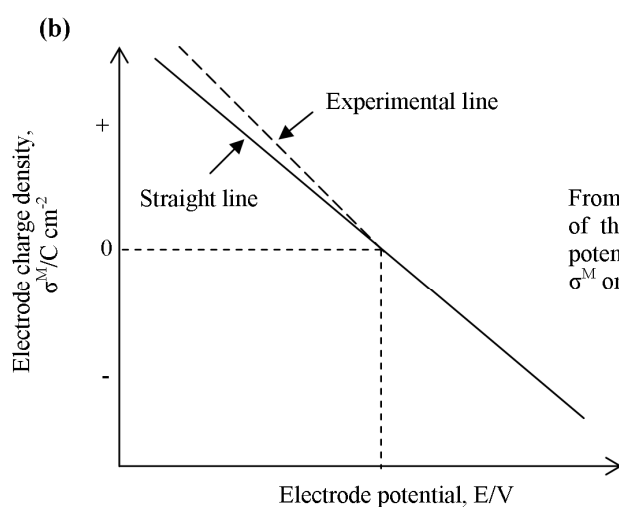


Fig. 1.4a shows that the charge on the electrode starts off with one sign and then changes its sign after passing through a zero charge value. The potential where it happens is the *potential of zero charge*, E_{pzc}



From Fig. 1.4b we can see that the slope of the electrocapillary curve at any cell potential, V is equal to the charge density, σ^M on the electrode.

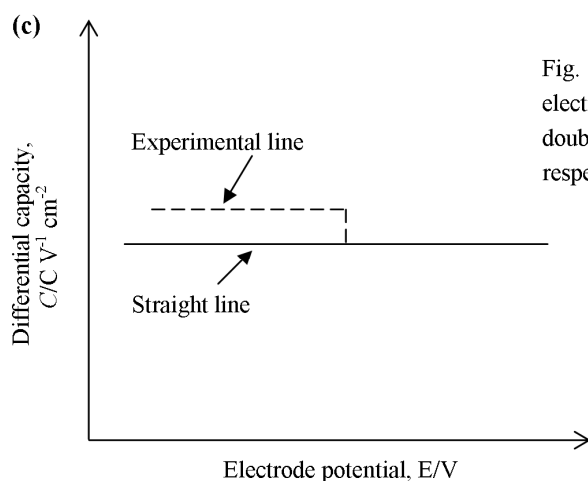


Fig. 1.4c shows the differential capacity vs electrode potential which is the plot of double derivative of surface tension with respect to electrode potential, $\left(\frac{\partial^2 \gamma}{\partial V^2}\right)$

Figure 1.4 Electrocapillary vs E curve. When the electrocapillary vs E curve (part 1.4a) is a perfect parabola, the electrode charge density varies linearly with potential difference (part 1.4b). A further differentiation gives a capacity that is potential independent (part 1.4c). However, experimental electrocapillary curves are not perfect parabolas [51].

The implication of the Eq. (1.26) lies in the fact that the second derivative of the surface tension with respect to the potential gives the capacity of *the electric double layer*. It shows that the slope of the curve of the electrode charge vs cell potential in Fig. 1.4(b) determines the value of the differential capacity of the double layer in Fig. 1.4(c). When the curve is ideally parabolic, it gives a constant capacitance.

It is a convenient to determine the PZC when electrocapillary measurements method is used for the liquid metal electrode, such as *a dropping mercury electrode* (DME). However, PZC being an important characteristic of interfaces, it is necessary to know the PZC for the interfaces that involve solid electrodes as well. It is not possible to determine the value of surface tension using a solid electrode by the electrocapillary method [51]. Therefore alternative methods of determining the value of PZC are needed.

1.2.9 Total capacitance of the electric double layer

In Section 1.2.4, we have described the electric double layer according to the *Gouy-Chapman-Stern model*. A potential-distance relation has been found to be an important characteristic of this model where we have a linear variation of the potential in the region from electrode surface to the location of the OHP, and an exponential potential drop in the region from OHP to the Gouy-Chapman diffuse layer.

Based on the Stern's unification of Helmholtz model of the electric double layer, where ions are in contact with the metal electrode, and the Gouy-Chapman theory of ions being agitated and scattered due to the thermal fluctuation, we can write an expression for the total capacitance for the electric double layer. We write the differentials of the potential difference across the interface with respect to the charge on the metal, σ^M give the following [41]-

$$\frac{\partial(\psi_M - \psi_{bulk})}{\partial \sigma^M} = \frac{\partial(\psi_M - \psi_H)}{\partial \sigma^M} + \frac{\partial(\psi_H - \psi_{bulk})}{\partial \sigma_G} \quad (1.27)$$

Each of the terms in Eq. (1.27) can be represented by the inverse of a deferential capacity and the equation can be rewritten as-

$$\frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_G} \quad (1.28)$$

Here, C is the total capacity of the interface, C_H is the Helmholtz capacity or the capacity of the Stern layer, and C_G is the capacity of the Gouy-Chapman diffuse layer.

Now for dilute electrolyte, C_G is much smaller than C_H and as a result the total capacity is determined by the smaller Gouy-Chapman capacity and has therefore a minimum at *the potential of zero charge* (pzc

or ψ_{pzc}) [45]. In other words, if the potential applied is negative, electrons flow into the surface and make the surface more negative. But, if a positive potential is applied, then the electrons move away from the surface and the surface becomes less negative. Therefore, there is a *potential* for particular electrode in a particular electrolyte solution, where the electrode surface has neither negative nor positive charge, the surface will have zero charge which is ψ_{pzc} .

With this we end our discussion of the *electric double layer*. Cyclic voltammetry is discussed next.

1.3 Cyclic voltammetry

1.3.1 Introduction

Cyclic voltammetry (CV) is one of the most frequently used electrochemical methods because of its relative simplicity and the amount of information it provides on the electrochemical processes. In cyclic voltammetry, a triangular waveform is applied as the potential to an electrode and the current is measured simultaneously by a current-voltage converter. The potential is normally generated by a function generator and applied to the cell through a potentiostat. Since the applied potential varies linearly with time, the slope is equivalent to the scan rate and the unit of $V s^{-1}$ or $mV s^{-1}$. The resulting current-potential behaviour constitutes the voltammogram. Many examples of voltammograms will be seen later in this thesis.

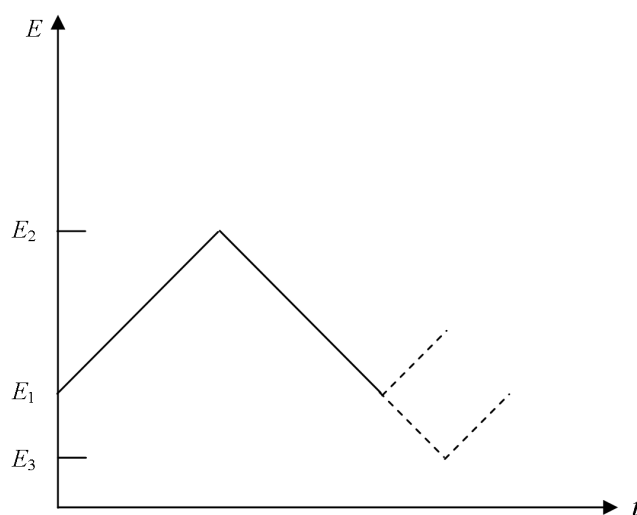


Figure 1.5 Potential-time behaviour at the working electrode following the application of triangular waveform in cyclic voltammetry. E_2 is potential limit in the forward scan and E_1 and E_3 are in the reverse scan [53].

The potential-time triangular waveform, used for sweep measurements is shown in Fig. 1.5. The lower and higher limits of potential, E_1 and E_2 can be varied depending on the purpose of the experiment. Linear sweep voltammetry (LSV) is the simplest of these techniques that involves scanning the electrode potential at a sweep rate, v between the potential limits, E_1 and E_2 , and then halt it. CV is the same as LSV at least initially, but on reaching E_2 , the scan is usually reversed. When the sweep reaches the initial potential E_1 , then it can be stopped, reversed or allowed to continue to a potential value of E_3 [53]. Sometime for initial qualitative experiments E_1 and E_2 are chosen in aqueous electrolyte to lie between the hydrogen and oxygen evolution potentials (where the solvent decomposes). In this way, any adsorbed impurities which may block the electrode process from taking place can be removed from the electrode surface by oxidation or reduction processes, which often called electrochemical cleaning. By scanning between these potentials, it is possible to obtain highly reproducible cyclic voltammograms of metals, such as Pt, Au or Pd, even though in most cases reproducible behaviour will depend on parameters, for example, electrolyte purity, electrode materials, and lower and higher limits of the potential sweep.

Once a reproducible cyclic voltammogram is obtained, the potential range examined may be narrowed to study a smaller region of interest in more detail. For the qualitative study, CV is carried out over a wide range of potential and scan rates, and more than one or several current peaks may appear [53].

In aqueous solution when the reactants and products of a chemical process are free to move and soluble and if such system is studied by CV, the reactions can be divided into two categories, and they are ***reversible*** and ***irreversible reactions***.

In an aqueous solution, if there is no reduction/oxidation-active species between the anodic and cathodic potential regions, E_p^A and E_p^C , then the observed potential-current hysteresis may refer to the formation and dissolution of chemisorbed hydride and oxide layers on the electrode surface (but not all metals absorb hydrogen and/or grow oxides). This is how cyclic voltammetry is also can be an effective tool to study surface processes.

1.3.2 Reversible processes

A *reversible reaction or process* is the one where both the anodic and the cathodic processes occur simultaneously at a given electrode potential and the current depends on the rate of oxidation (or anodic process) and the reduction (or cathodic) process. The transfer of an electron in a redox process can be expressed in the following form-



where O and R are the oxidized and reduced forms respectively, and n is the charge number of the electrons involved in the electrode process [53]. The electron transfer at the electrode surface for a reversible electrode process is fast such that when potential is varied, O and R immediately adjust to the ratio dictated by *the Nernst equation* [54]-

$$E_e = E_e^0 + \frac{RT}{nF} \ln \frac{C_O}{C_R} \quad (1.30)$$

Where E_e^0 is the standard electrode potential, E_e is the equilibrium potential, and the surface concentration of O and R are C_O and C_R respectively.

Usually when a slow linear potential sweep is applied, the voltammogram will appear as a steady state i vs E curve. But when the sweep rates are increased, then current peaks increase as well. Fig. 1.6 shows that the current at the electrode is a function of scan rate, and it increases as the scan rate increases. Current also depends on processes, such as, adsorption, electron transfer, chemical reaction or diffusion of product(s) in the cell. Therefore, to have an insight into the kinetics of electrode and the interfacial species it is necessary to vary scan rate.

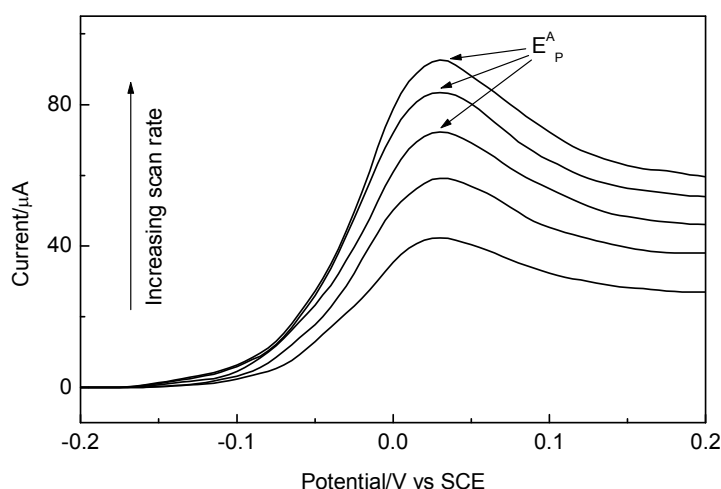


Figure 1.6 Diagram showing how current increases with increasing scan rate where E_p^A is the potential of the anodic current peak (modified from Ref. [53]).

For a *reversible process* as demonstrated in Fig. 1.7, when the potential is scanned in the reverse order, especially at slow scan rate, the current is expected to trace the forward sweep current with a change in sign. However, this may not be the case when the scan rates are faster. In faster scan rates there is significant concentration of reduced species, R present close to the electrode and they continue to be

formed on the reverse sweep until the potential reaches E_e^0 . Here, in order for the surface concentration to follow *Nernst equation*, as the potential approaches, E_e^0 , the R present close to the electrode starts to be oxidised back to O and a reverse current flows [53].

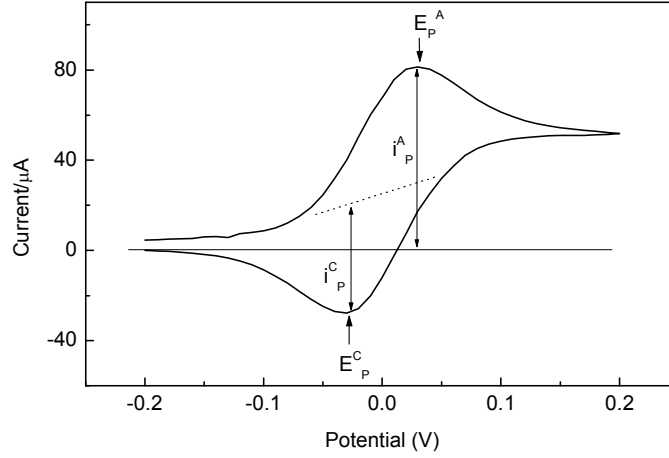


Figure 1.7 Cyclic voltammogram for a single electron transfer reaction showing the parameters of importance as diagnostic criteria. i_p^A and i_p^C are the anodic and cathodic peak current at the potential E_p^A and E_p^C respectively. It can be seen that $\frac{i_p^A}{i_p^C} = 1$ [53].

For a reversible electrochemical reaction of a single electron transfer, the voltammogram has certain defined characteristics which are often called *the diagnostic tests for reversible systems*. Some important characteristics of a reversible system are as follows-

(1) The potential separation between the anodic and cathodic current peaks can be determined from the *Nernst equation* and it is [55]-

$$\Delta E = E_p^A - E_p^C = \frac{59}{n} mV \quad (1.31)$$

where E_p^A and E_p^C are the anodic and cathodic peak current potential respectively.

(2) The ratio of the peak current densities is equal to the unity [53].

$$\left| \frac{i_p^A}{i_p^C} \right| = 1 \quad (1.32)$$

(3) The relation between the peak currents and the scan rate-

The relation between the potential scan rate, ν and the peak current density, i_p for a reversible electron transfer is of a directly proportional to analyte concentration c_O^∞ in mol cm^{-3} as described by *the Randles-Sevcik equation* [53]-

$$i_p = -0.4463nF\left(\frac{nF}{RT}\right)^{\frac{1}{2}}c_O^\infty D^{\frac{1}{2}}\nu^{\frac{1}{2}} \quad (1.33)$$

here i_p is the peak current density (A cm^{-2}), n is the number of electrons in reaction, ν is the potential sweep rate (V s^{-1}), F is the Faraday's constant (96485 C mol^{-1}), R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the absolute temperature (K), and D is diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$). If we assume the room temperature 298.15 K the Randles-Sevcik equation at 25°C reduces to the following [53]-

$$i_p = (2.69 \times 10^5)n^{\frac{3}{2}}c_O^\infty D^{\frac{1}{2}}\nu^{\frac{1}{2}} \quad (1.34)$$

The Randles-Sevcik equation for a single electron transfer system at particular analyte concentration can be written in a more concise form and that shows that the peak current is proportional to the square root of the sweep rate [53]-

$$i_p \propto \nu^{\frac{1}{2}} \quad (1.35)$$

These three criteria above are the main diagnostic test for the reversibility of a system. A reversible voltammogram can only be seen when both O and R are stable, and the kinetics of the electron transfer process are fast, such that at all potentials and potential sweep rates, the electron transfer process is in equilibrium; in other words, the surface concentration of O and R follow the *Nernst equation*.

1.3.3 Irreversible and quasi-reversible processes

In irreversible process as potential is applied, it fails to generate enough electrons on the electrode surface as required by the Nernst's equation due to the *slow* reaction kinetics and equilibrium is not maintained.

Two main diagnostic tests for totally irreversible electrode reaction are [43]:

(1) Total absence of reverse peak-

This is the most marked feature of a cyclic voltammogram of a totally irreversible system, but is not the conclusive proof of an irreversible electrode reaction because this can be due to a fast flowing chemical reaction. Therefore other tests must be carried out.

(2) The peak current density of the voltammogram, i_p^A is proportional to the square root of the sweep rate, ν , that is [43],

$$i_p^A \propto \nu^{\frac{1}{2}} \quad (1.36)$$

(3) The peak potential, E_p^A shifts by the amount, $-30/\alpha_C n_\alpha$ mV for each decade of increase in the scan rate, ν at 25° C [53, 56].

Diagnostic tests for quasi-reversible reaction [43]:

(1) The anodic or cathodic current density peaks, i_p^A or i_p^C increases with the increase in scan rate, ν , but is not proportional to it.

(2) The ratio between anodic peak current, i_p^A and cathodic peak current i_p^C is unity. Therefore, $\left| \frac{i_p^A}{i_p^C} \right| = 1$

provided that $\alpha_C = \alpha_A = 0.5$. α_A and α_C are the transport coefficients which depend on the diffusion coefficient, D of the system.

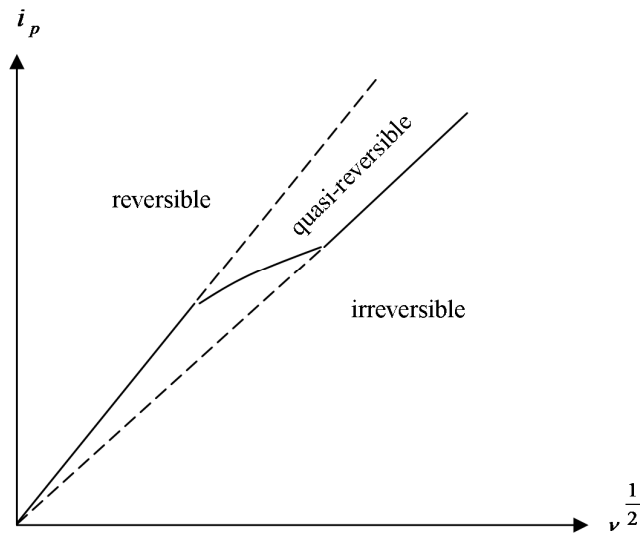


Figure 1.8 A plot of the dependence of the peak current on the square root of the potential sweep rate, showing the transition from reversible to irreversible behaviour of the reactions with increasing sweep rate [53].

It is not unusual that a system that is reversible at low sweeps rate, may become irreversible at higher sweep rates and may behave as a quasi-reversible system at sweep rates between them. This transformation from the reversible then quasi-reversible and irreversible, as the scan rate increases, takes place when the potential applied fails to generate enough concentrations of the redox species at the electrode surface predicted by the Nernst equation [53]. So the *Nernstian equilibrium* does not hold at the electrode surface. This transformation can be seen when the peak current, i_p is plotted against the square root of the sweep rate, v as shown in the Fig. 1.8 above.

1.3.4 Surface process- adsorption

Adsorption processes where adsorbed forms of O and R are electroactive can be studied by cyclic voltammetry. The interfacial behaviour of electroactive compounds especially the organic compounds which can adsorb on the electrode surface with their chemical characteristics intact is of paramount importance in electrochemistry [57]. Both the reactant and product can be involved in adsorption or desorption process [58]. The typical case of an adsorption is the case where adsorbed forms of O and R are both electro-active in the potential range under investigation. If the electron transfer is reversible then the cyclic voltammetry experiment gives the results that are illustrated in the Fig. 1.9 [59].

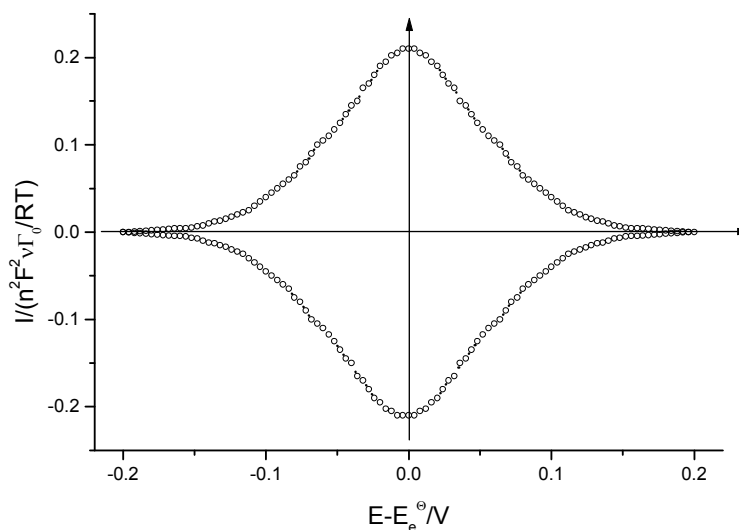


Figure 1.9 An example of cyclic voltammogram for the reduction of adsorbed O and reoxidation of the product R where the electron transfer is reversible [60].

The main characteristic of such a system is that the peak current is directly proportional to the surface coverage, Γ_0 and potential scan rate, v . Therefore the peak current density, i_p is [59, 60],

$$i_p = \frac{n^2 F^2 \Gamma_o A v}{4RT} \quad (1.37)$$

where R is the gas constant, F is Faraday constant, A is the area of the electrode and n is the number of electron in the process. The peak current density, i_p is proportional to the sweep rate, v .

We can find the area under the anodic or cathodic peak by converting the potential axis to a time axis, and then integrating current, i over time, t , and the area gives us the charge, Q . In this way we find an expression for surface coverage, Γ_o and the relation with charge is [59],

$$\Gamma_o = \left| \frac{Q}{nF} \right| \quad (1.38)$$

Fig. 1.9 shows the main characteristics of the cyclic voltammogram of a surface process- that the peaks are symmetrical, the current starts to rise from zero to a peak value and then falling again to zero, there is negligible or no peak separation and charge associated with anodic and cathodic process are equal but opposite in sign.

1.3.5 Three electrode cell configuration

In conventional cyclic voltammetry experiment, the electrochemical cell consists of three different electrodes. They are: working electrode, counter electrode, and reference electrode.

1.3.5.1 Working electrode

The working electrode is the electrode where, the reaction of interest takes place which can be a small disk or a small flag of a metal foil. One of the important features of an electrode is that it should not react chemically with the solution components [61]. Usually, surface of a working electrode should be smooth so that the geometrical area is well defined. It needs to be free from any undesired impurities and deposits on its surface, especially when reduction and oxidation reactions are taking place on its surface. Working electrodes are usually made of Au, Pt, Pd or glassy carbon. The choice of material depends on a range of considerations related to the reaction being studied.

For consistent results, it is essential to clean working electrodes and the roughness of the surface minimal. The pretreatment and cleaning procedure helps ensure a reproducible and a consistent surface area, and is free from any impurities [61].

1.3.5.2 Counter electrode

The counter electrode allows current to pass through the cell and the current passed is equal in magnitude, but opposite in sign, to that passed at the working electrode. The surface area of a counter electrode is usually chosen to be greater than the working electrode so that current density at the counter electrode is less than that of working electrode. It is often separated from the main cell so that the products of counter electrode's reaction with the electrolyte do not enter the main cell. Normally the counter electrode should be of same material as the working electrode to ensure working electrode or electrolyte are not contaminated, if it corrodes.

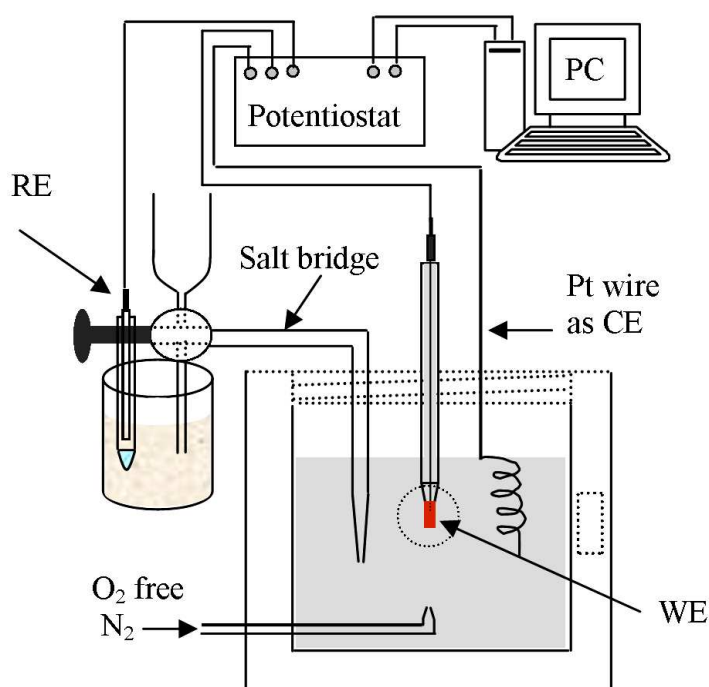
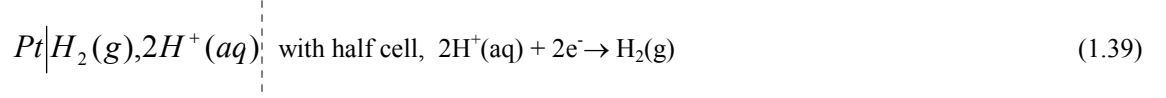


Figure 1.10 A schematic diagram of a three electrode electrochemical cell showing the Cu working electrode (WE), platinum counter electrode (CE) and reference electrode (RE).

1.3.5.3 Reference electrode

A reference electrode keeps a constant electrode-solution potential which does not fluctuate during experiment due to its chemical and structural composition. A wide variety of reference electrode systems are used, such as Hg/Hg₂Cl₂ or Ag/AgCl in contact with saturated KCl solution. It is necessary to relate the potential of a reference electrode to other reference electrodes [61]. The potential of a reference electrode is normally taken with respect to the *standard/normal hydrogen electrode* (SHE/NHE), which is accepted as the standard thermodynamic scale for oxidation and reduction potential.

A standard hydrogen electrode is simply H₂ gas at 1 bar pressure confined and in contact with a platinised Pt electrode dipped in acid solution. Alternatively the Pt electrode is dipped in an acidic solution and pure H₂ gas at 1 bar pressure is bubbled through it. The platinised Pt is needed to provide the surface on which the H₂ gas can be in contact with H⁺ (aq) ions to form the hydrogen electrode [62]-



The standard hydrogen electrode potential E_{H_2/H^+}^0 is accepted to be zero at all potential when the pressure of H₂ and the activity of H⁺ are both 1 (unity). Potentials of any other electrode systems are calculated with respect to the potential of SHE/NHE electrode system. The electrode potential of Hg/Hg₂Cl₂ couple in contact with saturated KCl solution is 0.242 V vs. SHE at 25°C. The relation can be expressed in the following way [63]-

$$E_{H_2/H^+}^0 = E_{Hg/Hg_2Cl_2}^0 + 0.242 \quad (1.40)$$

The potential of a reference electrode remains constant, even if a small amount of current does pass through it. The potential is controlled between the working and reference electrodes. When the potential difference is changed between the electrodes, the change of potential difference appears only at the working electrode. The reference electrode is often chosen to be Ag/AgCl or saturated calomel (Hg/Hg₂Cl₂) in contact with saturated aqueous KCl solution, which is called *saturated calomel electrode* (SCE).

Just as in the case of any other reference electrodes, the potential of SCE is governed by **the Nernst equation** [54],

$$E = E^0 - \frac{RT}{nF} \ln Q \quad (1.41)$$

where R is the universal gas constant, T is the absolute temperature in Kelvin, n is the number of electrons transferred in the reaction, F is the Faraday constant and Q is the reaction quotient or in other words- Q is the ratio of the product of the product activities raised to their stoichiometric numbers, to that of products of the reactant activities raised to their stoichiometric numbers. However, in the SCE one component is Hg, which is an element and the other is a solid compound (Hg₂Cl₂), so both have an activity of unity. The third component is Cl⁻ which is present in abundance in the saturated solution which is in contact with the calomel. Therefore, the *Nernst equation* for the reference electrodes, Ag/AgCl or Hg/Hg₂Cl₂ in contact with saturated KCl solution can be written as [64]-

$$E = E^0 - \frac{RT}{nF} \ln [Cl^-] \quad (1.42)$$

As a result, unless there is an unusually high current passed, the activity stays constant and so does the electrode potential. It is also important to note that modern potentiostat are designed in way so that no current is allowed to pass through the reference electrode. Therefore a reference electrode system ensures that when any potential change made in the cell (E_{cell}), it appears in the working electrode (E_{wkg}).

In the next section the nonlinear optical technique, second harmonic generation (SHG) will be discussed. SHG technique is used in this work together with cyclic voltammetry.

1.4 Epioptics- study of surfaces and interfaces by linear and nonlinear optical techniques

There are various diagnostic techniques available for the determination of the surface and interface structure and roughness etc. during and after the adsorption, desorption and oxide formation [65]. Conventional optical techniques, such as low energy electron diffraction (LEED) and reflection high energy electron diffraction (RHEED) have been used [66]. These electron beam techniques require an ultra high vacuum (UHV) environment in order to be applied, and electrons or photons act both as probe and signal. These issues can be resolved by the use of optical techniques, such as spectroscopic ellipsometry (ES) or reflectance difference/anisotropy spectroscopy (RDS/RAS) for the extraction of surface and interface information with monolayer or sub-monolayer resolution [65]. Beside these linear optical techniques, nonlinear optical techniques such as optical second harmonic generation (SHG) are also used to investigate surface and interfaces. In surface and interface analyses these epioptic techniques carry several important advantages over conventional techniques.

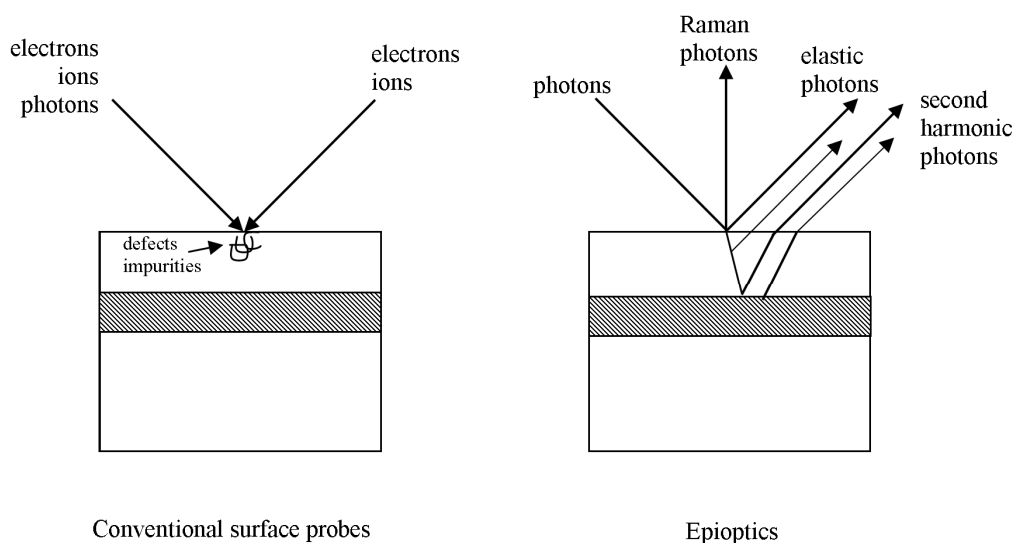


Figure 1.11 Comparison of conventional and epioptic probes. For conventional surface probe UHV is required but epioptic probes are applicable in all pressure and temperature regimes [65].

The use of optical diagnostic techniques for the studies of surfaces and interfaces has increased greatly over the decades. The advantages of epioptic techniques involving electromagnetic radiation over conventional surface spectroscopies are manifold. These techniques can be used in all pressure and temperature ranges, thereby eliminating the need of UHV. The possible material damage, the risk of contamination due to the charge particle beam, such as, electrons and ions can be avoided [65]. The electromagnetic radiation in or around the visible spectrum has high penetration depth for many materials and oxide layers, making them effective investigative tools for buried interfaces, especially when they are under optically transparent surface layers. Therefore the optical techniques are suitable tools to study all kind of interfaces including solid/liquid interfaces whilst under electrochemical control.

1.5 Linear optical techniques

The two successful linear optical techniques for surface/interface studies are spectroscopic ellipsometry (SE) and reflectance difference/anisotropy spectroscopy (RDS/RAS) and they are based on the measurements of the changes that occur when polarised electromagnetic waves reflects from an interface.

1.5.1 Spectroscopic ellipsometry (SE)

Spectroscopic ellipsometry (SE) uses the polarisation properties of light. When a beam of plane polarised light is reflected from a surface, upon reflection the light undergoes changes in phase and in the amplitude of electric and magnetic components. While the incident plane polarised light is reflected with difference in phase, it carries important information about the incident surface. The technique measures the transmission, T ; reflection, R ; and the ratio of the complex reflection coefficient, ρ as expressed in *Fresnel's equations*, for the p -polarised and s -polarised radiation to the sample surface, where the p -polarisation has the electric field vector in the plane of incidence and the s -polarisation has the vector normal to the plane of incidence.

As in Fig. 1.12, a beam of light is incident on a sample at an angle of incidence θ_i which is the angle between the input beam direction and the direction normal to the sample surface. At the solid/air interface the light will be partly reflected at angle θ_r and partly transmitted through the sample at an angle of θ_t . According to *Snell's law*, the incident, reflected and transmitted beams should be on the same plane. Therefore over a wavelength range, the reflection and transmission ratios respectively are-

$$R = \frac{I_r}{I_i} \quad (1.43)$$

and

$$T = \frac{I_t}{I_i} \quad (1.44)$$

where the I_i , I_r , and I_t are the intensity of the incident, reflected, and transmitted light respectively. It has been mentioned that ellipsometry measures the change in polarisation state of the reflected light from the surface of the sample.

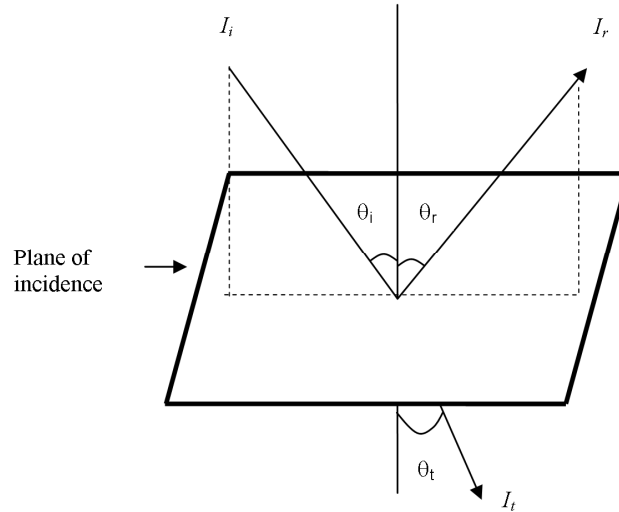


Figure 1.12 A schematic diagram showing the incident, reflected, and transmitted light and the angles they make at the surface under study, θ_i , θ_r and θ_t with the normal direction respectively in an ellipsometry experiment.

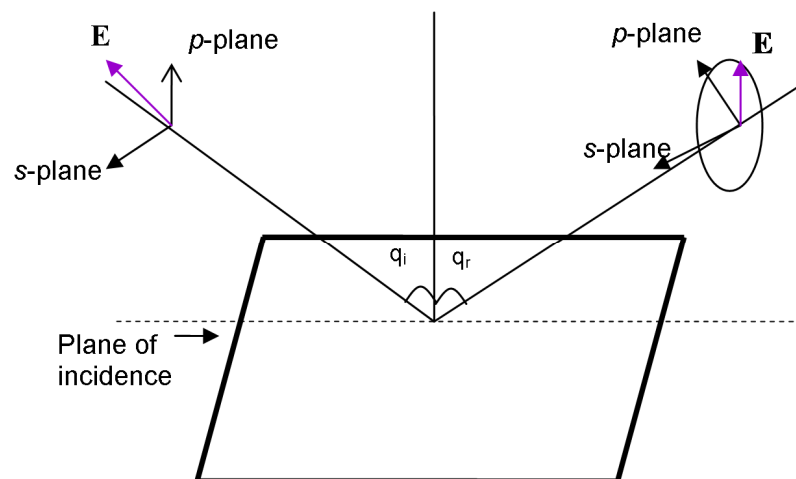


Figure 1.13 A schematic diagram of ellipsometry experiment showing the conversion of polarisation state (linear) of incident beam to the polarisation state of (elliptical) reflected beam (adapted from Ref. [67]).

The complex reflection coefficient, ρ is defined by the following equation [68]:

$$\rho = \frac{R_p}{R_s} = \tan \Psi \exp i\Delta \quad (1.45)$$

where R_p and R_s are the complex reflection coefficients of the polarised light parallel and perpendicular to the incident plane, respectively. Eq. (1.45) contains the phase information in the capital delta, “ Δ ”, and hence the ratio, ρ is a complex number. The Fig. 1.13 shows how a linearly incident beam converts to an elliptically polarised beam upon reflection on the sample surface. When the angle of incidence, θ_i is $0 < \theta_i < 90$, the Fig. 1.13 shows that the p -polarised light and s -polarised light will be reflected differently.

Spectroscopic ellipsometry (SE) is an *in situ* technique and it can complement electrochemical studies of surfaces and interfaces. SE is surface sensitive which makes it suitable for characterisation of oxide thickness at electrodes [69] and thin films [70] and their refractive indices. SE measures the dielectric constant of materials over a spectral range. Therefore the technique can be used for the determination of strain and composition, optical properties of oxide [71] and depth profiling of semiconductor samples and multilayer system [72, 73]. When this technique is repeated on different wavelengths with variable angles, it can provide valuable information.

1.5.2 Reflectance difference/anisotropy spectroscopy (RDS/RAS)

Reflection difference/anisotropy spectroscopy (RDS/RAS) is another linear optical technique for probing surfaces and interfaces in which the change in polarisation of reflected light from a material is measured. Linearly polarised light is incident upon the surface at near-normal incidence, such that the state of polarisation is at 45° to the two orthogonal directions of the sample. RDS/RAS measures the difference in reflection along these two directions and is expressed in the following way [74]-

$$\frac{\Delta r}{r} = \frac{2(r_x - r_y)}{(r_x + r_y)} \quad (1.46)$$

where $\frac{\Delta r}{r}$ is the complex reflectance anisotropy, and r_x and r_y are the complex Fresnel reflection coefficients. When the material under probe has a cubic crystal structure the bulk linear optical response to normal or near normal incidence light will be isotropic. Therefore for the same material with the same geometry, theoretically anisotropic reflectance can only arise from the anisotropy in the surface region or due to nonlinear effects [75]. That means observed reflectance anisotropy of cubic materials is usually attributed to the surface.

RDS/RAS has become an important surface and interface science technique and has been applied to the study of metal surfaces both in UHV and in air [74]. RAS can be applied to measure anisotropy in many systems but vast majority of works involving RAS have used it for probing anisotropy of single crystal surfaces [74]. RAS also has been applied for the studies of the metal/liquid interfaces and adsorption of organic molecules onto noble metal surfaces [76].

Despite the above mentioned advantage of the technique of ellipsometry and RDS/RAS, the functionality of these techniques is optical power density-limited and hence its sensitivity is poor at monolayer and sub-monolayer regime. Recently there has been dramatic increase of interest in *nonlinear* optical techniques as methods for studying electrochemical interfaces. While the above linear optical tools have widely been used to study surfaces and interfaces and electrified interfaces, yet some nonlinear optical techniques are intrinsically surface sensitive and surface specific and they are increasingly being used in all aspects of surface science; optical second harmonic generation (SHG) is an example of these techniques.

1.6 Nonlinear optical technique: second harmonic generation (SHG)

This section introduces optical second harmonic generation (SHG). A brief account of the principles of non-linear optics and optical second harmonic generation are presented here.

1.6.1 Introduction to nonlinear optics

Before the discovery of laser (Light Amplification by Stimulated Emission of Radiation) in the early 1960's [77], mathematical formulae with linear features were used to interpret optical phenomena, for example, refraction, reflection, or dispersion. Prior to the introduction of laser, optical phenomena were measured at relatively low incident electric fields; as such they were well described by linear optics. In conventional sources, the incident light has sufficiently low electric fields that the magnitude was low compared to the fields experienced by electrons in atoms. Classically, electrons in the constituent atoms of a medium respond linearly to the electromagnetic radiation, and the induced polarisation is proportional to the electric field of the radiation. But if a force is large enough, such that the applied field

strength E is of the order of the atomic electric field strength, $E_{at} = \frac{e}{a_0^2}$, where $-e$ is the charge of the

electron, and $a_0 = \hbar^2/(m_e e^2)$ is the Bohr radius of hydrogen atom, $\hbar$ is Planck's constant divided by 2π , and m_e is the mass of the electron; it may be possible to induce nonlinear response on the electrons [77, 78]. When in an atom or a molecule, an electron or a valence electron is bound to the core, and then if a large force is applied, the system will be driven beyond the linear harmonic response into a nonlinear, anharmonic regime. Following equation describes the motion of a damped anharmonic oscillator [78]-

$$\frac{d^2 \mathbf{x}(t)}{dt^2} + \Gamma \frac{d\mathbf{x}(t)}{dt} + \omega_0^2 \mathbf{x}(t) + D\mathbf{x}^2(t) = -\frac{e}{m} \mathbf{E} \quad (1.47)$$

where $\mathbf{x}(t)$ is the displacement from the equilibrium position, t is the time, Γ is the damping factor, $D\mathbf{x}^2(t)$ is the anharmonic term, $-e$ is the charge of an electron, m is the mass of the electron, and $\mathbf{E}$ is the electric field.

Fig. 1.14 below shows the polarisation effect in a linear dielectric (Fig. 1.14a) and, in a medium that lacks inversion symmetry in (Fig. 1.14b) [79]. Under electromagnetic light field, the polarisation has linear dependence on the applied optical field whereas when the applied electromagnetic field is strong enough that it can comparable to that of atomic electric field, then the resulting polarisation has nonlinear dependence on the applied optical field.

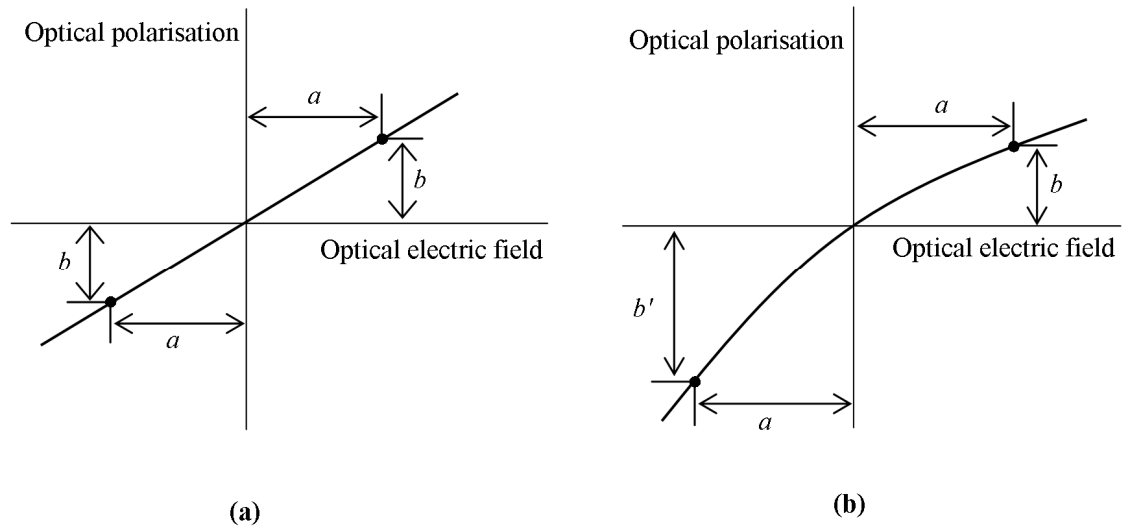


Figure 1.14 Relation between induced polarisation and the electric field that induces it, (a) in a linear dielectric and (b) in a crystal lacking inversion symmetry [79]

In order to drive the valence electrons of the constituent atoms into the nonlinear regime, light of high intensity is necessary. In the absence of a laser, it was not possible to see how the nonlinear optical properties of a medium depended on the intensity of the incident electromagnetic radiation as the high and ultra high intensity regime could not be experimentally obtained.

1.6.2 Nonlinear polarization

Classically, the electrical polarization vector, $\mathbf{P}$ of a given medium is assumed to be linearly proportional to the electric field strength of an incident electromagnetic wave,

$$\mathbf{P} = \varepsilon_0 \chi \mathbf{E} \quad (1.48)$$

where ε_0 is free space permittivity and χ is the susceptibility of the medium. That means χ is the measure of how easily the medium polarizes and to what extent in response to an electric field, $\mathbf{E}$. The linear electric susceptibility, χ is constant for a medium and is independent of the electric field, $\mathbf{E}$, and its magnitude is a function of the frequency of the applied radiation.

Within the formalism of a linear approximation, it is not possible to generate any new frequency through coupling of two or more optical waves of different frequencies. Although experimental nonlinear phenomena had not been seen until the laser was invented, theoretical effort had described what might happen [80]. The observation of second harmonic generation (SHG) at an optical frequency was first achieved in 1961 [81] which was an important contribution in the development of experimental nonlinear optics.

The observation of second harmonic generation in 1961 by Franken *et al.* [81] was followed almost immediately by several other coherent optical mixing effects such as, third harmonic generation (THG) [82], optical sum frequency generation (SFG) [83], optical difference frequency generation (DFG) [84, 85]. These experimental findings verified the validity of nonlinear polarisation theories [86].

A more general formalism for the electrical polarisation can be expressed as shown below to take these phenomena into account.

$$\mathbf{P} = \varepsilon_0 [\chi^{(1)} \mathbf{E} + \chi^{(2)} \mathbf{E}\mathbf{E} + \chi^{(3)} \mathbf{E}\mathbf{E}\mathbf{E} + \dots] \quad (1.49)$$

Here, $\chi^{(1)}$, $\chi^{(2)}$, and $\chi^{(3)}$ respectively are the first order linear, the second order nonlinear, and the third order nonlinear susceptibility.

In linear isotropic media under relatively low electric field strength the first term of Eq. (1.49) is dominant but the contribution to the polarisation from the higher order terms becomes significant at higher field strength. The implication of Eq. (1.49) can be further explored when incident radiation is expressed in the following form

$$\mathbf{E} = \mathbf{E}_0 \sin \omega t \quad (1.50)$$

By incorporating Eq. (1.50) into Eq. (1.49) we get the following-

$$\mathbf{P} = \varepsilon_0 \chi^{(1)} \mathbf{E}_0 \sin \omega t + \varepsilon_0 \chi^{(2)} \mathbf{E}_0^2 \sin^2 \omega t + \varepsilon_0 \chi^{(3)} \mathbf{E}_0^3 \sin^3 \omega t + \dots \quad (1.51)$$

Now for convenience we introduce *sine law* for $\sin^2 \omega t$ and replace θ with ωt and get the following relation-

$$\sin^2 \omega t = \frac{1 - \cos 2\omega t}{2} \quad (1.52)$$

Using Eq. (1.52) and corresponding formula for $\sin^3 \omega t$ into Eq. (1.51) we get

$$\mathbf{P} = \varepsilon_0 \chi^{(1)} \mathbf{E}_0 \sin \omega t + \frac{\varepsilon_0 \chi^{(2)}}{2} \mathbf{E}_0^2 (1 - \cos 2\omega t) + \frac{\varepsilon_0 \chi^{(3)}}{4} \mathbf{E}_0^3 (3 \sin \omega t - \sin 3\omega t) + \dots \quad (1.53)$$

Here we see that the polarisation can be expressed in terms of linear and higher order nonlinear susceptibilities. The second order, $\chi^{(2)}$ and the third order, $\chi^{(3)}$ nonlinear susceptibilities, induced in the medium, give rise to the higher frequencies associated with the incident radiation. For more rigorous theoretical treatment of the physical origin of nonlinear polarisation, readers may refer to the textbooks by Bloembergen [87], Shen [88], Yariv [89] or Boyd [90].

1.6.3 Optical second harmonic generation

Optical SHG is a special case of sum frequency generation (SFG) where the fundamental wave with frequency, ω is incident on a nonlinear medium and creates a new coherent wave at the SH frequency of 2ω . SHG can be described in terms of three-wave mixing where two monochromatic coherent optical waves with frequency, ω_1 and ω_2 interact with a third wave with frequency, ω_3 .

$$\omega_1 + \omega_2 = \omega_3 \quad (1.54)$$

From Eq. (1.49) the second order nonlinear polarisation can be written as

$$\mathbf{P}^{(2)}(2\omega) = \varepsilon_0 \chi^{(2)}(\omega, \omega) \mathbf{E}(\omega) \mathbf{E}(\omega). \quad (1.55)$$

Here $\mathbf{E}(\omega)$ is the incident fundamental optical field, and $\chi^{(2)}(\omega, \omega)$ is the second order nonlinear susceptibility tensor of a medium for SHG.

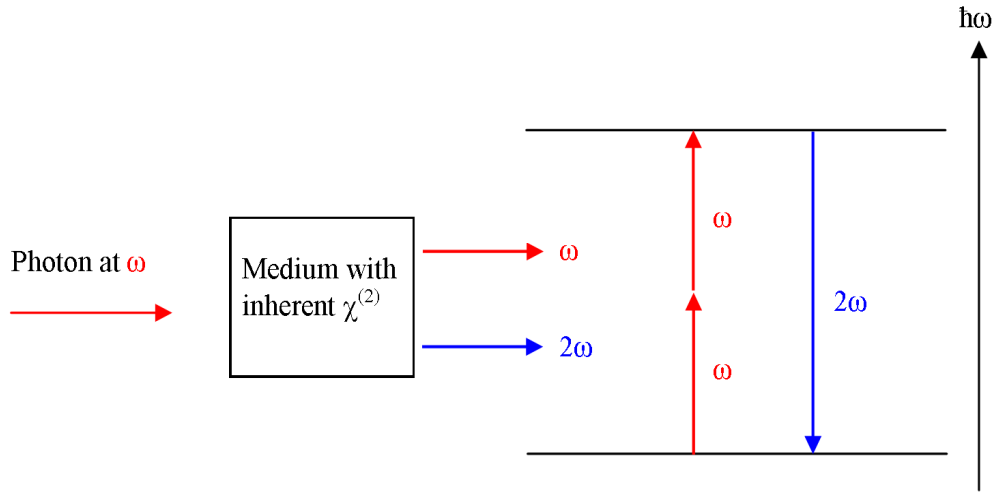


Figure 1.15 Schematic representation of the SHG process. Radiation of frequency ω generates a nonlinear polarisation in the material that has inherent nonlinear susceptibility and then re-radiate at a frequency of 2ω [88, 90].

Fig. 1.15 illustrates the energy level diagram in terms of photons that is in agreement with the conservation of energy. The elementary process of SHG is made of two stages as shown in Fig. 1.15. Under the influence of an intense optical field, two photons of fundamental wave at ω collapse and radiate a photon with twice the frequency, 2ω of initial photons. These semi-classical processes happen simultaneously in a single instant. In the process, energy and momentum of the system are conserved,

$$2\hbar\omega = \hbar(2\omega) \quad (1.56)$$

$$\text{and} \quad \hbar k^{(2\omega)} = 2\hbar k^{(\omega)} \quad (1.57)$$

here $\mathbf{k}$ is the wave vector, and $\hbar$ is Planck constant over 2π . Eq. (1.56) and (1.57) imply that when a fraction of the incident beam is converted into SH photons upon incident, the momentum and energy are conserved.

1.6.4 Nonlinear susceptibility and symmetry consideration

The nature of the susceptibility tensor of the medium depends on the symmetry of the medium, and the magnitude of each tensor element depends upon the chemical constitution and structure of the medium. In the dipole approximation the even order terms of Eq. (1.49) vanish for centrosymmetric media, e.g. Pt, Au, or Si. For centrosymmetric materials possessing inversion symmetry, the crystal structure remains unchanged upon inversion operation, $\mathbf{x} \rightarrow -\mathbf{x}$ [91]. For all centrosymmetric crystals the second order nonlinear polarisation, $\mathbf{P}_i^{2\omega}$ is given by

$$\mathbf{P}_i^{2\omega} = \chi_{ijk}^{(2)} \mathbf{E}_j^\omega \mathbf{E}_k^\omega \quad (1.58)$$

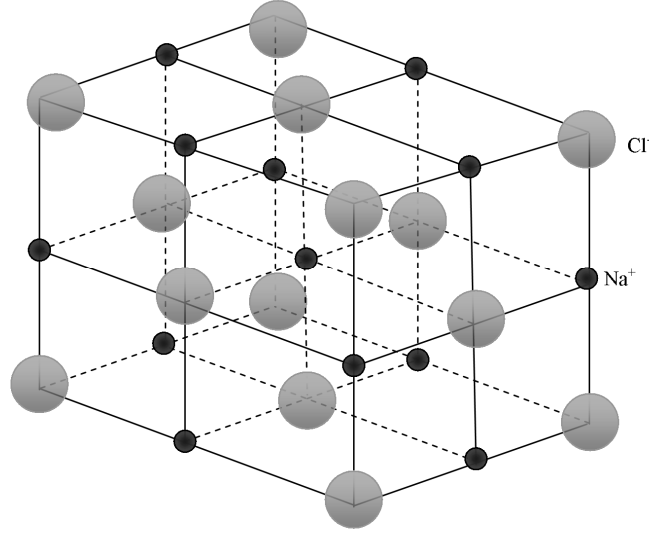


Figure 1.16 The face centred cubic (fcc) crystal structure of NaCl with one Cl^- ion sitting at $(0,0,0)$ and one Na^+ ion sitting at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The crystal is centrosymmetric, since an inversion of any ion about the central Na^+ ion leaves the crystal structure unchanged [89].

If the direction of the electric field is reversed then in Eq. (1.58), $\mathbf{E}_j^\omega$ becomes $-\mathbf{E}_j^\omega$, and $\mathbf{E}_k^\omega$ becomes $-\mathbf{E}_k^\omega$. As the crystal is centrosymmetric, the reverse electric field sees a crystal similar to the original one; the polarisation induced by it, $-\mathbf{P}_i^{2\omega}$ also must be of the same relationship to the original electric field. Therefore upon inversion operation Eq. (1.58) becomes-

$$-\mathbf{P}_i^{2\omega} = \chi_{ijk}^{(2)} (-\mathbf{E}_j^\omega)(-\mathbf{E}_k^\omega) \quad (1.59)$$

Now Eq. (1.58) and (1.59) can hold simultaneously if only the coefficient $\chi_{ijk}^{(2)}$ is zero. So it can be said that for crystals possessing inversion symmetry there is no second harmonic generation (SHG). In the crystal structure of NaCl as depicted in the Fig. 1.16, we see that the inversion of any ion about any neighbouring ion leaves the crystal unchanged.

In the limit of an electric dipole approximation, all centrosymmetric crystals and isotropic media, all tensor elements of even-order susceptibilities must be zero. SHG will not be seen in these kinds of media. However, in the vicinity where the inversion symmetry is broken, like surfaces and interfaces even-order terms will contribute towards the nonlinear response.

1.6.5 SHG as a surface probe

Under the electric dipole approximation, SHG is forbidden in the bulk of a centrosymmetric medium. Due to the large penetration depth of visible optical radiation into the bulk of the matter, magnetic dipole [92, 93] and higher order electric and magnetic multipole [94] terms from the bulk of the materials may contribute to the nonlinear response of the medium. But in general, the bulk quadrupole contributions to the nonlinear polarisation are negligible compared to that of surface dipole contributions. To study surface or interface of materials that have low nonlinear optical response from surface dipole polarisation, such as Si [94], bulk quadrupole contributions need to be considered. Therefore, it can be inferred that in the absence of an external electric field, the SHG response in centrosymmetric media is mainly due to surface electric dipoles for most materials. Under the electrical dipole approximation for the surface polarisation at the SH frequency is

$$\mathbf{P}_{sd,i}^{2\omega} = \chi_{ijk}^{(2),sd} \mathbf{E}_j^\omega \mathbf{E}_k^\omega \quad (1.60)$$

where $\chi_{ijk}^{(2),sd}$ is the surface dipole susceptibilities and $\mathbf{E}_j^\omega$ and $\mathbf{E}_k^\omega$ are the fundamental beam's electric fields in the j and k directions.

The second order nonlinearity mainly arises from the surface and/or interfaces where inversion symmetry is broken by the structural discontinuity of crystal lattice. SHG derives its sensitivity from the discontinuity of the electric field oriented normal to the surface [95, 96]. These types of discontinuities take place over the vicinity of few atomic layers and they give rise to the nonlinearity of polarisation [97]. The induced nonlinear polarisation from the surfaces and interfaces can be expressed in terms of an effective susceptibility, $\chi_{sd,ijk}^{(2),eff}$ as [98]-

$$\mathbf{P}_{sd,i}^{2\omega}(\mathbf{r}) = \chi_{sd,ijk}^{(2),eff} \mathbf{E}_j^\omega(\mathbf{r}) \mathbf{E}_k^\omega(\mathbf{r}) \delta(z - \xi) \quad (1.61)$$

In Eq. (1.61) the new term, $\delta(z - \xi)$ denotes an infinitesimally thin sheet of polarisation at an atomic scale distance, ξ [99, 100], such that $z - \xi$ approaches z , which is the distance measured normal to the surface. Fig. 1.17 illustrates the incidence of a fundamental beam on the surface of a material and reflecting, which induces a nonlinear polarisation on the electrons within the infinitesimally thin region of thickness, ξ .

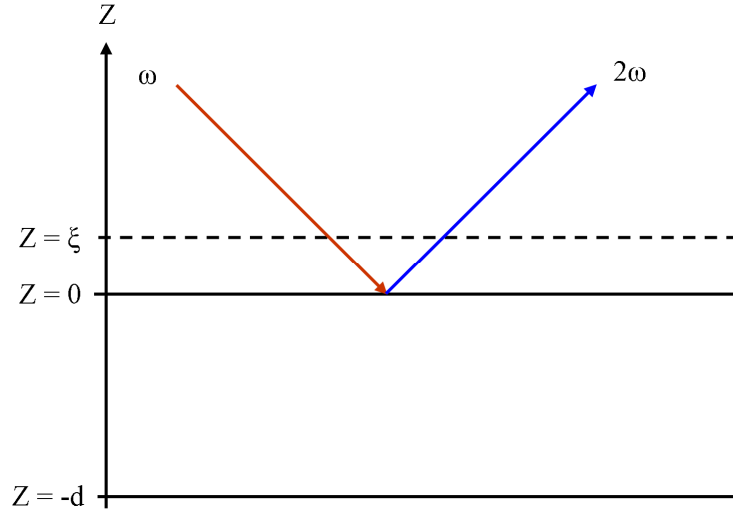


Figure 1.17 Schematic representation of SHG experimental geometry on a sample with thickness, d and an infinitesimally thin sheet of polarisation at a distance of ξ from the surface from which all surface and interface dipole contributions to SH originate. Z is the distance measured normal to the surface.

For SHG to be useful as a surface probe, the surface contribution has to be either dominant or deducible from the measurements. In usual reflection measurements the only entity one gets is $\chi_{ijk}^{(2),eff}$ and the contributions come from $\chi_{ijk}^{(2),sd}$. For a given material system there can be difficulties in distinguishing the surface contribution from the bulk or vice versa. It has however been largely possible to separate the surface and bulk contribution to the total SHG signal by rotating the sample under study and using different single crystals [94] and by comparing the measured s -polarised SH signal from Si(111) and Si(100) surface with a p -polarised excitation [101].

1.6.6 Electric-field induced second harmonic (EFISH) generation

In the previous sections of this chapter it has been understood that in the absence of an external electric field, SHG in the centrosymmetric media, such as Si and most metals, is due to surface/interface dipole and bulk quadrupole contributions [102, 103]. For centrosymmetric media, SHG is sensitive to dc electric fields as they break inversion symmetry permitting bulk dipole contribution to SHG. This applied electric field can enhance the nonlinear optical signal and it is termed as electric field induced second harmonic (EFISH) generation.

If a dc electric field is incorporated into the description of SHG, then one can think of three fields interacting and giving rise to the fourth one, which is observed by SHG. There needs to be a third order

nonlinear tensor inducing a polarisation strictly oriented in the normal direction to the surface of the media. This third order nonlinear tensor is $\chi^{(3)}$ and can be denoted as $\chi_{ijkl}^{(3),bd}$ and the resultant EFISH contribution to the SH polarisation is-

$$\mathbf{P}_{bd,i}^{2\omega} = \chi_{ijkl}^{(3),bd} \mathbf{E}_j^\omega \mathbf{E}_k^\omega \mathbf{E}_l^{dc} \quad (1.62)$$

where $\mathbf{P}_{bd,i}^{(2\omega)}$ is bulk dipole polarisation, $\mathbf{E}_j^\omega$ and $\mathbf{E}_k^\omega$ are the fundamental beam electric fields, and $\mathbf{E}_l^{dc}$ is the local dc electric field.

For the total reflected SH fields generated at the face of a centrosymmetric crystal we combine effective surface dipole (Eq. (1.61)) and EFISH contributed bulk dipole (Eq. (1.62)) and we get the following

$$\begin{aligned} \mathbf{P}_i^{(2\omega)} &= \mathbf{P}_{sd,i}^{(2\omega)}(\mathbf{r}) + \mathbf{P}_{bd,i}^{(2\omega)} \\ &= \chi_{sd,ijk}^{(2),eff} \mathbf{E}_j^\omega(\mathbf{r}) \mathbf{E}_k^\omega(\mathbf{r}) \delta(z - \xi) + \chi_{ijkl}^{(3),bd} \mathbf{E}_j^\omega \mathbf{E}_k^\omega \mathbf{E}_l^{dc} \end{aligned} \quad (1.63)$$

Eq. (1.63) can be further simplified as-

$$P(2\omega) = \chi^{(2)} E(\omega) E(\omega) + \chi^{(3)} E(\omega) E(\omega) E^{dc} \quad (1.64)$$

The third order term governed by the third order nonlinear susceptibility tensor ($\chi_{ijkl}^{(3),bd}$) in the above Eq. (1.63) is dependent on the dc electric field between the bulk medium (i.e., electrodes) and the overlayer or electrolyte. Although in general, $\chi_{ijkl}^{(3),bd}$ values are smaller than χ^2 values, they can be significant as the dc electric field gradient varies with applied potential. An applied dc electric field causes charge redistribution and thus a varying charge density exists at the interface.

The intensity of the fundamental optical radiation I^ω and the intensity at the second harmonic wavelength $I^{2\omega}$ are related via nonlinear susceptibilities and can be expressed as-

$$I^{(2\omega)}(t) = \left| \chi^{(2)} + \chi^{(3)} E^{dc}(t) \right|^2 (I^\omega)^2 \quad (1.65)$$

where $\chi^{(2)}$ counts for all the surface susceptibilities and $\chi^{(3)}$ is the effective third order nonlinearity arising from the quasi-static field that includes all terms that vary linearly with field strength [104]. It is possible to monitor the changes in local electric field at least qualitatively by simultaneously running cyclic voltammogram and SH spectroscopy experiment in the specially constructed spectro-electrochemical cell.

1.6.7 Nonlinear susceptibility at an interface- generation of SHG

The region of the interface, where SHG is allowed, is also the region precisely where electrochemical processes occur. When adsorption or desorption of the ions and neutrals takes place at the electrode, it alters the nonlinear susceptibility of the surface, $\chi_s^{(2)}$ and as a result SHG response is altered. Ions and other molecules may possess an inherent nonlinear susceptibility themselves, they can also interact with the surface through the formation of bonds or through acceptance or donation of charges, and all these interactions and their effects lead to a change in the nonlinear susceptibility of the surface, ($\chi_s^{(2)}$) which contributes to $\chi_{AS}^{(2)}$ which is the nonlinear susceptibility of the surface in presence of adsorbates and can be represented as-

$$\chi_{AS}^{(2)} = \chi_s^{(2)} + \chi_A^{(2)} + \Delta\chi_I^{(2)} \quad (1.66)$$

where $\chi_A^{(2)}$ is the nonlinear susceptibility of the surface adsorbates and, $\Delta\chi_I^{(2)}$ reflects the effects of the interaction between $\chi_s^{(2)}$ and $\chi_A^{(2)}$. The situation can be made more complex by the application of a dc electric field. Application of this dc electric field gives an extra dimension of the technique of SHG is termed as EFISH, which has been explained in the preceding section.

Besides EFISH there are other processes which are responsible and contribute to the overall SHG response in a system. When a metal electrode surface undergoes electrochemical changes, SHG signals are affected. Electrochemical oxide formation and reduction significantly change the surface of electrodes with a possible variety of oxide layered structures which are bound to influence SHG intensity. In the potential range of the double layer region of the cyclic voltammogram of an electrode, no faradaic current is passed; that means no oxidation or reduction process takes place; as a result the SHG intensity might be only from ionic adsorption or surface electrons. The SHG response may yet originate from the metal electrode due to the inherent nonlinear optical characteristics of the medium.

Another important contribution to SHG may arise from surface plasmon resonance. Surface plasmons are electromagnetic waves that propagate at the interface between metal and a dielectric and are characterised by the electric and magnetic field that exponentially decay on each side of the interface. These fields, and hence the optical response of the interface, are very sensitive to small changes in the dielectric properties of the region close to the interface [105]. Because the surface plasmon polariton is resonantly excited, and there may also be substantial field enhancement at the interface. The excitation of surface plasmons causes a sharp minimum in the *reflectivity-angle of incidence* curve, the shape of which is sensitive to the optical constants and the components of the interface [106]. Surface plasmon spectroscopy has also been used to study double layer effects and adsorption [107, 108]. In the absence of any oxidation or reduction process in the double layer region of the cyclic voltammogram of metal electrode, such as Au, the SH response can be influenced by the presence of surface plasmons.

1.7 SHG as a nonlinear optical technique for surface and interface studies

1.7.1 Introduction

This section describes the origin and the development of nonlinear optical techniques and how SHG from its first discovery in 1960's [81] has become an established technique to study the surfaces and interfaces today. The phenomenon of SHG was observed only after the invention of laser even though the prediction of it dates back to 1931, when it was reported in a paper by Goppert-Mayer on optical wave mixing [80]. Before the invention of laser any electromagnetic radiation sources were not intense enough to generate nonlinear response.

The first ever observation of SHG was done by Franken *et al.* [81] in 1961 by allowing 694.2 nm ruby laser through quartz crystal and measuring SH response at 347.1 nm on a photographic plate. This demonstration of the nonlinear optical phenomenon was followed by a surge of research which mainly concentrated in the theoretical understanding of nonlinear optics [83, 109]. Apart from research in theoretical understanding of second harmonic generation (SHG) in the 1970's, no significant progress was made that would help realise the full potential of the technique. In 1967, Electric field induced SH (EFISH) was discovered by Bloembergen and co-workers [110]. Their initial studies of the nonlinear response from Ag and Si demonstrated a strong variation when a dc electric field was applied. But the demonstration of enhancement of nonlinear susceptibility induced by the presence of surface plasmon resonance (SPR) was also an important finding of the decade by Simon *et al.* [90].

In the 1980's, the pioneering works by Sipe's group [100, 112] put forward a more thorough macroscopic theory for anisotropic second- and third-harmonics, obtained in reflection from the surface and bulk cubic centrosymmetric single crystals. This was followed by the work of Shen's group at UC Berkley [88, 113, 114] who suggested that the effective nonlinear susceptibility of a medium is the result of the combined susceptibilities of surface electric dipole and bulk quadrupole moment. These studies demonstrated the true potential of nonlinear optics for the investigation of surfaces and interfaces.

The fast pace growth of the field of nonlinear optical studies in the late 1980's onward is mainly due to the development of smart laser systems such as tuneable pulsed dye-laser system and tuneable Ti-Sapphire lasers. Whereas earlier studies were carried out using low repetition rate laser sources, such as YAG lasers with high pulse energies and nanosecond pulses, today's laser systems offer reliable and widely tuneable lasers with high repetition rate and femtosecond pulses. Therefore single wavelength and steady state studies with long data acquisition time have been replaced by spectroscopic studies with dynamics over a much shorter timescale and enhanced signal to noise ratio, and hence much shorter recording time. Thanks to the development of these advanced instrumentations, SHG has become a versatile tool to study physical, chemical and biological phenomena at surfaces and interfaces.

Nonlinear optical studies of surfaces and interfaces have grown steadily over the last 4 decades and today, the field of nonlinear optical studies of surfaces and interfaces present a vast area of research. Presenting a comprehensive historical preview of SHG work to date is beyond the scope and capacity of this project. There are several review papers on the nonlinear optical techniques and their applications in the research of surfaces and interfaces of semiconductors [99], metal electrodes [93, 115, 116] and biological samples [117] are available. However, the main focus of the remaining part of this chapter is on the development of SHG as a probe of the metal/solution interface whilst under electrochemical control, especially oxide formation and reduction at Cu and Au electrodes.

1.7.2 Electrochemical and second harmonic generation (SHG) studies of Cu

Due to its good thermal and electrical conductivity, Cu is one of the important metals and has been used in different industrial and technological applications. The oxidation of Cu is a much studied process as knowledge of the corrosion and passivation behaviour of the metal is of great importance. Cu also plays an important role in the recent development of chip design in the microelectronics industry and it is replacing Al as a conductor of choice in transistor systems [118, 119]. Recently Cu or Cu oxide thin films also drawing interests [120] and a recent study reported the demonstration of electrochromism from a Cu oxide thin film [121]. Electrochemical methods are applied to construct nanostructured Cu/Cu₂O multilayer structures which help demonstrate quantum confinement phenomenon [122].

It is widely accepted that in alkaline solutions when Cu is electrochemically oxidised a passivation layer is built from the Cu₂O structure over which an outer film constitute a CuO/Cu(OH)₂ structure [6, 8, 12, 17]. In agreement with the thermodynamic calculations of the Pourbaix diagrams, these structures are formed depending on solution pH, applied potential and polarisation time [12, 14, 16]. The formation processes of these structure can also be accompanied by the production of soluble species, such as Cu(I)- and Cu(II)-oxides [11, 14] and the solubility of these species depends on the pH and chemical composition of the electrolyte. The electrochemical behaviour of Cu has been extensively studied in moderate alkaline media, such as, carbonate-bicarbonate buffer [13, 14, 123, 124], borax buffer solution [8, 14, 17], and also in phosphate buffer [8], and acetate [125] but to a lesser degree. In order to understand the complex nature of the structure of Cu/Cu₂O and Cu/CuO interface, electrochemists had to look beyond the mechanistic studies of Cu oxidation by potentiodynamic and potentiostatic techniques.

In acidic solution the dissolution of the oxides is considerably fast such that it cannot provide any passivity. The growth and composition of the oxide films formed at higher pH have been investigated qualitatively and quantitatively by electrochemical methods and complemented by surface analytical methods, such as X-ray photoelectron spectroscopy (XPS) [8, 105], ion scattering spectroscopy [8], *in situ* Raman [127] and infrared [128] spectroscopy. The structure of the oxide layers has been investigated recently by scanning tunnelling microscopy (STM) [16, 129] and electrochemical atomic force microscopy (AFM) [130].

After the first ever electrochemical study on Cu by Muller [131], there have been several studies on electrochemical behaviour of Cu by Armstrong et al. [132, 133], Fleischmann [134], Dignam [5] and Ambrose [135] with some success in explaining the mechanism of Cu_2O and CuO formation but no clear distinction was made between Cu dissolution, surface reaction or passivation. Some reaction mechanisms were proposed but due to the absence of any structural data, especially as far as formation of surface Cu(II) oxide is concerned, the analysis remained tentative.

In 1976 Shoesmith *et al.* [6] investigated anodic oxidation of Cu in LiOH solution. Their galvanostatic and potentiostatic techniques were complemented by X-ray electron diffraction (XRD) and scanning electron microscopy (SEM). They proposed that when Cu is electrochemically oxidised, initially a layer of Cu_2O was formed but at higher potential thermodynamically stable CuO was formed and that was followed by formation of Cu(OH)_2 layers, of which base layer was grown by solid-state mechanism and an upper layer crystals nucleated and grown from solution. The studies by Strehblow *et al.* [8] on the passive behaviour of Cu in weakly acid and alkaline solution, and examination of the passive film by electron spectroscopy for chemical analysis (ESCA) and ion scattering spectroscopy (ISS) clarified the findings by Shoesmith. The studies by Strehblow found that when Cu cyclic voltammetry carried out in weakly alkaline buffer solution (borax buffer), the voltammogram shows two clear and well separated anodic and cathodic current peaks. The size and breadth of the peaks depend on the pH and the electrolyte composition.

From the ESCA and ISS data Strehblow's study further explained the hysteresis in the voltammogram and the growth mechanism and thickness of the oxide layers. Initially Cu_2O forms on Cu surface leading to the first oxidation peak, then when CuO/Cu(OH)_2 formed on top of it. The formation of CuO and/or Cu(OH)_2 disturbs the structure of underlying Cu_2O , so that it no longer can work as migration barrier of the Cu ions. However CuO reduces the dissolution as anodic oxidation of Cu to Cu(OH)_2 is no longer possible for thermodynamic reasons. This formation and dissolution process of Cu_2O may happen in a faster rate when pH of electrolyte solution is high. It has been noted that the total charge associated with the anodic current peaks is higher than that of associated with the cathodic current peaks, a sign that soluble Cu species are formed during the electrochemical cycle. This deduction is tested by Brisard *et al.* [15]. In their probe beam deflection experiment they found that the probe beam deflects close to the electrode-electrolyte interface due to the concentration gradient of the dissolved species from Cu electrode. Some of the ESCA studies suggest that the formation of the duplex structure of $\text{Cu}_2\text{O/CuO}$ for sufficiently positive potentials just before the oxygen evolutions [17]. For borax buffer the total oxide layer that contains both Cu_2O and CuO/Cu(OH)_2 does not exceed 40 Å [8]. A study by Abrantes *et al.* [10] largely agrees with Strehblow's results on the question of thickness of oxide layers obtained by photocurrent spectra measurements.

There have been numerous studies to determine the potential of zero charge (PZC) of Cu electrode. The PZC data for single crystals of noble metals such as Au, Pt are largely consistent. But the published data on the double layer properties of Cu single crystals in aqueous solution often differ markedly [136]. Some of the earliest studies on Cu electrochemistry reported that the PZC values of Cu was closed to 0 (zero) V

vs SHE [137, 138]. The PZC data found even under the identical experimental conditions differ by more than 0.05 V [139]. Recently, Lukomska *et al* [136] carried out a study on the PZC of Cu poly- and single crystals by impedance spectroscopy methods, in the frequency range of 1-100 Hz. The reported PZC values for (111), (100) and (110), and polycrystalline Cu were -0.70, -0.73, -0.75 and -0.73 V vs SHE respectively in 0.01 M NaClO₄. There are differences in PZC values of Cu as reported by different authors but a dependence of the PZC on electrolyte concentration and their pH is reported widely [136].

Recently, there has been a surge in the research Cu electrochemistry using surface analytical techniques. Due to the wide ranging use of Cu, anodic oxide films and corrosion behaviour of Cu have been studied in both acidic and alkaline media using XPS, SEM and spectroscopy ellipsometry (SE) [126, 129, 140]. Berlouis *et al.* [140] studied electrochemical behaviour of Cu in fluorine containing alkaline solution by SE. They have shown that fluorine ions could affect the growth of the oxide layer and that could in turn enhance the dissolution of Cu as the Cu(II) species occur as a result of stress corrosion cracking. The motivation of such studies is to understand corrosion behaviour and corrosion products for Cu in aqueous solutions of various pH values, from acidic to neutral and neutral to alkaline. One such study is carried out by Feng *et al.* [126]. They have found that corrosion products of Cu (mainly Cu₂O) tend to be porous in acidic medium with no protection for Cu from dissolution; thick and porous in solution with pH between 4 and 5, and in solutions with pH 6 to 9, the Cu oxide film starts to be protective and passivative and becomes spontaneously passivative at solution of pH 10 and above but below pH 13.

Using STM on Cu single crystals, the Marcus research group at *Laboratoire de Physico-Chimie des Surfaces, CNRS-ENSCP*, studied anodic oxide films [129]. The motivation of their research was to study the topographical characterisation of passive oxide layer by electrochemical STM. They reported on their investigation of the anodic Cu(I)/Cu(II) duplex passive layers grown on Cu(111) and Cu(001) in 0.1 M NaOH; the outer Cu(I) species part of the duplex film formed on both substrate is crystalline with terrace and step topography [141]. A granular and amorphous layer covering the crystalline CuO(001) oxide has been observed on Cu(001) but not on Cu(111). They assigned this difference to a film of Cu hydroxide, a corrosion product formed by a dissolution-precipitation mechanism. The absence of it on the passivated Cu(111) surface is explained by the higher stability of the Cu₂O(111) [141].

The interest on the adsorption of hydroxide, hydroxyl groups and ambient oxygen on metal surface such as Cu at room temperature is also growing due to its importance in oxidation, corrosion and protection against corrosion and possibly in electrocatalysis. In view of this, Marcus' group has recently investigated the initial oxidation or *premonolayer oxidation* of Cu in aqueous solution [129, 142]. They have reported *in situ* STM measurements of Cu (111) in 0.1 M NaOH solution and demonstrated that a reversible adsorption/desorption process occurred in the underpotential range of Cu₂O formation [129]. They noticed that the adsorption and desorption processes respectively roughen and smooth the substrate terraces and it occurred simultaneously with the current peaks in the voltammogram [142]. The reversible potential of formation of Cu₂O is -0.675 ± 0.02 V/SHE. In this kind of adsorption/desorption experiments, where a technique with monolayer and submonolayer sensitivity is needed, optical second harmonic generation (SHG) may have advantage over other electron beam techniques.

Second harmonic generation (SHG) is a recognised tool for the investigation of liquid/solid interfaces. Most of the early SHG studies of solid/liquid interfaces focussed on the ion adsorption [1, 143, 144] and surface film formation at metals using rotational anisotropy to examine single crystals and the study of surface reconstruction [2]. In the work of Tom *et al.*, [145], SH was generated in reflection from the Cu(111) single crystal surface using 7 ns pulses of 1060 nm radiation from Nd:YAG. A 3-fold rotational symmetry pattern was observed suggesting anisotropy compatible with the 3m symmetry of the (111) surface. A similar SHG study of Cu(111) was carried out by Shannon *et al.* [75] but the sample was examined under the potential bias in the ideally polarised region (IPR) and under similar electromagnetic radiation. The angular and potential dependence of SHG intensity were measured. They have observed a featureless cyclic voltammogram in the IPR and the same kind of SH response as with the rotational anisotropy study of Tom *et al.* [145]. In both cases the observed rotational anisotropy in SH response for Cu was attributed to the excitation of interband transitions since the energy of SH photons at 530 nm (2.3 eV) is large enough to promote *d*-band electrons into the surface plasmon conduction band. A few more studies were carried out on Cu to investigate the rotational anisotropy. Bradley *et al.* [146] carried out comparative SHG study of Cu(111) in UHV and in solution but no significant change in the rotational anisotropy in SHG response obtained in solution with ambient pressure and with UHV was observed. Koos *et al.* [147] compared the measured azimuthal anisotropy in the SHG response from various crystal faces of Ag, Cu, and Au and found that surface dipole contribution to the (111) anisotropy was at least 3, 4, and 10 times greater than the quadrupole anisotropy for Ag, Cu, and Au, respectively.

The hydrogen evolution reaction on metal surface by which H₂O is broken down electrochemically to form H₂ molecules in aqueous solutions, has always been an area of interest to electrochemists to understand the electrocatalytic properties of a metal [117]. Even though it is more common to study H₂ evolution at noble metals, such as Pt, Au or Pd for their importance in the operation of H₂/O₂ fuel cell, Hewitt *et al.* [148] applied SHG technique to study hydrogen evolution at polycrystalline Cu electrode. They reported that in their combined cyclic voltammetry and SHG experiment, SH signal intensity consistently follow the potential dependence of the current, that is, in going from pH 6.5 to 6.0 and then to pH 5.5, the oxygen evolution current at -1.6 V vs SCE increases but the SH signal decreases. Several explanations have been given for the variation of SH intensity. The variation in SHG intensity could be related to a coverage-induced response in the surface electrons of Cu and/or the bound *d* electrons respond to SH wavelength and are involved in the interband transition to the surface plasmons conduction band. At the same time the free electron density of the surface can be perturbed by partially charged Cu-H_{ad} bonds resulting in a change in the free electron component of the second order nonlinear susceptibility, $\chi^{(2)}$ which in turn may result in coverage-induced variations in the SH intensities [126]. The authors make no distinction between the bound and free electrons as to which electrons play more effective role in determining the optical response of the H_{ad} on Cu.

A study by Nagy *et al.* [149] used SHG to investigate the oxidation and reduction of Cu in aqueous halide electrolyte. In this study cyclic voltammetry was carried out on polycrystalline Cu electrode in Na-halide solutions, and in Na₂SO₄ and NaOH media. The SH response showed a large enhancement during the oxidation process in Na-halide solution. Optically resonant surface species are formed during and after

the Cu surface is oxidised to a certain degree in the halide environment. The authors proposed that these surface species probably associated with small clusters of Cu atoms which might be stabilised by CuX (X: Cl, Br) crystallites. In a previous study Guyot-Sionnest *et al.* [95] has shown that the surface contribution to SHG response is typically more than an order magnitude stronger than the corresponding bulk contribution. It should be noted here that a possible bulk contribution to SH response can be prominent only when a system or process shows strong potential dependence of nonlinear susceptibility due to the bulk dipole, $\chi_{bd}^{(2)}$. Taking these earlier findings into account, Nagy et al [149] drew conclusion for their system that the potential dependent contribution to the SHG response is negligible compared to the nonlinear susceptibility of the surface in presence of adsorbates, $\chi_{AS}^{(2)}$.

The study by Nagy *et al.* [149] further proposed a threshold condition for SH enhancement in terms of amount of oxidation charge necessary to trigger the enhancement. They called this charge “critical” amount of oxidation charges corresponding to this threshold as Q_C . According to the suggestion this critical amount of oxidation products is necessary to thermodynamically stabilize the optically sensitive adsorbates so that the nonlinear response could be seen. No credible explanation was provided in the paper nor any further surface analysis techniques was suggested to verify their speculation. Their suggestion of the “critical” charge also is in contrast to the findings of some earlier studies [75, 145].

There have been some SHG studies on the underpotential deposition (UPD) of foreign metals where Cu has been used as substrate [150] or on Cu thin films grown by underpotential deposition on other materials substrates such as, on Au by Bennahmias *et al.* [151]. These studies are not concerned with oxidation or reduction Cu. Schwab *et al.* [152] studied the intensity of SHG at the Cu (110) surface to determine the relative sizes of the different component of the second order susceptibility tensor that arise from the different faces of the crystal.

Even though the Cu electrochemistry was well understood by the end of 1980 as far as electrochemical oxidation and reduction is concerned, but there were few studies to investigate what kind of SH response can be seen from the oxidation and reduction of Cu at the electrode surface. One of the main reasons of the relative gap in the SH studies of Cu is the absence of smart lasers in the late 1980’s that are available today; the laser systems that are widely tuneable and have high repetition rates and femtosecond pulses. Even after the nonlinear optical technique of SHG became available, SHG studies of electrochemical oxide formation and reduction at Cu electrode surface has largely been overlooked. Our SHG study on Cu will highlight the *in situ* and real time capabilities of the technique and explore its monolayer and sub-monolayer sensitivity.

1.7.3 Electrochemical and second harmonic generation (SHG) Studies of Au

The electro-oxidation of noble metals has been a subject of scientific discussion because they are an ideal system for fundamental investigations in electrochemistry. The oxide growth at noble metals is of interest because it provides a model system in the examination of oxide growth at non-noble transition metals of industrial importance [22]. Because of the fact that dissolution can largely be avoided, the electrochemical studies on Au electrodes help determine important parameters, such as, the composition of the oxide film, its structure and growth mechanism [31]. There have been many studies of oxide formation at Au electrodes. Using potentiostatic and cyclic voltammetry techniques, Au can be oxidised to its Au(II) or Au(III) state, facilitating the formation of first α -oxide, and at higher potentials an overlying thicker β -oxide, respectively. Initially, research on the electrochemical behaviour of Au was to some extent confined to the α -oxide formation and removal, and electric double layer response [18, 19, 31, 153]. But as Au also exhibits an interesting and complex behaviour- the β -oxide formation, and research on its growth conditions, compositions and mechanism, and kinetics are also reported [28, 154].

Despite there being numerous studies on Au surface oxidation, a lively debate goes on, about the phenomenon of commonly occurring Au α -oxide film, AuO and Au(OH)₂ and concerning the nature of β -oxide, Au₂O₃. Previous research on the oxide formation on noble metals, especially Au, shows that the inner layer grows to a limiting thickness of one or several monolayers and the outer layer can grow without reaching a limiting thickness with Au being in a higher oxidation state [19, 20, 23, 28, 154, 155]. The thicker Au β -oxide can be grown potentiostatically at ca 2.00 V vs SHE or above, or by repetitive and fast potential cycling between a lower (1.0 V vs SHE) and an upper potential limit (2.1 V vs SHE) with sweep rate as high as 50 V s⁻¹ [23]. There have been different suggestions for the compositions of Au β -oxides such as Au₂O₃, Au₂O₃·H₂O or Au₂O₃·3H₂O, Au(OH)₃ [28].

Techniques such as *in situ* quartz crystal microbalance (QCMB) and ellipsometry have been used to study the growth of mainly Au α -oxide [28]. A QCMB study of Au α -oxide by Gordon *et al.* [156] in 0.1 M HClO₄ between 0.2 and 1.6 V vs SHE showed a large increase in the mass whilst scanning the positive potential around 0.5 V vs SHE before the oxide film formation, which was attributed due to the adsorption H₂O forming a monolayer Au(OH)₂. Another study by Bruckenstein *et al.* [157] in 0.2 M HClO₄ suggested the mass increase in the positive going scan in the pre-oxide region is due to the specific adsorption of ClO₄⁻. In a another investigation of the system by Stockel *et al.* [158] reported that the specific adsorption of the anions was the reason for the increase in mass in the region.

Ellipsometry also has been used to study premonolayer oxidation and anodically formed oxide films at Au electrode [23, 159, 160, 161]. Horkans *et al.* [138] reported that the α -oxide that is formed in the initial stages of growth at potentials <1.38 V vs SHE is not the same film that is grown at potentials >1.38 V. One of the earliest application of ellipsometry whilst under electrochemical control, Sirohi *et al.* [159] proposed that a chemisorbed species such as, Au(OH)₂ and/or AuO are formed in the potential region of 0.2 – 1.1 V vs SCE with Au₂O₃ formation taking place at more positive potentials. Another study by Tremiliosi-Filho *et al.* [23] observed that the α -oxide reaches a limiting thickness of three monolayers of

AuO or Au(OH)₂ whereas the β -oxide grew on top of the α -oxide film and without any limit. Up to 100 monolayers of β -oxide suggested to be Au₂O₃/Au(OH)₃, were reported to be formed in their work.

Burke *et al.* [21, 162] suggested a whole new theory namely *incipient hydrous oxide/adsorbate mediator* (IHOAM) as the mechanism for the premonolayer oxidation that results in the increase in charge in the pre-oxide region. The concept of premonolayer oxidation assumes the passage of some faradaic current associated with the incipient oxidation of the surface in the double layer region [163]. The theory of IHOAM further assumes no role of dissolved anions except OH⁻ and proposed the presence of β -oxide in the double layer region. No further evidence for the proposed mechanism was provided to verify the claim other than the authors' own.

A recent study Xia *et al.* [28] on the formation and reduction of the α -oxide and the overlying β -oxide films at Au electrode in 0.1 M H₂SO₄ solutions verifies some of the earlier findings [25, 27]. In the study of Au-oxides, Xia *et al.* [28] combined potentiostatic and cyclic voltammetric studies with ellipsometric and QCM techniques. The studies reported that α -oxide films formed both by holding at constant potentials and scanning the potential, are hydrated, even with overlying thick β -oxide layers. The composition of α -oxide films is AuO when grown at potentials below 1.5 V vs RHE, and both AuO and Au₂O₃ at potentials higher than 1.5 V and becoming only Au₂O₃ at very high potentials around ca. 2.1 V vs RHE. When β -oxide film was grown at constant potential it became hydrated with growth time and the ellipsometric data were consistent with the growth of Au₂O₃·H₂O and later with Au₂O₃·2H₂O.

The findings of Xia *et al.* [28] have been supported by a more recent study by Tremiliosi-Filho [31] but proposed that oxide growth follows two distinct laws, not only the inverse logarithmic mechanism as suggested by Xia *et al.* Each one of those two mechanisms arising from different oxide layers- the first is logarithmic growth for the oxide up to 2 monolayers of AuO, and the second is inverse-logarithmic growth for oxides with thickness is in the range of 2-3 monolayers. The logarithmic growth is proposed to be originating from the interfacial place exchange between O_{chem} and the top most Au surface atoms, whereas the inverse logarithmic growth law arises from the fact that the growth is restricted by the number of Au cation from the metal into the oxide at inner metal-oxide interface [31].

Beside the linear optical techniques such as ellipsometry spectroscopy (ES) and reflection anisotropy spectroscopy (RAS), nonlinear optical technique, for example second harmonic generation (SHG) is also being used to study Au surface. The focus of much of the early SHG works on metals was to study the adsorption and desorption processes and surface reconstruction [1, 2, 143, 144]. Au thin films deposited on semiconductor substrates (Si) [164] or on oxides of semiconductor (SiO₂) or other substrates [165] have also been investigated. SHG techniques were used to investigate electrochemical deposition and dissolution processes of catalytic-active metals, such as Pt, Pd, and Ru on inactive noble metal surfaces, such as Au electrode in aqueous solution [166]. The surface chemistry of Au has also seen a renewed interest through the discovery of usefulness of Au nanoparticles in catalysis. Due to the inherent asymmetry, size, and very high surface area, Au nanoparticles are suitable to be studied by surface-enhanced spectroscopy and nonlinear optical techniques, especially SHG.

SHG being sensitive to changes at surface is a suitable technique to study specific adsorption or anionic chemisorptions on noble metals, such as Au and Pt. In absence of any molecular transitions at the incident fundamental or second harmonic wavelengths, the SH intensity from Au or Pt is dominated by the nonlinear susceptibility of the surface metal atoms. Therefore, in the presence of the chemisorbed species on the metal surfaces the SHG signal provides a quantitative measure of surface coverage. Using rotational anisotropy and isotropy on Au single crystals Pettinger *et al.* [2] studied surface processes, namely surface reconstruction on Au(111) whilst the Au electrode held in halide-ion containing electrolytes. The study reports a 3-fold rotational anisotropy of Au(111) for SHG response and C_{3v} symmetry changes to a Cs symmetry as the result of mixture of one- and two-fold symmetry as the electrode is held at various constant potential. Simultaneous SHG and cyclic voltammetry data shows that SHG is responsive to the adsorption and desorption of the halide ions. Campbell *et al.* [143] reported similar results in their works on metals investigating the adsorption of ions such as halides and film formation such as adsorption of H on Pt [144, 167].

Optical surface SH response from thermally evaporated Au on a Si substrate with a native layer of SiO_2 was investigated by Krause *et al.* [164] and the magnitude of the second order susceptibility tensor elements and optical constants were determined for Au and compared with that of Cu, Ag. The film preparation and surface roughness are reported to have influenced the values of second order nonlinear susceptibility tensor, $\chi^{(2)}$ and the increasing roughness has increased the magnitude of the tensor. The authors concluded that while the nonlinear susceptibility, $\chi^{(2)}$ was material dependent, it was also dependent on individual film properties, such as roughness and thickness.

Kitahara *et al.* [165] reported a strong dependence of the resonance energy of SH generation, from Au film on NaCl (100), on the film thickness. The resonance peak of the SH intensity was reported to have found at $2\hbar\omega = 3.2$ eV for the island film of mean thickness of 0.4 nm while for the continuous film of thickness 40 nm, the resonance peak appeared at $2\hbar\omega = 2.4$ eV [20]. The study suggested that the SH intensity peak observed at $2\hbar\omega = 3.2$ eV originated from a resonant transition from occupied to unoccupied electronic levels of the (100) surface on top of the Au islands and the SH intensity peak observed at $2\hbar\omega (= 2.4$ eV) originated from the roughness induced linear dielectric property of the film [165].

SHG studies of noble metal nanoparticles has drawn interest for the potential application of Au nanoparticles in chemical catalysis, molecular electronics and biosensor and also to investigate the unusual crystal structure and anomalous behaviour. One of earliest SHG studies on Au nanoparticles was carried out by Antoine *et al.* [168] in order to investigate the nonlinear optical response of Au nanoparticle at the air/toluene interface. The study reported a strong surface plasmon enhanced SHG spectrum resonance in the range 450-600 nm of the second harmonic wavelength. Sandroock *et al.* [169] investigated centrosymmetric and noncentrosymmetric gold nanoparticle structures in a porous anodic aluminium oxide film. A higher SHG signal intensity from noncentrosymmetric nanoparticle structure than the centrosymmetric one was reported which was attributed to the local field enhancement to the

nonlinear second harmonic response of the nanostructure arising from surface plasmon resonance band centred around ca. 530-540 nm.

Despite SHG being an established nonlinear optical technique; and the fact that it can provide substantial information about surfaces and interfaces, relatively little attention has been given to the potential use of SHG techniques to study the electrochemical oxide formation and reduction at electrodes.

1.8 This work

The main focus of the work described in this thesis is to apply optical SHG to study the oxide formation and reduction at Cu and Au electrodes. Following is the thesis outline-

Chapter 1: This chapter introduces electrochemical interfaces, cyclic voltammetry and optical SHG. The nonlinear optical technique was described as an effective tool to study the electrochemical interfaces, in particular metal/electrolyte interfaces. The chapter also reviews the application of SHG technique in the study of oxide formation and reduction at Cu and Au electrodes.

Chapter 2: This chapter describes the experimental technique and the experimental set up.

Chapter 3: In this chapter, studies of electrochemical oxide formation and reduction at Cu electrodes are described. The results of simultaneous electrochemical and SHG experiments on Cu electrodes are presented. In order to investigate the SHG response, “window opening” cyclic voltammetry experiments on Cu electrodes carried out together with the SHG experiments. Finally, CV and SHG spectroscopy were carried out to check the validity of the conclusions, drawn from experiments carried out at a single wavelength.

Chapter 4: SHG studies of electrochemically formed α - and β -oxides at Au electrodes are described. An investigation of the growth and reduction of α - and β -oxide at Au electrodes in acidic solution, while the electrode is simultaneously irradiated by a diode pumped Ti-Sapphire oscillator, is reported here.

Chapter 5: This chapter reviews the findings of this work and discusses future work.

Chapter 2

Experimental

2.1 Introduction

In the research work described in this thesis, cyclic voltammetry and SHG measurements were carried out simultaneously, and current and SHG intensity were recorded as functions of applied potential. The theoretical aspects of cyclic voltammetry and phenomenological description of SHG have been provided in the previous chapter.

Two different spectroelectrochemical cells were constructed in-house from machined polytetrafluoroethylene (ptfe) to carry out experiments on Cu and Au. The electrode preparation and pretreatment regime were different for Cu and Au electrode and different potentiostats were used, and hence data collection procedures were also different. But the optical instrumentations and optical path were identical for all the experiments. Therefore, optical instrumentation is described in this chapter; the electrode and electrolyte preparation, pretreatment procedure, and the differences in design of spectroelectrochemical cells for Cu and Au are described in the experimental section of Chapter 3 and 4 respectively.

2.2 Experimental set up

As shown in Fig. 2.1 the laser beam from a Coherent Mira 900 Ti-Sapphire oscillator is guided to a beam splitter via two mirrors. A fraction of the laser beam is directed to an APE spectrum analyser to monitor the pulse width and pulse shape of the laser beam constantly. The beam then passed through a red pass filter, half-wave plate and a cube polarizer before reflecting from a mirror to the spectroelectrochemical cell. The electrode sample inside the spectroelectrochemical cell is placed in a way that the laser beam while maintaining the polarisation state is incident and reflected at 45° angle at the electrode surface. The spectroelectrochemical cell is mounted on a two way, x and y , translation stage. The laser beam is focussed on the electrode by a lens and after reflection the beam is passed through another lens, and the reflected fundamental and the SH beam were re-collimated. After the re-collimation, the reflected beam, which at this stage is comprised of both fundamental and SH photons, is passed through two dispersing prisms. After the dispersion, SH photons are separated and passed through an iris where the fundamental photons are dumped.

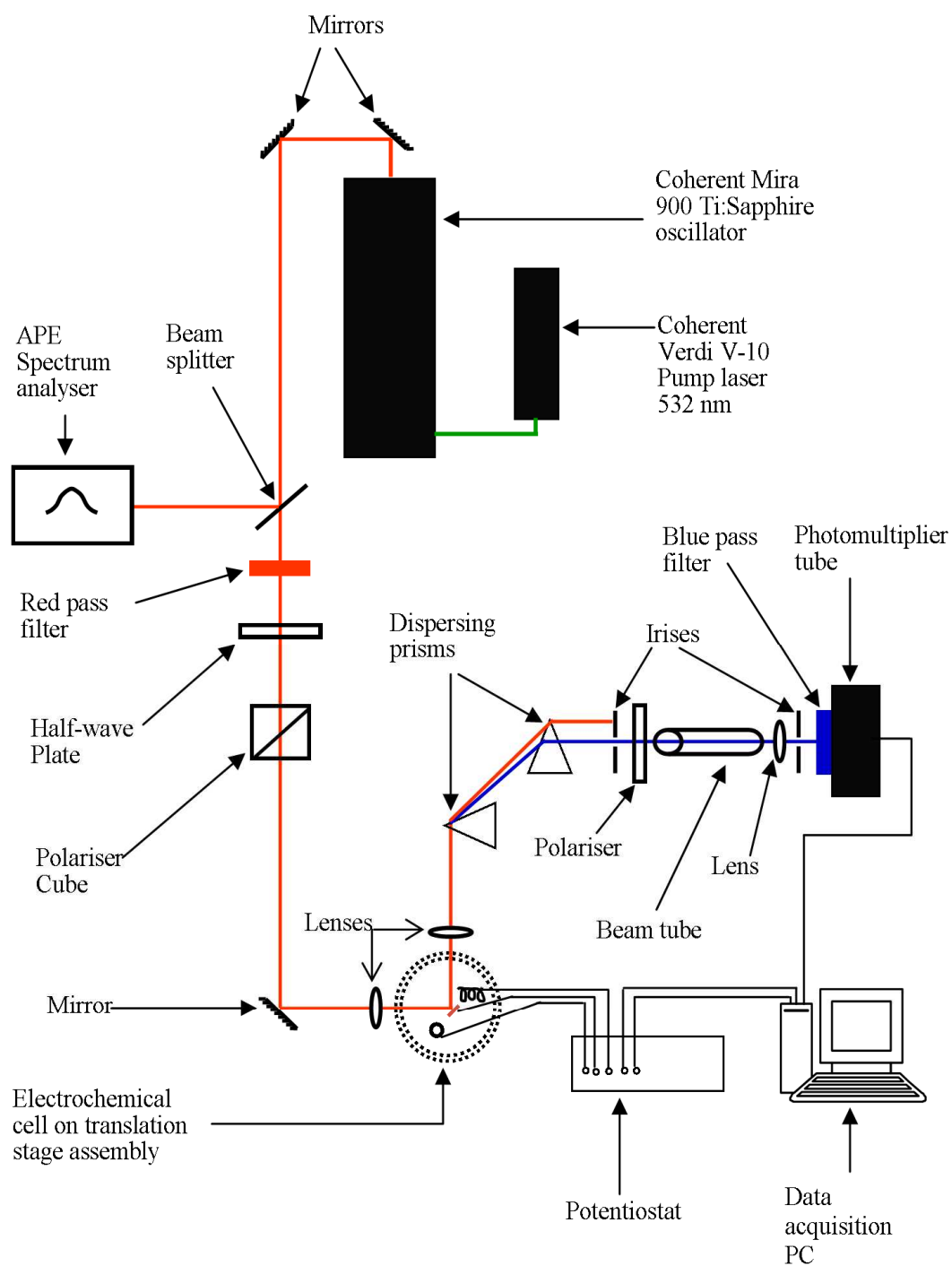


Figure 2.1 Schematic diagram of the optical arrangement for the simultaneous cyclic voltammetry and SHG experiments. The diagram illustrates the optical components that are used for experimental set up.

The beam of SH photons passes through a linear polariser aligned for *p*-polarisation to ensure that the *p*-polarisation state of the SH beam, and then a beam tube. Finally, the SH photons beam is focussed on the PM tube by a lens. Irises are also used to prevent any ambient photons from reaching the PM tube. A blue pass filter (350 – 550 nm) is fitted with the PM tube window to prevent any accidental exposure of the PM tube to the full power of the fundamental beam.

Three electrodes inside the spectroelectrochemical cell are connected to a potentiostat and then the current-voltage data from potentiostat and SH photon counts data from the PM tube are fed into a personal computer via a data acquisition board.

2.3 Optical components

The details of the experimental set up is illustrated in Fig. 2.1, and a description of each of the optical components in the experimental set up is described below roughly in the order they appear in the optical path from laser source to the PM tube and data acquisition pc.

2.3.1 Laser

The optical excitation was provided using a tuneable (720-990 nm) Kerr-lens mode-locked **Coherent Mira 900** Ti-Sapphire oscillator pumped by a 10 W diode solid state laser, Coherent Verdi V10. The repetition rate of the laser pulses was 76 MHz. The incident pulses of the laser were of the order of 200 fs pulse width with an average power of 600 W at the exit of the laser cavity. The incident beam was focussed to approximately 50 μm diameter at the electrode surface. In all cases, where not stated otherwise, the excitation wavelength of 780 nm (1.59 eV) was used. In all the experiments, if not otherwise mentioned, after the optical losses the average power of the laser beam was reduced to the range of ~ 300 mW when it is incident on the electrode surface. It was necessary to ensure that the intensity of the laser beam at the surface of the electrode was sufficient to generate SH signals.

2.3.2 Mirrors

25 mm diameter and 6 mm thick flat mirrors were used to position the laser beam when it exits the laser cavity and also to reflect, position and to direct the laser to the spectroelectrochemical cell. The mirrors used are broadband coated, $R > 99\%$ for 700 – 980 nm mirrors provided by SLS Optics.

2.3.3 Beam splitter

A visible and near infra-red plate beam splitter with no back surface reflection supplied by Comar optics was used to redirect a fraction of fundamental laser beam to an APE spectrum analyser. Using APE spectrum analyser the shape and width of the laser pulses were monitored and power intensity on the electrode sample was estimated.

2.3.4 Long pass filter

A long pass filter was used to absorb shorter wavelengths and to transmit longer wavelengths that coincide with the wavelengths of the fundamental laser beam. The long pass filter was LPF 700 purchased from CVI Optics. A UV-visible absorption spectrum was carried out on the long pass filter and absorption as a function of wavelength is plotted in Fig. 2.2. It shows that more than 99% of the short wavelength photons are absorbed. The filter was used specifically to block any residual 532 nm radiation from pump beam along with any SH radiation generated from the turning mirrors.

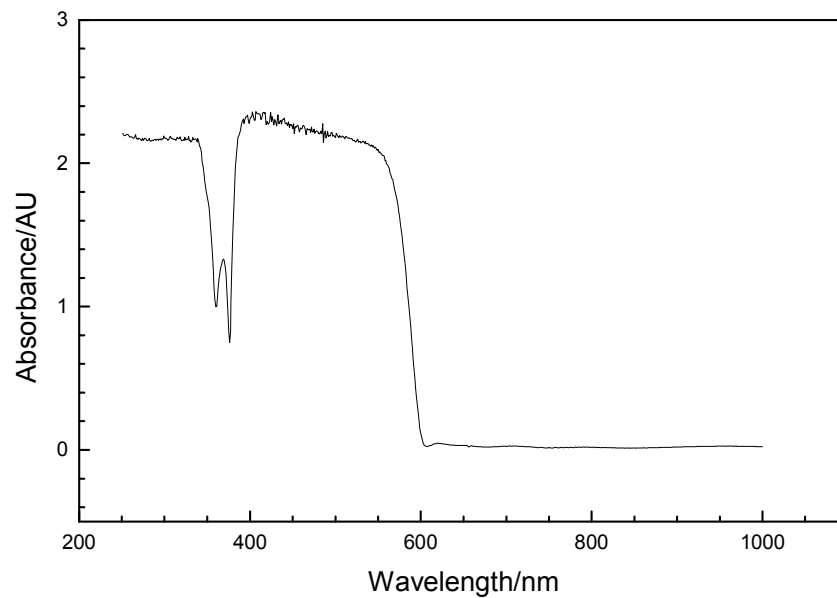


Figure 2.2 Absorption spectra of long pass filters. The filter allows the transmission of electromagnetic radiation between 600 – 1000 nm. It is used to attenuate any residual photons of the pump beam at 532 nm.

2.3.5 Half wave plate

The laser beam passes through a half wave plate placed just before the first polariser. The half wave plate was used to control the intensity of the incident beam at the sample surface whilst maintaining the polarisation state (*p*-polarisation) of the laser beam.

2.3.6 Polarizer

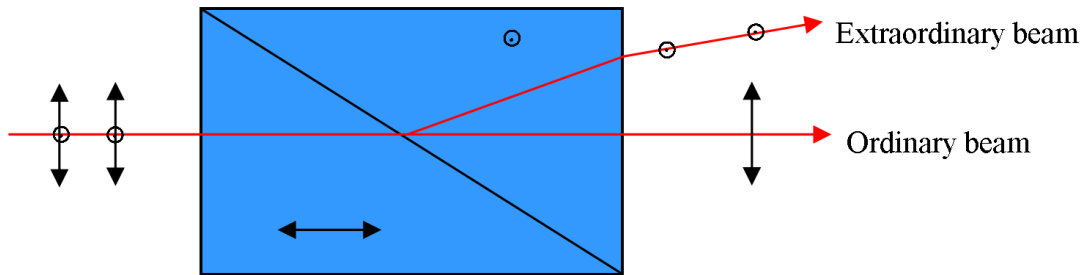


Figure 2.3 Diagram of a Rochon prism. It shows how the extraordinary beam is deviated and the ordinary beam is propagated.

A Rochon type polariser was used before the spectroelectrochemical cell in the optical path. It is made of two quartz prisms cemented together. Both ordinary and extra ordinary beams propagate collinearly down the optical axis in the first prism, but upon entering the second prism, the extra ordinary beam diverges and the ordinary beam transmits without any deviation as shown in Fig. 2.3. The second polariser placed in the optical path after the dispersing prisms was a plane polariser.

2.3.7 Lens

A 100 mm focal length lens (PLCX-25.4-38.6-C from CVI Optics) was used to focus the beam at the electrode sample at an angle of 45° . The reflected laser beam was re-collimated by using another lens of same kind. Finally, SH photon beam was focussed at the PM tube by a third lens of 75 mm focal length.

2.3.8 Dispersing prisms

A pair of dispersing prisms (Comer) were added to the optical path after the electrode sample which allowed the spatial separation of the SH photon beam from the fundamental ones. This was to ensure that the impingement of fundamental radiation on the PM tube was minimal. With the ratio of fundamental to second harmonic radiation typically around $10^{14}:1$ [99, 164], it was important to minimise the contribution of the fundamental beam to the measured signal.

2.3.9 Iris and beam tube

After the SH photons beam is separated from the fundamental beam, SH photons beam is passed through an iris, and a 10 cm beam tube to decrease the acceptance angle of the light and minimise the number of

stray photons from the unwanted ambient light sources. In this way the dark count was kept below 25 photons per second.

2.3.10 Blue pass filter

An unmarked “blue pass filter” with no mention of the wavelength range from the lab was used at the active window of the PM tube. Therefore an absorption spectrum was carried out to determine the wavelength range of the blue pass filter. The absorption as a function of wavelength is plotted in Fig. 2.4. The Fig. 2.4 shows that 99.99% of the photons outside the 350 – 550 nm wavelength range were absorbed by the filter.

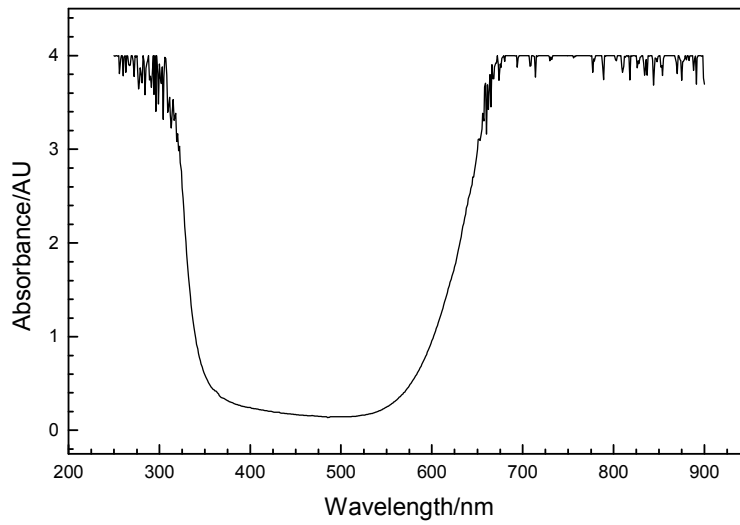


Figure 2.4 Absorption spectra of the blue pass filter. The filter allows the transmission of the electromagnetic radiation only between 350 – 550 nm and wavelengths of the SH photons fall within this range.

2.3.11 SH photon detector

A photomultiplier (PM) tube was placed just after the short pass filter. The PM tube used was a Hamamatsu H8259 module which comes with an integral amplifier and pulse shaping electronics that have high conversion efficiency and low dark count (typical- 30 s^{-1} and maximum- 80 s^{-1}) at the wavelengths ranging between 300 and 700 nm, and hence very high signal to noise ratio. Therefore the PM module is highly sensitive (sensitivity between 2.1×10^5 and 2.6×10^5) in the wavelength of interest (between 370-440 nm) and it completely blocks any fundamental photons above 700 nm of wavelengths [170]. These features make Hamamatsu H8259 a suitable choice of PM module to detect the second harmonic photons in the UV and short wavelengths region.

2.4 SHG measurement protocol

SHG experiments were carried out simultaneously with cyclic voltammetry. Pretreatment protocols followed for cyclic voltammetry experiments for Cu and Au are different from one another; therefore they are described in the relevant chapter. Following protocols were followed for the SHG experiments that were applicable to both Cu and Au experiments.

2.4.1 Near-constant intensity of laser beam

A protocol was followed to make sure that a constant intensity of fundamental beam power was maintained. The intensity of the incident radiation, I^ω in the unit of W cm^{-2} was estimated using the following relation-

$$I^\omega = \frac{P}{\tau_p \cdot A \cdot R} \quad (2.1)$$

measured values of the average power of the laser beam, P is the average power of the fundamental beam in watts, τ_p is the duration of the laser pulse in seconds, A is the area of laser spot in cm^2 , and R is the repetition rate of the laser in Hz.

An APE spectrum analyser was used to estimate first the bandwidth, $(\Delta\omega)$ then the pulse duration, $\Delta\tau_p$ using the following relation-

$$\Delta\omega\Delta\tau_p \geq K \quad (2.2)$$

where $\Delta\omega$ is the bandwidth of the pulse, $\Delta\tau_p$ is the pulse duration and K is the time bandwidth product and is dependent on the functional form of the pulse. It is assumed that the pulse has a Gaussian profile and therefore $K = 0.441$ [89]. We can rearrange Eq. (2.2) find an expression for the pulse duration, $\Delta\tau_p$ -

$$\Delta\tau_p \geq \frac{K\lambda_0^2}{\Delta\lambda c} \quad (2.3)$$

here λ_0 is the centre of the wavelength in m, $\Delta\lambda$ is the full width at half maximum (FWHM) of the wavelength in m, and c is the speed of light in m s^{-1} [88, 90]. From there the radiation intensity was estimated and experimental conditions were then adjusted to meet these condition.

2.4.2 Optical alignment

Alignment of the optical path to optimize the SHG conversion upon reflection at the electrode surface was paramount. Upon reflection, depending on the nonlinear susceptibility of the sample, a small fraction of the fundamental photons will be converted to SH photons and reradiate. The reflected beam consists of both fundamental and SH photons. Even though, fundamental and SH radiations were spatially separated using a pair of prisms, the SH radiation may not be intense enough for naked eye to follow. Therefore, to walk the SH photon beam from the spectroelectrochemical cell to the PM tube, a SH photon beam was generated by placing a nonlinear crystal, β -barium borate (BBO) in the optical path before the electrode sample outside the spectroelectrochemical cell. The SH efficiency of BBO is high to an extent that the SH beam is visible unaided. As a result, the radiated SH photon beam was seen on the back of a white visiting card. After the alignment of the optical components and optimization of the SH photon beam, SH photon beam was focussed at the active area of the PM tube at a low average laser power- typically from $\frac{1}{10}$ to $\frac{1}{8}$ of the total average laser power to avoid any accidental exposure of the PM tube to the intense SH beam due to the high conversion efficiency of the nonlinear crystal. Then the nonlinear crystal was removed from the optical path and full laser power was applied before running experiments and recording the data.

The SHG experiments were carried out using 780 nm incident laser beam unless otherwise mentioned. While carrying out SHG spectroscopic studies, where variable wavelengths were used, optical path was adjusted in each case. Because the wavelength range used was wide, the optical pathway had to be optimized for each wavelength. Due to the fact that laser system has different operational efficiency at different wavelengths and the output powers of the laser at different wavelength were not the same, the SH radiation intensities would also differ. Therefore, the SH intensity data were normalised by taking the highest SHG response as unity. A brief description of the normalisation procedure is provided at the relevant section.

2.4.3 Thermal stability in the laser lab

To reduce the effect of thermal expansion of optical components and optical cavity, thermal equilibrium in the laser cavity had to be ensured so that the fundamental radiation intensity does not fluctuate due to the fluctuation in the temperature. Therefore, the temperature in the laser lab and of the laser cooling system was kept constant at 18° C. Optimisation and fine alignment of the optical path were performed one hour after the laser is powered on, and then at least another 30 minutes' time would be elapsed before any data were recorded.

Chapter 3

Second harmonic generation studies of the oxidation of Cu electrodes

3.1 Introduction

In this chapter results of simultaneous electrochemical and SHG experiments on Cu electrodes are presented. For the specific example of Cu oxidation, which is the subject of this chapter, a brief overview of the general electrochemistry of Cu- the formation and reduction of Cu oxides and their structure is followed by a discussion of the Cu cyclic voltammogram in a weakly alkaline medium. Then SHG studies of Cu oxide formation and reduction are described. In order to investigate the SHG response, “window opening” cyclic voltammetry experiments on Cu with different maximum potentials have also been carried out together with the SHG experiments. Finally, CV and SHG spectroscopy were carried out, and SHG responses and current were recorded as functions of the applied electrode potential at various wavelengths to investigate the wavelength dependence of SH signal intensity. This is to check the validity of the conclusions, drawn from experiments carried out at a single wavelength.

3.2 Cu structure

This section presents a short discussion of the structure of Cu because the SHG response from Cu depends on the lattice structure and on its surface. Assuming that only non-faradaic processes are taking place in the electric double layer region of Cu voltammogram, any SH responses in that potential range are considered to be the result of the ion adsorption or inherent nonlinear properties of Cu. The crystal structure of Cu is a face centred cubic (fcc) [171] which is a simple cubic lattice with an additional lattice point in the middle, in this case, a Cu atom is at the centre of each of the six faces of the cube. This crystal structure puts Cu in the same category of metals, such as, Au or Pt. Therefore Cu may behave in a similar way just as Au and Pt in its response to SH intensity in the electric double layer region of the cyclic voltammogram in which no surface oxide formation takes place.

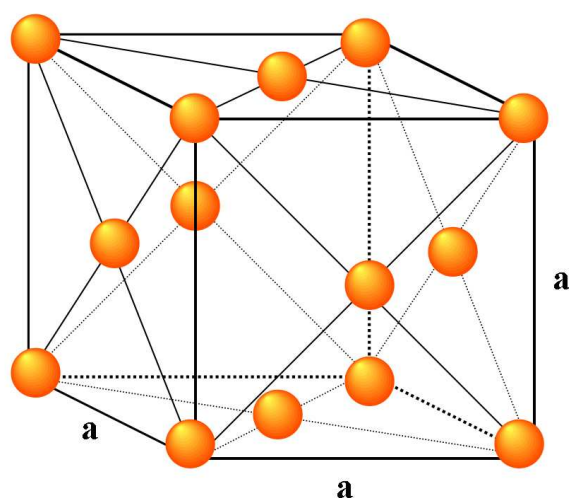


Figure 3.1 Face centred cubic (fcc) lattice structure of Cu atom. The diagram shows that one Cu atom is at the centre of each side and one each at the vertices. Every atom has 12 nearest neighbours which gives the highest packing density of 74%. For clarity in the figure the atoms have been drawn apart from each other.

There are 12 nearest neighbours for Cu crystal and four lattice points per unit cell in fcc crystals. When the atoms are assumed to be rigid spheres and their radius is equal to the one quarter of the diagonal distance between the atoms positioned at the corners of the unit cell, it gives highest packing density of 74% which is the highest among the *Bravais lattices*. Cu belongs to the $3m\bar{3}$ symmetry group [171]. The magnitude and the unit vectors of the lattice parameter are equal and the angles between the vectors are also equal. That means $a_1 = a_2 = a_3 = 361.49$ pm and $\alpha = \beta = \gamma = 90^\circ$ [172]. The nearest distance between two lattice points is $\frac{a}{\sqrt{2}}$. The electronic configuration of Cu is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$.

3.3 Cu electrochemistry

3.3.1 Introduction

In this section Cu electrochemistry will be discussed. The discussion will be restricted to the Cu electrochemistry in neutral or weakly alkaline media. Oxidation of Cu and the oxidation peak current depend on the pH of the electrolyte solutions [6, 8, 12, 14, 16]. The SHG response from Cu under electrochemical control will also depend on the structure, thickness, and the properties of Cu oxides. Therefore a brief discussion of the properties and structure of the two main oxides of Cu, Cu_2O and CuO , formed under these conditions, which show semiconducting behaviour, will also be presented here.

Since the first ever work by Muller [131], the electrochemical behaviour of Cu in weakly alkaline or acidic media has been the subject of many studies in order to realize the corrosion and passivation behaviour of Cu due to its technological applications [6, 8, 15]. In the studies of the electrochemical behaviour of Cu, the experimental conditions and surface preparation, qualitative understanding of anodic processes and quantitative analysis, and determination of charge transfer and metal dissolution are very important. Away from the traditional interest in Cu, interest in the studies of Cu electrochemical behaviour has significantly increased due to the use of Cu in microelectronic industries [173]. Cu is also increasingly being chosen to replace aluminium (Al) in multi-level interconnections due to its low resistivity and high electro-migration [174].

With increasing interest in nanomaterials, electrochemically deposited nano-scale Cu/Cu₂O multi-layers are being studied as potential candidates for the quantum confinement [122]. Having no inversion symmetry, nano-structured Cu/Cu₂O multi-layers are suitable for SHG studies. Additionally, Cu₂O which is a *p*-type semiconductor with a band gap of 2.17 eV [175] formed on Cu surface is drawing interest into the continued study of the electrochemical behaviour of Cu [176].

3.3.2 Cyclic voltammetry of Cu in neutral or weakly alkaline solution

In understanding the electrochemical oxidation of Cu either in weakly alkaline or acidic media, disagreement may persist [6] but it is generally accepted that the cyclic voltammogram of Cu displays two anodic peaks, AI and AII as illustrated in Fig. 3.2. The shape and position of these peaks are affected by the ions of the electrolytes and the pH of the solution. The two anodic peaks are largely well resolved in both acidic and alkaline media but in certain electrolytes, such as, phosphate or citrate buffer broad and weakly resolved anodic current peaks are observed due to anodic dissolution of the metal. Anodic dissolution and anodic current peaks in acidic solution increase by up to a hundred times compared to the current peaks in alkaline media [177]. In acid solution, the Cu ions are more likely to be soluble than in alkaline media where poorly soluble oxides and hydroxides are more likely to be found.

At slow scan rates the anodic current peaks, especially AII, tend to appear at a less positive potential due to dissolution, and the anodic current density increases. The positions and breadth of the reduction peaks, CII and CI are unaffected by the pH values of electrolyte. In general it is recognised that the current peaks, AI and CI correspond to the formation and reduction of Cu₂O; and AII and CII correspond to the formation and reduction of CuO [3, 6, 8, 9]. A typical cyclic voltammogram of polycrystalline Cu electrode, carried out in pH 9.2 borax buffer solution is presented in Fig. 3.2.

In contrast to the response seen below, Brisard *et al.* [15] reported three oxidation and reduction current peaks when Cu is oxidised in strong alkaline medium with pH 12-14. In their studies of Cu electrochemistry in strong alkaline medium Cu showed three different anodic current peaks with the third one appearing just before the AII current peak and is more like a shoulder in the potential region where Cu is passivated by CuO and Cu(OH)₂. As has been mentioned above and according to Pourbaix [178],

oxidation of metallic Cu is surprisingly complex and it involves both soluble and insoluble products and as a result three different oxidation states of Cu can be produced. A similar number of oxidation and reduction current peaks also have been reported by Fonseca *et al.* [179] in neutral solutions of pH 6-7. Fonseca *et al* [179] carried out Cu cyclic voltammetry in aqueous solution of Na₂SO₄ and the appearance of the third anodic peak in between AI and AII was attributed to the formation of CuSO₄·3Cu(OH)₂ which while being reduced gives rise to the third cathodic peak appearing in between CII and CI.

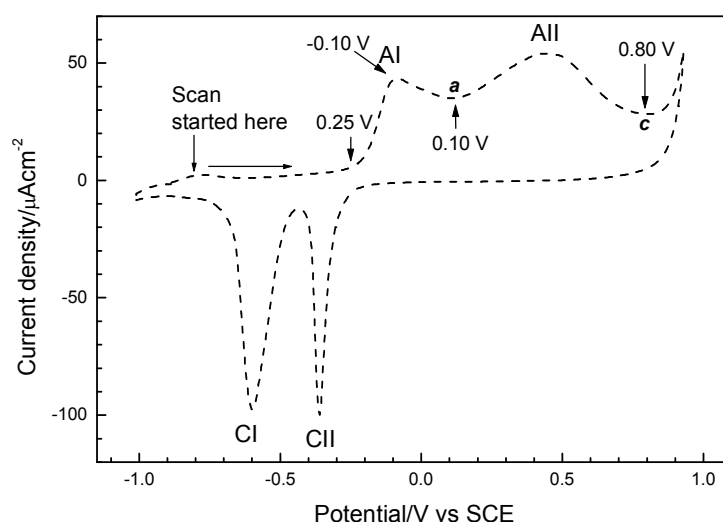


Figure 3.2 Cyclic voltammogram of polycrystalline Cu in alkaline medium at scan rate 5 mV s⁻¹ in 0.1 M borax buffer of pH 9.2.

In the cyclic voltammetry experiment, not all the oxidation processes are favoured in a particular potential range. Certain oxidation states are favoured at certain potentials and at certain pH values of the electrolyte solution. During the scan of the potential, the surface of Cu may go through corrosion and passivation, and the formation of surface layer is also seen. The stability of the surface layer and of the redox species that are stable in the system depend on the potential and the pH values of the solution. These relations between the electrode potential and the electrolyte pH can be depicted in diagrams. These diagrams with electrode potential and pH axes were calculated and proposed by Pourbaix [178] in the early 1950's.

3.3.3 Pourbaix diagrams of Cu

In 1963 the Belgian electrochemist and corrosion scientist, Marcel Pourbaix proposed *potential-pH diagrams* that could be used to show the thermodynamic stability of a metal at an electrode potential and pH of the electrolyte it is in. These potential-pH diagrams are called *Pourbaix diagrams*, which are useful to determine if a metal is stable at a particular combination of pH and potential by plotting the redox potential of a system on the vertical axis and the pH of the solution on the horizontal axis. Pourbaix diagrams can be constructed from calculations based on the *Nernst equation* and see the relationship

between possible phases of a system. A detailed description and guidance on how to construct Pourbaix diagrams can be found in the works of Pourbaix, "Atlas of Electrochemical Equilibria [178] and the importance of these diagrams in the study of metal corrosion in Ahmad's [180] work.

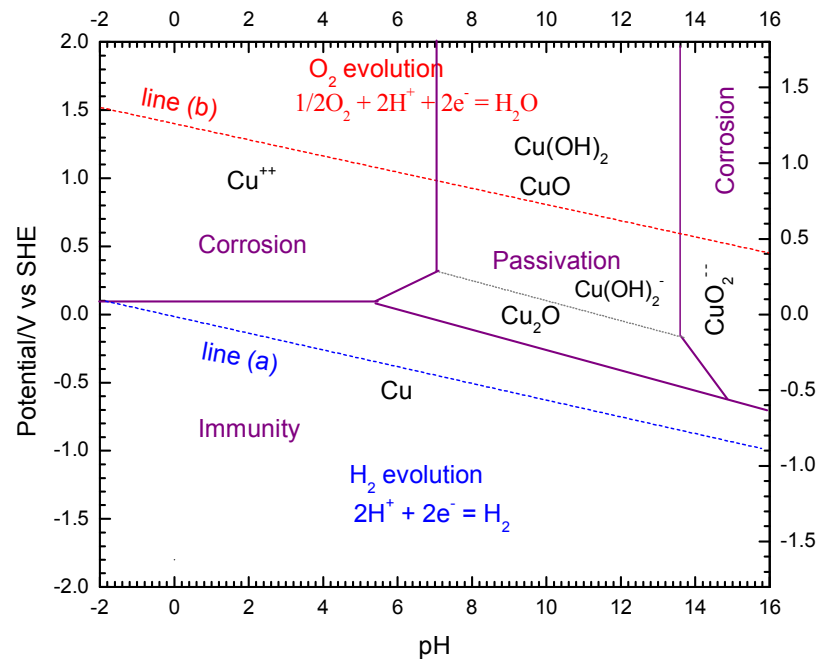


Figure 3.3 Pourbaix (Potential-pH) diagrams for Cu in H₂O or Na⁺ containing solution showing the redox species of Cu that are stable or undergo dissolution or corrosion [178].

Fig. 3.3 shows the Pourbaix diagrams for Cu in H₂O or Na⁺ ion containing solution. The diagrams show that Cu is not passivated in acid electrolytes and the Cu⁺- and Cu⁺⁺-oxides of Cu are only stable in weakly acidic and alkaline electrolytes [180]. The stability of these species extends above the line (a) in the diagram which is the boundary below which hydrogen evolution will occur and alkalisation of the solution will take place, and the line (b) is the boundary above which oxygen evolution and acidification of the solution occur when cyclic voltammetry experiment is carried out. The purple lines show the domains for immunity, corrosion and passivation when a potential is applied on the Cu electrode in solution. Therefore, by adjusting the pH of a solution and the applied potential, a particular form of oxidation product of Cu can be made stable [181]. But Cu is corroded by acid or strongly alkaline solutions containing oxidising agents. When the oxidation phase is a solid phase such as Cu₂O, CuO, or Cu(OH)₂, then this phase will form a surface layer. Cu₂O is insoluble in weakly alkaline solution and CuO is only slightly soluble in alkaline solutions. Therefore, neutral or slightly alkaline solutions passivate the metal and corrosion is checked by the formation of oxide films. On the other hand, when ionic species of Cu, for example Cu⁺⁺, is favourable then Cu will directly pass into the solution as Cu⁺⁺, which is dissolution of Cu and no surface layer will form. And finally if solid Cu is favourable in a particular potential regime then Cu will not oxidise and no surface layer will form in that region which is

the so-called *electrical double layer region*. According to the Pourbaix diagrams above, Cu undergoes corrosion when the pH is 6 or less, passivation when the pH of the solution is between 6 and 12 and corrosion again when the pH of the solution is above 12.5.

In the next few sections, Cu electrochemistry will be looked at and oxidation of Cu to form Cu₂O and CuO will be discussed. In the SHG studies of oxide formation at Cu electrodes whilst under electrochemical control, it is essential to know the structure and properties of Cu₂O and CuO. An understanding of the present state of knowledge in this area will underpin the discussion of the changes induced in the SHG signal by the surface chemistry. Because SHG is a surface sensitive diagnostic tool, the response will depend on the oxide layers that are formed at Cu surface as cyclic voltammetry is carried out on the Cu electrode.

3.3.4 Oxidation of Cu to the Cu(I) state and formation of Cu₂O

3.3.4.1 Oxidation mechanism

In 0.1 M borax buffer solution the first oxidation current peak, AI in Fig. 3.2 is due to the formation of a Cu₂O film on the surface as Cu oxidises to its Cu⁺ state in weak acid, neutral and weakly alkaline solutions (pH values ranging from 6 to 9) [8, 15], and hence the reactions on a Cu surface as the oxidation current increases and reaches the apex can be represented by the following reactions [8]-



In neutral solution with pH values up to 9 the relative abundance of OH⁻ is very low (~10⁻⁵ M), therefore Eq. (3.1) is more likely. Using the cyclic voltammogram in Fig. 3.2 as a guide, if one starts scanning from the potential of -0.80 V, it shows that the first oxidation current peak, AI occurs at -0.1 V. The broad oxidation current peak, AI shows that the reactions above are most likely to continue until the scanning of the potential reaches 0.15 V vs SCE. It is reported [6, 8, 15] that a passivating layer starts to form at potentials more positive than the first oxidation peak potential. After the initial oxidation, as the potential is scanned beyond the oxidation peak potential, further oxidation takes place as Cu⁺ ion driven by the applied potential and diffuse through the thin layer of Cu₂O that has already grown on the surface. Cu₂O formed at around the first oxidation peak potential is insoluble in neutral and weakly alkaline solution and can be reduced only by cathodic reduction [6, 8]. Fig. 3.4 shows a schematic diagram of Cu₂O at the Cu surface.

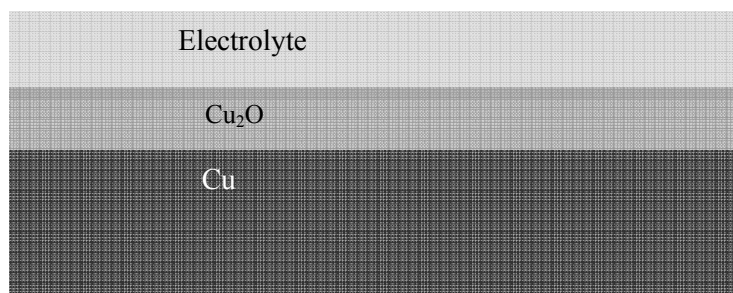


Figure 3.4 Schematic diagram showing Cu₂O thin film and Cu electrode surface as Cu is oxidised to grow Cu₂O in the Cu/electrolyte interface.

If the scan continues the passivating layer becomes thick enough to demonstrate an insulating behaviour. This insulating layer is more like a semiconductor and hence the oxidation current reaches the lowest value before oxidation of Cu to the Cu(II) state starts to take place. As the higher potentials are scanned, holes are driven to the surface of the Cu₂O layer, which is a p-type semiconductor and an anodic decomposition reaction can take place in the following form [6, 15]-



The extent to which this process takes place depends strongly on the pH of the solution. As CuO and/or Cu(OH)₂ starts to grow on the top the Cu₂O layer there is no apparent change in thickness for the inner Cu₂O layer as Cu continues to be oxidised to Cu(II) [8, 17]. The growth of this second oxide is discussed later.

3.3.4.2 Thickness and structure of the electrochemically formed Cu₂O

As with the most electrochemically produced oxides, the Cu₂O layer is only a few monolayers thick, porous, and passivating. Ruiz *et al.* [182] describes the electronic structure of this semiconducting thin film in terms of band structure and density of states. According to their study, the main contributions to the valence band come from the Cu's 3d and oxygen's 2p states. The charge required to form a monolayer of Cu₂O electrochemically can be estimated from the unit cell dimensions. Cu₂O crystallises in a cuprite structure [174], built up from a body centred cubic (bcc) lattice of oxygen atoms and a face centred cubic (fcc) lattice of Cu atoms [10]. Cu and oxygen align in a rare structure of linear O-Cu-O chains. Therefore in the structure of the oxide, Cu₂O, Cu sits at the position (0, 0, 0) with oxygen atom at (¼, ¼, ¼). The cuprite structure such as Cu₂O can be described as depicted in Fig. 3.5- the Cu₂O structure and is equivalent to two interpenetrating frameworks of molecules of cristobalite structure, i.e., SiO₂. The lattice size of Cu₂O molecule, $a = 4.27 \text{ \AA}$ and Cu₂O belongs to the space group of Pn3M [175] with a cubic crystal structure.

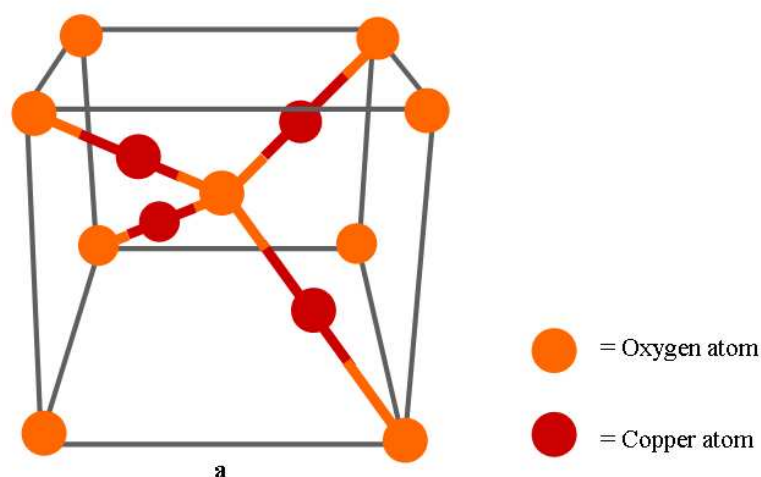


Figure 3.5 Crystal structure of Cu_2O . Orange balls represent oxygen atoms and the red ones copper atoms. Cu_2O crystallises in the cuprite structure formed by a bcc array of oxygen atoms with metal inserted between two consecutive oxygen layers [182].

Considering the Cu_2O size, the charge required to form a unit cell monolayer oriented on the basal plane is $300 \mu\text{C cm}^{-2}$ [183]. This charge calculation suggests that by the point when the first oxidation current reaches the peak, AI, at least 2-3 monolayers of Cu_2O are grown. An equal number of monolayers are grown as the potential scan continues to the point where the oxidation current reaches a minimum; this point is marked as “a” on Fig. 3.2. At potentials around the anodic current peak, AI, the oxide layer is up to $15 \text{ \AA}$ thick [8, 17]. In slight contrast to this, Abrantes *et al.* [10] have reported that two monolayers of Cu_2O are formed on the forward sweep leading to 0.8 V vs SCE, and two further monolayers of Cu_2O are subsequently added on to the Cu_2O layer on the reverse sweep while Cu^{++} -oxides undergoes reduction. They further reported that the thickness of the Cu_2O film could be up to $17 \text{ \AA}$, and the growth of Cu_2O monolayers is dependent of electrolytes and their pH values. A detailed calculation of oxidation and reduction charges for Cu electrode in borax buffer solution will be provided later in this chapter. This information on the thickness of the Cu_2O formed under these conditions will become relevant when the SHG responses are discussed.

3.3.5 Oxidation of Cu to the Cu(II) state and formation of $\text{CuO}/\text{Cu}(\text{OH})_2$

In the previous section, the mechanism of Cu_2O formation, and its structure and thickness have been discussed. In this section CuO formation, its thickness and structure will be discussed. The CuO forms on the top of the Cu_2O layer as Cu is oxidised to the Cu(II) state.

3.3.5.1 Cu to Cu(II) oxidation mechanism

After the first oxidation of Cu to its Cu^+ state and as the potential is scanned further, Cu is oxidised to the Cu(II) state. It is generally accepted that CuO is the main oxidation product. Strehblow *et al.* [8, 15] has demonstrated that CuO is present from the observation of a peak at binding energy of 943 eV in their ESCA (Electronic Spectroscopy for Chemical Analysis) experiment. The formation of CuO is governed by several different reaction mechanisms. At potentials leading to the anodic current peak, AII, in Fig. 3.2, Cu^{++} ions may be produced at the interface and then hydrolyze and precipitate on the Cu_2O porous film.



At moderate to high pH this hydroxide is not stable according to a recent recalculation of the Pourbaix diagram [178, 180] and should produce CuO instantly.



The studies by Strehblow *et al* [8] suggest that in weakly acid solution both CuO and $\text{Cu}(\text{OH})_2$ may form at the interface by oxidation through the combination of Eq. (3.4) and (3.7). As the Cu_2O is porous [182] at this potential CuO can be formed at bare Cu surface as well. The continuous formation of $\text{Cu}(\text{OH})_2$ around the potentials at and after the current peak, AII, disturbs the structure of underlying Cu_2O . As a result Cu_2O no longer serves as an effective barrier for Cu ion migration.



When the $\text{Cu}(\text{OH})_2$ is sufficiently thick and continuous then this layer causes the decrease of anodic current

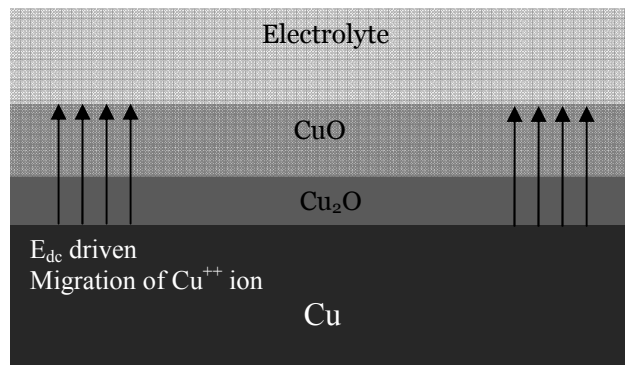


Figure 3.6 Schematic diagram of formation of CuO thin film where Cu^{++} ions are driven to the interface by applied dc electric field [141].

It is widely accepted [6, 8] that as Cu oxidises to the Cu^{++} state, both CuO and $\text{Cu}(\text{OH})_2$ are formed. Shoesmith *et al* [6] suggest that at comparatively low potentials the thermodynamically stable CuO is formed with a layer of $\text{Cu}(\text{OH})_2$ attached on top, and at higher potentials the formation $\text{Cu}(\text{OH})_2$ dominates but it happens in two stages- a base layer is grown by a solid state mechanism first and a top layer then develops where individual crystals are nucleated and grown from solution. Strehblow's [8] studies of Cu oxidation by means of ESCA and ion scattering spectroscopy (ISS) largely agree with this and to an extent complement the studies by Shoesmith's group.

3.3.5.2 Thickness and structure of the electrochemically formed $\text{CuO}/\text{Cu}(\text{OH})_2$ layer

When Cu is oxidised to higher potentials beyond the first oxidation current potential, CuO starts to grow and with higher potential a *meta-stable* and less compact $\text{Cu}(\text{OH})_2$ grows on top of the already grown CuO layer. ESCA experiments [6] show that the oxide thickness after the first oxidation current peak doubles if the potential is scanned beyond the second oxidation current peak, AII, and up to the point when oxidation current shows a minimum at ca.0.80 V vs SCE. This also proves that the Cu(II) oxide or hydroxide forms a passive layer covering the Cu(I) oxide underneath. Either CuO or $\text{Cu}(\text{OH})_2$, Cu(II) oxides may grow up to a thickness of 20 Å [8, 17].

Since the SHG response from the oxidised Cu surface will depend on the surface structure it is worth having a look at the crystal structure of CuO. The CuO lattice has a monoclinic symmetry [182] where each Cu atom will have four nearest neighbour oxygen atoms or vice versa with Cu atoms at the centre of an oxygen rectangle and oxygen atoms at the centre of a partially reoriented Cu tetrahedron. In a comparatively recent study by Åsbrink *et al.* [184] two possible space groups for CuO have been proposed which are $C2/c$ and Cc . The former is a centrosymmetric and the latter is a non-centrosymmetric space group. We know from our discussion in Chapter 1 that centrosymmetric media will not have a nonlinear response from the bulk but from the surface where the symmetry breaks down. In the case of a non-centrosymmetric medium a nonlinear response is expected from both the bulk and the surface or interface.

As described in this chapter, oxidation and reduction of polycrystalline Cu will be examined by SHG and cyclic voltammetry in weakly alkaline medium. SHG and cyclic voltammetry will be simultaneously carried out.

3.4 Experimental

3.4.1 Spectroelectrochemical cell

The spectroelectrochemical cell with 5.0 cm inner diameter was constructed in house from machined polytetrafluoroethylene (ptfe) with a ptfe screw lid and three glass windows placed over polyvinylidene fluoride o-ring to avoid leakage of the electrolyte solution. The glass windows were antireflection coated 2.5 cm diameter CaF_2 glass windows (CVI Optics) with high transmission curve for UV to IR light. The holes in the lid were spaced so that it was possible to put working and counter electrodes into the electrolyte and the reference electrode with a Luggin capillary system. A tapered glass jet with 0.5 mm diameter opening was inserted into the cell from the side and near the bottom and connected to an oxygen free nitrogen tank by tube. The spectroelectrochemical cell was mounted on a translational stage with two degrees of freedom of movement. The stage was at a fixed height from the laser table and could be translated in x - or y -direction to make incident and reflected beam orthogonal to each other and the sample at an angle of 45° with the incident beam and reflected beam. Fig. 3.7 shows the translation stage assembly used for the SHG experiments on Cu electrode. The assembly was crucial to ensure that good alignment was maintained throughout the experiment.

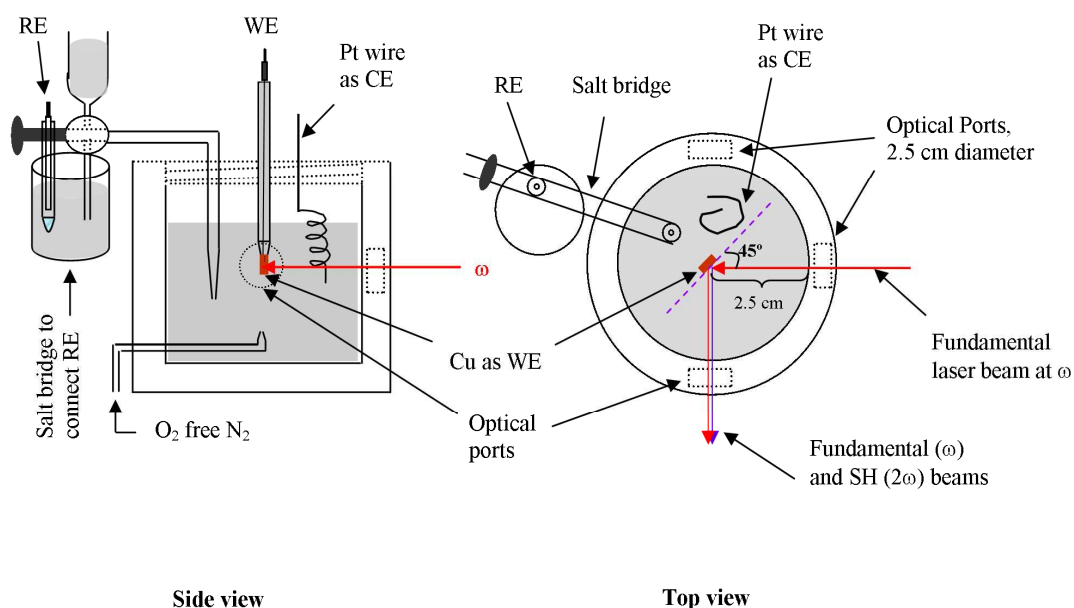


Figure 3.7 Schematic representation of the flow cell used for the combined cyclic voltammetry and optical experiments. Working electrode (WE) is a rectangular Cu foil with surface area of 0.20 cm^2 , counter electrode (CE) is a Pt wire, and reference electrode (RE) is $\text{Hg}/\text{Hg}_2\text{Cl}_2$ in contact with saturated KCl solution.

3.4.2 Electrode preparation

For the experiments on Cu, polycrystalline Cu electrodes were made by cutting samples of 0.20 cm² area from 0.5 mm thick, 5 cm x 5 cm puratronic 99.9999% Cu foil supplied by Alfa Aesar. A Cu wire, passed through a glass tube with a tapered end was soldered on the back side of the foil. The area around the Cu wire and soldering site was insulated with epoxy resin leaving the shiny reflecting side of Cu electrode exposed to electrolyte [3]. Electrodes were polished using 0.3 µm aluminium oxide strips and then wiped with wet cotton wool. Finally, the electrodes were rinsed with ultrapure water before any experiments were carried out.

A 0.5 mm diameter and 10 cm long Pt wire, polished in the same way as the Cu electrode was used as the counter electrode. In the experimental set up illustrated in Fig. 3.7 about 6 cm of the Pt wire was in contact with the electrolyte solution and the area of the counter electrode was calculated to be 1.20 cm². The reference electrode was a standard calomel (Hg/Hg₂Cl₂) electrode (SCE) in contact with saturated KCl solution. Potentials of all the cyclic voltammograms carried out in this work are measured against the potential of SCE in contact with saturated KCl solution unless otherwise stated.

3.4.3 Electrolyte

VWR International supplied Analab Normapur® analytical reagent 1 grade di-sodium tetraborate decahydrate (Na₂B₄O₇·10H₂O) and research grade sodium hydroxide (NaOH) were used to prepare 0.1 M borax buffer solution of pH 9.2 using ultrapure water from a Direct Q3-UV (Millipore) system with 18 MΩ.cm resistivity. The buffer solution used in the experiments described in this chapter may simply be referred as “borax buffer solution”. While making the borax buffer solution of di-sodium tetraborate decahydrate and sodium hydroxide at the desired pH of 9.2, the guidelines published in *CRC Handbook of Chemistry and Physics* [185] were followed and the alkalinity of the solution was checked with a pH meter.

3.4.4 Pretreatment protocol

Before any experiments were commenced oxygen was purged from the electrolyte solution by oxygen free nitrogen and a positive pressure of nitrogen on the electrolyte surface inside the cell was maintained. During the electrochemical cleaning the solution was continuously purged to remove any soluble gas. The main problem in maintaining a reproducible surface was to ensure that Cu surface was properly reduced after every scan or after a gap in time before a new scan was carried out.

3.5 Results and discussions

3.5.1 Cyclic voltammetry of Cu in borax buffer

A cyclic voltammogram of Cu obtained in 0.1 M borax buffer solution of pH 9.2 with scan rate 5 mV s^{-1} was shown in Fig. 3.2 and is reproduced here as in Fig. 3.9 below. Scanning of the potential started at -0.8 V and reversed at 0.9 V and then was scanned back to -1.0 V and finally was stopped at 0.8 V in the forward scan. Fig. 3.9 shows a cyclic voltammogram of Cu in weakly alkaline solution of moderate strength and is in good agreement with previous works [6, 8, 15, 17]. The cyclic voltammogram in Fig. 3.9 shows hysteresis and it illustrates two broad and easily distinguishable anodic peaks, AI and AII and two sharp and well-pronounced cathodic peaks, CII and CI. The two anodic peaks are well-separated and they appear at 0.10 and 0.46 V and the cathodic peaks appear at -0.23 and at -0.6 V respectively. The two main processes that can be identified for the Fig. 3.9 are- oxidation of Cu to the Cu^+ state to form Cu_2O and formation of Cu(II) species mainly CuO and $\text{Cu}(\text{OH})_2$ as Cu oxidises to the Cu^{++} state.

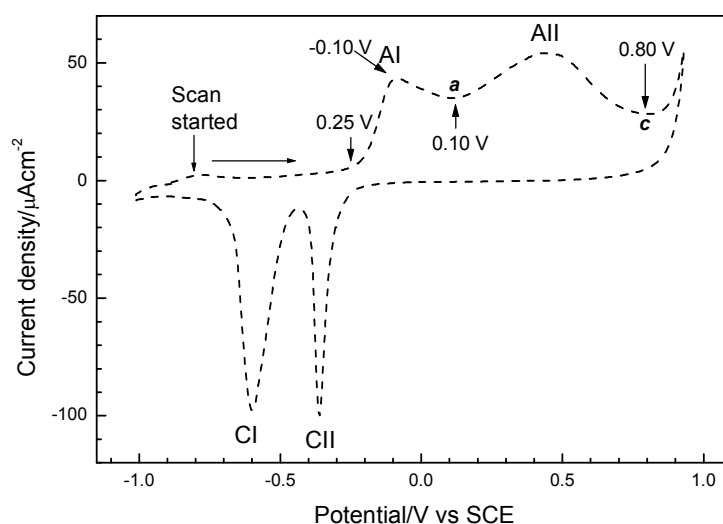


Figure 3.9 Current and voltage curve from a Cu electrode in 0.1 M borax buffer solution of pH 9.2 at scan rate 5 mV s^{-1} .

It is noticed from the figure above that the anodic peaks are broader compared to cathodic peaks and the area enveloped by the anodic current peaks is bigger than that enveloped by the cathodic current peaks. Integration of the current peaks for oxidation and reduction charges shows that the total amount of anodic charge passed, exceeds that of the cathodic charges by a significant amount. This suggests that alongside oxidation to produce Cu_2O and CuO as discussed in earlier sections, there is also significant dissolution of Cu taking place. This suggestion will be explored in detail later in a section within this chapter with charge calculations.

In the voltammogram showed in Fig. 3.9, the potential scan was started at -0.80 V and continues upward but no Faradaic current is observed until -0.50 V, beyond which the anodic current starts to increase as Cu oxidises to form Cu₂O. The growth of Cu₂O leads to the increase in anodic current and it reaches its maximum at -0.10 V, labelled as AI in Fig. 3.9. As scanning of the potential progresses forward, charge calculation will show that by 0.10 V a 2-4 Å thick layer of Cu₂O has already been deposited on the Cu electrode surface. As the potential is taken further, the anodic current starts to decrease suggesting that the highly insoluble Cu₂O (in weakly alkaline solution) sits on the Cu surface, and limits the availability of Cu atoms for oxidation. The oxide film acts as an insulator stopping further growth until the potential and hence the electric field increase, driving Cu⁺⁺ to the surface to allow further oxidation.

The anodic current starts to decrease and reaches its local minimum at 0.10 V, labelled as “a” in Fig. 3.9. At point “a”, initially CuO starts to form on top of the Cu₂O which leads to the second anodic current to increase and reach the peak, AII at 0.46 V. At the potentials around the peak, AII, both CuO and Cu(OH)₂ form on top of Cu₂O and also at any remaining “bare” Cu atomic sites. This oxidation is facilitated by the field driven transport of Cu cations from underneath the Cu₂O layer to the surface. After the second oxidation peak, AII, as the potential scan continues, the current decreases continuously and reached the minimum at 0.80 V. Oxygen evolution starts to occur at the potential of 0.8 V and onward. Under the conditions used in this experiment, it is possible that a 5-7 Å thick layer of Cu₂O is formed on the Cu surface and the combined oxide layer thickness can be up to 40 Å [8].

On the reverse sweep the current drops sharply to the level that of the double layer region. In the potential range of 0.90 to -0.20 V (in the reverse direction) no change occurs in terms of oxide layer until the scan reaches -0.20 V, where the reduction current starts to pass, and as the potential is scanned back, the reduction current peak, CII appears at -0.23 V and then the reduction current peak, CI occurs at -0.60 V. On continued sweep, the current reaches the value of its double layer region value and returns to its initial value at -0.80 V. The fact that at the end of the scan the current returns to its initial value demonstrates that in borax buffer electrolyte and at the moderate scan rate of 5 mV s⁻¹ the Cu surface reduces completely, as the slow scan allows sufficient time for the reduction process to occur. Cu electrochemistry discussed in this section involved only one scan rate. In the next section copper cyclic voltammetry is carried out at several different scan rates and the results are described below.

3.5.2 Cyclic voltammetry of Cu at various scan rates

CV of Cu has been carried out at 2, 5, 10, and 20 mV s⁻¹ and the results are discussed below. The CV's are illustrated in Fig. 3.10; potentials of the peak oxidation and reduction current are plotted as functions of scan rate in Fig. 3.10; and peak oxidation current, AI and AII, and reduction currents, CII and CI, are plotted against the scan rates in Fig. 3.12. Oxidation charge and reduction charge densities and the ratios of their differences over the anodic charge are tabulated in Table 3.1 as functions of the scan rates. Also oxidation peak current and reduction peak current densities, and the ratio of oxidation peak current to the corresponding reductions are tabulated as functions of the scan rate in Table 3.2.

Cyclic voltammetry experiments with variable scan rate as illustrated in Fig. 3.10 shows that peak current densities do change with the scan rates. We assume that the Cu oxidation is a surface process. When faster scan rate is applied, it is likely that a higher amount of oxidation charge will pass in a shorter span of time, this in turn, will cause an increase in the oxidation and reduction current. Therefore, we see in the figure below that the current density increase when faster scan rates are applied.

Table 3.1 shows that the amount of oxidation charge passed in the process is higher than the total reduction charge passed. This means that the oxidation products such as Cu_2O and/or CuO are partly soluble in the electrolyte solution. Our calculation of the ratios of the difference of anodic and cathodic charge to the total anodic charge shows that there is a significant dissolution takes place as Cu is oxidised to form Cu_2O and CuO .

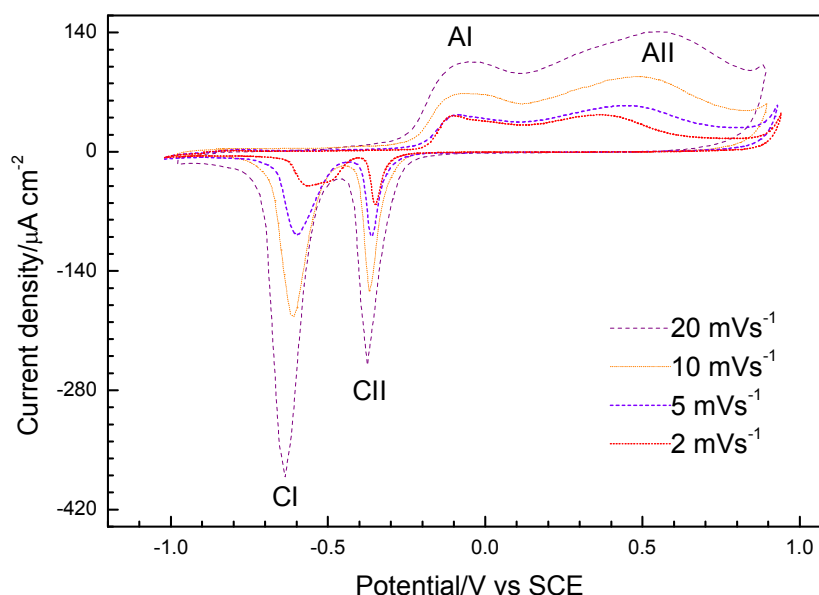


Figure 3.10 Anodic and cathodic polarisation curve of poly-Cu in 0.1 M borax buffer of pH 9.2 with various scan rates.

Scan rate: mV s^{-1}	Oxidation charge densities (q_+) $\mu\text{C cm}^{-2}$	Reduction charge densities (q_-) $\mu\text{C cm}^{-2}$	% Dissolution $\frac{q_+ - q_-}{q_+} \times 100$
2	1591	552	65.3%
5	2108	1076	49.0%
10	3762	1750	53.5%
20	6253	3463	44.6%

Table 3.1 Oxidation charge (q_+) and reduction charge (q_-) and the percentage dissolution when variable scan rates are applied for cyclic voltammetry of Cu.

Scan rate, ν (mV s^{-1})	Oxidation peak current densities (i_p^A) ($\mu\text{A cm}^{-2}$)		Reduction peak current densities (i_p^C) ($\mu\text{A cm}^{-2}$)		$\text{Ratios} = \left \frac{i_p^A}{i_p^C} \right $	
	AI	AII	CII	CI	AI/CI	AII/CII
2	42.3	43.5	62	39.7	1.06	0.70
5	43.5	54.0	100	97.5	0.44	0.54
10	68.5	88.0	163	194	0.35	0.54
20	105	141	250	382	0.27	0.57

Table 3.2 Oxidation peak current density, i_p^A , reduction peak current density, i_p^C and the ratio of oxidation and reduction peak current densities as functions of scan rate in Cu cyclic .

Table 3.2 shows oxidation peak current and reduction peak current densities. The tabulated ratios of

oxidation current density to reduction current densities, $\frac{i_p^A}{i_p^C}$ shows that only at the slow scan rate of 2 mV s^{-1}

the ratio is close to 1 (unity) for only the first oxidation current peak, AI and reduction current, CI, and which corresponds to the formation and reduction of Cu_2O . From our discussion of reversible process in

Section 1.3.2 we can say that for a system to be reversible the following relation should hold: $\left| \frac{i_p^A}{i_p^C} \right| = 1$,

i.e., the ratio of anodic peak current density to the cathodic peak current density should be unity. Therefore, the results of our experiments demonstrate that at slow scan rate electrochemical oxidation of Cu is, to a certain degree, a quasi-reversible process only if the potential scan is reversed after the first oxidation current peak. The process becomes irreversible at faster scan rate and when higher potential is scanned. Similar results are reported by Strehblow *et al.* [8, 17].

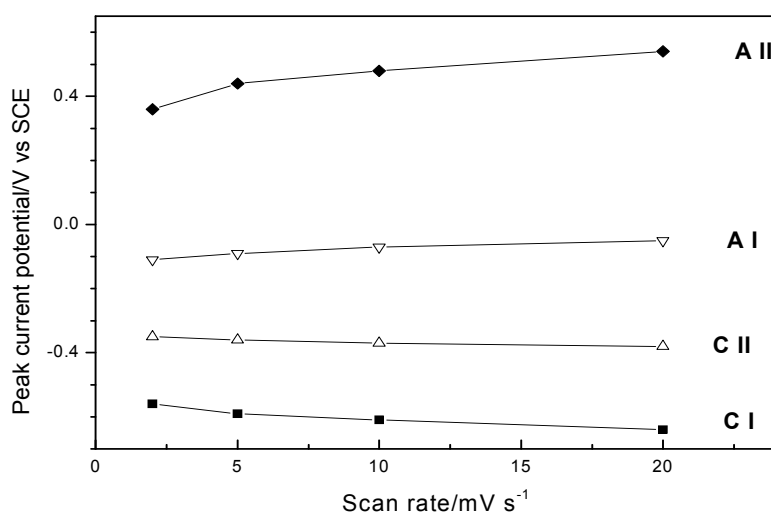


Figure 3.11 Scan rate dependence of potential position of the anodic and cathodic current peaks when Cu is oxidised in 0.1 M borax buffer solution of pH 9.2 at various scan rates.

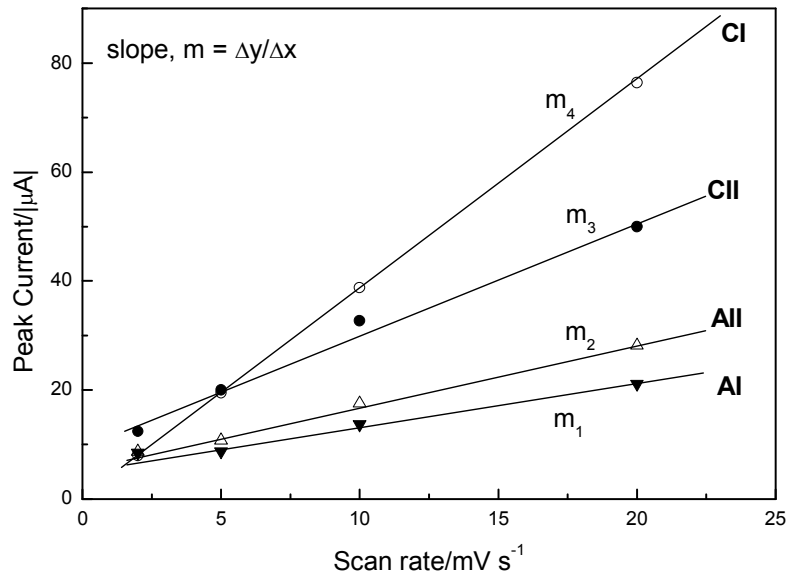


Figure 3.12 Scan rate dependence of anodic and cathodic peak current densities when Cu is oxidised in 0.1 M borax buffer solution of pH 9.2 at various scan rates.

Fig. 3.12 shows the peak current as a function of scan rates. The oxidation and reduction peak currents increase as the scan rates get faster. The linear relation between the peak currents and the scan rate is an indication that the peak current is proportional to the scan rates, v . In the figure, the slopes, m_1 , m_2 , m_3 and m_4 are constants for a system for a particular electrolyte with a particular electrolyte pH. Therefore for our system of surface process the relation,

$$i_p = m v \quad (3.8)$$

where v is scan rate and m is the slope holds. We know from our discussion in Section 1.3.4 that for the surface process, the peak current is [60]-

$$i_p = \frac{n^2 F^2 \Gamma_o A v}{4RT} \quad (3.9)$$

where R is the gas constant and F is Faraday constant, A is area of the electrode and n is the number of electron involved in the process.

The peak current i_p is proportional to the sweep rate, v . Except for the scan rate for a system the other parameters in Eq. (3.9) are considered constant. The “ m ” in Eq. (3.8) is equivalent to all the constants of Eq. (3.9). Therefore, for our system of Cu oxidation in 0.1 M borax buffer solution of pH 9.2, we can write,

$$i_p \propto \nu. \quad (3.10)$$

This indicates that Cu oxidation is a surface process and the peak current is proportional to the scan rate.

From our discussion we can draw the following conclusion-

- Dissolution takes place when Cu is oxidised in weakly alkaline electrolyte.
- Cu oxidation is a surface process.

3.5.3 Cyclic voltammetry of Cu: “window opening” experiments

In this section the results of a series of “window opening” experiments have been described and discussed. Fig. 3.13 shows cyclic voltammograms of Cu in 0.1 M borax buffer solution of pH 9.2 with the potential scan limits of -0.15, 0.05, 0.15, 0.50, and 0.85 V and the corresponding CV's are cv_1 , cv_2 , cv_3 , cv_4 and cv_5 . We observe that the first two CV's, cv_1 and cv_2 are reversed before the oxidation current minimum, labelled “a” after first oxidation peak and these two CV's show only first cathodic peak, CI in the reverse sweep. The third sweep, cv_3 is the first scan that leads to the second reduction peak, CII. In addition to the two anodic and two cathodic currents peak, cv_4 and cv_5 exhibit shoulders, labelled s_1 and s_2 . We see that in the reverse sweep, the reduction current peaks, CII and CI appear, develop and become more prominent, and shift to more negative potential as the reversing potential is extended. It can be seen that the peak AI and CI are related to the formation and reduction of Cu_2O and the peaks, AII and CII are the peaks related to the formation and reduction of CuO and/or $Cu(OH)_2$.

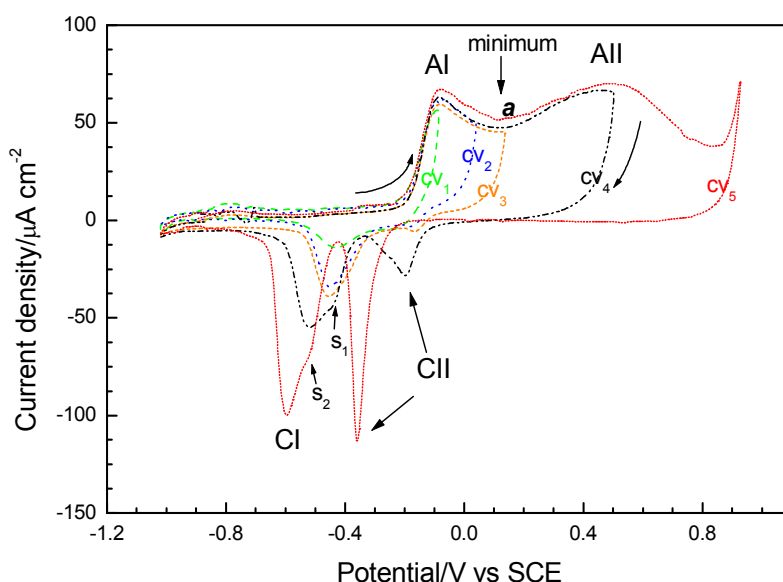


Figure 3.13 Cyclic voltammograms of Cu in 0.1 M borax buffer of pH 9.2 with various positive reversing potentials with sweep rate, 5 mV s^{-1} .

The first three scans are reversed before or at the minimum after the first oxidation current peak, it seems that Cu oxidation from Cu to Cu (II) state) starts to take place only if potential is scanned beyond 0.15 V. But the appearance and development of the reduction current peaks, both CII and CI with the successive scanning to the higher potential says that the formation of Cu_2O and CuO/Cu(OH)_2 overlaps and this overlapping starts to happen in the potential range right after first oxidation current peak, AI. When the potential is scanned initially further than the electrical double layer region, the formation of Cu_2O takes place and it continues and the rate of this oxidation is the fastest around the first oxidation current peak AI. The fact that the reduction peak, CI continues to develop during scans with reversing potential well beyond the first oxidation current peak, AI, is a strong evidence that Cu_2O continues to grow beneath the CuO layer. The shoulders s_1 and s_2 are most likely due to the reduction of Cu^{++} to Cu^0 involving the reduction of Cu(OH)_2 into Cu.

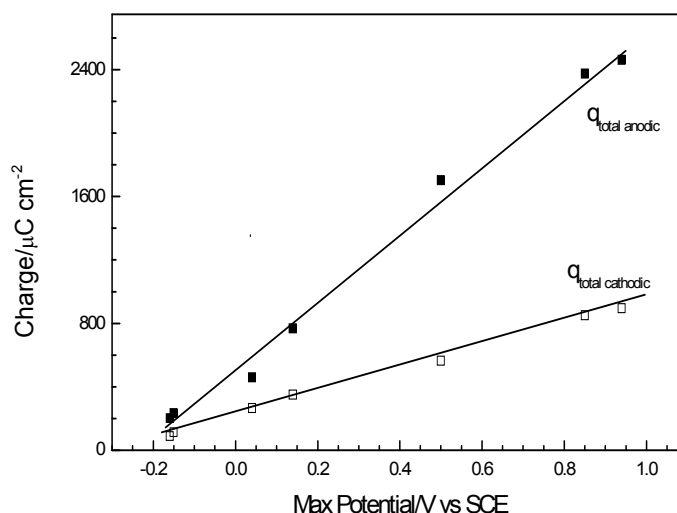


Figure 3.14 Total anodic and cathodic charges', obtained from cyclic voltammogram in borax buffer of pH 9.2, dependence on the maximum positive scanning potential.

Fig. 3.14 shows the dependence of the anodic and cathodic total charge $q_{\text{anodic total}}$ and $q_{\text{cathodic total}}$ on the reversing potential. At the initial stage when potential is scanned just up to the first oxidation current peak, the ratio of anodic and cathodic total charge is close to the unity. As the reversing potential scan is extended it shows that in the potential region of formation of the CuO/Cu(OH)_2 layer, soluble Cu(II) species are also produced which diffuse into the solution. Therefore, the cathodic charge is significantly less than the anodic charge passed and the difference in anodic and cathodic charge widens.

So far in this chapter experiments on Cu electrochemistry in weakly alkaline solution is discussed. Before carrying out simultaneous cyclic voltammetry and SHG experiments, two test experiments were carried out. These two experiments were- the nonlinear response at Cu electrode surface in the air, and the polarisation angle dependence of SHG in the weakly alkaline solution. The test experiments are discussed below.

3.5.4 Test for nonlinear optical response from Cu

In the introduction chapter, the SHG studies by various authors both under electrochemical control and in the air on polycrystalline and single crystals Cu electrode have been discussed. From literatures [148, 149] we know that Cu shows non-linear characteristics when irradiated by the ultra short pulsed laser illumination. To test the experimental set up, mainly the optics and the optical path used in this work; polycrystalline Cu electrode was examined by 780 nm laser beam to confirm that a nonlinear response could be observed with our experimental set up. The following two test experiments were performed:

- (1) Power dependence of SHG signal intensity from Cu surface
- (2) Polarisation dependence of SHG intensity from Cu surface

3.5.4.1 Power dependence of SHG intensity for Cu

In this experiment the Cu electrode was held in the air and the power of the incident beam was varied between 50 and 250 mW using a set of microscope slides as neutral density filters. Starting from 250 mW, power of the incident beam was lowered by adding microscope slides one by one. 780 nm from diode pumped Ti: Sapphire oscillator with $p_{in} - p_{out}$ laser geometry was used for the illumination.

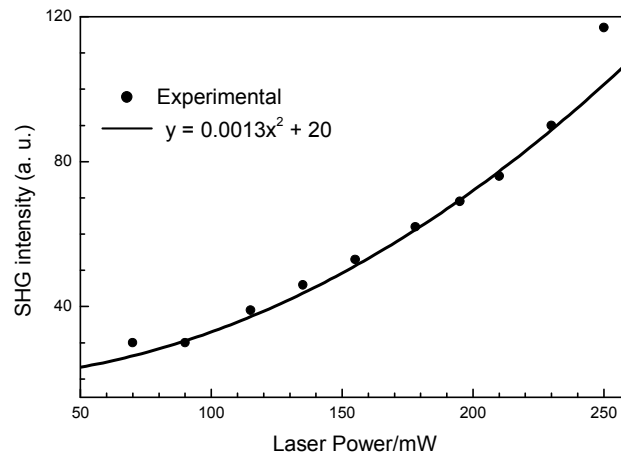


Figure 3.15 Optical SH intensity at the surface of Cu electrode as a function of power of incident laser beam. 780 nm laser illumination with $P_{in} - P_{out}$ laser geometry is used.

Fig. 3.15 shows the plot of SHG intensity obtained upon reflection of the incident beam at Cu surface as a function of power of the incident beam. The polynomial fit of the laser power and the (nonlinear polarisation, and the resulting) SHG intensity response data into the following quadratic equation $f(x) = ax^2 + c$, shows that the SHG intensity from Cu surface has a quadratic (nonlinear) dependence on the laser power [79]. The constant “ a ” in the equation is a parameter which is dependent on the nonlinear susceptibility of Cu. The constant “ a ” is similar to the second order nonlinear

susceptibility, $\chi^{(2)}$ in Eq. (1.49). We also know from the discussion in Section 3.2 that Cu has an fcc structure and the symmetry group 3m3 and it is an example of a centro-symmetric medium [146] but the symmetry breaks down at the surface, hence SHG is allowed for the Cu surface. As expected upon intense electromagnetic exposure SH is generated at Cu surface [149] and the SH intensity may show quadratic dependence on the laser power or on the photon energy [152]. The results of this experiment indicate that the optical experimental set up has been carried out correctly.

Another test experiments is to test how the SHG intensity may vary when the incident laser power is varied by varying the polarisation angle of the incident laser beam, which is described below.

3.5.4.2 Polarisation dependence of SHG intensity

The polarisation dependence of the SHG intensity was tested by rotating a polariser in front of the electrode sample and placing a second polariser after the sample fixed at *p*-polarisation state so that only *p*-polarised reflected SH photons are collected. The polariser before the electrode allowed both *s* and *p*-polarised laser light to pass through as the polariser was being rotated. But the polariser after the electrode sample, which was held at *p*-polarisation state allowed only *p*-polarised SH photons to pass. In this way the optical power of the fundamental laser was controlled. This experiment was carried out on a Cu electrode which was held at -0.8 V in 0.1 M borax buffer solution of pH 9.2 and the SH signal intensity was recorded. The input polariser was rotated and parked at 10° intervals to record the SHG intensity for the full rotation of 360°. Fundamental laser beam was blocked every time a new polarisation rotation angle was set and SHG recorded exactly after 60 s after the fundamental laser beam was unblocked.

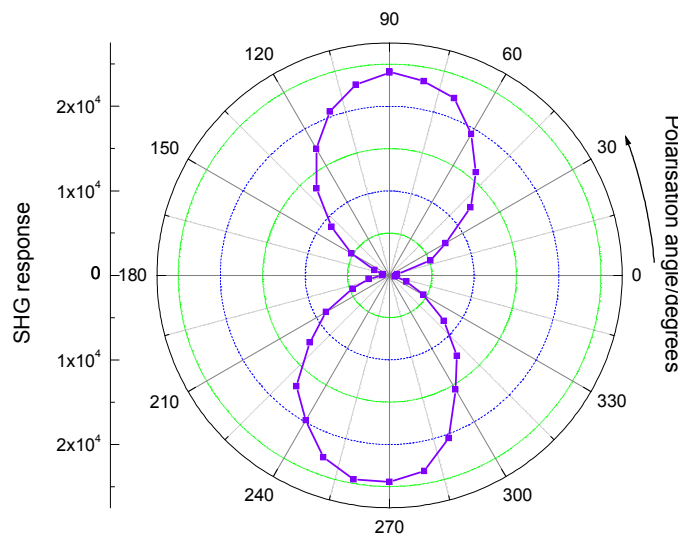


Figure 3.16 Polar plot of the input-polarisation angle dependence of the SHG signal intensity for Cu electrode held at -0.8 V in 0.1 M borax buffer of pH 9.2 under *p*-polarised laser illumination at 780nm.

In the given experimental geometry, the SHG intensity from the Cu electrode surface at the angle of rotation, α of the p -polarised output SH signal recorded at positions 0° and at 180° angle should ideally be coincided with the s -polarised input signals recorded at 90° and 270° respectively. But the reading on the plane polariser holder gives a misalignment of up to 5° with the actual linear polarisation angle. We can eliminate the error arising from this misalignment of polarisation angle by using a pair of linear polariser and restrict the polarisation of the electric field to the P_{in} and P_{out} geometry. The first linear polariser is placed before the fundamental laser beam is incident at the metal electrode and the second polariser is placed before the SH photon beam is guided to the photon counting device, the PM tube.

The results illustrated in Fig. 3.16 demonstrates that for s input incident laser beam there is negligible or no SHG response recorded at p output selection which is similar to the finding by Schwab *et al.* [152]. The SHG intensity curve gives a two-fold rotational pattern and can be expressed as and fitted to the following equation-

$$I \propto \sin^2 \alpha \quad (3.11)$$

where “ I ” is the SHG intensity and α is rotation angle of the input polariser [146]. This polarisation dependence of the SHG intensity led us to assume that the experimental set up is properly configured and is fit to investigate how the nonlinear response may vary when Cu is oxidised and the surface of the electrode changes.

3.5.5 Simultaneous SHG and cyclic voltammetry experiments on Cu

3.5.5.1 Introduction

In Sections 3.3 we have discussed Cu electrochemistry in general and in Section 3.5.1, 3.5.2, and in Section 3.5.3 we have discussed results of our experiments on Cu electrochemistry in 0.1 M borax buffer solution of pH 9.2. Here we have used optical SHG to study the formation and reduction of Cu oxides. Therefore, cyclic voltammetry experiments on Cu at various reversing potentials, the so called “window opening” experiment, were carried out and SHG responses from the Cu surface and the currents were recorded as functions of the applied electrode potential. During the experiment, although the Cu electrode was under intense laser illumination, no change in the cyclic voltammogram or any surge in anodic and cathodic current was noticed. This was tested by running cyclic voltammetry experiments with and without laser illumination. That means the influence of thermal and optical exposure of the Cu electrode on the oxidation or reduction current is negligible.

To simplify the discussion of the experimental results in this section, results are discussed in the following two parts-

- SHG and Cyclic Voltammetry: potential reversed at the top of the first oxidation current peak, AI
- SHG and complete Cyclic Voltammetry of Cu

3.5.5.2 SHG and cyclic voltammetry: potential reversed at the top of the first oxidation current peak, AI

Fig. 3.17 shows the plot of the SHG signal and the oxidation current as functions of the applied potential when the Cu cyclic voltammogram is obtained. After pretreatment, the scanning of the potential started at -0.80 V and then was reversed at the top of the first oxidation current peak, AI at -0.02 V and then scanned back to -1.0 V and finally scanned forward to -0.80 V and stopped.

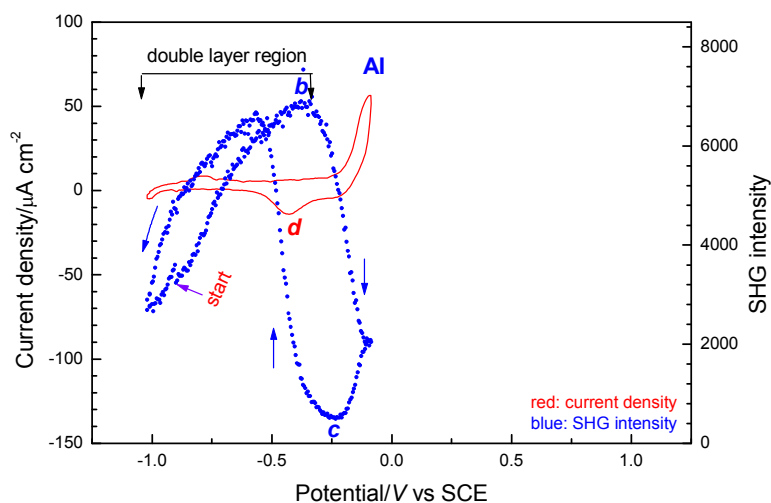


Figure 3.17 Cyclic voltammetry (CV) and SHG response for Cu in 0.1 M borate buffer of pH 9.2 at 5 mV s⁻¹. The *p*-polarised incident is at 780 nm. The scan was reversed at -0.02 V [3].

We know that the first oxidation current peak is associated with the oxidation of Cu to the Cu(I) state and in the process, Cu₂O is formed. In the *electric double layer region*, labelled in Fig. 3.17, no redox activity takes place. As the potential is scanned, the SHG signal increases slowly and continues to increase until it reaches the SHG peak at -0.37 V. The potential being scanned here is still within the double layer region. After the SH intensity peak, labelled as “*b*” in Fig. 3.17, the SHG intensity falls sharply and reaches a minimum at -0.02 V, at where the scanning of the potential was reversed, which is also the potential where first oxidation current peak, AI appear. When the potential scan is reversed, the current decreases sharply and SHG intensity decreases initially to a minimum, labelled as “*c*” but before the appearance of a small cathodic current peak, labelled “*d*”, the SHG intensity starts to increase. Eventually, SHG intensity and current return to their original values. Here, the contribution to the SHG intensity may come from several different phenomena which are discussed next.

3.5.5.2.1 Origins of SHG contributions

To discuss the origin of the SHG signal, we separate the induced optical polarisation into the nonlinear susceptibility tensor, $\chi^{(2)}$ into its resonant, $\chi_r^{(2)}$, and non-resonant, $\chi_{nr}^{(2)}$ contributions,

$$P(2\omega) = (\chi_r^{(2)} + \chi_{nr}^{(2)})[E(\omega)]^{(2)} + \chi^{(3)}(E(\omega))^2 E^{(dc)} \quad (3.12)$$

The potential was scanned in this section only up to the apex of the first oxidation current peak, AI as illustrated in Fig 3.17. Within this potential range, the most likely contributions to the SHG response are the following-

(a) A non-resonant contribution through $\chi_{nr}^{(2)}$.

A non resonant contribution is not dependent on the wavelength of the incident laser beam or on the applied dc-electric field [117].

(b) A resonant contribution through $\chi_r^{(2)}$ [117].

This contribution is dependent on the wavelength of the incident laser beam. Contributions from this category may arise from the following:

- The population/depopulation of surface states may affect any resonance contribution from the metal/electrolyte interface [93].
- Anion adsorption may bind surface electrons- affecting their ability to be polarised by the incident light [3, 75, 93].
- A resonant contribution may arise due to the band gap of the semiconductor grown on metal surface, such as the Cu surface.

(c) Contribution due to the applied electric field, $\chi^{(3)}$, which is the so called EFISH contribution [3, 4, 110, 117].

When cyclic voltammetry is carried out on Cu one or more of these contributions may be responsible for the increase or decrease of the SHG response.

3.5.5.2.2 SHG in the forward scan

The initial increase of SHG signal intensity in the *double layer region* is most probably due to increased ionic adsorption, which in turn influences the second order nonlinear susceptibility, $\chi^{(2)}$ of the surface. Marcus' group [129, 141, 186] has recently investigated the initial oxidation of Cu in aqueous solution. They have reported on the *in situ* STM electrochemical measurements of Cu (111) in 0.1 M NaOH and demonstrated that a reversible adsorption/desorption process occurred in the underpotential range of

Cu₂O formation around -0.675 ± 0.02 V vs SHE. Although this type of ion adsorption is restricted to one surface monolayer, it can change the surface's nonlinear susceptibility, $\chi^{(2)}$, which causes the initial increase of SHG signal. An EFISH contribution to the SHG signal intensity is also possible from the Cu surface itself in absence of any faradaic process in the *double layer region*. Before the surface oxidation and formation of Cu₂O take place, as observed in Fig. 3.17, the SHG signal starts to decrease. At this stage Cu₂O and to a lesser degree CuOH [183] start to develop on the Cu surface. As the Cu₂O layer continues to grow on the Cu surface, the anodic current increases and the SHG signal continues to decrease. The surface is affected by the presence of the dc field. This change in field causes a change in the surface electron density, which in turn, affect the second order nonlinear susceptibility of the interface, $\chi_I^{(2)}$. As a result, continued decline of SHG signal takes place. A similar decrease in SHG response has been reported by Campbell *et al.* [167] for Pt, where they have suggested that the oxide growth and the adsorbed anions displacements by the oxide layers caused the SHG response to reduce. The potential is reversed just before the anodic current reaches the apex of the first oxidation peak, AI which coincides with a tiny increase of SHG signal at the end of the scan.

3.5.5.2.3 SHG is sensitive to surface layers

In this section effectiveness of SHG as a sub-monolayer probe will be discussed based on the results we have presented above. The voltammogram illustrated in Fig. 3.17 shows that the potential was reversed at the top of the first oxidation current peak. At this point a significant amount of charge has passed. As explained in the earlier section, charge calculations in Section 3.5.2 and 3.5.3, and figures from the published results giving a literature value of $300 \mu\text{C cm}^{-2}$ for a monolayer of Cu₂O [183, 187] on the Cu surface indicates that by the end of the forward scan when SHG signal is about to rise, at least 2-3 monolayers of Cu₂O that have been formed. Considering the charge and molar volume data, at this potential and under the condition, the thickness of Cu₂O is at least 5-7 Å [8]. The fact, the SHG signal starts to rise just before the end of positive going potential, has significant implication as to what is the origin of SHG, and how sensitive SHG is to the surface layers. If we look at the Fig. 3.17, it is seen that the base count of SHG signal is 300 at the point when SHG signal starts to increase and the SHG signal count increased by more than 5,000 giving a signal to noise ratio of around 25. When Cu₂O is formed the signal change is around 6,000, which makes the SHG signal to be sensitive to sub-monolayer coverage. This result shows that there need only be as little as a tenth of a monolayer of Cu₂O present to see a change in the nonlinear response. This is in excellent agreement with the previous works on Pt and Ag [144] and an assurance that the technique of SHG is capable of showing sub-monolayer sensitivity.

3.5.5.2.4 SHG response from semiconducting Cu₂O

At this stage it is worth mentioning that Cu₂O is a semiconductor with a band gap of 2.10 eV [121]. When Cu₂O grows under the influence of potential it will clearly reach a point where the thickness is such that it

can show its semiconducting properties. As the Cu_2O is illuminated and the SH photon energies are greater than the band gap of Cu_2O , the electrons can be promoted from the valence band (VB) to the conduction band (CB). While this process is occurring, holes are left behind and on the surface of Cu_2O a surface charge region (SCR) is formed. But in the bulk of Cu_2O , recombination of the electron-hole pairs continues to happen. In presence of an electric field applied to the electrode, the SCR facilitates the separation of electron-hole pairs.

At the end of the positive scan in Fig. 3.17 there is a small increase in the SHG signal intensity. This is believed, on the evidence to be discussed further later in this chapter, to be due to a resonant contribution, $\chi_r^{(2)}$ from the semiconducting thin film, Cu_2O . When the frequency of an inter-band transition of semiconducting film or a surface electronic state is in resonance or near-resonance with either the incident or second harmonic frequency of the photons, there can be significant enhancement in the nonlinear optical responses. The 2.10 eV band gap of Cu_2O is smaller than the energy of a SH photon of ~ 390 nm, which is 3.18 eV. Thus a resonant contribution is possible when Cu_2O is sufficiently thick to behave as a semiconductor. This point will be discussed further in the next section where the potential scan is extended further to potentials where Cu oxidises to the Cu^{++} state.

Now going back to the discussion of Fig. 3.17 as the potential is reversed, reduction current is produced that coincides with a decrease in SHG signal. Finally, both the SHG signal intensity and current return to their original values.

3.5.5.3 SHG and complete cyclic voltammetry of Cu

3.5.5.3.1 Introduction

For the experiment discussed in this section, the potential is extended into potential regime of Cu(II) oxidation. The typical cyclic voltammogram displays two anodic peaks, AI and AII and two cathodic peaks CII and CI. SHG intensity also has been recorded. The recorded current and SHG intensity data were plotted as functions of applied electrode potential and are illustrated in Fig. 3.18.

Fig. 3.17 shows that the potential scan was commenced at -0.80 V. Both CV and SHG responses up to the top of the first oxidation current peak were described in Section 3.5.5.2. In Fig. 3.18 we see that when the potential scan is extended, the oxidation current starts to decrease and SHG signal intensity starts to increase. With further scanning of the potential, the decrease of anodic current continues until it reaches a minimum at 0.15 V. The increase of SHG signal intensity reaches a maximum at 0.20 V, which is also the potential from where the oxidation current starts to increase. The oxidation current increases until it reaches the second oxidation current peak, AII at 0.45 V, then the oxidation current decreases continuously until the oxygen evolution potential where it shows a sharp increase after 0.80 V. The SHG

response from point “*d*” starts to decrease and reaches its minimum at ca. 0.70 V and then increases until the end of the positive going scan.

In the reverse scan, the current drops sharply from the oxygen evolution higher current regime to the minimum positive value. Here at this stage, there are both Cu(I)- and Cu(II)-oxides present at the electrode surface. But no redox process takes place with scanning down of the potential, as the potential is not sufficiently negative to begin oxide reduction. As the potential is scanned back, the current does not change over the range of potential from 0.80 V to -0.10 V. Electrochemically nothing happens in this potential range in the reverse scan. The SHG response from point “*a*” traces back the SHG response as in the forward scan until the point “*d*” with a minimum at 0.73 V. In contrast to the current which does not change until -0.10 V, the SHG response increases continuously until the point “*b*” at -0.20 V. Just when reduction charge starts to pass before the reduction peak, CII, there occurs a sharp fall in SHG response (from “*b*” to “*e*”). The reduction current shows two cathodic current peaks, CII and CI, before returning to the original value at -0.80 V. In contrast, the SHG response follows a wide peak (“*e*” to “*g*”) and slowly recovers to its forward-scan-value at -0.80 V.

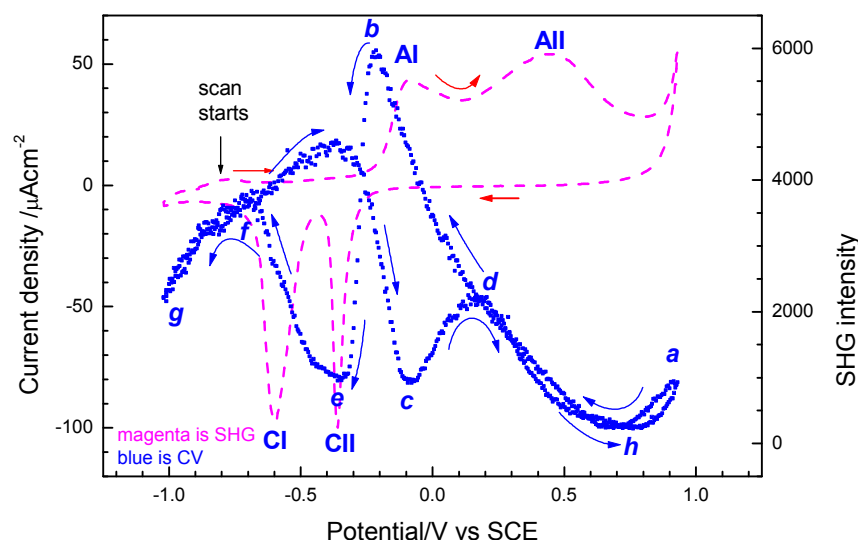


Figure 3.18 Cyclic voltammogram and SHG response for Cu in 0.1 M borax buffer solution of pH 9.2. Scan rate is 5 mV s⁻¹. The p-polarised incident laser beam of 780 nm from an amplified Ti: Sapphire oscillator is used [3].

Due to the complexity of Fig. 3.18, and the amount of information related to the CV and SHG response curve, this section will be discussed in the following parts-

- EFISH response from CuO between point “*a*” and “*b*”
- SHG change at point “*b*”,
- SHG intensity change between point “*c*” and “*d*” and
- Full recovery of SHG signals at the end of cyclic voltammogram.

3.5.5.3.2 EFISH response from CuO between point “a” and “b”

The complicated response seen in Fig. 3.18 can be more easily explained by considering what happens as the potential travels in the negative direction from the positive end of the scan. At the point labelled ‘a’, the scan is reversed and by the time that this point at the end of the anodic scan is reached, a duplex structure of Cu₂O and CuO with thickness in the range of 20-40 Å [8] has been formed; CuO is formed on the surface with a thinner layer of Cu₂O and/or CuOH underneath. On the negative going scan there is a large potential region (between 0.90 and -0.10 V) where the CuO layer is mostly unchanged until the reduction begins at -0.10 V. From point “a” to “b” in the reverse scan and from point “d” to “a” in the forward scan the SHG signal traces a parabola. The data in this region in both directions can be fitted to a parabola using a simple fitting programme. This is shown below in Fig. 3.19a and 3.19b. This observed parabolic dependence of SHG signal means that the response can be attributed to an electric field induced second harmonic (EFISH) response [3, 4].

Here, there is a dc electric field normal to the electrode surface in the z-direction as discussed in Section 1.6.5 of Chapter 1 and illustrated in Fig. 1.17. In fact, Strehblow *et al* [8] estimated a field strength of $4\text{--}7 \times 10^6 \text{ V cm}^{-1}$ for the CuO layer. The minimum value of intensity of SH occurs at 0.78 V when the potential is scanned in the forward direction and at 0.72 V in the reverse direction as seen in Fig. 3.19a and Fig. 3.19b.

To see the quadratic behaviour of SHG response between the point “a” to “b” in the reverse direction and “d” to “a” in the forward direction the experimental data were fitted to the following quadratic equation-

$$I^{2\omega} = I_0^{2\omega} + (V - V_0)^2 \quad (3.13)$$

where $I^{2\omega}$ is the intensity of the SHG signal, V_0 is the potential where the minima of the SHG signal intensity occur and V is the potentials positive or negative of the potential, V_0 .

The good quadratic fit of the data in both the forward direction between 0.40 and 0.90 V and in the reverse direction between 0.90 and 0.45 V confirms that the variation of the SHG intensities as functions of the applied potential in the regions is dominated by the EFISH term, $\chi^{(3)} E(\omega) E(\omega) E^{dc}$ in Eq. (3.12).

As discussed, there is a strong possibility that the applied dc electric field induces a nonlinear polarisation, and hence triggers an EFISH contribution to the SHG in the potential region where there is CuO present on the Cu surface during the potential scan. The potential where EFISH minimum is observed in the forward sweep shifts about 0.03 mV to the less positive potential in the reverse scan. This is due probably to the fact that when the forward potential scan is reversed at 0.90 V, a small scale oxidation still goes on [8, 10]. Potential range for EFISH response in the forward scan is shorter than the range in the reverse scan because the formation of CuO takes place over a much narrower potential range compared to the

potential range over which the formation of CuO takes place in the forward potential sweep before being reduced in the reverse scan.

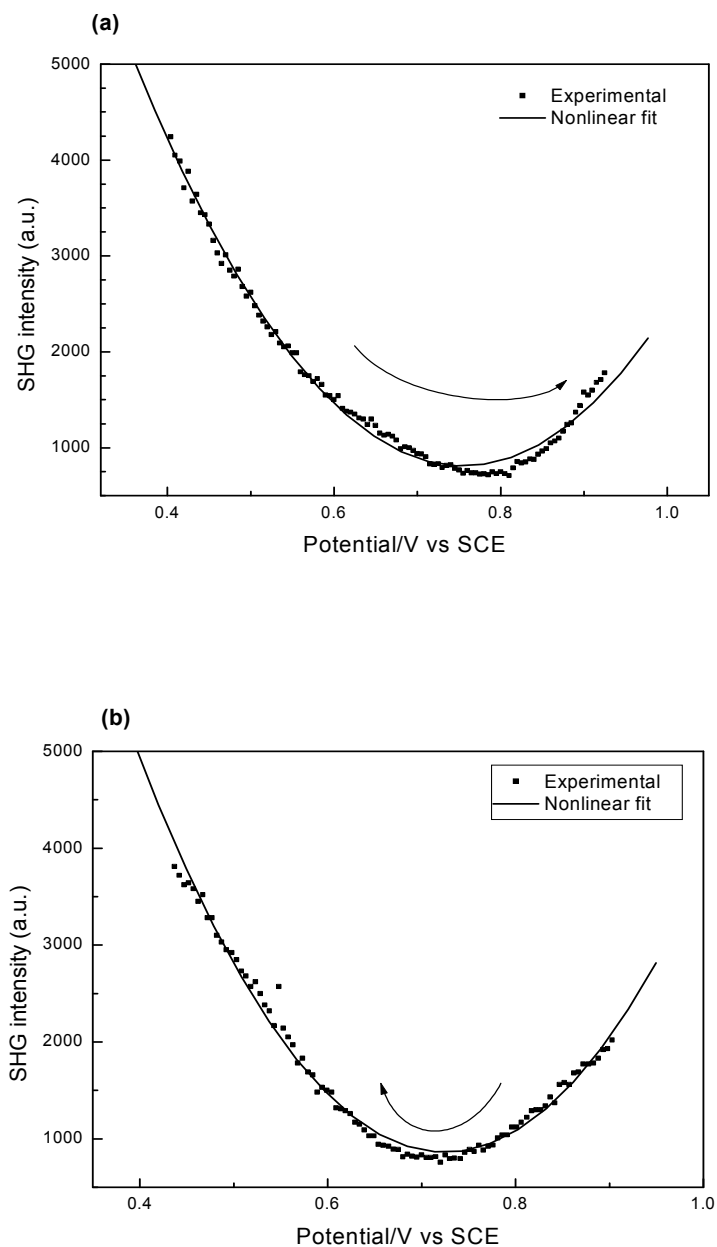


Figure 3.19 SH intensity response vs applied potential in the vicinity of lowest SHG signals where the variation in the SH intensity is dominated by the third-order nonlinear susceptibility, $\chi^{(3)}$ (EFISH). The parabolic fits demonstrate the quadratic dependence of the SH intensity on the applied field. Scan (a) is forward scan, and (b) is reverse scan.

Potential of zero charge (PZC) of semiconducting CuO

At the potential of zero charge (PZC), there is no net excess charge at the electrode surface. At potentials more negative than the PZC, the electrode surface has a negative excess charge, and at more positive potential there has a net positive surface charge. At PZC the number of charged particles or ions at the surface is zero resulting a decrease in the number of surface states, which is responsible for the decrease in the SH intensity. Therefore it is probable that the PZC might be located in the potential range where the SH intensity is mediated by the EFISH and a minimum. This point where the SH intensity is minimum is V_0 in the Fig. 3.19. The reported PZC values by Lukomska *et al.* [136] for (111), (100) and (110), and polycrystalline Cu in 0.01 M NaClO₄ were -0.70, -0.73, -0.75 and -0.73 V vs SHE respectively. These values are far from the potential values where the EFISH intensity minima occur and they are 0.78 V in the forward scan and 0.72 V in the reverse scan.

From Fig. 3.18 we can see that by the time we notice the minima of the EFISH mediated SH intensity, the growth of Cu₂O/CuO on the Cu electrode is in between 20-40 Å and this oxide layers shows semiconducting properties, such as band gap and interband transition of states when under optical illumination. The analogous of PZC is *the flat band potential* (E_{FB}) for a semiconductor. E_{FB} is the potential at which the potential induces zero net charge on the underlying semiconductor, and hence the excess charge on either side of semiconductor/electrolyte is zero. This is an indication that SHG technique could be used to determine the E_{FB} of semiconductors.

From the discussion we understand that the technique of SHG has the potential to determine the PZC of a metal electrode or the E_{FB} of a semiconductor. But these two parameters depend on the concentration and the kind of electrolyte, and also on the surface preparation. A thorough investigation of the PZC of Cu electrode and/or E_{FB} of semiconducting Cu₂O/CuO were not intended and was considered beyond the scope and capacity of the project due to the time constraint.

At the end of this section, we can draw the following conclusions:

- The CuO layer is the dominant contributor to the nonlinear polarisation, and hence SHG response in the potential ranges from 0.90 to -0.20 V in the reverse scan and 0.20 to 0.90 V in the forward scan.
- In the regions from “a” to “b” or “d” to “a”, the SHG signal is dominated by an EFISH contribution.
- The technique of SHG might be used to find the PZC of metal electrode and/or E_{FB} of semiconductors.

3.5.5.3 SHG change at point “b”

We have just seen the quadratic behaviour of the SHG signal as a function of applied potential which terminates at point “b”, the behaviour of the SHG signal as the potential proceeds further negative is discussed here.

Fig. 3.18 shows a sharp fall in the SHG signal, beginning at point “b”. It is noteworthy that only a submonolayer amount of charge (corresponding to the peak, CII) needs to be passed before the sharp drop in SHG signal occurs. The potential at point “b” is also the potential where the cathodic current increases sharply demonstrating that the CuO layer was being reduced in a faster rate than the rate it was formed.

The sharp decline in the SHG intensity, even though less than a monolayer equivalent charge being passed is perhaps due to a mechanism in which the initial reduction current converts an outer layer of CuO to Cu/Cu₂O causing a reversal/collapse of the field across the oxide layer and that triggers the collapse of the EFISH dominated SHG signal [3]. Therefore the following conclusions can be drawn on the SHG change at point “b”-

- A sharp decrease in SHG signal is observed.
- Submonolayer amount of charge is passed before the sharp decrease of SHG takes place.
- It is possible that reduction of the outer layer of CuO at point “b” is responsible for the collapse of the quadratic (EFISH) behaviour of SHG [3].
- The contribution from E^{dc} mediated EFISH terminates at point “b” in the reverse sweep.

3.5.5.4 SHG intensity change between point “c” and “d”

After the changes witnessed in Fig. 3.17 and discussed in Section 3.5.5.2, where potential was reversed at the top of the first oxidation peak, AI we reach point “c” in Fig. 4.18. At the point labelled “c”, the Cu₂O layer has grown to a thickness of up to 5-7 Å [8, 17], sufficient to facilitate the “tuning in” of the resonance contribution from Cu₂O. We recall the $(\chi_r^{(2)})[E(\omega)]^{(2)}$ term of Eq. (3.12). This resonance contribution causes the increase in the SHG signal. The SHG signal continues to increase as the Cu₂O layer gets thicker and the oxidation current drops to a minimum (because the layer is passivating). This increase of SHG signal until the point, “d” is due to the resonance contribution from Cu₂O layer as discussed earlier. However at point, “d”, the SHG signal starts to drop as the current begins to rise again after the first oxidation peak, AI. This rise in current is due to the start of formation of the CuO layer on top of the Cu₂O layer [3]. But at higher potentials the literature says that Cu(OH)₂ starts to grow as well. The formation of Cu(OH)₂ on the surface disturbs the structure of the underlying Cu₂O layer. Therefore, Cu₂O no longer acts as an effective migration barrier for the Cu⁺⁺ ions which can easily be driven to the surface by the applied potential. As previously mentioned, the further oxidation of Cu to its Cu(II) state is a field- driven process.

As the oxidation proceeds with increasing potential and CuO grows on top of the Cu₂O layer, the formation of CuO changes the surface and the development of the CuO layer alters the dominant factor, the resonance contribution, $(\chi_r^{(2)})[E(\omega)]^{(2)}$ responsible for SHG signals. The dominant factor for SHG changes from being the resonant contribution from Cu₂O to the EFISH from CuO. Due to the onset of EFISH, the SHG signal curve enters into the parabolic region at the point labelled, “*d*”, and follows the parabolic shape, passes through the minimum of SHG signal count and reaches the point “*a*” where the scan is reversed and the EFISH contribution continues until when an outer layer of CuO layer is reduced in the reverse scan, and disrupts the field and as a result SHG signals falls abruptly. To summarise the main steps of SHG change in the region between point “*c*” and “*d*” the following can be stated-

- As CuO starts to form, anodic current increases until the broad anodic peak, AII.
- The dominant contribution to the SHG signal alters from the resonant contribution of $(\chi_r^{(2)})[E(\omega)]^{(2)}$ at point “*c*” to the EFISH contribution $\chi^{(3)} E(\omega) E(\omega) E^{dc}$ from point “*d*” onwards in the forward direction [3].

3.5.5.3.5 Full recovery of SHG signals at the end of the cyclic voltammogram

In the previous sections we have discussed the phenomena suggested to be responsible for the changes in the SHG responses with potential for the whole of the positive going cycle and then the first part of the negative going cycle. We will now discuss what happens in the reminder of the negative going scan.

In Fig. 3.18 it is noticed that after point “*b*” in the negative going scan, with the onset of the reduction peak CII, SHG signal falls sharply. As reduction of CuO takes place the SHG signals recover partly. This is because as the CuO is reduced, at the surface the underlying Cu₂O is exposed and the resonance contribution from Cu₂O layer starts to influence the SHG signal again. Unlike in the case of reduction of CuO where the SH signal reduces sharply as soon as reduction of that layer begins, the reduction of Cu₂O in fact is seen to be accompanied by an increase in the SHG signal. In contrast to what was seen at the onset of CuO reduction, the SHG signal increases continuously until a large fraction of Cu₂O undergoes reduction. When this has happened, the SHG signal then merges with its original path, decreasing slightly as the potential returns to the starting point.

In this section it has been suggested that SHG signal changes markedly as the Cu is oxidised first to its Cu(I) state and form Cu₂O then CuO in a duplex structure. The formation of Cu₂O gives rise to a resonant contribution to the SHG signals because of the band gap of the semiconducting Cu₂O, and then the upper CuO layer produces an EFISH response and dominates the SHG signal in the potential region where CuO is present at the Cu surface. To verify the suggestion that EFISH is responsible for SHG response, the experiments are carried out by varying the wavelength of the incident laser beam, and the results are discussed in Section 3.5.7.

3.5.6 “Window opening” experiments: SHG and cyclic voltammetry of Cu

3.5.6.1 Introduction

In Section 3.5.3 “window opening” cyclic voltammetry experiments on Cu have been discussed. So far SHG signal from partially to fully oxidised Cu surface has been discussed in Section 3.5.5. A resonance contribution from Cu_2O and EFISH response from CuO to SHG were noticed and discussed in the preceding section. In this section, results of combined SHG and “window opening” cyclic voltammetry experiments are discussed below. The pretreatment procedure is similar to that has been discussed in Section 3.4.4.

In Fig. 3.20 to Fig. 3.24, the results of “window opening” with SHG experiments are illustrated. In each case potential was reversed before full oxidation of Cu took place except the one described in Fig. 3.24 where full Cu cyclic voltammetry was carried out. Scanning of the potentials was reversed for each of the cyclic voltammetry scans at -0.15, 0.05, 0.15, 0.50, and at 0.95 V. The oxidation and reduction current peaks show the typical behaviour that has been discussed in the Cu electrochemistry section.

The SHG data presented in Fig. 3.20, where potential was reversed at the top of the first oxidation peak, AI and in Fig. 3.24, which is a full cyclic voltammogram, have been discussed in Section 3.5.5.2 and in 3.5.5.3 respectively.

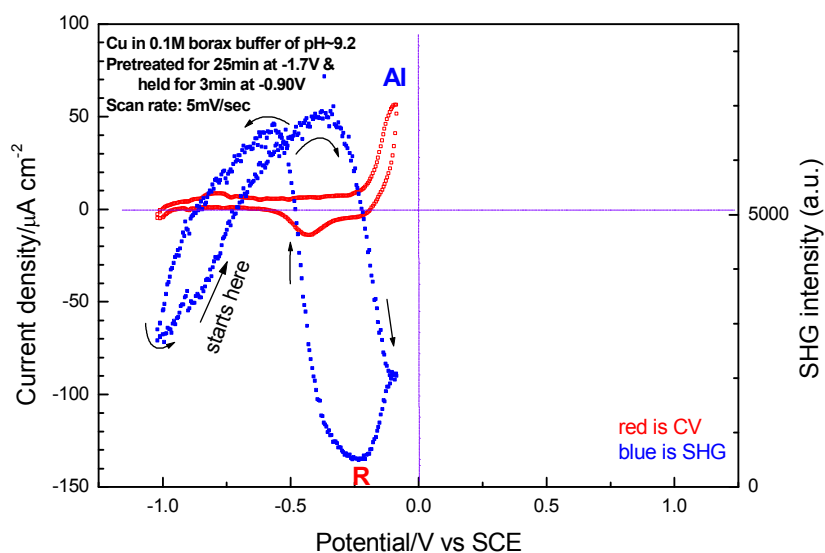


Figure 3.20 Simultaneous cyclic voltammetry and SHG from a Cu electrode in 0.1 M borax buffer of pH 9.2 with reversing potential of -0.16 V at 5 mV s^{-1} under *p*- polarised illumination at 780 nm from a Ti-Sapphire oscillator. Potential scan was reversed at -0.15 V.

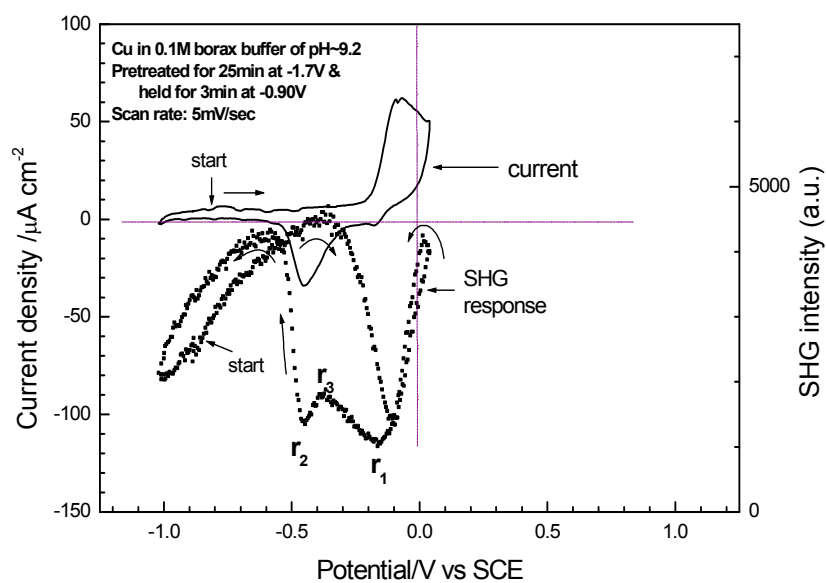


Figure 3.21 As for Fig. 3.20 except the reversing potential which is 0.05 V

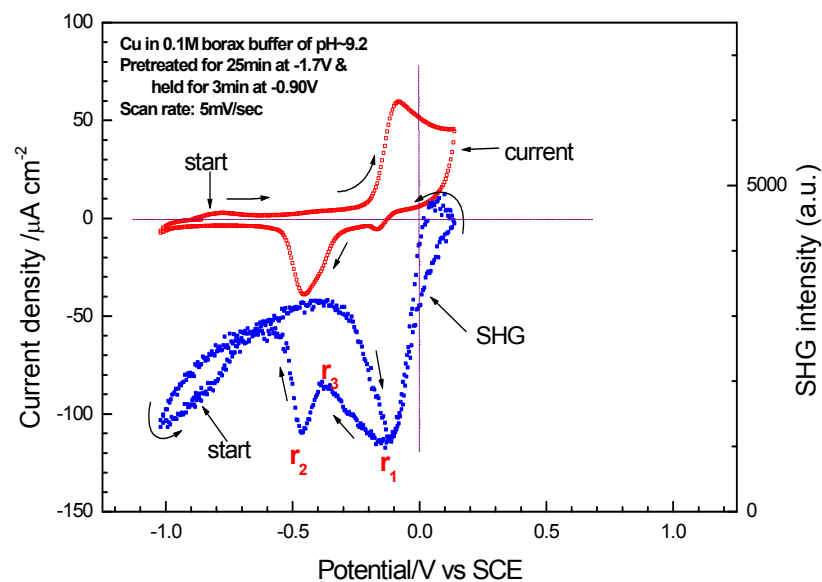


Figure 3.22 As for Fig. 3.20 except the reversing potential which is 0.15 V

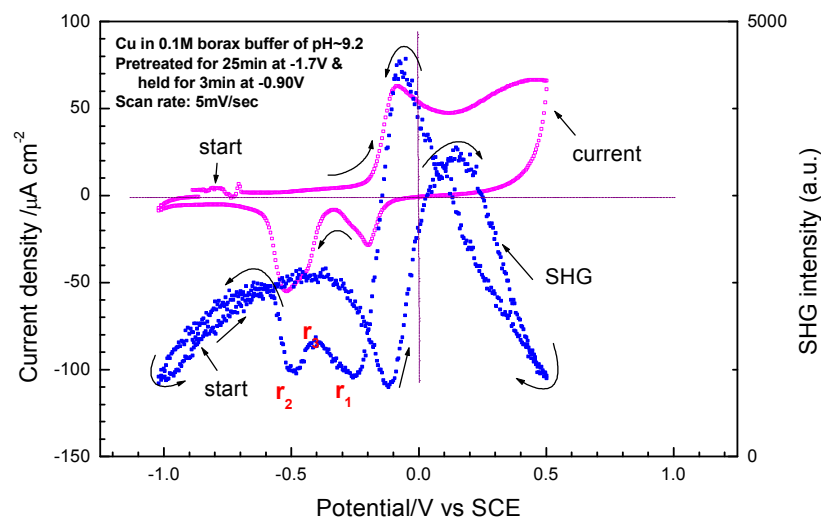


Figure 3.23 As for Fig. 3.20 except the reversing potential which is 0.5 V

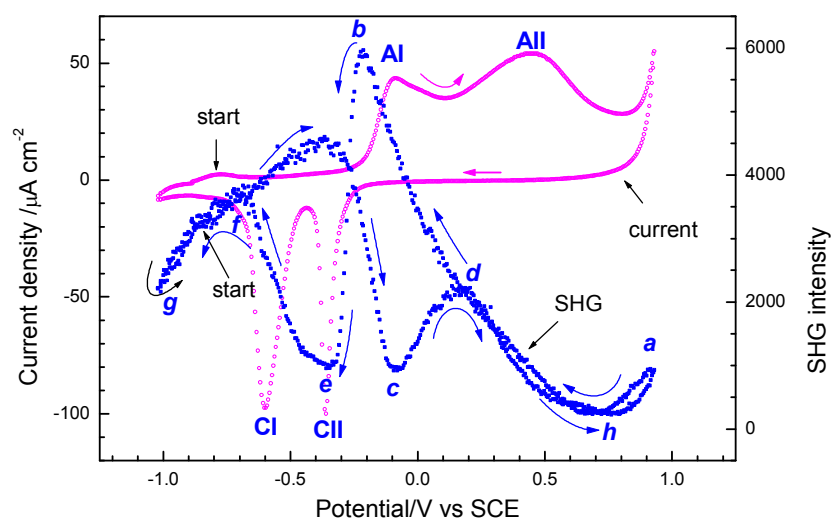


Figure 3.24 Simultaneous cyclic voltammetry and SHG from a Cu electrode in 0.1 M borax buffer of pH 9.2 with reversing potential of -0.16 V at 5 mV s⁻¹ under p- polarised illumination from 780 nm from a Ti-Sapphire oscillator. The potential scan was reversed at 0.95 V.

In the window opening experiments the upper potential limit is extended and the current and SHG responses are recorded. The oxidation and reduction currents were similar to those seen in Section 3.5.3. But a noteworthy change happened in the SHG responses. Initially, when the potential is reversed at the top of the first oxidation current peak, AI, it leads to a broad SHG peak (labelled “R” in Fig. 3.20) that occurs before a small reduction charge is passed. As the potentials in positive going scans are extended the initial single broad SHG peak splits into two peaks (troughs), labelled “r₁” and “r₂” in Fig. 3.21, 3.22 and in Fig. 3.23, and then the peak “r₂” disappears and “r₁” broadens to the feature labelled “e” as seen in Fig. 3.24. In the sections below the observed phenomena are discussed.

3.5.6.2 Single SH signal peak, labelled “R” in Fig. 3.20

A discussion of SHG intensity up to the point of maximum anodic current peak, AI was presented in Section 3.5.5.2. When the oxidation current starts to pass, we see SHG starts to decrease and just as current reaches the peak, AI as shown in Fig. 3.20; the SHG signal intensity reaches a minimum. The potential is reversed at the point when the resonance contribution to SHG signal from Cu₂O (after a growth of a layer 5-7 Å layer as suggested from literature data) should just be about to start. After the scan reversal, reduction charge starts to pass and the SHG changes are reversed with SHG recovering with a ca. 0.25 V delay compare to the forward scan SHG response.

3.5.6.3 Development of two SH signal peaks “r₁” and “r₂”

As the potential is extended, two SHG peaks appear as shown in Fig. 3.21 and the peaks develop with further scanning of the higher potential as in Fig. 3.22 and 3.23. The hysteresis and development of the reduction current indicate that when the potential is past the apex of the first oxidation current peak, AI, a small scale oxidation of Cu to its Cu(II) state also takes place and CuO starts to grow on top of the Cu₂O layer. Although there may be a thin layer of CuO present, not enough for a $\chi(3)E(\omega)E(\omega)E^{dc}$ mediated full EFISH contribution to the SHG signal is seen. So when the reduction of the thin layer of CuO starts, the SHG signal intensity decreases from the point labelled “r₃”. But soon after, SHG signal curve enters the resonant dominated SHG region from Cu₂O. Therefore when the potential is reversed, the SHG signal intensity is reduced sharply. But immediately SHG response increases because the resonance contribution from Cu₂O ‘tunes in’. As the reduction of Cu₂O to Cu becomes complete, the SHG signal increases and then finally merges with the initial path.

3.5.6.4 Disappearance of peak “r₂” (trough)

In this section the possible reasons for disappearance of SHG peaks “r₂” will be discussed. When the potential is scanned up to 0.50 V, the two SHG peaks, “r₁” and “r₂” are clearly seen in Fig. 3.21, 3.22 and in Fig. 3.23. But when the potential is extended beyond 0.50 V, and into the regime where oxidation current decays after the peak, AII; the SHG signal peak labelled “r₂” disappears. The potential-current curves of the window opening experiments suggest that after the oxidation current reaches the peak, AI, formation of both Cu₂O and CuO/Cu(OH)₂ continues, perhaps at different rates. On a Cu surface, Cu₂O formation takes place first and when the potential is extended, then formation of CuO layer takes place on top of the Cu₂O layer. But the growth of the Cu₂O layer underneath the CuO continues [6, 8, 17].

In absence of techniques such as ellipsometry, ESCA and electrochemical STM, it is difficult to exactly pinpoint the sequence of oxide formation and the reason behind the disappearance of the SHG peak “r₂”, when the potential is scanned beyond 0.50 V. But with the knowledge available to us from experiments

carried out, it is possible to suggest that the following could be the reasons for the disappearance of the peak “r₂”:

We have learnt that after the first oxidation current peak, AI, the formation of both Cu₂O and CuO takes place. Initially perhaps the interface between the oxides of different oxidation state of Cu remains well defined. But this well defined interface starts to collapse when interpenetration of Cu(I) and Cu(II) species takes place. So when the potential is reversed before a substantial interpenetration occurs, the SHG response can trace back the SHG response of the forward scan. Therefore existence of the peak “r₃” may suggest that there is a well defined interface present between the layers of Cu(I) and Cu(II) species. As a result, when the $\chi^{(3)}E(\omega)E(\omega)E^{dc}$ is no longer the dominant contributor to the nonlinear polarisation, SHG intensity decrease sharply with the reduction of submonolayer amount of CuO, the resonant contribution from Cu₂O tuned in and the SH signal immediately increases to form the peak “r₃”. This happens only when the oxide thickness is in the range of ca. 5-7 Å.

But when the CuO is formed with the potential scanned up to 0.95 V, the SH signal in the reverse scan has a slow increase as the CuO must undergo substantial reduction before the resonant contribution becomes dominant. Therefore we notice the overlap of the trough, “r₂” and the peak, “r₃” to form “e” as seen in Fig. 3.24. Eventually, SH signal curve merges with the initial path of SHG after the point where “r₁” appears. In the next section, results of wavelength dependent SHG will be discussed.

3.5.7 SHG spectroscopy of Cu oxidation and reduction

3.5.7.1 Introduction

Earlier in this chapter it was suggested that there were resonant contributions from initial Cu₂O layer and EFISH dominant contribution from upper CuO layer to the SHG response. The resonant contribution to the SHG response from Cu₂O should be wavelength dependent. It means that the resonant contribution to the SHG from Cu₂O at a particular wavelength can be “tuned out” at another wavelength. But EFISH contribution will not be dependent on the wavelength of the incident laser beam as it is driven by changes in the applied dc electric field, and hence it is field dependent. Whether the resonant contribution from Cu₂O will have any potential dependence will depend on the contribution from $\chi^{(3)}$ to the SHG. $\chi^{(3)}$ is field dependent but may also have a resonant contribution [3]. Results of the SHG experiments at different wavelengths will help verify the suggestions made.

Simultaneous CV and SHG experiments were carried out for the wavelengths of 730, 755, 780, 810, 840 and 880 nm. The energy of the fundamental and corresponding SH photons are tabled in Table 3.3.

Wavelength(λ) (nm)	Energy of fundamental photon (eV)	Energy of SH photon (eV)
730	1.70	3.4
755	1.64	3.28
780	1.59	3.18
810	1.54	3.08
840	1.48	2.96
880	1.41	2.82

Table 3.3 The energy of the fundamental photons and that of the SH photons.

Current and SH signal intensity plotted as functions of applied potential are illustrated, from Fig. 3.25 to Fig. 3.30. The experiments were carried out in the order from the shortest to the longest wavelength. An identical Cu cyclic voltammogram was reproduced before running experiment at any wavelengths. This is to ensure that the surface of the Cu electrode is identical at the start of every new scan. So that the dependence of SH intensities on wavelength is better understood. Fig. 3.31 shows the SH intensities obtained from the experiments with all six different wavelengths and the data are normalised in order to be able to compare. Finally, Fig. 3.32 and Fig. 3.33 are the nonlinear fits of the form $I^{2\omega} = I_0^{2\omega} + (V - V_0)^2$ of SH signal intensity in the forward and reverse scan respectively. These nonlinear fits are done only in the EFISH dominated region.

3.5.7.2 Data normalisation procedure

Six different experiments with six different wavelengths were carried out. In each of these experiments the scan rate was 5 mV s^{-1} and the potential range was between -0.90 and 0.90 V. Current in μA and SHG intensity in number were recorded as functions of applied electrode potential in V for each of the experiments. To compare the SHG data recorded at different wavelengths and to see the potential dependence of SHG intensity, the data were normalised.

The normalisation was devised so that the SHG signal is spanned over the range from 0 (zero) to 100. For each set of SHG data points for one wavelength, the lowest value of SHG intensity was found. This “*SHG value – I*” was then subtracted from all the values. This produces a set of SHG intensity data where the lowest number of SHG counts was 1.

The column of data generated by the procedure noted which was then divided by the highest value. This converts the data to a set of numbers lying between 0 (zero) and 1. The data lying between 0 (zero) and 1 were then multiplied by 100 to produce data lying between 0 (zero) and 100.

Potential/V vs SCE	Current/ μA	SHG counts/number for incident beam of wavelength λ				
		λ_1/nm	λ_2/nm	λ_3/nm	...	λ_n/nm
-0.90	0.03	23	24	27	...	29
-0.89	0.03	12	14	16	...	18
...	...	...	...	...	...	-
.89	0.90	7	9	11	...	13
.90	0.95	8	10	12	...	14
...	...	...	...	...	...	-
-0.89	0.03	23	25	27	...	28
-0.90	0.03	21	21	22	...	23

Table 3.4 Sample data to show the normalisation procedure to compare the variable wavelength SHG data by spanning them between 0 (zero) and 100, and to show them in one graph.

Finally, an offset (constant value) was added to each set of SHG data. This offset was different for each wavelength and was included simply to allow all the data to be shown on one graph, but the span of SHG intensity for each wavelength runs between 0 (zero) and 100.

3.5.7.3 Resonance contributions to the SH intensity

The characteristics feature of resonance contributions to the SH intensity is that the SH intensity is dependent on the wavelength of the incident laser beam and/or on the applied dc electric field. SH signal intensity at the points labelled “r”, “R” and the region “c to d” in Fig. 3.25 to 3.31 are three most probable regions where the SH signal might be influenced by the resonant contribution. Careful observation of the features of SH signal intensity in these three points/regions shows that the SH signal intensity features shift with the wavelength of incident laser beam. Region labelled “r” on the SHG signal curve corresponds to the double layer region on the voltammogram where no faradaic process takes place. The region labelled “R” in SHG curve corresponds to the point in the reverse direction on the cyclic voltammograms where the reduction of CuO starts to begin. Then the region “c to d” region of SHG curve which corresponds to the region on the voltammograms where the oxidation current start to decrease after the oxidation current peak, AI. At this stage, there is 5-7 Å thick layer of Cu₂O at the electrode surface.

The SHG peak and the shape of the region, labelled “r”, on the SHG curve shift to the higher potential when the experiments were carried out with the longer to the shorter wavelength incident laser beams. The peak positions of the region “r” on the SHG curve shifts ca. 60 mV between the experiments with 880 and 730 nm incident laser beams. This is an indication that probably this shift in the peak position of

the SHG intensity is due to the resonant contribution to the SHG intensity. As the region “r” of SHG curve falls in the *electric double layer* region of the cyclic voltammogram, therefore the resonance contribution may originate from the population/depopulation surface states or binding of the surface electrons by the process of anion adsorption.

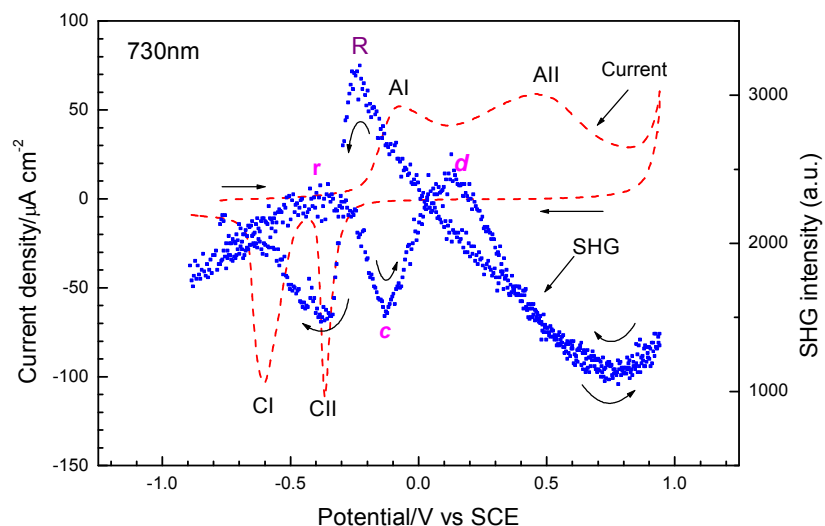


Figure 3.25 Cyclic voltammogram and SHG response at poly-Cu 0.1 M borax buffer of pH 9.2 at 5 mV s⁻¹ under *p*-polarised illumination from a Ti-Sapphire oscillator at 730 nm.

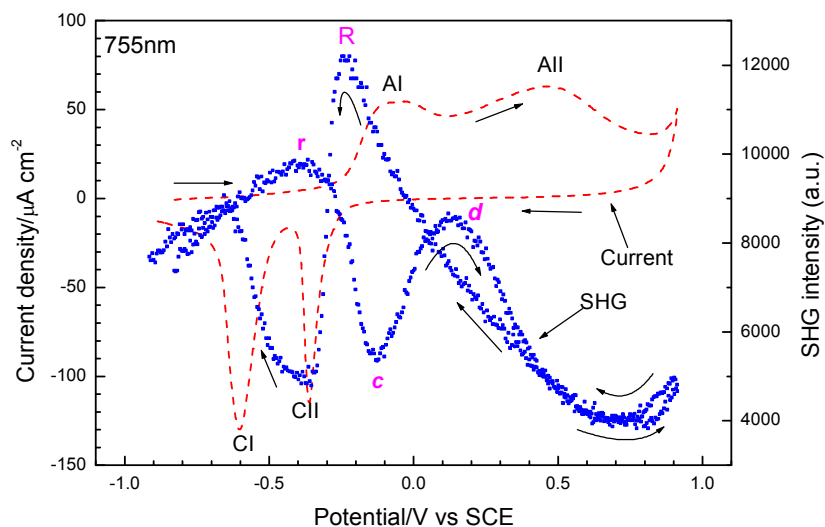


Figure 3.26 As for Fig. 3.25 except incident laser illumination at 755 nm.

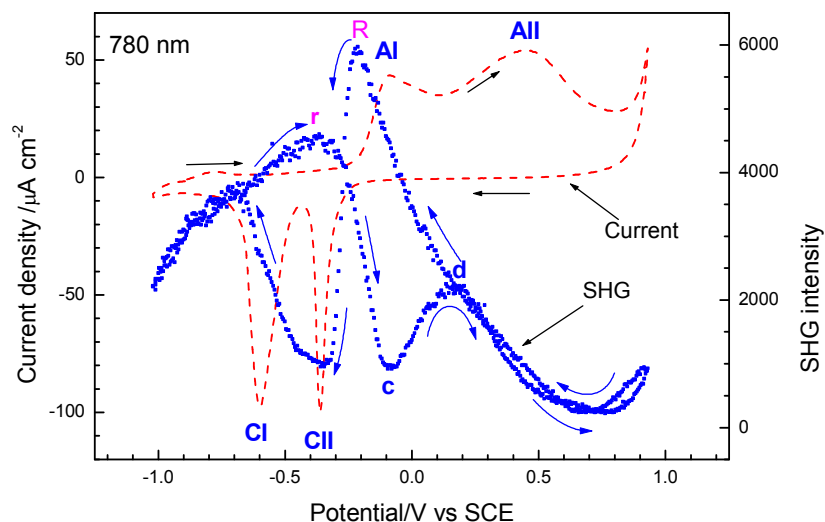


Figure 3.27 As for Fig. 3.25 except the incident illumination is at 780 nm.

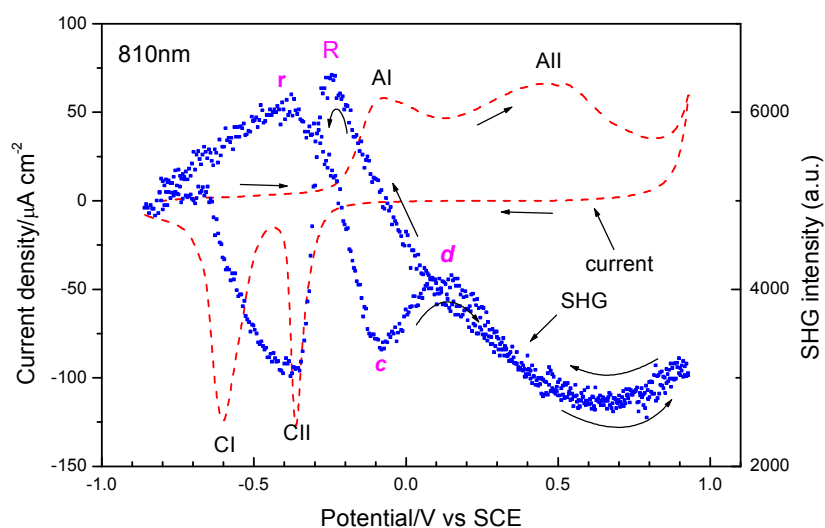


Figure 3.28 As for Fig. 3.25 except the incident beam used is of 810 nm.

After the initial increase of SH intensity around the region, labelled “r”, the SH signal intensity curve enters the potential regime where Cu_2O starts to grow. The growth of Cu_2O continues and the anodic current reaches the peak, AI; then the oxidation current decreases until the local minima at 0.15 V. The corresponding region on the SHG curve is denoted as region “c to d” in Figs. 3.25 to 3.31. As discussed earlier that Cu_2O is a semiconductor with the band gap of 2.10 eV [121], therefore it is probable that when variable wavelengths for incident laser beam are used there will be contribution to SH response due to resonant contribution, $\chi_r^{(2)}$ from Cu_2O . When the frequency of an inter-band transition of semiconducting film or a surface electronic state is in resonance or near-resonance with either the incident

or harmonic frequency of the photons, there can be significant enhancement in SH responses. The 2.10 eV band gap of Cu_2O is smaller than the energy of a SH photon, energy of which is in the range of 2.82-3.40 eV. Thus a resonant contribution is possible when Cu_2O is sufficiently thick to behave as a semiconductor. This resonant contribution to SHG signal probably will vary as incident beam of different wavelengths is used.

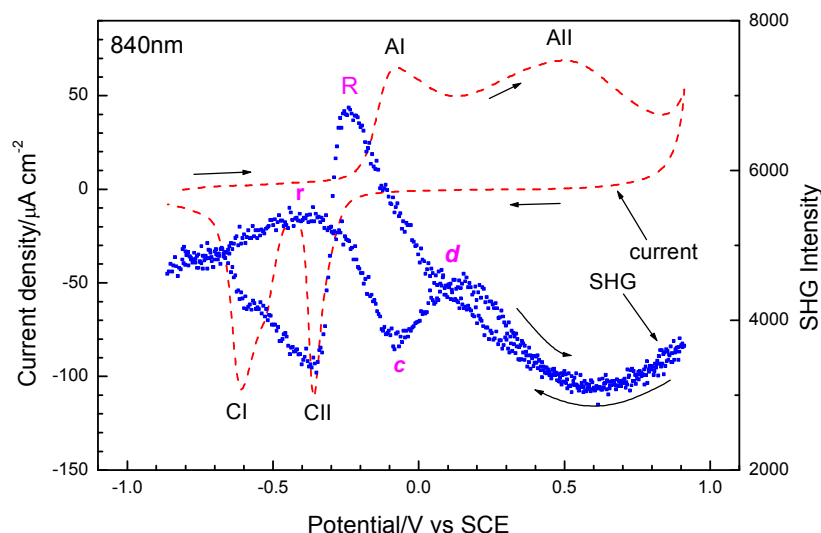


Figure 3.29 As for Fig. 3.25 except the incident beam used is of 840 nm.

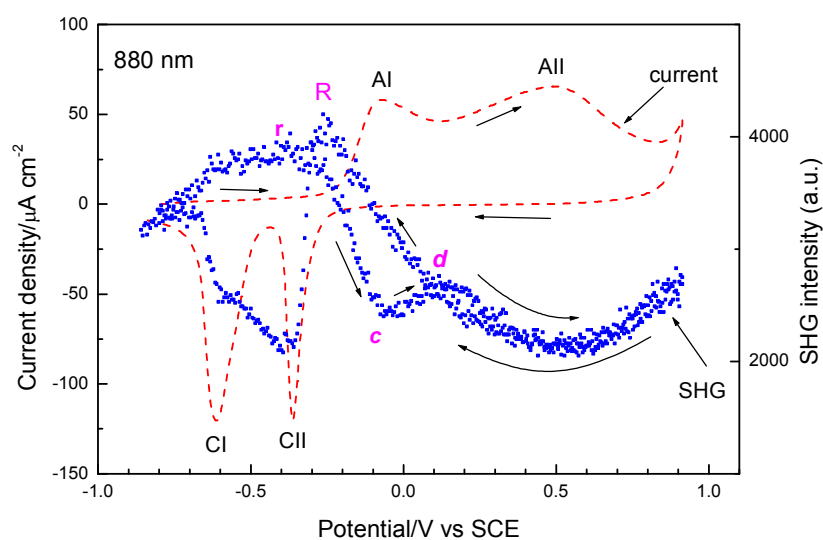


Figure 3.30 Cyclic voltammogram and SHG response at poly-Cu 0.1 M borax buffer of pH 9.2 at 5 mV s^{-1} under *p*-polarised illumination from a Ti-Sapphire oscillator at 880 nm.

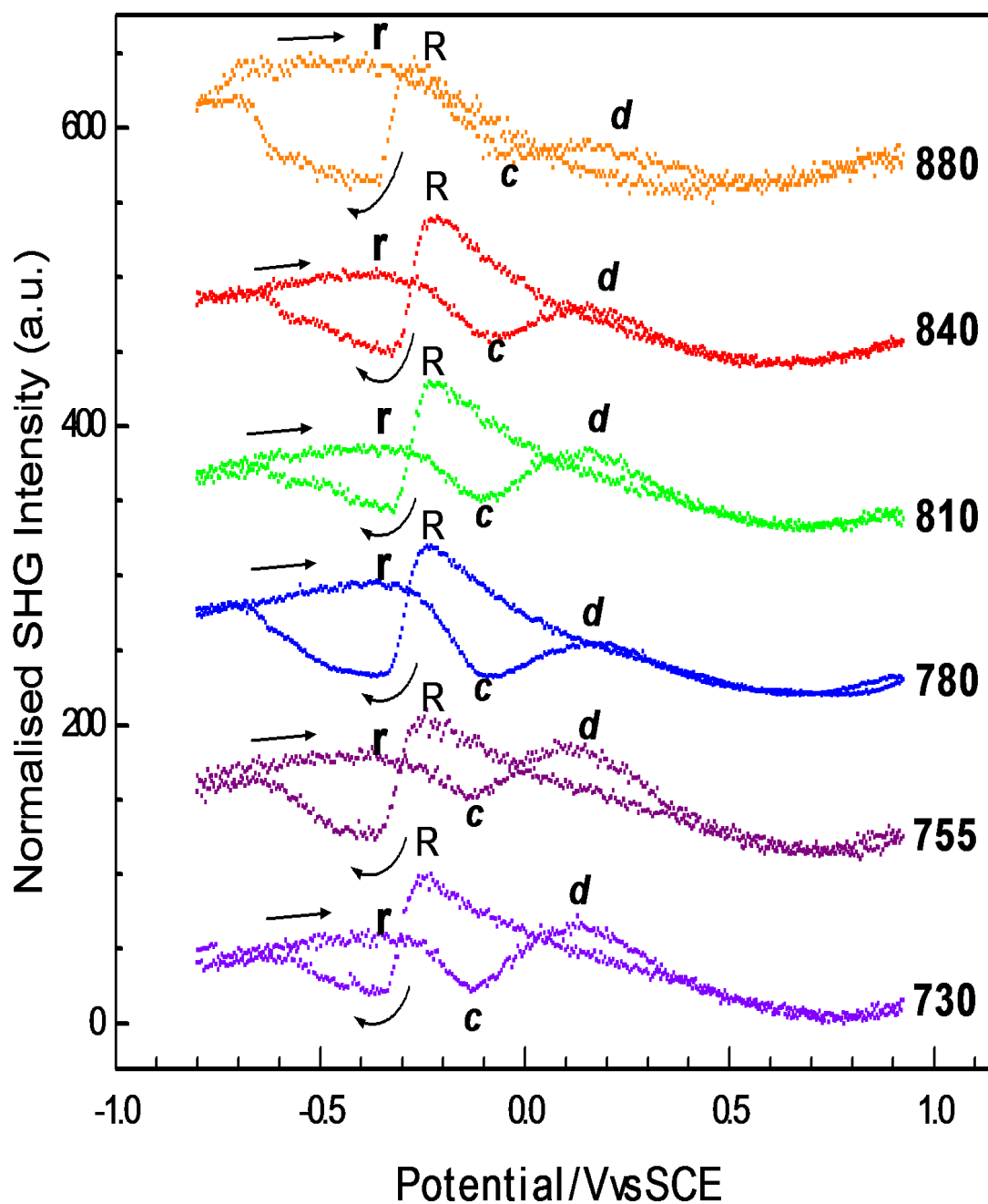


Figure 3.31 Wavelength dependence of SHG intensity from poly-Cu electrode under illumination from Ti: Sapphire Oscillator with $p_{in} - p_{out}$ geometry. Wavelength dependent SHG data are normalised. Current data of cyclic voltammogram are not plotted here.

Now a close observation of the region “ $c - d$ ” shows that the peak at “ d ” shifts to less positive potential as incident beam of the shorter wavelengths are used. The fact that the region “ c to d ” on the SHG curve shifted to the less positive potential in the positive going scan of the potential indicates that the resonance contribution region shifted as well. In the positive going scan the resonance contribution from Cu_2O to the SH intensity peaks around the point labelled “ d ”. In the reverse scan the resonance contribution peaks

around the point “**R**”. In both cases there is combined contribution to the SH intensity of the EFISH and the resonance contribution from Cu₂O due to the resonance of excitation of the interband transition with the frequency of the incident and/or SH radiation.

Our observation of the Fig. 3.31 points that the highest resonance contribution is noticed when the 780 nm fundamental incident beam was used for the experiment. The ratio of the SH intensity at point “**R**” to that of at point “**d**”, **R/d** is the highest for the fundamental incident beam of 780 nm. The resonance contribution to the SH intensity decrease when the shorter and the longer than 780 nm incident beam is used. That means the frequency of the SH photons, 2ω is no longer in resonant with the frequency of the excitation of the interband transition.

Now if the energy of a single SH photon at point “**c**” or “**d**” is E_{ph}^{total} then we can write,

$$E_{ph}^{total} = E_{ph}^{dc} + E_{ph}^{\lambda} \quad (3.14)$$

where E_{ph}^{dc} is photon energy due to dc field and E_{ph}^{λ} is the energy due to the incident photons. Therefore, from the Eq. (3.14) we see that when the energy of the incident photons get higher with the shorter wavelength of the incident laser beam, the resonance contribution in the region, “**c** to **d**” start to be less prominent.

The point “**R**” on the SHG curve seems not to shift when different incident beam with shorter or longer wavelength is used. Point “**R**” is the point on SHG curve that corresponds to the point on the voltammogram where the reduction of CuO starts in the reverse scan. This can be attributed to our suggestion that there is no resonance contribution from CuO and the formation and reduction of Cu(II) oxide is the region on the potential axis where it is speculated that the dominant contribution to the SHG is from EFISH which is discussed next.

3.5.7.4 EFISH: Field dependent SHG between 0.2 - 0.8 V

In Section 3.5.5.3 it was suggested that the SH intensity between the potential 0.2 and 0.8 V, where Cu was oxidised to form Cu(II) species, was dominated by the applied dc electric field mediated SH intensity. The experiment discussed in Section 3.5.5.3 was carried out only at 780 nm. The SH intensity in the potential range of 0.20 - 0.80 V fitted the quadratic equation $I^{2\omega} = I_0^{2\omega} + (V - V_0)^2$ as shown in Fig. 3.19a and 3.19b. But that alone is not sufficient to suggest that the SH intensity is dominated by the EFISH in that region without running the SHG spectroscopic experiments.

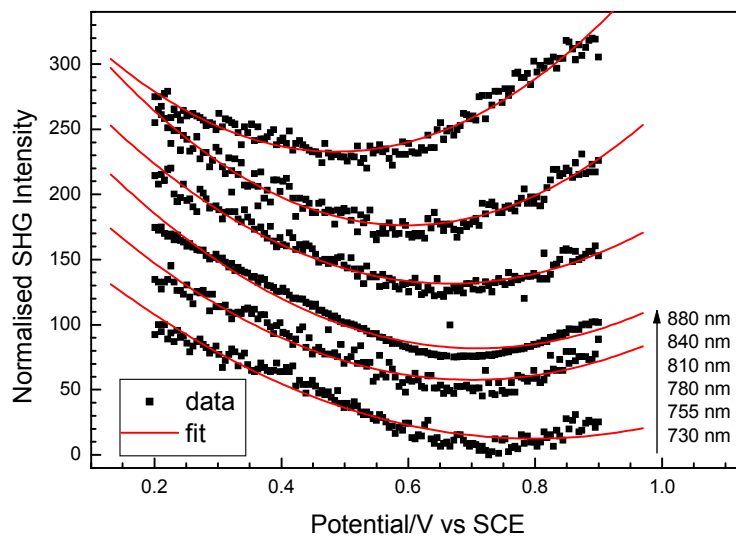


Figure 3.32 SH intensity response spectra vs. applied potential where the variation in the SH intensity is dominated by EFISH contribution. The parabolic fits of $I^{2\omega} = I_0^{2\omega} + (V - V_0)^2$ demonstrate the quadratic dependence of the SH intensity on the applied field in the forward direction of the scan. SHG data are normalised.

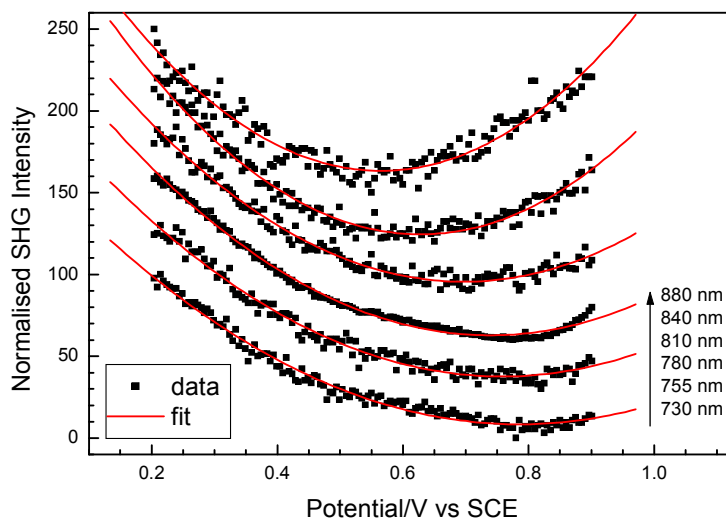


Figure 3.33 As for Fig. 3.32 except the SHG intensity data are taken from the reverse scan.

It is noticeable that the SH intensities at all the incident laser beams of variable wavelength (Fig. 3.25 to Fig. 3.31) maintains the quadratic shape over the potential range 0.20 - 0.80 V. The normalised data for all the wavelengths are plotted in Fig. 3.30. The truncated data concerned with the potential range where the EFISH contribution is suggested are plotted and fitted to the equation, $I^{2\omega} = I_0^{2\omega} + (V - V_0)^2$ with

well defined minimum, and they are plotted in Fig. 3.32 and 3.33 for the forward and reverse scan respectively. This shows that our earlier suggestion that E^{dc} mediated SH signal dominated the SHG in the potential range of 0.20 - 0.80 V in the both direction is verified.

3.6 Conclusion

Complete cyclic voltammetry of Cu together with “window opening” experiments were carried out with Cu electrode continuously exposed to the ultra fast laser illumination to yield SH photons at the Cu electrode surface through the process of oxidation and reduction. To our knowledge these experiments on the SHG studies of Cu oxide formation and reduction are the first ever SHG studies to look at metal oxide formation and reduction especially when the duplex structures are involved. As demonstrated in this chapter, SHG techniques have significant potential for the studies of oxide growth and reduction at Cu electrodes. Further studies can provide better understanding of the kinetics and mechanism of the oxide formation and reduction especially when complex and duplex oxide structures are involved. It is shown that SHG as a technique is suitable to investigate submonolayer coverage.

From the results, we conclude that submonolayer sensitivity of SHG technique to surface oxide growth is demonstrated. It was suggested that when Cu is oxidised to form Cu(I) species, SHG was influenced by the resonance contribution from Cu_2O . Further scanning of the potential allowed the formation of mainly CuO on top of the already formed Cu_2O layer. In the CuO formation region of the cyclic voltammogram, the SHG was dominated by electric field induced second harmonic (EFISH) Generation. By nature EFISH is independent of the wavelength of the incident laser illumination.

To reinforce the suggestion of a resonant contribution to the SHG signal from Cu_2O but EFISH dominant contribution from CuO, a SHG spectroscopic study was carried out. The results of these experiments offer a verification of the conclusions drawn from experiments carried out at a single wavelength. The SHG spectroscopic study shows that SHG intensity may have wavelength dependence at potentials where Cu_2O grows but it is wavelength independent in the EFISH dominant region between potential 0.20 and 0.80 V where mainly a CuO layer is on the surface.

Chapter 4

Second harmonic generation studies of the compact and hydrous oxide growth at Au electrodes

4.1 Introduction

4.1.1 Overview

In this chapter the results of the study of the oxide formation at poly-Au electrodes in aqueous medium by second harmonic generation (SHG) are discussed. An investigation of the growth and reduction of compact (α) and hydrous (β) oxide at Au electrodes in acidic solution, while the electrode is simultaneously irradiated by a diode pumped Ti-Sapphire oscillator, is reported here. Firstly, Au electrochemistry has been studied where the potential of the Au electrode has been scanned only up to the potential where the α -oxide is formed. This was followed by an examination of the growth of the comparatively thicker β -oxide. Au β -oxides were grown for various durations by holding the electrode at a much higher constant potential. Finally, the electrochemically grown β -oxide was reduced, and the reduction currents and SHG signals were recorded as functions of scanning potential.

This chapter represents, to our knowledge, the first ever SHG study of both compact and hydrous Au-oxides. In this chapter, as we will see later, the SHG signal responses and Au cyclic voltammograms have been recorded; the SHG responses are suggested as resulting from the propagation of a d -electron derived surface plasmon resonance (SPR) in the double layer region and due to the cessation of SPR in the α -oxide formation region of the voltammogram. When β -oxide was reduced, the SHG responses were thought to be influenced by an order/disorder transition at the α -/ β -oxide interface, and/or possibly due to the presence of surface traps at the interface [32]. As in the study of the oxidation of Cu presented in the previous chapter, SHG has once again been shown to be a sensitive and informative technique with sub-monolayer sensitivity for the α -oxide growth whilst also offering important and vital information on the reduction of the β -oxides.

4.1.2 Importance of Au electrochemistry

Due to its physical properties, especially electrochemical behaviour and for its dissolution resistance, Au is an ideal candidate for the investigation of solid electrodes in the aqueous media; both in base and in acid. Being one of the noblest and the most inert of the metals, understanding the electrochemistry of Au

helps understand the electrochemical behaviour of other metals. Au in general has weak chemisorption properties, a large *electric double layer* region, (the *electric double layer* region has been described in Chapter 1), with minimal electrochemical activities in most neutral electrolytes. The Au electrode oxidizes to form Au α -oxide at higher positive potentials. These are some of the properties that make Au unique among the metals.

One of the reasons why the use of Au has been high is that Au is a good electrical conductor. The miniaturisation of electronic devices and the increasing tendency of using precious materials in these applications have caused more consumption of Au in the electronic industries. There has been significant growth of the use of Au in information technology [188], telecommunications and safety-critical applications [189]. Au plated battery connections in mobile phones, edge-connectors in circuit boards and Au bonding wires in semiconductor packages [190] are some of the examples where Au is being used routinely. Some more recent uses of Au in electronics in everyday life are in Au plating and bonding wire in smart cards and in the automotive electronics for ignition control and other highly sensitive sensors.

Au also has a wide variety of applications in medicine. Due to its excellent biocompatibility and high degree of resistance to bacterial colonisation it is probably the most suitable metal to be used for implants in areas where there is a risk of infection such as dentistry. Another interesting application of Au is the concept of targeted drug delivery microchips [191]. Even though it is in decline but Au and Au-compounds were used for the treatment of rheumatoid arthritis [192]. Properties of Au and Au-compounds are also of great interest for the potential use in cancer treatments as possible replacements for Pt based drugs [191].

Not all of the applications cited above are directly related to electrochemistry, but the most important current and probable future application for which Au is of enormous interest is its ability to enhance the rate of an electrode reaction at a given overpotential or to lower the overpotential for a particular reaction without being consumed in the process. The electrochemistry and electrocatalytic properties of Au are hence used to obtain efficient utilisation of energy in an electrolytic cell or to obtain maximum chemical to electrical energy conversion in a fuel cell [193]. It has been claimed that Au catalysts can also be used for the production of H_2O_2 cost effectively at the point of use [194]. The low temperature activity of Au catalysts may play a role in the task of emission control [193] and more energy efficient fuel cells may be made. Therefore there is likelihood that Au will be an important catalyst in chemical processing, pollution control, and in fuel cell applications.

4.1.3 The field of Au nanotechnology

Another important area stimulating the study of the electrochemistry and other properties of Au is nanotechnology. Researchers in nanotechnology have been studying gold nanoparticles for their properties [193 and references therein]. Even though Au nanoparticles have been used in colour chemistry and photographic developments for quite some time, the present day interest and the extent of the study

into the nanoparticles of Au go far beyond the popular use of Au nanotechnology. Clusters of Au atoms whose dimensions are in the range of 0.5 to 50 nm show the characteristics of nanoparticles. Interatomic forces and interactions that are negligible at macro scales become dominant with the reduction of size, and nanoparticles exhibit anomalous or at least yet to be understood physical properties [195]. Due to their significant reduction in size relative to bulk Au, nanoparticles do not adhere to many bulk properties, for example they do not conform to behaviour, such as, fitting restrictive crystal structures such as *face centre cubic* (fcc) for Au. This lack of specific crystal structure causes a lack of symmetry or centrosymmetry in the nanoparticles. This particular deviation made nanoparticles a good candidate to be studied by nonlinear optical techniques notably by second harmonic generation (SHG). Nanotechnology based on Au nanoparticles will have potential use in medicine [191], solar energy [196], microelectronics [197], cytology and molecular biology [198] as well as in nanosized devices and sensors.

4.2 Au electrochemistry

The introduction to this chapter has demonstrated the widespread use and some emerging uses of Au, and the importance of Au electrochemistry. It is now appropriate to introduce and review the electrochemical behaviour of Au electrodes. A typical cyclic voltammogram recorded for polycrystalline Au in acid solution is shown in Fig. 4.1.

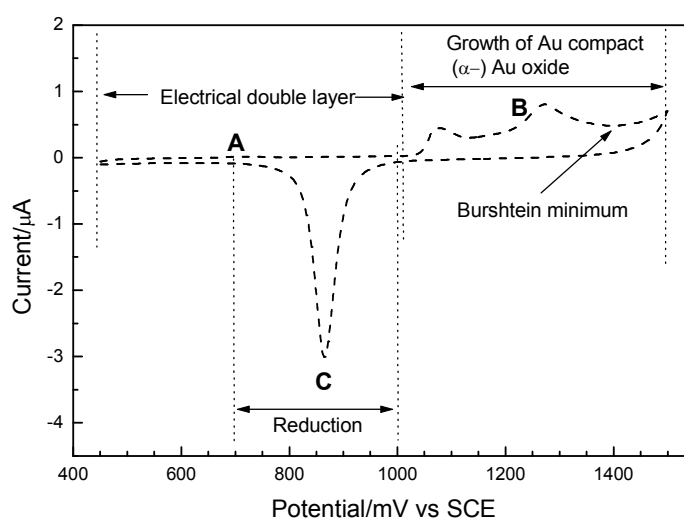


Figure 4.1 Cyclic voltammogram of poly-Au electrode in 0.1 M H₂SO₄ at 5 mV s⁻¹.

4.2.1 Au electric double layer

There remains a controversy about the *electric double layer region* of Au cyclic voltammogram as to whether the double layer current is entirely non-faradaic or if there are actually faradaic processes going on, leading to the formation of oxy-species well within the limit of the double layer region of the cyclic

voltammogram. This postulated oxide formation in the double layer region is called pre-monolayer oxidation. Several optical methods have been used to assert the claim of oxide formation in the double layer region, e.g., Auger electron spectroscopy (AES) by Huong *et al.* [199]. Huong *et al.* has ruled out earlier assumption that the presumed oxidation in the double layer region is the oxidation of impurity metal from the bulk, and suggested that the oxidation in the double layer region is from some active sites. Several studies by Angerstein-Kozłowska [19] investigated whether the initial stage of Au oxidation involves the discharge of adsorbed water to form AuOH. Burke *et al.* [21] suggested that the appearance of a small current peak in the double layer region could be due to the formation of an initial Au β -oxide species at the Au α -oxide/aqueous solution interface, accompanied by oxygen evolution which is catalysed in a transient manner. But in contrast to Burke's suggestion, some more recent studies [23, 28, 30] involving EQCM suggest that the initial step involves oxidation of non-adsorbed water forming AuO.

4.2.2 Au oxidation: Mechanism of Au α -oxide formation

Fig. 4.1 shows a typical cyclic voltammogram of polycrystalline Au. The monolayer oxide formation and reduction shown in the figure is a common type of behaviour for noble metals and the electrochemistry of Pt has a lot of similarities to that of Au. One important observation from Fig. 4.1 is that the potential range of monolayer oxide formation in the positive sweep (region B) and the monolayer α -oxide reduction in the negative sweep (region C) differ substantially. The oxide is not reduced immediately upon scan reversal but is reduced at potentials substantially more negative (or reducing) than those where the oxide is formed. This hysteresis is assumed to be due to post-electrochemical processes that take place after the initial oxidation. Conway [22] suggested that hysteresis in the monolayer α -oxide formation/reduction processes can be attributed to the gradual changes in the nature of the oxide film towards developing a quasi-3D structure by means of the *interfacial place exchange mechanism* [26]. As we will see more detail shortly, the formation of the Au α -oxide monolayer involves the development of dipolar species of $\text{Au}^{\delta+}.\text{OH}^{\delta-}$. As the monolayer develops and the coverage increases, these dipolar species repel each other [153]. This interaction raises the energy required to generate more of these species and a surface repulsive barrier is developed. As a result, formation of a full Au α -oxide monolayer requires scanning of the potential over a significant range, over which to develop sites of various potential energies which are present in a polycrystalline Au surface. This is why the monolayer α -oxide formation response in the cyclic voltammogram (region B) is an extended plateau region. Sites of differing energy suggest the appearance of several not so prominent current peaks, hence a plateau.

Burke *et al* [153] suggested that there is a post-electrochemical process which is illustrated in Fig. 4.2. The surface dipoles reduce lateral repulsive energy by rotation and place exchange as the potential is increased, which results in a stable surface deposit towards the end of the scan just before the oxygen evolution potential. In the negative scan a sharp cathodic peak is observed but at a potential much more negative than the potential of oxide formation. This is due to the fact that the place exchange must be reversed in the reverse scan and the extra potential is needed to drive the reversal of the place exchange process.

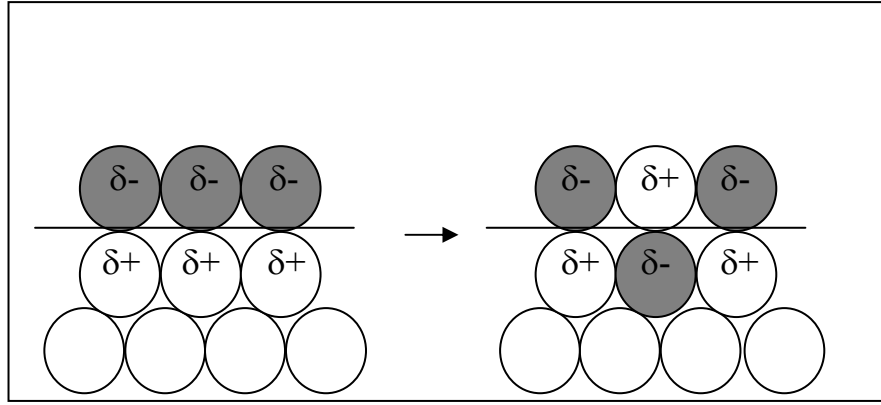


Figure 4.2 Schematic diagram of the post-electrochemical place exchange reaction in monolayer oxide formation. Surface metal atoms exchange position with oxygen species resulting reduction of repulsive electrostatic energy (from Ref. [153]).

During the oxide formation at Au electrode, it is the surface atoms that are responsible for the mechanisms that shape the hysteresis in the cyclic voltammogram [153]. Atoms that make the bulk of Au electrode have little significance in the oxidation process. There are two mechanisms [18, 22, 23] that might be involved in the formation of the Au α -oxide monolayer through place exchange. In the first mechanism electro-adsorption happens in the following way-

An adsorbed water molecule through oxidation loses a proton with formation of adsorbed hydroxyl group, OH_{ads} as shown in Eq. (4.1)



Electro-adsorption is followed by the interfacial place exchange between OH_{ads} and surface Au atoms as discussed earlier and shown above in Fig. 4.2



A further electron transfer then takes place leading to formation of AuO.



The second mechanism [31, 153] is a direct two electron transfer followed by place exchange



The two above mechanism both result in a partial charge transfer between Au and OH or O, $\text{Au}^{\delta+} - \text{OH}^{\delta-}$ or $\text{Au}^+ - \text{O}^{\delta-}$ [23].

4.2.3 Growth of Au α -oxide

In the previous section the formation mechanism of the Au α -oxide has been discussed. But given that, in the work reported later in this chapter, the potential of the electrode is held at high values where the Au β -oxide also grows and where there is significant oxygen evolution, it is important to discuss the extent of the overall growth of Au α -oxide in the process. The amount of Au α -oxide that can grow at the electrode surface with specific *geometrical surface area*, A_{geom} under specific condition is of particular importance in order to know the *real surface area*, A_{real} and *roughness factor*, RF of the electrode, and to know the extent of monolayer coverage at the surface of a specific electrode. Roughness factor, geometrical area, and real surface area are related in the following way

$$RF = \frac{A_{real}}{A_{geom}} \quad (4.6)$$

Often for some specific applications higher roughness factor for electrodes, such as Au and Pt are desired and upon special pretreatment and roughening of the surface, the A_{real} of an electrode can be made orders of magnitude greater than the A_{geom} .

Now coming back to our discussion of Au α -oxide, the growth of a complete monolayer of oxide on the Au electrode is important for the determination of *the real surface area* of the electrode. Different surface preparations result in varying microscopic roughness (normally incorporated into a roughness factor) of the Au electrode, i.e., the real surface area of an electrode is always greater than that of the geometrical area, and hence there is a need for a method to determine the real surface area. Several methods to determine the real surface area of solid electrodes exist and some of the methods can be specific to the type of electrode materials. In the study of polycrystalline Au, one method for the determination of the real surface area is to integrate the oxide reduction charge when the potential is reversed just before oxygen evolution at a feature in the cyclic voltammogram known as the *Burshtein minimum* [200]. Fig. 4.1 shows the Burshtein minimum point, denoted with an arrow. The technique assumes that a complete monolayer of compact oxide is achieved at this potential at a scan rate of 0.05 V s^{-1} . If this assumption is correct then all that is needed is an estimate of the number of surface atoms present per cm^2 and then it is possible to convert the charge to area. According to the Burshtein minimum method a charge of $400 \text{ } \mu\text{C cm}^{-2}$ is associated with the formation of an Au α -oxide monolayer [200].

However, another earlier study by Woods [201] proposed that the total charge for formation of one complete monolayer of Au α -oxide is $386 \text{ } \mu\text{C cm}^{-2}$. This figure is likely to vary because a polycrystalline surface will contain a variety of facets corresponding to a particular single crystal orientation; and therefore an interpretation has to be made as to how a polycrystalline surface is represented. The figure reported by Woods [201] was deduced by holding a clean Au electrode at 1.8 V for 100 s and then calculating the charge following a negative sweep. Most of the discussion above is about growing a monolayer of compact oxide in order to assess electrode area using a conversion factor, but it is important

to note that the growth of the surface oxide and its density are dependent on the experimental conditions such as oxidation potential, oxidation time and temperature. This aspect is important when we consider what might happen alongside β -oxide formation and the results that we will see later in this chapter.

Some recent studies to an extent support Wood's [201] finding. Crystallographic data show that the thickness of 1 monolayer of AuO is 5.0 Å [202]. The charge density of formation of 1 monolayer of AuO is also reported by several authors to be 386 $\mu\text{C cm}^{-2}$ [203, 204]. However, it must be noted that some more recent works suggest that the compact oxide can grow to more than one monolayer under appropriate conditions. For example, Tremiliosi-Filho *et al.* [23] reported that in acidic media at potentials less than 2.00 V vs RHE, Au α -oxide can grow up to a limiting thickness of 3 monolayers that is equivalent to a total charge of 1158 $\mu\text{C cm}^{-2}$. Xia *et al.* [28] reported that the total charge can be 1450 $\mu\text{C cm}^{-2}$. But elsewhere Tremiliosi-Filho *et al.* [31] report that in some cases the total α -oxide charge could be as much as 2000 $\mu\text{C cm}^{-2}$. This may indicate that at higher potential such as near 2.00 V vs RHE the β -oxide also starts to grow. Under the conditions described in reference [31], Au α -oxide (AuO) continues to grow without reaching any limiting thickness, or that the growth of α - and β -oxides overlap with the onset of β -oxide growth. Without having a well-defined second oxidation current that relates to the formation of β -oxide and due to oxygen evolution it is difficult to come to a definitive conclusion about the exact nature of α -oxide growth.

Depending on the real surface area and experimental procedure, the total charge required for one complete monolayer coverage of a unit surface area of an electrode can be altered. Therefore, from a practical viewpoint, the conditions for a monolayer oxide formation on electrode are important in characterising the surface and determining the real surface area.

4.2.4 Au β -oxide

Generally noble metals show interesting and complex β -oxide responses. Au β -oxide is regarded as being of low density and containing hydrated oxides that generally involve oxy- and/or hydroxyl-species. Investigations of β -oxide at Au electrode by Birss' group using ellipsometry and QCMB [28], and by using potential cycling techniques by Burke *et al.* [153] give important insight into the hydrous β -oxide responses of noble metals.

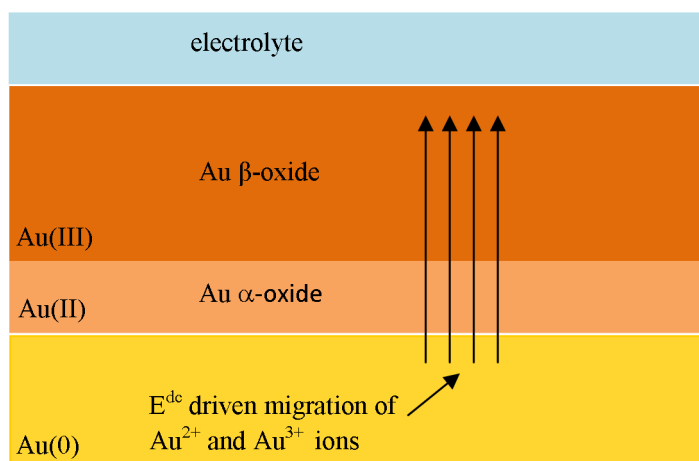


Figure 4.3 Schematic diagram of formation of hydrous Au_2O_3 on top of inner compact AuO where Au^{++} ions are driven to the top by applied dc electric field as shown by arrows in the figure.

Au hydrous oxide studies [28, 31, 153] found that to induce and maintain the growth of β -oxides, Au electrode needs to be held at a higher constant potential or subject to rapid potential cycling (this is discussed in more detail below). These β -oxides can be readily reduced back to the elemental state of Au at potentials negative of the reduction potential of compact α -oxide film. The experimental drawback in studying the electrochemical behaviour of Au β -oxide is that- electrochemically it can only be probed by investigating reduction behaviour. This is because strong oxygen evolution at growth potential complicates the recording of oxidation current. As β -oxides are of low density and are hydrated, it is difficult to characterise them in terms of their structure. A comprehensive account of β -oxide electrochemistry can be found in the review paper by Burke *et al.* [135].

4.2.5 Growth of Au β -oxide

Au β -oxides are reported to be formed at potential greater than 1.8 V vs SCE. This type of Au oxide is hydrous and thick, and its growth increases with time. There are two methods by which Au β -oxide can be grown [23, 28]-

- (1) By holding the Au electrode in 0.1 M H_2SO_4 solution at a constant potential above 2.1 V vs. RHE.
- (2) Au β -oxide can be formed by a rapid potential cycling between 1.0 and 2.1 V SHE with sweep rate as high as 50 V s^{-1} .

Usually, a surface cleaning will precede the actual growth of Au β -oxide growth. The electrochemical cleaning is typically performed by scanning the potential of the Au working electrode between 0.1 V and

1.6 V vs RHE. This was the normal protocol to obtain a good Au CV, such as the one shown in Fig. 4.1, prior to growing β -oxide. Then a repetitive potential cycling between a lower potential limit of 1.0 V and an upper potential limit of 2.1 V [28] is performed to grow the β -oxide. The sweep rate may vary from 1 V s⁻¹ to 50 V s⁻¹. The thickness of the Au β -oxide depends on several parameters, such as, the lower and upper potential limits, cycling rate, number of cycles, temperature, and the solution pH [28].

Neither of the two methods of producing Au β -oxide film noted above appears to give any added benefit in terms of the reproducibility of the film produced. As long as proper electrochemical cleaning methods are employed, reproducibility can be achieved [28]. For the experiments described later in this chapter, the Au β -oxides have been grown only by holding the Au electrode at 1.9 V vs SCE for various durations. When reduced, the Au β -oxide layer gives rise to two main reduction peaks irrespective of how it is grown. Before the reduction can be studied the potential must be lowered to the value where the oxygen can be purged from the solution because β -oxide growth occurs at the same time as the oxygen evolution. Then a scan in the negative direction allows one to examine the reduction of both Au α - and β -oxides. The potential scan sequence for the formation and reduction of Au β -oxide is illustrated in Fig. 4.10 in Section 4.2.2.

4.3 Experimental

The laser system used for the experiments on Au electrode has been described in Chapter 2. The spectroelectrochemical cell used for the experiments on Au electrode is slightly different than the one used for the experiments on Cu electrode.

4.3.1 Spectroelectrochemical cell

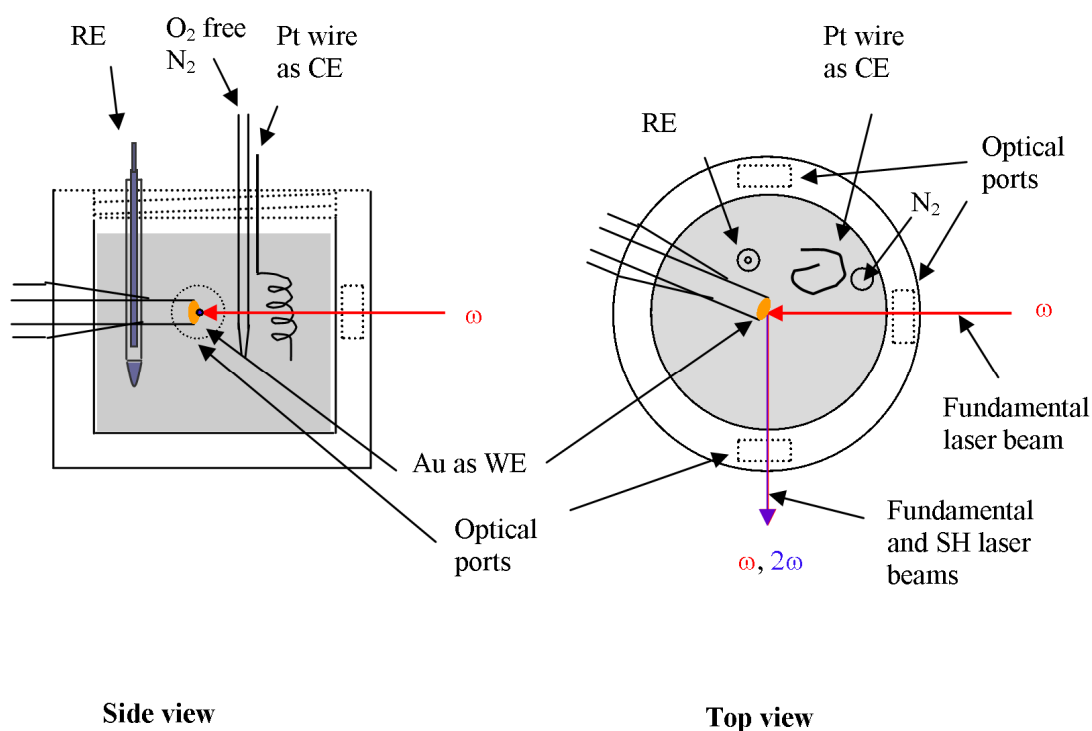


Figure 4.4 Schematic representation of the flow cell used for the combined cyclic voltammetry and optical experiments. Working electrode (WE) is an Au disk insulated in PTFE with surface area of 0.20 cm², counter electrode (CE) is a Pt wire, and reference electrode (RE) is Hg/Hg₂Cl₂ in contact with saturated KCl solution.

The spectroelectrochemical cell as illustrated in Fig. 4.4 was constructed in house from machined polytetrafluoroethylene (ptfe) with a plane glass lid attached with the side wall of the cell by screws. Three glass windows placed over polyvinylidene fluoride (PVDF) o-ring to avoid leakage of the electrolyte solution. The glass windows were antireflection coated CaF₂ glass windows (CVI Optics) with high transmission curve for UV to IR light. The holes on the lid were spaced so that it was possible to put counter electrode into the electrolyte and the reference electrode, and also for the degassing of the electrolyte. The Au working electrode was a polycrystalline disc of radius 0.25 cm insulated in Teflon

which was inserted into the cell through the threaded opening on the side wall of the cell. Then the spectroelectrochemical cell was mounted on a translational stage with two degrees of freedom of movement. The stage was at a fixed height from the laser table and could be translated in *x*- or *y*-direction to make incident and reflected beam orthogonal to each other and the sample at an angle of 45° with the incident and reflected beam.

4.3.2 Electrode preparation

The electrochemical experiments described and discussed in Section 4.4.1 were carried out on a 50 µm thick Alfa Aesar Au wire of purity 99.995% and supplied by VWR International. All other experiments discussed in this chapter were carried out on the Au working electrode of diameter 0.5 cm insulated by Teflon. Working electrodes were polished using 0.3 µm aluminium oxide strips and then wiped with wet cotton wool. Finally, the electrodes were rinsed with ultrapure water before any experiments were carried out. A polished 0.5 mm diameter and 10 cm long Pt wire was used as the counter electrode and the reference electrode was a saturated calomel (Hg/Hg₂Cl₂) electrode (SCE) in contact with saturated KCl solution. Potentials for all the cyclic voltammetry experiments carried out in this work are referred to the potential of SCE unless otherwise stated.

4.3.3 Electrolyte

Ultrapure water with resistivity 1.8 MΩ cm from a Direct Q3-UV (Millipore) system was used to prepare the solutions. All experiments on Au electrode were carried out in 0.1 M H₂SO₄ solution. H₂SO₄ solutions were made using VWR International supplied AnalaR Normapur® analytical grade 1 H₂SO₄.

4.3.4 Pretreatment protocol

Before any experiment was commenced the Au electrode was polished with 0.3 µm sized alumina coated strips. Following the polishing, the electrode was then washed several times with ultrapure water. Before experiments on Au, the electrode was cycled for 20 cycles between 0.1 and 1.6 V vs SCE at 1 V s⁻¹ whilst degassing the solution with oxygen free nitrogen. For the experiments carried out on Au α-oxide, potential was scanned starting from 0.4 V to maximum of 1.6 V and then reversed and voltammograms were recorded.

To grow thick Au β-oxide, after pretreatment the potential was taken to a constant value of 1.9 V vs SCE and held for a set time. 1.9 V is also the potential where oxygen is evolved at the Au surface. Once the desired duration had elapsed the potential was decreased to 1.4 V and held there for three minutes. During this holding time at 1.4 V degassing of solution with oxygen free nitrogen was continued to facilitate

removal of oxygen from the solution. Finally, the potential was scanned down from 1.4 to 0.4 V at 5 mV s⁻¹, and reduction current and SHG signal intensity were recorded as functions of the applied potential.

4.3.5 Data collection

Except while growing the hydrous oxide on the metal electrodes, an Oxford Electrode manual potentiostat was used to apply the potential, and current, potential, and SHG intensity were documented using a personal computer with a data acquisition card (NIDAQ-1200, National Instrument) and an in-house written programme [courtesy to Professor Anthony Kucernak's research group] using LabView (National Instruments) software.

When hydrous oxides were grown the electrochemical equipments and data recording procedure were modified slightly. The potential and current responses were regulated by a BAS 100 B/W Electrochemical Analyser (Bioanalytical System Ltd.). The SHG responses part was acquired by the method described above with potential of a dummy cell to track the SHG responses. Data files from the two systems were put together, and the SHG intensity and current-potential responses were discussed. The difference of timing between two collecting methods was less than 1 s which corresponds to less than 5 mV on the potential scale. Data were processed using Origin Data Analysis and Graphing Software.

4.4 Results and discussions

4.4.1 Au cyclic voltammetry in H₂SO₄

A simple cyclic voltammogram of a poly-Au electrode in 0.1 M H₂SO₄ solution is shown in Fig. 4.5 below. An important feature of Au cyclic voltammogram is that there is a large electric double layer region, labelled 'A' in Fig. 4.5 (a detailed description of the *electric double layer region* has been provided in Section 1.2.3 and 1.2.4 and illustrated in Fig. 1.1) typically extending from 0.4 V up to 1.0 V against an SCE reference electrode. In the positive going scan, anodic current starts to increase towards the end of double layer region and leads to the formation of the first oxidation current peak starting at 1.1 V which is due to the formation of the Au α -oxide layer. This broad region of oxidation current plateau extends up to ca. 1.5 V vs SCE. If the scanning potential is reversed then a single reduction peak labelled 'C' in Fig. 4.5 appears around 0.85 V. The breadth and sharpness of the reduction current peak depends on the reversing point of the positive going sweep. The distinctive feature of the response of Au electrode here is the broad anodic peak, labelled 'B', when the potential is scanned in the positive going direction. In contrast, the cathodic peak in the negative sweep is sharp, indicating a small window of potential where all of the oxidised Au is reduced.

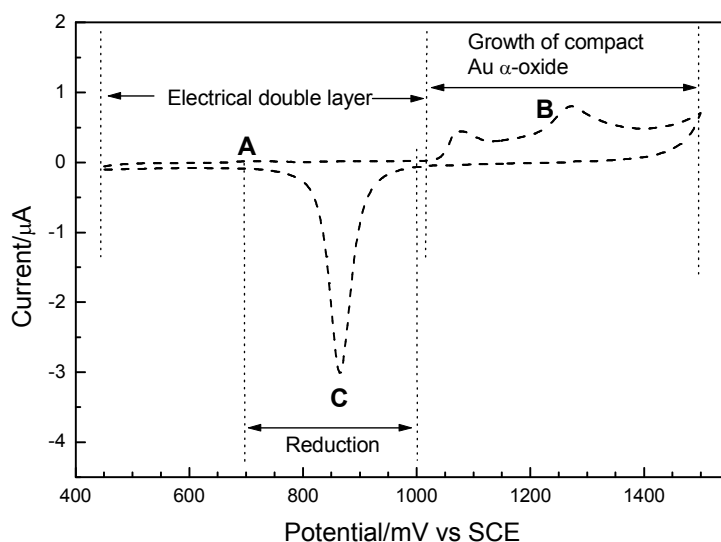


Figure 4.5 Cyclic voltammogram of polycrystalline Au electrode in 0.1 M H₂SO₄ at 5 mV s⁻¹ showing the double layer region, and growth and reduction of Au α -oxide.

If the scan is allowed to continue in the positive direction above a potential of 1.5 V, no major change occurs until significant oxygen evolution begins at around 1.7 V, followed by the formation of Au β -oxide at potentials of 1.9 V and above. Fig. 4.6 shows oxygen evolution occurring at ca. 1.7 V but oxygen evolution continues as the potential scan is extended further. In fact, the formation of Au β -oxide with oxygen evolution happens at higher potentials such as 1.9 V vs SCE.

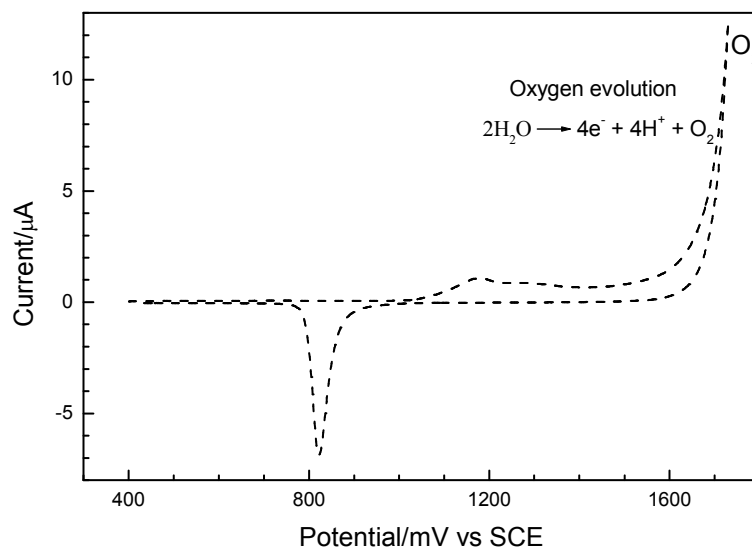


Figure 4.6 Cyclic voltammogram of polycrystalline Au electrode in 0.1 M H₂SO₄ at 5 mV s⁻¹, where the potential scan is taken well into the oxygen evolving regime.

The so called “window opening” experiments illustrated in Fig. 4.7 show that when large scale place exchange takes place but still within the Au α-oxide formation potential regime, the reduction happens at a more negative potential. In these experiments, the upper limit of potential scan is slowly increased so that the extent of oxidation at the surface is also increased. What the voltammogram shows here is that as the upper limit of potential scan is increased, the reduction peak potential shifts towards more negative potentials. This is demonstrated graphically when the positive going potential limit of the window opening experiments is plotted as a function of the reduction peak potential in Fig. 4.8. This figure shows largely a linear relation with a negative slope between the reversing potential and the reduction peak potential. This shows that as the coverage of oxide increases, the reduction process becomes more difficult because of the need to drive the reversal of place exchange. At low coverage, the extent of place exchange is small and so reduction is relatively easy. As the upper limit increases, the coverage increases and so does place exchange, and the reduction process becomes harder and the reduction peak moves to more negative potentials.

Table 4.1 together with Fig. 4.9 shows the charge calculation of the window opening experiments. As the experiments were carried out on a 0.50 μm thick Au wire with 1 cm length of the electrode dipped in the solution, the geometric surface area of the exposed surface area has been calculated to be 0.16 cm². When 1 (one) monolayer of charges in 1 cm² area are considered to be 400 μC, Fig. 4.9 shows that when potential is scanned up to 1.24 V vs SCE, 1.07 monolayer (427.58 μC) of AuO oxide formed at the electrode and it doubles when the potential is scanned up to 1.37 V vs SCE. When the potential scan is reversed at the end of the oxidation plateau (at 1.6 V), the number of monolayers formed is 3.79 which is associated with the total charge of 1518 μC cm⁻². The results in Fig. 4.9 demonstrate that the reduction

charge and the number of monolayer vs scanning potential limits curve is nonlinear at the beginning and linear after one monolayer of oxide is already formed.

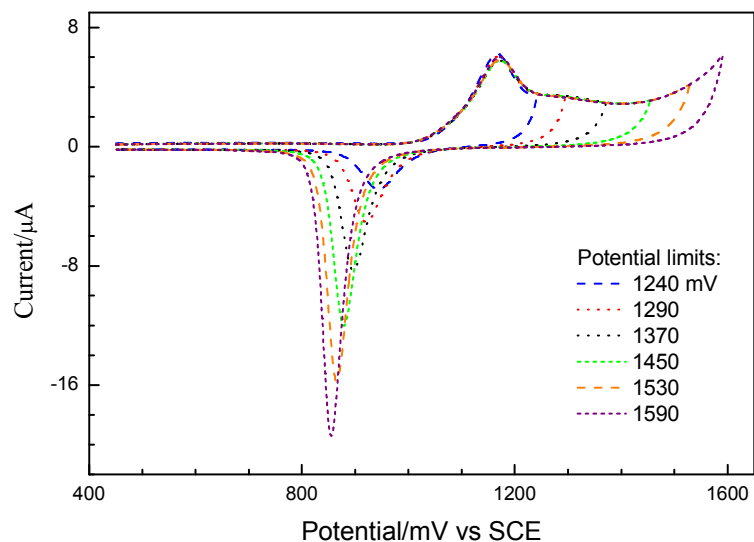


Figure 4.7 Cyclic voltammogram of polycrystalline Au electrode in 0.1 M H_2SO_4 at 5 mV s^{-1} with various positive potential limits.

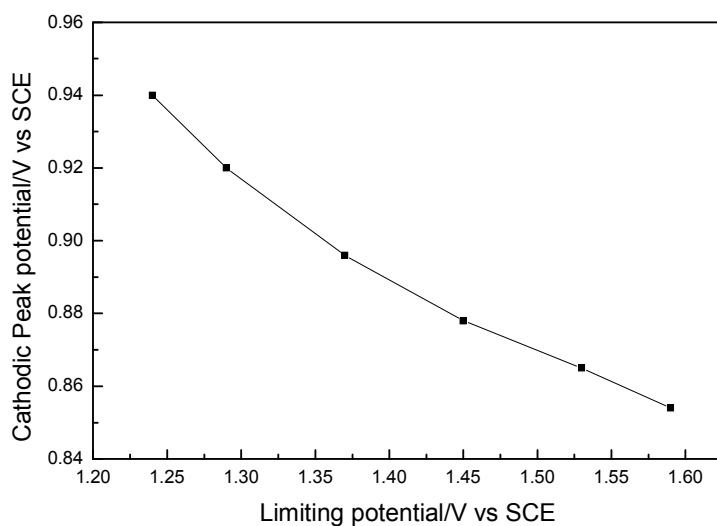


Figure 4.8 Plot of cathodic peak potential vs limiting potential. Cathodic peak potentials shift as the potential scan is reversed at more positive going scanning potentials for the CV of poly-Au in 0.1 M H_2SO_4 at 5 mV s^{-1} .

Scanning potential limits (V)	Total reduction charge (μC)	Charge density ($\mu\text{C cm}^{-2}$)	No. of monolayer (number)
1.24	67.13	427.58	1.07
1.29	98.69	628.60	1.57
1.37	135.48	862.93	2.16
1.45	172.45	1098.41	2.74
1.53	208.76	1329.68	3.32
1.59	238.48	1518.98	3.79

Table 4.1 Data of window opening cyclic voltammetry experiments on poly-Au electrode in 0.1 M H_2SO_4 . Total reduction charge, ($\mu\text{C cm}^{-2}$) and number of monolayers are tabulated as functions of scanning potential limits.

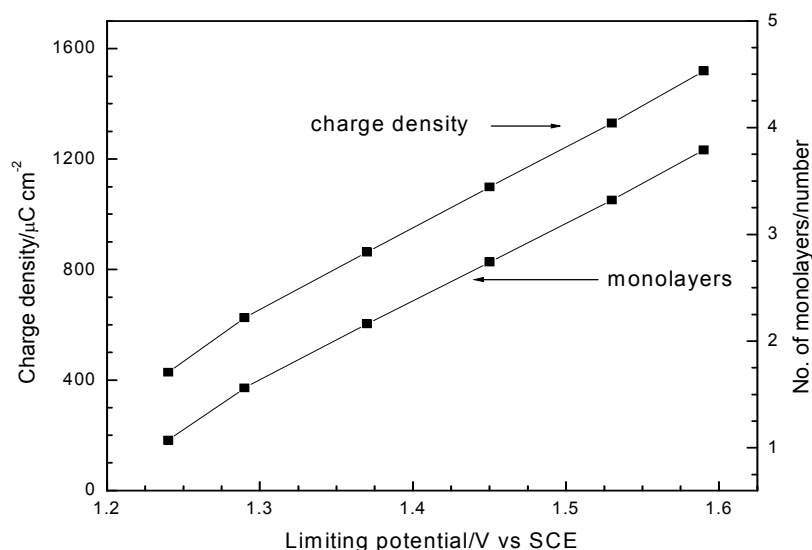


Figure 4.9 Reduction charge density ($\mu\text{C cm}^{-2}$) and number monolayer grown as functions of positive going potential limits in the cyclic voltammetry experiments on of poly-Au in 0.1 M H_2SO_4 at 5 mV s^{-1} .

We have earlier discussed that the AuO may grow to a limiting thickness of 3 monolayers. But our calculation shows that reduction charge exceeds the value $1,200 \mu\text{C cm}^{-2}$ which is associated with 3 monolayers. This indicates that the Au β -oxide should also develop under these conditions. But without a reduction peak for the Au_2O_3 reduction, it is not conclusive whether Au β -oxide also grows concurrently with Au α -oxide. Therefore, there are several possibilities that can be suggested-

- either that AuO could grow without any limiting thickness under the conditions described here, or

- reduction current peak for Au_2O_3 could be small and overlaps with the reduction current peak for AuO , [31] or
- the real surface area of the electrode is higher than the geometric surface area of the electrode, that means the roughness factor is higher than unity.

Due to the fact that higher oxidation peak current of Au is difficult to measure and without even a shoulder for Au_2O_3 reduction in the voltammogram, the second or third hypothesis is more likely the case.

4.4.2 Formation and reduction of Au β -oxide

The discussion in the preceding paragraph indicates that we cannot record oxidation current during the formation of the Au β -oxide because of concurrent oxygen evolution. But we can observe the reduction of Au β -oxide. After the usual pretreatment of the Au electrode, thick Au β -oxide films are grown at the electrode by holding the electrode at 1.9 V vs SCE for specified duration. After the specified time is elapsed the potential was then scanned down to 1.4 V at 5 mV s^{-1} . The electrode was then held at 1.4 V for 3 min whilst degassing continued to facilitate removal of oxygen. Finally, the Au β -oxide was reduced at 5 mV s^{-1} scan rate. The scanned potential sequence of Au β -oxide formation and reduction cyclic voltammetry experiment is illustrated in Fig. 4.10, and the data of Au β -oxide reduction experiment are recorded, and reduction current is plotted as a function of the potential and shown in Fig. 4.11.

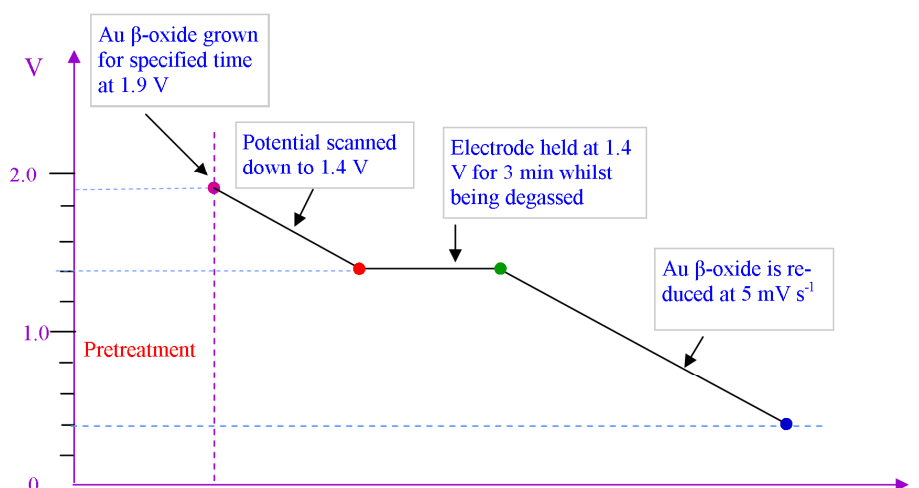


Figure 4.10 The potential scanning sequence during Au β -oxide formation and reduction cyclic voltammetry experiment. The β -oxide was grown by holding the electrode at 1.9 V vs SCE, then after degassing at 1.4 V the oxide was reduced.

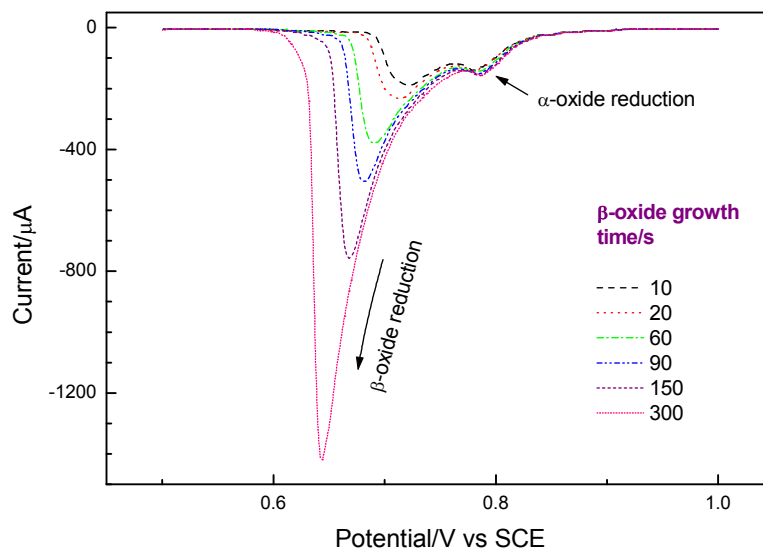


Figure 4.11 Reduction profiles for oxide films grown at poly-Au electrode by holding the electrode at 1.9 V vs SCE for various lengths of time in 0.1 M H₂SO₄. The reduction was carried out at 5 mV s⁻¹ [32].

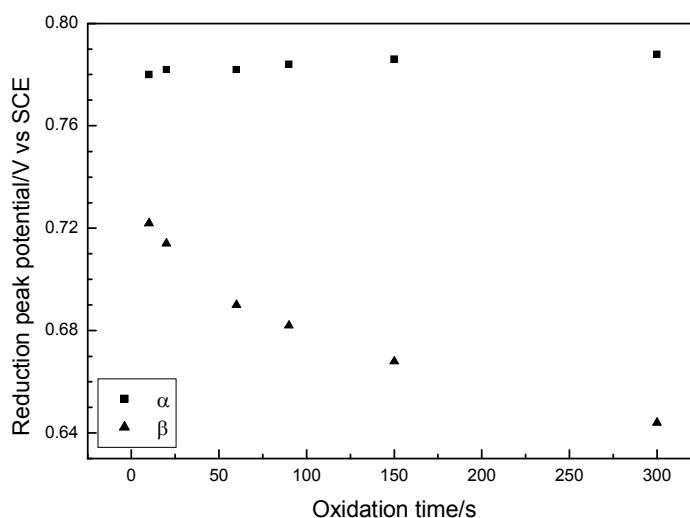


Figure 4.12 Reduction peak potentials of Au α- and β-oxide film formed on a poly-Au electrode in 0.1 M H₂SO₄ vs time of oxide growth at 1.9 V vs SCE.

In Fig. 4.11 the first reduction peak is due to the removal of the compact inner layer of Au α-oxide and the second peak is due to the reduction of Au β-oxide. The reduction peak attributed to the removal of Au β-oxide appears at a potential negative of the α-oxide peak potential. The reduction potential shifts from ca. 0.72 V at 10 s to ca. 0.64 V after 300 s of growth. This is an indication that the thickness and properties of the Au β-oxide film change as the oxide is grown for longer duration. Fig. 4.11 shows the usual behaviour that has been reported by Xia *et al.* [28]. When Au α-oxide is reduced, then there is a slight negative shift of the peak potential with a slight increase in peak current is noticed.

4.4.3 SHG and cyclic voltammetry of Au: Formation of Au α -oxide

SHG is applied to study both α - and β -oxide formation at Au electrodes. For the SHG experiments, *p*-polarised 780 nm laser illumination from a tuneable (720-990 nm) diode pumped Ti-Sapphire oscillator (Coherent Mira 900) with a repetition rate of 76 MHz was used. Further specifications are described in Chapter 2. In fact, identical laser illumination was used for experiments on both Cu and Au electrode.

Cyclic voltammograms and SH response data have been obtained, where Au electrode was under laser illumination. No change in the cyclic voltammogram whether in anodic or cathodic current peak was noted between those recorded with and without laser illumination. Therefore, any influence on oxidation or reduction current due to thermal and optical exposure of the electrode was negligible. This was due to the ultra short laser pulses that provide a high power density per unit area at low average power reducing the possibility of thermally damaging the electrode sample under study.

As shown in Fig. 4.13, the electrode potential, current and SHG responses from the Au electrode have been recorded. Fig. 4.13 shows a cyclic voltammogram and the associated SHG signals for the oxidation of Au in 0.1 M H₂SO₄. The potential scan was reversed at the upper limit of 1.5 V vs SCE around where the initial Au α -oxide is formed. The initial SHG response from the Au electrode is strong and the SHG response count is about 60,000 photons per second.

The SHG response remained relatively unchanged through-out the *electric double layer region* in the positive-going direction. As the potential becomes more positive, this featureless SHG response shows a sharp drop of almost a third of the SH photon counts, when some oxidation charge has just begun to pass (at the potential of 1.1 V). This sharp decline in the response of SHG happens over a very short range of potential, ca. 0.08 V. After this sharp fall at 1.1 V, the SHG signals continue to decrease with continued oxidation in a gradual way until the end of the positive going scan at 1.5 V. In the reverse scan the SHG response recovers steadily until the potential reaches 1.2 V. It is worth noting that between the potentials of 1.5 and 1.0 V, no significant cathodic charge is passed. The current is simply a small double layer current in the negative going direction. This is because the potential has not reached a value that is sufficiently enough to drive reduction of the oxide, and hence the recovery of the SHG intensity is less than a third of the initial intensity.

As we have noted above that in the initial stage of the reverse (negative going) scan, the SHG signal steadily recovers until the oxide reduction starts and cathodic charge starts to pass. But, as the reduction charge starts to pass and the reduction current reaches peak value there is a decrease in SHG signals in the shape of a small peak or a local minimum, labelled “A” in Fig. 4.13. The SHG signal then recovers immediately after the reduction current reaches the maximum (around the potential of 0.9 V in the negative going scan). After this small dip “A” the SHG signal then recovers almost all of its magnitude within a very short range of potential of around 40 mV. The recovery of the SHG signal occurs as a reversal of the trend that we have witnessed in the positive going scan.

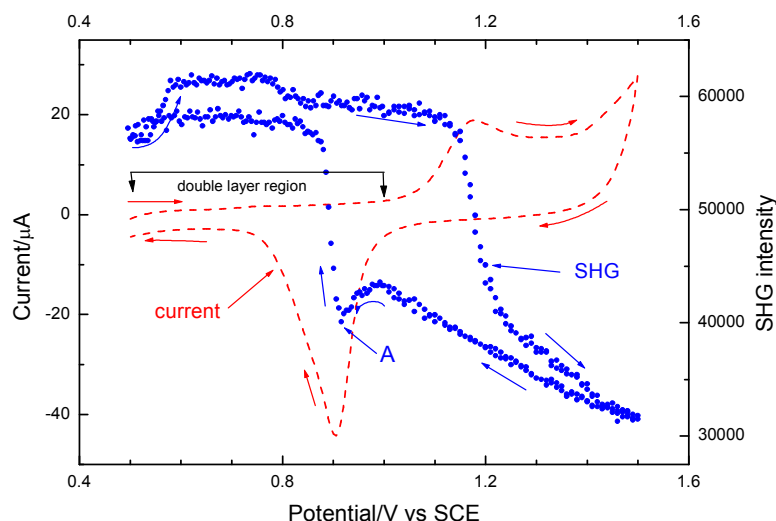


Figure 4.13 Cyclic voltammogram and SHG response for the oxidation of a poly-Au electrode under illumination at 780 nm from diode pumped Ti-Sapphire oscillator in 0.1 M H₂SO₄ at 5 mV s⁻¹. The upper potential limit is 1.5 V vs SCE [32].

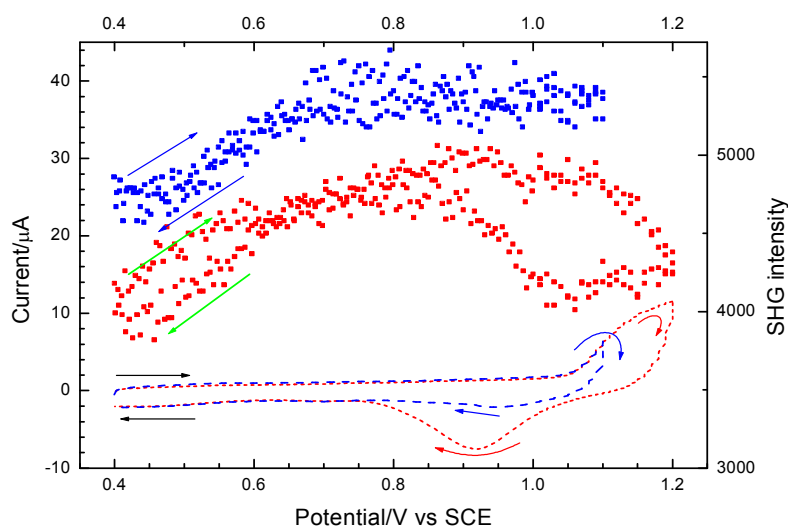


Figure 4.14 Potential vs current and SHG intensity at a poly-Au electrode in 0.1 M H₂SO₄ with maximum scanning potential of 1.1 V and 1.2 V vs SCE. Scan rate 5 mV s⁻¹ [32]. A much lower average laser power (~40 mW before it incident at Au surface) of the fundamental beam was used in this experiment. Lower average laser power was used during alignment which was not switched to full average laser power, typically 300 mW.

In Fig. 4.13 we noticed that when surface oxidation begins the interesting feature about SHG is that it decreases sharply. Conventional “window opening” experiments, shown above in Fig. 4.14, points that a small scale oxidation of Au that occur between the potential of 1.1 and 1.2 V is responsible for the

decrease in SH response. Fig. 4.14 shows when the potential is reversed at 1.1 V the SHG signal retraced the forward going intensity immediately without a decrease. But when the potential is scanned beyond 1.1 V, the SHG signal dropped sharply, this also the point where surface oxidation starts to occur, oxidation current rises and oxidation charge starts to pass. When the potential is scanned further and reversed at 1.2 V, the SHG signal recovers only when the potential is scanned back to 0.95 V, where the reduction peak appears. In the next section, this observed phenomenon will be explained with reference to how surface condition and oxide formation influence the SHG. There is a notable hysteresis in the optical response, when some oxidation has taken place.

4.4.3.1 SHG response in the electric double layer region

It has been mentioned in the introductory chapter that previous SHG works on noble metals, such as Au or Pt electrodes have mainly focussed on the electric double layer region, where no faradaic processes take place. Most of these earlier studies were on ion adsorption [2] and surface reconstruction [144] at single crystals. Campbell *et al.* [144] reported that adsorption of H and ionic species at Pt electrode did not influence SHG signals strongly. In the double layer region, a lack of potential dependent SHG was reported which was attributed to the potential independent coverage of the species from electrolyte solutions. The change in SHG signal in Fig. 4.13 within the double layer region is small. This change in the SH response might be due to the change in electron density, which may alter the second order nonlinear susceptibility, $\chi^{(2)}$ through the donation or acceptance resulting from ion adsorption. The Campbell [144] study did observe a decrease in SHG intensity the start of surface oxidation. The reason why the onset of surface oxidation causes this decrease was not explained in any great detail. In the next two sections we suggest what might influences the SH response in the electric double layer region.

4.4.3.2 Sharp decrease in SHG signal

Data of cyclic voltammetry covering the potential of compact Au-oxide growth and the conventional window opening experiment, and simultaneous SHG presented in Fig. 4.13 & 4.14 show that the SHG signal has a sharp drop when the potential has reached 1.2 V. Some comparatively recent studies that combine conventional cyclic voltammetry and EQCM suggest that the initial stage oxidation involves non-adsorbed water in the formation of AuO [23, 31]. As coverage increases, place exchange occurs between Au and O as discussed earlier in this chapter in Section 4.2.2. Here it is observed in Fig. 4.13 that the sharp decrease of SHG occurs before significant place exchange happens. Thus at the point at which SHG starts to drop, the Au surface is not fully covered with a monolayer of oxide, in fact coverage is much smaller than one monolayer and no significant place exchange is likely to have occurred. It is suggested below that the reason for the drop in the SHG is due to the effect of the initial stages of surface oxidation which reduce the probability of surface plasmon resonance [32].

4.4.3.3 Influence of surface plasmon on SHG response

Before going on to analyse the influence of surface plasmons on the SHG signal response a brief introduction to surface plasmons in connection to SHG response is presented here. Surface plasmons are collective oscillations of free electrons that propagate along the surface of the metals. Recently, surface plasmon resonance (SPR) has attracted attention due to its application to the study of the surface reactions and in the study of sensors [205, 206]. Moreover, recent developments in nanoparticles brought more attention to the surface plasmons of nanoparticles in order to characterise more fully the electronic properties of nanoparticles. We have seen in Chapter 1 that the nonlinear polarisation induced on a metal surface related to the square of the incident electric field by the second order nonlinear susceptibility, $\chi^{(2)}$ and can be expressed as the following:

$$P(2\omega) = \chi^{(2)}[E(\omega)]^2 \quad (4.7)$$

Taking into $\chi^{(r)}$ and $\chi^{(nr)}$ (resonant and non-resonant) polarizability into account Eq. (4.7) can be expressed as-

$$P(2\omega) = (\chi^{(nr)} + \chi^{(r)})[E(\omega)]^2 \quad (4.8)$$

If the excitation frequency, ω or second harmonic frequency, 2ω are resonant with any surface electronic state, then the resonant contribution of the nonlinear polarisability can be significant. Importantly, a study by Antoine *et al.* [168] found surface second harmonic generation (SSHG) was influenced by resonant plasmon excitation for Au nanoparticles that were adsorbed at an interface between air and toluene.

A detailed study on the surface plasmons on bulk Au by Barker [207] pointed out the existence of a surface plasmons because of a free standing wave at 550 nm. Barker [207] also mentioned that there were surface plasmons connected to the *d*-electrons at around 410 nm and in the region of 270-280 nm. In the work presented in this chapter, Au experiments were carried out at 780 nm excitation wavelength. Given that the experiments were carried out at room temperature and that the surface plasmons have significantly wide optical band width, the surface plasmons of 410 nm is in the considerably close to the value of SH frequency, 2ω at 390 nm and resonance enhancement is therefore likely.

The sharp drop in the SHG intensity observed between 1.1 and 1.2 V in the positive going direction results from the effect of the initial stage of formation of Au α -oxide at Au on the surface plasmons associated with the *d*-band electrons of Au. Surface chemistry (in other words the formation of an oxide on the surface) affects availability of the *d*-electrons due to the early stages of oxidation- as a result, plasmon excitation cannot take place and the resonance contribution to the overall induced polarisation drops; hence the observation of a sharp decrease in SHG signal.

4.4.3.4 SHG signals between 1.2 and 1.5 V and back to 0.4 V

After the sharp decrease of SHG signal between 1.1 and 1.2 V the rate of fall decreased and the SHG signal reached the minimum at the end of the scan. The data of “window opening” experiments plotted in Fig. 4.14 shows that the drop in SHG begins at a potential where the oxidation is still very much reversible. The involvement of *d*-electrons in bonding to the oxygen is enough to interrupt the surface plasmons propagation linked to the *d*-band electrons but complete coverage of oxide or indeed even the onset of place exchange does not need to occur before the propagation of the surface plasmons to be discontinued [32]. All that is needed is a moderate coverage of oxide at the Au surface to discontinue the propagation of surface plasmons, and hence stop the surface plasmon resonance contribution to the SH response.

When the potential is scanned further, there is further decrease of the SHG response but the rate of decrease slows down. This further decrease is associated simply with the increased coverage of oxide at the electrode surface. Results on Pt also showed a drop in SHG signal as the α -oxide developed [144].

When the potential is reversed, some cathodic charge begins to pass and the compact Au α -oxide starts to reduce. Therefore, the SHG signal also gradually recovers because the oxide coverage at the surface is being decreased. As the potential is scanned further in the negative direction, the Au surface is restored in parts and the SHG response increases when the surface plasmons are again able to propagate across the metal surface and the resonance contribution to the SHG comes into play [32]. The small peak marked “A” in Fig. 4.13 will be discussed in the next section, when a test experiment for SHG response from Au β -oxide is discussed.

4.4.3.5 Test of SHG response from Au β -oxide grown at 1.8 V vs SCE

In this section, a test experiment for the SHG response from Au β -oxide grown at 1.8 V vs SCE is discussed. In this experiment the electrode was cleaned electrochemically as described before. The potential was then held at 1.8 V vs SCE for 30 s. This test experiment was carried out to investigate the appearance of a small SHG peak (trough, labelled ‘A’) at 0.9 V in Fig. 4.13 in the negative going scan.

Conventional “window opening” experiments shown in the Fig. 4.14 and in Fig. 4.15 below demonstrate that there is no peak (trough) around 0.9 V when the upper limit of potential is restricted to values below 1.5 V. The results shown in Fig. 4.15, where the potential is scanned up to 1.4 V, the SHG signal stays almost the same between 1.4 and 0.9 V (in the reverse direction) after which SHG increases sharply and recovers almost all of its original SHG intensity. The small peak labelled ‘A’ in Fig. 4.13 appears only when the potential is scanned beyond 1.4 V and at least up to 1.5 V in the positive direction. We therefore attribute the appearance of this peak to the very small scale growth of Au β -oxide. Therefore, a test

experiment was carried out to see the extent of the growth of SHG peak by holding the electrode at a slightly higher potential than the potential where compact Au α -oxide is formed.

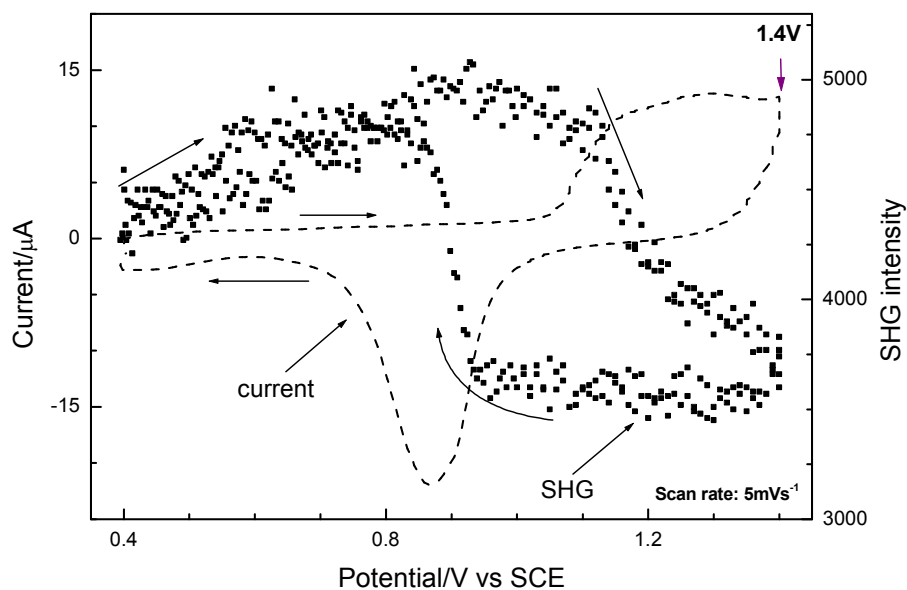


Figure 4.15 Simultaneous cyclic voltammogram and SHG response from polycrystalline Au in 0.1 M H₂SO₄ at 5 mV s⁻¹. The potential scan is reversed at 1.4 V vs SCE.

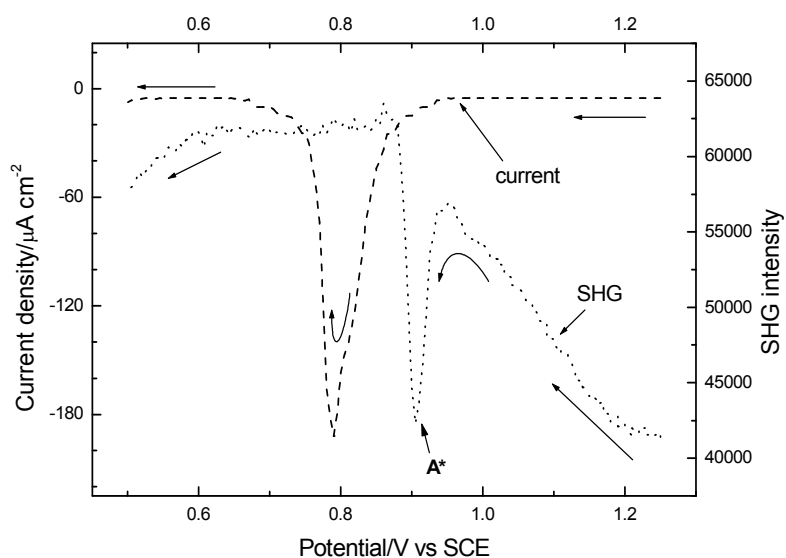


Figure 4.16 SHG response with the reduction profile of Au electrode in 0.1 M H₂SO₄ which was held at 1.8 V vs SCE for 30 s.

The test experiment results are shown in Fig. 4.15 and in Fig. 4.16, and are carried out by growing a very thin layer of Au β -oxide by holding potential at 1.8 V vs SCE for 30 s which is beyond the potential where Au α -oxide is produced but not into the potential regime of significant β -oxide growth. After growing the β -oxide at 1.8 V vs SCE, the potential was then scanned down to 1.25 V, held for 3 min whilst electrolyte being degassed and then the potential was scanned down to 0.50 V vs SCE.

The Fig. 4.16 shows that as the potential is scanned down from 1.25 V in the negative direction, SHG signal starts to rise and continues to rise until 0.95 V. At around 0.95 V when some reduction charge starts to pass the SHG signal drops sharply and a peak (trough) reaches a minimum over a very short range of potential of 0.06 V. It is likely that the “trough”, labelled “A*” in Fig. 4.16 is an extension of what was seen in Fig. 4.13, a small peak (trough), labelled “A”. The trough “A*” in Fig. 4.16 indicate that it may originate due to the presence of the interface between AuO and Au₂O₃. It is worth noting here that although the electrode was held at a constant potential of 1.8 V to grow a very thin layer of Au β -oxide on top of the α -oxide, the reduction profile in Fig. 4.16 shows only a reduction current peak at around 0.8 V which is most probably the current peak due to the reduction of Au α -oxide.

Therefore it can be said that formation of Au β -oxide at 1.8 V was insignificant or at least the β -oxide was not thick enough to exhibit any reduction current peak. A very thin Au β -oxide layer, reduction peak for which perhaps is overlapped in the α -oxide reduction peak, might have induced the sharp peak (labelled “A*”) in Fig. 4.16.

4.4.3.6 Conclusions

Following conclusions can be drawn from discussion of SHG studies on Au α -oxide-

- Initially surface plasmon resonance is responsible for the SHG response in the double layer region. Then ion adsorption is probably responsible for a small decrease in SHG in Au electrical double layer region but detailed study is needed to confirm this.
- Surface oxidation of Au atoms is suggested to inhibit the propagation of a d-electron surface plasmon. This surface plasmon provides a resonance contribution to the SHG intensity that is observed in the double layer region. Thus when it is inhibited because of the formation of partial monolayer of oxide, the SHG signal falls sharply.
- SHG shows promise as surface probe for sub-monolayer adsorption processes and also for chemical reactions at the surface which may affect the propagation of the surface plasmon associated with d-electrons.

4.4.4 SHG studies of Au β -oxide

4.4.4.1 Introduction

A set of current-voltage curves for the reduction profile of Au β -oxide grown for various durations at the potential of 1.9 V vs SCE is shown in Fig. 4.11. The potential scan sequence for growing β -oxide has been explained in Section 4.4.2 and illustrated in Fig. 4.10. After the growth of oxide films, the potential was scanned down to 1.4 V vs SCE and held at 1.4 V for 3 min while the electrolyte was degassed by N_2 . Finally, the Au β -oxide was reduced by scanning the potential from 1.4 V to 0.4 V at 5 mV s^{-1} . The resulting current and the corresponding SHG intensities were recorded. The successive reductions of the oxides leads to the unusual narrow peaks (troughs) in the SHG signals but these narrow peaks occur before any reduction charge is passed. When the thickness of β -oxide increases, the initial single sharp peak changes and develops to a pair of peaks and then merge into one broad peak. In the following section the results are discussed.

4.4.4.2 SHG response from Au β -oxide

Fig. 4.17 shows the SHG intensity that accompanies the reduction current profile of the oxide film grown electrochemically for 10 s at the potential of 1.9 V vs SCE. The current response shows two peaks due to the reduction of Au α -oxide followed by the reduction of the Au β -oxide. As expected for this degree of growth of β -oxide, the comparative sizes of the reduction peaks show that the β -oxide is not thick as the current voltage profile maintains the same feature as seen in Fig. 4.11. But what is interesting here is the appearance of a peak (trough) in the SHG response. When the potential is scanned in the negative going direction from 1.4 V vs SCE, the SHG signals start to increase until it reaches the point around 0.9 V. At around 0.9 V, before a monolayer of reduction charge is passed, the SHG response from the β -oxide starts to decrease and the rate of decrease becomes faster, forms a narrow peak (dip), which recovers within a potential range of just 0.15 V. This recovery happens before any significant oxide reduction charge is passed. As the potential is further decreased and reduction proceeds, no significant change is observed in the SHG signal. Finally, when oxide reduction is complete and no more reduction charge passes, the SHG signal decrease again slowly.

In order to investigate the processes leading to the SHG response, β -oxide growth was allowed to continue for various durations. The responses obtained are shown below for growth times of 90, 150, 270 and 300 s in Fig. 4.18, 4.19, 4.20, and 4.21 respectively.

Successive experiments with longer holding time for oxide growth show an interesting evolution of the SHG response. Current-voltage profiles show that the Au β -oxides have grown significantly and become considerably thicker than the inner Au α -oxide. The SHG signal now evolves into two peaks. In Fig. 4.18 where oxide is grown for 90 s, SHG signal initially increases between 1.4 to 0.9 V largely at a constant

rate. At around 0.9 V, reduction charge begins to pass; the SHG signal decreases sharply and then reaches a minimum, labelled “a₂” and the shoulder labelled “a₂”. Around the minimum SHG signal intensity starts to develop two separate minima. While recovering, SHG signal slows down just after 0.8 V and then recovers fully to the pre-peak intensity as the oxide reduction is complete and then follows a slowly decreasing path.

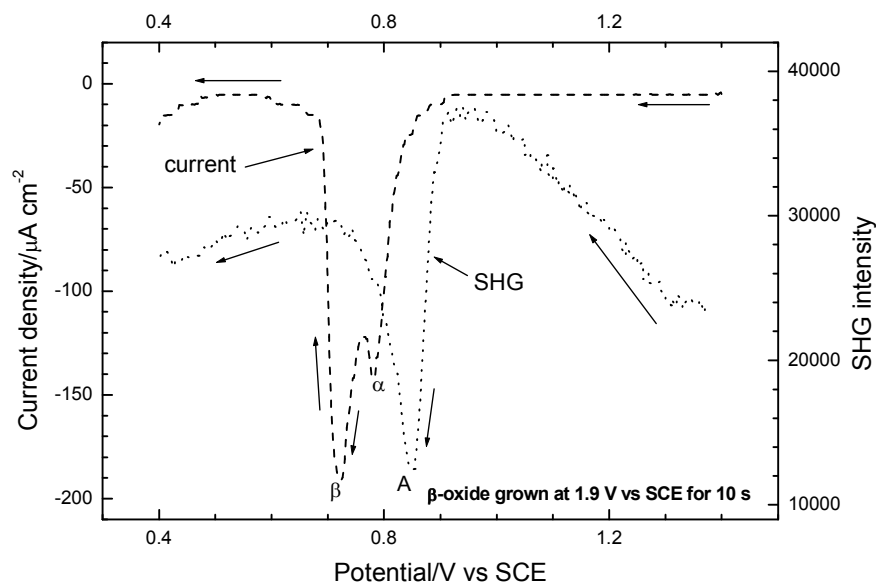


Figure 4.17 Cyclic voltammogram and SHG response for the reduction of Au β -oxide grown on poly-Au in 0.1 M H₂SO₄ at 1.9 V vs SCE for 10 s. The scan rate was 5 mV s⁻¹.

In Fig. 4.19 the holding time is increased further to 150 s, and the Au β -oxide gets thicker which results in an increase in the reduction current. The potential vs SHG signal curve shows that a pair of SHG signal peaks labelled “a₁” and “a₂” appearing between 0.87 and 0.80 V vs SCE in Fig. 4.19. Fig. 4.20 for which the holding time is 270 s shows that the SHG peaks are of equal size. First peak occurs before any significant reduction current is passed and the second peak also appears at a potential which is only slightly less negative than the potential where the Au α -oxide reduction peak occur.

Fig. 4.21, where the holding time is 300 s, shows that the two distinctive SHG peaks that were seen, when oxidation time was 150 and 270 s, now merge into a single broad peak (trough). The increase in SHG signal from 1.4 V as the potential is scanned in the negative direction is continuous until the potential of 0.95 V. Then the decrease in SHG response starts before all the reduction charge has been passed and SHG signal decreases sharply reaching its peak, labelled “A” roughly at a potential that is coincident with the Au α -oxide reduction peak, labelled “ α ”. Unlike in the reduction cases of oxides of lower thickness, the SHG signal in this case recovers more slowly and continues to recover as the Au β -oxides is reduced completely.

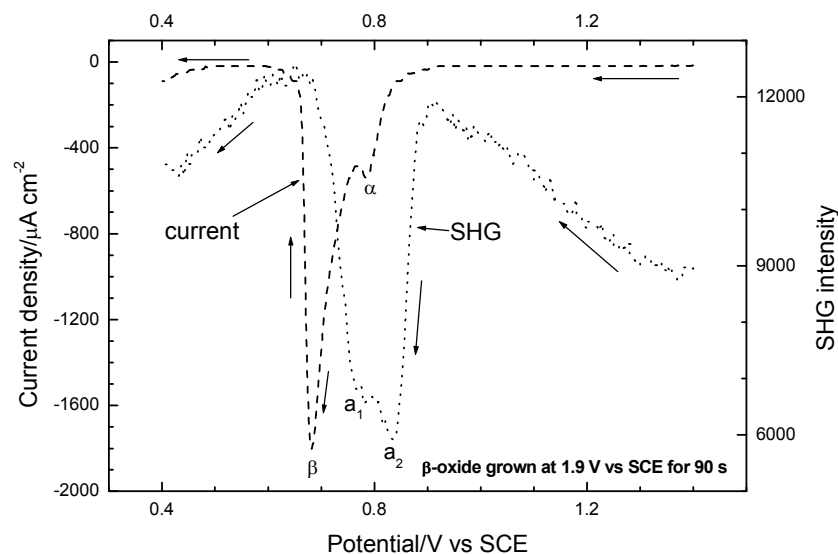


Figure 4.18 Cyclic voltammogram and SHG response for the reduction of Au β -oxide grown on poly-Au in 0.1 M H_2SO_4 at 1.9 V vs SCE for 90 s. The scan rate was 5 mV s^{-1} .

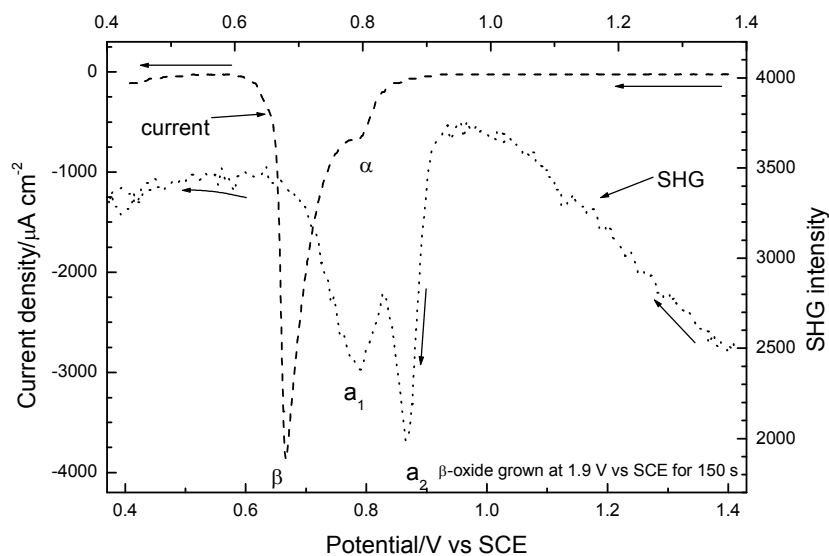


Figure 4.19 Cyclic voltammogram and SHG response for the reduction of Au β -oxide grown on poly-Au in 0.1 M H_2SO_4 at 1.9 V vs SCE for 150 s. The scan rate was 5 mV s^{-1} .

To compare the SHG data obtained while reducing the different Au β -oxide layers grown at 1.9 V vs SCE for variable durations, SHG response data from all β -oxides were normalised. The normalisation was devised so that each set of SHG signal data for each of the reduction scan is spanned over the range from 0 (zero) to 100. Then an offset (constant value) was added to each set of SHG data. This offset was different for each data set and was included simply to allow all the data to be shown on one graph, but the

span of SHG intensity for each of the Au β -oxide reduction SHG data set runs between 0 (zero) and 100. The normalised SHG data for the reduction experiments are plotted as a function of the scanning potential and illustrated in Fig. 4.22 below.

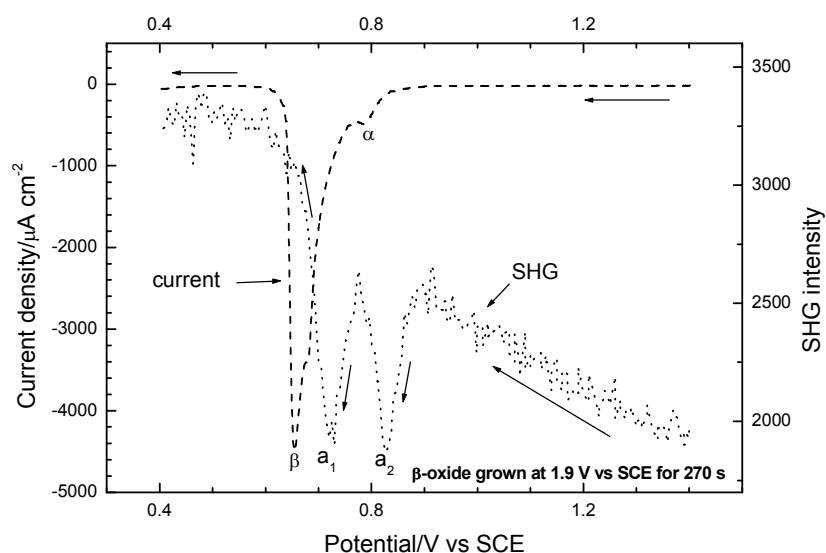


Figure 4.20 Cyclic voltammogram and SHG response for the reduction of Au β -oxide grown on poly-Au in 0.1 M H_2SO_4 at 1.9 V vs SCE for 270 s. The scan rate was 5 mV s^{-1} .

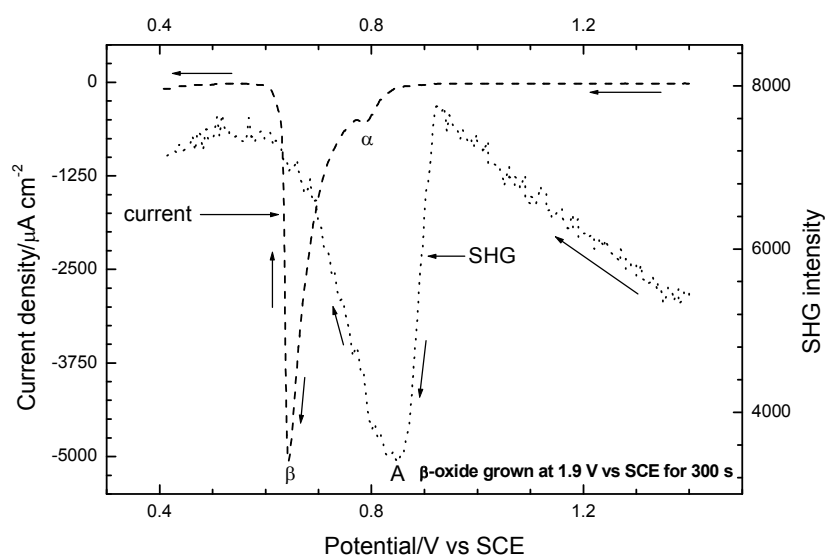


Figure 4.21 Cyclic voltammogram and SHG response for the reduction of Au β -oxide grown on poly-Au in 0.1 M H_2SO_4 at 1.9 V vs SCE for 300 s. The scan rate was 5 mV s^{-1} .

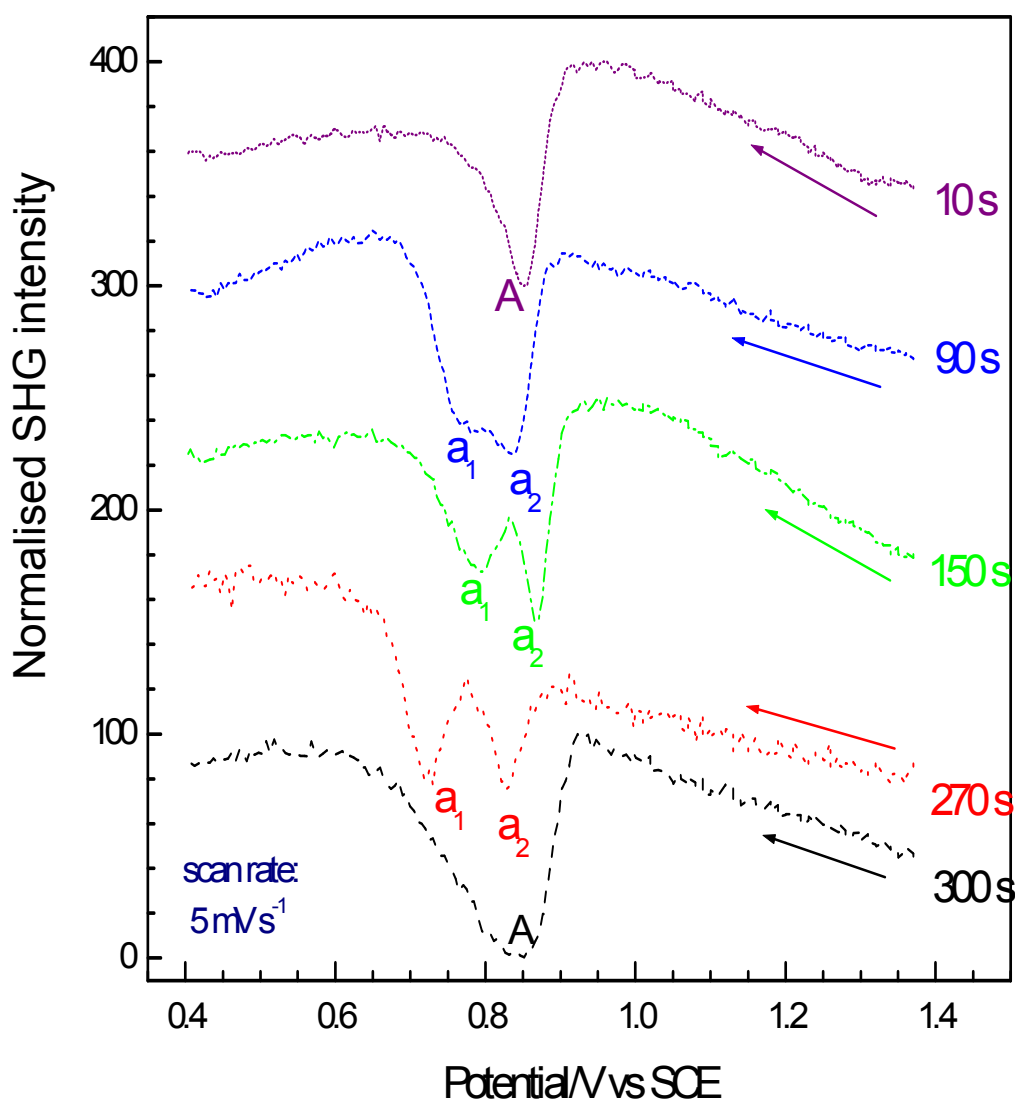


Figure 4.22 Normalised SHG intensities as functions of the applied potential. The oxides were grown at 1.9 V vs SCE for variable durations and then reduced at the scan rate of 5 mV s⁻¹.

Fig. 4.22 shows that there is a correlation between the breadths of the SHG signal peaks and the corresponding oxide growth time. As the time of oxide growth is increased and the Au β -oxide becomes thicker, a peak, labelled “A” in the SHG signal develops. As oxide growth time increases a pair SHG peak, labelled “a₁” and “a₂” appears and then develops. With longer oxidation time as the Au β -oxide layers thickens, we notice that peak “a₁” disappears or/and the two SHG peaks converge into one broad peak, labelled “A”. As the β -oxide thickens with increasing oxide growth time, peak “A” and “a₂” do not shift, but the peaks “a₁” shift to the less positive potential. The observed phenomena are discussed below.

4.4.4.3 A possible EFISH response from Au β -oxide

The structure and properties of oxides, such as the band gap of any semiconducting materials influence the SHG response [4]. The SHG response also depends on the second and the third order nonlinear susceptibilities as denoted by $\chi^{(2)}$ and $\chi^{(3)}$ respectively in the following equation from Chapter 1-

$$P(2\omega) = \chi^{(2)}E(\omega)E(\omega) + \chi^{(3)}E(\omega)E(\omega)E_{DC} \quad (4.9)$$

In Chapter 3 we have seen that for oxidation of Cu dramatic changes in the SHG were associated with the passing of oxidation charge and dramatic changes were observed during the reduction process, which is not the case in Au. In contrast to Cu-oxides, it appears that little is known about the electronic structure of Au-oxides. A recent theoretical calculation done by Shi *et al.* [97] on Au_2O_3 suggested that it is a semiconductor with a band gap of 0.85 eV. It is quite well known that semiconductors can have an EFISH contribution to the SHG. When the potential (and hence the electric field across the semiconductor) is varied, it is observed that Si [4] and CuO [3] show an EFISH contribution that leads to a parabolic shape of the SHG response. Therefore an EFISH contribution from inner Au α -oxide or outer β -oxide may be possible but cannot be proved.

If the SH response curve in Fig. 4.18 and 4.19 for the potential range of 1.4 to 1.0 V (in the reverse direction) could be considered as making up one of the arms of a parabolic response curve, it might be possible to suggest that the β -oxide shows an EFISH response. But in the absence of a minimum, it cannot be inferred because no higher potential can be scanned as the oxygen evolution would complicate the detection of SH photons. Therefore, it is hard to establish any definitive evidence for an EFISH response in the first part of the negative going scan, from 1.4 V to 1.0 V, but it cannot be ruled out. Nevertheless, the peaks (troughs) seen in the SHG responses when the potential continues to be made more negative, can be related to an EFISH contribution to the SH response.

In Fig. 4.18 and 4.19, the sharp decrease of SHG signal starts to occur at a potential where there are no faradaic processes. The electrode is covered with oxide and the potential, while decreasing, but has not yet reached a value where the oxide can be reduced. Thus, it is possible that the changing electric field across the oxide might be affecting the SHG. However, it is important to note that the SHG peaks are quite sharp: they occur within a narrow range of potential which has a half width of about 0.08 V [3]. But in the case of Au α -oxide reduction, the SHG curve is sharp and appears within a much narrower range of scanning potential than a normal EFISH response would [4]. The initial appearance of this SHG peak in Fig. 4.13 was due to a situation where there could only be a very thin layer of oxide at the electrode surface, and so it seems unlikely that an EFISH signal could arise here either. Thus it seems unlikely that an EFISH contribution to the SHG signal could be observed during Au α -oxide formation or reduction. The phenomenon which can be responsible for the SHG signal to increase initially (as the potential is made more negative) and then drop sharply and recover at the end will be discussed in the next section.

4.4.4.4 SHG due to interfacial order/disorder phenomenon

In the preceding section it has been argued that the evidence for an EFISH contribution from Au α -oxide to SHG is inconclusive and unlikely and it is highly unlikely in the case of β -oxide. This conclusion is reinforced by the fact that Fig. 4.18 shows the sharp decrease in SHG when only a thin layer of β -oxide present was being reduced. This thin layer of oxide has less capacitance than a thick oxide so it might not be able to support a separation of charges; hence the field across the oxide layer is smaller than it would be for a thicker oxide. This makes an EFISH contribution to the SHG peak unlikely. Therefore, an alternative explanation must be sought. An important point here in the discussion of this phenomenon is the peak in Fig. 4.13 labelled 'A', which appears when the positive going potential was set at 1.5 V in the cyclic voltammogram. Conventional "window opening" experiments illustrated in Fig. 4.14 and 4.15 do not show the peak when the potential is limited to 1.4 V. The peak appears when the potential limit was extended to 1.5 V and some oxygen evolution probably occurs. The test experiment shown in Fig. 4.16 shows that the peak (trough) is even more prominent when the electrode held at 1.8 V vs SCE for 30 s. But the reduction shows that there has not been any significant growth of Au β -oxide. Considering this phenomenon it can be suggested that the peak 'A' in Fig. 4.13 is connected to the *interface* between Au α -oxide and β -oxide. The peak is absent when only α -oxide is formed (as it is clear in Fig. 4.14 and 4.15) but appears in the reduction profile of the Au CV where the β -oxide would just start to form in the positive going scan around 1.5 V. Its appearance seems to be connected to the presence of both oxides at the surface and hence the existence of an interface between them.

Under the dipole approximation, an ordered system that lacks inversion symmetry causes a rise of SHG response. Therefore a reasonable and possible explanation of the decrease in SHG that occurs when β -oxide is reduced is that a phase change takes place at the interface between α -oxide and β -oxide. The interfacial species may go through ordered, disordered and then reordered cycles which then could be responsible for the observed SHG phenomenon. Changes in order that lead to SHG responses are quite well known from the literature. For example, some earlier SHG studies of metal surfaces were focussed on studies of phase transitions observed at single crystals [2, 144] using rotational anisotropy. Surface reorganisation at single crystals can be driven by an applied electric field or adsorption of various species like halides and pyridines as studied by Pettinger *et al.* [2].

As mentioned earlier in the chapter both AuO and Au₂O₃ are semiconductors. Therefore it might seem surprising that such large SHG signals are observed but it is well known that many semiconductors have large nonlinear optical coefficients [79, 208] and so can give rise to significant SHG signals. Furthermore, there is precedent for phase transitions in materials with similar structures to that of Au₂O₃. It should be noted that Au₂O₃ has Fdd2 symmetry and potassium dihydrogen phosphate (KDP) which is a well-known nonlinear optical material, undergoes a phase transition that results in a structure with Fdd2 symmetry [32, 209]. As KDP is a crystal with a high nonlinear coefficient, being in the same crystal symmetry group, Au₂O₃ is also likely to show nonlinear property and SHG could be seen from its surface before it is heavily hydrated.

4.4.4.5 $\text{Au}_2\text{O}_3\cdot\text{H}_2\text{O}/\text{Au}_2\text{O}_3\cdot 2\text{H}_2\text{O}$ interface giving rise to second SHG peak, “a₁”

With longer oxide growth time, Au β -oxide becomes thicker and two SHG peaks appear as shown in Fig. 4.19 and 4.20 labelled “a₁” and “a₂”. A combined electrochemistry, QCM and ellipsometry study by Xia *et al.* [28] suggest that the β -oxide is initially $\text{Au}_2\text{O}_3\cdot\text{H}_2\text{O}$ but with longer growth time it gets thicker and becomes more hydrated as an extra water molecule is embedded with the oxide to become $\text{Au}_2\text{O}_3\cdot 2\text{H}_2\text{O}$. Thus it could be suggested that we have three layers of oxides- the outermost layer probably a heavily hydrated $\text{Au}_2\text{O}_3\cdot 2\text{H}_2\text{O}$ layer, then an inner layer of less hydrated $\text{Au}_2\text{O}_3\cdot\text{H}_2\text{O}$ layer, and finally the innermost Au α -oxide layer as shown in Fig. 4.23 below. The ellipsometric results were modelled using this three-layer picture with the outer heavily hydrated oxide layer having a lower refractive index than the inner hydraous oxide [28, 32]. Therefore it is plausible to argue the possibility of a second interface being developed as the β -oxide gets thicker.

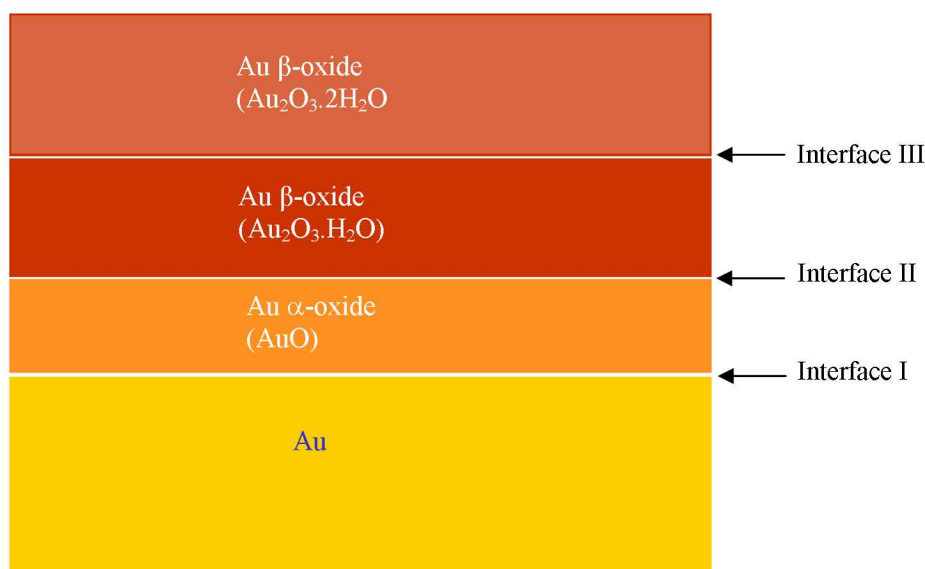


Figure 4.23 Schematic illustration of the interfaces between three-layer oxides. The outer Au β -oxide ($\text{Au}_2\text{O}_3\cdot 2\text{H}_2\text{O}$) layer is more hydrated than the inner Au β -oxide ($\text{Au}_2\text{O}_3\cdot\text{H}_2\text{O}$) and the third layer is the Au α -oxide (AuO).

Therefore in this complex oxide structure, it is also possible that a second order/disorder transition takes place just before the more hydrated Au β -oxide, $\text{Au}_2\text{O}_3\cdot 2\text{H}_2\text{O}$ starts to form on top of the initial Au β -oxide, $\text{Au}_2\text{O}_3\cdot\text{H}_2\text{O}$. This second order/disorder transition could then be responsible for the appearance of the second SHG peak, labelled “a₁” as shown in Fig. 4.19 and 4.20. The Au β -oxide layers grown here are thick, particularly when the holding time at 1.9 V vs SCE is longer. As a result, as explained earlier in this chapter and illustrated in Fig. 4.23, could be substantial cations migration through the complex oxide structure to allow the growth to happen. In addition to the above, Xia *et al.* [28] proposes that during the growth of β -oxide and associated oxygen evolution may alter the local acidity at the electrode solution

interface and that may lead to the film dissolution and a porous film is formed [32]. Therefore, it does not seem unlikely that as the oxide growth time increases various phenomenon including cation migration and changes in local acidity may cause the oxide film to become more porous and these distinct interfaces merge or break down leading a less well-defined single interface. This loss of distinct interfaces then causes the merging of two SHG peaks into one a broader one which can be easily seen in Fig. 4.22. However, the suggestion of order/ disorder phenomenon giving rise to peaks in the SHG signal is not the only possibility.

An alternative explanation of the SHG peaks can be provided by considering Au α -oxide and β -oxide as semiconductors. In the following section it will be explained how it is possible for SHG response and the peaks to arise due to local defects and electron trapping.

4.4.4.6 SHG response from local defects and electron trapping

The Au α - and β -oxide are two semiconducting materials that correspond to two different phases with differing band gaps [97]. An interface that is made of two semiconductors may be characterised by small regions where there will be Au atoms present with different oxidation states. Au atoms with different oxidation states cross the phase boundary and interpenetrate between the phases leading to the rise of local defects. These local defects can act as traps for electrons or holes and in effect, creating electronic states in the band gap.

If the potential needed to fill these traps is characterised by a shallow well, then the scan of potential can cause filling and then emptying these traps [32]. The phenomenon is explained by Eq. (4.8) where the observed SHG signals arises from both non-resonant, $\chi^{(nr)}$ and resonant, $\chi^{(r)}$ second order susceptibility. The drop in SHG signal over a narrow potential range could be explained as the detuning effect of the $\chi^{(r)}$, such that the filled electronic states are responsible for the resonant contribution and are emptied and then filled again causing the SHG response to drop and then recover again [32].

There can be another scenario here which is- if we assume that in the emptying-populating process if the final state is a hole, where the wholes are filled and emptied again as the electrons are mobile due to the influence of applied potential [32]. Interfacial studies by Shamir *et al.* [210] on Si and SiO₂ have shown that interfacial electron trapping is responsible for the SHG response where oxide layer with negative charge and holes that are formed at the interface. Strain in the form of heating due to continuous electron bombardment can also induces defects that act as traps for electrons which in turn can further enhance the SH signal intensity. Similar claim was also made by Dadap *et al.* [211] in their studies of femtosecond carrier induced screening of dc electric field induced second harmonic (EFISH) generation. Mitchell *et al.* [212] calculated the number of density of charge carriers generated in the semiconductor under illumination from a femtosecond laser source using the equation-

$$n_{eh} = \frac{2\pi F \alpha}{h\omega} (1 - R_p) \quad (4.10)$$

where n_{eh} is the number of electron-hole pairs, F is the fluence of the incident radiation, α is the absorption coefficient of the Si electrode at the fundamental laser frequency, ω , and R_p is the reflectivity at the fundamental laser frequency for p -polarised incident light. These studies in semiconductors-oxide interface strengthen the arguments that SHG response can originate from local defects and electron trapping. However, oxides of Si are some of the extensively studied systems. In contrast to that, detailed characterisations of semiconducting Au-oxide such as, AuO and Au₂O₃ have not been performed. Therefore, it is difficult to estimate, cross reference and quantify the electron-hole pairs for AuO or Au₂O₃. Nevertheless these semiconducting Au-oxides, when under femtosecond laser illumination are likely to produce electron-hole carriers and influence the SHG response.

4.5 Conclusion

It has been demonstrated that SHG can be used as a sensitive probe to monitor changes at the surface of Au electrodes during studies of electrochemical oxide formation and reduction. In addition, SHG response during the reduction process of Au β -oxide together with the underlying α -oxide can also be observed. In the process of Au α -oxide development, sub-monolayer sensitivity of SHG in the electric double layer has been noted. The development of AuO and the involvement of d -electrons associated with the bonding are suggested to be the cause of the sharp fall in the SHG response when the resonance contribution to the SHG from the surface plasmon related to the d -electrons is diminished [32].

When thicker β -oxide is grown on top of the already formed α -oxide by holding the potential at a constant point the corresponding stripping of the oxide layer give rise to narrow peaks (troughs) in the SHG intensity and this happens before a submonolayer reduction charge is passed. When the amount of β -oxide increases with holding time, an additional narrow SHG peak appears and, then both the peaks merge into a broad peak. The initial dip in the SHG response is suggested to be related to the interface between Au α -oxide and β -oxide which is likely to be linked to an order/disorder transition or populating and emptying of surface traps. As the β -oxide thickens with longer growth time, the appearance of two SHG peaks probably reflects the presence of an additional interface between Au₂O₃.H₂O and comparatively more hydrated Au₂O₃.2H₂O. When the Au β -oxide thickens further, it becomes porous with more interfacial water and the additional interface collapse, which results in the merger of two SHG peaks into a broad peak.

Chapter 5

Conclusion and future work

The research work reported in this thesis intended to study the electrochemical oxide formation at metal electrodes using nonlinear optical technique, second harmonic generation (SHG). The key findings of this work are outlined below.

5.1 SHG studies of oxide formation and reduction at Cu electrode

SHG intensity was recorded alongside cyclic voltammogram of Cu in weakly alkaline media. It has been shown that optical SHG can be used to follow the oxidation and reduction at Cu electrode in an especially constructed spectroelectrochemical cell. The monolayer and submonolayer sensitivity of the SHG technique helped investigate the oxide formation at Cu electrode and separate the SHG contribution from Cu₂O and CuO.

In the double layer region of the cyclic voltammogram, where no faradaic process is taking place, the change in SH response is due to the increased ionic adsorption or possibly due to an EFISH response from Cu itself. As Cu electrode oxidises, the formation of Cu₂O causes a resonant contribution to the SHG signal because of the band-gap of the semiconducting oxide. When the potential scan is extended further, the typical cyclic voltammograms show two anodic and two reduction currents peaks. The development of upper CuO layer produces an electric field induced second harmonic (EFISH) response. When the oxides layers are reduced, the EFISH mediated SHG intensity is continued until reduction charge starts to pass, with further reduction, the resonance contribution to the signal from underlying Cu₂O becomes dominant.

To verify these suggestion that there is a strong resonant contribution from the semiconducting Cu₂O to the SH intensity, SHG spectra experiments were carried out to see the wavelength dependence of the SHG response.

If we recall the Eq. (3.12)-

$$P(2\omega) = \left(\chi_r^{(2)} + \chi_{nr}^{(2)} \right) [E(\omega)]^{(2)} + \chi^{(3)} E(\omega)^2 E^{(dc)} \quad (5.1)$$

A non-resonant contribution through $\chi_{nr}^{(2)}$ to the SHG signal was noticed in the double layer region of Cu. A non resonant contribution is not dependent on the wavelength of the incident laser beam or on the applied dc-electric field.

A resonant contribution through $\chi_r^{(2)}$ was responsible for the fluctuation of SHG during the oxidation of Cu to the Cu(I) state to form Cu_2O and the reduction of it. This contribution is dependent on the wavelength of the incident laser beam. Contributions of this category may arise from population or depopulation of the surface states or a resonant contribution from the semiconducting Cu_2O due to the band gap of the semiconductor grown on the Cu surface.

When thicker oxide CuO was grown then the dominant contribution to the SHG signal alters from the resonant contribution, $(\chi_r^{(2)})[E(\omega)]^{(2)}$ from underlying Cu_2O to the EFISH contribution, $\chi^{(3)} E(\omega) E(\omega) E^{dc}$ from the top layer, which is CuO. The SHG data of the EFISH dominated potential regime are fitted into the following quadratic equation

$$I^{2\omega} = I_0^{2\omega} + (V - V_0)^2 \quad (5.2)$$

The accuracy of the fit confirms that the variation of SH intensity as a function of applied potential in the region, where CuO is present at the electrode surface, is dominated by $\chi^{(3)} E(\omega) E(\omega) E^{dc}$ term in equation.

The proposed resonant contribution to the SHG intensity from Cu_2O but EFISH mediated SH signal from CuO is verified by the wavelength dependence experiments which demonstrated that wavelength dependence at potentials close to the points where Cu_2O is present at the electrode surface but no wavelength dependence of SHG response at potentials where CuO is present at the electrode surface, especially near the EFISH minimum for CuO.

The sensitivity of the SHG response to the applied electric field may allow the determination of the *potential of zero charge* (pzc). The fact that we noticed the EFISH dominant SH intensity and a SH intensity minimum at V_o (in Fig. 3.18 and 3.19) when there is between 20-40 Å thick layer of semiconducting CuO formed at the electrode surface. Determination of PZC from the SH intensity will be similar to determination of the flat band potential (E_{FB}) of semiconducting CuO.

When applied in tandem with cyclic voltammetry, SHG can be used to detect the surface structure of the electrode, and oxidation and reduction of the surface oxide qualitatively. When complimented by STM and XPS, with submonolayer sensitivity SHG can also be a tool to investigate the oxide formation quantitatively and also the initial stage oxidation at Cu electrode.

5.2 SHG Studies of Au compact and hydrous oxide

The SHG studies of the oxidation of Au electrodes, and α - and β -oxide growth in acidic media have been carried out and reported here. When Au was initially oxidised to produce compact (or α -) oxide at Au surface, it causes a significant drop in SHG intensity even when only a fraction of oxide is grown. When thicker hydrous (or β -) oxide layers were grown at constant potentials on top of the α -oxide, the reduction of them are accompanied by remarkable narrow peaks in the SHG response that occur just before any reduction charge starts to pass. As the β -oxide layer gets thicker the initial narrow peak evolves into two peaks and then they merge into one broad peak. The SHG peaks are suggested to be an interfacial (between α - and β -oxide layers) order-disorder transition or due to the presence of surface traps.

In Au electrical double layer region of the cyclic voltammogram, ion adsorption may influence SHG through donation or acceptance of electron density altering the nonlinear susceptibility, $\chi^{(2)}$ and/or surface plasmon resonance is responsible for the SHG response. The initial surface oxidation of Au is suggested to inhibit the propagation of a d -electron surface plasmon resonance (SPR). Thus when SPR is inhibited because of the formation of the partial monolayer of oxide, the SHG signal falls sharply. SHG shows promise as surface probe for sub-monolayer adsorption processes and also for chemical reactions at the surface which may affect the propagation of the surface plasmon resonance associated with d -electrons.

Just as it was in the case of thicker Cu oxide (CuO) from where we have seen EFISH response, there could have been an assumption that similar EFISH mediated SHG response might be seen when Au β -oxide was formed. But the results of SHG response show that was not the case. It is quite well known for semiconductors that when the potential (and hence the electric field across the semiconductor) is varied, semiconductors can have an EFISH contribution to the SHG. But oxygen evolution at the growth potential of β -oxide prevents studying the formation of Au_2O_3 and look at the SHG response. Only reduction of Au_2O_3 could be studied by SHG. Therefore it is hard to establish any definitive evidence for an EFISH response from Au β -oxide.

Therefore, an alternative explanation for the SHG response from Au_2O_3 was suggested. One of the possible reasons for the decrease in SHG that occurs when β -oxide is reduced is that a phase change may take place at the interface between α -oxide and β -oxide. The interfacial species may go through ordered, disordered and then reordered cycles which then could be responsible for the observed SHG phenomenon. It is also possible that a second order/disorder transition takes place just before the more hydrated Au β -oxide, $\text{Au}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ starts to form on top of the initial less hydrated Au β -oxide, $\text{Au}_2\text{O}_3 \cdot \text{H}_2\text{O}$. This second order/disorder transition could then be responsible for the appearance of a second SHG peak.

In these studies SHG is shown to be a sensitive probe for the study of oxide formation at metal electrodes. It is clear that submonolayer sensitivity of SHG technique is achieved. If other methods, such as, SIMS depth profiling or XPS are combined with SHG, it can be potential technique for the quantitative measurements of oxide thickness.

5.3 Future work

5.3.1 Apply SHG to investigate the onset of oxidation

There have been several reports on the investigation of the initial oxidation of Cu using Scanning Tunnelling Microscopy (STM) in ultra high vacuum (UHV) [129, 142]. Instead of using UHV where all the non-chemisorbed species may evaporate, with its submonolayer sensitivity, *in situ* SHG techniques in room temperature may have advantage over the other investigative techniques. Application of SHG technique to the studies of initial oxidation on metal such as Cu, Au or Pt may play a key role in a broad range of applications including catalysis, corrosion and corrosion protection, and fuel cells.

If more time was available, the research reported in this thesis could be extended to the following areas-

5.3.2 SHG and electrochemical studies on Cu in acidic and alkaline media

In order to understand a more complete picture of the oxide formation and reduction at metal electrode electrochemical studies and SHG studies can be extended to the other weakly acidic and basic media. Cu electrode was studied only in weakly alkaline media. Cu electrochemistry differs significantly with the change of pH values of the solution. If we recall the Pourbaix diagrams illustrated in Fig. 3.3, we see that in weakly alkaline media Cu has got immunity between -2.0 and -0.2 V, and passivation regime above the potential of -0.2 V vs SHE and exposed to corrosion in the electrolyte solution of low and very high pH.

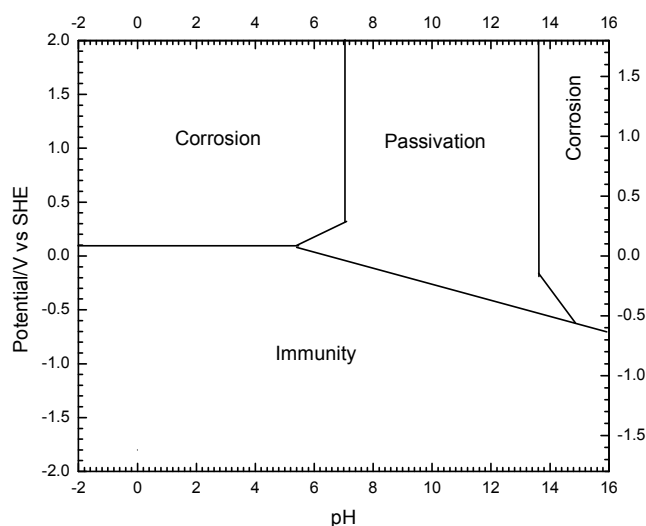


Figure 5.1 Simplified Pourbaix diagram of Cu in H₂O showing the corrosion, passivation and immunity domains of potential and pH [178].

In the modified Pourbaix diagram in Fig. 5.1 above, corrosive, passivation and immunity domains of Cu in terms of potential and pH are shown. Researchers in corrosion science have been using nonlinear optical techniques to study corrosion at metal surfaces [213]. With inherent surface sensitivity, second harmonic generation (SHG) is suitable to study the incipient oxidation and corrosion in a non-invasive way [214]. It would be interesting to perform the spatial mapping of the SHG signals on Cu electrode exposed to atmospheric condition, e.g., humidity, temperature etc., or to see how SHG response changes when Cu corrodes in the pH regime below 7 and above 13. With submonolayer sensitivity, SHG can be a suitable technique to study corrosion at Cu electrode. The application of SHG technique to the research of corrosion could easily be extended in tandem with the findings of our present work.

5.3.3 SHG and mechanistic studies on Cu and Au electrodes

Simultaneous SHG and cyclic voltammetry experiments were carried out in this research. This could be extended to the kinetic and mechanistic studies of Cu or Au electrode. Step potential experiments, for example chronoamperometry experiments in particular could be carried out in conjunction with SHG experiments. In potential step experiments, the potential of the working electrode is changed instantaneously then current-time response or potential transients under open circuit condition recorded. Different oxide of Cu can be formed at the electrode surface at a preset potential then the stability of the oxide can be investigated at another potential by analysing current or potential transients and SHG response.

5.3.4 SHG studies on deposited Cu or Au films on Si substrate

Another way this work can be extended is to deposit Cu or Au electrochemically or by sputtering on Si substrate of various thickness and study the simultaneous cyclic voltammetry and SHG response. Both substrate material, Si, and the sputtered layer of Cu and Au, and their oxide all show SHG response. In addition, Si and CuO also show electric field induced SHG (EFISH) [3, 4]. Controlling the thickness of the Cu and Au deposit on the Si substrate, it can be possible to separate the SHG contribution of the substrate from the contribution of the deposited Cu or Au thin films.

References

- [1] G.L. Richmond in: A.J. Bard (ed.), *Electroanalytical Chemistry*, vol. 17, Marcel Dekker Inc., 1991, p.87.
- [2] B. Pettinger, J. Lipkowski, S. Mirwald, A. Friedrich, *J. Electroanal. Chem.* 329 (1992) 289.
- [3] S.M.A. Baten, A.G. Taylor, C.P. Wilde, *Electrochem. Commun.* 9 (2007) 2393.
- [4] P. Hays, A.G. Taylor, J.A. Levitt, C.P. Wilde, *Electrochem. Commun.* 5 (2003) 883.
- [5] M.J. Dignam, D.B. Gibbs, *Can. J. Chem.* 48 (1970) 1242.
- [6] D.W. Shoesmith, T.E. Rummery, D. Owen, W. Lee, *J. Electrochem. Soc.* 123 (1976) 790.
- [7] S. Fletcher, R.G. Barradas, J.D. Porter, *J. Electrochem Soc.* 125 (1978) 1960.
- [8] H.-H. Strehblow, B. Titze, *Electrochim. Acta* 25 (1980) 839.
- [9] D.W. Shoesmith, S. Sunder, M.G. Baily, G.J. Wallace, F.W. Stanchell, *J. Electroanal. Chem.* 143 (1983) 153.
- [10] L.M. Abrantes, L.M. Castillo, C. Norman, L.M. Peter, *J. Electroanal. Chem.* 163 (1984) 209.
- [11] M.R.G. de Chialvo, J.O. Zerbino, S.L. Marchiano, A.J. Arvia, *J. Appl. Electrochem.* 16 (1986) 517.
- [12] U. Collisi, H.-H. Strehblow, *J. Electroanal. Chem.* 284 (1990) 385.
- [13] M.P. Sanchez, M. Barrera, S. Gonzalez, R.M. Souto, R.C. Salvarezza, A.J. Arvia, *Electrochim. Acta* 35 (1990) 1337.
- [14] M.P. Sanchez, R.M. Souto, M. Barrera, S. Gonzalez, R.C. Salvarezza, A.J. Arvia, *Electrochim. Acta* 38 (1993) 703.
- [15] G.M. Brisard, J.D. Rudnicki, F. McLarnon, E.J. Cairns, *Electrochim. Acta* 40 (1995) 859.
- [16] V. Maurice, H.-H. Strehblow, P. Murcus, *J. Electrochem. Soc.* 146 (1999) 524.
- [17] H.-H. Strehblow, V. Maurice, P. Marcus, *Electrochim. Acta* 46 (2001) 3755.
- [18] A. Damjanovic, A. Dey, J.O'M. Bockris, *J. Electrochem. Soc.* 113 (1966) 739.
- [19] H. Angerstein-Kozłowska, B.E. Conway, K. Tellefsen, B. Barnett, *Electrochim. Acta* 34 (1989) 1045.
- [20] L.D. Burke, J.F.O' Sullivan, *J. Electroanal. Chem.* 285 (1990) 195.
- [21] L.D. Burke, V.J. Cunnane, B.H. Lee, *J. Electrochem. Soc.* 139 (1992) 399.
- [22] B.E. Conway, *Prog. Surf.Sci.* 49 (1995) 331.
- [23] G. Tremiliosi-Filho, L.H. Dall'Antonia, G. Jerkiewicz, *J. Electroanal. Chem.* 422 (1997) 149.
- [24] L.D. Burke, P.F. Nugent, *Gold Bull.* 31 (1998) 39.
- [25] S.J. Xia, V.I. Birss, *Electrochim. Acta* 44 (1998) 467.
- [26] G. Jerkiewicz, in: A. Wieckowski, Editor, *Interfacial Electrochemistry*, Marcel Dekker, New York 1999, p. 559-576 (Chapter 32).
- [27] S.J. Xia, V.I. Birss, *Electrochim. Acta*, 45 (2000) 3659.
- [28] S.J. Xia, V.I. Birss, *J. Electroanal. Chem.* 500 (2001) 562.
- [29] L.H. Dall'Antonia, G. Tremiliosi-Filho, G. Jerkiewicz, *J. Electroanal. Chem.* 502 (2001) 72.
- [30] M. Tian, W.G. Pell, B.E. Conway, *Electrochim. Acta*, 48 (2003) 2675.

- [31] G. Tremiliosi-Filho, L.H. Dall'Antonia, G. Jerkiewicz, *J. Electroanal. Chem.* 578 (2005) 1.
- [32] S.M.A. Baten, A.G. Taylor, C.P. Wilde, *Electrochim. Acta*, 53 (2008) 6829.
- [33] A.J. Bard, L.R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, John Wiley & Sons, 2nd Ed. 2000, p. 9-13.
- [34] R. Greef, R. Peat, L.M. Peter, D. Pletcher J. Robinson, *Instrumental Methods in Electrochemistry*, Southampton Electrochemistry Group, Ellis Horwood Limited, Chichester, UK, 1990, p.19.
- [35] H. Helmholtz, *Pogg. Ann.* LXXXIX 89 (1853) 211.
- [36] H-J. Butt, K. Graf, M. Kappl, *Physics and Chemistry of Interfaces*, Wiley-Vch GmbH & Co. KGaA, Weinheim 2003, p. 42-53.
- [37] G. Gouy, *J. Phys. (Paris)* 9 (1910) 457.
- [38] D.L. Chapman, *Philos. Mag.* 25 (1913) 475.
- [39] G. Gouy, *Ann. Phys.* 7 (1917) 129.
- [40] P. Debye, E. Hückel, *Physikalische Zeitschrift* 24 (1923) 185.
- [41] J. O'M. Bockris, A.K.N. Reddy, M. Gamboa-Aldeco, *Modern Electrochemistry 2A Fundamentals of Electrode Processes*, London 2000, p. 876-886.
- [42] O. Stern, *Zeitschrift für Elektrochemie*, 30 (1924) 508.
- [43] D.C. Grahame, *Chem. Rev.* 41 (1947) 441.
- [44] R. Greef, R. Peat, L.M. Peter, D. Pletcher J. Robinson, *Instrumental Methods in Electrochemistry*, Southampton Electrochemistry Group, Ellis Horwood Limited, Chichester, UK, 1990, p.152.
- [45] R. Greef, R. Peat, L.M. Peter, D. Pletcher J. Robinson, *Instrumental Methods in Electrochemistry*, Southampton Electrochemistry Group, Ellis Horwood Limited, Chichester, UK, 1990, p.161-166.
- [46] J. Huang, PhD thesis: Characterization of Electrochemical Interfaces by Infrared Spectroscopy, Submitted to the Virginia Polytechnic Institute and State University, USA, 1996.
- [47] H-J. Butt, K. Graf, M. Kappl, *Physics and Chemistry of Interfaces*, Wiley-Vch GmbH & Co. KGaA, Weinheim 2003, p. 72.
- [48] H. Ibach, *Physics of Surfaces and Interfaces*, Springer, 2006, p. 121-124.
- [49] G. Lippmann, *Ann. Chim. Phys. (Paris)* 5 (1875) 494.
- [50] A.J. Bard, L.R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, John Wiley & Sons, 2nd Ed. 2000, p. 537-538.
- [51] J. O'M. Bockris, A.K.N. Reddy, M. Gamboa-Aldeco, *Modern Electrochemistry 2A Fundamentals of Electrode Processes*, London 2000, p. 854-862.
- [52] H. Ibach, *Physics of Surfaces and Interfaces*, Springer, 2006, p. 162.
- [53] R. Greef, R. Peat, L.M. Peter, D. Pletcher J. Robinson, *Instrumental Methods in Electrochemistry*, Southampton Electrochemistry Group, Ellis Horwood Limited, Chichester, UK, 1990, p. 178-188.
- [54] A.J. Bard, L.R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, John Wiley & Sons, 2nd Ed. 2000, p. 31.

- [55] A.J. Bard, L.R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, John Wiley & Sons, 2nd Ed. 2000, p. 231.
- [56] R.S. Nicholson, I. Shain, *Anal. Chem.* 36 (1964) 706.
- [57] J. O'M. Bockris, A.K.N. Reddy, M. Gamboa-Aldeco, *Modern Electrochemistry 2A Fundamentals of Electrodeics*, London 2000, p. 969.
- [58] J. Wang, *Analytical Electrochemistry*, 2nd Ed. Wiley-Vch, 2000, p. 36-37.
- [59] R. Greef, R. Peat, L.M. Peter, D. Pletcher J. Robinson, *Instrumental Methods in Electrochemistry*, Southampton Electrochemistry Group, Ellis Horwood Limited, Chichester, UK, 1990, p. 206-207.
- [60] A.J. Bard, L.R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, John Wiley & Sons, 2nd Ed. 2000, p. 591.
- [61] R. Greef, R. Peat, L.M. Peter, D. Pletcher J. Robinson, *Instrumental Methods in Electrochemistry*, Southampton Electrochemistry Group, Ellis Horwood Limited, Chichester, UK, 1990, p. 357-363.
- [62] A.J. Bard, L.R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, John Wiley & Sons, 2nd Ed. 2000, p. 50.
- [63] A.J. Bard, L.R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, John Wiley & Sons, 2nd Ed. 2000, p. 808.
- [64] H. Kahlert, Reference Electrode, Chapter III.2 in *Electroanalytical Methods: Guide to Experiments and Application*, Edited by F. Scholz, Springer 2005, p. 264.
- [65] J.F. McGilp, *J. Phys.: Condens. Matter* 2 (1990) 7985.
- [66] A. Ichimiya, P.I. Cohen, *Reflection High Energy Electron Diffraction*, Cambridge University Press, 2004.
- [67] A.J. Bard, L.R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, John Wiley & Sons, 2nd Ed. 2000, p. 687.
- [68] R.M.A. Azzam, N.M. Bashara, *Ellipsometry and Polarized Light*, North Holland, Amsterdam, 1997, p. 288.
- [69] J. Ijima, J. Lim, S. Hong, S. Suzuki, K. Kimura and M. Isshiki, *Appl. Surf. Sci.* 253 (2006) 2825.
- [70] H. Nishizawa, Y. Tateyama, T. Saitoh, *Thin Solid Films* 455-456 (2004) 491.
- [71] G. Papadimitropoulos, N. Vourdas, V.Em. Vamvakas, D. Davazoglou, *Thin Solid Films* 515 (2006) 2428.
- [72] C. Pickering, *Surf. Interf. Anal.* 31 (2001) 927.
- [73] K. Vedam, *Thin Solid Films* 313-314 (1998) 1.
- [74] P. Weightman, D.S. Martin, R.J. Cole, T. Farrell, *Rep. Prog. Phys.* 68 (2005) 1251.
- [75] V.L. Shannon, D.A. Koos, S.A. Kellar, P. Huifang, G.L. Richmond, *J. Phys. Chem.* 93 (1989) 6434.
- [76] C.I. Smith, A.J. Maunder, C.A. Lucas, R.J. Nichols, P. Weightman, *J. Electrochem. Soc.* 150 (2003) E233.
- [77] R.W. Boyd, *Nonlinear Optics*, 2nd Ed., Academic Press, 2003, p. 1.
- [78] Y.R. Shen, *The Principles of Nonlinear Optics*, Wiley-Interscience, 1984, p. 5.

- [79] A. Yariv, Optical Electronics in Modern Communications, 5th Ed. Oxford University Press, 1997, p. 275.
- [80] M. Goeppert-Mayer, Ann. Phys. 9, (1931) 273.
- [81] P.A. Franken, A.E. Hill, C.W. Peters, G. Weinreich, Phys. Rev. Lett. 7 (1961) 118.
- [82] R.W. Terhune, P.D. Maker, C.M. Savage, Phys. Rev. Lett. 8 (1962) 404.
- [83] M. Bass, P.A. Franken, A.E. Hill, C.W. Peters, G. Weinreich, Phys. Rev. Lett. 8 (1962) 18.
- [84] K.E. Niebuhr, Appl. Phys. Lett. 2 (1963) 136.
- [85] A.W. Smith, N. Braslou, J. Appl. Phys. 34 (1963) 2105.
- [86] J.A. Armstrong, N. Bloembergen J. Ducuing, P.S. Pershan, Phys. Rev. 127 (1962) 1918.
- [87] N. Bloembergen, Nonlinear Optics, 4 ed., World Scientific Publishing Co. Pte. Ltd., London 1996.
- [88] Y.R. Shen, The Principles of Nonlinear Optics, Wiley-Interscience, 1984.
- [89] A. Yariv, Optical Electronics in Modern Communications, 5th Ed. Oxford University Press, 1997.
- [90] R.W. Boyd, Nonlinear Optics, 2nd Ed., Academic Press, 2003.
- [91] A. Yariv, Optical Electronics in Modern Communications, 5th Ed. Oxford University Press, 1997, p. 280.
- [92] J. Reif, J.C. Zink, C. –M. Schneider, J. Kirschner, Phys. Rev. Lett. 67 (1991) 2878.
- [93] M.B. Raschke, Y.R. Shen, Curr. Opin.Solid State Mater.Sci. 8 (2004) 343.
- [94] H.W.K. Tom, T.F. Heinz, Y.R. Shen, Phys. Rev. Lett. 51 (1983) 1983.
- [95] P. Guyot-Sionnest, Y.R. Shen, Phys. Rev. B 38 (1988) 7985.
- [96] R.W.J. Hollering, M. Barmentlo, Opt. Commun. 88 (1992) 141.
- [97] H. Shi, R. Asahi, C. Stampfl, Phys Rev. B 75 (2007) 205125.
- [98] M.C. Downer, B.S. Mendoza, V.I. Gavrilenko, Surf. Interface Anal. 31 (2001) 966.
- [99] G. Lupke, Surf. Sci. Rep. 35 (1999) 75.
- [100] V. Mizrahi, J.E. Sipe, J. Opt. Soc. Am. B-Opt. Phys. 5 (1988) 660.
- [101] M.A. Verheijen, C.W. van Hasselt, Th. Rasing, Surf. Sci. 251-252 (1991) 467.
- [102] O.A. Aktsipetrov, A.A. Fedyanin, M.C. Downer, Notions and Perspective in Nonlinear Optics, Edited by O. Keller, Series in Nonlinear Optics, Vol. 3, World Scientific, Singapore, 1996, p. 301-339.
- [103] T.F. Heinz, in Nonlinear Surface Electromagnetic Phenomena, Edited by H.-E. Ponath, G.I. Stegeman, Modern Problems in Condensed Matter Science 29, Elsevier Science, Amsterdam, 1991, Chap. 5.
- [104] P. Guyot-Sionnest, A. Tadjeddine, J. Chem Phys. 92 (1990) 734.
- [105] J.R. Sambles, G.W. Bradberry, F. Yang, Contemporary Phys. 32 (1991) 173.
- [106] F. Yang, G.W. Bradberry, J.R. Sambles, Opt. Commun. 74 (1989) 1.
- [107] A. Otto, Surf. Sci. Lett. 101 (1980) A433.
- [108] A. Otto, Surf. Sci. Lett. 101 (1980) A433.
- [109] N. Bloembergen, P.S. Pershan, Phys. Rev. 128 (1962) 606.
- [110] C.H. Lee, R.K. Chang, N. Bloembergen, Phys. Rev. Letts. 18 (1967) 167.
- [111] H.J. Simon, D.E. Mitchell J.G. Watson, Phys. Rev. Lett. 33 (1974) 1531.

- [112] J.E. Sipe, D.J. Moss, H.M. van Driel, *Phys. Rev. B* 35 (1987) 1129.
- [113] Y.R. Shen, *Ann. Rev. Phys. Chem.* 40 (1989) 327.
- [114] Y.R. Shen, *Nature* 337 (1989) 519.
- [115] F. Chao, M. Costa, A. Tadjeddine, *J. Electroanal. Chem.* 329 (1992) 313.
- [116] J.F. McGilp, *Phys. Stat. Sol. A* 175 (1999) 153.
- [117] C.T. Williams, D.A. Beattie, *Surf. Sci.* 500 (2002) 545.
- [118] L. Arnaud, G. Tartavel, T. Berger, D. Mariolle, Y. Gobil, I. Touet, *Microelectron. Reliab.* 40 (2000) 77.
- [119] T.G. Koetter, H. Wendrock, H. Schuehrer, C. Wenzel, K. Wentzig, *Microelectron. Reliab.* 40 (2000) 1295.
- [120] M. O'Reilly, X. Jiang, J.T. Beechinor, S. Lynch, C. NiDheasuna, J.C. Patterson, G.M. Crean, *Appl. Surf. Sci.* 91 (1995) 152.
- [121] T.J. Richardson, J.L. Slack, M.D. Rubin, *Electrochim. Acta* 46 (2001) 2281.
- [122] E. Mishina, K. Nagai, D. Barsky, S. Nakabayashi, *Phys. Chem. Chem. Phys.* 4 (2002) 127.
- [123] A. Zhou, D. He, N. Xie, Q. Xie, L. Nie, S. Yao, *Electrochim. Acta* 45 (2000) 3950.
- [124] S.B. Ribotta, M.E. Folquer, L.M. Gassa, *J. Arg. Chem. Soc.* 91 (2003) 55.
- [125] M. Metikos-Hukovic, R. Babic, I. Paic, *J. Appl. Electrochem.* 30 (2000) 617.
- [126] Y. Feng, K. -S. Siow, W. -K. Teo, K. -L. Tan, A. -K. Hsieh, *Corrosion* 53 (1997) 389.
- [127] H.Y.H. Chan, C.G. Takoudis, M.J. Weaver, *J. Phys. Chem. B* 103 (1999) 357.
- [128] C.A. Melendres, G.A. Bowmaker, J.M. Leger, B.J. Beden, *J. Electroanal. Chem.* 449 (1998) 215.
- [129] V. Maurice, H.-H. Strehblow, P. Marcus, *Surf. Sci.* 458 (2000) 185.
- [130] N. Ikemiya, T. Kubo, S. Hara, *Surf. Sci.* 323 (1995) 81.
- [131] E. Muller, *Z. Elektrochem.* 13 (1907) 133.
- [132] R.D. Armstrong, G.M. Bulman, *J. Electroanal. Chem.* 25 (1970) 121.
- [133] R.D. Armstrong, *Corros. Sci.* 11 (1971) 693.
- [134] M. Fleischmann, D.J. Lax, H.R. Thirsk, *Trans. Faraday Soc.* 64 (1968) 3128.
- [135] J. Ambrose, R.G. Barradas, D.W. Shoesmith, *Electroanal. Chem. Interf. Electrochem.* 47 (1973) 65.
- [136] A. Lukomska, J. Sobkowski, *J. Electroanal. Chem.* 567 (2004) 95.
- [137] L.Y. Yegorov, I.M. Novoselskij, *Elektrokhimiya* 6 (1970) 521.
- [138] I.M. Novoselskij, N.I. Kanievskij, L.Y. Yegorov, *Elektrokhimiya* 8 (1972) 1480.
- [139] S. Trasatti, E.J. Lust, in: R.E. White, J.O.M. Bockris, B.E. Conway (Eds.), *Modern Aspects of Electrochemistry*, vol. 33, Plenum Press, New York, 1999.
- [140] L.E.A. Berlouis, D.A. Mamman, I.G. Azpuru, *Surf. Sci.* 408 (1998) 173.
- [141] J. Kunze, V. Maurice, L.R. Klein, H.-H. Strehblow, P. Marcus, *Corros. Sci.* 46 (2004) 245.
- [142] H. -H. Strehblow, V. Maurice, P. Marcus, *Electrochim. Acta* (2001) 3755.
- [143] D.J. Campbell, R.M. Corn, *J. Phys. Chem.* 91 (1987) 5668.
- [144] D.J. Campbell, R.M. Corn, *J. Phys. Chem.* 92 (1988) 5796.
- [145] H.W.K. Tom, T.F. Heinz, Y.R. Shen, *Laser Chem.* 3 (1983) 279.
- [146] R.A. Bradley, K.A. Friedrich, E.K.L. Wong, G.L. Richmond, *J. Electroanal. Chem.* 309 (1991) 319.

- [147] D.A. Koos, V.L. Shannon, G.L. Richmond, *Phys. Rev. B* 47 (1993) 4730.
- [148] T.D. Hewitt, D. Roy, *Chem. Phys. Lett.* 181 (1991) 407.
- [149] G. Nagy, D. Roy, *Langmuir* 9 (1993) 1868.
- [150] M.A. Lovell, M.J. Walters, D. Roy, *Electrochim. Acta*, 43 (1998) 2101.
- [151] M.J. Bennahmias, S. Lakkaraju, B.M. Stone, K. Ashley, *J. Electroanal. Chem.* 280 (1990) 429.
- [152] C. Schwab, G. Meister, J. Woll, A. Gerlach, A. Goldman, *Surf. Sci.* 457 (2000) 273.
- [153] L.D. Burke, P.F. Nugent, *Gold Bulletin* 30 (1997) 43.
- [154] L.D. Burke, P.F. Nugent, *J. Electroanal. Chem.* 444 (1998) 19.
- [155] L.D. Burke, M.E.G. Lyons, in: R.E. White, J. O'M. Bockris, B.E. Conway (Eds.) *Modern Aspects of Electrochemistry*, vol. 18, Plenum Press, New York, 1986, p. 169.
- [156] J.S. Gordon, D.C. Johnson, *J. Electroanal. Chem.* 365 (1994) 267.
- [157] S. Bruckenstein, M. Shay, *J. Electroanal. Chem.* 188 (1985) 131.
- [158] W. Stockel, R. Schumacher, *Ber. Bunsenges. Phys. Chem.* 93 (1989) 600.
- [159] R.S. Sirohi, M.A. Genshaw, *J. Electrochem Soc.* 116 (1969) 910.
- [160] J. Horkans, B.D. Cahan, E. Yeager, *Surf. Sci.* 46 (1974) 1.
- [161] M.E. Vela, J.O. Zerbino, A.J. Arriva, *Thin Solid Films* 233 (1993) 82.
- [162] L.D. Burke, *Electrochim. Acta* 39 (1994) 1841.
- [163] L.D. Burke, P.F. Nugent, *Electrochim. Acta* 42 (1997) 399.
- [164] D. Krause, C.W. Teplin, C.T. Rogers, *J. Appl. Phys.* 96 (2004) 3626.
- [165] T. Kitahara, H. Tanaka, Y. Nishioka, G. Mizutani, *Phys. Rev. B* 64 (2001) 193412.
- [166] T. Awatani, I. Yagi, H. Noguchi, K. Uosaki, *J. Electroanal. Chem.* 524-525 (2002) 184.
- [167] D.J. Campbell, M.L. Lynch, R.M. Corn, *Langmuir* 6 (1990) 1656.
- [168] R. Antoine, P.F. Brevet, H.H. Girault, D. Bethell, D.J. Schiffrin, *Chem. Commun.* (1997) 1901.
- [169] M.L. Sandrock, C.D. Pibel, F.M. Geiger, C.A. Foss Jr, *J. Phys. Chem. B* 103 (1999) 2668.
- [170] Hamamatsu Photonics UK Limited Publications, Photon Counting Head, H8259 Series, Feb 2008.
- [171] N. W. Ashcroft and N. D. Mermin, *Solid State Physics*, Holt, Rinehart, and Winston, New York, 1976.
- [172] M.E. Straumanis, L.S. Yu, *Acta Cryst. A* 25 (1969) 676.
- [173] J.M. Steigerwald, S.P. Murarka, R.J. Gutmann, *Chemical Mechanical Planarization of Microelectronics Materials*, Wiley, New York (1997).
- [174] M. Anik, *J. Appl. Electrochem.* 35 (2005) 1.
- [175] J. Ghijsen, L.H. Tjeng, J. van Elp, H. Eskes, J. Westerink, G.A. Sawatzky, M.T. Czyzyk, *Phys. Rev. B* 38 (1988) 11322.
- [176] L.M. Gassa, A.M. Castro-Luna, R.M. Torres-Sanchez, J.O. Zerbino, *Portugaliae Electrochim. Acta* 22 (2004) 81.
- [177] A.H. Moreira, A.V. Benedetti, P.L. Cabot, P.T.A. Sumodjo, *Electrochim. Acta* 38 (1993) 981.
- [178] M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, NACE, TX (1974), p. 384.
- [179] I. T. E. Fonseca, A.C.S. Marin, A.C. Sa, *Electrochim. Acta* 37 (1992) 2541.

- [180] Z. Ahmad, Principles of Corrosion Engineering and Corrosion Control, Butterworth-Heinemann, p. Oxford, Great Britain, 2006.
- [181] H. Liang, J-M. Martin, R. Lee, J. Electron. Mat. 30 (2001) 391.
- [182] E. Ruiz, S. Alvarez, P. Alemany, R. A. Evarestov, Phys. Rev. B 56 (1997) 7189.
- [183] F. King, C. D. Litke, Y. Tang, J. ElectroanalChem 384 (1995) 105.
- [184] S. Asbrink, A. Waskowska, J. Phys.: Condens. Matter.3 (1991) 8173.
- [185] CRC Handbook of Chemistry and Physics, 89th edition, edited by D.R. Lide, 2008-2009, p. 8-39.
- [186] F. Wiame, V. Maurice, P. Marcus, Surf.Sci. 601 (2007) 1193.
- [187] G.T. Burshtein, R.C. Newman, J. Electrochem.Soc. 128 (1981) 2270.
- [188] H.S. Choi, Y. Kang, H. Lee, C. Lee, Curr.Appl. Phys. 7 (2007) 522.
- [189] A. Boltasseva, T. Nikolajsen, K. Leosson, K. Kjaer, M.S. Larsen, S.I. Bozhevolnyi, 23 (2005) 413.
- [190] A.J.G. Strandjord, S. Popelar, C. Jauernig, Microelectronics Reliability 42 (2002) 265.
- [191] R. Bhattacharya, P. Mukherjee, Advanced Drug Delivery Reviews 60 (2008) 1289.
- [192] W.F. Kean, I.R.L. Kean, Inflammopharmacology 16 (2008) 112.
- [193] S. Wang, N. Kristian, S. Jiang, X. Wang, Electrochem.Comm.10 (2008) 961.
- [194] A. Jones, R. Grey, WO Patent 02/064500 A2 (2002), Arco Chemical Technology.
- [195] V. Sharma, K. Park, M. Srinivasarao, Mat. Sci. Eng. Rep. 65 (2009) 1.
- [196] W.H. Lai, Y.H. Su, L.G. Teoh, M.H. Hon, J. Photochem.Photobio. A: Chem. 195 (2008) 307.
- [197] C.W. Tan, A.R. Daud, M.A. Yarmo, Appl. Surf.Sci. 191 (2002) 67.
- [198] L. Tan, Q. Xie, X. Jia, M. Guo, Y. Zhang, H. Tang, S. Yao, Biosensors Bioelectron. 24 (2009) 1603.
- [199] G.N.V. Huong, C. Hinnen, J. Lecoeur, J. Electroanal.Chem. 106 (1980) 185.
- [200] A.M. Michri, A.G. Pshenichnikov, R. Kh. Burshtein, elektrokhiya 8 (1972) 364.
- [201] R. Woods: Electroanalytical Chemistry Vol. 9 edit. by A.J. Bard, Mercel Dekker, New York, 1997, p. 1.
- [202] P.G. Jones, H. Rumpel, E. Schwarzmman, G.M. Sheldrick, ActaCrystallographica B 35 (1975) 1435.
- [203] H. Angerste-Kozlowska, in: E. Yeager, J. O'M. Bockris, B. E. Conway (Eds.), Comprehensive Treatise of Electrochemistry, vol. 9, Plenum Press, New York, 1984 (Chapter 9).
- [204] B. E. Conway, W. B. A. Sharp, H. Angerstein-Kozlowska, E. E. Criddle, Anal. Chem 45 (1973) 1321.
- [205] J. M. Brockman, B. P. Nelson, R. M. Corn, Ann. Rev. Phys. Chem. 51 (2000) 41.
- [206] K. A. Willets, R. P. Van Duyne, Ann. Rev. Phys. Chem. 58 (2007) 267.
- [207] A.S. Barker, Phys. Rev. B 8 (1973) 5418.
- [208] N. Bloembergen, R.K. Chang. S.S. Jha, C.H. Lee. Phys Rev. 174 (1968) 813 (erratum: Phys. Rev. 178 (1969) 1528).
- [209] P. Simon, E. Gervais, E. Courtens, Phys. Rev. B 37 (1988) 1969.
- [210] M. Shamir, J.G. Mihaychuk, H.M. Van Driel, J. Vac. Sci. Technol.A 15 (1997) 2081.
- [211] J. I. Dadap, P. T. Wilson, M. H. Anderson, M. C. Downer, M. terBeek, Opt. Lett.22 (1997) 901.

- [212] S. A. Mitchell, S. Janz, J. A. Bardwell, Chem. Phys. Lett. 310 (1999) 361.
- [213] J. Hedberg, J. Henriquez, S. Baldelli, C.M. Johnson, C. Leygraf, J. Phys. Chem. 113 (2009) 2088.
- [214] J. Ying, F. Liu, P.P. Ho, R.R. Alfano, Opt. Lett. 25 (2000) 1189.

Publications

1. A second harmonic generation study of the oxidation of copper electrodes,
Shah M. A. Baten, Alan G. Taylor, C. Paul Wilde,
Electrochemistry Communications 9 (2007) 2393-2396.
2. Second Harmonic Generation studies of the oxidation of metal electrodes: Compact and hydrous oxide growth at gold electrodes in acid solution,
Shah M. A. Baten, Alan G. Taylor, C. Paul Wilde,
Electrochimica Acta 53 (2008) 6829-6834.

Conference paper

1. Shah M. A. Baten, C. Paul Wilde, Alan G. Taylor, Second Harmonic Generation (SHG) Studies of surface oxidation at electrode.
International Society of Electrochemistry Meeting, September 2007, Banff, Canada. (Presented by C. Paul Wilde).