Chapter 3

Experimental Details

3-1 Introduction

In this chapter, the various processing steps as well as the specific experimental details followed during the deposition of the respective thin films are described in detail. Another important aim of this study was the accurate characterization of the semiconductor thin films. The techniques used to investigate the structural features of the films were scanning electron microscopy (SEM) and x-ray diffraction (XRD). The optical features of the compound semiconductors were investigated by optical transmittance and absorption coefficient measurements. Four-point measurement was used to characterize the layers electrically. The most important applications of these techniques are also outlined in this chapter.

3-2 Preparation of the Substrates

In this study, Corning 1737F glass substrates were used as substrate material. The substrates were cut into a standard size of 1×1 inch. The quality of the substrate, prior to growth, is a crucial factor, which influence the material properties of the deposited thin film. In order to obtain glass substrates with a high degree of chemical cleanliness, the following standard procedure was followed：

1. Substrates were rinsed under running D.I water for at least 5 minutes.

2. Substrates were ultrasonically cleaned in acetone, alcohol and D.I. water.

Finally, the samples were blown dry with nitrogen before it was loaded into the deposition chamber.

3-3 Deposition Technologies

3-3.1 Introduction

In this study, a radio frequency (RF) magnetron sputtering system was used for the deposition of ZnO thin films. In the following sections, the sturcture of these deposition systems and growth procedures will be outlined.

3-3.2 RF Magnetron Sputtering

3-3.2.1 Deposition System

The sputtering system is composed of the following：(1) sputtering chamber, (2) vacuum pumps, consisting of one turbo pump (high vacuum pump) and one mechanical pump (low vacuum pump), (3) sputtering gas supply and flow controller, (4) substrate holder and lamp heater, and (7) pressure gauges. In this sputtering system, the target-substrate distance was about 12 cm. The wafers are placed on the top of the holder, which can rotate and be heated by the lamp heater. The wafer temperature was monitored by a thermal couple sitting

between the substrate and heating lamps, which was calibrated by another thermal couple in direct contact with the wafer when the wafer was not rotating.

High purity Argon (Ar) was introduced through a mass flow controller after the vacuum chamber was evacuated to the base pressure. The RF power (13.56MHz) was controlled by a RF power supply with an automatic matching network which can be tuned for minimum reflected power.

3-3.2.2 Target Preparation

The sputtering targets used in the experiment were ones that were specifically designed using high purity ZnO (99.99%) and Al_2O_3 (99.99%) powders. Five different ceramic targets with different weight ratio of Al_2O_3 and ZnO were prepared：(1) 0wt% Al_2O_3 (only ZnO powder), (2) 0.5wt% Al_2O_3, (3) 1wt% Al_2O_3, (4) 2wt% Al_2O_3, and (5) 4wt% Al_2O_3.

The mixed powders were first dry ball-milled for thirty minutes and wet ball-milled in alcohol for 24 hours to ensure the particle sizes of these powders will reduce to get the homogeneity of the mixing. Then we put the mixture in the oven to dry at 80℃ for 24 hours. Finally, the powders were milled by hands and were pressed into a shallow stainless steel disk to obtain AZO (ZnO:Al) targets of 3 inch in diameter.

3-3.2.3 Film Preparation

The AZO thin films were deposited on Corning 1737F glass substrate by RF magnetron sputtering from AZO targets with a diameter of 3 inch. The sputtering chamber was evacuated to a base pressure of 8×10^{-6} Torr. Prior to the each deposition, the AZO target was pre-sputtered (50W) for 10 minutes to clean the target surface. The AZO films were first been deposited at various power and working pressure. Then we choose fixed deposition power and working pressure to prepare the AZO films at various substrate temperatures, deposition time, and different ratio of argon and oxygen atmosphere with a total flow of 10 sccm.

The material qualities of the sputtered ZnO films (electrical and optical properties) were strongly influenced by the deposition parameters and conditions of the radio frequency plasma. In order to optimize this rather complex system, the individual parameters were individually optimized.

3-4 Characterization of Deposited Layers

3-4.1 Introduction

In this study, a variety of characterization techniques were used to evaluate the structural, optical and electrical properties of the thin films. Of particular interest was the determination of the thin film thicknesses, crystallinity, optical parameters, and the

conductivity of the various films.

3-4.2 Film Thickness

The growth rate and the thickness of the samples were determined by SEM (Scanning Electron Microscopy) cross-sectional analysis.

3-4.3 Four-Point Probe

In this study, the resistivity of the film was determined from the sheet resistance measurement by a four-point probe (NAPSON, RT-7).

For semiconductor layer, the most common method of measuring this sheet resistance is the four-point probe method. The Rs is known as the sheet resistance of one square of the film that is independent of the size of the square. A small current from a constant-current source (I) is passed through the outer two probes and the voltage (V) is measured between the inner two probes [17]. The sheet resistance is given as：

$$Rs = 4.53\frac{V}{I} \times CF, \qquad (3\text{-}1)$$

where CF is the correction factor. Then we can determinate the value of resistivity：

$$\rho = Rs \times t \,, \qquad (3\text{-}2)$$

where t is the thickness of the film.

3-4.4 Optical Properties

The transmittance spectra was recorded using UV/VIS spectrophotometer (Hitachi, U-3500). Optical characterization is a non-destructive technique to obtain optical parameters such as absorption coefficient (α) as function of wavelength, and optical band gap (Eg).

We can obtain the optical band gap from the measurements of absorption coefficient, which is given by

$$\alpha = \frac{4\pi\, k'}{\lambda}\,, \qquad (3\text{-}3)$$

where k' is the extinction coefficient, and λ is the wavelength [15].

The absorption coefficient of a direct band gap semiconductor near the band edge, for photon energy $h\nu$ greater than the band gap energy Eg of the semiconductor, is given by the following equation：

$$\alpha \approx (h\nu - Eg)^{1/2}, \qquad (3\text{-}4)$$

where h is Planck's constant and ν is the frequency of the incident photon. By plotting the square of the absorption coefficient α^2, versus photon energy $h\nu$, the band gap Eg can be found from extrapolation.

3-4.5 Structural Characterization

3-4.5.1 X-ray Diffraction (XRD)

X-ray diffraction is a very important experimental technique that has long been used to address all issues related to the overall structure of bulk solids, including lattice constants, identification of unknown materials, orientation of single crystals, orientation of polycrystals, defects, stresses, etc. In this study, a Cu $K\alpha_1$ (1.54056 Å) source was used. And it was operated at 30kV and 20mA.

By using Bragg's law (equation 3-5) for diffraction, the reflected x-rays from the respective atomic planes can be measured by the detector.

$$n\lambda = 2\,d\sin\theta\,, \qquad (3\text{-}5)$$

where $n\lambda$ is an integral number of wavelengths, d is the distance between two successive crystal planes and θ is the Bragg angle.

In addition, the average grain size can be calculated by X-ray diffraction line

broadening using the Scherrer formula：

$$D = \frac{K \times \lambda}{\Delta(2\theta) \times \cos\theta_B}, \qquad (3\text{-}6)$$

where D is the average grain size, Δ(2θ) is full width at half max of a peak in radian, K is the shape factor of the average crystallite (expected shape factor is 0.9), λ is the wavelength (usually 1.54056 Å) for Cu Ka_1, and θ_B is the Bragg angle.

3-4.5.2 Scanning Electron Microscopy (SEM)

In this study, the surface morphology, microstructure and film thickness were examined by Hitachi S-4700I (High-Resolution Cold Field Emission Scanning Electron Microscope & Energy Dispersive Spectrometer, SEM&EDS) with the resolution of 1.5Å.