Chapter II: Experimental and Characterization techniques

Abstract

This chapter describes the different fabrication and characterization techniques used in the present work. In the present work, IBSD was used to deposit Ag and Au thin films on Quartz, Borosilicate glass and carbon coated Cu grids substrate and also on sol-gel deposited TiO$_2$ and ZrO$_2$ thin films. The deposited films were characterized using atomic force, scanning electron and transmission electron microscopy, UV-Vis-NIR spectrophotometry and x-ray diffraction. The details of experimental conditions and characterization techniques are presented here.
Chapter II: Experimental Techniques

2.1. Ion Beam Sputter Deposition

The surface atoms of a solid can be sputtered by exposing them to a beam of energetic particles of energy between 0.1 to 5 KeV. If the sputtered atoms are deposited on a substrate, then the process is called Ion Beam Sputter Deposition (IBSD). The overall amount of deposited energy (and therefore the number of sputtered atoms) is sensitive to the surface. The use of ion beams for processing, as opposed to directly extracting ions from plasma to bombard a sample, has numerous advantages for the controlled processing of materials with ion bombardment. The parameters of ion beam, the flux, the energy, the species and charge state and the direction (and divergence) are all easily quantified and controlled. IBSD typically operates in the pressure range of $1 \times 10^{-5}$ Torr to $1 \times 10^{-3}$ Torr, which makes it compatible with a number of other physical and chemical processes used in thin film material processing. This is not possible in other plasma based sputtering techniques which work at much higher pressures. One other significant advantage to operation in this relatively low pressure region is that the mean free paths of both the incident ions and also of the sputtered atoms are long. There is little scattering due to gas phase collisions and as such the complication of charge exchange modification of the ion flux is minor.

Many researchers have worked on ion beam deposition techniques for many different applications. A brief review of literature on IBSD is presented. Todorov et al. have deposited monolayer thick silver films on an Ni(100) surface using direct ion beam deposition of $^{107}$Ag+ ions with 20 eV kinetic energy and the substrate at 25°C. The film deposition was performed by means of a mass-selected, low energy, ultra-high vacuum ion beam system with a well-defined ion energy. The films were analyzed in situ by time of-flight scattering and recoiling spectrometry (TOF-SARS) and by low energy electron diffraction (LEED). They have used classical ion trajectory simulations to model the TOF-SARS spectra. It is found that the results of the TOF-SARS spectra and azimuthal scans are consistent with the growth of a monolayer Ag film with a fcc (111) structure on the Ni(100) surface. The deposited films exhibited a faint hexagonal c(2×8) LEED pattern. It is observed that molecular dynamic simulations of the deposition process are in
agreement with the experimental observations. The growth of such isotopically pure metal monolayers at room temperature with controlled orientations provides the opportunity for exploring a variety of unique physical properties [1]. Nguyen et al. have developed high-reflection (HR) and multilayer antireflection (AR) coatings using ion-beam sputtering deposition (IBSD) for long-wave infrared (LWIR) (\(\lambda \sim 9.4 \mu m\)) quantum cascade lasers (QCL). The high quality, high-density material achieved by IBSD allows for flexible and robust optical coatings especially compared to electron beam evaporation (EBE). It was observed that similar to the engineering of the QCL emission wavelength, both AR and HR coating structures can be customized, by slight adjustment of the layer thicknesses, for other lasers emitting at any wavelength in the LWIR. The metallic HR coating achieved a measured reflectance of 96.70%, and the multilayer AR coating achieved a measured reflectance of 1.64%, within 3% of theoretical simulation. They have provided a solution to the processing sequence due to problems that arise from the high-temperature deposition process. Finally, the coatings were applied to a \(\lambda \sim 9.4 \mu m\) QCL [2]. Liu et al. have used Time–power monitoring technique for monitoring the thickness of optical films during ion beam sputter deposition with the routine parameters of the main ion source are 1200 V/ 300 mA for Ta2O5 and 1000 V/500 mA for SiO2 respectively. They baked the vacuum chamber at 80°C for 2 h and the baking is stopped during the coating process. In the beginning stage of sputtering, it was observed that the change of composition and microstructure in the top layer of targets results in the change of the sputter rate. For different materials, their sputter characteristics are different. With the increase of the layer number, the deposition rate for Ta2O5 increases, while the deposition rate for SiO2 decreases, and both deposition rates eventually stabilize. It has been shown that the results of a single layer coating were in fairly good agreement with those of multilayer coatings. The results show that the film thickness can be controlled accurately by adjusting the deposition time at the beginning of deposition. This paper has also provided a simple and effective way to optimize the thickness match of the high- and the low-index layers for a multilayer stack [3]. Balu et al. have deposited chromium films by IBSD technique with varied process parameters. The ion energy in this case was 1 KeV with an incident angle of 45° at different fluxes. The energetics involved in the process has been observed as the important criteria that influence the structural evolution. Deposition rate has been found to play a major role in the initial structure formation indicating the necessity of a critical deposition rate. It has been observed that (1 1 0) orientation sustains even at higher substrate temperatures as high as 700°C. The structural
transformation of (1 1 0) to (2 0 0) orientation occurs when the process parameters favor the formation of island growth, which was carried out using oblique incidence technique. With higher angle of incidence, the film shows (2 0 0) preferential orientation, which is considered to be the plane of better lattice match to Co-based alloys. The surface morphology shows a ripple nature with comparatively lower surface roughness. From the above investigations, it is clear that the energetics of the process controlled by various factors, such as deposition rate, substrate temperature and film thickness associated with oblique incidence, plays the major role in the structural transformation from (1 1 0) to (2 0 0) orientation in Cr thin films [4]. Huang et al. have deposited Silicon nitride films on Al/glass, NaCl, KBr, and silicon substrates by single ion beam sputter deposition. They prepared the films at various N$_2^+$ ion beam voltages over the range from 500 to 1200 V. The resulting films were characterized by using secondary ion mass spectrometry, Fourier transform infrared spectroscopy, transmission electron microscopy, and transmission electron diffraction. The stoichiometry of these silicon nitride films was controlled by adjusting the ion beam voltage. It was observed that the films deposited under conditions of ion beam voltage below about 700 V were nitrogen rich while films made with beam voltages in excess of 900 V were silicon rich. The film structure changed with the substrate temperature from amorphous at room temperature to nanocrystalline/amorphous at 300°C. The lowest occupied (LO) phonon band for stoichiometric Si$_3$N$_4$ was approximately 1124 cm$^{-1}$ and the stoichiometry of thin silicon nitride films could be assessed with the LO phonon position [5]. Lim et al. have reported on Cu films deposited by ion beam deposition with or without a negative substrate bias voltage were found to have different states of dependence of electrical resistivity on film thickness. Here, a/Cu-enriched plasma was generated by an application of a negative bias voltage of -300 V to the Cu target. In this report, they have attempted to evaluate the effects of the film thickness, average grain size, impurities, and morphological defect on the resistivity increase of Cu films in addition to the surface scattering of the Fuch-Sondheimer model and the grain boundary scattering of the Mayadas-Shatzkes model. When the theoretical model was fit to the experimental data, the Cu films deposited at a substrate bias voltage of $-50$ V showed that the electrical resistivity was in good agreement with the theoretical curve under the condition that the film thickness was 2.3 times larger than the average grain size and when $p=0$ and $R=0.24$. For the Cu films deposited without a substrate bias voltage, however, there was a slight deviation between the theoretical curve and the measured resistivity below a 100 nm thickness, even at the condition of the film thickness.
that was six times larger than the average grain size, which is considered to result from
the effect of solute impurities in the Cu films. Therefore, it was found that the impurity
effect on the electrical resistivity could not be neglected. It was also confirmed that the
morphological defect, such as a columnar structure with noticeable gaps in the Cu films
deposited without the substrate bias voltage, caused a great increase in resistivity even
above the 100 nm thickness [6]. Sasase et al. have deposited ‘Environmentally friendly’
semiconductor β-FeSi2 thin films by the ion beam sputter deposition (IBSD) method on
Si(100) substrate. The authors used Ar\(^+\) ion energy of 35 KeV and Ar\(^+\) ion current density
of 250 µA/cm\(^2\). The difference in crystallinity of the FeSi\(_2\) obtained has been investigated
using Fe and Fe–Si targets at various substrate temperatures. When the Fe target was
used, highly (100)-oriented β-FeSi2 films with relatively smooth surfaces were formed at
700°C. On the other hand, such films were scarcely observed when the Fe–Si target was
used. Sharp edge grains were observed, which consisted of a mixture of α and β phases or
α single phase. In the latter case, it is found that α-FeSi2 is formed at \(T_s\) above 600°C,
which is lower than the conventional transformation temperature for the β \(\rightarrow\) α phase [7].
Nitti et al. have used the ion-sputtering technique with Ar ions of energies 350 and 700
eV, with a fixed ion current of 50 mA to deposit CsI thin films having a target
stoichiometry not affected by the ion energy of the sputtering gas. It was observed that the
film composition and growth rate were tunable with the experimental conditions. In
particular, the analytical results of the morphological and structural properties of the
films, in comparison to those of evaporated films confirmed the capacity of the ion beam
technique to control and improve these properties. The comparative analysis of all film
properties suggests that the different surface morphology of sputtered films with respect
to evaporated films can be assumed as the main cause of the lower QE of sputtered CsI
films. The more compact surface texture of sputtered films can determine a lower
illuminated and photoemissive effective surface area [8]. Gallasch et al. have deposited
V\(_2\)O\(_5\) thin films by means of dc-ion beam sputtering deposition technique. The films were
grown by means of accelerating the ions at acceleration voltage of 600 V towards the
target. The samples were characterized by X-ray diffractometry and transmission electron
microscopy to determine the influence of various deposition parameters. Using electron
energy loss spectroscopy, the oxidation state of vanadium was quantified based on the
chemical shift of absorption edges. It is observed that measurement of in-plane direct
current showed the electronic conductivity varies over several orders of magnitude
depending on the preparation conditions. The desired structure suitable for battery
applications was achieved by sputtering under partial pressure of oxygen and suitable post-annealing under ambient atmosphere and they also demonstrated the reversible intercalation of Li into the produced thin films [9]. Ronning et al. have grown boron carbide (B₃C) thin films via direct ion beam deposition using mass selected ¹¹B⁺ and ¹²C⁺ ions. The films were deposited on silicon and ITO-coated quartz glass substrates with an ion energy of 100 eV at room temperature. The B⁺:C⁺ ion ratio during deposition was varied between 0:1 (pure carbon) and 1:0 (pure boron), and the resulting composition of the films matched this ratio, as observed by X-ray photoelectron spectroscopy (XPS). A detailed analysis of the XPS-spectra revealed that the deposited films undergo a transition from sp³-bonded diamond-like carbon to a boron carbide phase with a lower density with increasing B concentration. The formation of carbbide bonds has been observed by means of XPS, and the valence band spectra showed a strong transition from the amorphous semiconductor ta-C to metallic boron. This transition was also observed by optical and electrical measurements [10]. Shimura et al. have reported photoluminescence (PL) from β-FeSi₂ thin film grown by ion beam sputter deposition (IBSD) method. For the first time, they observed several small PL peaks in the as-grown IBSD films at around 0.77 and 0.83 eV below 100 K. By thermal annealing at 1153 K for more than 24 h, these films showed a strong peak at around 0.81 eV with increased intensity by more than an order of magnitude at 6 K. These annealed samples showed luminescence up to room temperature, while no PL was observed above 100 K for the as-grown films [11]. Ichinohe et al. have fabricated a light emitting Si-doped glass (Si-DG) film using ion beam sputter-deposition (IBSD) technique. They have used Ar ions of energy 1 KeV, and the ion current density was adjusted to 0.5 mA cm⁻². It is observed that the photoluminescence (PL) intensity increased with increasing annealing temperature up to approximately 900°C but it often decreased above the critical temperature. According to the high-resolution transmission electron microscope (TEM) observations, Si crystallites with a diameter of approximately 3 nm were found in the film after the heat treatment, indicating that the formation of Si crystallites is closely related to the luminescence intensity. The luminescent Si-DG film showed extremely broad PL spectra and the full width at half-maximum (FWHM) typically being approximately 1 eV. To obtain a much sharper bandwidth for light emission, the Si-DG film was sandwiched by a metal (Ag) film and a dielectric multilayered reflector. The FWHM value of the PL spectrum was reduced to approximately 0.1 eV after fabricating the resonator using a 20-paired CeO₂/Si-DG multilayered reflector [12]. Tam et al. have fabricated binary component Ni–
Si films of different compositions on AISI 304L stainless steels by means of ion-beam sputter (IBS) deposition. In this study, they have co-sputtered commercial purity nickel (Ni) (>99.9%) metal disc and silicon (Si) (100) wafer targets by means of low energy argon ion beams (≤500 eV) generated simultaneously from two Kaufman type ion source. They have analyzed the compositions of the thin films and the chemical states by means of X-ray photoelectron spectroscopy (XPS) and the phase formation is studied and discussed in view of Pretorius' effective heat of formation (EHF) model. The chemical state analyses were carried out by fitting the core level spectra of Ni 2p\textsubscript{3/2} and Si 2p peaks with an asymmetry Gaussian–Lorentzian sum function. They observed that chemical state analyses from the XPS curve-fittings agree well with the compound predictions using the Pretorius's EHF model. The valence band spectra from the Ni–Si film series samples show that the bonding changes from predominantly metallic to covalent bonding as the Si content increases. This could also be concluded from the corresponding Ni 2p\textsubscript{3/2} and Si 2p core level spectra through the assessment and study of FWHM values and peak symmetry parameters. For the very short-range ordered structure in the Ni–Si thin films, the line broadening effect and limited film thickness (~100 nm) make it impossible to ascertain the structure of the Ni–Si films by means of GIXRD [13]. Ensinger et al. have deposited alumina and tungsten carbide powder with gold and platinum by ion beam sputter deposition (IBSD). For the uniform deposition, the powder grains were agitated in a rotating conical vessel. It contained a sputter target which was irradiated by a beam of rare gas ions of energy 60 keV maintaining the ion currents onto the sputter target ranged from 30 to 100 µA. Metal atoms sputtered from the target were deposited onto the powders. The amount of deposited noble metals was determined by means of atomic absorption spectrometry. It increased monotonically with the sputter ion fluence. Under the given conditions, up to 0.3 wt.% gold were deposited onto alumina, while tungsten carbide received up to 0.016 wt.% platinum. While alumina remained non-conductive, the electrical conductivity of tungsten carbide was found to increase up to a factor 4 by platinum deposition. Electrochemical measurements showed that the electrochemical activity of tungsten carbide was considerably enhanced by platinum deposition and they claim that this material may be used as an electrocatalyst [14]. Kojima et al. deposited SiO\textsubscript{2}/Ta\textsubscript{2}O\textsubscript{5} multilayers on Si(100) by ion-beam sputter deposition. In this case, the used ion energy was from 50-1200 eV. They have characterized the layer thickness and interfacial roughness of the multilayers by using a grazing incidence x-ray reflectivity technique. In particular, the differences in structural features between the Ta\textsubscript{2}O\textsubscript{5} on SiO\textsubscript{2}...
interface and the SiO₂ on Ta₂O₅ interface, as well as the possible inhomogeneity of the SiO₂ layers, were successfully revealed. It is observed that the x-ray reflectivity results are consistent with the high-resolution electron microscopy observations [15]. Mahendra Kumar et al. have reported on the pure amorphous silicon thin films deposited by ion beam sputter deposition onto borosilicate glass substrates at ambient temperature by using Ar ion energy of 600 eV. They derived the optical constants from spectral transmittance measurements in the range of 350-2500 nm. It is observed that all the samples, regardless of thickness, show a Raman peak centered between 460 and 480 cm⁻¹. The root-mean-square variation in the bond angles, ∆θ, obtained from Raman spectra, indicates the presence of relatively good short range order in amorphous silicon thin films. It is found that the refractive index at 1.4 eV decreases from 4.35 to 3.52 with an increase in thickness from 30 to 130 nm. The band gap varies with thickness and at a thickness of 130 nm the band gap is found to be 1.3 eV, which increases to 1.8 eV at 30 nm. The narrow band gap values of ion beam sputtered a-Si thin films indicate that they can be explored for photovoltaic applications [16].

It is evident from the review of literature that IBSD is a very effective technique to provide a large variety of thin films with enhanced properties. Majority of the work focuses on the use of Ar ions of energies >500 eV. There is very limited work on investigations of growth of films at energies <500 eV. The focus of current work is, therefore, to investigate growth of films at Ar ion energies << 500 eV.

2.2. Parameters used for IBSD in this study

Ion beam sputter deposition is an effective approach for creating or enhancing strong, stable, uniform and direct adhesion of thin films deposited on substrates which is very useful for applications. The ion beam sputter deposition system used in this work is home built and consists of a Kaufman type DC ion source (of Oxford Applied Research, Model DC25, 100 – 1500 eV model). This ion beam is capable of producing ion beams of 2.5 cm in diameter. The main reason of using such a low energy ion beam sputtering is to obtain self ordered nanostructured thin films. Figure 2.1(a) shows the schematic diagram of ion beam sputter deposition system used in the current work.
Figure 2.1(a). Schematic diagram of ion beam sputter deposition system.

The ion source consists of cylindrical type chamber (anode) where cathode (tungsten filament) is mounted and surrounded by magnet and water cooled chamber which is attached to two grids (called screen grid and extractor grid). Ar gas is passed through the ion source itself. When current is applied to the filament, it emits electron and the emitted electron collide with the Ar gas which is ionized. The direction of magnetic field causes the emitted electrons to move in helical path so that they collide with more Ar gas increasing the ionization process. Ions are then extracted by the extractor grid and accelerated towards the target. They bombard the target and sputter the material. The screen grid screens the electron from coming out of the ion source. Photographic images of the system are shown in figs. 2.1 (b) to (e).
Fig. 2.1. (b) View of the 16 inch dia UHV chamber with capability to sputter 3 targets without breaking vacuum (c) Kaufman type ion source (DC25 of Oxford Applied Research, UK) (d) Full view of ion beam sputter deposition coating unit and (e) the inner view of the chamber during sputter deposition.
Ion beam sputter deposition has many advantages over other physical vapor deposition techniques like thermal evaporation and normal glow discharge sputtering. Some of the advantages are listed below:

<table>
<thead>
<tr>
<th>Ion beam sputter deposition</th>
<th>Glow discharge system</th>
<th>Thermal evaporation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Can sputter at high vacuum like $10^{-4}$ to $10^{-5}$ Torr.</td>
<td>Sputtering takes place at pressure $&gt; 10^{-3}$ Torr.</td>
<td>Can evaporate at $10^{-5}$ Torr or lower pressure.</td>
</tr>
<tr>
<td>Can sputter metals and insulator.</td>
<td>Can not sputter insulator unless RF is used.</td>
<td>Can evaporate metals and insulator but stoichiometry is a problem.</td>
</tr>
<tr>
<td>There is no contamination in the film as the Ar gas is passed in the ion source itself and ions are extracted.</td>
<td>Ar gas is filled in the chamber so there will be scattering and contamination.</td>
<td>Contamination due to reaction between evaporant and heat source (such as W, Ta or Mo boat).</td>
</tr>
<tr>
<td>Has independent control on energy, current density and angle of incidence of ions.</td>
<td>No independent control possible.</td>
<td>Energy and flux is related to source temperature, angle of incidence can be controlled.</td>
</tr>
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</table>

In the present work, the Ag and Au films were deposited with the following conditions:

Pumping unit : Rotary + turbo pump  
Base pressure : $2 \times 10^{-6}$ Torr  
While sputtering : $4.5 \times 10^{-4}$ Torr  
Ion source to target distance : 15 cm  
Target to substrate distance : 14 cm  
Substrate temperature : RT to 300$^\circ$C.  
Ion energy : 150, 200, 250, 300, 400 and 600 eV  
Ion current : 0.2 A.  
Extractor voltage : - 40 V.  
Substrates: Boro silicate glass substrates and fused silica.
2.3. Characterization Techniques

2.3.1. Thickness measurement

The thickness of the samples was measured using stylus profilometer (also known as profilometer) (Model XP-1, Ambios Technology, USA). Surface profilometry is a direct, simple and fast measurement technique for determining the physical thickness of thin films [17]. The only requirement is the existence of a step as shown in figure 2.2. In this study, the step was made by covering a part of the substrate using a thin stainless steel shadow mask during deposition. This method involves loading a stylus (generally a diamond stylus) slightly in contact with the film surface and gently dragging it across the step as shown in figure 2.2. The vertical deflection measures the change in step height (film thickness) and the trace is recorded with high accuracy.

![Figure 2.2](image.png)

**Figure 2.2.** Illustration of stylus profilmometry to measure film thickness.

2.3.2. X-Ray diffraction

X-ray diffraction is a well-known technique for characterizing the crystal structure of materials. X-rays have a wavelength of the order of Angstroms ($10^{-10}$ m), which is comparable to the inter-atomic spacing in crystalline solids. Therefore, a diffraction pattern can be observed when a beam of x-rays is directed on a crystalline material (where the atoms are arranged periodically). This diffraction pattern is directly related to the crystal structure of the material under observation. The diffraction of x-rays by a crystalline material is illustrated in figure 2.3.

In the present work, two types of X-ray diffractometers with different x-ray source were used to characterize the samples. One was equipped with Co Kα ($\lambda=1.7889\text{Å}$) radiation in a wide angled powder X-ray diffractometer (INEL Model CPS120) and a position
sensitive detector while the other one was a conventional X-ray diffractometer operating in the Bragg-Brentano geometry with Cu K$_\alpha$ ($\lambda=1.54056$ Å) radiation (Philips PW 1830 diffractometer). Calibration using a Si standard was done to account for the instrumental line broadening and the value was approximately 0.05° for the former and 0.10 for the later. The patterns were compared with standard patterns (JCPDS) and the phases and degree of crystallinity was determined. A slow scanning rate of 0.5°/min was used to extract data for the measurement of crystallite size. These results gave important information regarding the variation in the crystalline orientation of films lattice constants, crystallite size, strain etc. as a function of processing conditions.

2.3.2.1. Calculation of crystallite sizes from x-ray diffraction patterns

*Bragg’s Law:*

In figure 2.3 below, consider rays 1 and 1a in the incident beam. They strike atoms K and P in the first plane of atoms and are scattered in all directions. Only in the directions 1’ and 1a’, the scattered beams are completely in phase (because QK – PR = PK Cos θ - PK Cos θ = 0) and are capable of reinforcing one another.

This relationship is true of all the planes separately, and we have to find the condition for reinforcement of rays scattered by atoms in different planes. Let us take rays 1 and 2 scattered by atoms K and L, and the path difference for rays 1K1’ and 2L2’ is

$$ML + LN = d \sin \theta + d \sin \theta$$

(2.1)

If this path difference is equal to a whole number n of wavelengths,

*Figure 2.3. Diffraction of X-rays by periodically arranged atoms in a crystalline material.*
\[ n\lambda = 2d \sin \theta \]  

(2.2)

where, \( \theta \) is the diffraction angle, \( \lambda \) is wavelength of the X-ray and \( n \) is the order of reflection, which may take any integral value consistent with \( \sin \theta \) but not exceeding unity.

This relation was first formulated by W. L. Bragg and is known as the Bragg law [18]

\[ \frac{n\lambda}{2d} = \sin \theta < 1 \]  

(2.3)

i.e., \( n\lambda \) must be less than \( 2d \). For \( n = 1 \) the condition for diffraction at any observable angle \( 2\theta \) is \( \lambda < 2d \).

For most sets of crystal planes \( d \) is of the order of 3 Å or less, which means that \( \lambda \) cannot exceed about 6 Å.

Scherrer’s formula is used to estimate the crystallite size, \( t \) given by,

\[ t = \frac{0.93\lambda}{\beta \cos \theta_{\beta}} \]  

(2.4)

\[ \beta = \frac{1}{2} (2\theta_1 - 2\theta_2) \]

where, \( \beta \) is angular width, in terms of \( 2\theta \) and is measured in radian at an intensity equal to half the maximum intensity and is called full width at half maximum (FWHM) (shown in figure 2.4 below)
2.3.3. Scanning Electron Microscopy (SEM)

SEM is a widely used technique to study surface topography of the samples. A schematic diagram of SEM is shown in figure 2.5. SEM consists of an electron source, a series of lens system which produces a finely focused beam on the specimen surfaces, two pairs of deflection coils (scanning coils) at right angles to each other, connected to a saw-tooth wave generator system, so that the finely focused electron beam can be rastered on the sample surface. The secondary electrons are gathered in a collector, amplified and fed to a cathode-ray display tube or a computer.

A high energy (typically 10-30 keV) electron beam, thermionically emitted from a tungsten filament is focused to a spot size of 1 nm to 5 nm by the condenser lenses. The focused beam passes through a pair of scanning coils, which raster the beam across the surface. The incident electrons cause low energy secondary electrons generation. The secondary electrons emitted from the sample are detected by a scintillator-photomultiplier device and the resulting signal is rendered into a two-dimensional intensity distribution that can be viewed and saved as a digital image. The most common imaging mode monitors low energy (<50 eV) secondary electrons which originates within a few nanometers from the surface. In the current work we have used Carl Zeiss Model FEG-Scanning Electron Microscope (Model Ultra 55).
2.3.4. Scanning Probe Microscopy (SPM)

Scanning probe microscopy (SPM) covers several related technologies for imaging and measuring surfaces on a fine scale, down to the level of molecules and groups of atoms. SPM technologies share the concept of scanning an extremely sharp tip (3-50 nm radius of curvature) across the sample surface. The tip is mounted on a flexible cantilever, allowing the tip to follow the surface profile.

When the tip moves in proximity to the investigated object, forces of interaction between the tip and the surface influence the movement of the cantilever [19]. These movements are detected by selective sensors. Various interactions can be studied depending on the
mechanics of the probe. Our interest is in the atomic force microscope (AFM). The atomic force microscope (AFM) probes the surface of a sample with a sharp tip (often less than 100Å in diameter). The tip is located at the free end of a cantilever that is 100 to 200µm long. Forces between the tip and the sample surface cause the cantilever to bend, or deflect. A detector measures cantilever deflections as the tip is scanned over the sample, or the sample is scanned under the tip. The measured cantilever deflection is mapped as the surface topography [20]. AFM can be used for insulator and semiconductor as well as electrical conductors [21]. The schematic diagram of AFM is shown in figure 2.6.

![Schematic diagram of atomic force microscopy (AFM)](image)

**Figure 2.6.** Schematic diagram of atomic force microscopy (AFM) [22].
Several forces contribute to the deflection of an AFM cantilever. The force most commonly associated with atomic force microscopy is an inter-atomic force called the Van der Waals force depending upon the distance between tip and sample as shown in figure 2.7.

Two distance regimes are labeled in figure 2.7 the contact regime and the non-contact regime. In the contact regime, the cantilever is held less than a few angstroms above the sample surface and the interatomic force between the cantilever and sample is repulsive [23]. In the non-contact regime, the cantilever is held about tens to hundreds of angstroms away from its attractive regime (largely a result of the long-range Van der Waals interactions).

![Figure 2.7. Nature of forces in the Contact and Non-contact mode of AFM operation.](image)

2.3.4.1. Non-contact AFM

Non-contact AFM (NC-AFM, otherwise known as dynamic force microscope, DFM) is one of the modes of operation in AFM, where the cantilever is vibrated near the surface of the sample. The spacing between the tip and sample for DFM is of the order of tens to hundreds of angstroms. This spacing is indicated in the Van der Waals force curve in figure 2.7 as the non-contact regime. DFM is desirable because it provides a means for measuring sample topography with little or no contact between the tip and sample. Similar to contact-AFM, DFM can also be
used to measure the topography of the insulator and semiconductors as well as electrical conductors. The total force between the tip and sample is very low, generally $10^{-12}$N. Since the force between tip and sample in the non-contact regime is low, it is more difficult to measure this region than in the contact regime. In addition, the cantilever used in DFM is stiffer than those used for contact AFM because soft cantilevers can be pulled easily onto the sample surface. Hence, both these factors make the DFM signal difficult to measure. Thus, a sensitive, AC detection scheme is used in this operation. In the non-contact mode, the system vibrates a stiff cantilever near its resonant frequency (typically from 100 to 400 kHz). Then, it detects the changes in the resonant frequency or vibration amplitude as the tip comes near the sample surface. The sensitivity of this detection scheme provides sub-angstrom vertical resolution in the image, as with contact AFM.

The relationship between the resonant frequency of the cantilever and variations in sample topography can be explained as follows. The resonant frequency of a cantilever varies as the square root of its spring constant. In addition, the spring constant of the cantilever varies with the force gradient experienced by the cantilever. Finally, the force gradient, which is the derivative of the force Vs distance curve changes with the tip-to-sample separation. Thus, change in the resonant frequency of the cantilever can be used as a measure of change in the force gradient, which changes with the tip-to-sample spacing, or sample topography. DFM does not suffer from the tip or sample degradation effects that are sometimes observed after taking numerous scans with contact AFM. As mentioned above, DFM is preferable to contact AFM for measuring soft samples. In the case of rigid samples, contact and non-contact AFM for images may look the same. In the present study Seiko SPA-400 scanning probe microscope was used in the DFM mode to obtain the surface morphology of Ag, Au, Ag/Au, Au/Ag, Ag/TiO$_2$, Au/TiO$_2$, Ag/ZrO$_2$, Au/ZrO$_2$, and In/Ag thin film samples.

2.3.5. Transmission Electron Microscopy (TEM)

Electron microscopes use electron beams to provide images of nanoscale objects. In transmission electron microscopy (TEM), the specimen is illuminated with an electron beam. The electron beam that transmits through the specimen produces a transmitted, optical image, much like conventional optical microscopy. The wavelength of electron is much smaller than that of light, therefore the optimal resolution attainable for TEM image...
is several orders of magnitude higher than that for a light microscope. Not all the electrons are transmitted through the sample, some are also scattered or diffracted. The scattered and diffracted electrons form the image contrast as denser or thicker parts of the sample scatter as well as absorb, more electrons, thus appearing as darker areas in the image [24-25].

In the present work we have used Transmission electron microscope (model: Tecnai 20 G2 STwin, FEI electron microscope operated at 20 kV using Gatan CCD camera) to investigate nano particle nucleation and growth and to determine crystal structure of Ag and Au thin films.

2.3.5.1. Imaging Modes of a TEM

The imaging system of a TEM consists of at least three lenses (Figure. 2.8): the objective lens, the intermediate lens (or lenses), and the projector lens. The intermediate lens can magnify the first intermediate image, which is formed just in front of this lens, or the first diffraction pattern, which is formed in the focal plane of the objective lens, by reducing the excitation [24]. In many microscopes, an additional diffraction lens is inserted between the objective and intermediate lenses to image the diffraction pattern and to enable the magnification to be varied in the range 102 to 106. The bright-field mode (BF) with a centered objective diaphragm is the typical TEM mode, with which scattering contrast and diffraction contrast can be produced with objective apertures \( \alpha_o \) between 5 and 20 mrad. For high-resolution phase contrast, the aperture should be larger (\( \alpha_o \geq 20 \) mrad) to transfer high spatial frequencies. The only purpose of the diaphragm in this mode is to decrease the background by absorbing electrons scattered at very large angles. The resolution is limited by the attenuation of the contrast-transfer function (CTF) caused by chromatic aberration and not by the objective aperture \( \alpha_o \). Normally, the specimen is irradiated with small illumination apertures \( \alpha_i \leq 1 \) mrad. For high resolution, an even smaller aperture \( \alpha_i \leq 0.1 \) mrad is necessary to avoid additional attenuation of the CTF by partial spatial coherence. When unconventional types of contrast transfer are desired, it is often necessary to change the illumination condition by tilting the beam or using hollow-cone illumination, for example.
In the *dark-field mode* (DF), the primary beam is intercepted in the focal plane of the objective lens. Different ways of producing dark-field conditions are in use. The shifted-diaphragm method (Fig. 2.9 b) has the disadvantage that the scattered electrons pass through the objective lens on off-axis trajectories, which worsens the chromatic aberration. The most common mode is therefore that in which the primary beam is tilted (Fig. 2.9 c) so that the axis strikes the centered diaphragm. The image is produced by electrons scattered into an on-axis cone of aperture $\alpha_0$. This mode has the advantage that off-axis aberrations are avoided. There is thus no increase of chromatic error.

Asymmetries in the dark-field image can be avoided by swiveling the direction of tilt around a cone, or conical illumination can be produced by introducing an annular diaphragm in the condenser lens. Another possibility is to use a central beam stop that intercepts the primary beam in the back focal plane for this, a thin wire stretched across a circular diaphragm may be employed (Fig. 2.9 d). DF micrographs need a longer exposure time because there are fewer scattered electrons. For high resolution, the contrast-transfer function (CTF) of DF is nonlinear, whereas the CTF of the BF mode is linear for weak-phase specimens. The DF mode can also be employed to image crystalline specimens with selected Bragg-diffraction spots.

Increasing the objective aperture in the BF mode allows us to transfer the primary and one Bragg-reflected beam through the diaphragm [24]. These beams can interfere in the final image. The fringe pattern is then an image of the crystal-lattice planes. Optimum results are obtained for this mode when the primary beam is tilted by the Bragg angle $+\theta_B$. The Bragg-reflected beam that is deflected by $2\theta_B$ passes through the objective lens with an angle $-\theta_B$ relative to the axis.

In the *crystal-lattice imaging mode*, more than one Bragg reflection and the primary beam form a lattice image that consists of crossed lattice fringes or an image of the lattice and its unit cells if a large number of Bragg reflections are used. This mode is most successful for the imaging of large unit cells, which produce diffraction spots at low Bragg angles so that the phase shifts produced by spherical aberration and defocusing are not sufficiently different to cause imaging artifacts. Further operating modes of a TEM are described in other sections: scanning transmission mode, Lorentz microscopy and the analytical modes.
of x-ray microanalysis, electron energy-loss spectroscopy, and electron diffraction [24]. The Photograph of TEM used in this work is given in figure 2.10.

**Figure 2.8.** Ray diagrams for a TEM in (a) the bright-field mode and (b) selected area electron diffraction (SAED) mode [24].

**Figure 2.9.** (a) Bright-field mode with a centered objective diaphragm and production of a dark-field mode by (b) a shifted diaphragm, (c) a tilted beam, and (d) a central beam stop [24].
2.3.5.2. Electron diffraction (ED)

Electron-diffraction methods are employed for the identification of substances by measuring the lattice-plane spacing and for the determination of crystal orientations in polycrystalline films (texture) or single-crystal foils. Extra spots and streaks, caused by antiphase structures or plate-like precipitates, for example, may also be observed when imaging a selected area. The selected-area diffraction technique, in which an area of the order of 0.1–1 μm across is selected by a diaphragm in the first intermediate image, is a standard method [24].

2.3.5.3. Selected-Area Electron Diffraction (SAED)

The cone of diffracted electrons with an aperture of the order of a few tens of milliradians (mrad) can pass through the small pole piece bores of the final lenses only if the back focal plane of the objective lens that contains the first diffraction pattern is focused on the screen. Figure 2.8(b) shows the ray diagram of this technique. A selector diaphragm of diameter $d$ situated in the intermediate image plane (magnification $M \approx 20–50$) in front of the intermediate or diffraction lens selects an area of the specimen of diameter $d/M$. This area can be chosen in the normal bright-field mode (figure. 2.8 a), in which the primary beam passes through the objective diaphragm. When the excitation of the intermediate lens is decreased, its focal length is increased and the diffraction pattern in the focal plane of the objective lens can be focused on the final screen after removing the objective diaphragm (figure. 2.8 b). The excitations of the later projector lenses are unchanged. These lenses magnify either the intermediate image or the diffraction pattern behind the intermediate lens. The diameter of the area selected cannot be decreased below 0.1–1 μm owing to the spherical aberration of the objective lens. The intermediate images of the Bragg reflections (dark-field images) are shifted relative to the bright-field image by a distance [24]

$$\Delta s = (C_s \theta_g^3 - \Delta z \theta_g) M, \quad (2.5)$$

which depends on the defocusing $\Delta z$ and the constant $C_s$ ($\theta_g = 2\theta_B$ and $\theta_B$ is the Bragg angle). It is of course possible to compensate for the shift by a suitable choice of the defocus $\Delta z$, but only for one Bragg reflection, not for the whole diffraction pattern.
simultaneously. The consequence is that Bragg reflections of high order with large \( \theta \) do not come from the area that was selected in the bright-field mode. Thus, for \( 2\theta_B = 50 \) mrad and \( Cs = 1 \) mm, the shift is \( 0.125 \) \( \mu \)m. The diffraction angle \( \theta \) decreases linearly with \( \lambda \) as the electron energy is increased. A further selection error can result if the position of the intermediate image is shifted when the intermediate lens changes over from the imaging to the diffraction mode.

**Figure 2.10.** Photograph of the Transmission electron microscope (model: Tecnai 20 G2 STwin, FEI electron microscope operated at 20 kV using Gatan CCD camera) (established at CFN, UoH) used in the current study.

Diffraction patterns from smaller areas can only be obtained by using the rocking-beam technique or by producing a small electron probe. The resolution \( d/\Delta d \) of an SAED pattern can be defined in terms of the smallest lattice-spacing difference \( \Delta d \) that can be resolved and may be estimated from the ratio \( \Delta r/r \). Here \( r \) denotes the distance from a diffraction spot to the center of the diffraction pattern in the focal plane of the objective lens, \( r = 2\theta_B f = \lambda f/d \) (\( f \): focal length), and \( \Delta r \) is the diameter of the spot, which is equal to the diameter \( 2a_i f \) of the primary beam \( (a_i \): illumination aperture):

\[
d/\Delta d = r/\Delta r = \lambda/2a_id \quad (2.6)
\]
Thus, for $\lambda = 3.7 \text{ pm (100 keV)}$, $d = 0.1 \text{ nm}$, and $\alpha = 0.1 \text{ mrad}$, we find $d/\Delta d = 200$. The resolution can be increased only by reducing $\alpha$, but this reduces the pattern intensity. The spherical aberration of the objective lens can cause barrel and spiral distortion of the SAED pattern but this is, however, smaller than 1%; an elliptic distortion can arise due to astigmatism of the intermediate lens. The most severe distortion is caused by the projector lens. For the accurate determination of lattice spacing $d$, the diffraction (camera) length $L$ must be calibrated by using a diffraction standard [24]. The photographic image of the TEM used in the current study is shown in fig.2.10.

2.3.6. Optical Characterization

2.3.6.1. Ultra Violet-Visible Spectrophotometer

Optical properties of the Ag, Au and Ag, Au /dielectric bilayer and metal bilayer thin films were studied using a JASCO V-570 UV-VIS-NIR double beam Spectrophotometer. The optical studies of thin films are mainly concerned with basic optical phenomena including absorption, reflection and transmission and also the interaction of photon energy with matter and consequent changes in electronic states [26]. The important parameters that can be obtained from the measured spectral absorption data include absorption coefficient and optical band gap. In the present study the data were collected in the range 190 to 2500 nm, with air as reference.

The Ultra Violet -Visible-Near Infrared (UV-VIS-NIR) spectrophotometer uses two light sources, a deuterium (D$_2$) lamp for ultraviolet region and a halogen lamp for visible and NIR region. The light from the source lamp gets reflected from mirror 1 and beam passes through slit 1 and hits a diffraction grating. The grating can be rotated allowing for a specific wavelength to be selected. At any specific orientation of the grating, only monochromatic (single wavelength) beam successfully passes through slit 2. A filter is used to remove unwanted higher order diffracted beam. The light beam hits a second mirror before it gets split by a half mirror (half of the light is reflected, the other half gets transmitted). One of the beams is allowed to pass through a reference sample (air in the present case), the other passes through the film coated substrate. The intensities of the light beams are then measured at the end as shown in figure 2.11. The photometer (not
shown) computes the ratio of the sample signal to reference signal \((I/I_0)\) to obtain the transmittance.

An electronic transition consists of the promotion of an electron from an orbital of a molecule in ground state to an unoccupied orbital by absorption of a photon. The molecule is then said to be in an excited state.

Experimentally, the efficiency of light absorption at a wavelength \(\lambda\) by an absorbing medium is characterized by the absorbance \(A(\lambda)\) or the transmittance \(T(\lambda)\), defined as [27]

\[
A(\lambda) = \log_{10} \frac{I_0^\lambda}{I_\lambda} = -\log T(\lambda) \tag{2.7}
\]

\[
T(\lambda) = \frac{I_\lambda}{I_0^\lambda}
\]

where \(I_0^\lambda\) and \(I_\lambda\) are the light intensities of the beams and entering and leaving the absorbing medium, respectively.
Usually the absorbance of a sample follows the Beer-Lambert law

\[ A(\lambda) = \log_{10} \frac{I_0}{I_\lambda} = \varepsilon(\lambda)lc \]  

(2.8)

where \( A \) is the measured absorbance, \( I_0 \) is the intensity of the incident light at a given wavelength, \( I \) is the transmitted intensity, \( L \) the path length through the sample, and \( c \) the concentration of the absorbing species. For each species and wavelength, \( \varepsilon \) is a constant known as the molar absorptivity or extinction coefficient. This constant is a fundamental molecular property in a given solvent, at a particular temperature and pressure, and has units of \( 1/\text{M} \cdot \text{cm} \) or often \( \text{AU}/\text{M} \cdot \text{cm} \).
References


22. www.pscl.me.ntu.edu.tw


