

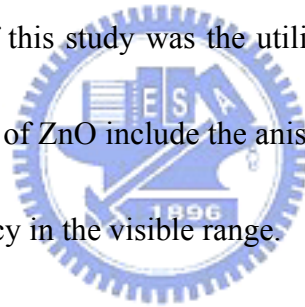
Chapter 2

Material Properties of ZnO thin films

2-1 Introduction

Transparent conducting oxides (e.g. zinc oxide (ZnO) and indium tin oxide (ITO)) have received a vast amount of attention in the last few years. The reason for the attention is quite obvious. These materials are both transparent and conductive with a wide variety of applications in both industry and research.

An important aspect of this study was the utilization of ZnO thin films for solar cell application. Interesting aspects of ZnO include the anisotropy in crystal structure, a wide band gap, and the optical transparency in the visible range.



In this chapter, attention will be given to the growth techniques generally applied for depositing ZnO thin films. Attention is also given to the structural, optical and electrical properties of this important semiconducting material.

2-2 Fabrication Techniques for ZnO Thin Films

2-2.1 Introduction

ZnO can be deposited by a variety of techniques such as radio-frequency magnetron sputtering, direct current magnetron sputtering, spray pyrolysis, evaporation, chemical vapor

deposition (CVD), pulsed laser deposition (PLD), and sol-gel process.

2-2.2 Sputtering Deposition Techniques

Sputtering is one of the most versatile deposition techniques used for the deposition of transparent conducting oxides (TCO) [14]. Sputtering, when compared to other techniques, produces layers with higher purity and better-controlled composition. It also produces films with greater adhesive strength, homogeneity and permits better control of film thickness.

Sputtering processes involve the creation of gas plasmas (usually an inert gas such as argon) between an anode and cathode. The cathode is used as the source of sputtered particles whereas the anode is usually the substrate holder. The source material is subjected to intense bombardment by ions. Using the momentum transferred from the bombarding ions, particles are ejected from the surface of the source (cathode) and then diffuse away from it, depositing a thin film onto the substrate. Sputtering is usually performed at pressures of 10^{-2} - 10^{-3} Torr.

In standard sputtering processes, there are usually two modes of powering the sputtering system. These two modes are direct current (DC) or by radio frequency (RF). In DC sputtering, a direct voltage is applied between the cathode and anode. This method works well with conductive targets (e.g. aluminum). The second method (RF sputtering) involves the use of a radio frequency source with atypical frequency of 13.56 MHz. This method is preferred for both conductive as well as non-conductive targets.

2-2.3 Sputtering Deposition of ZnO Films

One of the deposition techniques mostly used is magnetron sputtering, either from metallic targets in the reactive mode or from ceramic targets in pure argon atmosphere. In general, the structural properties as well as electro-optical properties are strongly dependent on the processing conditions, such as gas phase composition, plasma conditions, deposition temperature and deposition geometry. A special advantage of the magnetron sputtering method is the possibility to prepare films of high quality concerning specific resistance and transparency at temperatures below 100°C.

In this study, we deposit ZnO thin films by RF sputtering in pure argon ambience from ceramic targets. These intrinsic films, however, are electrically unstable. It is therefore essential to dope ZnO to ensure stability. Dopants such as aluminum are normally used. These dopants are added as a metallic oxide powder to the ZnO powder. Doping concentration of between 1 and 5% is usually sufficient to achieve good quality films.



2-3 Crystal Structure of ZnO Lattice

ZnO crystallizes primarily in the hexagonal wurtzite structure that exhibits strong piezoelectric characteristics. For this reason, *c*-axis oriented ZnO thin films are of interest for the production of surface and bulk acoustic wave devices. In addition, the crystal structure is strongly dependent on the deposition parameters.

2-4 Influence of Deposition Parameters on the Material Properties of ZnO

2-4.1 Influence on Electrical Properties

It is well known that heavily doped ZnO is a degenerate *n*-type semiconductor with an optical bandgap of about 3.37 eV. Depending on the presence of impurities (dopants), the resistivity can vary widely. As well as resistivity, carrier concentration and mobility in the thin film also can vary depending of the deposition parameters and doping.

The free charge carriers in undoped ZnO results from shallow donor levels associated with oxygen vacancies and interstitial zinc [Pöpll et al., 1990 and 1991]. Regardless of the deposition method, all undoped ZnO conducting films have unstable electric properties in the long term. This instability of the undoped, conductive ZnO is related to the change in surface conductance under oxygen chemisorption and desorption. On the contrary, ZnO thin films with impurity-doping can improve their stability as well as their electrical properties.

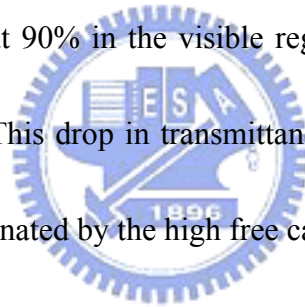
2-4.2 Influence on Structural Properties

For solar cell applications, a strong *c*-axis orientation (002) perpendicular to the substrate is required. The single orientation in polycrystalline ZnO can easily be obtained by controlling the deposition parameters.

2-4.3 Influence on Optical Properties

For the application of ZnO as a transparent conductive window layer in solar cells, it is important that this layer transmit a maximum amount of light through to the underlying absorber layer. ZnO films are in general transparent between the wavelength range of 0.3 and 2.5 μm , and the plasma edge lies between 2 and 4 μm depending on the carrier concentration. In addition, It is well known that a shift in the band gap edge appears with an increase in the carrier concentration. This shift is known as the Burstein-Moss shift.

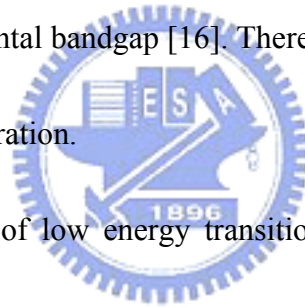
AZO films are also wide bandgap semiconductors ($E_g = 3.4 \sim 3.9 \text{ eV}$), which show good optical transmittance in the visible and NIR (near-infrared) region. Besides, the transmittance drops from about 90% in the visible region to zero in the infrared part of the spectrum for the doped case. This drop in transmittance is known as free carrier absorption. This type of absorption is dominated by the high free carrier concentration.



2-5 Optical Properties in Near-UV Region

The fundamental optical band gap edge of the heavily doped ZnO showed a blueshift in high carrier concentration, which can be explained in terms of Burstein–Moss band-filling effect (BM shift) [15]. As previously mentioned, ZnO can be heavily doped with various impurities such as aluminum (Al) to obtain the required doping concentration and resistivity. The bandgap widening that occurs in these heavily doped crystals is due to the lowest states of the conduction band that are blocked.

For TCOs, the band-to-band transitions are affected by the concentration of free carriers because the materials are degenerate. The states at the bottom of the conduction band are filled (the Fermi level has moved into the conduction band). The optical band gap is defined as the minimum energy needed to excite an electron from the valence band to the conduction band. In pure undoped crystals, the optical band gap equals the energy separation between the band edges. On heavy doping, the donor electrons occupy states at the bottom of the conduction band, since Pauli principle prevents states from being doubly occupied, this means that the energy required to activate an electron from the valence band to the conduction band is more than the fundamental bandgap [16]. Therefore, the optical band gap will increase with increasing carrier concentration.



This type of blocking of low energy transitions is known as Burstein–Moss effect which indicates that the bandgap becomes wider as the carrier concentration increases, that is,

$$E_g = E_{g_0} + \Delta E_g , \quad (2-1)$$

where E_{g_0} is the intrinsic bandgap and ΔE_g is a positive quantity whose magnitude is increased for the increasing carrier concentration. ΔE_g includes a BM shift that is partially balanced by a narrowing of the intrinsic band (bandgap shrinkage) due to the many-body interactions on the conduction and valence bands.

We should take into account not only band widening due to the blocking of states in the conduction band (Burstein–Moss effect) but also the bandgap narrowing effect resulting from electron–electron and electron–impurity interactions. However, for the range of carrier concentrations used in this analysis (about less than 10^{20} cm^{-3}), this is probably not a major issue because the electrons are unlikely to be scattered by each other.

If one considers only the blocking of the lowest states in the conduction band and neglects scattering effects, then

$$E_g \approx E_{g0} + \Delta E_g^{\text{BM}}, \quad (2-2)$$

where ΔE_g^{BM} is the bandgap shift given by the Burstein-Moss theory, that is,

$$\Delta E_g^{\text{BM}} = \frac{h^2}{8m^*} \left(\frac{3}{\pi}\right)^{2/3} n_e^{2/3}, \quad (2-3)$$

where h is Planck's constant, m^* is the electron effective mass in conduction band, and n_e is the carrier concentration.

2-6 Free-Carrier Absorption

Impurity-doping ZnO thin films have high transmittance in the visible region. But the

transmittance drops from about 90% in the visible region to zero in the infrared part of the spectrum for the doped case. This drop in transmittance is known as free-carrier absorption. This type of absorption is dominated by the high free-carrier concentration in the layers.

The resistivity of ZnO:Al films can be controlled by extrinsic doping, and can be decreased up to the semimetallic regime by increasing the carrier concentration up to about $1.5 \times 10^{21} \text{ cm}^{-3}$. However, an undesired consequence of having such high carrier concentration is that it considerably increases the free carrier absorption in the near-infrared range [15]. This adversely affects the application in thin-film solar cells with microcrystalline silicon absorber layers, where a high optical transmittance is required for the wavelength range between 400 and 1100 nm.



A more effective use of ZnO:Al films as a front contact in microcrystalline silicon solar cells requires an increased transparency in the near-infrared region while maintaining a low resistivity. We can increase the conductivity of TCOs without compromising the optical properties by increasing the mobility rather than the free-carrier concentration.