OPTICAL PROPERTIES OF ULTRATHIN METAL OXIDE AND METAL FILMS: EFFECTS OF FREE ELECTRONS, QUANTUM CONFINEMENT AND LOCALIZED SURFACE PLASMON RESONANCE

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Dedicated to my parents
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Summary

Knowledge of optical properties of a material is crucial for design and optimization of the nanoscale devices. In this thesis, a study of the effects of free electrons, quantum confinement and localized surface plasmon resonance (LSPR) on optical properties of metal oxide and metal thin films is presented. Ultrathin metal oxide thin films including undoped ZnO, Al-doped ZnO (AZO) and amorphous indium gallium zinc oxide (a-IGZO) were deposited using RF magnetron sputtering technique. Ultrathin Au films were deposited using electron beam evaporation technique. Optical properties including dielectric function, optical constant and band gap energy of the thin films were investigated with spectroscopic ellipsometry (SE) based on various optical dispersion models.

The effect of free electrons on optical properties of AZO and a-IGZO thin films has been investigated. The comparison study of the free electrons between the undoped ZnO and AZO shows that free electrons could greatly suppress the excitonic absorption near the band edge and result in an expansion of band gap due to the free electrons effect. It has been observed that thermal annealing at temperature range of 400-700°C could greatly change the free electrons concentration of the AZO films, which directly influences the free electrons absorption and band edge absorption. The thickness dependence of optical properties of a-IGZO films has also been observed. The evolution of the dielectric function is shown due to the change of free electrons concentration in the films.
The effect of quantum confinement on optical properties of ZnO and a-IGZO thin films has been investigated. The ultrathin ZnO film exhibits a significant reduction in dielectric function and an expansion of band gap with decreasing film thickness. The evolution of the dielectric function is shown related to the changes in the interband absorption, discrete-exciton absorption, and continuum-exciton absorption, which can be attributed to the quantum confinement effect on both the band gap and exciton binding energies. Thickness dependence of optical properties of a-IGZO thin films has also been observed. The evolution of the dielectric function is explained as the net result of both the free electrons effect and quantum confinement effect.

The effects of LSPR and quantum confinement on optical properties of ultrathin Au films have been investigated. A significant evolution of the LSPR, interband transition energies, plasma energy and conductivity with the film thickness is observed. The evolution is attributed to the changes in the size, shape and spacing of the self-assembled Au nanoparticles (NPs) as well as the aggregation of the Au NPs in the Au films.
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## Nomenclatures

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$\varepsilon_1$</td>
<td>Real part of complex dielectric function</td>
</tr>
<tr>
<td>$\varepsilon_2$</td>
<td>Imaginary part of complex dielectric function</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Absorption coefficient</td>
</tr>
<tr>
<td>$n$</td>
<td>Refractive index</td>
</tr>
<tr>
<td>$k$</td>
<td>Extinction coefficient</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Band gap energy</td>
</tr>
<tr>
<td>$E_p$</td>
<td>Plasma energy</td>
</tr>
<tr>
<td>a-IGZO</td>
<td>Amorphous indium gallium zinc oxide</td>
</tr>
<tr>
<td>nc-Si</td>
<td>Si nanocrystal</td>
</tr>
<tr>
<td>nc-Ge</td>
<td>Ge nanocrystal</td>
</tr>
<tr>
<td>Ar</td>
<td>Argon</td>
</tr>
<tr>
<td>AZO</td>
<td>Al-doped ZnO</td>
</tr>
<tr>
<td>BM</td>
<td>Bursterin-Moss</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>E-beam</td>
<td>Electron beam</td>
</tr>
<tr>
<td>FB</td>
<td>Forouhi-Bloomer</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>LSPR</td>
<td>Localized surface plasmon resonance</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular beam epitaxy</td>
</tr>
<tr>
<td>MSE</td>
<td>Mean square error</td>
</tr>
</tbody>
</table>
\begin{tabular}{ll}
N\textsubscript{2} & Nitrogen \\
O\textsubscript{2} & Oxygen \\
ODQC & One-dimensional quantum confinement \\
PLD & Pulse laser deposition \\
PVD & Physical vapor deposition \\
RF & Radio frequency \\
SE & Spectroscopic ellipsometry \\
SEM & Scanning electron microscopy \\
Si & Silicon \\
SiO\textsubscript{2} & Silicon dioxide \\
TCO & Transparent conductive oxide \\
TL-Drude & Tauc Lorentz-Drude \\
UV-VIS & Ultraviolet-visible \\
V\textsubscript{o} & Oxygen vacancy \\
XRD & X-ray diffraction \\
ZnO & Zinc oxide \\
\end{tabular}
Chapter 1 Introduction

Optical properties of a material are greatly governed by its intrinsic effect and extrinsic effect. The intrinsic effect is related to the electronic transitions between the valence band and the conduction band, while the extrinsic effect can be related to the impurity or defects. As compared to the bound electrons, the nearly free electrons are much easier to be excited and play an important role in determining the optical properties of the material. Transparent conductive oxides (TCOs) are semiconductor materials with relative high carrier concentration. TCOs have been attracted much attention in recent years due to its promising application in optoelectronics. [1, 2] Optical properties of TCOs are greatly influenced by its carrier concentration, e.g., free electrons. The abundant free electrons could greatly change the optical properties of TCOs, in particular, the free electrons absorption and near band edge absorption. [3] On the other hand, with the abundant free electrons, metal nanostructures could exhibit prominent absorption peak which is absent in their bulk counterpart. This characteristic absorption peak is related to the collective oscillation of conduction electrons inside the nanostructures, known as localized surface plasmon resonance (LSPR). [4] The confinement of electrons could also greatly alter the optical properties of the nanostructures due to the quantum confinement effect. [5, 6] Therefore, it is interesting to study the role of free electrons in an oxide film and a metal film, and knowing the evolution of the optical properties of ultrathin film is definitely important for various applications. This thesis presents a study of the effects of free electrons, quantum confinement and LSPR on optical properties of metal oxide and metal thin
films. This chapter introduces the background, motivation, and major contributions of this work. Details of the study are presented in the following chapters.

1.1 Glamour of Transparent Conductive Metal Oxides

A transparent conductive metal oxide (TCO) is a wide band gap semiconductor material with relatively high carrier concentration. Most of useful TCOs are n-type semiconductors that usually have the band gap greater than 3 eV. [2] Unlike traditional metallic conductor, TCOs can be easily tuned from insulating via semiconducting to conductor, while remains optical transparent in visible. Thus, TCOs are especially usefully for flat panel display technology, e.g., transparent conductive electrode and thin film transistor (TFT). Sn-doped In$_2$O$_3$ (ITO) is the most widely used transparent conductive electrode today due to its high conductivity and high transparency. [1] A high performance TFT based on indium gallium zinc oxide (IGZO) has been demonstrated by Nomura et al. [7] TCOs also play an important role in the rapid growth of green nanotechnology for utilizing the solar energy, such as smart window [8, 9] and photovoltaics [10]. A TCO-based low-thermal emittance (Low-E) coating could effectively reflect the infrared light without compromising the visible light. The energy efficient window is especially usefully for indoor cooling as the solar heating can be greatly reduced. Moreover, TCOs are considered as alternative plasmonic materials for replacing conventional metal in near-infrared applications due to the abundant free electrons [11]. The confinement of electrons also greatly changes the optical properties of TCOs. In this thesis, the effects of free electrons and quantum
confinement on optical properties of metal oxide thin films including undoped ZnO, Al-doped ZnO (AZO) and amorphous indium gallium zinc oxide (a-IGZO) are investigated.

1.2 Beauty of Plasmonics

Plasmonic nanostructures have been intensively investigated and shown plenty of amazing effect and fascinating phenomenon, such as local field enhancement [12], nano-waveguiding [13] and biomolecule sensing [14]. All this is possible because the plasmonics can confine the light on the order of or smaller than the wavelength of light through the coupling between the light and conduction electrons at metallic interface or in metal nanostructure. The study of this light-matter interaction leads to fast growth of plasmonics, and open up new way to manipulate the light beyond the diffraction limit. Detection and probing single molecule have been realized [15], and even treatment of cancer becomes possible [16]. There are two build blocks in plasmonics, surface plasmon polaritons (SPP) and localized surface plasmon resonance (LSPR). SPP is the excitation of conduction electrons at the interface between a metal and a dielectric, while LSPR is related to the collection oscillation of conduction electrons inside the metal nanostructure, e.g., metal nanoparticles. In this thesis, a study on the localized surface plasmon resonance (LSPR) of ultrathin Au films is presented. The influences of LSPR and electron confinement on optical properties of ultrathin Au films are investigated.
1.3 Objective and Scope of Research

In this work, metal oxide thin films including undoped ZnO, Al-doped ZnO (AZO) and amorphous indium gallium zinc oxide (a-IGZO) were fabricated using RF magnetron sputtering technique. Ultrathin Au films were fabricated using electron beam (E-beam) evaporation technique. The main objectives of this work are to investigate the effects of free electron and quantum confinement on optical properties of metal oxide films, and the effects of localized surface plasmon resonance (LSPR) and electron confinement on optical properties of metal thin films. The scope of the research and the approach are as follows:

1. Synthesis of metal oxide thin films including ZnO, AZO and a-IGZO with various thicknesses from a few nanometers to 100 nm using RF magnetron sputtering technique. Synthesis of Au thin films with various thicknesses from a few nanometers to 12 nm using E-beam evaporation technique.

2. Structural and optical characterizations of the deposited thin films with X-ray diffraction (XRD), scanning electron microscope (SEM), absorption spectroscopy and spectroscopic ellipsometry (SE).

3. Experimental determination of optical properties including dielectric function, optical constant and band gap energy of the deposited films with absorption spectroscopy and spectroscopic ellipsometry.

4. Study of the effect of free electrons on optical properties of AZO and a-IGZO thin films.
5. Study of the effect of thermal annealing on optical properties of AZO thin films.


7. Study of the effects of aggregation and electron confinement on optical properties of Au nanoparticles in ultrathin Au films.

1.4 Major Contributions of the Thesis

In this thesis, metal oxide thin films such as ZnO, AZO and a-IGZO and noble metal Au film have been successfully synthesized. Detailed investigations on optical properties of the deposited thin films have been performed. The major contributions of this thesis are listed as follows:

1. A comparison of the free electrons effect between the undoped ZnO and AZO has been conducted.
   a) Band gap energy and excitation binding energy of both the ZnO and AZO thin films with various thicknesses have been determined with optical absorption spectroscopy.
   b) Strong excitonic absorption has been observed in ZnO thin films. Blue shift of absorption band edge and suppression of excitonic absorption have been observed in AZO thin films.
   c) The effect of the free electrons on band gap energy and exciton binding energy of AZO films has been examined.
2. Effect of thermal annealing on optical properties of AZO thin films has been investigated.
   a) Complex dielectric function and band gap energy of the as-deposited and annealed AZO films have been determined with spectroscopic ellipsometry.
   b) Expansion of band gap has been observed in the annealed AZO films.
   c) The effect of the annealing temperature on dielectric function and band gap energy of the annealed AZO films has been examined.

3. Influence of thickness on optical properties of a-IGZO films has been investigated.
   a) Complex dielectric function and band gap energy of a-IGZO thin films with various thicknesses have been determined with spectroscopic ellipsometry.
   b) Expansion of band gap with increasing film thickness has been observed.
   c) The thickness dependence of dielectric function and band gap has been examined.

4. Effect of quantum confinement on optical properties of ultrathin ZnO and a-IGZO thin films has been investigated.
   a) Complex dielectric function, exciton binding energy and band gap energy of the ultrathin ZnO thin films have been determined with spectroscopic ellipsometry.
   b) Dielectric function suppression has been observed in ultrathin ZnO films. The size dependence of band gap energy and exciton binding energies has been examined.
   c) Evolution of dielectric function of a-IGZO films with film thickness has been observed. The thickness dependence of band gap energy has been examined.
Chapter 1 Introduction

5. Effects of localized surface plasmon resonance (LSPR) and electron confinement on optical properties of ultrathin Au films have been investigated.

a) Complex dielectric function, LSPR and interband transition energies of the ultrathin Au films have been determined with spectroscopic ellipsometry.

b) Evolution of LSPR with film thickness has been observed. A significant blue shift of interband transition has been observed in ultrathin Au film with thickness of 1-3 nm.

c) The effects of aggregation and electron confinement on LSPR, free electrons concentration have been examined.

1.5 Organization of the Thesis

In this thesis, studies of optical properties of metal oxide films are mainly focus on undoped ZnO, Al-doped ZnO (AZO) and amorphous indium gallium zinc oxide (a-IGZO) thin films. Study of optical properties of metal film is mainly focus on Au films.

In chapter 1, background of conductive metal oxide and metal thin films and their potential application in optoelectronics are introduced. Objectives and scope of this study as well as major contributions of this thesis are presented.

In chapter 2, reviews of synthesis, characterizations, optical properties and applications of metal oxide and metal thin films are presented. Optical properties of ZnO and a-IGZO thin films are briefly reviewed, e.g., free electrons effect on complex dielectric function. Optical properties including bulk dielectric function and surface
plasmon of the Au film are also reviewed. The effect of quantum confinement on optical properties of semiconductor nanocrystals is briefly reviewed. Finally, applications of metal oxide and metal nanoparticles are introduced.

In chapter 3, investigations of free electrons effect on optical properties of AZO and a-IGZO films are conducted. First, a comparison study of free electrons effect between the undoped ZnO and AZO thin films is presented. Then, the influence of thermal annealing on optical properties of AZO films is discussed. Finally, the thickness dependence of optical properties of a-IGZO thin films is discussed.

In chapter 4, investigations of quantum confinement effect on optical properties of ultrathin ZnO and a-IGZO films are conducted. First, a comprehensive study of quantum confinement effect on dielectric function of ultrathin ZnO films is presented. Then, the one-dimensional quantum confinement (ODQC) effect on optical properties of ultrathin a-IGZO films is discussed.

In chapter 5, investigations of LSPR and quantum confinement effect on optical properties of ultrathin Au films are conducted. First, a study of aggregation effect on dielectric function of ultrathin Au films is presented. Then, the evolution of LSPR and electron confinement effect with film thickness in ultrathin Au films is discussed.

In chapter 6, the research work carried out in this thesis is summarized. Recommendations for future work are also given in this chapter.
Chapter 2 Literature Review

2.1 Introduction

Transparent conductive oxides (TCOs) have attracted a lot attention due to its promising applications in optoelectronics such as thin film solar cell and flat-panel display. [1] The abundant free electrons play an important role in determining the optical properties of the oxide films as a result of the free electrons effect. Noble metals such as Au and Ag have also gain much interests in the field of plasmonics, e.g., surface plasmon resonance (SPR). SPR is related to the collective oscillation of conduction electrons at metal surface. For metal nanoparticles, the plasmon mode is known as the localized surface plasmon resonance (LSPR), which is strongly dependent of size, shape and surrounding environment of the nanoparticles. [12] On the other hand, in a nanoscale device, quantum confinement effect could greatly change the material electronic and optical properties. [17] Thus, knowledge of optical properties of the nanomaterials is of great important for accurate design and modeling of nanoscale devices. In this chapter, brief reviews of synthesis, characterizations, optical properties and applications of metal oxide and metal thin films are presented.

2.2 Synthesis Techniques for Thin Films

Thin film technology has been widely used in area of electronic devices, optical coatings and instrument hard coatings for more than a half century. [18] The synthesis of thin film is a well-established material technology. Thin films can be deposited on a substrate by physical vapor deposition (PVD) and/or chemical vapor deposition
(CVD). The common technique used to synthesize the metal oxide and metal films is physically sputtering a material target in a vacuum environment. Deposition of high quality metal oxide films were also reported using fine control techniques, such as pulsed-laser deposition (PLD) [19], molecular-beam epitaxy (MBE) [20], and metal organic chemical vapor deposition (MOCVD) [21]. In this section, various deposition techniques used to synthesize ZnO, IGZO and Au thin films will be briefly reviewed.

### 2.2.1 Sputtering

Sputtering is the one of most popular growth techniques for thin film deposition. The deposition is carried out with Ar ion bombardment of the target material in vacuum. The sputtered species condense on a substrate and gradually form into a continuous layer. The growth rate of the film is dependent on deposition conditions, such as gas follow rate, substrate temperature, and substrate bias. DC-sputtering is typically used to deposit the metallic materials. The major advantage of DC-sputtering is multi-components can be deposited. The disadvantage is low deposition rate and difficult to sputter the dielectric material due to the charging problem. In order to overcome this issue, RF sputtering is developed. The positive charge will stay in plasma zone and prevent the accumulation of charges at cathode and make sputter dielectrics become possible. [18]
The growth of oxide films such as ZnO and IGZO has been intensively investigated using RF-magnetron sputtering technique, due to its low cost, simplicity, and low operating temperature.\cite{22-24} The deposition is usually carried out at room temperature in pure Ar or Ar+O\textsubscript{2} ambient with the background pressure of 10\textsuperscript{-3}-10\textsuperscript{-2} torr.\cite{22, 24} ZnO thin films can be also grown with reactive DC-sputtering from a Zn target in an Ar+O\textsubscript{2} gas mixture. O\textsubscript{2} is used as reactive gas and Ar is used as the sputtering gas.

2.2.2 Evaporation

The evaporation generally includes two types, thermal evaporation and electron beam (E-beam) evaporation. Thermal evaporation is a relatively old deposition technique. The source material is heated above its melting point by hot filaments or RF induction. The evaporated atoms travel at high velocity and deposit onto the substrate above the crucible. The major disadvantage of thermal evaporation is contamination of the
deposit film due to contact of target material with filament. In advanced E-beam evaporation technique, high energy electron beam is used as heating element to prevent the contamination issue, as shown in Fig. 2.2. The focused electron beam enables the evaporation of metals and dielectrics with high melting points. [25] However, this technique cannot use to deposit composite materials due to different melting temperature of the composites.

The growth of Au thin film by E-beam evaporation starts from the nucleation of Au atom on a substrate. The densification of Au atom leads to the formation of Au nanoparticles. With increasing deposition, Au nanoparticles gradually aggregate into large-scale coalescence, and eventually a continuous film is formed. [27]

2.2.3 Pulsed Laser Deposition

Pulsed laser deposition (PLD) is an advanced PVD deposition technique, which making use of high power pulsed laser beam to ablate the target materials. The target
material is vaporized in plasma form and dense on a substrate. The evaporation of PLD composes both the thermal process and the plasma process. [18] PLD has the advantage of creating high energy source particle, which is enable high quality film growth at low substrate temperature. Wide range of materials can be deposited with PLD, including oxides, metal, semiconductors and even polymers. [28] The major disadvantage of this technique is the ablation of smaller droplets due to the fast heating and cooling processes of the target. [28] It has been reported that these droplets can be prevented from reaching the substrate surface with the off-axis geometry. [29]

Fig. 2.3 Pulsed laser deposition system.[18]

For the growth of oxide films by PLD technique, UV excimer lasers (KrF: \( \lambda = 248 \text{ nm} \) and ArF: \( \lambda = 193 \text{ nm} \)) and Nd: yttrium aluminum garnet (YAG) pulsed lasers (\( \lambda = 355 \text{ nm} \)) are usually used for ablation of the oxide target in an oxygen environment. [22] High quality ZnO and IGZO thin films growth by PLD have been reported elsewhere. [30-32] It has been also reported that PLD is capable to grow Au nanostructure with carefully controlling the laser ablation energy. [33, 34]
2.2.4 Molecular Beam Epitaxy

Molecular beam epitaxy (MBE) is a much more reliable evaporation technique as compared to thermal evaporation and sputtering. The deposition process is precisely controlled by the deposition parameters. With the help of reflection high energy electron diffraction (RHEED), real-time monitoring of film growth becomes possible. However, an ultra-high vacuum environment is required for MBE process. MBE is widely used for the controlled deposition of alloys and compounds. [35]

![Molecular beam epitaxy (MBE) system.][18]

For oxide thin film growth by MBE, metals and oxygen are typically used as the source materials. Metals are evaporated from an effusion cell onto the substrate surface. Oxygen radicals are usually generated from an RF plasma source and emitted onto the film surface to permit the oxidization. [36] Epitaxial growth of high quality ZnO using hydrogen peroxide (H$_2$O$_2$) as oxygen precursor has been reported. [37]
2.2.5 Chemical Vapor Deposition

Chemical vapor deposition (CVD) is a technique based on chemical reaction of supplied gaseous compound, and commonly used for dielectric and polysilicon deposition. The fundamental concept of CVD is to form nonvolatile solid film on the substrate through reaction of vapor phase chemicals. The major advantage of CVD is large scale production of high quality films at low costs. Typically, CVD can be classified into three categories based on the operating temperature: atmospheric pressure CVD (APCVD), low pressure CVD (LPCVD) and plasma enhanced CVD (PECVD). When metal organic precursors are used, the technique is known as MOCVD.

MOCVD is widely used in the fabrication of epitaxial GaN-based optoelectronic devices. [38, 39]. For ZnO growth by MOCVD, it has been reported that metal organic source of zinc acetylacetonate or dimethyl zinc in combine with oxygen can provide a high quality growth of ZnO films on sapphire substrate. [40-42] The potential of nitrous oxide used as oxygen precursor has been also demonstrated for high quality ZnO film growth. [43] Besides the bulk ZnO growth, ZnO nanostructures such as nanowires [44] and nanopillars [45] have been successfully grown by MOCVD. The growth of IGZO by MOCVD has been also demonstrated. [46]

2.3 Characterizations of Thin Films

Optical response of the thin film is greatly influenced by its structural and material properties. Thus, characterizations are essential for study of the thin film properties. In
this section, common structural characterization techniques such as X-ray diffraction (XRD) and scanning electron microscopic (SEM) are briefly introduced. Optical characterization techniques such as absorption spectroscopy and spectroscopic ellipsometry (SE) are also reviewed.

2.3.1 Structural Characterizations

2.3.1.1 X-ray Diffraction (XRD)

X-ray diffraction is a technique used to characterize the material crystalline structure on an atomic scale. The scattering of X-ray at lattice atoms result in a diffraction pattern, which provides the information of material crystalline structure. The basic components of an X-ray diffractometer include the X-ray source, X-ray detector and sample. [47] $\theta$–2$\theta$ geometry is the most commonly used configuration in X-ray diffractometer, where $\theta$ is the angle between the sample and X-ray source and 2$\theta$ is the angle between the X-ray source and the detector. In the scans of $\theta$–2$\theta$ geometry, X-ray source is fixed and detector moves along the circle.

![Fig. 2.5 Geometry of an X-ray diffractometer.[47]](image-url)
Figure 2.6 shows the XRD pattern of the sputtered ZnO thin film on quartz and SiO₂ substrate. The dominated Bragg peak at (002) indicates the polycrystalline growth of wurtzite structure along the c-axis [48]. The average grain size $D$ in the oxide thin films can be estimated from the broadening of the Bragg peak in the XRD patterns based on the Scherrer’s equation [49]

$$D = \frac{0.9 \lambda}{\beta \cos \theta},$$

where $\lambda$ is the wavelength of the X-ray, $\beta$ is the full width of the half maximum (FWHM) of the Bragg peak, and $\theta$ is the Bragg angle. The FWHM $\beta$ is a good indicator of the crystallinity of the thin films. Thickness dependence of FWHM of the Bragg peak is typically observed in the oxide films. The narrower the Bragg peak, the higher the crystallinity of the film.

2.3.1.2 Scanning Electron Microscopic (SEM)
Scanning electron microscopy (SEM) is a powerfully electron microscopy, which use energetic electron beam to scan over the sample surface and produce an image from the detected secondary electrons. The electron-sample interactions generate variety of signals including secondary electrons, backscattered electrons, diffracted backscattered electrons and characteristic X-rays. [50] Secondary electrons are used for imaging the sample surface. Backscattered electrons are used for illustrating the phase contrasts in composite materials. Diffracted backscattered electrons are used for determining the crystal structure. Characteristic X-rays are used for identifying the sample composition. The secondary electrons are very sensitive to the sample surface. Therefore, a topography image of the sample surface can be obtained based on the amount of secondary electrons collected from sample surface.

![SEM image of Au thin film with thickness of 4 nm.](image)

**Fig. 2.7** SEM image of Au thin film with thickness of 4 nm.

Figure 2.7 shows the high resolution image of Au film with thickness of 4 nm. The magnification and resolution of an SEM are much better than that of an optical microspore due to smaller wavelength of the electron.
2.3.2 Optical Characterizations

2.3.2.1 Ultraviolet-visible Spectroscopy

Ultraviolet-visible (UV-Vis) spectroscopy is also known as the absorption spectroscopy or reflectance spectroscopy. It can measure the transmittance or reflection of the thin film material in ultraviolet and visible region. This technique is especially useful for study of electronic transition of a material, e.g., band-to-band transition in semiconductors or intraband transition in metals. As shown in Fig. 2.8, optical band gap $E_g$ of the ZnO thin film can be roughly estimated from the traditional Tauc method of linearly extrapolating the absorption edge. [51-53]

![Tauc plot for as-deposited and annealed ZnO thin films at various annealing temperatures.](image)

It has been reported that the excitons could greatly influence the band edge absorption of ZnO films. [54, 55] Metal nanoparticles such as gold and silver nanoparticles could exhibit a remarkable visible absorption peak due to the effect of localized surface plasmon resonance (LSPR). [4, 56] Therefore, UV-Vis spectroscopy
is very useful for investigating the excitonic absorption of an oxide film and LSPR of a metal nanoparticle film.

2.3.2.2 Spectroscopic Ellipsometry (SE)

Spectroscopic ellipsometry (SE) is a non-destructive optical characterization technique that measures the light reflection or transmission from samples. The fundamental working principle of ellipsometry is to measure the ratio of p- and s-polarized light upon light reflection on the sample, described by [57]

\[
\frac{R_p}{R_s} = \tan(\Psi) \exp(i\Delta).
\]  (2.2)

where \(\Psi\) and \(\Delta\) are related to the ratio of Fresnel reflection coefficients \(R_p\) and \(R_s\) for the p- and s-polarized light, respectively. SE provides a high precise measurement than other conventional instruments, e.g., film thickness sensitivity \(\sim 0.1 \text{Å} \) [58] SE allows characterization of optical properties such as dielectric function and band gap of a thin film material, as well as structural properties such as thickness, morphology, and alloy composition of the film. The SE data analysis consists three main parts: construction of optical model, modeling of dielectric function of the thin film and spectra fitting of ellipsometric angles (\(\Psi, \Delta\)). Figure 2.9 shows the SE spectra fitting of the measured ellipsometric angles for both the Ga-doped ZnO (ZnO:Ga) and Sn-doped In\(_2\)O\(_3\) (In\(_2\)O\(_3\):Sn) thin films with different carrier concentration. [59]
Optical properties of metal oxide film have been intensively studied with SE based on various models including Forouhi-Bloomer (F-B) model, [51] the Tauc-Lorentz (T-L) model [59] and Holden’s model. [60, 61] For study of optical properties of metal film, classical Lorentz-Drude model [62] has been widely used.

2.4 Optical Properties of ZnO and IGZO Thin Films

Optical properties of an oxide film are greatly influenced by its intrinsic and extrinsic effect. It has been reported that coulomb interaction of the oxide film could greatly modify its electronic transitions near the band edge, leading to the excitonic effect. [63] Extrinsic factors such as dopants or defects could also greatly change the oxide carrier concentration and alter its optical behavior due to the free electrons effect. In this section, optical properties of ZnO and IGZO thin film will be briefly reviewed.
2.4.1 Exciton in ZnO Thin Film

The formation of exciton is due to the coulombic interaction of electron-hole pair, which introduces a hydrogen-like state, with the energy given by [63]

\[ E_n = E_g - \frac{R_\beta}{n^2}, \]  

(2.3)

where \( E_n \) is the exciton energy, \( E_g \) is the band gap energy, \( R_\beta \) is the exciton binding energy, and \( n \) is the state number. Equation 2.3 shows that the free exciton can be created more easily than the free electron-hole pairs by absorbing photons due to the smaller formation energy. As compared to III-V wide band gap material, ZnO has a relative large exciton binding energy of \( \sim 60 \) meV. [64] However, the bonding of exciton is very easily weakened by the thermal energy \( K_T \). For ZnO, the free exciton absorption at exciton energy \( E_1 \) can only be resolved in low temperature absorption spectra into three peak A, B and C, which are corresponding to three valence bands of wurtzite semiconductor \( \Gamma_7, \Gamma_9 \) and \( \Gamma_7 \), respectively. [54, 65] The near band edge absorption is dominated by the transitions from these three valence band. As shown in Fig. 2.10, all energy transitions are allowed for \( E \perp c \), while the B valence and conduction bands are forbidden for \( E \parallel c \).
Chapter 2 Literature Review

The transition energies of the intrinsic exciton can be measured with the low temperature absorption, [54, 66] reflection, [67] and photoluminescence. [68, 69] In 1960, Thomas [66] measured the excitonic structure of ZnO with the low temperature reflection and absorption of ZnO crystals grown from the vapor phase, and three peaks arising from exciton transitions were observed. Later on, Reynolds et al. [67] reported free exciton transition for the first time. Teke et al [69] also observed the free excitons of the annealed ZnO with the PL measurement at 10 K in $E \perp c$ polarization geometry. As shown in Fig. 2.11, the excited states of free exciton $A$ are observed at $FX_{A}^{n=1} = 3.3771$ eV and $FX_{A}^{n=2} = 3.4220$ eV, respectively.
Exciton can be bound to the neutral or charged donors and acceptors, [68] which are related to the dopants or defects. For direct band gap materials, the bound exciton is typically referring to the donor-bound exciton (DBE) and acceptor-bound excition (ABE) due to the dominant coupling of the like particles in the bound exciton states. [70] The recombination of bound excitons could result in a sharp line in PL spectrum, which has been reported for ZnO in the energy range of 3.348 – 3.374 eV. [69] As shown in Fig. 2.12, donor-bound excitons were observed at high energy region while acceptor-bound excitons presence in low energy region.

Fig. 2.11 Free excitonic fine structure region of the 10 K PL spectrum for the annealed ZnO. [69]
There is another characteristic donor-bound exciton transition, known as the two-electron satellite (TES) transition. The TES transition is a complicated process, such that the donor-bound exciton is recombined and donor is leaving in the excited state. It has been reported that the energy difference between the ground state of donor-bound exciton state and its excited state can be used to determine the donor binding energy. [68, 71] Detail study of TES in ZnO can be found in ref. [69, 71, 72].

2.4.2 Free Electrons Effect in Conductive Metal Oxide Thin Films

Electrical or optical properties of an oxide film are greatly influenced by its carrier concentration due to the free electrons effect. The carrier concentration in the oxide can be easily tuned by doping impurities. Nominally undoped ZnO is an n-type semiconductor with carrier concentration of $10^{16} - 10^{17} \text{ cm}^{-3}$ due to the presence of intrinsic or extrinsic defects, which were generally attributed to native defects, such as the Zn-on-O antisite, the Zn interstitial, and the O vacancy. [22] N-type ZnO is much easier obtained by substituting Zn with group-III elements such as Al, Ga or In. Al-
doped ZnO (AZO) has recently emerged as an important transparent conductive oxide (TCO), which can be used as transparent electrodes for optoelectronic applications. [73] AZO generally has the carrier concentration in the range of $10^{19} - 10^{21}$ cm$^{-3}$. [2] With such high concentration of free electrons, excitonic absorptions could be significantly suppressed by the free-electron screening. [74, 75] It has been reported that when the carrier concentration in the oxide exceeds the Mott critical density ($10^{18}–10^{19}$ cm$^{-3}$ in ZnO), a semiconductor-to-metal transition occurs and conduction band filling with free electrons shifts the onset of band-edge absorption towards higher energies as a result of the Burstein-Moss (BM) effect. [3, 59, 76]

As shown in Fig. 2.13, T. MAKINO et al. [3] reported a blue shift of absorption edge of Ga-doped ZnO thin film with increasing electron concentration. The blue shift of the absorption edge indicates the expansion of the band gap due to the BM effect. On the other hand, the suppression of excitonic absorption is observed in Ga-doped
ZnO films with electron concentration larger than \( 7 \times 10^{18} \text{ cm}^{-3} \) due to the free-electron screening effect. The screening could greatly modify the columbic interaction and result in a reduction of exciton binding energy. [74]

Optical response of the free electrons in metal oxide films has been successfully modeled by the classical Drude model [77]. It has been reported that the free electrons absorption increases with increasing electron concentration in the oxide films. [59] As shown in Fig. 2.14, in the low energy region (< 1.5 eV), the increase of imaginary parts (\( \varepsilon_2 \)) of dielectric function of Ga-doped ZnO and Sn-doped In$_2$O$_3$ thin films indicate an increase of free electrons absorption as a result of increase of electron concentration in the films.

![Fig. 2.14 Dielectric functions of (a) Ga-doped ZnO (ZnO:Ga) and (b) Sn-doped In$_2$O$_3$ (In$_2$O$_3$:Sn) films as a function of electron concentration.][59]
The intrinsic donor-like defects such as oxygen vacancy and hydrogen impurity can greatly change the carrier concentration. [78, 79] It has been shown that oxygen vacancy \( (V_o) \) can be created more easily in ZnO thin film by thermal annealing due to its lowest formation energy among the donor-like defects. [80] For IGZO thin films, the oxygen vacancy \( (V_o) \) could behave very differently, as \( V_o \) is dependent of the film crystallization. It has been reported that \( V_o \) does not produce free electrons in crystalline IGZO \((c\text{-IGZO})\) as a result of fully occupation of \( V_o \) level. [81, 82] However, in amorphous IGZO \((a\text{-IGZO})\), due to the local amorphous network, \( V_o \) can form either deep fully-occupied localized states near the valence band maximum or donor states. [83, 84]

### 2.4.3 Dielectric Function of ZnO Thin Film

As discussed in sections 2.4.1 and 2.4.2, the complex dielectric function and band gap of the oxide film can be greatly altered by its intrinsic and extrinsic effects. Normally an oxide film exhibits strong optical absorption above the band gap due to the band-to-band absorption. The excitonic effect could greatly change the near band edge absorption due to the columbic interactions. The dielectric function of ZnO thin film is generally described by \( \varepsilon(E) = \varepsilon_1(E) + i\varepsilon_2(E) \), where \( \varepsilon_1(E) \) and \( \varepsilon_2(E) \) are the real and imaginary parts of dielectric function, respectively. Optical constants including refractive index \( (n) \) and extinction coefficient \( (k) \) of the ZnO thin films can be calculated from the value of dielectric function \( (\varepsilon_1, \varepsilon_2) \) with the following formulas
Bond [85] and Mollow [86] have first reported the refraction index of single crystal ZnO using the minimum deviation method. Hu et al. [87] also calculated the dielectric function of ZnO thin film with the optical transmission based on the Kramers-Kronig technique. As compared to Kramers-Kronig technique, ellipsometric technique is more accurate for determining the dielectric function of the oxide films, as it does not rely on the optical measurement (transmittance or reflectance could be inaccurate sometimes). Dielectric function of bulk ZnO films has been intensively studied with ellipsometric technique based on various optical models. [51, 59, 88] Yoshikawa and Adachi studied the dielectric function of ZnO with modeling the interband absorption, discrete excitonic absorption and continuum excitonic absorption in wurtzite ZnO thin films. [65] As shown in Fig. 2.15, Yoshikawa and Adachi’s model provides an excellent description of refraction index of the ZnO thin film.

\[ n = \sqrt{\frac{\varepsilon_1^2 + \varepsilon_2^2 + \varepsilon_1}{2}} \]

\[ k = \sqrt{\frac{\varepsilon_1^2 + \varepsilon_2^2 - \varepsilon_1}{2}} \]  

(2.4)
Fig. 2.15 Refraction index of ZnO for $E \perp c$ below the fundamental absorption edge.\[65\] The circles and triangles represent the experiment data obtained by Bond [85] and Mollwo [86], respectively.

Djurišić et al. [88] also derived the dielectric function of ZnO based on the Elliott’s formula [63]. As shown in Fig. 2.16, the modeled dielectric function of ZnO shows excellent agreement with experimental data.

Fig. 2.16 The real and imaginary parts of the index of refraction of ZnO for $E \perp c$.\[88\] The circle indicates the experimental data [89].
2.4.4 Dielectric Function of IGZO Thin Film

Indium gallium zinc oxide (IGZO) has attracted a lot attention for next generation transparent and flexible optoelectronic devices due to its high carrier mobility and high transparency. Intensive electrical studies have been carried out on the IGZO thin films. However, there is still lack of optical study of the complex dielectric function. In general, the dielectric function \((\varepsilon_1, \varepsilon_2)\) of an oxide film can be parametrically described by Forouhi-Bloomer (FB) model [91, 92] or Tauc-Lorentz (TL) model. [93, 94] It has been reported that TL model could have a better description of dielectric function of amorphous materials over FB model. [93] In TL model, the imaginary part of dielectric function \(\varepsilon_2\) is formulated based on the single-electron model, such that a single-electron transition is considered.

\[
\varepsilon_2(E) = \begin{cases} 
AE_0C(E - E_g)^2 & \text{if } E > E_g \cr 
\frac{(E^2 - E_0^2)^2 + C^2E^2}{E} \cdot \frac{1}{E} & \text{if } E < E_g
\end{cases}
\]

(2.5)

where \(A\), \(C\), \(E_0\), \(E_g\) are oscillator strength, broadening parameter, peak transition energy and band gap energy, respectively. The real part of the dielectric function can be obtained by Kramers–Kronig integration of \(\varepsilon_2\). [95]
Fig. 2.17 (a) Real and (b) imaginary parts of the dielectric function of the IGZO (In:Ga:Zn = 3:x:1) films with different Ga ratio modeled with TL model [96].

Figure 2.17 shows the dielectric function of IGZO (In:Ga:Zn = 3:x:1) thin films with different Ga ratio reported by Tae Jung Kim et al. [96]. The dielectric function and band gap of the IGZO thin films were modeled with spectroscopic ellipsometry (SE) based on the TL model. As discussed in section 2.4.2, the high electron concentration could greatly change the optical properties of the oxide due to the free electrons effect. A doped oxide such as IGZO could exhibit significant free electrons absorption in the low energy region (< 2 eV), which is not considered in TL model, as shown in Fig. 2.17. Therefore, the contribution of free electrons absorption (described by classical Drude model) should be included in TL model. It has been reported that TL-Drude...
model has an excellent description of dielectric function of Ga-doped ZnO and Sn-doped In$_2$O$_3$ films. [59]

2.5 Optical Properties of Au Thin Film

Optical properties of noble metals such as Ag, Cu and Au have been studied for many years. [97-99] Typically, metal thin films exhibit high reflectivity due to its abundant free electrons, which result in a dominant free electrons effect. On the other hand, the interaction between the light and the conduction electrons leads to astonishing phenomenon of plasmon. The plasmon mode greatly depends on the geometries of metals, e.g., volume plasmon in bulk metal and surface plasmon at interface between the metal and dielectrics. In this section, optical properties of bulk Au and plasmon will be briefly reviewed.

2.5.1 Dielectric Function of Bulk Au

Optical properties of bulk Au have been successfully described by the classical Lorentz-Drude model. The complex dielectric function of Au ($\varepsilon_m = \varepsilon_{\text{Lorentz}} + i\varepsilon_{\text{Drude}}$) can be modeled with both the Lorentz and Drude dispersion functions [58, 77]

$$\varepsilon_{\text{Lorentz}}(E) = \sum_{j=1}^{k} \frac{A_j}{E_j^2 - E^2 - i\Gamma_j E}.$$  \hspace{1cm} (2.6)

$$\varepsilon_{\text{Drude}}(E) = (1 - \frac{A}{E^2 + i\Gamma_0 E}).$$ \hspace{1cm} (2.7)

where ($A$, $\Gamma_0$) and ($A_j$, $\Gamma_j$) are (oscillator strength, broadening parameter) for the Drude and Lorentz dispersion functions, respectively. $E_j$ is the resonance energy of
the Lorentz oscillator. The Drude term is used to describe the intraband absorption of free electrons, while the Lorentz term is used to describe the interband absorption of bound electrons. In quantum-mechanical expression, the Lorentz dispersion function \( \varepsilon_{q,\text{Lorentz}} \) is described by the following equation [62, 100]

\[
\varepsilon_{q,\text{Lorentz}}(E) = \sum_{j=1}^{k} \frac{f_j E_p^2}{E_{q,j}^2 - E^2 - i \Gamma_{q,j} E},
\]

(2.8)

where \( f_j \) is the oscillator strength and \( \Gamma_{q,j} \) is the broadening parameter \( E_p \) is the plasma energy, \( E_{q,j} \) is the resonance energy. Eq. (2.8) was derived based on the single-electron model, such that \( f_j \) obeys the sum rule \( \sum_{j=1}^{k} f_j = 1 \). [100]

Figure 2.18 shows the complex dielectric function of bulk Au calculated with Brendel–Bormann model and Lorentz-Drude model. [62] The experimental data is from Dold and Mecke [101] and Theye [102].

Figure 2.18 Real and imaginary parts of the dielectric function of bulk Au calculated with Brendel–Bormann model and Lorentz-Drude model. [62] The experimental data is from Dold and Mecke [101] and Theye [102].
increase of $\varepsilon_2$. In the high energy region (> 2.5 eV), optical response of Au is completely altered by the interband absorption of bound electrons. It has been reported that the $d$-state interband transitions make a positive contribution to $\varepsilon_1$ so that the plasma energy shifts to the lower energy, as shown in Fig. 2.19. [103]

![Fig. 2.19 Contributions of free and bound electrons to the $\varepsilon_1$ of Ag. The plasma frequency is indicated as $\omega_p$.][103]

2.5.2 Plasmon

2.5.2.1 Volume Plasmon

Plasmons are the collective oscillation of conduction electrons excited by the light. Volume plasmons are the oscillation of the charge density and propagating through the volume of the metal. [12] The plasma frequency $\omega_p$ is defined as [12]
where $e$, $m^*$, $\varepsilon_{\infty}$, $\varepsilon_0$ are the electron charge, electron effective mass, high frequency dielectric constant, and free space permittivity, respectively. The dielectric function of bulk metal can be written in the simplified Drude mode as [12]

$$\varepsilon(w) = 1 - \frac{\omega_p^2}{\omega^2}. \quad (2.10)$$

As can be observed from the Eq. (2.10), the dielectric function becomes zero at plasma frequency. For $\omega > \omega_p$, the dielectric function of metal is real, and the medium does not absorb the light energy. For $\omega < \omega_p$, the dielectric function of metal is negative, and the medium is highly reflective. The plasma oscillations occur at the plasma frequency $\omega_p$, which is the natural frequency of oscillation of the electrons, known as the volume plasmons. It has been reported that volume plasmons do not couple to transverse electromagnetic waves due to longitudinal nature of the excitation. [12]

### 2.5.2.1 Surface Plasmon Polaritons

Surface plasmons are the oscillation of conduction electrons at metal surface. There are two types of excited surface plasmons. One is surface plasmon polaritons (SPP) [104, 105] and the other is localized surface plasmon resonance (LSPR) [4, 106, 107]. SPP is the excitation of conduction electrons at the interface between a metal and a dielectric, as shown in Fig. 2.20.
SPP only exists for TM wave as the TE wave cannot generate the charges at the interface. [12] The SPP dispersion relation can be described by [105]

\[ k_{spp} = k \sqrt{\frac{\epsilon_d \epsilon_m}{\epsilon_d + \epsilon_m}}. \] (2.11)

where \( \epsilon_d \) is the permittivity of dielectric, \( \epsilon_m \) is the permittivity of metal, and \( k \) is the wave vector in free space. The frequency of SPP wave is described by [105]

\[ \omega_{spp} = \frac{\omega_p}{\sqrt{1 + \epsilon_d}}. \] (2.12)

It can be observed from Eq. (2.12) that the SPP frequency is lower than the bulk plasma frequency. Figure 2.21 shows the SPP dispersion relation. As shown in the figure, the wave vector of SPP wave is larger than that of light in free space, indicating a momentum mismatch between the SPP wave and light. Thus, light illuminating a metal surface cannot directly couple to SPP. This mismatch can be overcome by special phase-matching techniques such as grating [108] or prism coupling [13, 109].
Fig. 2.21 SPP dispersion and prism coupling. [12]

The excitation of SPP wave occurs at the interface between the metal and the dielectric. Thus, multilayer structures such as Metal-Insulator-Metal or Insulator-Metal-Insulator can support the SPP modes at each interface, as shown in Fig. 2.22. Fig. 2.22(a) shows a thin metal slab is sandwiched between two thick dielectric layers. The overlap of evanescent fields of the two SPP waves leads to two couple modes including one symmetric mode and one antisymmetric mode. The symmetric mode is known as long-range SPP (LRSPP) mode. The propagation length of LRSPP can reach the order of centimeters [110, 111] due to smaller attenuation of electric field. For asymmetric mode, the loss of field is higher as the electric fields penetrate more deeply into the metal. Therefore, the asymmetric mode is also known as the short-range SPP (SRSPP), and the propagation length is very short due to the strong attenuation of the field in the metal.
2.5.2.1 Localized Surface Plasmon Resonance

Localized surface plasmon resonance (LSPR) is non-propagating excitation of the conduction electron of the metal nanoparticles coupled to the applied electromagnetic field. LSPR is strongly dependent of the nanoparticle size, shape, inter-particle spacing and surrounding medium. [4, 112, 113] Unlike the propagating SPP wave where the phase-matching technique is required, LSRP can be excited by direct light illumination. The interaction of light with nanoparticles can be simply described by a classical harmonic oscillator, as shown in Fig. 2.23.
As shown in the figure, in the quasi-static regime, for metal nanoparticle size much smaller than the incident wavelength, the resonance of conduction electrons could be excited collectively without considering the retardation effect of the applied electromagnetic field. For Au and Ag nanoparticles, the resonance is observed in the visible light spectrum. [114]

Figure 2.24 shows the extinction spectrum and AFM images of Ag nanoparticles with different sizes on ITO.[115]

Figure 2.24 shows the extinction spectrum and AFM images of Ag nanoparticles with different size. The strong extinction observed in visible is due to the resonance of
conduction electrons inside the nanoparticles, which greatly enhance the absorption and scattering of the electromagnetic fields. In the quasi-static regime, the field distribution of a spherical particle in an electrostatic field can be calculated with Laplace equation in spherical coordinate $(r, \theta)$. The potential $\Phi_{out}$ outside the spherical particle is described by [116]

$$\Phi_{out} = -E_0 r \cos \theta + \frac{p \cdot r}{4\pi \varepsilon_0 \varepsilon_m r^3}.$$  \hspace{1cm} (2.13)

$$p = 4\pi \varepsilon_0 \varepsilon_m a^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} E_0.$$  \hspace{1cm} (2.14)

where $E_0$ is the applied electric field vector, $\varepsilon_m$ is the permittivity of the surrounding medium, $\varepsilon_0$ is the free space permittivity, $\varepsilon$ is the permittivity of metal. $p$ and $r$ are the polarization vector and position vector, respectively. As can be observed from Eq. (2.14), the polarization reaches its maximum at a resonant condition that $|\varepsilon + 2\varepsilon_m|$ is a minimum. This condition is known as the Fröhlich condition. The resonance of polarization indicates an enhancement of the dipolar field, which leads to many promising applications of metal nanoparticles, such as bio-sensing and wave guiding. [117-119]

For particle with larger dimensions, the quasi-static approximation fails due to the significant retardation effect of the field over the particle volume. In 1908, Mie developed a complete theory of the scattering and absorption of electromagnetic radiation by a sphere. [120] The Mie theory has been widely used to describe the LSPR of a metallic nanoparticle. [121, 122] Detail discussion on Mie theory can be found in books such as Bohren and Huffman [123] and Kreibig and Vollmer [124].
2.6 Quantum Confinement Effect in Semiconductor Nanostructures

Optical properties of semiconductor materials with size of a few nanometers could be greatly different from their bulk counterparts due to the quantum confinement effect. The nanostructures can be classified into three types based on the confinement dimension including quantum well (1-D confinement), quantum wire (2-D confinement) and quantum dot (3-D confinement). The fundamental of quantum physics can be found in many reference books [77, 125, 126] and will not be discussed here. In this section, the effect of quantum confinement on optical properties of semiconductor nanocrystals including Si nanocrystals, Ge nanocrystals and ZnO nanocrystals will be briefly reviewed.

2.6.1 Quantum Confinement Effect in Si and Ge Nanocrystals

Owing to the quantum confinement effect, electronic and optical properties of Si nanocrystals and Ge nanocrystals have been intensively studied in last few years. [127-130] Many theoretical calculations showed that the nanocrystal size greatly influences both the optical transitions and the oscillator strengths. [6, 129]

![Energy diagram for the Kohn–Sham eigenvalues of Ge (left) and Si (right) as a function of atom numbers. [6]](image)
Figure 2.25 shows the calculated transition energies and oscillator strengths of the HOMO–LUMO transitions for Ge nanocrystals (nc-Ge) and Si nanocrystals (nc-Si) passivated with hydrogen as a function of atom numbers. [6] As shown in the figure, an increase of transition energy with reducing atom numbers due to the quantum confinement effect has been clearly observed in both nc-Ge and nc-Si. The size dependence of optical gap of nc-Si has been also reported by Öğüt. S et al. [128] As shown in Fig. 2.26, the nc-Si exhibits a significant expansion of band gap with reducing nanocrystal size.

![Fig. 2.26 Calculated quasiparticle gaps (dotted line), optical gaps (shown by × fitted to the solid line). [128] The experimental absorption data (□, ◊) for Si nanocrystal are from ref. [131].](image)

In general, the size dependence of band gap of nanocrystal can be empirically described as [132, 133]

\[
E_{g}^{\text{opt}}(d) = E_{g}^{\text{opt}}(\infty) + c / d^m.
\]

(2.15)

where \(E_{g}^{\text{opt}}\) is the band gap of the nanocrystal, \(E_{g}^{\text{opt}}\) is the band gap of bulk material (1.1 eV for bulk Si), and \(d\) is the nanocrystal size. The constants \(c\) and \(m\) are the
fitting parameters. For nc-Si, Delerue et al. reported the size dependence with $c = 3.37$ and $m = 1.39$ [132], and Weissker et al. proposed the value of $c = 2.96$ and $m = 1.0$ [133]. It has also been reported that optical constant or dielectric function of nanocrystal reduces with reducing nanocrystal size due to the quantum confinement effect. [133, 134]

![Fig. 2.27 Dielectric functions of Ge (a) and Si (b) nanocrystals with a varying number N of atoms. N=5, solid line; N=17, dotted line; N=41, dashed line; N=83, long-dashed line; N=147, dot dashed line; N=239, solid line; and N=363, dotted line. The vertical arrows in the absorption spectra indicate the single-particle HOMO-LUMO gaps.][133]

The arrows indicate the single-particle HOMO-LUMO gaps.

Figure 2.27 shows the dielectric function of nc-Si and nc-Ge calculated with different number of atoms. [133] It can be observed in the figure that the magnitude of both the real and imaginary parts of the dielectric function decreases with reducing nanocrystal size. The blue shift of absorption edge of $\varepsilon_2$ with decreasing nanocrystal size indicates the expansion of band gap due to the quantum confinement effect. The expansion is found more significant in a smaller nanocrystal due to the stronger...
confinement effect. On the other hand, the reduction of dielectric function over wide energy range also leads to the reduction of static dielectric constant $\varepsilon_r$. It has been known that the reduction in $\varepsilon_r$ could cause an increase in coulomb interaction energy between electrons, holes, and ionized shallow impurities and therefore can significantly modify the optical absorption and the transport phenomenon of a nanometric device. [5] The static dielectric constant of nanocrystal can be evaluated by integrating the imaginary part $\varepsilon_2(E)$ based on Kramer-Kronig relations at zero energy [134]

$$\varepsilon_s = 1 + \frac{2}{\pi} \int_0^\infty \frac{\varepsilon_2(E) / E}{dE.} \quad (2.16)$$

Figure 2.28 shows the static dielectric constant of spherical nc-Si as a function of radius. The size dependence can be simply described with the modified Penn model. [135]

$$\varepsilon_s(a) = 1 + \frac{\varepsilon_b - 1}{1 + (\Delta E / E_g)^2}. \quad (2.17)$$

where $a$ is the size of nanocrystal, $\varepsilon_b$ is the bulk static dielectric constant, $\Delta E$ is least energy separation and $E_g$ is the energy gap (4 eV for Si). It is important to note that the fundamental $\Gamma-\Delta$ gap at 1.1 eV plays almost no role in the dielectric function. [135] As shown in Fig. 2.28, the static dielectric constant of nc-Si decreases with reducing nanocrystal size as a result of the quantum confinement effect, which increases the separation of discrete states and leads to an increase of the energy denominator and a subsequent reduction in dielectric function. [135]
It has been discussed above that the electronic and optical properties of nc-Si and nc-Ge are greatly influenced by the nanocrystal size due to the quantum confinement effect. The surface and interface properties of nanocrystal could also change its electronic and optical properties. Detail discussions of quantum confinement effect on optical properties of Si nanostructures can be found in review articles [138-141].

2.6.2 Quantum Confinement Effect in ZnO Nanostructures

ZnO nanostructures such as quantum wires and quantum dots have attracted a lot attention in UV/blue optoelectronic applications due to its wide band gap and large exciton binding energy. [142, 143] As discussed in section 2.6.1, a confined nanostructure exhibits an expansion of band gap due to the quantum confinement effect.
Figure 2.29 (a) TEM image of uniform-sized ZnO nanorods with an average size of 5 nm (thickness) by 30 nm (length). (b) Comparison of photoluminescence spectra between ZnO nanorods and bulk powders drop-coated on glass substrates. [144]

Figure 2.29(b) shows the comparison of photoluminescence (PL) spectra between ZnO nanorods and bulk ZnO powders on glass substrates. [144] As shown in the figure, as compared to bulk ZnO where the emission observed at the peak energy of 3.25 eV, ZnO nanorods exhibit a blue shift of emission at peak energy of 3.3 eV. The blue shift is a direct evidence of expansion of band gap due to the quantum confinement effect. It has been shown that size dependence of band gap shift can be described based on the effective mass approximation [145]

$$\Delta E_g (R) = \frac{\pi^2 \hbar^2}{2R^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{\varepsilon R} + E_{so}(R).$$ \hspace{1cm} (2.18)
where $\Delta E_g$ is the shift of the lowest excited exciton state in the spherical nanoparticle with a radius of $R$. $m^*_e$ is the effective mass of the electron, $m^*_h$ is the effective mass of the hole, $\varepsilon$ is the dielectric constant and $E_{sol}$ is the solvation energy. In Eq. (2.18), the first term is the band gap shift due to the quantum confinement effect. The second term is the coulomb interaction related with exciton binding energy. The band gap shift calculated from Eq. (2.18) is comparable with the PL result. [144]

It has been also shown that the quantum confinement effect could greatly increase the coulomb interaction of electrons and holes, leading to an increase of exciton binding energy. [146-148] As shown in Eq. (2.18), the exciton binding energy increases with $R^{-1}$. It was reported that the exciton binding energy of ZnO nanorod with a diameter of 2.2 nm is 6–10 times larger than that of bulk ZnO. [149]

![Fig. 2.30 Exciton binding energies of ZnO quantum dots as a function of size. [150]](image)

Figure 2.30 shows the exciton binding energy of ZnO quantum dots as a function of quantum dot radius. As can be observed in the figure, as compared to bulk ZnO with exciton binding energy of 60 meV, ZnO quantum dots with radius of ~ 1-6 nm
Chapter 2 Literature Review

exhibit a greatly increase of exciton binding energy (~3-10 times) due to the quantum confinement effect. The large exciton binding energy could greatly enhance the bonding of electron-hole pairs and stabilize the exciton state. A stable exciton state promises a more efficient exciton-related emission. Thus, ZnO nanostructures are potential candidates for laser application.

2.7 Applications of Metal Oxide Thin Films

Metal oxide semiconductors have attracted special attention due to its promising application in memory storage and optoelectronics. Oxide-based resistive random access memories (RRAM) have gained a lot of interests recent years because of their potentials for nonvolatile memory application. On the other hand, conductive metal oxides such as Al-doped ZnO and indium gallium zinc oxide (IGZO) have been also intensively studied due to their potentials for next generation transparent electronics. In this section, applications of metal oxide will be briefly introduced.

2.7.1 Resistive Random Access Memory

Metal oxide based resistive random access memory (RRAM) is very promising for nonvolatile memory (NVM) application due to its simple structure, low power consumption, fast switching and compatibility with metal-oxide-semiconductor (CMOS) technology. [151, 152] Nominally, metal oxides are insulator, when sandwiched between two metal electrodes, exhibit an abrupt switching between a low resistance state (LRS) and a high resistance state (HRS) under electrical bias. The resistive switching behavior is very attractive for NVM application and widely
observed in various metal oxides such as SrTiO$_3$ [153], ZnO [154], TiO$_2$ [155, 156], NiO [157], Al$_2$O$_3$ [158] and HfO$_2$ [159].

![Fig. 2.31 (a) Schematic of metal-insulator-metal (MIM) structure for metal oxide RRAM, and I–V curves of two modes operation: (b) unipolar and (c) bipolar.[160]](image)

Usually, a forming voltage is required to initiate the switching due to the highly resistive state of the as-prepared sample. The switching modes of metal oxide can be classified into two modes: unipolar and bipolar. Figure 2.31 show the I–V characteristic of metal-oxide based RRAM for the two switching modes. As shown in the figure, unipolar switching only depends on the magnitude of the applied voltage but not on the polarity, while bipolar switching depends on the polarity of the applied voltage. The origin of the switching behavior could be very complicated. It is not only dependent on the oxide materials but also dependent on the metal electrodes and their interfacial properties. [160] There are two proposed models for resistive switching. One is filament-type conducting, which is related to the formation and rupture of conductive filaments in the oxide matrix. The other is interface-type conducting, which is related to the switching at interface between the metal electrode and the oxide. For filament-type, the switching is believed mainly due to the thermal redox and/or anodization near the interface between the metal electrode and the oxide. [161,
162] For interface-type, various models has been proposed such as electrochemical migration of oxygen vacancies [163, 164], trapping of charge carriers [165, 166], and a Mott transition induced by carriers doped at the interface.[167, 168] Detail discussion on switching mechanism of RRAM can be found in reviews by Waser et al [152, 169] and Sawa [151].

2.7.2 Transparent Conductive Electrode

Owing to the wide band gap nature, metal oxide thin films are optical transparent in visible spectrum. As discussed in section 2.4.2, most of metal oxides are n-type semiconductors, and their conductivities can be easily tuned by doping group-III elements such as Al, Ga or In. Therefore, transparent conductive oxide (TCO) can be used as transparent electrodes, which are the essential parts for thin film solar cells and flat panel display.[1] The most widely used TCO today is indium tin oxide (ITO). As compared to other TCOs, ITO has higher conductivity and good etching behavior. However, due to the limited availability of In, the cost of ITO is high. Therefore, there is a high demand for searching alternative n-type TCO materials. Recently, Al-doped ZnO (AZO) and Ga-doped ZnO (GZO) have emerged as important transparent conductive metal oxides, which can replace the expensive ITO. The free-electron concentration of AZO is usually in the range of 10^{19} - 10^{21} cm^{-3}. [2] Ternary oxides such as Zn_{2}SnO_{4} [170], MgIn_{2}O_{4} [171], Zn_{2}In_{2}O_{5} [172] and GaInO_{3} [173] were also developed. It has been shown that ZnO-based TCOs could be alternatives for ITO due to its low cost, good etching behavior and low toxicity. [174]
2.7.3 Transparent Thin Film Transistor

Another important application of metal oxide is the transparent thin film transistor (TFT). As compared to amorphous Si TFT and organic TFT, oxide-based TFT has much better electronic performance such as low cost, good reliability and high mobility. [175] In 2003, ZnO TFTs demonstrated by Hoffman et al [176], Garcia et al [177] and Masuda et al [178] shows that the oxide-based TFTs could be a viable technology for flat panel display. Later, Nomura et al. [7] presented a high performance TFT with effective mobility of 80 cm²V⁻¹s⁻¹, turn-on voltage of −0.5 V and on/off ratio of 10⁶ using indium gallium zinc oxide (IGZO). They have also demonstrated a room-temperature fabrication of transparent TFTs on flexible substrate using amorphous IGZO (a-IGZO). [32] In the following years, amorphous oxide semiconductors and their TFTs have been intensively studied due to its potential application in next generation flat-panel display. [179, 180] Amorphous oxide semiconductors such as a-IGZO can be deposited in low temperature to have a highly flat surface. As compared to polycrystalline oxide semiconductors, amorphous oxide semiconductors do not suffer from grain boundary problem, e.g., interface traps and scattering centers at grain boundary. Therefore, amorphous oxide-based TFT has higher mobility.
Figure 2.32 shows the typical device structures for fabrication of amorphous oxide semiconductor TFTs. As shown in the figure, TFT structure is a stacking order of gate electrode, channel layer and source and drain contacts. The top-gate structure has a good protection of channel layer from degradation due to atmospheric exposure; however, two patterning mask steps are required. [180] The bottom-gate structure is commonly used in laboratory research due to easy patterning of channel layer with a single mask step. The two inverted staggered structures shown in Fig. 2.32, are typically used for a-Si:H TFTs, and have been proposed for a-IGZO TFTs. [24]

2.8 Applications of Metal Nanoparticles

Metallic nanoparticles such as gold and silver nanoparticles exhibit remarkable localized surface plasmon resonance (LSPR) due to the collective oscillation of conduction electrons inside the nanoparticles. The highly localized field around the nanoparticles can lead to numerous plasmonic applications, such as biological sensing and optical wave guiding. In this section, applications of metal nanoparticles will be briefly introduced.
2.8.1 Localized Surface Plasmon Resonance Sensing

Owing to the characteristic of LSPR, metal nanoparticles can be effectively used for molecular detection or environmental sensing. [181, 182] LSPR is strongly dependent of the nanoparticle size, shape, inter-particle spacing and surrounding medium. [124] LSPR can be identified from the optical spectra of metal nanoparticles in two different ways. One is the pronounced extinction band in the extinction spectrum, and the other is the substantial scattering of light.

![Graph showing Extinction, Absorption, Far Field Scattering Cross Section, and Near Field Scattering Efficiencies for Ag nanoparticle with 22 nm radius immersed in water.](image)

As shown in Fig. 2.33, both the two effects resulted from the resonance of electrons can be used for sensing application. The direct excitation of LSPR with light makes LSPR sensor [184] much favored than the SPR sensor [185]. The fundamental working principle of LSPR sensor is based on the evolution of LSPR of metal nanoparticles caused by analyte adsorption, e.g., wavelength shift of LSPR. [15, 186] The high sensitivity of LSPR to the local environment makes the detection of small
molecules become possible, e.g., DNA [182, 187] It has also been reported that metal nanoparticles can be used for colored labelling, as shown in Fig. 2.34. [188, 189]

![Fig. 2.34 Color image of a sample of gold nanorods (red) and 60 nm nanospheres (green) in dark-field illumination (inset upper left). Inset shows the TEM images of a dense ensemble of nanorods and a single nanosphere.][188]

2.8.2 Surface Enhanced Raman Scattering

One of the important applications of the LSPR is the surface enhanced Raman scattering (SERS), which exploits the highly localized light fields generated in the near-field of metallic nanostructures for amplifying the Raman signal. SERS is an important analytical technique in biophysics and biochemistry. In a normal Raman scattering process, the photon is not in resonance with the Raman transition. Therefore, the ordinary Raman signal is extremely weak; typically cross sections are of the order $10^{-30}$ cm$^2$/molecule. [190] When placing Raman-active molecules within the near-field of a metallic nanostructure, the resonant Raman scattering shows strong signal than the normal Raman scattering. The local field enhancement factor can be up to $10^{14}$. [12, 191] Thus, SERS is an effective tool for sensing molecules and capable of
detecting single molecule. [14, 190, 192] Figure 2.35 shows a SERS spectrum of a single haemoglobin molecule. [193]

![Graph](image)

Fig. 2.35 SERS spectrum of a single haemoglobin molecule on a silver nanoparticle dimer (see inset) measured in 200 s at 514.5 nm excitation laser wavelength using ~20 μW laser power.[193]

2.8.3 Metal Nanoparticle Waveguide

Owing to the down scale of optical devices, the integrated nanophotonic devices and circuits requires the electromagnetic energy to be guided on a scale that could overcome the diffraction limit of light. [194] Metal nanoparticle waveguide has been proposed for guiding electromagnetic energy below the diffraction limit. [195, 196] The guiding of electromagnetic energy is realized based on the near field coupling of arrays of closely packed metal nanoparticles. The coupling of plasmon mode leads to strong localization of electromagnetic energy between the adjacent metal...
nanoparticles. [196] The coupling of adjacent particles can be excited from two different polarizations: transverse mode and longitudinal mode.

Figure 2.36 shows the schematic of two coupling modes in a single nanoparticle chain. Transverse modes are observed with dipole moments perpendicular to the nanoparticle chain axis and longitudinal modes are observed with dipole moments along the propagation direction. The dispersion relation for the two plasmon modes has been calculated by M. L. Brongersma et.al [197, 198], as shown in Fig. 2.37.

Fig. 2.37 Dispersion relation for transverse modes (T) and longitudinal modes (L).[198]
Besides electromagnetic energy can be guided below the diffraction limit, another advantage of the metal nanoparticle waveguide over planar waveguide is low radiation loss around the corners of waveguide. Figure 2.38(a) shows a 60° corner waveguide of Au nanoparticle with size of 50 nm fabricated using e-beam lithography (EBL). Figure 2.38(b) shows a straight waveguide of Au nanoparticle with size of 30 nm. [198] The loss in metal nanoparticle waveguide can be attributed to both the radiation loss into the far field and internal damping loss. It has been shown that the excitation of plasmon modes between the nanoparticles due to the near-field coupling results in a strong localization of electromagnetic energy, leading to negligible radiation loss. [196, 198] Therefore, a nearly 100% of power transmission around 90° corner is viable based on the metal nanoparticle waveguide.

![Fig. 2.38 (a) SEM image of a 60° corner in a plasmon waveguide. The Au nanoparticles are ~ 50 nm in diameter and spaced by ~75 nm (center-to-center). (b) Straight waveguide made by 30 nm diameter colloidal Au nanoparticles. [198]](image-url)
2.9 Summary

In this chapter, literature reviews of thin film technologies including thin film synthesis and thin film characterization have been presented. Optical properties of ZnO, IGZO and Au thin films and their applications are briefly reviewed. It has been shown that the abundant free electrons could greatly alter the optical properties of the oxides. It has been also shown that metal nanoparticles such as Ag and Au nanoparticles exhibit remarkable LSPR due to collective oscillation of conduction electrons, which is absent in their bulk counterpart. LSPR is strongly dependent of the nanoparticle size, shape, inter-particle spacing and surrounding medium. On the other hand, it has been shown that quantum confinement effect could greatly change the optical properties of the nanostructure, e.g., expansion of band gap and suppression of dielectric function with reducing nanocrystal size. Investigations of effects of free electrons, quantum confinement and LSPR on optical properties of metal oxide and metal films will be presented in the following chapters.
Chapter 3 Free Electrons Effect in Conductive Metal Oxide Thin Films

3.1 Introduction

Conductive metal oxides such as Al-doped ZnO (AZO) and amorphous indium gallium zinc oxide (a-IGZO) have recently emerged as important transparent conductive oxides, which have wide applications in optoelectronics such as thin film solar cells and flat-panel display. [2, 176, 180] AZO is an n-type semiconductor material, and its free-electron concentration is usually in the range of $10^{19}$-$10^{21}$ cm$^{-3}$ due to the extrinsic Al dopant. [2] With such high concentration of free electrons, excitonic absorptions could be significantly suppressed by the free-electron screening. [74, 75] In addition, when the carrier concentration in the oxide exceeds the Mott critical density ($10^{18}$–$10^{19}$ cm$^{-3}$ in ZnO), a semiconductor-to-metal transition can occur and its conduction band can be partially filled with free electrons, resulting in a band gap expansion due to the Burstein-Moss effect.[59] The suppression of excitonic absorptions and Burstein-Moss shift due to high concentration of free electrons could significantly alter the optical properties of oxide films, in particular, the absorption spectrum in the region near the band gap energy. The situation is further complicated as carrier concentration has a strong dependence on the film thickness. [59, 199] On the other hand, the intrinsic donor-like defects such as oxygen vacancy and hydrogen impurity can significantly affect the carrier concentration [78], which can be greatly...
influenced by an annealing process. In this chapter, investigations of free electrons effect on optical properties of AZO and a-IGZO films are presented.

3.2 Numerical Determination of Optical Properties of Thin Films

Optical response of the medium is described by its dielectric function. Dielectric polarization \( P \) of the medium is dependent of applied electric field \( E \), described as

\[
P = \chi \varepsilon_0 E.
\]  

where \( \chi \) is the electric susceptibility and \( \varepsilon_0 \) is the permittivity of the free space.

Dielectric constant of the medium can be expressed as

\[
\varepsilon = 1 + \frac{P}{\varepsilon_0 E} = 1 + \chi.
\]  

Typically, the dielectric constant of the medium is a complex number, which is described by its real \( (\varepsilon_1) \) and imaginary \( (\varepsilon_2) \) parts.

\[
\varepsilon = \varepsilon_1 + i\varepsilon_2.
\]  

The dielectric constant can be also expressed in terms of its complex refractive index \( (N) \)

\[
\varepsilon = N^2 = (n + ik)^2.
\]  

where \( n \) is the refraction index and \( k \) is the extinction coefficient. The dielectric constant is dependent of the photon energy and the dispersion relation is known as the
dielectric function. The dispersions of optical constants including $n$ and $k$ can be also calculated from Eq. (3.4).

Dielectric function of the metal oxide and metal thin films can be determined with absorption spectroscopy or spectroscopic ellipsometry based on proper optical dispersion models. The two techniques will be briefly introduced in the following section.

### 3.2.1 Optical Absorption Spectra Modeling

Absorption coefficient ($\alpha$) of a thin film is related with its extinction coefficient ($k$) by

$$\alpha = \frac{4\pi k}{\lambda}. \quad (3.5)$$

where $\lambda$ is the wavelength of the photon. Absorbance ($A$) of the thin film can be calculated using absorption coefficient ($\alpha$) based on Beer–Lambert equation [77]

$$A = \frac{\alpha d}{\ln 10}. \quad (3.6)$$

where $d$ is the thin film thickness. One can calculate the absorbance ($A_{\text{cal}}$) with Eqs. (3.4) - (3.6) using the value of ($\varepsilon_1, \varepsilon_2$). To determine the dielectric function of the thin film, dummy dielectric function ($\varepsilon_{D,1}, \varepsilon_{D,2}$) is first calculated with an optical dispersion model with some empirical values. With the dummy dielectric function, the actual dielectric function ($\varepsilon_1, \varepsilon_2$) can be determined by freely varying the fitting parameters of the optical dispersion model to minimize the mean-squared-error (MSE) [57] of the
comparison between the calculated absorbance \( A_{\text{cal}} \) and the experimentally measured absorbance \( A_{\text{exp}} \).

\[
MSE = \frac{1}{M-P-1} \sum_{j=1}^{M} (A_{\text{cal}} - A_{\text{exp}})^2.
\]  

(3.7)

where \( M \) and \( P \) are the number of measurement points and analytical parameters, respectively. The spectral fitting procedures for determination of the dielectric function of the thin film are summarized in Fig. 3.1.

![Fig. 3.1 Spectral fitting procedures for absorption spectra modeling.](image)

3.2.2 Ellipsometric Modeling

As discussed in section 2.3.2.2, spectroscopic ellipsometry provides more precise measurement and characterizations than other conventional instruments. As compared to absorption spectra modeling, ellipsometric modeling provides more accurate description of optical properties such as band gap and dielectric function of the
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materials, but requires more complicated data analysis. In general, the measured ellipsometry angles ($\Psi, \Delta$) are defined as $\rho = R_p / R_s = \tan(\Psi)\exp(i\Delta)$, where $R_p$ and $R_s$ are the Fresnel reflection coefficients for the p- and s-polarized light, respectively. 

[57] For a three-phase model (i.e., air/thin film/substrate), $\rho$ is the function of wavelength $\lambda$, thin film thicknesses $d$, complex refraction index of the air ($N_0$), thin film ($N_1$) and substrate ($N_2$), and the incident angle $\theta_0$.

$$\tan(\Psi)\exp(i\Delta) = \rho(N_0, N_1, N_2, d, \lambda, \theta_0). \quad (3.8)$$

For a multilayer structure, the reflection coefficient $r_{j,j+1}^a$ ($a = s, p$, $j = 0,1,2...$) at interface between the $j$ th and $(j+1)$ th layers for $s$- and $p$- polarized light are given by the Fresnel equation [57]

$$r_{j,j+1}^s = \frac{N_j \cos \theta_j - N_{j+1} \cos \theta_{j+1}}{N_j \cos \theta_j + N_{j+1} \cos \theta_{j+1}}. \quad (3.9)$$

$$r_{j,j+1}^p = \frac{N_{j+1} \cos \theta_j - N_j \cos \theta_{j+1}}{N_{j+1} \cos \theta_j + N_j \cos \theta_{j+1}}. \quad (3.10)$$

The total complex reflection coefficient $R_{j,j+1}^a$ ($a = s, p$, $j = 0,1,2...$) at each interface between the $j$ th and $(j+1)$ th layers is described by [57]

$$R_{j,j+1}^a = \frac{r_{j,j+1}^a + R_{j+1,j+2}^a X_{j+1}}{1 + r_{j,j+1}^a R_{j+1,j+2}^a X_{j+1}}. \quad (3.11)$$

where

$$X_{j+1} = \exp(i \frac{4\pi}{\lambda} N_{j+1} d_{j+1} \cos \theta_{j+1}). \quad (3.12)$$

The refraction angle $\theta_j$ ($j = 0,1,2...$) at each interface can be calculated from the Snell’s equation [57]
\[ N_0 \sin \theta_0 = N_1 \sin \theta_2 = \ldots = N_j \sin \theta_j \]  
(3.13)

In above equations, \( N_j \) (\( j = 0, 1, 2 \ldots \)) is the complex refractive index of the \( j \)th layer, \( N_0 \) is the refraction index of air, \( \lambda \) is the wavelength and \( d_j \) (\( j = 0, 1, 2 \ldots \)) is the thickness of \( j \)th layer. For top air layer, \( N_0 = 1 \) and \( d_0 = 0 \) are assumed in all SE analysis. From Eqs. (3.9) – (3.13), one can calculate the ellipsometry angles \( (\Psi_{cal}, \Delta_{cal}) \) at interface between the air and first layer

\[\tan(\Psi_{cal}) \exp(i\Delta_{cal}) = \frac{R_{0,1}^p}{R_{0,1}^s}. \]  
(3.14)

The mean-squared-error (MSE) for the ellipsometric modeling is expressed as [58]

\[ \text{MSE} = \frac{1}{M-P-1} \sum_{j=0}^{M} \left[ \frac{(\Psi_{cal} - \Psi_{exp})^2}{\sigma^2_{\Psi_{exp}}} + \frac{(\Delta_{cal} - \Delta_{exp})^2}{\sigma^2_{\Delta_{exp}}} \right]. \]  
(3.15)

where \( M \) and \( P \) are the number of measurement points and analytical parameters, respectively, \( \sigma^2_{\Psi_{exp}}, \sigma^2_{\Delta_{exp}} \) are the measurement errors for \( (\Psi, \Delta) \), respectively. The ellipsometric modeling procedures are summarized in Fig. 3.2.

---

**Fig. 3.2 Spectral fitting procedures for ellipsometric modeling.**
3.3 Free Electrons Effect in Al-doped ZnO Thin Films

In this section, a comparison of the free electrons effect between the undoped ZnO and Al-doped ZnO (AZO) is conducted. The undoped ZnO thin films show strong excitonic absorptions at room temperatures; while the excitonic absorptions are greatly suppressed in AZO. As compared to the undoped ZnO, the AZO films exhibit an expansion in the band gap and a reduction in the exciton binding energies due to the free electron screening effect.

3.3.1 Sample Preparation

The undoped ZnO and AZO thin films were deposited on quartz substrates by RF magnetron sputtering of a pure ZnO target (99.99% purity) and an AZO target (2% Al2O3, 99.99% purity), respectively, under the same deposition condition. The chamber was pumped down to $7 \times 10^{-6}$ Torr prior to the deposition process. The sputtering deposition was carried out at room temperature in argon ambient with the background pressure of $9 \times 10^{-3}$ Torr, and the RF power was maintained at 80 W. The pure argon environment was to ensure that the influence of oxygen on the structural and optical properties of the deposited films is minimized. [203, 204] The thicknesses of the as-deposited films for both the undoped ZnO and AZO were 20, 40, 90 and 185 nm, as determined by spectroscopic ellipsometry. The crystalline structures and surface morphology of the thin films were investigated by X-ray diffraction (XRD) and scanning electron microscope (SEM), respectively. Optical absorbance
measurement was carried out with an UV-Vis spectrophotometer in the wavelength range of 250-800 nm.

Figure 3.3(a) shows the XRD and SEM measurements of the 20 nm and 90 nm undoped ZnO thin films; and Fig. 3.3(b) shows the same measurements of the 20 nm and 90 nm AZO thin films. The XRD patterns indicate the polycrystalline growth of wurtzite structure along (002) direction. There is no obvious shift of Bragg peak observed in both films. This indicates the strain induced at interface between the quartz substrate and the as-deposited films is insignificant. The average sizes of the grains in the oxide thin films can be estimated from the broadening of the Bragg peak.
Chapter 3 Free Electrons Effect in Conductive Metal Oxide Thin Films

in the XRD patterns based on the Scherrer’s equation [49]. The estimated grain size $D_{XRD}$ as a function of the film thickness for both undoped ZnO and AZO thin films is shown in Fig. 3.3(c). The in-plane average grains size $D_{SEM}$ estimated from the SEM images as a function of film thickness for both undoped ZnO and AZO thin films is shown in Fig. 3.3(c) also. As can be observed in Fig. 3.3(c), the $D_{SEM}$ is generally comparable with the $D_{XRD}$.

3.3.2 Absorption Spectra Modeling

Excitonic absorption can be described by the Elliott theory [63] for hydrogenic excitons. As exciton absorption can significantly influence a band-edge absorption spectrum, an excitonic theory instead of the traditional Tauc method of linearly extrapolating the absorption edge should be used for more accurate determination of the band gap energies. The discrete states of the exciton lines can be modeled with a broadened Lorentzian line shape [205]

$$\varepsilon(E) = \sum_{\beta=A,B,C} \left[ \sum_{n=1}^{\infty} \frac{A_{\beta n}^d}{n^3} \frac{1}{E_{g\beta} - \frac{R_{\beta}}{n^2} - i\Gamma_{n,\beta}^d} \right]. \quad (3.16)$$

where $\varepsilon$ is the complex dielectric function, $A_{\beta n}^d$ is the discrete exciton strength parameter, $R_{\beta}$ is the exciton binding energy, $\Gamma_{n,\beta}^d$ is the broadening parameter of the $n$ th discrete state (since the intensity falls with $n^3$, only the ground state $n = 1$ is considered in this work), and $E_{g\beta}$ is the band gap energy corresponding to distinct exciton peaks A, B and C. The discrete absorption below the band gap is summed with the continuum absorption above the band gap, which has the form [65]
where $A_\beta^c$ is the continuum exciton strength parameter, $\Gamma_{\beta}^c$ is the broadening parameter. Eqs. 3.16 and 3.17 were used to model both the absorption of the undoped ZnO and AZO thin films, as shown in Figs. 3.4(a) and 3.4(b), respectively.

### 3.3.3 Effect of Free Electrons Screening on Exciton Binding Energy

Figures 3.4(a) and 3.4(b) show the absorption spectra in the UV-visible range at room temperature of the undoped ZnO and AZO thin films, respectively, with the
thicknesses of 20 nm and 90 nm; and Fig. 3.4(c) shows the comparison of the absorption between the undoped ZnO and AZO for the thickness of 20 nm. It can be observed from Fig. 3.4 that there is remarkable difference in the absorption spectrum between the undoped ZnO and AZO thin films. The difference between the undoped ZnO and AZO can be attributed to the large difference in the carrier concentration. As shown in Fig. 3.4(a) for the undoped ZnO thin films, a broaden absorption peak is observed at $\sim 3.5$ eV, which is attributed to the excitonic absorptions. In contrast, as shown in Fig. 3.4(b), such peak is not evident in the AZO thin films. This indicates that the abundant free electrons (the carrier concentration in 90 nm AZO is in the order of $10^{18}$ cm$^{-3}$ as determined from the Hall effect measurement) in the AZO thin films greatly suppress the excitonic absorptions as a result of the free-electron screening effect. It has been known that the three valence bands of wurtzite ZnO result in the formation of the excitons labeled in order of the valence bands as “A”, “B”, and “C” [206]. The three excitons can be resolved usually at low temperatures; they can merge into a broadened peak at room temperature due to the broadening caused by the exciton-phonon interactions [207], which is the case observed in Fig. 3.4(a).
As can be observed in Fig. 3.5, the exciton binding energies of the AZO thin films are significantly smaller than that of the undoped ZnO thin films for the same grain size. For example, for the average grain size $D = 15.5$ nm (film thickness = 90 nm), the binding energies of excitons A, B and C of the AZO thin film are lower than that of the undoped ZnO thin film by 18, 17, 14 meV, respectively. One may estimate a screened binding energy with the empirical formula $R_b = R_{b0} - kN^{1/3}$, where $R_b$ is the screened binding energy, $R_{b0}$ is the unscreened binding energy, $N$ is the carrier concentration, and the suggested $k$ value of n-type ZnO is $\sim 1.2 \times 10^{-5}$ meVcm. [3, 75] The 90 nm AZO thin film has an electron concentration in the order of $10^{18}$ cm$^{-3}$ as determined from the Hall measurement; thus the estimated reduction in the binding energy due to the screening effect is $\sim 12$ meV, which is comparable with the above
differences in the binding energies between the undoped ZnO and AZO thin films. Note that the carrier concentration of the undoped ZnO thin film with the same thickness is 2 – 3 orders lower than that of the AZO thin film and thus the screening effect can be ignored for the undoped ZnO thin films.

### 3.3.4 Effect of Burstein-Moss Shift on Band Gap Energy

![Band gap energies of the undoped ZnO and AZO films as a function of the average grain size](image)

Figure 3.6 shows the band energies of the undoped ZnO and AZO films as a function of the average grain size $D$. As can be observed in the figure, the band gap energies of the AZO thin films are larger than that of the undoped ZnO thin films for the same grain size. For example, for the average grain size of 15.5 nm, the band gap energy of the AZO thin film is ~ 50 meV larger than that of the undoped ZnO thin film. The band gap expansion in the AZO films as compared to the undoped ZnO thin films can be explained by the concept of Bursterin-Moss(BM) shift [8, 59]. In the AZO thin films with abundant free electrons in the conduction band, as the direct consequence of Pauli exclusive principle, the filled electron states at the bottom conduction band
prevent further electron filling lower energy states, and electron filling can occur only at higher energy states. As a result, the fundamental edge of absorption transitions shifts to a higher energy. As shown in Fig. 3.6, the band gap of the AZO thin films is larger than the counterpart of the undoped ZnO thin films by 60 meV, which is due to the BM shift discussed above. The difference of 60 meV in the bandgap energy between the undoped ZnO and AZO thin films can be considered as an average value for different grain sizes. Note that the bulk value of 3.46 eV is larger than the reported value of ~ 3.4 eV [64]. This is due to fact that the bulk value is evaluated based on the largest band gap energy at exciton peak C (corresponding to the largest exciton absorption energy).

3.3.5 Conclusion

Both band gap energies and exciton binding energies of ultrathin undoped and Al-doped ZnO (AZO) films with different thicknesses on quartz substrate have been determined from optical absorption measurement based on the Elliott’s exciton absorption theory. As compared to the undoped ZnO films, the AZO films exhibit an expansion in the band gap and a reduction in the exciton binding energies due to the free electron screening effect, which significantly suppresses the excitonic absorption and results in a blue shift of the absorption edge.
3.4 Effect of Thermal Annealing on Optical Properties of Al-doped ZnO Thin Films

In this section, a study of the annealing effect on the optical properties of Al-doped ZnO (AZO) thin films is presented. The band gap and dielectric function of both the as-deposited and annealed AZO thin films have been determined with spectroscopic ellipsometry (SE). As compared to the as-deposited thin film, the annealed thin films exhibit both the Burstein-Moss shift and free-electrons effect, i.e., the band gap energy increases with higher electron concentration, which results in a higher free electron absorption. The annealing-temperature dependence of dielectric function is shown related to the change in the free-electron concentration of the oxide films, which is greatly influenced by the annealing temperature. The change in the electron concentration can be attributed to the change of the donor-like defect concentration in the oxide films as a result of annealing.

3.4.1 Sample Preparation

The AZO thin films were deposited with the RF magnetron sputtering technique onto a 30 nm SiO₂ buffer layer which was thermally grown on a p-type Si wafer. The deposition was carried out with a RF power of 80 W at room temperature in a pure argon ambient (background pressure of $9 \times 10^{-3}$ Torr) using an AZO target (2% Al₂O₃, 99.99% purity). The as-deposited AZO thin films with the nominal thickness of 90 nm were annealed in N₂ ambient using rapid thermal annealing (RTA) at the temperatures in the range of 400 - 700°C with a step of 50°C for 30 sec. The crystalline structure
and surface morphology of the as-deposited and annealed AZO thin films were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM), respectively. The as-deposited AZO thin films have an average grain size $D_{\text{as-dep}}$ of ~20 nm while the annealed films have an average grain size $D_{\text{annealed}}$ of ~26 nm as estimated from both the XRD and SEM measurements. The $D_{\text{annealed}}$ is about the same for all the annealed films, i.e. there is no obvious dependence of the grain size on annealing temperature observed at the annealing temperatures of 400-700°C. The grain sizes are relatively larger (>10 nm). Thus the influence of quantum confinement effect on the optical properties of the deposited thin films is insignificant. The SE measurement was conducted with an ellipsometer in the wavelength range of 280-1100 nm.

### 3.4.2 Ellipsometric Modeling

The SE analysis is based on the five-phase model (i.e., air/surface-roughness layer/AZO layer/SiO$_2$ buffer layer/Si substrate). The surface-roughness layer is modeled with Bruggeman effective medium approximation (EMA) [208]. It has been reported that the Yoshikawa and Adachi’s model [65] provides an excellent description of the dielectric function of ZnO thin films, in particular, the excitonic absorption near the band edge. The formation of excitons are attributed to the three valence bands of wurtzite ZnO, labeled in the order of the valence bands as “A”, “B”, “C” [206]. It has been shown that high electron concentration could greatly suppress the formation of excitons due to the free-electron screening effect [74, 75]. In this work, the
suppression of excitonic absorption is observed in both as-deposited and annealed AZO thin films with carrier concentration in the range of $10^{19}$ - $10^{20}$ cm$^{-3}$. Therefore, the dielectric function of AZO thin films, $\varepsilon(E) = \varepsilon_1(E) + i\varepsilon_2(E)$, is modified based on the Yoshikawa and Adachi’s model [65]

$$\varepsilon(E) = \varepsilon_{\text{int}}(E) + \varepsilon_{\text{Drude}}(E).$$

(3.18)

where $\varepsilon_{\text{int}}(E)$ and $\varepsilon_{\text{Drude}}(E)$ are the complex dielectric function due to the interband absorption and the free-electrons (Drude) absorption, respectively. The interband absorption $\varepsilon_{\text{int}}(E)$ is modeled with the sum of a simplified critical point model and a Lorentz oscillator,

$$\varepsilon_{\text{int}}(E) = \varepsilon_{\text{CP}}(E) + \varepsilon_{\text{LZ}}(E).$$

(3.19)

The critical point model $\varepsilon_{\text{CP}}(E)$ is to model the interband absorption at the three valence bands A, B, C near the band edge, described by [65]

$$\varepsilon_{\text{CP}}(E) = \sum_{\alpha = A, B, C} A_{0\alpha}^{\text{cp}} E_{g\alpha}^{-1.5} f(\chi_{0\alpha}).$$

(3.20)

where $f(\chi_{0\alpha}) = \chi_{0\alpha}^{-2}[2-(1+\chi_{0\alpha})^{1/2}-(1-\chi_{0\alpha})^{1/2}]$,

$$\chi_{0\alpha} = (E + i\Gamma_{0\alpha}^{\text{cp}}) / E_{g\alpha},$$

where $A_{0\alpha}^{\text{cp}}$ is the interband strength parameter, $\Gamma_{0\alpha}^{\text{cp}}$ is the broadening parameter, $E_{g\alpha}$ is the band gap energy corresponding to the $E_o$ gaps at the three valence bands A, B and C. It has been found in this work that the SE spectral fitting can be greatly improved by adding a Lorentz oscillator. The Lorentz oscillator $\varepsilon_{\text{LZ}}(E)$ is used to model the interband absorption above the band gap, given by [77]

76
\[
\varepsilon_{LZ}(E) = \frac{A_{LZ}}{E_i^2 - E^2 - i\Gamma_{LZ}E},
\]

where \( A_{LZ} \) and \( \Gamma_{LZ} \) are the strength and broadening parameters, respectively. \( E_i \) is the interband transition energy above the band gap. The contribution of free-electrons absorption \( \varepsilon_{\text{Drude}} \) can be described by the Drude model [77]

\[
\varepsilon_{\text{Drude}}(E) = \varepsilon_{\infty} - \frac{A_D}{E^2 + i\Gamma_D E},
\]

where \( A_D = \varepsilon_{\infty}E_p^2 \), \( \varepsilon_{\infty} \) is the high frequency dielectric constant, \( A_D \) and \( \Gamma_D \) are the strength and broadening parameters, respectively, and \( E_p \) is the plasma energy.

Fig. 3.7 SE spectral fittings of the as-deposited (a) and annealed (RTP 500°C) (b) AZO thin films deposited on SiO\(_2\) buffer layer. SEM images of the thin films are also shown in the figure. The dash lines are used to show the blue shift of the spectra due to the annealing at 500°C.

Figure 3.7 shows the comparison of the experimental spectra of the ellipsometric angles (\( \Psi \) and \( \Delta \)) between the as-deposited AZO thin film and the AZO thin film annealed at 500°C. It can be observed in the figure that the annealing leads to a blue
shift in the SE spectra. The blue shift can be attributed to the increase of electron concentration, which typically results in a blue shift of optical band gap as a result of the Burstein-Moss effect [59]. It has been reported that thermal annealing could greatly affect the carrier concentration in AZO thin films through the activation of Al dopant [209] or due to the change of the concentration of donor defects such as oxygen vacancies [80, 201]. On the other hand, annealing can increase the film crystallization.

The HRSEM images of the two samples (i.e. the above-mentioned as-deposited and annealed AZO thin films) are also shown in Fig. 3.7. It can be observed from the images that the average grain size of the annealed film is larger than that of the as-deposited one.

3.4.3 Influence of Annealing Temperature on Dielectric Function

![Fig. 3.8 Real part ($\varepsilon_1$) and imaginary part ($\varepsilon_2$) of the complex dielectric function of the AZO thin films annealed at the temperatures of 400-550°C (a) or 500-700°C (b). The arrow indicates the increase of annealing temperature. The complex dielectric function of the as-deposited AZO thin film is also included for comparison.](image)
Figure 3.8 shows the evolution of the complex dielectric function, which are obtained from the SE spectral fitting, of the annealed AZO thin films as a function of the annealing temperature. It can be observed in the figure that annealing temperature has a significant impact on the dielectric function, which can be attributed to a change in the free electron concentration as a result of annealing. It has been reported that annealing can greatly affect the free electron concentration in AZO thin films [210], which can lead to a change in the onset of the band-edge absorption due to the Burstein-Moss (BM) effect. The BM effect leads to a blue shift in the absorption or an expansion of the band gap. As discussed in section 3.3.4, the expansion of the band gap can be described by a conduction band filling theory based on the Pauli exclusive principle. The filled electron states at the bottom conduction band prevent further electron filling at low energy states, and electron filling can occur only at higher energy states. As a result, the fundamental absorption edge shifts to a higher energy. As shown in Fig. 3.8(a), the blue-shift of imaginary part ($\varepsilon_2$) of the complex dielectric function of the AZO thin films annealed at 400-550°C is a direct evidence of the band gap expansion due to the increase of electron concentration in the annealed AZO thin films as a result of the BM effect. On the other hand, an increase of electron concentration also leads to an increase of free-electrons (Drude) absorption in the film, as demonstrated by the increase in $\varepsilon_2$ at the low energy side (e.g., $\lesssim 1.5$ eV) (see Fig. 3.8(a)).
3.4.4 Influence of Annealing Temperature on Free Electrons Concentration

The optical electron concentration \( N_{opt} \) can be calculated from the value of the plasma energy \( E_p \) yielded from the SE spectral fittings with the expression below [59]

\[
E_p = \left( \frac{\hbar^2 e^2 N_{opt}}{m^* \varepsilon_\infty \varepsilon_0} \right)^{1/2}.
\]  

(3.23)

where \( \hbar \), \( e \), \( m^* \), \( \varepsilon_\infty \), \( \varepsilon_0 \) are the reduced Planck constant, electron charge, electron effective mass, high frequency dielectric constant, and free space permittivity, respectively. In the calculation of \( N_{opt} \), the effective mass of electron \( m^* = 0.28m_0 \) [72] and \( \varepsilon_\infty = 2 \) (obtained from the SE spectral fitting) were used. Figure 3.9 shows the comparison between the calculated electron concentration \( N_{opt} \) and the measured free-electron concentration \( N_{Hall} \) (obtained from the Hall effect measurement) of the AZO thin films annealed at various temperatures. As shown in the figure, the values of \( N_{opt} \) are comparable with that of \( N_{Hall} \), and \( N_{opt} \) and \( N_{Hall} \) have a similar annealing-temperature dependence. It can be observed in Fig. 3.9 that the electron concentration is maximized in the annealing temperature range of 450 to 550°C (the electron concentration obtained from the Hall effect measurement is at the level of \( \sim 5 \times 10^{20} \) cm\(^{-3} \) in this annealing temperature range). The influence of annealing temperature on the electron concentration is consistent with the evolution of the dielectric function of the AZO thin films with annealing temperature as shown in Fig. 3.8, which is due to both the Burstein-Moss shift and free-electrons absorption.
It has been shown that donor-like defects such as oxygen vacancy and Zn interstitial sites can greatly influence the electron concentration [211]. As shown in Fig. 3.9, as compared to the as-deposited AZO film, the annealed films exhibit an increase of electron concentration. Thermal annealing could increase the carrier concentration in AZO thin films through the activation of Al dopant [209] or change the concentration of donor defects such as oxygen vacancies [80, 201]. Oxygen vacancy can be created more easily than other defects by annealing due to its lowest formation energy among the donor-like defects [78]. It has been also reported that annealing can generate an oxygen poor region near the film surface, leading to a significant increase of electron concentration [200, 212]. On the other hand, annealing at high temperatures could also remove oxygen vacancies or other defects, which may
explain the reduction of electron concentration with annealing temperature when the temperature is higher than \( \sim 550 \, ^\circ \text{C} \).

### 3.4.5 Influence of Annealing Temperature on Band Gap Energy

![Fig. 3.10 Average band gap energy of AZO thin films as a function of annealing temperature. The band gap energy of the as-deposited AZO thin film is also included for comparison.](image)

Figure 3.10 shows the evolution of the average band gap energy of the AZO thin films as a function of annealing temperature. As shown in the figure, as compared to the as-deposited film, the annealed films exhibit a different degree of expansion in the band gap energy. As discussed earlier, the free electron concentration is greatly influenced by the annealing temperature as a result of the activation of Al dopant and the creation/annihilation of donor-like defects in the annealed AZO films. It has been shown that electron concentration in the oxide films exceeds the Mott critical density \((10^{18} - 10^{19} \, \text{cm}^{-3} \text{ for ZnO})\), a semiconductor-to-metal transition occurs and conduction band filling with free electrons shifts the onset of band-edge \([3]\). As the concentration
reaches the order of $\sim 10^{20} \text{ cm}^{-3}$, the modification of electronic states results in a band
gap renormalization due to the mutual exchange and coulomb interactions between the
free electrons, and leads to narrowing of the band gap [76]. The band gap shift should
be considered as the net result of the above two competing effects. As shown in Fig.
3.10, the evolution of the band gap of the annealed AZO films shows a dominant BM
effect.

3.4.6 Conclusion

Influence of thermal annealing on the optical properties of AZO thin films has been
investigated. An evolution of dielectric function of the AZO thin films with annealing
temperature is observed, which is attributed to the changes in both the BM effect and
the free-electron absorption as a result of the change of free-electron concentration of
the AZO thin films. The change of the electron concentration could be attributed to the
activation of Al dopant and the change of donor-like defect concentration in the films.

3.5 Thickness Dependence of Optical Properties of Amorphous
Indium Gallium Zinc Oxide Thin Films

In this section, a study of the evolution of optical properties of amorphous indium
gallium zinc oxide (a-IGZO) thin films with film thickness is presented. The band gap
and complex dielectric function of the a-IGZO thin films with various film thicknesses
have been determined with spectroscopic ellipsometry (SE) based on the Tauc-
Lorentz-Drude (TL-Drude) model. It is observed that the complex dielectric function
is strongly dependent of the film thickness. The thicker films (thickness $> \sim 35$ nm)
exhibit both the Burstein-Moss shift and enhancement of free-electrons absorption with increasing film thickness, which are related to the increase of electron concentration in a thicker film.

### 3.5.1 Sample Preparation

IGZO thin films with various thicknesses were deposited on a HF-cleaned $p$-type Si wafer. The deposition was carried out by RF magnetron sputtering technique using a IGZO target (In:Ga:Zn mole ratio = 1:1:1). The sputtering was conducted with a RF power of 100 W at room temperature in Ar ambient (background pressure of $3 \times 10^{-3}$ Torr). The complex dielectric function of the IGZO thin films was determined with spectroscopic ellipsometry (SE) in the wavelength range of 280-1100 nm. The nominal film thicknesses of the IGZO thin films under study are 5, 11, 20, 35, 50, 60 and 100 nm, respectively. The electron concentration of the thin films was measured with the Hall effect measurement. For the ultrathin films thinner than 35 nm, the Hall effect measurement was not able to yield a reliable value of the electron concentration (which was estimated to be lower than $2 \times 10^{17}$ cm$^{-3}$); for the thin films thicker than 35 nm, the electron concentration was measured to be in the order of $\sim 10^{18}$ cm$^{-3}$.
3.5.2 Ellipsometric Modeling

Figure 3.11 shows the measured ellipsometric angles ($\Psi$ and $\Delta$) of the IGZO film with the thickness of 50 nm for three different incident angles. The SE analysis is based on the four-phase model (i.e., air/surface-roughness layer/IGZO layer/Si substrate). The surface-roughness layer is modeled with the Bruggeman effective medium approximation (EMA) [208] as a mixture of the IGZO layer and the air void, as expressed below

$$\frac{\varepsilon_{\text{IGZO}} - \varepsilon_i}{\varepsilon_{\text{IGZO}} + 2\varepsilon_i}f + \frac{\varepsilon_{\text{air}} - \varepsilon_i}{\varepsilon_{\text{air}} + 2\varepsilon_i}(1-f) = 0.$$  \hspace{1cm} (3.24)
where $\epsilon_i$ is the effective complex dielectric function of the surface-roughness layer, $f$ is the volume fraction of IGZO in the surface-roughness layer, $\epsilon_{air}$ is the dielectric constant of air void ($\epsilon_{air} = 1$ assumed in all SE analysis), and $\epsilon_{IGZO} = \epsilon_1 + i\epsilon_2$, where $\epsilon_1$ and $\epsilon_2$ are the real part and imaginary part of the complex dielectric function, respectively, is the complex dielectric function of IGZO. Here $\epsilon_{IGZO}$ is the parameter to be determined from the SE analysis. The complex dielectric function ($\epsilon_{IGZO}$) of the IGZO thin films was determined with SE spectral fitting based on the TL-Drude model. [59] It has been shown that TL-Drude model can provide an excellent spectral fitting for various metal-doped oxide thin films such as Ga-doped ZnO and Sn-doped In$_2$O$_3$. [59]

The TL-Drude model is formulated by combining the Tauc-Lorentz (TL) term [93] and Drude term. The TL term is used to model the band-to-band energy absorption, while the Drude term is used to model the free-electron absorption. The imaginary part ($\epsilon_2$) of dielectric function of the TL-Drude model is described by

$$
\epsilon_2(E) = \begin{cases} 
\frac{A_{TL}E_0C(E-E_g)^2}{(E^2-E_0^2)^2 + C^2E^2} \cdot \frac{1}{E} + \frac{A_D\Gamma_D}{E^3 + \Gamma_D^2 E}, & \text{for } E > E_g \\
\frac{A_D\Gamma_D}{E^3 + \Gamma_D^2 E}, & \text{for } E < E_g 
\end{cases}
$$

where ($A_{TL}$, $C$) and ($A_D$, $\Gamma_D$) are (oscillator strength, broadening parameters) for the TL and Drude terms, respectively. $E_0$ is the peak transition energy, and $E_g$ is the band gap energy. The real part ($\epsilon_1$) of the dielectric function of the TL-Drude model can be obtained by the Kramers-Kronig integration of $\epsilon_2$. 

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Figure 3.12 shows the complex dielectric function of the IGZO thin film with thickness of 35, 50, 60 and 100 nm. As discussed earlier, the ultrathin IGZO films (thickness $< \sim 20$ nm) has the electron concentration of lower than $\sim 2 \times 10^{17}$ cm$^{-3}$, which is far below the Mott critical density ($10^{18}$-$10^{19}$ cm$^{-3}$) to observe the BM effect. [3] Therefore, the discussion of free electron effect in IGZO thin films is mainly focused on films with thickness thicker than $\sim 35$ nm.
3.5.3 Influence of Thickness on Band Gap Energy

Figure 3.13 shows the band gap energy of the IGZO thin films yielded from the SE modelling. A significant dependence of band gap on film thickness is observed. As the electron concentration increases with the thickness and reaches the order of ~ $10^{18}$ cm$^{-3}$, the thicker film (> 35 nm) exhibits a significant expansion in band gap energy with increasing film thickness. It has been shown that when electron concentration in an oxide film exceeds the Mott critical density (e.g., $10^{18}$–$10^{19}$ cm$^{-3}$ in ZnO), a semiconductor-to-metal transition occurs, and filling of the conduction band with free electrons leads to a band gap expansion as a result of the BM effect [213]. As shown in Fig. 3.13, a significant increase of the band gap energy is observed for the IGZO thin films thicker than ~35 nm. The increase of the band gap energy with increasing film thickness can be explained by the BM effect as a result of a higher electron concentration in a thicker IGZO film. In other words, for the thicker films, the BM effect is dominant. The explanation of the band gap expansion by the BM effect is
consistent with the large increase of the plasma energy with film thickness as discussed below.

### 3.5.4 Influence of Thickness on Free Electrons Concentration

![Graph showing the plasma energy (E_p) as a function of film thickness.](image)

Fig. 3.14 Plasma energy ($E_p$) of the IGZO thin films as a function of the film thickness.

As indicated by Eq. (3.25), the value of the parameter $A_D$ of the Drude term for free electrons can be obtained from the SE modeling. In the Drude theory, $A_D$ is expressed by [59]

$$A_D = \varepsilon_\infty E_p^2$$

(3.26)

where $\varepsilon_\infty$ is the high frequency dielectric constant and $E_p$ is the plasma energy. The plasma energy can be calculated with Eq. (3.26) by using $\varepsilon_\infty = 1$ and the $A_D$ values yielded from the SE fittings. Figure 3.14 shows the plasma energy ($E_p$) of the IGZO thin films yielded from the SE modeling as a function of film thickness. As can be observed in the figure, the plasma energy increases with increasing film thickness. The
increase of $E_p$ indicates an increase of free-electron concentration in the IGZO films as $E_p$ is proportional to $\sqrt{N_f}$ where $N_f$ is the free-electron concentration [59]. The large dependence of carrier concentration on film thickness could be attributed to the improvement of polycrystalline grain structures with increasing film thickness [214-216]. A large increase of electron concentration could significantly influence the band-to-band absorption in the film. As the concentration reaches the order of $\sim 10^{20} \text{ cm}^{-3}$, the modification of electronic states results in a band gap renormalization due to the mutual exchange and coulomb interactions between the free electrons, and leads to narrowing of the band gap [76]. As shown in Fig. 3.14, the plasma energy ($E_p$) of the IGZO thin film with the thickness of 100 nm is $\sim 1.11 \text{ eV}$, which is much larger than the value (0.82 eV) of the 50 thin film, showing a large increase of the electron concentration. However, the 100 nm film does not exhibit a large increase in the band gap energy as compared to the 50 nm film, as shown in Fig. 3.13. This indicates that in the thicker thin films with a high electron concentration, the band gap change should be considered as the net result of the competition between the BM shift and the band gap renormalization.
Fig. 3.15 Imaginary part ($\varepsilon_2$) of the complex dielectric function of the IGZO thin films calculated with Eq. (3.25) in the energy range of 0.5-1.5 eV where the free-electron absorption is significant. The arrow indicates the increase of film thickness.

Figure 3.15 shows the imaginary part ($\varepsilon_2$) of the complex dielectric function of the IGZO thin films calculated with Eq. (3.25) in the energy range of 0.5-1.5 eV where the free-electron absorption is significant. It is observed in the figure that $\varepsilon_2$ increases with film thickness. This indicates an increase of free-electron absorption in a thicker film due to the increase of electron concentration, which agrees with the increase of $E_p$ with film thickness.

3.5.4 Conclusion

The complex dielectric function and band gap energy of amorphous indium gallium zinc oxide thin films (a-IGZO) with various thicknesses have been determined with spectroscopic ellipsometry based on the Tauc-Lorentz-Drude model. Evolution of both the dielectric function and band gap with film with thickness thicker than ~ 35 nm has
been observed, which is explained as the result of the free-electron effect (i.e., the Burstein-Moss shift and free-electron absorption).

3.6 Summary

In this chapter, the effect of free electrons on optical properties of Al-doped ZnO (AZO) and amorphous indium gallium zinc oxide (a-IGZO) has been investigated with absorption spectroscopy and spectroscopic ellipsometry based on various optical dispersion models. The comparison study between the undoped ZnO and AZO thin films shows that the high concentration of free electrons could greatly suppress the excitonic absorption near the band edge as a result of the free electrons screening effect. The abundant free electrons in the oxide films also result in an expansion of band gap due to the Burstein-Moss (BM) effect. The study of the annealing effect on AZO thin films shows that the annealing temperature could greatly change the film electron concentration. As compared to the as-deposited AZO films, the annealed AZO films exhibit both the Burstein-Moss shift and free-electrons effect. The change in the electron concentration can be attributed to the change of the donor-like defect concentration in the oxide films as a result of annealing. The study of the optical properties of a-IGZO thin films with film thickness shows that the electron concentration has a strong dependence on the film thickness. The large dependence of carrier concentration on film thickness could be attributed to the improvement of polycrystalline grain structures with increasing film thickness. The evolution of both
the dielectric function and band gap with film with thickness is explained as the free-electron effect (i.e., the Burstein-Moss shift and free-electron absorption).
Chapter 4 Quantum Confinement Effect in Ultrathin Metal Oxide Films

4.1 Introduction

When metal oxide films and associated devices are scaled down to nanoscale regime, due to the quantum confinement effect, the nanoscale structures exhibit some unique properties different from their bulk counterparts. The size dependence, which provides us the possibility to tune the material properties, is of great interest to be studied. In section 3.3, it has been shown that the band gap and exciton binding energies of undoped ZnO and Al-doped ZnO films increase with decreasing grain size, as shown in Fig. 3.5 and Fig. 3.6 respectively. [217] The expansion of band gap and exciton binding energies could be attributed to the quantum confinement effect in a small grain size. On the other hand, it was reported that quantum confinement effect has a significant influence on the dielectric functions of the Si and Ge nanocrystals embedded in a SiO$_2$ matrix, e.g. the magnitude of the dielectric functions is reduced with decreasing nanocrystal size. [218, 219] Therefore, it would be interesting to examine the film-thickness dependence of the complex dielectric function of the ultrathin metal oxide films as quantum confinement effect could play an important role in such system. In this chapter, investigations of quantum confinement effect on optical properties of ZnO and amorphous indium gallium zinc oxide (a-IGZO) are conducted.
4.2 Effect of Quantum Confinement on Optical Properties of Ultrathin ZnO Films

In this section, the complex dielectric function of ultrathin ZnO films as a function of the film thickness has been investigated with spectroscopic ellipsometry (SE). It is observed that the complex dielectric function is strongly dependent of the film thickness, e.g., the magnitudes of both real and imaginary parts of the complex dielectric function decrease with decreasing film thickness and are significantly smaller than that of bulk ZnO. It is shown that the phenomenon can be attributed to the quantum confinement effect on both the band gap and exciton binding energies of the ZnO thin films.

4.2.1 Sample Preparation

ZnO thin films with various thicknesses were deposited onto a 30 nm SiO$_2$ buffer layer which was thermally grown on a HF-cleaned $p$-type Si wafer by dry oxidation. The oxide buffer layer was used to minimize the substrate-induced stress effect [48] and provide a film configuration (ZnO/SiO$_2$) that is similar to the one (ZnO thin film/quartz substrate) used in the optical absorbance measurement. The ZnO deposition was carried out by RF magnetron sputtering using a pure ZnO target (99.99% in purity). The sputtering was conducted with a RF power of 80 W at room temperature in argon ambient with a background pressure of $9 \times 10^{-3}$ Torr (the base pressure was $7 \times 10^{-6}$ Torr). The pure argon environment was to ensure that the influence of oxygen on the structural and optical properties of the deposited films is minimized. [203]
crystalline structure and surface morphology of the ZnO thin films were investigated by X-ray diffraction (XRD) and scanning electron microscope (SEM), respectively. The average grain sizes of the ZnO thin films estimated from the XRD measurement are comparable with that from the SEM measurement; and both measurements indicate that the average grain size increases with increasing film thickness. Spectroscopic ellipsometric (SE) measurement was carried out with an ellipsometer in the wavelength range of 250-1100 nm with a step size of 5 nm at the three incident angles of 65°, 70° and 75°, respectively. The thickness values obtained from the SE fittings for the various films are very close to the nominal values of 10, 20, 40, 90, and 185 nm, respectively. Optical absorbance measurement was carried out with an UV-Vis spectrophotometer on the samples of ZnO thin films deposited on quartz substrate in the wavelength range of 250-800 nm.
4.2.2 Ellipsometric Modeling

Fig. 4.1 SE spectral fittings of the 10 nm (a) and 40 nm (b) ZnO thin films deposited on the SiO2 buffer layer for three different incident angles. SEM images of the thin films are shown in the figure. The five-phase model used in the SE modeling is shown in the inset of (a) also.

The SE analysis is based on the five-phase model (i.e., air/surface-roughness layer/ZnO layer/SiO2 buffer layer/Si substrate) shown in the inset of Fig. 4.1(a). The surface-roughness layer is modeled with an effective layer consisting of air voids and ZnO based on the Bruggeman effective medium approximation (EMA) [208]

\[
\frac{\varepsilon_{\text{ZnO}} - \varepsilon_i}{\varepsilon_{\text{ZnO}} + 2\varepsilon_i} f + \frac{\varepsilon_{\text{air}} - \varepsilon_i}{\varepsilon_{\text{air}} + 2\varepsilon_i} (1 - f) = 0. \tag{4.1}
\]

where \(\varepsilon_i\) is the effective complex dielectric function of the surface-roughness layer, \(f\) is the volume fraction of ZnO in the surface-roughness layer, \(\varepsilon_{\text{air}}\) is the dielectric
constant of air void \( \varepsilon_{air} = 1 \) assumed in all SE analysis), and \( \varepsilon_{ZnO} = \varepsilon_1 + i \varepsilon_2 \), where \( \varepsilon_1 \) and \( \varepsilon_2 \) are the real part and imaginary part of the complex dielectric function) is the complex dielectric function of ZnO. Here \( \varepsilon_{ZnO} \) is the parameter to be determined from the SE analysis. Detail of the modeling and determination of \( \varepsilon_{ZnO} \) is discussed below.

Dielectric function of bulk ZnO films has been intensively studied based on various models such as the Forouhi-Bloomer (F-B) model [51], the Tauc-Lorentz (T-L) model [59] and Holden’s model [60, 61]. It has been known that the presence of excitons near the band edge significantly influences the dielectric function in the energy range. [220] The formation of excitons are attributed to the three valence bands of wurtzite ZnO, labeled in order of the valence bands as “A”, “B”, and “C”. The three excitons usually merge into a broadened peak at room temperature due to the broadening caused by the exciton-phonon interactions.[206] In this work, the dielectric function of the ZnO thin films is determined based on the model proposed by Yoshikawa and Adachi [65]

\[
\varepsilon(E) = \varepsilon_\infty + \varepsilon_{int}(E) + \varepsilon_d(E) + \varepsilon_c(E). 
\] (4.2)

where \( \varepsilon_\infty \) is the high frequency dielectric constant, \( \varepsilon_{int}(E) \) is the complex dielectric function due to the interband absorption, and \( \varepsilon_d(E) \) and \( \varepsilon_c(E) \) are the complex dielectric function due to the discrete and continuum excitonic absorptions, respectively. \( \varepsilon_{int}(E) \) is modeled with a simplified critical point model at \( E_0 \) transition due to the three valence bands A, B, C, described by Eq. (3.20). \( \varepsilon_d(E) \) is modeled with a broadened Lorentzian line shape and described by Eq. (3.16). \( \varepsilon_c(E) \) is described by Eq. (3.17).
The ellipsometric angles ($\Psi$ and $\Delta$) are functions of wavelength, thicknesses $d_s$, $d_{ZnO}$ and $d_{SiO_2}$ of the surface-roughness layer, ZnO layer and SiO$_2$ buffer layer, respectively, volume fraction $f$ of ZnO in the surface-roughness layer, and dielectric functions of SiO$_2$, bulk Si and ZnO thin films. In the calculations of $\Psi$ and $\Delta$, the complex dielectric functions of both SiO$_2$ and bulk Si from Ref. [221] were used; and Eq. (4.2) was used to calculate the complex dielectric function of the ZnO thin films. As there were large fluctuations in the experimental data for wavelengths shorter than 285 nm due to the high noise level in short wavelengths, the spectral fitting was carried out in the wavelength range of 285-1100 nm by freely varying the fitting parameters to minimize the mean-squared-error of the comparison between the calculated and experimentally measured $\Psi$ and $\Delta$. Excellent fittings with goodness of fit $\chi^2 < 20$ were achieved for all the film thicknesses. As examples, Figure 4.1 shows the SE spectral fittings of the ZnO thin films with the thicknesses of 10 and 40 nm. By using the values of the parameters yielded from the spectral fittings in the wavelength range of 285-1100 nm, we calculated the real part ($\varepsilon_1$) and imaginary part ($\varepsilon_2$) of the complex dielectric function of the ZnO films with Eq. (4.2) in the extended photon energy range of ~ 1.1 - ~ 5 eV (i.e., the wavelength range of 250 nm – 1100 nm). The calculated $\varepsilon_1$ and $\varepsilon_2$ of the ZnO thin films with various thicknesses are shown in Fig. 4.2. With the $\varepsilon_1$ and $\varepsilon_2$ values, we were also able to calculate the absorption coefficient $\alpha$ [77] of the ZnO thin films in the photon energy range of ~ 1.1 - ~ 5 eV. Figure 4.3 shows the comparison between the calculated and measured $\alpha$ for the ZnO thin film with the thickness of ~ 20 nm. Note that the
normalized value of the absorption coefficient instead of the absolute value is used in the figure. This is to eliminate the effect of some difference in the film thickness between the sample used in the SE analysis and the one used in the absorbance measurement. As can be observed in the figure, the calculation generally agrees well with the experimental result (note that there is a small departure for photon energies lower than ~ 3 eV, which could be due to the fact that defect absorption is not included in the modeling). This indicates that the models used in the SE analysis are accurate and the above approach is reliable.

Fig. 4.2 (a) Real part (\( \varepsilon_1 \)) and (b) imaginary part (\( \varepsilon_2 \)) of the complex dielectric function of the ZnO thin films with various thicknesses obtained from the spectral fittings. The bulk value (Ref. 65) is included for comparison.
4.2.3 Influence of Grain Size on Band Gap Energy and Exciton Binding Energy

As can be observed in Fig. 4.2, the film thickness has a significant impact on the dielectric function of ZnO thin films. As compared to the bulk counterpart [65], the ultrathin ZnO films exhibit a significant reduction in the magnitudes of both real and imaginary parts of the complex dielectric function, which can be attributed to the quantum confinement effect. The quantum confinement effect could be mainly related to the small sizes (a few nanometers) of the grains in ZnO thin films. The reduction is found more significant in a thinner film due to the stronger confinement in a smaller grain, e.g., as compared to bulk ZnO, the ZnO thin film with the thickness of 20 nm (average grain size $D = 6.8$ nm) shows a significant reduction of $\sim 26\%$ and $\sim 37\%$ in the real and imaginary parts of the complex dielectric function at the photon energy of 3.3 eV, respectively; while the ZnO thin film with the thickness of 90 nm (average
grain size $D = 15.5$ nm) only shows a reduction of $\sim 16\%$ and $\sim 29\%$, respectively. The peaks also show a small blue shift with reduction in the film thickness.

\[ \text{Fig. 4.4 a) Exciton binding energies and b) band gap energy of the ZnO thin films obtained from the SE analysis as a function of the average grain size $D$ ($D$ is determined from the SEM images). The insets show the same size dependence of exciton binding energies and band gap energy of the ZnO thin film obtained from an absorption study (Ref. 217). The trend lines of the size dependence are for guiding the eyes only.} \]

Figure 4.4 shows the exciton binding energies and band gap energy of the ZnO thin films obtained from the SE spectral fittings as a function of average grain size. As shown in the figure, a strong quantum size effect can be observed. Both the exciton binding energies and band gap energy increase with decreasing grain size. Band gap expansion due to quantum confinement is a well-known phenomenon. [207, 219] The increase in exciton binding energies is due to the confinement of electron-hole wave function in the small dimensions.[222] The confinement enhances the coulombic interaction of an exciton, giving rise to an increase in the exciton binding energy.[147]
Chapter 4 Quantum Confinement Effect in Ultrathin Metal Oxide Films

As shown in Figs. 4.4(a) and 4.4(b), the size dependence of average exciton binding energies and band gap energy could be roughly described by the trend lines of $R_{AV} (meV) = 60 + 926 / D(nm)^{1.62}$ and $E_g (eV) = 3.46 + 3.23 / D(nm)^{1.65}$, respectively. These results are consistent with our previous absorption study [217] which is shown in the insets of Fig. 4.4. On the other hand, it is also worthy to point out that in addition to the confinement in the nanocrystals, one-dimension confinement (i.e., the confinement in the thickness direction) in a continuous thin film may also play a role.

4.2.4 Effect of Quantum Confinement on Dielectric Function

Fig. 4.5 Contributions of the interband absorption ($\varepsilon_{int,imag}$) (a), discrete-exciton absorption ($\varepsilon_{d,imag}$) (b) and continuum-exciton absorption ($\varepsilon_{c,imag}$) (c) to the imaginary part ($\varepsilon_2$) of the complex dielectric function of the ZnO thin films with the thicknesses of 20 and 90 nm. The bulk values (Ref. 65) are included for comparison.
In a confined nanostructure, the reduction of optical constant or dielectric function is typically associated with the band gap opening. [134] In a classic description, the reduction of dielectric function could be explained by the reduction of electron polarization induced by the distortion of electrons in the atoms as the result of the band gap expansion; while quantum mechanically, it could be explained by the increase of the band gap energy, which makes it more difficult for electrons to transit from the valance band to the conduction band. Figure 4.5 shows the contributions of the interband absorption ($\varepsilon_{int,imag}$), discrete-exciton absorption ($\varepsilon_{d,imag}$) and continuum-exciton absorption ($\varepsilon_{c,imag}$) to the imaginary part ($\varepsilon_2$) of the complex dielectric functions of the ZnO thin films with the thicknesses of 20 and 90 nm. The corresponding counterparts of bulk ZnO [65] are also included for comparison. As can be observed in the figure, all the absorptions ($\varepsilon_{int,imag}$, $\varepsilon_{d,imag}$ and $\varepsilon_{c,imag}$) exhibit a film-thickness dependence, i.e., they are smaller and show a blue shift for a thinner film, which is responsible for the film-thickness dependence of dielectric function shown in Fig. 4.2. It is noticed from Fig. 4.5 that $\varepsilon_{int,imag}$ and $\varepsilon_{c,imag}$ have a more significant film-thickness dependence than $\varepsilon_{d,imag}$. It has been known that the continuum excitonic absorption will become proportional to $(E - E_g)^{1/2}$ when $E >> E_g$, in the form similar to the interband absorption above the $E_g$. [63] Therefore, for a thinner ZnO film, with the band gap expansion as a result of quantum confinement effect, both the interband absorption ($\varepsilon_{int,imag}$) and continuum-exciton absorption ($\varepsilon_{c,imag}$) decrease. It can be also understood that increase in the transition energy makes the transition more difficult resulting in reduction in the polarizability. It
can be concluded that the reduction in \( \varepsilon_2 \) is mainly due to the reduction in both the interband absorption \( (\varepsilon_{\text{int,imag}}) \) and continuum-exciton absorption \( (\varepsilon_{\text{c,imag}}) \). For the contribution of the discrete-exciton absorption \( (\varepsilon_{\text{d,imag}}) \), the situation is more complicated. As shown in Fig. 4.5(b), as compared to the bulk counterpart, both the 20 and 90 nm ZnO thin films exhibit a reduction in the oscillator strength of the discrete-exciton absorption. However, the reduction of the 20 nm sample is not more significant than that of the 90 nm sample. This is because increase in the exciton binding energy (see Fig. 4.4(a)) due to quantum confinement effect results in stabilization of the exciton. [146]

4.2.5 Conclusion

The complex dielectric function, band gap energy and exciton binding energies of ultrathin ZnO films deposited by RF magnetron sputtering have been obtained from the SE analysis based on the Yoshikawa and Adachi’s model. As compared to bulk ZnO, the ultrathin films exhibit a significant reduction in both real and imaginary parts of the dielectric function, accompanied by the increase in both band gap energy and exciton binding energies. The reduction in the complex dielectric function is mainly attributed to the reduction in the interband absorption and continuum-exciton absorption due to the band gap expansion induced by the quantum confinement effect; while discrete-exciton absorption is not significantly reduced due to the increase in the exciton binding energy, which is also the consequence of the confinement effect.


4.3 Effect of One-dimensional Quantum Confinement on Optical Properties of Amorphous Indium Gallium Zinc Oxide Thin Films

In section 3.5, we examined the free electrons effect on the dielectric function of the amorphous indium gallium zinc oxide (a-IGZO) films with thickness thicker than ~ 35 nm. In this section, a study of the evolution of optical properties of a-IGZO thin films with film thickness thinner than ~ 20 nm is presented. The band gap and complex dielectric function of the IGZO thin films have been observed strongly dependent of film thickness. The ultrathin films (thickness < ~ 20 nm) show a blue shift of both the real and imaginary parts of the complex dielectric function and an expansion of band gap with decreasing film thickness due to the quantum confinement effect.

4.3.1 Sample Preparation and Ellipsometric Modeling

IGZO thin films with various thicknesses of 5, 11 and 20 nm were deposited on a HF-cleaned p-type Si wafer. Details of the sample preparation have been reported in section 3.5.1. The complex dielectric function and film thickness of the IGZO thin films was determined with spectroscopic ellipsometry (SE) based on the Tauc-Lorentz-Drude (TL-Drude) model [59] in the wavelength range of 280-1100 nm. Details of the SE modeling have been discussed in section 3.5.2. Figure 4.6 shows the measured ellipsometric angles (\( \Psi \) and \( \Delta \)) of the IGZO film with the thickness of 20 nm for three different incident angles. Figure 4.7 shows the AFM image of the a-IGZO film with thickness of 5 nm.
Fig. 4.6 SE spectral fitting of the 20 nm IGZO thin film based on the TL-Drude model for the angles of incidence of $65^\circ$, $70^\circ$ and $75^\circ$.

Fig. 4.7 AFM image of the a-IGZO thin film with thickness of 5 nm.
4.3.2 Influence of Thickness on Dielectric Function

Figure 4.8 Real part ($\varepsilon_1$) and imaginary part ($\varepsilon_2$) of the complex dielectric function of the IGZO thin films with thicknesses of 5, 11, and 20 nm. The arrow indicates the increase of film thickness.

Figure 4.8 shows the complex dielectric function of the IGZO thin films with thicknesses of 5, 11, and 20 nm. As shown in the figure, the film thickness has a significant impact on the dielectric function of the IGZO thin films. It has been reported that when the thickness of ZnO and Ge thin films scales down to 20 nm, the ultrathin films exhibit an expansion of band gap and a reduction of dielectric function due to the quantum confinement effect. [223, 224] As shown in Fig. 4.8 for the IGZO thin films thinner than ~ 20 nm, the ultrathin films exhibit a blue shift in both real and imaginary parts of dielectric function with decreasing film thickness. The blue shift
indicates an expansion of band gap, which can be attributed to the quantum confinement effect [5]. As discussed earlier, the ultrathin IGZO films (thickness < ~20 nm) has the electron concentration of lower than \(\sim 2 \times 10^{17} \text{cm}^{-3}\), which is far below the Mott critical density (\(10^{18}-10^{19} \text{cm}^{-3}\)) to observe the BM effect [3]. Therefore, the observed blue shift of dielectric function shown in Fig. 4.8 is mainly attributed to the quantum confinement effect, which leads to a band gap opening. Unlike the nanocrystalline ZnO thin film where the electrons are confined in a three dimensional environment (e.g., nanocrystalline grain size) [224], ultrathin amorphous IGZO films could exhibit the confinement of electrons along the thickness direction (i.e., the one-dimensional quantum confinement (ODQC) effect). It has been shown that thickness dependence of band gaps of ultrathin amorphous materials can be described by the ODQC effect [223, 225].

### 4.3.3 Influence of Thickness on Band Gap Energy

![Fig. 4.9 Band gap energy of ultrathin IGZO films as a function of film thickness.](image)
Figure 4.9 shows the band gap energy of the ultrathin IGZO films yielded from the SE modelling with goodness of fit $\chi^2 < 20$. A significant dependence of band gap on film thickness is observed. As shown in the figure, the ultrathin films ($< \sim 20$ nm) exhibit an expansion of band gap energy with decreasing film thickness, which can be mainly attributed to the ODQC effect in the ultrathin amorphous IGZO films.

4.3.4 Conclusion

The complex dielectric function and band gap energy of amorphous indium gallium zinc oxide thin films with various thicknesses have been determined with spectroscopic ellipsometry based on the Tauc-Lorentz-Drude model. The ultrathin films with thickness thinner than $\sim 20$ nm exhibit a blue shift of dielectric function and an expansion of band gap, which is explained in term of the one-dimensional quantum confinement effect.

4.4 Summary

In this chapter, the effect of quantum confinement on optical properties of ZnO and amorphous indium gallium zinc oxide (a-IGZO) thin films has been investigated with spectroscopic ellipsometry (SE). The ultrathin ZnO films exhibit a significant reduction in both real and imaginary parts of the dielectric function and an increase in both band gap energy and exciton binding energies. The evolution of the dielectric function of the ZnO thin films with film thickness can be attributed to the quantum confinement effect on the band gap and exciton binding energies. On the other hand, the ultrathin a-IGZO films exhibit a blue shift of both the real and imaginary parts of
the complex dielectric function and an expansion of band gap due to quantum confinement effect. Unlike the nanocrystalline ZnO thin film where the electrons are confined in a three dimensional environment (e.g., nanocrystalline grain size), ultrathin a-IGZO films exhibit the confinement of electrons along the thickness direction (i.e., the one-dimensional quantum confinement (ODQC) effect).
Chapter 5 Localized Surface Plasmon Resonance and Quantum Confinement Effect in Ultrathin Au Films

5.1 Introduction

Metallic nanoparticles such as gold and silver nanoparticles exhibit remarkable visible-absorption peak which is absent in their bulk counterpart. This characteristic absorption peak is related to the collective oscillation of conduction electrons inside the nanoparticles, known as localized surface plasmon resonance (LSPR). LSPR is strongly dependent of the nanoparticle size, shape, inter-particle spacing and surrounding medium. [4, 56] Therefore, LSPR is very useful for sensing and spectroscopy applications. [113, 226, 227] It has been shown that structural geometry of individual particles and the aggregate topology have significantly impact on the optical response of nanoparticles, in particular, the surface plasmon resonance. [124, 228] For example, red-shift of LSPR due to the inhomogeneous polarization of nanoparticles [229, 230], and splitting of LSPR due to the near-field coupling between neighboring nanoparticles. [231, 232] On the other hand, it has been reported that for metallic nanoparticles with small size (e.g. < 10 nm) the quantum confinement effect could be significant, [233] e.g., a dominant interband absorption over plasmon resonance may occur with decreasing particle size. [234] Self-assembled metal nanoparticles could be formed in an ultrathin metal film. The size, shape and inter-particles spacing of the nanoparticles are dependent of the film thickness. In addition, both the formation of conductive percolation paths between the neighboring
nanoparticles and the aggregation of nanoparticles, which could delocalize the free electrons inside the nanoparticles, are also dependent of the film thickness. Therefore, it would be interesting to examine the influence of the film thickness on the LSPR and the electron confinement effect in ultrathin noble metal films. In this chapter, investigations of LSPR and quantum confinement effect on optical properties of ultrathin Au films are presented.

5.2 Effect of Aggregation on Dielectric Function of Ultrathin Au Films

In this section, a systematic study of aggregation effect on the dielectric function of ultrathin Au films consisting of self-assembled gold nanoparticles (Au NPs) on SiO2 is presented. It has been observed that Au NPs aggregate into large-scale coalescence with increasing film thickness, and inter-links between the particles are gradually formed. A continuous film is observed with the film thickness of 10 nm; and discontinuous Au NP thin films are formed for the films thinner than ~ 10 nm. Size dependence of the optical properties (complex dielectric function $\varepsilon_n$, refractive index $n$ and extinction coefficient $k$) of Au NPs has been studied. The result shows that the aggregation effect has a significant influence on the LSPR and Drude (free electrons) absorption of the Au NP films.

5.2.1 Sample Preparation

A $p$-type silicon wafer was first cleaned by diluted HF solution to remove the native oxide. Subsequently, a 30 nm SiO2 buffer layer was grown on the silicon substrate by dry oxidation. Au films with nominal thicknesses of 4, 5, 6, 8, 10 nm were deposited
on the SiO₂ layer or a quartz substrate by electron beam evaporation in the pressure of
4×10⁻⁶ mbar. The deposition rate was maintained at 0.1 Å per second. The oxide
buffer layer was used to prevent the silicidation reaction between the deposited Au
films and the Si substrate and provide a film structure configuration (Au NP film / SiO₂ layer) that is similar to the one (Au NP film / quartz substrate) used in the optical
absorbance measurement. The film surface morphology was investigated using high
resolution scanning electron microscope (HRSEM). Optical absorbance measurement
was carried out with an UV-Vis spectrophotometer on the samples of Au NP films
deposited on quartz substrate in the wavelength range of 250-2500 nm. The quartz
substrate is used as the reference baseline for all the absorbance measurement.
Complex dielectric function of the Au NPs was obtained with spectroscopic
ellipsometry (SE) on the samples of Au NP films deposited on the SiO₂ layer in the
wavelength range of 250-1200 nm.

Fig. 5.1 HRSEM images of the ultrathin Au films with the nominal thicknesses of 4-8
nm on the SiO₂ layer.
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Figure 5.1 shows the HRSEM images of the Au NP films with the film thicknesses of 4, 5, 6 and 8 nm, respectively. As shown in the figure, the Au films with the thicknesses of 4, 5 and 6 nm exhibit a large-scale coalescence of Au NPs and a high surface coverage on SiO₂. The average size and irregularity of the Au NPs increase with increasing film thickness. The formation of non-spherical particles (worm-like particles shown in Fig. 5.1) is the direct evidence of aggregation of Au NPs on the SiO₂ layer due to touching and merging of adjacent particles. The formation of inter-links between the coalescences of Au NPs is greatly enhanced as the film continues growing, and a continuous film is eventually formed as the film thickness reaches ~ 10 nm.

5.2.3 Absorbance Measurement

![Absorbance spectra](image)

Fig. 5.2 Absorbance spectra of the ultrathin Au films with various thicknesses on quartz substrate.

Figure 5.2 shows the absorbance spectra of the ultrathin Au films with various thicknesses on quartz substrate in the photon energy range of 0.5-5 eV at room...
temperature. The influence of the film thickness on the absorbance spectrum is evident in the figure. A difference in the film thickness means a difference in the degree of aggregation, which can be translated to the differences in the particle size, shape and interparticle distance. Unlike the bulk Au where the Drude absorption (free-electrons) dominates in the infrared, metal nanoparticle film exhibits LSPR in the visible region. As shown in Fig. 5.2, the aggregation effect is obvious in the region with photon energies lower than ~2.5 eV where the Drude absorption and the LSPR occur. As the film thickness decreases, the Drude absorption is reduced, while the LSPR is enhanced. A LSPR band can be observed for the films thinner than 8 nm. The enhancement of the plasmon resonance is associated with the reduction of Drude absorption as a result of the decrease of aggregation of Au NPs in a thinner film. In a thicker film, the formation of inter-links (conductive percolation paths) between the Au NPs due to the aggregation of Au NPs can delocalize the free electrons inside the particles, the concentration of free electrons is higher, and thus the Drude absorption is more significant. However, the aggregation will suppress the LSPR of the Au NPs. On the other hand, a red-shift of the LSPR with increasing film thickness is observed. The phenomenon can be attributed to the inhomogeneous polarization of the nanoparticles with larger sizes, which enhances the higher-order-mode oscillations at lower energies.

[229] Note that the red shift of LSPR of the 6 nm film relative to the 5 nm film is difficult to observe in Fig. 5.2 due to the overlap of the Drude absorption and the LSPR band as result of the significant aggregation of Au NPs in a thicker film (> 4 nm) (however, it could be revealed by a curve fitting program).
5.2.2 Ellipsometric Modeling

To quantitatively understand the contributions of the LSPR and Drude band to the optical response of the aggregated nanoparticles film, the complex dielectric function of the aggregated Au NPs were determined with the spectroscopic ellipsometry (SE). The ellipsometric angles (Ψ and Δ) were measured on the samples of Au NP thin films on the SiO2 layer in the wavelength range of 250-1200 nm with a step size of 5 nm at an incident angle of 75°. The Au NP thin film system can be treated as a quasi-homogeneous effective-medium material, which can be described with an effective medium approximation (EMA). Maxwell-Garnett (MG) EMA [235] and Bruggeman EMA [208] are the common approaches to describe the dielectric properties of particles embedded in a dielectric host matrix. However, both MG and Bruggeman EMAs are valid only for a low particle volume fraction and fail to describe particle-particle interactions in the scenario of a high volume fraction. Cohen et al [236] has proposed a generalized EMA, which has the form [236]

\[
\frac{\varepsilon_c - \varepsilon_m}{(\varepsilon_c - \varepsilon_m)\hat{L} + \varepsilon_m} = (1-Q) \frac{\varepsilon_i - \varepsilon_m}{(\varepsilon_i - \varepsilon_m)\hat{L} + \varepsilon_m}.
\]

(5.1)

where \(\varepsilon_c\) is the effective complex dielectric function of the Au NP film, \(\varepsilon_m\) is the complex dielectric function of Au NPs, \(\varepsilon_i\) is the complex dielectric function of the surrounding dielectric material (here it is air), and \(\hat{L}\) is the effective depolarization factor of the surrounding dielectric material, \(Q\) is the filling factor of Au NPs. The effective depolarization factor \(\hat{L}\) here can be interpreted as the quantity that describes the lateral interactions in the Au NP/dielectric system. [236, 237]
In the dielectric function of the aggregated Au NPs, the free electrons absorption can be described by the Drude dispersion function, and both the LSPR peaks and interband transitions can be represented with a Lorentz dispersion function, as given below [62]

\[
\varepsilon_\omega(E) = (1 - \frac{f_0 E_p^2}{E^2 + i\Gamma_0 E}) + \sum_{j=1}^{i} \frac{f_j E_j^2}{E_j^2 - E^2 - i\Gamma_j E} \tag{5.2}
\]

where \((f_0, \Gamma_0)\) and \((f_j, \Gamma_j)\) are (oscillator strength, broadening parameter) for the Drude and Lorentz dispersion functions, respectively. \(E_p\) is the plasma energy, \(E_j\) is the resonance energy. As shown in Fig. 5.2, there are two broaden absorption peak observed at \(~3.05\) eV and \(~4.32\) eV, which can be attributed to the interband transitions from \(d\)-valance band to the empty states in the \(s\) and \(p\) bands above the Fermi level. [238, 239] It is observed in the figure that the interband transitions are not largely affected by the structural properties of the nanoparticles. In order to simplify the optimization process during the SE spectral fitting, the two interband transitions of the aggregated Au NPs are modeled with two Lorentz dispersion functions with the resonance energies fixed at 3.05 and 4.32 eV, respectively.
Chapter 5 Localized Surface Plasmon Resonance and Quantum Confinement Effect in Ultrathin Au Films

Fig. 5.3 SE spectral fittings of the Au NP films with the film thicknesses of 4-8 nm on the SiO2 layer that is thermally grown on a silicon substrate. The ellipsometric angles $\Psi$ and $\Delta$ are measured at the incident angle of $75^\circ$.

Figure 5.3 shows the SE spectral fittings of the measured ellipsometric angles $(\Psi, \Delta)$ for the Au NP films with the film thicknesses of 4-8 nm using Eqs. (5.1) and (5.2) and based on the four-phase model (i.e., air/Au NP film/SiO2/Si). In the calculation of $\Psi$ and $\Delta$, the complex dielectric functions of SiO2 and bulk Si from [221] were used. The effective dielectric function of the Au NP films is calculated with Eq. (5.1) under the assumption that air void ($\varepsilon_i = 1$) is embedded in the Au NP films with the Au NPs as the host material. The filling factor $(Q)$ of the Au NPs in the Au NP films on SiO2 estimated from the SEM images are $\sim 76\%$, $83\%$, $85\%$, and $90\%$ for the Au NP films with the film thicknesses of 4, 5, 6, and 8 nm, respectively. The measured ellipsometric data $(\Psi, \Delta)$ were fitted in the wavelength range of 280-1200 nm by minimizing the mean-squared-error of the difference between the calculated and experimentally measured $\Psi$ and $\Delta$. [57] As shown in Fig. 5.3, the calculated $\Psi$
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and $\Delta$ yielded from the best spectral fittings show good agreement with the measured data ($\Psi$ and $\Delta$) in the wavelength range of 400-1200 nm. Figures 5.4(a) and 5.4(b) show the real ($\varepsilon_{r,1}$) and imaginary ($\varepsilon_{r,2}$) parts of the complex dielectric function of the Au NPs of the Au NP films with various film thicknesses yielded from the SE spectral fittings, respectively. The real ($\varepsilon_{e,1}$) and imaginary ($\varepsilon_{e,2}$) parts of the effective complex dielectric function calculated with Eq. 5.1 for the Au NP films with the film thicknesses of 4-8 nm are shown in Figs. 5.4(c) and 5.4(d), respectively.

Fig. 5.4 (a) Real part ($\varepsilon_{r,1}$) and (b) imaginary part ($\varepsilon_{r,2}$) of the complex dielectric function of the Au NPs of the Au NP films with the film thicknesses of 4-8 nm. The complex dielectric functions of the continuous Au film with the thickness of 10 nm and the bulk Au (Ref. 62) are included in the two figures for comparison. (c) The real part ($\varepsilon_{e,1}$) and (d) imaginary part ($\varepsilon_{e,2}$) of the effective complex dielectric function of the Au NP films with the film thicknesses of 4-8 nm.
5.2.3 Effect of Aggregation on Optical Constants

Figures 5.5(a) and 5.5(b) show the refraction index ($n$) and extinction coefficient ($k$) of the Au NPs of the Au NP films, which are obtained from the calculation using the complex dielectric function of the Au NPs shown in Figs. 5.4(a) and 5.4(b). The optical constants of the continuous Au film with the thickness of 10 nm and the bulk Au are also included in Fig. 5.5 for comparison. It can be observed from the figure that the optical constants ($n$, $k$) of the Au NPs become more similar to that of bulk Au as the film thickness increases, as a result of aggregation of the Au NPs into large-scale of coalescence, which eventually leads to a continuous film. As shown in Fig. 5.5(b), the Au NP films with the film thicknesses of 4, 5 and 6 nm exhibit a broaden
absorption peak in the energy range of 1-2.5 eV due to the collective oscillation of the conduction electrons inside the Au NPs. The broadening of LSPR can be attributed to the splitting of plasmon resonance, which was modeled with two Lorentz oscillators (SPR1 and SPR2) in the SE analysis. The resonance energies of SPR1 and SPR2 as a function of the film thickness are shown in Fig. 5.6. It has been shown that the near-field coupling of the nanoparticle pairs could cause the splitting of plasmon band as a result of excitation of multipole mode in non-spherical particles. [232] The origin of the splitting could be attributed to the hybridization of plasmon of the individual nanoparticles, and the strength of the hybridization strongly depends on the geometry of the composite particles. [240, 241] The splitting of plasmon band could also be attributed to the inhomogeneous polarizations of nanoparticles, [242, 243] which typically result in a red-shift of plasmon resonance. As shown in Fig. 5.6, both the SPR1 and SPR2 show a red-shift with increasing film thickness. In a classic description, the red shift of plasmon band indicates a reduction of oscillation of electrons due to the reduction of restoring force as a result of inhomogeneous polarizations in a particle with large size and irregular shape. Therefore, the LSPR could be greatly influenced by the aggregation topology of the nanoparticles. On the other hand, the formation of percolation paths in a thicker film leads to an increase of the Drude (free electrons) absorption, which could overlap with the LSPR band and result in an increase of absorption at low energies. This argument is supported by the results shown in Fig. 5.5(b). For the Au film with thickness of 10 nm, the LSPR band disappears and is superseded by the Drude absorption. This indicates a complete...
transition from an aggregated Au NP film to an electrically continuous Au film. Therefore, the dielectric function of the continuous Au film with thickness of 10 nm is close to that of bulk Au, as shown in Fig. 5.4.

5.2.4 Effect of Aggregation on LSPR and Free Electrons Absorption

Fig. 5.7 Contributions of the Drude band (a) and LSPR band (b) to the extinction coefficient $k$ of the Au NPs of the Au NP films with film thicknesses of 4-8 nm.
Figures 5.7(a) and 5.7(b) show the contributions of the Drude band ($k_{Drude}$) and LSPR band ($k_{LSPR}$) to the extinction coefficient ($k$) of the Au NPs of the Au NP films with different thicknesses, respectively. As discussed earlier, the aggregation of the Au NPs has significant impact on the particle size, shape and interparticle distance, which directly influence the optical response of the Au NP film. As shown in Fig. 5.7(a), the Drude absorption increases with increasing film thickness. This is a direct evidence of the increase of free electrons concentration in a thicker film due to the delocalization of electrons in the aggregated Au NPs. The aggregation of nanoparticles is more significant in a thicker film. On the other hand, the delocalization of electrons suppresses the LSPR in a thicker film, which is indeed observed in Fig. 5.7(b).

5.2.4 Conclusion

Aggregation effect on the LSPR and Drude absorption of Au NPs of Au NP films with various film thicknesses has been investigated with SE. The splitting of the plasmon resonance is observed for the ultrathin films thinner than ~ 8 nm, which could be attributed to the near-field coupling of the Au NPs and/or the inhomogeneous polarizations of the nanoparticles. In a thicker film, the aggregation of the Au NPs leads to the delocalization of electrons in the Au NPs, causing an increase in the free-electron concentration and thus an increase in the Drude absorption; however, the delocalization reduces the LSPR band.
5.3 Evolution of the Localized Surface Plasmon Resonance and Electron Confinement effect in Ultrathin Au Films

In section 5.2, we examined the aggregation effect of self-assembled gold nanoparticles (Au NPs) in ultrathin Au films on the dielectric function of the Au films. As an extension to the study, in this section, evolution of the LSPR as well as the electron confinement effect on both interband transitions and free-electron absorption in ultrathin Au films with the film thickness is investigated by spectroscopic ellipsometry (SE). A significant evolution of the LSPR, interband transition energies, plasma energy and conductivity with the film thickness is observed. The evolution is attributed to the changes in the size, shape and spacing of the self-assembled gold nanoparticles (Au NPs) as well as the aggregation of the Au NPs in the Au films.

5.3.1 Sample Preparation and Ellipsometric Modeling

Ultrathin Au films with various thicknesses of 1-12 nm were deposited by electron beam evaporation on a 30 nm SiO$_2$ layer thermally grown on a $p$-type silicon substrate (for the optical absorbance measurement, the Au films were deposited on a quartz substrate). Details of the sample preparation have been reported in section 5.2.1. It is worthy to point out that the thickness of ultrathin Au films including both continuous and discontinuous films were determined with SE modelling. The thickness of nanoparticle film (discontinuous film) yielded from SE modelling is the nominal value, which does not imply the nanoparticle film is continuous. In section 5.2.2, we have developed the SE modeling technique to determine the complex dielectric
function of the Au NPs in ultrathin Au films. The Au NP thin film system is modeled as a quasi-homogeneous effective medium material consisting of Au NPs and air voids. The complex dielectric function $\varepsilon_m$ of Au NPs may include the contributions from the free electron absorption (described with the Drude function), LSPR (represented by Lorentz oscillators) and interband transitions (represented by Lorentz oscillators). The SE spectral fitting shows that a single oscillator (SPR1) is required to describe the LSPR contribution for the film thickness of 1, 2 and 3 nm; in contrast, two oscillators (SPR1 and SPR2) are required for the film thickness of 4, 5, 6 and 8 nm, indicating that there is a new mode of LSPR for these films (note that there may be also new LSPR existing for the films thinner than 4 nm, but such resonance is too weak to be detected in the SE analysis). It is worthy to point out that the modeling of LSPR with one or two Lorentz oscillators is a first-order approximation as the actual LSPR structure could be complicated due to the irregular shapes of the particles in the films. On the other hand, as discussed in section 5.2.3, the absorbance measurement shows that there are two interband transitions. Therefore, two oscillators are used to describe the interband transitions in the SE modeling. As examples, the SE modeling for the Au films with the thickness of 1, 2, 3 and 12 nm are shown in Fig. 5.8. The modeling agrees well with the SE measurement; in addition, the LSPR peak energies obtained from the SE modelling are also comparable with that obtained from the absorbance measurement.
It has been shown that the film thickness has a significant impact on the aggregation topology of the Au NPs [27]. A difference in the film thickness means a difference in the degree of aggregation of nanoparticles, which leads to a difference in the particle size, shape and inter-particle spacing. As can be observed in the HRSEM images shown in the insets of Fig. 5.8, discrete nanoparticles exist in the 1 nm Au film; and doublet, triplet and higher order nanoparticles are gradually formed with the thicknesses of 2 and 3 nm due to the touching and merging of adjacent particles. As shown in Fig. 5.1, the Au films with the thicknesses of 4, 5, 6 and 8 nm exhibit a large-scale coalescence of Au NPs. The size and irregularity of the Au NPs increase with increasing film thickness. A continuous film is eventually formed as the film thickness
reaches ~ 10 nm. The surface coverage (filling factor $Q$) of Au NPs on the SiO$_2$ layer was estimated from the HRSEM images using the open software ImageJ [244], and the result is shown in Fig. 5.9.

![Fig. 5.9 Surface coverage (filling factor $Q$) of Au NPs on the SiO$_2$ layer as a function of the Au film thickness.](image)

### 5.3.2 Absorbance Measurement

![Fig. 5.10 Normalized absorbance spectra of the Au thin films (1, 2, 3 and 12 nm) on quartz substrate. The spectra are normalized to the maximum absorption intensity in the measured wavelength range of 250-2500 nm.](image)
Chapter 5 Localized Surface Plasmon Resonance and Quantum Confinement Effect in Ultrathin Au Films

Figure 5.10 shows the normalized absorbance spectra of the Au films with the thicknesses of 1, 2, 3, and 12 nm on quartz substrate in the wavelength range of 250-1200 nm (1.03-4.96 eV). It can be observed from the figure that the film thickness has a significant impact on the LSPR (the peak structures below the photon energy of ~ 2.5 eV) and interband transitions (the structures above the photon energy of ~ 2.5 eV). In the Au thin films with the thicknesses of 1, 2 and 3 nm, Au NPs are formed due to the discontinuity in the films, leading to the emergence of LSPR of Au NPs. The peak energies of the LSPR of the three films with the thicknesses of 1, 2 and 3 nm are 2.17, 2.05 and 1.91 eV, respectively, which are close to the corresponding values obtained from the SE modeling. On the other hand, for the Au film with the thickness of 12 nm, there are two broaden absorption peaks at ~ 406 nm (3.05 eV) and ~ 287 nm (4.32 eV), respectively, which are attributed to the interband transitions from the d-valance band to the empty states in the s, p bands above the Fermi level, indicated as interband 1 ($L_3 \rightarrow L_2$) [245] and interband 2 ($L_2 \rightarrow L_1$) transitions [238, 239], respectively. A blue shift of interband transitions can be also observed for the films with the thicknesses of 1, 2 and 3 nm, as shown in Fig. 5.10.
5.3.3 Evolution of the Localized Surface Plasmon Resonance

![Figure 5.11](image)

Fig. 5.11 Evolution of LSPR of Au NPs as a function of film thickness. SPR2 for the films thinner than ~ 4 nm and LSPR for the films thicker than ~ 8 nm are too weak to be detected in the SE analysis. The solid curves are used for guiding the eyes only.

Figure 5.11 shows the evolution of the LSPR of the Au NPs yielded from the SE modeling with the film thickness. As can be observed in the figure, the film thickness has a significant impact on the LSPR due to the difference in the degree of aggregation of the nanoparticles. As pointed out earlier, the LSPR strongly depends on the particle size, shape and inter-particle spacing, which directly influence the restoring forces of oscillating electrons inside the nanoparticle [229]. It has been shown that for Au NPs with sizes much smaller than the wavelength of incident light, dipolar plasmon resonance is dominated [124]. The single LSPR (SPR1) shown in Fig. 5.11 for the Au films with thicknesses of 1, 2 and 3 nm is due to the collective oscillation of electrons inside the discrete nanoparticles. As discussed in section 5.2, a large-scale coalescence of Au NPs is observed in the Au films with the thicknesses of 4, 5, 6 and 8 nm due to
touching and merging of adjacent particles into aggregated nanoparticles. It has been shown that plasmonic interaction between nanoparticles increases with increasing overlap of adjacent particles and leads to a splitting of LSPR [246]. The splitting of plasmon band could also be attributed to the polarizations parallel and perpendicular to a non-spherical particle [242]. The two resonances (SPR1 and SPR2) shown in Fig. 5.11 for the Au films with the thicknesses of 4, 5, 6 and 8 nm could be attributed to the hybridization of plasmon of the individual nanoparticles due to the increase of near-field coupling of Au NPs [240] and/or the inhomogeneous polarizations of the nanoparticles [242]. It is worth to point out that there may be also new LSPR existing for the Au films with thicknesses of 1, 2 and 3 nm, but such resonance (SPR2) is too weak to be modeled due to the weak coupling of Au NPs where the inter-particle distance is large. Thus, in our SE modeling, SPR1 is more related to the particle shape and size, while SPR2 could be related to the complicated coupling of nanoparticles and or other mechanisms such as inhomogeneous polarizations of the nanoparticles.

As shown in Fig. 5.11, the coalescence of the Au NP films with thickness larger than 4 nm leads to non-spherical particles. The non-spherical particles could lead to a very complicated situation of coupling, e.g., there may be coupling between the adjacent particles and coupling within the overlapped particles. Therefore, the coupling in the Au films with the thicknesses of 4-8 nm could be much more complicated than the situation of the coupling between two perfect spherical nanoparticles. Note that in an aggregated nanoparticle film, the coupling strength is not only increased with reducing inter-particle distance, but also reduced due to the reduction of resonance caused by
the delocalization of the conduction electrons as a result of the formation of conduction percolation paths. Thus, the two resonances (SPR1 and SPR2) observed in this work could be a net result of the two competing effects.

As can be observed in Fig. 5.11, both SPR1 and SPR2 show a red-shift with the film thickness. The red-shift can be attributed to the increase in the particle size and irregular shapes in a thicker film. In a classic description, larger particles with irregular shapes leads to smaller force constants and thus smaller restoring forces for electron oscillations in the particles; therefore the oscillation frequencies (thus the resonance energies) are lower (note that in classical mechanics, oscillation frequency of simple harmonic motion is proportional to square root of force constant). On the other hand, there is no LSPR observed in continuous Au films with thicknesses of 10 and 12 nm. This is due to the fact that the aggregation of nanoparticles is very significant in such thicker films. The formation of conductive percolation paths between neighboring nanoparticles can greatly delocalize the electrons inside the particles, leading to the suppression of LSPR.
5.3.4 Effect of Quantum Confinement on Interband Transition Energies

![Graph showing interband transition energies](image)

Fig. 5.12 Interband transition energies of Au NPs determined from the SE spectral fitting as a function of film thickness. The solid curves are used for guiding the eyes only.

Figure 5.12 shows the thickness dependence of the interband transition energies of Au NPs. The interband transition energies shown in Fig. 5.12 were obtained from the SE spectral fitting in which the two interband transitions are modeled with two Lorentz oscillators respectively. The interband transition energies were also determined from the absorbance measurement. The peak energies of the interband absorbance were located with a curve fitting program (i.e., the peak analysis function in the software Origin®). The results yielded from the two techniques are consistent. As shown in the figure, for the Au films thinner than ~ 4 nm, the energies of both interband transition 1 and interband transition 2 increase with decreasing film thickness. It has been shown that confinement of electrons in the Au NPs could lead to a discretization of energy levels and result in an increase of interband transition energy [233, 247]. It has been
also reported that nanoparticles with size smaller than 10 nm presents a quantum size effect [234]. Therefore, the blue shifts of the interband transition energies with decreasing film thickness can be attributed to the quantum confinement effect of the small Au NPs presented in the Au films thinner than ~ 4 nm.

### 5.3.5 Effect of Confinement on Free Electrons Concentration

The confinement of electrons inside the nanoparticles can lead to a decrease in the concentration of the free electrons (conduction electrons). Unlike the thicker Au films (e.g. the 10 and 12 nm films) where the free-electrons absorption is dominant in the optical absorption as a result of the formation of conductive percolation paths between the neighboring nanoparticles, thinner Au NP films (e.g. the 1, 2 and 3 nm films) exhibit weak or negligible Drude (free electrons) absorption due to the reduction of conduction electrons as a result of the localization of electrons inside the nanoparticles, as shown in Fig. 5.10. The weak or negligible Drude (free electrons) absorption indicates a large reduction in the free-electron concentration in the discrete NP films with the thicknesses of 1, 2 and 3 nm. As pointed out earlier, the film thickness has significant impact on the aggregation topology of Au NPs (e.g. particle size, shape and inter-particle spacing), which can influence the free-electron concentration of the Au NP films [248]. The low electron concentration could significantly reduce the free-electron screening effect in the Au NP film, and result in dominant interband transitions instead of the Drude absorption [249].
The confinement effect on the free-electron concentration in the Au NPs can be also revealed from the thickness dependence of the plasma energy $E_p$ of the Au films obtained from the SE modeling. Figure 5.13 shows the plasma energy as a function of the film thickness. As can be observed in the figure, the plasma energy decreases with decreasing film thickness. The decrease of $E_p$ indicates a decrease of free-electron concentration in the Au NPs as $E_p$ is proportional to $\sqrt{N_f}$ where $N_f$ is the free-electron concentration [59]. This is consistent with the reduction of the Drude absorbance with decreasing film thickness as discussed above. On the other hand, it can be also noted from Fig. 5.13 that as the film thickness increases, $E_p$ increases towards the value (9.03 eV) [62] of bulk gold.

Besides the free-electron concentration, the mobility of the conduction electrons in the Au films may be also affected by the confinement of electrons inside the
nanoparticles. It has been suggested that when the particle size is comparable to the mean free path of the electrons inside the nanoparticles, the collisions of the conduction electrons with the particle surface contribute to an additional collision process [250]. This will lead to a decrease in the mobility. To investigate this issue, the thickness dependence of the conductivity ($\sigma$) of the Au films has been examined. The ratio of $\sigma / \sigma_m$, where $\sigma_m$ is the maximum conductivity, which is obtained from the measurement of the sheet resistance of the Au films on quartz substrate, is plotted in Fig. 5.13 for various film thicknesses. As shown in the figure, unlike the plasma energy ($E_p$) of the Au NPs, which increases gradually with thickness, $\sigma / \sigma_m$ shows an abrupt insulator-to-metal transition at the percolation threshold of thickness of 6 nm. This indicates that the conductivity of the Au films is more influenced by the electron mobility rather than the free-electron concentration inside the nanoparticles.

As shown in Fig. 5.13, for the Au films with the thicknesses of 1-3 nm, the conductivity of the films is extremely low and electrons are mainly confined inside the particles. As film thickness increases up to the percolation threshold of 6 nm, the conduction paths between the neighboring particles can greatly delocalize the electrons, and thus lead to a sharp increase of electron mobility. On the other hand, for a densely packed nanoparticle film, the formation of conduction path between the nanoparticles does not greatly change the surface filling factor $Q$ [27]; therefore, the percolation threshold may not be strongly related to the surface filling factor.
5.3.6 Conclusion

The LSPR, interband transitions and plasma energy of Au NPs as well as the conductivity of the Au films are found to be strongly dependent of the film thickness. The thickness dependence can be understood in terms of the near-field coupling and inhomogeneous polarization of nanoparticles, quantum confinement effect on the energy bands, and the effects of electron confinement in Au NPs on the free-electron concentration and electron mobility. These factors are affected by the nanoparticle size, shape and spacing as well as the aggregation of the nanoparticles, which all are dependent of the film thickness.

5.4 Summary

In this chapter, the effects of localized surface plasmon and quantum confinement on optical properties of ultrathin Au films consisting of self-assembled Au nanoparticles are investigated. It has been shown that the film thickness has a significant impact on the aggregation topology of the Au NPs. In the SE analysis, single LSPR was observed for the Au films consisting of discrete Au NPs; two resonances were observed when the Au NPs aggregate into large-scale coalescence; and no LSPR was observed with continuous gold films. A red-shift of LSPR with increasing film thickness was observed. In the Au films thinner than ~ 4 nm where Drude (free electrons) absorption was weak or negligible, a blue shift of interband transitions with decreasing film thickness was observed, which can be attributed to the quantum confinement effect. The plasma energy of free electrons gradually increased towards the bulk value of 9.03
eV [62] with increasing film thickness, which is mainly due to the increase in the free-electron concentration as a result of the delocalization of electrons in the Au NPs. However, the conductivity of the Au films shows an abrupt insulator-to-metal transition at the percolation threshold of thickness of ~ 6 nm, indicating that the conductivity is more influenced by the electron mobility rather than the electron concentration inside the nanoparticles.
Chapter 6 Conclusion and Recommendations

6.1 Conclusion

Conductive metal oxides have been intensively studied due to its promising application in optoelectronics. The abundant free electrons could greatly alter the optical properties of the oxide films. Noble metals such as Au and Ag have also gained much attention in plasmonics due to its potential application in bio-sensing and optical interconnects. On the other hand, owing to the trend of down scaling, the nanoscale structures exhibit some unique properties different from their bulk counterparts. Thus, knowledge of optical properties of a material is crucial for us. In this thesis, investigations of effects of free electron, quantum confinement and localized surface plasmon resonance on optical properties of the ultrathin metal oxide and metal films have been carried out. This section briefly summarizes the overall work presented in this thesis.

6.1.1 Free Electrons Effect in Conductive Metal Oxide Thin Film

Optical properties including dielectric function and band gap of Al-doped ZnO (AZO) have been investigated with both absorption spectroscopy and spectroscopic ellipsometry. The result shows that the abundant free electrons could greatly influence the optical properties of the oxide films, e.g., suppression of excitonic absorption due to the free electrons screening effect and expansion of band gap due to the Burstein-Moss (BM) effect. It has been found that the annealing at temperature range of 400-700°C could greatly change the electron concentration of the AZO films, which greatly
influence the onset of band edge absorption and free electrons absorption. The change in the electron concentration can be attributed to the change of the donor-like defect concentration in the oxide films as a result of annealing. Thus, thermal annealing could be an effective tool for tuning the carrier concentration of the metal oxide films. On the other hand, the study of the optical properties of a-IGZO thin films shows that the film thickness could also greatly influence the free electrons concentration in the metal oxide films. The dependence of carrier concentration on film thickness could be attributed to the improvement of polycrystalline grain structures with increasing film thickness.

6.1.2 Quantum Confinement Effect in Ultrathin Metal Oxide Film

The effect of quantum confinement on dielectric function of ultrathin ZnO films has been investigated with spectroscopic ellipsometry (SE). The result shows that nanocrystalline grain size has a significant impact on the band gap energy and exciton binding energies of ZnO films due to the quantum confinement effect, which result in a reduction of dielectric function of the oxide films. On the other hand, the evolution of dielectric function of amorphous indium gallium zinc oxide (a-IGZO) films with film thickness has been observed. The evolution is explained as the result of the confinement of electrons along the thickness direction (i.e., the one-dimensional quantum confinement (ODQC) effect). It has been shown that thickness dependence of band gaps of ultrathin amorphous materials can be described by the ODQC effect.
6.1.3 Localized Surface Plasmon Resonance and Quantum Confinement Effect in Ultrathin Au Films

The evolution of the LSPR as well as the electron confinement effect on both interband transitions and free-electron absorption in ultrathin gold films with the film thickness has been investigated with spectroscopic ellipsometry (SE). It has been shown that the aggregation of Au nanoparticles increase with increasing film thickness. A difference in the degree of aggregation leads to a difference in the particle size, shape and inter-particle spacing, which directly influence the near-field coupling of the nanoparticles as well as the formation of conductive percolation path in the film. On the other hand, in Au film with thickness of 1-3 nm where the free electrons absorption is weak, a blue shift of interband transitions with decreasing film thickness is observed, which can be attributed to the quantum confinement effect. This indicates that the metal nanoparticles with size smaller than 10 nm could exhibit a dominant quantum confinement effect.

6.2 Recommendations

The work presented in this thesis has enriched the understanding of the optical properties of metal oxide and metal thin film, and open up possibilities for their potential applications in optoelectronics. As an extension to the study, the following recommendations are proposed.
6.2.1 Study of Optical Properties Using Other Theoretical Calculations and Tools

In this thesis, optical properties including dielectric function and band gap of metal oxide and metal films have been determined with the spectroscopic ellipsometric (SE) based on various optical dispersion model. The SE analysis provides an important approach for the study of energy transition and optical absorption in nanomaterials. Nevertheless, to quantitatively study the optical properties, theoretical calculation is needed, not only to verify the accuracy of the SE analysis, but also to quantitatively understand the background physics of the phenomenon. Study of electronic structure of ultrathin metal oxide and metal films by using first principle calculation is recommended in future work. The electronic structure could quantitatively explain the electrical and optical properties of the nanomaterials. Low temperature photoluminescence study of ultrathin ZnO films is also recommended, as the excitonic structure of ZnO can be only resolved in low temperature measurement due to the thermal broadening. Theoretical calculations such as Mie theory, discrete dipole approximation (DDA), finite difference time domain (FDTD) are also recommended for the study of size dependence of optical properties of metal nanoparticles.

6.2.2 Study of Surface Plasmon Resonance in Conductive Metal Oxide

As discussed in the chapter 3, the abundant free electrons concentration could greatly change the optical properties of the oxide films. It has been reported that when the electron concentration reaches $10^{20} - 10^{21}$ cm$^{-3}$, surface plasmon resonance (SPR) could be observed in the conductive metal oxides. [251] Unlike noble metal where the SPR
Chapter 6 Conclusion and Recommendations

is observed in visible spectrum, transition metal oxides exhibit the SPR in the infrared spectrum. [252, 253] Thus, heavily doped metal oxides such as Al-doped ZnO and Ga-doped ZnO could be alternative plasmonic materials for replacing the conventional metals in near-infrared, e.g., exhibit surface plasmon resonance (SPR) in infrared and remain optical transparent in visible. As compared to conventional metal plasmonics, the oxide-based plasmonic materials have the advantages of low loss, high performance, tunable optical properties and compatible with standard fabrication procedures. [11] Fabrication of heavily doped metal oxide nanostructures and study their surface plamson resonances are highly recommended in future work.

6.2.3 Development of Plasmonic Waveguide Based on Metal Nanoparticles

One of the promising applications of SPR of the noble metal nanoparticles is the plasmonic waveguide. As discussed in section 2.8.3, the guiding of electromagnetic energy is realized based on the near field coupling of arrays of closely packed metal nanoparticles. It has been shown that the plasmonic waveguide can overcome the issues like the diffraction limit and bend loss of traditional waveguide due to the down scaling the devices. [198] Thus, metal nanoparticle waveguide is considered as potential candidate for next generation on-chip optical interconnect. Simulation and fabrication of metal nanoparticle waveguide are recommended.

6.2.4 Study of Coupling between Metal Nanoparticle and Metal Oxide

Metal nanoparticles have the ability to localize and strongly enhance an incident electromagnetic field due to the surface plasmon resonance. It has been shown that the
SPR electron and energy could transfer from the metal to surrounding oxides and greatly modify their optical properties. [254, 255] It has been also reported that the coupling between the emission of ZnO with the surface plasmon resonance of Au nanoparticles could greatly enhance the photoluminescence of ZnO. [256] Therefore, it would be interesting to examine the optical properties of the nanocomposite material, as the coupling could play an important role in such hybrid system.
Bibliography


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Switching Mechanism in Single-Crystal TiO2 Resistive Memory on Silicon,


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