

Inelastic electron tunnelling
spectroscopy
using nanoscale tunnel junctions

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Declaration

The work presented in this thesis entitled “ Inelastic electron tunnelling spectroscopy using nanoscale tunnel junctions ” conducted from January 2011 to December 2013. Other works which where reviewed from an external source has been appropriately referenced and acknowledged. No portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of Imperial College London or any other university or other institute of learning.

Yasaman Hamidizadeh

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Publications

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To my beloved husband, Behnam

Abstract

Inelastic Electron Tunnelling Spectroscopy (IETS) [1–5] provides a means to characterise the phonon spectrum of a molecule by measuring the phonon-assisted tunnelling current through a potential barrier impregnated with target molecules. Traditionally, this technique has used Metal - Insulator - Metal (MIM) junctions, and the molecules of interest are adsorbed on to the insulator during junction fabrication. At low applied voltage V , tunnelling through the barrier is elastic. However, inelastic tunnelling caused by electron interaction with vibrational states in the adsorbed molecules can create additional conduction channels, occurring when V reaches a value of $\frac{\hbar\omega}{e}$, where ω is a molecular vibrational mode. These lead to peaks in the d^2I/dV^2 vs. V characteristics for each additional channel, giving a spectrum of the molecular vibration modes. As energy separations in the vibrational spectrum are relatively small compared to the electronic spectrum, the full vibrational spectrum is measured only at $T < 30K$. However, it may be possible to measure part of the spectrum even at room temperature, raising the possibility of a molecular detector.

This project is concerned with fabricating nanoscale tunnel junctions based on Si nanowires (NWs) made by electron-beam lithography (EBL), for the purpose of IETS measurements, at $300K$. A Si / SiO₂ tunnel barrier / Al structure is used, where the Al NW crosses an oxidised Si NW. This allows the fabrication of tunnel junctions down to $50\text{ nm} \times 120\text{ nm}$ in area and tunnelling occurs across a 10 nm thick SiO₂ layer. The reduction in device dimensions to the nanoscale may increase the sensitivity of the device to molecules adsorbed on the tunnel junction. Furthermore, the use of Silicon on insulator (SOI) material allows modulation of the tunnel junction using the back gate formed by the SOI substrate, control

of the Fermi energy and electron concentration in the NW, and hence the IETS characteristics of the device. In principle, an IETS sensor may be possible using such a configuration.

In principle, a switchable IETS measurements are performed at $300K$ for ammonium hydroxide (NH_4OH), acetic acid (CH_3COOH), and propionic acid ($C_3H_6O_2$) molecules. The $I-V$, $dI/dV-V$, and d^2I/dV^2-V characteristics of the tunnel junction are measured before and after the adsorption of molecules on the junction using vapour treatment or immersion. Peaks can be observed in the d^2I/dV^2-V characteristics in all the cases following molecules adsorption. These peaks may be attributed to vibrational modes of $N-H$ and $C-H$ bonds.

Simulation of IETS characteristics modelled based on a combination of elastic, inelastic tunnelling and Schottky barriers at the Si / SiO₂ / Al interface in the device. A comparison has been made between the simulation results and experimental measurements which showed very good agreement. This device modelling can be used to predict experimental characteristics and allow thermal broadening of the IETS peaks to be investigated.

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Nomenclature

List of Abbreviations

IETS	Inelastic Electron Tunnelling Spectroscopy
MIM	Metal - Insulator - Metal
Si NWs	Silicon Nanowires
EBL	Electron-Beam Lithography
FET	Field Effect Transistor
ISFET	Ion-Sensitive Field-Effect Transistor
NT	Nanotube
CMOS	Complementary Metal-Oxide Semiconductor
STM	Scanning Tunnelling Microscope
SIM	Semiconductor - Insulator - Metal
SBs	Schottky Barriers
IR	Infrared
MeNC	Methyl Isocyanide
MMM	Metal - Molecule - Metal
BDT	Benzenedithiolate

MCBJ	Mechanically Controllable Break Junction
SATJs	Self-Assembling Tunnel Junctions
MTJs	Magnetic Tunnel Junctions
TO	Transverse Modes
LO	Longitudinal Modes
MMS	Metal - Molecule - Silicon
1-D	One Dimensional
WKB	Wentzel, Kramers and Brillouin method
VLS	Vapour Liquid Solid
MACE	Metal Assisted Chemical etching
SEM	Scanning Electron Microscope
SOI	Silicon - on - Insulator
IPA	Isopropyl Alcohol
PMMA	Poly Methyl Methacrylate
MIBK	Methyl Isobutyl Ketone
RIE	Reactive Ion Etching
ECP	Exposure Control Program

List of Symbols

V	Voltage
$\hbar$	Reduced Planck's constant
ω	Angular frequency
U	Potential energy of the barrier

E	Total energy of the particle
ν	Frequency
$g(\omega)$	Vibrational density of states
Φ_B	Potential barrier height
d	Width
$\Psi(x, t)$	Wave function at position x and time t
k	Wave vector
p	Momentum of the particle
m^*	Effective Mass
r	Reflected coefficient
a_i	Transmitted coefficient
$T(E)$	Transmission probability
R	Reflection coefficient
$E_{c,L}$	Conduction band energy of the left metal
$E_{c,R}$	Conduction band energy of the right metal
E_z	Perpendicular energy
E_t	Transverse energy
j_i	Incident current density
e	Elementary charge
$D(k)$	Density of states
$f_{L,R}$	Fermi-Dirac distribution function of left/right metal
$v(k_L)$	Velocity
$j_{L \rightarrow R}$	Tunnelling current density from left to right

$j_{R \rightarrow L}$	Tunnelling current density from right to left
$J_{elastic}$	Elastic tunnelling current density
$I_{elastic}$	Elastic current
U_{int}	Perturbing potential
U_z	Barrier potential
L	Length of the barrier
$I_{inelastic}$	Inelastic tunnelling current
S_v	Unit step
α	Molecular bond polarizability
k_B	Boltzmann constant
W	Line width
χ_s	Electron affinity in semiconductor
ε_s	Electric field
ε_{max}	Electric field on the interface of the metal and semiconductor
μ	Electron mobility
$j_{s \rightarrow m}$	Current density from semiconductor to metal
$G(E)$	Density of states of the semiconductor conduction band
ζ_s	Shift in Fermi level due to applied voltage
T	Temperature
E_F	Fermi energy
A^*	Richardson coefficient
R_t	Tunnel junction resistance
C	Capacitor

Chapter 1

Introduction

In recent years, there has been great interest in nanometre-scale chemical and biological sensors using Si nanowires (Si NWs) [6–9]. Semiconductor devices have been used to realise chemical and biological sensors since 1962 and in particular, the planar field effect transistor (FET) has been used as the basis of chemical and biological sensors [10]. In this regard, Seiyama *et al.* showed that the adsorption and desorption of gases on various semiconducting thin films surfaces can be monitored by direct change in the conductance. Planar FET technology can be configured to create such a device by using a solution and an ion-selective membrane for the gate electrode, creating the Ion-Sensitive Field-Effect Transistor (ISFET) [11]. Electron exchange occurs at the ion-selective membrane, inducing a potential at the gate as a function of the ion concentration in the solution, in turn controlling the FET channel.

The sensitivity of the ISFET can be improved by defining nanoscale FETs. Here, the binding of chemical or biological species to a nanowire (NW) or carbon nanotube (CNT) surface can

alter the local electrical characteristics by the depletion or accumulation of carriers within the “bulk” of the nanometre diameter structure (versus only the surface region of a planar device). Therefore, the sensitivity of the sensors is increased, such that even single-molecule detection becomes possible [6, 10]. Although carbon NT FETs have been used as gas sensors, the lack of flexible methods for the modification of NT surfaces, which are required to prepare interfaces selective for binding a wide range of chemical or biological species, may limit their development as nanosensors [6]. Si NWs based sensors can have specific advantages over other chemical and biological sensors [6, 12]. In contrast with other systems such as carbon NTs, Si NWs are compatible with complementary metal-oxide semiconductor (CMOS) technology and may be used to define high-performance MOSFETs, allowing direct large-scale integration of NW sensors [13].

In early works in this field, the use of Si NWs as a basis for nanoscale sensors was demonstrated by Lieber and Cui in 2001 [14]. Following their initial work on the growth of high quality Si NWs using CVD, Lieber and Cui fabricated Si NW-based sensors to detect different chemical and biological species down to single molecules and 10 pM sensitivity [6, 13, 14]. Since then, numerous other groups have investigated nanometre-scale chemical and biological sensors using Si NWs [13]. State-of-the-art Si NW-based chemical sensors may be classified into two types, based on their operating principles. These are conduction-detection sensors (Fig.1.1(a)) [6–9], and mass-detection sensors (Fig.1.1(b)) [15].

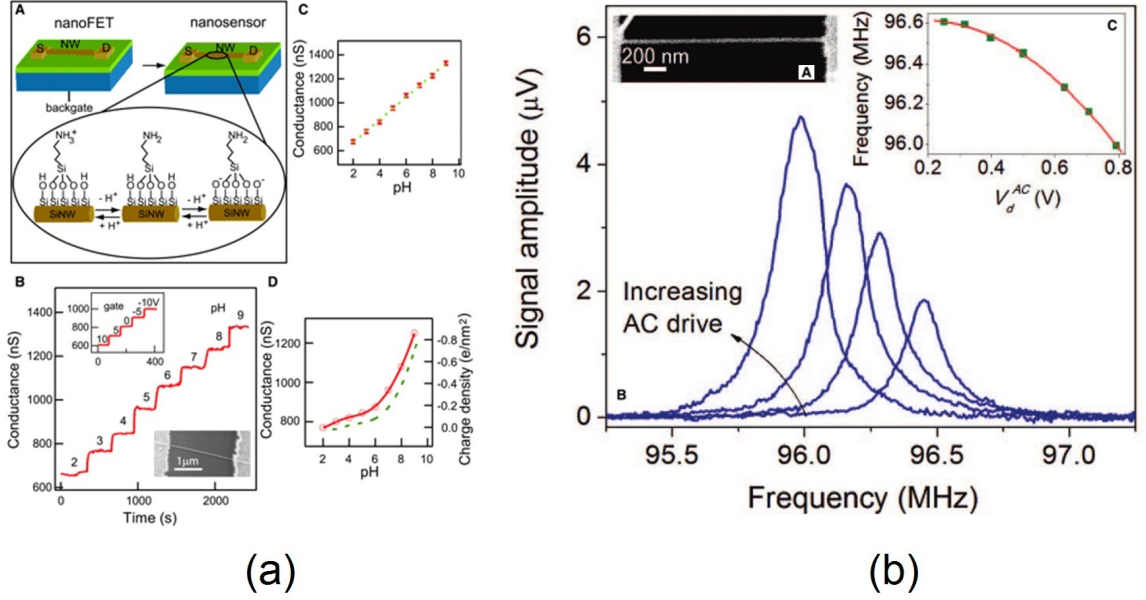


Figure 1.1: (a) Conduction-detection sensors [6–9] vs. (b) mass-detection sensors [15]: (a) Si NW pH sensor: (A) The schematic diagram of a NW FET converted into NW nanosensors; (B) Conductance of an APTES-modified Si NW vs. time; (C) Conductance vs. pH; (D) Conductance of unmodified Si NW vs. pH [6]. (b) (A) SEM image of a 40 nm thick and 1.8 μm long Si NW and a DC resistance of 80 kΩ; (B) The DC voltage is fixed at $V_d^{DC} = 0.2$ V and the AC drive is set at $V_d^{AC} = 0.50, 0.63, 0.71$, and 0.79 V for the curves, respectively; (C) The resonance frequency vs. V_d^{AC} [15].

In both types, the surface of the NWs is functionalised with particular silane-coupling agents as linker molecules [6], in order to make either an H-terminated Si surface or a native-oxide-covered Si surface active to the targeted molecules. A high-quality surface functionalisation layer is essential, primarily for sensor selectivity but also for sensors sensitivity. However, while various functionalisation methods [16–18] have been examined for Si NWs, based on both liquid-phase and vapour-phase surface processes, it is unclear if any of the existing techniques can cover the NW surface uniformly at the nanoscale. Technically-challenging and often costly surface functionalisation is a crucial issue, creating a bottleneck in realising reliable, cost-effective Si NW-based chemical sensors.

A second issue in present Si NW-based chemical sensors is that adsorbed chemical molecules cannot be identified directly from the detected change in the conductance or resonant frequency. Other chemical interactions may also be possible, reducing sensor selectivity. Existing sensors monitor only the concentration of particular chemical molecules selectively bonded onto the functionalised surface.

A third issue in present Si NW-based chemical sensors is the lack of simple techniques to make the sensor reusable. Joule heating caused by forcing a high current density through the NW has been proposed to remove the adsorbed molecules on the NW surface, but this process inevitably ablates the functionalisation layer covering the NW surface as well. Therefore, sensors after this refresh operation require re-functionalisation, making the device impractical for commercial application.

There are numerous investigations [6, 7] of Si NW conduction-detection sensors for biological applications, driven by the possibility of label-free, fast and sensitive detection. In contrast, there is relatively limited work on Si NW ion and chemical sensors. NWs with [6, 14] or without [19] silane functionalisation may be used as pH sensors, where protonation/deprotonation of the NW surface occurs with varying pH. Si NW functionalised with calmodulin can sense Ca^{2+} ions [6]. Other devices have detected NO_2 [20], oxygen [21], ammonia [22], and water vapour [22]. Si NWs based molecular detection was reported by Sheu *et al.* [23]. Here, gold nanoparticles were deposited on the oxide surface of the Si NWs and then functionalized with amino groups, which served as linkers to select target molecules. The target molecules were bound with gold nanoparticles on the surface of the Si NWs and

resulted in a voltage shift [9, 16]. Arrays of Si NWs, functionalised with different silanes, have been used to form an “electronic nose” to detect acetone and hexane vapours [19].

In contrast to present approaches to Si NW sensors, it may be possible to detect target molecules directly by using the molecular phonon spectrum, removing the need for surface functionalisation. Inelastic Electron Tunnelling Spectroscopy (IETS) provides a means to characterise the phonon spectrum of molecules by measuring phonon-assisted tunnelling current through a potential barrier impregnated with the molecules of interest [1–4]. Traditionally, this technique has used metal - insulator - metal (MIM) junctions and molecules are adsorbed on to the insulator during junction fabrication. It is also not commercially useful as it needs to be re-supplied during fabrication. At low applied voltage V , tunnelling through the barrier is elastic. However, inelastic tunnelling caused by electron interaction with vibrational states in the adsorbed molecules creates additional conduction channels, with a change in energy $\hbar\omega$. These lead to peaks in the d^2I/dV^2 vs. V characteristics for each additional channel, providing a spectrum of the molecular vibrational modes.

As energy separations in the vibrational spectrum are relatively small compared to the electronic spectrum, in many cases the full vibrational spectrum can be measured only at low temperature, $T < 30K$ [20]. However, it may be possible to measure part of the spectrum even at room temperature, raising the possibility of a molecular detector.

IETS may provide a spectroscopic technique with high sensitivity and selectivity [5] for gas sensing [24]. However, the use of IETS for sensing applications requires molecule adsorp-

tion only after device fabrication. Bommisetty *et al.* have measured and contrasted the full IETS characteristics for an NH_3 doped, $20\mu m \times 20\mu m$ Al / Al_2O_3 / Pb junction at 4K, with the corresponding characteristic at 300K [22, 25]. Two large peaks corresponding to Al–O and NH_3 phonons persist even at 300K, providing a means to identify the underlying molecules bonds (Fig.1.2) [6].

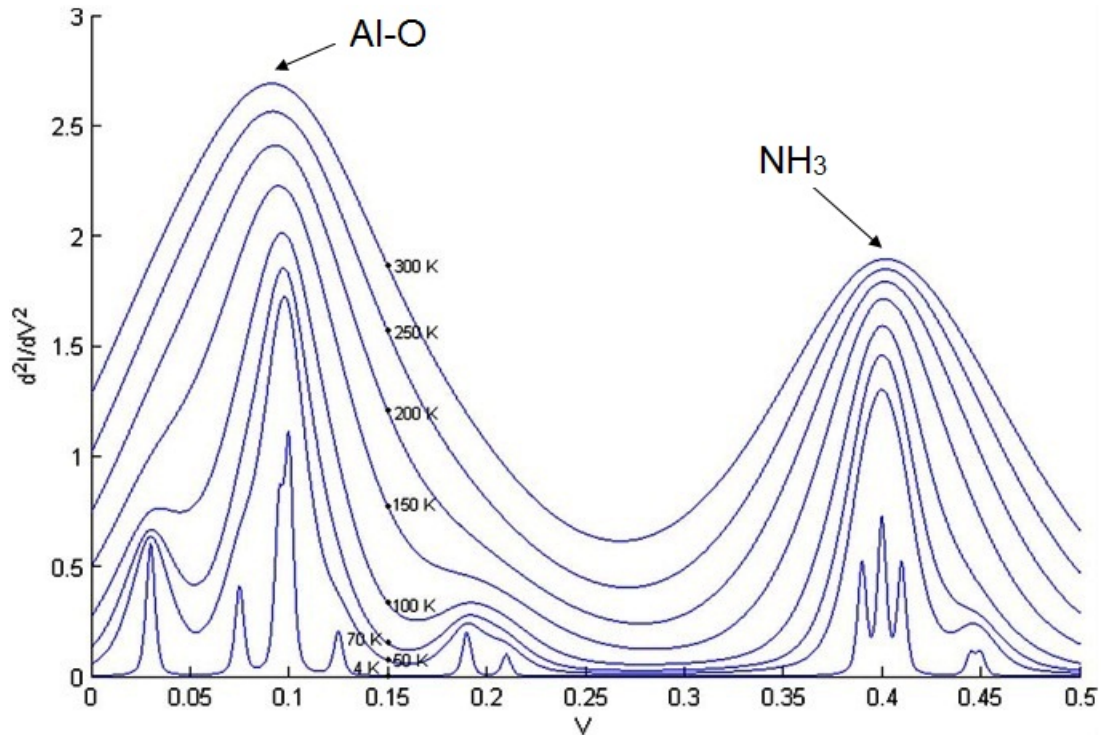


Figure 1.2: Thermal broadening of IETS in an NH_3 doped Al / Al_2O_3 / Pb junction. (Bottom curve: 4K is experimental, all other curves are theoretically calculated by thermal broadening of this, Upper curves: 300K) [24].

More recently, the IETS molecular spectra have been measured using scanning tunnelling microscopy (STM - IETS) [26–28]. This allows the characterisation of single molecules with simultaneous imaging of the surface with atomic resolution [26], e.g. STM measurements have been performed on single acetylene molecules (Fig.1.3) [26].

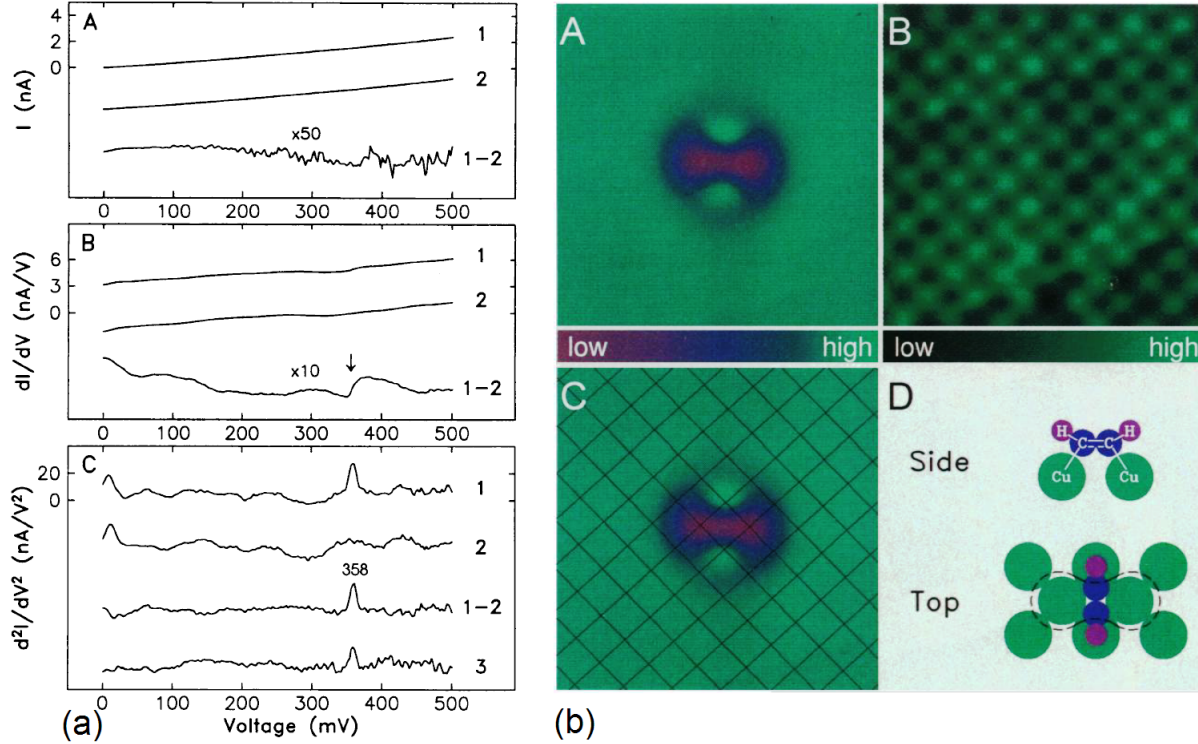


Figure 1.3: (a) STM - IETS characteristics [26] - (b) STM image of: (A) C_2H_2 molecule on the $Cu(100)$ surface at 8K, (B) The molecule in (A) was transferred to the tip by applying a voltage, (C) The atoms in (B) were fitted to a lattice, (D) Schematic diagram of the molecules orientations from side and top views [26].

Single molecule spectra have also been measured using micro meter scale metal - molecule - metal junction measurements of alkyl and π -conjugated molecules [29], and nanoscale alkanedithiol monolayers [30].

1.1 Aims and Research Goals

The main objective of this project is to investigate IETS measurements on nanoscale semiconductor - insulator - metal (SIM) tunnel junctions (Si NW / SiO_2 / Al NW). The use of a Si NW provides a means to define a more robust tunnel junction with the potential for gate control. The molecules of interest are adsorbed on to the insulator after device fabrication.

At low applied voltage, the tunnelling process is similar to a MIM device (Fig.1.4(a-b)).

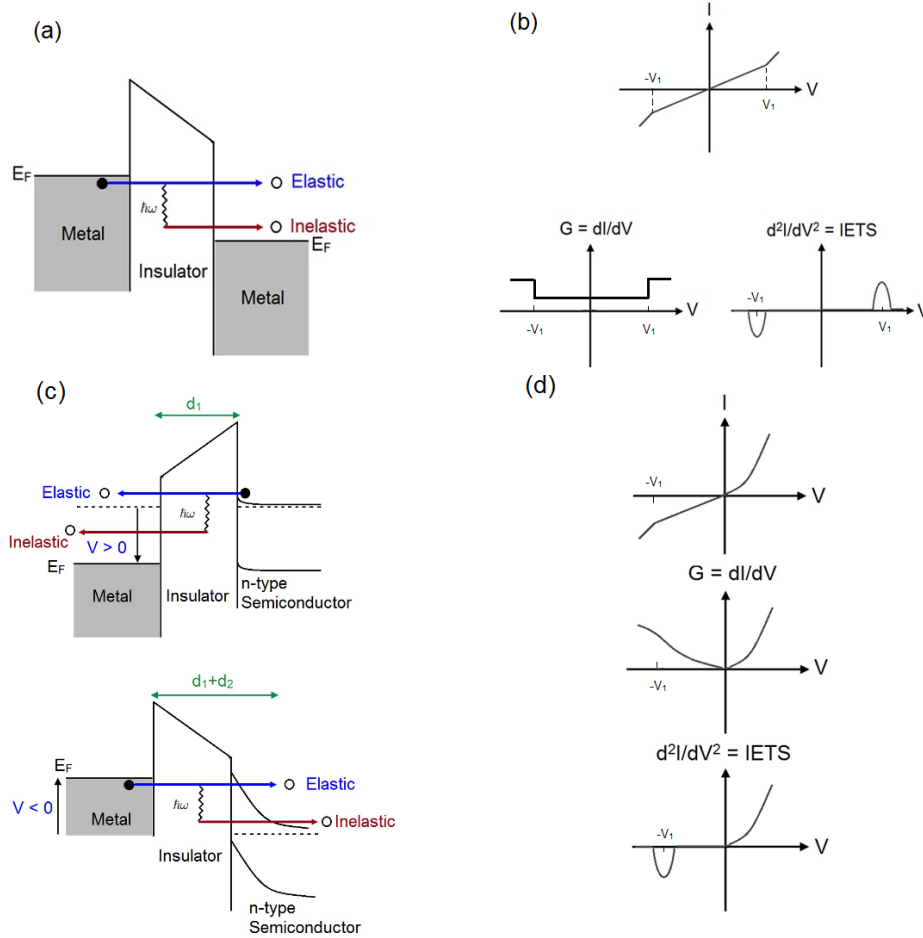


Figure 1.4: Schematic diagram of: (a) elastic and in elastic tunnelling, and (b) IETS signals on a MIM tunnel junction device, (c) reverse and forward biased elastic and in elastic tunnelling, and (d) IETS signals on a SIM tunnel junction device.

However, as the applied voltage increases, the electrical characteristics are affected by the Schottky barrier formed at the Si NW surface. With a reverse biased Schottky barrier, IETS peaks may be measured at reduced current, with less likelihood of damaging the tunnel junctions (Fig.1.4(c-d)).

The thesis discusses IETS measurements performed on well-characterised molecules such as ammonium hydroxide (NH_4OH), acetic acid (CH_3COOH) and propionic acid ($C_3H_6O_2$)

at room temperature. The $I - V$, $dI/dV - V$ and $d^2I/dV^2 - V$ characteristics of the tunnel junction are measured before and after the adsorption of ammonium hydroxide (NH_4OH), acetic acid (CH_3COOH) and propionic acid ($C_3H_6O_2$) molecules using vapour treatment for NH_4OH molecules, and immersion for CH_3COOH and $C_3H_6O_2$ molecules. Following this, IETS characteristics are modelled based on a combination of elastic, inelastic tunnelling and Schottky barriers at the Si / SiO₂ / Al interface in the device. A comparison has been made between the simulation results and experimental measurements which showed very good agreement and further confirmed aspects of the experimental data.

1.2 Overview and Scope of Thesis

This thesis is divided into 7 chapters, and outlines of the chapters following this introduction are given below.

Chapter 2 provides a literature review, surveying past and present work in the field of IETS. The basic theoretical background for quantum tunnelling, inelastic electron tunnelling, vibration (phonon) spectra of molecules and tunnel junction devices for IETS will be presented here. A review of recent work on highly nanoscale tunnel junction and molecular electric devices will also be presented.

Chapter 3 gives an overview of the theoretical background for IETS. This starts with the transmission probability of elastic tunnelling for a single rectangular barrier, and a barrier with arbitrary shape using WKB approximation method. The electrical current is then

calculated. Following this, the inelastic tunnelling transmission probability, and current density is studied. This is followed by detailed derivations of the theoretical underpinnings of the transport across Schottky Barriers (SBs), which determines the behaviour of the majority of the work presented in this thesis. Finally, the total IETS current for semiconductor - insulator - metal (SIM) tunnel junction will be calculated and studied based on these models.

Chapter 4 consists of a detailed discussion of the fabrication process developed for preparation of nanoscale crossed Si NW / SiO₂ / Al NW tunnel junction for IETS measurements. The Si NWs fabricated in the present work, are defined using electron beam lithography (EBL). The Si NW / SiO₂ / Al NW devices use Si NWs with widths down to $\sim 50\text{ nm}$. The NWs are thermally oxidised at 1000°C to create a SiO₂ layer $\sim 10\text{ nm}$ thick. An Al NW $\sim 120\text{ nm}$ in width is defined to perpendicularly cross the SiO₂ / Si NW in each device, forming a nanoscale Si NW / SiO₂ / Al NW tunnel junction $\sim 50\text{ nm} \times 120\text{ nm}$ in area. An overview of electron beam lithography techniques is presented first. Furthermore, a detailed description of the fabrication steps necessary to define Si NW / SiO₂ / Al NW tunnel junction devices is provided. Finally, a detailed discussion of fabrication issues for the Si NW / SiO₂ / Al NW tunnel junction devices used for the IETS measurements in this thesis is presented.

Chapter 5 discusses electrical measurements of the fabricated Si NW / SiO₂ / Al NW tunnel junction devices. The traditional AC modulation technique for IETS measurement is presented in here. This is followed by a discussion of IETS measurements, performed at 300 K , for ammonium hydroxide (NH_4OH), acetic acid (CH_3COOH), and propionic acid

($C_3H_6O_2$) molecules. In this regard the $I - V$, $dI/dV - V$, and $d^2I/dV^2 - V$ characteristics of the tunnel junction are measured before and after adsorption of molecules on the junction.

Chapter 6 explores the IETS equations formulated in Chapter 3, with the effect of the various experimental variables simulated, and used to further confirm aspects of the experimental data of Chapter 5. IETS current equations are coded into a Matlab software programme to calculate the $I - V$, $dI/dV - V$, and $d^2I/dV^2 - V$ characteristics for a metal - insulator - metal (MIM) tunnel junction structure, and a semiconductor - metal - insulator (SIM) tunnel junction structure. The Matlab simulation results for SIM tunnel junctions is then used to study the IETS characteristics observed in Chapter 5.

Chapter 7 presents conclusions for this project, alongside recommendations for future works.

Chapter 2

Literature Review

This chapter provides an introduction to Inelastic Electron Tunnelling Spectroscopy (IETS), where the inelastic tunnelling of electrons is mediated by molecules vibrational states within the tunnel junction. IETS was first proposed and observed in 1966 by Jacklevic and Lambe [1–5]. They observed a new phenomenon during an experimental study of metal - insulator - metal (MIM) tunnel junctions. In this phenomenon, tunnelling electrons interacted with vibrational states of molecules adsorbed at a metal-oxide interface, and caused an increase in the conductance characteristics of the MIM tunnel junction at certain voltages ($eV = \hbar\omega$). Jacklevic and Lambe observed peaks in the d^2I/dV^2 vs. V characteristics at $4.2K$. These peaks correspond to the vibrational frequencies of the molecules contained within the MIM tunnel junction [1]. As energy separations in the vibrational spectrum are relatively small compared to the electronic spectrum, in many cases the full vibrational spectrum can be measured only at low temperature, $T < 30K$ [4]. However, it may be possible to measure part of the spectrum even at room temperature, raising the possibility of a molecular detector [24].

Since then, other groups showed great interest in the studies of IETS using metal - insulator - metal (MIM) junctions. More recently, the IETS molecular spectra have been measured using scanning tunnelling microscopy (STM - IETS) [26–28]. This allows the characterisation of single molecules with simultaneous imaging of the surface with atomic resolution [26], e.g. STM measurements have been performed on single acetylene molecules [26]. Single molecule spectra have also been measured using micro-meter scale metal - molecule - metal junction measurements of alkyl and π -conjugated molecules [29], and nanoscale alkanedithiol monolayers [30].

In order to have a better understanding of IETS, the basic concepts of quantum tunnelling, elastic and inelastic electron tunnelling will be discussed first in this chapter. An overview of past and present work in the IETS field alongside with the recent works on highly nanoscale tunnel junction and molecular electric devices will then be presented.

2.1 Tunnelling Phenomena

Quantum tunnelling is used to describe the quantum mechanical property where a particle tunnels through a potential barrier from one classically-allowed region to another. Here, the potential barrier is a region where the electron is classically forbidden to exist [31]. In the forbidden or barrier region, the potential energy of the barrier, U , is greater than the total energy of the particle, E [5]. This quantum mechanical phenomenon is a direct consequence of the wave-particle duality of matter. According to the wave-particle duality of matter, particles have the forms both of particles and waves. Tunnelling phenomena have now been

studied theoretically and experimentally in a vast number of systems over many decades, from radioactive decay to nanoscale semiconductor devices such as tunnel diodes, quantum dots, etc [32, 33].

With regards to tunnelling in solid-state devices, Fowler and Nordheim observed electron field emissions from metals into vacuum [34, 35]. These tunnelling effects are of particular interest in system such as Metal - Insulator - Metal (MIM) and Metal - Insulator - Semiconductor (MIS) tunnel junctions at high voltages [33]. Two other major early successes in tunnelling devices are the work of Giaever [36] on the measurement of the superconductor energy gap using the tunnelling method, and the explanation of the $p - n$ tunnel diode reported by Esaki [37]. IETS extends these experiments into a region where electron energy changes due to an electron interaction with vibrational states in the adsorbed molecules [1–5]. In order to have a better understanding of IETS, the basic concepts of elastic and inelastic electron tunnelling will be discussed briefly in the next section.

2.1.1 Elastic Tunnelling

Elastic Tunnelling, where an electron tunnels without a change in energy, is the basic form for quantum tunnelling. This is also the mechanism for charge flow through the insulator layer in MIM junctions at low bias [2]. When a small positive voltage V is applied to the top electrode (Fig.2.1(a)), all the potential drop occurs across the barrier. Here, the two Fermi levels of the metals are separated by the energy eV , and electrons tunnel through the barrier “elastically” i.e. without an energy change. This implies that electrons in the

left-hand metal are capable of a horizontal transition (without losing any energy) from filled states in the left-hand metal into empty states in the right-hand metal [2] (Fig.2.1(b)).

During this process, the current increases linearly with small applied bias V . Particles are capable of tunnelling through classically forbidden barriers as long as the transmission probability is non-zero. The expression for the transmission probability and elastic tunnelling current will be discussed in detail in Chapter 3.

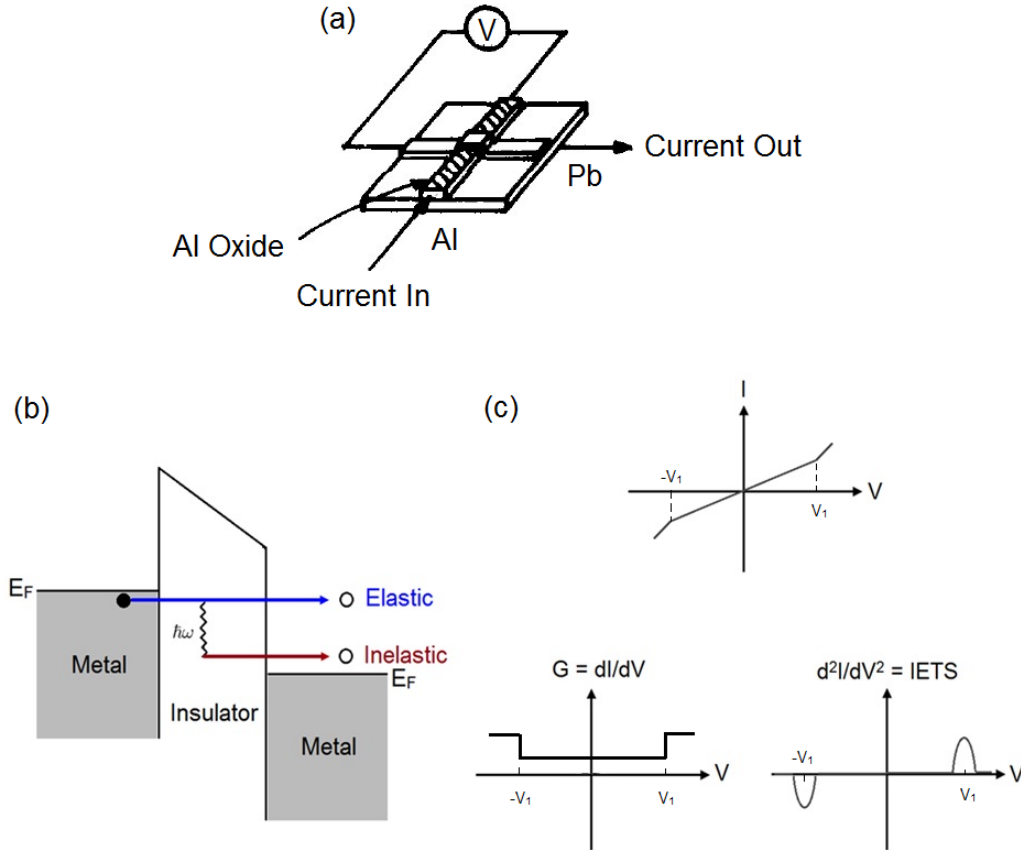


Figure 2.1: Schematic diagrams of: (a) An Al / Al₂O₃ / Pb tunnel junction under applied bias V , (b) elastic and inelastic tunnelling, and (c) IETS signals for a MIM tunnel junction device.

2.1.2 Inelastic Tunnelling

Inelastic tunnelling can occur when impurities with energy $E = h\nu$ (h is Planck's constant) and vibrational modes with frequency ν , lying within the insulator layer, interact with tunnelling electrons. Here, when the applied bias V is large enough such that $eV \geq h\nu$, the electron can lose an energy of $h\nu$ to excite the vibration mode and tunnel into another empty state [2]. This process creates additional conduction channels for tunnelling electrons and therefore increases the transmission probability. This leads to a change in conductance dI/dV vs. V and peaks in the d^2I/dV^2 vs. V characteristics for each additional channel, providing a spectrum of the molecular vibrational modes (Fig.2.1(b-c)). The expression for the transmission probability and inelastic tunnelling current will also be studied in detail in Chapter 3. Here, vibrational spectra consist of a transitions from a particular vibrational state to another vibrational state in the same electronic term (Fig.2.2) [38].

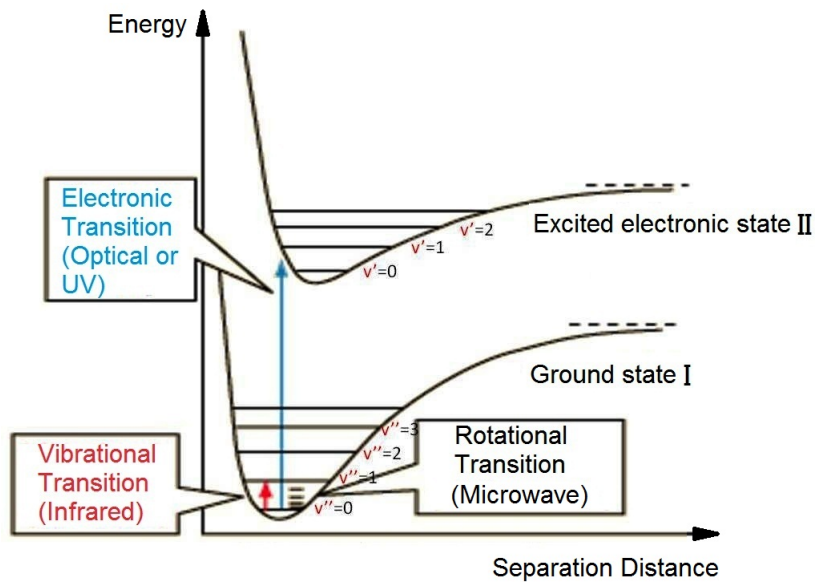


Figure 2.2: *Vibrational and rotational levels of two electronic excitation states of a molecule [39].*

These spectra can be observed with Infrared spectroscopy and Raman spectroscopy [38]. Figure 2.2 illustrates the vibrational and rotational levels of two electronic excitation states of a molecule. Here, rotational spectra are due to the transitions between two rotational levels of a particular vibrational level. These spectra lie in the microwave or far infrared regions (Fig.2.3). The electronic spectra are due to transitions between the vibrational level of electronic ground state to another vibrational level of excited electronic state. These spectra can be observed in the near infrared, the visible, or the ultraviolet regions (Fig.2.3) [38].

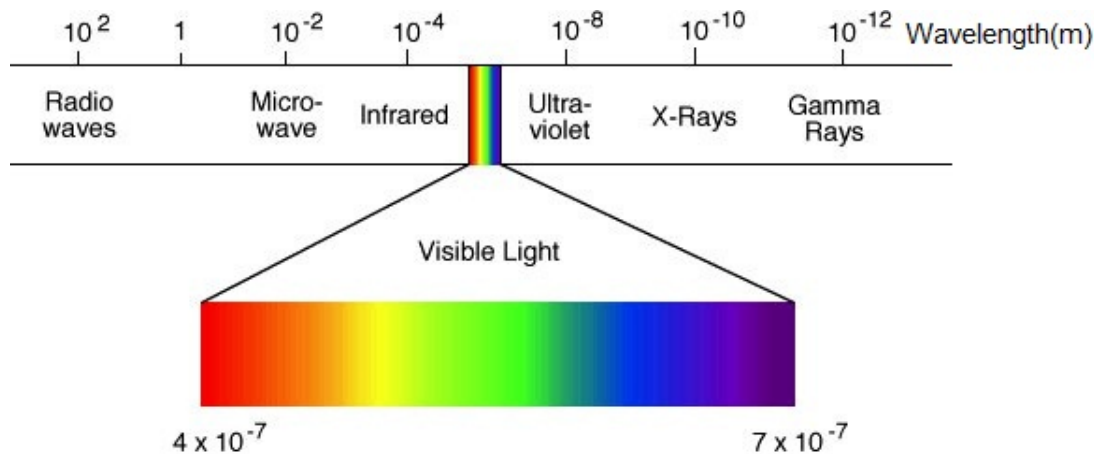


Figure 2.3: The spectrum of electromagnetic radiation [40].

2.2 Inelastic Electron Tunnelling Spectroscopy

2.2.1 IETS on Metal - Insulator - Metal Tunnel Junctions

IETS was first proposed in 1966 by Jacklevic and Lambe [1–5], who observed peaks at 4.2K in the d^2I/dV^2 vs. V characteristics of tunnel junction impregnated with molecules species (Fig.2.4). These peaks were related to the vibrational excitations of the molecular impurities

contained within the, $\sim 1 \times 1 \text{ mm}^2$ Al / Al_2O_3 / Pb tunnel junction, in the voltage range of 0 – 1 V. Here, the “dopant” was exposed on the oxide layer in a vacuum system at a pressure of 10^{-1} torr for several minutes.

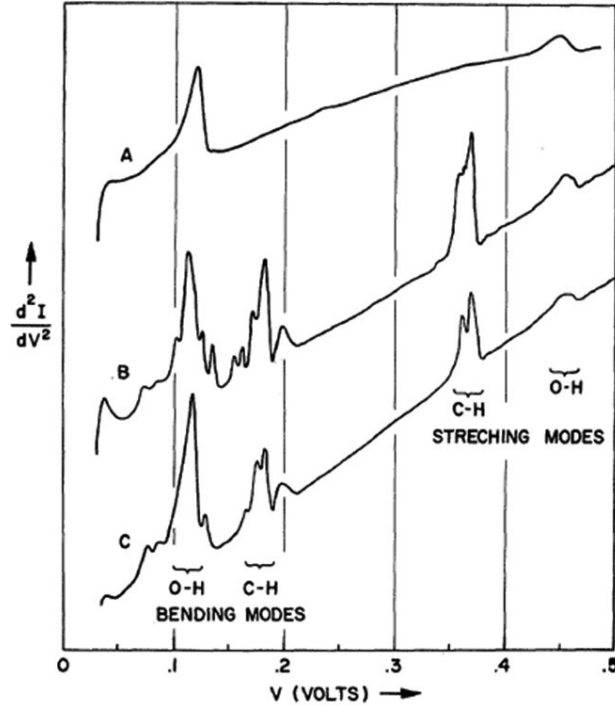


Figure 2.4: Early IETS measurements on Al / Al_2O_3 / Pb tunnel junction at 4.2K. Curve A is obtained from a “clean” junction. Curves B and C are obtained from junctions exposed to propionic acid ($\text{C}_3\text{H}_6\text{O}_2$) and acetic acid (CH_3COOH), respectively [1].

Jacklevic and Lambe obtained curve A from a “clean” junction. Curves B and C were obtained from junctions exposed to propionic acid ($\text{C}_3\text{H}_6\text{O}_2$) and acetic acid (CH_3COOH), respectively [1]. The peaks observed in the region of 0.050 – 0.5V, which corresponds to the infrared (IR) region of $25 - 2.5 \mu\text{m}$. Scalapino and Marcus [41] then modelled these experiments theoretically to explain the characteristics using inelastic tunnelling theory and an IR dipole mechanism. They predicted that the intensities in a tunnelling spectrum should be the same as in an IR spectrum. Leger *et al.* have observed the excitation of electronic

transitions at voltages above 1V by IETS [42]. They have also studied the possibility of deducting precise information from IETS measurements using Mg / MgO / Pb tunnel junction [43]. An alternative method of doping called liquid doping was introduced by Hansma and Coleman [44]. Here a drop of a solution containing the dopant was placed on the oxide surface and then the excess spun off.

An early estimate of IETS sensitivity has been given by Lewis *et al.* [45]. They calculated that $\sim 2 \times 10^{10}$ molecules on 1 mm^2 junction would be detectable using the signal-to-noise ratio for peaks in an IETS spectrum of formic acid. Langman and Hansma have detected $\sim 5 \times 10^9$ molecules on $\sim 0.025 \text{ mm}^2$ junction (3% of a monolayer of benzoic acid) in an experiment primarily designed to test the linearity of peak intensity on surface coverage [46]. In other work, the application of IETS to analytical chemistry and surface interaction has been studied in detail by Keil *et al.* [2]. The IETS technique has also been extended to biological molecules by Clark and Coleman [47] in 1976, where nucleic acid derivatives were detected by IETS. The IET spectra of hexanoic acid, chemisorbed on to an oxidised Al film, were measured later that year [48]. The theory for the intensity of vibrational modes in IETS of organic molecules in MIM junctions has been developed by using a transfer Hamiltonian formalism [49]. Symmetry selection rules in IETS have been studied by J. Kirtley and P. K. Hansma [50]. In this case, IETS was performed on a highly symmetric molecule, anthracene, to show that the vibrational frequency measured by tunnelling matches well with previous optical measurements [50]. The first direct measurement of IETS sensitivity has been studied by Kroeker and Hansma [51], using an experiment to measure the sensitivity directly. They deposited a known fraction of a monolayer of deuterated benzoic acid on to a tunnel

junction, and then attempted to detect this fraction of a monolayer in the IETS spectra of the tunnel junctions. They found that the detection limit for the fraction of a monolayer is 1 %.

IETS may provide a spectroscopic technique with high sensitivity and selectivity [5] for gas sensing [24]. However, the use of IETS for sensing applications requires molecule adsorption only after device fabrication. Jaklevic and Gaerttner resolved this fabrication problem [52], by introducing external doping of Al / Al₂O₃ / Pb tunnel diodes. According to their report, small organic molecules in the presence of water vapour would penetrate through the top metal (Pb) of completed junctions. The IET spectra obtained from these vapour-infused diodes were comparable to the traditionally doped devices [3]. In their subsequent works, they showed that the completed Al / Al₂O₃ / Pb tunnel junctions could be infused with various species from either water vapour or aqueous solution [3, 53, 54]. In addition, they obtained IET spectra of Al / Al₂O₃ / Pb tunnel junctions exposed with small quantities of hydrogen and deuterium gas [55].

Other groups investigated that the intensity of the peaks is related to the concentration of adsorbed solution. As the solution concentration decreased, the intensity of the peaks in the tunnelling spectra decreases as well [53]. As an example, Langan *et al.* considered an Al / Al₂O₃ / Pb tunnel junction, doped with benzoic acid in aqueous solution of 1.0 and 0.1 mg/ml. The IETS spectra, taken at 4.2K are shown in Fig.2.5.

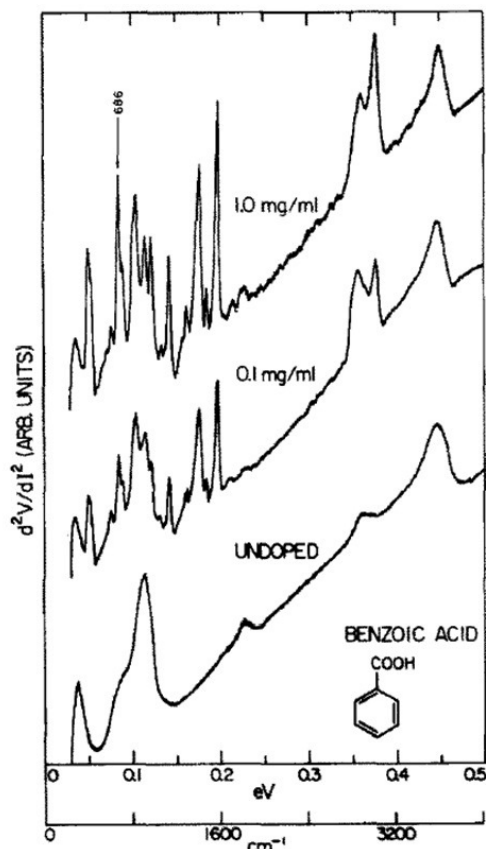


Figure 2.5: d^2I/dV^2 vs. V plot, showing the effect of concentration of a liquid doping solution on the intensity of the tunnelling peaks [46].

Figure 2.5 illustrates that as the concentration of liquid doping solution is increased, the intensity of the tunnelling peaks increases. The position of the peaks can shift, based on the metal used for the top electrode [53]. Different research groups have noted that with different top metal electrodes, the vibrational modes can change dramatically. Kirtley and Hansma have studied the effect of the top metal electrode on the peak positions [49, 56]. They observed that in tunnel junctions with top metal electrodes with smaller atomic radii, the peak positions are down-shifted. Beyman *et al.*, showed that the metals with similar atomic radii gave similar spectra [53, 57]. In this case, the vibrational modes of CO on iron / aluminium oxide barrier with different top metals were investigated (Fig.2.6).

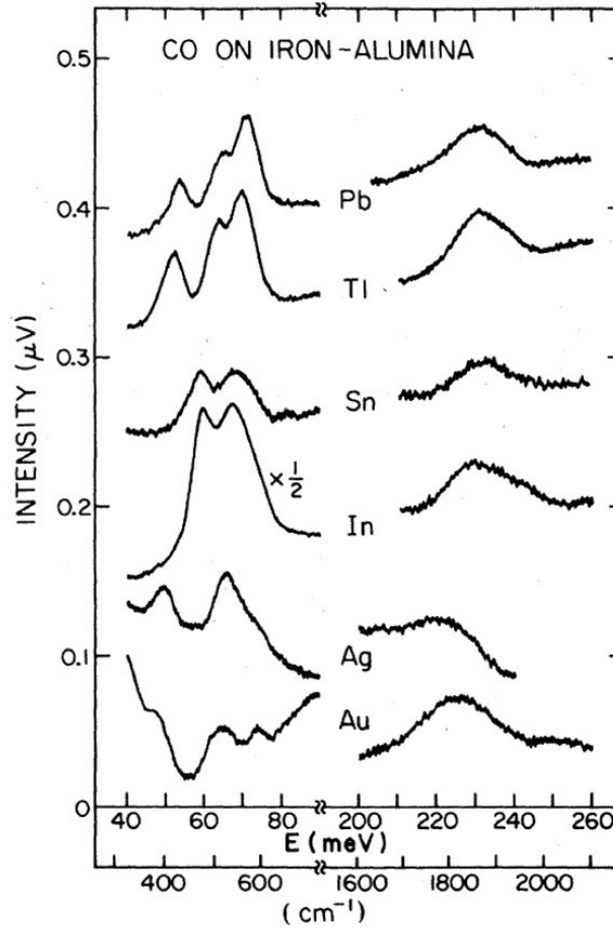


Figure 2.6: *The effect of top metal electrode [57].*

Figure 3.13 illustrates that electrodes with similar radii range give similar spectra. Here, the radii of Pd and Tl are 1.745 and 1.71 Å respectively. It is seen that, these have similar vibrational spectra. Similar behaviour can be observed for Sn and In with 1.582 and 1.57 Å radii, and for Ag and Au with 1.442 and 1.439 Å radii [53, 57].

Some groups reviewed the different methods of doping and also described an essential construction for an inelastic electron tunnelling spectrometer [58–60]. Other groups reproduced their results on Al / Al₂O₃ / Pb tunnel junction [61–63]. In these works, it was noted that water vapour played a critical role in the infusion process. Here, the water vapour etched

the grain boundaries in the Pb electrode and created a path for entry of the add-species into the Al / Al₂O₃ / Pb tunnel junction. As the sensor electrode must be chemically and mechanically stable as well as infusible, Pb was therefore not an ideal material for the sensor electrode. In this regard, Jaklevic has mentioned in some of his works that Sn and Au can be used as a top electrode for infusion, however spectra were not presented [4]. Mazur *et al.* obtained IET spectra from infused Al / Al₂O₃ / Au tunnel junctions [4, 64] (Fig.2.7).

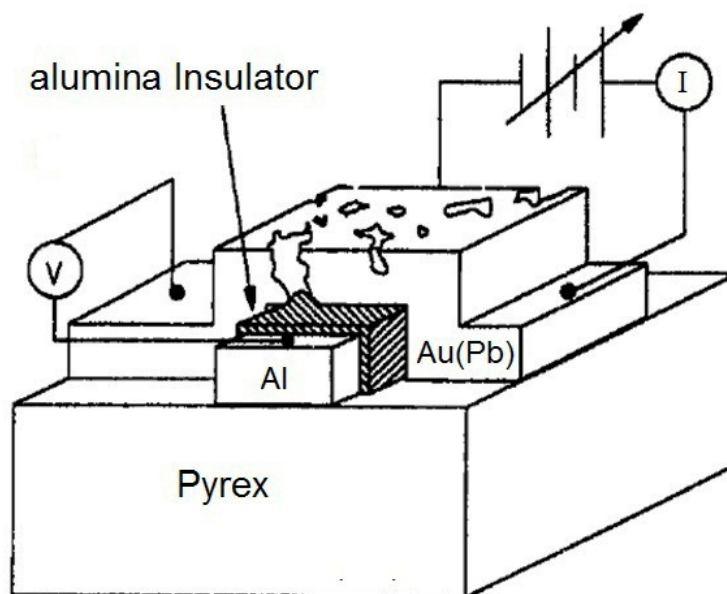


Figure 2.7: Schematic diagram of an infusible Al / Al₂O₃ / Au tunnel junction [64]

In subsequent work, Mazur *et al.* focused on infusion of species that do not react with Au. They studied the infusion of formic acid through Al / Al₂O₃ / Au and Al / Al₂O₃ / Pb / Au tunnel junctions for various concentration of formic acid. A two-layer top electrode structure was used for the first time, which produced a good conductor layer and played a critical role in determining the sensitivity of the device to gas-phase formic acid [4].

2.2.2 IETS Sensors

Bommisetty *et al.* have measured and contrasted the full IETS characteristics for an NH_3 doped, $\sim 20 \mu m \times 20 \mu m$ Al / Al_2O_3 / Pb junction at $4K$, with the corresponding characteristic at $300K$ [24, 25]. Two large peaks corresponding to $Al - O$ and NH_3 phonons persisted even at $300K$, providing a means to identify the underlying molecules bonds [25] (Fig.2.8). In Fig.2.8, only the $4K$ curve is experimental and the remaining curves are theoretically calculated by incorporating thermal broadening.

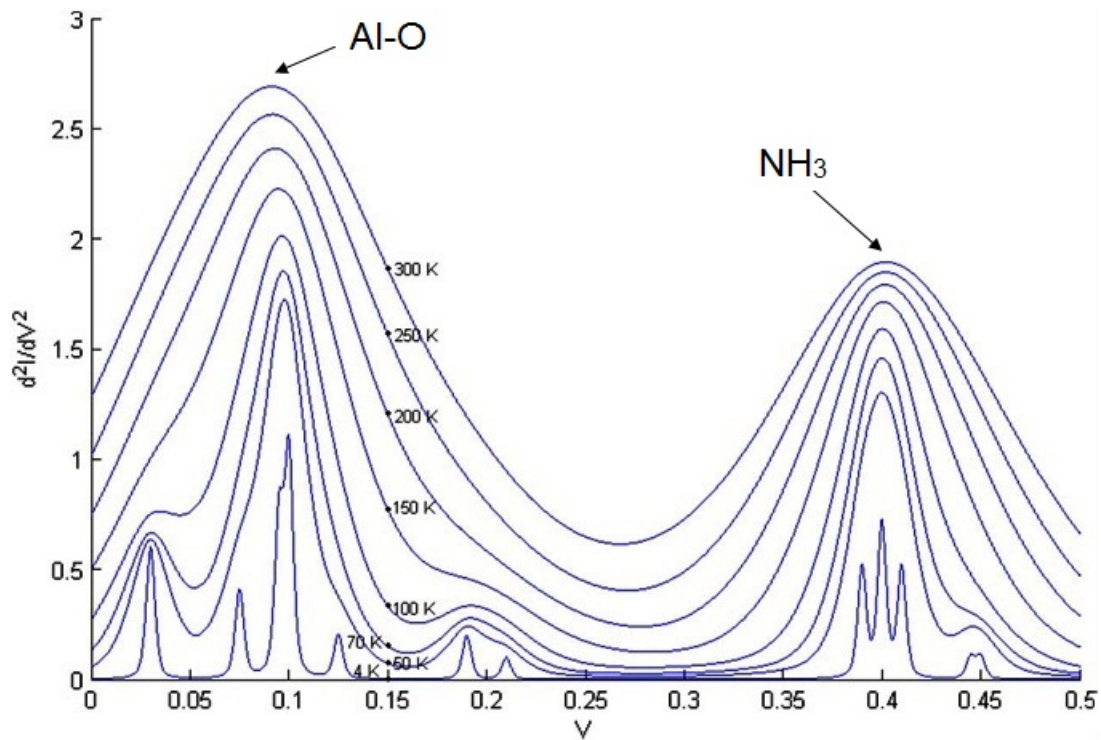


Figure 2.8: Thermal broadening of IETS in an NH_3 doped Al / Al_2O_3 / Pb junction. (Bottom curve: $4K$ is experimental, all other curves are theoretically calculated by thermal broadening of this, Upper curves: $300K$) [24].

Bommisetty *et al.* then measured IETS in an Al / Al_2O_3 / Pb junction $77K$, and at room temperature [24] (Fig.2.9). Here, the $Al - O$ peak at room temperature is broader compared

to the peak at $77K$ due to the thermal broadening effect.

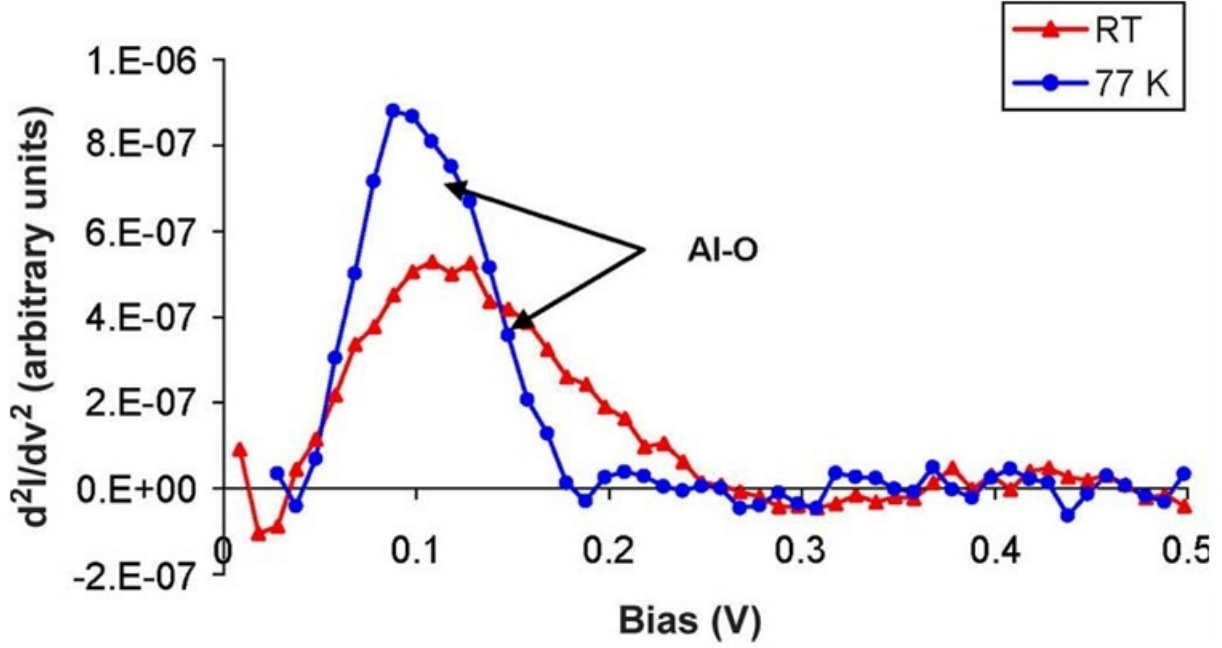


Figure 2.9: IETS spectra of $Al / Al_2O_3 / Pb$ junction at $77K$, and room temperature [24].

The $Al / Al_2O_3 / Pb$ junction was then exposed at $77K$ to ammonia gas in dry air. Figure 2.10 illustrates the IETS spectra at $77K$. Here, the data from the NH_3 doped $Al / Al_2O_3 / Pb$ junction at $4K$ are theoretically adjusted based on thermal broadening effect to $77K$. The Al phonon and $Al - O$ stretch peak positions are similar in both spectra. The first excitation mode of NH_3 is measured at $\sim 280 mV$, while the adjusted peak position based on data's at $4K$ is at $\sim 200 mV$. Bommisetty *et al.* claimed that despite significant differences in measurement temperature, the positions of major peaks were similar, therefore it is possible to detect NH_3 using IETS at $77K$.

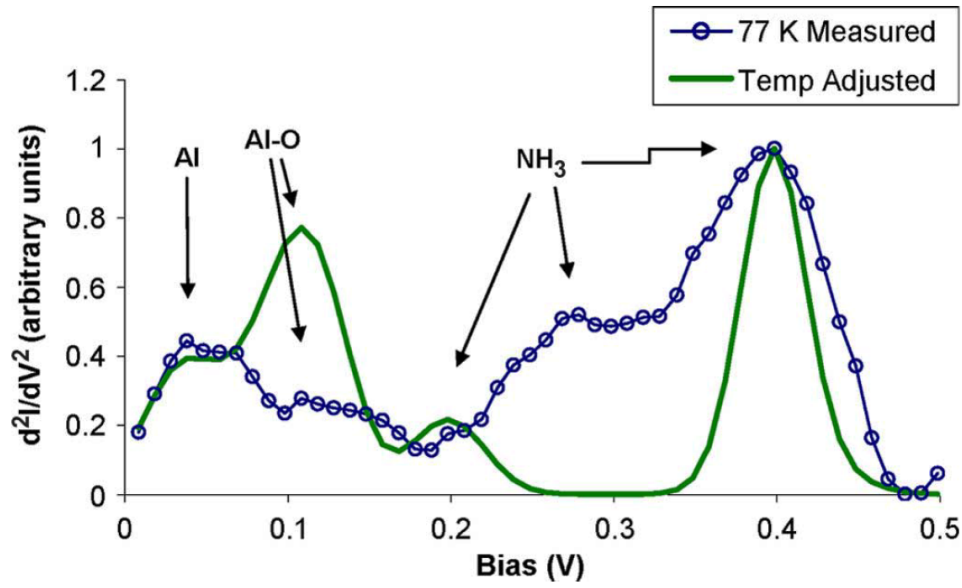


Figure 2.10: *IETS spectra of Al / Al₂O₃ / Pb junction exposed to ammonia gas at 77K [24].*

The measurement was then repeated for NH_3 doped Al / Al₂O₃ / Pb junction at room temperature (Fig.2.11).

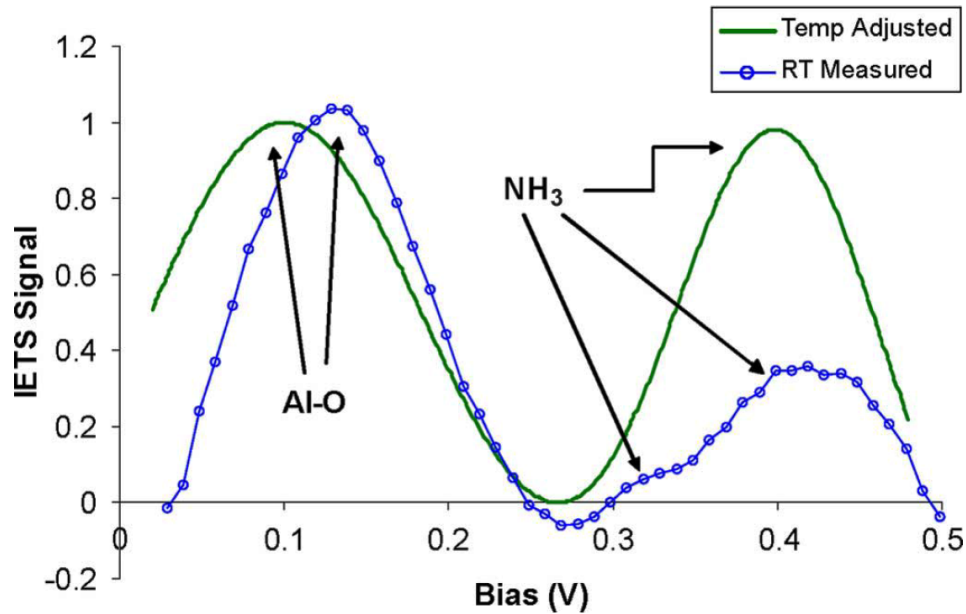


Figure 2.11: *IETS spectra of Al / Al₂O₃ / Pb junction exposed to ammonia gas at room temperature [24].*

Here, the measured peak positions are slightly shifted to the right. Figure 2.11 shows significant difference in the peaks heights.

IETS also provides an application to areas of surface chemistry and catalysis [65–67]. In this regard, Weinberg and Evans studied the reaction of ethanol with an aluminium oxide surface by IETS [68]. Here, IETS was performed as a function of the temperature at which molecules were adsorbed on to the oxide surface. These studies were followed by the IETS of selected Alcohols and Amines on plasma-grown aluminium oxide [69–72]. Adsorption of unsaturated hydrocarbons on supported metal catalysts has also been studied by IETS [73].

Other groups have investigated IETS in further detail [25, 74, 75]. Here, IETS was compared with Raman spectroscopy [76], applications of IETS [77, 78] considered, and IETS measurements circuits using AC modulation techniques were reviewed [79–82]. A comparison has been made between experimental study of relative intensities in IETS of formic and acetic acid chemisorbed on alumina, and the Scalapino and Marcus theory of tunnelling intensities [83]. Here, the observed and calculated intensities did not show good agreement. Godwin *et al.* [84] and Yang *et al.* [85] suggested that a possible explanation is that the interaction mechanism between electron and molecule was not well described by Scalapino and Marcus theory [83].

The mechanisms for frequency shifts in IETS have been studied by C. J. Adkins and A. K. Sleight [86], where two mechanisms were analysed. The first one resulted from the presence of the top metal electrode in the tunnelling structure which had been discussed previously by

Kirthley and Hansma [56]. Kirthley and Hansma showed that the position of the peaks could shift, based on the metal used for the top electrode. This shift was due to the interaction between the molecular system and its dipole image in the top electrode, which could cause frequency shifts of several percent. Here, an oscillating charge outside of the metal surface induced an image charge inside the metal, which their interaction potential was proportional to $\frac{1}{d}$ (Fig.2.12). Here, d is the separation between the charge and surface of the metal.

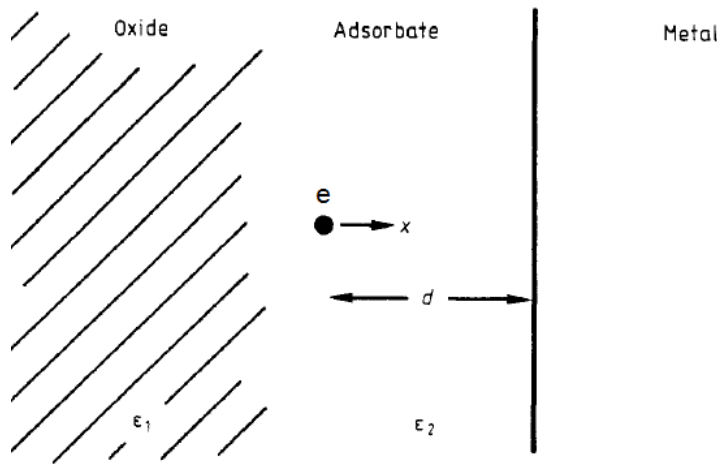


Figure 2.12: Schematic diagram of interaction mechanism between an atom of an adsorbed species carrying partial charge of e with it's image in the metal electrode [86].

This interaction potential shifted the resonance frequency down. Kirthley and Hansma explained this peak shift by studying the OH stretch modes of adsorbed hydroxyl ions for Mg and Al bottom metal oxides. The interaction potential between the charge and it's image was approximated as:

$$U_{int} = \frac{-e^2}{2d\epsilon_1} \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1} \sim \frac{-e^2}{2d\epsilon_1} \quad (2.1)$$

Here, ϵ_1 is the dielectric constant of the oxide and ϵ_2 is the frequency-dependent real part of the dielectric constant of the metal. They also approximated the the $O - H$ bending with a

Morse potential [56]:

$$U(r - r_e) = D_e(1 - \exp(-\beta|r - r_e|)) \quad (2.2)$$

For the OH^- group, where $\beta = 1.6 \times 10^8 \text{ cm}^{-1}$ and $D_e = 4.7 \text{ eV}$, the energy shift is:

$$\Delta E \sim -\frac{\hbar q^2}{(2M\beta^2 D_e)^{1/2} 2\epsilon_1 d_0^3} \left(1 + \frac{3}{2}\beta d_0\right) \quad (2.3)$$

Here, M is mass of a proton, q is dipole moment of OH^- group which is $\sim 0.71e$, d_0 is the distance from proton in the $O-H$ group to the metal surface and it's measured in angstroms ($\text{\AA}$), and $\epsilon_1 = 8$ is the dielectric constant of Al_2O_3 . The $O-H$ peak positions on Al_2O_3 can be varied from 455 to 473 meV . The exact position depends on the temperature. Schwartz measured the $O-H$ peak position on Al_2O_3 at room temperature. Using the peak positions for $O-H$ on Al_2O_3 in the absence of a top metal electrode ($455 + 3 \text{ meV} \sim 455 \text{ meV}$), Kirthley and Hansma fitted Eq.2.3 to experiment to obtain the values of d_0 [56]. Therefore, the energy shift is [56]:

$$\Delta E = (5.91/d_0^3)(1 + 2.4d_0) \text{ meV} \quad (2.4)$$

The second mechanism, resulted from the electric field that was applied during measurement. Adkins and Sleight showed that the applied electric field changed frequencies by the same mechanism as that previously been used to explain the top-electrode effects. Based on their

model, the potential energy of the atom has three components [86]:

$$\text{Molecular Potential } U_0 = \sum a_n x^n \quad (2.5)$$

$$\text{Image potential } U_i = \sum b_n x^n$$

$$\text{Applied Field } U_E = c_1 x$$

In the presence of interaction, the displaced equilibrium position x_0 is [86]:

$$x_0 = -\frac{(c_1 + b_1)}{2(a_2 + b_2)} \quad (2.6)$$

Adkins and Sleigh, obtained a fractional frequency shift by extracting the harmonic restoring force about $x = x_0$:

$$\frac{\Delta\omega}{\omega_0} = \frac{b_2}{2a_2} - \frac{3}{4} \frac{(c_1 + b_1)(a_3 + b_3)}{a_2(a_2 + b_2)} \quad (2.7)$$

Here, ω_0 is the frequency of atomic vibration for the adsorbed species before perturbation by the top electrode or by the applied field, c_1 is the driving-force term for the polarity shift, b_1 is corresponding to a contribution to x_0 from the attraction of the image and b_2 is corresponding to a modification of the harmonic term in the potential at $x = 0$.

2.2.3 STM - IETS

Hipps and Mazur investigated scanning tunnelling microscopy (STM) based IETS with the capability of measurement at high temperature (77K) to study surface science [3]. More recently, the IETS molecular spectra have been measured using scanning tunnelling microscopy

(STM - IETS) at low temperature [26–28, 87, 88]. Here, the MIM tunnel junction device is replaced with the STM tunnel junction, which consists of a sharp metal tip, a vacuum gap of several angstroms ($\text{\AA}$), and a surface with the adsorbed molecules (Fig.2.13) [26].

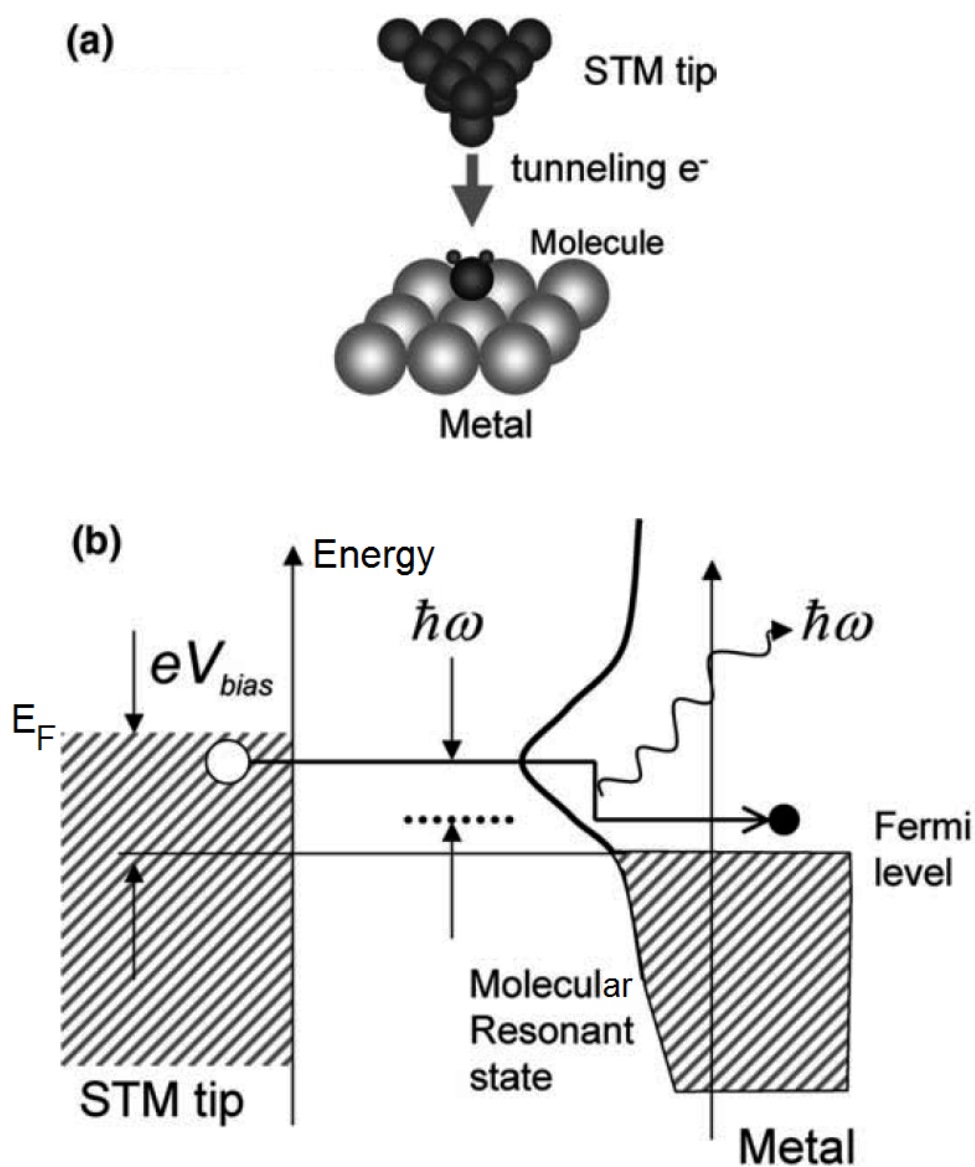


Figure 2.13: Schematic diagram of STM setup [87].

This allows the characterisation of single molecules with simultaneous imaging of the surface with atomic resolution e.g. STM measurements have been performed on single acetylene molecules (Fig.2.14) [26], single methyl isocyanide (MeNC) molecule on the Pt surface at 4.7K [89], single pentanedithiol molecules covalently bound to gold electrodes [90], single propene molecule [91], and alkanethiol self-assembled monolayers [92].

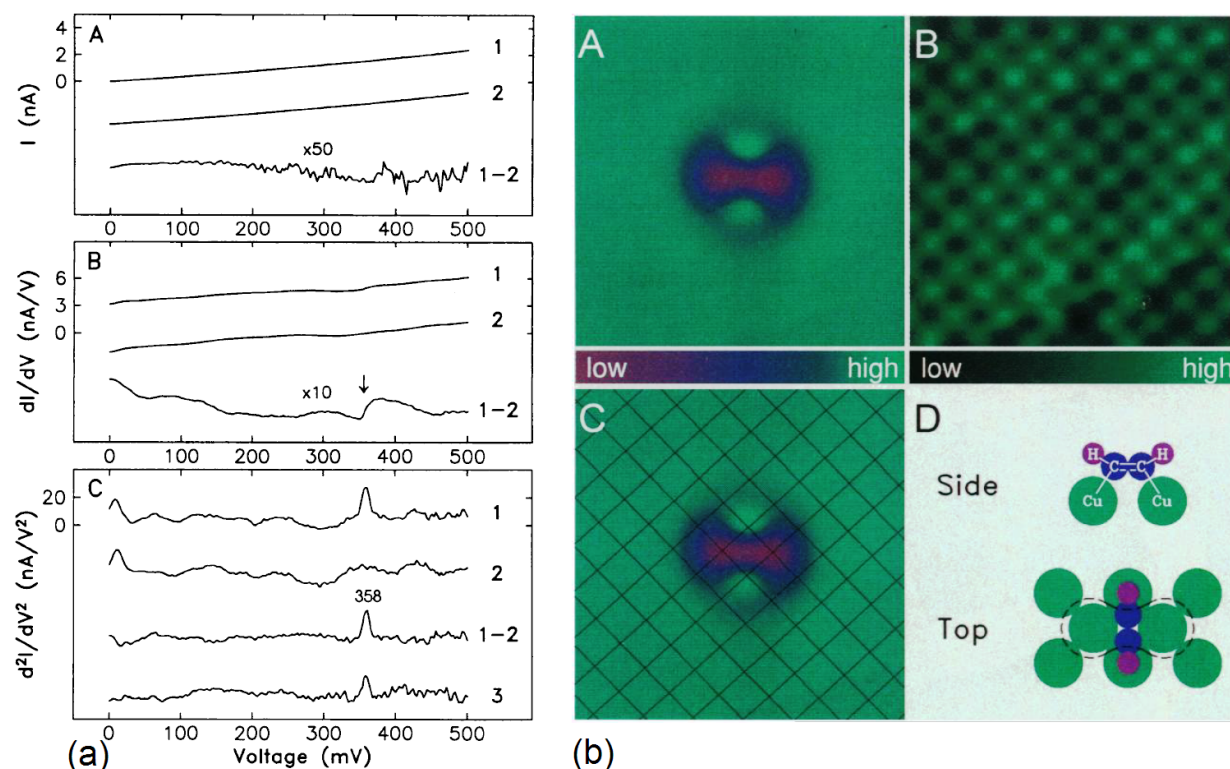


Figure 2.14: (a) STM - IETS characteristics [26]: (A) $I - V$ ((1) shows curve over the center of molecule, (2) over the bare copper surface, and (1 - 2) is the difference curve), (B) $dI/dV - V$ (The difference in conductance (1 - 2) shows a sharp increase at a bias of 358 mV (shown by arrow)), (C) $d^2I/dV^2 - V$ (The difference spectrum shows a peak at 358 mV). (b) STM image of: (A) C_2H_2 molecule on the Cu(100) surface at 8K, (B) The molecule in (A) was transferred to the tip by applying a voltage, (C) The atoms in (B) were fitted to a lattice, (D) Schematic diagram of the molecules orientations from side and top views [26].

2.2.4 Metal - Molecule - Metal Junctions

Single molecule spectra have also been measured using micrometer scale metal - molecule - metal (MMM) junction [93] e.g. alkyl and π -conjugated molecules [29], nanoscale alkanedithiol monolayers [30, 94], benzenedithiolate (BDT) molecules [95, 96], and amine-ended and thiol-ended octanes [97].

Furthermore, Yu *et al.* [98] have performed IETS measurements at $5K$ using single-molecule transistors. Here, *Au* electrodes with a $\sim 2nm$ gap were formed by electromigration in a $\sim 15nm$ *Au* line. The gap is bridged using a Co^{2+} ion, bonded with coordinated ligands on either side and then covalently attached using di- or trithiolate to the *Au* electrodes. The vibrational states could be tuned using a gate electrode. Other groups also measured IETS vibrational spectra of metal - molecule - metal junctions using electromigrated nanogap electrodes (Fig.2.15) [99].

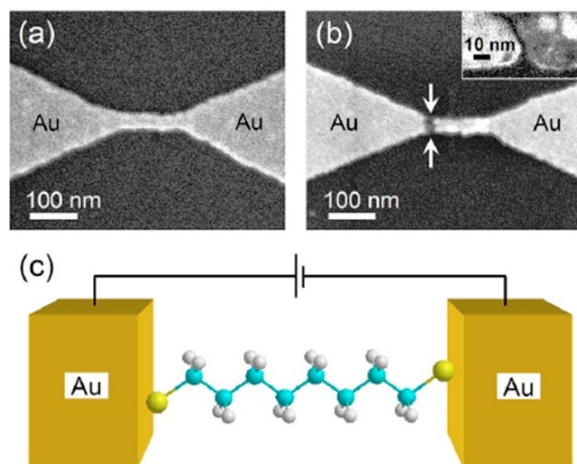


Figure 2.15: SEM image of: (a) a continuous Au wire before electromigration, (b) a broken Au wire after electro-migration. (c) Schematic diagram of a MMM junction [99].

Single molecule spectra can also be measured using nanoscale mechanically controllable break junction (nano - MCBJ) [100]. This technique was capable of simultaneous measurement of conductance and IETS [101]. Recently, vibrational spectroscopy of single - molecule junctions has been measured by direct DC current measurements instead of traditional AC modulation technique (Fig.2.16) [102]. The measurement techniques will be discussed in details in Chapter 5.

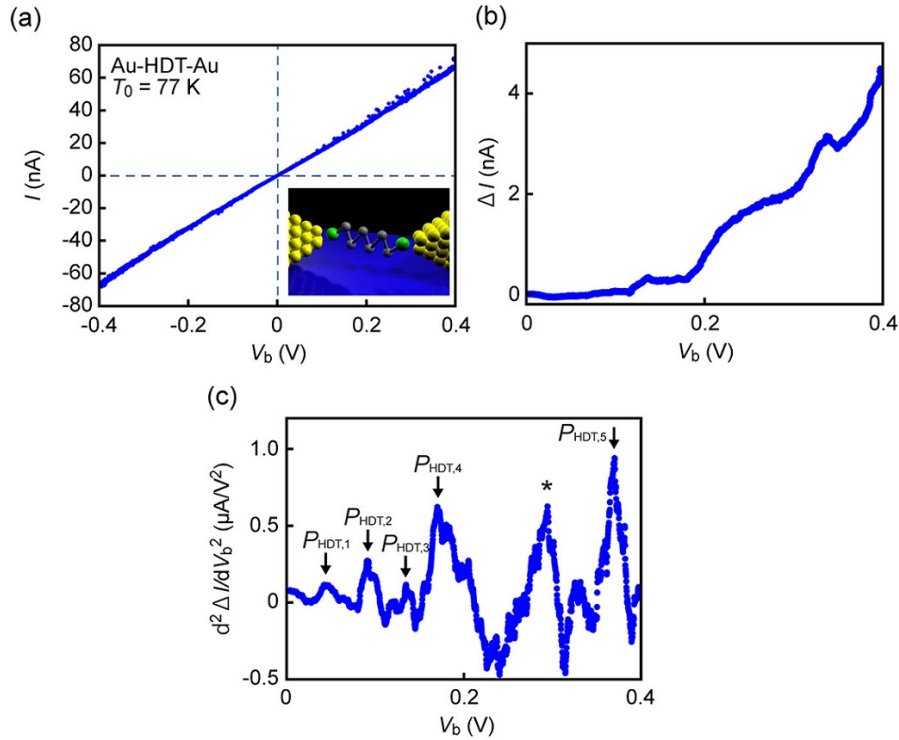


Figure 2.16: Single-Molecule junction measurements at 77K by direct DC measurement: (a) Elastic current vs. voltage, (b) Inelastic current vs. voltage, and (c) IETS spectra [102].

IETS molecular spectra have been measured with standard AC modulation techniques using self-assembling tunnel junctions (SATJs) [103, 104]. In this setup, the MIM junction has been replaced with two long metallic wires whose separation was set by an atomically thin gas barrier film and the molecules of interest could either be deposited directly onto the metal surfaces or co-adsorbed with the film [105].

2.2.5 IETS on Semiconductor - Insulator - Metal Tunnel Junctions

The study of IETS has also been extended to semiconductor - insulator - metal (SIM) tunnel junctions and magnetic tunnel junctions (MTJs) [106]. Here, Balk *et al.* obtained tunnelling spectroscopy characteristics from different SIM tunnel junctions such as Si / SiO₂ / Al (Fig.2.17(a)), and Si / SiO₂ / Pb tunnel junction at 4.2K [107]. Figure 2.17(b) shows, the conductivity for Si / SiO₂ / Al tunnel junction before and after annealing in dry nitrogen at 400°C for 20 minutes.

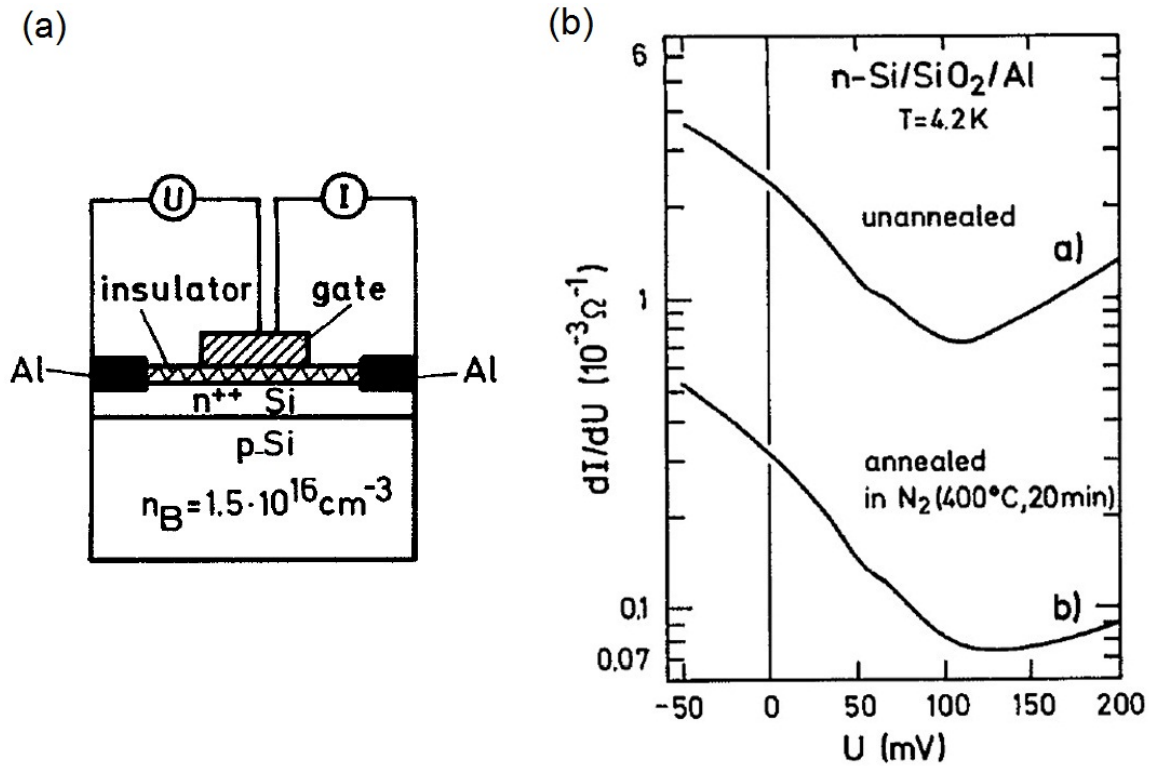


Figure 2.17: Conductivity of Si / SiO₂ / Al tunnel junction at 4.2K [107]

Figure 2.17(b) illustrates the reduction in conductivity, and also a shift in the minimum to higher voltages for the annealed junction [107]. Balk *et al.* also obtained IETS characteristics

using Si / SiO₂ / Pb tunnel junctions (Fig.2.18) [107].

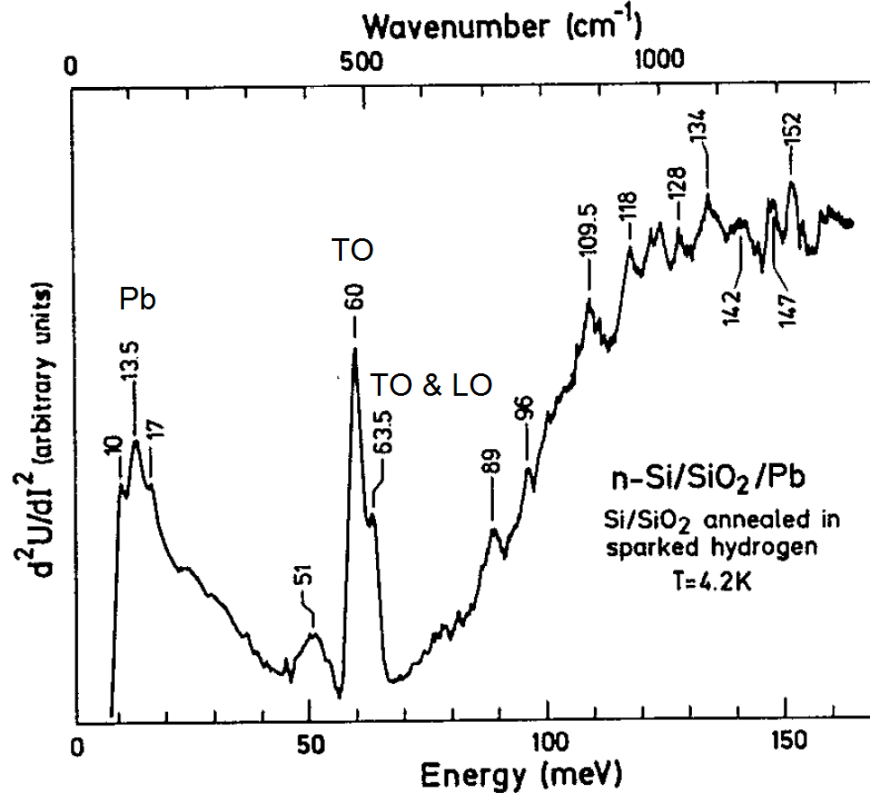


Figure 2.18: IETS spectra of Si / SiO₂ / Pb tunnel junction at 4.2K [107].

Here, the Si / SiO₂ / Pb tunnel junction was annealed in sparked hydrogen at 350°C for 1 hour. Figure 2.18 illustrates the Pb phonon peak at ~ 13.5 meV. The peak at ~ 60 meV was attributed to the excitation of an optical phonon transverse modes (TO), and the peak at ~ 63.5 meV corresponded to the interaction of tunnelling electrons with optical phonon longitudinal modes (LO) and TO phonons. Peaks at ~ 52 meV were attributed to a Si–O–Si bending mode, and peaks at ~ 134 meV and 147 meV attributed to different Si–O stretching vibrations modes. Here, IETS on SIM tunnel junctions was limited to energy below 200 meV [107, 108].

The study of IETS SIM tunnel junctions has been reviewed in more detail in this chapter. Generally, only a few authors used SIM junctions to study IETS [109]. Salace and Petit studied the capability of the IETS technique applied to a SIM junction to detect molecular vibrations, such as $Si-H$ bonds [109], where molecular vibration spectra were observed on $Al / SiO_2 / Si$ tunnel junction at $4.2K$ (Fig.2.19).

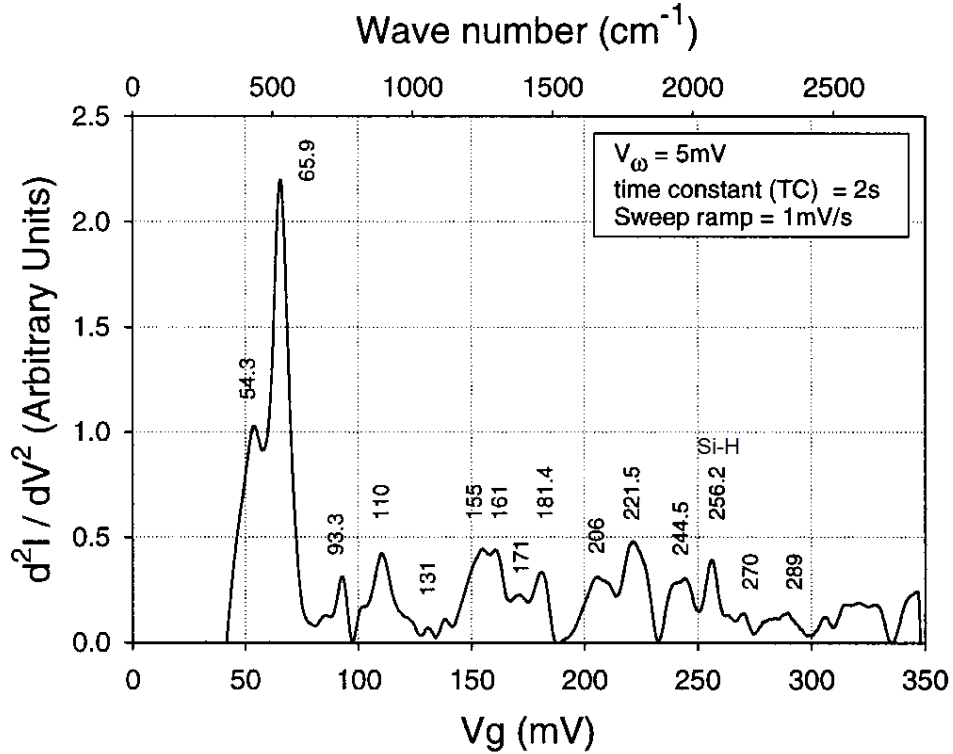


Figure 2.19: IETS spectra of $Al / SiO_2 / Si$ tunnel junction at $4.2K$ [110].

Here, the energy limit has extended up to $350 meV$. Therefore, $Si-H$ bond can be observed in IETS spectra at $\sim 256.2 meV$. The $Si-H$ peak was observed previously at $\sim 257 meV$ on a MIM tunnel junction device with SiO deposited on alumina [110].

Wang *et al.* [111] have reported the first IETS experiment on integrated metal - molecule - silicon (MMS) devices at $4.2K - 35K$. Here, molecules assembled directly to Si contacts in

$2 \times 2 \mu\text{m}^2$ to $11 \times 11 \mu\text{m}^2$ Si - molecule - Au devices (Fig.2.20).

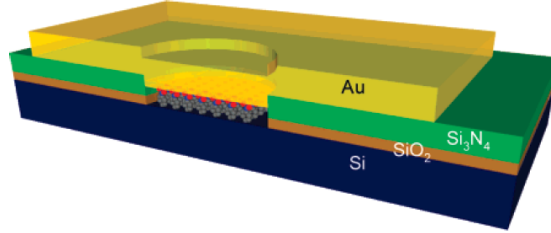


Figure 2.20: Schematic diagram of the integrated MMS device. The thickness of the SiO_2 and silicon nitride insulating layers are 50 and 200 nm, respectively. The well patterns have dimensions ranging from $2 \times 2 \mu\text{m}^2$ to $11 \times 11 \mu\text{m}^2$ [111].

Figure 2.21 illustrates the IETS spectra of Si / C18 / Au devices measured at various temperatures (4.2, 20, and 35K), showing the thermal broadening effect.

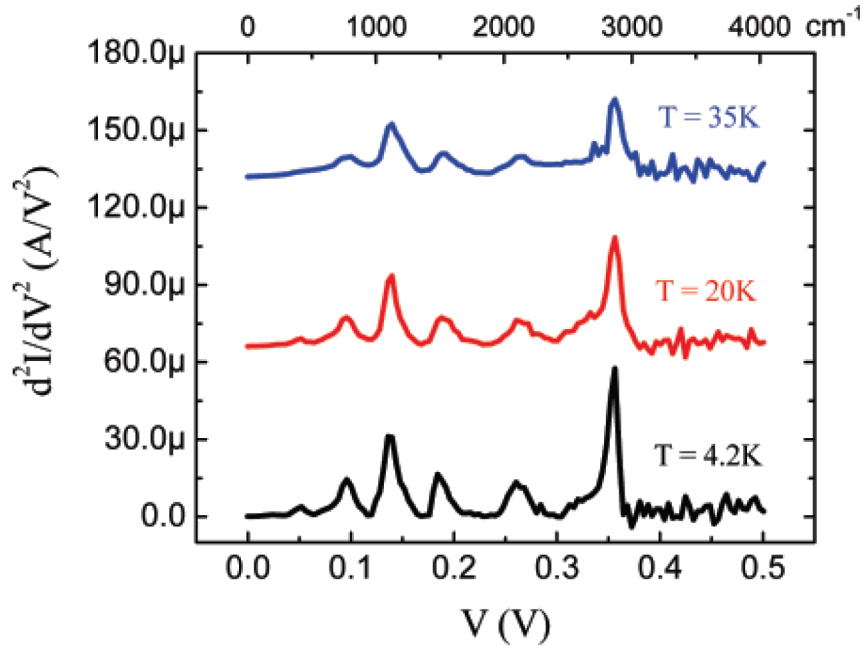


Figure 2.21: IETS spectra of the Si / C18 / Au device obtained at different temperatures (4.2, 20, and 35 K), showing the thermal broadening effect of the spectra lines [111].

2.3 Summary

This chapter provides an introduction to Inelastic Electron Tunnelling Spectroscopy (IETS), where the inelastic tunnelling of electrons is mediated by molecules vibrational states within the tunnel junction. IETS was first proposed and observed in 1966 by Jacklevic and Lambe [1–5]. They observed a new phenomenon during an experimental study of metal - insulator - metal (MIM) tunnel junctions. In this phenomenon, tunnelling electrons interacted with vibrational states of molecules adsorbed at a metal-oxide interface, and caused an increase in the conductance characteristics of the MIM tunnel junction at certain voltages ($eV = \hbar\omega$). Jacklevic and Lambe observed peaks in the d^2I/dV^2 vs. V characteristics at 4.2K. These peaks correspond to the vibrational frequencies of the molecules contained within the MIM tunnel junction [1].

Since then, other groups showed great interest in the studies of IETS using metal - insulator - metal (MIM) junctions. This chapter provides a literature review, surveying past and present work in the field of IETS. The basic theoretical background for quantum tunnelling, inelastic electron tunnelling, vibration (phonon) spectra of molecules and tunnel junction devices for IETS have been presented here. Then a review of recent work on highly nanoscale tunnel junction and molecular electric devices have been presented.

Chapter 3

Theory of Inelastic Electron Tunnelling Spectroscopy

This chapter provides an overview of the theoretical background for IETS. Initially, the chapter considers the transmission probability of elastic tunnelling for a single rectangular barrier, and for a barrier with arbitrary shape using the WKB approximation method. The elastic tunnelling current density is then considered and the elastic tunnelling current derived from the current density equation. Following this introduction to elastic tunnelling, the inelastic tunnelling transmission probability, and current density is studied considering three different interaction mechanisms: infrared dipole mechanism, bond polarizability of the molecule mechanism, and transfer Hamiltonian theory mechanism. This is followed by a study of IETS spectral line-widths, which are independent of the interaction mechanisms. Based on theoretical studies of IETS, the width of a spectral peak is comprised of two width-broadening effects, and a natural intrinsic line-width. Here, the two width-broadening effects are thermal broadening and modulation broadening.

Discussion of these effects is followed by derivations of the theoretical equations underpinning of the transport across Schottky Barriers (SBs). Three different carrier transport mechanisms (diffusion, thermionic emission, and quantum tunnelling) will be studied. Finally, the total IETS current for semiconductor - insulator - metal (SIM) tunnel junctions will be calculated, and studied in details.

3.1 Elastic Tunnelling

As discussed in the previous chapter, elastic tunnelling, where particles tunnel without a change in energy, is the basic mechanism for the quantum tunnelling of particles. In this section, the expression for the transmission probability in this process will be discussed in detail, for a single rectangular barrier, and for a barrier with an arbitrary shape. In the later case, the WKB approximation method will be reviewed. Following this, determination of the elastic current density will be discussed. Finally, the elastic tunnelling current will be derived from the current density equation.

3.1.1 Elastic Transmission Probability

The transmission probability in the elastic tunnelling process is used to describe the probability of a particle tunnelling through a potential barrier without a change in energy. The expression for the transmission probability in this process, differs depending on the shape of the potential barrier. Here, the transmission probability will be studied for a single rectangular barrier (Fig.3.1(a)), and for a barrier with an arbitrary shape using the WKB [112] approximation method (Fig.3.1(b)).

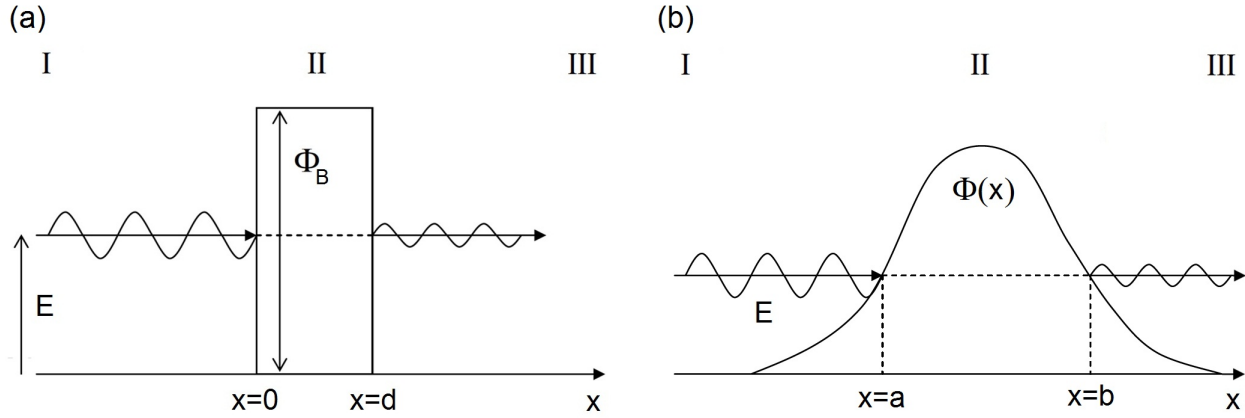


Figure 3.1: Schematic representation of tunnelling through (a) single rectangular barrier vs. (b) a barrier with an arbitrary shape.

Single Rectangular Barrier

To begin, we consider the simplest example of tunnelling, which is electron penetration through a one dimensional (1-D) single rectangular potential barrier (Fig.3.2) [31, 112]. Here, a single rectangle barrier with a height in energy of Φ_B and a width in space of d will be considered (Fig.3.2). When an electron with energy E is incoming from the left side of the barrier, this can quantum-mechanically tunnel through the barrier. Basic quantum mechanics allows the particle such as an electron to be mathematically defined by the wave function $\Psi(x, t)$, where x is position of the particle and t is time. While typically, Gaussian wave packets are used to define a particle, essential features of the tunnelling process may be derived using a travelling wave approximation.

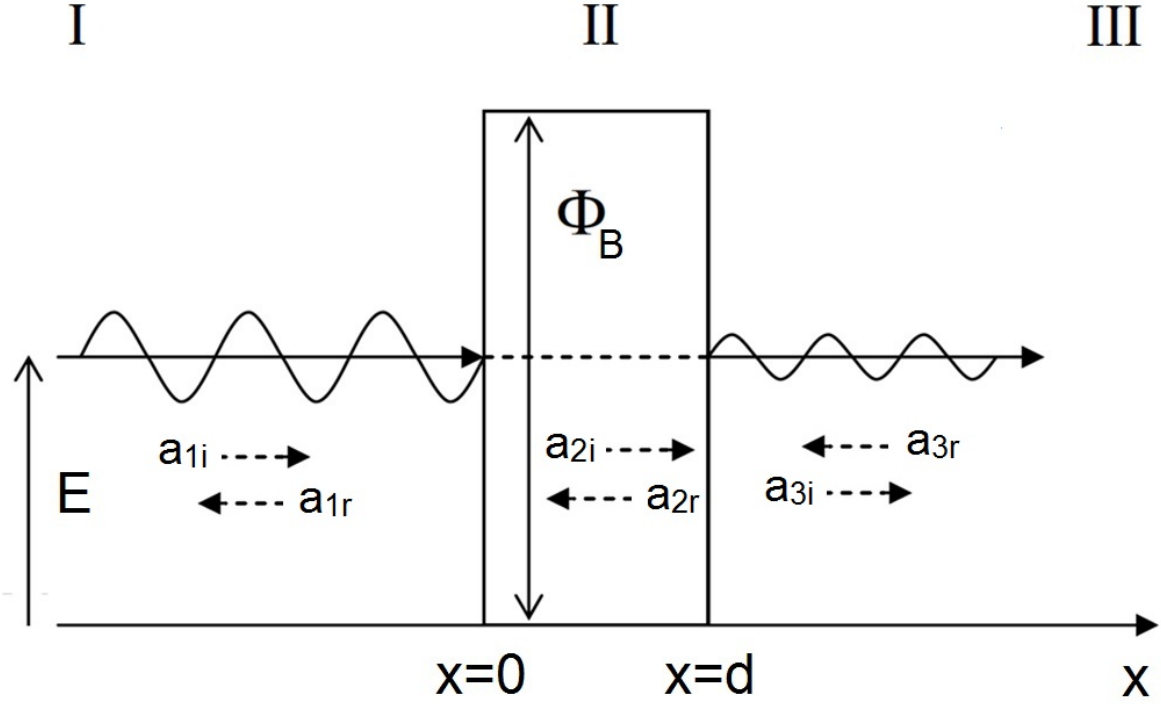


Figure 3.2: Schematic representation of tunnelling through a single rectangle barrier.

Here, we assume Ψ is a travelling wave with wave vector k and frequency ω :

$$\Psi(x, t) = A \exp i(kx - \omega t) \quad (3.1)$$

From Planck's formula [113], and the de Broglie hypothesis [114], the energy of a non-relativistic free particle with angular frequency $\omega = 2\pi\nu$ and reduced Planck's constant $\hbar$, in a region where potential energy is equal to zero ($U = 0V$), is defined with a kinetic energy equation:

$$\text{Kinetic Energy : } E = \frac{p^2}{2m} \implies E = \hbar\omega = \frac{\hbar^2 k^2}{2m} \quad (3.2)$$

where p is the momentum of the particle and m is the mass of the particle.

Furthermore, the energy of a particle with angular frequency ω and wave vector k in a region with potential energy (U), is defined as:

$$\text{Total energy} = \text{Kinetic energy} + \text{Potential energy}$$

Therefore:

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} + U \quad (3.3)$$

where $\hbar$ is the reduced Planck's constant, m is the mass of the particle, and U is the potential energy of the particle.

Taking the derivatives of the wave function $\Psi(x, t)$ from (Eq.3.1):

$$\begin{cases} \frac{\partial \Psi(x, t)}{\partial t} = -i\omega \Psi(x, t) \\ \frac{\partial^2 \Psi(x, t)}{\partial x^2} = -k^2 \Psi(x, t) \end{cases} \quad (3.4)$$

and relating it to the (Eq.3.3) shows the energy equation in another form.

By substituting the (Eq.3.4 $\times \Psi(x, t)$) in (Eq.3.3) the Schrödingers' equation becomes the 1-D, time dependent Schrödingers' equation [115]:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + U \Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t} \quad (3.5)$$

where $\Psi(x, t)$ is the wave function at position x and time t , $\hbar$ is the plank constant, m is the mass of the particle and U is the potential energy of the particle. The time independent

1-D Schrödingers' equation may be solved based on the specific boundary conditions. For tunnelling through a single rectangular barrier (Fig.3.2), The potential energy is given by:

$$\begin{cases} U(x) = \Phi_B, & 0 < x \leq d \\ U(x) = 0, & x < 0 \text{ and } x > d \end{cases} \quad (3.6)$$

Space dependent wave functions in regions I, II and III are different based on the specific boundary conditions (Fig.3.2).

In region I the space dependent wave function consists of the incident wave travelling from the left and the reflected wave travelling from the right:

$$\begin{aligned} \Psi_1 &= a_{1i} \exp(ik_1x) + a_{1r} \exp(-ik_1x) \\ &= \exp(ik_1x) + r \exp(-ik_1x) \end{aligned} \quad (3.7)$$

Here, a_{1i} is related to the incoming particle from left and may be taken as equal to one and a_{1r} is related to the reflecting particle and is equal to the amplitude reflection coefficient r , which is a complex number. The wave vector k_1 is related to the energy as $k_1 = \sqrt{\frac{2m_1E}{\hbar^2}}$.

In region II the space dependent wave function consists of the transmitted wave and the reflected wave:

$$\Psi_2 = a_{2i} \exp(ik_2x) + a_{2r} \exp(-ik_2x) \quad (3.8)$$

Here, a_{2i} is related to the transmitted particle from left and a_{2r} is related to the reflected particle. The wave vector k_2 is related to the energy and potential barrier as

$$k_2 = \sqrt{\frac{2m_2(\Phi_B - E)}{\hbar^2}}.$$

In region III, the space-dependent wave function is the transmitted wave:

$$\Psi_3 = a_{3i} \exp(ik_3x) + a_{3r} \exp(-ik_3x) \quad (3.9)$$

Here, we assumed that same material is used in region I and III, therefore $k_1 = k_3$. We also considered that the wave is incident from the left side of the potential barrier and also assumed that there is no wave from the right hand side of the barrier, therefore a_{3i} is the transmitted coefficient and $a_{3r} = 0$. The wave vector k_1 is related to the energy as

$$k_1 = \sqrt{\frac{2m_3E}{\hbar^2}}.$$

For tunnelling through a single rectangular barrier (Fig.3.2), boundary conditions are applied at $x = 0$ and $x = d$. Here, the two boundary conditions that are applied at $x = 0$ are

$$(1) \Psi_1 = \Psi_2 \text{ and } (2) \frac{1}{m_1} \frac{d\Psi_1}{dx} = \frac{1}{m_2} \frac{d\Psi_2}{dx}.$$

The first boundary condition at $x = 0$ for $m_1 = m_2$ is:

$$(1) \Psi_1 = \Psi_2 \longrightarrow 1 + r = a_{2i} + a_{2r} \quad (3.10)$$

The second boundary condition at $x = 0$ is:

$$(2) \frac{d\Psi_1}{dx} = \frac{d\Psi_2}{dx} \longrightarrow k_1(1 - r) = k_2(a_{2i} - a_{2r}) \quad (3.11)$$

where k_1 and k_2 are wave vectors in regions I and II respectively.

Similar boundary conditions as $x = 0$ are applied at $x = d$, i.e. (1) $\Psi_2 = \Psi_3$ and

$$(2) \frac{1}{m_2} \frac{d\Psi_2}{dx} = \frac{1}{m_3} \frac{d\Psi_3}{dx}.$$

The first boundary condition at $x = d$ for $m_2 = m_3$, based on $\Psi_2 = \Psi_3$ is:

$$(1) a_{2i}e^{ik_2d} + a_{2r}e^{-ik_2d} = a_{3i}e^{ik_1d} = t \quad (3.12)$$

The second boundary condition at $x = d$ is:

$$(2) k_2(a_{2i}e^{ik_2d} - a_{2r}e^{-ik_2d}) = k_1t \quad (3.13)$$

Solving (Eqs. 3.10 - 13) simultaneously, allows the amplitude transmission coefficient t to be calculated as below:

$$t = \frac{4k_1k_2}{(k_1 + k_2)^2 e^{-ik_2d} - (k_1 - k_2)^2 e^{ik_2d}} \quad (3.14)$$

where k_1 and k_2 are wave vectors in regions I and II respectively. This equation (Eq. 3.14)

allows us to calculate the transmission coefficient for intensity [116]:

$$T = |t|^2 = \frac{4k_1^2 k_2^2}{(k_1^2 + k_2^2)^2 \sinh^2 k_2 d + 4k_1^2 k_2^2} \quad (3.15)$$

where k_1 is the wave vector at regions I and III, and k_2 is the wave vector at region II as above.

The reflection coefficient for intensity [116] can also be calculated as:

$$R = 1 - T = \frac{(k_1^2 + k_2^2)^2 \sinh^2 k_2 d}{(k_1^2 + k_2^2)^2 \sinh^2 k_2 d + 4k_1^2 k_2^2} \quad (3.16)$$

The transmission coefficient $T \neq 0$ (Eq.3.15), indicates that the electron can tunnel through a potential barrier which $\Phi_B > E$. If we assume $k_2 d \gg 1$, then $\sinh(k_2 d) \approx \frac{1}{2}e^{k_2 d} \gg 1$, and the transmission coefficient T can be approximated as [33]:

$$T \approx e^{-2k_2 d} = \exp\left[\frac{-2d}{\hbar} \sqrt{2m(\Phi_B - E)}\right] \quad (3.17)$$

For a barrier with small d , the transmission probability decreases exponentially with the increase in barrier thickness and the square root of the barrier height. The transmission probability coefficient is then plotted versus energy for a single rectangular barrier (Fig.3.3).

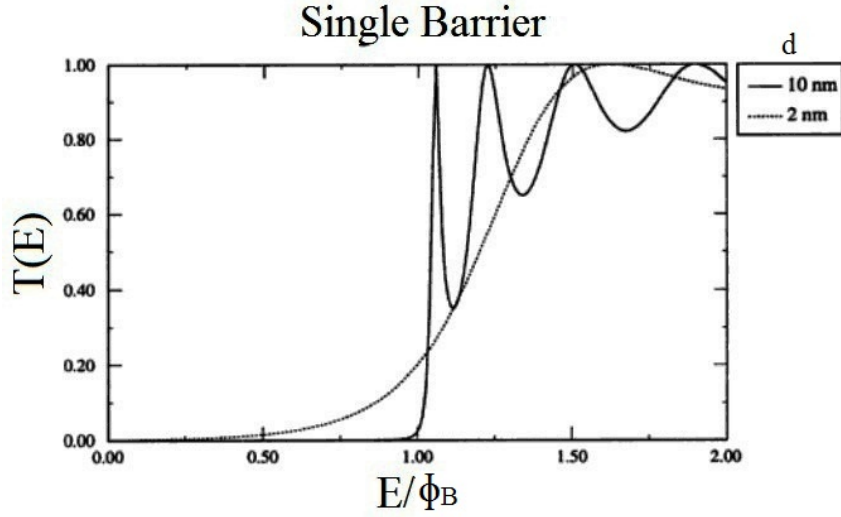


Figure 3.3: *Transmission coefficient vs. energy for a simple symmetric single rectangular barrier for two barrier widths [35].*

Here, as the energy difference below the barrier increases, the transmission probability decay strongly. For the energies above the barrier height, as energy E becomes larger, the transmission coefficient is oscillatory approaching unity [35].

Barrier with Arbitrary Shape (WKB Method)

Finding the tunnelling transmission coefficient for a barrier with an arbitrary shape is more complicated. Wentzel, Kramers, and Brillouin proposed a method (WKB method) for finding approximate solutions to linear partial differential equations with varying coefficients such as Schrödingers' equation [112]. For a potential barrier of $U = \Phi(x)$, which changes slowly with x (Fig.3.4), the Schrödingers' equation becomes:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + \Phi(x) \Psi = i\hbar \frac{\partial \Psi}{\partial t} \quad (3.18)$$

and according to the WKB method, the wave function solutions of the Schrödingers' equation can be approximated as a simple plane wave:

$$\Psi(x) = A \exp(ik(x)x) + B \exp(-ik(x)x), \quad \text{where } k(x) = \frac{2\pi}{\lambda(x)} = \sqrt{\frac{2m(E - \Phi(x))}{\hbar^2}} \quad (3.19)$$

Here, the wave vector $k(x)$ changes slowly with x and is related to the energy E as:

$$\begin{cases} k(x) = \sqrt{\frac{2m(E - \Phi(x))}{\hbar^2}} & \text{for } E > \Phi(x) \\ k(x) = -i\sqrt{\frac{2m(\Phi(x) - E)}{\hbar^2}} & \text{for } E < \Phi(x) \end{cases} \quad (3.20)$$

where E is the total particle energy, $\Phi(x)$ is the potential barrier energy, $\hbar$ is the reduced Planck's constant and m is the mass of the particle.

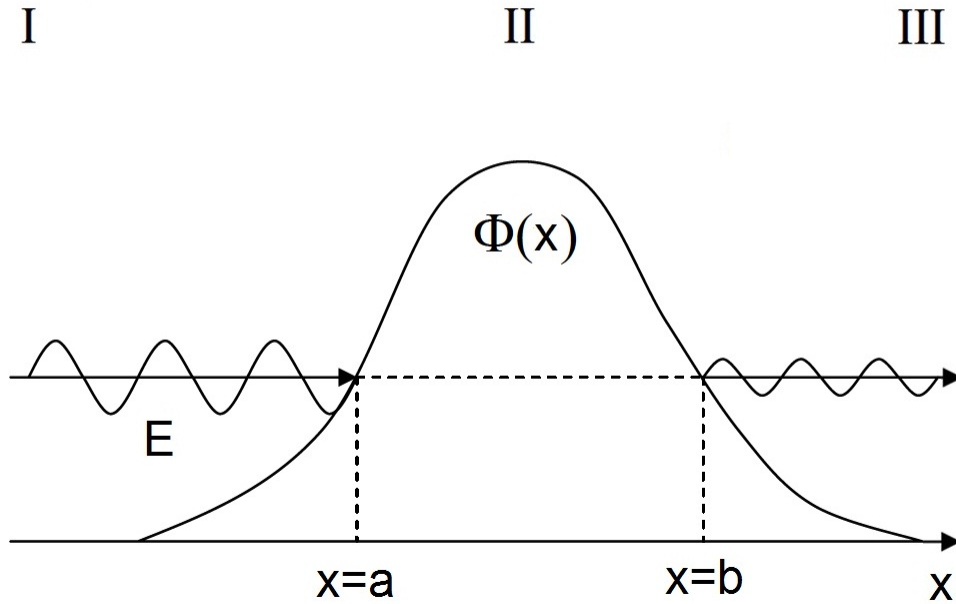


Figure 3.4: Schematic representation of tunnelling through a barrier with an arbitrary shape.

Hence, by taking $S(x) = \hbar k(x)$, the Schrödingers' equation becomes:

$$-\hbar^2 \frac{\partial^2 S}{\partial x^2} - \left(\frac{\partial S}{\partial x} \right)^2 + (k(x))^2 = 0 \quad (3.21)$$

where $k(x)$ is the wave vector. The WKB approximation assumes that the potentials are varying slowly. If this is the case, $k(x)$ is also slowly varying and so $S(x)$ is slowly varying. Thus, the 0^{th} order WKB approximation assumes that $\left(\frac{\partial^2 S}{\partial x^2} \approx 0 \right)$. Schrödingers' equation then becomes:

$$\left(\frac{\partial S}{\partial x} \right)^2 = (k(x))^2 \quad (3.22)$$

Therefore, by substituting the (Eq.3.20) in $S(x) = \hbar k(x)$ for the classically forbidden region ($E < \Phi(x)$), $S(x)$ is:

$$S(x) = \pm \int -i \sqrt{\frac{2m(\Phi(x) - E)}{\hbar^2}} dx + C_0 \quad (3.23)$$

where E is the total particle energy, $\Phi(x)$ is the potential barrier energy, $\hbar$ is the reduced Planck's constant and m is the mass of the particle. By substituting $S(x)$ in (Eq.3.20) the wave-function $\Psi(x)$ becomes:

$$\Psi(x) = e^{i(\pm \int -i \sqrt{\frac{2m(\Phi(x) - E)}{\hbar^2}} dx + C_0)} \quad (3.24)$$

Here, the transmission probability T for a barrier with an arbitrary shape $U = \Phi(x)$ has been expressed as:

$$T = \exp \left[\frac{-2}{\hbar} \int \sqrt{2m(U - E)} dx \right] \quad (3.25)$$

The reflection and transmission coefficients vs. energy can then be plotted as (Fig.3.5).

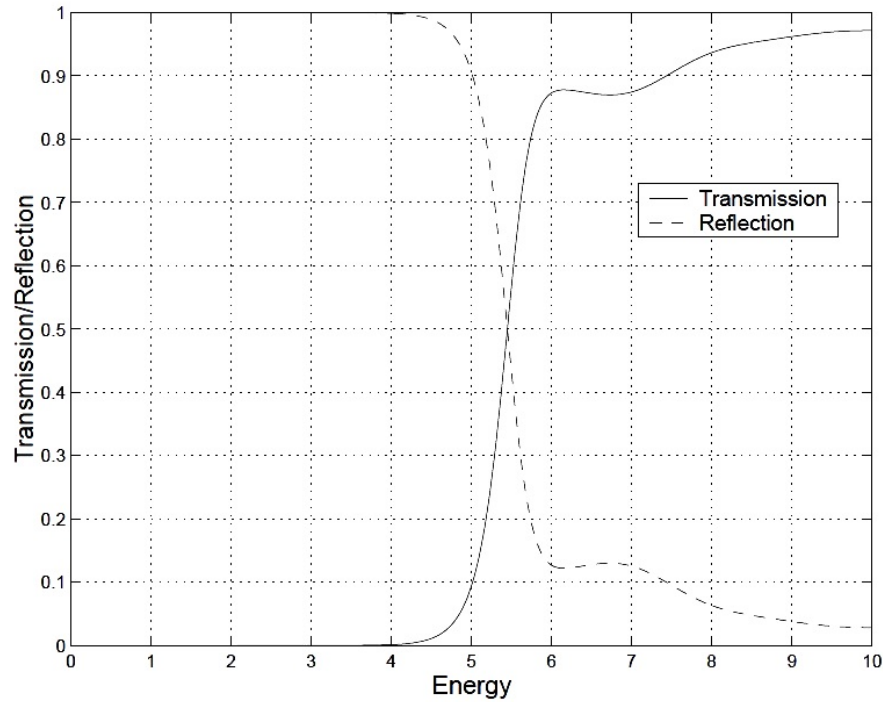


Figure 3.5: *Transmission and Reflection coefficients vs. energy for a single rectangular barrier [117].*

3.1.2 Elastic Tunnelling Current

As IETS usually has been studied on a metal - insulator - metal (MIM) tunnel junction, in this section we will derive the elastic tunnelling current density for such a tunnel junction. The elastic tunnelling current will then be calculated based on the elastic tunnelling current density.

To deduce the elastic tunnelling current density, a distribution function has to be introduced to include the occupancy of current-carrying states incident on, and transmitted through the barrier [35]. In this model, the contacts on the left and right sides of the barrier are assumed to be in equilibrium such that they can be described by the Fermi-Dirac distribution

function. Figure 3.6 illustrates the energy band diagram of a MIM junction with a rectangle barrier under bias V . The applied bias V separates the Fermi energy levels in the left and right hand side of electrodes by eV .

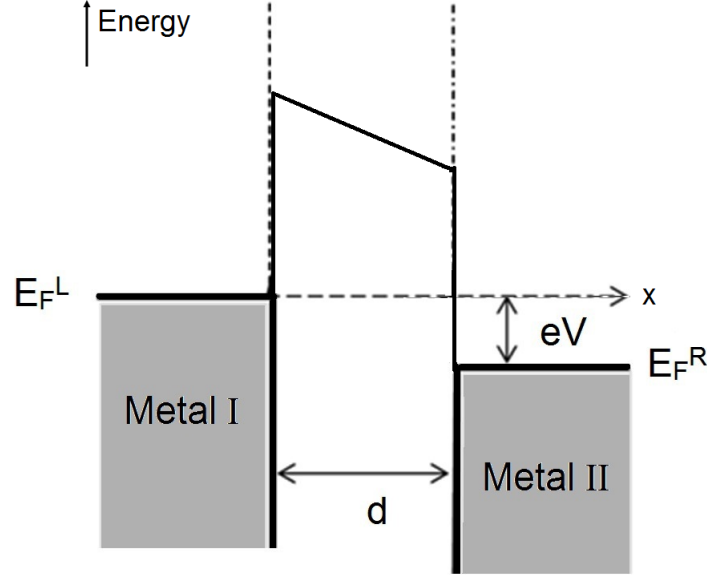


Figure 3.6: Band diagram for a MIM tunnel junction under bias V .

Here, the zero-reference of the potential energy in the system is Fermi level in the left metal, $E_F^L = 0$. The energy of a particle before tunnelling is [35, 118]:

$$E = E_x + E_\rho = \frac{\hbar^2 k_{x,L}^2}{2m^*} + \frac{\hbar^2 k_{\rho,L}^2}{2m^*} \quad (3.26)$$

where E is separable into longitudinal E_x (x-direction) and transverse E_ρ (y and z-directions) components and k_x and k_ρ are the longitudinal and transverse components of the wave vector ($k_\rho^2 = k_y^2 + k_z^2$). Here $\hbar$ is the reduced Planck's constant and m^* is the effective mass of the particle.

The energy of a particle after tunnelling is:

$$E = \frac{\hbar^2 k_{x,R}^2}{2m^*} + \frac{\hbar^2 k_{\rho,R}^2}{2m^*} + E_F^R \quad (3.27)$$

Here, E_F^R is the Fermi energy at the right hand side metal electrode.

During the tunnelling process, the transverse momentum is assumed to be conserved ($k_{\rho,L} = k_{\rho,R}$). Therefore, the transverse energy is equal on both sides ($E_{\rho,L} = E_{\rho,R}$) and the longitudinal energy is given by:

$$E_x = \frac{\hbar^2 k_{x,L}^2}{2m^*} = \frac{\hbar^2 k_{x,R}^2}{2m^*} + E_F^R \quad (3.28)$$

In this model, the incident current density on the barrier in an extremely small volume of momentum space $dk_{x,L}$ around $k_{x,L}$ is given by [35, 118]:

$$j_i = -eD(k_{x,L})f_L(E)(1 - f_R(E))\nu_x(k_{x,L})dk_{x,L} \quad (3.29)$$

where e is the elementary charge, $D(k_{x,L})$ is the density of states, f_L is the distribution function on the left contact and $\nu(k_L)$ is the velocity. Here, the density of states is $D(k_{x,L}) = \int_0^\infty \int_0^\infty D(k_{x,L}, k_{y,L}, k_{z,L}) dk_{y,L} dk_{z,L}$, where $D(k_{x,L}, k_{y,L}, k_{z,L})$ is the density of states for a 3-D system and is equal to $\frac{2}{(2\pi)^3}$. The velocity ν_x is perpendicular to the barrier from the left as $(\nu_x(k_{x,L}) = \frac{1}{\hbar} \frac{\partial E(k_{x,L})}{\partial k_{x,L}} = \frac{\hbar k_{x,L}}{m^*} = \frac{p_x}{m^*})$, and $\nu_x(k_{x,L})dk_{x,L} = \frac{1}{\hbar} dE_{x,L}$.

Using the (Eq.3.29), weighted by the transmission coefficient $T(E_{x,L})$, the tunnelling current

density from left to right is given by [33]:

$$j_{L \rightarrow R} = \frac{e}{4\pi^3\hbar} T(E_{x,L}) dE_{x,L} \int_0^\infty \int_0^\infty f_L(E) (1 - f_R(E)) dk_{y,L} dk_{z,L} \quad (3.30)$$

where $T(E_{x,L})$ is the transmission coefficient, and f_L is the distribution function on the left metal contact.

Similarly, the tunnelling current density from right to left is [33]:

$$j_{R \rightarrow L} = \frac{e}{4\pi^3\hbar} T(E_{x,R}) dE_{x,R} \int_0^\infty \int_0^\infty f_R(E) (1 - f_L(E)) dk_{y,R} dk_{z,R} \quad (3.31)$$

$T(k_{x,R})$ is the transmission coefficient, and f_R is the distribution function on the right metal contact.

Using polar coordinates for the transverse wave vector components (y,z), $k_\rho = \sqrt{k_y^2 + k_z^2}$ and $\theta = \arctan(\frac{k_y}{k_z})$, the current density (Eqs.3.31-32) becomes [118]:

$$j_{L \rightarrow R} = \frac{4\pi m^* e}{h^3} \int_{E_{min}}^{E_{max}} T(E_{x,L}) dE_{x,L} \int_0^\infty f_L(E) (1 - f_R(E)) dE_\rho \quad (3.32)$$

and

$$j_{R \rightarrow L} = \frac{4\pi m^* e}{h^3} \int_{E_{min}}^{E_{max}} T(E_{x,R}) dE_{x,R} \int_0^\infty f_R(E) (1 - f_L(E)) dE_\rho \quad (3.33)$$

The transmission coefficient is symmetric at a given energy E_x , therefore $T(E_{x,L}) = T(E_{x,R})$.

Therefore, the net flow of the current through the barrier can be expressed as the difference

of the tunnelling current density from left to right and right to left [33]:

$$J = \frac{4\pi m^* e}{h^3} \int_{E_{min}}^{E_{max}} T(E_x) dE_x \int_0^\infty [f_L(E) - f_R(E)] dE_p \quad (3.34)$$

The 0th order WKB approximation assumes that, the distribution functions are given by the Fermi-Dirac distribution function:

$$f_{L,R}(E) = \frac{1}{1 + e^{(E - E_F^{L,R})/k_B T}} \quad (3.35)$$

where E is the total energy, $E_F^{L,R}$ is the Fermi energy of the left and right metal contact, k_B is the Boltzmann's constant, and T is the temperature. The difference between the two Fermi energies can be given as: $E_F^L - E_F^R = eV$.

The Tsu-Esaki formula [119] for calculating the elastic tunnelling current density is derived by substituting (Eq.3.35) in (Eq.3.34):

$$J_{elastic} = \frac{em^* k_B T}{2\pi^2 \hbar^3} \int_0^\infty dE_x T(E_x) \ln\left(\frac{1 + e^{(E_F^L - E_x)/k_B T}}{1 + e^{(E_F^L - eV - E_x)/k_B T}}\right) \quad (3.36)$$

Integrating the current density with respect to the cross-sectional area of the tunnelling channel A , yields the elastic tunnelling current as below:

$$I_{elastic}(V) = J_{elastic}(V) \times A \quad (3.37)$$

3.2 Inelastic Tunnelling

Inelastic tunnelling, where particles tunnel through the barrier with a change in energy, is the other basic mechanism for the quantum tunnelling of particles. In this section, three different interaction mechanisms for inelastic tunnelling will be studied: infrared selection rules mechanism, Raman selection rules mechanism, and transfer Hamiltonian theory mechanism.

The expression for the transmission probability will then be considered and the inelastic tunnelling current will be derived from current density equation. This will be followed by the study of IETS spectral line-width, which is independent of the interaction mechanisms. Based on theoretical studies of IETS, the width of a spectral peak is comprised of the natural intrinsic line-width, and two width-broadening effects. The two width-broadening effects, thermal broadening and modulation broadening, will also be discussed.

3.2.1 Inelastic Transmission Probability and Inelastic current

Initial models for inelastic electron tunnelling were proposed by Scalapino and Marcus in 1967 [41]. They studied the infrared dipole mechanism, in which vibrations can be detected if the dipole momentum p_z is changed in a molecule. Scalapino and Marcus, considered a situation where a small perturbing potential $U_{int}(z)$ is added to a rectangular barrier potential $U(z)$. U_{int} was assumed to be the interaction energy between the electron and a molecule with a dipole moment p_z , which was located near one of metal contacts in the junction. Here, the image dipole must also be included and yields an effective dipole moment

$2p_z$ in the $\vec{z}$ direction [120] (Fig.3.7):

$$U_{int} = \frac{2ep_z\vec{z}}{(\vec{z}^2 + r_{\perp}^2)^{3/2}} \quad (3.38)$$

where $\vec{z}$ and $r_{\perp}$ are the perpendicular and parallel direction to the surface of MIM junction ($r_{\perp} = \sqrt{x^2 + y^2}$).

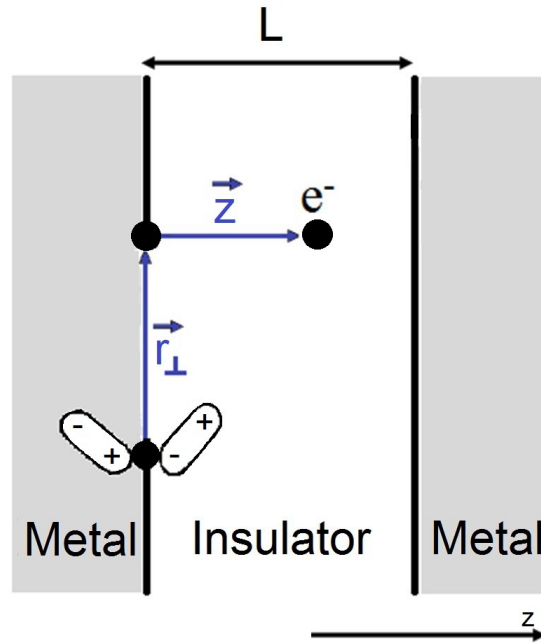


Figure 3.7: Schematic diagram showing Scalapino and Marcus interaction mechanism.

They also assumed:

$$U_z - (E - E_{\perp}) = \Phi \quad (3.39)$$

Here, U_z is the barrier potential, E is the total electron energy, $E_{\perp}$ is the kinetic energy associated with the component of motion parallel to the barrier, and Φ is the maximum barrier height.

In this case, the transmission probability can be approximated as [120]:

$$T = [(\frac{2m^*}{\Phi})^{\frac{1}{2}} \frac{ep_z}{\hbar L} g(\frac{r_{\perp}}{L}) + 1] \exp[-(\frac{2m\Phi}{\hbar^2})^{\frac{1}{2}} L] \quad (3.40)$$

where m^* is the mass of the particle, Φ is the maximum barrier height, e is the elementary charge, $\hbar$ is the reduced Planck's constant, L is the thickness of barrier, and $g(x) = \frac{1}{x} - \frac{1}{\sqrt{(1+x^2)}}$. Here, the first term in the brackets in (Eq.3.41) leads to the inelastic tunnelling probability and the second term leads to the elastic transmission probability as in (Eq.3.27).

Scalapino and Marcus then considered a simple molecule with a single vibrational frequency ω_0 . The energy needed to excite the molecule from the ground state to its first excited vibrational state is then $\hbar\omega_0$ and the inelastic current can be calculated as:

$$\begin{aligned} I_{inelastic}(\omega_0, V) &= (\frac{dj}{dV})_0 [\frac{4\pi me}{\hbar^2 \Phi}] \ln|\frac{L}{r_0}| \quad [|\langle 1|p_z|0 \rangle|^2] \quad (3.41) \\ &\times \int_{-\infty}^{\infty} dE f(E) [1 - f(E + eV - \hbar\omega_0)] \\ &\times N_1(E) N_2(E + eV - \hbar\omega_0) \end{aligned}$$

Here, N_1 and N_2 are effective tunnelling densities of states which are equal to unity for normal metals, $f(E)$ is the Fermi function, $[|\langle 1|p_z|0 \rangle|^2]$ is the dipole matrix for the vibrational

transition from the ground state to its first excited vibrational state. Here, $2\pi L^2 \ln(\frac{L}{r_0})$ term results from the integration of $g(\frac{r_\perp}{L})$ term over an area extending from radius r_0 to radius L . For $r_\perp > L$, g^2 is small. This represents an effective cross section for tunnelling [120]. Here, $(\frac{dj}{dV})_0$ is the elastic conductance per unit area for a normal junction [120, 121]:

$$(\frac{dj}{dV})_0 = \frac{e(\frac{2m(U_z - E_z)}{\hbar^2})^{1/2}}{4\pi^2 L \hbar} \exp(T_{elastic}) \quad (3.42)$$

where $T_{elastic}$ is as (Eq.3.27).

To represent a real excitation spectrum, the total inelastic current due to N molecules will be calculated from summing the above expression as below:

$$I_{inelastic}(V) = N(\frac{dj}{dV})_0 [\frac{4\pi me}{\hbar^2 \Phi}] \ln|\frac{L}{r_0}| [\Sigma_\nu | < \nu | p_z | 0 > |^2] \quad (3.43)$$

$$\times \int_{-\infty}^{\infty} dE f(E) [1 - f(E + eV - \hbar\omega_\nu)]$$

$$\times N_1(E) N_2(E + eV - \hbar\omega_\nu)$$

dI/dV can then be calculated as:

$$\frac{dI}{dV} = N(\frac{dj}{dV})_0 [\frac{4\pi me}{\hbar^2 \Phi}] \ln|\frac{L}{r_0}| [\Sigma_\nu | < \nu | p_z | 0 > |^2] S_\nu(eV) \quad (3.44)$$

Here, S_ν is a unit step at $eV = \hbar\omega_\nu$.

The d^2I/dV^2 can be calculated as:

$$\left(\frac{d^2I}{dV^2}\right) = N\left(\frac{dj}{dV}\right)_0 \left[\frac{4\pi me}{\hbar^2\Phi}\right] \ln\left|\frac{L}{r_0}\right| \left[|\Sigma_\nu| < \nu|p_z|0 >|^2\right] \delta_\nu(eV - \hbar\omega_\nu) \quad (3.45)$$

where $\delta_\nu(eV - \hbar\omega_\nu)$ is a Dirac delta function. Here, the last term in the bracket of the d^2I/dV^2 ($|\Sigma_\nu| < \nu|p_z|0 >|^2 \delta_\nu(eV - \hbar\omega_\nu)$), corresponds to the infrared absorption spectrum. Scalapino and Marcus used (Eq.3.44) to estimate the size of such effects for a coverage of one molecule per $10 \text{ \AA}^2$. Here, a value for $|\Sigma_\nu| < \nu|p_z|0 >|^2 \sim 3.3 \times 10^{-48} C^2 cm^2$ was used previously [120].

Scalapino and Marcus, studied the specific case of adsorption of H_2O in an Al / Al_2O_3 / Pb junction. They integrated (Eq.3.46) over voltage V to calculate the change in conductance for the $O - H$ bending mode with the energy $\hbar\omega_v \sim 0.11 \text{ eV}$, and the oscillator strength of the v^{th} band $f_v \sim 10^{-5}$. They assume $\frac{L}{r_0} = 30$, $\Phi = 2 \text{ eV}$, and $\sin^2\theta = \frac{1}{2}$ where θ is the angle between the $O - H$ dipole and normal to the junction surface.

$$\frac{dI}{dV} = N\left(\frac{dj}{dV}\right)_0 \left[\frac{4\pi me}{\hbar^2\Phi}\right] \ln\left|\frac{L}{r_0}\right| \frac{e^2 f_v}{2m\omega_v} A, \quad \text{where } A = \sin^2\theta \text{ (bending mode)} \quad (3.46)$$

Here, dI/dV shows that the conductance is increased by order of 1% [41, 120]. Therefore, if $|\Sigma_\nu| < \nu|p_z|0 >|^2$ is assumed to be equal to $3.3 \times 10^{-48} C^2 cm^2$, the conductance is increased by 1% [120]. They predicted that the intensities in a tunnelling spectrum should be the same as in an infrared spectrum. Furthermore, peaks that cannot be observed in IR spectra can be observed in the tunnelling spectra [33].

Jacklevic and Lambe studied another mechanism which extended the interaction mechanism to include the Raman active modes, in which vibration can be detected if the polarizability α is changed in a molecule [120]. Here, the interaction is based on the potential due to the bond polarizability of the molecule and not to a change in the dipole moment. The interaction energy in this case is:

$$U_{int} = \frac{-4e^2\alpha\vec{z}^2}{(\vec{z}^2 + r_{\perp}^2)^3} \quad (3.47)$$

where α is the molecular bond polarizability, e is the elementary charge, and $\vec{z}$ and $r_{\perp}$ are the perpendicular and parallel direction to the surface of MIM junction.

The transmission probability can be approximated as [120]:

$$T \sim [(\frac{2m}{\Phi})^{1/2} \frac{\alpha e^2}{4\hbar L^3} t(\frac{R_{\perp}}{L}) + 1] \exp[-(\frac{2m\Phi}{\hbar^2})^{1/2} L] \quad (3.48)$$

where $t(x) = \frac{1}{x^2}[\frac{1-x^2}{(1+x^2)^2} + \frac{1}{x}\tan^{-1}(\frac{1}{x})]$. Therefore, the inelastic current can be expressed as:

$$I_{inelastic}(V) = N(\frac{dj}{dV})_0 [\frac{4\pi m e^3}{\hbar^2 \Phi 16 L^6}] [\int_{r_0}^L t^2 r_{\perp} dr_{\perp}] [\Sigma_{\nu} | < \nu | \alpha | 0 > |^2] \quad (3.49)$$

$$\times \int_{-\infty}^{\infty} dE f(E) [1 - f(E + eV - \hbar\omega_{\nu})]$$

$$\times N_1(E) N_2(E + eV - \hbar\omega_{\nu})$$

Their calculation showed that the conduction steps due to Raman interaction are comparable with those from infrared active modes. Therefore, both Raman active and infrared active vibration modes can be observed in inelastic tunnelling spectra [120].

While the above approximations provided a clear understanding of the interaction mechanisms in IETS, the calculations used were somewhat over-simplified. Kirtley *et al.* proposed another method (KSH method) to study the interaction mechanism in IETS using the transfer Hamiltonian theory [33, 53]. They assume that these existing sets of partial charges, are localized on the atoms in the molecule. Therefore, the interaction potential between the tunnelling electron and the vibrating molecule (U_{int}) is the sum of the Coulomb potentials due to the partial charges:

$$U_{int} = -\sum_n \frac{e^2 Z_n}{|\bar{R}_n - \bar{r}|} \quad (3.50)$$

Here, $Z_n e$ is the partial charge related to the n^{th} atom and $\bar{R}_n$ is the n^{th} atom position in the molecule. They used the image charge in the nearest metal surface as in Scalapino and Marcus' model and also included the image in the farther metal surface [53], yielding:

$$U_{int} = \sum_{p=-\infty}^{\infty} \sum_n \frac{-e}{\varepsilon} \bar{\mu}_n^k \cdot \nabla_n \left[\frac{1}{|\bar{r} - \bar{R}_n - 2pL\hat{z}|} - \frac{1}{|\bar{r} - \bar{R}_n - (2pL - 2\alpha_n)\hat{z}|} \right] \quad (3.51)$$

where the local dipole is $\bar{\mu}_n^k = e Z_n^k \delta \bar{R}_n^k$, the barrier distance is L , the width of the n^{th} atom from a metal surface is a_n , and ε is the dielectric constant [53].

The calculation of inelastic tunnelling probability and inelastic current for this model is

complex [121] and will not be reproduced here. The results predicted by the KSH method are consistent with those from the Scalapino and Marcus model, when the molecules are relatively close to one metal surface. They showed that vibrations with net dipole moments normal to the surface should couple more strongly with the tunnelling electrons than those with net dipole moments parallel to the surface. However, this is no longer true for dipoles deep within the tunnelling barrier [53]. The KSH method also relaxes the intensity preferences of theory of the Scalapino and Marcus. The Scalapino and Marcus theory only allowed vibrational modes with net oscillating dipole moments or infrared active modes [53].

3.2.2 Spectral Line-Widths

The study of spectral line-widths is independent of the details of the interaction mechanisms discussed in Section 3.2.1. Based on theoretical studies of IETS, the line-width of a spectral peak is comprised of a natural intrinsic line-width, and two width-broadening effects. The two width-broadening effects are thermal-broadening and modulation-broadening, where the former is due to the Fermi level smearing effect and the latter is due to the dynamic detection techniques typically used to obtain the second harmonic signals [33]. These two broadenings will be discussed in detail in the following.

Thermal Broadening

The thermal broadening effect was first proposed by Jacklevic and Lambe [120]. They studied IETS in a MIM junction with metals in normal states at finite temperature. Therefore the inelastic tunnelling current expression as (Eq.3.50) can be simplified by taking the density

of states N_1 and N_2 as unity [122]:

$$I_{inelastic}(\nu) = C \int_{-\infty}^{\infty} dE \left(\frac{1}{1 + e^{\frac{E}{k_B T}}} \right) \left(1 - \frac{1}{1 + e^{\frac{[E + e(V - U_\nu)]}{k_B T}}} \right) \quad (3.52)$$

where C contains all the tunnelling parameters independent of energy E and temperature T . Here, $U_\nu = \frac{\hbar\omega_\nu}{e}$. Therefore, a simplified expression for the inelastic electron tunnelling current is:

$$I_{inelastic}(\nu) = C e(V - U_\nu) \frac{\exp\left(\frac{e(V - U_\nu)}{k_B T}\right)}{\exp\left(\frac{e(V - U_\nu)}{k_B T}\right) - 1} \quad (3.53)$$

By taking derivatives of the inelastic electron tunnelling current vs. voltage, $d^2 I_i / dV^2$ can be expressed as:

$$\frac{d^2 I_{inelastic}(\nu)}{dV^2} = C \frac{e^2}{k_B T} \left[e^\alpha \frac{(\alpha - 2)e^\alpha + (\alpha + 2)}{(e^\alpha - 1)^3} \right], \quad \text{where } \alpha = \frac{e(V - U_\nu)}{k_B T} \quad (3.54)$$

The $\frac{1}{e^2} \frac{d^2 I_{inelastic}(\nu)}{dV^2}$ function is plotted in Fig.3.8. As illustrated in Fig.3.8., the maximum value of the thermal function is $\frac{1}{6k_B T}$. Therefore, the half of maximum value is $\sim 0.084k_B T$. By substituting this value into (Eq.3.55) and solving the equation for V , the $\pm V$ values at half maxima would be $\hbar\omega = \pm 2.7k_B T$. Thus the full line-width of the thermal function at half maximum is $V_+ - V_- = 5.4k_B T$ [33].

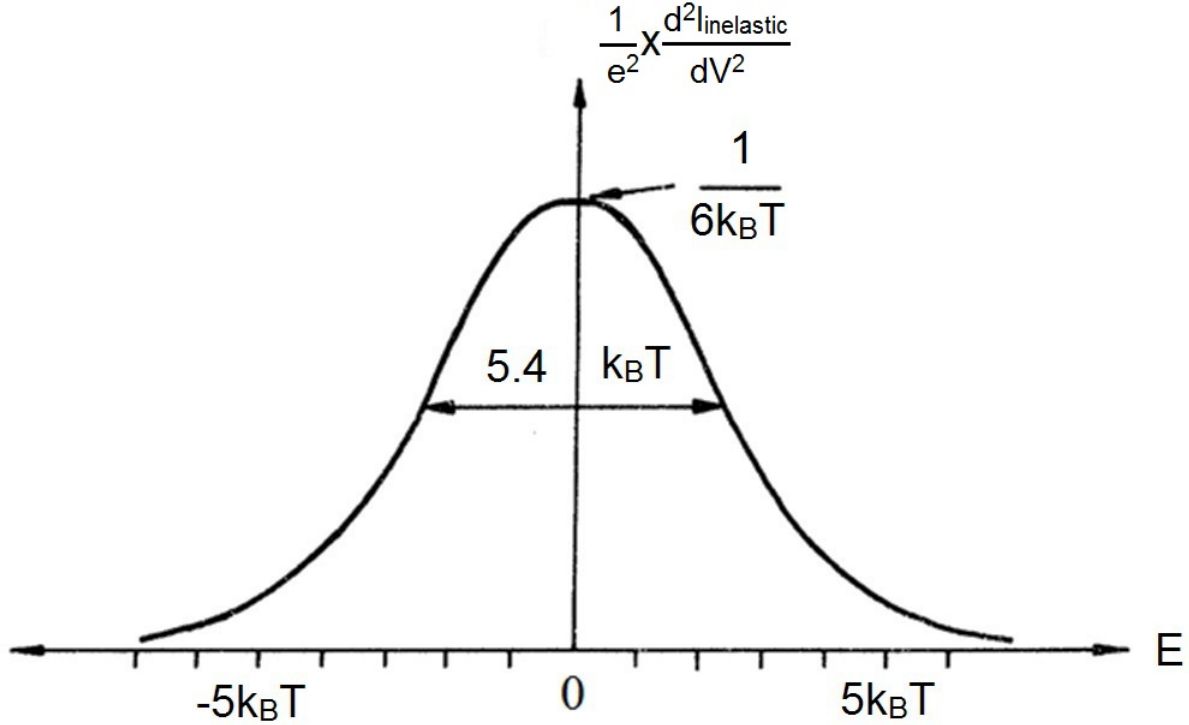


Figure 3.8: Theoretical broadening of the IETS lines due to the thermal broadening effect [33].

Finite-Modulation Technique Broadening

The earliest study of the broadening effect caused by the finite modulation technique was proposed by Klein *et al.* [43]. Finite modulation technique is typically used to detect a second derivative of inelastic tunnelling current $d^2 I_{inelastic}/dV^2$. Klein *et al.* assumed a current as a function of time:

$$I(\omega) = f(eV_0 + eV_\omega \cos(\omega t)) \quad (3.55)$$

In this function, V_0 is the bias voltage, eV_ω is the modulation amplitude at frequency ω and $I = f(eV)$ is the junction characteristic. Therefore, the current at the second harmonic

frequency is (where τ is the period) [33, 43]:

$$I_{2\omega} = \frac{2}{\tau} \int f(eV_0 + eV_\omega \cos(\omega t)) \cos(2\omega t) dt \quad (3.56)$$

and the second derivative is calculated as:

$$\frac{\pi}{2} V_\omega^2 I_{2\omega} = \int_{-eV_\omega}^{eV_\omega} f''(eV_0 + E) \frac{(e^2 V_\omega^2 - E^2)^{3/2}}{3} dE \quad (3.57)$$

where $f''(eV)$ is the exact second derivative and $E = eV_\omega \cos(\omega t)$.

It then appears that the second derivative obtained from experiments called $F''(eV)$, is different from the calculated second derivative $f''(eV)$. The experimental second derivative is:

$$F'' = \left(\frac{4}{V_\omega^2}\right) I_{2\omega} \quad (3.58)$$

which is a convolution product of the exact second derivative $f''(eV) = \frac{d^2 I}{d(eV)^2}$ and an instrumental function Φ :

$$F'' = f'' \times \Phi \quad (3.59)$$

Here the instrumental function Φ is:

$$\begin{cases} \Phi(E) = \frac{8}{3\pi} \frac{1}{(eV_\omega)^4} (e^2 V_\omega^2 - E^2)^{3/2}, & \text{for } |E| < eV_\omega \\ \Phi(E) = 0, & \text{for } |E| > eV_\omega \end{cases} \quad (3.60)$$

where eV_ω is the modulation amplitude at frequency ω and E is the energy. Figure 3.9 illustrates the instrumental function, where the half-width of the instrumental function is $1.22V_\omega$.

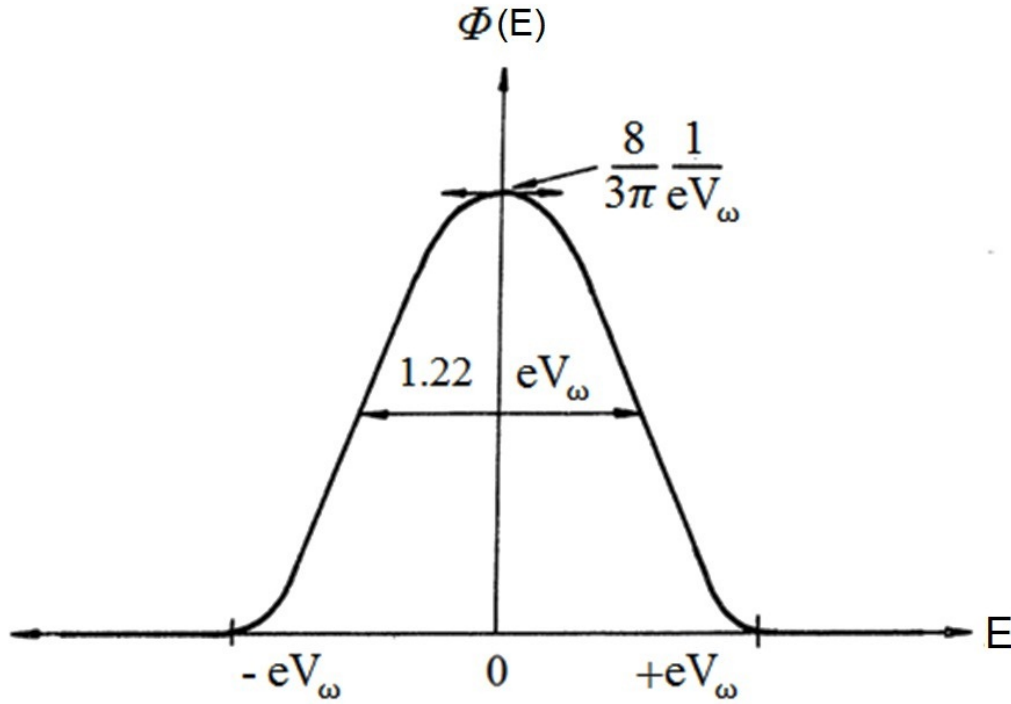


Figure 3.9: *Theoretical broadening of the IETS lines due to the finite modulation technique [33].*

The experimental broadening of the lines due to the finite modulation technique can have more influence than the thermal broadening effect [33, 74]. This is because the thermal broadening effect can be reduced by lowering the measurement temperature. In order to make the modulation broadening comparable to the thermal effect, the modulation voltage should be less than 1.18 mV . To summarize, the spectral line-width consists of three broadening effects: the natural intrinsic line-width W_{Natural} , the thermal broadening W_{Thermal} which is proportional to $5.4k_B T$, and the modulation broadening $W_{\text{Modulation}}$ which is proportional

to $1.22V_w$. Therefore, the total spectral line-width is [33, 120]:

$$W_{total} = \sqrt{W_{Natural}^2 + W_{Thermal}^2 + W_{Modulation}^2} \quad (3.61)$$

3.3 Carrier Transport Across Schottky Barrier

In this thesis, IETS measurements are extended to Metal - Insulator - Semiconductor (MIS) tunnel junctions. As the metal - semiconductor junction can form a potential barrier called Schottky Barrier (SB), it is essential to study the carrier transport mechanisms across SBs. In this section, the different current transport mechanisms across SBs will be studied, and the expression for the SBs current density will be calculated.

The current across a SB is mainly due to majority carriers, electron for n -type semiconductors and holes for p -type semiconductors [123]. In the following discussions, an n -type semiconductor isolated from a nearby metal with a larger work function is considered (Fig.3.10(a)) [12]. In this situation, the difference in Fermi levels is notable. The metal work function is Φ_m and the electron affinity in the semiconductor is χ_s . We also assume that Φ_m is greater than the work function in the semiconductor, $\chi_s + \xi$, such that electron travels from the semiconductor to the metal. When the metal and semiconductor contacts are brought together, as Fig.3.10(b), this forces the Fermi levels into coincidence by transfer of electrons across the interface. This modification of carrier density in proximity to the interface is then reflected in bending of the conduction and valence band edges upward, forming the “Schottky” potential barrier Φ_B [12].

Three different carrier transport mechanisms exist for an electron to be transported across this SB [12]:

- (1) Diffusion of carriers from the semiconductors into the metal.
- (2) Emission of carriers across the potential barrier from the semiconductor into the metal.
- (3) Quantum tunnelling through the barrier.

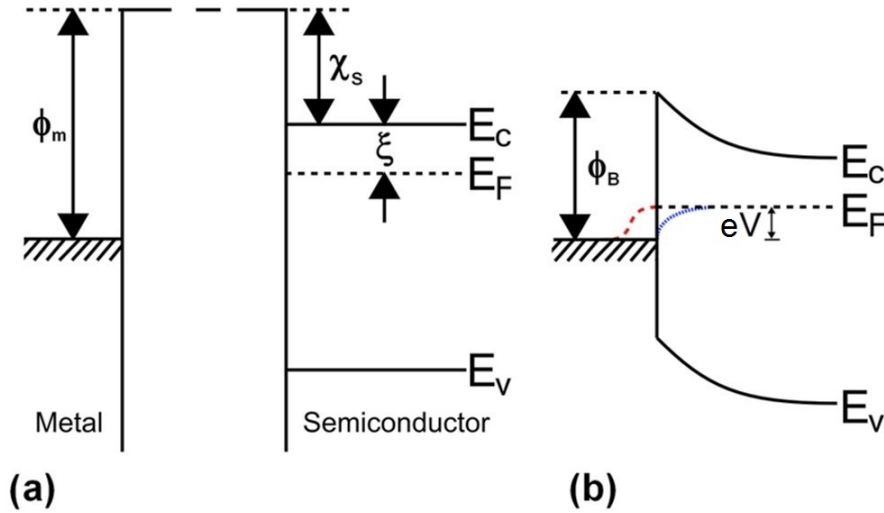


Figure 3.10: (a) Isolated metal and semiconductor regions. (b) Metal and semiconductor regions in perfect contact under bias. (Electron quasi-Fermi level according to diffusion theory (blue) and thermionic-emission theory (red)) [12].

In a given junction, a combination of all three mechanisms could exist. However, only one current mechanism dominates. Here at room temperature, emission over the barrier represents the most likely mechanism to dominate the conduction characteristics. Quantum tunnelling is small in comparison to emission and is not likely to dominate unless measured at low temperatures. Diffusion mechanisms rely on minority carrier and so will be significantly

less than the majority carrier emission [12, 124].

3.3.1 Diffusion Current

The diffusion current is due to the recombination of carrier particles (electron and holes) of a semiconductor. These move from a place with higher concentration to lower concentration. Therefore, the change in concentration of the carrier particles caused a current flow called diffusion current.

Diffusion theory shows that the current density can be expressed as [124, 125]:

$$J_n = \frac{eD_nN_c}{k_BT} \sqrt{\frac{2e(\Phi_i - V_a)N_d}{\varepsilon_s}} \exp\left(-\frac{e\Phi_B}{k_BT}\right) \left(\exp\left(\frac{eV_a}{k_BT}\right) - 1\right) \quad (3.62)$$

where e is the elementary charge, D_n is the diffusion constant, N_c and N_d are doping density, ε_s is the dielectric constant, Φ_B is a height of potential barrier, Φ_i is the built-in voltage and V_a is the applied voltage. Here, the electric field on the interface of the metal and semiconductor ε_{max} is:

$$\varepsilon_{max} = \sqrt{\frac{2e(\Phi_i - V_a)N_d}{\varepsilon_s}} \quad (3.63)$$

and as the current depends on the applied voltage (V_a), and on the height of potential barrier Φ_B , the expression for current density can be rewritten as:

$$J_n = e\mu N_c \varepsilon_{max} \exp\left(-\frac{e\Phi_B}{k_BT}\right) \left(\exp\left(\frac{eV}{k_BT}\right) - 1\right) \quad (3.64)$$

where μ represents the electron mobility.

3.3.2 Thermionic Emission

The thermionic emission current is due to transportation of electrons with energy larger than potential barrier height Φ_B , velocity v in the direction of barrier, across the interface from one material to the next. Therefore, the barrier shape has no influence and only the electrons with energy larger than $E_F + e\Phi_B$ are considered. The current density from the semiconductor to the metal ($J_{s \rightarrow m}$) is then the sum of these electrons multiplied by their velocity in the direction of transport (v_x) [12, 125]:

$$J_{s \rightarrow m} = \int_{E_F + e\Phi_B}^{\infty} e v_x dn(E) \quad (3.65)$$

where e is the elementary charge, v_x is the velocity in the direction of transport and $dn = G(E)F(E)dE$. Here, $G(E)$ is the density of states in the semiconductor conduction band and calculated as:

$$G(E) = \frac{4\pi(2m^*)^{3/2}}{h^3} \sqrt{E - E_c} \quad (3.66)$$

where m^* is the effective mass of electron, E is the total energy and E_c is the conduction band energy and $F(E)$ is the distribution of energy of the carriers (under the assumption that $E - E_F \gg k_B T$):

$$F(E) = \exp\left(-\frac{E - E_F}{k_B T}\right) \quad (3.67)$$

where E_F is the Fermi energy, k_B is the Boltzmann constant and T is the temperature. Here, dn has been calculated from combination of Eqs.(3.67) and (3.68):

$$dn = \frac{4\pi(2m^*)^{3/2}}{h^3} \sqrt{E - E_c} \exp\left(-\frac{E - E_F + e\xi}{k_B T}\right) dE \quad (3.68)$$

where ξ is the shift in Fermi level due to applied voltage.

The electrons in the conduction band have been assumed to only have kinetic energy:

$$E - E_c = \frac{1}{2}m^*v^2 \quad dE = m^*v dv \quad (3.69)$$

where m^* is the effective mass of electron and v is the velocity. Substituting (Eq.3.69) into (Eq.3.68) yields:

$$dn = 2\left(\frac{m^*}{h}\right)^3 \exp\left(-\frac{e\xi}{k_B T}\right) \exp\left(-\frac{m^*v^2}{2k_B T}\right) (4\pi v^2 dv) \quad (3.70)$$

Here, m^* is the effective mass of electron, e is the elementary charge, ξ is the shift in Fermi level due to applied voltage, k_B is the Boltzmann constant, T is the temperature, and v is the velocity. By using Cartesian instead of Spherical coordinates, $J_{s \rightarrow m}$ can be expressed as:

$$J_{s \rightarrow m} = 2e\left(\frac{m^*}{h}\right)^3 \exp\left(-\frac{e\xi}{k_B T}\right) \int_{v_{0x}}^{\infty} \exp\left(-\frac{m^*v_x^2}{2k_B T}\right) dv_x \quad (3.71)$$

$$\begin{aligned} & \int_{-\infty}^{\infty} \exp\left(-\frac{m^*v_y^2}{2k_B T}\right) dv_y \int_{-\infty}^{\infty} \exp\left(-\frac{m^*v_z^2}{2k_B T}\right) dv_z \\ &= \left(\frac{4\pi e m^* k_B^2}{h^3}\right)^2 T^2 \exp\left(-\frac{e\xi}{k_B T}\right) \exp\left(-\frac{m^*v_x^2}{2k_B T}\right) \end{aligned}$$

Here, an electron velocity to overcome the potential barrier height (Φ_B) is calculated as:

$$\frac{1}{2}m^*v_{0x}^2 = e(\Phi_B - \xi - V) \quad (3.72)$$

where e is the elementary charge, ξ is the semiconductor Fermi energy from the conduction band edge, and V is the applied voltage. This yields:

$$J_{s \rightarrow m} = \left(\frac{4\pi em^*k_B^2}{h^3} \right)^2 T^2 \exp\left(-\frac{e\Phi_B}{k_B T}\right) \exp\left(\frac{eV}{k_B T}\right) \quad (3.73)$$

The current density from the metal to the semiconductor ($J_{m \rightarrow s}$) has been calculated in the same manner. The only difference is that, on the metal side of the interface, the applied bias voltage does not affect the barrier height. Therefore, the bias voltage is assumed to be $V = 0V$ and the current density from the metal to the semiconductor ($J_{m \rightarrow s}$) can be expressed as:

$$J_{m \rightarrow s} = -\left(\frac{4\pi em^*k_B^2}{h^3} \right)^2 T^2 \exp\left(-\frac{e\Phi_B}{k_B T}\right) \quad (3.74)$$

where m^* is the effective mass of electron, e is the elementary charge, k_B is the Boltzmann constant, T is the temperature, and Φ_B is the potential barrier height. The total current density is then the sum of the current density from the semiconductor to the metal ($J_{s \rightarrow m}$) and the current density from the metal to the semiconductor ($J_{m \rightarrow s}$) (Richardson's Equation):

$$J = A^* T^2 \exp\left(-\frac{e\Phi_B}{k_B T}\right) \left(\exp\left(\frac{eV}{k_B T}\right) - 1 \right) \quad (3.75)$$

where A^* is the effective Richardson coefficient ($A^* = \frac{4\pi em^* k_B^2}{h^3}$), T is the temperature, e is the elementary charge, k_B is the Boltzmann constant, Φ_B is the potential barrier height, and V is the applied voltage.

3.3.3 Quantum Tunnelling

The quantum tunnelling current is due to the wave-particle duality of electrons. The quantum tunnelling current density is the electron charge multiplied by their velocity v_R (called Richardson velocity), the carrier's density n , and the tunnelling transmission probability T_P . Therefore, the quantum tunnelling current density can be expressed as [124]:

$$J_n = ev_R n T_P, \quad v_R = \sqrt{\frac{k_B T}{2\pi m^*}} \quad (3.76)$$

Here, the tunnelling transmission probability T_P can be calculated by using the time independent Schrödingers' equation [126]:

$$\frac{\hbar^2}{2m^*} \frac{\partial^2 \Psi}{\partial x^2} + U(x) \Psi = E \Psi \quad (3.77)$$

Here $\Psi(x, t)$ is the wave function at position x and time t , $\hbar$ is the reduced Planck's constant, m^* is the effective mass of the particle, E is the energy of the particle, and U is the potential energy of the barrier. This equation can be solved using WKB approximation method as we

discussed earlier in section [(3.1.1) - Barrier with Arbitrary Shape]:

$$\Psi(x + dx) = \Psi(x) \exp(-ikdx), \quad \text{where } k = \frac{2\pi}{\lambda} = \sqrt{\frac{2m^*(U(x) - E)}{\hbar^2}} \quad (3.78)$$

where k is the wave vector. Here, the wave function at $x = L$ can be written as:

$$\Psi(L) = \Psi(0) \exp\left(-\int_0^L \frac{\sqrt{2m^*(U(x) - E)}}{\hbar} dx\right) \quad (3.79)$$

Here, the transmission probability T can be calculated as:

$$T = \frac{\Psi(L)\Psi^*(L)}{\Psi(0)\Psi^*(0)} = \exp\left(-2 \int_0^L \sqrt{\frac{2m^*e(U(x) - E)}{\hbar^2}} dx\right) \quad (3.80)$$

where e is the elementary charge, $\hbar$ is the reduced Planck's constant, m^* is the effective mass of the particle, and L is the length of barrier.

The tunnelling transmission probability T can be expressed as (where ε is the electric field ($\varepsilon = \frac{\Phi_B}{L}$) [124]:

$$T = \exp\left(-\frac{4}{3} \frac{\sqrt{2em^*}}{\hbar} \frac{\Phi_B^{3/2}}{\varepsilon}\right) \quad (3.81)$$

Here, by substituting (Eq.3.81) in (Eq.3.76), the quantum tunnelling current density can be written as:

$$J_n = en \sqrt{\frac{k_B T}{2\pi m^*}} \exp\left(-\frac{4}{3} \frac{\sqrt{2em^*}}{\hbar} \frac{\Phi_B^{3/2}}{\varepsilon}\right) \quad (3.82)$$

3.4 Total IETS Current

In the previous sections, the expressions for the elastic current (Eq.3.37), inelastic current (Eq.3.53), and SB current (Eq.3.75) have been discussed. Since these currents increase proportionally with the voltage V , the total current I for a MIS tunnel junction can then be referred as the sum of these three currents (Fig.3.11):

$$I_{total} = I_{elastic} + I_{inelastic} + I_{thermionic\ emission} \quad (3.83)$$

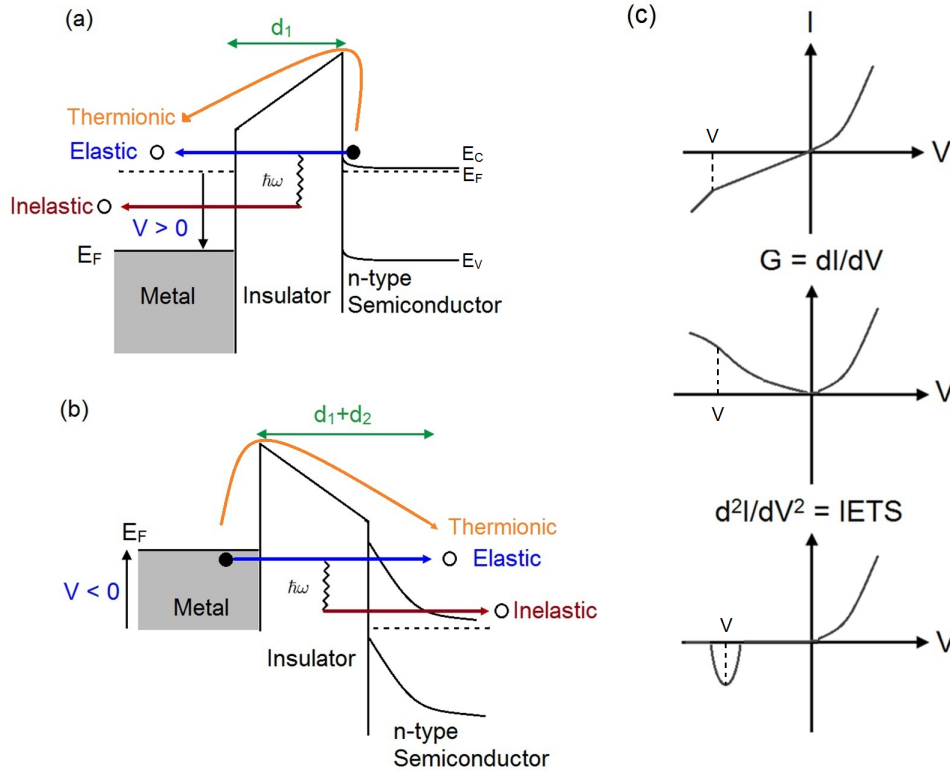


Figure 3.11: (a) Inelastic tunnelling forward bias, (b) inelastic tunnelling reverse bias, and (c) IETS signals (The $I - V$ characteristics, conductance $G = dI/dV - V$ and IETS peaks $d^2I/dV^2 - V$) for semiconductor - insulator - metal tunnel junction.

Here, the thermionic emission current ($I_{thermionic\ emission}$) is given by the Richardson equation for the case of a SB. The second derivation of the $I - V$ characteristics (d^2I/dV^2) displays

the molecular spectrum of the adsorbed molecule on the tunnel junction (Fig.3.11(c)). This is due to the unique vibrational frequencies of the molecules. The inelastic process can only start to occur when the applied bias reaches $eV = \hbar\omega$. Therefore, the peak at the threshold voltage $eV = \hbar\omega$ corresponds to a specific vibrational frequency. The peaks width can be broaden due to thermal broadening effect (discussed in section 3.2.2.) but this does not affect the position of the peaks.

3.5 Summary

This chapter gives an overview of the theoretical background for IETS. The chapter begins with a discussion of the transmission probability of elastic tunnelling for a single rectangular barrier, and hence for a barrier with arbitrary shape using the WKB approximation method. The electrical current through these barriers is then calculated. Following this, the inelastic tunnelling transmission probability, and current density have been studied considering three different interaction mechanisms: infrared dipole mechanism, bond polarizability of the molecule mechanism, and transfer Hamiltonian theory mechanism. This has been followed by a study of IETS spectral line-widths, which are independent of the interaction mechanisms.

Detailed derivations of the theoretical underpinnings of the transport across Schottky Barriers (SBs) are then provided, which determines the behaviour of the majority of the work presented in this thesis. Finally, the total IETS current for semiconductor - insulator - metal (SIM) tunnel junction has been calculated and studied based on these models.

Chapter 4

Fabrication Methodology

This chapter describes the fabrication methods developed for the preparation of nanoscale crossed Si nanowire (NW) / SiO₂ / Al NW tunnel junctions for IETS measurements. Traditionally, large area metal - insulator - metal (MIM) junctions (minimum size $\sim 20\ \mu m \times 20\ \mu m$) have been used in the IETS measurements and the molecules of interest are adsorbed on to the insulator during junction fabrication. In contrast to earlier experiments, throughout this thesis we investigate IETS measurements using nanoscale tunnel junctions. Here, the IETS characteristics of molecules such as ammonium hydroxide (NH_4OH), acetic acid (CH_3COOH), and propionic acid ($C_3H_6O_2$) molecules are measured using a nanoscale Si NW / SiO₂ / Al NW structures at 300K.

Many different techniques may be used to fabricate Si NWs including both “bottom-up” methods and lithographic “top-down” methods. A brief review of different Si NWs fabrication methods is provided in this chapter. The Si NWs fabricated in the present work, are defined in silicon-on-insulator (SOI) material using electron beam lithography (EBL). The Si

NW / SiO₂ / Al NW devices fabricated in the present work, have Si NWs with widths down to $\sim 50\text{ nm}$. The NWs are thermally oxidised at 1000°C to create a SiO₂ layer $\sim 10\text{ nm}$ thick. An Al NW $\sim 120\text{ nm}$ in width is defined to perpendicularly cross the SiO₂ / Si NW in each device, forming a nanoscale Si NW / SiO₂ / Al NW tunnel junction $\sim 50\text{ nm} \times 120\text{ nm}$ in area. The reduction in device dimension to the nanoscale increases the sensitivity of our devices to molecules adsorbed on the tunnel junction. Furthermore, the use of SOI material can potentially allow modulation of the tunnel junction using the back gate formed by the SOI substrate. The back gate voltage may control the Fermi energy and electron concentration in the NW, and hence modulate the IETS characteristics. The EBL technique for preparation of tunnel junction used in this thesis is presented in this chapter. Furthermore, a detailed description of the fabrication steps necessary to define Si NW / SiO₂ / Al NW tunnel junction devices is provided. Finally, a detailed discussion of fabrication issues for the Si NW / SiO₂ / Al NW tunnel junction devices used for the IETS measurements in this thesis is presented.

4.1 Device Fabrication

Traditionally, large area MIM junctions have been used in the IETS measurements, where the molecules of interest are adsorbed on to the insulator during junction fabrication. In this section, first standard methods for sample preparation for IETS measurements are presented. Following this, fabrication of the Si NW / SiO₂ / Al NW tunnel junctions used throughout this thesis is described in detail. Finally, an overview of the EBL system and methods used for preparation of the device is provided.

4.1.1 Traditional Metal-Insulator-Metal Tunnel Junction Devices

The traditional method for MIM sample preparation for IETS measurements has been described in detail by various research groups [3, 5, 53]. Typically, sample preparation was done in a high vacuum chamber. The vacuum is presented by either oil diffusion-pumped system with liquid nitrogen trapping (base pressure of $\sim 10^{-7} \text{ Torr}$) or ion-pumped oil free system (base pressure of $\sim 10^{-9} \text{ Torr}$). Both systems were equipped with a gas-discharge metal electrode for thermal evaporation of the top metal contact. Immediately after initial pump down, this system operated with O_2 gas to clean-up impurities. Most research groups have used oil diffusion-pumped system for establishing the vacuum. Oil diffusion-pumped system is less clean, and carbon contamination is possible. Many types of insulating materials have been used by different research groups as substrates. These include fused silica substrates [120], fused alumina substrates, sapphire substrates and ordinary microscope glass slides [3, 5, 53]. Among these materials glass microscope slides are typically used by researchers as substrates because these are cheap and available. The slides were thermally tested by rapid immersion in liquid nitrogen and discard all with the cracks. Then cleaned in HNO_3 / H_2O_2 . Afterwards, a thin strip of metal (usually Al or Mg) was deposited on the substrate using resistive heating of metal filaments or suitable crucibles. The insulator layer was then either deposited or grown on the top of the metal electrode. Various mechanisms were possible for adsorption of molecules on the tunnel junction. In many cases, the molecules of interest were adsorbed on the insulator layer during junction fabrication, by doping the oxidized metal strip with the molecule of interest. This can be done by two different techniques: liquid phase (adsorption from solution) doping or gas phase (direct vapour deposition). In

the liquid phase technique (Fig.4.1(a)), the molecules were applied to the junction by either dipping the sample in a container of solution or by placing a drop of solution on the junction and spinning this off. In the gas phase technique (Fig.4.1(b)), the oxidised metal strip was exposed with the vapour of the dopant directly in a vacuum chamber. Finally, the MIM junction was completed by evaporating the top metal electrode (most often Pb, Tl, Sn, or Ag) [3, 5, 53].

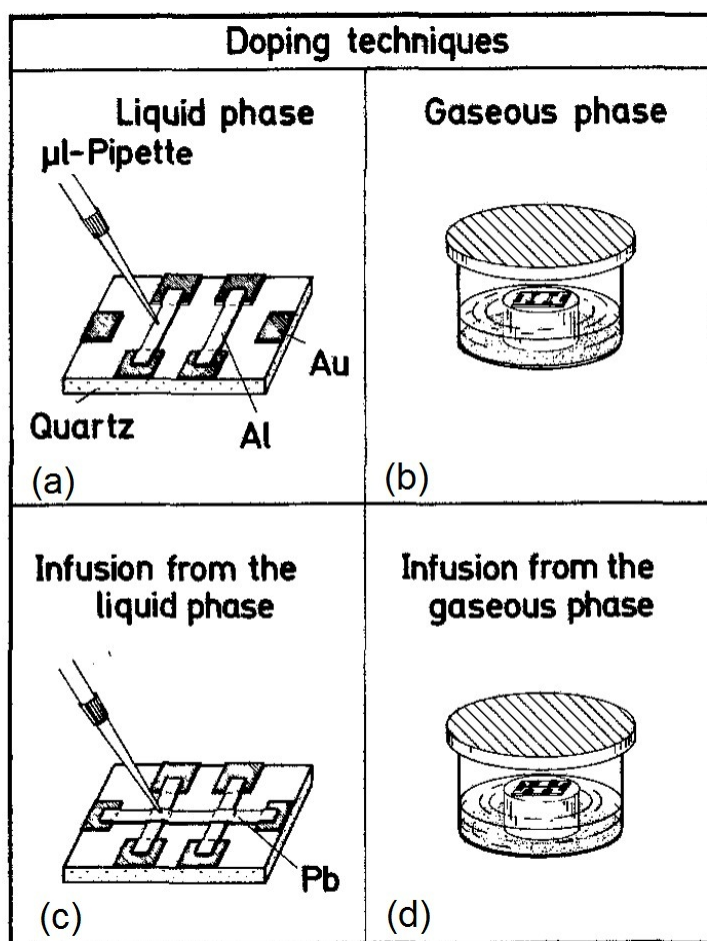


Figure 4.1: Schematic representation of different doping techniques: (a) liquid phase technique, (b) gas phase technique, (c-d) infusion technique [59].

The molecules of interest could also be adsorbed on the junction after device fabrication (infusion doping) (Fig.4.1(c-d)). This technique relied on the production of a porous top

metal electrode. The molecules could then diffuse through the pores of the completed MIM tunnel junction device [61, 127, 128]. After the tunnel junction was completed (Fig.4.2), typically four terminal measurements were used to measure the IETS characteristics.

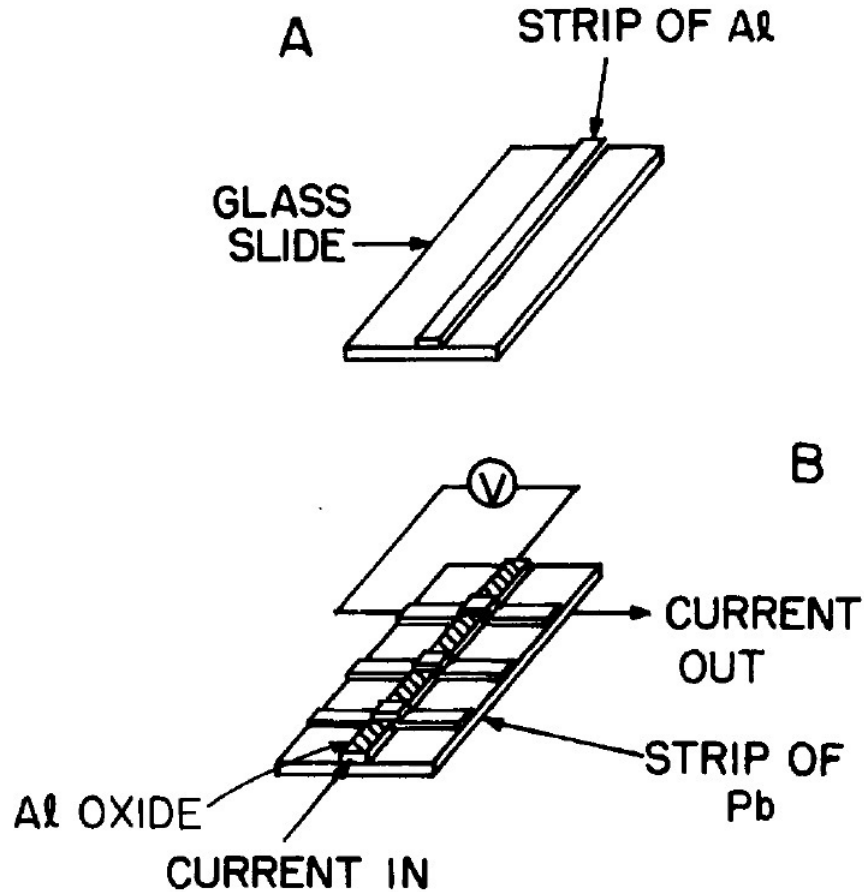


Figure 4.2: *Fabricated structure of tunnel junction used in IETS [2].*

4.1.2 Si NW Fabrication Techniques

Traditional methods for sample preparation for IETS measurements have been discussed in the previous section. In contrast to these earlier experiments, the tunnel junctions used in this thesis are based on crossed Si NWs / Al NWs. In the last decade, Si NWs have been widely investigated for nanoelectronics, sensors, bioelectronics and energy applications [6–

9, 129]. Many different techniques have been used to fabricate the Si NWs, including both “bottom-up” method synthesis [130, 131] and “top-down” lithographic methods [132–135].

Electron beam lithography (EBL), a traditional high resolution “top-down” lithographic technique [132–135], provides both the necessary nanoscale resolution and pattern flexibility for Si NW definition. Here, the NWs range can be as small as $\sim 10\text{ nm}$ in diameter, fabricated by a progression of EBL and etching steps on the target sample. However, as single-beam EBL techniques are comparatively slow, they are not appropriate for the high-throughput necessary in industry. Alternatively, NWs can be fabricated using optical lithography alone, however this may require the use of complex optical lithography and a subsequent chemical/plasma etch to achieve diameters of $\sim 10\text{ nm}$ or less [12, 136]. Selective etching of Si at the edges of a pattern defined by optical lithography may also be used to define NW.

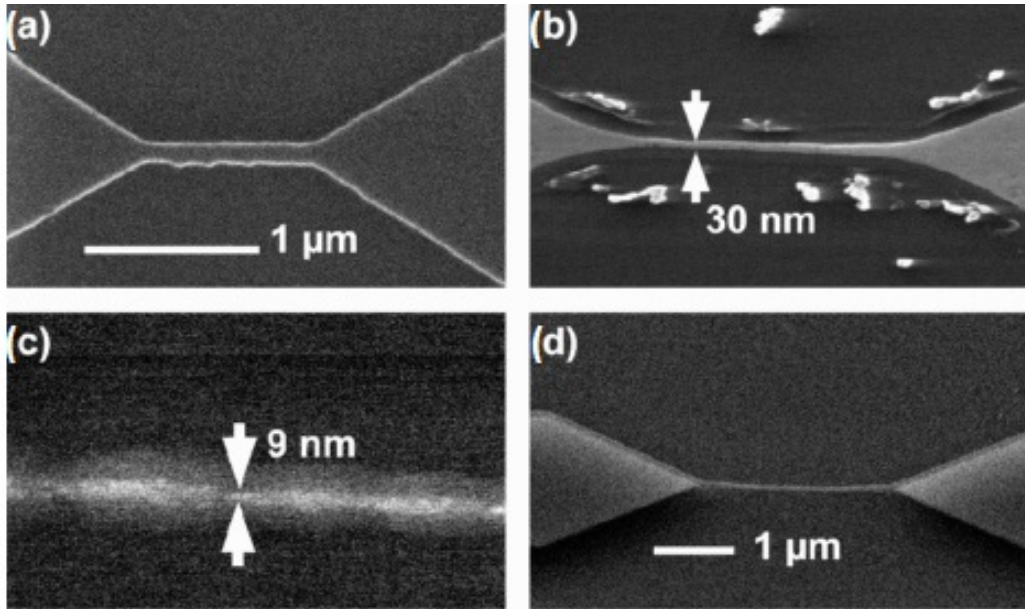


Figure 4.3: *Top SEM views of Si NWs before (a) and after etching (b-d) [137].*

Alternatively, “bottom-up” techniques have the ability to break free of lithographic limitations, provided nanostructures can be self-assembled and are not externally patterned. These techniques are also able to synthesise a range of materials [138–141]. Nanostructures made by self-assembly can have some advantages over lithographically defined structures, for example they may be well controlled in morphology and reasonably defect free, and have good electrical properties such as high carrier electron mobility. However, their integration into large devices is more difficult because of difficulties in their manipulation to create circuits [142].

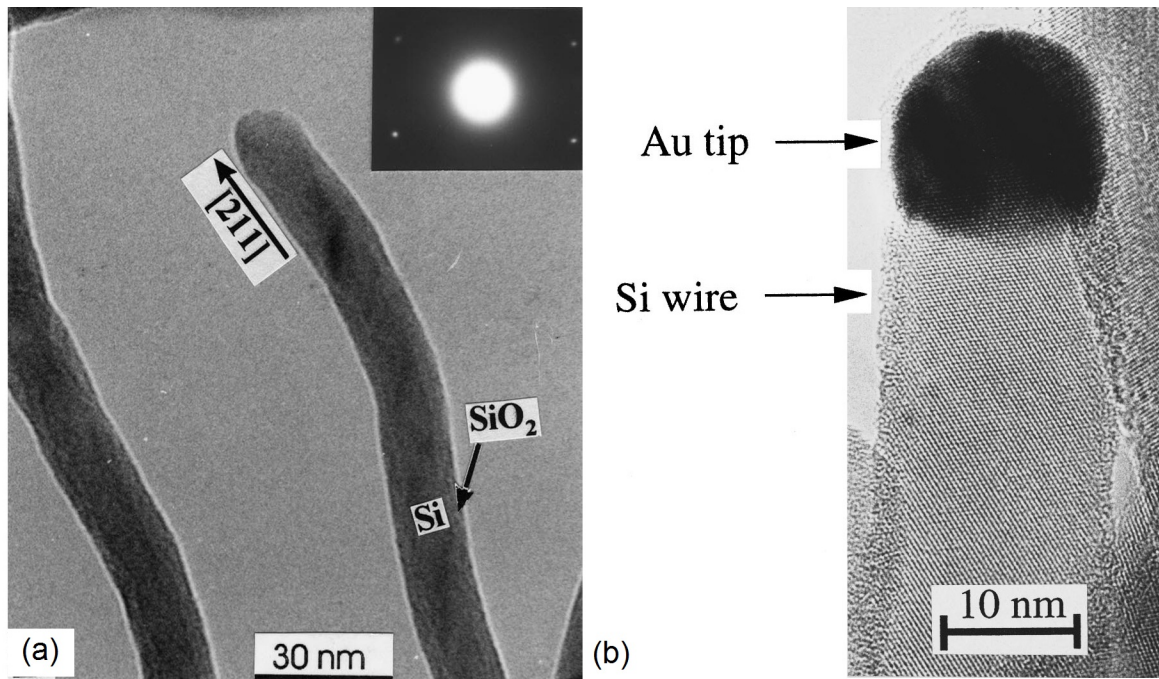


Figure 4.4: (a) TEM of OAG Si NW [143] (b) TEM image of single VLS grown Si NW [130].

The “bottom-up” techniques can be divided into vapour-phase techniques e.g. oxide assisted growth (Fig.4.4(a)) [130] and vapour liquid solid (VLS) mechanism (Fig.4.4(b)) [131], and liquid-phase techniques e.g. supercritical fluid-liquid-solid synthesis (Fig.4.5(a)) [144, 145] and metal assisted chemical etching (MACE) (Fig.4.5(b)) [146].

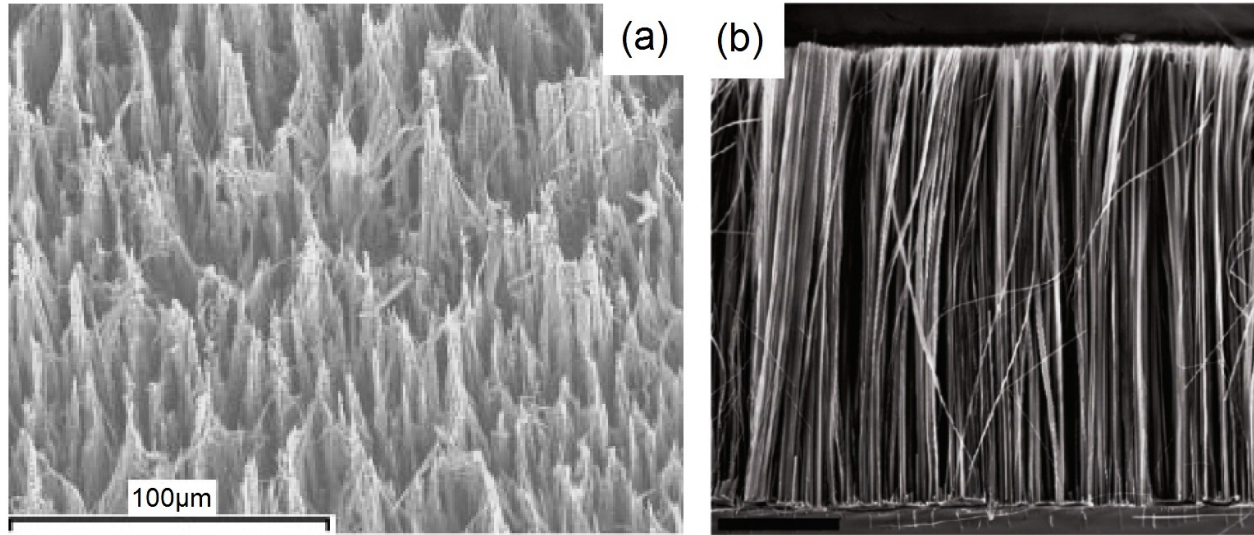


Figure 4.5: (a) SEM image of large-area Si NW arrays grown by supercritical fluid-liquid-solid synthesis [145] (b) SEM image of MACE prepared Si NW array cross section [146].

Finally, in order to make the most from both “top-down” and “bottom-up” techniques, a combination of traditional lithography and additional treatments has also been used to form large numbers of nanostructures [147, 148]. Very high resolution is possible, e.g. Sub 10 nm conducting channels have been created in Si with a combination of different techniques such as EBL, anisotropic etching and selective oxidation [149].

The Si NWs in this thesis are fabricated in SOI material using EBL. Therefore, we will limit the following section solely to this traditional “top-down” lithographic technique.

4.1.3 Electron-Beam Nanolithography

Electron-beam lithography (EBL), the principles of which are illustrated schematically in Fig.4.6, is the most commonly used fabrication technique for nanostructures for electronic applications [150]. EBL is the process of scanning a beam of electrons in a pattern across a surface covered with a thin film or “resist”, to chemically “expose” the resist, such that it is possible to selectively remove either the exposed or the non-exposed regions of the resist (“developing”) in a chemical situation. If the exposed portion of the resist is removed, the resist is then referred to as “positive-tone”, and if the un-exposed portion of the resist is removed, it is “negative-tone”.

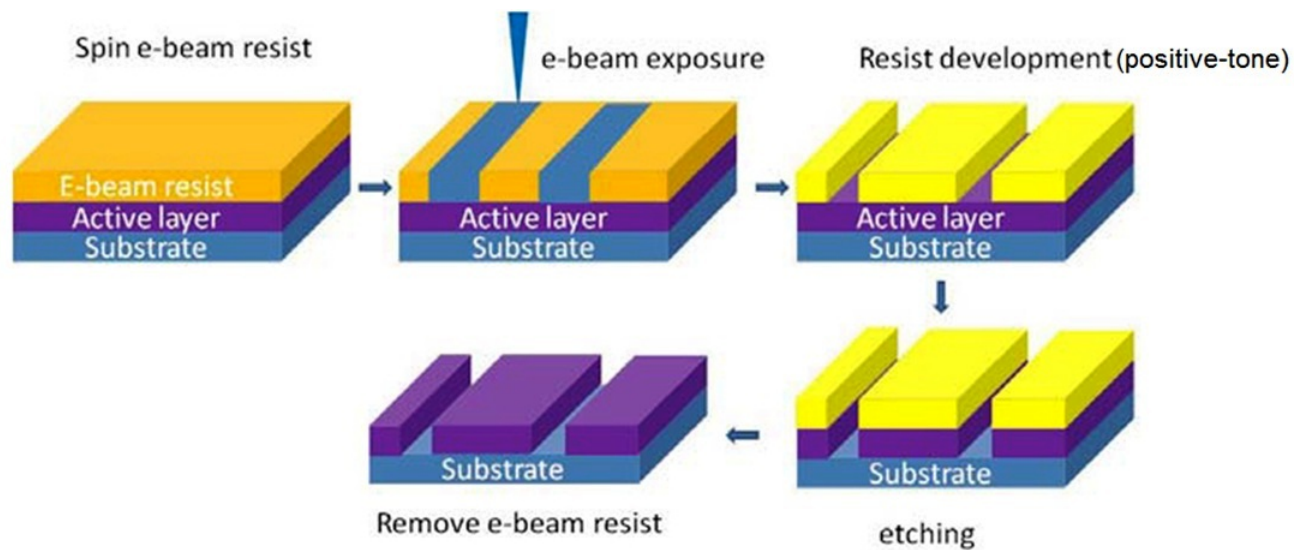


Figure 4.6: Overview of the E-beam Lithography steps [150].

The EBL process may be used to create very small features in the resist and these can subsequently be transferred to the substrate material, often by etching. In order to achieve high-resolution e-beam lithography, the resist layer should be as thin as possible and the scanning area (the “writing field”) should be restricted, to prevent defocusing of the beam.

High electron energy, low beam current, low pattern density and a stable lithographic environment are further preferred conditions [140].

Here, an overview of the e-beam lithography system in our laboratory is illustrated in Fig.4.7.

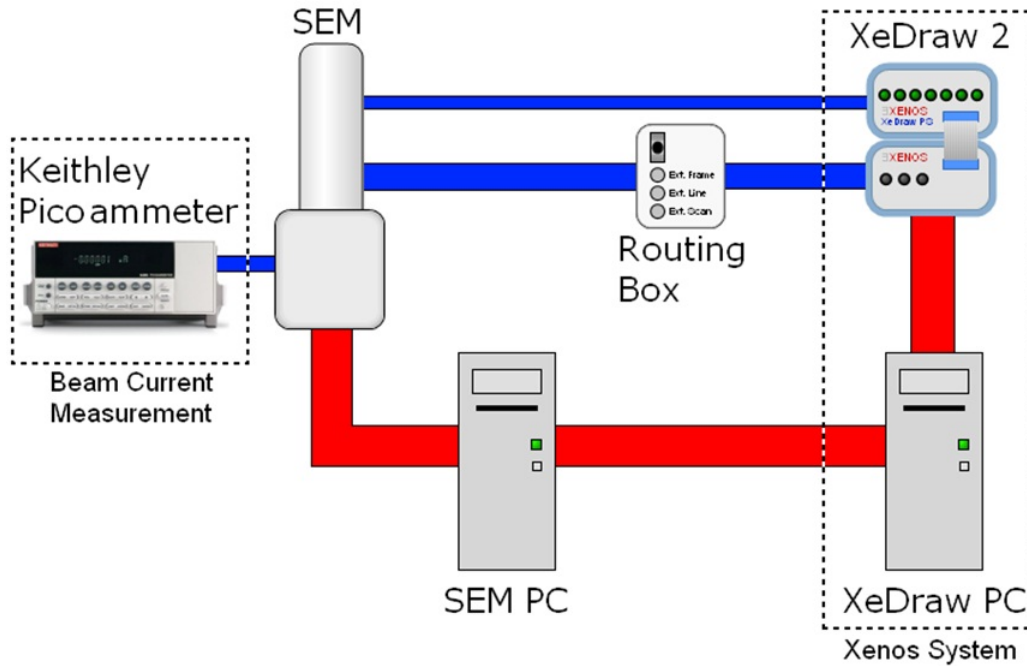


Figure 4.7: Overview of the Xenos e-beam lithography system [151].

Xenos XeDraw 2 e-beam pattern generator was used in conjunction with a scanning electronic microscope (SEM). Figure 4.8 illustrates how the SEM instrument works in general. It produces a largely magnified image by using electrons instead of light. A beam of electrons is produced at the top of the microscope by an electron gun. The electron beam follows a vertical path through the microscope, which is held within a vacuum. The beam travels through lenses and scanning coil, which create a magnetic field using fluctuating voltage, in order to focus the beam down towards the sample. Once the beam hits the sample, elec-

trons and X-rays are ejected from the sample. Here, a secondary electron detector attracts scattered electrons. The brightness of image depends on the number of secondary electrons that reach to the detector. A backscattered electron detector, is detecting the backscattered electrons which reflect off from the sample's surface, and the other sensor detects the X-rays which emitted from beneath the sample's surface. The collected data from the detectors is then sent to a monitor which shows the final image of the sample [152].

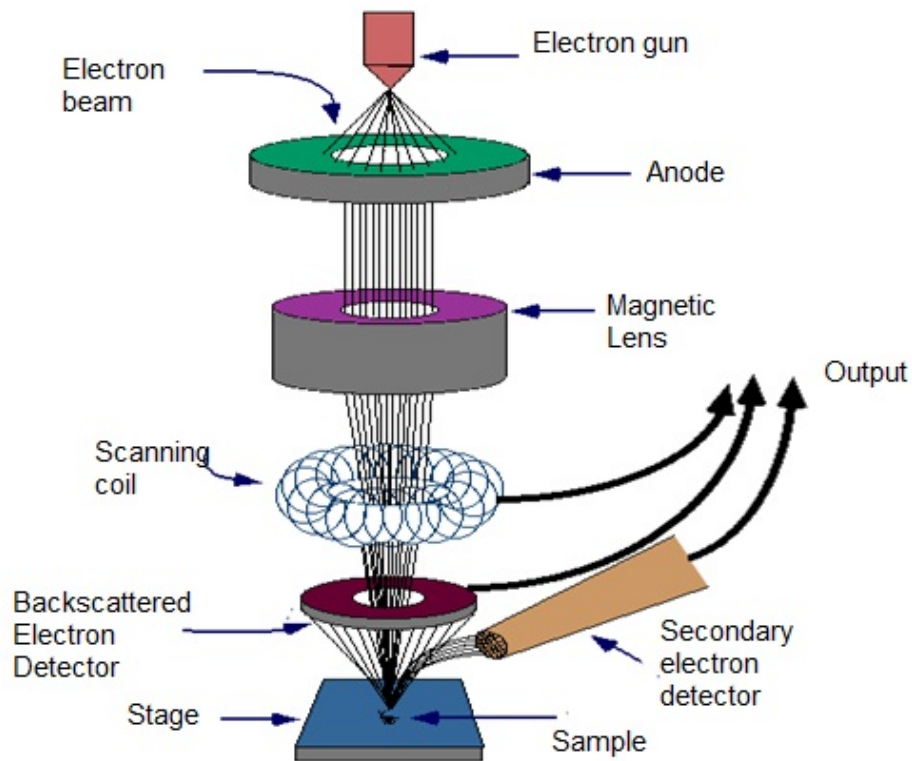


Figure 4.8: *Schematic diagram of scanning electron microscope system [152].*

Here, our Xenos XeDraw 2 e-beam pattern generator was used in conjunction with a LEO 1450VP SEM, which has a tungsten hairpin filament with an accelerating voltage range of 200 V to 30 kV. The Xenos e-beam lithography system consists of the XeDraw 2 pattern

generator, a PC, and a Keithley picoammeter. The pattern generator controls the position of the SEM beam in order to expose a particular pattern. The patterns are programmed in advance by using software provided with the Xenos XeDraw 2 system (Fig.4.9).

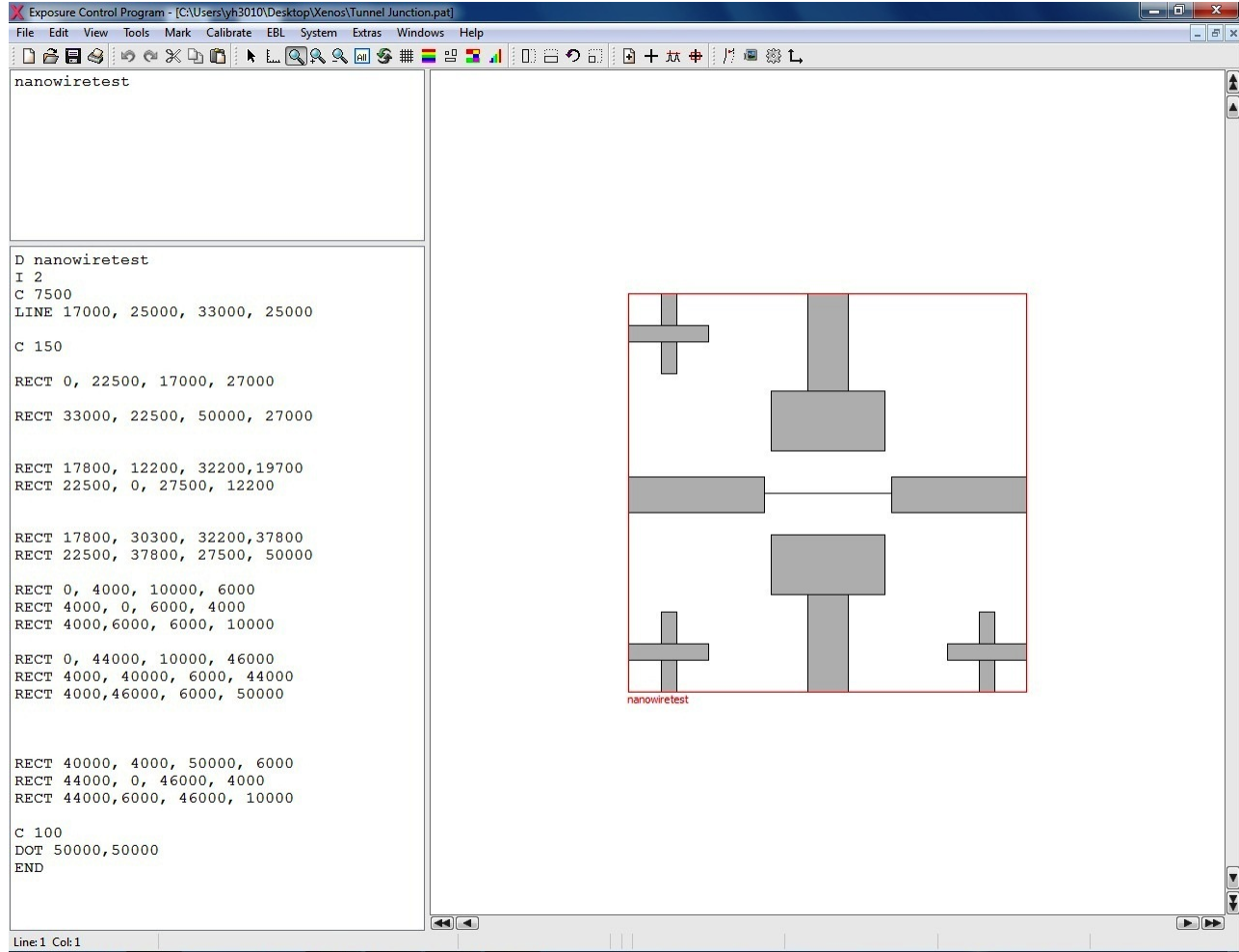


Figure 4.9: Single Si NW pattern obtained by XeDraw 2 pattern generator.

Here, in order to generate the pattern using XeDraw 2 pattern generator, three steps need to be taken: first the increment “ I ” has to be set. It defines the step size of the beam in units of pixels. In Fig.4.9, “ I 2” means that, the beam is moved to only every second point. Then, the “dwell time” “ C ” has to be set. It defines the time a single point is exposed, e.g. 200 ns.

Finally, the pattern is coded using different geometric figures, e.g. rectangle (RECT), line, and dot. Here, for a rectangle shape, the first two numbers defines the coordination of the left corner, and the second set shows the upper right corner [151]. The illustrated code in Fig.4.9, defines a single NW pattern with three alignment marks.

The picoammeter is used to measure the beam current at a Faraday cup installed in the SEM stage (Fig.4.10). The Faraday cup provides a means to measure the current in a beam of charged particles.

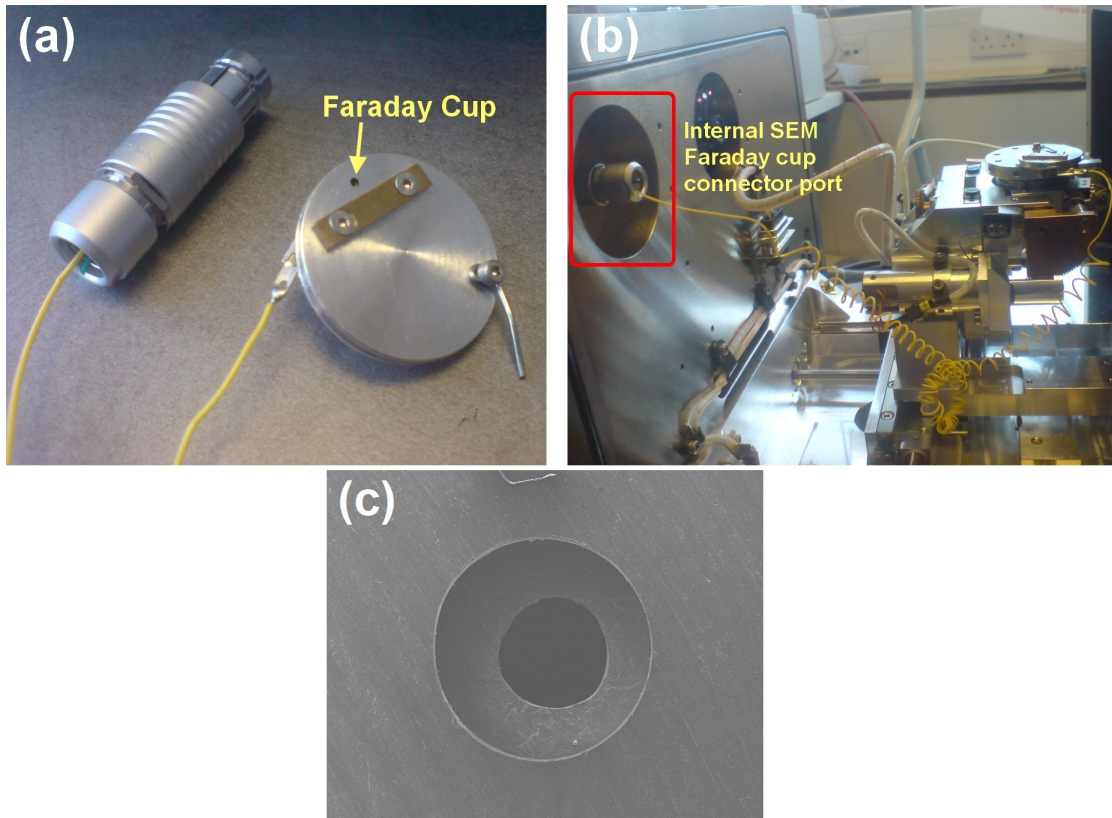


Figure 4.10: (a) Custom SEM stage with in-built Faraday cup (marked), shown with connector, (b) Image of stage and connector installed in SEM chamber, (c) SEM image of Faraday cup.

This consists of a conducting metallic chamber or cup, which intercepts the electron beam.

An electrical lead is attached to the chamber, which allows the current to be measured using a picoammeter. This beam current value is then used to calculate the “dwell time” per pixel of the beam necessary to provide a set dose to the resist. After e-beam exposure the resist may be developed to remove exposed portions (positive-tone process). Further stages of metal evaporation, lift-off, and wet or dry etching can then transfer the pattern into the substrate.

4.2 Nanoscale Tunnel Junction Fabrication

In this section, the Si NW / SiO₂ / Al NW tunnel junction fabrication process flow is presented. The process flow is divided into the fabrication of Si NWs, and the fabrication of the crossed Si NW / SiO₂ / Al NW tunnel junction. A detailed description of these stages is provided. Finally, a discussion of the fabrication issues and problems faced during the fabrication process is presented in detail.

4.2.1 Overview of Process

Figure 4.11 shows a schematic diagram of the Si NW / SiO₂ / Al NW tunnel junction devices, fabricated for the IETS measurements. The lower section of the device consists of a Si NW, fabricated in silicon-on-insulator (SOI) material. The Si NW is thermally oxidised to create a SiO₂ layer $\sim 10\text{ nm}$ thick, in order to form the tunnel junction. An Al NW $\sim 120\text{ nm}$ in width is then defined such that it crosses the Si NW, forming the nanoscale Si NW / SiO₂ / Al NW tunnel junction device. The fabricated tunnel junctions are then used for IETS measurements of molecules such as NH_4OH , CH_3COOH , and $\text{C}_3\text{H}_6\text{O}_2$, adsorbed

on the junction. These molecules are chosen as they have previously been characterised in large-area MIM tunnel junctions and these IETS characteristics are well-known. Comparison with the characteristics of our Si NW / SiO₂ / Al NW devices allows confirmation of IETS operation in nanoscale devices. Electrical results will be provided in Chapter 5.

The reduction in device dimensions to the nanoscale may increase the sensitivity of the device to molecules adsorbed on the tunnel junction. Furthermore, the use of SOI material allows modulation of the tunnel junction using the back gate formed by the SOI substrate, control of the Fermi energy and electron concentration in the NW, and hence the IETS characteristics of the device. In principle, an IETS sensor may be possible using such a configuration.

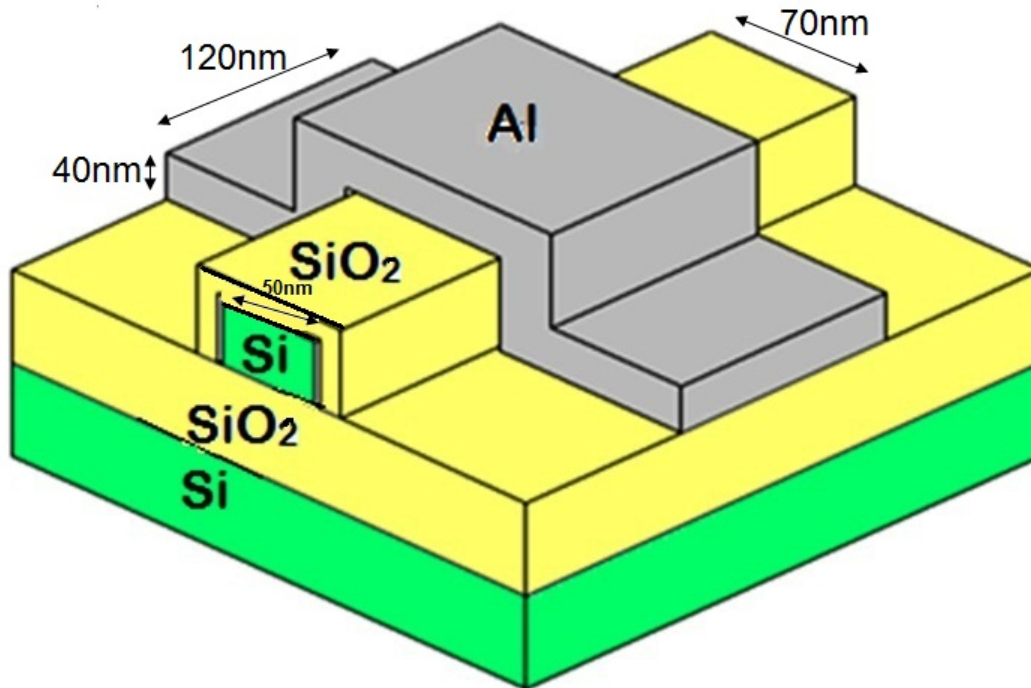


Figure 4.11: *Schematic diagram of cross nanowire tunnel junction.*

The process flow for the fabrication of Si NW / SiO₂ / Al NW tunnel junctions for IETS measurements is summarised as follows (Further details in Appendix A):

- 1) First EBL stage, using PMMA resist, on SOI substrates. This needs patterns for the Si NWs, and larger Si lead-in regions to allow electrical contact to the nanowires.
- 2) Evaporation of Al as a hard mask for RIE.
- 3) Reactive ion etching (RIE) using SF_6 , to transfer EBL resist pattern into top Si of SOI material.
- 4) Wet etch to remove Al mask metal.
- 5) Thermal oxidation of Si NWs at $1000^\circ C$ to define a SiO₂ tunnel junction.
- 6) Second EBL stage for fabrication of the Al NW, to cross the Si NW as shown in Fig 4.11. This requires alignment of the Al NW EBL pattern to the underlying Si NW.
- 7) Fabrication of Ohmic contacts. This requires a third EBL pattern.
- 8) IETS measurements across the Si NW / SiO₂ / Al NW tunnel junction, at $300K$.

The detailed description of the necessary steps for the device fabrication, and the various fabrication issues encountered, will be discussed in the remaining portion of this chapter.

4.2.2 Si NW Fabrication

Figure 4.12 illustrates an overview of our EBL Si NW fabrication process. In the first stage of the fabrication process, an n -type, highly-doped SOI wafer (doping density $\sim 10^{19} - 10^{20} cm^{-3}$) was selected as the base substrate. Then, a $\sim 1 \times 1 cm^2$ chip of the

highly-doped n -type SOI material is rinsed with acetone and isopropyl alcohol (IPA), and blow-dried with N_2 . The chip is then baked at $150^\circ C$ for 15 minutes in order to dry it completely and if necessary, stored in a dust-proof container. Following this sample cleaning stage, poly methyl methacrylate (PMMA) e-beam resist with a molecular weight of 950,000, diluted 2% in anisole, is spun on a highly-doped n -type SOI at 5000 rpm for 50 seconds. This gives a resist layer thickness of $\sim 100\text{ nm}$ (value from data sheet). The chips, coated with PMMA is then baked at $170^\circ C$ for 1 hour to dry and harden the PMMA.

Following this, a Si NW pattern was written using EBL [19, 153, 154]. A Xenos XeDraw 2 E-beam pattern generator was used, in conjunction with a LEO 1450VP SEM. This system allows the definition of features well below 100 nm in size, e.g. a “single pass” EBL line exposure can expose patterns of the order of the electron beam diameter. The minimum line width written in this work is $\sim 50\text{ nm}$. The exposed pattern is then developed in 3 : 1 isopropyl alcohol (IPA): methyl isobutyl ketone (MIBK) for 60 seconds at $23^\circ C$. In order to stop further developing, the chip was rinsed in IPA and then blow-dried with N_2 .

The SEM aperture size was at the largest size ($100\text{ }\mu\text{m}$), and the working distance (the distance from the bottom edge of the SEM objective lens to the sample surface) was set to a value of around 7 mm . The accelerating voltage was 20 kV .

A 40 nm thick Al layer was then evaporated at a pressure $< 1.1 \times 10^{-6}\text{ mbar}$ and lift-off in acetone used to create a $\sim 50\text{ nm}$ wide Al NW. This created a hard mask for reactive ion etching (RIE) of the top Si layer. SF_6 was used as the RIE gas at 100 mTorr for 40 seconds,

at RF power of 100 W and an etch depth of 200 nm was obtained. The Al mask was then removed using wet etching for 30 seconds. Here, the wet-etch contained mixtures of $1 - 5\%$ HNO_3 for Al oxidation, $65 - 75\%$ H_3PO_4 to dissolve the Al_2O_3 , $5 - 10\%$ CH_3COOH for wetting and buffering and H_2O dilution. Si NWs with lengths $\sim 1\text{ }\mu\text{m}$ and widths down to $\sim 50\text{ nm}$ were fabricated by this process.

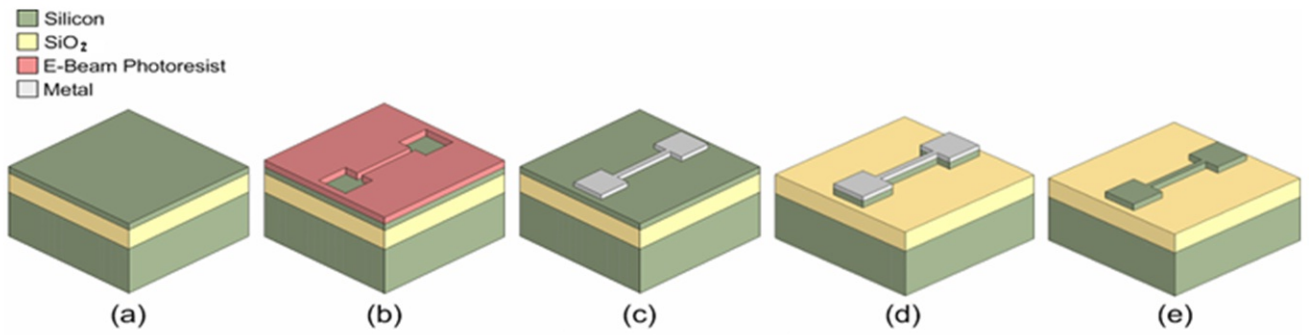


Figure 4.12: Overview of our e-beam Si NW fabrication by EBL. (a) The process begins with an SOI wafer on which an e-beam resist will be deposited. (b) This will be exposed by e-beam and developed, metal line then be evaporated to form a hard mask for a later RIE step. (c) Lift-off will leave behind the desired nanowire and contact pattern. (d) This will be used as an etch mask for RIE to remove unwanted Si. (e) The metal is wet etched, leaving behind a Si nanowire with large pads [155].

Figure 4.13(a-b), illustrates the pattern obtained by XeDraw 2 pattern generator (Fig.4.13(a)), and the optical micrograph of the the resist pattern before metal evaporation (Fig.4.13(b)).

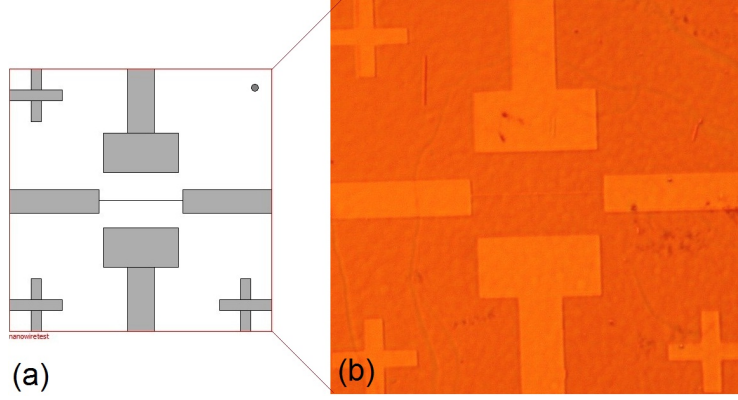


Figure 4.13: (a) Single Si NW pattern obtained by XeDraw 2 pattern generator. (b) Optical image of the resist pattern before metal evaporation.

The optical micrograph of a processed wafer immediately after thermal evaporation and lift-off of Al can be seen in Fig.4.14(a). Figure 4.14(b) shows an SEM image of another Si NW fabricated by this process after RIE.

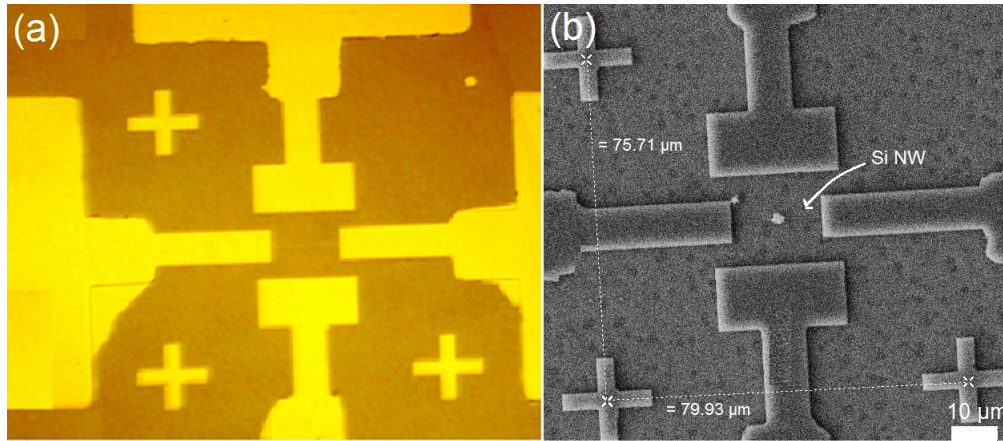


Figure 4.14: (a) Optical image of Si NW after thermal evaporation and lift-off of Al. (b) SEM image of another Si NW after RIE.

Here, the optical image (Fig.4.14 (a)) shows the exposed areas, consisting of a single pass line for the NW (A), the contact regions on each side (B) and three alignment marks (C) after the evaporation and lift-off of the 40 nm thick Al layer. The line has exposure dose of $\sim 5 \text{ nC/cm}$ and the contact areas has exposure dose of $\sim 375 \mu\text{C/cm}^2$. Figure 4.14 (b)

illustrates an SEM image of another Si NW after RIE to transfer the pattern into the Si.

4.2.3 Tunnel Junction Fabrication using EBL

Figure 4.15 illustrates an overview of our e-beam crossed junction fabrication process. Here, the Si NWs were thermally oxidised at 1000°C to create a SiO_2 surface layer $\sim 10\text{ nm}$ thick. A second PMMA e-beam resist layer with a molecular weight of 950,000, diluted 2% in anisole was then spun on the chip at 5000 rpm for 50 seconds. This gives a layer thickness of $\sim 100\text{ nm}$. The sample, coated with PMMA, was then baked at 170°C for 1 hour to dry and harden the PMMA. A second EBL stage was then used to define a 40 nm thick and $\sim 120\text{ nm}$ wide Al NW such that it crossed the Si NW, forming the nanoscale Si NW / SiO_2 / Al NW tunnel junction. Adding the Ohmic contacts was the final stage of fabrication process. This required a third EBL pattern. Finally, 120 nm of Al was thermally evaporated to form the contact areas following lift-off. The fabricated Si NW / SiO_2 / Al NW tunnel junction was then used for IETS measurements at 300 K .

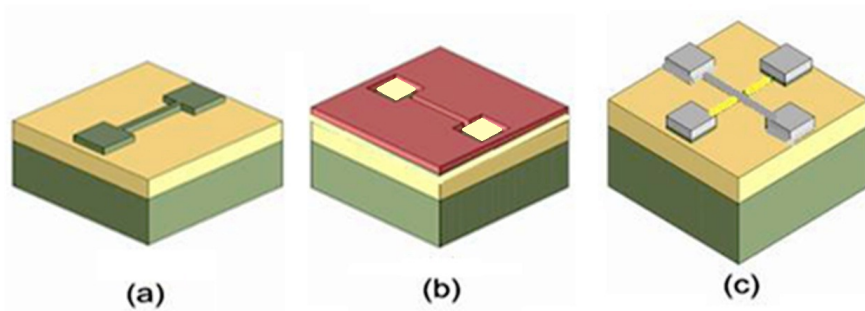


Figure 4.15: Overview of our e-beam crossed junction fabrication work flow.

Figure 4.16 illustrates the fabricated Si NW / SiO_2 / Al NW tunnel junction with Ohmic contacts.

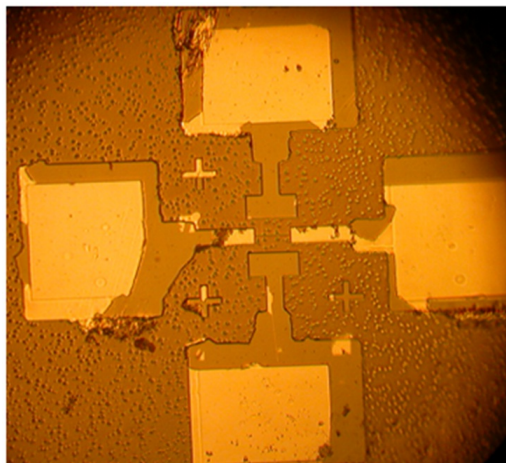


Figure 4.16: *Optical image of the fabricated Si NW / SiO₂ / Al NW tunnel junction with Ohmic contacts .*

The reduction in device dimension to the nanoscale is expected to increase the sensitivity of the device to molecules adsorbed on the tunnel junction. Various mechanisms are possible for adsorption of molecules on the tunnel junction. As the top Al layer is only $\sim 40\text{ nm}$ thick, this can be porous [61, 64, 127, 128]. Molecules may then diffuse through the pores in a manner similar to previous work on large area IETS structures with thin Al contacts ($\sim 50\text{ nm}$) [131]. In particular, molecules in the presence of water vapour can penetrate the top metal of the completed tunnel junction more easily [130, 131, 142, 144]. A second possible mechanism involves the deposition and diffusion of molecules from the exposed SiO₂ surface at the side edges of the tunnel junction. Furthermore, the use of SOI material raises the possibility of back gate control of the NW carrier concentration, and hence of the IETS characteristics.

Figure 4.17 shows optical and scanning electron micrograph of selected crossed Si NW / SiO₂ / Al NW tunnel junction fabricated by this process. An optical image of tunnel junction device after alignment and successful evaporation and lift-off of 40 nm of Al can be seen in

Fig.4.17(a). Figures 4.17(b-c) illustrates SEM images of two different devices.

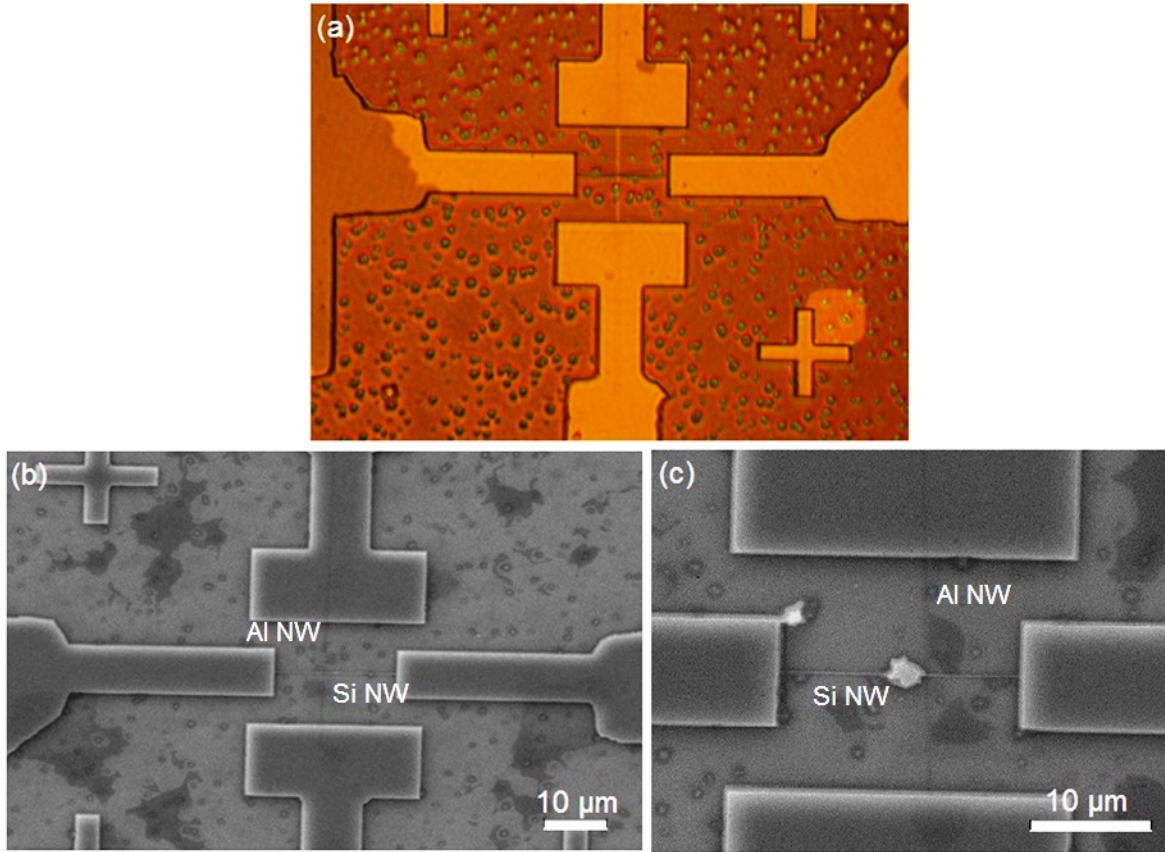


Figure 4.17: (a) Optical image of tunnel junction device after oxidation and alignment, (b) SEM image of tunnel junction device after oxidation and alignment, (c) Magnified crossed tunnel junction device .

Here, damage to the underlying Si substrate of the SOI material in Fig.4.17(a) occurs after RIE step.

Figure 4.18 illustrates the SEM micrograph of a completed Si NW / SiO₂ / Al NW tunnel junction device. Here, some problems with lift-off can be seen in Fig.4.18, however enough metal remains for contacts to allow measurement.

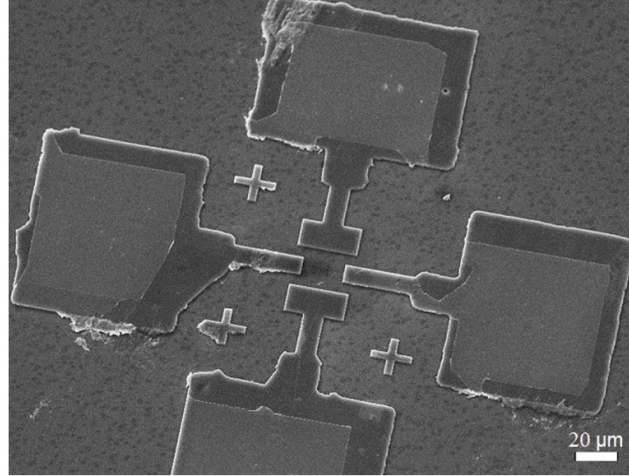


Figure 4.18: SEM image of Si NW / SiO₂ / Al NW tunnel junction.

Figure 4.19 illustrates the completed Si NW / SiO₂ / Al NW tunnel junction device in further magnifications. Here, the Si NW width goes down to $\sim 50\text{ nm}$ and the width of Al NW is $\sim 120\text{ nm}$. The cross sectional area of the Si NW / SiO₂ / Al NW tunnel junction is $\sim 6 \times 10^{-15}\text{ m}^2$.

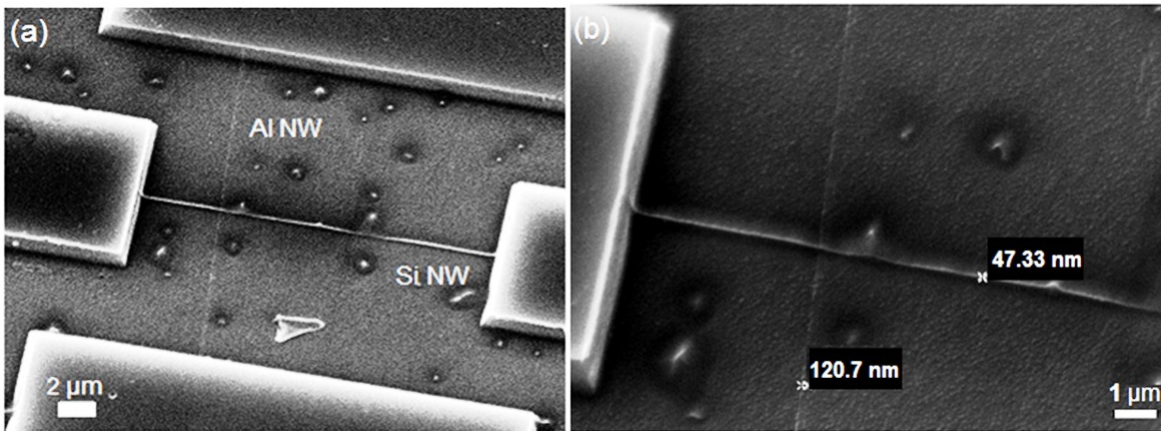


Figure 4.19: (a) Magnified SEM image of final Si NW / SiO₂ / Al NW tunnel junction, (b) SEM image of final Si NW / SiO₂ / Al NW tunnel junction widths.

4.2.4 Fabrication Issues

This section discusses the development of the fabrication process in detail, including the problems faced and the solution adopted. During the development of the nano-tunnel junction fabrication process, certain issues arose that had to be solved to achieve a good quality Si NW / SiO₂ / Al NW tunnel junctions. Some of the most important of these issues will be discussed in this section.

Exposure and Development Issues

In initial experiments, single-pass lines EBL lithography of Si NW with two contact areas at each end, using PMMA with a molecular weight of 950,000, which was diluted 6% in anisole, as an electron beam resist. The resist was spun on to a Si wafer at 5000 rpm for 50 seconds; giving a layer thickness of $\sim 300\text{ nm}$ (based on data sheets). Schematic diagram of the initial single Si NW device defined by XeDraw 2 pattern generator is illustrated in Fig.4.20.

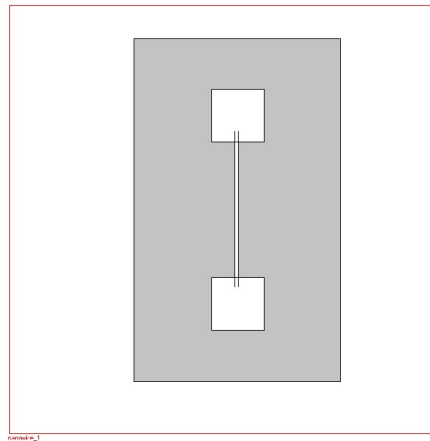


Figure 4.20: Schematic diagram of the initial single Si NW device defined by XeDraw 2 pattern generator.

The Si NW fabrication was started with a similar exposure dosage for large area and single-pass lines. Initially, the exposure dosage was set at $\sim 2800 \mu C/cm^2$. The exposed pattern was then developed for 140 seconds. Unfortunately, this resulted in round and overdeveloped Si NW device (Fig.4.21).

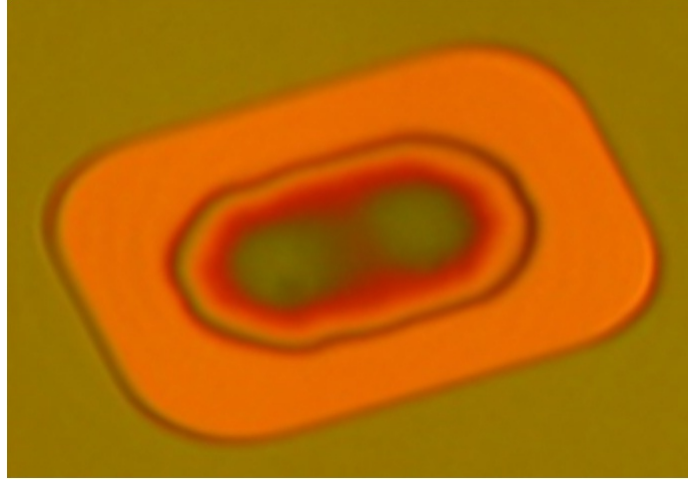


Figure 4.21: *Initial EBL lithography: Optical micrograph of an overexposed and overdeveloped pattern.*

Here, the image is slightly angled due to the sample's position under the optical microscope. Figure 4.21 illustrates that there is not an Si NW in between the contacts. The outer rectangle, and the two contacts are looked round. The rounded area implies that the exposure dosage was high. The pattern was also overdeveloped because of the long development time. According to the failure of achieving Si NWs with high exposure dose for area and line, a dose trial was performed by reducing the exposure dosage from $\sim 2800 \mu C/cm^2$ to $\sim 390 \mu C/cm^2$, in seven steps. The development time was also reduced to 30 seconds. Here, the exposure dosage of $\sim 390 \mu C/cm^2$ gives the best contact region, illustrated in Fig.4.22. However, even in this case, the NW did not develop properly. It was believed that this problem was caused by the exposure dosage of the single-pass line used to define a Si NW. Therefore,

the exposure doses were adjusted independently for the single-pass line used to define the Si NW, and the contact regions on either side.

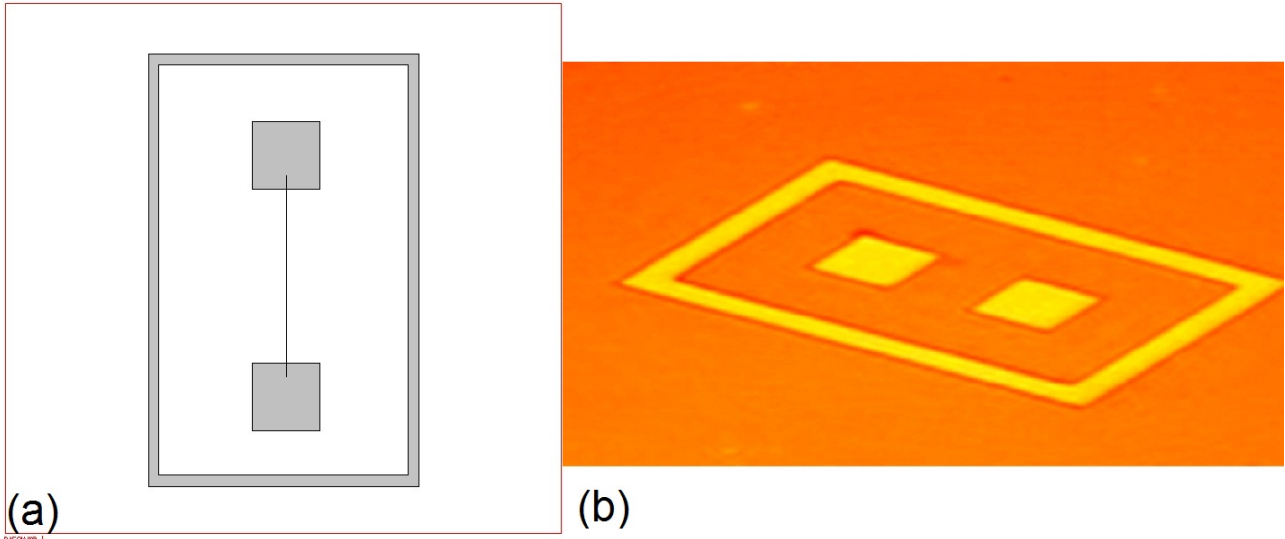


Figure 4.22: *Initial EBL lithography: (a) Schematic diagram of the initial single Si NW device defined by XeDraw 2 pattern generator, (b) Optical micrograph of sharp exposed area, without NW.*

Figure 4.22(a) shows another pattern for single Si NW with two contact areas defined by XeDraw 2 pattern generator. Figure 4.22(b) illustrates the optical micrograph of this pattern without NW. Here, the image is slightly angled due to the sample's position under the optical microscope.

The area dosage was then reduced to $\sim 375 \mu C/cm^2$, and a dose trial was used for the lines in order to find out the best line dosage. The line dosage was set between $\sim 4 - 10 nC/cm$. The development time was 30 seconds. Afterwards, $40 nm$ of Al was thermally evaporated on the pattern and lift-off in acetone used to remove excess Al. Figure 4.23 shows the new Si NW device after thermal evaporation of $40 nm$ Al and lift-off in acetone.

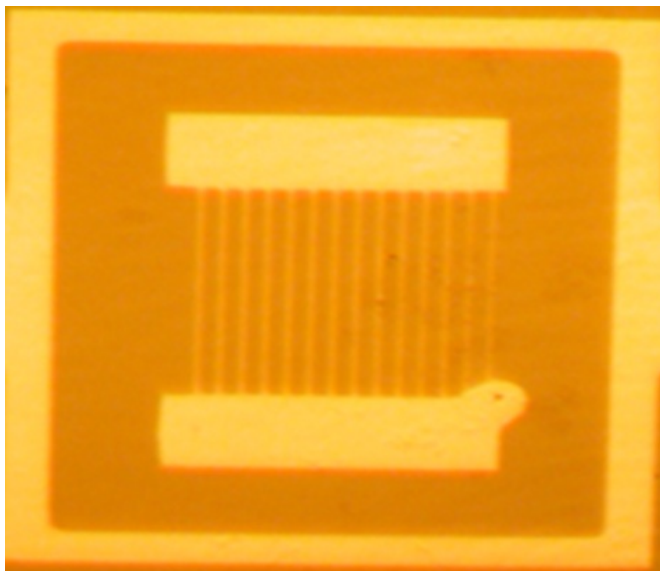


Figure 4.23: *Optical image of dose trial for Si NWs, after thermal evaporation and metal lift-off (Exposure dosage varies from $\sim 4 - 10 \text{ nC/cm}$, from right to left in steps of 1 nC/cm . Here, pairs of lines exposed with the same dosage.)*

Figure 4.23 illustrates an exposed area with 14 single pass lines, and two contact regions on either side. Each line has a different exposure dose to make sure that the correct dosage exists at some point in the pattern ($\sim 4 - 10 \text{ nC/cm}$). All the lines have developed and lifted-off correctly, can be clearly observed in the micrograph.

Here, the large circle on one of the contact areas was not present in the writing pattern file and is an artifact of the writing system. Features such as this can occur because of the following problem.

For a single field exposure, the XeDraw 2 scans the electron beam over the field, and then returns the SEM to normal image scanning when complete. For a multi-field exposure, a beam blanker is required by the XeDraw 2 to interrupt the beam exposing the sample while

the next pattern field is being processed by the XeDraw PC. Without this blanker, the electron beam continues to strike the sample during the delay between field exposures. It is this effect that causes the exposed “dot” seen above. Our SEM unfortunately had no beam blanker installed. RIE was then carried out in order to etch the Si NW. Figure 4.24 shows SEM image of NWs obtained after 30 seconds of RIE, using SF_6 gas.

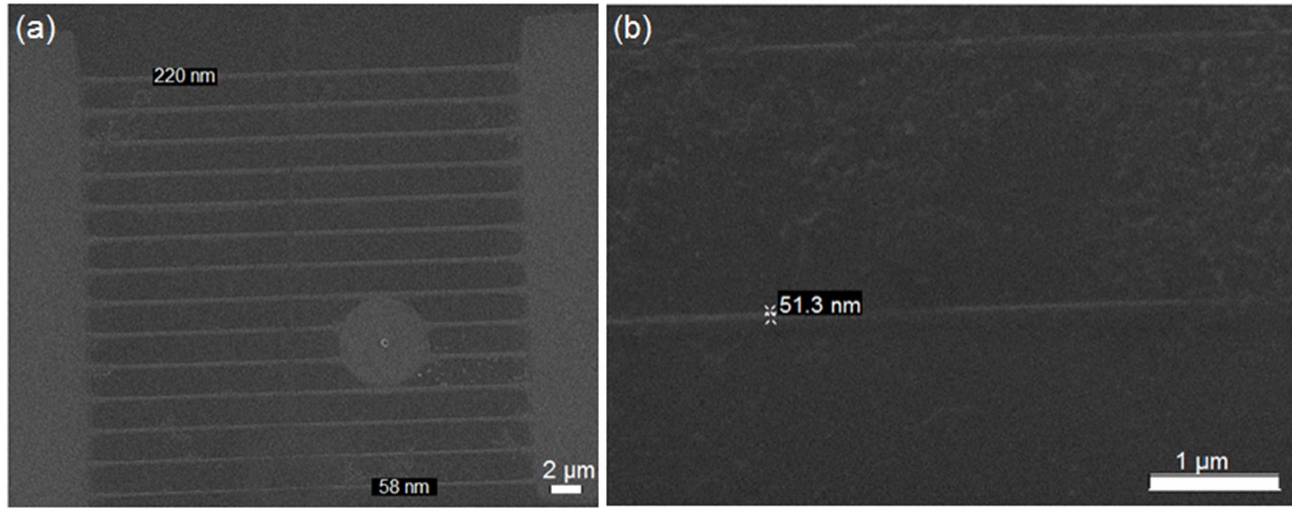


Figure 4.24: SEM image of dose trial device.

Figure 4.24(a) also illustrates the effect of different exposure dosage, leading to NWs with different wire widths. Figure 4.24(b) shows a $\sim 50\text{ nm}$ width nanowire, fabricated with an exposure dose of $\sim 5\text{ nC/cm}$. The same process was then successfully repeated in order to confirm the reproducibility of the Si NW.

Lift-off Issues

In order to have thinner Si NWs, a thinner resist layer was required. Therefore, PMMA was diluted 2% in anisole after achieving several successful NWs with a same method as

above. Alignment marks were then added to the pattern in order to start fabrication of cross NW devices using a second e-beam lithography pattern, aligned to the Si NW. The area dosage was reduced to around $\sim 175 \mu\text{C}/\text{cm}^2$, and the single-pass line dosage was set at $\sim 5 \text{ nC}/\text{cm}$. The development time was 60 seconds. Then 40 nm of Al was thermally evaporated on the pattern and lift-off in acetone used to remove excess Al. Here, the lift-off was unsuccessful and NWs were broke during the lift-off. However, RIE was carried out in order to etch the Si, in order to try the alignment process. Figure 4.25(a) shows an optical micrograph of the new pattern without NWs, after 20 seconds of RIE using SF_6 gas (RIE is expected to etch the Si to a depth of 200 nm).

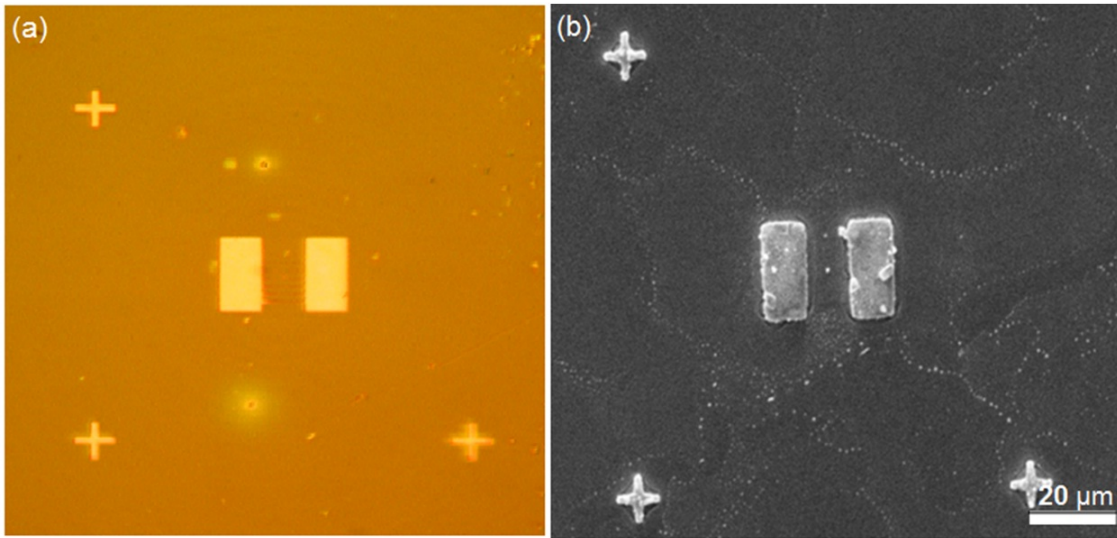


Figure 4.25: (a) Optical image of device without Si NW, with alignment marks after RIE, (b) SEM image of the device with alignment marks.

Figure 4.25(b) illustrates an SEM image of the device with alignment marks, before spinning the second layer of PMMA. The Al mask was then removed using wet etching. The Si NWs were then thermally oxidised at 1000°C to create a SiO_2 surface layer of $\sim 10 \text{ nm}$ thick.

Alignment Issues

Fabrication of the Al NW, aligned to the Si NW, required a second layer of PMMA to be spun and baked on the chip. The sample was then placed in the SEM for the Al NW alignment and exposure. Figure 4.26 illustrates the SEM image of the Si NW pattern and alignment marks under the second layer of the resist. Alignment of second wire was started using the “image mark” method. In this method, the alignment marks have to be detected by initially obtaining an image of the sample.

In order to use the alignment marks in an SEM micrograph of the original pattern, first the position of alignment marks had to be found using the stage position indicated by the SEM.

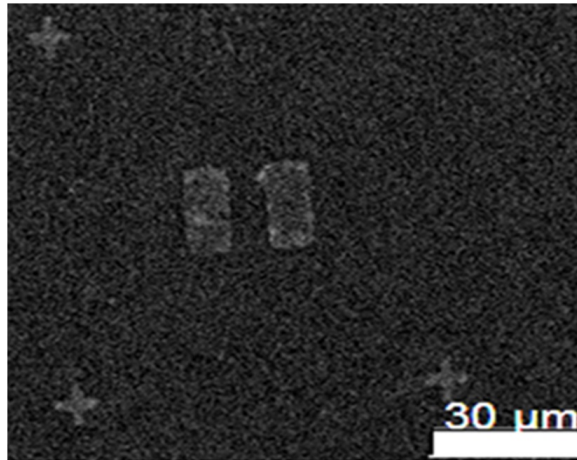


Figure 4.26: *SEM image of the pattern under second layer of PMMA.*

The alignment mark parameters then had to be set using a “mark editor” programme in the XeDraw system. The length of the mark was set to 5000 pixels, and the width to 1000 pixels. The correlation detection threshold was set to 70% and other parameters were set as default. After setting all the parameters, the 1st mark was scanned and exposure control program

(ECP) was used to successfully detect this mark. The detected mark was then saved. The whole pattern was then scanned in order to find the remaining two marks, similar to the saved mark.

Initially, the XENOS system was able to detect the first mark, but it could not find the remaining two marks. As the process did not work following repeated attempts, the “cross mark” alignment method was tried. In this method, the expected position of the marks is pre-defined in the EBL control file. By zooming on the whole pattern manually, the system was able to find the alignment marks by scanning the proposed coordinations. Accordingly, alignment was preformed using the “cross mark” method. By running the control file in this method, the XENOS system found the first and second marks reliably but detection of the third mark was unreliable. However, the detection of two marks, while not ideal, was sufficient for device fabrication. Following EBL exposure, the sample was then developed for 30 seconds to confirm the exposure.

Initial alignment experiments suffered from various problems, Fig.4.27 illustrates the optical micrograph of a pattern after the alignment of the second pattern, but with a 90° rotation error, and over exposure.

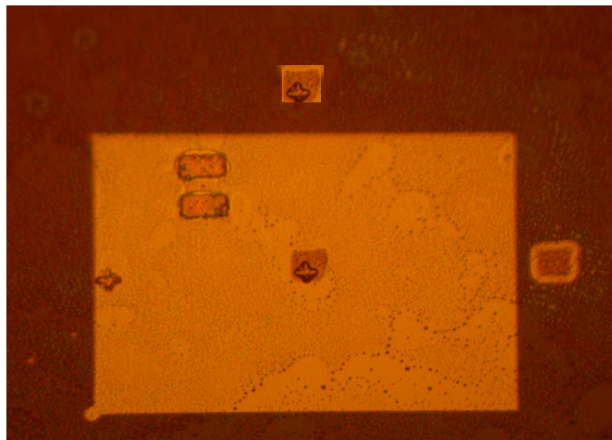


Figure 4.27: *Optical image of pattern after unsuccessful alignment due to rotation error.*

Figure 4.27 shows that the scanned area and pattern position were rotated by 90° . Rotating the pattern by 90° degree, allowed detection of the three marks and then complete the exposure process. There is also a rectangle over the pattern caused by the long scanning exposure time. Figure 4.28 illustrates a further attempt at alignment, with the exposed pattern after development. Here, the scanned areas were close but not exactly on the alignment mark. This suggested a calibration error, where the distance between the marks in the alignment control file needed to be reduced.

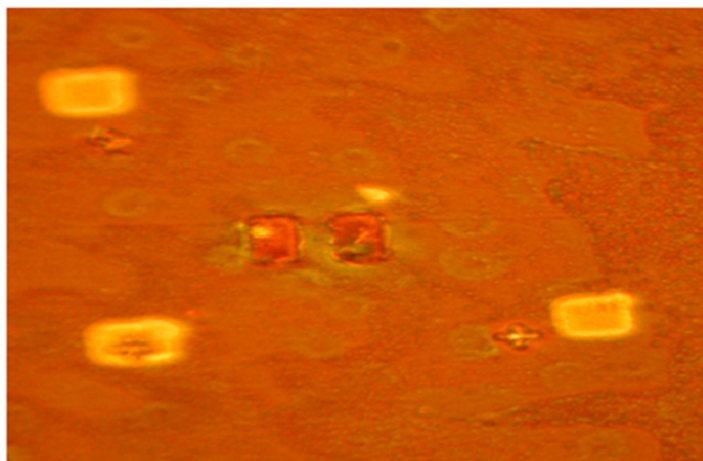


Figure 4.28: *Optical image of pattern after unsuccessful alignment due to calibration errors.*

Following these initial attempts, the distance between the marks was measured under the SEM. Figure 4.29 illustrates the measured distance between the marks.

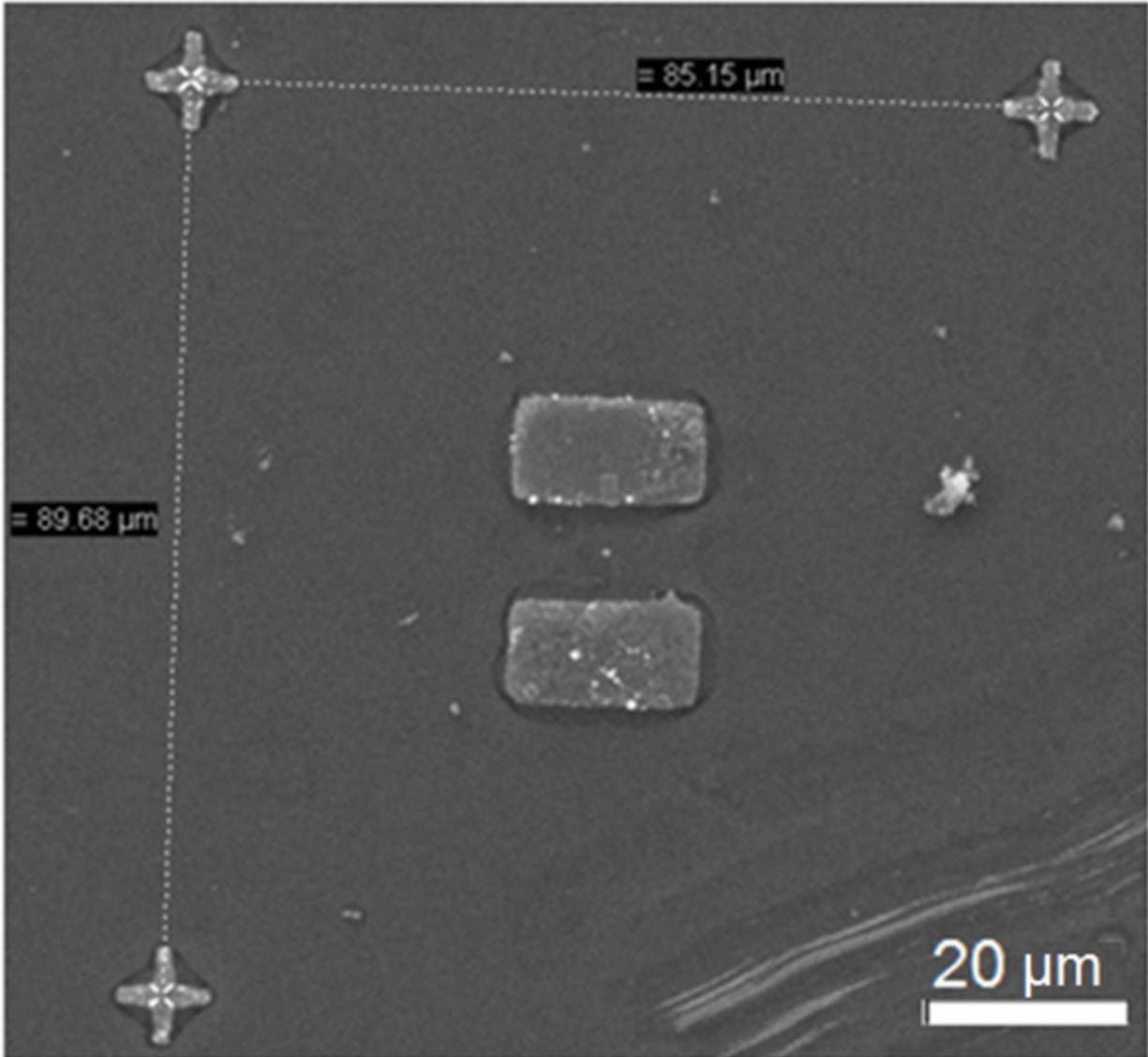


Figure 4.29: *SEM image of the distance between the alignment marks.*

It can be seen that distance between the marks is only $\sim 85 \mu\text{m}$, instead of the $100 \mu\text{m}$ distance defined in the pattern file. Therefore, the marks coordinates in the alignment control file were changed and the lengths reduced by 20%. The detection process was then repeated and this time, alignment of the second NW pattern was successful. The sample

was then developed for 30 seconds. Figure 4.30 illustrates the pattern after the alignment process.

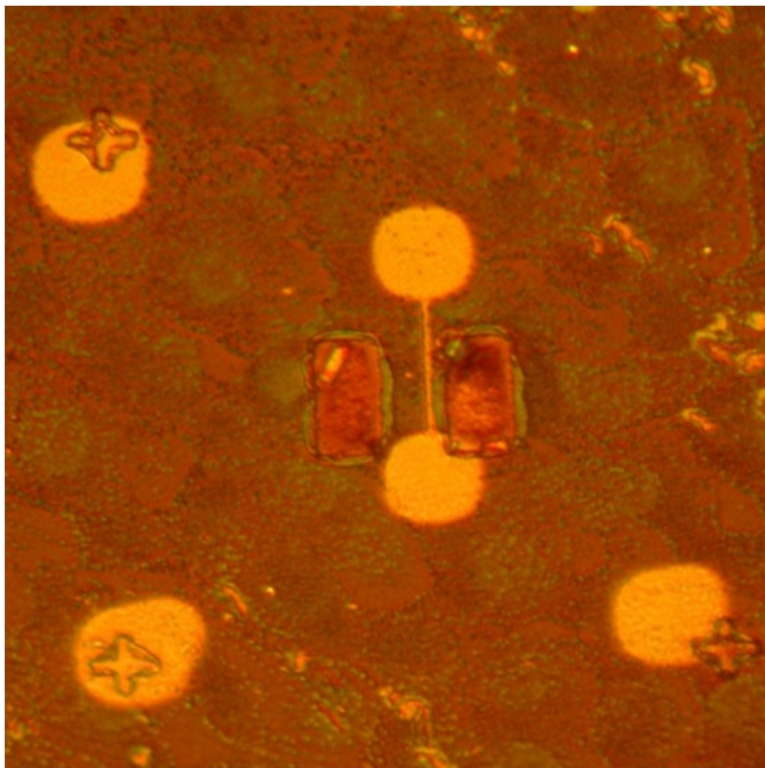


Figure 4.30: *Optical image of crossed junction device after successful alignment.*

Here, a first mark was successfully aligned. Then the system moves the stage according to the commands in the control file to find the next mark. However it can consistently fail to do so even when supplied with accurately measured distances. The root of this problem is due to the many sources of error present within the system. Two particular sources of error are the cause of the majority of issues; SEM image error, and stage error. Firstly, any measurement of distance made using an SEM image contains error based upon the current level of beam focussing/zoom level (characterised as a variation in measured distances as large as 10% over a doubling of the magnification level). The second and larger source of error is the stage movement. The stage used in the current SEM system can overshoot its

positioning by a distance as large as several microns. The quality of the motor and control system is such that accurate stage positioning is not possible (Fig.4.31) [151].

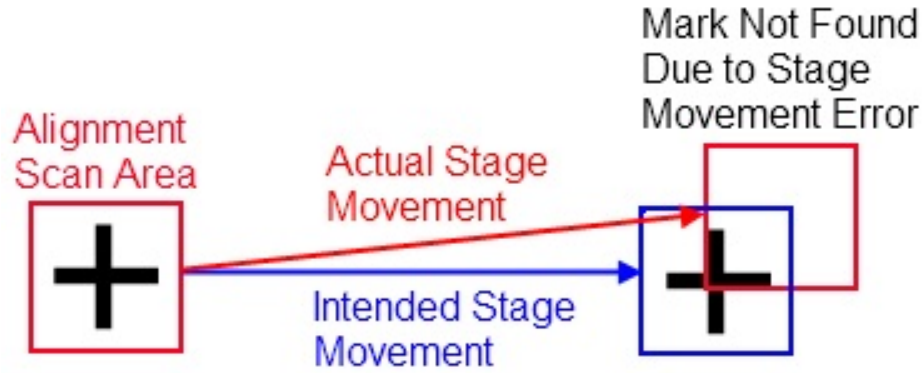


Figure 4.31: *Error in stage movement can cause mark alignment to fail [151].*

The process was repeated in order to examine the reproducibility of the crossed junction device. Figure 4.32 shows selected optical micrographs of aligned Al NW / Al NW tunnel junction fabricated by the above process.

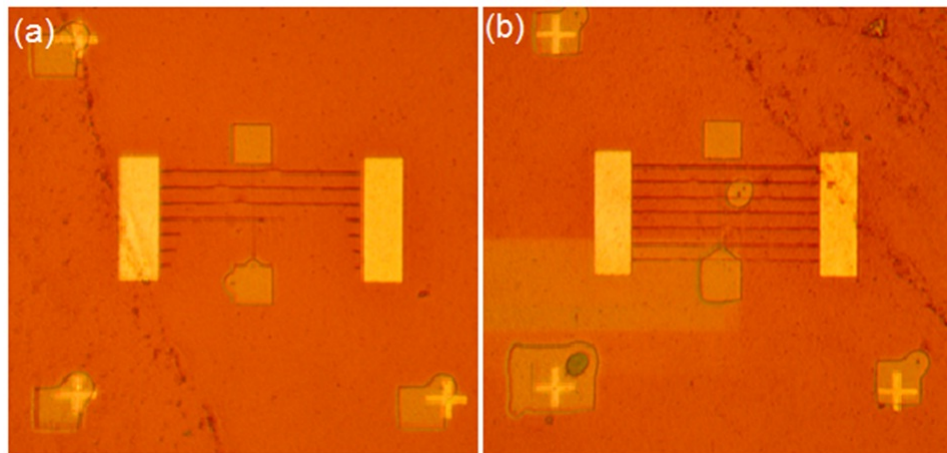


Figure 4.32: *(a)-(b) Optical micrograph of two different successful alignment processes.*

Figure 4.33 shows the SEM images of the above patterns in further magnification.

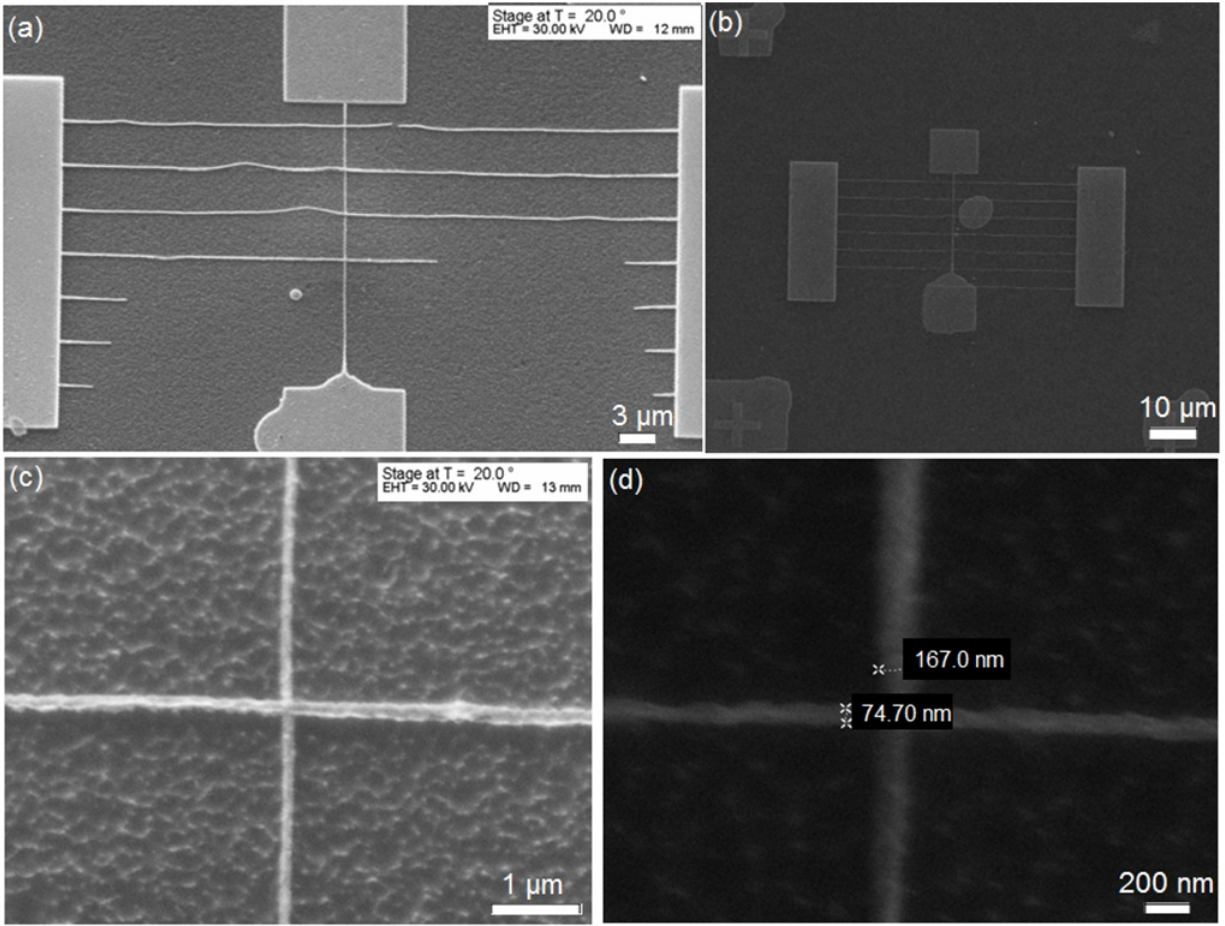


Figure 4.33: (a) Top view of SEM micrograph of crossed NW device in Fig.4.32(a). (b) Top view of SEM micrograph of crossed Al NW / Al NW device in Fig 4.32(b). (c) Magnified view of the cross junction. (d) NW widths.

Adding Ohmic Contacts Issues

After successfully alignment of the second e-beam lithography pattern to the Si NW, a new set of patterns was designed to add an Ohmic contacts to complete the device. The new pattern was introduced as Fig.4.34. Four different trench widths were defined to find the best trench size. (Trench size from left to right: 300, 400, 500, 600 nm.)

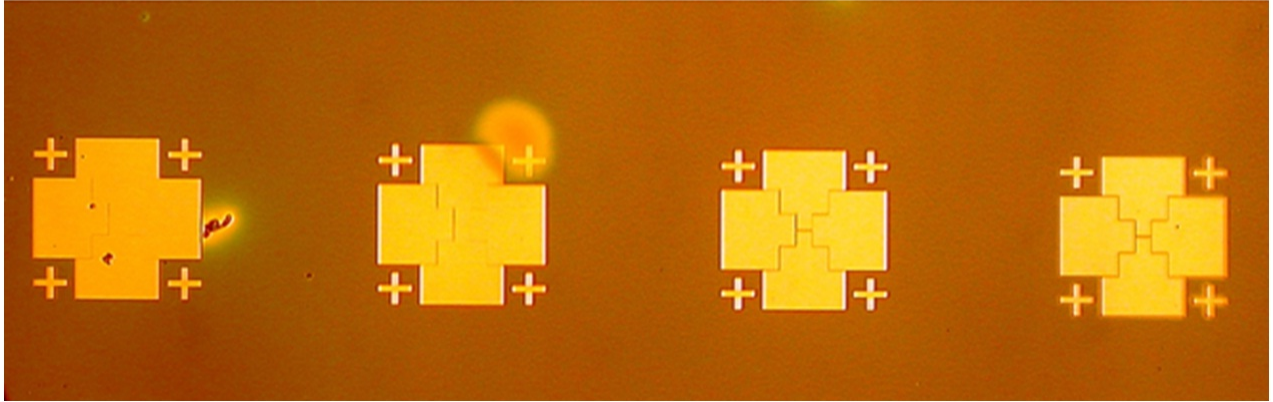


Figure 4.34: *Optical image of Si NW with different trench widths after being exposed and developed.*

Based on the micrograph the best trench size among them is 600 nm . 40 nm of Al was then evaporated onto the sample for contact region. Figure 4.35 shows an optical image of the 600 nm trench pattern structure after lift-off of Al. Here, the lift-off process was not successful and the contact areas were not isolated.

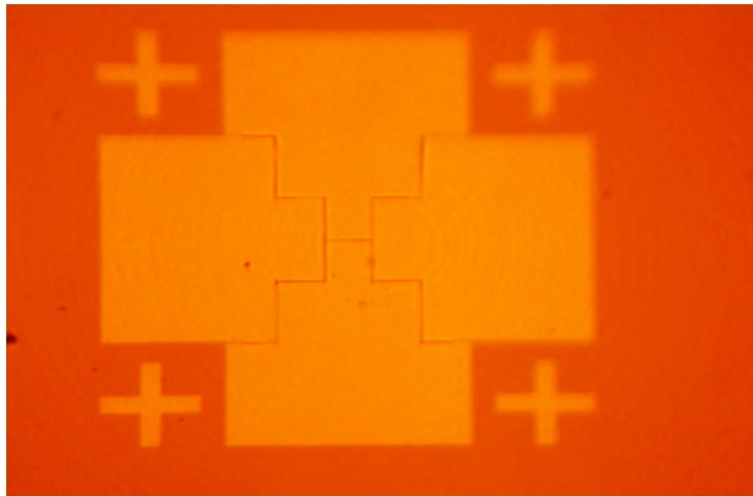


Figure 4.35: *Optical image of the pattern with 600 nm trench size after lift-off.*

Based on this experiment, the pattern trench size had to be wider, so a new pattern was exposed with wider trench size (700 nm). Figure 4.36 illustrates the new pattern after being developed.

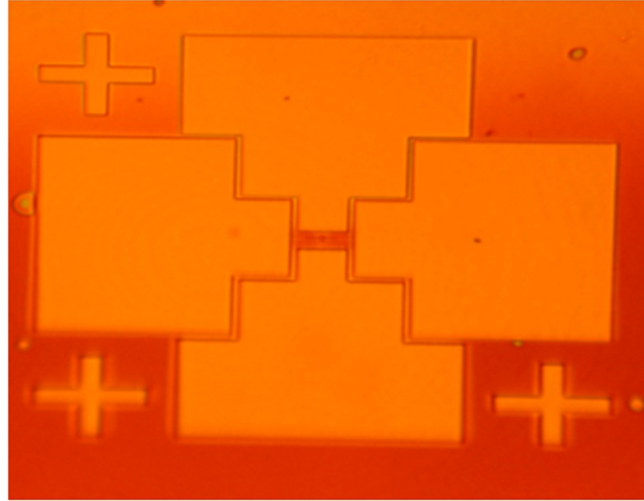


Figure 4.36: *Optical image of Si NW device with 700 nm trench size.*

The optical microscope image (Fig.4.36) illustrates that the contact areas are clearly defined. Here, the sample was developed for 50 seconds, and 20 nm of Al was evaporated on to form the contact areas. Finally, the sample was reactive ion etched for 50 seconds. Figure 4.37 illustrates the pattern after Al lift-off.

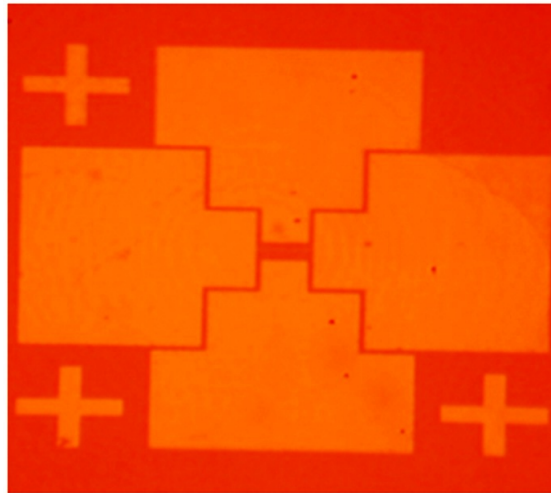


Figure 4.37: *Optical image Si NW device with 700 nm trench size after lift-off.*

Figure 4.37 shows that the lift-off in acetone and ultrasonic bath was successful. However, increasing the trenches size can make the lift-off easier. Here, based on the successful results

of the previous experiment, finally the experiment was repeated on highly-doped n -type SOI chips. The trenches size were set to $6\ \mu\text{m}$. Area exposure dose was set to $\sim 250\ \mu\text{C}/\text{cm}^2$, and single pass line exposure dose was $\sim 5.0\ \text{nC}/\text{cm}$. The pattern was exposed over 40 minutes and then developed for 50 seconds. The next step was to add the outer contact areas for ohmic contacts. In order to add these, the location of the pattern had to be found under the SEM and then the contact area “rectangles” had to be added separately. The beam voltage was set to $20\ \text{kV}$. Before starting the exposure process, the coordinates of the starting point (bottom-left corner) were saved. The pattern was then exposed for 47 minutes. Finally, the stage was moved to the pattern four corners separately, in order to add the outer contact areas. The sample was then developed for 50 seconds. Figure 4.38 illustrates the full pattern after being developed.

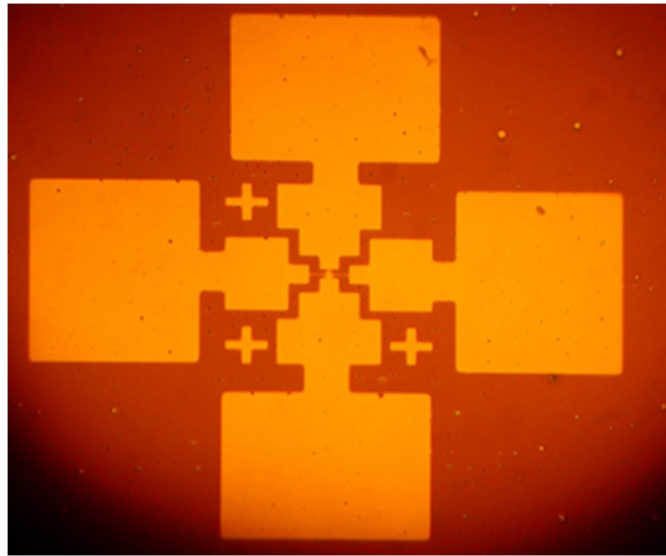


Figure 4.38: *Optical image new Si NW device with $\sim 6\ \mu\text{m}$ trench size and outer contact areas after being developed.*

Figure 4.38 shows that, the wire developed correctly, the contact areas were isolated from each other, and the outer contact areas were attached to the initial pattern properly. Then

40 nm of Al was evaporated on the chip. Figure 4.39 illustrates the optical micrograph of the device after evaporation and lift-off.

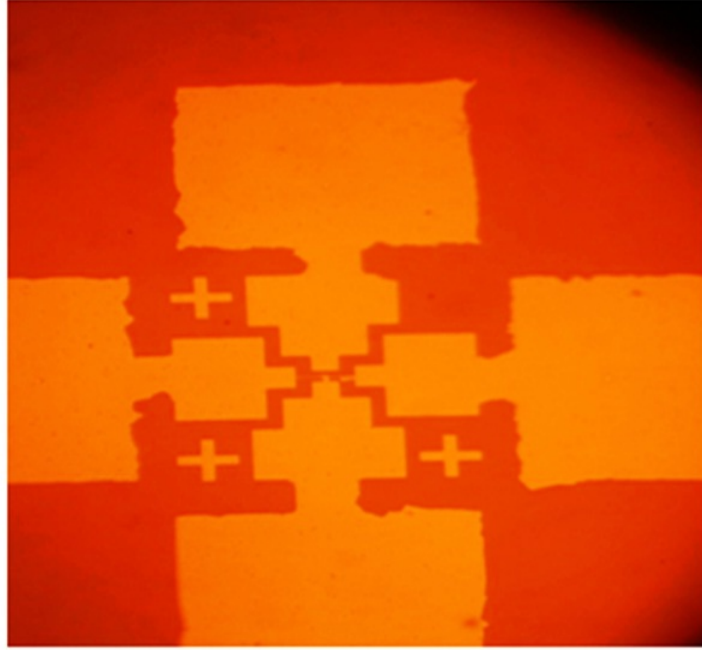


Figure 4.39: Optical image new Si NW device with 6 μm trench size and outer contact areas after Al evaporation and lift-off.

After lift-off and RIE, wet etching was used for 30 seconds to remove the Al metal from the surface. Here, the wet-etch contained mixtures of 1 – 5% HNO_3 for Al oxidation, 65 – 75% H_3PO_4 to dissolve the Al_2O_3 , 5 – 10% CH_3COOH for wetting and buffering and H_2O dilution. Si NWs with lengths $\sim 1\ \mu\text{m}$ and widths down to $\sim 50\ \text{nm}$ were fabricated by this process. This was followed by oxidation order to define the SiO_2 tunnel junction. Figure 4.40 shows the device after oxidation.

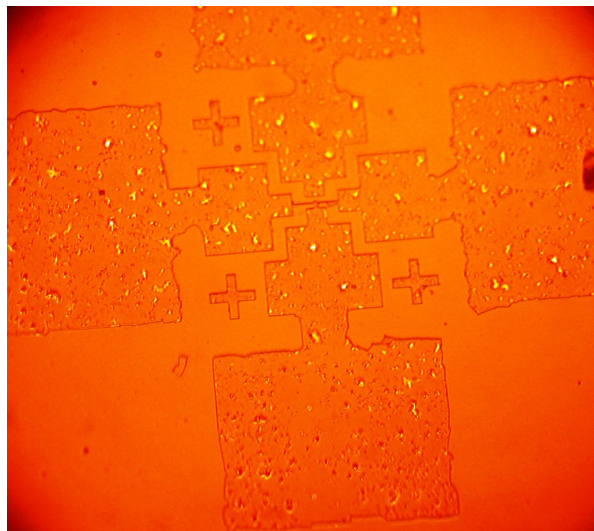


Figure 4.40: *Optical image of Si NW device with 6 μm trench size and outer contact areas after oxidation.*

Here, due to incomplete removal of Al mask from the device surface, the device is contaminated with Al after thermal oxidation. The device was then imaged with SEM (Fig.4.41).

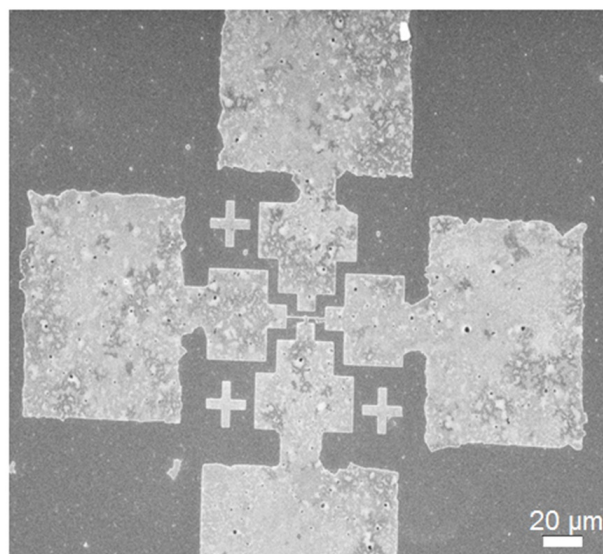


Figure 4.41: *Optical image of Si NW device with 6 μm trench size and outer contact areas after oxidation.*

As the damage to the sample after oxidation, affects the Si NW device, it can not be used for IETS measurements.

Therefore, the entire experiment was repeated. We also slightly changed the pattern file to make the lift-off and alignment easier (Fig.4.42).

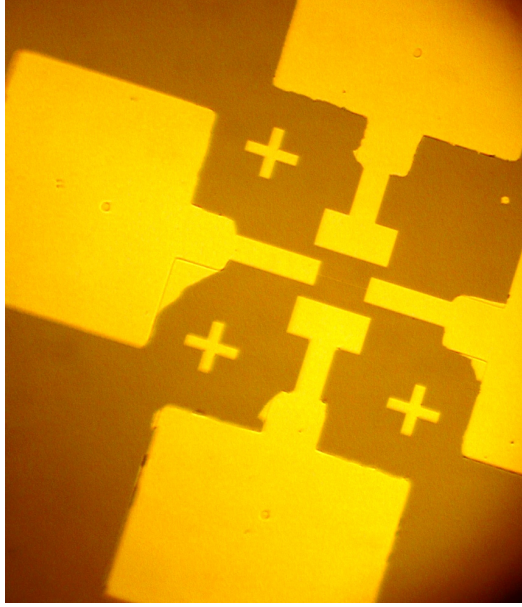


Figure 4.42: *Optical image of the final Si NW device with outer contact areas after Al evaporation and lift-off.*

Figure 4.42 illustrates the Si NW device after Al evaporation and lift-off. Reactive ion etching was then used to transfer the pattern to the substrates. Afterwards, wet etching was used for 30 seconds to remove the Al metal from the surface. The second EBL stage was then carried out to define a 40 nm thick and $\sim 120\text{ nm}$ wide Al NW such that it crossed the Si NW, forming the Si NW / SiO_2 / Al NW tunnel junction.

Figure 4.43 shows the SEM image of the Si NW / SiO_2 / Al NW tunnel junction device.

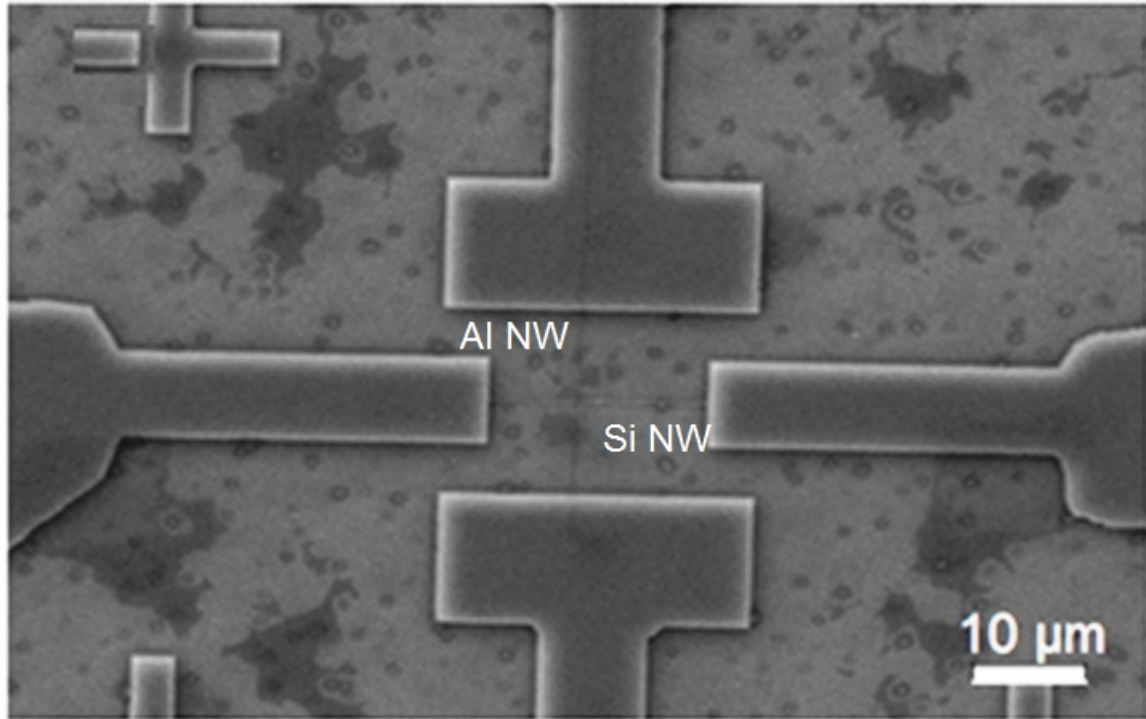


Figure 4.43: SEM image of Si NW / SiO₂ / Al NW tunnel junction.

Here, the underlying Si substrate of the SOI material is damaged after thermal oxidation. However, it does not affect the device region and can be used for IETS measurements.

Adding the Ohmic contacts was the final stage of fabrication process. This required a third EBL pattern. For this purpose the third layer of PMMA with a molecular weight of 950,000 (Diluted 6% in anisole) was spun and baked on the sample. Then, EBL was used to form contact areas and complete the device. Here, 120 nm of Al was thermally evaporated and lifted-off, to form the contact areas on the fabricated Si NW / SiO₂ / Al NW tunnel junction device. Figure 4.44 shows the device after successful evaporation and lift-off of Al as an Ohmic contacts.

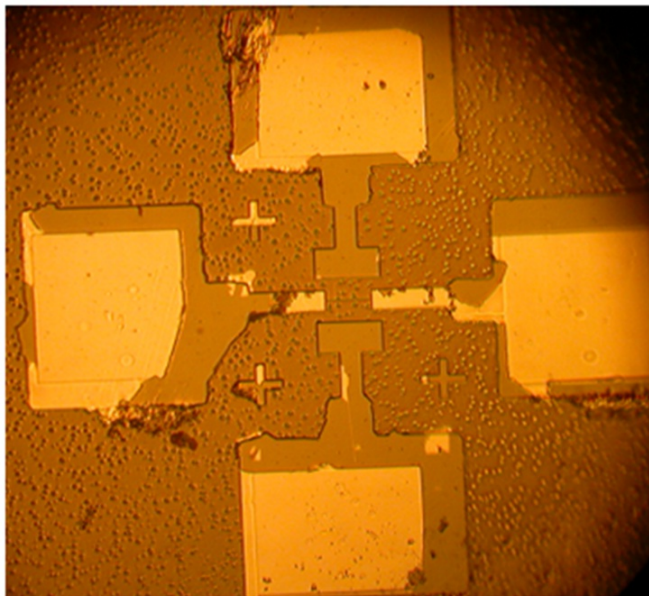


Figure 4.44: *Optical image of Si NW / SiO₂ / Al NW tunnel junction device with Al Ohmic contacts.*

The completed Si NW / SiO₂ / Al NW tunnel junction device was then imaged with the SEM (Fig.4.45)

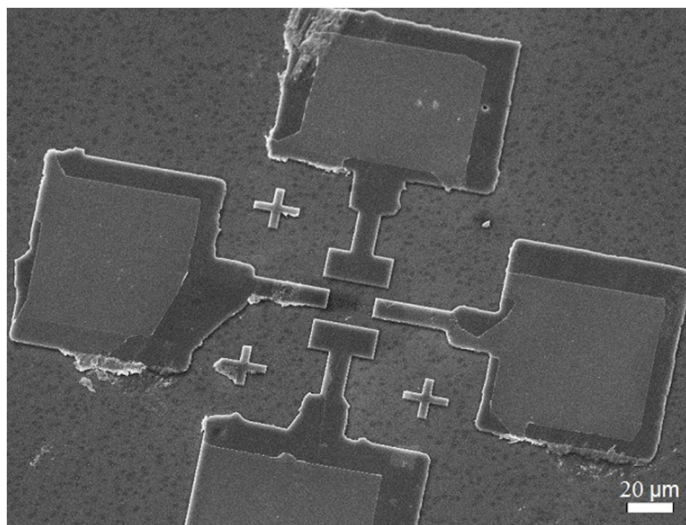


Figure 4.45: *SEM image of the completed Si NW / SiO₂ / Al NW tunnel junction with Al Ohmic contacts.*

The completed Si NW / SiO₂ / Al NW tunnel junction device was then imaged with the

SEM in high magnification (Fig.4.46). Here, the Si NW width is only $\sim 50\text{ nm}$ and the width of the Al is $\sim 120\text{ nm}$. The cross sectional area of the tunnel junction is $\sim 6 \times 10^{-15}\text{ m}^2$.

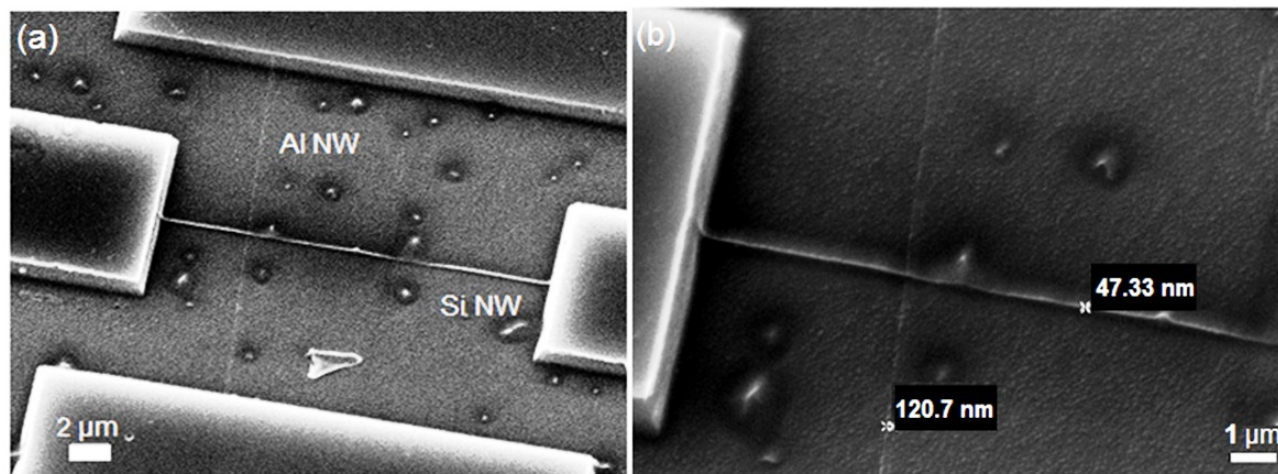


Figure 4.46: (a) Magnified SEM image of Si NW / SiO₂ / Al NW tunnel junction, (b) SEM image of Si NW / SiO₂ / Al NW tunnel junction with estimated NW widths.

Eight devices were fabricated using the above fabrication process. The Si NW / SiO₂ / Al NW tunnel junction devices were ready for the IETS measurements of well-characterised molecules such as NH_4OH , CH_3COOH , and $\text{C}_3\text{H}_6\text{O}_2$ adsorbed on the junction to demonstrate the successful operation of our device. These results will be discussed in Chapter 5.

4.3 Summary

This chapter consists of a detailed discussion of the fabrication process developed for preparation of nanoscale crossed Si NW / SiO₂ / Al NW tunnel junction for IETS measurements. Many different techniques may be used to fabricate the Si NWs including both “bottom-up” methods and lithographic “top-down” methods. A brief review of different Si NWs fabrication methods have been provided in this chapter. The Si NWs fabricated in the present

work, have been defined using electron beam lithography (EBL). The Si NW / SiO₂ / Al NW devices use Si NWs with widths down to $\sim 50\text{ nm}$. The NWs are thermally oxidised at 1000°C to create a SiO₂ layer $\sim 10\text{ nm}$ thick. An Al NW $\sim 120\text{ nm}$ in width is defined to longitudinally cross the SiO₂ / Si NW in each device, forming a nanoscale Si NW / SiO₂ / Al NW tunnel junction $\sim 50\text{ nm} \times 120\text{ nm}$ in area. Here, tunnelling occurs across the 10 nm thick SiO₂ layer. The molecules of interest are adsorbed on to the insulator after device fabrication.

An overview of electron beam lithography technique has been presented here. Furthermore, a detailed description of the fabrication steps necessary to define Si NW / SiO₂ / Al NW tunnel junction devices have been provided. Finally, a detailed discussion of fabrication issues have been presented. Here, the exposure and development issues, have been solved by using dosage trials. The lack of beam blanker, has been solved by intentionally parking the beam at a known position in the pattern. The alignment issues were solved by using “cross mark” method and rotating the sample to match with the pattern file coordinates.

Chapter 5

IETS Measurements

This chapter describes the experimental IETS measurement and analysis of fabricated nanoscale Si NW / SiO₂ / Al NW tunnel junction devices in detail. First, a discussion is provided of the experimental technique for measurement of our tunnel junction. This is followed by a discussion of IETS measurements performed at 300K, for ammonium hydroxide (NH_4OH), acetic acid (CH_3COOH), and propionic acid ($C_3H_6O_2$) molecules. In this regard, the $I - V$, $dI/dV - V$, and $d^2I/dV^2 - V$ characteristics of the tunnel junction are measured before and after the adsorption of molecules on the junction using vapour treatment or immersion. In all cases, peaks can be observed in the $d^2I/dV^2 - V$ characteristics following molecules adsorption. These peaks are compared to previous results on large area tunnel junctions and attributed to vibrational modes of $N - H$ and $C - H$ bonds.

5.1 Measurement Techniques

5.1.1 AC lock-in Measurement Technique

It is possible to measure IETS characteristics directly, with AC modulation techniques using lock-in amplifiers [2, 3]. In this technique, the dV/dI and d^2V/dI^2 vs. V characteristics are directly measured, and peaks in the d^2V/dI^2 vs. V data give the IETS spectrum. The peak positions and widths are sufficient to obtain a molecular spectrum for the adsorbate. A basic measurement circuit for IETS is shown in Fig.5.1. Here, a low-distortion oscillator provides a small AC voltage of amplitude ν and frequency f , a DC voltage source provides bias voltage V_b , and a lock-in amplifier measures signals at f and $2f$.

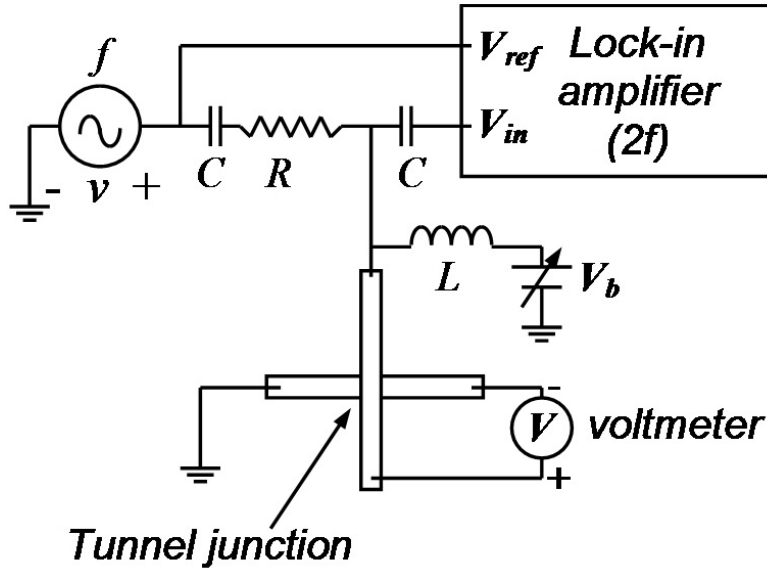


Figure 5.1: AC lock-in measurement circuit [156].

The DC junction voltage V is measured using a high-impedance voltmeter. A resistance $R \gg$ the tunnel junction resistance R_t leads to an approximately constant DC bias current I_0 and AC modulation current (amplitude i_0) across the junction. At frequency f , the DC

blocking capacitors C has small impedance and the inductor L has large impedance. We may then use a Taylor series to expand V as follows:

$$\begin{aligned}
 V(I) &= V(I_0 + i\cos(2\pi ft)) \\
 &= V(I_0) + \left(\frac{dV}{dI}\right)_{I_0} i\cos(2\pi ft) + \left(\frac{1}{2}\right)\left(\frac{d^2V}{dI^2}\right)_{I_0} i^2\cos^2(2\pi ft) + \dots \\
 &= V(I_0) + \left(\frac{dV}{dI}\right)_{I_0} i\cos(2\pi ft) + \left(\frac{1}{4}\right)\left(\frac{d^2V}{dI^2}\right)_{I_0} i^2(1 + \cos(2\pi(2f)t)) + \dots
 \end{aligned} \tag{5.1}$$

The junction voltage then includes components at f and $2f$:

$$V_f = \left(\frac{dV}{dI}\right)_{I_0} i\cos(2\pi ft) \tag{5.2}$$

and

$$V_{2f} = \frac{1}{4}\left(\frac{d^2V}{dI^2}\right)_{I_0} i^2(1 + \cos(2\pi(2f)t)) \tag{5.3}$$

These components are inversely proportional to $\sigma = dI/dV$ and to d^2I/dV^2 and may be detected by the lock-in amplifier directly. V_{2f} gives the IETS characteristics of the device. A voltage range of $0 - 0.5 V$, corresponding to a spectral range from $0 - 4000 \text{ cm}^{-1}$, is typically

sufficient to characterise vibrational spectra [2]. However, the $I - V$ characteristics must be separately measured to obtain a full set ($I, dI/dV$ and d^2I/dV^2) of data for the system. A much larger voltage range ($\sim 1 - 10 V$, corresponding to spectral range $8000 - 80000 \text{ cm}^{-1}$) is necessary to characterise the elastic tunnelling spectrum. In this case, potentially direct resonant tunnelling through molecular states can be observed, in either the $I - V$ or $dI/dV - V$ data. Here, the molecular states are confined by the double barrier structure formed by the sections of the tunnel barrier to the right and left of the molecule.

5.1.2 DC Measurement Technique

Recently, a DC measurement technique has also been used to measure IETS characteristics directly [102]. This section provides the experimental technique for IETS measurement of our fabricated Si NW / SiO₂ / Al NW tunnel junction devices. Here, four-terminal $I - V$ characteristics are directly measured, and the $dI/dV - V$, and $d^2I/dV^2 - V$ characteristics are then calculated from the obtained data. The basic four-terminal measurement circuit is shown in Fig.5.2.

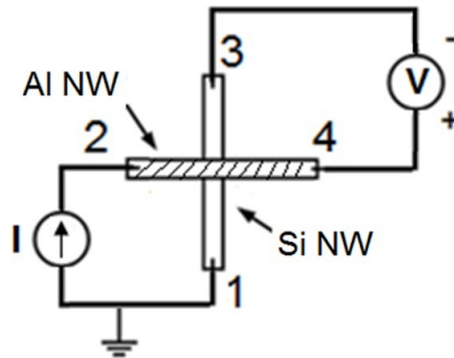


Figure 5.2: *The four-terminal dc measurement circuit.*

In this thesis, four terminal $I - V$ characteristics (1000 measurement points) were obtained

using an Agilent 4155B parameter analyzer. In this technique, current was forced through the tunnel junction using terminals 2 (Al NW) and 1 (Si NW), and the voltage was measured between terminals 4 (Al NW) and 3 (Si NW). Here, the measurement terminals have high-impedance inputs with no current flow, therefore no voltage drop occurs across the measurement lines. This is an advantage which allows accurate measurements at low resistance values. The $dI/dV - V$ and $d^2I/dV^2 - V$ characteristics are then calculated from the obtained data. Here, peaks can be observed in the $d^2I/dV^2 - V$ characteristics following molecules adsorption.

5.2 Results and Discussions

Nanoscale Si NW / SiO₂ / Al NW tunnel junction devices were fabricated according to the fabrication process described in Chapter 4. Here, IETS measurements were performed at room temperature to obtain four terminal $I - V$ characteristics (1000 measurement points) for two such devices. The $dI/dV - V$ and $d^2I/dV^2 - V$ characteristics were then calculated from the data. The noise floor in our $I - V$ measurement was ~ 10 pA, allowing direct extraction of $d^2I/dV^2 - V$ curves. Here, the electrical characteristics of a “clean” tunnel junctions were measured first at 300K. Then the tunnelling spectra were measured for NH_4OH , CH_3COOH , and $C_3H_6O_2$ molecules.

NH_4OH was deposited on the device by vapour treatment and CH_3COOH and $C_3H_6O_2$ by immersion. It was possible to wash the device in acetone / IPA and recover the original “clean” measurement. This is in strong contrast to previous IETS measurements, where

molecules were introduced during tunnel junction fabrication [1–4].

5.2.1 Vapour Treatment from Ammonium Hydroxide (NH_4OH)

Electrical characteristics of a “clean” tunnel junction were measured first at $300K$. The $dI/dV - V$ and $d^2I/dV^2 - V$ were then calculated numerically. As the devices could not be immersed directly in ammonium hydroxide, vapour treatment was used to deposit NH_3 vapour molecules on the device. Here, the two devices were left in a petri dish in an ammonium hydroxide atmosphere for two hours. Measurements were then repeated and compared to those from the “clean” devices (Fig.5.3(a-c) - Fig.5.5(a-c)).

Figure 5.3(a-c) and Fig.5.5(a-c) show the IETS characteristics of two different Si NW / SiO_2 / Al NW tunnel junctions, before and after adsorption of NH_4OH molecules at $300K$.

Figure 5.3(a) illustrates the $I - V$ characteristics of the first tunnel junction before and after adsorption of NH_4OH molecules. Figure 5.3(b) displays the $dI/dV - V$ characteristics, and Fig.5.3(c) shows the $d^2I/dV^2 - V$ characteristics of the first device. The $I - V$ characteristics (Fig.5.3(a)) are diode-like, due to the presence of a “Schottky-like” barrier at the Al NW / Si NW interface.

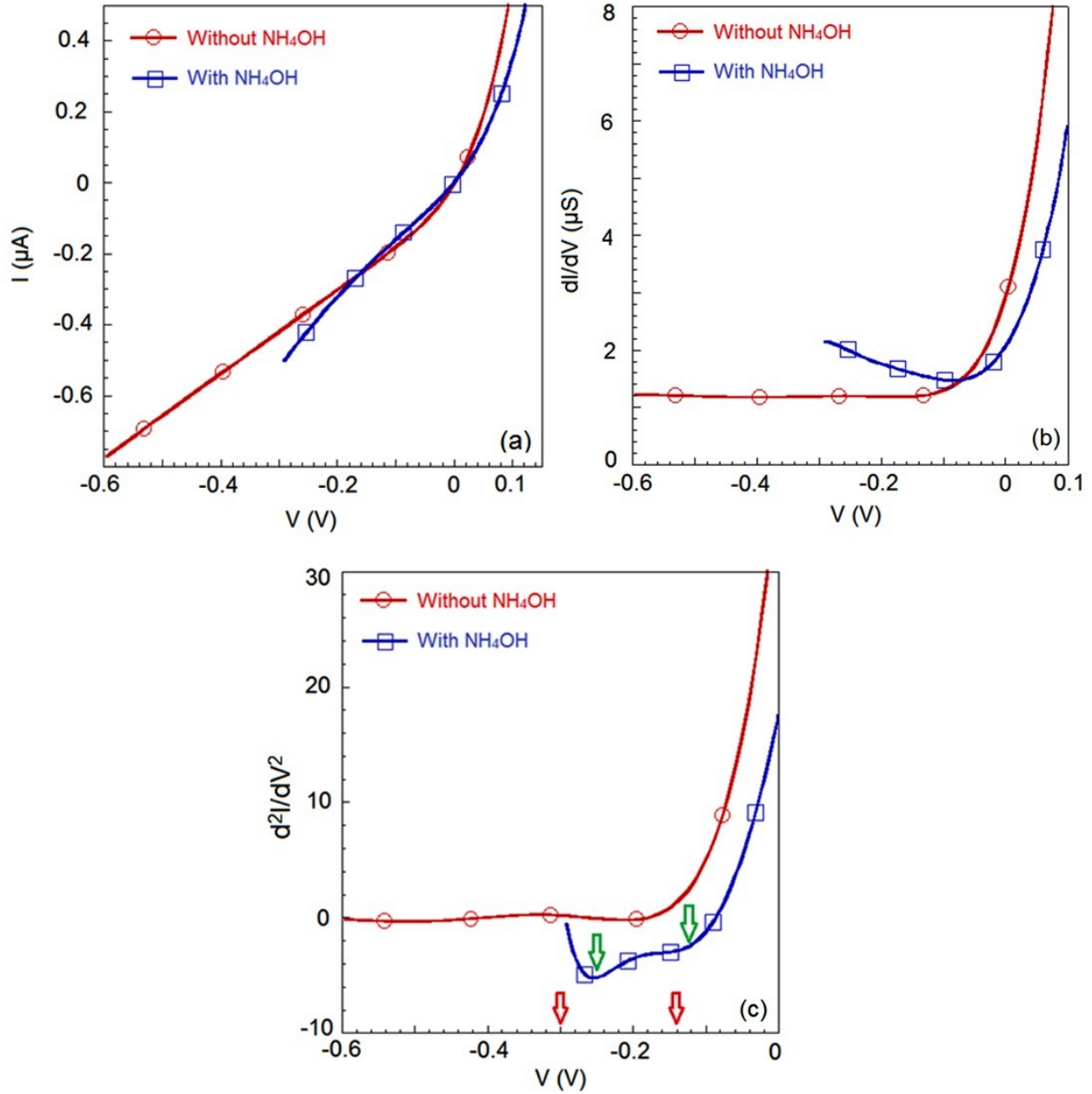


Figure 5.3: IET spectrum of NH_4OH on a first $\text{Si NW} / \text{SiO}_2 / \text{Al NW}$ tunnel junction at 300K (1000 measurement points, Rectangles and circles used as marker to indicate different curves): (a) The $I - V$ characteristics of the tunnel junction before and after adsorption of NH_4OH molecules, (b) The $dI/dV - V$ characteristics, (c) The $d^2I/dV^2 - V$ characteristics of the device (Green arrows indicate excitation modes of N - H bonds in a SIM ($\text{Si NW} / \text{SiO}_2 / \text{Al}$) device at 300K vs. Red arrows indicate previously reported excitation modes of N - H bonds in a MIM ($\text{Al} / \text{Al}_2\text{O}_3 / \text{Pb}$) device at 4.2K).

As we measure the data using a four-terminal measurement, this implies that the potential barrier must lie along the current path, i.e. at the Al NW / SiO₂ interface and is not remote from the junction or elsewhere in the Si NW (Fig.5.4).

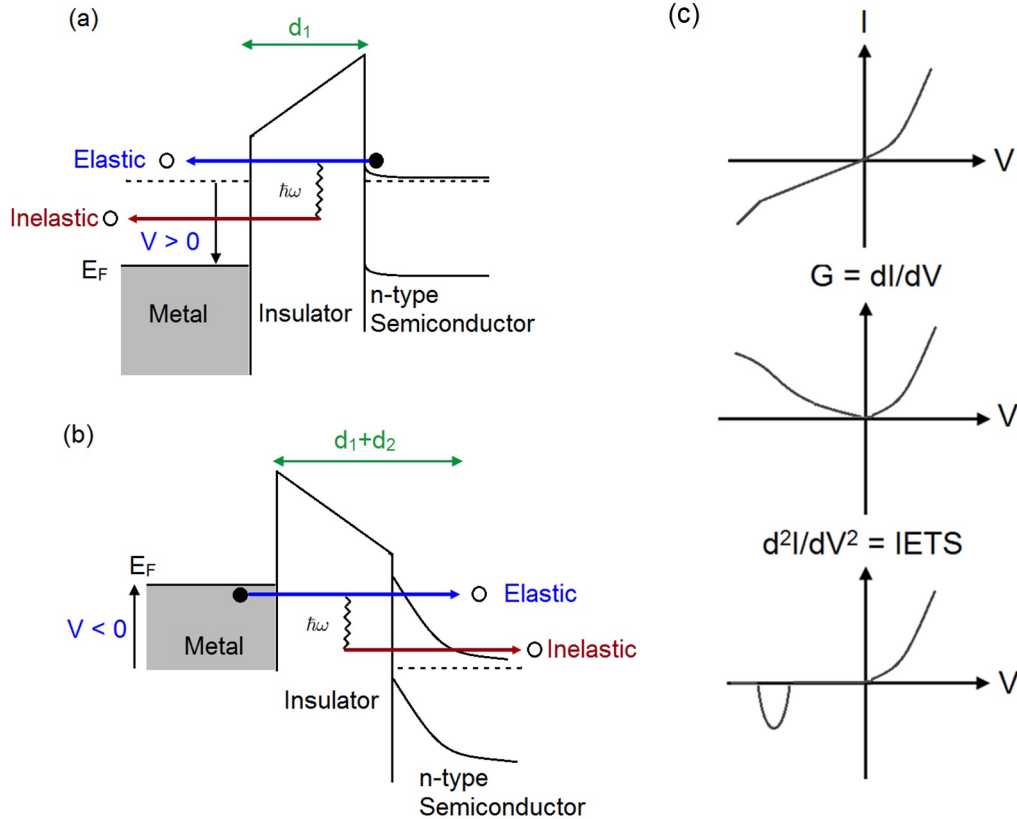


Figure 5.4: (a) Inelastic tunnelling forward bias, (b) Inelastic tunnelling reverse bias, (c) IETS signals for semiconductor - insulator - metal tunnel junction.

The device's current reduces slightly following NH_4OH treatment. In the $d^2I/dV^2 - V$ characteristics (Fig.5.3(c)), peaks are observed at $\sim -0.12\text{ V}$ and -0.25 V (upper arrows). The Peak at $\sim -0.25\text{ V}$ may be attributed to the first excitation modes of an $N-H$ bond at room temperature. The lower arrows at $\sim -0.15\text{ V}$ and -0.3 V indicate previously reported excitation modes of $N-H$ bonds in a MIM (Al / Al₂O₃ / Pb) device at 4.2 K [157].

Figure 5.5(a-c) shows the IETS characteristics of the second Si NW / SiO₂ / Al NW tunnel junction device, before and after adsorption of NH₄OH molecules at 300K.

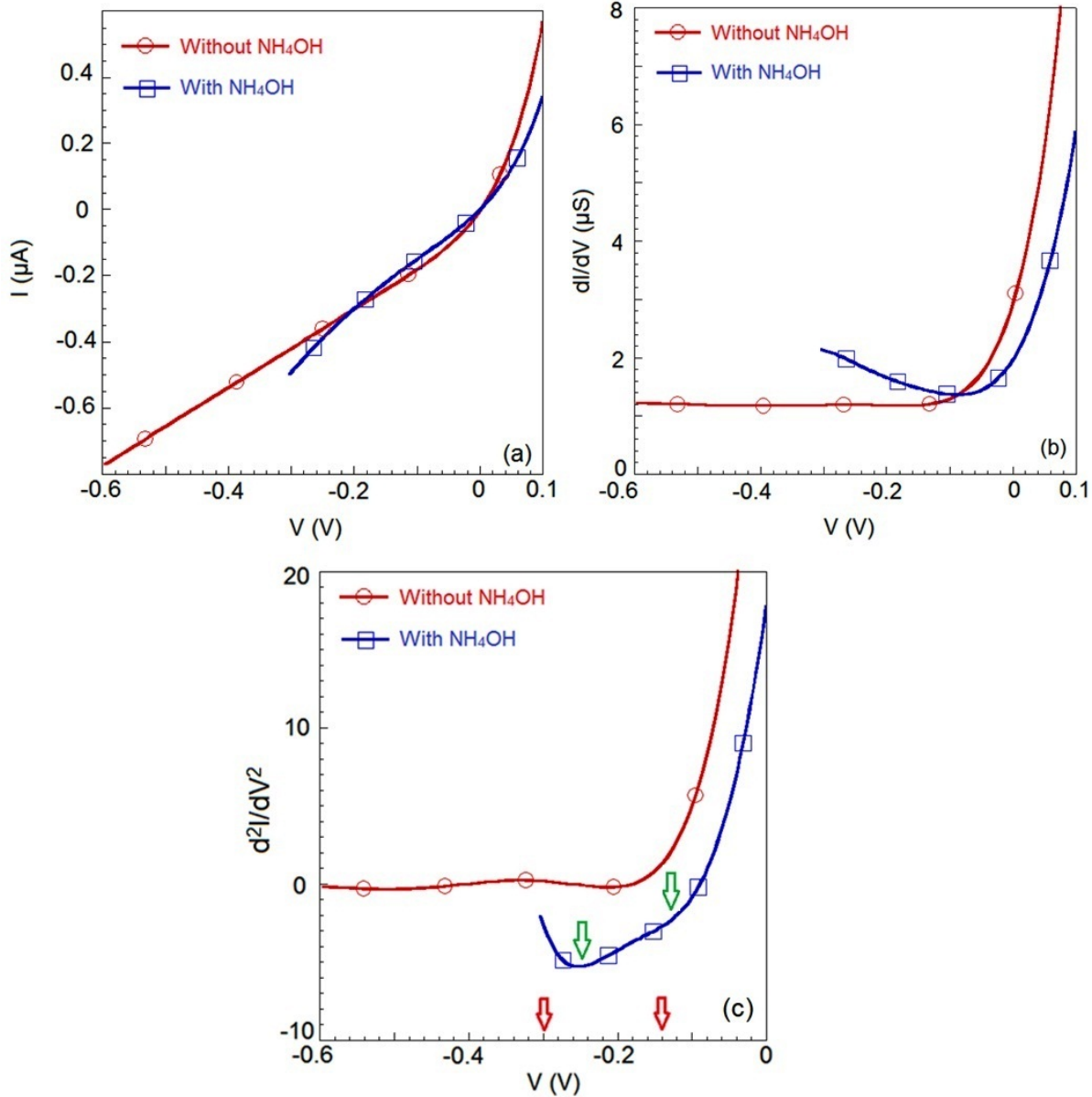


Figure 5.5: IET spectrum of NH₄OH on a second Si NW / SiO₂ / Al NW tunnel junction at 300K (1000 measurement points, Rectangles and circles used as marker to indicate different curves): (a) The $I - V$ characteristics of the tunnel junction before and after adsorption of NH₄OH molecules, (b) The $dI/dV - V$ characteristics, (c) The $d^2I/dV^2 - V$ characteristics of the device (Green arrows indicate excitation modes of N - H bonds in a SIM (Si NW / SiO₂ / Al) device at 300K vs. Red arrows indicate previously reported excitation modes of N - H bonds in a MIM (Al / Al₂O₃ / Pb) device at 4.2K).

Figure 5.5(a) illustrate the $I - V$ characteristics of the second tunnel junction before and after adsorption of NH_4OH molecules. Figure 5.5(b) displays the $dI/dV - V$ characteristics, and Fig.5.5(c) shows the $d^2I/dV^2 - V$ characteristics of the second device. The $I - V$ characteristics (Fig.5.5(a)) are diode-like, due to the presence of a “Schottky-like” barrier at the Al NW / SiO_2 interface (Fig.5.4).

In the $d^2I/dV^2 - V$ characteristics (Fig.5.5(c)), peaks are observed at $\sim -0.12V$ and $\sim -0.25V$ (upper arrows). These may be attributed to the first and second excitation modes of an $N - H$ bond at room temperature. The lower arrows at $\sim -0.15V$ and $-0.3V$ indicate previously reported excitation modes of $N - H$ bonds in a MIM Al / Al_2O_3 / Pb device at $4.2K$ [157]. The peaks in our data are shifted slightly relative to previous data.

Table 5.1 compared our experimental results on SIM (Si NW / SiO_2 / Al NW) tunnel junction devices at room temperature with previously reported excitation modes of $N - H$ bonds in a MIM (Al / Al_2O_3 / Pb) device at $4.2K$ [157]:

Table 5.1: Experimental Results for Ammonium Hydroxide

	$1^{st} \text{ Excitation}$	$2^{nd} \text{ Excitation}$
SIM Device I at 300K	$-0.12V$	$-0.25V$
SIM Device II at 300K	$-0.12V$	$-0.25V$
MIM Device at 4.2K	$-0.15V$	$-0.3V$

In contrast to early IETS measurements, it is possible to wash the device in acetone / IPA and recover the original “clean” measurement. This is due to the possibility of molecules adsorption after tunnel junction fabrication. In early IETS measurements molecules were introduced during the tunnel junction fabrication [1–4].

5.2.2 Acetic Acid (CH_3COOH)

The IETS characteristics of tunnel junctions with acetic acid adsorption were then measured for the same set of devices following “cleaning” (Fig.5.6 and Fig.5.7).

Figures 5.6-7(a-c) shows the $I - V$, $dI/dV - V$ and $d^2I/dV^2 - V$ characteristics respectively, for both the “clean” devices, and the devices with acetic acid adsorption. Acetic acid was adsorbed on the “clean” devices by immersion at room temperature for 5 minutes.

In a manner similar to the measurements of Fig.5.3(a) and Fig.5.5(a), the $I - V$ characteristics are diode-like, both before and after immersion, and the device current reduces following immersion. The $dI/dV - V$ characteristics of the devices (Fig.5.6-7(b)) shows a reduction in conductance, and non-linearities which correspond to the peaks in the $d^2I/dV^2 - V$ characteristics (Fig.5.6-7(c)).

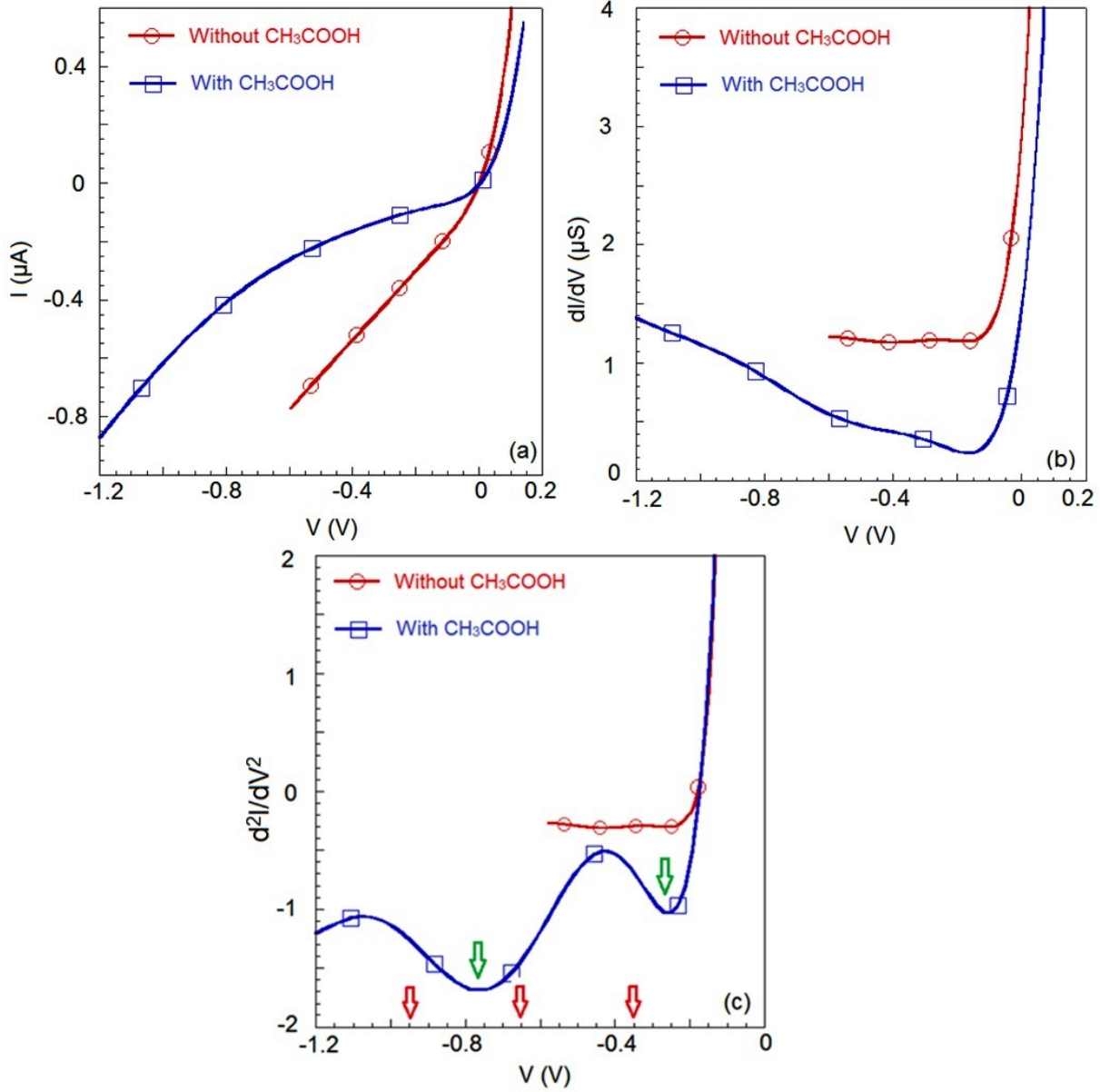


Figure 5.6: IET spectrum of CH_3COOH on a first Si NW / SiO_2 / Al NW tunnel junction at 300K (1000 measurement points, Rectangles and circles used as marker to indicate different curves): (a) The $I - V$ characteristics of the tunnel junction before and after adsorption of CH_3COOH molecules, (b) The $dI/dV - V$ characteristics, (c) The $d^2I/dV^2 - V$ characteristics of the device (Green arrows indicate excitation modes of C - H bonds in a SIM (Si NW / SiO_2 / Al) device at 300K vs. Red arrows indicate previously reported excitation modes of C - H bonds in a MIM (Al / Al_2O_3 / Pb) device at 4.2K).

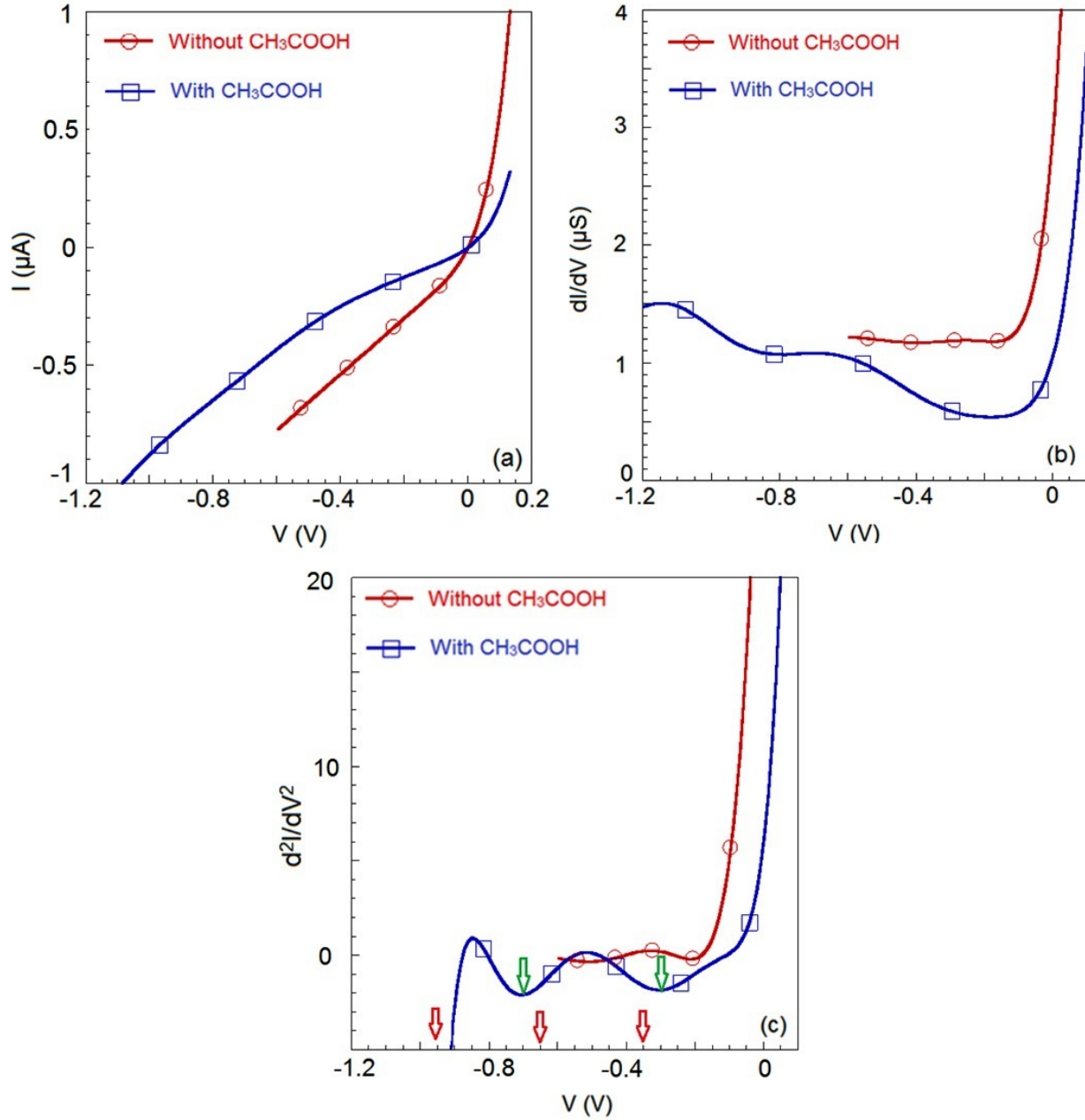


Figure 5.7: IET spectrum of CH_3COOH on a second Si NW / SiO_2 / Al NW tunnel junction at 300K (1000 measurement points, Rectangles and circles used as marker to indicate different curves): (a) The $I - V$ characteristics of the tunnel junction before and after adsorption of CH_3COOH molecules, (b) The $dI/dV - V$ characteristics, (c) The $d^2I/dV^2 - V$ characteristics of the device (Green arrows indicate excitation modes of C - H bonds in a SIM (Si NW / SiO_2 / Al) device at 300K vs. Red arrows indicate previously reported excitation modes of C - H bonds in a MIM (Al / Al_2O_3 / Pb) device at 4.2K).

In Fig.5.6(c) and Fig.5.7(c), the upper arrows indicate the measured peaks at $\sim -0.25 V$ and $-0.75 V$. The lower arrows illustrate the previously reported excitation modes of $C - H$ at $\sim -0.36 V$, $-0.65 V$, and $-0.95 V$ in a MIM device at $4.2 K$ [120].

Table 5.2 compared the measured excitation modes of $C - H$ bonds in a SIM (Si NW / SiO_2 / Al NW) tunnel junction devices at room temperature with previously reported excitation modes of $C - H$ bonds in a MIM (Al / Al_2O_3 / Pb) device at $4.2 K$ [120]:

Table 5.2: Experimental Results for Acetic Acid

	$1^{st} \text{ Excitation}$	$2^{nd} \text{ Excitation}$
SIM Device I at 300K	$-0.25V$	$-0.75V$
SIM Device II at 300K	$-0.25V$	$-0.75V$
MIM Device at 4.2K	$-0.36V$	$-0.65V$

However, according to simulations (see Chapter 6) the 1^{st} peak does not correspond to any of the $C - H$ excitation modes. This peak may be due the $N - H$ bonds trapped in SiO_2 layer on the sample. The 2^{nd} peak can be attributed to the second excitation mode of a $C - H$ bond at room temperature (Chapter 6).

5.2.3 Propionic Acid ($C_3H_6O_2$)

The devices were then again washed in acetone / IPA and the original “clean” measurements obtained. Following this, IETS characteristics of tunnel junctions with propionic acid adsorption were measured (Fig.5.8 and Fig.5.9). Figure 5.8(a-c) and Fig.5.9(a-c) shows the $I - V$, $dI/dV - V$ and $d^2I/dV^2 - V$ characteristics respectively, for both the “clean” devices, and the devices with propionic acid adsorption. Propionic acid was adsorbed on the “clean” devices by immersion at room temperature for 5 minutes.

In a manner similar to the measurements of Fig.5.3(a), Fig.5.5(a), Fig.5.6(a) and Fig.5.7(a), the $I - V$ characteristics are diode-like, both before and after immersion, and the device current reduces following immersion. Figure 5.8(b) and Fig.5.9(b), the $dI/dV - V$ characteristics of the devices, shows a reduction in conductance and nonlinearities which correspond to the peaks in the $d^2I/dV^2 - V$ characteristics.

In Fig.5.8(c) and Fig.5.9(c), the upper arrows illustrate measured peaks at $\sim -0.2 V$, $-0.5 V$, and $-0.85 V$. The lower arrows illustrate the previously reported excitation modes of $C - H$ at $\sim -0.36 V$, $-0.65 V$, and $-0.95 V$ in a MIM device at $4.2K$ [157].

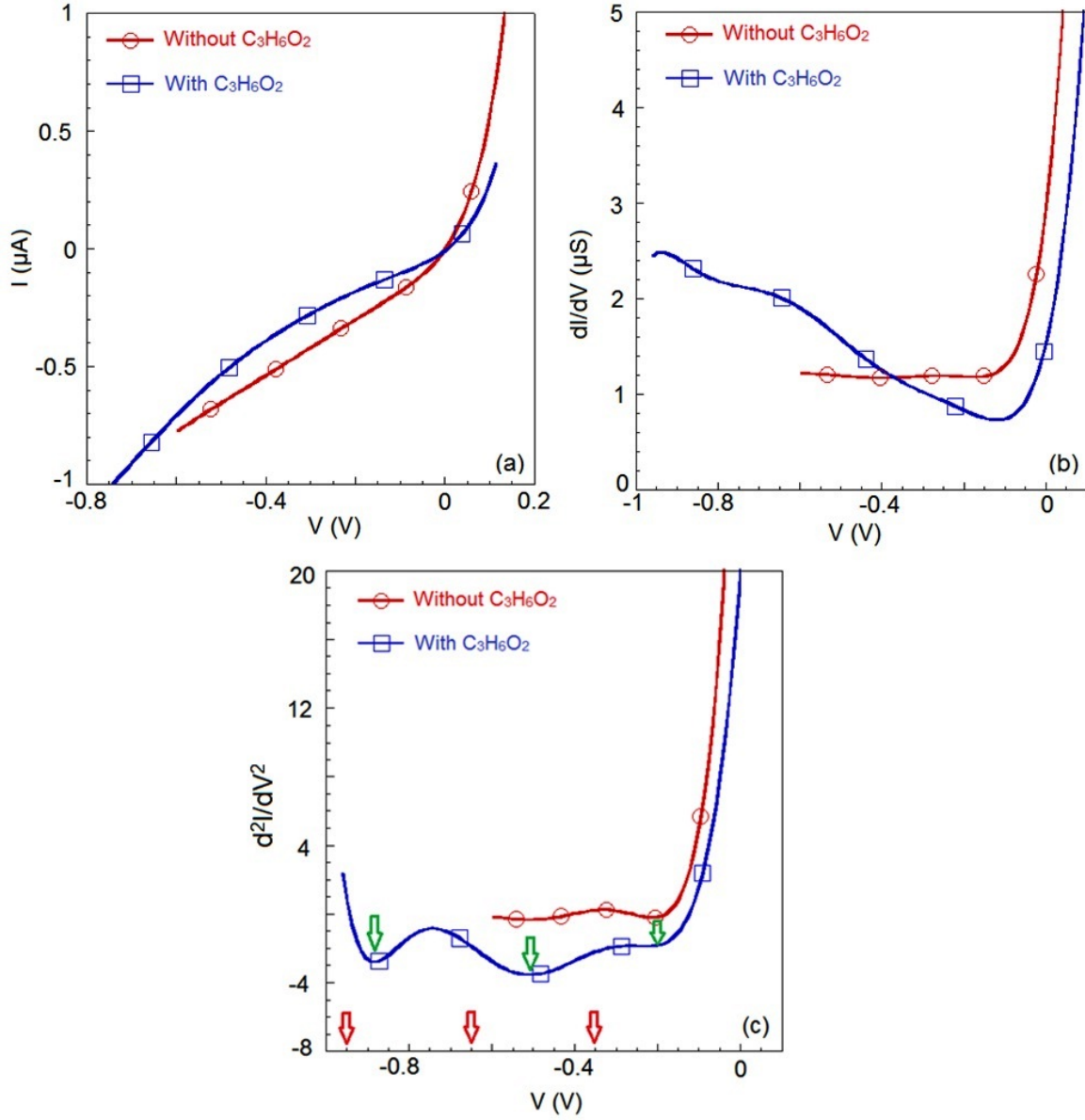


Figure 5.8: IET spectrum of $C_3H_6O_2$ on a first Si NW / SiO_2 / Al NW tunnel junction at 300K (1000 measurement points, Rectangles and circles used as marker to indicate different curves): (a) The $I - V$ characteristics of the tunnel junction before and after adsorption of $C_3H_6O_2$ molecules, (b) The $dI/dV - V$ characteristics, (c) The $d^2I/dV^2 - V$ characteristics of the device (Green arrows indicate excitation modes of C - H bonds in a SIM (Si NW / SiO_2 / Al) device at 300K vs. Red arrows indicate previously reported excitation modes of C - H bonds in a MIM (Al / Al_2O_3 / Pb) device at 4.2K).

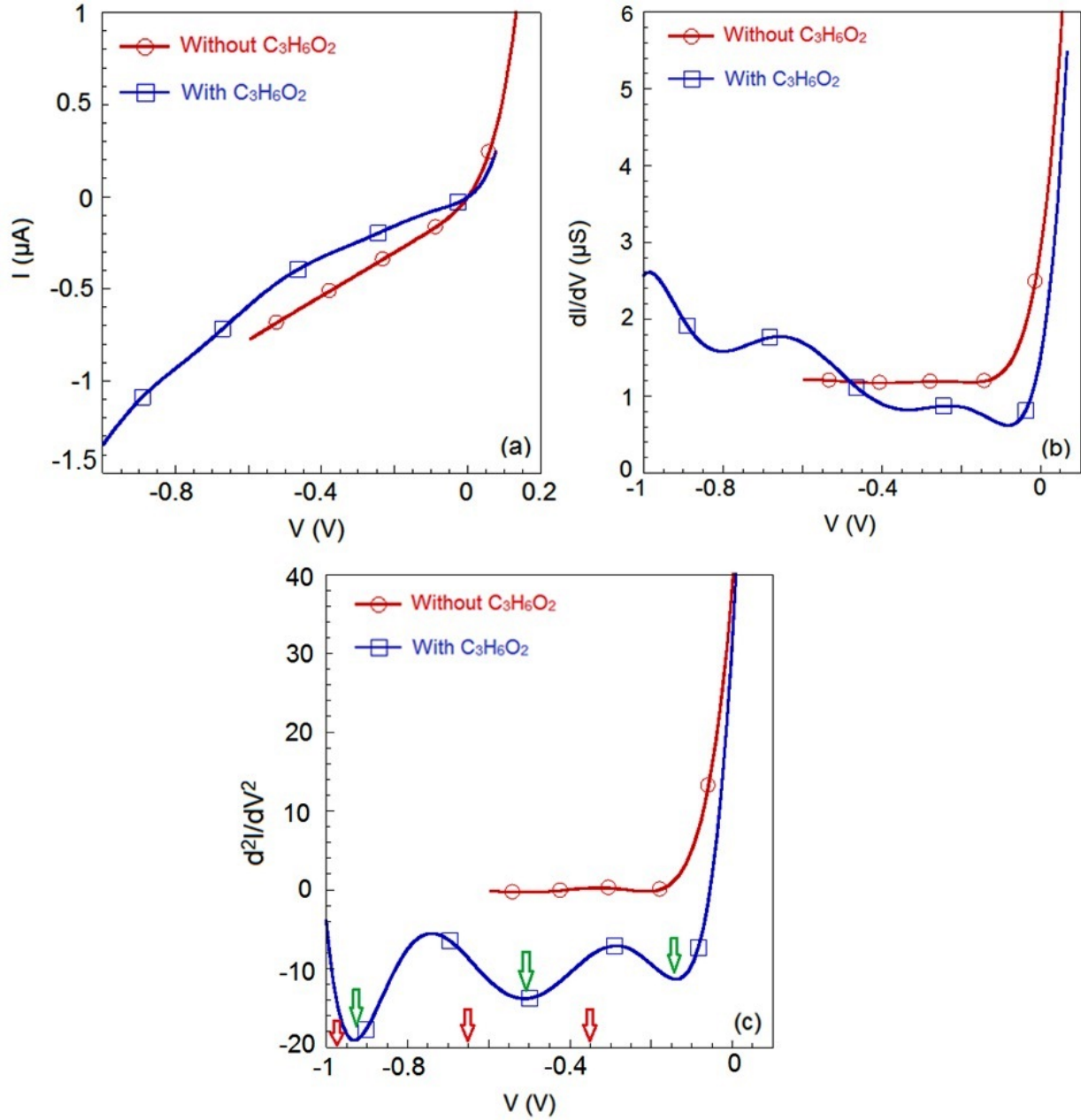


Figure 5.9: IET spectrum of $C_3H_6O_2$ on a second Si NW / SiO_2 / Al NW tunnel junction at 300K (1000 measurement points, Rectangles and circles used as marker to indicate different curves): (a) The $I - V$ characteristics of the tunnel junction before and after adsorption of $C_3H_6O_2$ molecules, (b) The $dI/dV - V$ characteristics, (c) The $d^2I/dV^2 - V$ characteristics of the device (Green arrows indicate excitation modes of C-H bonds in a SIM (Si NW / SiO_2 / Al) device at 300K vs. Red arrows indicate previously reported excitation modes of C-H bonds in a MIM (Al / Al_2O_3 / Pb) device at 4.2K).

Table 5.3 compares the measured excitation modes of $C - H$ bonds in a SIM (Si NW / SiO₂ / Al NW) tunnel junction devices at room temperature with previously reported excitation modes of $C - H$ bonds in a MIM (Al / Al₂O₃ / Pb) device at 4.2K [120]:

Table 5.3: Experimental Results for Propionic Acid

	1^{st} Excitation	2^{nd} Excitation	3^{rd} Excitation
SIM Device I at 300K	$-0.2V$	$-0.5V$	$-0.85V$
SIM Device II at 300K	$-0.2V$	$-0.5V$	$-0.85V$
MIM Device at 4.2K	$-0.36V$	$-0.65V$	$-0.95V$

However, according to simulations (see Chapter 6) the 1^{st} peak does not correspond to any of the $C - H$ excitation modes. Here, this peak may be due the $N - H$ bonds trapped in SiO₂ layer on the sample. The 2^{nd} and 3^{rd} peaks can be attributed to the first and second excitation modes of a $C - H$ bond at room temperature (Chapter 6). The peaks separation in our measured data is $\sim -0.3V$, which corresponds well to the separation between the 1^{st} and 2^{nd} excitation modes of $C - H$ bond on an Al / Al₂O₃ / Pb tunnel junctions [120]. The position of the peaks are also compared with peak positions for $Si - H$, $Si - CH_3$, and $Si - OH$ bonds to make sure that measured peak positions corresponded to the $C - H$ bonds.

5.2.4 Discussion

In this chapter we have presented the IETS measurement and analysis of a fabricated nanoscale Si NW / SiO₂ / Al NW tunnel junction devices. Here, IETS measurements were performed at 300K, for ammonium hydroxide (NH_4OH), acetic acid (CH_3COOH), and propionic acid ($C_3H_6O_2$) molecules. In this regard, the $I-V$, $dI/dV-V$, and d^2I/dV^2-V characteristics of the tunnel junction are measured before and after the adsorption of molecules on the junction using vapour treatment or immersion.

In all cases, peaks can be observed in the $d^2I/dV^2 - V$ characteristics following molecule adsorption. These peaks are compared to previous results on large area tunnel junctions, and attributed to vibrational modes of $N-H$ and $C-H$ bonds.

Comparison

The measured IETS characteristics of the fabricated Si NW / SiO₂ / Al NW tunnel junction devices before and after the adsorption of molecules on the junction, shows trends that were expected in our devices. These include the effect of the SB, and change in slope of the $I-V$ characteristics at specific points, leading to peaks in the d^2I/dV^2 curves (Fig.5.10). At low applied voltage V , tunnelling through the barrier is elastic. However, inelastic tunnelling caused by electron interaction with vibrational states in the adsorbed molecules created additional conduction channels, with a change in energy $\hbar\omega$. These lead to an increase in conductance $dI/dV - V$ characteristics (Fig.5.10(b)) at voltages corresponding to the vibration state energies, and peaks in the $d^2I/dV^2 - V$ characteristics (Fig.5.10(c)) for each

additional channel, giving a particular spectrum of the molecular vibration modes. Strong steps were not observed in the $dI/dV - V$ characteristic due to thermal smearing at the measurement temperature of $300K$. Changes in the slope of the characteristics are observed, leading to peaks in the $d^2I/dV^2 - V$ characteristics.

Figure 5.10 illustrates the schematic diagram of the $I - V$, $dI/dV - V$, and $d^2I/dV^2 - V$ characteristics of the Si NW / SiO₂ / Al NW tunnel junction after the adsorption of molecules.

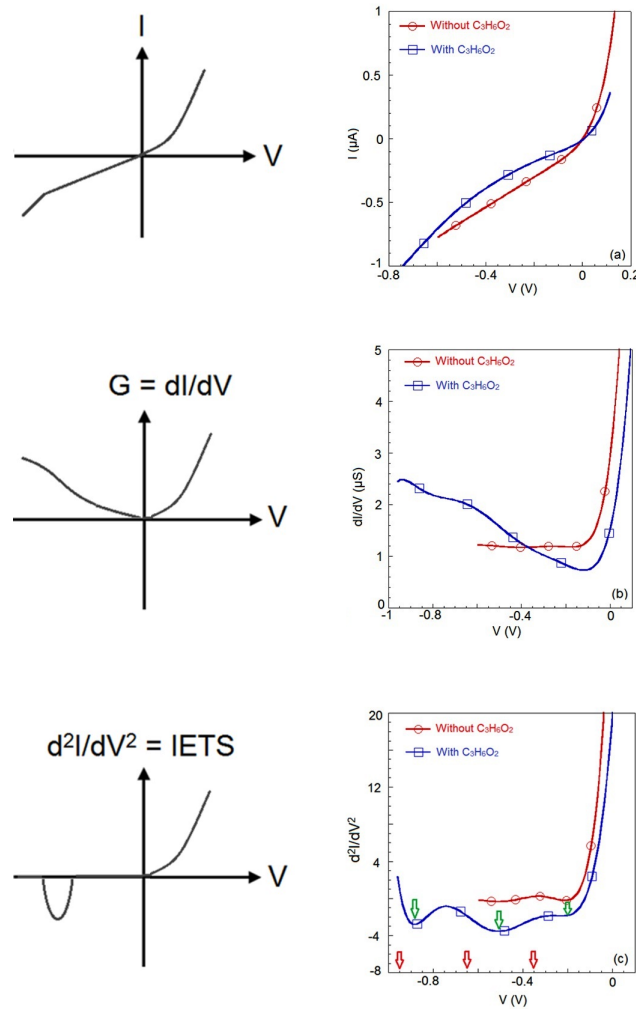


Figure 5.10: (a) Inelastic tunnelling forward bias, (b) Inelastic tunnelling reverse bias, (c) IETS signals for semiconductor - insulator - metal tunnel junction.

It also shows the measured IETS characteristics of $C_3H_6O_2$ molecules adsorbed on our fabricated Si NW / SiO_2 / Al NW tunnel junction device. Here, the diode-like $I - V$ characteristic (Fig.5.10(a)), is due to the presence of a “Schottky-like” barrier at the Al NW / SiO_2 interface. The $dI/dV - V$ characteristics of the devices show steps in conductance, and non-linearities which correspond to the peaks in the $d^2I/dV^2 - V$ characteristics.

Table 5.4 illustrated the measured excitation modes of $C - H$ bonds in two SIM (Si NW / SiO_2 / Al NW) tunnel junction devices at room temperature. It also shows the previously reported excitation modes of $C - H$ bonds in a MIM (Al / Al_2O_3 / Pb) device at 4.2K [120]:

Table 5.4: Experimental Results - Excitation Modes of $C - H$

	1^{st} Excitation	2^{nd} Excitation	3^{rd} Excitation
SIM Device I at 300K	$-0.2V$	$-0.5V$	$-0.85V$
SIM Device II at 300K	$-0.2V$	$-0.5V$	$-0.85V$
MIM Device at 4.2K	$-0.36V$	$-0.65V$	$-0.95V$

Here, according to simulations (see Chapter 6) the 1^{st} peak does not correspond to any of the $C - H$ excitation modes. This peak may be due the $N - H$ bonds trapped in SiO_2 layer on the sample. The 2^{nd} and 3^{rd} peaks can be attributed to the first and second excitation modes of a $C - H$ bond at room temperature (Chapter 6). Here, the peak positions on both devices are the same. The peaks separation in our measured data is $\sim -0.3V$, which corresponds well to the separation between the 1^{st} and 2^{nd} excitation modes of $C - H$ bond

on an Al / Al₂O₃ / Pb tunnel junctions [120].

Estimated Number of Molecules in the Tunnel Junction

The number of molecules adsorbed on the Si NW / SiO₂ / Al NW tunnel junction is then estimated after adsorption of ammonium hydroxide (NH_4OH). The density of NH_4OH with molecular weight of 35.05 g/mol at room temperature is 0.9 g/cm³. Therefore the molar density of NH_4OH is equal to 0.026 mol/cm³. This corresponds to $= 0.026 \times 6.22 \times 10^{23} \text{ molecules} = 1.82 \times 10^{22} \text{ molecules/cm}^3$. As the device could not be immersed directly in ammonium hydroxide, vapour treatment is used to deposit NH_3 vapour molecules on the device. Here, the device was left in a petri dish in an ammonium hydroxide atmosphere (Volume of large container $\sim 20 \text{ cm} \times 20 \text{ cm} \times 20 \text{ cm} = 8000 \text{ cm}^3$) for two hours (Fig.5.11). The NH_4OH atmosphere was created by the complete evaporation of NH_4OH with volume $\sim 50 \text{ cm}^3$ ($20 \text{ cm} \times 20 \text{ cm} \times 0.125 \text{ cm} = 50 \text{ cm}^3$). Therefore, the number of molecules in ammonium hydroxide liquid can be estimated as:

$$1.82 \times 10^{22} \times 50 = 9.1 \times 10^{23} \text{ molecules}$$

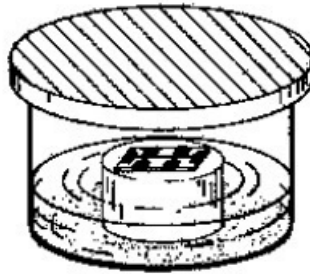


Figure 5.11: Schematic diagram of the vapour treatment.

Here, the inter molecules separation is $= \frac{1}{\sqrt[3]{1.82 \times 10^{27}}} = 8.19 \times 10^{-10} m = 0.819 nm$.

Various mechanisms are possible for adsorption of molecules on the fabricated Si NW / SiO₂ / Al NW tunnel junction. Here, we assumed the deposition and diffusion of molecules from the exposed SiO₂ surface at the side edges of the tunnel junction. Therefore, the number of molecules adsorbed on the tunnel junction with side edges area of $(50 + 120 + 50) \times 2 = 440 nm$ can be estimated as:

$$\frac{440}{0.819} \sim 500 \text{ molecules}$$

The reduction in device dimension to the nanoscale has increased the sensitivity of the device to molecules adsorbed on the tunnel junction.

5.3 Summary

This chapter discusses electrical measurements of the fabricated Si NW / SiO₂ / Al NW tunnel junction devices. The traditional AC modulation technique for IETS measurement has been presented in here. This is followed by a discussion of DC IETS measurements, performed at 300K, for ammonium hydroxide (NH_4OH), acetic acid (CH_3COOH), and propionic acid ($C_3H_6O_2$) molecules. In this regard the $I - V$, $dI/dV - V$, and $d^2I/dV^2 - V$ characteristics of the tunnel junction have been measured before and after adsorption of molecules on the junction. Here, the peak positions in the calculated $d^2I/dV^2 - V$ characteristics corresponds to the $N - H$ and $C - H$ bonds.

Finally, the number of molecules adsorbed on the tunnel junction has been estimated (~ 500

molecules). In this thesis, the reduction in device dimension to the nanoscale has increased the sensitivity of the device to molecules adsorbed on the tunnel junction from $\sim 10^{13}$ molecules to ~ 500 molecules.

Chapter 6

Simulation

In this chapter, the IETS equations formulated in Chapter 3 are explored, with the effect of the various experimental variables simulated and used to further confirm aspects of the experimental data of Chapters 5.

IETS current equations in Chapter 3 have been coded into Matlab software programme to calculate the $I - V$, $dI/dV - V$, and $d^2I/dV^2 - V$ characteristics for metal - insulator - metal (Al / Al₂O₃ / Pb) tunnel junction structure. The obtained Matlab simulation results for Al / Al₂O₃ / Pb tunnel junction are then compared with the previously reported experimental IETS characteristics [120].

After verification of the basic operation of the code by using a metal - insulator - metal (Al / Al₂O₃ / Pb) tunnel junction structure, for which experimental data is available [120], we modified these to model the semiconductor - insulator - metal (Si NW / SiO₂ / Al NW) tunnel junction structure. The Matlab simulation results for Si NW / SiO₂ / Al NW tunnel

junction structure are then used to study the IETS characteristics observed in Chapters 5.

6.1 Metal - Insulator - Metal Tunnel Junction

In this section, the simulation of a traditional MIM tunnel junction device for IETS, is used to further confirm aspects of the experimental data of previously reported IETS characteristics [120]. Here, the IETS current equations are simulated to calculate the $I - V$, $dI/dV - V$, and $d^2I/dV^2 - V$ characteristics for a $C - H$ bonds adsorbed on Al / Al₂O₃ / Pb tunnel junction device.

The energy levels of the vibrations of the adsorbed molecules can be approximated as [38]:

$$E_\nu = \hbar\omega_e(\nu + \frac{1}{2})[1 - \chi_e(\nu + \frac{1}{2})] \quad (6.1)$$

where E_ν is not the transition energy required to excite the molecules from one state to another. Here ω_e is the vibrational constant, and χ_e is the anharmonicity constant, which are specific for different molecules [122].

The transition energy from the ground state ($\nu = 0$) to another higher energy level can then be calculated as:

$$\Delta E = E_{\nu=m} - E_{\nu=0}, \quad \text{where } m = 1, 2, 3, .. \quad (6.2)$$

where the transition energy from ground state to the ν^{th} excitation state is:

$$\Delta E_{0 \rightarrow \nu} = \nu \omega_e [1 - \chi_e(\nu + 1)] \quad [Unit : cm^{-1}] \quad (6.3)$$

The Eq.6.3 is used in the simulation to calculate the threshold energy $\hbar\omega_e$. The energy unit is then converted to electron-volts (eV):

$$\Delta E = \frac{\Delta E_{0 \rightarrow \nu}}{8065.48} \quad [Unit : eV] \quad (6.4)$$

Here, we assumed that $C - H$ bonds ($\omega_e = 2860.75$, and $\chi_e = 0.022526$) adsorbed on Al / Al_2O_3 / Pb tunnel junction device. Therefore by modelling (Eqs.6.3-4), the excitations occurs at $0.339 V$, $0.661 V$, and $0.959 V$ (Table.6.1).

Table 6.1: $C - H$ Excitation Modes

ν	$\Delta E_{0 \rightarrow \nu} [cm^{-1}]$	$\Delta E_{0 \rightarrow \nu} [V]$
$0 \rightarrow 1$	2731.86	0.339
$0 \rightarrow 2$	5334.85	0.661
$0 \rightarrow 3$	8504.92	0.959

The total IETS current (I_{total}) in MIM tunnel junction device is:

$$I_{total} = I_{elastic} + I_{inelastic} \quad (6.5)$$

Here, the elastic current $I_{elastic}$, can be calculated as:

$$I_{elastic}(V) = \int_0^\infty J_{elastic}(V) dA \quad (6.6)$$

where the elastic tunnelling current density $J_{elastic}$ is derived in Chapter 3 as:

$$J_{elastic} = \frac{4\pi em^* k_B T}{(2\pi)^3 \hbar^3} \int_0^\infty dE_z T(E_z) \ln\left(\frac{1 + e^{\frac{E_F^L - E_z}{k_B T}}}{1 + e^{\frac{E_F^L - eV - E_z}{k_B T}}}\right) \quad (6.7)$$

For clarity, the included terms are as follows: e is the electron charge, m^* is the effective mass of particle, $\hbar$ is the reduced Planck's constant, E_F^L is the Fermi energy at left contact, k_B is the Boltzmann's constant, T is temperature, and the transmission probability $T(E_z)$ for a potential barrier Φ_B is:

$$T(E_z) = \exp\left[-\frac{2d}{\hbar} \sqrt{2m^*(\Phi_B - E)}\right] \quad (6.8)$$

Here, we assumed that the bias energy is larger than the product of Boltzmann's constant multiplied by absolute temperature ($eV \gg k_B T$), and the source electrode has a higher Fermi energy than the drain electrode ($E_F^L > E_F^R$), which are separated by: $eV = E_F^L - E_F^R$.

Therefore the elastic tunnelling current density equation (Eq.6.2) has been simplified as:

$$J_{elastic} = \frac{4\pi em^*}{\hbar^3} \int_{E_F^R}^{E_F^L} dE_z T(E_z) (E_F^L - E_F^R) \quad (6.9)$$

Then, the inelastic current $I_{inelastic}$, is considered as:

$$I_{inelastic} = Ce(V - U_\nu) \frac{\exp(\frac{e(V - U_\nu)}{k_B T})}{\exp(\frac{e(V - U_\nu)}{k_B T}) - 1} \quad (6.10)$$

where C contains all the parameters independent of energy E and temperature T (see section 3.2.2 (Eqs.3.53-55)). Here, $U_\nu = \frac{\hbar\omega_v}{e}$, and therefore the second derivatives of the inelastic electron tunnelling current is given by:

$$\frac{d^2 I_{inelastic}}{dV^2} = C \frac{e^2}{k_B T} [e^\alpha \frac{(\alpha - 2)e^\alpha + (\alpha + 2)}{(e^\alpha - 1)^3}], \quad \text{where } \alpha = \frac{e(V - U_\nu)}{k_B T} \quad (6.11)$$

The simulation based on the above equations is then performed for $C - H$ bonds adsorbed on Al / Al₂O₃ / Pb tunnel junction device with parameter values as Table 6.2.

Table 6.2: Simulation Variables for MIM Tunnel Junction

Variable	Description	Value
m^*	Effective Mass of electron	$9.11 \times 10^{-31} kg$
e	Elementary charge	$1.6 \times 10^{-19} C$
$\hbar$	Reduced plank constant	$1.055 \times 10^{-34} Js$
U_v	Potential barrier height	$12 eV = 1.92 \times 10^{-18} J$
L	Barrier length	$10 nm$
E_F^L	Fermi energy of left metal (Pb)	$10 eV = 1.6 \times 10^{-18} J$
V	Applied voltage	$-1 < V < 1$
T	Absolute temperature	$4.2 - 300 K$

The values of the simulation variables are chosen initially from those used in previous experimental reports [120]. Here, the barrier length is given a value of $10 nm$, similar to our fabricated Si NW / SiO₂ / Al NW tunnel junction in Chapter 4. The Fermi energy of the Pb is approximated as $10 eV$ (original value = $9.47 eV$ [158]). The temperature T is varied between $4.2 K$ to $300 K$.

The elastic current ($I_{elastic} - V$), inelastic current ($I_{inelastic} - V$), conductance ($dI/dV - V$), and IETS spectra ($d^2I/dV^2 - V$) is then simulated based on variables in Table.6.2, for the $C - H$ bonds on the Al / Al₂O₃ / Pb tunnel junction. Here, the $C - H$ has vibrational constant $w = 2860.75 cm^{-1}$, and anharmonicity constant $x = 0.022526 cm^{-1}$ [159]. In this section the $I - V$, $dI/dV - V$, and $d^2I/dV^2 - V$ plots are presented at $4.2 K$, $20 K$, $70 K$, $200 K$,

and $300K$ respectively.

In Figure 6.1 the IETS simulated results for $C - H$ bonds adsorbed on $Al / Al_2O_3 / Pb$ tunnel junction, are plotted at $4.2K$.

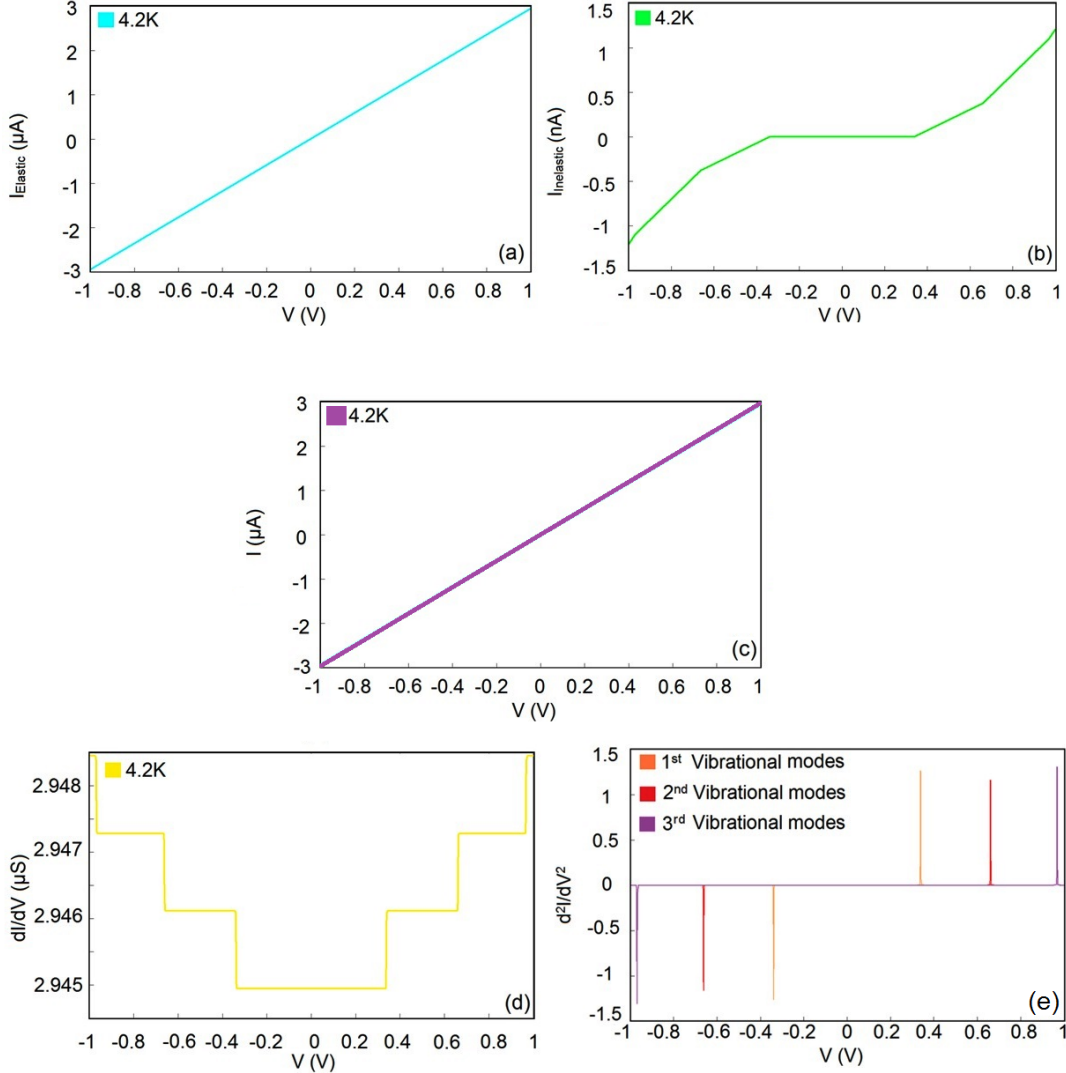


Figure 6.1: Simulated IETS Spectra of $C - H$ bonds on $Al / Al_2O_3 / Pb$ tunnel junction at $4.2K$.

Figure 6.1(a) illustrates the elastic $I - V$ characteristics of $C - H$ bonds on the $Al / Al_2O_3 / Pb$ tunnel junction. It shows linear behaviour due to the small voltage range, as we expected.

The inelastic $I - V$ characteristic, shows changes in the slope at three threshold voltages $eV = \hbar\omega$ (Fig.6.1(b)). Figure 6.1.(c) illustrates the total $I - V$ characteristics. Here, the slope changes are not visible, because the $I_{elastic} \gg I_{inelastic}$. These changes can be seen as steps in conductance plot (Fig.6.1(d)), and as peaks in IETS spectrum plot (Fig. 6.1(e)). The previously reported excitation modes of $C - H$ are at $\sim -0.36 V, -0.65 V$, and $-0.95 V$ in a MIM device at $4.2K$ [120]. These peaks positions are matched with the simulated peaks positions at $4.2K$.

Here, the percentage error of the 1st peak position in the simulated results compared to experimental data [120] is:

$$Percentage\ Error = \frac{0.339 - 0.36}{0.36} \times 100\% = -5.83\%$$

In the following sections, the effect of changing temperature, barrier length, and Fermi energy and barrier height on the device characteristics is investigated.

Temperature Effect

The temperature is allowed to vary within a $4.2K$ to $300K$ range. Here, this modification is studied for $I - V$, $dI/dV - V$, and $d^2I/dV^2 - V$ characteristics of $C - H$ bonds adsorbed on the $Al / Al_2O_3 / Pb$ tunnel junction. As the slope changes were not visible in $I_{total} - V$ characteristics, the $I - V$ characteristics plotted for the inelastic current.

Figure 6.2 illustrates the $I_{inelastic} - V$ characteristic for different temperatures in $4.2K$ to $300K$ range.

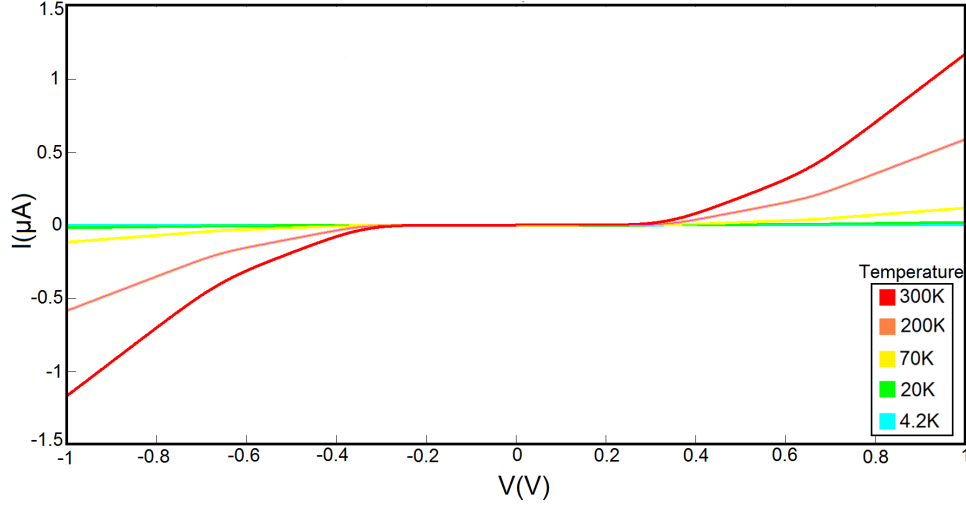


Figure 6.2: Simulated inelastic current of $C - H$ bonds on $Al / Al_2O_3 / Pb$ tunnel junction at $4.2K$, $20K$, $70K$, $200K$, and $300K$.

Here, the inelastic current changes at $\sim -0.36 V$, and $-0.65 V$ correspond to the additional conduction channels being created at threshold voltages ($eV = \hbar\omega$). Figure 6.2 shows that, the position of the threshold voltages remains unchanged, and there is only a change in slopes. By gradually increasing the temperature, the changes in inelastic current becomes more obvious.

The temperature effect is then studied on conductance (dI/dV) vs. voltage (V) characteristics for a $C - H$ bonds on $Al / Al_2O_3 / Pb$ tunnel junction at $4.2K$, $20K$, $70K$, $200K$, and $300K$ (Fig.6.3). Figure 6.3 shows that, although the dI/dV raises by increasing the temperature, but the position of threshold voltages at $\sim -0.36 V$, and $-0.65 V$ still remains unchanged, shows similar behaviour in different temperatures as we expected.

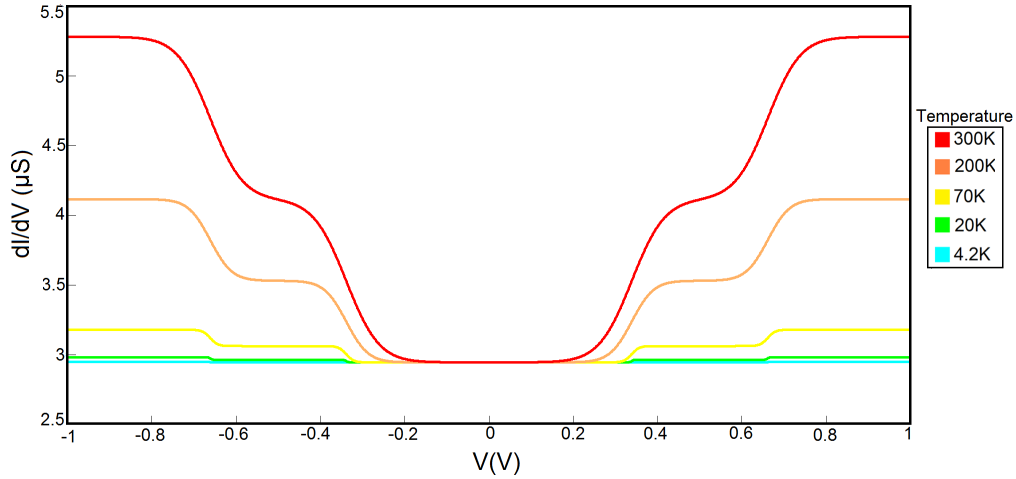


Figure 6.3: Simulated $dI/dV - V$ of $C - H$ bonds on $Al / Al_2O_3 / Pb$ tunnel junction at 4.2K, 20K, 70K, 200K, and 300K.

The temperature effect is then studied on IETS spectra (d^2I/dV^2) vs. voltage (V) characteristics for a $C - H$ bonds on $Al / Al_2O_3 / Pb$ tunnel junction at 4.2K, 20K, 70K, 200K, and 300K (Fig.6.4).

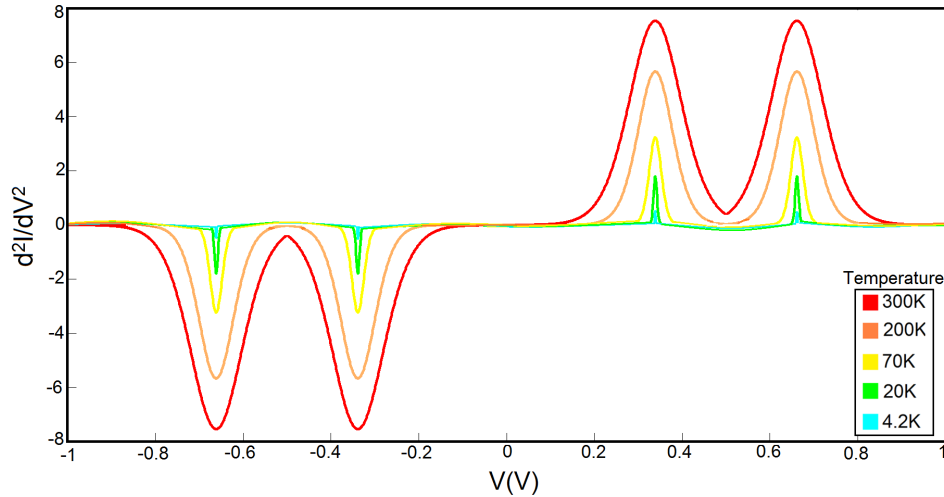


Figure 6.4: Simulated $d^2I/dV^2 - V$ of $C - H$ bonds on $Al / Al_2O_3 / Pb$ tunnel junction at 4.2K, 20K, 70K, 200K, and 300K.

Here, Fig.6.4 shows that by increasing the measurement temperature the line-width of IETS spectra becomes broadened due to the thermal broadening effect.

The positions of the peaks at $\sim -0.36 V$, and $-0.65 V$ in the simulated plots are matched with the previously reported measurements of the $C - H$ bonds on Al / Al₂O₃ / Pb tunnel junction. Therefore the code can be used to simulate the IETS spectra of the Si NW / SiO₂ / Al NW tunnel junction, to further confirm the operation of our fabricated Si NW / SiO₂ / Al NW tunnel junction in Chapter 4.

Varying Barrier Length

The effect of changing the length of barrier on the device characteristics is investigated in this section. The initial Al / Al₂O₃ / Pb tunnel junction barrier length was set $L = 10 nm$. Here, the barrier length is reduced and then increased to study the effect of changing the barrier length.

The barrier length is first reduced to $L = 5 nm$. Figure 6.5 illustrates the IETS characteristics of the $C - H$ bond adsorbed on Al / Al₂O₃ / Pb tunnel junction with barrier length of $L = 5 nm$ at $4.2K$. Here, reducing the barrier length shows an increase in current in $I - V$ characteristics, which is due to the increase in transmission probability (Fig.6.5(a)). The position of the threshold voltages remains unchanged in the conductance plot (Fig.6.5(c)) and IETS peaks (Fig.6.5(d)) compared to simulation results with $L = 10 nm$ as we expected.

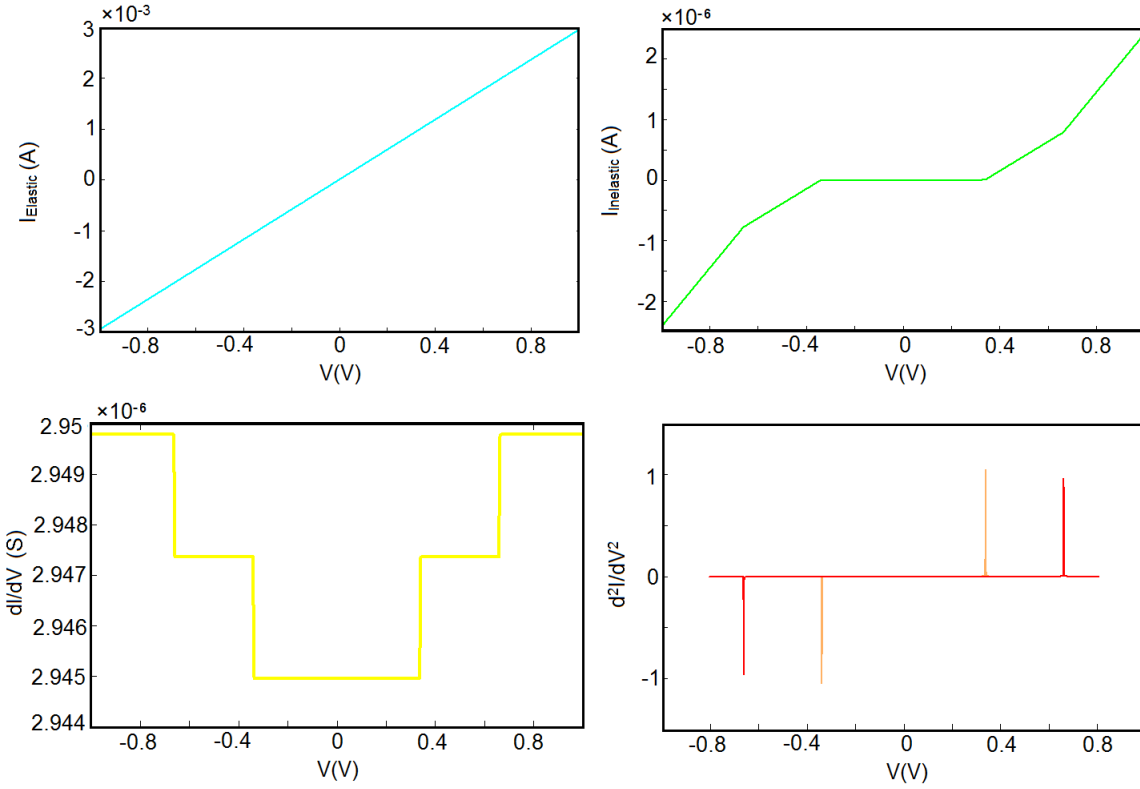


Figure 6.5: Simulated $d^2I/dV^2 - V$ of $C - H$ bonds on $Al / Al_2O_3 / Pb$ tunnel junction with 5 nm barrier length at 4.2K.

Figure 6.6 illustrates the slope changes in $I_{Inelastic} - V$ vs. $I_{Elastic} - V$ characteristics using a log plot.

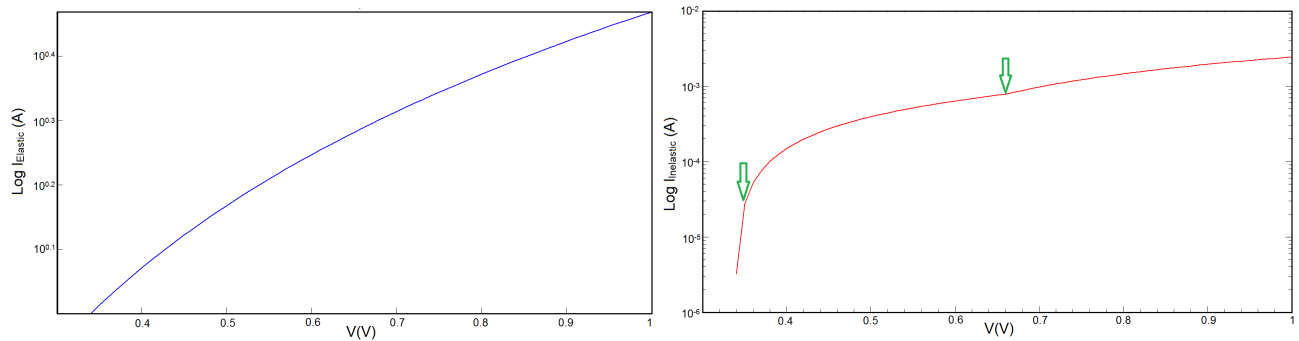


Figure 6.6: Slope changes in $I_{Inelastic} - V$ vs. $I_{Elastic} - V$ characteristics using a log plot of $C - H$ bonds on $Al / Al_2O_3 / Pb$ tunnel junction with 5 nm barrier length at 4.2K.

The slope changes is shown with an arrow in $I_{Inelastic} - V$ characteristics at $\sim -0.36 V$, and

-0.65 V , which corresponds to the $C-H$ bonds 1^{st} and 2^{nd} excitation modes on Al / Al_2O_3 / Pb tunnel junction.

The barrier length is then increased to $L = 15\text{ nm}$. Figure 6.7 illustrates the IETS characteristics of the $C-H$ bond adsorbed on Al / Al_2O_3 / Pb tunnel junction with barrier length of $L = 15\text{ nm}$ at 4.2 K . Figure 6.7 illustrates the IETS characteristics of the $C-H$ bond adsorbed on Al / Al_2O_3 / Pb tunnel junction with potential length of $L = 15\text{ nm}$ at 4.2 K .

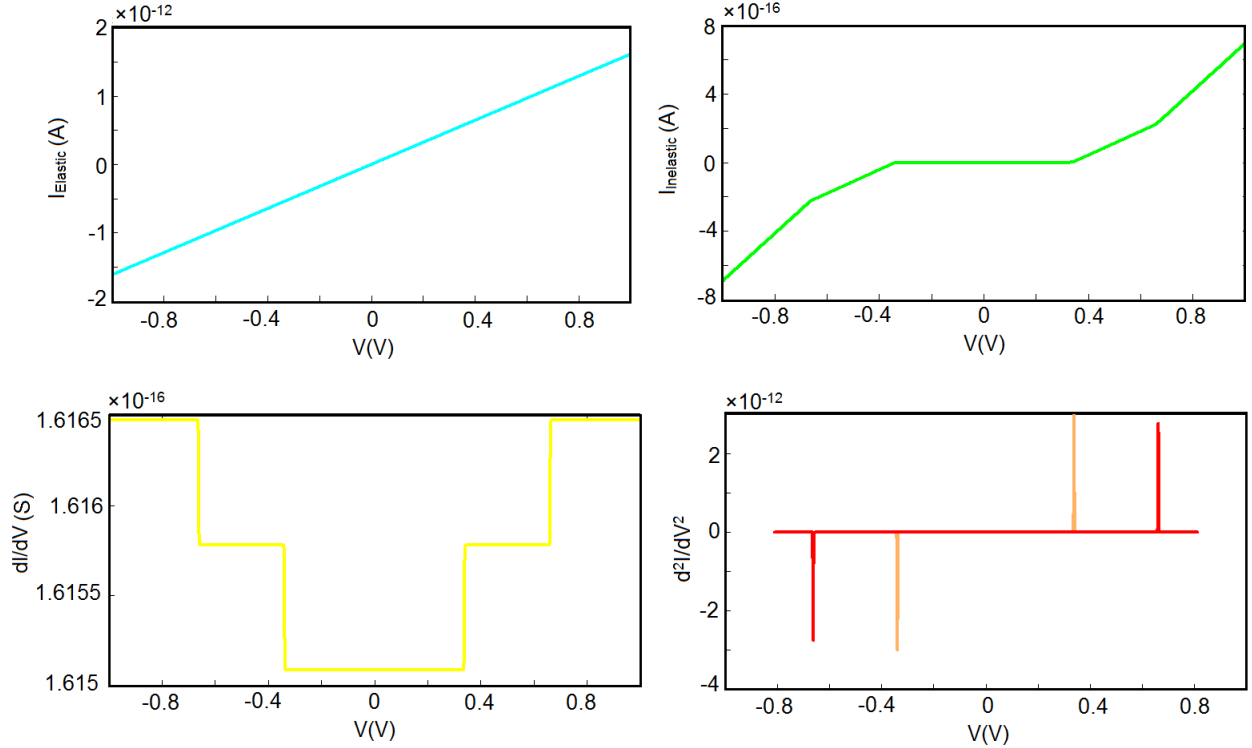


Figure 6.7: Simulated $d^2I/dV^2 - V$ of $C-H$ bonds on Al / Al_2O_3 / Pb tunnel junction with 15 nm barrier length at 4.2 K .

Here, increasing the barrier length shows a decrease in current in $I - V$ characteristics, which is due to the decrease in transmission probability (Fig.6.7(a)). The position of the threshold

voltages remains unchanged in the conductance plot (Fig.6.7(c)) and IETS peaks (Fig.6.7(d)) as we expected. These results confirms that the position of the peaks are independent of the barrier length.

Fermi Energy and Barrier Height Effect

The effect of changing the Fermi energy and barrier height on the device characteristics is then investigated. The initial Al / Al₂O₃ / Pb tunnel junction potential barrier height was set $U_\nu = 12\text{ eV}$, and the Fermi energy of the left metal was $E_F^L = 10\text{ eV}$. Here, the potential barrier height is increased to $U_\nu = 15\text{ eV}$, and the the Fermi energy of the left metal is changed to $E_F^L = 7\text{ eV}$ to increase the energy difference between potential barrier and Fermi energy.

Figure 6.8 illustrates the IETS characteristics of the $C-H$ bond adsorbed on Al / Al₂O₃ / Pb tunnel junction with potential barrier height $U_\nu = 15\text{ eV}$, and the the Fermi energy of the left metal $E_F^L = 7\text{ eV}$ at 4.2 K .

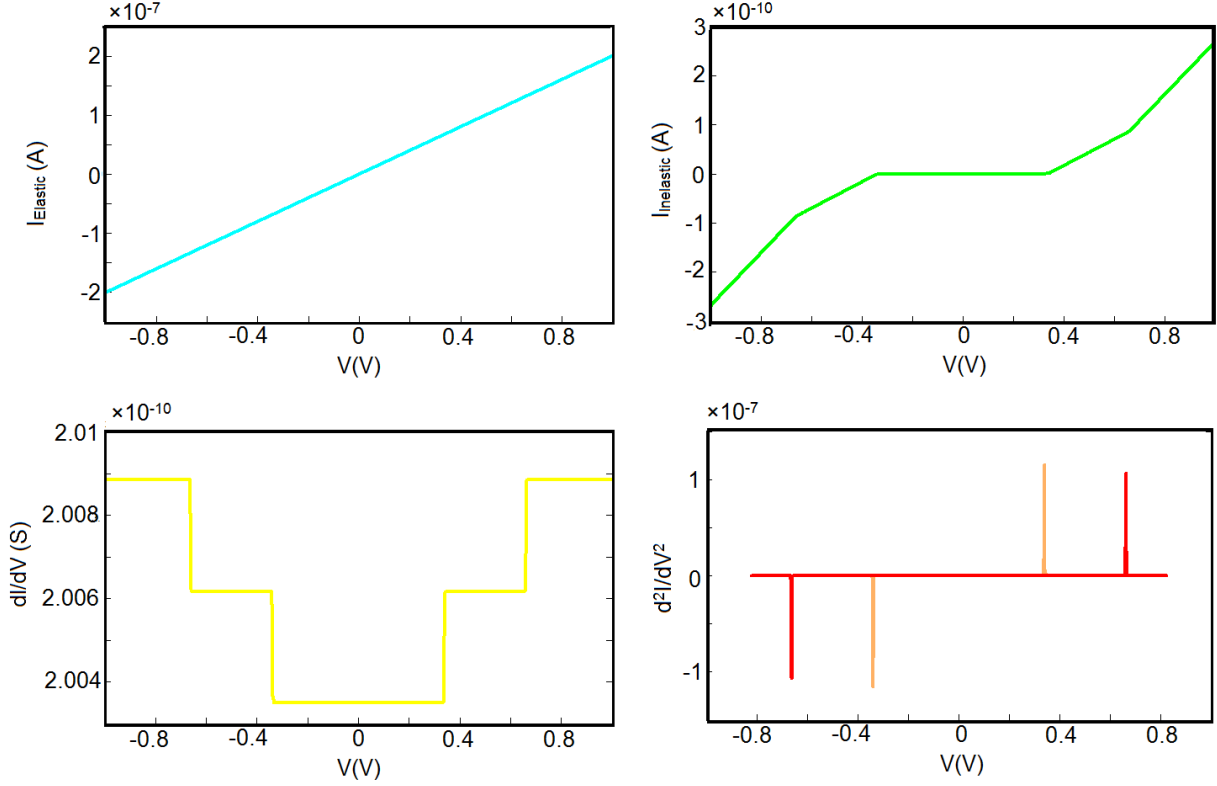


Figure 6.8: Simulated $d^2I/dV^2 - V$ of $C-H$ bonds on $Al / Al_2O_3 / Pb$ tunnel junction with potential barrier height $U_\nu = 15$ eV, and the the Fermi energy of the left metal $E_F^L = 7$ eV at 4.2K.

Here, the increase in energy difference between potential barrier and Fermi energy caused the reduction in tunnelling current (Fig.6.8(a-b)). The position of threshold voltages remains unchanged in the conductance plot (Fig.6.8(c)), and IETS peaks (Fig.6.8(d)) as we expected. This confirms that the position of the peaks are independent of the barrier height and Fermi energy.

6.2 Semiconductor - Insulator - Metal Tunnel Junction

After verification of the code by using the Al / Al₂O₃ / Pb tunnel junction structure [120] in the previous section (Section 6.1), the code is modified to be employed for the SIM (Si NW / SiO₂ / Al NW) tunnel junction structure. This structure is used to further confirm aspects of the experimental data of Chapters 5.

Here, the total IETS current in this tunnel junction is:

$$I_{total} = I_{elastic} + I_{inelastic} + I_{SB} \quad (6.12)$$

The model uses the same equations for the elastic and inelastic tunnelling current (Eq. 6.2-6.7). For the SB current, the thermionic emission current has been used as it is the most likely mechanism:

$$I = AA^*T^2 \exp\left(-\frac{e\Phi_B}{k_B T}\right) \left(\exp\left(\frac{eV}{k_B T}\right) - 1\right) \quad (6.13)$$

where A^* is the effective Richardson coefficient ($A^* = \frac{4\pi em^*k_B^2}{h^2}$).

The simulation based on the above equations is then performed for $C - H$ bonds adsorbed on Si / SiO₂ / Al tunnel junction device with parameter values as Table 6.3.

Here, the values of the simulation variables are chosen based on our fabricated Si NW / SiO₂ / Al NW tunnel junction in Chapter 4. The temperature T is varied between 4.2K to

300K.

Table 6.3: Simulation Variables for SIM Tunnel Junction

Variable	Description	Value
m^*	Effective Mass of electron	$9.11 \times 10^{-31} kg$
e	Elementary charge	$1.6 \times 10^{-19} C$
$\hbar$	Reduced plank constant	$1.055 \times 10^{-34} Js$
A^*	Richardson coefficient	$320000 Am^{-2} K^{-2}$
Φ_B	Potential barrier height	$12 eV = 1.92 \times 10^{-18} J$
L	Barrier length	$10 nm$
A	Tunnel junction area	$50 nm \times 120 nm$
E_F^L	Fermi energy of left metal (Al)	$11.7 eV = 1.87 \times 10^{-18} J$
V	Applied voltage	$-1 < V < 1$
T	Absolute temperature	$4.2 - 300 K$

The total current ($I - V$), conductance ($dI/dV - V$), and IETS spectra ($d^2I/dV^2 - V$) is then simulated based on variables in Table. 6.3, for the $C - H$ bonds on the Si NW / SiO₂ / Al NW tunnel junction. Here, the $C - H$ has vibrational constant $w = 2860.75 cm^{-1}$, and anharmonicity constant $x = 0.022526 cm^{-1}$ [159].

In this section the $I - V$, $dI/dV - V$, and $d^2I/dV^2 - V$ plots are first presented at 300K to

be compared with the data from Chapter 5.

In Fig.6.9 the IETS simulated results for $C - H$ bonds adsorbed on Si NW / SiO_2 / Al NW tunnel junction, are plotted at $300K$.

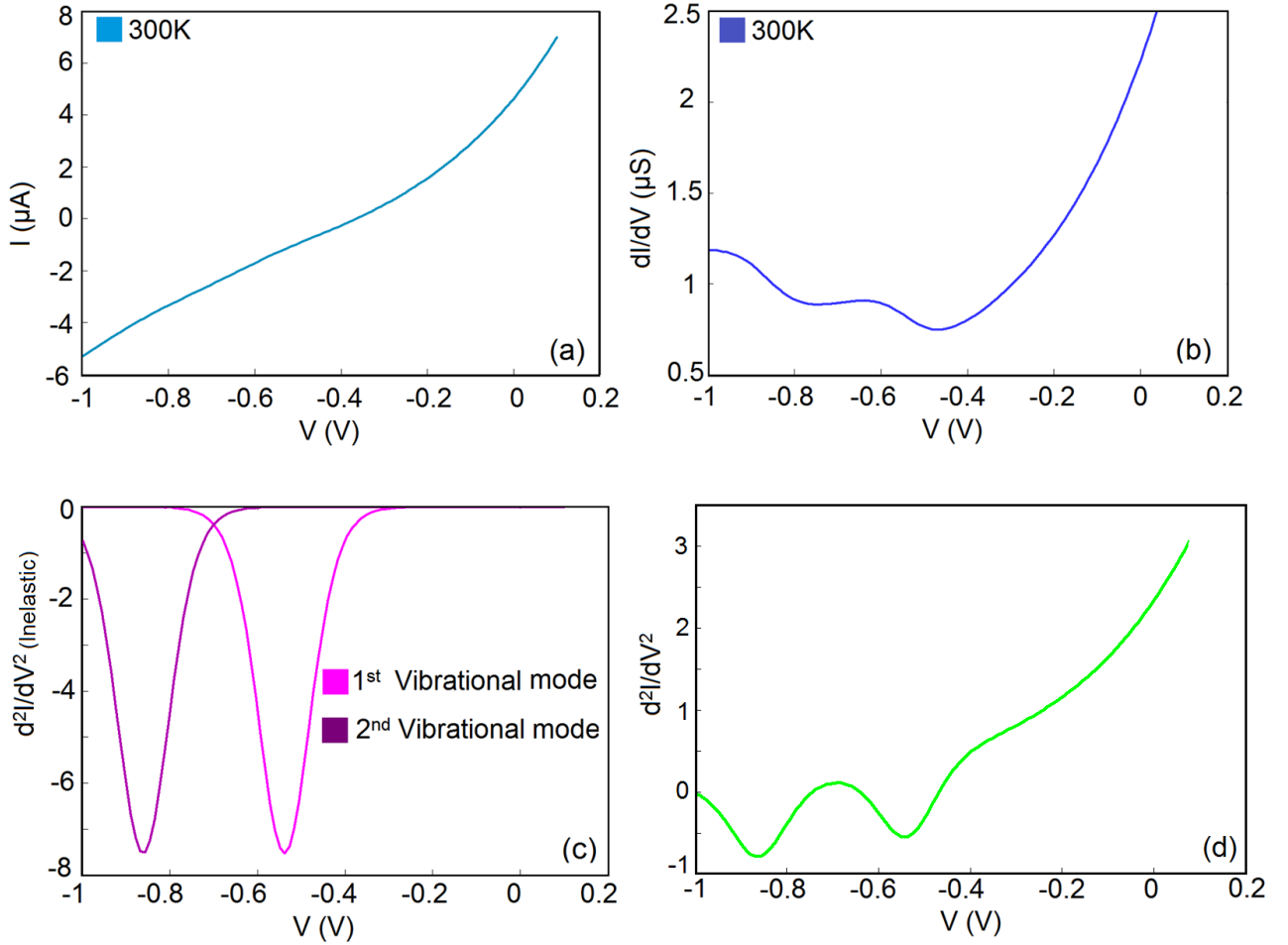


Figure 6.9: Simulated IETS Spectra of $C - H$ bonds on Si NW / SiO_2 / Al NW tunnel junction at $300K$: (a) $I - V$, (b) $dI/dV - V$, (c) $d^2I/dV^2 - V$ of Inelastic current, (d) $d^2I/dV^2 - V$ of total current.

Figure 6.9 illustrates the simulated IETS characteristics of $C - H$ bonds adsorbed on Si NW / SiO_2 / Al NW tunnel junction at $300K$. The $I - V$ characteristic (Fig.6.9(a)) is diode-like, due to the presence of a Schottky barrier at the Si NW / SiO_2 interface. The

conductance plot (Fig.6.9(b)) shows steps at two threshold voltages $\sim -0.55 V$, and $-0.85 V$ (where $eV = \hbar\omega$). These changes can be observed as peaks $\sim -0.55 V$, and $-0.85 V$ in IETS spectrum plot (Fig.6.9(c-d)). Figure 6.9(c) shows the $d^2I/dV^2 - V$ of Inelastic current, and Fig.6.9(d) shows the $d^2I/dV^2 - V$ of total current. The simulated IETS characteristics of Si NW / SiO₂ / Al NW junction has similar behaviour as the IETS characteristics of $C - H$ bonds on our fabricated Si NW / SiO₂ / Al NW tunnel junction at 300K (Fig.6.10).

The simulated and measured $I - V$ characteristics in Fig.6.10(a), are both diode-like as was expected. The conductance ($dI/dV - V$), shows steps at two threshold voltages $\sim -0.55 V$, and $-0.85 V$ (Fig.6.9(b) and Fig.6.10(b)). The comparison (Fig.6.10(c)) shows that the position of the simulated peaks are similar to the 2nd and 3rd peak positions in the IETS spectra of $C - H$ bonds on our fabricated Si NW / SiO₂ / Al NW tunnel junction at 300K. This proves that the 2nd and 3rd peak positions at $\sim -0.55 V$, and $-0.85 V$, correspond to the 1st and 2nd excitation modes of $C - H$ bonds adsorbed on the Si NW / SiO₂ / Al NW tunnel junction respectively. It also shows that the 1st peak does not correspond to any of the excitation modes, and could be due to the experimental noise.

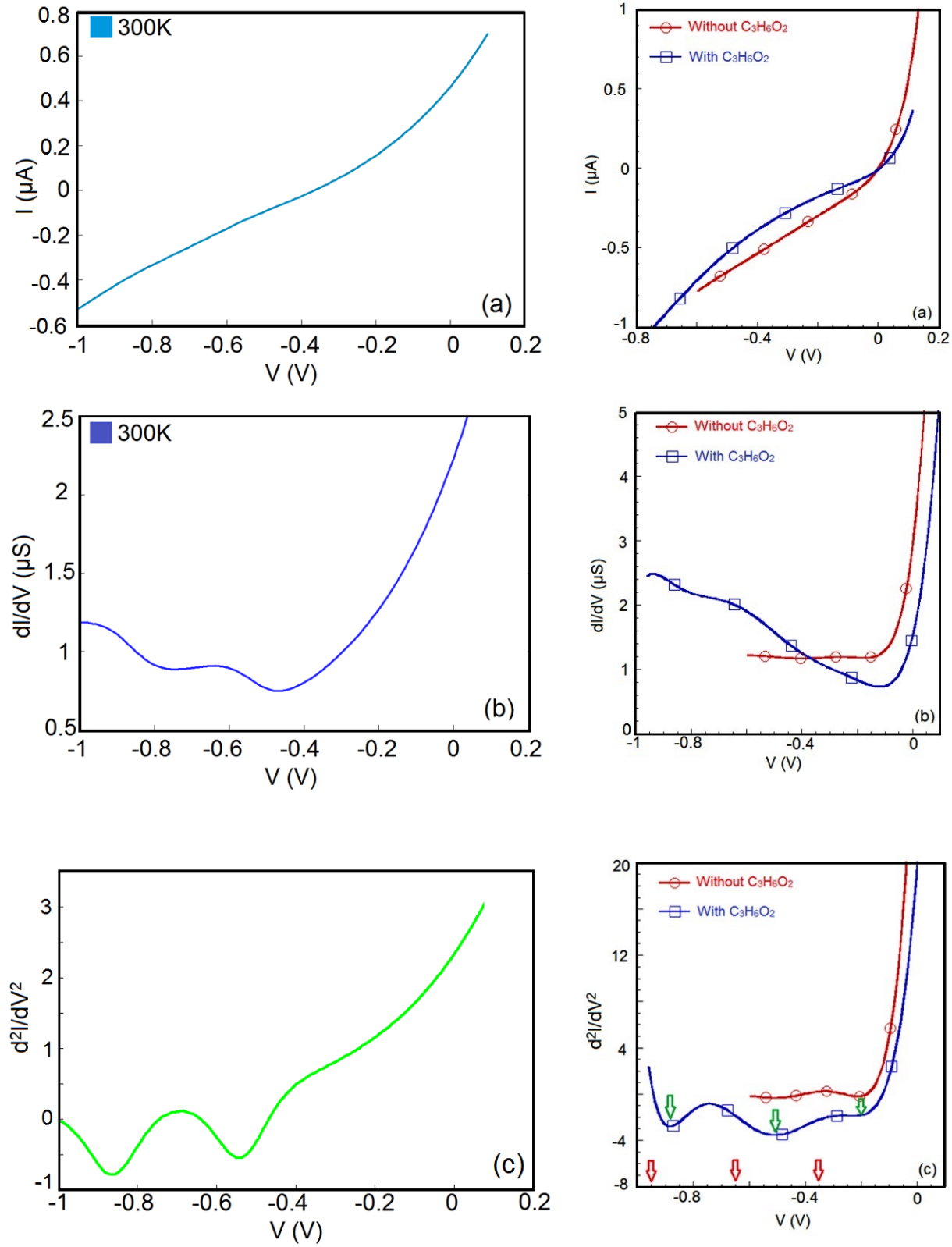


Figure 6.10: IETS Spectra of C-H bonds on Si NW / SiO₂ / Al NW tunnel junction at 300K: (a) $I - V$, (b) $dI/dV - V$, (c) $d^2I/dV^2 - V$

The temperature is then allowed to vary within a $4.2K$ to $300K$ range. Here, this modification is studied for $d^2I_{Inelastic}/dV^2 - V$ characteristics of $C - H$ bonds adsorbed on the Si NW / SiO_2 / Al NW tunnel junction (Fig.6.12).

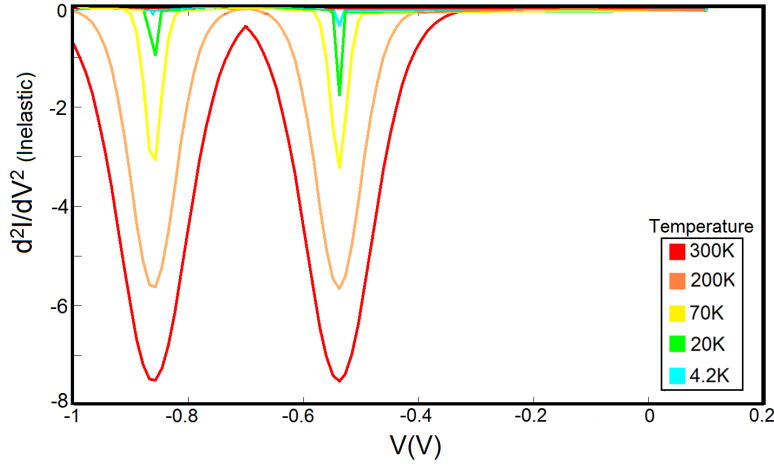


Figure 6.11: Simulated $d^2I_{Inelastic}/dV^2 - V$ of $C - H$ bonds on Si NW / SiO_2 / Al NW tunnel junction at $4.2K$, $20K$, $70K$, $200K$, and $300K$.

Figure 6.12 illustrates the effect of temperature on IETS spectra of $C - H$ bonds on Si NW / SiO_2 / Al NW tunnel junction. It shows that the increase in the measurement temperature broadens the spectral line-width, which is due to the thermal broadening effect.

The IETS measurements performed on the Si NW / SiO_2 / Al NW tunnel junction at $300K$ for CH_3COOH , and $C_3H_6O_2$ molecules, agree with the positions of the peaks at $\sim -0.55 V$, and $-0.85 V$ in the simulated plots. Here, the peak separations are similar to previous reported work on micro meter scale MIM tunnel junction at low temperature. These confirm the correct performance of our fabricated Si NW / SiO_2 / Al NW tunnel junction in Chapter 4.

6.3 Summary

This chapter explores the IETS equations formulated in Chapter 3, with the effect of the various experimental variables simulated, and used to further confirm aspects of the experimental data of Chapters 5. IETS current equations have been coded into a Matlab software programme to calculate the $I - V$, $dI/dV - V$, and $d^2I/dV^2 - V$ characteristics for a metal - insulator - metal (MIM) tunnel junction structure (Al / Al₂O₃ / Pb). The Matlab simulation results for $C - H$ bonds adsorbed on Al / Al₂O₃ / Pb are then compared with the previously reported experimental IETS characteristics. The effect of changing temperature, barrier length, and Fermi energy and barrier height on the device characteristics have been then investigated.

After verification of the basic operation of the code by using a Al / Al₂O₃ / Pb tunnel junction structure, for which experimental data is available [120], the code has been modified to model the semiconductor - insulator - metal (Si NW / SiO₂ / Al NW) tunnel junction structure. The Matlab simulation results for Si NW / SiO₂ / Al NW tunnel junction structure has been then used to study the IETS characteristics observed in Chapters 5.

Here, the simulated and measured $I - V$ characteristics are both diode-like as it was expected. The conductance ($dI/dV - V$), shows steps at two threshold voltages $\sim -0.55 V$, and $-0.85 V$. The comparison between simulated and measured $d^2I/dV^2 - V$, shows that the position of the simulated peaks are similar to the 2nd and 3rd peak positions in the IETS spectra of $C - H$ bonds on our fabricated Si NW / SiO₂ / Al NW tunnel junction at 300K.

This proves that the 2^{nd} and 3^{rd} peak positions at $\sim -0.55 V$, and $-0.85 V$, correspond to the 1^{st} and 2^{nd} excitation modes of $C - H$ bonds adsorbed on the Si NW / SiO_2 / Al NW tunnel junction respectively. It also shows that the 1^{st} peak does not correspond to any of the excitation modes, and it could be due to the experimental noise.

Chapter 7

Conclusion and Further Work

7.1 Conclusion

This thesis has investigated nanoscale tunnel junction for Inelastic Electron Tunnelling Spectroscopy (IETS) measurement. Traditionally, this technique has used metal - insulator - metal (MIM) junctions and molecules are adsorbed on to the insulator during junction fabrication. At low applied voltage V , tunnelling through the barrier is elastic. However, inelastic tunnelling caused by electron interaction with vibrational states in the adsorbed molecules creates additional conduction channels, with a change in energy $\hbar\omega$. These lead to peaks in the d^2I/dV^2 vs. V characteristics for each additional channel, providing a spectrum of the molecular vibrational modes. As energy separations in the vibrational spectrum are relatively small compared to the electronic spectrum, in many cases the full vibrational spectrum can be measured only at low temperature $< 30K$. However, it may be possible to measure part of the spectrum even at room temperature, raising the possibility of a molecular detector.

In this work, IETS measurements were performed for nanoscale semiconductor - insulator - metal (SIM) tunnel junctions (Si NW / SiO₂ / Al NW) at 300K for ammonium hydroxide (NH₄OH), acetic acid (CH₃COOH), and propionic acid (C₃H₆O₂) molecules. Our use of a Si NW provides a means to define a more robust tunnel junction with the potential for gate control. In first stage of the fabrication process, an *n*-type highly-doped silicon-on-insulator (SOI) wafer (doping density $\sim 10^{19} - 10^{20} \text{ cm}^{-3}$) was selected as the base substrate. $1 \times 1 \text{ cm}^2$ chip of the highly-doped *n*-type SOI material have used for device fabrication. Nanowire lithography patterns were written using EBL in PMMA resist.

A 40 nm thick Al layer was then used to form a hard-mask for reactive ion etching (RIE). Here, the Al was evaporated and lifted-off a $\sim 50 \text{ nm}$ wide Al NW, for RIE of the top Si layer. SF₆ was used as the RIE gas and etch depths of 200 nm were used. The Al mask was then removed using wet etching. Si NWs with lengths $\sim 1 \mu\text{m}$ and widths down to $\sim 50 \text{ nm}$ were fabricated by this process.

The NWs were then thermally oxidised at 1000°C to create a SiO₂ surface layer $\sim 10 \text{ nm}$ thick. A second EBL stage was then used to define a 40 nm thick and $\sim 120 \text{ nm}$ wide Al NW such that crossed the Si NW, forming the nanoscale Si NW / SiO₂ / Al NW tunnel junction. Adding the Ohmic contacts was the final stage of fabrication process. This required a third EBL pattern aligned to the previous patterns. Finally, 120 nm of Al was thermally evaporated and following lift-off, formed the contact areas on the fabricated device. The tunnel junction area was $\sim 50 \text{ nm} \times 120 \text{ nm}$ and tunnelling occurred across the 10 nm thick SiO₂ layer. The molecules of interest were adsorbed on to the insulator after device fabrication.

The $I - V$, $dI/dV - V$, and $d^2I/dV^2 - V$ characteristics of the tunnel junction were measured before and after the adsorption of the NH_4OH , CH_3COOH , and $C_3H_6O_2$ molecules using vapour treatment or immersion. At low applied voltage, the tunnelling process was similar to a MIM device. However, as the applied voltage increased, the electrical characteristics were affected by the Schottky barrier formed at the Si NW surface. The reduction in device dimension to the nanoscale was expected to increase the sensitivity of the device to molecules adsorbed on the tunnel junction. Various mechanisms were possible for adsorption of molecules on the tunnel junction: The top Al layer was only $\sim 40\text{ nm}$ thick and can be porous. Molecules could then diffuse through the pores in a manner similar to previous work on large area IETS structures with thin Al contacts ($\sim 50\text{ nm}$). In particular, molecules in the presence of water vapour could penetrate the top metal of the completed tunnel junction more easily. A second possible mechanism, involved the deposition and diffusion of molecules from the exposed SiO_2 surface at the side edges of the tunnel junction. The number of molecules adsorbed on the tunnel junction was estimated as ~ 500 molecules. Furthermore, the use of SOI material raised the possibility of back gate control of the NW carrier concentration, and hence of the IETS characteristics.

With a reverse biased Schottky barrier, IETS peaks could be measured at reduced current, with less likely hood of damaging the tunnel junctions. Peaks could be observed in the $d^2I/dV^2 - V$ characteristics in all the cases following molecules adsorption. These peaks were attributed to the vibrational modes of $N - H$ and $C - H$ bonds. The peak separations were similar to previous reported work on micro meter scale MIM tunnel junction at low

temperature.

Simulation of the IEST measurements of $C-H$ bonds on Al / Al_2O_3 / Pb tunnel junction were then performed to better understand the device characteristics. The simplified current density equation, elastic and inelastic tunnelling current equations were modelled in Matlab. The positions of the peaks at $\sim -0.36 V$, $-0.65 V$, and $-0.95 V$ in the simulated plots were then matched with the previously reported measurements of the $C-H$ bonds on Al / Al_2O_3 / Pb tunnel junction. Hence, the code was used to simulate the IETS spectra of the $C-H$ bonds on a Si NW / SiO_2 / Al NW tunnel junction. Here, the total current was:

$$I_{Total} = I_{Elastic} + I_{Inelastic} + I_{SB}$$

where I_{Total} is the total current, $I_{Elastic}$ is the elastic current, $I_{Inelastic}$ is the inelastic current, and I_{SB} is the Schottky barrier current.

The model used the same equations for the elastic and inelastic tunnelling current as is developed for MIM device. For the SB current, the thermionic emission current was used. The $I-V$, $dI/dV-V$, and d^2I/dV^2-V plots were then plotted at $4.2K$, $20K$, $70K$, $200K$, and $300K$.

The measured $I-V$, $dI/dV-V$, and d^2I/dV^2-V characteristics of the tunnel junction after the adsorption of the CH_3COOH , and $C_3H_6O_2$ molecules were compared with the simulated plots at $300K$. Peaks could be observed at $\sim -0.55 V$ and $-0.85 V$ in the

$d^2I/dV^2 - V$ characteristics in all the cases following molecules adsorption at room temperature. These peak positions matched with the simulated peaks positions. These peaks were attributed to the first and second excitation modes of a $C - H$ bond at room temperature.

7.2 Further Work

The research presented in this thesis has raised several lines of research which should be pursued. These are discussed in detail in this section:

Low Temperature Measurements

Firstly, as the full vibrational spectrum can be measured only at low temperature $< 30K$, the IETS measurements can be performed for nanoscale SIM tunnel junctions (Si NW / SiO₂ / Al NW) for NH_4OH , CH_3COOH , and $C_3H_6O_2$ molecules at low temperature $< 30K$. This requires gating of SB using a back-gate. Low temperature measurements, in particular can be used to investigate possibility of measuring full IETS of single-molecule.

Fabrication

The device sensitivity can be investigated by fabricating thinner NWs. In this thesis, the reduction in device dimension to the nanoscale is increased the sensitivity of the device to molecules adsorbed on the tunnel junction from $\sim 10^{13}$ molecules to ~ 500 molecules. Fabrication of reduced dimension devices with gate control may allow investigation of the IETS characteristics of smaller numbers of molecules. Then the effect of reduction in device dimension on peak shape can be investigated.

Various top metal electrodes can be then used, to investigate the effect of top metal electrodes on IETS characteristics. The position of the peaks can shift, based on the metal used for the top electrode.

Then the effect of the concentration of an adsorbed molecule can be investigated. We expected to see that as the solution concentration is increased, the intensity of the tunnelling peaks increases as well. Furthermore, we can study the effect of adsorption time on the IETS measurements. Finally, IETS measurements can be performed for different molecules.

Simulation

Some assumptions were made during the simulation in this thesis to simplify the simulation coding:

The simplified current density equation was modelled in Matlab. Here, we assume that the left electrode has a higher Fermi energy than the right electrode, which are separated by $eV = E_{F,L} - E_{F,R}$. If this is not the case, the simplified current density equation can not be applied to calculate the elastic tunnelling current. Therefore, in future works the model has to use the Tsu-Esaki equation.

Transfer matrix method for calculating tunnel junction probability can be used. This method may allow enhancement of model by including the effect of molecules potential on tunnel barrier.

Also in this thesis, the molecular peak intensities in the spectrum was not calculated properly. This is important if the concentration of the impurities within the insulator has to be determined. The KSH method can be used as a suitable model to calculate the intensities.

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Appendix A

Si NW / SiO₂ / Al NW Tunnel

Junction Fabrication Process

1. PMMA 950k photoresist diluted 2% in anisole, spun onto *n*-type, highly doped SOI wafer (doping density $\sim 10^{19} - 10^{20} \text{ cm}^{-3}$): 5000 rpm spin speed, 500 rpm acceleration, for 50 seconds.
2. Bake on hotplate at 170°C (1 hour)
3. 1st EBL - Si NW pattern: Area Exposure dose $\sim 375 \mu\text{m}/\text{cm}^2$, Line Exposure dose $\sim 3 - 5 \text{ nC}/\text{cm}$
4. Develop in IPA : MIBK (3:1) at 23°C (60 seconds)
5. Rinse in IPA
6. Blow dry with N_2
7. Thermal Evaporation of 40 nm of Al at $< 1.1 \times 10^{-6} \text{ mbar}$: Hard mask for RIE
8. Sample left in Acetone (20 minutes)
9. ultrasonic

APPENDIX A. SI NW / SiO_2 / AL NW TUNNEL JUNCTION FABRICATION PROCESS

10. Lift-off
11. Blow dry with N_2
12. RIE using SF_6 at 100 mTorr for 40 seconds, at RF power of 100 W : Etch depth $\sim 200\text{ nm}$
13. Wet Etch for 30 seconds

Chemical	Ratio	Dissolve
HNO_3	1 – 5 %	Al Oxidation
H_3PO_4	65 – 75 %	Al_2O_3
CH_3COOH	5 – 10 %	Wetting and Buffering

14. Si NW thermally oxidised at 1000°C to create a SiO_2 surface layer : 10 nm thick
15. PMMA $950k$ photoresist diluted 2% in anisole spun onto sample: 5000 rpm spin speed, 500 rpm acceleration, for 50 seconds
16. Bake on hotplate at 170°C (1 hour)
17. 2nd EBL - Al NW pattern: define an Al NW such that it crossed the Si NW, using Alignment
18. Develop in IPA : MIBK (3:1) at 23°C (60 seconds)
19. Rinse in IPA
20. Blow dry with N_2
21. Thermal Evaporation of 40 nm of Al metal at $< 1.1 \times 10^{-6}\text{ mbar}$: Al NW
22. Sample left in Acetone (20 minutes)

23. ultrasonic
24. Lift-off
25. Blow dry with N_2
26. PMMA 950*k* photoresist diluted 6% in anisole spun onto sample: 5000 rpm spin speed, 500 rpm acceleration, for 50 seconds
27. Bake on hotplate at 170°C (1 hour)
28. 3rd EBL - Ohmic contact: Area Exposure dose 375 $\mu m/cm^2$
29. Thermal Evaporation of 120 *nm* of Al metal at $< 1.1 \times 10^{-6}$ *mbar*: Ohmic contact
30. Sample left in Acetone (20 minutes)
31. Lift-off
32. Blow dry with N_2