Characterization of structural and optical properties of Zinc Oxide thin films

Liu, Yuchan

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Characterization of Structural and Optical Properties of Zinc Oxide Thin Films

Liu Yuchan

School of Mechanical and Aerospace Engineering

A thesis submitted to the Nanyang Technological University
in fulfilment of the requirement for the degree of
Master of Engineering

2005

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Abstract

The objective of this thesis is to determine the optical properties of ZnO thin films with spectroscopic ellipsometry in a wide spectral region covering the both regimes of below and above the ZnO bandgap. Three dispersion models, namely, Sellmeier dispersion model, Cauchy model and Forouhi-Bloomer model, were used and evaluated to determine the optical constants of ZnO thin films below the energy band gap. On the other hand, two ellipsometric models, namely, two-phase model and three-phase point-by-point fit, were used to determine the optical constants above the band gap. Cauchy model is found to be the most suitable model for extracting the optical constants for photon energies below the ZnO bandgap while the point-by-point fit with the refractive index and extinction coefficient calculated from the two-phase model as the initial values can be used to reliably determine the optical constants for photon energies above the bandgap. Based on the above studies, the optical properties including optical constants, dielectric functions, reflectance, and absorption coefficient in the wavelength range of 250 – 1100 nm, covering both regions of below and above the bandgap, have been determined. Annealing effects on the optical properties and the structures of ZnO thin films have also been studied. It is observed that annealing causes a large reduction in the refractive index and the real part of the dielectric function. Atomic force microscopic study reveals that annealing changes the surface roughness, grain size and size distribution of the ZnO thin films significantly. The reduction in refractive index and dielectric function may be attributed to the increase of the volume fraction of voids in the thin films as a result of annealing,

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List of Symbols

χ	Wavevector
E_g	Energy band gap
E_{ip}	Electric field of incident light in p- direction
E_{is}	Electric field of incident light in s- direction
E_{rp}	Electric field of reflected light in p- direction
E_{rs}	Electric field of reflected light in s- direction
ρ	Ratio of Fresnel reflection coefficients
ψ	Amplitude change of polarization
Δ	Phase change of polarization
δr^p	Phase change for the p- component on reflection
δr^s	Phase change for the s- component on reflection
r^p	Fresnel reflection coefficient for the p - component
r^s	Fresnel reflection coefficient for the s- component
R_p	Complex reflection coefficient for the p- component
R_s	Complex reflection coefficient for the s- component
N	Complex refractive index
n	Refractive index
k	Extinction coefficient
X	Parameter
ϕ_0	Incident angle at the interface of air/thin film
ϕ_1	Refractive angle at the interface of air/thin film

ϕ_2	Refractive angle at the interface of thin film/substrate
d	Thickness of thin film
λ	Wavelength of light
α	Absorption coefficient
E	Photon energy
ε	Complex dielectric function
ε_1	Real part of dielectric function
ε_2	Imaginary part of dielectric function
R	Reflectance at normal incident
d_{hkl}	Perpendicular spacing between the lattice planes
η	Integer
θ	Diffraction angle
$\bar{S}$	Arithmetic mean of the sum of absolute deviations of the calculated ψ and A from the measured ones over the spectral range
A	Fitting parameter
B	Fitting parameter
C	Fitting parameter
σ	The extinction coefficient amplitude in Cauchy model
β	The exponent factor in Cauchy model
γ	The band edge in Cauchy model
$n(\infty)$	The refractive index when the photon energy $E = \infty$ in Forouhi-Bloomer model
f	Error function

Chapter 1 Introduction

1.1 Background

Zinc oxide (ZnO) is a versatile II–VI semiconductor material and has been used for a variety of applications such as varistors, phosphors, gas sensors, surface acoustic wave devices, solar cells windows or transparent contacts. With its direct band gap of about 3.3 eV at room temperature [1,2], ZnO has also drawn attention for its promise on applications in short wavelength optoelectronic devices. Comparing with other wide band gap materials, such as ZnSe, GaN, and SiC, ZnO has numerous advantages for device applications including higher chemical and thermal stability, higher radiation hardness, and lower growth temperature. These properties are favorable for the fabrication and for long lifetime operation of devices. In addition, the binding energy of the exciton of ZnO (60 meV) is large [2], which allows efficient excitonic emission at high temperature. As the oscillator strength of excitons is much larger than that of direct electron-hole transitions and the energy distribution of optical gain by excitonic recombination is much narrower than that of band edge free carrier recombination, thus a lasing process based on the excitonic effect is expected to have a higher gain and a lower threshold than that of an electron-hole plasma [3,4]. However, the exciton binding energy, for most semiconductor materials, is so small that excitonic effects only play a role at low temperature. For example, GaN is known to be a good material for the fabrication of the optical devices such as light emitting diodes or laser diodes, but its binding energy of exciton is only 25 meV at room temperature [5]. In contrast, ZnO has an exciton binding energy of about 60 meV, which is 2.4 times of that of GaN. As a result, ZnO-related materials have received

considerable attention. Just recently, many researches aiming at the application of ZnO's photoluminescent property have been carried out [5-11]. Since ZnO is surface-smooth and transparent in the visible light, it can be utilized for light waveguide [12]. In addition, ZnO film has a high transmittance in the visible region and a low electrical resistivity, hence it is an ideal window material for solar cell and flat panel displays. Therefore, it is believed that ZnO will be one of the most promising materials for optoelectronic devices in the UV region and optical or display devices in the future.

In 1997, stimulated emission and optically pumped laser action in ZnO epitaxial films were observed at room temperature by the research groups in Tohoku University, Tokyo Institute of Technology and The Institute of Physical and Chemical Research in Japan and Hong Kong University of Science and Technology [13, 14]. This discovery makes the research community in the area of optoelectronics very excited. Subsequently, many researches have been focused on the fabrication of ZnO thin films by different methods for photoluminescence investigation. To date, it has been proved that high quality ZnO thin films can emit light under stimulation and can be grown by molecular beam epitaxy [2, 4, 6, 8, 13, 14], magnetron sputtering [15, 16], pulsed laser deposition [17], reactive thermal evaporation [18], spray pyrolysis [19, 20], metal organic chemical vapor deposition [21], sol-gel process [22] and filtered cathodic vacuum arc [23].

Characterization of ZnO is important to the evaluation of the film quality, process control, device design and understanding the function mechanisms of the device. Most of the characterizations are carried out using XRD, optical transmittance

and photoluminescence spectrum measurements [5-9, 24, 25]. Not much work, however, has been done on the study of optical constants (refractive index and extinction coefficient), dielectric function, energy band gap, and surface roughness. With the increasing use of ZnO, it is known that gaining the precise information of the optical properties is critical for designing optical and optoelectronic devices. Development of a methodology to characterize the optical properties of ZnO thin film is therefore essential. In addition, surface structure may affect the optical properties of thin film. For example, rougher surface exhibits larger volume fraction of voids on the surface, which can effectively reduce the refractive index. Hence, it is also important to investigate the surface morphology of ZnO thin films prepared under various process conditions.

1.2 Objective of this project

This project aims to develop a non-destructive methodology to extract the information of optical constants, dielectric function, reflectance, absorption coefficient and film thickness, and to study the effects of annealing on the optical properties, grain size and surface roughness of ZnO thin films.

1.3 Scope of this project

ZnO thin film is deposited on silicon wafer by filtered cathodic vacuum arc (FCVA) technique and subsequently annealed under different conditions. Spectroscopic ellipsometry (SE) is employed to measure the change in the polarization state, i.e., ψ (ψ) and Δ (Δ), of the light reflected off the surface of the

film for the wavelengths ranging from 250 nm to 1100 nm. Five modeling techniques, namely: Sellmeier dispersion model [55, 60], Cauchy mathematical expression [42], Forouhi-Bloomer model [62], two-phase model and point-by-point fit [42], are applied to help developing the appropriate model for the determination of optical constants at photon energies below and above the band gap as well as the film thickness of ZnO thin films. X-ray diffractometer (XRD) is used to investigate the crystalline structure of the thin films, and atomic force microscopy (AFM) is used to characterize the surface morphology and measure the surface roughness, grain size and size distribution of the thin films. Finally, the effects of annealing on the optical properties and surface structures of the ZnO thin films are also investigated.

1.4 Achievement of this project

The performance of the five modeling techniques mentioned in Section 1.3 in the spectral fitting was evaluated. The optical properties at the photon energies below and above the band gap and the film thickness of ZnO thin films were extracted successfully. The spectral dependence of the refractive index and extinction coefficient obtained in this piece of work is very similar to that of RF-sputtered ZnO film [56]. In addition, the value of film thickness of the un-annealed ZnO film extracted from the ellipsometric study is in agreement with that measured by AFM. Therefore, an accurate and reliable methodology based on the ellipsometry for determining the optical properties and film thickness of ZnO thin films has been demonstrated in this project. The optical properties including optical constants, dielectric function, reflectance and absorption coefficient of ZnO thin films in the

wavelength range of 250 – 1100 nm (1.1 – 5.0 eV), which covers both regions of above and below the ZnO band gap, have been determined successfully.

In addition, annealing effects on the optical properties and the structures of ZnO thin films are investigated also. It is observed that the annealing can cause a large reduction in the refractive index and the real part of dielectric function. On the other hand, atomic force microscopic study reveals that annealing can lead to a very significant change in the surface roughness, grain size and size distribution. It is proposed that the reduction in the refractive index and the dielectric function is due to the increase of the volume fraction of voids in the ZnO thin films as a result of annealing.

1.5 Organization of this thesis

In this thesis, Chapter 1 introduces the applications of ZnO thin films, explains why ZnO thin film is one of the most promising materials for the fabrication of the next-generation optoelectronic devices in the *UV* region and optical or display devices. Subsequently, it is pointed out that the characterization of ZnO thin films, especially development of a methodology to characterize its optical properties, is essential for the applications of ZnO thin films. Chapter 2 provides a literature review on physical and optical properties of ZnO and various technologies for fabricating ZnO films. Then it reviews previous research on characterization of ZnO films, namely, investigation of crystalline structure of the films with X-ray diffraction, study of photoluminescent emission, determination of optical properties and film thickness with ellipsometry, and study of surface morphology and measurement of surface

roughness with atomic force microscopy. In addition, Chapter 2 also describes the basic principle of ellipsometry, reviews the existing models for extracting optical constants of ZnO thin films and evaluates their performance in the spectral fitting. Chapter 3 describes the deposition process for the preparation of the samples used in this project. The details of the experiments conducted by SE, XRD and AFM are included. Modeling with Sellmeier dispersion model is also comprised in Chapter 3. Chapters 4 and 5 study the determination of the optical constants of ZnO thin films for photon energies below and above the band gap energy, respectively. Chapter 6 discusses the merging of the spectral range of wavelengths > 375 nm (i.e., photon energies below the band gap of ZnO) with the range of wavelengths < 375 nm (i.e., photon energies above the band gap of ZnO). Such a merging provides a complete spectral dependence of optical constants of ZnO film in a wide wavelength range of 250 - 1100 nm (or photon energies of 1.1 - 5.0 eV). The optical properties of the un-annealed ZnO thin film including the optical constants, dielectric functions, reflectance, and absorption coefficient in the wavelength range of 250 – 1100 nm are also presented. Chapter 7 is concerned with the influence of annealing on the optical properties, surface roughness, grain size and size distribution of the ZnO thin films. In chapter 8, we present some conclusions and recommendations for future works.

Chapter 2 Literature Review

2.1 Physical and optical properties of ZnO

Zinc oxide (ZnO) is a 11-VI compound. It is a direct band gap semiconductor, in which the lowest point of the conduction band and the highest point of the valence band occur at the same value of wavevector (χ) (Figure 2.1). ZnO is a wide band gap (about 3.3 eV at room temperature) semiconductor and it has a binding energy of the exciton of 60 meV. It also exhibits other properties such as transparent in visible light range, piezoelectric characteristic, acoustic-to-optical behavior and electro-optical behavior. It is a most promising material in the application of optoelectronics in UV range. We compare the relevant physical and optical properties of ZnO with those of other wide band gap semiconductors in Table 2.1.

Figure 2.1. The direct band gap structure. The lowest point of the conduction band occurs at the same value of wavevector (χ) as the highest point of the valence band [40].

Table 2.1. Comparison of the properties of ZnO with those of other wide band gap semiconductors [2,26].

Material Property	ZnO	ZnS	ZnSe	GaN
Crystal structure	Wurtzite	Wurtzite Zinc blende	Wurtzite Zinc blende	Wurtzite Zinc blende
Wurtzite lattice constants at 300K a (nm) c (nm)	0.3249 0.5207	0.3823 0.6261	0.398* 0.653*	0.3189 0.5185
Wurtzite density at 300K (g / cm ³)	5.66	4.1	...	6.10
Zinc blende density at 300K (g / cm ³)	...	4.11*	5.26*	5.65*
Phase stable at 300K	Wurtzite*	Wurtzite & Zinc blende*	Zinc blende*	Zinc blende*
Melting point (K)	2248	2103	1793	1973
Wurtzite structure thermal conductivity (mW·cm ⁻¹ ·K ⁻¹) at 300K	600	460	...	656
Refractive index Zinc-blende structure Wurtzite	 2.008*	2.368* 2.356*	2.5*	2.72*
Energy gap E _g (eV) at 300K Zinc-blende structure Wurtzite	 ... 3.37, direct	3.68, direct* 3.8, direct	2.70, direct ...	2.394, direct* 3.39, direct
Exciton binding energy E _b (meV)	60	39	20	21
Dielectric constants ε(0) ε(∞)	8.75 3.75	9.6 5.7	9.1 6.3	8.9 5.35

* Data are obtained from reference [27].

2.2 Techniques for fabrication of ZnO thin films

ZnO thin films can be grown by various techniques such as molecular beam epitaxy, magnetron sputtering, pulsed laser deposition, reactive thermal evaporation,

spray pyrolysis, metal organic chemical vapor deposition, sol-gel process and filtered cathodic vacuum arc. Normally, high quality ZnO films were grown at relatively high substrate temperature varying from 450° C to 750° C by molecular beam epitaxy on sapphire substrates [2,4,6,8,13, 14]. In this section, we describe briefly some of the major techniques that were commonly used for fabricating ZnO thin films.

2.2.1 Molecular Beam Epitaxy (MBE)

Molecular beam epitaxy (MBE) was developed in the early 1970s as a means of growing high-purity epitaxial layers of compound semiconductors [28, 29]. Since then it has evolved into a popular technique for growing III-V compound semiconductors as well as several other materials. MBE can produce high-quality layers with very abrupt interfaces and good control of thickness, doping, and composition. Because of its high control ability, MBE is a valuable tool in the development of complex electronic and optoelectronic devices.

In MBE, the constituent elements of a semiconductor in the form of “molecular beams” are deposited onto a heated crystalline substrate to form thin epitaxial layers. The “molecular beams” are typically from thermally evaporated elemental sources, or some other sources including metal-organic group III precursors (MOMBE), gaseous group V hydride or organic precursors (gas-source MBE), or their combinations (chemical beam epitaxy or CBE). To obtain high-purity layers, it is critical that the material sources are extremely pure and the entire process is done in an ultra-high vacuum (UHV) environment. Another important feature of MBE is that the film growth rate is typically in the order of a few Å/s and the beams can be

shuttered in a fraction of a second, allowing nearly atomically abrupt transitions from one material to another. A generic MBE system is illustrated in Figure 2.2. Sample block / substrate is heated and rotated. The source materials (e.g., Zn) are evaporated in effusion cells (also named as Knudsen cells) and exit from effusion cells. Fast shutters are interposed between the substrate and the sources. The beam fluxes are controlled by close monitoring of the source temperature and the use of fast-acting shutters.

Figure 2.2. Schematic diagram of a typical MBE system [30].

In 1997, high quality of ZnO thin films were successfully grown on sapphire substrates by the research groups in Tohoku University, Tokyo Institute of Technology and The Institute of Physical and Chemical Research in Japan and Hong Kong University of Science and Technology [13, 14] using plasma-enhanced

molecular beam epitaxy and laser molecular beam epitaxy techniques. Light emitting in ultraviolet (UV) range at room temperature was observed from these ZnO epilayers.

2.2.2 Magnetron sputtering

Sputtering is a process where material is dislodged and ejected from the surface of a solid due to the momentum exchange associated with surface bombardment by energetic particles [31]. A source of coating material called the target is placed into a vacuum chamber along with the substrates. The chamber is evacuated to a base pressure typically in the range of 5×10^{-4} to 5×10^{-7} Torr, and the pressure is increased to 10^{-2} to 10^{-4} Torr by inserting working gases. The bombarding species are generally ions of a heavy inert gas. Argon is the most commonly used. The sputtered material is ejected primarily in atomic form. The substrates are positioned in front of the target so that they intercept the flux of sputtered species. Figure 2.3 demonstrates simply the sputter coating process.

In a magnetron sputter deposition process, magnetic fields are used to form an electron trap which, in conjunction with the cathode surface, confines the $\mathbf{E} \times \mathbf{B}$ electron drift current to a closed-loop path near the surface of the target. This “race-track” effectively increases the number of ionizing collisions per electron in the plasma and hence increases the plasma density. The magnetic confinement near the target results in higher achievable current densities at lower pressure (10^{-3} - 10^{-2} torr), nearly independent of voltage. This manner of cathode operation is capable of providing much higher deposition rates with less electron bombardment of the

substrate and therefore less heating [32]. The research groups in Akita University, Ritsumeikan University and Matsushita Electric Industrial Co., Ltd of Japan [9, 15], and Stanford University of USA [16] have used magnetron sputtering technique to produce good quality ZnO thin films.

Figure 2.3. A schematic diagram of sputter coating process [31].

2.2.3 Filtered Cathodic Vacuum Arc (FCVA)

Filtered cathodic vacuum arc deposition belongs to vacuum arc evaporation technique. Cathodic vacuum arc (CVA) evaporation employs a vacuum arc to generate vapor emission from target, which is the cathode, in an arc discharge circuit. Material is eroded from the target in several forms, for instance, ions and

microdroplets. Ionized vapor of the target material is deposited onto the substrate, which is normally biased negatively with respect to the chamber and the anode. A basic CVA system is illustrated in Figure 2.4. It consists of a vacuum chamber, a cathode (target), an arc power supply, an arc igniter, an anode, and a substrate bias power supply. During the cathodic arc process, macro-particles of 0.1-10 μm are unavoidable by-products, which can easily reach the substrate and cause contamination of the films [33 - 35]. This drawback hinders broad application of films prepared by the cathodic vacuum arc in optical and electronic regimes, where uniformity and smoothness are prerequisites. Macro-particles can be removed by the use of suitable filters, so called “filtered arc evaporation process”. A filtered cathodic vacuum arc coating system with a magnetic macro-particle filter developed by Shi et al. [36], in which consists of an off-plane double-bend (OPDB) filter, can filter efficiently out unwanted macro-particles.

Figure 2.4. A basic CVA system.

The filtered cathodic vacuum arc (FCVA) technique has been used successfully in producing ultra-hard and dense tetrahedral amorphous carbon films [37]. Recently it has also been reported that polycrystalline ZnO films can be produced by FCVA simply using a zinc elemental target under an O₂ reactive atmosphere [23, 38, 39]. FCVA is a low-cost deposition technique. The deposition process is simple, and a high quality of ZnO film can be deposited at a low temperature such as 200 °C or even room temperature [23, 38, 39]. Low temperature deposition is preferred in some processes in order to avoid reactive and elemental diffusion of different layers and to protect substrates such as polymers [39]. The structure and stoichiometry of the ZnO films are determined by the oxygen pressure, and the increase of the oxygen pressure improves the stoichiometry and the crystalline quality of the ZnO films [39]. The crystalline quality can be evaluated through monitoring the evolution of the XRD full width at half maximum (FWHM) with the oxygen pressure [39]. In this study, we employed FCVA technique to prepare high quality ZnO thin films for the study of their optical properties.

2.3 Characterization of ZnO thin films

Most of the characterizations have been done on crystalline structures, optical transmittance and photoluminescence [5-9, 24, 25]. Not much work, however, has been done on optical constants and dielectric functions.

2.3.1 Crystalline structure analysis with XRD

ZnO is a solid having a wurtzite structure. X-ray diffraction (XRD) is a good tool to study the crystalline structure, It was extensively used to understand the

crystalline structure of ZnO thin films prepared by different techniques. Chen et al. [2] employed molecular beam epitaxy technique to grow ZnO film on c-plane sapphire and observed that ZnO (002) peak is at $2\theta = 34.4^\circ$ and its full width at half-maximums (FWHMs) is 0.026° , which yields a d spacing of $2.607 \text{ \AA}$, in agreement with the lattice constant of ZnO ($c = 2d = 5.213 \text{ \AA}$). Ma et al. [18] applied thermal evaporation method to deposit ZnO and ZnO:Al films onto glass substrates. They used XRD to study both films and found that ZnO film was polycrystalline and oriented perpendicular to the substrate surface (c-axis orientation) but ZnO:Al film had only the (002) diffraction peak. Figure 2.5 shows the XRD spectra of ZnO and ZnO:Al films obtained by Ma et al. In addition, Sato et al. [15], Shen et al. [5], Chen et al. [6], Ohtomo et al. [24], and Sun et al. [17] used pulsed laser deposition, magnetron sputtering to fabricate ZnO films and also observed the (002) dominant peak in the XRD spectra.

Figure 2.5. X-ray diffraction spectra of (a) a ZnO film and (b) a ZnO: Alfilm with Al/Zn=0.5 at % [18].

2.3.2 Photoluminescent (PL) emission of ZnO thin films

When light illuminates onto a sample, it is absorbed and imparts excess energy into the material in a process called “photo-excitation.” One way that this excess energy can be dissipated by the sample is through the emission of light (photoluminescence). More specifically, photo-excitation causes electrons within the material to move into excited states. When these electrons return to their equilibrium states, the excess energy is released and may include the emission of light (a radiative process) or may not (a non-radiative process). The energy of the emitted light (or photoluminescence) is related to the difference in energy levels between the two electron states involved in the transition, i.e., between the excited state and the equilibrium state. By measuring the energy of this emitted light, one can determine the energy band gap and detect impurity levels and defects. Analysis of photoluminescence helps to understand the underlying physics of the recombination mechanism.

In 1997, the research groups in several universities in Japan and Hong Kong [13, 14] reported firstly the observation of room temperature UV laser emission on crystallite, nano-sized ZnO thin films. This makes the research community in the area of optoelectronics very excited because it represents an important step towards the development of nanometer photoelectronics. Subsequently, much research has been focused on the fabrication of ZnO thin films by different methods for photoluminescence investigation [5-8, 24, 25, 39]. Chen et al. [2] produced ZnO thin films by MBE and showed that PL emission properties of ZnO epilayers vary from sample to sample, even when they were produced under similar conditions. However,

the main features of the PL spectra are similar for all samples, and can be divided into three categories: the near band edge emission, the low energy tail extending from the near band edge emission, and the deep-level emission. A representative PL spectrum at low temperature of a ZnO epilayer is shown in Figure 2.6. The dominant peak is at 3.347 eV with FWHM of about 3 meV, which is attributed to the recombination of excitons bound to neutral donors or acceptors [41]. A broad deep-level emission is seen around 2.5 eV which passes over into the long emission tail of the near band edge emission. The deep-level emission is usually related to structural defects and impurities. As the temperature increases, the free exciton emission increases and finally dominates the PL spectra at room temperature. Figure 2.7 shows the PL spectra at room temperature. We can see from Figures 2.6 & 2.7 that the deep-level emission is extremely weak for the ZnO films grown by MBE, The typical intensity ratio of the near band edge emission to deep-level emission is about 500 at 10K and 20 at room temperature.

Figure 6. Low temperature PL spectrum obtained from a ZnO epilayer grown on Al₂O₃ (0001) at 600°C. The inset displays detail of the near band edge region [2].

Figure 2.7. Room temperature PL spectrum of a ZnO epilayer grown on Al_2O_3 (0001) at 600°C . Even at room temperature, the integrated deep-level emission is as weak as 1/20 of the intensity of the free exciton emission [2].

2.3.3 Study of surface morphology of ZnO thin films

Surface morphology and surface structure are very important for optical applications. Shiosaki et al. used planar magnetron RF sputtering to fabricate ZnO for waveguide application [12]. They observed that the surface of ZnO films deposited by this technique was so smooth that it should have low optical waveguide losses. However, they found that the measured optical waveguide losses of the films were one order of magnitude higher than those prepared by chemical vapor deposition. Xu et al. [23] used filtered cathodic vacuum arc (FCVA) to produce ZnO films and used AFM to characterize the surface of the film. They noticed that a very uniform nanocrystalline structured ZnO film can be achieved at a deposition temperature of 230°C . Under floating conditions, the grain size of the films increased with the increase of substrate temperature and bias voltage. With the bias voltage increased to

200 V, they observed an amorphous phase with irregular features. Wang et al. [39] also employed AFM to evaluate the surface finish of ZnO deposited by FCVA and noticed that the films were composed of well faceted grains and the sizes of the grains generally decreased with the increase of oxygen pressure during the deposition. The room mean square roughness decreased from 3.9 nm to 0.9 nm. Yu et al. [44] reported that post-deposition annealing can generate a highly disordered structure inside the as-deposited ZnO thin films and this formation of irregular ZnO grains can create lateral facets (i.e., laser cavities) so that closed-loop scattering and coherent amplification of lights are realized, hence high-intensity UV lasing is possible in the ZnO thin film waveguides.

Atomic force microscope (AFM) is a member of the family of scanning probe microscopy. It was developed by Binnig, Quate, and Gerber as collaboration between IBM and Stanford University in 1986. It is a sensitive tool to probe the surface of materials and its resolution can reach to 0.05 nm in the vertical direction and 10 nm in the lateral direction. It can provide the information of surface topography in three dimensions unlike scanning electron microscope providing two-dimensional information. It is also able to measure surface roughness and the size of grains. AFM is therefore a good candidate for analyzing surface structure and surface morphology of ZnO thin films used for UV lasing, waveguide, and optical applications.

2.3.4 Determination of optical properties of ZnO thin films with spectroscopic ellipsometry

Except photoluminescence spectrum, optical properties of materials also include optical constants such as refractive index (n) and extinction coefficient (k), reflectance, absorption coefficient, and dielectric function. Spectroscopic ellipsometry is a good tool to study the above properties of thin films. In this section, we review the basic of ellipsometry and what information can be extracted from ellipsometric spectra.

2.3.4.1 The physics of ellipsometry

Ellipsometry is an optical technique that relies on the optical physics of layered media. As we know, light is an electromagnetic wave and has many interesting properties. One of these properties is polarization. Ellipsometry uses polarized light for measurement. In ellipsometric experiments it is common to use the so-called p- and s- directions as the two orthogonal basis vectors to express beam polarization (Figure 2.8). The p- direction is defined as the direction lying in the plane of incidence, which contains the incident and reflected beams and the vector normal to the sample surface. The s- direction lies perpendicular to the p- direction such that the p- direction, s- direction, and direction of propagation define a right-handed Cartesian coordinate system. The electric field of incident light can be described by two components E_{ip} and E_{is} and that of the reflected light can be indicated by E_{rp} and E_{rs} . Before reflection, the E_{ip} and E_{is} components are in phase (for linearly polarized light). When polarized monochromatic light reflects off a surface, both the phase and amplitude change, depending on the optical nature of the material [43].

The quantification of the phase change of E_s relative to E_p (Δ) and the amplitude change (ψ) is measured in the ellipsometric experiment.

Figure 2.8. Representation of linear polarized light into components parallel and normal to the plane of incidence for incident and reflected light [43].

Figure 2.9. Multiple reflections of light at all interfaces on the system of single film above substrate [43].

Figure 2.9 shows multiple reflections at all the material interfaces, where additional phase and amplitude changes occur. All changes are in terms of Δ and ψ ,

and the analysis is based on the optical properties of the materials. For a bare reflecting surface, the form for Δ and Ψ is as follows:

$$\Delta = \delta r^p - \delta r^s \quad \text{and} \quad \tan \psi = |r^p| / |r^s| \quad (2.1)$$

with the complex reflection coefficient, ρ , given as

$$\rho = \tan(\psi) \exp(i\Delta) = r^p / r^s \quad (2.2)$$

where δr^p is the phase change for the p- component on reflection and similarly for the s- component as δr^s , r^p and r^s are the Fresnel coefficients that are obtained from matching the tangential E and H fields across an interface and are given as

$$r^p = E_{rp} / E_{ip} = (N_1 \cos \phi_0 - N_0 \cos \phi_1) / (N_1 \cos \phi_0 + N_0 \cos \phi_1) \quad (2.3)$$

$$r^s = E_{rs} / E_{is} = (N_0 \cos \phi_0 - N_1 \cos \phi_1) / (N_0 \cos \phi_0 + N_1 \cos \phi_1) \quad (2.4)$$

where N_0 and N_1 are the complex refractive index for air and film.

Equations (2.3) and (2.4) show that the r values are the ratio of the electric field components. Ellipsometry measures the changes in polarization of the reflected light but the absolute light intensity, it is therefore a very sensitive surface technique. For multiple layers, the output signal detected by detector is due to the contribution from all reflected beams (Figure 2.9). As a result, the complex reflection coefficient R , for a single film on substrate, is obtained from the following equations:

$$R_p = (r_{01}^p + r_{12}^p X) / (1 + r_{01}^p r_{12}^p X) \quad (2.5)$$

$$R_s = (r_{01}^s + r_{12}^s X) / (1 + r_{01}^s r_{12}^s X) \quad (2.6)$$

$$\text{where } X = \exp(-j4\pi N_1 d \cos \phi_1 / \lambda) \quad (2.7)$$

λ is the wavelength of light; r_{01}^p and r_{01}^s are the Fresnel coefficients for the p- and s-polarized lights, respectively at the interface between the air and the film; and r_{12}^p and r_{12}^s are the Fresnel coefficients for the p- and s-polarized lights, respectively at the

interface between the film and the substrate; d is thickness of film and ϕ_1 is the refractive angle at the interface between air and film.

For film covered substrate, ρ is similarly defined as in Eq. (2.2) but using R_p and R_s as

$$\rho = \tan(\psi) \exp(i\Delta) = R_p / R_s \quad (2.8)$$

In general, the fundamental equation of ellipsometry that relates the measurables with the accessible optical information is

$$\rho = \tan(\psi) \exp(i\Delta) = \rho(N_0, N_1, N_2, d, \lambda, \phi_0) \quad (2.9)$$

The middle term contains the measurables ψ and Δ and the last term on the right contains all the accessible parameters of the measurement, namely, complex optical constants, film thickness, wavelength of light, and incident angle.

2.3.4.2 What does ellipsometry measure and how can it be obtained?

Ellipsometry measures the changes in polarization state of the light reflected off the surface of a sample. The measured values are expressed as psi (ψ) and delta (Δ). As shown in Eq. (2.9), psi (ψ) and delta (Δ) are the functions of complex optical constants, film thickness, wavelength of light, and incident angle. From the measurements of ψ and Δ , values of complex optical constants N and film thickness d can be obtained. However, before one can interpret the accurately measured ψ and Δ pairs, a representative optical model is required. From the model for the system, regression analysis is used to obtain the desired parameters in the model. We will discuss the model being used for ZnO thin films in the next section.

The definition of the complex refractive index N for any pure homogeneous substance is as

$$N = n + i k \quad (2.10)$$

where n is the real part of the refractive index and k is the extinction coefficient, which relates to the absorption coefficient (α) by

$$\alpha = 4\pi k / \lambda \quad (2.11)$$

where λ is wavelength. Thus from N , we can obtain the optical absorption spectrum in terms of k , or perhaps more commonly α , as a function of incident photon energy or wavelength (λ). The relationship of photon energy and wavelength is described in Eq. (2.12).

$$E = 1.24 \times 10^{-6} / \lambda \quad (2.12)$$

where E is photon energy and its unit is eV, the unit of λ is meter.

In addition, the complex dielectric function has the following relationship with the complex refractive index N :

$$\epsilon = \epsilon_1 + i\epsilon_2 = N^2 = (n + ik)^2 \quad (2.13)$$

Therefore, we can find the relationships between the real and imaginary parts of the dielectric function and the refractive index (n) and extinction coefficient (k), as given below

$$\epsilon_1 = n^2 - k^2 \quad (2.14)$$

$$\epsilon_2 = 2nk \quad (2.15)$$

As the refractive index (n) and extinction coefficient (k) of the film are obtained from the fittings of model, the real and imaginary parts of the dielectric function of the film can be easily calculated with Eqs(2.14) and (2.15).

2.4 Optical models for ZnO thin film with ellipsometry

In ellipsometric study, the two measurables are ψ and Δ , which are functions of optical constants, film thickness, incident angle, and wavelength of light as described in Eq. (2.9). In order to extract useful parameters, the optical system being investigated (a bare reflecting surface or film covered surface; a homogeneous or inhomogeneous; etc) needs to be approximated. From this approximation or model for the system, an algorithm can be used to invert Eq. (2.9) to obtain the desired parameters in the model such as film thickness, optical constants, and other model-dependent variables. In other words, we find a set of the variable parameters which yields calculated data very closely matching our measured optical data such as ψ and Δ in this case. If the best-fit set of parameters is unique, physically reasonable, and not strongly correlated, we can conclude that the best-fit model probably represents the physical reality of the sample reasonably well.

There have been various studies of the optical properties of ZnO crystal and films [51 - 54]. Recently, Washington et al. [55], Rebien et al. [56], and Sun et al. [17] tried to determine the optical constants of ZnO films with different approaches. Washington et al. and Sun et al. assumed that the extinction coefficient (k) of ZnO thin film is zero at photon energies below the band gap, and then used a three-phase Sellmeier dispersion model to fit for extraction of optical constants and thickness of ZnO films. In reference [55], we can see that the fittings of $\tan \psi$ and $\cos \Delta$ for the photon energies below 3.26 eV do not agree with the experimental data very well especially in the range close to band edge 3.3eV (Figure 2.10). Washington et al. also

used two-phase direct model to compute the dielectric constants above energy band gap. They then plotted the dielectric constants obtained from Sellmeier model and two-phase model together to represent dielectric constants as a function of photon energy below and above energy band gap (Figure 2.11). We can notice from Figure 2.11 that the changes of ϵ_1 and ϵ_2 at the energy band edge are discrete and abrupt and ϵ_2 is zero below the band gap, which corresponds to zero extinction coefficient. However, the sub-band gap absorption near the fundamental absorption edge (3.3 eV) may not be neglected due to excitonic effects [1,57 - 59]. It is shown that the extinction coefficient is ~ 0.1 at 3.2 eV [56]. This indicates that the sub-band gap absorption is still significant. A neglect of the absorption may lead to a large error in the determination of the refractive index and the thin film thickness from ellipsometry. Sun et al. also demonstrated refractive index and extinction coefficient in the wavelength range of 350 – 1000 nm only and that extinction coefficient (k) is zero below energy band edge (Figure 2.12).

Figure 2.10. Experimental data for $\tan \psi$ and $\cos \Delta$ shown as solid line. Below the band gap, interference oscillations due to multiple internal reflections are observed. The best fit using Sellmeier model is represented as diamond symbol [55].

Figure 2.11. The complex pseudo dielectric functions derived from three-phase Sellmeier model with $k = 0$ below 3.26 eV and two-phase direct computation above 3.26 eV [55].

Figure 2.12. Refractive index and extinction coefficient of ZnO film on sapphire as a function of wavelength [17].

Rebien et al. [56] studied the optical properties of ZnO thin films prepared by ion layer reaction and RF magnetron sputtering techniques. They conducted spectroscopic ellipsometry (SE) measurements from 0.75 to 4.5 eV at incident angles of 55° , 65° , and 75° and used spectral point-by-point fit to extract refractive index and extinction coefficient below and above energy band gap as well as film thickness and surface roughness. They observed that there was an exponential absorption tail in the spectrum of extinction coefficient. Figure 2.13 demonstrated the refractive index and extinction coefficient of ZnO film deposited by RF sputtering, as a function of photon energy obtained by Rebien et al. As there is no information about the quality and details of their ellipsometric spectra (ψ and Δ) fittings, it is hard to justify whether their result is accurate enough because different approaches could have some difference in the fitting results.

Figure 2.13. Optical functions of sputtered ZnO film by Rebien et al. [56] and those obtained by other research groups.

The above-mentioned models are empirical and mathematical expressions. From the analysis of electron transitions, Forouhi and Bloomer published a formulation of the optical function of amorphous semiconductors and insulators [61], and later, using the same formalism, extended their work to crystalline semiconductors [62]. They obtained an expression for the refractive index and the extinction coefficient. This model is a physics-based model in which the extinction coefficient is obtained from electron transition between two energy states and the refractive index is then derived from the Kramers-Kronig relation. The model can be used for the spectral ranges of both below and above the band gap. Forouhi and Bloomer have used these equations to determine the $n(E)$ and $k(E)$ spectra for crystalline Si, Ge, GaP, GaAs, GaSb, InP, InAs, InSb, SiC, cubic C, and $\alpha\text{-SiO}_2$ over a wide range of energies ($\sim 0 - 20$ eV). ZnO is II-VI compound crystalline semiconductor and Forouhi and Bloomer model should be able to apply to ZnO for determination of its optical constants but there is no such work reported.

2.5 Summary

ZnO is one of the most promising materials for the fabrication of next-generation optoelectronic devices in the UV region and optical or display devices. It can be fabricated by various techniques such as molecular beam epitaxy, magnetron sputtering, pulsed laser deposition, filtered cathodic vacuum arc, etc. Characterization of ZnO thin films is important for the evaluation of the film quality, control of process, design for applications, and for understanding the mechanism of the devices. Precise knowledge of the optical properties of the material is critical for designing optoelectronic and optical devices. Spectroscopic ellipsometry is a good tool to

determine the optical properties of materials. An applicable optical model is required for the extraction of the desired parameters from ellipsometric spectra. Establishment of an appropriate model is critical to obtain accurate parameters such as optical constants, dielectric function, reflectance, absorption coefficient, and film thickness. The research reported in this aspect was not much. The assumption stating that the extinction coefficient (k) of ZnO thin film is zero for photon energies below the band gap by Washington et al. and Sun et al. is questionable because sub-band gap absorption may not be neglected due to excitonic effects. The results obtained by Rebien et al. are hard to be justified, as there is no information about the quality and details of their ellipsometric spectral (ψ and Δ) fittings. Investigation of the application of Forouhi and Bloomer model for ZnO thin film is needed as mentioned in section 2.4. In addition, study of surface morphology and surface structure are important for UV lasing, waveguide, and optical applications. Therefore, development and evaluation of a non-destructive methodology to extract optical constants, dielectric function, reflectance, absorption coefficient and film thickness, to measure surface roughness, grain size and size distribution, and to study the effects of annealing on the above properties of ZnO thin films is essential.

Chapter 3 Experiment and Methodology

3.1 Preparation of ZnO thin films

In this project, we employed filtered cathodic vacuum arc (FCVA) technique to prepare high quality ZnO thin films. Before deposition, n-type (100) silicon substrate was cleaned ultrasonically using acetone, methanol and de-ionized water, subsequently blown by nitrogen gas. A schematic diagram of the vacuum arc apparatus for ZnO deposition used in this project is shown in Figure 3.1. The cathode was a 99.99% purity zinc target with a diameter of 60 mm mounted onto a water-cooled copper plate. The off-plane double-bend (OPDB) filter was inserted between the plasma source and the main chamber to remove effectively the macro-particles produced in the cathodic arc plasma. An arc current of approximately 15 mA was used and the oxygen partial pressure during the deposition was about 2×10^{-4} Torr. The temperature of substrate was controlled at 230°C. During the deposition, a bias of 0 V was applied to the substrate. The thickness of the films was 200 – 400 nm. After deposition of ZnO thin films, samples were put into a furnace for annealing. Firstly, the samples inside the furnace were heated up from room temperature to 900 °C within 20 minutes. Then, the samples were annealed for a period of time (t_a) at a constant temperature of 900°C. Finally, the samples were cooled down to room temperature inside the furnace. This annealing process was used to minimize the build-up of thermal strain and stress at the interface of ZnO / Si.

Figure 3.1. A filtered cathodic vacuum arc system [23]

3.2 Study of crystalline structure of ZnO thin films with XRD

Fundamentally, X-rays are a portion of the electromagnetic spectrum having wavelengths from 10^{-10} to 10^{-8} m (1 to 100 Å), but only 0.3 to 2.5 Å is used for x-ray diffraction. As electromagnetic radiation, x-rays have wave and particle properties. Derivation of all angle dependent phenomena, such as diffraction, is based on their wave characteristics.

Basically, x-ray diffraction is a phenomenon of electromagnetic radiation scattered from a periodic arrangement of scattering centers that has the spacing of the same order of magnitude as the wavelength of the radiation. Interference of the scattered rays in most directions results in cancellation and absence of detectable

beams. However, in a few selected directions, reinforcement of all the scattered rays occurs, and a strong beam results. Figure 3.2 illustrates the diffraction occurring on a single crystal with inter-planar spacing of d_{hkl} . The lattice is considered to be planes of lattice points, and x-ray beam acts as if it reflects off these planes. Constructive interference occurs only when incident angle and diffraction angle (θ) satisfy Bragg's law (Eq. 3.1). In other words, a diffraction spot will occur only when the diffracted waves interfere in a constructive fashion, that is, when the phase of the bottom wave lags the top wave by 360° (2π radians).

$$n\lambda = 2d_{hkl} \sin \theta \quad (3.1)$$

where d_{hkl} is the perpendicular spacing between the lattice planes, λ is the wavelength of radiation, n is integer, and θ is diffraction angle.

Figure 3.2. Basic principle of single crystal diffraction

The intensity of the diffraction peaks is measured as a function of the diffraction angle (2θ) and depends on the preferred orientation of specimen and the atomic types and distribution. The diffraction peak corresponds to specific crystal plane in the crystal lattice. The diffraction pattern is used to identify the phases present in the samples and provide information on the physical state of the sample, such as grain size, texture, and crystal perfection. Most x-ray diffraction techniques are rapid and non-destructive.

Philips X' Pert x-ray diffractometer was employed to study the crystalline structure of ZnO thin films in this project. Figure 3.3 shows the diagram of the instrument. The anode target of the x-ray tube was copper. The x-ray was $\text{Cu K}_{\alpha 1}$ and $\text{K}_{\alpha 2}$ radiations with wavelengths of $1.54056 \text{ \AA}$ and $1.54439 \text{ \AA}$. The high tension and current were set to 40 kV and 30 mA, respectively. θ - 2θ scanning mode was used to characterize the phase and crystallographic structure. The divergence slit of 1° , beam mark of 10, and the anti-scatter slit of $1''$ were chosen for θ - 2θ scan. The ZnO thin films as-deposited, annealed at 900°C for 10 seconds, 2 minutes, 10 minutes, 30 minutes, and 60 minutes were scanned and the dominant peak at 34.4° for ZnO thin films was observed. Figure 3.4 shows the XRD spectrum of the as-deposited ZnO thin film. The spectra for other samples are similar to that of the as-deposited sample. Therefore, the ZnO thin films were (002) hexagonal structure.

Figure 3.3. Philips X' Pert x-ray diffractometer was employed to study the crystalline structure of ZnO thin films.

Figure 3.4. XRD spectrum of the as-deposited ZnO thin film shows that the dominant peak was at 34.4°.

3.3 Study of surface morphology with AFM

Basically, AFM probes the surface of a sample with a sharp tip less than 100 nm in diameter, forces between the tip and sample surface cause the cantilever to bend or deflect, measurements of cantilever deflections allow a computer to generate a map of surface topography. AFM has three types of operation modes, namely, contact mode AFM, tapping mode AFM, and non-contact mode AFM. Tapping mode AFM operates by scanning a tip attached to the end of an oscillating cantilever across the sample surface. Figure 3.5 illustrates the configuration of the control loop of tapping mode AFM. The cantilever is oscillated at or near its resonance frequency with amplitude ranging typically from 20 nm to 100 nm. The tip lightly “taps” on the sample surface during scanning, contacting the surface at the bottom of its swing. The laser light emitted from a solid state diode is reflected off the back of cantilever and collected by a position sensitive detector (PSD) consisting of two closely photodiodes whose output signal is collected by a differential amplifier (Figure 3.6). The feedback loop maintains a constant oscillation amplitude of cantilever by maintaining a constant RMS of the oscillation signal acquired by the split photodiode detector. The vertical position of the scanner at each (x, y) data point in order to maintain a constant “setpoint” amplitude is stored by the computer to form the topographic image of the sample surface. By maintaining a constant oscillation amplitude, a constant tip-sample interaction is maintained during imaging.

Figure 3.5. The configuration of tapping mode AFM [64].

Figure 3.6. The detection of beam deflection by split photodiode detector [64].

Comparing with other AFM operation modes, tapping AFM has advantages of higher lateral resolution on most samples (5 nm to 10 nm), lower forces and less damage on the sample, and lateral forces eliminated. Therefore, tapping mode AFM (Digital Instruments Scanning Probe Microscope Dimension 3000) was used to study the surface morphology and measure the grain size of ZnO thin films in this project. Before scanning, the samples were cleaned by blowing with nitrogen gas. Single crystal silicon probes produced by etching techniques were used for the measurement. The nominal tip radius of curvature was 5 – 10 nm. The spring constant was 20 – 100 N/m and resonant frequency was 200 – 400 kHz. The length of cantilever was 125 μm and the cantilever is uncoated. The probe was mounted into the cantilever holder and subsequently installed onto SPM scanner. The laser light emitted from solid state diode was aligned onto the back of cantilever by adjusting the laser aiming screws and the laser light reflected off the back of cantilever was moved to the center of the detector by adjusting mirror adjustment screws (Figure 3.7). The cantilever was tuned to find its resonant frequency before scanning. The scan area was set to 1 μm x 1 μm and the scan speed was 1 Hz. One image consisted of 512 lines. The setpoint was set to 1 - 2 V and the proportional gain and integral gain were within the range of 0.3 to 0.8 to ensure that the tip tracked the sample surface properly but without feedback oscillation introduced in the scan. Height image and phase image were captured for studying surface morphology and surface structure of ZnO thin films. In addition, AFM was also employed to measure the thickness of ZnO film for the as-deposited sample to verify the appropriateness of the optical model developed for extraction of optical properties and thickness of ZnO thin film described in Chapter 4.

Figure 3.7. Schematic diagram of AFM scanner [64].

3.4 Experiment with spectroscopic ellipsometer

As mentioned in Chapter 2, characterization of optical properties of ZnO thin films is critical for optoelectronic and optical devices. Spectroscopic ellipsometer (SE) is a non-destructive and accurate tool to extract optical properties of thin films when an appropriate optical model is utilized. Chapter 2 has depicted the basic principle of ellipsometry and therefore we will not repeat it in this section. J. A. Woollam Co., Inc. VASE spectroscopic ellipsometer was employed to study the optical properties of ZnO thin films in this project. The system of the ellipsometer is demonstrated in Figure 3.8 and the schematic diagram of the system is shown in Figure 3.9. The system consists of light source (Xenon arc lamp), polarizer, sample stage, continuously rotating analyzer, and silicon photodiode detector. Optical fiber is

used to couple the light beam from the output of light source to the input of polarizer. Polarizer converts light with any polarization state into linearly polarized light oriented along the transmitting axis. The linearly polarized light illuminates onto the sample and reflected off the sample. The polarization state of the reflected beam was measured by the combination of rotating analyzer and detector. The range of the goniometer attached to this SE is $0^\circ - 90^\circ$ and the incident angle was set to 70° and 75° in this study. The spectral wavelength range was from 250 nm to 1100 nm (ultraviolet – near infrared) with a step of 5 nm. Before measurement, a clean bare silicon wafer was used to calibrate the system. For the calibration and spectroscopic scan, a silicon alignment detector was used to align the sample. The system measures the spectra of Ψ and Δ as functions of wavelength.

Figure 3.8. The system of J. A. Woollam Co., Inc. spectroscopic ellipsometer.

Figure 3.9. The schematic diagram of the J. A. Woollam Co., Inc. variable angle of incident spectroscopic ellipsometer (VASE).

3.5 Simulation

In Sections 2.3.4 and 2.4, we have described the physical principle of ellipsometry and listed a series of equations for ellipsometric study. As mentioned in these two sections, ellipsometry measures the changes in polarization state of the light reflected off the surface of a sample. The measured values are psi (ψ) and delta (Δ) as functions of wavelength (λ). As shown in Eq. (2.9), psi (ψ) and delta (Δ) are functions of complex optical constants, film thickness, wavelength of light, and incident angle. We duplicate this equation below for easy reference.

$$\rho = \tan(\psi) \exp(i\Delta) = \rho(N_0, N_1, N_2, d, \lambda, \phi_0) \quad (2.9)$$

In this project, ZnO thin film was deposited on silicon wafer. Therefore N_0 , N_1 , and N_2 are the complex refractive indexes of air, ZnO thin film, and silicon substrate, respectively, while d is the thickness of ZnO thin film, and λ and ϕ_0 are wavelength and incident angle of light. N_0 , N_2 , λ and ϕ_0 are known variables. From measurements of ψ and Δ , values for complex refractive index N_1 and film thickness d can be obtained if the optical system being investigated is approximated and proper optical dispersion model is utilized. In other words, N_1 can be described as a function of λ and there are a few parameters in the dispersion model. Several dispersion models, namely: Sellmeier dispersion model, Cauchy mathematical expression, and Forouhi-Bloomer model, were investigated in this study. As an example, we provide some discussions for Sellmeier model here. In Sellmeier model, extinction coefficient (k) is zero, and the refractive index (n) is given by Eq. (3.1), in which A and B are the fitting parameters.

$$n^2(\lambda) = 1 + A\lambda^2 / (\lambda^2 - B^2) \quad (3.1)$$

We find a set of the variable parameters (A , B , and d in Sellmeier dispersion model) which yields calculated ψ and Δ very closely matching our measured ψ and Δ . To realize this purpose, we defined an error function as indicated in Eq. (3.2) to represent the quality of the match between the data calculated from the model and the experimental data, and used a program written with MATLAB to search a set of variable parameters so as to obtain a minimum error function such that the calculated ψ and Δ were very closely matching our measured ψ and Δ . During this process, a set of variable parameters with proper values can be obtained so that the complex

refractive index and thickness can be extracted. The error function used in this study is as below:

$$f = \sum_{i=1}^N [(\tan \psi_{\text{exp}} \cos \Delta_{\text{exp}} - \text{real } \rho_{\text{cal}})^2 + (\tan \psi_{\text{exp}} \sin \Delta_{\text{exp}} - \text{Im } \rho_{\text{cal}})^2]^{1/2} \quad (3.2)$$

where N is the number of (ψ, Δ) pairs.

MATLAB (Matrix Laboratory) is a high-performance language for technical computing. It integrates computation, visualization, and programming in an easy-to-use environment where problems and solutions are expressed in familiar mathematical notation. Typical uses include math and computation, algorithm development, data acquisition, modeling, simulation, prototyping, data analysis, exploration, visualization, scientific and engineering graphics. Minimization function, i.e., **fminsearch**, was used in this project. The algorithm is shown in Figure 3.10. The MATLAB programs written for this project based on Sellmeier model are attached in appendix I - IV. The programs for other models are very similar to that for Sellmeier model so they are not shown in this thesis.

Figure 3.10. The algorithm used for regression analysis of ellipsometric data with optical models.

Chapter 4 Determination of Optical Constants of ZnO Thin Films for Photon Energies below the Band Gap

4.1 Introduction

As mentioned in Chapters 1 and 2, Zinc oxide (ZnO) is a multifunctional semiconductor material that has been used in various areas. With a wide band gap ($E_g = 3.3$ eV) ZnO is a promising material for short-wavelength light-emitting devices and daylight-blind *UV* detectors [13, 45]. Since it has a high transmittance in the visible region and low electrical resistivity, ZnO film is an ideal window material for solar cell and flat panel displays [46]. Recently, a transparent light-emitting diode [47] as well as room temperature lasing [48 - 50] have been demonstrated. It seems that ZnO is getting more and more attention in optoelectronic and optical applications. It is known that precise knowledge of the optical properties of the material is critical for designing optoelectronic and optical devices.

There have been various studies of the optical properties of ZnO crystal and films [51 - 54]. Recently, Washington et al. [55] and Rebien et al. [56] tried to determine the optical constants of ZnO films with different approaches. However, for ZnO thin films, there are large discrepancies in the optical constants among various studies. One of the reasons is that the thin film structures (such as film density) may be different in different studies with different thin film deposition techniques or different thin film deposition conditions. However, the biggest issue is that the approaches used for the determination of the optical constants of the ZnO thin films

from spectroscopic ellipsometry were not carefully justified in these studies. For example, in ref. [55], to determine the optical constants of the ZnO thin films for photon energies below the band gap, it is assumed that the extinction coefficient (k) of the ZnO thin film is zero, and then a three-phase Sellmeier dispersion model is used to fit the ellipsometric spectra for determining the refractive index (n) and the thickness (d) of ZnO films. However, the sub-band gap absorption at the fundamental absorption edge (-3.3 eV) may not be neglected due to excitonic effects [1, 57-59, 63]. It is shown that the extinction coefficient is ~ 0.1 at 3.2 eV [56]. This indicates that the sub-band gap absorption is still significant. A neglect of the absorption may lead to a large error in the determination of the refractive index and the thin film thickness from ellipsometry. The following is another example of improper use of optical model in the ellipsometric analysis of ZnO films. In ref. [66], two-phase model is used to fit the ellipsometric spectra to obtain dielectric functions and refractive index of ZnO thin films in a wide spectral range (1.5 eV - 5.5 eV). Such an approach is questionable. ZnO thin films are transparent for the spectral range below the band gap (-3.3 eV). However, two-phase model assumes that the thin film is infinite and all the light is absorbed within the film. Therefore two-phase model is invalid for ZnO thin films in the spectral range below the band gap. The application of invalid model may lead to a large error in the extraction of dielectric functions and refractive index. This can be observed from the oscillation of dielectric functions and refractive index for the photon energies below band gap as shown in ref.[66].

In this chapter, a systematic investigation on the determination of the optical constants of ZnO thin films for the photon energies below the band gap with various models, namely, the Sellmeier dispersion model [55, 60], Cauchy model [42] and

Forouhi-Bloomer model [61, 62], is presented. The Sellmeier dispersion model and Cauchy model are empirical models. The former assumes the extinction coefficient (k) as zero while the latter assumes an exponential absorption tail at the absorption edge. In contrast, Forouhi-Bloomer model is a physics-based model in which the extinction coefficient is obtained from electron transition between two energy states.

4.2 Ellipsometric model and analysis

For ZnO thin films deposited on Si substrate, as the photon energies used in the present ellipsometric study is bigger than the silicon band gap (1.1 eV), the Si substrate, which is $\sim 1\text{mm}$, can be treated as infinite. Therefore, the material system in this study can be described with a three-phase model, i.e., air/ZnO film/Si substrate for the ellipsometric study, as shown in Figure 4.1. Each phase is characterized by its complex refractive index, $N_i (= n_i + jk_i, i = 0, 1, 2$, where n is the refractive index and k is the extinction coefficient) in ellipsometric analysis. Note that $N_0 = 1$ for air and $N_2 = N_{\text{Si}}$ (i.e., Si complex refractive index, which is known) for the Si substrate. Our task is to determine the complex refractive index (i.e., $N_1 = n_{\text{ZnO}} + jk_{\text{ZnO}}$) and thickness (d) of the ZnO thin films from ellipsometric analysis. For easy reference, the relevant formulas of the three-phase model in Chapter 2 are duplicated in this section.

Figure 4.1. Three-phase model.

The ratio ρ of the complex reflection coefficients (R_p and R_s) of the p- and s-polarized lights for the system is given by

$$\rho = R_p / R_s = \tan(\psi) \exp(j\Delta) \quad (2.8)$$

where ψ and Δ are the ellipsometric angles. For the three-phase system shown in Fig.4.1, the complex reflection coefficients (R_p and R_s) can be described as

$$R_p = (r_{01}^p + r_{12}^p X) / (1 + r_{01}^p r_{12}^p X) \quad (2.5)$$

$$R_s = (r_{01}^s + r_{12}^s X) / (1 + r_{01}^s r_{12}^s X) \quad (2.6)$$

$$\text{where } X = \exp(-j4\pi N_1 d \cos\phi_1 / \lambda) \quad (2.7)$$

λ is the wavelength of light; r_{01}^p and r_{01}^s are the complex Fresnel reflection coefficients for the p- and s-polarized lights, respectively at the interface between the air and the ZnO film; and r_{12}^p and r_{12}^s are the complex Fresnel reflection coefficients for the p- and s-polarized lights, respectively at the interface between the ZnO film and the Si substrate. The Fresnel Coefficients are given by

$$r_{01}^p = (N_1 \cos\phi_0 - N_0 \cos\phi_1) / (N_1 \cos\phi_0 + N_0 \cos\phi_1) \quad (4.1)$$

$$r_{12}^p = (N_2 \cos\phi_1 - N_1 \cos\phi_2) / (N_2 \cos\phi_1 + N_1 \cos\phi_2) \quad (4.2)$$

$$r_{01}^s = (N_0 \cos\phi_0 - N_1 \cos\phi_1) / (N_0 \cos\phi_0 + N_1 \cos\phi_1) \quad (4.3)$$

$$r_{12}^s = (N_1 \cos\phi_1 - N_2 \cos\phi_2) / (N_1 \cos\phi_1 + N_2 \cos\phi_2) \quad (4.4)$$

The angles ϕ_i ($i=0, 1$, and 2) are related by the Snell's law

$$N_0 \sin\phi_0 = N_1 \sin\phi_1 = N_2 \sin\phi_2 \quad (4.5)$$

The parameters in the above equations are complex numbers.

By using a dispersion model and assuming the ZnO film's extinction coefficient $k = 0$ or an exponential absorption tail at the absorption edge, one can

determine the optical constants (refractive index n and extinction coefficient k) of the ZnO film for the photon energies below the ZnO band gap (~ 3.3 eV) and the ZnO film thickness d as well from a spectral fitting (best fitting) based on the above equations with wavelengths longer than the absorption edge (~ 375 nm). In the following sections, the spectral fittings with various dispersion models are discussed, and a comparison among the models is given.

4.3 Sellmeier dispersion model

Sellmeier dispersion model [55, 60] is an empirical model and is the most commonly used to describe the spectral dependence of the refractive index (n) in the transparent region below the band gap. In this model, the extinction coefficient (k) is assumed to be zero, and the refractive index n is given by

$$n^2(\lambda) = 1 + A\lambda^2 / (\lambda^2 - B^2) \quad (3.1)$$

where A and B are the fitting parameters.

The spectral fittings with the above model for different samples of ZnO thin films deposited on Si substrate with different annealing condition have been carried out. In the following discussions, the fittings with the sample annealed at 900°C for 3 hours is firstly examined and then the un-annealed sample is studied. The un-annealed sample is defined as Sample A and the sample annealed at 900°C for 3 hours is defined as Sample B for easy reference in the following section. Figure 4.2 shows the best fittings of the ψ and Δ in the wavelength range of $375 - 1100\text{nm}$ for the annealed sample (Sample B). The fitting yields $A = 2.431$, $B = 219.7$ nm and the ZnO film

thickness $d = 318.2\text{ nm}$. The refractive index (n) of the ZnO film obtained from the fitting is shown in Figure 4.3.

Figure 4.2. Comparison of Ψ and Δ between experiment and model; calculation based on the Sellmeier model for the sample annealed at 900°C for 3 hours.

Figure 4.3. Refractive index (n) of the ZnO film obtained from the fittings shown in Figure 4.2.

As can be seen in Figure 4.2, all the spectral features and structures can be fitted. But there are still some departures. We thought that the departures may be due to the existence of a native silicon oxide on the Si surface or a very thin SiO_2 layer grown on the Si substrate during the annealing of the ZnO film. To check the influence of this silicon oxide layer at the interface between the ZnO film and the Si substrate, the four-phase model depicted in Figure 4.4 is used in the ellipsometric fittings. As a SiO_2 layer is added in the ellipsometric calculation, Eqs. (2.5) - (2.7) and Eqs. (4.1) - (4.5) should be modified. However, the calculation procedure is very similar to that using the three-phase model, and therefore the details are not given here. It is worth mentioning that in the spectral fittings the refractive index of SiO_2 is known and the extinction coefficient of SiO_2 is zero.

Figure 4.4. Four-phase model with a very thin SiO_2 layer at the interface.

The influence of the thickness (d_{SiO_2}) of the SiO_2 layer on the spectral fittings has been studied. To describe the quality of a fitting, we use the arithmetic mean ($\bar{S}$)

of the sum of absolute deviations of the calculated Ψ and Δ from the measured ones over the spectral range as given below

$$\bar{S} = \frac{1}{N} \sum [|\psi_{\text{cal}}(\lambda_i) - \psi_{\text{exp}}(\lambda_i)| + |\Delta_{\text{cal}}(\lambda_i) - \Delta_{\text{exp}}(\lambda_i)|] \quad (4.6)$$

where N is the number of the experimental (Ψ , Δ) pairs, $\psi_{\text{cal}}(\lambda_i)$ and $\psi_{\text{exp}}(\lambda_i)$ are the calculated and measured values of ψ at each wavelength (λ_i), respectively, and $\Delta_{\text{cal}}(\lambda_i)$ and $\Delta_{\text{exp}}(\lambda_i)$ are the calculated and measured values of A at the same wavelength, respectively. For the $d_{\text{SiO}_2} < 2$ nm, the introduction of the SiO_2 layer has little impact on the fitting; however, the introduction of the SiO_2 layer with $d_{\text{SiO}_2} > 2$ nm makes the fitting worse (one example with $d_{\text{SiO}_2} = 2.5$ nm is shown in Figure 4.5). This indicates that the thickness of the SiO_2 layer cannot be larger than 2 nm.

Figure 4.5. Worse of the spectral fitting due to the introduction of SiO_2 layer with $d_{\text{SiO}_2} = 2.5$ nm.

The $\bar{S}$ as a function of d_{SiO_2} is shown in Figure 4.6. As can be seen in this figure, the value of $\bar{S}$ is at its minimum when $d_{\text{SiO}_2} = \sim 1.5$ nm. This suggests that there may be a SiO_2 layer with a thickness of ~ 1.5 nm at the interface. It is worth pointing out that a native oxide on Si surface is usually less than 1 nm. The slightly thicker SiO_2 layer may be due to the Si oxidation during annealing as the oxygen residual may diffuse into the interface. Figure 4.7 shows that the introduction of the 1.5 nm SiO_2 layer has only a slight influence on the refractive index of the ZnO film as obtained from the spectral fitting (i.e., a small reduction of 0.06 – 0.07 in the refractive index over the spectral range). Therefore, in the following studies, it is not necessary to consider the influence of the SiO_2 layer.

Figure 4.6. Influence of d_{SiO_2} on the $\bar{S}$

Figure 4.7. Influence of the SiO₂ layer with $d_{\text{SiO}_2} = 1.5 \text{ nm}$ on the calculation of the refractive index (n) of the ZnO film.

Figure 4.8 shows the spectral fittings for the un-annealed sample (Sample A) without considering the SiO₂ layer (i.e., $d_{\text{SiO}_2} = 0$), and the refractive index of the ZnO film is shown in Figure 4.9 (the solid line). The fitting yields $A = 2.612$, $B = 224.627 \text{ nm}$ and the ZnO film thickness $d = 296.6 \text{ nm}$. The influence of the interface layer for the un-annealed sample has also been examined. Figure 4.10 shows the influence of the d_{SiO_2} on the $\bar{S}$. This figure suggests that the SiO₂ layer should be less than 0.7 nm. The refractive index of the ZnO film obtained from the spectral fitting with $d_{\text{SiO}_2} = 8.7 \text{ nm}$ is shown in Figure 4.9 (the circular symbols). As can be seen in this figure, the interface layer has no significant influence on the determination of the refractive index. Therefore, in the discussions of the following sections and chapters, we will not consider the influence of the interface layer.

Figure 4.8. Spectral fitting for the un-annealed sample with $d_{\text{SiO}_2} = 0$.

Figure 4.9. Refractive index of ZnO film of the un-annealed sample obtained from the spectral fittings with $d_{\text{SiO}_2} = 0$ (the line) and $d_{\text{SiO}_2} = 0.7 \text{ nm}$ (the circular symbols).

Figure 4.10. Influence of d_{SiO_2} on $\bar{S}$ for the un-annealed sample.

4.4 Cauchy model

In the Cauchy model [42], over part of the spectral range for many materials (dielectrics, semiconductors, and non-metals), the refractive index (n) and extinction coefficient (k) can be described by a slowly varying function of wavelength (λ) and an exponential absorption tail, respectively:

$$n(\lambda) = A + B/\lambda^2 + C/\lambda^4 \quad (4.7)$$

$$k(\lambda) = \sigma \exp \{ \beta [12400(1/\lambda - 1/\gamma)] \} \quad (4.8)$$

The six fitting parameters in the model are A , B , C , the extinction coefficient amplitude σ , the exponent factor β , and the band edge γ . It is an empirical model. This model should be particularly useful for ZnO thin films as its exponential absorption tail can describe the sub-gap absorption well at the band gap edge due to the excitonic absorption.

The sample A (the un-annealed sample) is used to investigate the quality of the spectral fittings with the Cauchy model. As discussed in section 4.3, the interface layer has no significant influence on the fittings, it is therefore not considered here. The fitting yields $A = 1.8982$, $B = 0.0035546 \text{ (nm}^2\text{)}$, $C = 0.0070677 \text{ (nm}^4\text{)}$, $\sigma = 0.14775$, $\beta = 8.612$, and the ZnO film thickness $d = 305.5 \text{ nm}$ with the fixed band edge $\gamma = 375 \text{ nm}$. The spectral fitting with the Cauchy model is shown in Figure 4.11. The refractive index and the extinction coefficient of the ZnO film are shown in Figure 4.12 and Figure 4.13, respectively. A comparison between the Sellmeier model and the Cauchy model will be given in Section 4.6.

Figure 4.1 1. Spectral fitting with the Cauchy model for the un-annealed sample that is the same as the one of Figure 4.8 in Section 4.3.

Figure 4.12. Refractive index (n) of the ZnO film of the un-annealed sample obtained with Cauchy model.

Figure 4.13. Extinction coefficient (k) of the ZnO film of the un-annealed sample obtained with Cauchy model.

As shown in Figure 4.13, an absorption tail extended from the band edge (375 nm or ~ 3.31 eV) to a wavelength of ~ 410 nm (or ~ 3.02 eV) can be seen. The absorption tail could be due to the excitonic effect or electron transitions between the valence band (and or conduction band) and shallow defect/impurity energy levels within the band gap. The details are not known yet. On the other hand, as the sub-band gap absorption has been considered in the Cauchy model, the quality of the spectral fitting with the Cauchy model is better than that with the Sellmeier model (in particular, a significant improvement is reached for the fitting of ψ). This is evident from the comparison between Figure 4.8 and Figure 4.11.

4.5 Forouhi-Bloomer model

From the analysis of electron transitions, Forouhi and Bloomer published a formulation of the optical functions of amorphous semiconductors and insulators [61], and later, using the same formalism, extended their work to crystalline semiconductors [62]. They obtained an expression for the refractive index and the extinction coefficient, given by

$$n(E) = n(\infty) + (HE + I)/(E^2 - BE + C) \quad (4.9)$$

$$k(E) = A(E - E_g)^2 / (E^2 - BE + C) \quad (4.10)$$

where $H = (A/Q)[-B^2/2 + E_g B - E_g^2 + C]$ (4.11)

$$I = (A/Q)[(E_g^2 + C)B/2 - 2E_g C] \quad (4.12)$$

$$Q = (1/2)(4C - B^2)^{1/2} \quad (4.13)$$

A , B , C , E , and $n(\infty)$ are treated as fitting parameters. E_g represents the band gap, while $n(\infty)$ is the refractive index when the photon energy $E = \infty$. This model has been used for the spectral ranges of both below and above the band gap. In the following, we can see that the model can fit the experimental data reasonably well in the spectral range below the band gap. However, in the spectral range above the band gap, this model is not able to give a reasonable fitting, which could be due to the complexity of the band structures.

Figure 4.14 shows the spectral fitting with the Forouhi-Bloomer model for the same un-annealed sample (Sample A) as in Section 4.3 (Figure 4.8) and Section 4.4 (Figure 4.11). The fitting yields $A = 1.18 \times 10^{-3}$, $B = 8.80$, $C = 19.38$, $n(\infty) = 1.67$, the ZnO film thickness $d = 316.0$ nm with fixed ZnO band gap $E_g = 3.30$ eV. The d value

is comparable with those obtained with the Sellmeier model and the Cauchy model with a difference less than 10 nm. As can be seen in Figure 4.14, Forouhi-Bloomer model is able to describe the experimental result reasonably well. The refractive index of the ZnO film is shown in Figure 4.15. The refractive index is smaller than those obtained with the Sellmeier model and the Cauchy model. The detail will be discussed in Section 4.6. The extinction coefficient obtained from the Forouhi-Bloomer model is shown in Figure 4.16. The extinction coefficient obtained is less than 0.001 in the whole spectral range of 375 – 1100 nm, indicating that the ZnO film is transparent in this spectral range.

Figure 4.14. Spectral fitting with the Forouhi-Bloomer model for the same sample (Sample A) used in Figure 4.8 and Figure 4.11.

Figure 4.15. Refractive index of ZnO film obtained from the fitting shown in Figure 4.14.

Figure 4.16. Extinction coefficient of the ZnO film obtained from the fitting shown in Figure 4.14.

4.6 Comparison among the models

In order to make an easy comparison of their performance, the above spectral fittings with the Sellmeier model, Cauchy model and Forouhi-Bloomer model for the un-annealed sample are compiled in Figure 4.17.

Figure 4.17. Comparison of the spectral fittings among the three models.

It is evident from Figure 4.17 that the quality of the match between the data calculated from the Cauchy model and the experimental data is the best among the three models. In particular, the Cauchy model can describe well the spectral behaviors of ψ and Δ near the band edge (i.e., the wavelength range of 375 - 410 nm). This could be attributed to the fact that the exponential absorption tail in the Cauchy model can describe properly the sub-band gap absorption near the band edge. The superiority of the Cauchy model is also evident from the comparison of the $\bar{S}$ value among the models in Table 4.1 (note that a smaller $\bar{S}$ means a better spectral fitting). Therefore, in Chapters 5 and 6, all the data analysis and discussions are based on Cauchy model.

Table 4.1. Comparison of $\bar{S}$ and d among the models for the un-annealed sample.

Model	Sellmeier model	Cauchy model	Forouhi-Bloomer model
$\bar{S}$	7.44	4.50	6.80
d (nm)	296.6	305.5	316.0

The ZnO film thickness (d) of the un-annealed sample obtained with the three models is shown in Table 4.1. The difference in the d value among the models is less than 10 nm (or 3%) with the mean d value of 306.0 nm. The thickness of the un-annealed sample was 309.9 nm as measured by AFM (Figure 4.18), which is very similar to that obtained from Cauchy model. These comparable results support strongly that the spectral fitting with Cauchy model is accurate and reliable.

Figure 4.18 (a). Thickness measurement by cross-section with AFM for the un-annealed sample.

Figure 4.18 (b). AFM three-dimensional image of ZnO film deposited on silicon wafer (the un-annealed sample).

Figure 4.19 shows the comparison of the refractive index of the ZnO film of the un-annealed sample among the three models. The difference of the n value among the models is less than ~ 0.1 for the spectral range of 375 - 1100 nm. At the wavelengths close to the band edge (375 - 410 nm), the Cauchy model yields the highest n values; however, in the transparent range (~ 410 - 1100 nm) beyond the absorption tail, the n values obtained by the Cauchy models are between those obtained by the Sellmeier model and the Forouhi-Bloomer model.

Figure 4.19. Comparison of refractive index of ZnO film of the un-annealed sample among the three models.

4.7 Summary

In this chapter, the models and formulation of ellipsometry used in this study are described. For ZnO thin film deposited on Si substrate, a three-phase model, i.e.,

air/ZnO film/Si substrate, can describe well the material system in the ellipsometric calculation. Although a very thin silicon oxide layer (the SiO_2 layer is less than 0.7 nm for the un-annealed sample while it is about 1.5 nm for the sample annealed at 900 °C for 3 hours) may exist at the interface between the ZnO film and the Si substrate, the interfacial SiO_2 layer doesn't make a significant influence on the spectral fittings.

Three different dispersion models, namely, the Sellmeier model, Cauchy model and Forouhi-Bloomer model, have been used to fit the experimental data of the spectral dependence of ψ and Δ , and their performance in the spectral fittings is evaluated. The Sellmeier model has the simplest form with only two fitting parameters, and it ignores any sub-band gap absorption (i.e., the extinction coefficient $k = 0$). The Cauchy model is relatively more complicated as it has 5 fitting parameters if the band edge is fixed, but its exponential absorption tail can describe well the sub-band gap absorption close to the band edge. Both the Sellmeier model and the Cauchy model are empirical models. In contrast, the Forouhi-Bloomer model is based on the physics of electron transitions in a semiconductor. This model has 4 fitting parameters if the band gap is fixed, and it can also yield the extinction coefficient in the sub-band gap range. The Cauchy model has the highest quality in the spectral fittings among the three models. The variation of the ZnO film thickness obtained among the models is less than 3% and the thickness value obtained by Cauchy model is comparable with that measured directly by AFM. The difference in the refractive index of the ZnO film among the models is less than ~ 0.1 for the whole spectral range (375 – 1100 nm).

Chapter 5 Determination of Optical Constants of ZnO Thin Films for Photon Energies above the Band Gap

5.1 Introduction

In Chapter 4, we have discussed the determination of optical constants of ZnO films below the band gap (3.30 eV or a wavelength of 375 nm). In the present chapter, we will discuss the determination of the optical constants above the band gap. As there is a strong absorption above the band gap due to the electron transitions between the valence band and the conduction band in a semiconductor, it was frequently assumed that the semiconductor thin film under study can be treated as an infinite bulk material (i.e., the light cannot penetrate into the substrate and thus there is no influence from the substrate) without a careful justification [55, 60, 63]. For example, in ref.[55], to determine the optical constants of the ZnO thin films with thicknesses ranging from 80 to 800 nm above the band gap, it is assumed that the thickness of the films approaches infinity such that the light is completely absorbed within the film. Based on such an assumption, absorption peaks at ~3.32 eV and 3.38 eV (which were attributed to various transition processes) were obtained in the absorption spectrum. Such a study is questionable. It is suspected that the absorption peaks at ~3.32 eV and 3.38 eV observed in ref.[55] could be due to the influence of the substrate as a result of internal reflection. Therefore, the validity of the two-phase model for determining optical constants above the band gap will be justified first, and then the application of three-phase point-by-point fit will be discussed in the following sections.

5.2 Two-phase model

In Chapter 4, we have discussed the three-phase model, i.e., the system of air/ZnO film/Si substrate. This model should be used for the spectral range below the ZnO band gap as the ZnO film is transparent in this spectral range and the influence of the substrate must be considered. Actually, the three-phase model is valid generally. For the spectral range above the band gap, with a high absorption in the ZnO due to the inter-band transitions (i.e., the transitions between the conduction band and the valence band), the ZnO film can be treated as infinite if the film is thick enough such that all the light is absorbed within the film. In this case, the three-phase model can be reduced to the two-phase model as depicted in Figure 5.1.

Figure 5.1. Reduction from the three-phase model to the two-phase model when the function $X = 0$ (X is described in Eq. 2.7).

To facilitate the discussion on the two-phase model, we should start from the three-phase model. For easy reference, the formulas of the three-phase model, i.e., equations (2.5) – (2.8) in Chapter 2, are duplicated below:

$$\rho = R_p / R_s = \tan(\psi) \exp(j\Delta) \quad (2.8)$$

$$R_p = (r_{01}^p + r_{12}^p X) / (1 + r_{01}^p r_{12}^p X) \quad (2.5)$$

$$R_s = (r_{01}^s + r_{12}^s X) / (1 + r_{01}^s r_{12}^s X) \quad (2.6)$$

$$\text{where } X = \exp(-j4\pi N_1 d \cos\phi_1 / \lambda) = M \exp(j\delta) \quad (2.7)$$

Note that $N_1 = n_1 + jk_1$ and both N_1 and ϕ_1 are complex numbers. If k and d of the ZnO film are large enough, the magnitude of X (i.e., M) is close to zero. The d -dependence of M and the angle δ are shown in Appendix V where one can see that $M \approx 0$ when $d \approx 250$ nm for $\lambda = 300$ nm. In the case of $M \approx 0$, light is absorbed completely in the ZnO film and there is no light reaching the ZnO/Si interface. Then Eqs. (2.5) and (2.6) for the complex reflection coefficients (R_p and R_s) of the p- and s-polarized lights can be simplified as

$$R_p = r_{01}^p \quad (5.1)$$

$$R_s = r_{01}^s \quad (5.2)$$

where the Fresnel complex reflection coefficients for the p- and s-polarized lights at the interface of air / ZnO film are given by

$$r_{01}^p = (N_1 \cos\phi_0 - N_0 \cos\phi_1) / (N_1 \cos\phi_0 + N_0 \cos\phi_1) \quad (4.1)$$

$$r_{01}^s = (N_0 \cos\phi_0 - N_1 \cos\phi_1) / (N_0 \cos\phi_0 + N_1 \cos\phi_1) \quad (4.3)$$

From Eq.(2.8), Eqs.(5.1) and (5.2), and Eqs.(4.1) and (4.3), one can obtain the ratio ρ of the complex reflection coefficients (R_p and R_s) for the system as below

$$\rho = R_p / R_s = r_{01}^p / r_{01}^s \quad (5.3)$$

$$= [(N_1 \cos\phi_0 - N_0 \cos\phi_1)(N_0 \cos\phi_0 + N_1 \cos\phi_1)] / [(N_1 \cos\phi_0 + N_0 \cos\phi_1)(N_0 \cos\phi_0 - N_1 \cos\phi_1)]$$

As the refractive index $N_0 = 1$ for air, from Eq.(5.3) we can obtain the following relationship

$$[(1-\rho)/(1+\rho)]^2 = (N_1^2 - \sin^2\phi_0)/(\sin^2\phi_0 \tan^2\phi_0) \quad (5.4)$$

$$\text{or } N_1^2 = \sin^2\phi_0 + [(1-\rho)/(1+\rho)]^2 (\sin^2\phi_0 \tan^2\phi_0) \quad (5.5)$$

where $\rho = \tan(\psi)\exp(j\Delta)$.

Therefore, based on the two-phase model, from an ellipsometric measurement (i.e., the measurement of Ψ and Δ at a given wavelength), the complex refractive index $N_1 (=n_1 + jk_1)$ of the ZnO film can be easily calculated with Eq.(5.5), and thus the refractive index (n) and the extinction coefficient (k) of the ZnO film are obtained. In contrast to the calculation with the three-phase model, the calculation of N_1 with the two-phase model is much simpler as N_1 can be directly calculated with Eq(5.5).

For the un-annealed sample (Sample A), the ψ and Δ in the spectral range of 250 – 450 nm are shown in Figure 5.2. The oscillations in the ψ and Δ for the photon energy below the band gap (i.e., wavelengths longer than 375nm) due to the influence of the Si substrate can be observed in this figure. We have tried to calculate the refractive index and extinction coefficient of the ZnO film with Eq.(5.5) in the spectral range of 250 – 450 nm. Obviously, the two-phase model [and thus Eq.(5.5)] is not appropriate for the wavelengths longer than 375 nm as the film is transparent although there are still some absorption near the band edge. However, it would be interesting to compare the n and k calculated with Eq.(5.5) with those obtained from the Cauchy fittings discussed in Chapter 4 for the wavelengths longer than 375 nm but close to the band edge. The n and k calculated with Eq.(5.5) for the spectral range of 250 – 450 nm are shown in Figures 5.3 and 5.4, respectively.

Figure 5.2. Experimental Ψ and D in the spectral range of 250 – 450 nm for the un-annealed sample (Sample A). The lines in the figures are for tracing only (not fitting result).

Figure 5.3. Refractive index of ZnO film calculated with Eq.(5.5) from the experimental Ψ and Δ shown in Figure 5.2.

Figure 5.4. Extinction coefficient of ZnO film calculated with Eq.(5.5) from the experimental Ψ and Δ shown in Figure 5.2.

The strong oscillation in n and k in the wavelength range longer than the band edge shown in Figures 5.3 and 5.4 indicates that the two-phase model is invalid in this wavelength range. In the wavelength range shorter than the band edge, the calculation of n and k could be acceptable as ZnO has a strong absorption in this wavelength range. However, it should be justified. In the following sections, it will be shown that for the sample with a ZnO thickness of 305.5 nm (as obtained from the Cauchy fitting that is discussed in Chapter 4) the two-phase model is valid and thus the n and k calculated with Eq.(5.5) agree with those from the point-by-point fittings satisfactorily.

5.3 Justification of the two-phase model

To justify the validity of the two-phase model for ZnO films at the wavelengths shorter than the band edge, the dependence of ψ and Δ on the film thickness (d) at different wavelengths and incident angles has been calculated with the three-phase model which is valid generally. The calculations are carried out with Eqs. (2.5) – (2.8) and Eqs. (4.1) – (4.5). In the calculations, the values of the optical constants of the ZnO film obtained from the point-by-point fitting are used. These values have been proven to be accurate (see the discussions in Section 5.4). The dependence of ψ and Δ on film thickness with different incident angles (50° and 70°) at the wavelength of 250 nm is shown in Figure 5.5. In addition, the change of ψ and Δ due to the variation of wavelength is shown in Figure 5.6.

Figure 5.5. Influence of incident angle on the film thickness dependence of Ψ and Δ at the wavelength of 250 nm calculated by three-phase model.

Figure 5.6. ψ and Δ vs. film thickness, with the variation of wavelength. ψ and Δ are calculated by three-phase model with the incident angle at 70° .

As can be seen in these two figures, large oscillation in Ψ and Δ occurs when the film thickness is less than $\sim 200\text{nm}$; and Ψ and Δ become constant when the film thickness is larger than $\sim 300\text{nm}$. This oscillation indicates the existence of the internal reflection. This means that the light can reach the interface of ZnO film / Si substrate, the influence of the Si substrate cannot be ignored, and thus the two-phase model is invalid for film thickness less than $\sim 200\text{nm}$. However, when Ψ and Δ become constant, there is no internal reflection anymore, i.e. the light cannot reach the interface. In this case, there is no influence from the substrate, and thus the material system can be described by the two-phase model. On the other hand, the film thickness dependence of Ψ and Δ is affected by the incident angle and the wavelength. As can be seen in Figure 5.5, a smaller incident angle requires a slightly larger d at which Ψ and Δ start to become constant. This is because the light can penetrate deeper in the film with a smaller incident angle. The wavelength influence on the film thickness dependence is evident in Figure 5.6. For the wavelength of 250 nm , Ψ and Δ become constant at the film thickness of $\sim 200\text{ nm}$; at the wavelength of 300 nm , and Δ become constant at the film thickness of $\sim 250\text{ nm}$; and at the wavelength of 375 nm , Ψ and Δ become constant at the film thickness of $\sim 350\text{ nm}$. The wavelength influence is related to not only the ratio of (d/λ) but also the spectral dependence of the refractive index and extinction coefficient of the ZnO film [see Eq.(2.7)]. Especially, a smaller extinction coefficient means a greater penetration depth and thus a greater d at which Ψ and Δ start to become constant.

The refractive index and extinction coefficient of the ZnO film calculated with Eq.(5.5) of the two-phase model by using Ψ and Δ shown in Figure 5.6 are shown in

Figures 5.7 and 5.8, respectively. The oscillation of n and k for $d < \sim 300$ nm indicates that the two-phase model is invalid for film thickness less than ~ 300 nm. However, for $d > \sim 300$ nm, the n and k become constant and approach the “real” n and k values at the wavelength concerned, indicating that the two-phase model is valid. Note that the “real” n and k values are actually the corresponding values obtained from the point-by-point fitting based on the three-phase model (see the next section). Actually, the film thickness dependence of n and k shown in Figures 5.7 and 5.8 is just a translation of the film thickness dependence of Ψ and Δ shown in Figure 5.6.

From the above discussion, it is clear that the two-phase model is valid for the sample with the ZnO film thickness of 305.5 nm used in the present study in the wavelength range of shorter than 375 nm because d is larger than 300 nm. Therefore, the refractive index and extinction coefficient obtained with the two-phase model in this wavelength range should be accurate enough. This has been confirmed by the satisfactory agreement with the result of the point-by-point fitting, as discussed in the next section.

Figure 5.7. Film thickness dependence of refractive index of ZnO film calculated with the two-phase model [Eq.(5.5)] as a function of wavelength.

Figure 8. Film thickness dependence of extinction coefficient of ZnO film calculated with the two-phase model [Eq.(5.5)] as a function of wavelength.

5.4 Point-by-point fitting

The point-by-point fitting is based on the three-phase model with Eqs. (2.5) – (2.8) and (4.1) – (4.5) described in Chapter 4. With the known film thickness, the refractive index and extinction coefficient of ZnO film can be obtained from the fitting to the experimental ψ and Δ at a single wavelength in the wavelength range of shorter than 375 nm. The fitting is carried out with one wavelength at a time.

Theoretically, from Eqs. (2.5) – (2.8) and (4.1) – (4.5) for the three-phase model, with the film thickness and the optical constants (refractive index and extinction coefficient) of the Si substrate known, ψ and Δ at a given wavelength (λ) are functions of only n and k :

$$\psi = \psi(n, k) \quad (5.6)$$

$$\Delta = \Delta(n, k) \quad (5.7)$$

where $\psi(n, k)$ and $\Delta(n, k)$ are very complicated and they cannot be described with an analytical form. In the point-by-point fitting, one set of (n, k) is searched such that the ψ and Δ calculated with Eqs.(5.6) and (5.7) are closest to the experimental ψ and Δ . The best fitting can be carried out by minimizing an error function. An error function could be in various forms, but the fitting results are not very different.

In the point-by-point fitting, for a single incident angle, as the number of unknowns (n and k) is exactly equal to the number of equations [Eqs.(5.6) and (5.7)], the best fitting may not be able to yield a correct result in some cases due to the existence of various errors such as experimental errors in ψ and Δ and the error in the film thickness. In particular, the influence of the error in the film thickness could be

serious. In contrast, in a spectral fitting with a model, the number of fitting parameters is usually much less than the number of measurement points, and the fitting is largely constrained. One example of this kind of problems in the point-by-point fitting is shown in Figures 5.9 and 5.10. The sample used is the one annealed at 900 °C for 3 hours (Sample B). The ZnO film thickness is obtained from the spectral fitting in the transparent range (375 -1100 nm). As can be seen in Figure 5.9, the quality of the point-by-point fitting is excellent. However, the fitting yields a negative n value (Figure 5.10) which is incorrect in physics.

Figure 5.9. Point-by-point fitting for the sample annealed at 900 °C for 3 hours (Sample B). The ZnO film thickness is obtained from the spectral fitting in the transparent range (375 - 1100nm).

Figure 5.10. Refractive index and extinction coefficient of ZnO film obtained from the point-by-point fitting shown in Figure 5.9.

In order to increase the constraint for the point-by-point fitting, multiple incident angles are used. Figure 5.11 shows the fitting for the un-annealed sample (Sample A) with two incident angles (70° and 75°) with the film thickness obtained from the Cauchy fitting in the spectral range of 375 - 1100 nm. The refractive index and extinction coefficient obtained from this fitting are shown in Figure 5.12. Although the n and k obtained are positive, the quality of the fitting is poor. We have

found that the initial values used in the fittings play a critical role in the quality of the fittings. The reason for this could be due to the fact that the error function has multiple minimum points and the search algorithm is not able to look for the true minimum point.

Figure 5.11. Point-by-point fitting for Sample A (the same sample as in Figure 5.2) using two incident angles (70° and 75°) with the film thickness obtained from the Cauchy fitting in the spectral range of 375 – 1100nm.

Figure 5.12. Refractive index and extinction coefficient of the ZnO film obtained from the point-by-point fitting shown in Figure 5.11.

In Section 5.3, it has shown that for the film thickness greater than 300 nm the refractive index and extinction coefficient calculated with Eq.(5.5) (the two-phase model) are close to their real values in the wavelength range of 250 – 375 nm. Therefore, the refractive index and the extinction coefficient calculated with Eq.(5.5) can be used as the initial values for the point-by-point fitting, and this should improve the quality of the point-by-point fitting. To prove this idea, the following experiment has been designed. To get the initial values from the calculation with Eq.(5.5), we

used a new sample named Sample C (its ZnO film thickness is not known, but we are sure it is thicker than 300 nm based on the deposition time of thin films). Our objective is to obtain the optical constants for Sample A by using the point-by-point fitting. The purpose of using a different sample (Sample C) is to avoid any self-consistence in the fittings such that the above-mentioned idea is proved for a general situation. Actually, the initial values can be obtained with the same sample, and this is more convenient. The refractive index and extinction coefficient of Sample C calculated with Eq.(5.5) of the two-phase model are shown in Figure 5.13. In this figure, they are also compared with those shown in Figures 5.3 and 5.4 for Sample A. As can be seen in Figure 5.13, the optical constants at the wavelengths shorter than 375 nm are slightly different between the two samples.

Using the n and k of Sample C shown in Figure 5.13 as the initial values, the point-by-point fitting has been carried out on the same experimental data presented in Figure 5.11, and the fitting is shown in Figure 5.14. This fitting is much better, comparing with that shown in Figure 5.11. This indicates that initial values are close to the real values. The refractive index and extinction coefficient obtained from the point-by-point fitting are shown in Figure 5.15, and they are also compared with those obtained from the calculation with Eq.(5.5) of the two-phase model for the wavelengths shorter than 375 nm. As can be seen in the figure, the agreement between the two-phase model and the point-by-point fitting is excellent. This is consistent with the discussion on the film thickness dependence of the two-phase model in Section 5.3. It has been already clarified in Section 5.3 that in the spectral range of 250 – 375 nm the two-phase model is valid for a film thicker than 300 nm. For the sample (Sample A) used here, the film thickness is 305.5 nm, and thus the optical constants

above the band gap calculated with the two-phase model are accurate enough. The good agreement between the two-phase model and the point-by-point fitting indicates that the point-by-point fitting is correct and accurate.

Figure 5.13. Refractive index and extinction coefficient of Sample A and Sample C calculated with Eq45.5) of the two-phase model.

Figure 5.14. Point-by-point fitting for Sample A (the same experimental data shown in Figure 5.11) by using the n and k of Sample C shown in Figure 5.13 as the initial values.

Figure 5.15. Comparison of the optical constants of Sample A between the two-phase model (see Figures 5.3 and 5.4) and the point-by-point fitting (see Figure 5.14) by using the n and k of Sample C shown in Figure 5.13 as the initial values.

5.5 Summary

In this chapter, two approaches to determine the optical constants of ZnO films above the band gap (i.e., the wavelengths shorter than 375 nm) are discussed. The first approach is based on the two-phase model. In the spectral range of wavelengths shorter than the band edge (375 nm), ZnO films have a strong absorption due to the band-to-band transition. Therefore, it is possible that the light is absorbed completely within the ZnO film if the film is thick enough and thus there is no light reaching the ZnO/Si substrate interface. In this case, the material system can be described with the two-phase model, and the refractive index and the extinction coefficient of the ZnO film can be easily calculated. A detailed discussion on the film thickness dependence of the two-phase model is provided in this chapter. It is shown that in the spectral range of 250 – 375 nm the two-phase model is valid for a film thicker than 300 nm and the optical constants calculated with the two-phase model are accurate.

The second approach is the point-by-point fitting. The point-by-point fitting is based on the three-phase model. With the film thickness obtained from a Cauchy fitting in the transparent range (i.e. the wavelengths longer than the band edge or 375 nm), the refractive index and extinction coefficient of ZnO film can be obtained from the fitting to the experimental ψ and Δ by using a single wavelength. The choosing of suitable initial values is critical in the point-by-point fitting. For a ZnO film thicker than 300 nm, a practical way to choose the initial values is to calculate the n and k with the two-phase model and then use them as the initial values. It has been proved that this way works satisfactorily.

For Sample A which has the film thickness of 305.5 nm, the refractive index and extinction coefficient calculated with the two-phase model are in good agreement with those obtained by point-by-point fitting. This indicates that in this case both the two-phase model and the point-by-point fitting are valid and are able to yield accurate optical constants of the ZnO film.

Chapter 6 Optical Properties Derived from the Optical Constants of ZnO Thin Films

6.1 Introduction

In Chapter 4, the determination of the refractive index and extinction coefficient of the ZnO films for the photon energies below the ZnO band gap (or the wavelengths are longer than 375nm) by using various models is discussed. It is shown that the performance of the Cauchy model is the best among the models as the exponential absorption tail in the Cauchy model can properly describe the sub-band gap absorption near the band edge. In Chapter 5, it has been shown that the optical constants at the photon energies above the band gap (i.e., wavelengths shorter than 375 nm) can be determined from the point-by-point fitting by using the refractive index and extinction coefficient calculated from the two-phase model as the initial values.

In present chapter, the discussion of the merging of the two spectral ranges, i.e., wavelengths > 375 nm and wavelengths < 375 nm, for the optical constants of the un-annealed ZnO film will be carried out. Subsequently, the optical properties of the un-annealed ZnO film including the optical constants, dielectric functions, reflectance, and absorption coefficient in the wavelength range of 250 – 1100nm will be presented.

6.2 Optical properties of un-annealed ZnO film

Figure 6.1 shows the merging of the Cauchy fitting in the wavelength range of 375-1100 nm and the point-by-point fitting in the wavelength range of 250 - 375 nm for the ellipsometric spectra of the un-annealed ZnO film. The refractive index and extinction coefficient of the ZnO film obtained from the Cauchy fitting and the point-by-point fitting in the two spectral ranges are shown in Figure 6.2. The optical constants obtained in this piece of work are compared with those of ZnO film prepared by RF sputtering reported by Rebien et al. [56]. The spectral dependence of the refractive index and extinction coefficient of this work is very similar to that of Rebien et al., although there is some difference in the magnitude of the optical constants. As there is no information about the quality and details of their fittings, it is hard to justify whether their result is accurate enough (as discussed in Chapters 4 and 5, different approaches could have various fitting results). On the other hand, film density could affect the optical constants, and different film deposition conditions may lead to different film density.

In general, normal-incidence reflectance spectrum of the ZnO film can be calculated with the following equation [40]:

$$R = [(n-1)^2 + k^2] / [(n+1)^2 + k^2] \quad (6.1)$$

The result is shown in Figure 6.3. The ZnO film has a poor reflectivity. For wavelengths longer than about 700 nm (i.e. photon energy smaller than 1.77 eV), the reflectance is less than 10%, and there is no absorption (this will be shown in Figure

6.5) Therefore, the ZnO film is highly transparent in this spectral range as its transmittance is higher than 90%.

Figure 6.1. Merging of the Cauchy fitting and the point-by-point fitting for the unannealed ZnO film.

Figure 6.2. Refractive index and extinction coefficient of the un-annealed ZnO film obtained from the Cauchy fitting and the point-by-point fitting. The triangles in the figure represent the result of Rebien et al. [56]

Figure 6.3. Reflectance spectrum of the un-annealed ZnO film.

In solid-state physics, dielectric function $\epsilon(E)$ (where E is energy) is introduced to describe the response of a solid to an electromagnetic field (such as under light illumination). The dielectric function depends sensitively on the electronic band structure of a solid. Study of the dielectric function by optical spectroscopy is very useful in the determination of the overall band structure of a solid [40]. Generally, the dielectric function is a complex number, i.e., $\epsilon(E) = \epsilon_1(E) + i\epsilon_2(E)$ where $\epsilon_1(E)$ and $\epsilon_2(E)$ are the real and imaginary parts of the dielectric function, respectively. The imaginary part is related to energy dissipation in the solid, and $\epsilon_2(E) = 0$ if there is no absorption in the solid. The physics of the dielectric function and its relationship with the band structure are beyond the scope of this thesis, and will not be discussed here.

The dielectric function is not directly accessible experimentally from optical measurements. However, it has the following relationship with the complex refractive index $N = n + ik$ as discussed in Chapter 2:

$$\epsilon = \epsilon_1 + i\epsilon_2 = N^2 = (n + ik)^2 \quad (2.13)$$

Therefore, we can find the relationships between the real and imaginary parts of the dielectric function as well as the refractive index (n) and extinction coefficient (k) with the equations presented below:

$$\epsilon_1 = n^2 - k^2 \quad (2.14)$$

$$\epsilon_2 = 2nk \quad (2.15)$$

As the refractive index and extinction coefficient of the ZnO film have been obtained from the fittings, the real and imaginary parts of the dielectric function of the ZnO film can be easily calculated with Eqs.(2.14) and (2.15). The dielectric function as a function of photon energy is shown in Figure 6.4.

The absorption coefficient (α) of ZnO film can be calculated with the following formula as mentioned in Chapter 2:

$$\alpha = 4nk / \lambda \quad (2.11)$$

where λ is the wavelength. The absorption spectrum of the un-annealed ZnO film is shown in Figure 6.5. As can be seen in the figure, there is some sub-band gap absorption near the band edge. The absorption tail could be due to the exciton binding energy (~ 60 meV) or defects or impurities levels within the band gap of the ZnO film.

Figure 6.4. Real and imaginary parts of the dielectric function of the un-annealed ZnO film as a function of photon energy.

Figure 6.5. Absorption spectrum of the un-annealed ZnO film.

6.3 Summary

In this chapter, we have discussed the merging of the two spectral ranges, i.e., wavelengths > 375 nm and wavelengths < 375 nm, to obtain the optical constants of the un-annealed ZnO film. The reliability of the obtained optical constants is carefully justified. In addition, the optical constants obtained in this piece of work are also compared with those of ZnO film prepared by RF sputtering reported by Rebien et al. The spectral dependence of the refractive index and extinction coefficient of this work is very similar to that of Rebien et al., although there is some difference in the magnitude of the optical constants. The difference could be due to the difference in film structures and density. In addition, the fitting approaches may also be accountable for some of the difference.

Chapter 7 Annealing Effect on Optical Properties and Surface Morphology of ZnO Thin Films

7.1 Introduction

In chapters 4 and 5 we have discussed the determination of the refractive index and extinction coefficient of ZnO film for the photon energies below and above the ZnO band gap. In chapter 6, we have also discussed the merging of the two spectral ranges, i.e., wavelengths > 375 nm and wavelengths < 375 nm, for the optical properties of un-annealed ZnO film. In the present chapter, the influence of thermal annealing on the optical properties of the ZnO films, including the optical constants, dielectric functions, reflectance, and absorption coefficient in the wavelength range of 250 – 1100 nm, will be discussed. Finally, the influence of thermal annealing on the surface morphology and surface structure will be presented also.

7.2 Annealing effect on the optical properties

In Chapter 6, the optical properties of the un-annealed ZnO film have been determined. In this section, the optical properties of the ZnO films annealed at 900 °C for 10 seconds, 2 minutes, 10 minutes, 30 minutes and 60 minutes are also determined respectively, and the results are compiled. The influence of annealing on the refractive index, extinction coefficient and reflectance in the wavelength range of 250 – 1100 nm are shown in Figures 7.1, 7.2, and 7.3, respectively. The influence of annealing on the real and imaginary parts of the complex dielectric function and the absorption

coefficient in the photon energy range from 1.1 eV to 5 eV are shown in Figures 7.4, 7.5, and 7.6, respectively. As can be seen in the figures, the optical properties of the film annealed for 10 seconds are similar to those of the as-deposited film. However, after annealing for 2 minutes or longer time, the optical properties, such as the refractive index, the reflectance and the real part of the complex dielectric function, exhibit significant changes as compared to those of the un-annealed sample. Particularly, in the wavelength ranging from 375 nm to 1100 nm or the photon energy ranging from 1.1 eV to 3.3 eV, the values of the refractive index, the reflectance and the real part of the complex dielectric function decrease with the increase of annealing time. However, there are only little changes in the extinction coefficient, the imaginary part of the complex dielectric function and the absorption coefficient after annealing. The changes in the refractive index, the reflectance and the real part of the complex dielectric function may be caused by the change in the surface structure of ZnO films after annealing. For example, the volume fraction of voids on the surface of films will increase with annealing, which is confirmed from AFM studies as discussed in the next section. The increase in the volume fraction of the voids can effectively reduce the refractive index and the real part of dielectric function. This explains the reductions of refractive index, reflectance and real part of dielectric function with increasing annealing time. However, there is no such study reported in the literature so far.

Figure 7.1. Annealing effect on refractive index of ZnO films.

Figure 7.2. Annealing effect on extinction coefficient of ZnO films.

Figure 7.3. Annealing effect on reflectance of ZnO films.

Figure 7.4. Annealing effect on the real part of the complex dielectric function of ZnO films.

Figure 7.5. Annealing effect on the imaginary part of the complex dielectric function of ZnO films.

Figure 7.6. Annealing effect on the absorption coefficient of ZnO films.

7.3 Annealing effect on the surface morphology

As mentioned in Chapter 3, atomic force microscope (AFM) has been used to study the surface morphology of ZnO thin films that are un-annealed and annealed at 900°C for 10 seconds, 2 minutes, 10 minutes, 30 minutes, and 60 minutes, respectively. Figure 7.7 shows the influence of thermal annealing on the surface structure. In Figure 7.7, the left image was obtained by monitoring the variation of height of sample surface and the right image was obtained by capturing the change of phase of the oscillation of cantilever during scanning. Figure 7.8 demonstrates the influence of annealing on the surface morphology. Figure 7.9 illustrates the distribution of the grain size of ZnO thin films before and after annealing. Table 7.1 shows the influence of annealing on the surface roughness and the mean value of grain size. As can be seen in these figures and the table, the surface of the un-annealed sample was very smooth and the value of roughness was about 1 – 1.2 nm in Ra. The grains on the surface were fine and the mean size was about 25 nm. The size distribution of the grains follows a symmetric Gaussian distribution, as shown in Figure 7.9 (a). For the sample annealed for 10 seconds, the surface roughness was similar to that of the un-annealed sample, the grains were still fine and the mean size was also 25 nm, and the size distribution follows the same Gaussian function too. However, when annealing time was increased to 2 minutes or longer, the surface structure of the samples has been changed significantly as compared to the un-annealed sample. The grains were grown much bigger, the grain boundaries were fewer, the size of the grains was not uniform and the distribution of the sizes was asymmetric, as shown in Figures 7.9 (c)-(f). In addition, the surface of the samples annealed for 2 minutes or longer was rougher than that of the un-annealed sample and

exhibited large height variation as shown in Figure 7.8. Therefore, it is obvious that thermal annealing for 2 minutes or longer can change significantly the structure and morphology of the surface and increase the size of the grains. This trend is especially clear when annealing time was 30 minutes or longer, In this case, the surface of ZnO film became much rougher and the height variation became much larger. On the other hand, obviously, these structural changes lead to the increase of the volume fraction of the voids in the ZnO films. The increase of the volume fraction of voids in the ZnO films with annealing could be explained in terms of atomic diffusion process during the annealing. The atomic diffusion causes the merging and migration of smaller ZnO grains, leading to the growth of both the ZnO grains and voids. Such an atomic diffusion process depends on the annealing temperature and duration. The increase in the volume fraction of the voids is responsible for the reductions in the refractive index and the real part of dielectric function, as mentioned in the previous section. In other words, the changes in the thin film structures after annealing are the causes for the changes in the optical properties. However, the details are still not known yet. There is no such study reported in literature so far.

Figure 7.7 (a) Un-annealed sample

Figure 7.7 (b) Sample annealed at 900°C for 10 seconds

Figure 7.7 (c) Sample annealed at 900°C for 2 minutes

Figure 7.7 (d) Sample annealed at 900°C for 10minutes

Figure 7.7 (e) Sample annealed at 900°C for 30 minutes

Figure 7.7 (f) Sample annealed at 900°C for 60 minutes

Figure 7.7. AFM height and phase images of ZnO thin films of the un-annealed and annealed samples.

Figure 7.8 (a) Un-annealed sample

Figure 7.8 (b) Sample annealed at 900°C for 10 seconds

Figure 7.8 (c) Sample annealed at 900°C for 2 minutes

Figure 7.8 (d) Sample annealed at 900°C for 10 minutes

Figure 7.8 (e) Sample annealed at 900°C for 30 minutes

Figure 7.8 (f) Sample annealed at 900°C for 60 minutes

Figure 7.8. AFM three-dimensional images of ZnO thin films of the un-annealed and annealed samples.

Figure 7.9 (a) Un-annealed sample

Figure 7.9 (b) Sample annealed at 900°C for 10 seconds

Figure 7.9 (c) Sample annealed at 900°C for 2 minutes

Figure 7.9 (d) Sample annealed at 900°C for 10 minutes

Figure 7.9 (e) Sample annealed at 900°C for 30 minutes

Figure 7.9 (f) Sample annealed at 900°C for 60 minutes

Figure 7.9. Distribution of the grain size of ZnO thin films of the un-annealed and annealed samples.

Table 7.1. Annealing effect on surface roughness and grain size of ZnO films.

Annealing time	Ra (nm)		Rq (nm)		Rmax (nm)		Mean grain size (nm)
	Area 1	Area 2	Area 1	Area 2	Area 1	Area 2	
0 s	1.033	1.211	1.290	1.508	10.354	12.615	25.0
10 s	1.328	1.442	1.645	1.789	17.252	18.049	25.5
2 min.	2.760	2.869	3.459	3.556	28.537	26.158	59.5
10 min.	2.952	2.307	3.658	2.910	23.377	21.251	74.1
30 min.	5.146	5.537	6.216	6.801	40.585	44.036	79.3
60 min.	6.716	6.521	8.456	8.155	52.529	48.643	88.0

7.4 Summary

In this chapter, the optical properties including the optical constants, dielectric functions, reflectance, and absorption coefficient in the wavelength ranging from 250 nm to 1100 nm, for the as-deposited and annealed ZnO films, have been determined and compared with each other. The influence of annealing on the optical properties has clearly been demonstrated, in particular, annealing for 2 minutes or longer results in a reduction in the refractive index, reflectance and real part of complex dielectric function. The changes in the optical properties are attributed to the changes in the thin film structures caused by the annealing. It was clearly observed that annealing can change the surface structure and surface morphology significantly. The annealing can increase the grain size, change the size distribution and roughen the surface of the films. These changes lead to the increase of the volume fraction of the voids on the surface of thin films. The increase of the volume fraction of the voids can effectively

reduce the refractive index and the real part of the dielectric function. This can explain the annealing effects on the optical properties observed in this work.

Chapter 8 Conclusions and recommendations

8.1 Conclusions

ZnO thin film with surface roughness of about 1 nm can be fabricated on silicon wafer by filtered cathodic vacuum arc technique. Spectroscopic ellipsometry is a good tool to determine the optical properties of ZnO thin films. An appropriate optical model is required for extracting optical constants, dielectric function, reflectance, absorption coefficient, and film thickness from ellipsometric spectra. For ZnO thin films deposited on Si substrate, a three-phase model, i.e., air/ZnO film/Si substrate, can describe well the material system in the ellipsometric calculation. For the photon energies below the band gap (i.e., wavelengths longer than 375 nm), three optical dispersion models, namely Sellmeier model, Cauchy model, and Forouhi-Bloomer model, can be used to fit the experimental ellipsometric spectra. The Cauchy model shows the highest quality in the spectral fittings among these three models as the exponential absorption tail in the Cauchy model can properly describe the sub-band gap absorption near the band edge. For the photon energies above the band gap (i.e., wavelengths shorter than 375 nm), the optical constants can be determined from the point-by-point fitting by using the refractive index and extinction coefficient calculated from the two-phase model as the initial values. Based on the above studies, the optical properties including optical constants, dielectric functions, reflectance, and absorption coefficient in the wavelength range between 250 nm and 1100 nm (covering both regions of below and above the band gap) have been determined. In addition, the spectral dependence of the refractive index and extinction coefficient obtained in this work is very similar to that of ZnO film prepared by RF sputtering

reported by Rebien et al. [56]. The value of the thickness of ZnO film extracted from ellipsometric study is in good agreement with that measured directly by AFM. Therefore, an accurate and reliable methodology based on the ellipsometry for determining the optical properties and film thickness of ZnO thin films has been developed in this project.

Annealing for more than 2 minutes results in a large reduction in the refractive index and the real part of the dielectric function. Atomic force microscopic study reveals that annealing changes the surface roughness, grain size and size distribution of the ZnO thin films significantly. The reduction in the refractive index and dielectric function may be attributed to the increase of the volume fraction of voids in the thin films as a result of annealing.

8.2 Recommendations

The optical properties of ZnO thin films have been determined in this work. Although it is beyond the scope of this work, a study on the physics of the optical properties would be useful and interesting. For this propose, a physics-based model should be developed to model the optical properties. On the other hand, a further study on the influence of the thin film structures on the optical properties should be useful. Actually, in this work we have observed that the reduction in the refractive index and the real part of the dielectric function corresponds to the change in the thin film structure as a result of annealing. In a further study, a quantitative relationship between the change in the optical properties and the change in the thin film structures can be established based on the effective medium approximation theory [65] in terms

of the change of the volume fraction of the voids in the thin films. The information of the voids can be obtained from AFM and transmission electron microscopy (TEM) characterization.

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Appendices

MATLAB (Matrix Laboratory) has been used to fit the ellipsometric spectra to determine the refractive index, extinction coefficient, and thickness of ZnO thin film in this project. The programs based on Sellmeier model are described in the appendices I – IV, respectively. The programs for other models are similar to those for Sellmeier model thus we do not repeat it in these appendices.

Appendix I Main program based on Sellmeier model

```
%Program name: Main-Program
%This program is based on Sellmeier model (three-phase)

input data -----
Input-data; %run the Input-data sub-program to load all data files required for calculation.

%-----

x0=[2 53 350.00221;%input initial values for the fitting parameters x0(a, b, d)

save x0_values.xls x0 -ascii -double %save initial values for the fitting parameters

num-data = numel(LAMDA); %number of data points

%This part uses fminsearch to search for one set of fitting parameters x(a, b, d) such
%that the error function f is minimized.
%The calculation of the error function is carried out with the
%sub-program "error_function".

options = optimset('LargeScale','off');
x =
fminsearch(@error_function,x0,options,psi_exp70deg,delta_exp70deg,nsi,ksi,LAMDA,num_data)
x = x';
```

```

save x_values.xls x -ascii -double %Save the final fitting parameters in excel file: x_values.xls

%Using the final fitting parameters x(a,b,d) to calculate psi and delta
for aa = 1 : num-data
    fy(1)=70*pi/180;    %incident angle in air is 70 degree
    cal_n_k_psi_delta    %use this subprogram to calculate refractive index and
extinction Coefficient of ZnO, and psi and delta at each wavelength
    PSI70(aa,1)=psiCal_degree; %store the calculatedpsi of each wavelength in the
calculated psi vector:PSI70(aa,1)
    DELTA70(aa,1)=deltaCal_degree; %store the calculated delta of each wavelength in the
calculated delta vector:DELTA70(aa,1)

    n(aa,1) =nZnO; %store the calculated refractive index of ZnO at each wavelength in the vector:
n(aa,1)
    k(aa,1) =kZnO; %store the calculated extinction coefficient of ZnO at each wavelength in the vector:
k(aa,1)

    ReIE(aa,1)=nZnO*nZnO - kZnO*kZnO; %calculate the real part of the dielectric function of ZnO
and store it in the vector ReIE(aa,1)
    ImE(aa,1) =2*nZnO*kZnO; %calculate the imaginary part of the dielectric function of
ZnO and store it in the vector ImE(aa,1)

end

%plot the graph of experimentaland calculated psi vs wavelength
subplot(6,1,1)
plot(LAMDA,PSI70,'b')
hold on
plot(LAMDA,psi_exp70deg,'r')
ylabel('psi')
legend('psi-Cal','psi-Exp')

%plot the graph of experimental and calculated delta vs wavelength
subplot(6,1,2)

```



```
plot(LAMDA,DELTA70,'b')
hold on
plot(LAMDA,delta_exp70deg,'r')
ylabel('delta')
legend('delta-Cal','delta-Exp')
```

%plot the graph of the refractive index and extinction coefficient of ZnO vs wavelength

```
subplot(6,1,3)
plot(LAMDA,n,'b')
ylabel('n')
subplot(6,1,4)
plot(LAMDA,k,'r')
ylabel('k')
```

%plot the graph of the real and imaginary parts of the dielectric function of ZnO vs wavelength

```
subplot(6,1,5)
plot(LAMDA,RelE,'b')
legend('Rel E')
ylabel('Rel E')
subplot(6,1,6)
plot(LAMDA,ImE,'r')
ylabel('Im E')
legend('Im E')
xlabel('wavelength (m)')
```

save n_result.xls n -ascii -double %save the refractive index of ZnO in Excel file: n_result.xls

save k_result.xls k -ascii -double %save the extinction coefficient of ZnO in Excel file: k_result.xls

save cal_delta.xls DELTA70 -ascii -double %save the calculated delta in Excel file: cal_delta.xls

save cal_psi.xls PSI70 -ascii -double %save the calculated psi in Excel file: cal_psi.xls

save exp_delta.xls delta_exp70deg -ascii -double %save the experimental delta in Excel file:

exp_delta.xls

save exp_psi.xls psi_exp70deg -ascii -double %save the experimental psi in Excel file: exp_psi.xls

save New_LAMDA.xls LAMDA -ascii -double %save the extract wavelengths in Excel file:

New_LAMDA.xls

saveas(gcf,'Graphs.jpg') %save the above plots in a file named "Plots.jpg" in JPG format

Appendix II Input all known data

% Program Name: Input-data

% This program loads all the data required, extracts the data in specified wavelength range, and stores
% the extracted data in the designated data vectors.

% Load the data

load lamdaSi.dat %load the wavelength data

load psi.dat %load the psi data of experiment

load delta.dat %load the delta data of experiment

load nsi.dat %load the refractive index data of Si

load ksi.dat %load the extinction coefficient data of Si

bb=1;

clear LAMDA

% Select the data corresponding to the wavelengths from the 22th wavelength
% to the last wavelength,

% To store the selected data in the data vectors including wavelength

% vector: LAMDA(bb,1), refractive index of Si vector: nsi(bb,1); extinction coefficient

% of Si vector: ksi(bb,1); psi vector: psi_exp70deg(bb,1); and delta vector:

% delta_exp70deg(bb,1).

for ii=22:numel(lamdaSi)

LAMDA(bb,1) = lamdaSi(ii)*1e-9; % wavelength in the unit of meter

nsi(bb,1) = nsi(ii);

ksi(bb,1) = ksi(ii);

psi_exp70deg(bb,1) = psi(ii);

delta_exp70deg(bb,1) = delta(ii);

bb=bb+1;

end

Appendix III Sub-program to calculate refractive index, extinction coefficient, psi, and delta based on Sellmeier formulation

```
%Name of this subqrogram: cal_n_k_psi_delta

%Firstly, this program calculates the refractive index of ZnO based on Sellmeier
%model by using the fitting parameters a, b and d

%Then this program calculates psi and delta of the three-phase system
%(i.e., air/ZnO film/Si substrate) with the ellipsometric equations.

%This part is to assign the values to the fitting parameters (a,b,d) from
%the x vector
a=x(1);
b=x(2)*1e-9;
d=x(3);

%This part is to calculate the refractive index of ZnO using Sellmeier model
nZnO = sqrt(1 + a*LAMDA(aa)*LAMDA(aa)/(LAMDA(aa)*LAMDA(aa)-b*b));
kZnO = 0; %Sellmeier model assumes k=0
EZnO = (nZnO^2 - kZnO^2) + 2 * nZnO * kZnO * i; %Calculate dielectric function of ZnO

n1 = nZnO;
k1 = 0;

Nsi = nsi(aa) + ksi(aa)*i; %complex refractive index of Si
No = 1; %complex refractive index of air
Ni = [No; n1+k1*i; Nsi]; %complex refractive index of each phase [air, ZnO, Si]

%This part calculate the complex angles of each phase using Snell's law:
%air j=1; ZnO j=2; Si j=3
for j=2:1:3
    fy(j,1) = asin(Ni(1)*sin(fy(1)) / Ni(j));
end

%This part calculates Fresnel complex-amplitude reflection coefficients for
%the s-polarized light at air/ZnO interface (j=1) and ZnO/Si interface
```

```

%(j=2)
for j=1:1:2
rs(j,1)=(Ni(j)*cos(fy(j)) - Ni(j+1)*cos(fy(j+1))) / (Ni(j)*cos(fy(j)) + Ni(j+1)*cos(fy(j+1))) ;
end

%This part calculates Fresnel complex-amplitude reflection coefficients for
%the p-polarized light at air/ZnO interface (j=1) and ZnO/Si interface
%(j=2)
for j=1:1:2
rp(j,1)=(Ni(j+1)*cos(fy(j)) - Ni(j)*cos(fy(j+1))) / (Ni(j+1)*cos(fy(j)) + Ni(j)*cos(fy(j+1))) ;
end

X(1,1)=exp(-i*4*pi*Ni(2)*d*1e-09*cos(fy(2)) / LAMDA(aa)) ;

%This part calculates the complex reflection coefficient Rs for s-light
j = 1;
Rs(j,1)=(rs(j) + rs(j+1)*X(j)) / (1 + rs(j)*rs(j+1)*X(j));
%-----

%This part calculates the complex reflection coefficient Rp for p-light
Rp(j,1)=(rp(j) + rp(j+1)*X(j)) / (1 + rp(j)*rp(j+1)*X(j));
%-----

%This part calculates the ellipsometric angles

rho = Rp(1)/Rs(1); %The ratio of the complex reflection coefficients (Rp and Rs) of the p and s-lights

psiCal = atan(abs(rho));          %psi

deltaCal = abs(angle(rho));       %delta

psiCal_degree = psiCal/pi * 180;   %psi in degree
deltaCal_degree = deltaCal/pi * 180; %delta in degree
%-----

```

Appendix IV Sub-program for calculation of the error of fitting over the spectral range

```
%Name of this sub_program: error_function
%This sub-program is to calculate the error function over the spectral range

function f = error_function(x,psi_exp70deg,delta_exp70deg,nsi,ksi,LAMDA,num_data)

f=0;
for aa = 1 : num_data
    m=1;
    psi_exp70 =psi_exp70deg(aa)*pi / 180; %experimental psi
    delta_exp70 =delta_exp70deg(aa)*pi / 180; %experimental delta

    fy(1)=70*pi/180; %incident angle
    cal_n_k_psi_delta; %use the subqrogram "cal_n_k_psi_delta" to calculatepsi and delta

    rho_70deg = rho;

    f = f + sqrt((tan(psi_exp70)*cos(delta_exp70) - real(rho_70deg))^2 +
(tan(psi_exp70)*sin(delta_exp70) - imag(rho_70deg))^2);

end
```

Appendix V Dependence of the magnitude(M) and angle (δ) of the parameter X on the ZnO film thickness (d) at the wavelength of 300 nm