

Imperial College London

Department of Materials

Nanoscale Films for Near Infrared Active Plasmonic Devices

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Thesis submitted for the degree of

DOCTOR OF PHILOSOPHY

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ABSTRACT

As optoelectronic components become nano-dimensional, controlling the coupling between light and matter at the nanoscale has become a major technological challenge, as well as the subject of theoretical studies. The aim of this work is threefold. First, to assess the suitability of ferroelectric thin films - Barium Strontium Titanate (BST), and Strontium Barium Niobate (SBN), as active media for plasmonic devices. Second, to find suitable thin film electrodes for such devices, by exploring and optimizing the plasmonic behaviour of already known conductive materials, conductive oxides (Strontium Ruthenate - SRO), and transitional metal nitrides (Titanium nitride - TiN). Third, to optimize the deposition process of metallic (Silver – Ag) films, so as to improve their smoothness, and thus their suitability for plasmonic applications and lithography in general.

SBN ceramic targets were sintered. SBN and BST films were deposited by PLD and ellipsometry and normal incidence reflectometry were used to examine their optical tunability. Ellipsometry was further used to measure the effects of the residual strain of the BST thin films on their optical properties. BST and SBN films were found to exhibit a birefringence under bias along the direction of growth. A residual strain variation along the films' direction of growth was inferred from an observed non-linear change in the refractive index of BST films along that same direction.

SRO and TiN films were fabricated using PLD and reactive magnetron sputtering, respectively. The effects of the deposition pressure upon structure, charge carrier concentration and mobility, and optical properties were studied using X-ray diffraction (XRD), Hall-effect measurements, and ellipsometry. The optical properties of SRO were explained based on electron concentration and structure. SRO was confirmed as a promising plasmonic material, for applications in the near infrared range and at elevated temperatures. The influence of the deposition temperature upon the optical properties of TiN films was shown. Films grown at high temperature (800°C) had quasi-metallic optical properties, while films grown at room temperature exhibited well defined plasmon bandwidth, between two distinct Epsilon-near-zero (ENZ) frequencies, which has been linked to the uniform oxidation of the samples.

Finally, Ag thin films were deposited using magnetron sputtering, in an Ar/He atmosphere. The effect of the sputtering gas ratio on the films structure, morphology and reflectivity was studied using XRD, Atomic force microscopy (AFM) and visual-range normal incidence reflectometry. The addition of Helium to the sputtering atmosphere was found to reduce the roughness of Ag films and improve their reflectivity, due to the Penning effect present in the Ar-He plasma.

The work undertaken has, by developing new plasmonic materials (SRO, oxidized TiN), and expanding the knowledge of the behaviour (BST) and fabrication (Ag) here has paved the way for the development of active plasmonic devices.

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LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
ASP	Acoustic Surface Plasmon
BET	Brunauer–Emmett–Teller
BST	Barium Strontium Titanate BaSrTiO_3
BTO	Barium Titanate BaTiO_3
EO	Electro-optic
FHWM	Full width at half maximum
IMI	Insulator–Metal–Insulator
IR	Infra Red
LAO	Lanthanum Aluminate LaAlO_3
LN	Lithium Niobate LiNbO_3
LT	Lithium Tantalite LiTaO_3
MIM	Metal-Insulator-Metal
MP	Multipole Surface Plasmon
PLD	Pulsed Laser Deposition
SEM	Scanning Electron Microscopy
SBN	Strontium Barium Niobate SrBaNbO_3
SNOM	Scanning Optical Near-Field
SPP	Surface Plasmon Polaritons
SPR	Surface Plasmon Resonance
SRO	Strontium Ruthenate SrRuO_3
STO	Strontium Titanate SrTiO_3
TiN	Titanium Nitride
XRD	X-Ray Diffraction

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ACKNOWLEDGMENTS

I am deeply grateful to everyone who has helped, supported and encouraged me in this work: my supervisors - Dr. Peter K. Petrov and Prof. Neil McN. Alford, our partners in the Active Plasmonics project and my fellow graduate students.

CHAPTER 1

INTRODUCTION

My first encounter with independent experimental work, and Imperial College, was closely related to phenomena at the nanoscale, thrilling my imagination like a game. It involved studying the dynamic and distribution of Oxygen in Silicon-on-Insulator (SOI) structures, which had been obtained by ion implantation at 150 keV, using the ion accelerator at Imperial College, as a result of the collaboration with my University in Bucharest. My interest in surface phenomena and technology took me to the University of Paris VI for an MsC, where I had the chance to study the behaviour of a certain ferromagnetic material on graphene substrates.

The opportunity to work, as a PhD student, in the Department of Materials at Imperial College, gave me the chance to learn and work with another deposition technique: Pulsed Laser Deposition. During my PhD work I expanded my knowledge of thin films and characterization while working on materials relevant to plasmonics, an exciting emerging technology.

The aim of this work carried out in the Materials Department at Imperial College is threefold. First, the assessment of the suitability of ferroelectric thin films - Barium Strontium Titanate (BST), and Strontium Barium Niobate (SBN), as active media for plasmonic devices. Second, an exploratory work followed by optimization of the plasmonic behavior of two already known thin film electrode materials, such as conductive oxides (Strontium Ruthenate - SRO), and transitional metal nitrides (Titanium nitride - TiN). The third and last one is related to the optimization of thin Ag thin films used as electrodes, in terms of reduced roughness at low thickness values compatible with plasmon applications.

1.1 Motivation

Optoelectronic components are able to operate at much higher frequencies than conventional integrated circuits, which are limited by high conduction losses to the GHz range. Reducing the size of these components and integrating them with conventional planar technology would lead the way to many novel applications in both electronics and photonics.

Until now, the resolution limit of optical instruments, spanning from microscopes to telescopes, was limited by the diffraction limit, i.e. the possibility to control the electromagnetic radiation on length scales down to a little below its wavelength, meaning a few hundred nanometres for visible light. This limit derives from the diffraction of light on an aperture. Due to light waves interference there is a minimum distance between the two positions where the diffracted light interfere constructively, and respectively destructively. From the Fourier transform it results the smallest size Δx to which a plane light wave can be focused in one dimension is of the order of $\Delta x \approx 2\pi/\Delta k_x = \lambda_0/2$, where $\Delta k_x = 4\pi/\lambda_0$ represent the maximum possible spread of the wavevector component k_x along the x direction, and λ_0 is the wavelength in vacuum. Conversely, this length scale also governs the smallest distance between two objects for which the objects can be individually resolved in a microscope. Ernst Abbe was the first to formulate a proper derivation of the diffraction limit in 1873 [1]. In this approach the electromagnetic field propagating in a homogeneous medium (having a dielectric constant ϵ , is expanded in plane waves $e^{i\mathbf{k}\cdot\mathbf{x}}$, the wavevector $\mathbf{k}$.

Plasmonic technology aims to control light down to nanometre length scale, by taking advantage of the localised collective oscillations of electrons along metallic surfaces. Plasmonics, emerged as a new area of research in recent years, as a result of developments in nanotechnology and nanoelectronics. It deals with the generation, propagation and detection of plasmonic waves, which are collective electronic excitations generated by an electromagnetic field that excites a metal/dielectric interface. Following the interaction, the electromagnetic fields are confined to the surface and propagate along the interface; they are called surface plasmon polaritons (**SPP**) [2], [3]. A SPP is in fact a collective electron density oscillation at the interface between a metal and a dielectric. Due to this field confinement and enhancement at a metal/dielectric interface, the SPP play a key role in material science, optics, biology, and more recently in nanoelectronics and nanophotonics [4], [5].

The propagation length of a SPP δ_{SP} is determined by the loss in the metal. As an example, comparing Al and Ag at $\lambda = 500$ nm, $\delta_{SPP}^{(Al)} = 2$ μ m, while $\delta_{SPP}^{(Ag)} = 20$ μ m, due to the higher absorbance in Al. The δ_{SPP} value increases with λ , so that for 1.55 μ m one gets $\delta_{SP}^{(Ag)} = 1000$ μ m [2].

One important feature is that SPP wavelength (λ_{SPP}) is always smaller than the electromagnetic excitation wavelength λ_0 , depending on the relative permittivities of the metal and dielectric media [3]. Up to now, the research has been mostly limited to frequencies in the visible and IR spectral regions, near the metallic plasma frequencies, where, into a thin region at the metal surface, the electric field of SPPs is strongly confined, and consequently can guide efficiently the light on very small length scales. Several applications, demonstrated till now just in the lab environment, include sub-wavelength optics and microscopy, non-linear optics, data storage, photolithography, and bio-photonics.

As the reduction in size of integrated circuit components, the performance of metal wire interconnects is expected to degrade in a number ways, such as increased delay time for signal propagation, power dissipation and cross-talk amongst wires, derived from fundamental physical limitations of transmitting information along metal wire interconnects by electric charging and discharging. Considering that elements in conventional circuits are much smaller than the associated wavelength of electrons under the conditions of operation, Engheta [6] explored the way concepts used to describe circuits might be extended to optical frequencies, when dealing to nanoparticles, and introduced optical nano-elements as nanoinductors, nanoresistors and nanocapacitors. A further step was circuit analysis in metal-optics [7], showing that one difference between the plasmonic and classical electrical cable lines consists in that the first one employs kinetic inductance (arising from the inertia of the electrons in a metal), instead of magnetic (Faraday) inductance. Kinetic inductance dominates over Faraday inductance when the characteristic dimensions are smaller than the collisionless skin depths [8]. Compared to classical electrical cables, SPPs can accommodate higher frequencies, so their future in the efficient transmission of information can be anticipated.

Conway and co-authors [9] made a quantitative comparison between the performance of metal wire interconnects, operated in the traditional manner by electric charge and discharge, versus the performance of metal wires operated as surface plasmon waveguides. They demonstrated that plasmonic interconnects offer reduced signal latency compared to conventional interconnects. However, they found that high density plasmon wire interconnects, needed for reducing cross-talk amongst them, significantly increases energy dissipation per transmitted bit, above and beyond that required for electric charge/discharge interconnects at the same density. Eventually, even if surface

plasmons are not an obvious replacement for intermediate electric interconnects, there is potential for their use in other integrated circuit applications [9].

In the visible and the Infra-Red (IR) optical spectrum, plasmonic devices have dimensions in the range of 300–1000 nm. These small SPP features make possible the integration at the nanoscale, in the same chip, of the optical and electronic components, and so generating circuits with high speed and flexibility.

Nowadays, optical fibers and waveguides are able to carry digital information with a capacity three orders of magnitude greater than that of copper electronic interconnects, however their dimension is still very large compared to nanoelectronic devices. There is also a more physical impediment for further miniaturization in optical devices: diffraction phenomena destroy the confinement of propagating light when their dimensions approach λ_0 . A proposed method to circumvent this natural limitation is to convert light into SPP waves, which can overcome the diffractive limit, as the SPP wavelength is always smaller than λ_0 . The SPP devices are called therefore sub-wavelength components. In these devices the incoming light is to be converted into SPP and then processed (i.e. modulated, focused, propagated at a remote location, etc.) and then reconverted at the output back into light with diffractive properties, as schematically represented in Figure 1.1 [10]. So, by merging photonics and electronics, nanoscale plasmonic chips could be implemented for high data rate processing or very effective sensing applications [11]. Currently, SPP waveguides are one of the most studied issues in the field of plasmonics.

Among the most studied approaches for guiding SPP fields are metal/dielectric interfaces, chains of nanoparticles or nanowires. The metal-insulator-metal (MIM) and its complementary, the insulator–metal–insulator (IMI) waveguides, are basic configurations used for SPP propagation [12]. These consist of a dielectric strip sandwiched between metal regions (MIM), and respectively a metal strip surrounded by semi-infinite dielectrics (IMI). Although an increase of the plasmon propagation lengths has only been observed in IMI structures, accompanying the decrease of the width of the metallic strip, it is only in MIM structures that sub-wavelength extension of SPP fields can be achieved. Simulations for two coupled waveguides show, similarly, that subwavelength pitches and high confinement are obtained only in a repetitive MIM structure, whereas longer propagation lengths associated with larger pitches are characteristic for repetitive IMI structures. The pitch is defined as the period of the MIM (or IMI) configuration, or, alternatively, as the distance between the centres of adjacent waveguides [12].

Hybrid metal ferroelectric insulator multilayer structures are a promising direction of research, allowing for the active response of a dielectric to be controlled by an applied voltage. How-

ever, greater plasmon confinement associated with a reduction in size subjects such devices to great intrinsic losses and low propagation lengths.

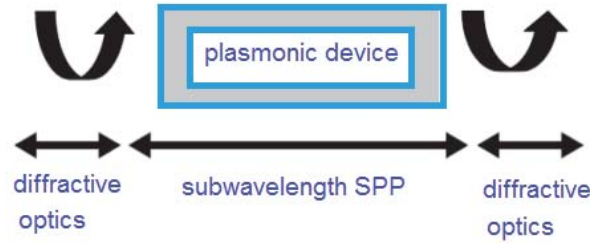


Figure 1.1: Basic configuration of a plasmonic chip that uses diffractive optics to excite the SPP and to extract the emitted light [10].

As a result, plasmonics combines integration at the nano-scale obtained in nanoelectronics, with the high bandwidth specific for photonics, by coupling the photon's energy with the free-electron gas [5, 13 - 15].

Metamaterials [16], Transformation Optics (in which values of chosen parameters of metamaterials are varied spatially to bend electromagnetic waves and energy) [17, 18] and plasmonics are steering the advances of unique, innovative devices with novel functionalities such as optical invisibility cloaks [17, 19, 20], superlenses [16, 21, 22], planar magnifying hyperlenses [23, 24], hyperlenses [25, 26], sub-wavelength waveguides [15, 27] or optical nano-antennas [28 - 30].

An active plasmonic device enables the external active control of plasmonic propagation. Depending on output, active plasmonic devices can be divided in two categories: one where metallic structures acting as a nanoantenna control or tune the device's performance [31, 32], and plasmonic response devices [33, 34], where the response of the plasmonic structure is controlled/tuned by an external component. Up-to-date, capabilities to enable external active control over the plasmonic response in real time—so-called active plasmonic response devices (plasmonic modulators and switches), still remain a major challenge [35, 36].

As optoelectronics components become nano-dimensional, the coupling between matter and light at the nanoscale is important both for fundamental research and applications in nanotechnology. The study of materials in relation to their possible applications in plasmonics is of tremendous importance.

1.2 Thesis outline

Chapter 2 is a monograph concerning the state of the art, describing the theory of surface plasmons from a semi-classical perspective, combining classical electrodynamics with the Drude electron-gas model. Three active plasmonic devices, the plasmonic waveguide, the plasmonic interferometer and the plasmonic modulator are presented because of their suitability as test-bed devices for the evaluation of their constituent materials. A brief overview of techniques used to couple electromagnetic radiation and surface plasmons is also given. Another part is concerned with active media of plasmonic devices, presenting a succinct description of the ferroelectric symmetry groups and explaining the dielectric behaviour of perovskite materials, as exemplified by BST, and tungsten bronze structured materials like SBN. A brief overview of the Landau theory of ferroelectric transitions is also given, followed by a concise account of the electro-optical effect in ferroelectrics, as exemplified by BST. Also presented is the motivation behind the choice of materials for the thin film electrodes of plasmonic devices: metals, conducting oxides, and transitional metal nitrides.

Chapter 3 discusses the fabrication techniques used for plasmonic thin films (pulsed laser deposition and magnetron sputtering), ceramic targets, and the methods used for their characterisation.

Chapter 4 describes the work done on ferroelectric thin films. It contains the introduction of fabricated ferroelectric SBN targets (described in detail in Annex 1), subsequently used for the deposition of ferroelectric thin films. The optical properties of SBN and BST films deposited by pulsed laser deposition are discussed, as well as the results of the electro-optical effects measurements which have been carried out.

Chapter 5 is concerned with the work carried out on electrode materials for thin film plasmonic devices, namely SRO and TiN. Section 5.1 describes the deposition process of SrRuO_3 , and the effects of the deposition parameters on the films structure are described. The relation between the films structure and charge carrier concentration and mobility, and the dielectric constants is also discussed. The relation between charge carrier dynamics and optical constants in the near-infrared range was elucidated. Section 5.2 describes the ongoing work with TiN thin films: the deposition process and the effects of the deposition parameters on films structure. In the following section the effect of the deposition parameters upon the charge carrier concentration and mobility, conductivity, and optical constants are described and discussed. The latest results from ongoing work are pre-

sented in Annex 2. Section 5.3 describes the work carried out to optimize the deposition process of Ag thin films. The effects of addition of He to the sputtering gas upon the films structure, morphology, electrical and optical properties are described.

Chapter 6 contains the conclusions of the undertaken work. The conclusions of previous chapters are systemized and critically evaluated.

Chapter 7 contains the future work plans, as imposed by the conclusions from the previous chapter. It contains the future experiments to be carried out involving all the materials previously explored.

1.3 Original contribution

- Ellipsometry was used to determine optical tunability in a ferroelectric thin film; the impact of strain upon the ferroelectric properties of ferroelectric films was described.

L. Braic, B. Zou, D.Y. Lei, N. Vasilantonakis, A.V. Zayats, S.A. Maier, N.M. Alford, P.K. Petrov *The Effect of Ferroelectric Tunability and Strain on the Optical Properties of Barium Strontium Titanate Thin Films*, poster presentation, UK Ferroelectrics 2015, 27-28 July 2015.

- The optical properties of SrRuO_3 thin films were investigated, showing their suitability for near infrared plasmonic applications.

L.Braic, B.Zou, P.K. Petrov, M.I. Rusu, A.E. Kiss, R. Savastru, C.E.A. Grigorescu, N.M. Alford *Thickness Dependence of Structural, Electrical and Optical Properties of SrRuO_3 Thin Films on MgO* , poster presentation, ROCAM-2012 seventh international edition, 28-31 August Brasov, Romania

L.Braic, N.Vasilantonakis, B.Zou, S.A. Maier, N.M. Alford, A.V. Zayats, P.K. Petrov *Optimizing Strontium Ruthenate Thin Films for Near Infrared Plasmonic Applications*, Scientific Reports **5**, article number 9118, doi: 10.1038/srep09118

- The optical properties of TiN films deposited at room temperature were investigated for the first time, and a limited plasmonic bandwidth, between two different Epsilon-Near-Zero (ENZ) frequencies was observed.

Manuscript in preparation.

- Helium was added to the process gas for the RF-magnetron deposition of Ag thin films, and was found to significantly reduce their roughness.

Manuscript in preparation.

CHAPTER 2

STATE OF THE ART

This chapter presents a summary of the reviewed literature related to surface plasmon polaritons and their properties, active plasmonic devices and materials for active plasmonic devices.

Surface plasmon polaritons are surface electromagnetic waves that propagate along a metal/dielectric interface. Their propagation requires the two media to have dielectric constants of opposite signs. In the visible and infrared wavelength region, this condition is met by e.g. air/metal and water/metal interfaces (where the real dielectric constant of a metal is negative and that of air or water is positive). Typical metals that support surface plasmons are silver and gold, but metals such as copper or titanium nitride can also support surface plasmon generation.

2.1 Surface Plasmon Polaritons and their Properties

This section gives a brief outline of the theory of surface plasmons from a semi-classical perspective, combining classical electrodynamics with the Drude electron-gas model. Plasmon losses in metals are also described, together with the effects of surface roughness.

2.1.1. Drude Free-Electron-Model: A Brief Introduction

The interaction between metals and electromagnetic fields can be accurately described using Maxwell's equations. This is because the high density of free carriers in metals determines tiny separation of the electron energy levels, as compared to thermal excitations at room temperature ($\sim kT$). As such, in the following the classical theory will be used.

The short description of the optical properties of metals will be done in the frame of Maxwell equations. This phenomenological approach allows one not to consider the fundamental interactions

between charged particles inside media and electromagnetic fields, because the rapidly varying microscopic fields are averaged over distances much larger than the underlying microstructure.

Maxwell equations:

$$\nabla \cdot \mathbf{D} = \rho_{ext} \quad (2.1.1a)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (2.1.1b)$$

$$\nabla \times \mathbf{E} = -\partial \mathbf{B} / \partial t \quad (2.1.1c)$$

$$\nabla \times \mathbf{H} = \mathbf{J}_{ext} + \partial \mathbf{D} / \partial t \quad (2.1.1d)$$

link the electric field ($\mathbf{E}$), the dielectric displacement ($\mathbf{D}$), the magnetic field ($\mathbf{H}$) and the magnetic induction ($\mathbf{B}$), with the external charge and current densities ρ_{ext} and $\mathbf{J}_{ext}$. Let us consider both the external and internal charge and current densities [5]:

$$\rho_{tot} = \rho_{ext} + \rho; \quad \mathbf{J}_{tot} = \mathbf{J}_{ext} + \mathbf{J},$$

where the external set drives the system while the internal one responds to external stimuli.

The electric field and the dielectric displacement are linked via polarization ($\mathbf{P}$):

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} \quad (2.1.2a)$$

and the magnetic field and the magnetic induction via magnetization ($\mathbf{M}$):

$$\mathbf{H} = \frac{1}{\mu_0} \epsilon_0 \mathbf{B} - \mathbf{M} \quad (2.1.2b)$$

where ϵ_0 and μ_0 are the electric permittivity and magnetic permeability of vacuum, respectively. Since magnetic media are not explored in this work, magnetization will not be further considered. The polarization $\mathbf{P}$ describes the electric dipole moment per unit volume inside the material (originating from the alignment of microscopic dipoles with the electric field), and so, it is related to the internal charge density ($\nabla \cdot \mathbf{P} = -\rho$). However, charge conservation ($\nabla \cdot \mathbf{J} = -\partial \rho / \partial t$) requires that the internal charge and current densities are linked via

$$\mathbf{J} = \partial \mathbf{P} / \partial t \quad (2.1.3)$$

By inserting equation (2.1.2a) into eq. (2.1.1a) we obtain:

$$\nabla \cdot \mathbf{E} = -\rho_{tot} / \epsilon_0 \quad (2.1.4)$$

meaning that the macroscopic electric field includes all polarization effects, i.e. both the external and the induced fields are absorbed into it.

In the following, we will consider only linear, isotropic and nonmagnetic media. One can define the constitutive relations:

$$\mathbf{D} = \epsilon_0 \epsilon \mathbf{E} \quad (2.1.5a)$$

$$\mathbf{B} = \mu_0 \mu \mathbf{H} \quad (2.1.5b)$$

with $\epsilon_0 \approx 8.854 \times 10^{-12}$ F/m and $\mu_0 \approx 1.257 \times 10^{-6}$ H/m. ϵ is called the dielectric constant or relative permittivity and $\mu = 1$ the relative permeability of the nonmagnetic medium. The linear relationship (2.1.5a) between $\mathbf{D}$ and $\mathbf{E}$ is often also implicitly defined using the dielectric susceptibility, which describes the linear relationship between $\mathbf{P}$ and $\mathbf{E}$ via equation (2.1.6):

$$\mathbf{P} = \epsilon_0 \chi \mathbf{E} \quad (2.1.6)$$

Inserting (2.1.2a) and (2.1.6) into (1.5a) yields $\epsilon = 1 + \chi$.

The last important constitutive linear relationship we need to mention is that between the internal current density $\mathbf{J}$ and the electric field $\mathbf{E}$, defined via the conductivity σ by

$$\mathbf{J} = \sigma \mathbf{E} \quad (2.1.7)$$

The optical properties of metals are broadly governed by the response of free electron gas. Over a wide range of frequencies the optical properties of metals can be explained by a plasma model, where a gas of free electrons of density n moves against a fixed background of positive ion cores. Elaborated by Paul Drude, this simple, but successful theory explains the electrical and thermal conduction in metals, by applying the kinetic theory of gases to free electrons. To maintain the neutral charge of the whole metal, the negative charge of the electrons is considered to be compensated by much heavier particles, considered as immobile. As such, it is a step by step development of the theory of kinetic gases applied to the free electron gas, so even though the typical densities for metals are about three order of magnitude greater than in a classical gas, the initial assumptions in the Drude theory do not depart too much from the kinetic theory of gases [37].

The basic assumption of Drude model are:

- (1) The collisions between electrons and ions are instantaneous, uncorrelated events.
- (2) All other interactions (i.e. potentials from ions or other electrons) except for applied fields, are neglected. This means that electrons travel in straight lines between scattering events.
- (3) Probability of an electron having a collision in a time interval dt is dt/τ ; τ does not depend on the electron position or momentum.
- (4) Electrons are assumed to maintain the thermal equilibrium with their surroundings only through collisions.

Regarding the second assumption of the model, interactions not considered are incorporated into the effective electron mass m^* . Under the influence of the external field the electrons oscillate, and their motion is damped via collisions occurring with a characteristic frequency $\gamma=1/\tau$, where τ is

the relaxation time of free electron gas ($\tau \sim 10^{-14}$ s at room temperature, corresponding to $\gamma = 100$ THz).

In order to calculate the current induced into the metal by an electric field variable in time:

$$\mathbf{E}(t) = \mathbf{E}_0 e^{-i\omega t} \quad (2.1.8)$$

The equation of motion for an electron of position $\mathbf{x}(t)$, is:

$$m \cdot \ddot{\mathbf{x}} + m \cdot \gamma \cdot \dot{\mathbf{x}} = -e\mathbf{E} \quad (2.1.9)$$

A particular solution of this equation describing the oscillation of the electron is $\mathbf{x}(t) = \mathbf{x}_0 e^{-i\omega t}$, in which the complex amplitude incorporates any phase shifts between the driving field and the electron response via [5]:

$$\mathbf{x}(t) = \frac{e}{m(\omega^2 + i\gamma\omega)} \mathbf{E}(t) \quad (2.1.10)$$

The displacement of the electrons contributes to the macroscopic polarization $\mathbf{P} = -ne\mathbf{x}$ as:

$$\mathbf{P} = \frac{n \cdot e^2}{m(\omega^2 + i\gamma\omega)} \mathbf{E}(t) \quad (2.1.11)$$

Inserting the above equation (2.1.11) into equation (2.1.2a) we obtain:

$$\mathbf{D} = \epsilon_0 \left(1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \right) \mathbf{E} \quad (2.1.12)$$

where

$$\omega_p^2 = \frac{n \cdot e^2}{\epsilon_0 \cdot m^*} \quad (2.1.13)$$

is the plasma frequency of the free electron gas. So, we obtain the dielectric function of the free electron gas:

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \quad (2.1.14)$$

The real and imaginary parts of the complex dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ are:

$$\epsilon_1(\omega) = 1 - \frac{\omega_p^2 \cdot \tau^2}{1 + \omega^2 \cdot \tau^2} \quad (2.1.15a)$$

$$\epsilon_2(\omega) = \frac{\omega_p^2 \cdot \tau}{\omega(1 + \omega^2 \cdot \tau^2)} \quad (2.1.15b)$$

where we re-introduced the relaxation time τ .

In the following, we will consider the energy domain where $\omega < \omega_p$, for which the metals retain their metallic character, and will discuss different regimes with respect to the collision frequency γ .

a) For large frequencies close to ω_p , $\omega \cdot \tau \gg 1$, determining negligible damping. In this region the dielectric function is predominantly real:

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2} \quad (2.1.16)$$

and it can be considered as the dielectric function of the undamped free electron plasma. However the noble metals behaviour in this region is altered by the interband transitions, determining an increase of ε_2 .

b) For very low frequencies: $\omega \cdot \tau \ll 1$, and $\varepsilon_2 \gg \varepsilon_1$, the real and imaginary part of the complex refractive index are of comparable magnitude, and are given by:

$$n \approx k = \sqrt{\frac{\varepsilon_2}{2}} = \sqrt{\frac{\tau \cdot \omega_p^2}{2\omega}} \quad (2.1.17)$$

In this region, metals are mainly absorbant, with an absorption coefficient α :

$$\alpha = \sqrt{\left(\frac{2\omega_p^2 \cdot \tau \cdot \omega}{c^2}\right)} \quad (2.1.18)$$

Combining eqs. (2.1.18) and (2.1.13) we obtain:

$$\alpha = \sqrt{(2\sigma_0 \cdot \omega \cdot \mu_0)} \quad (2.1.19)$$

where $\sigma_0 = \frac{n \cdot e^2 \cdot \tau}{m^*}$ is the DC conductivity.

The Beer's law of absorption implies that for low frequencies the field intensity inside the metal diminishes exponentially according to $e^{-\frac{z}{\delta}}$, δ being the skin depth:

$$\delta = \frac{2}{\alpha} = \frac{c}{k\omega} = \sqrt{\frac{2}{\sigma_0 \cdot \omega \cdot \mu_0}} \quad (2.1.20)$$

A more rigorous discussion of the low-frequency behavior based on the Boltzmann transport equation is given in reference [38], showing this description to be valid as long as the mean free path of the electrons $l \ll \delta$. At room temperature, for typical metals $l \approx 10$ nm and $\delta \approx 100$ nm, thus justifying the free-electron model.

Figure 2.1.1 illustrates reflection as a function of frequency. A sharp discontinuity in reflectivity appears at $\omega = \omega_p$, known as the plasma reflecting edge.

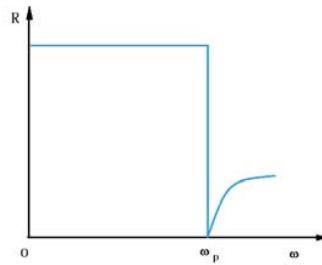


Figure 2.1.1: The plasma reflection edge.

c) At higher frequencies ($\omega \tau \leq \omega_p \tau$), the complex refractive index is predominantly imaginary (leading to a reflection coefficient $R \approx 1$ [39]), and σ acquires more and more complex character, blurring the boundary between free and bound charges.

It should be pointed out that the dielectric function obtained in the Drude model (eq. 2.1.14) accurately describes the optical response of metals only for photon energies below the threshold of transitions between electronic bands. For some noble metals, interband effects already start to occur at energies above 1 eV ($\sim \lambda \approx 1 \mu\text{m}$). The results indicate the Drude model is not adequate for describing either ϵ_1 or ϵ_2 at high frequencies, and for Au, its validity already breaks down at the boundary between the near-infrared and the visible. Above their respective band edge thresholds, photons are very efficient in inducing interband transitions, where electrons from the filled band below the Fermi surface are excited to higher bands. Theoretically, these can be described using the same approach as direct band transitions in semiconductors [37, 38]. The main consequence is an increased damping and competition between the two excitations at visible frequencies. However, this inadequacy of the model can be overcome by introducing in the equation of motion (2.1.9) the following term: $m \cdot \omega^2 \cdot \mathbf{x}$, yielding [5]:

$$m \cdot \ddot{\mathbf{x}} + m \cdot \gamma \cdot \dot{\mathbf{x}} + m \cdot \omega^2 \cdot \mathbf{x} = -e\mathbf{E} \quad (2.1.21)$$

Interband transitions are thus described using the classical picture of a bound electron with resonance frequency ω_0 and eq. (2.1.21) can then be used to calculate the resulting polarization.

To summarize, the electrical polarization can be described by the material's complex electrical permittivity or dielectric function, denoted by $\epsilon(\omega)$. While the real part of the dielectric function ($\text{Re}\epsilon$) describes the strength of the polarization induced by an external electric field, the imaginary part ($\text{Im}\epsilon$) describes the losses encountered in polarizing the material. Thus, a low loss material is associated with small values of $\epsilon(\omega)$. Primary loss mechanisms in the NIR, visible, and soft UV frequencies may be broadly classified as arising from phenomena related to conduction electrons and bound electrons (interband effects) [40]. Losses for conduction electrons arise from electron-electron and electron-phonon interactions, and from scattering due to lattice defects or grain boundaries. The success of the Drude theory is related to the fact that the conduction electrons have a nearly continuum of available states, their interaction with an electromagnetic field being well approximated by classical theory.

2.1.2 Stepping outside the ideal case: roughness effects

As presented above, the SPPs represent electromagnetic surface waves, having their maximum intensity at the surface, while decaying exponentially along the direction normal to the surface. One important phenomenon, considered in several applications (e.g. enhanced photo-effect by SPs, surface enhanced Raman scattering), is related to the SPs coupling with the photons via corrugated surfaces. It was first demonstrated by the excitation of the SPs on rough silver surfaces, after it was observed that the emitted light was about 100 times stronger in the resonance than out of it [41], and this was correlated with the strong diminishment of the reflected light, which indicated an increase of the electromagnetic field in the surface, accompanied eventually by the complete transformation of the incident light in SPPs. On rough surfaces the SPPs are scattered and consequently their displacement will transform from that of an extended wave to a disordered one, and thus their propagation along the surface resembles a diffusion process. If the frequency of the incident light ω is higher than the frequency of the SPPs ω_{sp} , then the SPPs are excited via roughness coupling, because the disorder induced by scattering determines an increase of the density of the electromagnetic field, which is becoming higher than the one associated to a regular extended SPPs wave on a smooth surface.

For rough surfaces the attenuation of SPPs depends on the wavelength and is related to the angular width of the minimum in the reflected monochromatic light [42, 43]. The amount of light converted into SPPs eventually produces heat, due to the above mentioned "diffusion-like process". If excited with white light, SPPs of different frequencies will propagate and will be extinguished after different distances, so they can be observed by optical microscopy as "color jets", due to some frequencies being damped faster than other ones [44].

Figure 2.1.2 [45] presents the reflectivity at normal incidence of Ag surfaces with different roughnesses. A second minimum is observed for rough surfaces, its intensity and full width at half maximum (FWHM) increasing with the roughness.

The attenuation length is affected by the scattering of SPPs on the surface roughness, and also on scratches, and inhomogeneities of the surface or the adjacent medium, as also observed in thin metallic films [46, 47]. The absorption in the adjacent medium determines additional attenuation, and this effect was used to measure that medium's absorption coefficient, and has found widespread applications, mainly related to sensors [48, 49].

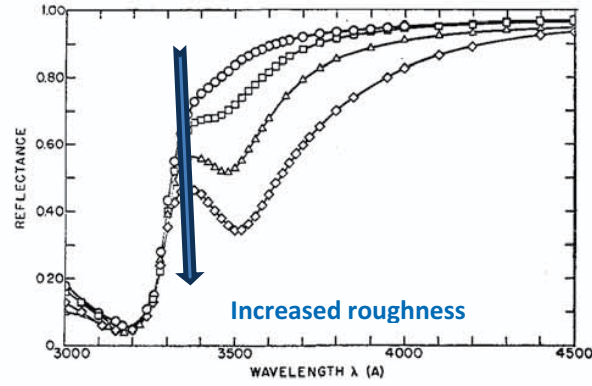


Figure 2.1.2: The reflectivity at normal incidence of Ag surfaces with different roughness values [45]. A dip in the reflectance appears around 345 nm, becoming more pronounced and moving toward 350 nm as the film's roughness increases. The dip at 320 nm, caused by interband transitions, is not affected by roughness.

To consider the influence of the surface roughness on the propagation of SPPs, a fairly simple system can be studied: a three layer system consisting of: a glass prism ($n = 0$); a metal film ($n = 1$) with a complex dielectric permittivity $\epsilon_1 = \epsilon_{1,r} + \epsilon_{1,i}$ and thickness d_1 , and an adjacent dielectric medium ($n = 2$), which can also have losses, so that $\epsilon_2 = \epsilon_{2,r} + i\epsilon_{2,i}$. It is assumed that the metal film at the interface with the dielectric medium ($n = 2$) exhibits a certain roughness [43].

In an experimental study [44] was used a Kretschmann-Raether configuration (presented in the next sub-chapter), the prism making possible the coupling of the incident light to the surface plasmon mode [41, 43]. Two different wavelengths were used in the experiment: 633 nm (He-Ne laser, 3 mW) and 805 nm (Ti:sapphire laser, 20 mW), as presented in Figure 2.1.3.

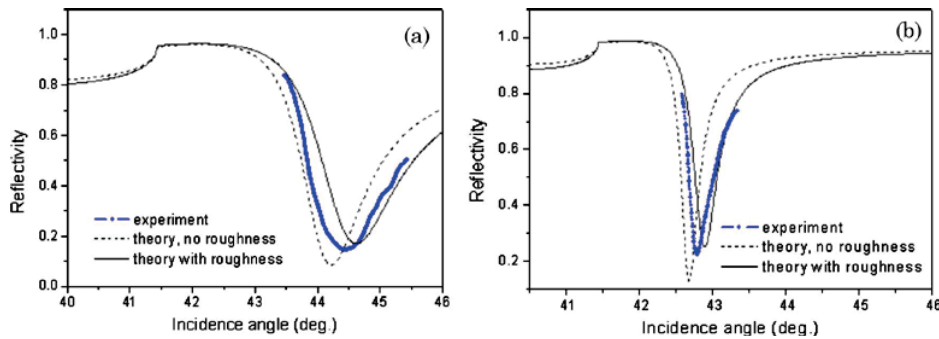


Figure 2.1.3: Measured and calculated (for smooth and rough surfaces) SPP curves for two wavelengths: (a) 633nm; (b) 805 nm [44].

SPPs are the source of some counterintuitive optical properties of materials. The behaviour can, however, be explained by classical electrodynamics, while considering the Drude model of an ideal electron gas. The value of the considered materials dielectric constant determines the SPP propagation and losses. In case of anisotropic materials, the values of the dielectric constant in the region closest to the interface play a larger role. This is, however, not the case for materials with a complex electronic structure, and the interaction of SPPs with surface states in such materials are the subject of continuing theoretical and experimental investigations. Also, the surface roughness affects SPP's and as such can affect their optical manifestations, by broadening their spectral range, reducing their intensity and propagation length.

2.2 Active plasmonic devices

The section describes three active plasmonic devices, the plasmonic waveguide, the plasmonic interferometer – whose transfer function changes when subjected to an electric signal, and the active plasmonic modulator. They were chosen because of their suitability as test-bed devices for the evaluation of their constituent materials. A brief overview of techniques used to couple electromagnetic radiation and surface plasmons is also given, illustrating the Kretschmann and Otto prism coupling geometries, the use of a Scanning Optical Near-Field (SNOM) probe, of diffraction gratings and the effect of surface features.

2.2.1 Plasmonic Waveguides

As introduced in sub-chapter 2.1, surface plasmons are the quanta of collective plasma oscillations localized at the interface between a metal and a dielectric. Because metals are lossy, under optical illumination the bound surface plasmon modes of a single metal/dielectric interface can propagate over several microns [41, 50]. In such a geometry, if using visible and near-infrared excitation frequencies, the field skin depth (representing $1/e$ decay length) increases exponentially with wavelength in the dielectric, while remaining approximately constant in the metal (~ 25 nm). Based on this observation, it was introduced a new class of plasmon waveguides, consisting of an insulating

core and conducting cladding (Figure 2.2.1), allowing the propagation of the surface plasmon modes that are strongly confined in the insulator region with an acceptable propagation length [51]. The field components at the metal-dielectric interface are illustrated in Figure 2.2.2: the magnetic field is perpendicular to the direction of propagation and the electric field is normal to the interface. The evanescent decay of the field perpendicular to the interface is also illustrated in Figure 2.2.2, where δ_d and δ_m denote the decay length into the dielectric and metal, respectively. This is a visual representation of the way the SPPs are bound to the metal-dielectric interface. Due to this high confinement, a large field enhancement takes place close to the surface. In such metal-insulator-metal (MIM) structures the light is guided due to the differences in the refractive index of the metal cladding and dielectric core [52].

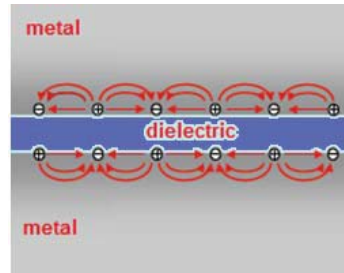


Figure 2.2.1: The electric field lines in a MIM waveguide.

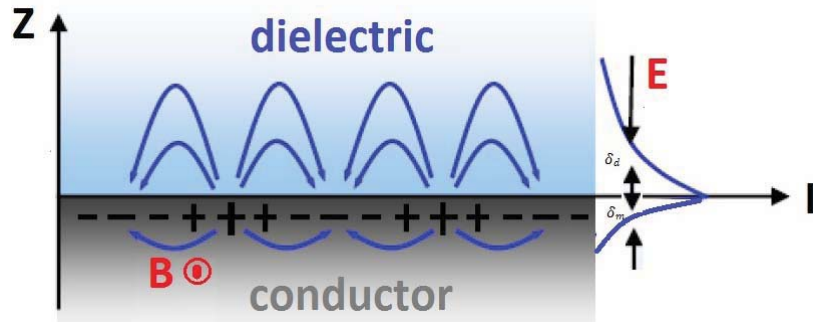


Figure 2.2.2: The electric field lines of a surface plasmon at a metal – dielectric interface.

Therefore, MIM waveguides are promising for the design of nanoscale all-optical devices with relatively easy fabrication according to the current state of the art [53, 54]. Several MIM waveguides based on SPPs, for example, bends and splitters, Mach–Zehnder interferometers, and couplers have been designed theoretically and demonstrated experimentally [55 - 59]. Some photonic band gap structures have also been proposed, such as plasmon Bragg reflectors, Bragg gratings with periodical-ly varied width [60, 61]. Given the perspective of integrating various functional components within

several micrometers, the size of devices must be decreased in order to meet the demand of high integration. All of the above devices are based on light bent by subwavelength metal slit structures.

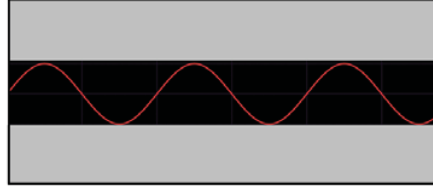


Figure 2.2.3: Schematic of a typical device fabricated using the basic MIM geometry.

In such a MIM structure the insulator layer can be replaced by a suitable active material, so that one can take also advantage of the electro-optic effect under an applied electric field. When applying an electric field across the such a device containing a ferroelectric as active material, the output can be tuned across the visible and infrared portions of the electromagnetic spectrum (Figure 2.2.3). If the active material is a semiconductor, an applied electrical field determines the modulation of the optical signal based on the change of the carrier density distribution within the active region.

In such a three layer structure one can change each of the materials, as well as their relative thickness; this may enable to tune the dispersion properties of the device as well as the resonance and filtering properties over a wide range of the electromagnetic spectrum. In addition, by changing the dimensions of the in-coupling and out-coupling structures, as well as the distance between them, it is possible to select different waveguide mode profiles that are present within the structure.

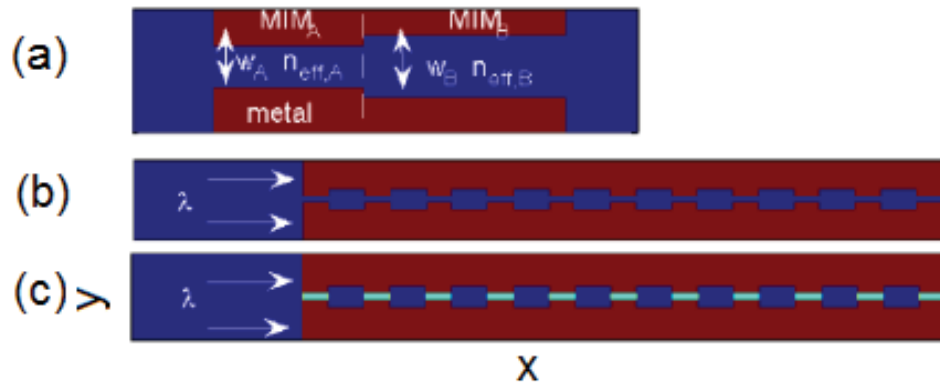
By active modulation of these plasmons with an applied external field, it is possible to design a wide range of devices, color filters (using refractive index modulation), modulators (modifying the carrier density) and optical logic gates.

As a cornerstone photonic device, the waveguide structures have been investigated theoretically and experimentally. Recently, Wang et al. reported a planar metal hetero-waveguide constructed by alternately stacking two kinds of metal gap waveguide with periodically modulated effective refractive index, leading to SPPs band gap structure [61]. Hosseini and Massoud proposed a low-loss plasmonic Bragg reflector consisting of alternatively stacked MIM waveguide with different dielectric materials [62]. Han devised the surface plasmon Bragg grating formed by a periodic variation of the width of the insulator in a MIM waveguide [60]. Liu investigated a wide band gap Bragg reflector by modulating the MIM waveguide slit and inserting dielectric materials with higher refractive index in the grating sections with narrow slit width [63]. As presented in [63], one can consider a MIM wave-

guide, which is a planar metallic waveguide with two semi-infinite metallic walls and the middle layer between the two walls is a dielectric film with width w , as shown in Figure 2.2.4a.

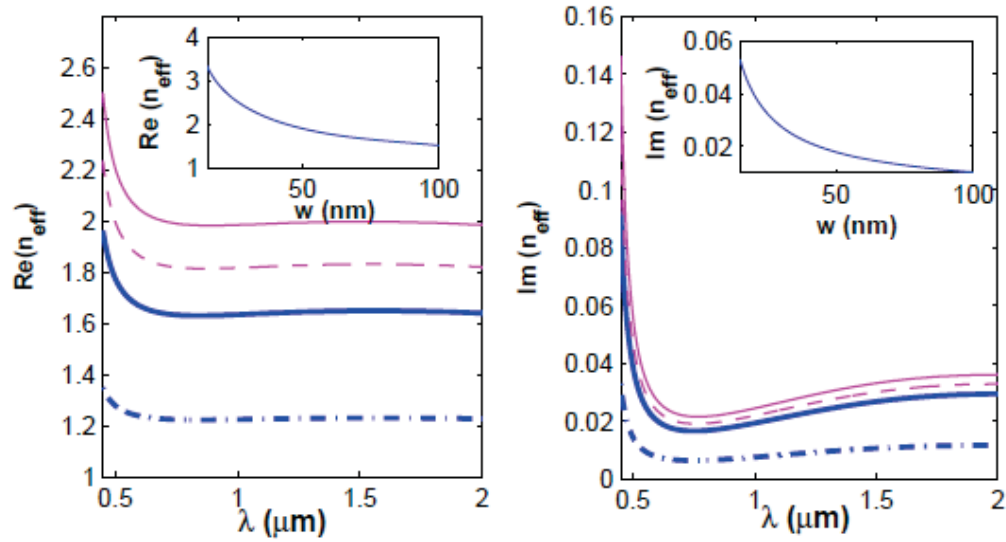
Figs. 2.2.5a and 2.2.5b plot the complex effective refractive indices of SPPs in the MIM waveguide for variant wavelengths. Two insets shown in Fig. 2.2.5a and 2.2.5b display the dependence of n_{eff} on the slit width at $\lambda = 1.55 \mu\text{m}$. In fact, in the range of visible and near-infrared frequency, the dependence of n_{eff} on w is very similar. It is clear that the value of n_{eff} , both the real and imaginary parts, increase with smaller slit widths. Regarding the real part, it shows that two MIM waveguides with different slit widths lead to the contrast of effective refractive indices.

Obviously, the contrast of n_{eff} can be fulfilled by symmetrically engraving two grooves on the two surfaces of a single MIM waveguide, which is shown in Fig. 2.2.4a. In particular, if the grooves are arranged periodically along to the axis of the slit, i.e., the direction of SPPs propagation, as shown in Fig. 2.2.4b and 2.2.4c, a periodic change of effective refractive indices can be produced. From Figure 2.2.5a, the periodic modulation of effective refractive index for the studied Bragg reflector (between two thick, blue lines or between dash-dot and thin red line) is greater than the planar MIM structure with periodic dielectric. Moreover, the bandgap will be further widened by filling the dielectric with higher refractive index in the narrower slits (Figure 2.2.4c). This character means the plasmonic Bragg reflector in Fig. 2.2.4c) will have a wider bandgap than that of Bragg reflector where modulation is achieved only by controlling the slit with and dielectric constant.

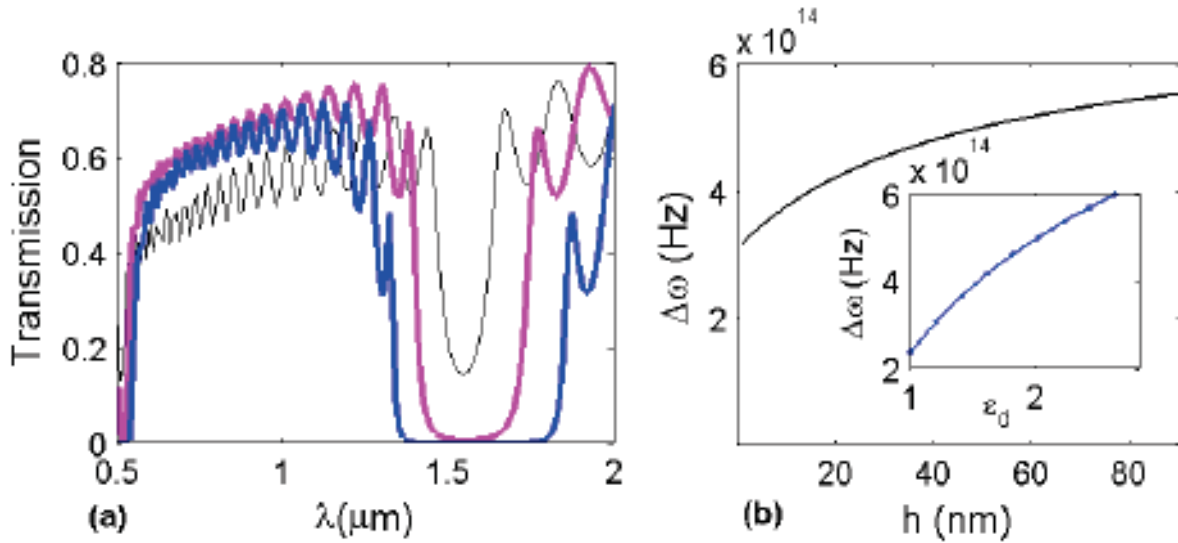


Figures 2.2.4: (a) Schematics of two MIM waveguides with slit widths w_A, w_B , respectively, produced by engraving two grooves on the surfaces of a single MIM waveguide, d_A and d_B are designating the waveguide thicknesses and the red section is metal. (b)-(c) Schematic of plasmonic Bragg reflector, alternately filled with air/air and SiO_2 /air, respectively [63].

On the other hand, as shown in Figure 2.2.5b, the imaginary part of the dielectric constant of the MIM waveguide with the wider slit (dash-dot blue line) will always be smaller than that of the narrow one (solid blue line, dashed red line and solid red line), which implies energy loss in the planar plasmonic Bragg reflector will be greater than in the standard Bragg reflector. Figure 2.2.6a shows the transmission spectrum of a Bragg reflector consisting of 10 periods. The thin (black) line represents the MIM Bragg reflector with periodic changes of dielectric in the slit, width $w = 30$ nm. The thick red and blue solid lines stand for the structure shown in Figure 2.2.5b and 2.2.5c, respectively. The slit widths are $w_A = 30$ nm, $w_B = 10$ nm, respectively. In Figure 2.2.6(b) is presented the bandgap as a function of slit width difference $h = w_B - w_A$, filled with dielectric in the narrow MIM waveguides ($\epsilon_d = 2.5$). [63].



Figures 2.2.5: Variation of the real (a) and imaginary (b) parts of n_{eff} with wavelength for SPPs mode in the MIM waveguide. The two insets show the real and imaginary of n_{eff} as a function slit width, at $1.55 \mu\text{m}$ wavelength. The thin solid, thin dash lines (red) and thick solid line (blue) correspond to the MIM waveguide with dielectric SiO_2 ($\epsilon_d = 1.46$), $p\text{-SiO}_2$ ($\epsilon_d = 1.23$), air ($\epsilon_d = 1.0$), and slit width $w = 30$ nm. The thick dash-dot line presents MIM structure filled with air, $w = 100$ nm [63].



Figures 2.2.6: (a) Transmission spectrum of Bragg reflector consisting of 10 periods; (b) Bandgap as a function of slit width difference $h = w_B - w_A$, filled with dielectric in the narrow MIM waveguides ($\epsilon_d = 2.5$) [63].

In the MIM structure presented above, the bandgap can be widened by filling with higher refractive index dielectric materials in the narrow slit of the proposed structure. This type of MIM structure is expected to have application in SPP-based devices such as distributed Bragg SPP emitter, filters and other nanophotonic devices, especially for the demand of broad bandgap elements [63].

Interfacing plasmonic elements (modulators, waveguides, etc.) with conventional photonic components, such as optical fibres and planar dielectric waveguides is important both for practical applications, as well for research experiments in the field of plasmonic waveguiding, as easier coupling schemes will facilitate rapid experimental characterization of waveguides for optimization purposes when geometrical configuration or the materials parameters are varied.

The photon and SPP wavevectors can be matched by using either photon tunnelling as in the total internal reflection geometry (Kretschmann and Otto configurations) or diffraction effects (Fig. 2.2.7 a, b, c, d, e, f) [64]:

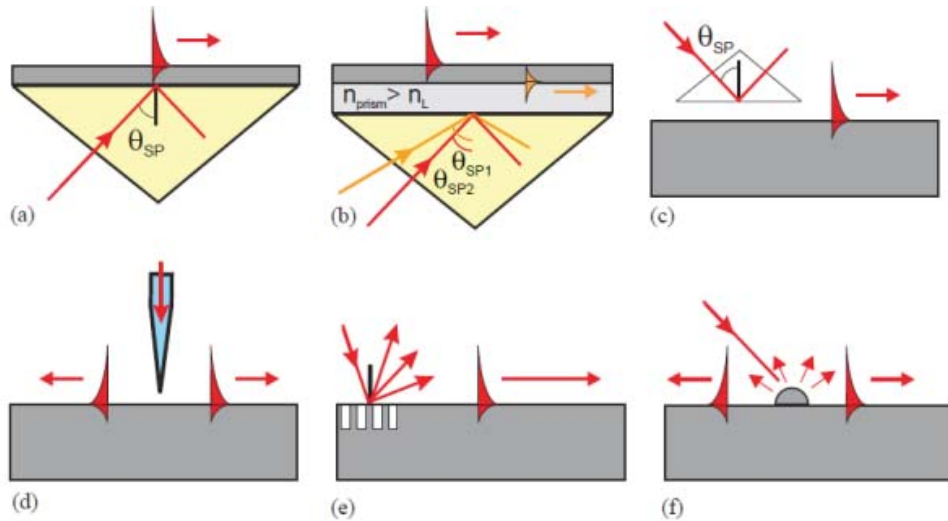
a) In the Kretschmann configuration, a metal film is illuminated through a dielectric prism at an angle of incidence greater than the critical angle of total internal reflection. At the angle of incidence θ at which the in-plane component of the photon wavevector in the prism coincides with the SPP wavevector at the air-metal interface, resonant light tunnelling through the metal film occurs, and light is coupled to surface polaritons. Under these resonant conditions, a sharp minimum is ob-

served in the reflectivity from the prism–metal interface as light can be coupled with almost 100% efficiency to the SPP field.

b) For a thicker metal film, the efficiency of the SPP excitation decreases as the tunnelling distance increases. With an additional dielectric layer with a refractive index smaller than the one of the prism (two-layer geometry), the photon tunnelling through this one can provide resonant excitation of SPP on the inner interface. Both SPP modes (on the surface and the interface) can be excited in such a configuration.

c) In the Otto configuration, for bulk metals, the prism for the total internal reflection is placed close to the metal surface and photon tunnelling occurs through the air gap between the prism and the surface.

d) Using illumination through a SNOM fibre tip, circular SPP waves can be locally generated at the surface. This configuration can be treated either as a tunnelling or as a diffraction mechanism for SPP excitation. This technique is somewhat analogous to the Otto configuration but allows local (with sub-wavelength precision) excitation of SPPs at the position of the SNOM tip.



Figures 2.2.7: SPP excitation configurations:

(a) Kretschmann geometry, (b) two-layer Kretschmann geometry, (c) Otto geometry, (d) excitation with a SNOM probe, (e) diffraction on a grating, and (f) diffraction on surface features [64].

e) If a diffraction grating is created on part of an otherwise smooth metal film, components of the diffracted light whose wavevectors coincide with the SPP wavevector will be coupled to surface

plasmon polaritons. Such an excitation configuration can provide efficient coupling to both air–metal and substrate–metal SPP modes of a metal film if the film thickness and grating profile depth are suitably related.

f) Yet another approach to the optical excitation of SPP is through diffraction of light from surface features. This is a Kretschmann configuration, with the difference that the metal film (strip) covers only a portion of the base of the prism. The SPP are excited at both edges of the metal strip on both of its interfaces, and propagate in the direction of the illuminating light (from the left edge) as well as in the opposite direction (from the right edge). However, on a randomly rough surface, the SPP excitation conditions can be achieved without any special arrangements, because in the near-field region are present diffracted components of light with all wavevectors [41, 64].

2.2.2 Active Plasmonic Interferometer

The active plasmon interferometer is a device capable of controlling the wavevector of surface plasmon polaritons along the interface between two media by actively controlling the properties of at least one of the two. Active dielectric interferometers consist of sub-wavelength apertures fabricated on a metal film deposited on top of a dielectric material, with electro-optic effects being used to tune the properties of the dielectric [65]. Active magneto-plasmonic devices have also been demonstrated [66].

The transmission of light through subwavelength apertures in metal surfaces has been of scientific interest for a very long time. In 1784, Lord Rayleigh observed that intensity of single-wavelength light emitted through such apertures could be modified by changing the apertures' shape [67]. In modern times, it was observed that surface plasmons play a crucial role in these phenomena [68]. As such, passive plasmonic interferometers have been constructed from pairs of slits [69, 70]. It has been shown [65, 71] that surface plasmon polaritons propagating along the interface between a dielectric and a metallic film can interact with light transmitted through apertures in the film and lead to an interference in the intensity of light transmitted through the dielectric-metal system.

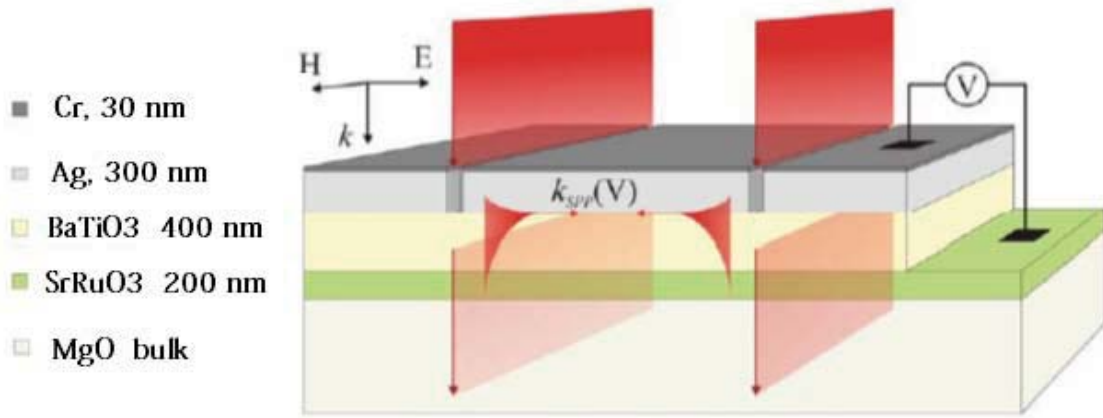


Figure 2.2.8: Double slit metal ferroelectric plasmonic modulator [72].

Dicken [72] has demonstrated a thin film active plasmonic interferometer, deposited on a MgO substrate. SrRuO₃ was used as a bottom contact electrode and Barium Titanate (BaTiO₃) as the active dielectric. The top electrode consisted of a Ag/Cr metal heterostructure, the role of the Cr layer being to prevent plasmon formation at the Ag/air interface. As the aperture array is illuminated with TM-polarized radiation (B field parallel to the long axis of the slit), a fraction of the incoming electromagnetic energy is taken up by surface plasmon polariton modes at the Ag/BaTiO₃ interface, and the rest is either reflected or transmitted. Surface plasmons interfere with the transmitted light at each slit depending on value of their phase parameter at that location. The propagation vector of the surface plasmon polaritons is determined by the dielectric properties of both media. Therefore changing the refractive index of the dielectric layer will change the transmitted intensity profile.

Controlled SPP propagation along materials' surfaces makes plasmonic devices possible. Being able to control those properties by an external stimulus, such as an electric signal or temperature makes these devices active. Such technology holds great promise for a number of applications, and, as such must be further developed.

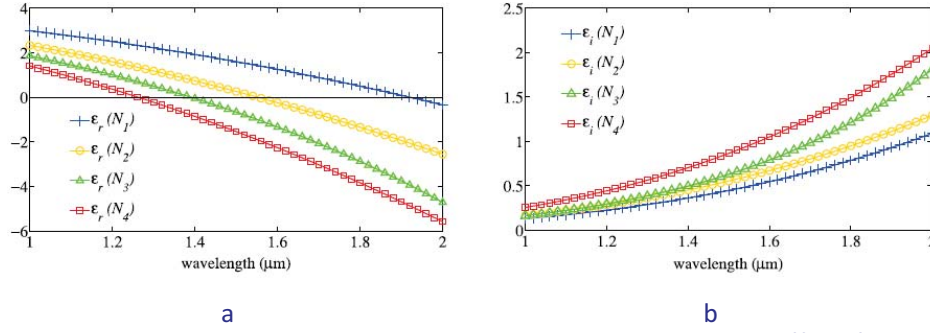
2.2.3 Active Plasmonic Modulator

Transparent conductive oxides (TCOs), specifically indium tin oxide (ITO), due to its electrically-tunable permittivity, is a material of interest for the near-infrared optical applications [73 - 76]. Its permittivity can be tuned by actively adjusting the carrier density, therefore this material respond to applied electric signals with absorption modulation. Its optical response in this domain is mainly due to free electrons, so the permittivity can be accurately modeled by using Drude theory. Due to the accumulation of electrons via electrical gating and subsequent variation of the electron concentration, the plasma frequency can be shifted from the mid- to the near-infrared. As a result, the change of the optical properties of ITO from dielectric-like to metallic make feasible the realization of new optical modulator designs.

The ITO modulator based on high-confined hybrid plasmon waveguides has demonstrated an extinction ratio of 5 dB with a 5- μm device length at the wavelength of 1.31 μm [75], which was further improved to be 6 dB μm^{-1} [77].

In this slot-waveguide modulator the optical loss of the fundamental TM mode (α_m) is assumed to be mainly due to the free-carrier absorption in the active ITO layer. This loss can be approximated by the product of the optical mode confinement factor (Γ) and the material absorption of the bulk ITO (α_b): $\alpha_m = \Gamma \cdot \alpha_b$, where $\alpha_b = 2k_0 \cdot \text{Im}[\epsilon^{1/2}]$. Γ depends on $|\epsilon|$ and the waveguide structure characteristics, such as active layer thickness, buffer material and thickness [78]. If the permittivity is tuned to induce absorption modulation, then both Γ and α_b are modified. A smaller $|\epsilon|$ can enhance the electric field magnitude confined in the ITO layer due to the continuity of the normal component of the electric displacement field ($D = \epsilon E$). Consequently, for obtaining a state with high optical loss, which enables a higher extinction ratio, it is important to engineer the conditions for which a minimum value for $|\epsilon|$ is obtained. To get this it is desirable to tune the permittivity of the ITO material to be around zero, which is referred as the “epsilon-near-zero” (ENZ) state.

Zhao and co-workers [79] fabricated ITO films, whose permittivity values were directly measured using spectroscopic ellipsometry. The measured real and imaginary parts of the ITO films permittivity, with different carrier concentrations ($N_1 = 4.33 \times 10^{20} \text{ cm}^{-3}$, $N_2 = 6.67 \times 10^{20} \text{ cm}^{-3}$, $N_3 = 8.31 \times 10^{20} \text{ cm}^{-3}$ and $N_4 = 9.58 \times 10^{20} \text{ cm}^{-3}$), derived from the measured plasma frequency, not directly measured, are shown in Fig. 2.2.9. The corresponding ENZ wavelengths are located at 1920, 1550, 1390 and 1270 nm for the samples with carrier concentrations ranging from N_1 to N_4 , respectively.



Figures 2.2.9: Permittivity of ITO with different carrier concentrations ($N_1 = 4.33 \cdot 10^{20} \text{ cm}^{-3}$, $N_2 = 6.67 \cdot 10^{20} \text{ cm}^{-3}$, $N_3 = 8.31 \cdot 10^{20} \text{ cm}^{-3}$ and $N_4 = 9.58 \cdot 10^{20} \text{ cm}^{-3}$), measured by spectroscopic ellipsometry. The thickness of ITO in the tested samples is 35 nm. (a) the real part of the complex permittivity; (b) the imaginary part of the complex permittivity [79].

Based on the previous experimental results and analysis in [73] and [74], which demonstrated that the change of the carrier concentration inside a thin ITO layer up to 10^{22} cm^{-3} can be achieved by carrier accumulation at the ITO/oxide interface under a few volts applied across the metal/oxide/ITO structure, the authors assumed that the fabricated ITO films would be tunable by adjusting the applied voltage. Consequently, Zhao and co-workers [79] assumed the electrically tunable permittivity of the active ITO layer between the states with different carrier concentrations (N_1 to N_4). A schematic of the proposed high-confinement slot-waveguide modulator based on engineered ENZ ITO films is presented in Figure 2.2.10. The structure consists of a Si strip waveguide (220 nm thick) on a buried oxide layer, an active ITO layer (10 nm thick), two SiO_2 buffer layers (10 nm thick) and a poly-Si capping layer (160 nm thick). The entire width of the modulator is 500 nm.

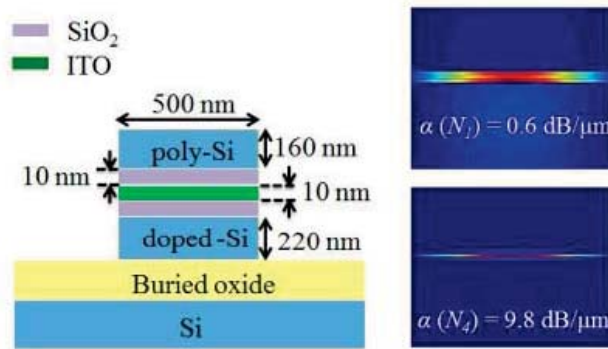


Fig. 2.2.10: Schematic of the modulator structure and the profiles of the fundamental TM mode at $\lambda = 1310 \text{ nm}$ [79].

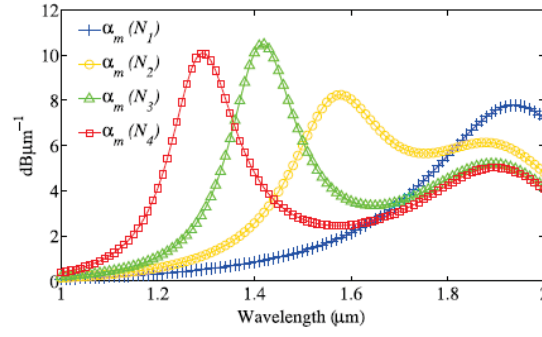


Fig. 2.2.11: Modulator absorption loss for different carrier concentrations [79].

The optical intensity of the TM modes is well confined in the slot, which effectively enhances the overlap of the optical modes and the ITO active medium. As shown in Figure 2.2.10, the electrical intensity of the fundamental TM mode is confined in the $\text{SiO}_2/\text{ITO}/\text{SiO}_2$ slot with ITO of N_1 , resulting in a small absorption loss ($0.6 \text{ dB}/\mu\text{m}^{-1}$) at the wavelength of $1.31 \mu\text{m}$. When the carrier concentration is tuned to be N_4 , the real part of the permittivity of the ITO film is near zero, and the electrical intensity is mostly confined only in the ENZ ITO material, so that a high absorption loss ($9.8 \text{ dB}/\mu\text{m}^{-1}$) is obtained. One can observe that in the wavelength interval of interest (the entire optical fiber communications band), the absorption loss α_m is quite low for ITO with carrier concentration of N_1 , while is relatively high for the other carrier concentrations (N_2 to N_4). As shown in Fig. 2.2.11, the maximum optical loss for ITO films with N_2 , N_3 and N_4 are achieved at 1.58 , 1.42 , and $1.29 \mu\text{m}$, respectively.

2.3 *Materials for Active Plasmonic Devices*

This section is concerned with the active media of plasmonic devices. It gives a brief description of the ferroelectric symmetry groups and explains the dielectric behaviour of perovskite materials, as exemplified by BST, and tungsten bronze structured materials like SBN. A brief overview of the Landau theory of ferroelectric transitions is also given. This is followed by a brief account of the electro-optical effect in ferroelectrics as exemplified by BST.

2.3.1 *Active Materials e.g. Ferroelectrics*

Crystals are divided into 32 classes of point groups according to the symmetry they possess. Of these 32 groups, 21 are non-centrosymmetric and develop an electric potential difference when a stress is applied on them. These are the piezoelectric materials. 10 of 20 non-centrosymmetric groups present spontaneous polar axis, which depend on the temperature. These 10 groups are pyroelectric. Ferroelectrics are a subset of pyroelectrics, their spontaneous polarization is reversible by the application of an electric field (Figure 2.3.1). At high temperatures ferroelectrics generally present a paraelectric high symmetry state, in which the unit cell is centrosymmetric, exhibiting a simple dielectric response to applied fields. As the temperature goes down below the critical Curie point T_C , the materials undergo a structural phase transition to a lower symmetry ferroelectric phase, in which at least two symmetry-equivalent orientation states are possible, separated by an energy barrier U_0 . In this phase, the materials exhibit a hysteresis-type behaviour when subjected to applied fields.

There are several ferroelectric, but Barium Titanate (BaTiO_3) is the focus of the following presentation, being one of the most studied and used ferroelectrics. It belongs to a category of materials called perovskites (ABO_3) – Figure 2.3.2. The high symmetry phase (above T_C) is cubic, and below that temperature they become tetragonal. In the cubic state the “A” atoms located in the center of the unit cell, the “B” atoms are located in the 8 corners, while the Oxygen lie in the 6 face-centered positions. When the cubic BaTiO_3 is cooled down below the Curie point, there is a contraction along the a-axis of the cell and a corresponding elongation along the c-axis. As a result, the oxygen atoms are moving towards the center of the unit cell, forcing the Ba atoms to move either above or below

the central plane of the oxygen atoms. This produces the spontaneous polarization which defines ferroelectrics.

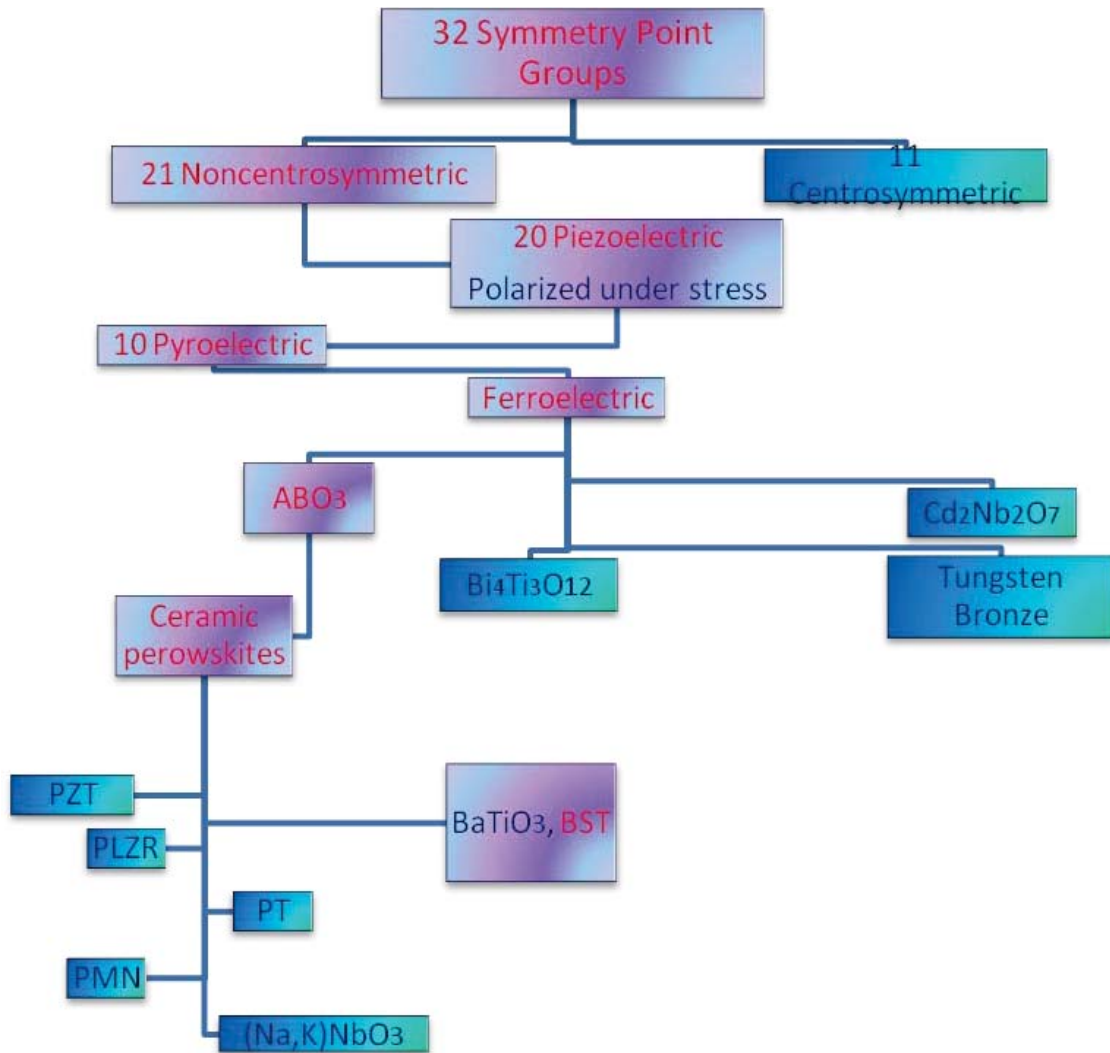


Figure 2.3.1: Classification of crystals according to the symmetry and polarisation they possess.

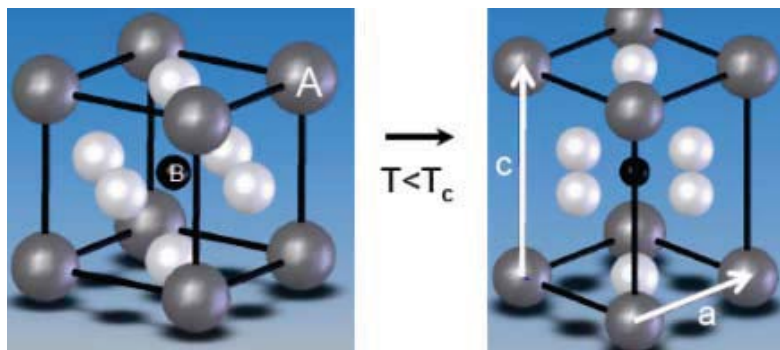


Figure 2.3.2: The ABO_3 perovskite unit cell above (left) and below (right) the Curie temperature.

Barium Strontium Titanate is, essentially, a solid solution of BaTiO_3 and SrTiO_3 . As both BaTiO_3 and strontium titanate (STO) have a perovskite structure, BST preserves this structure. BaTiO_3 has a ferroelectric to paraelectric transition temperature at 130°C , while SrTiO_3 is paraelectric down to absolute zero [80]. In the BST solid solution, the substitution of Ba with Sr atoms causes the Curie point to decrease linearly. According to Jaffe [80] the Curie point drops to 0°C at 34% Sr content, corresponding to a decrease of 3.8°C per molar percent of Sr. According to Ezhilvalavan [81], for the Sr addition into BaTiO_3 the linear drop of T_c is smaller, of about 3.4°C per molar percent of Sr, therefore 30 mol% Sr ($x=0.7$) would shift the Curie temperature down to room temperature. More recently, Kong have shown [82] that for room temperature applications, the composition is usually around $x = 0.63 - x = 0.5$, with T_c close to 0°C . If an electric field is applied, the variation domain of the Curie temperature is expanded to around 200 K for $x \approx 0.5$, as theoretically predicted by Kukreti et al. [83].

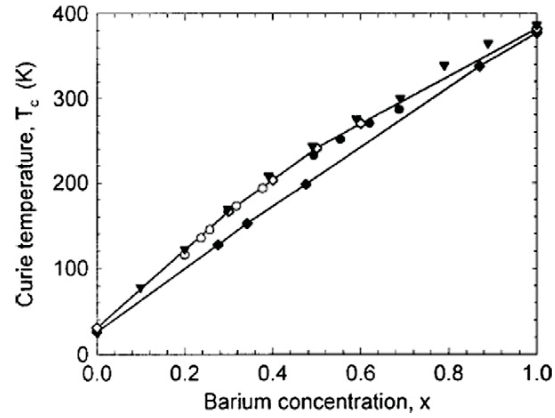


Figure 2.3.3: Curie temperature of $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ as function of x [82].

2.3.2 Landau - Ginzburg - Devonshire Theory of Ferroelectrics – a brief overview

The polarization vector $\mathbf{P}$ (C.m^{-2}) induced in a dielectric, non isotropic material by an applied external field $\mathbf{E}$ (V.m^{-1}) is given by the relation:

$$P_i = \chi_{ij} \varepsilon_0 E_j \quad (2.3.1)$$

where χ_{ij} (F.m^{-1}) is the dielectric susceptibility of the material and ε_0 ($8.854 \cdot 10^{-12} \text{ F.m}^{-1}$) is the permittivity of free space (vacuum). The relation above is true only in the linear limit for a general (non-linear) material, as in general the polarization depends on higher-order terms of the electric field.

The total surface charge density induced in the dielectric by the applied external field is described by the dielectric displacement vector $\mathbf{D}$ (C.m^{-2}), which is related to the external electric field and the polarization vector:

$$D_i = \varepsilon_0 E_i + P_i \quad (2.3.2)$$

Considering the two equations presented above, there is a simple relation between the dielectric displacement vector and the electric field:

$$D_i = \varepsilon_0 E_i + \chi_{ij} \varepsilon_0 E_j = \varepsilon_0 (\delta_{ij} E_j + \chi_{ij} E_j) = \varepsilon_0 (\delta_{ij} + \chi_{ij}) E_j = \varepsilon_{ij} E_j \quad (2.3.3)$$

where δ_{ij} is the Kronecker's symbol, $\varepsilon_{ij} = \delta_{ij} + \chi_{ij}$ is the dielectric permittivity of the material.

In a polar material the electric charge may be induced by an external electric field, by a temperature change (pyroelectric effect), and by mechanical stress (piezoelectric effect). In a similar way, mechanical strain in a piezoelectric material may be induced by an electric field (converse piezoelectric effect), by an external stress (Hooke's law), and by a temperature change (thermal expansion of the material). This coupling of different effects places important experimental constraints on property measurements, *which is a major fact to be carefully considered in our experiments*.

The coupling between the electrical, thermal and elastic parameters of a material can be understood by using the thermodynamic approach, with the resulting equations of state giving the relations between material's parameters measured under different experimental conditions.

As known from the first and second laws of thermodynamics, the reversible change dU in the internal energy U of an elastic dielectric material subjected to a small change of the strain dx , electric displacement dD , and entropy dS , may be expressed as a linear combination of the above mentioned small changes, as follows:

$$dU = TdS = X_{ij} dx_{ij} + E_i dD_i \quad (2.3.4)$$

with T being the temperature of the material. As in most experimental situations, we work under isothermal conditions, while considering the electric field and mechanical stress to be independent variables, so it is natural and convenient to change the initial set of independent variables (S, x, T) to (T, X, E) . In order to do this change, a Legendre transformation of the internal energy U is done, by adding to U the expression: $-TS - Xx - ED$. The resulting free energy function (Gibbs free energy) is:

$$G = U - TS - X_{ij} x_{ij} - E_i D_i \quad (2.3.5)$$

The differential of G can now be written as:

$$dG = -SdT - x_{ij}dX_{ij} - D_iE_i \quad (2.3.6)$$

The first derivative of G with respect to the external electric field is the dielectric displacement D:

$$D_i = -\left(\frac{\partial G}{\partial E}\right)_{T,X} \quad (2.3.7)$$

The relation includes only linear effects, so in the case of strong electric fields or strongly non-linear materials such as ferroelectrics, the relation must be extended to include higher order terms.

The main characteristic of the ferroelectrics (polar materials) is their spontaneous polarization (related to the electric dipole moment per unit volume), and the possibility to reverse its direction by the application of a suitable electric field. Ferroelectrics possess at least two equilibrium orientations of the spontaneous polarization vector in the absence of an external electric field [84 - 86].

Most ferroelectrics undergo a structural phase transition from a high-temperature nonferroelectric (or paraelectric) phase into a low-temperature ferroelectric phase (Figure 2.3.4). Such a phase transition is observed in both PbTiO_3 and BaTiO_3 . The permittivity curve represents data measured on a BaTiO_3 ceramic. The arrows show possible directions of the spontaneous polarization (in two dimensions). The unit cell is represented by a square in the cubic phase and rectangle in the tetragonal phase [87].

The paraelectric phase may be piezoelectric or nonpiezoelectric and is rarely polar [84]. Being a high temperature phase, its symmetry is always higher than the symmetry of the ferroelectric phase. The temperature of the phase transition is called the Curie point, T_C . Above the Curie point the dielectric permittivity falls off with temperature according to the known Curie–Weiss law:

$$\varepsilon = \varepsilon_0 + \frac{C}{T-T_0} \approx \frac{C}{T-T_0} \quad (2.3.8)$$

where C is the Curie constant and T_0 is the Curie–Weiss temperature ($T_0 < T_C$).

BaTiO_3 ferroelectrics undergo several phase transitions into successive ferroelectric phases. Only the transition temperature into the first ferroelectric phase is called the Curie point. The observed transition is a second order phase transition.

The transition into a ferroelectric phase usually leads to strong anomalies in the dielectric, elastic, thermal and other properties of the material [84], being accompanied with changes in the dimensions of the crystal unit cell. The associated strain is called spontaneous strain, representing the relative difference in the dimensions of the ferroelectric and paraelectric unit cells [88]. Figure 2.3.4 illustrates some changes that can occur in a ferroelectric material while it undergoes the transition from the paraelectric cubic into a ferroelectric tetragonal phase.

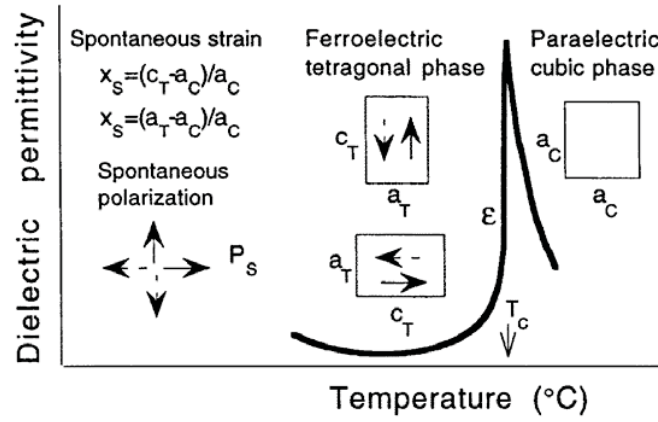


Figure 2.3.4: Illustration of the changes in a ferroelectric material which transforms from a paraelectric cubic into ferroelectric tetragonal phase with temperature [87].

For a ferroelectric material the polarization $\mathbf{P}$ can be expressed as a function of the electrical field $\mathbf{E}$: if an unpolarized sample of ferroelectric material is subjected to an increasing electric field at a temperature slightly below its Curie-Weiss point, the dipoles inside the ferroelectric start to be aligned with the electric field, the polarization following the “initial curve” which describes the variation of the electric field $\mathbf{E}$. However, when the electric field $\mathbf{E}$ increases beyond a certain value (specific for each material), the polarization remains almost constant, as all the dipoles inside the material are already aligned with the applied electric field. This maximum value of the polarization is known as the saturation polarization $\mathbf{P}_s$.

After the polarization reaches its maximum value, if the electric field is reduced to zero, the dipoles start to lose the former alignment, because in the absence of an external field they are bound to the existing preferred directions within the individual crystallites. Eventually the dipoles cannot return to the original alignment (i.e. from before applying the electrical field), remaining in positions most closely aligned with the original field, as no external energy is given to the system to reach the initial state. The state is defined by a relative high degree of dipole alignment, determining a non-zero value of the polarization, known as the remnant polarization $\mathbf{P}_r$, lower than $\mathbf{P}_s$. If the electric field is again increased, this time in the opposite direction, the polarization of the sample decreases (as the dipole receive enough energy for changing their position with respect to the preferred direction within the crystallites), falling to zero and then increasing again in the opposite (negative) direction, until it reaches the full value of the saturation polarization, but with an opposite sign $-\mathbf{P}_s$. The excursion of the polarization with the electric field is now predictive, so that if the electric field is reduced to zero again, the polarization falls to the remnant polarization $-\mathbf{P}_r$. This behavior

described by the associated curve is known as the hysteresis effect (Figure 2.3.5). The variation of dielectric displacement $\mathbf{D}$ as a function of electric field strength follows very closely the curve for polarization, a hysteresis curve for $\mathbf{D}$ being also observed, corresponding precisely with the effect observed for polarization. This behavior is associated with a second order phase transition. The symbols are explained in the text. The actual loop is measured on a (111)-oriented 1.3 microns thick sol-gel deposited $\text{Pb.Zr}_{0.45}\text{Ti}_{0.55}/\text{O}_3$ film. Regarding electro-optical or active plasmonic devices, hysteresis becomes a problem when the device is switched at higher frequencies. It also makes the device's behavior less predictable in practical use, because as its' response is not only a function of input, but also of past states. Therefore, provided they exhibit a strong enough electro-optic effect, paraelectric materials should be preferred as modulators, due to the absence of hysteresis.

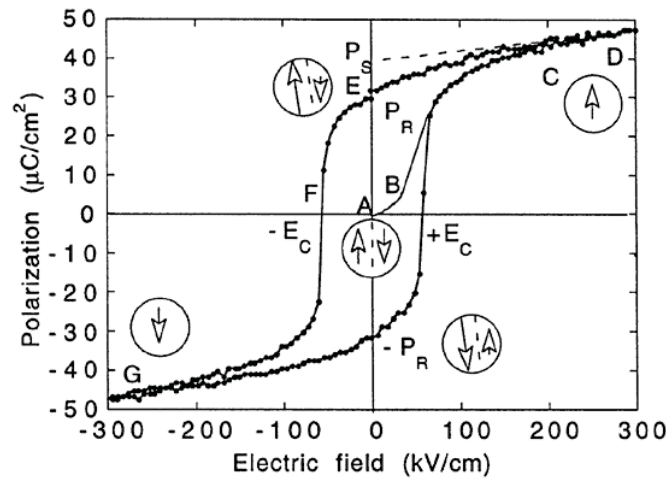


Figure 2.3.5: Ferroelectric P – E hysteresis loop. Circles with arrows represent the polarization [87].

An attempt to formulate a general theory of second-order phase transitions, starting from the Ehrenfest theory based on the free energy of the system (as a thermodynamic concept) is represented by Landau theory. In the Ehrenfest theory, phase transitions are classified based on the behaviour of the free energy as a function of other thermodynamic variables. For processes characterised across the transition by the continuity of the first derivative of the free energy with respect to an external field, this first order derivative is associated with an “order parameter”, as it presents no sudden changes during the transition. However, the second derivative of the free energy with respect to the external field is observed to be discontinuous at the transition, so these phase transi-

tions are known as second-order phase transitions. The ferromagnetic phase transition is such a transition.

The Landau theory for the second order phase transitions is based on few simple assumptions:

- there is an order parameter, which has a non-zero value for temperatures below the phase transition temperature; the order parameter can describe the differences in the symmetry of the two phases - before and after the phase transition;
- the free energy of the system can be expressed analytical as a Taylor series of the order parameter;
- the coefficients in the Taylor series are continuous functions of temperature.

For mathematical reasons, it is also assumed that the order parameter has a small value near the transition temperature and presents a slow variation in the space coordinates. This mathematical constraint proves to be consistent with the physical phenomena related to the second order phase transition, if the parameters are correctly chosen.

Landau developed his theory to study ferroelectricity. By using a thermodynamic approach the developed theory lacks a microscopic perspective, belonging to the class of mean-field-type theories. Nevertheless the Landau theory has successfully described the phenomenological behaviour of phase transitions in materials like superconductors and ferromagnets. The Ginzburg-Landau theory was later developed, using the same thermodynamic approach for the second order phase transitions, to describe superconductivity. Devonshire [84], considering the analogous behaviour of ferroelectric and ferromagnetic materials, and developed the Landau theory to study ferroelectricity. Since then, the Landau Devonshire theory has been instrumental in studying the phenomena of first and second order phase transitions in bulk ferroelectrics, and has also been extended to the study of such phenomena in thin films and multilayers.

For ferroelectrics, the first derivative of the free energy with respect to the external electric field is the electric displacement (rel. 2.3.9), the ferroelectric state being expressed as a deviation of the electric displacement $\mathbf{D}$ from the paraelectric state.

Considering an uniform, infinite ferroelectric crystal, and assuming that its non-polar paraelectric phase is centrosymmetric, that all stresses are zero, and that $\mathbf{D}$, and thus $\mathbf{P}$ and $\mathbf{E}$, are directed along one of the crystallographic axes, the Gibbs free energy of the system (in the vicinity of the critical temperature - T_c) can that be expressed as a Taylor expansion in the order parameter:

$$G = D^2 \frac{\alpha}{2} + D^4 \frac{\eta}{2} + D^6 \frac{\zeta}{2} \quad (2.3.9)$$

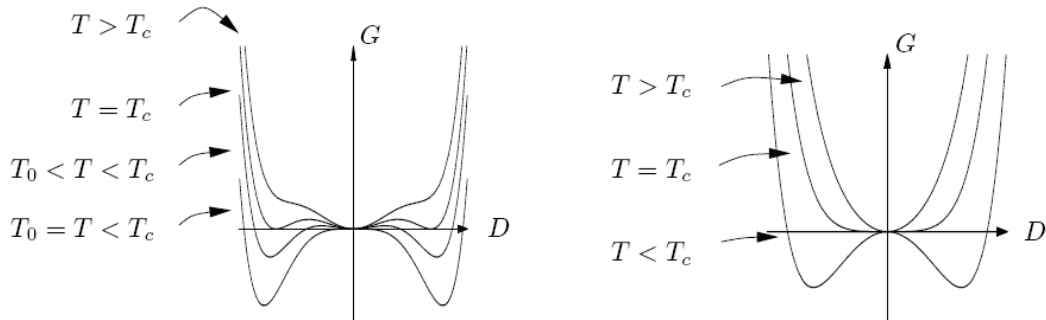
α , η and ζ are temperature-dependent parameters characteristic of the material, although this temperature dependence is small and can be neglected for η and ζ , while $\alpha = \beta (T - T_0)$ is taken to follow a linear temperature dependence close to the transition [84] (with T_0 being the Curie-Weiss temperature). Minimizing the free energy with respect to the displacement gives the equilibrium criterion:

$$\frac{dG}{dD} = \beta \frac{T - T_0}{D} - |\eta| D^3 + \zeta D^5, \quad (2.3.10)$$

which defines the transition from the paraelectric to the ferroelectric phase, marked by a divergence of the dielectric constant. Both first and second order transitions can be observed in different materials. In the former, where η is negative and ζ positive, both the free energy itself, G , as well as its derivative dG/dD are zero at:

$$T_c = T_0 - \frac{3}{16} |\eta|^2 (\beta \zeta)^{-1} \quad (2.3.11)$$

and there is a discontinuity in the remnant polarization, as shown in Figure 2.3.6. In a second order transition, where η is positive and ζ zero, the polarization is a continuous function of the temperature going to zero at $T_c = T_0$ as shown in Figure 2.3.6.



Figures 2.3.6: The free energy G as a function of displacement D for a first order transition (left) at which $T_c = T_0 - 3/16 \cdot |\eta|^2 \cdot (\beta \zeta)^{-1}$ and the polarization is a discontinuous function of the temperature, and a second order transition (right) for which $T_c = T_0$ and the polarization is a continuous function of the temperature.

2.3.3. Electro-Optic Effects in Ferroelectric Thin Films

An external electrical field, when applied to a dielectric medium, e.g. a crystal, produces a redistribution of bound charges (electron polarization), and as well as a slight deformation of the crystal lattice (ionic polarization) [89]. The cumulative effect of all internal charge displacement is a

macroscopic polarization of the material, which can be described by a net charge distribution. Usually the changes vary with the direction of the crystal, and as a result the electric field and the dielectric displacement vector (which defines the orientation of the polarization) will have different directions, so their relation will be expressed as:

$$D_i = \varepsilon_{ij} E_j \quad (2.3.12)$$

where the sum is made over all three values of j : x , y and z . In ferroelectric materials, there is no one-to-one correspondence between polarization and the electrical field because of hysteresis.

The above equation can be also written using a matrix representation:

$$\begin{pmatrix} D_x \\ D_y \\ D_z \end{pmatrix} = \begin{pmatrix} \varepsilon_x & 0 & 0 \\ 0 & \varepsilon_y & 0 \\ 0 & 0 & \varepsilon_z \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} \quad (2.3.13)$$

where the principal permittivities lie on the diagonal of the permittivity matrix. In the following the index ellipsoid will be introduced; it is a mathematical construct whose geometric characteristics represent the vibration directions of $\mathbf{D}$ and the phase velocities of the two allowed plane waves corresponding to a given optical wave with a propagation vector $\mathbf{k}$ in a crystal. The index ellipsoid is a quadratic surface of the stored electric energy density Ω_e of a dielectric [90, 91]:

$$\Omega_e = \frac{\varepsilon_0}{2} (E_x^2 \varepsilon_x + E_y^2 \varepsilon_y + E_z^2 \varepsilon_z) \quad (2.3.14)$$

The stored energy density has to be positive for any value of the electric field, so that the surface is mathematically described an ellipsoid [90 - 92]. Considering the relation between the electric field $\mathbf{E}$ and the displacement $\mathbf{D}$, and introducing the following substitutions:

$$x = \frac{D_x}{(2\Omega_e \varepsilon_0)^{1/2}}; \quad y = \frac{D_y}{(2\Omega_e \varepsilon_0)^{1/2}}; \quad z = \frac{D_z}{(2\Omega_e \varepsilon_0)^{1/2}} \quad \text{and} \quad n_x^2 = \frac{\varepsilon_x}{\varepsilon_0}; \quad n_y^2 = \frac{\varepsilon_y}{\varepsilon_0}; \quad n_z^2 = \frac{\varepsilon_z}{\varepsilon_0},$$

the ellipsoid can be expressed in principal coordinates as:

$$\frac{x^2}{n_x^2} + \frac{y^2}{n_y^2} + \frac{z^2}{n_z^2} = 1 \quad (2.3.15)$$

The equation represents the general index ellipsoid for an optically biaxial crystal. If $n_x = n_y$, the surface becomes a revolution ellipsoid, representing an uniaxial crystal, in which one of the two allowed eigenpolarizations will always be an ordinary wave with its Poynting vector parallel to the wave vector $\mathbf{k}$ and $\mathbf{E}$ parallel to $\mathbf{D}$ for any direction of propagation. An isotropic crystal ($n_x = n_y = n_z$) is represented by a sphere with the principal axes having equal length. Any wave propagating in this crystal will exhibit ordinary characteristics.

If the polarization $\mathbf{P}$ ($P_i = \chi_{ij} \varepsilon_0 E_j$) is not linearly proportional to the electric field $\mathbf{E}$, the medium is termed nonlinear and is described by the field of nonlinear optics. To a good approximation

(for sufficiently weak fields, assuming no permanent dipole moments are present), P is usually given by a Taylor series expansion of E , the coefficients of which are: the linear susceptibility - $\chi_{ij}^{(1)}$, the second-order susceptibility - $\chi_{ijk}^{(2)}$, and the third-order susceptibility - $\chi_{ijkl}^{(3)}$:

$$\frac{P_i}{\epsilon_0} = \sum_j \chi_{ij}^{(1)} E_j + \sum_{jk} \chi_{ijk}^{(2)} E_j E_k + \sum_{jkl} \chi_{ijkl}^{(3)} E_j E_k E_l \quad (2.3.16)$$

The linear electro-optic Pockels effect is represented by a third rank tensor $\chi_{ijk}^{(2)}$. The permutation symmetry of this tensor is $\chi_{ijk}^{(2)} = \chi_{jik}^{(2)}$, with $i, j, k = 1, 2, 3$. In general, the coefficients have very little dispersion in the optical transparent region of a crystal.

The quadratic electro-optic effect is represented by a fourth rank tensor $\chi_{ijkl}^{(3)}$. The permutation symmetry of this tensor is $\chi_{ijkl}^{(3)} = \chi_{jikl}^{(3)} = \chi_{ijlk}^{(3)}$, with $i, j, k, l = 1, 2, 3$.

Electro-optic (EO) modulators based on lithium niobate (LN) or lithium tantalite (LT) single crystals are currently used in photonic backbone networks [93, 94]. However, the low EO-coefficients of the LN and LT single crystals demand a long optical path in order to modulate the intensity of optical signals by an electric bias. This makes any further downsizing of these modulators, necessary in order to keep up with ever-evolving miniaturization standards, difficult to achieve. Even if one existing alternative - potassium tantalate–niobate (KTN) single crystal - exhibits relatively high EO-coefficients, the growth technique (top seed solution growth) is prohibitively expensive [95, 96]. Other candidates for this role are thin film transparent ceramics. If we focus on lead-free materials (excluding La-added lead zirconate–titanate (PLZT) thin films [97, 98], barium strontium titanate ((Ba, Sr)TiO₃ - BST) can be regarded as a new material for EO-modulators. Studies on BST thin films used in tunable capacitors used in the microwave region have already been reported [99, 100]. There are also some papers describing the relatively high EO-effect observed in BST thin films [101, 102]. Another requirement related to these class of applications is the low insertion loss of the modulators, which demands the minimization of light scattering at grain boundaries, which eventually requires the growth of epitaxial films.

BST thin films epitaxially grown on MgO or STO single crystals exhibit strain induced by the lattice with the substrates [103]. Due to this strain, the unit cell of the film material becomes slightly elongated along the c -axis; if, as a result of the film's growth, the c -axis is perpendicular to the surface, the strain will induce a spontaneous polarization along its direction. The EO-effect of BST films should be affected by the switching of this spontaneous polarization, if the anisotropy induced by the

lattice distortions is neglected. The authors of reference [104] used a transmission geometry (Figure 2.3.7), in which the birefringence of the substrate cannot be separated from that of the studied films. As a results, the birefringence induced in the substrate by EO effect was measured first, and later, the birefringence of the substrate was found to be negligible compared to the total birefringence. The observed small birefringence in the as-deposited films was enhanced by the application of an in-plane electric field before the measurement (Figure 2.3.8). This was explained by the switching of c-axis of some of the lattices from the OZ to the OX direction. The birefringence caused by these lattices had the optical axis along the Z direction. The electric field dependence of the birefringence was nearly parabolic, without a hysteresis shape, which was consistent with the slim hysteresis curve (P vs. E) – Figure 2.3.9. The obtained result led the authors to consider the EO-effect in BST epitaxial films to be dominantly determined by the Kerr effect, and to reduce the birefringence (Figure 2.3.10). The Kerr coefficient of the BST film was determined to be $3.44 \times 10^{-17} \text{ m}^2/\text{V}^2$.

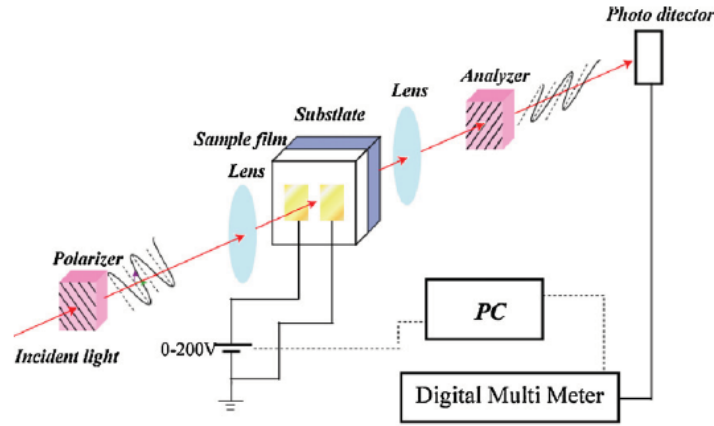


Figure 2.3.7: Schematic illustration of the system developed for measuring EO-effect as a function of the electric field, enabling the measurements of films' birefringence in "transmission" geometry, @ $\lambda=1.55 \mu\text{m}$ [104].

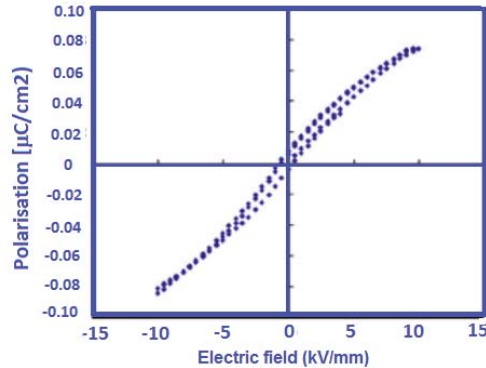


Figure 2.3.8: Variation of polarization vs. electric field in BST film (adapted from reference [104]).

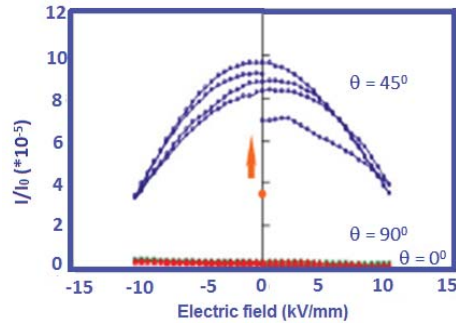


Figure 2.3.9: Electric field dependence of the intensity of transmitted light (I), normalized to the intensity of the incident light (adapted from ref. [104]).

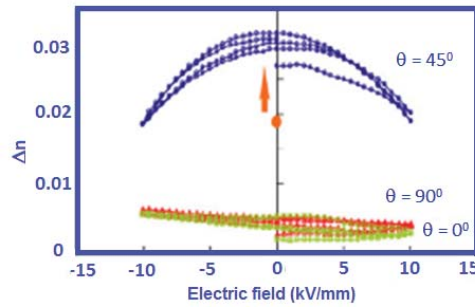


Figure 2.3.10: Electric field dependence of the birefringence (Δn) (adapted from ref. [104]).

Ferroelectric thin films exhibit dielectric tunability when subjected to coercive fields at frequencies up to the GHz range. Their dielectric constants, from the stationary case all the way to the NIR range can be controlled by such a coercive field. This is due to ionic polarization, and as such it depends upon a materials crystalline orientation; for perovskite-type structures, this is along the c -axis. Therefore, the best electro-optic modulation should be found in textured films grown along this direction.

2.4 Electrode Materials for Plasmonic Devices/Conductive Materials for Passive Plasmonic Structures

This section describes the motivation behind the choice of materials for the thin film electrodes of plasmonic devices: metals, conducting oxides, and transitional metal nitrides.

2.4.1 Metallic Electrodes

Light control at the nanoscale, made feasible by plasmonics, may be impeded by absorption losses in metals. Until now, gold and silver have been most commonly used [105, 106]. Aluminium and copper may also be suitable metals [107, 108].

The excitation and propagation of plasmons is controlled by the electrical polarization. The electrical polarization can be described by the material's complex electrical permittivity or dielectric function, denoted by $\epsilon(\omega)$. The real part of the dielectric function (denoted by ϵ_1 or ϵ') describes the strength of the polarization induced by an external electric field. The imaginary part (denoted by ϵ_2 or ϵ'') describes the losses encountered in polarizing the material. Thus, a low loss material is associated with small values of ϵ'' .

The main loss mechanisms in the NIR, visible, and soft-UV frequencies are related to conduction electrons and bound electrons (interband effects) [109]. Interband transitions occur due to absorption of incident photons which makes bound electrons shift from a lower energy level to the Fermi surface, or from near the Fermi surface to the next higher empty energy level, resulting in losses at optical frequencies. Electron-electron and electron-phonon interactions, and scattering due to lattice defects or grain boundaries are responsible for conduction electrons losses. It is possible to treat these phenomena using the classical theory of the conduction electrons, because of the near-continuum of available states. According to the Drude theory of the free electron gas [37, 5], the complex dielectric function of a material depends on the mean relaxation time of the electrons τ (eqs. 1.15). The energy losses of conduction electrons due to lattice defects or grain-boundary scattering, determine the dependence of the relaxation time τ on the size of the plasmonic particles, so that for a spherical particle of radius R the relaxation rate $1/\tau$ can be approximated as: $1/\tau = 1/\tau_\infty + A(v_F/R)$, where $1/\tau_\infty$ is the relaxation constant of the bulk material and v_F is the Fermi velocity; A depends on details of the scattering process, and is typically on the order of one [109 –

111]. Table 2.4.1 presents the Drude model parameters (plasma frequency and relaxation rate $1/\tau$) for plasmonic metals, for frequencies lower than the frequency of onset for the interband transitions (ω_{int}). For simplicity, in the following it is assumed that $1/\tau = 1/\tau_{\infty}$.

Table 2.4.1: Drude model parameters for some plasmonic metals.

Metal	ω_p (eV)	$1/\tau$ (eV)	ω_{int} (eV)
Ag [112 – 114]	9.2	0.02	3.90
Au [112, 114]	8.9	0.07	2.30
Cu [112 – 114]	8.7	0.07	2.10
Al [115, 116]	12.7	0.13	1.41

The free electron population provides negative real permittivity values, an essential property of any plasmonic material. As a result, the first choice for plasmonic devices generally is represented by metals, having an abundance of free electrons.

Silver has the smallest $1/\tau$ value, being the best-performing choice at optical frequencies. Gold, a chemically inert material, has a larger $1/\tau$ value than silver, is usually the metal preferred in lower NIR frequencies applications, because it has high interband losses in the visible spectrum for wavelengths (≤ 500 nm). The third material, copper, also exhibits large interband losses over most of the visible spectrum. So, for applications around the optical frequencies, silver represents the material of choice for plasmonic applications. It was used for demonstrating the extraordinary optical transmission [117], and the fabrication of hyperlenses [118], superlenses [119, 120], and of a negative-refractive-index material in the visible range [121]. The use of silver is somehow hindered, mainly because the losses in silver films are strongly dependent on the surface roughness [109], which is known to be high when deposited on dielectric surfaces.

Silver films are obtained by various physical vapour deposition (PVD) techniques, as electron-beam/thermal evaporation and magnetron sputtering. Both methods ensure the same surface roughness, as this feature is depending on the nucleation and growth mode of silver on different surfaces.

2.4.2 Conductive Oxides e.g. SrRuO_3

In any electro-optic experimental set-up the properties of the biasing electrodes are closely linked to those of the tunable thin film. The deposition process takes place at high temperatures and the growth of thin films should be controlled to allow the tailoring of the crystalline structure and composition of the film which are critical to their electrical and optical properties. An induced strain into the tunable film is also necessary and again the behavior of the electrodes (at least the bottom one which is interposed between the substrate and the film) is critical. If the electrodes also need to be transparent, metal coatings which can interfere with the film composition (by oxygen content depletion via gettering), and are also opaque, are not acceptable, at least for the direct deposition onto the electro-optically tunable film. The oxygen depletion, caused by gettering into the metallic electrode (with metal oxide formation) induces an unwanted polarization fatigue in the ferroelectric thin film. In this fatigue state, the acceptor centers and oxygen vacancies form dipoles that can reorient at high fields (lead vacancies and oxygen vacancies form similar dipoles). Because these dipoles are slower to reorient than are the lattice displacements producing remnant polarization, they contribute significantly to waiting time effects; by failing to reorient during short switching pulses, they provide opposing dipoles that compensate much of the lattice polarization and reduce the amount of switched charge in the film [122]. In fig. 2.4.1 [123] it is easy to observe the fatigue wear of a PZT film with YBCO electrodes and Pt ones.

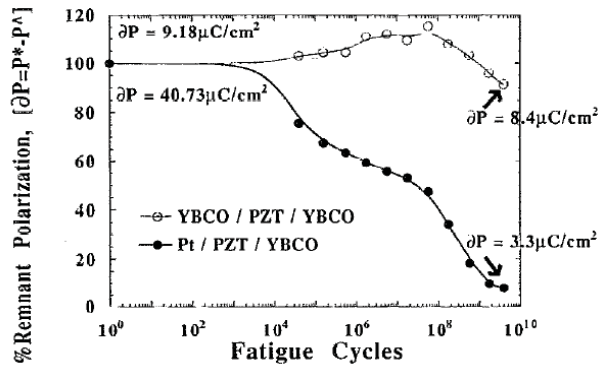


Figure 2.4.1: Remnant polarization vs number of cycles of applied pulsed voltage [123].

When looking for conductive and transparent electrodes, one has to consider that materials transparent in the visible range should have an optical band-gap greater than about 3 eV. As a general rule, transparent materials are insulators, while opaque materials are conductive. An exception

from the rule are the transparent conducting oxide semiconductors (TCOs), such as impurity doped In_2O_3 , SnO_2 , and ZnO , which have optical band-gaps greater than 3 eV, and carrier concentrations up to 10^{21} cm^{-3} , providing a high transparency in the visible range, accompanied by electrical conductivity. The properties of these doped semiconductors are depending quite strong on the level of doping.

Conductive oxides can be engineered through the deposition conditions (rate, crystalline structure) to have very low optical absorption in the visible range [124]. This can negatively impact electrical conductivity in the oxide, but is a great advantage for many optical device designs.

Another material suitable to be used as electrode is the strontium ruthenate (SRO), which is conductive enough to provide high-frequency switching voltages, and not to act as a sink for oxygen from the ferroelectric ceramic. SRO is a perovskite-type conductive metallic oxide with a pseudo-cubic lattice parameter of 3.93 Å, and with a room-temperature resistivity of $280 \mu \Omega \text{ cm}$ [125]. These are intrinsic properties of the materials, and are not depending on the doping; so that SRO may provide an optimum solution for the electrode choice in electro-optic devices.

SrRuO_3 has become the most popular epitaxial electrode for complex oxide heterostructures [126]. SRO has favorable fatigue characteristics, is chemically and thermally stable and also is a nearly isotropic conductor, being superior in terms of crystallinity and surface smoothness. For example, a strain engineering approach using epitaxial strain was used to dramatically enhance the properties of BaTiO_3 deposited on SrRuO_3 electrodes [127]. A BST/SRO (as bottom electrode)/ LAO (substrate) structure deposited by PLD is described in [128]. A dielectric constant around 500 and dielectric loss less than 0.01 at a frequency of 10 kHz were measured on capacitors with a configuration of Ag/BST/SRO. Electrical measurements on such epitaxial BST films showed a breakdown voltage above 10^6 V/cm and a leakage current density of less than $5 \cdot 10^{-8} \text{ A/cm}$ at a field intensity of $2 \cdot 10^5 \text{ V/cm}$. The PLD deposition technique was optimised in order to provide a suitable ablation plume configuration for the 248 nm KrF excimer laser (energy density of 1 J/cm^2 at repetition rates of 5-8 Hz). The working oxygen pressure was 20 Pa and the substrate temperature was 700°C for SRO and 740°C for BST. Deposition conditions were optimized not only to obtain high crystallinity thin films but also to maintain good electrical and dielectric properties of the BST thin films.

SrRuO_3 , a material with a perovskite-type crystal structure, has been the subject to intense research due to its high thermal and electrical conductivity, high thermal and chemical stability (up to 1200 K in oxidizing or inert-gas atmospheres [129]), and highly stable pseudocubic structure,

which only becomes cubic at 685 K [130]. For these reasons SrRuO_3 is widely used as electrode material for ferroelectric devices and semiconductors [131, 132], and as a standard substrate for the epitaxial growth of SrTiO_3 [133 - 137], LaAlO_3 [138], MgO [139], Yttrium stabilized zirconia YSZ [140], and even Si [141]. It is also used in heterostructure electronic devices as buffer layer for deposition of high-temperature superconductors and ferroelectrics materials [142, 143].

SrRuO_3 exhibits carrier dynamic similar to that of the cuprate superconductors, which is not well described by a simple Drude model [144 - 156]. The similarity is associated with a much higher conductivity in the mid-infrared range, than predicted by the Drude theory for metals. It should be mentioned that, in general, the experimental results for itinerant electron systems on the kinetic energy K of the electrons, as derived from optical conductivity data [149] are in good agreement with the band-structure calculations, so that their ratio is about one. However, the strong interactions involving charge and spin-orbit coupling, which are specific for many intermetallic compounds with d and f electrons, generate effects that depart the results from the ones obtained by band-structure calculations. These effects are competing with the modifications induced by the itinerancy of electrons in these systems, leading to the lower values of the $K(\text{exp})/K(\text{band})$. These effects on the $K(\text{exp})/K(\text{band})$ are presented in Fig. 2.4.2, where the SrRuO_3 present a value more close to the one specific of the correlated metals [150, 151].

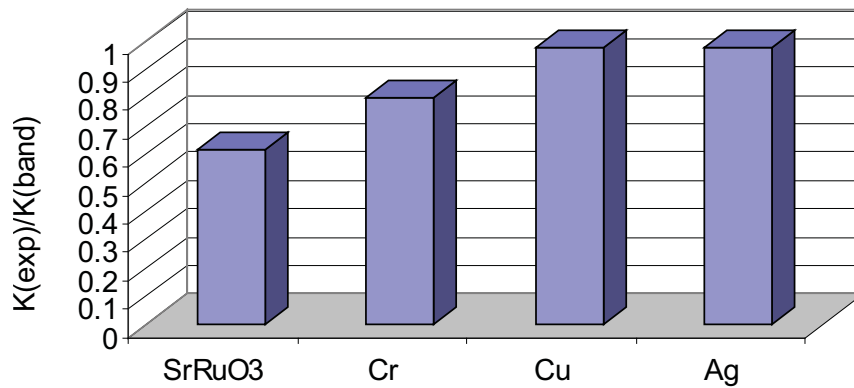


Figure 2.4.2: Ratio of the experimental kinetic energy and the kinetic energy from band theory $K(\text{exp})/K(\text{band})$ for Cr, Cu, Ag and Au and for SrRuO_3 . For clarity the data points are offset in the vertical direction.

The values are obtained from the following references: paramagnetic Cr [151], Ag and Cu [152].

The error bars (not shown) are estimated to be of about ± 0.05 .

The optical properties of SrRuO_3 include two unusual features: infrared reflectance increase almost linearly with the wavelength and the intensity of the Raman scattering is frequency-

independent. These are associated with a much higher conductivity in the mid-infrared range, than the Drude theory for metals would suggest. It was also shown that the mid-infrared conductivity band is common feature of all ruthenium oxides [145 - 147], including SrRuO_3 [148].

2.4.3. Transition Metal Nitrides e.g. Titanium Nitride

Transition metal nitrides form a wide range of refractory materials, and titanium nitride (TiN) is the best known and widest used from this extended family. This compound is not found in nature, and bulk nitrides are rarely used. TiN is usually a metallic compound at compositions up to the mononitride stoichiometry (e.g., $\text{Ti}_x\text{N}_{1-x}$). As all the nitrides of second group transition metals, TiN maintains its B1 cubic structure well below the mononitride stoichiometry, i.e. till about $x=0.45$. A relatively recent find is the existence of the Ti_3N_4 amorphous phase, which coexists with TiN_{1-x} nanocrystals - which are embedded in the amorphous matrix [153]. The existence of an amorphous TiN phase had been reported earlier, indicating an amorphous mixture of TiN_{1-x} and Ti_2N phases [154].

TiN films are known to present excellent properties like wear and corrosion resistance, low friction coefficient, and an appealing golden colour, due to their high hardness, elasticity, luster and metallurgical stability. TiN films are currently used in microelectronics mainly as diffusion barrier, due to their chemical stability, including resistance for forming silicides, and high electrical conductivity. TiN is an interesting thin film material, as it offers fabrication and integration advantages which could be useful in integrating plasmonics with nanoelectronics.

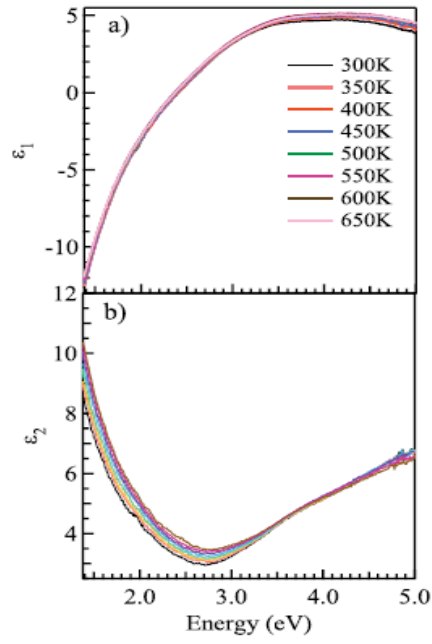
TiN is also widely used as a wear resistant coating on tools because of its earlier mentioned mechanical resistance, low friction coefficient and high melting point. The high Drude like reflectance in the infra red and high absorption in the visible and near infra red region makes TiN films similar to the metallic gold ones [155].

The optical and electronic properties of TiN thin films obtained by reactive magnetron sputtering have been investigated by spectroscopic ellipsometry [156], and recently TiN was proposed and is being explored as a material for plasmonic applications in the visible and near infra red wavelengths [105, 106]. The use of TiN instead of Ag is preferable, due to its high thermal stability, as the behaviour of SPR is affected by temperature induces changes in a material's refractive index.

Titanium nitride films deposited in different sputtering ambient, which was varied from 100% nitrogen to 20% nitrogen and 80% argon, exhibited just a small decrease of the carrier concentration under nitrogen-rich deposition conditions, so its metallic property was preserved. This behaviour is unique, as the other studied nitrides (ZrN, HfN, TaN) exhibited optical properties that changed from dielectric behavior to metallic behavior, as the partial pressure of the nitrogen decreased in the sputtering ambient [106]. It should be underlined that most of the transition nitrides exhibit larger carrier relaxation rates, as compared to noble metals, which determine increased optical losses. The interstitial defects, if present in these nitrides, determine interband transition losses, in the visible and ultraviolet ranges. However, by a careful choice of the deposition conditions, the plasma frequency, the Drude relaxation rate, and the strength of the interband transitions may be tailored. It was shown that the deposition at different temperatures of TiN films determined changes in its optical properties: for the TiN films deposited at higher temperatures the plasma frequency is higher (800 °C vs. 500 °C), and the Drude relaxation rate is lower [106], pointing out to the need of cautious optimization of the deposition conditions for obtaining low-loss TiN films.

The deposition conditions can change the Drude relaxation rate, the plasma frequency and the strength of the interband transitions. For example, a shift in the specular reflectance spectra minimum from 4.83 to 2.47 eV, has been observed and attributed to a change in the stoichiometry of the TiN sputtered films [157]. Also, sputtered TiN films deposited at 500 °C exhibited lower plasma frequency ($\omega_p=5.953$ eV) than films deposited at 800 °C ($\omega_p=7.9308$ eV) [106]; also the Drude relaxation rate is higher for films deposited at lower temperatures, showing that the optimization of the conditions of deposition is necessary if low-loss TiN films are to be obtained.

The temperature dependencies of the optical properties of TiN films deposited by magnetron sputtering were studied by spectroscopic ellipsometry; the data were modeled based on the Drude Lorentz dispersion law. The small changes in the optical properties with temperature, as shown in Figure 2.4.3 indicated that TiN films can be used in SPR applications at high temperatures [158]. This finding is also supported by the small variation observed for the thermo-optic coefficient of TiN films on a large range of temperatures, as presented in Figure 2.4.4.



Figures 2.4.3: Plot of the a) real and b) imaginary parts of the dielectric constants for measurement temperatures 300 K to 650 K [158].

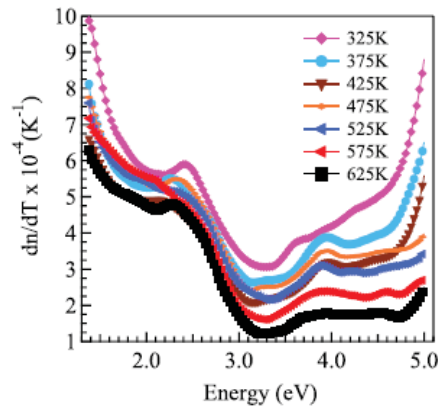


Figure 2.4.4: Thermo-optic coefficient (dn/dT) of TiN thin film for $T_{\text{averaged}} = (T_1 + T_2)/2$, from 325 K to 625 K [157].

CHAPTER 3

Fabrication and Characterisation Techniques

3.1. The Deposition of Thin Films for Plasmonic Structures and Devices

3.1.1 Pulsed Laser Deposition

Pulsed Laser Deposition (PLD) is one of the most versatile approaches to film deposition, particularly in oxide research [159]. In this technique, a pulsed laser is focused onto a target of the material to be deposited. For sufficiently high laser energy density, each laser pulse vaporizes or ablates a small amount of the material. The vaporized material, containing neutrals, ions, electrons etc., is known as a laser-produced plasma plume and expands rapidly away, forward directed, from the target surface (velocities typically $\sim 10^6$ cms⁻¹ in vacuum). Film growth occurs on a substrate upon which some of the plume material re-condenses. The kinetic of the film growth depends on the material flux, substrate material and, temperature, pressure of background gas (vacuum, inert/reactive), laser fluence and repetition rate, target to substrate distance [160]. All these allow the growing film properties to be manipulated, to suit individual applications. Relatively high deposition rates (typically hundreds Å/min), can be achieved at moderate laser fluences [161]. The film thickness can be accurately controlled by the number of laser pulses applied on the target. Typically, the deposition rate per laser pulse will be on the order of 0.001 to 1 Å. PLD provides for a laser shot-to-shot control of the deposition process that is ideal for multilayer and interface formation where sub-monolayer control is needed. Instead of a film deposition rate (Å/s) a per pulse rate is defined. Because the laser is used as an external energy source, the process is extremely clean and can run in both inert and reactive background gases. The transfer of the composition and stoichiometry from targets to substrate can be achieved for most ablated material combinations.

The major drawback of the PLD is the inherent generation of microdroplets which condense on the substrate significantly altering the surface smoothness. However the density and dimensions

of the particulates on the substrate are strongly influenced by the specific deposition parameters and quality films can be obtained after some refinement.

A typical PLD system configuration for ceramic oxides deposition is shown schematically in Figure 3.1.1.

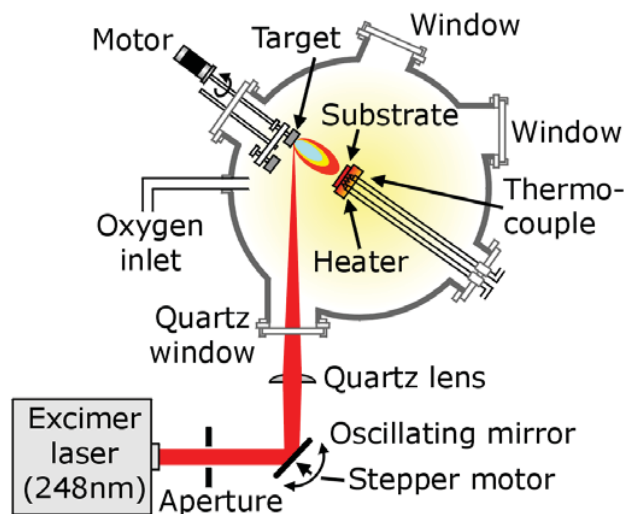


Figure 3.1.1: Schematic diagram of a pulsed-laser deposition system.

The deposition chamber is pumped with oil-free pumps, down to 10^{-6} mbar and is equipped with an oxygen introduction line and pressure control devices capable of operating up to the atmospheric pressure, allowing for the post deposition heat treatment of the coated samples. The sample stage has an integrated heater allowing a tight control of the substrate temperature during deposition and during postdeposition heat treatment. The substrate temperature control is a nontrivial issue during the film growth process. Therefore, a silver paste applied between the sample holder and the substrate can be very effective. Alternatively, the heating of the substrate holder can be provided by another laser source with the beam targeting the back of the holder.

The target rotator (carrousel) can accommodate one or more targets and allows in-situ changing of the ablated material by exposing them to the incoming laser beam alternatively. The efficient ablation of the target material requires the non-equilibrium excitation of the ablated volume to temperatures well above that required for evaporation. This generally requires the laser pulse to be short in duration, high in energy density, and highly absorbed by the target materials. There are different laser types which can be accommodated to a deposition chamber in order to provide an optimum laser beam – target interaction. For ceramic oxide targets, this is most easily achieved via the use of short wavelength lasers operating in the ultraviolet wavelength. The most

attractive are excimer lasers operating at 193, 248, or 308 nm wavelength with pulse duration of the order of tens of nanoseconds and an energy range up to several hundred mJ/ pulse [162].

i. Mitigating the fabricated films' roughness

One potential drawback of PLD is the ejection of micron-size particles (droplets) in the ablation process. If these particles are deposited onto the substrate, they present obvious problems in the formation of multilayer device structures. The use of highly dense ablation targets tends to reduce particle formation but does not eliminate this problem completely. Several techniques have been developed to further reduce particle density. Approaches that focus on preventing the particles from reaching the substrate surface include velocity filters [163], off-axis laser deposition [164], and line-of-sight shadow masks [165]. For instance, the shadow mask technique involves placing a disc shaped mask between the ablation target and the substrate. The mask effectively blocks all of the particles from reaching the substrate, while only fractionally attenuating the flux from the ablation plume. Unfortunately, the shadowing method can adversely alter the composition of the deposit from the plume. Another interesting approach suggested for eliminating particles involves the use of two laser beams focused on separate targets situated perpendicular to each other. The two ablation plumes collide and form a new stream containing light plume components and almost no droplets [166].

The laser fluence has a significant impact on the particulate size and density. It can be changed by varying the laser power or the laser spot size. There is a threshold laser fluence below which the target material is not ablated. One of the mechanisms that reduce the ablation rate is plasma shielding of the target [167], and it is best suited to laser-ablation deposition using longer wavelength.

The laser wavelength is directly related to the effectiveness of the absorption of the laser power into the target. For most metals, the absorption coefficient decreases with decreasing laser wavelength. Thus, the laser penetration depth in metal is larger in the UV range than in the infrared range. For other materials, the variation of absorption coefficient with wavelength is more complex due to various absorption mechanisms, such as lattice vibration, free carrier absorption, impurity centers, or bandgap transition [168, 169].

The primary effect of the laser wavelength on particulate generation is mostly due to the difference in the absorption coefficient when different laser wavelength are used. Larger particulates are generated when using longer laser wavelength [169].

During pulsed laser deposition, the use of background gas can be divided into passive or active use. The passive use is mostly to compensate for some loss of a constituent element. For example, the deposited oxides tend to be deficient in oxygen. Typically 10 - 50 mTorr of background oxygen in chamber is required for ferroelectrics oxides. The background gas pressure can influence the size of the microdroplets as the gas molecules interact with the ablated species and influence their condensation conditions and so the formation of fine or large particulates on the substrate. This interaction can be used also in a controlled manner to produce a certain distribution of particulates on the substrate [170]. The decreasing of the background gas pressure implies a decrease in size and a narrower size distribution of the condensed particulates [171].

The effect of inert ambient gas pressure increases collisions between the ejected species and the ambient gas as the pressure increases. At 1 mTorr pressure, the mean free path is about 5 cm. The mean free path of ejected species becomes 0.05 cm at a higher pressure of 100 mTorr. In vacuum, there are no collisions between ejected species virtually, so particulates are predominantly formed from solidified liquid droplets, and the vapor species are deposited as a uniform background film in the same time.

However, when the ambient gas pressure increases, the vapor species can have enough collisions. Thus, nucleation and growth of vapor species can occur, before they arrive at the substrates. This suggests that the ultrafine particulates are formed from the vapor species instead of liquid droplets.

The quality of the vacuum is directly influencing the quality of the growing film because gaseous impurities in the deposition chamber will stick on the surface of the growing film being included into its composition. If there is a multilayer structure with nanometer scale dimensions the characteristics can be significantly influenced. As a countermeasure, a UVH chamber structure and purging with oxygen (in our case - part of the substrate surface preparation procedure) will be effective.

The effect of target to substrate distance is mainly reflected in the angular spread of the ejected flux. Depending on the position of the substrate, different particulate appearance may occur. The specific effects of target to substrate distance and ambient pressure are related. The plume dimension decreases as the background gas pressure increases due to the increased collisions between the laser-produced plume and the background gas. When the target to substrate distance is smaller than the plume length, there is no remarkable difference in particulate size and density. As the target to substrate distance increases, a few larger particulates appear [172].

ii. Growth of epitaxial oxide thin films

Epitaxial oxide films can be deposited with PLD using single, stoichiometric targets of the material of interest. The thickness distribution of the thin film is quite non-uniform due to the highly forward-directed nature of the ablation plume and due to the texturing of the ablated target surface, spatial inhomogeneities in the laser spot, and laser absorption by the plasma [173]. To extend the film thickness uniformity over larger surfaces, rotation of the substrates and laser beam rastering on the target surface are applied.

PLD technique involves a set of specific sequences. It begins when the laser beam strikes the target surface and its energy is transferred to the solid material. The energy amount transferred to the target is dependent on the absorption coefficient of the material at the specific wavelength of the laser beam. The laser beam is focused on the target surface in order to have a suitable energy density. The target material melts and evaporates and a very dense plasma cloud appears in front of its surface. Because the laser beam is still on, a plasma beam interaction develops and the beam absorption into the evaporated material leads to a strong ionisation of the vapors. The plasma cloud interacts with the incoming beam following the classical rules of the radiation (at a certain frequency) transmission/absorption through a plasma (at a certain concentration). If the laser beam frequency is appropriate a strong absorption takes place and a so called Knudsen layer appears [174]. At the end of the laser pulse, in front of the target surface there is a very dense, small volume plasma cloud. The cloud will expand preferentially in a direction normal to the surface, towards the substrate. A shock wave is generated directing the plasma preferentially forward. At this stage there is no longer any external energy pumped into the plasma plume. The quality of the resulting thin film on the substrate is strongly dependent on the expanding conditions of the plasma (nature and pressure of the background gas) and on the substrate surface condition (crystalline structure, temperature) .

What makes the PLD different comparing to thermal evaporation and sputtering is the possibility to transfer to the substrate the stoichiometry of a complex, composed target [175], as is the case of complex oxides (perovskites). The ablation process is well described also in [176].

A background gas is often introduced which serves two purposes. First, the formation of an oxide film will require oxidizing species (typically molecular oxygen) as a component of the flux. The amount of oxygen required for phase formation will depend on the thermodynamic stability of the desired oxide phase. Interaction of ablated species with the background gas often produces suboxide species in the ablation plume. These sub-oxide species facilitate oxide phase formation. In addition, to actively participating in the chemistry of oxide growth, the background gas can be used to reduce

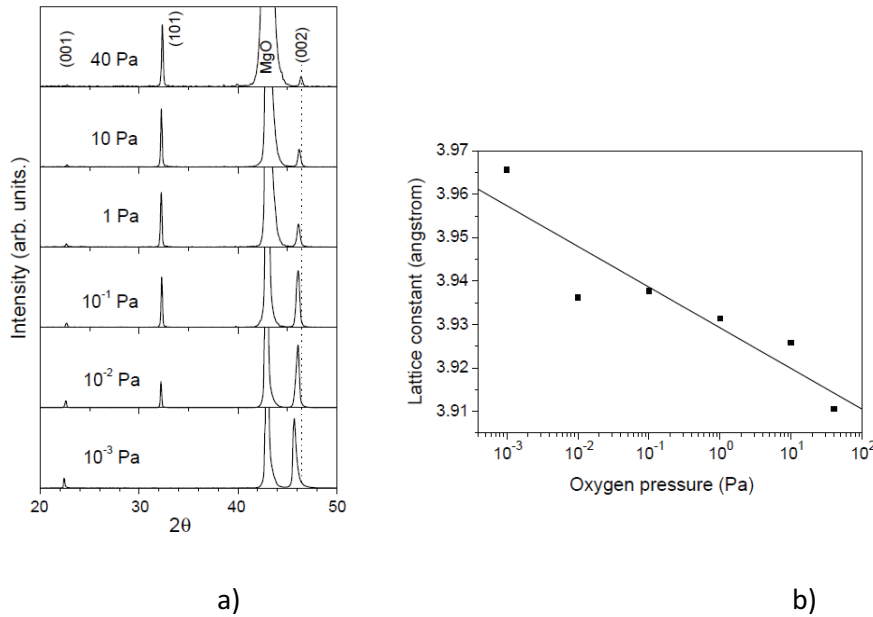
the kinetic energy of the ablated species which can reach several 100 eV. These energies are sufficiently high to create defects in the growing film. The background gas can be used to moderate the plume energies to less than 1 eV. At these energies the effect of the condensing ions on the film compressive stress generated by interstitial defects is also reduced. The vapors formed by laser ablation compress the surrounding background gas resulting in the formation of a shock wave. Interaction with the ambient gas slows the ablation plume expansion. Modeling indicates that the vapor/gas interaction is more pronounced in the radial direction, resulting in a focusing of the expanding plume [177]. The ablated material distribution depends on laser–target interaction, laser peak fluence, intensity profile, laser spot aspect ratio and physical properties of the target. For the deposition of oxide materials, target selection can have significant impact on film growth properties, as epitaxy, phase formation, and deposition rate. At a minimum, ablation requires a target material with a high optical absorption coefficient at the operating laser wavelength.

The PLD technique is mostly used with ablation targets that are polycrystalline ceramics. The biggest advantage of ceramic targets is the ease of target fabrication for multi-cation species. In general, the phase of the target does not need to be the same as that of the desired film. Only the cation stoichiometry needs to be identical to that of the films, assuming stoichiometric transfer and negligible evaporation from the film surface. For ceramic oxide targets, high density target materials are preferable, as this will reduce particulate formation during the ablation process. As an alternative to polycrystalline ceramics, the use of single crystals as ablation targets has been investigated, and shown to be effective at further reducing of droplet density [178].

One of the representative combination of films/ substrates used in electro-optic tunable applications is BST on MgO. $B_xS_{1-x}T$ is a solid solution of $BaTiO_3$ and $SrTiO_3$ and if the deposition conditions are carefully selected, PLD technique can conduct to a crystalline structure on the substrate, which can be engineered to show electro-optic tunability [179].

As electro-optic tunability is supposed to be controlled by the strain induced into the BST film by the lattice misfit with the substrate (e.g. (001) MgO), it should be influenced by the deposition process. The most important parameters are the substrate temperature, the oxygen pressure inside of working chamber and, the laser pulse's superficial energy density. After the completion of the deposition process by a preselected number of laser pulses at a given energy and duration, the coated substrates will cool down in an oxygen atmosphere. The characteristics of the BST film are in close relation with the working oxygen pressure which controls the plume evolution (i.e. the species energy and composition). A systematic study of the $B_xS_{1-x}T$ ($x = 0.02$) film growth on (001) MgO substrates, in a pressure range $10^{-3} - 300$ mTorr [180], at 850°C , revealed the strong dependence of the

film properties on the oxygen working atmosphere concentration. Oxygen vacancies, which affect the microstructure and properties of BST thin films, are introduced inevitably in the PLD-deposited oxide thin films for the lower deposition oxygen pressure. The lower the oxygen pressure, the higher the content of oxygen vacancies, increasing the concentration of trapped electric charges. Moreover, existence of oxygen gas in the ambient has a strong influence on expansion of the laser-produced plasma plume and modifies the kinetic energy of the ablated species, resulting in differences on characteristics of thin film, such as surface morphology, growth rate, orientation, stoichiometric composition. The effects of stoichiometric deviations, including oxygen vacancies upon the optical properties of ferroelectric films have not been reported yet. The strategy pursued in this work is to study, at least at first, stoichiometric BST and SBN films, as free from crystalline defects as it is possible to obtain.



Figures 3.1.2: Oxygen pressure influence on: a) XRD pattern and b) on the lattice constant of the BST film grown at 850 °C on (001) MgO substrates [180].

Figure 3.1.2a shows the transition of the XRD pattern from the (101) to (002) as the oxygen pressure decreases and Figure 3.1.2.b presents the variation of the lattice constant with the process pressure.

The interface between the MgO substrate and the BST growing film is strongly influencing the film properties. Delage [181] clearly pointed out the effect of a sub-oxidised BST layer over the BST film permittivity (Figure 3.1.3). It is quite reasonable to assume that a change in stationary permittivity would be accompanied by a change of the optical response under electric bias.

As the above summarized literature shows, PLD allows the deposition of very promising complex oxide films for the development of experimental plasmonic devices.

As for the development of the functional oxide thin films for active plasmonic devices, BST is the first candidate material and the existing reports are very encouraging taking in account *the already existing* experience in PLD deposition of both BST and SRO at Imperial College, other reviewed materials should be listed as candidates for active plasmonics – LN and $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$.

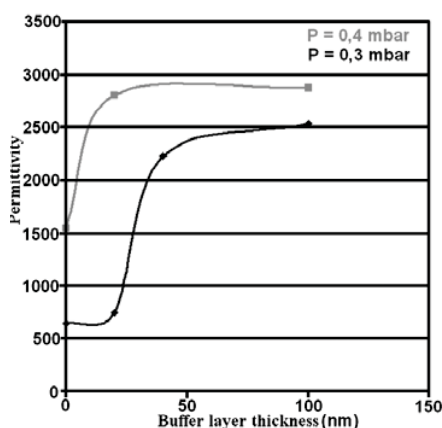


Figure 3.1.3: BST film permittivity vs. sub-oxide buffer layer thickness [181].

The properties of bulk crystal LN were extensively investigated for the successful development of optical data transmission devices and e.g. Ti diffused optical guides are currently in use. LN is, however difficult and very parameter sensitive if we want to deposit it as crystalline thin film. However, LN can be deposited by PLD [182 – 184] or RF magnetron [185] if deposition configuration (power, position of the substrate and distances) and target composition are appropriate. It has to be mentioned that Li is much more volatile than Nb and the composition of the target is usually enriched in Li by more than 10% in excess. The deposition temperature and working oxygen pressure are also critical parameters. No matter which parameters were chosen, the main characterisation techniques are XRD and propagation loss measurement, usually by prism coupling. SBN thin film deposition by RF magnetron sputtering and subsequent electro-optical investigation is extensively presented in an excellent series of papers [182 – 184] and a comparison with BST and LN is made, concluding the non linear properties of SBN epitaxial thin films are competitive with those of $(\text{Ba,Sr})\text{TiO}_3$ thin films for dielectric tunability and with those of crystalline LiNbO_3 for electro-optic properties.

PLD is one of the most appropriate technique to produce high quality films of ferroelectric oxides. The specific transfer of the composition and stoichiometry of an ablated target material to a

substrate is the main argument for the use of PLD in this application. Other features of the PLD are – the pulsed nature of the deposition process which allows the film thickness control by the number of the laser pulses applied on the target and the kinetic energy control of the plume species by the nature and pressure of the background gas. The process is very clean due to the external position of the energy source, usually the working chamber and the associated devices and components being UHV compatible. Concerning the experimental set-up configurations, the substrate holders are able to provide elevated temperatures with a precise controlled value during film growth so as to obtain the desired crystal structure. Despite the forward-directed plume, the film's thickness uniformity can be enhanced by the rotational movement of the substrate holder. The ablated targets can be alternated in front of the laser beam allowing the deposition of multilayered films. Some aspects as the relation between the laser wavelength and the energy absorption into a specific target material and the inherent production of particles which can ruin the surface morphology of the thin film can be counted as drawbacks of the PLD but, however, the effects can be substantially reduced.

Summarizing, the film properties which must be the subject of optimization for plasmonic applications are ideal stoichiometry, aiming for the elimination of oxygen vacancies and crystalline defects, (001) orientation, and as much as possible low roughness.

3.1.2 Magnetron Sputtering

In sputter deposition, energetic ions created in an RF or DC plasma of a glow discharge bombard a metal or oxide target surface – the cathode of the discharge. Ions are accelerated across the voltage drop inside the plasma sheath in front of the cathode towards energies which exceed the sputtering threshold on the plot of the sputtering yield vs. energy. This process ejects atoms from the target that subsequently deposit on a nearby substrate surface.

To enhance the sputtering yield and to decrease the ambient working pressure, the magnetron configuration consists in a magnetic closed field geometry, providing conditions to capture the electrons released by the cathode in a „race track” where they will strongly oscillate and tremendously increasing in this way the ionization efficiency (Figure 3.1.4).

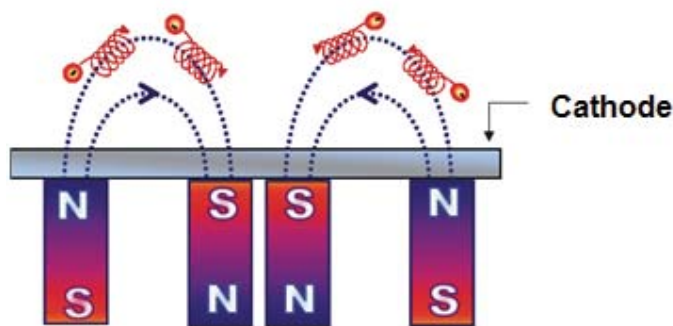
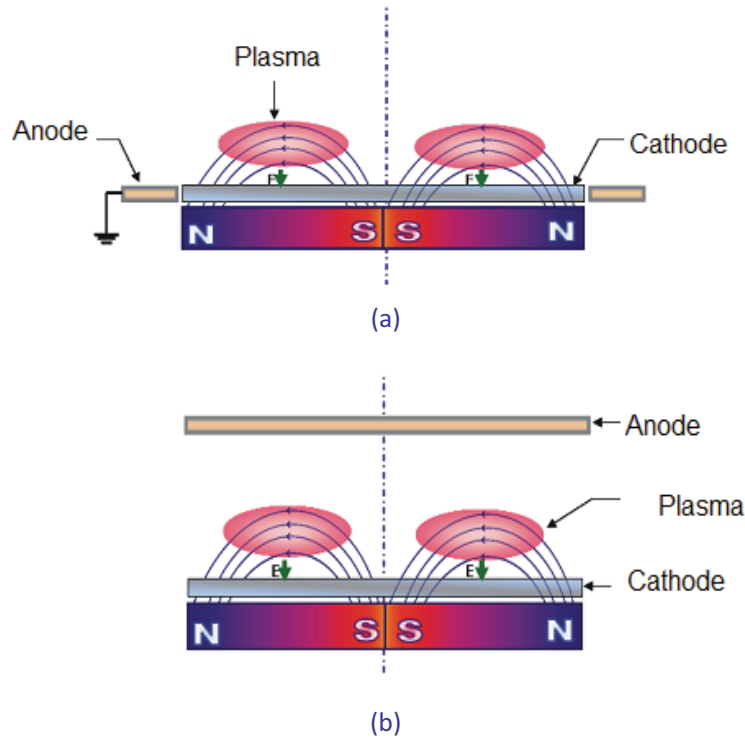


Figure 3.1.4: Schematic of the electron movement along the lines of the magnetic field in a planar magnetron.

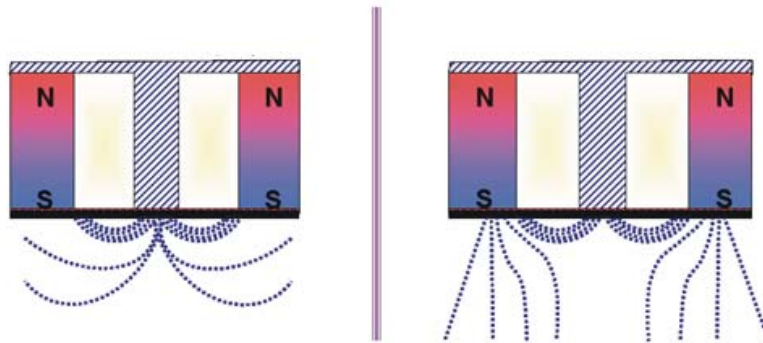
The magnetron configuration works at lower pressure and lower voltage comparing to the glow discharge but at much larger discharge current. Nowadays the magnetron heads are quite compact due to the development of the rare earth magnets able to withstand temperatures up to 150°C . A schematic of a magnetron head figuring also the sputtering process and two deposition configuration (plane parallel and coplanar) are presented in Figure 3.1.5.

The magnetron sputtering process is enhanced by the plasma confinement in the vicinity of the cathode, due to the presence of the magnetic field. However, too strong a confinement may not be beneficial because the plasma cannot be dispersed into the direction of the substrate, subsequently resulting in a low deposition rate and a reduced ion bombardment of the surface of the growing film. To address this issue one solution is to modify the configuration of the magnetic field, for example the center magnet has a weaker intensity than the outer ones, configuration known as unbalanced magnetron (Figure 3.1.6). In this configuration, contrary to the balanced magnetron also presented in Figure 3.1.6, not all the magnetic field lines are being closed between the central and outer poles, so that some field lines are directed towards the substrate. In the unbalanced magnetron configuration part of the secondary electrons follow these open field lines, and consequently the plasma flow out towards the substrate, being no longer confined in the magnetron target region. Thus, the resulting flux of sputtered ions/atoms from the target represents also a source of ions for substrate bombardment [186].

Usually, a shutter should be provided in front of the cathode to screen it from other vapour sources in the deposition chamber and to allow the target conditioning before deposition on the substrate.



Figures 3.1.5: Schematics of a magnetron target in (a) - coplanar and (b) plane parallel configurations.



Figures 3.1.6: The schematics of balanced (left) and un-balanced (right) magnetron deposition configuration.

Magnetron sputtering is currently and successfully used in many application areas, particularly in microelectronics and surface engineering, for the production of films and coatings. Some of the advantages of the technique are that it is simple and reliable, and capable of meeting the economic and functional requirements in industrial productions. Further, the sputtering deposition process operates under physical conditions which makes it possible to synthesize films with new physical and functional properties.

i. DC Magnetron Sputtering

The deposition of metallic thin films as parts of a plasmonic device can be easily performed by DC magnetron sputtering. The DC magnetron sputtering technique allows the deposition of very smooth metallic films with well controlled rate. The metallic coatings can be deposited in a continuous shape and subsequently etched to form electrodes as parts of plasmonic devices.

The DC magnetron technique was successfully applied to reactive sputtering deposition of complex oxides. In [187], an extensive report on the reactive deposition of PZT from composed metallic targets is presented with a detailed description of the composed target engineering and of the optimised deposition parameters found after the role of the deposition pressure, gas mixture and thermalizing of the sputtered species was investigated.

If an inert gas (usually argon) is used as working gas to maintain the discharge, the target material is transferred to the substrate (not necessarily reproducing the target stoichiometry). If the working inert gas is blended with a reactive gas (e.g. nitrogen or oxygen) the resultant thin film on the substrate is a nitride or an oxide of the target material. The process is called reactive magnetron deposition and there are a multitude of deposition recipes based on it. If a metal target is sputtered in a reactive mode the plasma quickly reacts with its surface and the process is controlled by the equilibrium between the sputtering yield of the resulting compound on the cathode's surface and the reactive gas percent into the working gas mixture. The sputtering in pure argon gas is called metallic mode and is easily controllable. If the content of the reactive gas is increased, the target is partially covered by a nitride (oxide) which has a much lower secondary electron emission coefficient and also a much lower sputtering yield. The process shifts into the ceramic mode and can also be relatively easy controlled. Unfortunately, if we would like to obtain a thin film with a controllable stoichiometry at still large deposition rate, we must work into the transition regime between the two modes and the process is unstable. This difficulty can be eliminated only by automatic control loops which measure by optical emission spectroscopy the concentrations of the metal atoms and of the reactive gas atoms. A feed-back is provided to the electrical supplies to adjust the discharge current in a very short time and keep the process stable. The DC magnetron deposition of the titanium nitride is a well-known example of such a reactive process.

ii. RF Magnetron Sputtering

Several sputter deposition techniques have been used in the growth of oxide films including a well-known on-axis magnetron sputtering, ion-beam sputtering [187] and off-axis magnetron sputtering. In the on-axis geometry, the substrate and target are facing one another. This is the optimal geometry for maximum deposition rate, but can result in film damage due to the bombardment of the film surface with energetic species from the plasma. An alternative is an off-axis geometry [188], in which the substrate surface is oriented perpendicular to the surface of the sputter target. This removes the film from the plasma region, eliminates sputter damage, and generally results in films with fewer defects. Unfortunately the off-axis approach also significantly reduces the growth rate that can be achieved by sputter deposition.

One disadvantage with sputter deposition is that the stoichiometry of a multi-component film is not necessarily that of the target material due to differences in sputtering yields for different elements. To compensate this drawback, it is necessary to prepare non-stoichiometric targets and to find the suitable composition by a set of trials. Also, to compensate the lack of oxygen into the film, a mixture of argon and oxygen is used as process gas.

The magnetron deposition of the insulator materials from ceramic targets cannot be performed in DC configurations due to the irreversible electrostatic charge accumulation on the cathode surface which suppress the gas breakdown and the plasma formation. If an RF potential is applied on the ceramic cathode, having the vacuum chamber wall at ground, the discharge is established and maintained by the energy transfer to the plasma electrons. Ions are not influenced by the RF potential. The spatial charge distribution in front of the cathode allows the ions from the RF plasma to be accelerated and to hit the cathode surface at energies above the sputtering threshold to sputter the material from it. However, due to the alternative electric bias of the electrodes the ions are practically accelerated to the cathode only in the negative half-cycle resulting in a lower sputtering rate. The ceramic cathode targets are usually simply pressed in a copper tray or can be hot pressed and then sintered in disc shaped parts which should be polished and thinned at an appropriate thickness for the type of the magnetic configuration of the magnetron.

Referring to the oxide ceramic targets, some considerations are important in RF sputtering, as the composition of the target, the Ar/O₂ ratio and pressure, the RF power, the substrate temperature during deposition and during the post annealing and the distance from the cathode to the substrate.

The pressed targets are easier to make and are used mainly to find the right composition (e.g. the value of x in Ba _{x} Sr_{1- x} TiO₃) in order to prepare a film with designed stoichiometry. Considering the

last approach, generally, some of the component oxides will be added in excess to the powder for the target, in order to compensate for their loss during the deposition process. E.g. - a powder based target was prepared and the compositions were $\text{Pb}_{1-x}\text{La}_x\text{Ti}_{1-x}/4\text{O}_3$ where $x = 0.05, 0.10$, and 0.15 . PbO powder was added in excess (10 molar %) on these compounds to prevent the lack of Pb [189].

However, such targets show a number of disadvantages such as target cracking due to localised heating during sputtering, oxygen deficiency and stoichiometric variations on the target surface after repeated use [190].

Considering the deposition parameters, even if it is often assumed that a high-energy flux associated with operation at low sputtering pressures (1 Pa) is advantageous for the formation of dense films, the case of complex oxides is different, due to their complex crystallographic structure. It was found [191] that thermalisation or dissipation of energy by collisions during transport through the plasma provided a much better control over composition, in the case of oxides. This can be reached by operating at relatively high pressures (5 Pa) and keeping the substrates - targets distance large enough to ensure complete thermalisation of the sputtered species. Another important parameter is the RF input power fed onto the cathode, as a high input power leads unavoidably to polycrystalline growth instead of favouring the epitaxial growth. That is because of too many particles from the target that arrive at the sample surface. Furthermore, by using high gas pressures the mean free path length is short, hence the kinetic energy of the particles becomes too low to move sufficiently on the surface and the structure also degrades. As a result, a compromise might be found to obtain high quality films of complex oxides.

If a preferential orientation for an epitaxially grown films is wanted to be obtained by the magnetron sputtering technique, the cooling conditions after deposition should be examined, and not only the lattice mismatch with the substrate and the thermal expansion.

If the RF power is turned off at the end of the deposition process, the compressive stress vanishes, and the preferred c-axis orientation generated during growth begins to convert into a-axis orientation. However, the lower the deposition temperature, more difficult to turn the orientation, due to the increasing lattice anisotropy. If the cooling rate is low and the deposition temperature high, the films have enough time to release the tensile stress and hence to relax in the favourable a-axis orientation. By contrary, for high cooling rates and low deposition temperatures, the lattice anisotropy becomes large in a short time preventing any re-orientation.

The mechanical stress in the sputtered films, induced by intrinsic stress due to lattice mismatch and thermal stress caused by different thermal expansion coefficients, can be subsequently relieved by thermal treatment; this however can led to the formation of hillocks or craters, but this

depends strongly on the material type, temperature gradients and composition of the atmosphere during annealing.

RF magnetron sputtering is currently applied for thin film deposition from insulator targets. Usually the RF supplies work at the standard industrial frequency 13.56 MHz. Deposition rates of 0.5 nm/min are easy to control at a working pressure of 1 Pa. The substrate is maintained at 600 – 750° C during the deposition then the film is cooled down in situ under oxygen flow [192].

Magnetron sputtering is a mature and very versatile technique of thin film deposition. Sputtering is based on the physics of the interaction of ions and neutral atoms with the surface of a solid target at an energy value which allows a maximum for the process yield Y (number of ejected atoms per energetic incident ion/atom). Basically the sputtering appears at the surface of the cathode electrode in a glow discharge but it needs high voltage across the discharge inter-electrode volume. Also the bombardment flux of ions and energetic neutrals is rather low. The magnetron configuration enhances the ionization in front of the cathode by a few order of magnitude by adding a magnetic field with a closed configuration – a race track – for the electrons. The elongated electron free path allows a much higher ionization probability in front of the cathode. The magnetron discharge will work at a much lower applied voltage and at much higher discharge currents and also – very important - at much lower pressure in the 10^{-2} - 10^{-3} mbar range. The discharge is maintained usually in an inert gas (argon) but also different gas combinations are used mainly for the so called reactive magnetron deposition (e.g. argon + oxygen – to produce oxides, argon + nitrogen – to produce nitrides thin films). The magnetron head can be DC-biased when the cathode (target) is conductive or an RF signal can be applied for insulating targets. The RF energy is absorbed only by electrons which ionize the background gas. The positive charge distributions is similar to the DC powered discharge allowing the flux of energetic ions and neutral atoms to bombard the surface of the insulating target and thus sputter the material. No electric charge can accumulate and stop the deposition process. Uniform film thickness can be easily achieved by using large cathodes. Also, the film's growth can be controlled by the background gas pressure, substrate temperature, deposition rate. Very smooth films of metals, oxides, nitrides etc. can be produced in a controlled manner.

3.2 Characterisation Techniques

The section describes the materials characterization techniques used in the present work. The structure of materials is investigated via X-ray diffraction (XRD), surface area analysis based on Brunauer–Emmett–Teller (BET) theory and dilatometry.

The surface is subjected to atomic force microscopy (AFM), scanning electron microscopy (SEM) and stylus profilometry measurements.

The electrical properties of conductive plasmonic materials are investigated with four probe conductivity measurements and Hall-effect mobility measurements. Their optical properties are investigated with normal incidence reflectivity and ellipsometry.

A brief account of the underlying theory and typical experimental set-up used by these techniques is given. Their adaptation to the materials under study in this work is also discussed.

3.2.1 Structural characterisation

i. X-Ray Diffraction

X-ray diffraction (XRD) is a powerful non-destructive technique used for the study of the crystallographic phases and orientations within a material, detection of phase transformations, measurement of residual stress, thickness measurement, etc. It takes advantage of the interaction of the electromagnetic radiation with wavelength (0.15 - 0.4 nm, depending on the material used for the anode of the X-ray tube) comparable to atomic spacings [193], when incident upon a crystalline sample is scattered by the atoms in the system and undergo constructive interference. In fact the interaction of X-rays with the atoms in a sample determines their scattering in all directions, and if amorphous no preferential direction will be visible.

In a crystalline solid, because the atoms are arranged in regular three dimensional lattices/arrays, constructive interference of the scattered X-rays will take place. This can be described mathematically by the von Laue equations for diffraction, as observed in Figure 3.2.1:

$$\begin{aligned} a (\cos \gamma_1 - \cos \delta_1) &= h\lambda \\ b (\cos \gamma_2 - \cos \delta_2) &= k\lambda \end{aligned} \quad (3.2.1)$$

$$c (\cos \gamma_3 - \cos \delta_3) = l\lambda$$

where δ_i is the incident X-ray beam, γ_i is the diffracted X-ray beam, a , b and c are lattice spacings, h , k and l are natural numbers, and λ is the wavelength of the incident X-ray beam [194].

The implementation of the Laue equations (Eq. 3.2.1) is challenging due to the large number of parameters to be defined: six angles, three lattice spacing (a , b and c), and three natural numbers. A mathematically more accessible function was given by W. L. Bragg, who proposed a physical model in which a diffraction peak occurs if the length of the photon's path between any two scattering centers in a unit cell is a integer multiple of the photon wavelength. W.L. Bragg approach on the diffracted image was based on the correct understanding of the phenomenon [195].

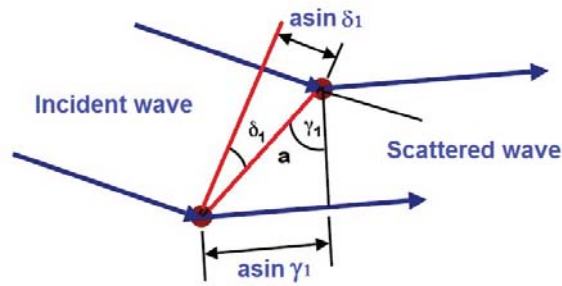


Figure 3.2.1: Incident and scattered waves on two atoms in an array at distance "a", picturing the Laue equations.

If d_{hkl} is the distance between the atomic planes in a crystalline solid, defined by the hkl Miller indices, θ_B is the angle between the incident X-ray beam and the crystal lattice planes, and λ is the X-ray wavelength, then the coherent scattering of high energy photons may be described, in analogy by visible light diffraction from a grating by the relation (Figure 3.2.2):

$$2 d_{hkl} \sin(\theta_B) = n\lambda \quad (3.2.2)$$

where "n" is the order of diffraction [196]. For the purpose of simplicity, the usual calculation involves only two rows of atoms, and the transition from constructive to destructive interference is gradual as the angle θ changes. In reality, there are many rows of atoms subject to X-ray interaction, so that the constructive interference peaks become very sharp with mostly destructive interference in between. This increase in the peaks' definition, which can be well fitted with a Lorentz or Lorentz-Voigt distribution, is very similar to the sharpening of the diffraction peaks in seen classical optics, when increasing the number of slits in a diffraction grating.

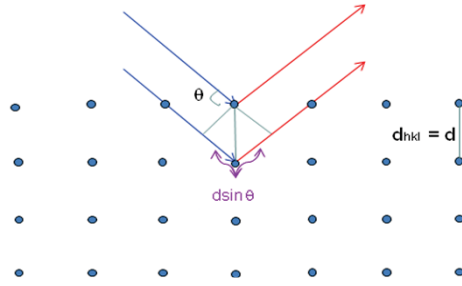


Figure 3.2.2: Illustration of Bragg diffraction law: two beams with the same wavelength and phase are scattered of two different atoms in a crystalline solid and within it; compared to the first beam, the second one has a longer path, with an extra length of $2d\sin\theta$. The constructive interference takes place only if this extra-length is equal to an integer multiple of the wavelength of the radiation.

Angular scan (θ - 2θ scan)

The symmetric Bragg-Brentano (θ - 2θ) geometry is usually used for determining the structural quality of different materials, including thin films of sufficient thickness. In this experimental arrangement both the X-ray source and the detector are moving simultaneously, and both the incident and diffracted beams have identical inclinations with respect to the substrate surface. As can be seen in Figure 3.2.2 in this simple geometry the bisecting line of the angle between the two beams is always normal to the sample surface, maintaining a fixed position. It is easily observed that the detector receives only the reflections generated by the planes parallel to the substrate surface. The information about the crystallographic structure can be obtained not only from the peak positions, but also from their intensity and shapes. If the sample has a preferential texture (exhibits preferential growth in one specific lattice direction), the relative height of the peaks will be modified. Using this geometry the preferred orientation of crystallites can be accurately determined.

Grain size

If studying different materials with different grain refinement (e.g. as obtained in bulk ceramic sintering), it can be observed that the full width at half maximum (FWHM) of the peaks increases, as the grain size becomes smaller. So, the broadening effect is due to the finite size of the crystallite grains. The averaged grain size can be determined in this geometry using Scherrer's formula [197]:

$$d = K \lambda / (\beta \cos\theta) \quad (3.2.3)$$

where β is the FWHM or integral breadth of the peak in radians, and K a constant, which depends on how the width is determined, the shape of the crystal, and the size distribution. The most common values for K are: 0.94 for FWHM of spherical crystals with cubic symmetry, 0.89 for integral breadth of spherical crystals with cubic symmetry. Despite $K=1$ being widely used (because both 0.94 and 0.89 round up to 1), K value can range from 0.62 to 2, depending on different crystal forms and different structures of the unit cells [198]. For the usual forms of the grains (spherical, plate-like and rod-like grains) K remains on the order of 1 [199]. Even if in this approach the strain contribution is not taken into account, the width of the XRD peak gives a good estimation of the grain size especially for small crystallite size [200].

It should be mentioned that in real crystals the residual microstrains determines peak broadening with increasing diffraction angle θ , which leads to an growing underestimation of the vertical grain size. Consequently the higher diffraction orders are not suitable to be used. These microstrains are produced by point defects (e.g. dislocations, interstitials, vacancies, etc.), which generate local variations of the lattice parameter around its average value. Another cause of microstrains is related to point anisotropy between grains, which may give rise to peak shift and line broadening if they vary from point to point in the film.

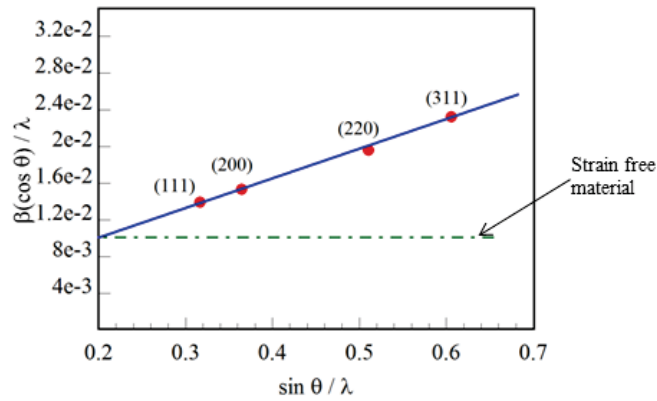


Figure 3.2.3: Example of the Williamson-Hall plot for calculating the crystallite size and the lattice strain for a cfc type structure [200].

To separate the peak broadening which is due to the averaged grain size from broadening due to the mean square strain, one should consider that the crystallite size is not a function of the reflection order, while for the strain it is. The Williamson-Hall method [201], not to be detailed in the following, uses the simple angular scans to determine both the grain size and the microstrain, by linearly adding a term related to the microstrain, as follows:

$$\beta \cos \theta / \lambda = 1/d + 4\varepsilon \sin \theta / \lambda \quad (3.2.4)$$

where β is the line broadening (FWHM), ε is the strain and d is the unknown grain size in the direction normal to diffracting planes. A “Williamson-Hall plot” of $\beta \cos\theta/\lambda$ vs. $2 \sin\theta/\lambda$, is a straight line with a slope of 2ε and an intercept of $1/d$ (Figure 3.2.3) [200].

Texture coefficient

The diffractogram obtained in Bragg-Brentano geometry indicates which crystallographic planes are parallel to the substrate, so the preferential out-of-plane orientation can be determined. The fraction of grains with a $[hkl]$ out-of-plane orientation is proportional to the area under the (hkl) diffraction peak. Since the intensity of the diffraction peak depends on the structure factor, the measured peak area must be corrected with the relative peak intensity of the corresponding powder as reported in the Joint Committee for Powder Diffraction Standard - International Centre for Diffraction Data (JCPDS-ICCD) card. The formula to calculate the fraction of grains with a $[hkl]$ out-of-plane orientation is:

$$T_{hkl} = \frac{\frac{A_{hkl}}{I_{hkl}}}{\frac{1}{n} \sum_{hkl} \left(\frac{A_{hkl}}{I_{hkl}} \right)} \quad (3.2.5)$$

with A_{hkl} the area under the hkl peak and I_{hkl} the reference standard (random) peak intensity values for the same reflection hkl . The standard intensity values should ideally be determined for a randomly oriented coating material but this is not possible usually for thin films, so the JCPDS-ICCD values of peak intensity are used as the standard. The term in the denominator represents an average over all observed (hkl) reflection of the ratio of measured to standard peak intensity values [201].

ii. Surface area measurement - BET

Surface-area measurement method depends on the adsorption of gases onto a particle surface at low temperature. No other type of adsorption method can provide a more extended characterization of porous solids as gas adsorption. The mass of gas adsorbed is measured as a function of gas pressure at a fixed temperature (typically liquid nitrogen). The method developed by Brunauer, Emmett, and Teller (BET) [202] for estimating the particle size relies on determining the surface area of the powder, which is calculated from the N_2 -isotherm observed at the boiling point of nitrogen.

The concept of the BET theory represents an extension of the Langmuir theory (a theory for monolayer molecular adsorption), to multilayer adsorption with the following hypotheses: (a) gas

molecules physically adsorb on a solid in layers infinitely; (b) there is no interaction between each adsorption layer; and (c) the Langmuir theory can be applied to each layer.

The model of BET theory assumes that the adsorbate starts by attaching itself to the surface sites with the highest free energy. As the pressure is increased, it becomes attached on the next energy level sites. The model also takes account of the 2nd, 3rd and higher layer adsorption. This BET theory for multi-layer adsorption is the expansion of Langmuir equation, which is for the single layer adsorption.

The BET equation is:

$$p/[V_a(p_0 - p)] = (V_m C)^{-1} + (C-1)p/(p_0 V_m C) \quad (3.2.6)$$

where: p - gas pressure; p_0 = saturation vapour pressure for adsorbate at the adsorption temperature; V_a - adsorbate volume at relative pressure p/p_0 ; V_m - adsorbate volume per unit mass of solid for monolayer coverage, and C - BET constant.

The theory well fits in the relative pressure ranges between 0.05 and 0.35. A plot of $p/[V_a (p_0 - p)]$ vs. p/p_0 gives a straight line from versus which V_m and C can be determined. The monolayer adsorption amount (V_m) and C parameter are calculated from the slope and intercept of BET-plot by using the least square fitting. According to BET theory V_m represents the amount of nitrogen necessary to form a monomolecular layer on the particle. Because one nitrogen molecule requires a surface area of 0.162 nm^2 , the surface area of the particle can be easily estimated in square meters per gram. C parameter represents the surface interaction energy, so it must take a positive value. The specific surface area S_{BET} of the powder can then be calculated using the equation:

$$S_{\text{BET}} = N_A \sigma V_m / V' \quad (3.2.7)$$

where N_A is Avogadro's number, V' is the molar volume = $22,410 \text{ cm}^3/\text{mole}$, and σ is the cross-sectional area of the adsorbate molecule (0.162 nm^2 for N_2). Assuming spherical particles, and the powder density ρ , their radius a can be simply obtained from:

$$a = 3/(\rho S_{\text{BET}}) \quad (3.2.8)$$

Even if the BET theory is based on an over-simplified model of multilayer adsorption, it is still used as a standard procedure for effective surface area determination. Precautions should be taken if the material is ultramicroporous, with pores of molecular dimensions [203].

iii. Thermo-dilatometry

The sintering process can be observed as the ceramic is heated, by measuring the length of the sample as a function of temperature; this method is known as thermo-dilatometry. If the structure of the ceramic is changing during the heating process, sudden length variations are observed, corresponding to the phase transition [204]. By using thermo-dilatometry measurements it is possible to determine a suitable temperature gradient for producing a constant rate of shrinkage. It is the way the thermo-dilatometry may enable the optimization of material processing and provide information about the thermal behaviour of ceramics at high temperature.

Sintering is a process taking place at high temperature transforming individual ceramic particles into a compact polycrystalline body, being used to obtain bulk ceramic components [205, 206]. In an agglomerate of fine powder particles, their large free surface creates an excess of the free energy, which represents the driving force of the sintering process. During the solid-state sintering process the powder particles develop necks with their neighbours, and in a certain time interval the junctions or contact area between them increases, and consequently the internal free surface of the powder compact is decreased [206, 207]. Sintering is accompanied by the reduction of the porosity during the densification process, which is in turn connected with shrinkage of the sample measurable by the dilatometer [208].

3.2.2 Surface morphology

i. Surface profilometry

Stylus profilometry is commonly used to estimate step heights (and thus film thickness) and surface roughness. The stylus is moved in contact mode across the studied surface, and the vertical displacement of the stylus is converted to a height value in Z equivalent to the step height in the feature studied. For performing the conversion, different mechanical and electronic devices are used.

The principle is somehow similar to the one used in early phonograph players. The sample is located in an X, Y, θ stage it should have a good resolution, as this is determining the resolution of the actual measurement. Topography is the main measurement the tool is capable of. By dragging the stylus over a certain line across the wafer, the surface topography can be determined from the output of the stylus. The principle consists of an electromagnetically sensing of the mechanical movement of a stylus as it traces the topography of a film step.

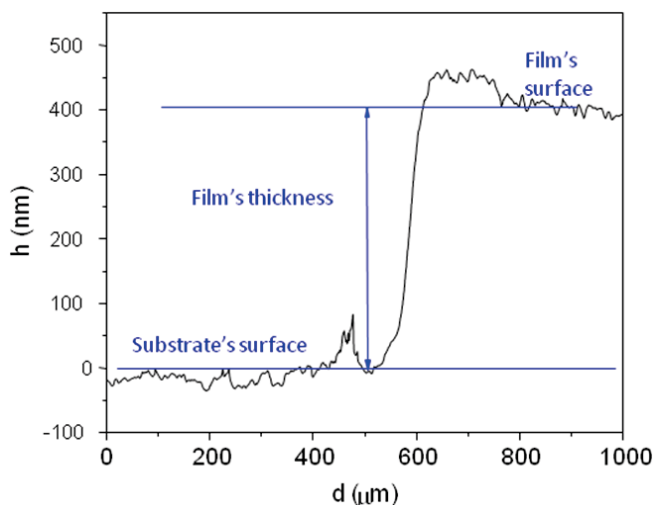


Figure 3.2.4: Example of thickness determination of a film by using the surface profiler Dektak 8000.

For studying the surface topography, the use of stylus profilers represents an wide accepted option. A Dektak 8000 profilometer with a low-inertia Stylus Sensor and variable programmable stylus force (1 - 100 mg) was used to measure the films thickness. The range of the scan length was 50 μm - 200 mm. The profilometer was used to measure film thickness by scanning surface irregularities (heights and trench depths). The device relies on a small-diameter stylus moving along a surface; the stylus moves vertically to measure the encountered surface features, while having a constant displacement in the horizontal plan. Stylus force and stylus radius are inter-dependant, the choice of both being subject to the inspected material hardness, and environmentl consitions, the most important one being the vibrations. It is to note that looking for a higher accuracy, the reduction of the stylus radius will determine the increase of the stylus pressure. The total stylus force is the sum of static and dynamic force. While the static force may be selected by the user, the dynamic force depends on the effective stylus mass and on the velocity of descent. If the stylus pressure is too high, it may determine plastic or elastic deflection, which may affect measurement repeatability. The resolution on the horisontal axis is determined primarily by the size of stylus, and also by the instrument filtering, data rate, scan speed, and scan length.

For film thickness measurement it was used a tip size of 5 μm , and the scanning on the horizontal axis was done over a scan length of 1 cm). Moreover, the estimated surface roughness by profilometry was found to be in agreement with the AFM measurements. In Figure 3.2.4 is presented the result of the measurement of a film thickness.

ii. Atomic Force Microscopy

Atomic force microscopy (AFM) is a scanning-probe technique that was developed in the 1980's in order to overcome the limitation of having to use conductive materials in scanning tunneling.

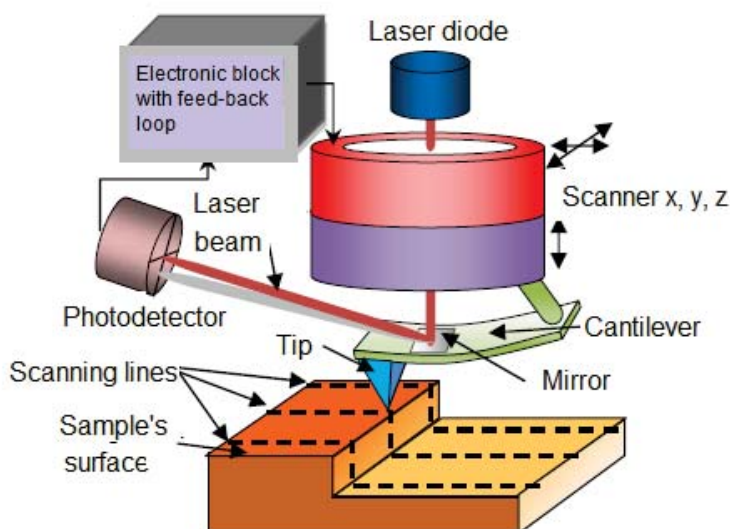


Figure 3.2.5: Schematic representation of the working principle of AFM.

A laser beam is directed onto the back of the cantilever, and is reflected onto a photodiode detector. This is a four-quadrant, position-sensitive detector, which is capable of detecting simultaneously the normal deflection and the lateral deflection signals.

The principle of an atomic force microscope is similar to a stylus profiler, but the probe forces on the surface are much smaller. Smaller probes can be therefore used, and much higher resolution can be achieved. At the same time, the vertical expansion is limited, consequently the method is useful for scans of low surface roughness. The AFM consists of a tip which makes soft physical contact with the sample (Figure 3.2.5). When the tip approaches the sample surface, strong repulsive forces appear which cause the cantilever bending. As the spring constant of the cantilever is lower than the effective spring constant holding the atoms of the sample together, the tip scan across the surface generate an accurate topographic map of the investigated surface. The topographical images can be visualized in real time.

The surface morphology was analyzed using an Atomic Force Microscope from Park Instruments operating mainly in contact mode. Different scanning heads were used ($5\text{ }\mu\text{m} \times 5\text{ }\mu\text{m}$; $20\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$ and $50\text{ }\mu\text{m} \times 50\text{ }\mu\text{m}$), depending on the analyzed area of the sample.

3.2.3 Optical Characterisation

An isotropic material is characterized, in term of optical constants, by the real and the imaginary part of the complex index of refraction. The complex index of refraction, as well as the complex dielectric function of a solid are closely connected with the material's electronic structure. Hence, the accurate experimental determination of the complex index of refraction is of great importance. Even up to date, the optical constants of materials have either not been determined, or determined in narrow wavelength range. Currently there is an increased need for an accurate knowledge of their optical constants, as the complex index of refraction gives information about of the optical band gap (for semiconductors and insulators) and plasma frequencies. Also, the value of the refractive index is needed for the design of optical components, optical coatings and new plasmonic devices.

Considering a homogeneous and plane-parallel film, the knowledge, at each wavelength, of the values of the real and imaginary parts of the complex refractive index, permits the unique determination of the optical constants of the film. To do that, two independent measurements are necessary, for solving the equations containing $n(\lambda)$ and $k(\lambda)$. However, real films are not completely homogeneous, and their roughness cannot be neglected.

i. Normal Incidence Reflectometry

One method to determine the complex refractive index consists of measuring the reflectance at or close to normal incidence over a sufficiently large range of wavelengths and then performing a Kramers - Kronig inversion [209, 210]. The light from an external source is emitted towards the film's surface, and measured after it is reflected normal by the film surface and by the interface between the film and the substrate. Transmitted light can also be measured, if the substrate is transparent.

By using light that is perpendicular to the film one can ignore the polarization effects (since most films are rotationally symmetric). One drawback is the absence of a reference beam, which makes the measurement dependent upon absolute, rather than relative values, leaving it exposed to errors arising from fluctuations in the spectre emitted by the lamp. However, most such fluctuations are faster than the signal integration time used. Another one is the lower optical path, through the

sample, due to the fixed normal incidence geometry, which makes this technique suitable for the analysis of thick films. The simple determination of the film thickness by normal incidence reflectometry measurements is suitable only for films with known, isotropic optical constants, such as those obtained by sol-gel or spin-coating. The main advantage of this set-up is the absence of moving parts, which negates the need for an alignment procedure.

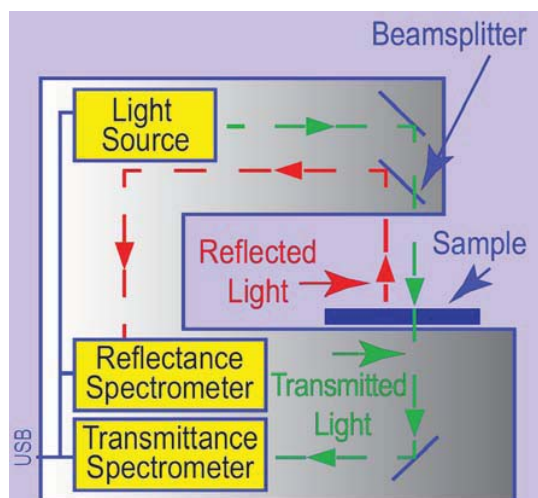


Figure 3.2.6: Schematic representation of the working principle of Filmetrics equipment (adapted from www.filmetrics.com)

ii. Ellipsometry

The optical constants of thin films can be measured by different methods, as spectrophotometry, interferometry, critical angle, transmittance (envelope) and ellipsometry. The comparison of the results obtained by different techniques, when investigating the same film, resulted in considerable discrepancies.

Ellipsometry measures the state of polarization of the transmitted or reflected light beam from a material. If a plane polarized wave is reflected from an optically smooth medium, its polarization change to an elliptical one, carrying information about the optical properties of the materials, as a result of the interaction (Figure 3.2.7).

The technique is independent of the absolute intensity, making the ellipsometric measurement very precise and reproducible. As a result, ellipsometry can be used to measure any physical property of an optical system that will induce a change in polarization state of the incident light wave, making it a versatile and precise characterisation method, useful in a wide variety of applications.

The one weakness of ellipsometry is the need to model the raw data, the models being physically based on energy transitions or simply by using free parameters to fit the experimental data.

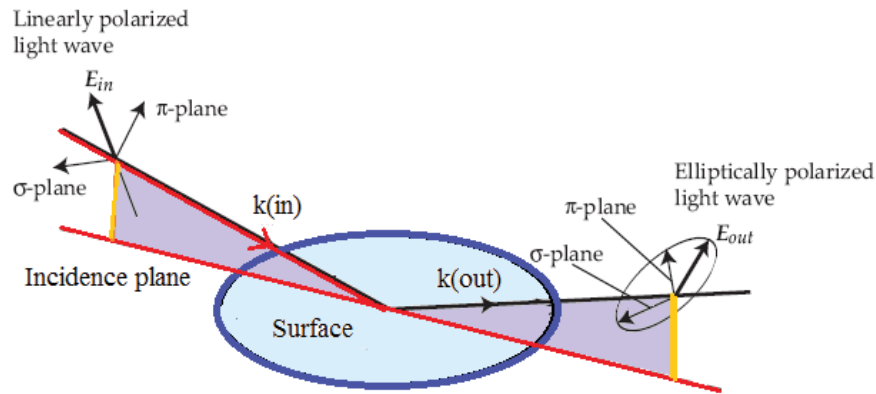


Figure 3.2.7: The general principle of an ellipsometric measurement, showing the change of the linearly polarized light, after reflection from the sample surface [adapted from <http://www.jawoollam.com/>].

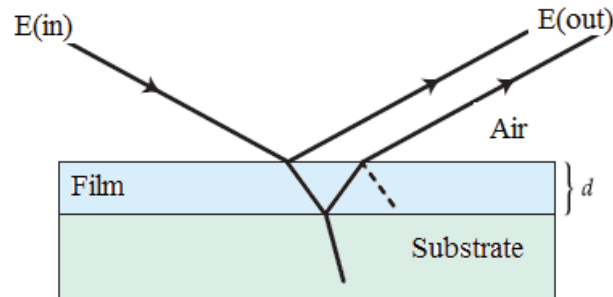


Figure 3.2.8: Illustration of a thin film on top of a substrate.

The main sources of systematic errors are: geometrical misalignment, wavelength errors arising from the non-ideal transfer characteristic of the modulator, depolarisation effects, which are mainly due to scattering, or problems with the initial calibration.

Summarizing, normal incidence reflectometry is a faster technique, especially suited for reflectivity measurements and for observing qualitative changes in the optical properties of materials, while ellipsometry, although more accurate, depends on parameter modelling in order to obtain quantitative results.

3.2.4 Electrical characterisation: Four probe electrical measurements including Hall effect mobility measurements

Electrical characterization of materials progress over time in three levels of understanding. In the beginning (early 1800's) both the resistance R and conductance G of a material were considered

as measurable physical quantities, their values being obtained from two-terminal current-voltage (I-V) measurements. It was observed that the modification of the sample shape determined different results, which determined the introduction of a new material property (resistivity or conductivity), which was independent on the specific sample geometry. Later, by the early 1900's, it was observed that different materials exhibit the same resistivity, while the “same” material might exhibit different values of resistivity, depending on its synthesis route. Several theories of electrical conduction were elaborated, but until the advent of quantum mechanics, no generally acceptable solution to the problem of electrical transport was developed. The quantum mechanics based theory introduced the definitions of carrier density n and mobility μ , which are capable up to date of explaining even the most complex electrical measurements.

The basic physical principle underlying the Hall effect is the well-known Lorentz force. For a bar-shaped semiconductor of n-type, the carriers are predominately electrons of bulk density n . If a constant current I flows along the longitudinal axis, from left to right in the presence of a z-directed magnetic field, the electrons initially drift away from the current direction toward the negative axis perpendicular to the longitudinal one, resulting in an excess negative surface electrical charge on this side of the sample. This charge results in a potential drop across the two sides of the sample, known as the Hall voltage. The magnitude of the Hall voltage is:

$$V_H = \frac{IB}{qnd} \quad (3.2.9)$$

where I is the current, B is the magnetic field, d is the sample thickness, and q (1.602×10^{-19} C) is the elementary charge. In some cases, it is convenient to use layer or sheet density ($n_s = nd$) instead of bulk density. One then obtains the equation:

$$n_s = IB/q|V_H| \quad (3.2.10)$$

The sheet resistance R_s of a semiconductor can be determined by use of the Van der Pauw resistivity measurement technique. Since sheet resistance involves both sheet density and mobility, one can determine the Hall mobility from the equation

$$\mu = \frac{|V_H|}{R_s IB} = \frac{1}{qn_s R_s} \quad (3.2.11)$$

If the conducting layer thickness d is known, one can determine the bulk resistivity ($\rho = R_s d$) and the bulk density ($n = n_s/d$).

As originally devised by Van der Pauw [211], it is used an arbitrarily, simply connected, thin-plate sample containing four very small ohmic contacts placed on the periphery (preferably in the

corners) of the plate. The objective of the resistivity measurement is to determine the sheet resistance R_s . As demonstrated by Van der Pauw, there are two characteristic resistances R_A and R_B , associated with the corresponding terminals shown of the thin-plate sample, which are related to the sheet resistance R_s through the Van der Pauw equation:

$$e^{-\pi R_A/R_s} + e^{-\pi R_B/R_s} = 1 \quad (3.2.12)$$

which can be solved numerically for R_s .

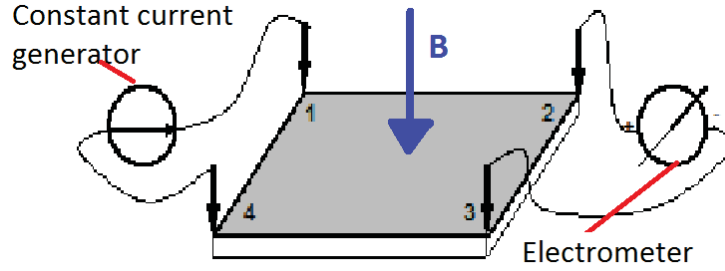


Figure 3.2.9: Illustration of Van der Pauw measurement set-up.

The bulk electrical resistivity ρ can be calculated using the formula:

$$\rho = R_s d \quad (3.2.13)$$

To obtain the two characteristic resistances, one applies a dc current I into contact 1 and out of contact 2 and measures the voltage V_{43} from contact 4 to contact 3 as shown in Figure 3.2.9. Next, one applies the current I into contact 2 and out of contact 3 while measuring the voltage V_{14} from contact 1 to contact 4. R_A and R_B are calculated by means of the following expressions:

$$R_A = V_{43}/I_{12} \text{ and } R_B = V_{14}/I_{23} \quad (3.2.13)$$

To measure the Hall voltage V_H , a current I is forced through the opposing pair of contacts 1 and 3 and the Hall voltage V_H ($= V_{24}$) is measured across the remaining pair of contacts 2 and 4. Once the Hall voltage V_H is acquired, the sheet carrier density n_s can be calculated via $n_s = IB/q|V_H|$ from the known values of I , B , and q .

There are practical aspects which must be considered when carrying out Hall and resistivity measurements. Primary concerns are:

(1) Contact quality, size, and uniformity. Large differences between the contacts' resistances, above 2-3 orders of magnitude, make the measurement impossible. The contacts transfer function must be linear (ohmic);

(2) sample uniformity and accurate thickness determination;

(3) thermal effects due to non-uniform temperature, leading to a parasitic thermoelectric current; together with the applied stationary magnetic field, leads to the appearance of an electric field, perpendicular to both the magnetic field and the thermal gradient, and thus to the sample's surface, known as the Nernst effect. This is easily addressed by averaging the results of measurements taken at opposite polarities;

(4) photoconductive and photovoltaic effects which can be minimized by measuring in a dark environment. Also, the sample lateral dimensions must be large compared to the size of the contacts and the sample thickness. Small errors arising from the sample's anisotropy or contact dissimilarities can be mitigated by averaging the results of measurements taken after reversing the field and switching the contacts. Finally, one must accurately measure sample temperature, magnetic field intensity, electrical current, and voltage.

CHAPTER 4

FERROELECTRIC OXIDE FILMS: FABRICATION AND PROPERTIES

Chapter 4 describes the deposition and characterization of ferroelectric SBN-50 and BST thin films. The films' structure and morphology is explored, and their optical properties are evaluated. An electrical bias has been found to induce birefringence in the films. The influence of strain on the films' structure and optical properties is considered and discussed.

4.1 The Fabrication of Ferroelectric Thin Films

BST and SBN-50 have been fabricated using a NEOCERA Pioneer 120 PLD system, shown in Figure 4.1.1.

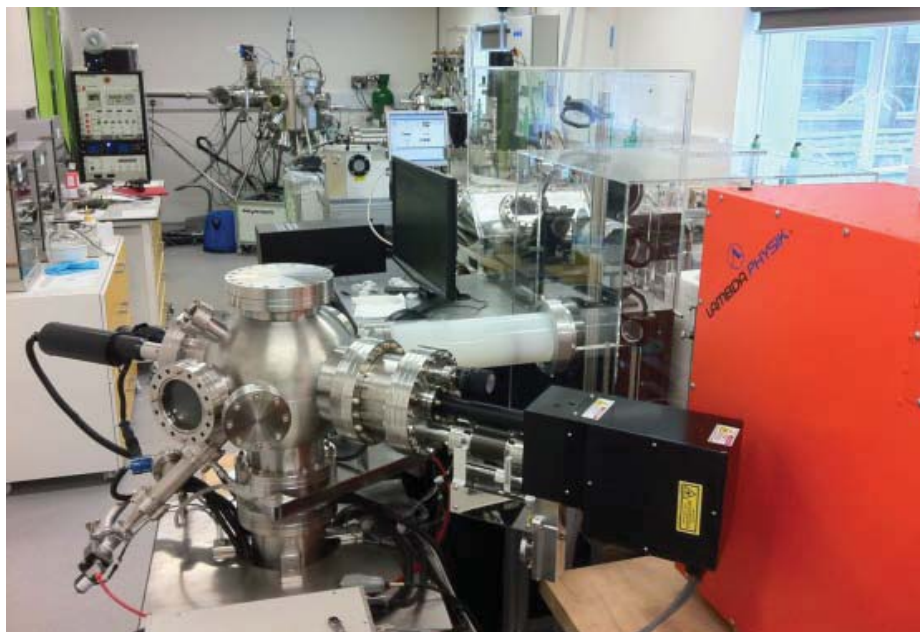


Figure 4.1.1: The NEOCERA Pioneer 120 PLD system,
excimer laser LAMBDA PHYSIK – KrF, 248 nm - not figured.

Figure 4.1.2 shows a snap-shot of the plasma plume. The substrate (sample) is glued to the heater with alumina diluted silver paste, to ensure the best heat transfer. The plasma plume is generated by an excimer laser (LAMBDA PHYSIK – KrF, 248 nm).

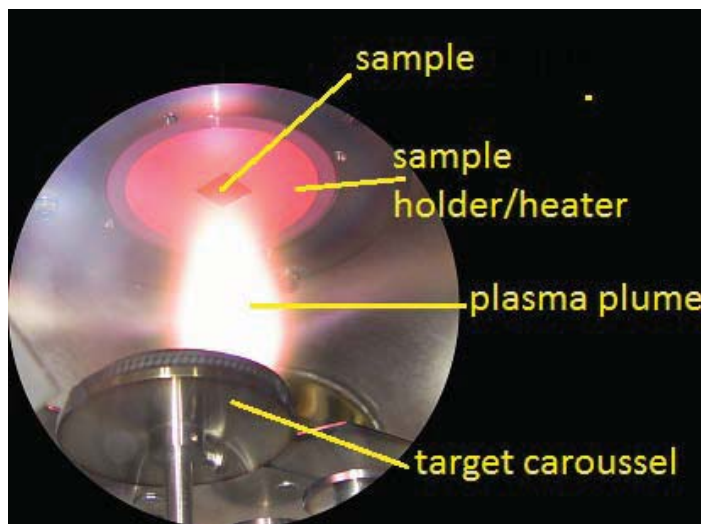


Figure 4.1.2: Plasma plume into the NEOCERA Pioneer 120 deposition chamber (courtesy of NEOCERA Inc. USA).

The target holder is fitted with BST or SBN and SRO targets switchable for the alternative deposition of the two materials. The BST thin films were deposited on MgO substrates. A bottom electrode of SRO was deposited first, then the ferroelectric film, and then another SRO electrode. To avoid the electrical contact between the SRO electrodes, the edges of the BST film were covered with vacuum compatible TiO_2 paste.

Prior to deposition, the substrates were washed for 5 minutes in isopropyl alcohol in an ultrasound bath, and blow dried with nitrogen. The substrates were attached to the substrate holder onto the resistive heater by alumina-diluted silver paste. The chamber was closed and pumped down to 10^{-6} Torr base pressure, after which the substrates were heated to deposition temperature at a rate of 10°C per minute. The process was carried out at 700°C for SRO films and at 740°C for the BST films. The substrates were then annealed in oxygen at 400 Torr for 30 mins, in order to remove any residual organic contamination, water, and to ensure the surface is epi-ready. The chamber was then pumped down to base pressure again. After this, oxygen was introduced in the chamber, and the pressure was controlled by adjusting mass-flow rate and pumping speed. The process pressure was set at 50 mTorr for SRO films and at 300 mTorr for BST films.

The laser frequency was 8 Hz at 520 mJ/pulse. The laser fluency was 0.8 J/cm^2 . The oxygen working pressure was 50 mTorr. After deposition the films were annealed under an oxygen atmosphere, at 400 mbar at deposition temperature and then cooled down. After being removed from the chamber, the deposited substrates were washed in an ultrasound bath using isopropyl alcohol and then in acetone for 5 minutes each.

SBN-50 films were also deposited as part of thin film capacitors using SRO electrodes. The deposition process was the same as for BST films, with a few differences. Unlike BST films, which were fabricated using commercially sourced targets, SBN-50 ceramic targets were sintered for this purpose, and the related work is described in Annex I. STO substrates were used, the temperature was varied from 650 to 750 °C, and multiple 1 hour sessions of oxygen relaxation at deposition temperature [212] and 400 mTorr were carried out after each run of 2000 laser pulses in order to limit the number of oxygen vacancies in the film. Considering a film thickness of 250 nm for a total of 10000 pulses, this corresponds to a maximum increase in the thickness of the SBN of 50nm between the annealing sessions.

Additionally, for all samples, the SRO contacts were coated by magnetron sputtering with silver through a metallic mask to provide a better contact with the biasing external electrodes used for electro-optical spectroscopic ellipsometry measurements.

4.2 The Structural Properties and Morphology of Ferroelectric Thin Films

4.2.1 Phase analysis

The XRD pattern shows well crystallized ($h00$) BST films. However, looking at the SRO, a small (211) peak can be distinguished. The concentration of the (211) phase increases with the oxygen pressure during film deposition, becoming significant at over 100mTorr. Table 2 presents 20 positions of the XRD maxima in Figure 4.2.3.a, as compared to the following JCPDS - ICDD cards:

- MgO	card no. 00-045-0946
- SRO orthogonal (SrRuO_3)	card no. 00-043-0472
- SRO cubic (SrRuO_3)	card no. 01-087-1246
- SRO tetragonal ($\text{Sr}_3\text{Ru}_2\text{O}_7$)	card no. ca00-047-0609
- BST cubic 50-50	card no. 00-039-1395

Table 4.2.1: XRD lines from Figure 4.2.1a, as compared with the JCPDS - ICDD cards:

Material	SRO	BST 20-80	BST 50-50	BST 80-20
Experimental value (2Θ)	42.95	43.02	42.90	42.57
JCPDS values MgO (200); Intensity-100	42.92	42.92	42.92	42.92
JCDPS values SRO orthorhombic (221); Inten- sity-1	42.96	42.96	42.96	42.96
Experimental value (2Θ)	45.78	46.19	45.18	45.51
JCPDS values BST 50-50 (200); Intensity-74	45.94	45.94	45.94	45.94
JCPDS values BST60-40 (200); Intensity-25	45.73	45.73	45.73	45.73
JCPDS values BST tetragonal (200); Intensity- 43	45.58	45.58	45.58	45.58
JCDPS values SRO orthorhombic (040); Inten- sity-35	46.18	46.18	46.18	46.18
JCDPS values SRO tetragonal (100); Intensity-7	45.81	45.81	45.81	45.81
Experimental value (2Θ)	71.32	71.9	70.32	70.92
JCPDS values SRO cubic (221); Intensity-0.6	71.34	71.34	71.34	71.34
JCPDS values BST 50-50 (300); Intensity-10	71.67	71.67	71.67	71.67
Material	SRO	BST 20-80	BST 50-50	BST 80-20
JCPDS values BST60-40 (221); Intensity-2	71.32	71.32	71.32	71.32
JCPDS values BST tetragonal (212); Intensity-6	70.94	70.94	70.94	70.94
Experimental value (2Θ)	94.04	94.04	94.04	93.68
JCPDS values MgO (400); Intensity-8	94.05	94.05	94.05	94.05
Experimental value (2Θ)	101.93	103.13	100.4	101.28
JCPDS values BST 50-50 (400); Intensity-8	102.63	102.63	102.63	102.63

All BST films exhibited textured growth along the $(00l)$ axis.

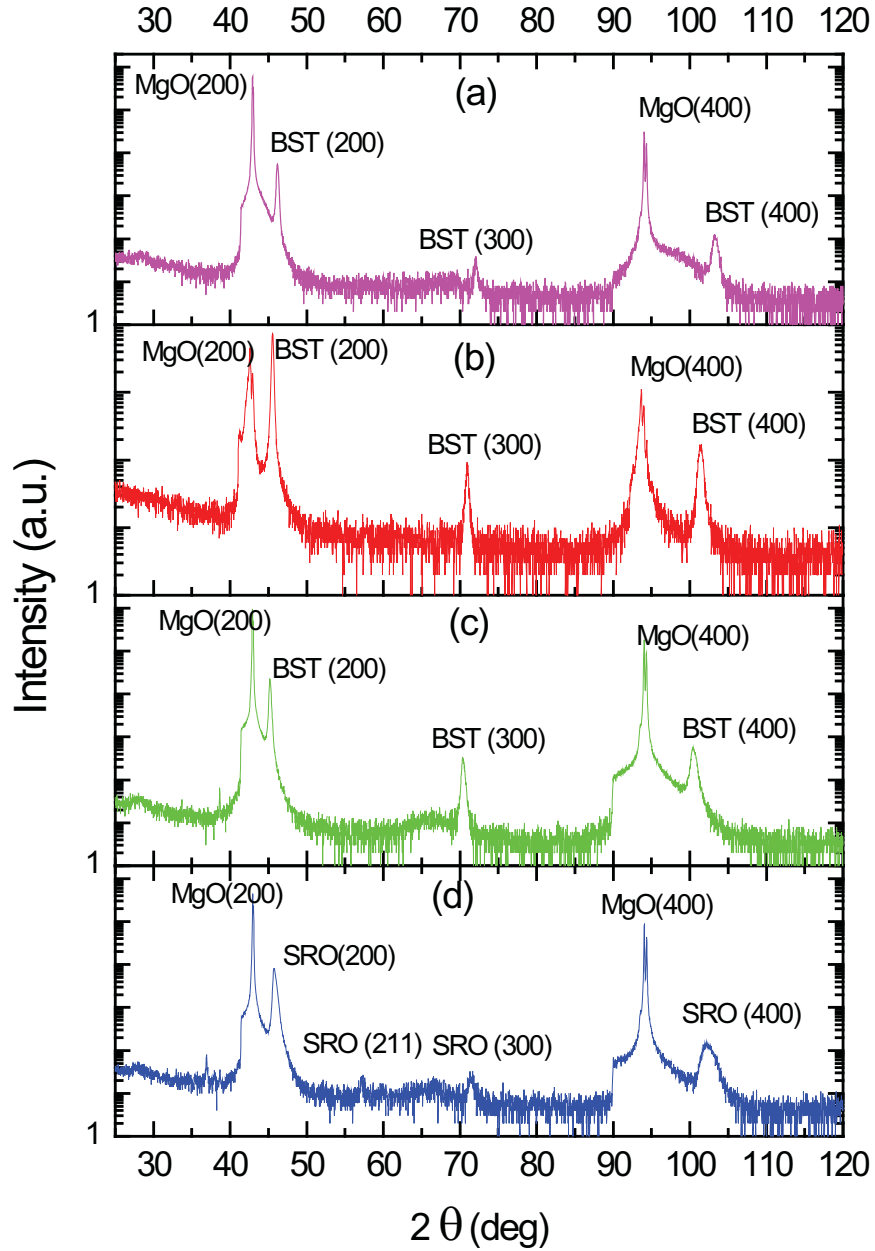


Figure 4.2.1a: XRD pattern of $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ ($x = 0.2, 0.5, 0.8$) and SRO thin films.

SBN films fabricated at 750 °C exhibited growth along a few high-Miller index directions, as well as an extra phase. Given the small size of these peaks when compared to those of the SRO bottom electrode, the film might consist of these crystallites embedded in an amorphous matrix. Films fabricated at lower temperatures were amorphous. Most likely, a deposition temperature higher

than 750 °C would have led to better crystallization. However, in our case, it would have exceeded the substrate holder's recommended operating range.

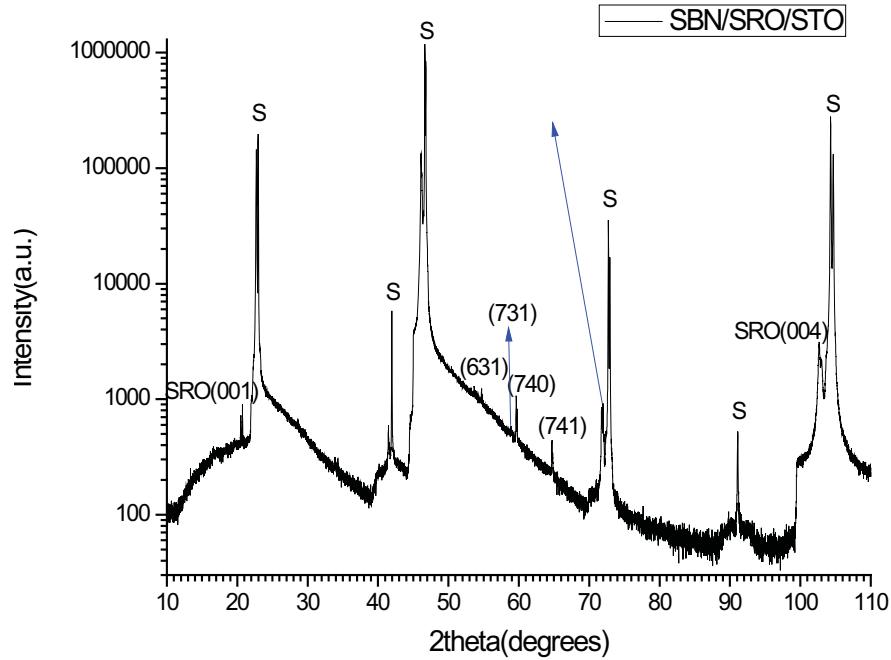


Figure 4.2.1b: XRD pattern of SBN50 films deposited on SRO covered STO substrates.

4.2.2 Surface morphology - AFM scans

MgO substrate surface characterization

The MgO substrates (10 X 10 X 0.5 mm) roughness was investigated by AFM. Figure 4.2.2 shows a scan of a MgO substrate. The roughness is below the size of the unit cell, and thus generated by the surface reconstruction due to the miscut angle.

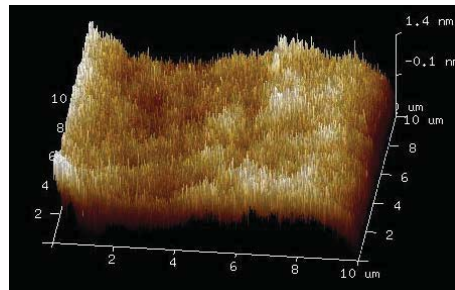
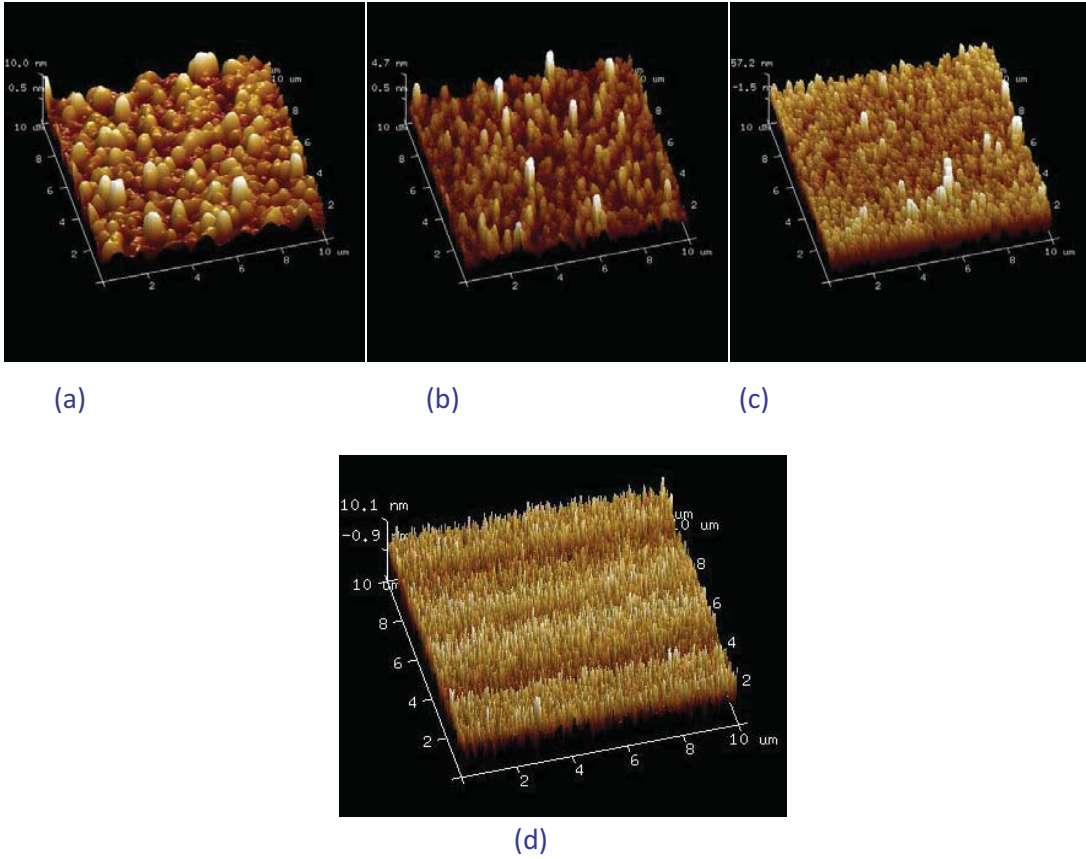


Figure 4.2.2: AFM scan of MgO substrate, (100), 0.5μm x 0.5μm, average roughness $R_a = 0.07$ nm; rms roughness $R_q = 0.3$ nm.

Surface characterization of BST and SBN films



Figures 4.2.3: AFM scan, (100), $10\mu\text{m} \times 10\mu\text{m}$, of (a) BST20 – $R_a=2.3\text{ nm}$; (b) BST50 – $R_a=1.2\text{ nm}$; (c) BST80 – $R_a=12.1\text{ nm}$; (d) SBN50 – $R_a= 3.5\text{ nm}$.

The deposited BST and SBN films were also subjected to AFM scans, using a Veeco Innova machine (Figure 4.2.3). It was observed that while for BST20 and BST 50 the roughness was very small, 2.2 nm and respectively 1.2 nm, the roughness of BST80 was around 12.1 nm. It might be that the BST 80 films had undergone a Curie transition while cooling, considering the Curie temperature of BST 80 film is 45.5°C [213].

The smoothness of the BST50 films marked them as the most suitable for electro-optic effect measurements.

4.3 Optical Properties of Ferroelectric Thin Films

The presence of bias-induced birefringence in the deposited samples was checked using a Filmetrics normal incidence reflectometer. Using MgO (001) substrate, a stack of thin films was designed to allow an easier biasing of the electrodes and also a simple positioning onto the table of the reflectometer. The stack (Figure 4.3.1 a) and b)) has a SRO layer as bottom electrode, a BST layer and again a SRO layer as upper electrode. The edges of the upper SRO layer are recessed (by coating with TiO_2 paste during deposition) to avoid the contact with the bottom layer. Eventually, two Ag electrodes were deposited by magnetron sputtering for the contact with external biasing electrodes.



Figure 4.3.1: The BST /SRO stack (a); the upper view of the stack – the light beam from the ellipsometer lies on the diagonal opposite to the Ag contacts (b).

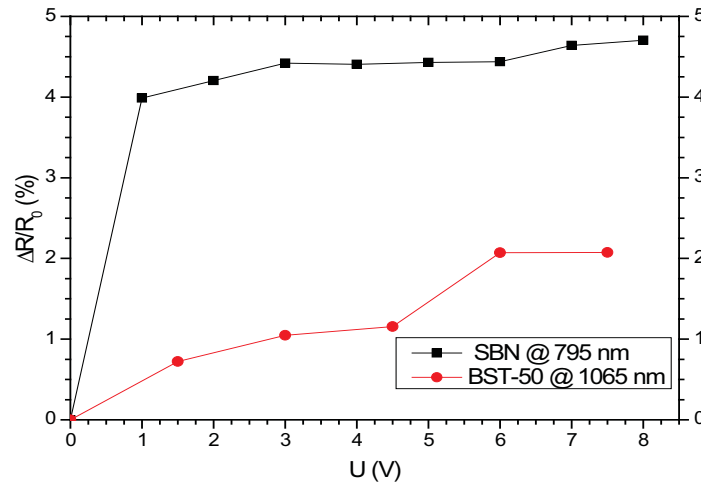


Figure 4.3.2: The maximum relative reflectivity change as a function of applied bias for SBN50 and BST50.

Figure 4.3.2 shows the relative reflectivity change as a function of applied bias, confirming the presence of an electro-optic effect. For maximum accuracy, the changes in relative reflectivity were measured at local maxima of the thin film interference, which in this case, takes place at normal incidence. Due to the different optical constants and thicknesses of BST and SBN films, these maxima are located at different wavelengths. However, this is not enough to ascertain the exact change in the refractive index of the measured samples. In order to quantify the bias induced birefringence, a WVASE32 Spectroscopic Ellipsometry System was used to investigate the changes in the refracting index of the deposited films, due to the applied electrical bias and temperature variation. The wavelength range explored was 400 – 1600 nm [214, 215]. The experimental set up was similar to the employed for normal incidence reflectometry.

4.3.1 Modelling Ellipsometric Data

The ferroelectric oxide layer, was treated as a homogenous Cauchy layer, as it is the standard first choice when dealing with materials which are transparent in most of the visible range. The Cauchy equation gives the refractive index as:

$$N(\lambda) = A_n + B_n/\lambda^2 + C_n/\lambda^4$$

where A is the constant term, B gives the curvature of the refractive index profile and C adds extra curvature at short wavelengths.

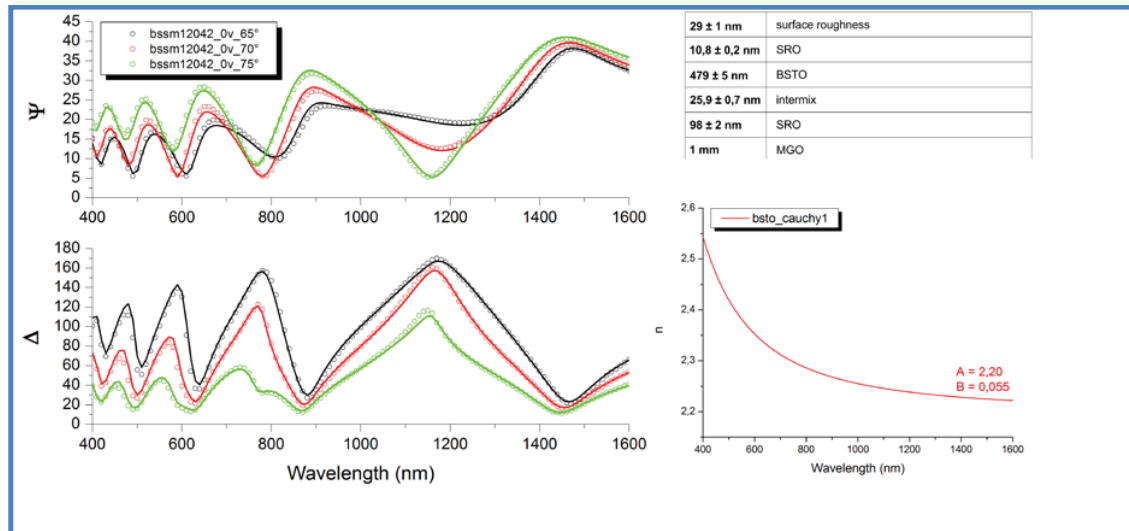


Figure 4.3.3: Perfect fitting of the measured data without bias (left figures) was obtained using a simple model (top right). The real refractive index was measured (bottom-right).

The refractive index of the BST film was obtained by fitting the measured ellipsometric data with a simple multilayer optical model, using the WVASE32 software package. This incorporated an intermixing layer between the dielectric film and the bottom electrode, corresponding to the roughness of the latter, as well as surface roughness. As the values of surface roughness were greater than the thickness of the top electrode, no intermix between the dielectric and top electrode was incorporated.

The optical properties of the conductive electrodes were described using the Tauc-Lorentz oscillator model. This model builds upon the standard Lorentz oscillator model, incorporating a small asymmetry. In addition to the three parameters of the Lorentz oscillator - the photon energy at the centre of band (at the position of maximum amplitude, for the Tauc-Lorentz oscillator), the broadening parameter (FWHM) and the value of the maximum amplitude, it incorporates a fourth, the energy where ε'' goes to zero.

The refractive index of thin-film SRO electrodes was extracted from the measured data using the VWASE32 software. The same n & k parameters can be used to fit the data collected from 100 nm thick SRO films, as used in the EO optical measurements performed on BSTO, and 50 nm thick films, which had been the first attempt at SRO electrodes. The exploration the SRO film's optical constants was not the focus of this work. It is presented in the next chapter, where a different series of samples was fabricated for this purpose.

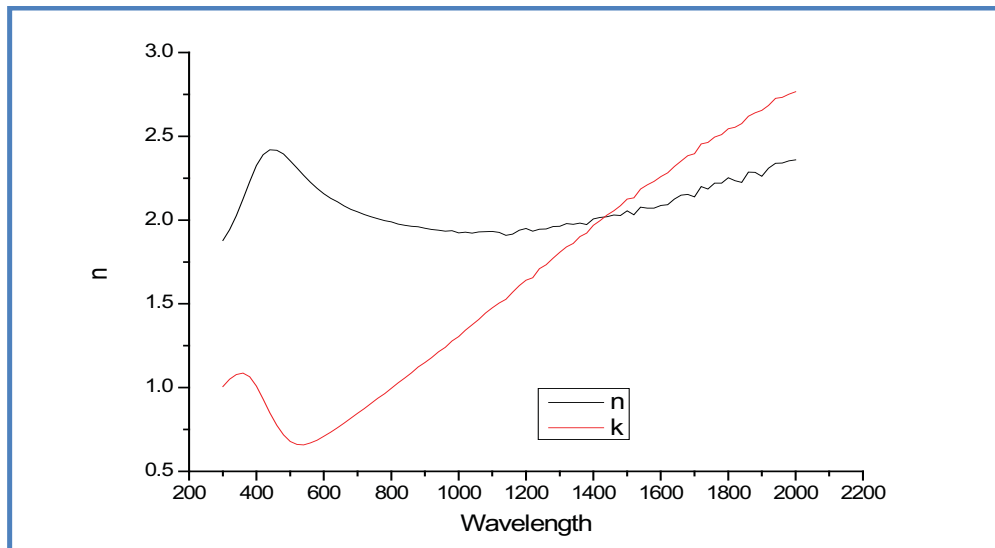


Figure 4.3.4: The refractive index and loss coefficient for the SRO obtained for a 100 nm thick electrode, the same as used in the EO measurement on BST.

4.3.2 Electro-Optical and Thermo-Optical Tunability

Figure 4.3.5(a) shows the bias dependant refractive index of the BST50 film. This is close with the results obtained earlier in our group on BST50 [216]. However, this effect is combined with a thermo-optic effect, due to the heat generated by the leakage current. In order to proper understand these effects, a series of heating-cooling cycles were performed without applying any bias to the sample as shown in Figure 4.3.5 (b). Although the initial heating cycle leads to a decrease of 0.005 in the refractive index, while varying the temperature from 30 to 90 °C the subsequent cycles only produced a change of 0.001, in the 60 – 90 °C region. It could be that the change of the refractive index is due to the strain built up in the film and interfaces while cooling after deposition, which was fully eliminated in the subsequent thermal cycles.

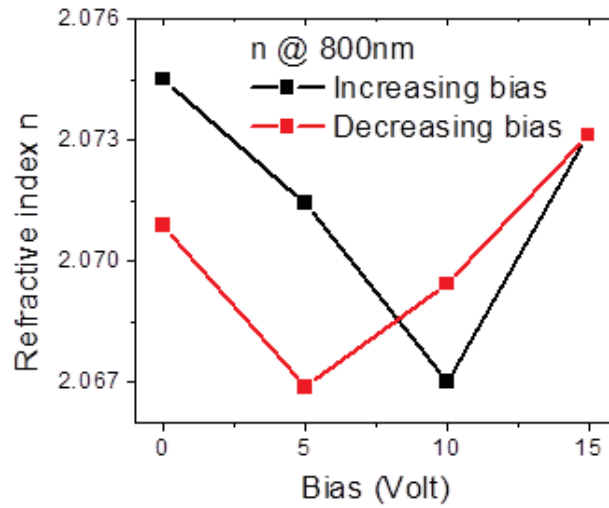


Figure 4.3.5 a: Variation of the refractive index with the bias voltage, for the BST50 film.

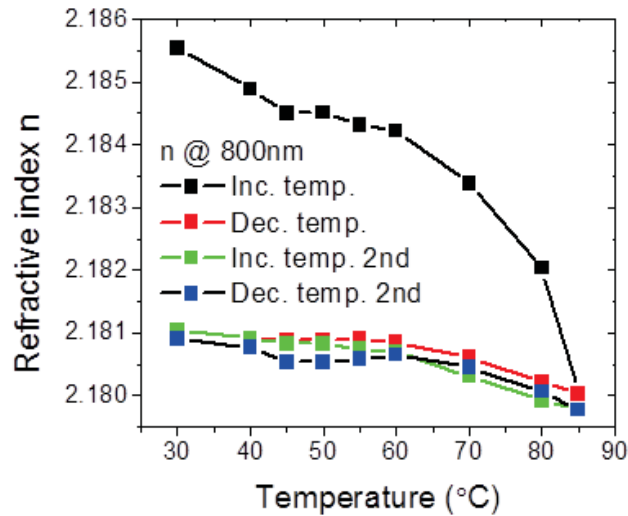


Figure 4.3.5 b: Variation of the refractive index with the temperature, for the BST50 film.

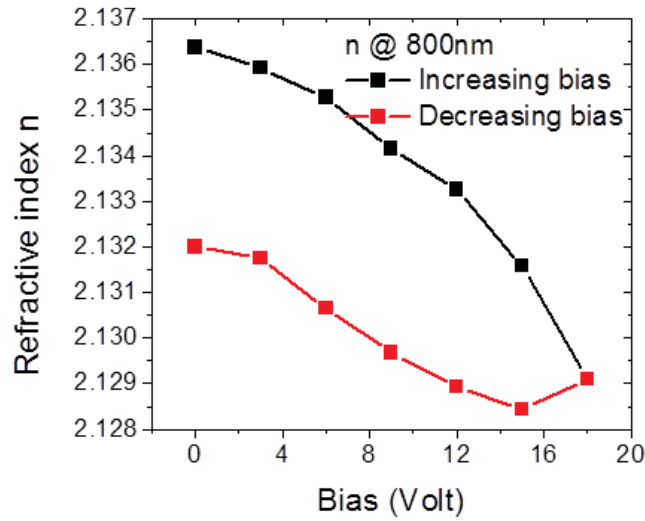


Figure 4.3.6a: Variation of the refractive index with bias voltage, at 20-30°C for the BST50 film.

In order to eliminate most of the heating, the sample was glued with silver paste to a radiator and a cooling fan was used, allowing a better measurement of the electro-optic effect. A Peltier cooler requires a consistent heat flow to be stable. This would not be the case at low applied bias, unless the sample is cooled below the dew point, which would not be acceptable for optical measurements. Even so, the temperature of the sample, as measured by a contact thermocouple and a pyrometer did not exceed 30°C. The different values in the refractive index (Fig 4.3.6.a) under no bias as compared to the previous measurements are due to the different model of the thin film stack being used. A hysteresis can be observed (Fig. 4.3.6.a and 4.3.6.b), as expected of a ferroelectric under induced polarization.

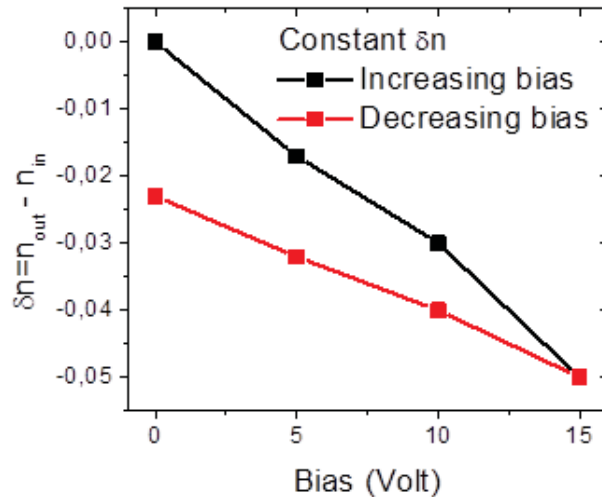
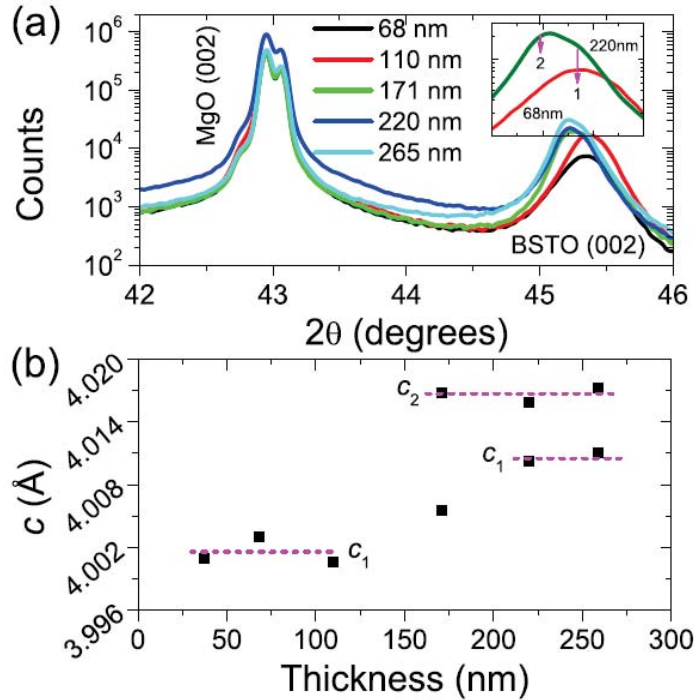


Figure 4.3.6b: Variation of the birefringence with bias voltage, for the BST50 film.

The largest birefringence ($\delta n = n_{in} - n_{out}$) induced by electro-optic effect obtained in our measurements is 0.05, which is comparable to the value of 0.03 estimated by Dicken et al. [217].

4.3.3 Considering Strain in Ferroelectric Thin Films.

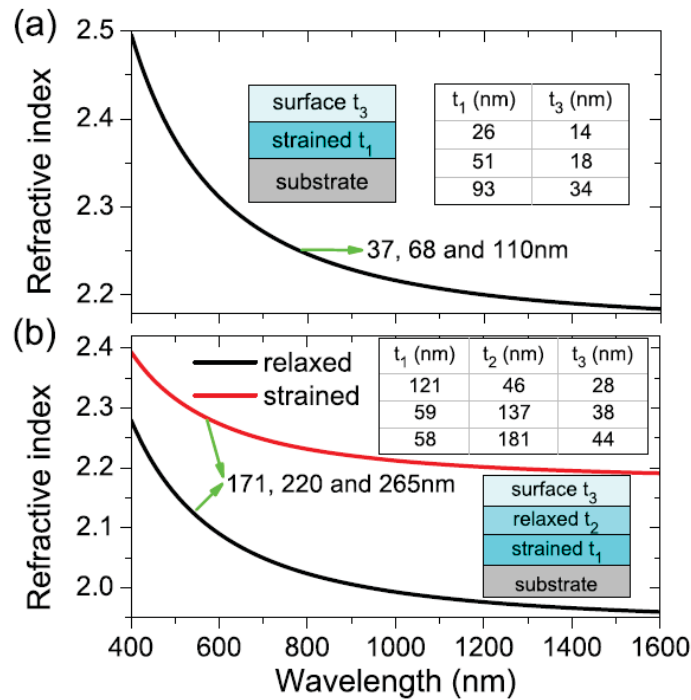
Heteroepitaxial strain in ferroelectric thin films is known to have a significant impact on both their low and high frequency dielectric properties. Because heteroepitaxial strain varies along the films direction of growth in a non-linear and not necessarily monotonous way, the film's local dielectric properties can be considered to be inhomogeneous. Therefore, a homogenous and isotropic model does not necessarily provide an accurate description of the optical properties of such materials. To this end, spectroscopic ellipsometry was used to determine the evolution of strain with film thickness and the strain distribution within the film [216]. BST50 films of different thicknesses were grown on MgO substrates, in conditions similar to those described above, as part of the training on the PLD system.



Figures 4.3.7: (a) XRD pattern of BST50 films of various thicknesses; (b) the calculated value of the c -parameter as calculated from the position of the (002) peak [216].

Figure 4.3.7 shows the modelled variation of the c parameter as a function of film thickness. The thinner films (68 nm and 110 nm-thick BSTO films) exhibit a single symmetric (002) peak that can be well fitted to a Gaussian function, from which a lattice parameter c_1 was extracted (Figure 4.3.7b).

The peaks for thicker films exhibit a significant shift to smaller angles, presenting a considerable broadening. This is due to the strain gradient present in such films [212]. Based on the observed broadening, these peaks were modelled as doublet, which was fitted using a superposition of two Gaussians with one peak centered close to position observed in the thinner films and the other located at a smaller angle. This is emphasized in the inset of Figure 4.3.7 (a) showing a magnified version of the (002) diffraction peaks for the 68 nm and 220 nm-thick films. The c -parameter for each film was calculated from the measured (00l) peak positions, being shown in Figure 4.3.7 (b) as a function of film thickness. In the figure, BSTO films thinner than 171 nm are represented with one lattice parameter c_1 , while thicker films are represented with two effective lattice-spacings c_1 and c_2 with $c_2 > c_1$.



Figures 4.3.8: (a) Refractive index obtained for 37 nm, 68 nm, and 110 nm thick BST50 films

(b) Refractive indexes of the strained and relaxed portions of the film, and the fitted thickness of each part [216].

Figure 4.3.8 shows the fitted thicknesses of the various regions of the film. Films up to at least 110 nm thick are modelled as a strained interface layer, with a surface layer on top. Films from 171 to 265 nm thick are modelled as a stack consisting of a strained interface layer, a relaxed middle

layer and a surface layer. The proportion of the film which is relaxed increases with the film's thickness. Still, such a sharp change in refractive index along the vertical axis is not necessarily plausible. However, this work has shown that ellipsometry can be used to gauge strain in BST films.

Figure 4.3.9 shows the evolution of the strained layer's thickness with the thickness of the BST50 film. The major drawback of this model is that it includes too many variables. While the non-uniform profile of strain, and thus, refractive index, along the films direction of growth has been established, the validity of any such actual profile is questionable. Therefore, adding possibly more variables to account for the differing contributions of different regions to the observed electro-optic response would not yield reliable results.

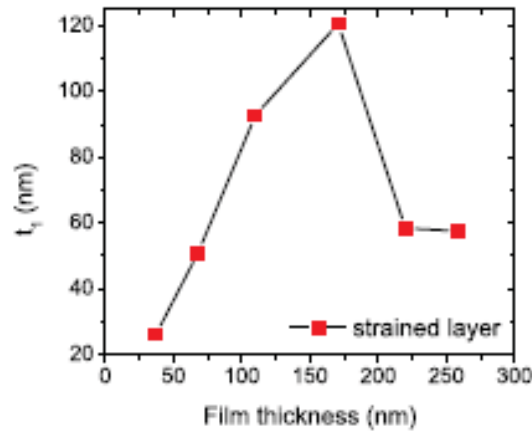


Figure 4.3.9: The thickness of the strained layer as a function of total film thickness [216].

4.4 Summary and Conclusions

BST and SBN films, of optical quality have been grown on SRO electrodes on MgO substrates. BST exhibited a clear orientation along the c -axis, as required for electro-optical applications. Therefore, we have demonstrated the ability to fabricate epitaxial MgO/SRO/BST heterostructures for electro-optical measurements. SBN films were polycrystalline, and weakly crystallized, probably due to the insufficient deposition temperature. It is important that both BST and SBN films, despite the latter's polycrystalline orientation, were found to exhibit an electro-optical response, making them suitable for use as active plasmonic materials. Ellipsometry has been used to measure the effective response of the BST film in a homogenous and isotropic approximation. However, residual strain has been shown to influence the film's optical properties, and its variation along the films' direction of growth is characterised by a non-uniform profile, which is strongly influenced by the film's total

thickness. Given the exponential attenuation, along the films's direction of growth, of a surface plasmon propagating along the surface (Fig. 2.2.1), the properties close to the interface, and their changes with applied bias or temperature, are the most relevant to plasmonic devices. This, and the film's non-uniform nature, mentioned above, limit the usefulness of effective optical properties extracted using a uniform film model. Therefore, further work is needed in order to accurately measure the change in dielectric constant at and close to the interface between the ferroelectric and the top electrode.

CHAPTER 5

Materials for Passive Plasmonic Structures

Chapter 5 is concerned with the work carried out on electrode materials form thin film plasmonic devices, namely SRO, TiN and Ag. Section 5.1 describes the deposition process of SrRuO_3 , and the effects of the deposition parameters on the films structure, upon charge carrier concentration and mobility, and upon the dielectric constants. The relation between charge carrier dynamics and optical constants in the near-infrared range was elucidated. Section 5.2 describes the ongoing work with TiN thin films: the deposition process and the effects of the deposition parameters on films structure. In the following section the effect of the deposition parameters upon the charge carrier concentration and mobility, conductivity, and optical constants are described and discussed. Section 5.3 describes the ongoing work with thin Ag films: the deposition process and the effects of the He addition to the deposition atmosphere on films structure, surface roughness, the electrical resistivity and optical reflectivity are described and discussed.

5.1 *SrRuO₃ Thin Films*

5.1.1 Fabrication of SrRuO_3 Thin Films

Light-scattering is a critical issue in the plasmonic structures due to the resonant nature the light – matter interaction, which may be reduced by dissipative losses. At optical frequencies these losses may be particularly significant.

To solve the problem, several solutions are considered in the literature, including the search for better plasmonic media among metals, metallic alloys, semiconductors and conductive oxides [218 – 220]. Another approach aims to compensate losses by using a combination of metamaterials with various optical gain media [221 – 223]. These solutions are created as a response to an ideal situation, in which the Joule losses are the most important. However, the dissipation rates measured experimentally are higher than expected from Ohm's law alone, being generated by the surface

roughness and grain boundary scattering due to the polycrystalline nature of the deposited films [224]. Therefore, plasmonic losses are expected to be considerably smaller in heteroepitaxial films.

For hetero-epitaxial film growth to occur, the lattice mismatch between the in-plane lattice parameter of SrRuO_3 and that of the single crystal substrate should be minimised. Otherwise, the lattice mismatch generates a strain which can affect the structural, electrical and optical properties of the SrRuO_3 films. The best lattice mismatch for the SrRuO_3 thin film are obtained for SrTiO_3 (0.6 %) and LaAlO_3 (1.7%). A fine match should also exist between the relative dielectric constants of the films and substrate. The single crystal SrTiO_3 exhibits high relative dielectric constant ($\epsilon \approx 300$ at 300 K), limiting the use at high frequencies. On the other hand, LaAlO_3 is prone to form crystallographic defects [e.g., twin planes along (100)], restricting its use, especially in microwave devices.

The mono-crystalline MgO substrates, having a low relative dielectric constant ($\epsilon_r(\omega=0) \approx 10$ at 300 K; $\tan\delta \approx 10^{-5}$) seem to be more appropriate for the plasmonic applications of SrRuO_3 , despite their relatively large lattice mismatch ($\sim 6.7\%$).

There are few reports on SrRuO_3 films grown on MgO by pulsed laser deposition. Choi et al., reported the growth of SrRuO_3 films at different substrate temperatures and oxygen pressures; (001)- or (h00)-oriented films were obtained only at pressure higher than 150 mTorr [225]. Another issue is related to the fact that in the previous reported XRD studies on SrRuO_3 films grown on MgO substrates, the presented XRD patterns only shows data at $2\theta < 55^\circ$, leaving a substantial part of the measurement range unexplored. Summarizing, the existing data in the literature are not sufficient for providing a comprehensive study about the effect of the oxygen pressure on the SrRuO_3 growth process on MgO substrate, aiming for plasmonic application. Previous work in our group [226] has studied the relationship between deposition parameters, structural and electrical properties of SrRuO_3 films. The aim of the work presented here was to build upon those results and relate the structural properties to the electron structure and optical constants, thus evaluating SrRuO_3 as a plasmonic material [227].

SrRuO_3 thin films were deposited by a PLD (Neocera Pioneer 120) system with a KrF excimer laser ($\lambda = 248$ nm). The system allows automated process sequences (from pumping down to final thermal treatment of the films). A sintered SrRuO_3 target $\phi = 2''$ and 5 mm thick (PVD Products), was used to deposit the films on (001)-oriented single crystal MgO substrates with an area of 1 cm^2 (Crystal GmbH, Berlin). The target rotated clockwise at constant velocities during the deposition process. The target rotation is necessary for reducing target erosion and uneven consumption of its surface. As documented before, the target rotation hinders the deposition of the particulates on the substrate, resulting in a decrease of the films roughness [228].

The substrates were prepared according to the same procedure described in the former chapter. Prior to each deposition process, the deposition chamber was pumped down to 8×10^{-6} Torr, and the SrRuO₃ target was ablated for surface conditioning. The deposition set-up is similar to that used by our group in earlier work on the same material [226]. The deposition parameters used in the experiment fit in a slightly narrower range around those which have produced the best crystalline structure and electrical conductivity, while fluence was slightly increased from 0.8 to 1.0 Jcm⁻², with the aim of achieving perfect (00l) growth.

After pump-down, the substrates were heated to deposition temperature, and then annealed at deposition temperature in oxygen, at a pressure of 500 mTorr, for 30 minutes. The chamber was then pumped down to base pressure again, while maintaining the substrate's temperature. During deposition, the oxygen pressure was varied between 20 and 300 mTorr. The as-grown films were in situ post-annealed for 20 min at the deposition temperature at 700 Torr oxygen pressure and then slowly (10 °C/min) cooled down to room temperature. Then the optimum conditions were used for the preparation of all the studied SrRuO₃ films.

All SrRuO₃ films were analysed ex-situ in open atmosphere, at room temperature.

An X-ray diffraction system (Bruker D2 Phaser), equipped with a graphite monochromator coupled with a scintillation counter detector using Cu K_α radiation ($\lambda = 1.5405$ nm) was used in the Bragg-Brentano mode in order to investigate the crystallographic structure and phase composition of the films. The 2θ range was 15 – 110°, and the step size was set at 0.03.

Atomic force microscopy (AFM) was performed on a Bruker INNOVA instrument. The microscope was vibration-damped. Commercial pyramidal phosphorus doped silicon tips (Veeco model RTESPA), mounted to a cantilever with a length, resonance frequency and nominal force constant in the range of 115 - 135 μm, 295 – 349 kHz and 20 - 80 N/m respectively, were used.

The film thickness of all samples was measured using a Dektak 150 surface profilometer from a step height in a masked area on the substrate, using a low-inertia stylus sensor (12.5 μm radius). Each measurement was taken on 4.0 mm scan length with 49 μN contact force and 100 μm/s scan speed. Five profilometry measurements were made for each specimen and a mean value was calculated. The deposition rate was measured and the number of pulses was adjusted for each deposition pressure so that the thickness of each sample was 100 ± 5 nm.

Figure 5.1.1 shows the XRD patterns for the samples grown at different oxygen pressures. All films exhibited a predominant (00l) orientation. The peaks identified at ~41.6° and ~90.59°, and ~42.9° and ~93.9° correspond to the (002) and (004) planes of the cubic SrRuO₃ and MgO, respectively [229]. The peaks around 55° and 66° were identified as tetragonal RuO₂ (211) and (310), respec-

tively [230]. The peak at 57.4° was identified as SrRuO_3 (123) belonging to the orthorhombic structure [231]. The intensity of MgO peaks changes from pattern to pattern due to randomly positioning of the samples relative to the azimuthal angle. The ‘shoulder’ observed adjacent to substrate peaks, at lower angles, is a higher order diffraction maximum, which becomes visible because of the logarithmic scale and the good quality of the single crystal substrate. It is not visible at higher angles because of the inevitable imperfection of the samples alignment, which leads to a small translation movement associated with the rotation.

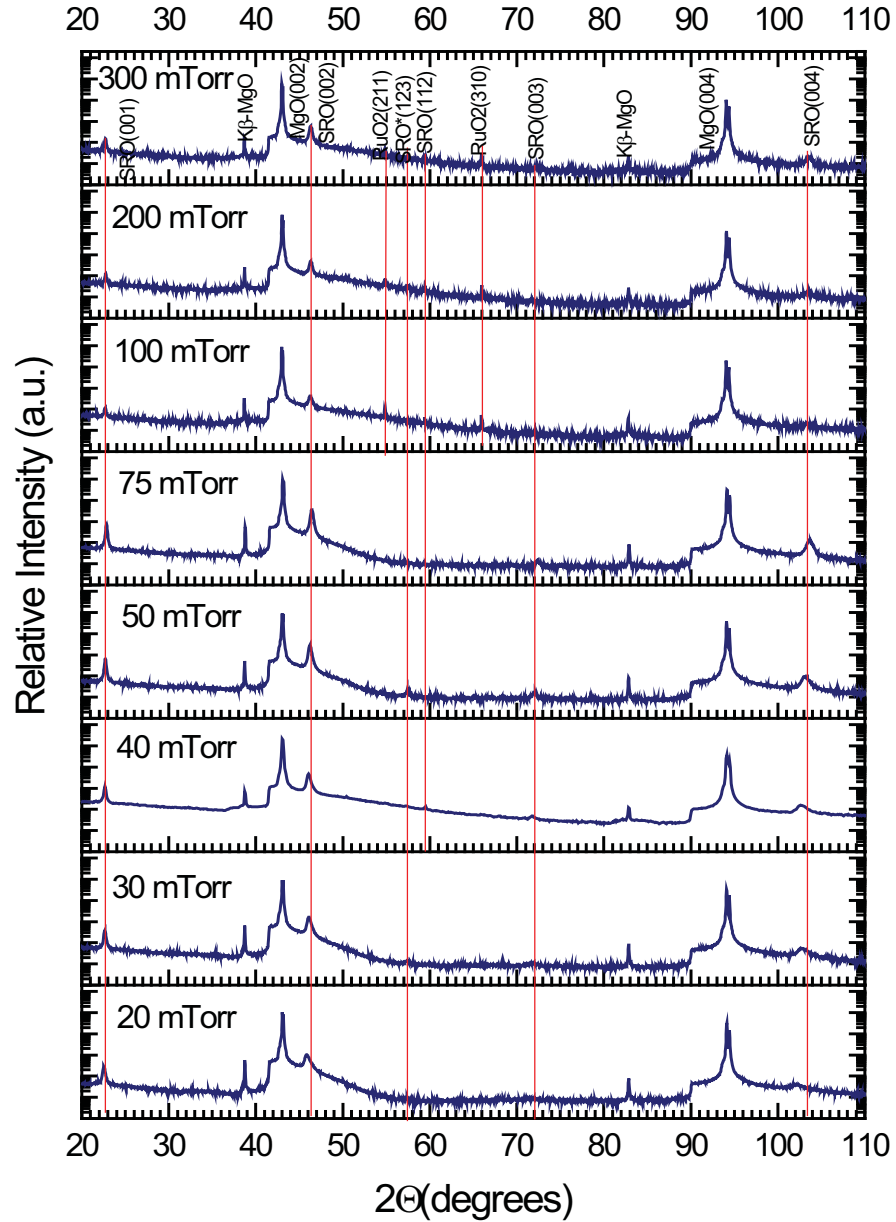


Figure 5.1.1: XRD patterns of SrRuO_3 films grown on MgO (001) substrates at different oxygen pressures.

In the samples deposited at high oxygen partial pressures (100 – 300 mTorr) inclusions of (112) and (123) oriented orthorhombic phase as well as RuO_2 were observed. No other inclusions were observed in the film deposited at 75 mTorr. Below this pressure, growth along the (123) direction can be observed. These results are in agreement with previously published results regarding SRO films on MgO substrates.

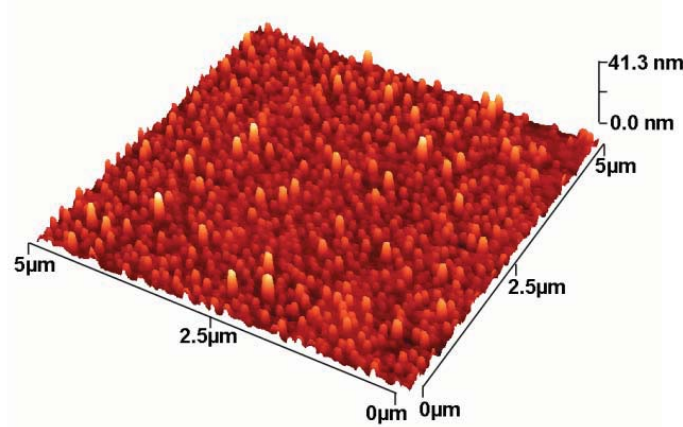


Figure 5.1.2: AFM image obtained in contact mode of the SrRuO_3 film on MgO substrate grown at 75 mTorr oxygen pressure ($\text{rms}=5 \text{ nm}$, $R_t=41.3 \text{ nm}$).

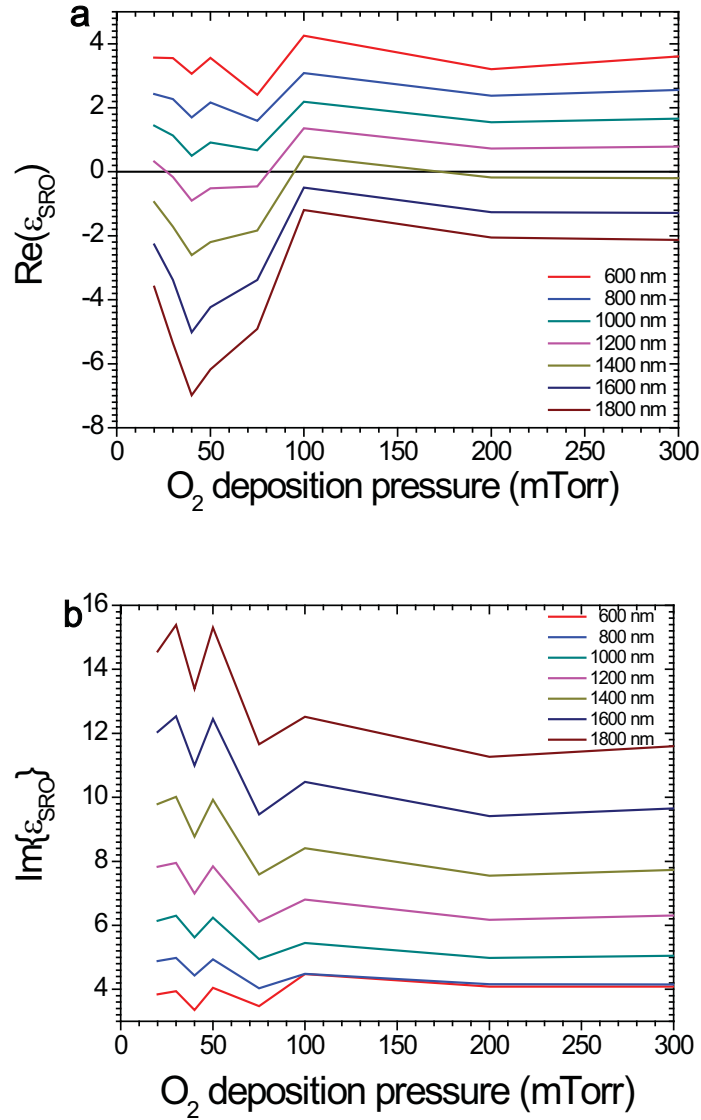
Figure 5.1.2 shows the surface morphology of the film deposited at 75 mTorr, as measured by contact-mode AFM. All the films exhibited a smooth surface, with a surface rms roughness of 5-10 nm, making them suitable for optical applications. Figure 5.1.2 also shows the maximum height of the profile $R_t = 41.3 \text{ nm}$, defined as $R_t = R_v + R_p$, which are the maximum valley depth (R_v) and the maximum peak height (R_p). The reduction of the SRO film's thickness below a certain limit ($\sim 30 \text{ nm}$) would be accompanied by an increase of the surface roughness [232].

5.1.2 Properties of SrRuO_3 Thin Films

The electrical resistivity and charge carrier concentration and mobility of the films were investigated by Ecopia HMS-3000 Hall measurement system with Van der Pauw geometry at 0.55 T magnetic field, using soldered indium contacts.

The optical characterisation of the films was done using a Horiba Jobin-Yvon Uvisel 2 ellipsometer. Phase-modulation reflection ellipsometry was used for all measurements at a 70° angle of incidence. For all measurements, the signal was acquired from an elliptical spot size (2 mm x 0.7 mm). After the acquisition, the data were post-processed to determine optical parameters of the films in the wavelengths range 300 – 2000 nm. The MgO substrate optical constants [233] and thick-

ness of SrRuO_3 were considered known and only the refractive index was fitted via the Marquardt minimization algorithm [234]. No pre-defined function (Drude, Tauc-Lorentz etc.) was used for the determination of the optical constants of SrRuO_3 ; they were all directly fitted to the experimental data via the ‘point-by-point’ method. This was done in order to insure the extracted results depend only upon experimental data, without being affected by predetermined theoretical constrains, which would result from a model.



Figures 5.1.3 a: Variation of the (a) real $\text{Re}\{\epsilon_{\text{SRO}}\}$, and (b) imaginary $\text{Im}\{\epsilon_{\text{SRO}}\}$ parts of the dielectric constant, versus oxygen pressure, for the all SrRuO_3 films.

Figures 5.1.3 present the variation of the real ($\text{Re}\{\epsilon_{\text{SRO}}\}$) and imaginary ($\text{Im}\{\epsilon_{\text{SRO}}\}$) parts of the dielectric constant versus the oxygen pressure, for all SRO films. Further discussion is centred on the films properties at four wavelengths: 400, 600, 800 and 1000 nm. It is easily observed that the behaviour at low wavelengths (400 and 600 nm) is different from the one exhibited at higher wavelengths. For the high deposition pressures (≥ 100 mTorr) the absorption has higher values for the wavelengths 800 and 1000 nm, and lower ones at shorter wavelengths (400 and 600 nm).

Figures 5.1.4 present the variation of the real and imaginary parts of the dielectric constants versus wavelength, for the SRO films deposited at different oxygen pressures. The real part of the dielectric constant for the films deposited at lower pressures (≤ 75 mTorr) present a maximum located at lower wavelengths, as compared to the films deposited at pressures (≥ 100 mTorr), the maximum of $\text{Re}\{\epsilon_{\text{SRO}}\}$ being shifted to shorter wavelengths.

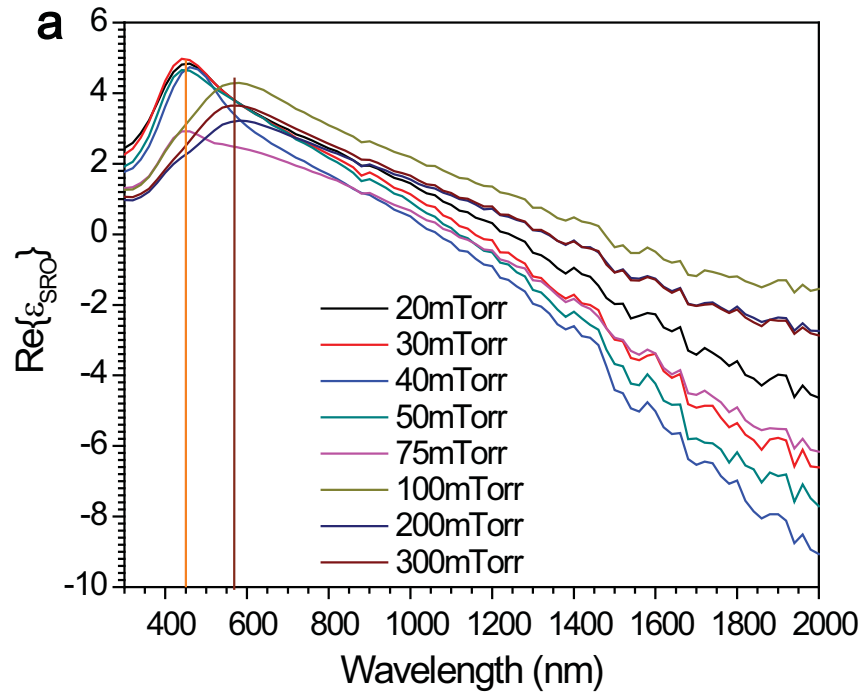


Figure 5.1.4 a: Variation of the real $\text{Re}\{\epsilon_{\text{SRO}}\}$ part of the dielectric constant versus wavelength, for the SrRuO_3 films deposited at different pressures

The minimum values of $\text{Re}\{\epsilon_{\text{SRO}}\}$ are not easy to be accurately located, by this simple analysis. However, the variation of $\text{Im}\{\epsilon_{\text{SRO}}\}$ clearly shows a maximum and a minimum, the values being shifted to higher wavelengths for the films deposited at pressures oxygen ≥ 100 mTorr. Note that for

the film deposited at 75 mTorr, with the best crystalline structure, $\text{Re}\{\epsilon_{\text{SRO}}\}$ presents a second maximum shifted to higher wavelengths.

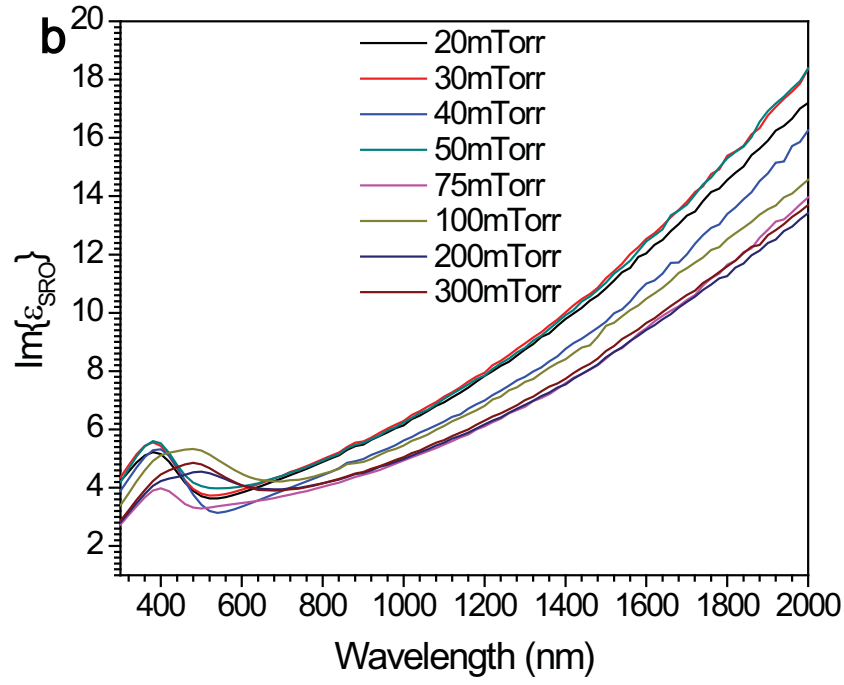
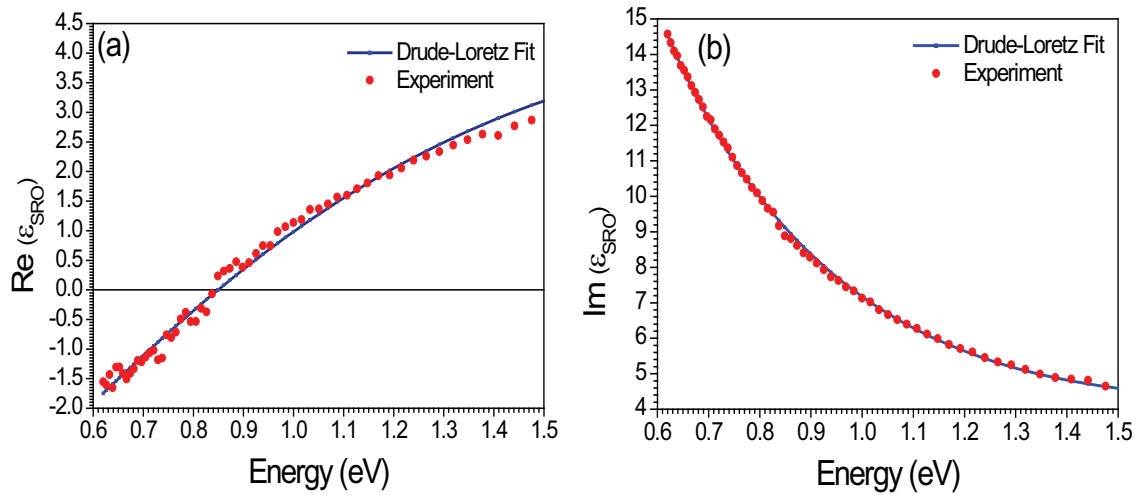


Figure 5.1.4 b: Variation of the imaginary $\text{Im}\{\epsilon_{\text{SRO}}\}$ part of the dielectric constant versus wavelength, for the SrRuO_3 films deposited at different oxygen pressures.



Figures 5.1.5: Experimental and fitted values of the (a) real and (b) imaginary dielectric constants of the 100 nm thick SrRuO_3 film on MgO substrate grown at 100 mTorr oxygen pressure.

Figure 5.1.5 shows in detail, as an example, the experimentally determined optical constants for the film prepared at 100 mTorr O₂ pressure. The real part of the dielectric constant monotonously increases, while the imaginary part decreases in this spectral range. In order to understand the nature of the optical properties, the spectral dependence of the permittivity was fitted using the Drude model with a Lorentz-type oscillator to account for the interband transition in ruthenate materials [235]:

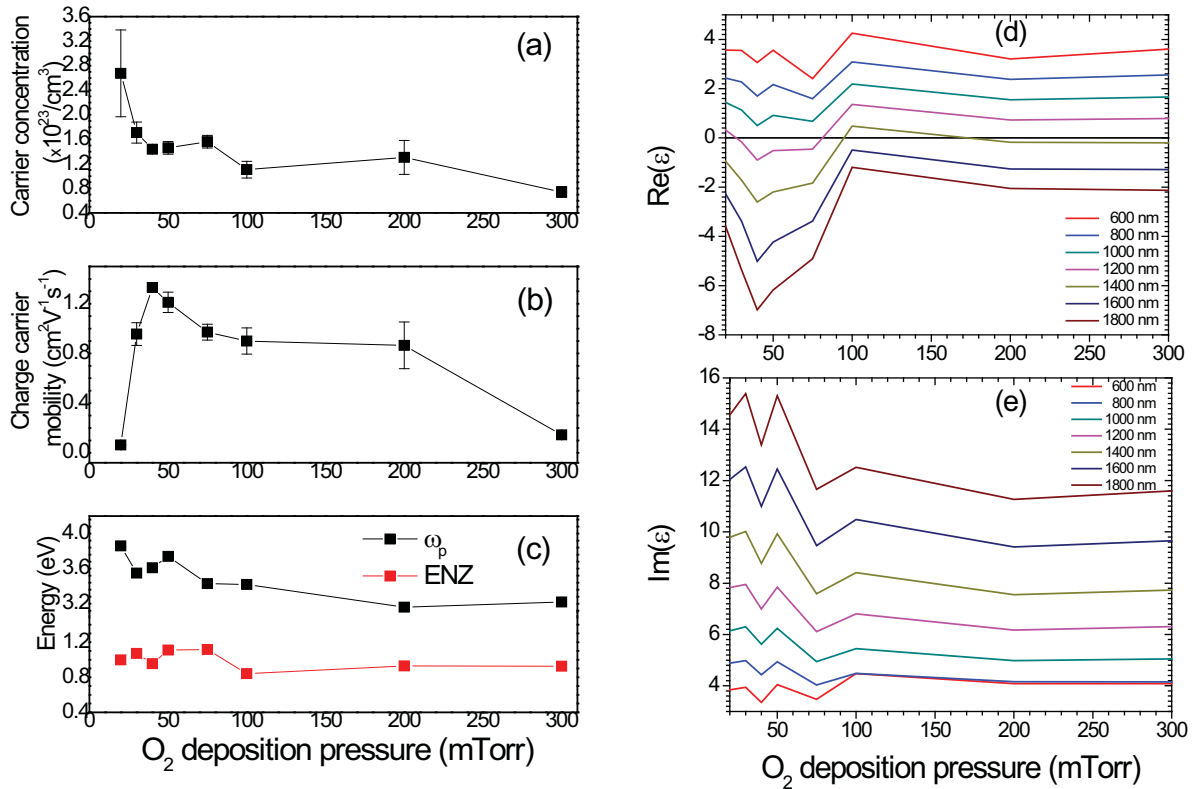
$$\varepsilon_{SRO} = \varepsilon_b - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma_1} - \frac{A^2}{\omega^2 - \omega_0^2 + i\omega\Gamma_2} \quad (5.1)$$

where ε_b is the background permittivity, ω_p is the plasma frequency, ω_0 is the frequency of the interband transition, A is a constant, and Γ_1 and Γ_2 are the damping frequencies for the free and bound electrons, respectively. The best fit (Figure 5.1.5) was obtained for $\varepsilon_b = 2.67$, $\omega_p = 3.41$ eV, $A = 6.98$ eV, $\omega_0 = 3.38$ eV, $\Gamma_1 = 0.98$ eV and $\Gamma_2 = 3.23$ eV with the goodness of fit test $\chi^2 = 1.33$. The fitting parameters were re-evaluated for all the other films and are in good agreement with optical measurements and the above parameters. The contribution of the additional RuO₂ phases to the results in the examined wavelength range (0.6 – 1.5 eV) was negligible.

The obtained spectral dependencies show that in the near infrared (NIR) regime (< 1.4 eV), the Drude part of the permittivity dominates, describing well the spectral behavior of both the real and imaginary part of the SRO film dielectric constant (Figure 5.1.5). As wavelength increases, $\text{Re}\{\varepsilon_{SRO}\}$ reaches the epsilon-near-zero (ENZ) frequency at 0.84 eV (1470 nm), so that for the photon energies below the ENZ frequency, $\text{Re}\{\varepsilon_{SRO}\}$ becomes negative in the measured spectral range up to 2000 nm. Conversely, for the same wavelength range, losses (i.e., $\text{Im}\{\varepsilon_{SRO}\}$) increase monotonously. In the UV-VIS spectral range (>1.4 eV), non-monotonous behavior is observed which is related to the interband transition resonance, in good agreement with Lee et al. [236]. Around the ENZ wavelength, losses of SRO are higher than Indium Tin Oxide (ITO) thin films [237], however, SRO exhibits better temperature stability and minimal surface roughness (few nm) compared to ITO and its hybrids (typically tens of nm), making it more suitable for high-temperature and perfect for absorber applications. The values of the plasma ENZ frequency, for all the deposition pressures, are presented in Figure 5.1.6c.

The dependence of the carrier concentration (n), mobility (μ), and of the SrRuO₃ films with oxygen pressure is shown in Figures 5.1.6. All the studied films exhibit n-type conductivity and ohmic transfer function. The electron concentration (Figure 5.1.6a) decreases with the increasing pressure. The highest concentration of electrons is exhibited at the lowest deposition pressure, possibly due to

non-equilibrium carriers generated by non-stoichiometric defects. Their concentration reduces at higher pressures, with the improvement of the films' crystal structure, hinting at the influence of trapped charges, produced by defects in the thin films or at the film/substrate interface. This is further confirmed by the electron mobility (Figure 5.1.6b), which is the largest for the deposition pressures about 40 – 50 mTorr, while dropping sharply for low O_2 pressures and slowly decreasing for larger ones, drastically dropping at 300 mTorr. This observation manifests that the electron mobility in the SRO films is mainly influenced by the oxygen vacancies which are usually present in the films deposited at low O_2 pressure as well as the scattering on grains boundaries with different orientation which were observed in the films deposited at high (100 – 300 mTorr) O_2 pressure. Since the charges concentration remains the same, this may be ascribed to a strain induced internal electric field that immobilizes the free charge carriers. Overall, the charge carrier concentration in the studied SRO films is on average approximately 10 times higher than that of Au or Ag, while the carrier mobility is about 100 times lower.



Figures 5.1.6: The dependence on oxygen pressure of (a) carrier concentration n , (b) carrier mobility μ , (c) plasma, and ENZ frequencies, (d) real part, and (e) imaginary part of the dielectric constants, for all SrRuO₃ films.

As observed in Figure 5.1.6c the plasma frequency, extracted from the fitted experimental data, decreases as the oxygen pressure increases. The slight fluctuations of $\omega_{p,eff}$ are probably related to free charges trapped by the defects, which are slightly different at different deposition pressures. The cross-over (ENZ regime) from dielectric to plasmonic behavior takes place in the spectral range 1.11 – 1.47 eV, depending on the oxygen pressure (Figure 5.1.6c).

The refractive index exhibited by films deposited under these conditions shows strong fluctuations with pressure, because of the varying electron structure of the defects in the crystal. For films deposited above 75 mTorr, the extinction coefficient, refractive index and electron concentration appear to be constant for most deposition pressures.

Comparing the electron concentrations and plasma frequencies of the SRO and plasmonic metals, one can notice the increased effective electron mass in SRO as should be expected [238, 239]. In the spectral range 1.11 – 1.47 eV, identified as ENZ regime, the transition from the dielectric (positive permittivity) to the plasmonic (negative permittivity) behavior depends on the oxygen pressure (Figure 5.1.6). For all the studied SrRuO₃ films, the plasmonic behaviours were observed in the infrared spectral range. In this spectral range, the absorption ($\text{Im}\{\epsilon_{SRO}\}$) is comparable to that of Au, for the films deposited at higher than 75 mTorr oxygen pressures.

The optical response corresponds well to the electric properties (Figure 5.1.3) with the decreased $\text{Re}\{\epsilon_{SRO}\}$ for low pressures, below 100 mTorr, corresponding to the increased carrier concentration and, thus, stronger free-electron contribution in Eq. (5.1). The decrease in mobility (and thus, increased scattering) can be attributed to the increasing $\text{Re}\{\epsilon_{SRO}\}$ for pressures lower than 40 mTorr. Please note that DC and optical-frequency scattering loss may not necessarily be the same. Nevertheless, the electron concentration is high enough to provide negative permittivity at infrared wavelengths for all deposition parameters. The optical losses (the imaginary part of the dielectric constant), show a decreasing trend with the deposition pressure (Figure 5.1.6), again in agreement with the electron concentration and the Drude model (Eq. 5.1). This behaviour is increasingly pronounced for longer wavelengths where the free-electron (Drude) part of permittivity becomes dominant.

This work has shown that by adjusting the deposition conditions of SRO films, i.e the oxygen deposition pressure, the films electron concentration, and thus plasma frequency and ENZ can be changed. Further, assuming the electron concentration of SRO thin films to be electrically tunable, it would be feasible to fabricate a slot-waveguide modulator based on engineered SRO films with a conveniently engineered ENZ. Such a device would consist of a smooth, thin SRO film buried between two dielectric layers (e.g. SiO₂), analogue to the proposed high-confinement slot-waveguide modulator based on engineered ENZ ITO films, shown in Figure 2.2.10. This part will be further ex-

plored, by finding the adequate method and deposition conditions for obtaining very thin, continuous and smooth SRO films.

5.1.3 Summary and Conclusions

In conclusion, thin SRO films of optical quality were grown on MgO (001) by pulsed laser deposition. The influence of the oxygen pressure (20 – 300 mTorr) on structure, charge carrier dynamics and optical properties were investigated. The best crystalline structure, characterized by the absence of extra phases or directions of growth, was obtained at the oxygen deposition pressure of 75 mTorr. The investigated films exhibit plasmonic behavior in the near-infrared spectral range with the plasma frequency at 3.16 – 3.86 eV and epsilon-near-zero behavior at 1.11 – 1.47 μm , depending on the deposition conditions. Oxygen pressure of 100 – 200 mTorr provides best electronic and optical properties, in this range of deposition parameters, for plasmonic applications of the films. The obtained parameters show the suitability of SrRuO_3 thin films for plasmonic and metamaterial design applications which may range from the heat generating nanostructures in the near-infrared spectral range to metamaterial-based ideal absorbers and epsilon-near-zero components, which is difficult to achieve in the near-infrared with conventional plasmonic metals. In all these applications, the interplay between real and imaginary parts of the permittivity in a given spectral range is needed for optimization of the performance. This material [227] is also compatible with and used in standard semiconductor technology and provides high temperature stability to up to 1200 K needed in many plasmonic applications, such as heat-assisted magnetic recording [240, 241].

5.2 *TiN Thin Films*

5.2.1 Deposition of TiN Thin Films

Titanium nitride (TiN) thin films were deposited on n-type c-Si (001) substrates ($10 \times 10 \text{ mm}^2$) by RF reactive magnetron sputtering by using a MANTIS Deposition System.

Before deposition, the Si substrates were cleaned for removing any possible contaminants from the surface: the substrates were dipped into acetone for 3 minutes with ultrasonic agitation and then dried by nitrogen; then the substrates were immersed in isopropanol for 3 minutes also

with ultrasonic agitation, followed by nitrogen drying. Finally, they were washed in deionized water (DI) for 30 seconds and dried again in nitrogen. After cleaning, the Si substrates were attached to the sample holder.

The samples deposited at room temperature (RT), were attached to the substrate holder by carbon tape, while for the samples deposited at high temperature (800°C) silver paste was used. The power fed on the Ti cathode was maintained constant, at 200 W, the deposition pressure was also constant (1.5 mtorr). The deposition time was set at 120 mins for the samples deposited at RT, denoted in the following as samples “R” and at 240 minutes for the films deposited at high temperature, denoted in the following as samples “H”, as presented in Table 5.2.1.

During the deposition the total mass flow rate was maintained constant (60 sccm), while the ratio N₂/Ar was varied.

Table 5.2.1 Mass flow rates of argon and nitrogen during the deposition of R and T - TiN samples

Sample notation	Gas mass flow ratios (sccm)	
	Ar	N ₂
H1; R1	50	10
H2; R2	40	20
H3; R3	30	30
H4; R4	20	40
H5; R5	10	50
H6; R6	0	60

5.2.2 Properties of TiN Thin Films

The thickness of the films, measured by surface profilometry, are presented in Table 5.2.2.

Table 5.2.2 Thickness of TiN films deposited at high (Hi) and low (Ri) temperatures

TiN Sample	H1	H2	H3	H4	H5	H6	R1	R2	R3	R4	R5	R6
Thickness (nm)	63±1	69±1	67±1	64±1	54±1	53±1	63±1	43±1	45±1	44±1	41±1	39±1

The thickness of the samples decreased at high nitrogen flows for both series of samples, as can be observed for the samples H5, H6, R4, R5 and R6. This behaviour may be ascribed to the decrease of the sputtering yield due to two different causes: (a) the decreased mass of the nitrogen, compared to the one of the argon [242, 243], and (b) the poisoning of the Ti target with TiN, which has lower sputtering yield and lower secondary emission coefficient than titanium [244, 245]. The decrease of the thickness is more pronounced in the case of the films deposited at low temperature, due to the reduced reactivity of the nitrogen due to temperature dependent nitriding kinetics on target and substrate surfaces [246, 247].

The crystalline structure of the films was measured by using a Bruker D2 Phaser A26-X1 XRD equipment. A Jandel four probe system was used to determine the sheet resistance of the TiN thin films. The current – voltage characteristics were obtained, the cut-off value of the voltage was set as 21 V. Since all TiN thin films were deposited on (001) Si substrates, the XRD pattern of the Si substrate was acquired in order to distinguish between Si peaks and TiN peaks.

Usually TiN thin films deposited by reactive sputtering develop strong preferred textures, (111) or (002), according to the deposition conditions [248, 249]. The (111) orientation is more likely to develop in films deposited with intense ion bombardment, due to either relatively high substrate bias, or due to specific deposition conditions favouring the energetic ion [250].

The diffractograms of the samples deposited at high temperature (series H) are presented in Figure 5.2.1 and the diffractograms of samples deposited at room temperature (series R) are shown in Figure 5.2.2. Since the X-ray count associated with the peaks of the Si substrate is much higher than for those of the TiN films, only the angular interval of the (111) and (002) maxima is shown.

The diffractograms in Figure 5.2.1 clearly illustrates (002) main preferred orientation of all TiN films in series H. Growth along the (111) direction was not for samples grown at low nitrogen concentrations: H1 (50Ar/10N₂) and H2 (40Ar/20N₂). The (111) is barely observable, for H3 (30Ar/30N₂) and H4 (20Ar/40N₂). For the samples H5 (10Ar/50N₂) and H6 (60N₂), the (111) peaks can be easily observed, especially for the H6 (0Ar/60N₂) sample grown in pure a nitrogen atmosphere. Considering the gas composition in the deposition chamber, it can be considered that for films grown in rich nitrogen atmosphere, the surface energy exceeds the strain energy, and consequently the crystallites exhibit a preferred (002) orientation. This fact may be ascribed to the lower energy of ions bombarding the growing film, due to the reduced momentum of nitrogen atoms, as compared to the argon ones [250].

The diffractograms of the samples in series R, grown at low temperature, indicate that in all films the surface energy is dominant, the crystallites exhibiting a preferred (002) orientation, while

the (111) peaks are missing. This observation may be explained by the reduced thickness of these films, as compared to those deposited at 800 °C, because the texture may change at higher thickness [251]. The R6 films seem to be amorphous at the micro-scale, as no diffraction peak could be observed.

At low nitrogen flow rates the position of the (002) peak, is shifted towards higher angles as compared with the reference data [252]. For the H5 and H6 samples it moves to lower angles, approaching the position corresponding to the ideal lattice constant (*c*) values. For samples deposited at low nitrogen flows, the (002) peak was shifted to higher angles, and then gradually shifted toward the reference value (JCPDS - ICDD file no. 38-1420). This may be caused by the difference of the lattice constant between each sample.

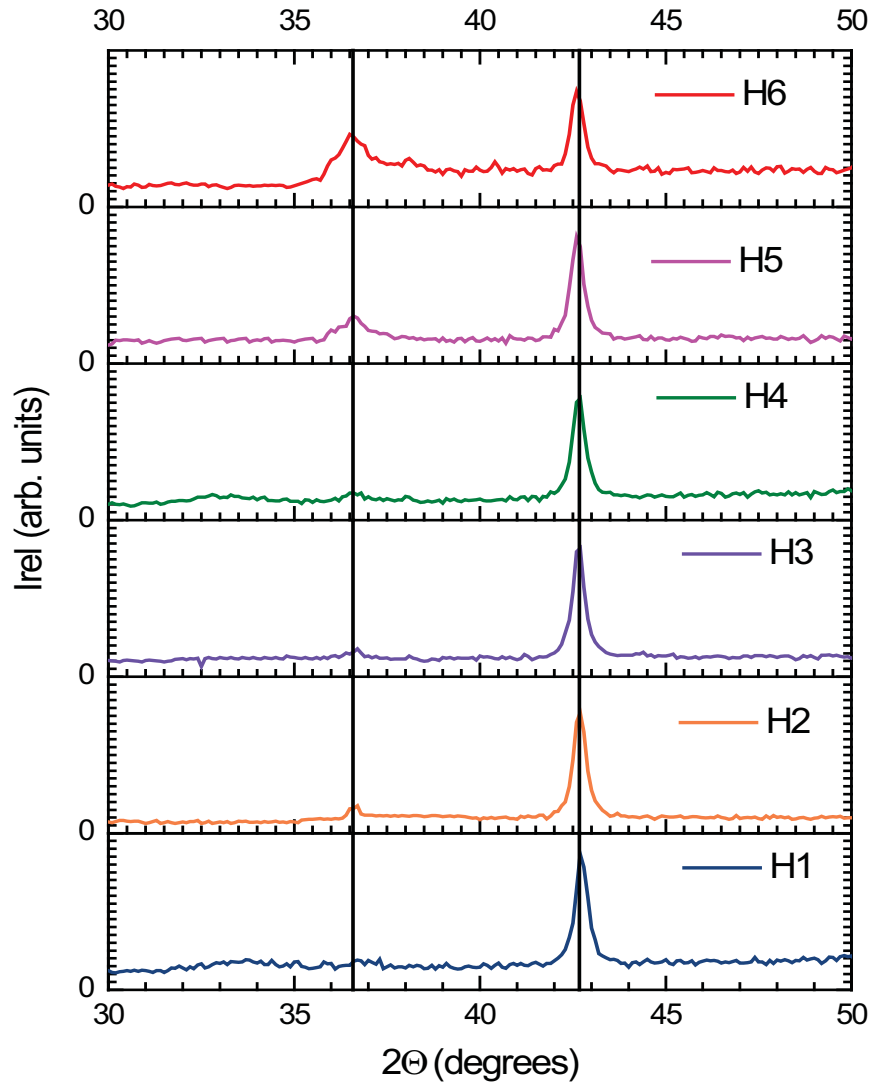


Figure 5.2.1: XRD patterns of the H1 - H6 samples. Vertical straight lines indicate the position of (111) and (200) maxima as in JCPDS - ICDD file no. 38-1420.

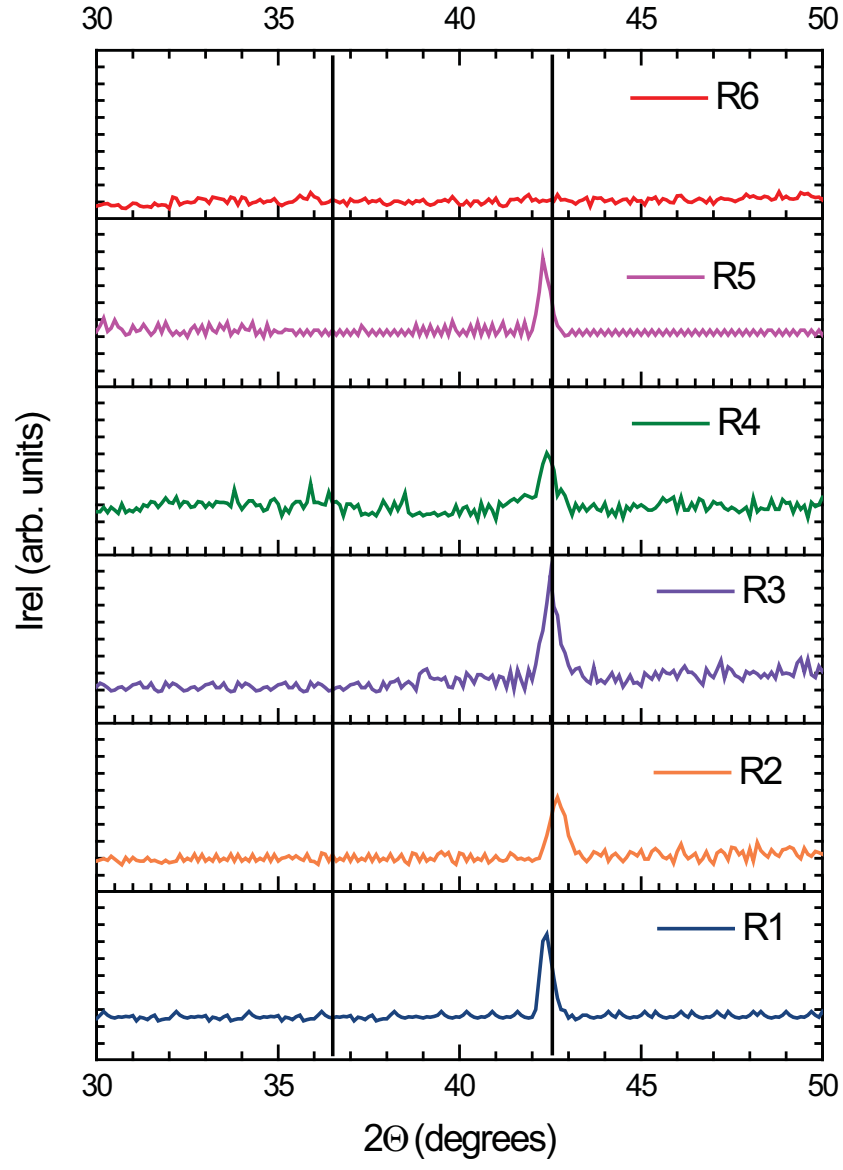


Figure 5.2.2: XRD patterns of the R1 - R6 samples. Vertical straight lines indicate the position of (111) and (200) maxima as in JCDPS - ICCD file no. 38-1420.

Table 5.2.3 The strain in TiN films deposited at high (Hi) and low (Ri) temperatures

TiN Sample	H1	H2	H3	H4	H5	H6	R1	R2	R3	R4	R5
Strain ϵ	-0.53	-0.36	-0.431	-0.47	-0.07	0.06	-0.24	-0.48	0.01	0.35	1.09

The lattice constant of the R group, as determined from the diffractograms, is shown in Figure 5.2.3a. The lattice constant decreases from R1 to R2 and then continuously increases from R3 to R5. This change gives an explicit account for the observed shift of the (002) peak position, determined by nitrogen occupying interstitial sites, and thus inflating the cubic lattice.

The variation of the interplanar distance “a” (Figures 5.2.3), lattice constant “c” (Figures 5.2.4) and grain size “D” (Figures 5.2.5) are shown for both series of TiN films. The interplanar distance values are more constant for the H series films, while the R series films present a higher spread of the interplanar values, with associated higher errors, due to the low intensity of the peaks in the diffraction patterns. The ideal value of the interplanar distance (black line) is also presented in the figures. This same trend is also observed for the lattice constant, as shown in in Figure 5.2.4, along with the ideal value of the lattice parameter, $c = 4.241 \text{ \AA}$ [252]. The films from both series deposited at low and intermediate nitrogen flow rates exhibit lattice constant values close to the ideal value. As the concentration of nitrogen in the deposition chamber increased, the nitrogen began taking interstitial positions in the TiN lattice, increasing its parameter.

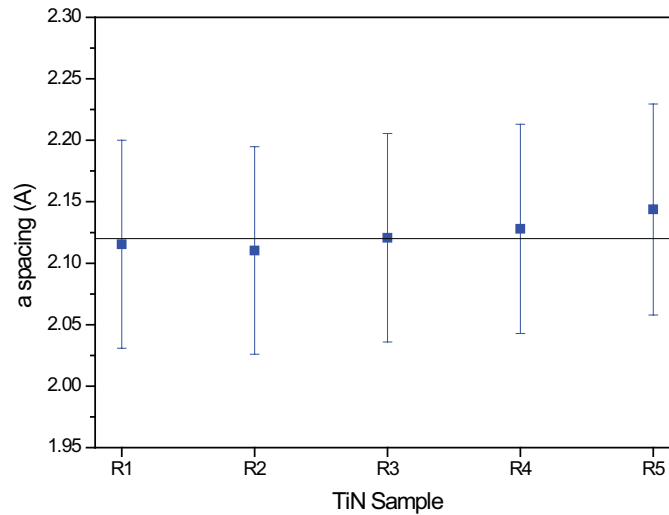


Figure 5.2.3.a: The interplanar spacing “a” for TiN films – series R; the black line indicates the ideal value of the interplanar distance a_0 [252].

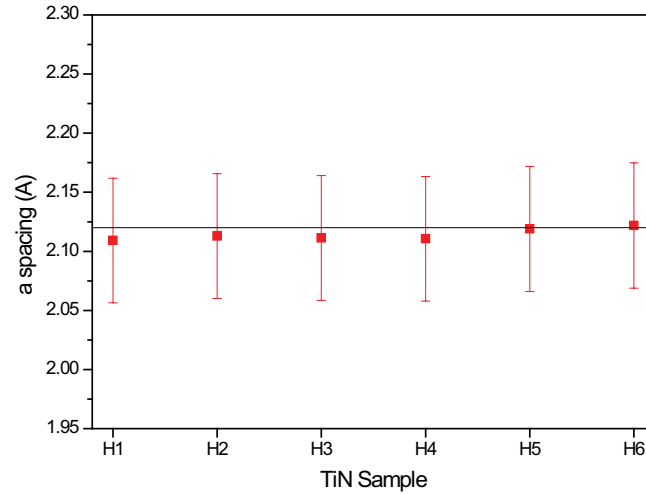


Figure 5.2.3.b: The interplanar spacing "a" for TiN films – series H; the black line indicates the ideal value of the interplanar distance a_0 [252].

The above assertions should be considered with much attention, because of the error values. The grain size as shown in Figure 5.2.5 comparatively for the R and H series films, clearly indicate that the films grown at low temperature exhibit a higher degree of amorphisation. The H6 films present a tendency toward amorphisation, comprising of (002) and (100) oriented crystallites, with low dimensions, approaching the ones obtained for R series films.

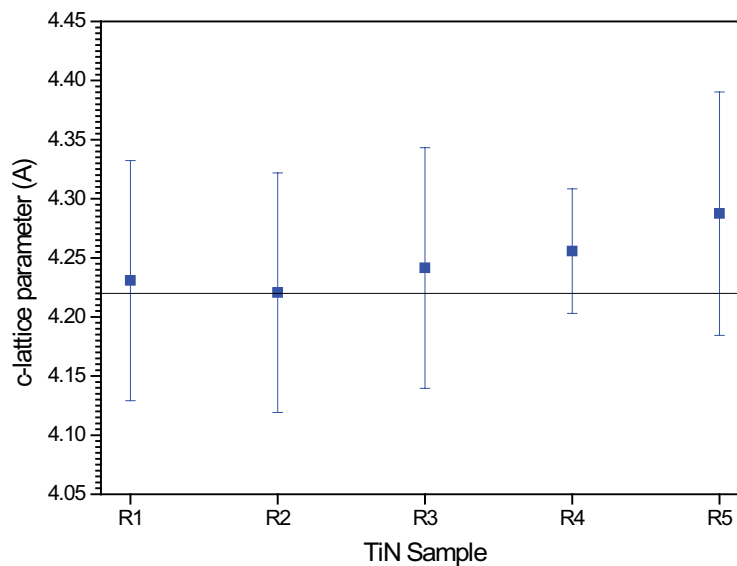


Figure 5.2.4.a: The lattice parameter "c" for TiN films –series R; the black line indicates the ideal value of the lattice parameter " c_0 " [252].

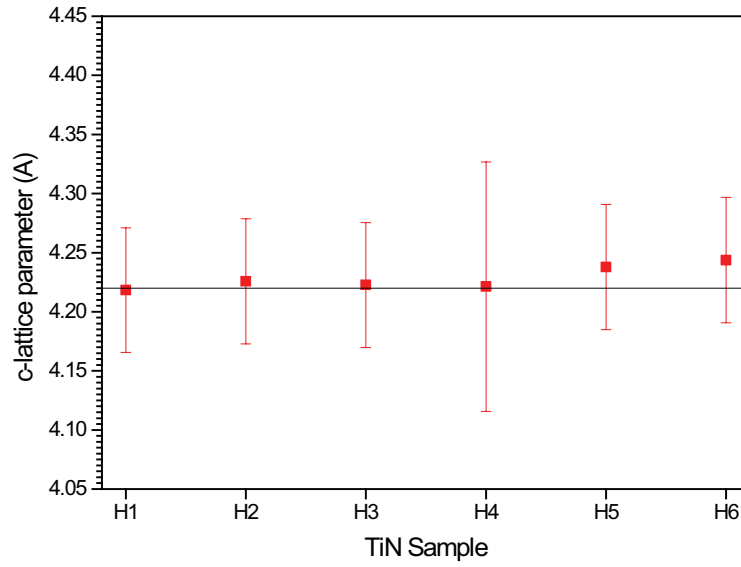


Figure 5.2.4.b: The lattice parameter "c" for TiN films –series H; the black line indicates the ideal value of the lattice parameter " c_0 " [252].

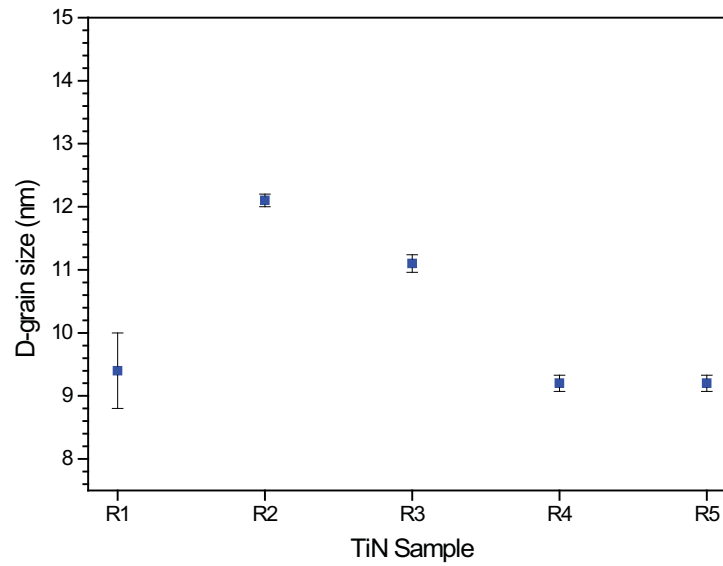


Figure 5.2.5.a: The grain size "D" for TiN films – Series R.

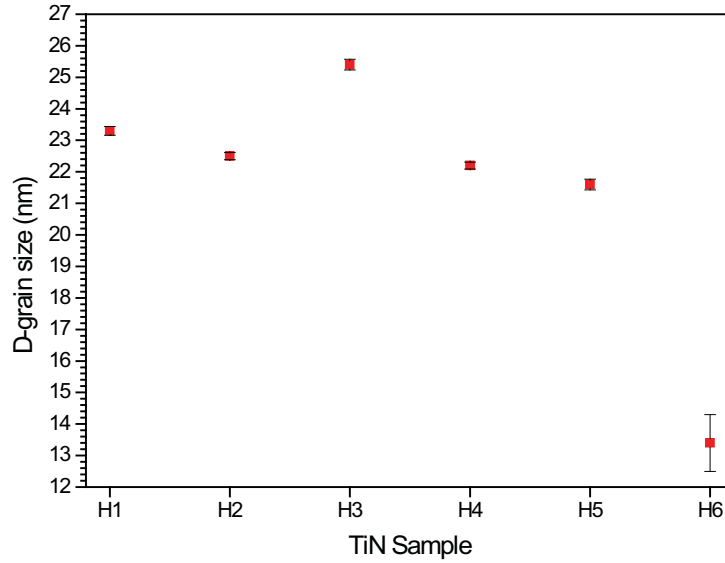


Figure 5.2.5.b: The grain size “D” for TiN films – Series H.

Titanium nitride films are known to exhibit high electrical conductivity, and as such they are used in microelectronics as diffusion barrier layers for metallic electrodes. Aiming to use TiN films as electrodes in plasmonic devices, the films electrical properties were investigated using the Van der Pauw method. The following figures show the carrier (electron) concentrations (Figures 5.2.6 (a) – series H, and (b) – series R), the carrier mobility (Figures 5.2.7 (a) – series H, and (b) – series R), and the resistivity values (Figures 5.2.8 (a) – series H, and (b) – series R).

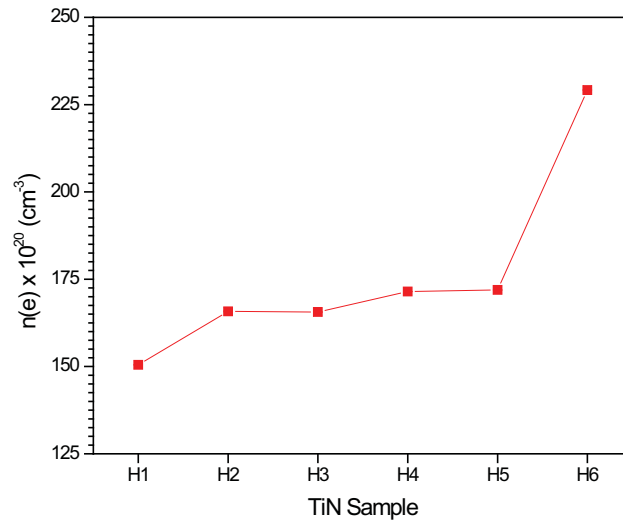


Figure 5.2.6 a: The carrier concentration "n(e)" for TiN films: series H.

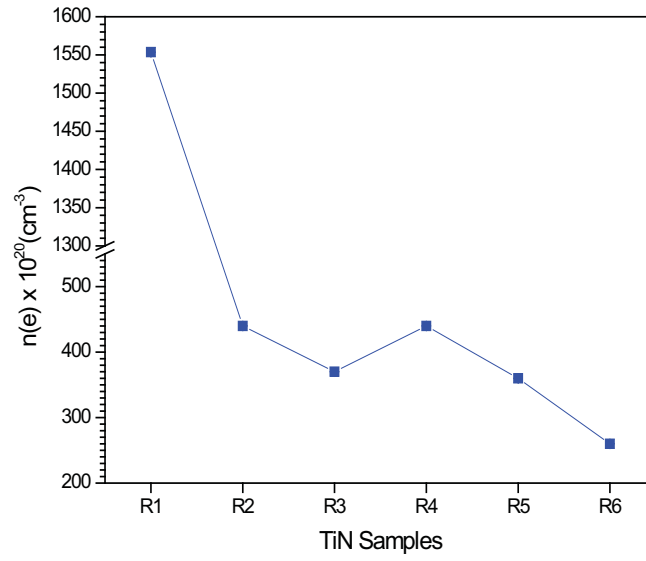


Figure 5.2.6 b: The carrier concentration " $n(e)$ " for TiN films: series R.

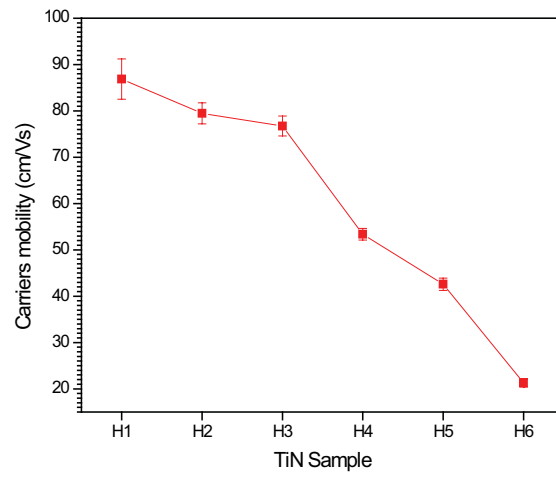


Figure 5.2.7 a: The carrier mobility for TiN films: series H.

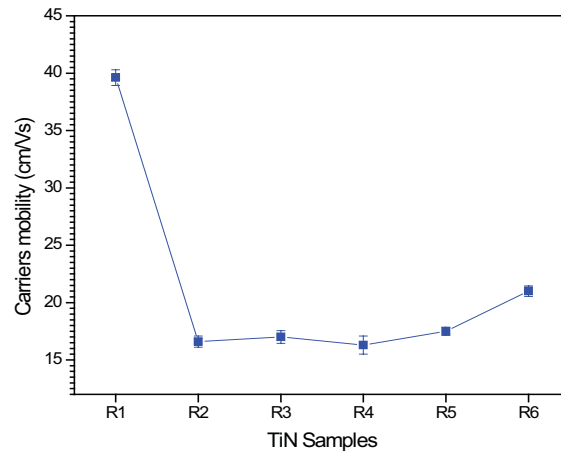


Figure 5.2.7 b: The carrier mobility for TiN films: series R.

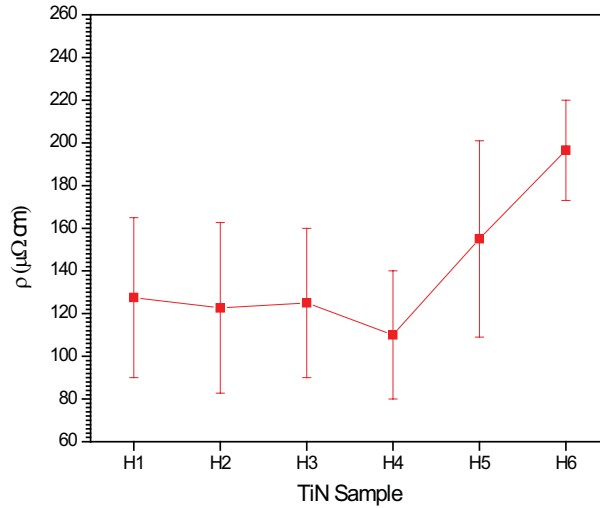


Figure 5.2.8 a: The resistivity " ρ " for TiN films: series H.

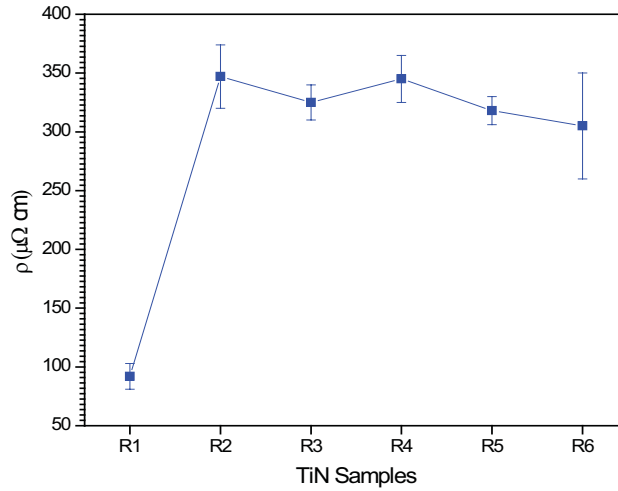


Figure 5.2.8 b: The resistivity " ρ " for TiN films: series R.

The films from series H exhibit relatively constant carrier concentrations, except for H6, which shows an increase in concentration, probably related to the almost ideal lattice parameter. On the contrary, the films from series R exhibit a different trend: the R1 sample, with a more pronounced metallic character exhibits high electron concentration, which decreases as the nitrogen concentration increased in the deposition chamber and, hence, in the deposited films. The saturation values of the electron concentration for the films R2 to R6 are higher than the values obtained for the H series films, indicating that R series films have a more metallic character. The low substrate temperature impeded the mobility of the atoms/ions arriving on the surface of the growing films, so that the films grew with defects, which acted as secondary nucleation sites, especially at grain boundaries, limiting

the further migration of newly arrived atoms/ions, determining low crystallite sizes and, eventually, the films amorphisation, as clearly observed in the case of sample R6 [253, 254].

The observed decrease in carrier mobility at higher nitrogen partial pressures in samples from both series may be ascribed to the films amorphisation which was progressing as the nitrogen concentration increased. The resistivity values obtained for the films of both series may be accounted for by the diminishing of the mobility and increased amorphisation brought about by the increase of the nitrogen concentration in the deposition chamber. The low value of resistivity obtained for the R1 film, indicating its metallic character, is quite remarkable. The lower values of the resistivity exhibited by the H series films, as compared to the R series, may be ascribed to the higher mobility of the carriers in these samples, due to larger grains and consequently to reduced scattering at grain boundaries. All room temperature grown samples exhibited electron concentrations of the order of 10^{22} (Figures 5.2.6), similar to the values reported in literature for titanium nitride and oxynitride [255 - 258].

In the following, the optical characteristics of TiN films are presented: the real and imaginary dielectric constants of TiN films – series H (Figures 5.2.9), and the real and imaginary dielectric constants of TiN films – series R (Figures 5.2.10), being figured also the real and imaginary parts of the dielectric constant of Au, for direct comparison. Also, there are presented the ENZ values for series H (Figure 5.2.12), for series R (Figure 5.2.13), the plasmon bandwidth (Figures 5.2.14 for series R films).

Considering the TiN films grown at high temperature, the observed decrease of the real dielectric constant (depending inversely proportional to the wave phase velocity in the film) with the increase of nitrogen partial pressure, is accompanied as expected by the increase of the imaginary dielectric constant. This behaviour is similar to the ones presented by Patsalas in a review on the optical properties and plasmonic performance of titanium nitride [259], in the interval: 250 - 820 nm. For wavelengths larger than 400 nm, the negative values of $\text{Re}\{\epsilon\}$ are ascribed to the interaction of light with the conduction electrons of TiN, i.e. to intraband absorption, while for shorter wavelengths the observed positive values of $\text{Re}\{\epsilon\}$ are associated with the interband absorption; these bands are also observed in the $\text{Im}\{\epsilon\}$ spectra. The dielectric constants of the TiN samples from series H (Figure 5.2.9) indicate a definite metallic behavior, showing a $\text{Re}\{\epsilon\}$ which is continuously decreasing, with negative values throughout most of the visible and infrared ranges, while the imaginary part constantly increases almost linearly, similar to the imaginary part of the series R TiN samples (Figure 5.2.10). This behavior corresponds to what was already been reported for TiN films grown at high temperatures [105], being similar to that of gold (figure 5.2.11).

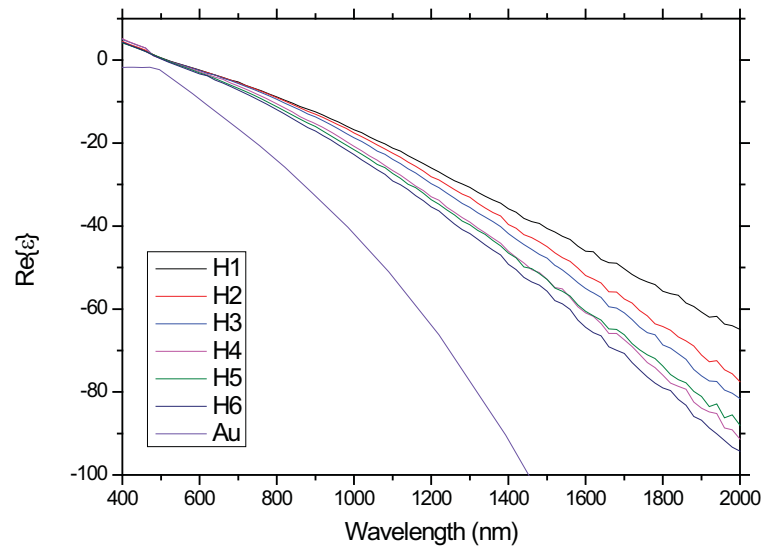


Figure 5.2.9 a: The real part of the dielectric constant of TiN films, series H;
Au constant is also presented for comparison.

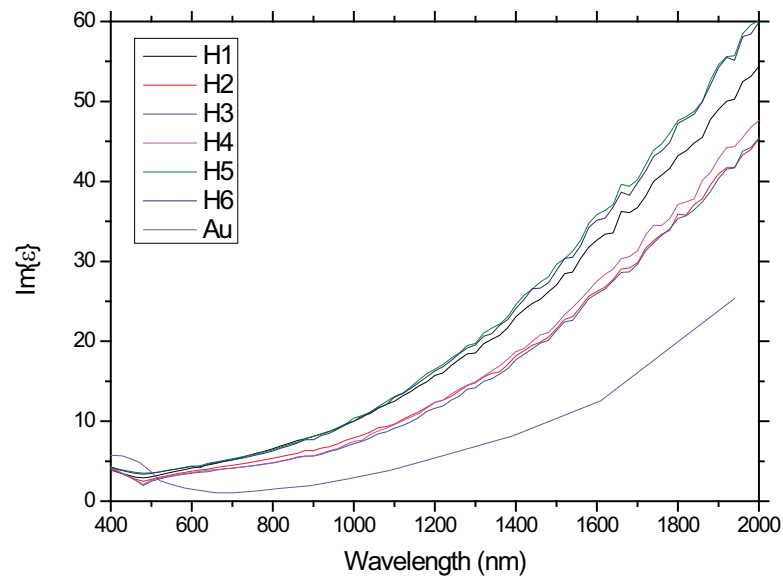


Figure 5.2.9 b: The imaginary part of the dielectric constant of TiN films, series H;
Au constant is also presented for comparison.

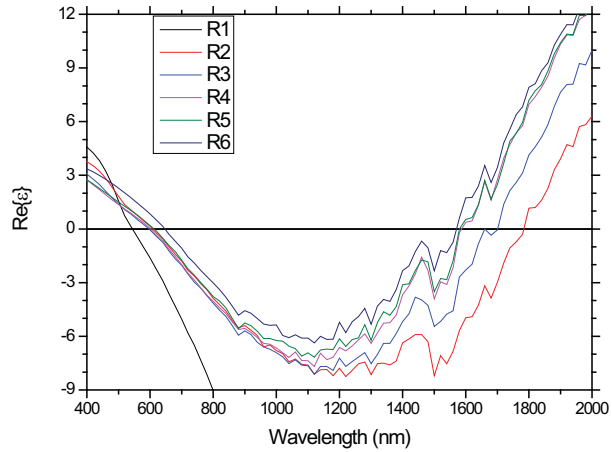


Figure 5.2.10 a: The real part of the dielectric constant of TiN films, series R.

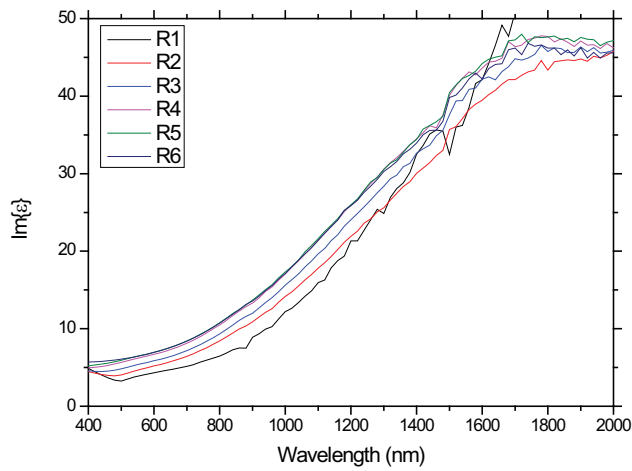


Figure 5.2.10 b: The imaginary part of the dielectric constant of TiN films, series R.

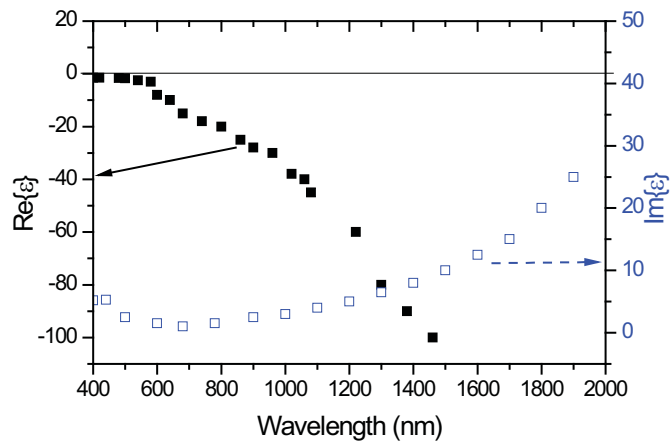


Figure 5.2.11: The real and imaginary parts of the Au dielectric constant (adapted from [105]).

The most remarkable result is the existence of two ENZ values for the R series films. It is very likely that these films are not chemically saturated with nitrogen and that, after the deposition process, contain many broken-bond-type defects, which become oxidized in air, leading to the formation of a TiN_xTiO_y system. The widespread presence of these oxidation centres is most likely responsible for the almost amorphous structure, high electron concentrations and low carrier mobility exhibited by the films.

The tunable double ENZ behaviour of the room temperature deposited samples may be attributed to the mixture of TiN and TiON phases in the films. This unusual phenomenon is not influenced by the films' crystallinity (as similar tunable double ENZ behaviour in both amorphous and crystalline films were observed), however this effect was not observed in samples deposited at high temperatures. Moreover, the XPS studies show that for the RT fabricated films, the ratio between TiN and TiO doesn't depend on the depth, as the films are quite thin, as shown in Annex II. At the same time for high-temperature sputtered films, even if the ratio does not depend on the depth from the surface, as resulted from XPS measurements, the films present a single, well defined ENZ value.

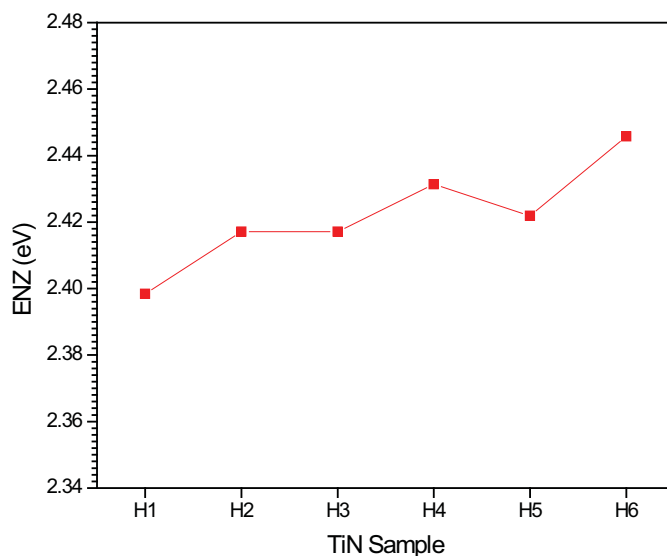


Figure 5.2.12: ENZ values for TiN films: series H.

The partial pressure of N_2 (within the N_2 -Ar sputter gas mixture) and the deposition temperature govern the nitride saturation of the growing TiN film. Reducing the amount of nitrogen results in the formation of TiN_x , which reacts, when exposed to air, forming TiO_x and TiON compounds. Varying the content of the deposition gas mixture, one can control the amount of TiN, TiO_x and TiON

in these films and therefore change the optical properties of the samples (Figure II.1- Annex II). Disappearance of the 2ENZ behavior in the samples deposited at high temperature is due to the (nearly) complete TiN structure saturation caused by the temperature enhanced nitrogen diffusion.

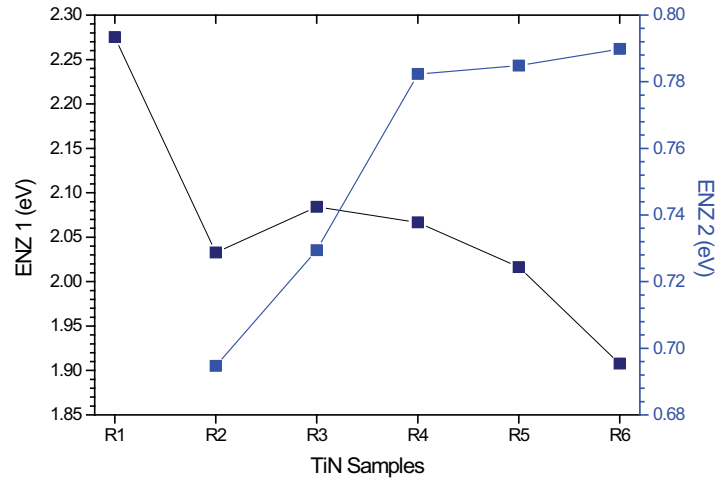


Figure 5.2.13: ENZ-1 and ENZ-2 values for TiN films – series R.

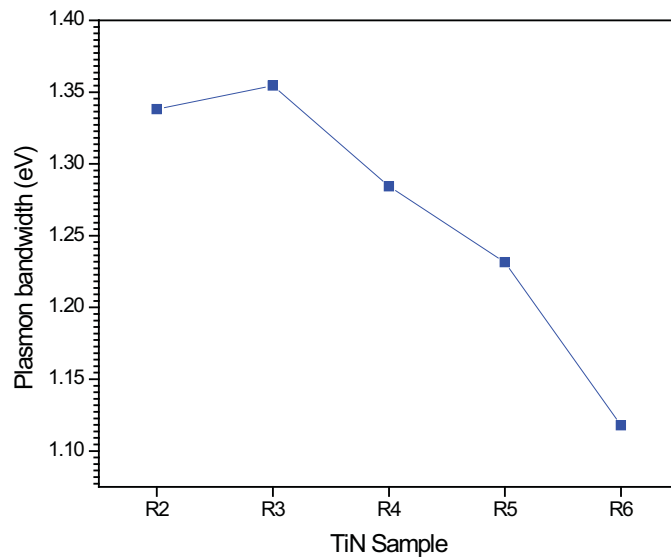


Figure 5.2.14: Plasmon bandwidth values for TiN films: series R.

5.2.3 Summary and Conclusions

TiN thin films of optical quality were grown on intrinsic Si (001) by reactive magnetron sputtering. The influence of the partial pressures of nitrogen (1:5 – 1) on structure, charge carrier dynamics and optical properties were investigated for films deposited at room temperature and at 800° C. Films deposited at high temperature exhibited optical properties similar to Au and Ag, and similar electron concentrations. Electrical mobility, however, was much lower. Films grown at room temperature had even lower mobility, but higher electron concentrations, due to the higher number of defects.

Although the resistivity and corresponding phases of all groups were obtained and analysed, a comparison to determine whether they are qualified or not is lacking. As some resistivity of TiN thin films from other researchers' works have already been presented in introduction section. It is encouraging to notice that the resistivity of the H group in this project is way lower than either Jeyachandran's or Bui's work [260, 261]. This is due to the higher deposition temperature which makes the TiN thin film highly crystallized and orientated. Meanwhile, the resistivity of R1 (50Ar/10N₂) and R2 (40Ar/20N₂) are in good agreement with Jeyachandran's work that under low nitrogen concentration and room temperature the resistivity keeps stable at $210 \pm 20 \mu\Omega\cdot\text{cm}$. Based on all results and analysis, some conclusions can be made on the conductive property of TiN thin film with certainty. Firstly, not only can resistivity be reduced at higher deposition temperatures, but stoichiometry can also be improved. Secondly, the (111) orientation, which only formed under 800 °C, contributes to higher conductivity in a much greater degree than (002). More specifically, at higher deposition temperatures (H group) the resistivity goes down from $56.1 \pm 1.3 \mu\Omega\cdot\text{cm}$ to $22.3 \pm 1.3 \mu\Omega\cdot\text{cm}$ with increasing nitrogen and under room temperature (R group) circumstance the resistivity goes up from $233.3 \pm 1.4 \mu\Omega\cdot\text{cm}$ to $843.5 \pm 3.0 \mu\Omega\cdot\text{cm}$ with more nitrogen content. Although some fluctuations may exist in the results, they are within acceptable range and will not affect the observed trend.

Films fabricated at 800°C exhibited optical constants broadly similar to metals. However, the films grown at room temperature most likely consisted of a new TiN_x:TiO_y system, and exhibited 2 distinct ENZ regions, demarcating a well-defined plasmon bandwidth, which has not yet been reported in literature. Further investigations will be needed in order to understand the electron structure behind this behaviour.

5.3 Ag Thin Films

Most metals do not wet insulating surfaces such as glass or silicon, and in such a case, a thin film grown by PVD methods, such as thermal evaporation, magnetron sputtering or pulsed laser deposition, passes through a sequence of morphological changes as the film thickens.

Ag, a relatively abundant material, is also one of the most used conventional plasmonic materials, and efforts have been made to fabricate smooth metal-dielectric interfaces. As most of the metals, Ag does not wet insulating surfaces. Regardless of the type of PVD methods used for Ag thin film deposition (thermal evaporation, magnetron sputtering or pulsed laser deposition), it passes through different morphological changes as the film thickens, following the Volmer - Weber growth model.

The atomic smoothness of the metallic film is crucial for reducing the plasmonic losses. For plasmonic applications it was shown that the optimal thickness of the film is about 50 nm, explained in terms of the balance obtained between the increased absorption in the metal and the increased optical field-enhancement due to surface plasmon-polariton excitation as the thickness is increased [262].

Different strategies were followed for reducing the surface roughness of the Ag films grown on dielectric substrates, because silver exhibits high surface roughness, no matter the type of the deposition method used [263]. A sufficiently thin film consists of isolated and compact islands. As the film is growing thicker, the islands grow and coalesce into larger and compact islands. At some critical island size, islands that touch no longer fully coalesce into near equilibrium compact shapes. As the thickness continuously increase these shapes stop to grow and form elongated structures, which connect and form a percolating structure; eventually a continuous, hole-free film is formed as the channels separating the structures are filled in with new deposited material.

Despite different attempts in modifying the deposition parameters, no reduction of the surface roughness was obtained. The thermal stability of Ag thin films is very poor, and due to surface diffusion of Ag atoms, enhanced by the temperature, the Ag layer becomes agglomerated, as holes or hillocks tend to grow within it [264]. As a result, the increase of the deposition temperature determined the increase of the roughness. Related to the substrate bias effect, it is widely acknowledged that a minimum roughness is obtained for a specific biased voltage. It is related to the energy and subsequent mobility of the bombarding ions/atoms on the growing film surface, and it has to be determined experimentally [265]. A low substrate bias provides less mobility of the ions/atoms,

while a high value proved to have detrimental effects, through re-sputtering of the films and defect formation.

The use of the High Power Impulse Magnetron Sputtering (HiPIMS) technique showed a reduction of the roughness for very thin films of ~ 12 nm from 2.4 nm to 1.8 nm, if using relative low currents (11 A), but a highly ionised plasma [266].

An important step forward consisted of depositing a very thin Ge nucleation layer, which proved to be effective in reducing the surface layer roughness [267], making possible the use of silver layers in plasmonic applications [268].

The aim of the study is to find out straightforward and cost effective deposition conditions for reducing the roughness of Ag films deposited on insulating surfaces, for using it in plasmonic and metamaterials applications. The magnetron deposition method was used for this purpose, as it is widely used in the optical industry.

The use of different sputtering gases when using the magnetron deposition method may determine different film's characteristics. Schucan et al. have deposited Nb thin films and observed that He addition determined the decrease of the deposition rate and of the grain size [269]. The same grain refinement was observed for Ti films deposited in a He/(Ar+He) mixture of 95%, as determined from the partial pressure values, by Pang and co-workers [270].

Novotny et al. [271], carried out a systematic study on the influence of Ne, Ar and Kr as sputtering gases, on Ag films properties and the RF magnetron sputtering plasmas. The 25 nm thick Ag thin films were deposited on floated fused silica substrates. It was shown that the deposition rate for Ar and Ne were approximately the same, while it decrease to about two thirds for Kr, due to the rarefaction effect determined by the low thermal conductivity of the Kr gas, and to the enhanced scattering of Ag by collisions with the heavy Kr ions/atoms [272]. They concluded that a higher energy of the atoms/ions impinging on the growing surfaces decrease the surface smoothness, because the lowest surface roughness R_q (2.9 nm) was obtained in Ne discharge, as compared to the value (3.9 nm) obtained for films produced in Ar or Kr discharge. However, this assumption seems not to be correlated with the roughness increase of the Ag films when the substrates are bombarded with low energy ions, as in the case of HiPIMS magnetron deposition using relatively low current values [266].

Thick Ag films (500 nm) were deposited by DC magnetron sputtering method, using pure Ne, Ar, Kr and Xe high purity gases on Si, float glass and float glass pre-coated with non-conducting ZnO by West and co-workers [273]. Comparing the discharges in Ne and in heavier inert gases, it was observed that in Ne discharge the Ag films were bombarded with the highest flux of ions at the highest

accelerating potential, while the impulse transfer through Ne ions and atoms was the lowest. This was confirmed by the fact the lowest deposition rate obtained in Ne discharge. The lowest roughness for 500 nm thick films was obtained in Ne discharge, as reported also by Novotny et al. for thin (25 nm) films [271]. For the thin silver films, West et al. [273] reported the smallest roughness for the films deposited in Kr atmosphere (~ 0.6 nm), the films obtained using Ne and Xe showed similar roughness values (~ 0.7 nm), the highest value being obtained when using Ar (~ 0.85 nm). The authors concluded that for the early stages of growth, it is not possible to present an explanation, as the knowledge is limited for the films near coalescence. This fact contradicts the data reported by Novotny et al. [271]. The differences may be ascribed to different deposition conditions related to the ion current density on the substrate and different plasma potential in the two deposition systems.

One can conclude that a growing film receives energy and momentum from the bombarding species produced by the sputtering gas - the sputtered metal, by backscattering, with a plus of energy and momentum if the substrate is negatively biased [274 – 276]. Detailed experimental studies were conducted for W films sputtered in various inert gases [277 – 279].

No data are available in the literature concerning the deposition of silver films in mixture of argon and helium. The deposition of films in pure He discharge was not reported, because due to the high ionization potential of the He atom, it is difficult to create and to sustain a stable discharge. However, it was reported the use of helium as mixture gas with nitrogen, for the deposition of titanium nitride films [280]. The investigation of the crystalline structure of the films, done by XRD and TEM revealed that all the deposited films in the usual a mixture of argon with nitrogen developed a distinct (111) texture, showing a strong columnar growth morphology with highly faceted grains, not fully dense. The films deposited in pure nitrogen or in a mixture of argon, nitrogen and helium presented a higher density and developed a strong (002) texture; the difference between the films was in the shape of the grains, equi-axed grains were obtained in pure nitrogen, while in a Ar+N₂+He mixture the grains were elongated and not faceted.

The main idea in this work was to increase the ionization degree of the magnetron plasma in a conventional magnetron deposition system, and to find the best deposition conditions for reducing the roughness of Ag thin films when deposited on insulating substrates. It should be mentioned that the floated substrates are biased at the plasma potential, which has a positive value, of about 15-30 V, depending on the gas and discharge conditions. Usually, the higher the ionization potential, the higher value is obtained for the plasma potential. The difference between negatively biased and

floated substrates may be significant, as a gentle balance of the ions energy impinging on the growing film is needed.

He, as compared to Ar, has a very low sputtering yield of Ag, since it is much lighter. As a result, in the He-Ag collisions, the metal energy loss is very much diminished, resulting in a moderate increase of the metallic ions/atoms energy impinging on the growing film, even on floated substrates.

The role of the He ions and metastable atoms in an Ar+He plasma may be shortly described by the following two elementary processes:

- asymmetric charge transfer $\text{He}^+ + \text{Ar} \rightarrow \text{Ar}^+ + \text{He}$ (1)
- metastable – neutral ionization $\text{He}^* + \text{Ar} \rightarrow \text{He} + \text{Ar}^+ + \text{e}^-$ (2)

The process (1) may determine an increase of heavy gas ions; it is to mention that reverse reaction is strongly endoenergetic [281], so it has a negligible cross-section. The process (2) determines an increase of the plasma ionization; the reverse process is most unlikely because a three body-collision is needed.

Table 5.3.1 The ionization energies and the first metastable states for the noble gases.

Atom	First metastable state (eV)	Ionization energy (eV)
Helium	19.8	24.6
Neon	16.6	21.6
Argon	11.0	15.7
Krypton	5.0	14.0

It should be underlined that in low pressure electrical discharges, as magnetron discharge, the ionization of a particle occurs by impact on a metastable particle with an excitation energy higher than its own; this is known as the Penning effect. It is known that He-Ar and He-Ne mixtures exhibit the Penning effect, as they present favourable energy-level combinations, as presented in the Table 5.3.1. On the other hand, He-Ne and Ar-Kr mixtures do not have the favourable energy-level combination, so the Penning effect is missing.

5.3.1 Deposition of Ag Thin Films in Ar and He mixture

The films were deposited on a magnetron deposition system equipped with five magnetrons in a confocal configuration, the substrates being placed at the top of the deposition chamber, for avoiding any contamination from possible flakes resulted from delaminated coatings from chamber parts. The chamber is cylindrical, 500 mm height, and diameter of 500 mm. The substrates holder rotates during the deposition, for depositing films with high thickness uniformity, despite their position on the 3" holder. The sketch of the deposition system is presented in Figure 5.3.1.

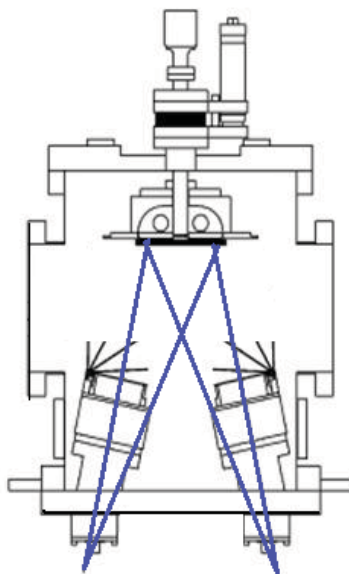


Figure 5.3.1: Schematic view of the magnetron deposition system with confocal arrangement of the cathodes.

One cathode, with a diameter of 2 inches of Ag (99.995% purity) from K.J. Lesker comp. was used. The distance between the cathode and the substrates was 18 cm.

The base pressure in the deposition chamber, prior to the deposition was 6×10^{-5} mTorr. The total gas pressure during the deposition was kept constant at 5 mTorr. Ar (99.99%), or a mixture of Ar (99.99%) and He (99.999%) was used as a sputtering gas. The absolute pressure was measured with a MKS 626 Barocel capacitance manometer. During the film deposition the ratios of the mass flow rates F_R of the sputtering gases $\text{He}/(\text{Ar}+\text{He})$ were varied from 0/10 to 8/10 standard cubic centimetres per minute (sccm).

The substrates were floated during the entire deposition process. The substrates were not heated, and the substrates temperature, as measured continuously by a backside non-contact thermocouple, was maintained at 35°C . The films were deposited on three different substrate types:

fused silica (Alpha Aesar) (25 x 25 x 1) mm³ for structural and optical characterisation, and on (0001) cut sapphire substrates (Crystec, GmbH), (10 x 10 x 0.5) mm³ for roughness investigation and electrical measurements.

The Ag target was sputter cleaned in vacuum by Ar ion bombardment for 10 min, at a pressure of 20 mTorr. During deposition the Ag target was fed from a 13.56 MHz AJA-Seren's RF generator with auto-matching network, working in the constant power mode, delivering 30 W to the Ag cathode. The RF regime was chosen due to the lower deposition rate, as compared to the DC mode. A lower deposition rate permits a superior control of the film thickness, by controlling the deposition time, when thin films are to be deposited. The deposition time was 1100 sec.

He/Ar+He flow ratios (F_R), measured in standard cubic centimetres per minute (sccm) were varied, as presented in Table 5.3.1.

The deposition rates (DR) were determined from the measured film thickness and the deposition time. The film thickness of all samples was measured using a Dektak 150 device from a step height in a masked area on the substrate, using a low-inertia stylus sensor (0.2 µm radius). Each measurement was taken on 2.0 mm scan length with 30 µN contact force and 50 µm/s scan speed. Five profilometry measurements were made for each specimen and the mean value was calculated.

The phase composition, crystalline structure, texture and crystallite size were determined via X-ray diffraction in Bragg-Brentano geometry, using a Rigaku MiniFlex-II diffractometer (CuK α radiation).

Table 5.3.2: Deposition parameters for the Ag films deposited in a mixture of Ar and He

Sample	Ag-1	Ag-2	Ag-3	Ag-4	Ag-5
F_R (He/Ar+He) (sccm)	0/10	2/10	4/10	6/10	8/10

Atomic force microscopy (AFM) was performed on a Bruker INNOVA instrument. The microscope was vibration-damped. Commercial pyramidal phosphorus doped silicon tips (Veeco model RTESPA), mounted to a cantilever with a length, resonance frequency and nominal force constant in the range of 115 - 135 µm, 295 – 349 kHz and 20 - 80 N/m respectively, were used. Measurements were done on 1 × 1 µm², taken in 4 different positions for each sample. The amplitude roughness parameters (R_a - arithmetic average, RMS – root mean square) were obtained by using the Veeco Innova analysis software. The reflection spectra were measured using a Jasco V300 UV/Vis/NIR spectrometer. The electrical resistivity of the films, the charge carrier concentration and their mobility

were investigated by Ecopia HMS-3000 Hall measurement system with Van der Pauw geometry at 0.55 T magnetic field, using silver paste contacts.

5.3.2 Properties of Ag Thin Films obtained in Ar and He mixture

In Table 5.3.3 are presented the thickness of the films and their deposition rate. The deposition rate decreased as the He partial pressure increased, because the impulse transfer through He ions and atoms is lower due to the lower mass of He, as compared to Ar.

Table 5.3.3: Thickness and deposition rate of Ag films deposited in a mixture of Ar and He

Sample	Thickness δ_{Ag} (nm)	Deposition rate (nm/min)
Ag-1	53.8 ± 0.2	0.72
Ag-2	57.3 ± 0.2	0.76
Ag-3	60.2 ± 0.2	0.80
Ag-4	67.6 ± 0.2	0.90
Ag-5	78.9 ± 0.2	1.05

The XRD patterns of the Ag films are presented in Figure 5.3.2. The most intense peaks were located at 2θ angle of $\sim 38.15^\circ$ and of $\sim 44.3^\circ$, assigned to the Ag (111) and (200) reflections, respectively [282]. In Figure 5.3.4. is presented the variation of the texture coefficient $T_{C(111)} = T_{(111)} / (T_{(111)} + T_{(200)})$, which shows an increase as the He partial pressure increased in the deposition chamber. The strength of (1 1 1) and (2 0 0) orientations was represented by the texture coefficient $T_{C(111)} = \{I_{(1\ 1\ 1)} / [I_{(1\ 1\ 1)} + I_{(2\ 0\ 0)}]\}$, where I is the integrated intensity of the corresponding Bragg peak from a Gaussian fit. The increase in texture coefficient $T_{C(111)}$ at He addition indicate that the strain energy is increasing, detrimental to the surface energy, and this may be due to the imperfections originating from defects introduced in the lattice by the presence of He atoms, occupying probably interstitial sites, due to their reduced radius.

Because Ag has a cubic structure, one may assume that the models used for other NaCl – type structures can be applied to study the Ag thin films. A transition from a [111] to a [002] out-of-plane orientation was observed when increasing the ion-to-atom ratio [283 - 286]. As He has a higher ionization energy than Ar, it may determine the increase of the number of ions in the plasma, and consequently a higher number of ions will bombard the surface of the growing Ag film. As a result, in Ar-

He mixture it is expected to get an increase ion-to-atom ratio, and consequently a transition to a [002] out-of-plane orientation [283 - 286]. The observed increase of $T_{c(111)}$ indicates that the lattice defects play a major role and are overcoming the effect of energetic ion bombardment.

The vertical grain sizes, calculated using the Scherrer formula from the (111) and (200) reflections, are presented in Figure 5.3.3, and present decreased values as He partial pressure increases in the deposition system. The observed decrease indicates the amorphisation of the films deposited in He rich atmosphere. The amorphisation may be explained by the inclusion in the deposited film of He atoms, acting as secondary nucleation sites and promoting the grain growth [287]. The amorphisation determined the decrease of the intensity of all the other reflections, which were well observed for the films deposited in pure Ar atmosphere. Considering the grain sizes determined from (111) and (200) peaks, it results that the grains are not equiaxed, their vertical dimension exceeding the lateral one.

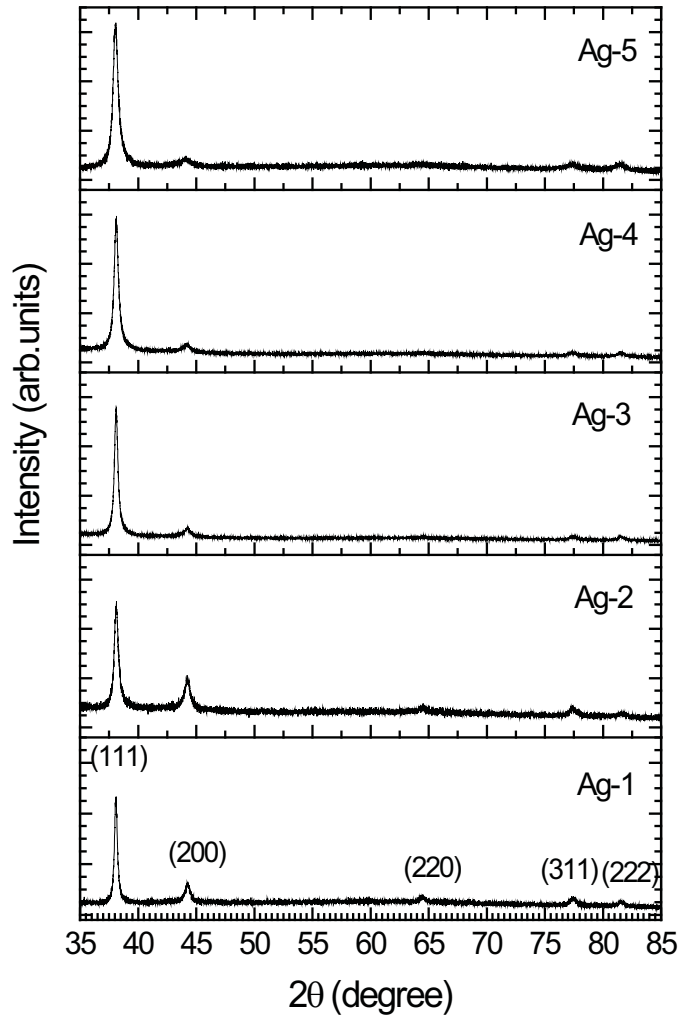


Figure 5.3.2: XRD patterns of Ag films grown at different He/(Ar+He) mass flow ratios.

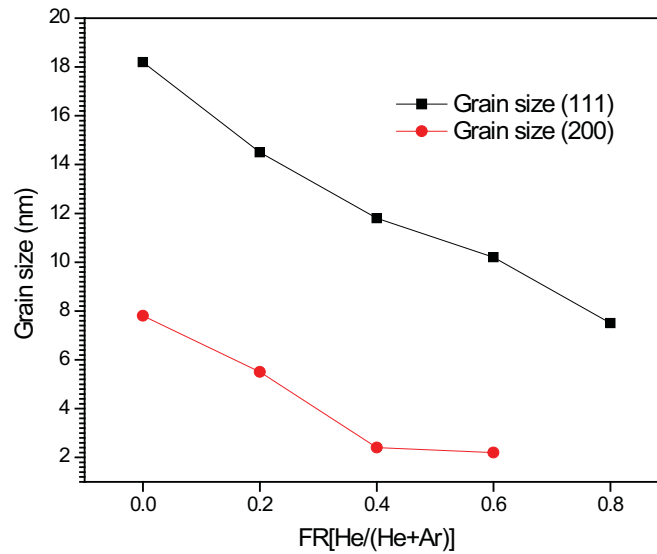


Figure 5.3.3: The vertical grain size variation of the Ag films grown at different He/(Ar+He) mass flow ratios.

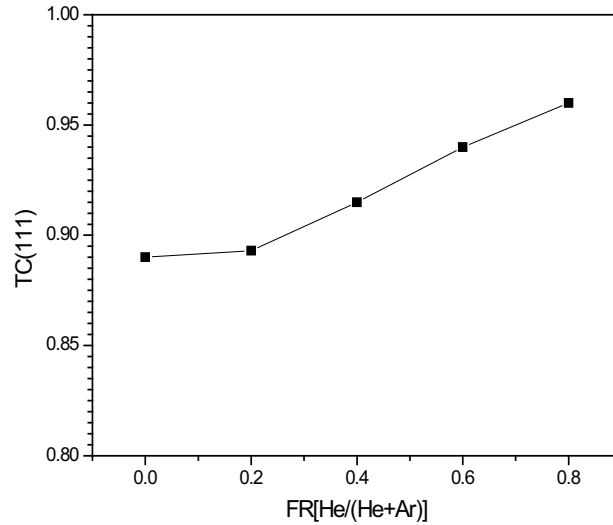


Figure 5.3.4: The variation of the texture coefficient $TC_{(111)} = T_{(111)} / (T_{(111)} + T_{(200)})$ for Ag films grown at different He/(Ar+He) mass flow ratios.

The roughness of the films, expressed as the rms roughness was found to decrease as the He concentration in the deposition gas increased (Figure 5.3.5). It is to note that the rms roughness decreased from 2.8 nm for sample Ag-1 (deposited in pure Ar atmosphere) to 0.1 nm for samples Ag-4 and Ag-5. One explanation for this decrease may be related to the decrease of the grain size of the crystallites. Another explanation may be related to the processes in the plasma discharge, also explaining the increase of the deposition rate with the addition of He (Table 5.3.3). Due to their small atomic mass, the velocity distribution function of He atoms is shifted toward higher values. Because

of the lower mass and higher mean speed of He atoms, they present a smaller scattering cross-section to sputtered Ag atoms/ions, determining the observed increase of the deposition rate. It can therefore be expected that as the ratio of He in the sputtering gas increases, the sputtered silver atoms would also undergo less collisions leading to a lower probability of agglomeration and growth on the substrate.

It could also be that due the higher kinetic energy of incoming Ag atoms, irregular surface ad-features, of lower binding energy, are sputtered away, in a similar fashion to assisted deposition.

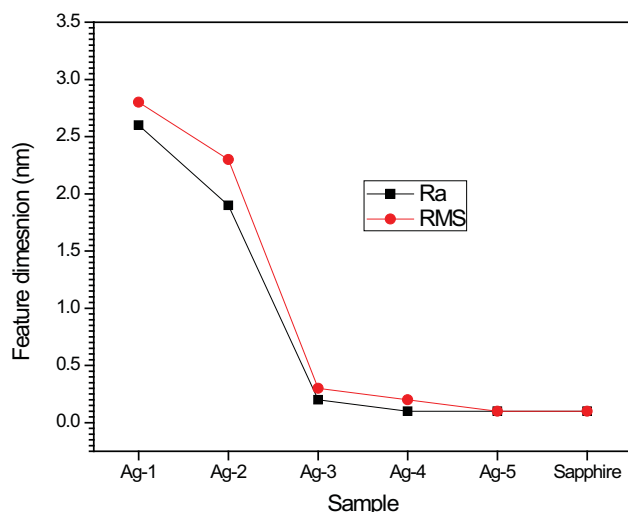
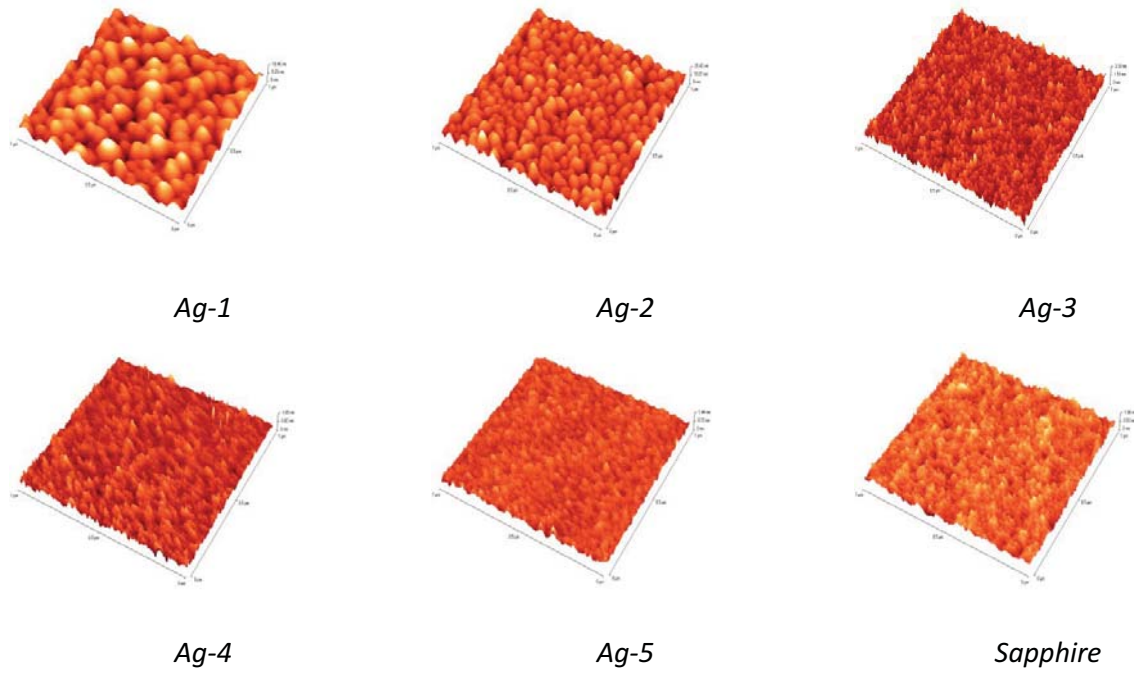


Figure 5.3.5: The variation of the Ra and RMS roughness of the Ag films deposited at different He/(Ar+He) mass flow ratios, and of the sapphire substrate.

Consequently, a decrease in the size of surface features is to be expected, with the addition of a lower mass sputtering gas [288]. Figure 5.3.6 presents the AFM images of the deposited samples, including the bare sapphire substrate.

The Ag films were further investigated by VIS reflectometry (Figure 5.3.7), which showed that the reflectivity of the films increase as the He concentration increased in the deposition atmosphere, for all the samples. At $\lambda = 450$ nm the reflectivity increase is about 12 % due to $F_R\{\text{He}/(\text{He}+\text{Ar})\}$ increase from 0 to 8. This increase is related to the smaller roughness of the Ag films deposited in the presence of He and the increased thickness of the films deposited in He rich environment.



Figures 5.3.6: AFM images of the deposited samples, including the bare sapphire substrate.

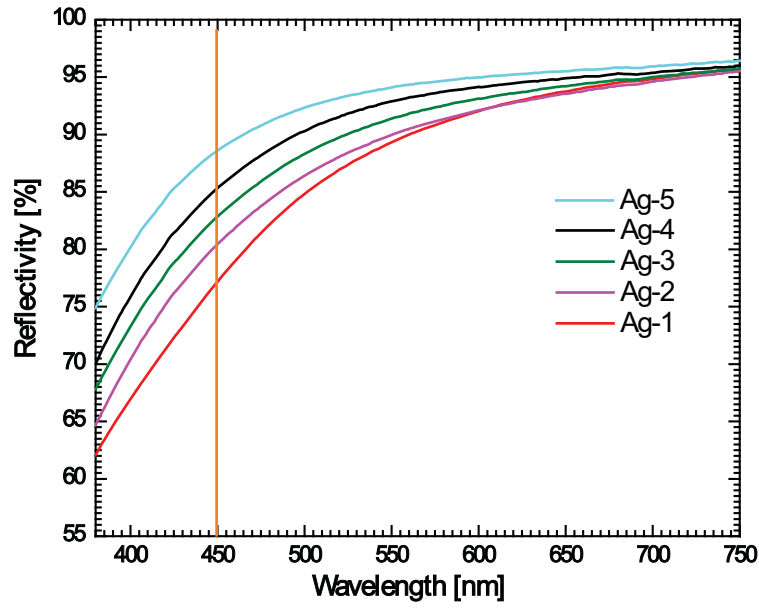


Figure 5.3.7: Variation of the reflectivity of the Ag films deposited at different He/(Ar+He) mass flow ratios.

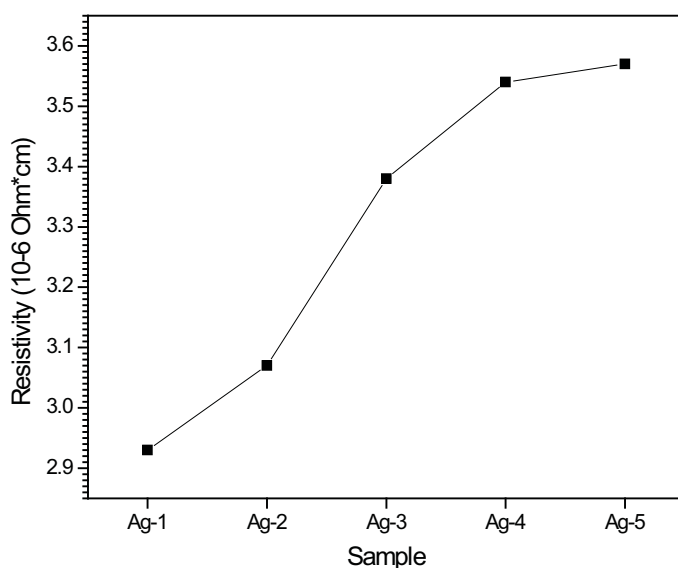


Figure 5.3.8: Variation of the resistivity of the Ag films deposited at different He/(Ar+He) mass flow ratios.

The Ag films were further investigated for their resistivity. The results, presented in Figure 5.3.8, indicated. As expected, the slight increase of the measured resistivity values, due to the amorphisation and increase of the grain boundaries density. The measured resistivity values are in good agreement with the results of Sarakinos et al. [266], reporting values around $3 \cdot 10^{-6} \Omega \cdot \text{cm}$. We consider that the observed decrease of conductivity, which is less than 20%, does not affect the films suitability for use as electrodes in plasmonic applications.

5.3.3 Summary and Conclusions

The roughness of thin Ag films can limit their applications as electrodes in plasmonic and optoelectronic devices, as well as in various nanophotonics applications. Harnessing the Penning effect, the addition of Helium in the deposition ambient determined the increase of the deposition rate, films' rms roughness decreased to that of the sapphire substrate, 0,1nm. The increasing He flow lead to the films amorphisation, accompanied by the decrease of the grain size. Together, these changes lead to an increase of the visible reflectivity, while the electrical resistivity exhibited a moderate increase. The higher resistivity will increase plasmon losses in film bulk. However, the lower roughness should reduce plasmon propagation losses along the interface. This is can be considered an optimization of the films for plasmonic, as well as general microelectronic and optical applications.

CHAPTER 6

CONCLUSIONS

The work undertaken as part of this project has lead to several advancements in the field of thin film optoelectronic materials, paving the way for the development of active plasmonic devices.

Regarding active media, BST and SBN films, of optical quality have been grown on SRO electrodes on MgO substrates. It has been shown that both BST and SBN exhibit an electro-optical response under these conditions, and that SRO/BST and SRO/SBN heterostructures can be used in electro-optic or active plasmonic devices. The residual strain along the film's direction of growth has been inferred from their optical properties, and found to vary along a non-uniform profile, influenced by the films' thickness. Ellipsometry has been used to measure the effective bias-induced birefringence of the film in a homogenous and isotropic approximation. The performance of plasmonic devices is, however, strongly influenced by the properties of the interface. Quantifying the birefringence profile along the sample's thickness is neither straightforward, nor entirely necessary. Further work should consist of incorporating these materials into various electro-optic devices. Assessing the behaviour of these devices would allow the electro-optic response of the material to be evaluated, within the context of each intended application. The sintering of SBN ceramic targets for PLD use has been a valuable training opportunity.

Regarding electrode materials, the suitability of SRO and TiN for plasmonic devices was successfully explored, and the deposition of Ag thin films has been further optimized for plasmonic applications.

Thin SRO films of optical quality were grown on MgO (001) by pulsed laser deposition. The influence of the oxygen pressure on structure, charge carrier dynamics and optical properties was investigated. The best crystalline structure, characterized by the absence of extra phases or directions of growth, was obtained at the oxygen deposition pressure of 75 mTorr. The investigated films exhibit plasmonic behavior in the near-infrared spectral range with the plasma frequency at 3.16 – 3.86 eV and epsilon-near-zero behavior at 1.11 – 1.47 μm , depending on the deposition conditions. Therefore, it should be possible that bias induced charge accumulation across a thin enough SRO film

would allow for the tuning of the epsilon-near-zero behavior in the near infrared range, opening the way for the development of an electro-absorption modulator. An Oxygen pressure of 100 – 200 mTorr provides best electronic and optical properties, in this range of deposition parameters, for plasmonic applications of the films. The obtained parameters show the suitability of SrRuO_3 thin films for plasmonic and metamaterial design applications, which may range from the heat generating nanostructures in the near-infrared spectral range to metamaterial-based ideal absorbers and epsilon-near-zero components, which is difficult to achieve in the near-infrared with conventional plasmonic metals. In all these applications, the interplay between real and imaginary parts of the permittivity in a given spectral range is needed for optimization of the performance. This material [227] is also compatible with and used in standard semiconductor technology and provides high temperature stability to up to 1200K needed in many plasmonic applications, such as heat-assisted magnetic recording [240, 241]. Since it can be used as an epitaxial bottom electrode for both SBN and BST, it follows that SRO can also be used as a top electrode in a devices using these materials as active media. Therefore, this work has shown that SRO has many potential applications in plasmonics and nano-optics, far beyond that of an epitaxial bottom electrode for ferroelectric films, for which it was initially considered.

TiN thin films of optical quality were grown on intrinsic Si (001) by reactive magnetron sputtering. The influence of the relative flow rates of reactive gas ($1/6 - 1$) on structure, charge carrier dynamics and optical properties were investigated for films deposited at room temperature and at 800° C. Films deposited at high temperature exhibited optical properties similar to Au and Ag, and similar electron concentrations. Electrical mobility, however, was much lower. Films grown at room temperature had even lower mobility, but higher electron concentrations, due to the higher number of defects.

Films fabricated at 800° C exhibited optical constants broadly similar to metals. However, the films grown at room temperature exhibited 2 distinct ENZ regions, demarcating a well-defined plasmon bandwidth, which has not been previously reported. This is most likely due to the presence of a titanium oxinitride or even titanium sub-oxide alongside titanium nitride in the films. The electron structure behind these unusual optical properties has to be explored, possibly using synchrotron radiation. It is a possibility that the double epsilon-near-zero behavior of these films could be controlled, just like for ITO and, potentially, SRO, thin time allowing for a duplex electroabsorption modulator.

Furthermore, TiN, just like SRO can be grown, heteroepitaxially, on top of BST or SBN, allowing their use as electrodes in active plasmonic devices.

Ag films were deposited in a mixture of He and Ar. Harnessing the Penning effect, the addition of He in the deposition ambient determined the increase of the deposition rate, an amorphisation of the films, accompanied by the decrease of the grain size, and the subsequent decrease of the roughness and increase of the visible reflectivity, while the electrical resistivity exhibited a moderate increase. This can be considered an optimization of the films for plasmonic, as well as general micro-electronic applications.

CHAPTER 7

FUTURE WORK

Perhaps the most exciting part of this project is the technological and scientific possibilities it has opened for research in plasmonics and nanophotonics. Further refining the characterization of the electro-optical effect in active media will, probably take the shape of plasmonic test-bed devices incorporating these materials, either a simple prism-coupling set-up, or a more complex interferometric device. Studying the behaviour of these devices at higher modulation frequencies will also be crucial, if they are to be technologically relevant. Obtaining smoother ferroelectric films, with a more uniform strain distribution should also be a goal, and several alternative fabrication techniques, like e-beam evaporation or magnetron sputtering could be considered as well. Also, microwave sintering will be attempted, in order to improve the density and uniformity of BST and SBN targets.

After this has been achieved, incorporating TiN and SRO electrodes will be a next step. Given that TiN is already used as a buffer layer, observing the change in the performance of such a device after a number of fatigue cycles and correlating it with the chemical changes at the interface would be a next step. Observing the behaviour of these electrode materials, together with other conducting oxides and metal films, at high temperatures would also be interesting. Another interesting and open-ended direction has been opened by the observed optical behaviour of SRO and TiN:TiON films. Using these materials as media for electro-absorption modulators should be a priority.

Aside from their applications in novel devices, some interesting issues about the physics of these materials remain to be solved. Most puzzling is the double ENZ observed in TiN. X-Ray Photoelectron Spectroscopy will be used to understand the chemical and electron structure of these samples, and hopefully their optical properties. The behaviour of plasmons in these materials is still not fully understood. Based upon calculated plasmon wavelengths, and discoidal surface structures of similar size will be created from these materials, in order to study the effects of plasmon confinement. Femto-second absorption spectroscopy will then be used to estimate plasmon damping rates and quantum generating efficiency.

Finally, the optical properties of Ag films fabricated under He partial pressures should be further studied via prism coupling or spectroscopic ellipsometry, so as to fully ascertain their suitability for plasmonic applications, which is increased by their smoothness but also hindered by their higher resistivity.

Such developments, together with the ever greater control of materials local properties, will be of increasing importance when designing plasmonic devices at ever smaller sizes, towards the goal of convergence with integrated electrical circuits.

Annex I

Fabricating Strontium Barium Niobate Ceramic Targets

Annex 1 describes the fabrication of ferroelectric Strontium-Barium Niobate targets. The PLD process requires sintered ceramic targets. BST thin films were deposited using available targets. The choice of Strontium Barium Niobate as an alternative material, however, required that targets of the proper stoichiometry be sintered. The preparation of precursor powders, the carrying out of the solid state reaction and the characterisation of the resulting material are described. The pressing of the green body, the sintering curve and the morphology of the sintered pellet are also discussed.

Strontium Barium Niobate (abbreviated as SBN) has a tungsten-bronze-type structure and exhibits excellent dielectric and optics properties [289 – 291].

The microstructure and ultimately the electrical and optical properties of the ferroelectric ceramics are mainly determined by the method of synthesis [292 – 294]. Different synthesis processes are known and used for obtaining ferroelectric ceramics, as conventional solid-state reaction process [295], co-precipitation or partial co-precipitation methods [296, 297], mechano-chemical synthesis, sol-gel process [298], hydrothermal synthesis, micro emulsion, combustion, thermal pyrolysis spray, molten salt etc. For obtaining a high quality ceramics, related to purity, homogeneity and microstructure, the above mentioned methods present specific advantages and disadvantages. The solid-state reaction route is one of the most used way of synthesis, because has the lower cost and is highly reliable, as compared to the other methods.

SBN targets were obtained by a solid-state reaction process, with the various steps followed for the synthesis being shown in a flow chart (Figure I.1), each stage/phase being discussed in the following.

A. Stoichiometric Proportion of Precursors

SBN ceramic was prepared by mixing the precursors powders in stoichiometric proportion, considering the final product $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_3$. The choice of the precursors was done according to the final product, consisting of mixtures of carbonates (SrCO_3 , BaCO_3) and oxide (Nb_2O_5).

B. Ball Milling

During the ball milling process, the materials were ground into fine powder and the different components are mixed uniformly. The rate of the grinding process is inversely proportional with the particle size of the precursors. Because the grinding rate depends on the contact surface between the precursor powders and the grinding media, it is obvious that the size should be minimised in order to maximize the surface area. An optimum size must be chosen for the grinding media, as the energy transfer between the media and precursor particles should also be maximised. For an efficient process, it is also necessary to have the precursors particles embedded in a grinding medium.

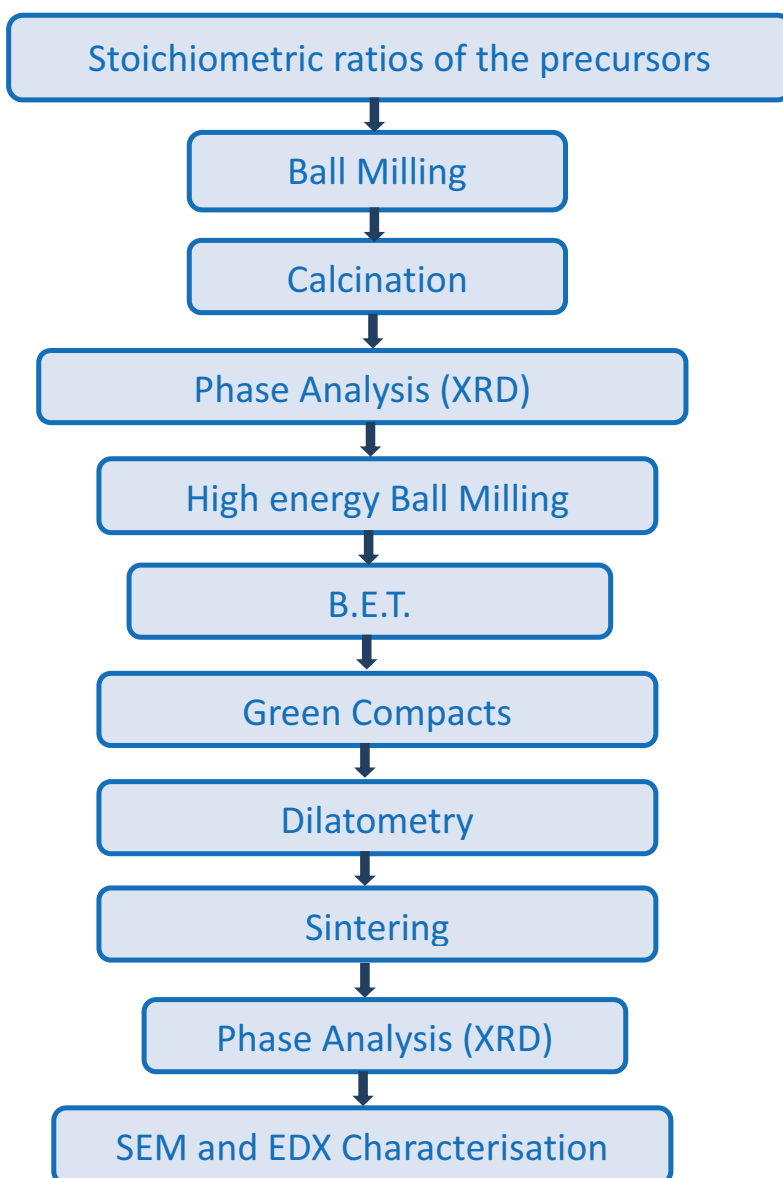


Figure I.1 Stages/Phases followed in a conventional solid state reaction process.

Another requirement for the grinding medium is related to its chemical inertness in relation with the precursors and environment. The container where the ball milling takes place must be both mechanically adequate (strong and tough), and not chemically react with its content and the environment.

The grinding process itself, fundamentally, is a transfer of mechanical energy into surface energy, which can be briefly explained as follows. During the milling process, the particles are subject to mechanical stresses at their contact points, due to compression, impact, or shear with the mill medium or with other precursor particles. As a consequence of the mechanical stresses, elastic and inelastic deformation may occur. If the stress exceeds the ultimate strength of the particle, it will be fractured. So, the mechanical energy supplied to the particles during the milling process is used to create new surfaces and also to produce other physical changes of the particulate matter, as inelastic deformation, increase in temperature and lattice rearrangements within the grains of the particulate matter. Other changes, e.g. in the chemical properties, especially at the surface can take place, especially after prolonged milling or under high energy milling conditions.

C. Calcination

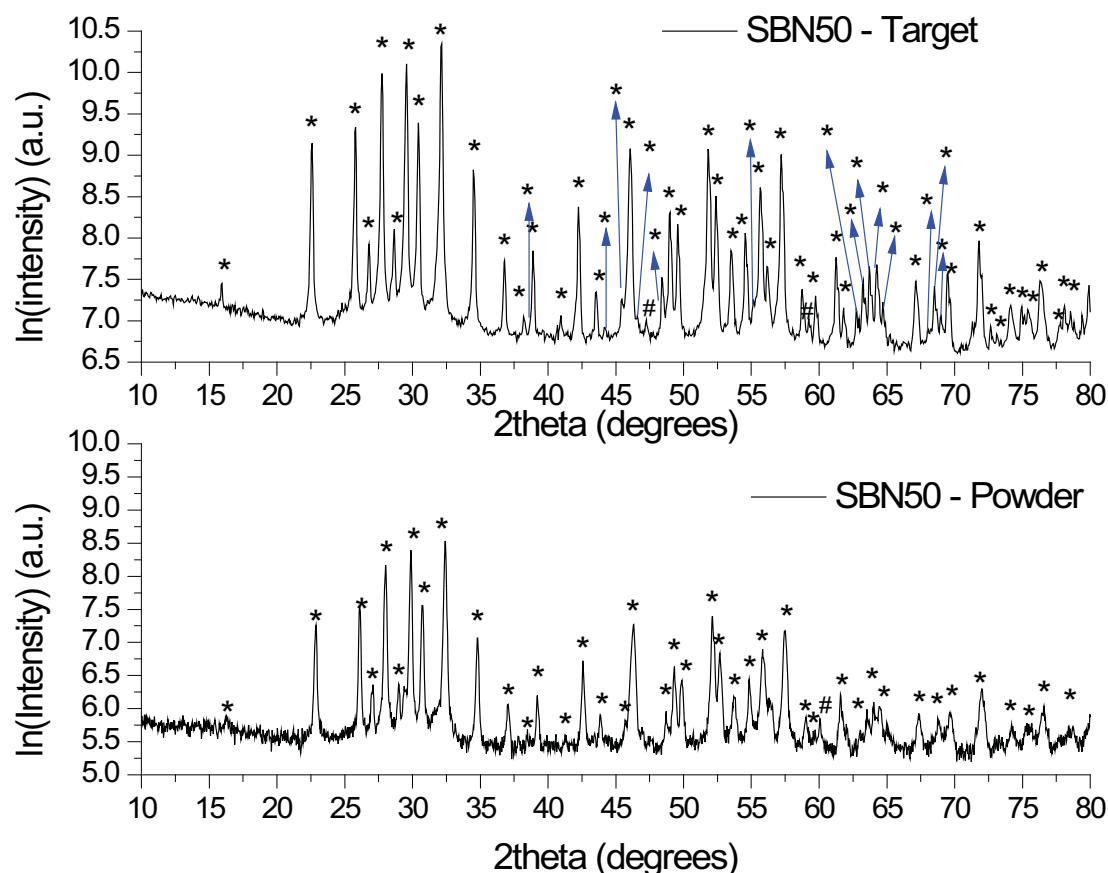
During the calcination process, the constituent carbonates and oxides decompose and react to form the phase of the required compound. In the calcinations process, four physical processes are involved: linear expansion of the particles, solid phase reaction, contraction of product, and grain growth. The phase formation of a compound takes place by solid-phase reaction, involving chemical reactions through atomic diffusion among grains at temperature below the melting points of the precursors [299].

Because decomposition reactions are endothermic, the system must be heated for sustaining the reaction. Usually, the calcination temperature has an intermediate level, being high enough to sustain the reaction, and low enough to facilitate subsequent grinding. If volatile materials are used, the calcination temperature must be kept set low enough to changing the compounds stoichiometry. This should, however, not be a concern with SBN50. The calcination process was carried out in air at 1200° C.

D. Phase Analysis

After the calcinations process, the assessment of the compound structure is needed, to further proceed with an adequate compound. Figures I.2 show the phase composition of the calcined powder,

and the sintered target. It can be clearly seen it is almost single phase, with a negligible content of unidentified phases. The target sintered from this powder is, however, single phase SBN50.



Figures I.2 The XRD patterns of SBN-50 powder calcined at 1200° C and of SBN targets, sintered in two stages, at 1260° C and 1380° C, indexed according to JCPDS - ICDD card 039-0265 corresponding to the tetragonal SBN 50.

E. High Energy Ball Milling

The grinding of the compound, free of carbonates is continued. As the oxide powders resulted from the calcinations process should diminish their size, and because their mechanical strengths is higher than that of the carbonates, the milling process is done at higher energy. In our case, the powders were milled for 6 hours at 240 rpm, at 20 cm from the rotation centre.

F. B.E.T. (Brunauer Emmett Teller)

Before evaluating the sintering behaviour of the material, it is useful to estimate the average size of the powders. Fine powders should be used, as sintering is improved at lower particle sizes, as embodied in the work of Herring [300]. For this purpose, the BET method was employed to measure

surface area, with the average particle size being derived using the formula $6/(S_{\text{surface}} \times \rho)$ which assumes monodispersed spheres.

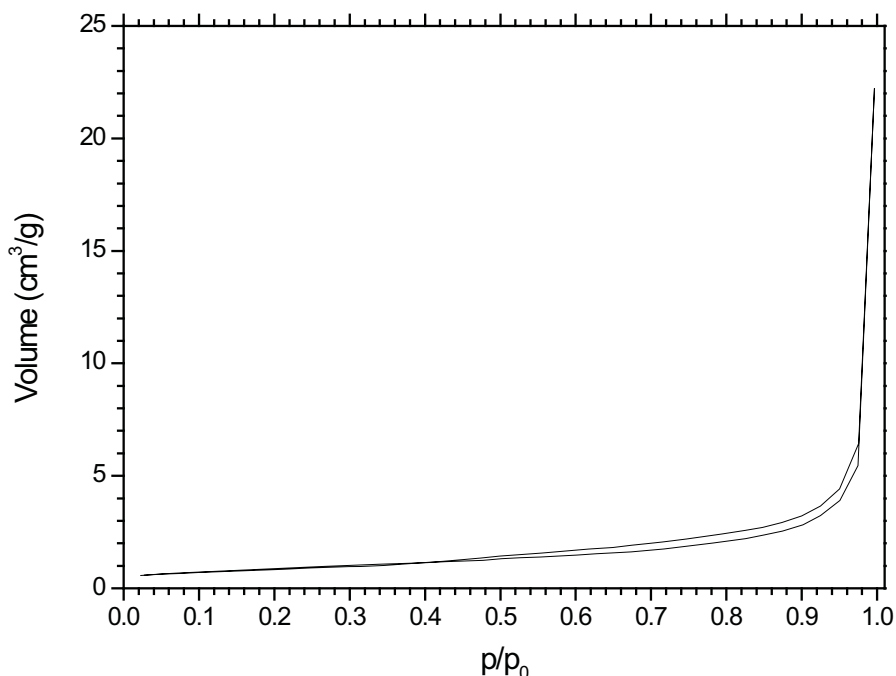


Figure I.3 BET Isotherm of the SBN50 powders after high energy milling.

BET analysis was carried out using N_2 gas; it yielded a surface area of $3.24 \text{ m}^2/\text{g}$, corresponding to an average particle size of $0.285 \text{ }\mu\text{m}$.

G. Green Compacts

The green compact is obtained by compressing the calcined powder, using moulds of the desired shape. The further sintering behaviour of green compacts depends on its structure [301]. Different shaping techniques can be used, e.g. uniaxial or isostatic pressing, calendering, extrusion, jigging, injection moulding, silk screening, slip casting, band casting, etc. In this work SBN green compacts, with simple disc shapes were obtained by uniaxial pressing technique from the calcined powder.

The process is shown in Figure I.4. It is carried out in a die having cylindrical open cavity. First, an air tight lower punch is placed in the cylindrical cavity. Then, the die is filled with the calcined powder which is to be compacted and after that an upper punch is placed on top. With the help of the upper punch, pressure in the range of 25-40 MPa is applied. The removal of green compact

should be done with care to avoid mechanical cracks which would lead to layering of the sintered products. Die and punch surfaces should be highly polished in order to reduce wall friction. Generally, die is made of hardened steel and punches are made of tungsten carbide mirror finish to minimize wear and maintain surface finish.

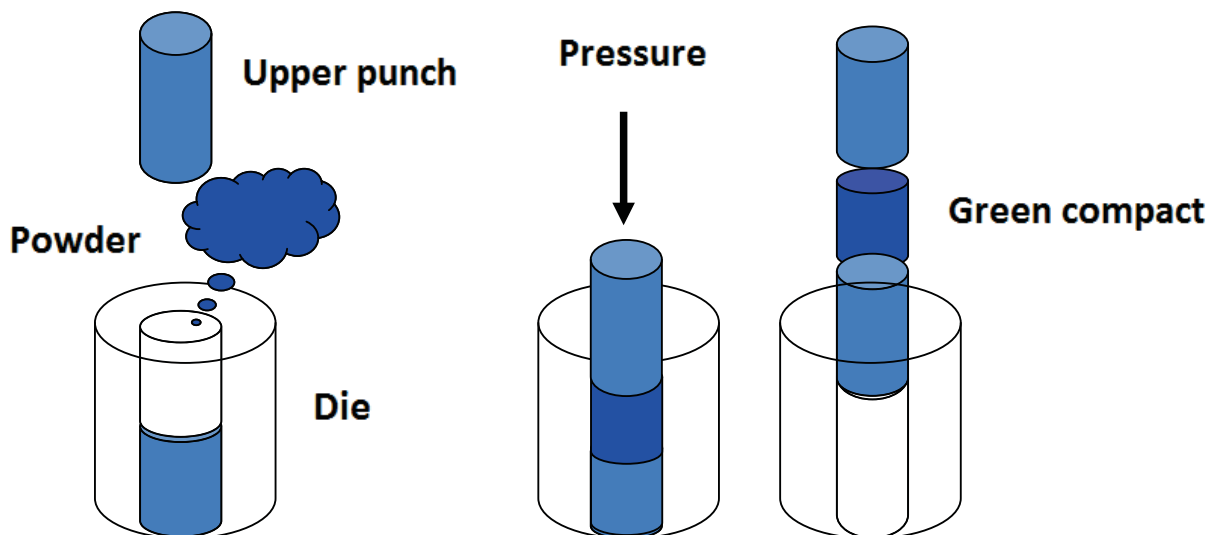


Figure I.4. Illustration of steps involved in preparation of green compacts.

The green body was pressed using a 1 inch diameter die, at a pressure of 0.5 tons per square inch. The density was evaluated by weighing the sample and measuring its geometrical proportions. It was evaluated at 3.75 g/cm. By considering the theoretical density of SBN50, of 6.5 g/cm (JCPDS 039-0265 tetragonal SBN 50), the green body's density is 57%. A smaller green body, with a diameter of 5mm, was pressed at the same pressure, and used to measure the sintering behaviour of the compound.

H. Sintering

Sintering is the densification process in which the green compact is heated to a temperature, which is generally in the range of 0.5 to 0.75 times of the melting temperature of the compounds present in green compact [302]. Figure I.5. illustrates the volume reduction process of calcined powders after shaping and after sintering. When green compacts are heated at such temperatures, the joining of the particles and the reduction in the porosity of the green compact occurs by solid state atomic diffusion.

The driving force for sintering is the reduction in surface free energy of the consolidated mass of particles. This reduction in energy can be accomplished by atom diffusion processes that lead to

either densification of the body (by transport of matter from inside the grains into the pores) or coarsening of the microstructure (by rearrangement of matter between different parts of the pore surfaces without actually leading to a decrease in the pore volume).

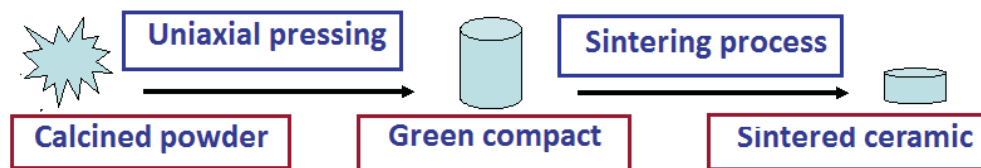


Figure I.5. Schematic diagram illustrating the effect of sintering on the volume.

There are at least six different mechanisms of sintering in polycrystalline materials which lead to bonding and growth of necks between the particles and hence affecting the strength of the powder compact during sintering. The six different mechanisms are:

1. Surface diffusion
2. Lattice diffusion (from the surface)
3. Vapour transport
4. Grain boundary diffusion
5. Lattice diffusion (from the grain boundary)
6. Plastic flow

The first three of the total six mechanisms mentioned above are non-densifying mechanisms as they lead to neck growth without densification. Occurrences of these diffusions reduce the curvature of the neck surface (i.e., the driving force for sintering) and hence reduce the rate of the densifying mechanisms. Fourth and fifth mechanisms are the most important densifying mechanisms in polycrystalline ceramics as the diffusion from grain boundary to the pore permits both neck growth as well as densification. Plastic flow by dislocation motion also leads to neck growth and densification, however this is more common in the sintering of metal powders. In addition to these mechanisms, the diffusion of the different ionic species making up the compound is coupled to preserve the stoichiometry and electro-neutrality of the compound. As a result, it is the slowest diffusing species along its fastest path that controls the rate of densification [302].

In this work, the sintering process was first attempted in a Netzsch series 3300 dilatometer. The dilatation of the green body was measured from room temperature up to 1400⁰ C, as shown in

Figure I.6. Although no offset point was observed by that stage, the experiment was stopped due to the proximity of the materials' melting point, estimated around 1490° C [303].

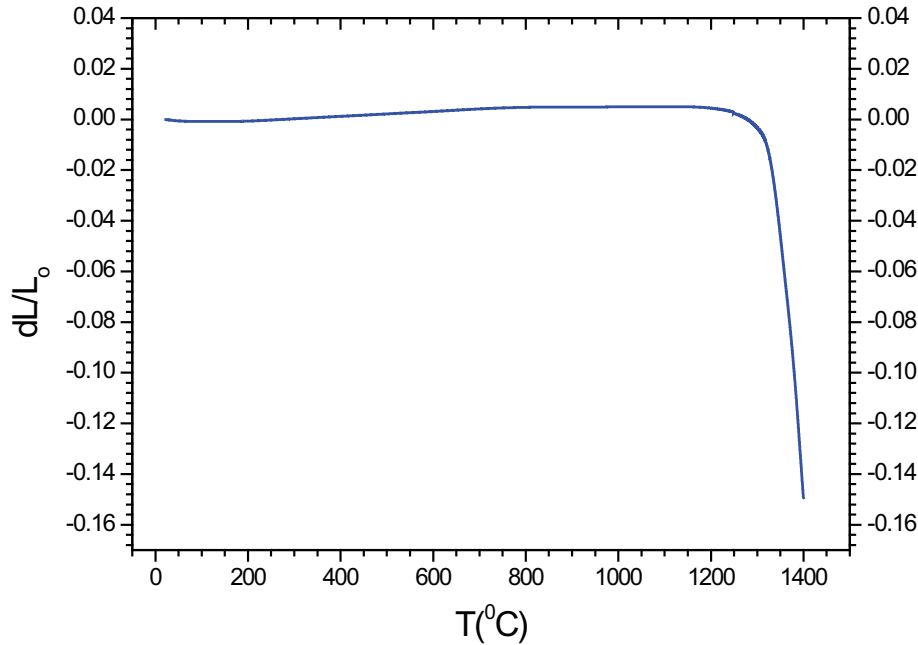


Figure I.6: Sintering curve of SBN-50 green body.

In general, the higher the sintering temperature, the larger the grains grow, as the grain growth is caused by atomic diffusion. One solution has been to incorporate a presintering step [304] in the fabrication of one of the targets. To this end, the green body was heated at a rate of 5°C /min to the estimated onset temperature of 1260 °C, where a presintering treatment was applied for 4 hours. This was followed by sintering at 1380 °C for another 4 hours. The green body density was determined to be 56% of theoretical density and a shrinkage of 14% (Figure I.6) leads to an estimated sintered density of 88% of theoretical density, considering that $\rho_{fin} = (L_{in}/L_{fin})^3 \rho_{in}$.

After this, the sample was cooled to room temperature at the same rate. As seen in Figure I.2, the sintered target is pure SBN-50. After this, the target was polished using P1200 sandpaper, and subjected to scanning electron microscopy (SEM) analysis.

I. Target Microstructure

The elemental composition and microstructure of the SBN-50 sample were analysed by a Hitachi 3030 SEM equipment with a Bruker Energy Dispersive X-ray Spectrometer (EDS).

The elemental composition is presented in Table I.1, showing a stoichiometric composition, and in Figure I.7 is presented the obtained EDS spectrum.

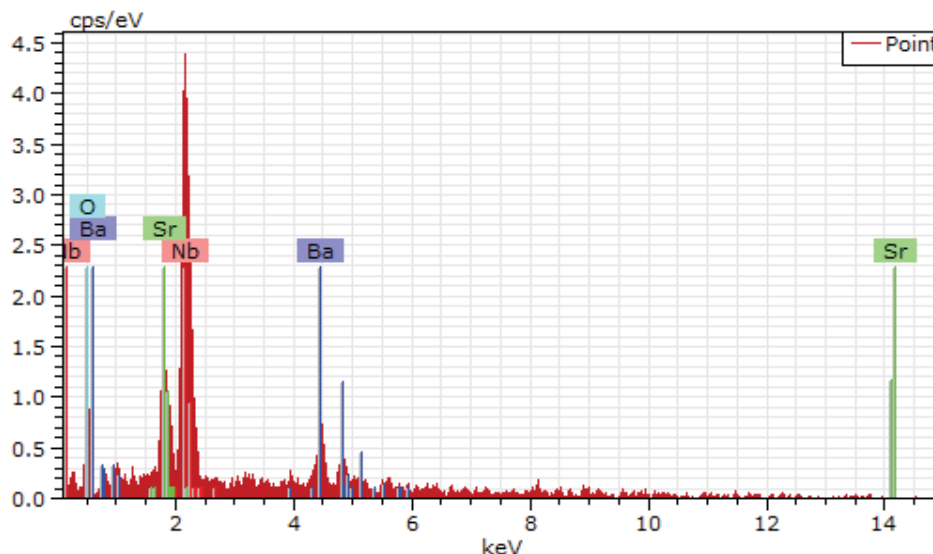


Figure I.7: EDX analysis of the SBN-50 sample composition.

The surface of the SBN-50 sample, fabricated without presintering, exhibits voids and scratch marks from the polishing process (Figure I.8). At higher magnification, cracks become visible (Figure I.9). The surface of the target appears to be heavily melted. Even at low magnification (Figure I.10) some large cracks are visible on the surface, rendering it unfit for use as a PLD target. Nevertheless, running a linear intercept across the image allows the density to be estimated at 92%; this is in close agreement with the dilatometry results and marks the target's fit for PLD use.

Table I.1: The elemental concentration of the SBN-50 sample, determined by EDS

Element	Concentration (at. %)
Oxygen	58.2 ± 4.12
Niobium	27.38 ± 1.68
Strontium	7.26 ± 0.48
Barium	7.11 ± 0.52

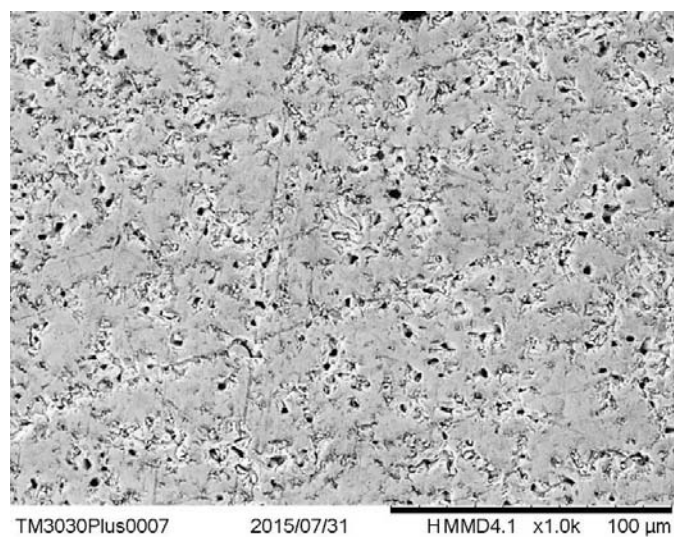


Figure I.8: SBN-50 sample, fabricated without presintering (x 1000 magnification).

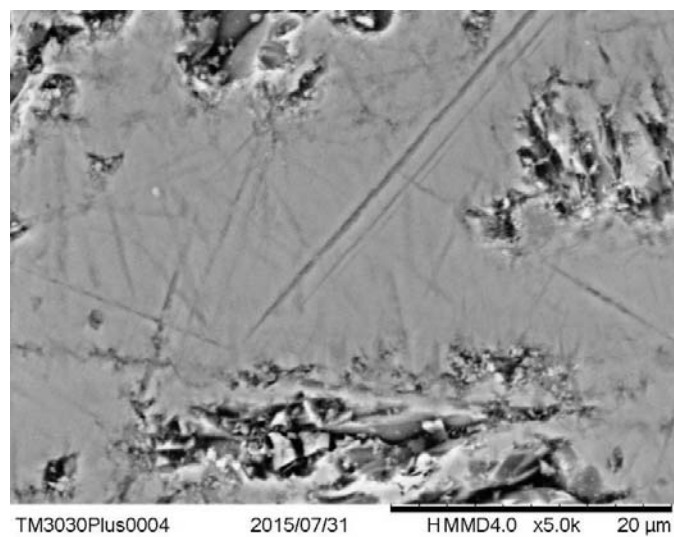


Figure I.9: SBN-50 sample, fabricated without presintering (x 5000 magnification).

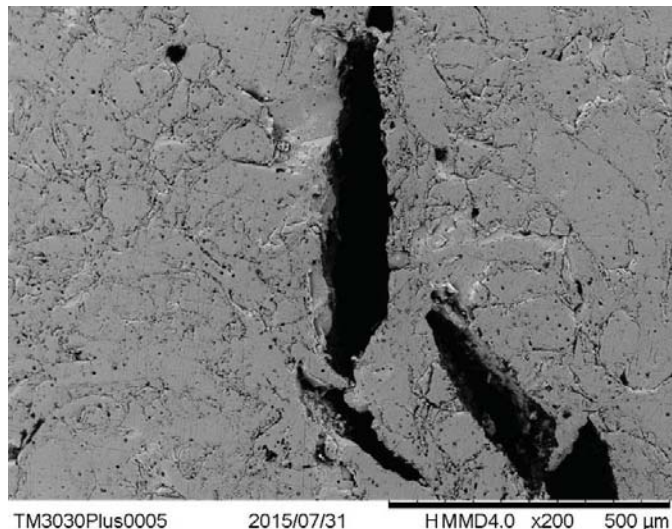


Figure I.10: SBN-50 sample, fabricated without presintering (x 200 magnification).

The presintered target has a rough, granular surface. Some voids are visible, and the sharp edges are indicative of high temperature sintering. However, no melting is visible. No large scale cracks have been observed, making the pellet suitable for use as a PLD target (Figure I.11). At higher magnification (Figure I.12) the grains are visible, and their size was found to be between 5-10 μm in size, with sharp edges, typical of materials sintered at high temperature. Even at this scale, no molten regions could be seen.

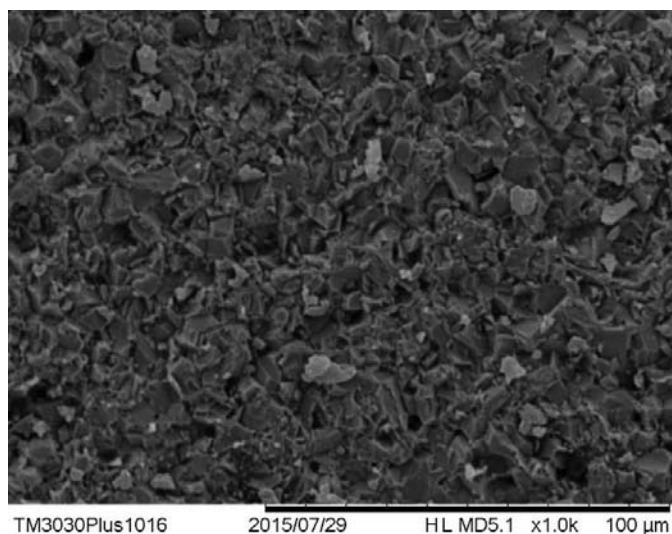


Figure I.11: Presintered SBN-50 sample, (x 1000 magnification).

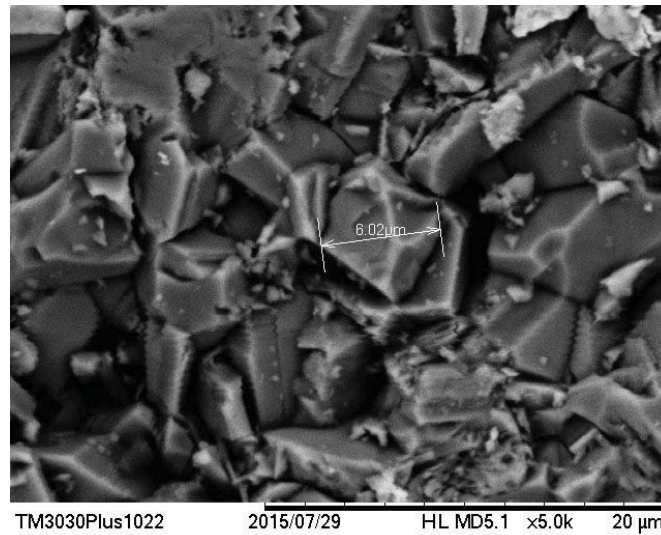


Figure I.12: Presintered SBN-50 sample, (x 5000 magnification).

Summary and Conclusions

SBN-50 ceramics were sintered with and without a presintering process. The ceramics produced without presintering present on the surface deep voids and cracks, presenting a specific morphology for a heavily melted material. On the contrary, the surface of the SBN-50 ceramic produced with a presintering process exhibit a coarse, granular surface. Some voids are still visible. The grain size values ranged in the interval 5 - 10 μm, with sharp edges, typical for materials sintered at high temperature. Because no large scale cracks or molten regions were substantiated, the pellet was suitable to be used as a PLD target. Starting from a green body density of 56%, the density of the sintered target was estimated, according to Herring's formula, to be 88-92%.

Annex II

Titanium oxynitride thin films with double epsilon-near-zero behaviour

Annex 2 expands the characterisation of the deposited TiN films, by incorporating the results of X-Ray Photoemission Spectroscopy (XPS) measurements which have been carried out after the main body of this work had been submitted.

A. XPS Data Collection

All XP spectra were recorded using a K-alpha+ XPS spectrometer equipped with a MXR3 Al K_{α} monochromated X-ray source ($h\nu = 1486.6$ eV). X-ray gun power was set to 72 W (6 mA and 12 kV). All spectra were recorded using a pass energy of 200 eV for survey spectra and 20 eV for high-resolution spectra. The instrument sensitivity was 3×10^6 counts $\cdot$ s $^{-1}$ when measuring the Ag 3d $_{5/2}$ photoemission peak for an atomically clean Ag sample recorded at a pass energy of 20 eV and 72 W (6 mA and 12 kV) emission power. The Ag 3d $_{5/2}$ full width at half maximum (FWHM) was 0.49 eV for the same instrument settings. Binding energy calibration was made using Au 4f $_{7/2}$ (83.96 eV), Ag 3d $_{5/2}$ (368.21 eV) and Cu 2p $_{3/2}$ (932.62 eV). Charge compensation was achieved using the FG03 flood gun using a combination of low energy electrons and the ion flood source. Argon etching of the samples were done using the standard EX06 Argon ion source using 1000 V accelerating voltage and 10 μ A ion gun current. All Ti 2p XP spectra were acquired in ultra-high vacuum, using 50 eV pass energy and 0.1 eV step size. Acquisition times were 2 min 15 sec per spectrum. All N 1s XP spectra were acquired in ultra-high vacuum, using 50 eV pass energy and 0.1 eV step size. Acquisition times were 1 min 30 sec per spectrum.

Samples were prepared by pressing the sample onto carbon based double side sticky based tape and analyzed at an electron take-off angle normal to the surface with respect to the analyzer.

B. XPS Data Analysis

Casa XPS was used for data interpretation. Shirley or two point linear background subtractions were employed depending on background shape. Thermo scientific sensitivity factors were used for quantification analysis. Peaks were fitted using GL(30) line shapes; a combination of a Gaus-

sian (70%) and Lorentzian (30%). All XP spectra were charge corrected by referencing the fitted contribution of C-C graphitic like carbon in the C 1s signal to 285 eV.

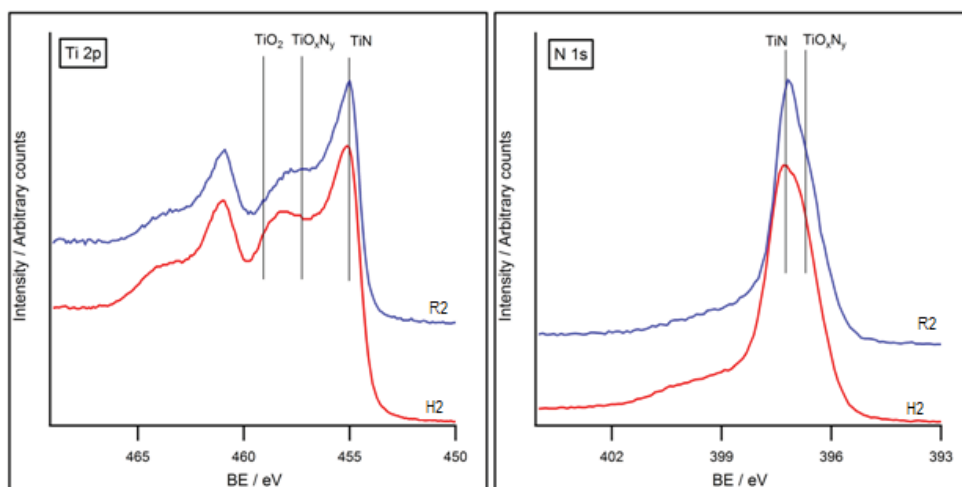


Figure II.1: Ti 2p XPS spectra of samples deposited H2, and R2 after a few consecutive sputtering cycles. The lines mark characteristic binding energies of different Ti chemical states.

The XPS studies show that for films from both series, the ratio between TiN and TiO doesn't depend on the depth.

The partial pressure of N_2 (within the N_2 -Ar sputter gas mixture) and the deposition temperature govern the nitride saturation of the growing TiN film. Reducing the amount of nitrogen results in the formation of substoichiometric TiN_x , which reacts, when exposed to air, forming TiO_x and TiON compounds. Varying the content of the deposition gas mixture, one can control the amount of TiN, TiO_x and TiON in these films, determining changes of the optical properties of the samples. Considering the series H films, due to enhanced diffusion of nitrogen atoms during films' growth determine complete TiN structure saturation, inhibiting the formation of titanium sub-oxides and oxynitride.

In order to verify this hypothesis the samples from H series were compared to the ones from R series. Figure II.1 shows the Ti 2p and N 1s XPS spectra of samples R2 and H2. The spectra show signals at the characteristic binding energies of TiN_x , TiON, and TiO_x [255, 305]. Table II.1 shows the calculated relative atomic percentages of the three different chemical states of Ti in the samples. Series H samples consist mainly of titanium nitride, with a small amount of titanium dioxide (2.6%) and oxy-nitride (7%). Samples from series R exhibit a considerable content of titanium dioxide (18.6%), and a similar (in comparison to the H series samples) amount of titanium oxynitride (10.1%). Depth profiling (Figure II.2) shows the film composition to be uniform, except for the stronger oxida-

tion near the surface (no capping layer has been used). The ion sputtering rate has been estimated around 2-2.5 nm/min.

Table II.1: Chemical binding of Ti in the samples fabricated at 20% N₂ partial pressure. The fitting procedures used to calculate the percentages in this table are shown in the supplementary information.

Sample	TiN (%)	TiON (%)	TiO ₂ (%)
H2	90.4	7.0	2.6
R2	71.3	10.1	18.6

The higher state of Ti in the samples fabricated at room temperature, is due to the greater proportion of broken-bond defects or unreacted Ti atoms, to which atmospheric oxygen then becomes attached. The N 1s peak at ~397 eV for all the TiON films (Figure II.2) in the present case can be attributed to nitrogen in the Ti-N bonds [306]. The very intense nature of this N 1s component peak is indicative of nitride formation in the film. The small N 1s peak at higher binding energy (~399 eV) has been associated to terminally bound nitrogen that is released during nitridation of Ti-O sites or in surface oxynitrides [306]. This peak has been noted by several authors for nitrides and oxynitrides of Ti grown by various methods [306, 307]. In fact, in a theoretical paper, Graciani et al. [308] argue that the most stable way of growing good quality Ti oxynitrides is through nitrogen incorporation in the most stable alpha-TiO phase, which is isostructural with TiN. According to their calculations, it is much easier to implant Nitrogen into the TiO than into TiO₂, which is the usual way of growing TiON [306], and Oxygen vacancy sites are the only places where Nitrogen implantation is thermodynamically favorable. In terms of density of states, the same authors argue that the gap between 2p (N/O) and 3d Ti bands increases with the concentration of Oxygen and decreases as the concentration of N increases. This can be seen in our electrical measurements where the actual resistivity of the samples decreases as the concentration of Nitrogen increases and in the evolution of the small N1s peak at ~399 eV and the Ti2p peak at ~455 eV. Nonetheless, no structural phase separation has been detected in these films deposited on MgO.

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