CHAPTER 5

INVESTIGATIONS ON ALUMINIUM AND NITROGEN CO-DOPED p-TYPE ZINC OXIDE THIN FILMS

5.1 INTRODUCTION

ZnO has a low power threshold for optical pumping at room temperature and UV emission resulting from a large exciton binding energy of 60 meV. Its band structure and optical properties are very similar to those of GaN, which is known to be a good material for the fabrication of optical devices like LED or LD. It is widely accepted that ZnO is a promising material for realizing UV laser at room temperature. By mixing MgO with ZnO one can have an effect of broadening the optical band gap (Cohen et al 2004). On the other hand, ZnO doped with Al can also lead to a tunable band gap. ZnO:Al thin films with high c-axis oriented crystalline structure along (002) plane are useful for device fabrication in broadband UV photo-detectors with high tunable wavelength resolution. Generally, c-axis oriented ZnO:Al thin films are fabricated using RF magnetron sputtering (Fu et al 2004, Zhou et al 2004), chemical vapour deposition (Barnes et al 2005), pulsed laser deposition (Mass et al 2003) and sol-gel process (Westin et al 2004, Musat et al 2004). Many research groups have reported p-type ZnO samples by doping with nitrogen. Indeed, nitrogen is a natural choice for an acceptor dopant, since it has about the same ionic radius as that of oxygen, and thus should readily substitute for the latter. In support of this scenario, SIMS measurements show that N can be doped to a level of more than $10^{19}$ cm$^{-3}$
(Look et al 2002), and electron paramagnetic resonance measurements confirm that N substitutes for O, in the ZnO lattice (Carlos et al 2001, Garces et al 2002). N-doped p-type ZnO samples have been grown using techniques such as CVD (Minegishi et al 1997), MOCVD (Wang et al 2003), MBE (Look et al 2002), PLD (Guo et al 2002) and sputtering both DC (Huang et al 2003) and RF (Singh et al 2003). Clearly the variety of growth techniques, dopants and substrates used in these endeavours bodes well for the future of this material.

ZnO is well known for its transparency when made into thin films and is expected to find wide use as transparent electrodes for many devices, such as electrochromic displays, electroluminescent displays, liquid crystal displays and solar cells. The performances of these devices greatly depend on the properties of the electrodes. Thus it is very important to improve the manufacturing process and the properties of the transparent electrodes.

Interest in the study of ZnO for optoelectronic applications has been enhanced by the reports in growing p-type ZnO layers and fabrication of p-n junctions (Ryu et al 2000, Lok et al 2002 and Ryu et al 2003). The properties of ZnO indicate that it could be used in almost all applications in which GaN is being used, if p-type ZnO were available. However, in II-VI compound semiconductors including ZnO, the control of hole conduction is difficult. The resistance to p-type doping is the self compensation of shallow acceptors resulting from various naturally occurring or spontaneously generated donor defects such as oxygen vacancies or zinc vacancies or zinc interstitials. Theoretical predictions by Yamamoto et al (2001) suggest that high-hole concentration p-type ZnO thin films can be realized by the codoping phenomenon, which requires the simultaneous presence of two dopants. Nitrogen has been established as a more soluble group-V element and as also possessing the shallowest acceptor level compared to P and As.
Yamamoto et al; 2001 have reported that the two pairs (Ga, N) and (Al, N) are more effective candidates than the other pairs for use in co-doping. In addition, doping with Al and N is better than doping with Ga and N because the corresponding III-N and III-O bonds are stronger for Al (Wang and Zunger 2003). Bian et al (2004) achieved p-type ZnO by co-doping with indium and nitrogen using ultrasonic spray pyrolysis technique. Theoretical studies on Ga-N co-doping revealed that by co-doping Ga and N a fully occupied impurity band can be formed above the valence band maximum, which significantly lowers the ionization energy of the N-acceptors. p-type ZnO by doping with S shows a shallower acceptor state (Persson et al 2006). However, there are still many deficiencies in the p-type layer when compared with n-type ZnO. Such deficiencies include radiative and nonradiative defects and/or impurities, which degrade the near band edge luminescence. To better understand and improve the film’s optical properties and meet the application of ZnO in short wavelength spectral range, it is essential to collect information of these defects and impurities.

5.2 EXPERIMENT

Thin films of Al and N co-doped ZnO were deposited on glass substrates using sol–gel method and spin-coating technique. Zinc acetate dihydrate was used as the precursor while aluminium chloride and ammonium acetate were used as source materials for aluminium and nitrogen dopants, respectively. The precursor and the dopant source were dissolved in 2-methoxyethanol (solvent) and monoethanolamine (stabilizing agent) at room temperature. The concentration of zinc acetate was 1 mol.l-1 and the molar ratio of monoethanolamine to zinc acetate was kept at 1:1. Using a magnetic stirrer, the solution was stirred at 353 K for 30 min. A clear homogeneous solution was obtained. The films were spin coated on glass substrates at 3000 rpm for 30 s. After each spin coating, the substrates were
dried at 523 K for 15 minutes for evaporating the solvent and to remove the organic components present in the films. The entire process was repeated 15 times. The films were then annealed at 773 K for 30 minutes.

The structural property of the films were evaluated using X-ray diffraction studies (D/MAX 2100H, Rigaku, Japan, 40 kV, 30 mA) with Cu Kα1 radiation of wavelength 1.54056 Å. To study the optical properties of the films, room temperature photoluminescence spectra were recorded using a He–Cd laser of excitation wavelength 325 nm. The Raman scattering experiments were carried out at room temperature utilizing the 632 nm line of the He-Ne laser as excitation source with power 17mW. The electrical properties of the deposited films were obtained by HALL measurement in the Vander Pauw configuration.

5.3 X-RAY DIFFRACTION STUDIES

The structural properties of the films were investigated using X-ray diffraction spectroscopy (XRD). Figure 5.1 shows the XRD pattern of undoped and doped ZnO thin films deposited on glass substrates. The undoped and the doped films show peaks corresponding to (10\(\bar{0}\)0), (0002), (10\(\bar{1}\)1), (10\(\bar{2}\)2), (11\(\bar{2}\)0), (10\(\bar{2}\)3) and (11\(\bar{2}\)2) planes. The diffraction peaks match the hexagonal wurtzite ZnO structure. The intensity of the (0002) plane is much stronger than that of the (10\(\bar{0}\)0) and (10\(\bar{1}\)1) planes in both the deposited films. When Al is doped in the ZnO film, the intensity of the diffraction peaks decreases, while the FWHM of the diffraction peaks increases. This indicates that when Al is doped into the ZnO thin films, the crystallinity gets affected. The increase in the FWHM of the Al doped ZnO thin films can be attributed to the stress induced due to the difference in the ionic sizes of Zn and Al.
The crystallite size $D$ was calculated from the (0002) peak width using the Scherrer’s formula

$$d = \frac{0.9\lambda}{\sqrt{\beta^2 - \beta_0^2 \cos \theta}}$$  \hspace{1cm} (5.1)$$

where $\beta$ is the measured broadening of the (0002) diffraction peak, full width at half its maximum intensity (FWHM), $\beta_0$ is the FWHM of the spectral width caused by instrumental broadening (0.1° in our experiment), $\lambda$ is the wavelength of the x-rays (1.5406 Å) and $\theta$ is the angle of diffraction. The average grain size and lattice parameters of the deposited films are given in Table 5.1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameters (Å)</th>
<th>Interplanar spacing (Å)</th>
<th>FWHM (°)</th>
<th>Average crystal size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>3.2487</td>
<td>5.1923</td>
<td>2.596</td>
<td>0.49</td>
</tr>
<tr>
<td>(Al, N) ZnO</td>
<td>3.2560</td>
<td>5.1960</td>
<td>2.598</td>
<td>0.62</td>
</tr>
</tbody>
</table>

Table 5.1 Lattice parameters (a, c), interplanar spacing (d), FWHM (β) and average crystal size (D) of undoped and (Al, N) co-doped ZnO thin films annealed at 773 K
Figure 5.1 XRD spectrum of a) Undoped ZnO and b) (Al, N) co-doped ZnO thin films.

5.4 UV-VISIBLE SPECTROSCOPY STUDIES

The effect of Al and N co-doping on the optical properties of ZnO thin films has been investigated. Figure 5.2 shows transmission spectra of the undoped and Al, N doped ZnO thin films. Both the films exhibited a transmission of more than 80% in the visible region with a sharp fundamental absorption edge. The optical absorption edge has a blue shift to the region of higher photon energy in the Al, N co-doped ZnO thin films. In general, the blue shift of the absorption onset of Al and N co-doped ZnO films is
associated with the increase of the carrier concentration blocking the lowest states in the conduction band, well known as the Burstein Moss – effect (Burstein 1954 and Moss 1954).

![Figure 5.2 UV-VIS spectra of a) Undoped ZnO and b) (Al, N) co-doped ZnO thin films annealed at 773 K](image)

**Figure 5.2** UV-VIS spectra of a) Undoped ZnO and b) (Al, N) co-doped ZnO thin films annealed at 773 K

### 5.5 PHOTOLUMINESCENCE STUDIES

The photoluminescence spectrum of ZnO thin films, in general, exhibit three prominent peaks. The near band edge (NBE) emission is around 380 nm, the green emission around 510 nm and the red emission around 650 nm (Bagnall et al 1998). The UV-NBE emission is due to the band-band transition while the latter two groups are related to the DL emission which
mainly results from the VO and Zni in the ZnO lattice structure. Figure 5.3. shows the room temperature photoluminescence spectra of undoped ZnO and (Al, N) co-doped ZnO thin films. The spectrum for the undoped film shows a NBE emission at 3.26 eV and a broad emission in the visible region. Zhang et al (2001) have suggested that the broad emission in the visible region due to the deep-level emission arises from the intrinsic defects in ZnO. However, the PL spectrum of the undoped ZnO thin film exhibits the NBE and DL emission peaks. Studies show that despite of the substrate types and the growth temperatures, broad DL emission exists in undoped ZnO thin films due to the presence of oxygen and zinc defects (Lim et al 2004). When Al and N were introduced into the film, the defect PL from oxygen or zinc defects was suppressed. These results indicate a very low concentration of defects in the Al, N co-doped ZnO thin films and that the deposited films are of good optical quality. It is also found from PL measurements that the peak of NBE emission of (Al, N) co-doped ZnO thin films has a blue shift to higher energy. This is believed to be due to the Burstein-Moss effect caused by the doping of Al and N into the ZnO thin films. In heavily doped ZnO thin films, the donor electrons occupy states at the bottom of the conduction band. The blue shift in the UV emission is attributed to the quantum confinement effect which states that the bandgap energy of a semiconductor increases with decrease in crystal size. Wang et al 2003 have observed quantum confinement effects when the particle size decreases from 60nm to 20 nm. In our case, the crystal size decreases from 27 nm (for the undoped ZnO thin film) to 21 nm (for the Al doped ZnO thin film). Hence it is evident that the blue shift of UV emission is caused by the quantum confinement effect due to the decrease in the crystal size (Valle et al 2004).
Figure 5.3 Room temperature PL spectra of a) Undoped ZnO and b) (Al, N) co-doped ZnO thin films annealed at 773 K

5.6 RAMAN SPECTROSOOPY STUDIES

The Raman spectra of the undoped and (Al, N) co-doped ZnO thin films are shown in figure 5.4. Wurtzite structure ZnO has the C6v symmetry group and has eight sets of optical phonon modes at Γ point of the Brillouin zone, classified as 2A1, 2B1, 2E1 and 2E2. Among these eight modes, A1+E1+2E2 modes are Raman active (Tong et al 2006). The 2B1 modes are Raman inactive while the remaining A1+E1 modes are infrared active. In addition, the A1 and E1 modes are polar and split into transverse optical (TO)
and longitudinal optical (LO) phonons. The frequencies of the optical modes in ZnO are $A_{1}(\text{TO})=379$ cm$^{-1}$, $A_{1}(\text{LO})=574$ cm$^{-1}$, $E_{1}(\text{TO})=410$ cm$^{-1}$, $E_{1}(\text{LO})=583$ cm$^{-1}$, $E_{2}(\text{Low})=379$ cm$^{-1}$, $E_{2}(\text{High})=439$ cm$^{-1}$. The $E_{2}(\text{High})$ mode is the band characteristic of the wurtzite phase. The position of the $E_{2}(\text{High})$ mode of the undoped and Al, N co-doped ZnO thin films were observed at 434 cm$^{-1}$. The $A_{1}(\text{TO})$ and the $A_{1}(\text{LO})$ phonon modes were observed at 377 cm$^{-1}$ and 580 cm$^{-1}$ respectively. Presence of $A_{1}$ mode indicates that this mode is associated with defects like oxygen vacancy, Zinc interstitial or their complexes.

Figure 5.4  Raman spectrum of a) Undoped ZnO and b) (Al, N) co-doped ZnO thin films deposited at 773 K.
5.7  ELECTRICAL PROPERTIES

It is well known that undoped ZnO is naturally n-type because of the existence of intrinsic defects like oxygen vacancies and zinc interstitials. To increase the carrier concentration, group III element doping is normally used. It has also been observed that by doping with Al, Ga etc., the resistivity of ZnO could be reduced to a very low value. On the other hand, due to the self-compensating effect in wide-band-gap semiconductors, it is difficult to prepare p-type ZnO films with low resistance. Group V elements like N, P, As and Bi have been successfully used to develop p-type ZnO (Heo et al 2004, Ryu et al 2000 and Ducler et al 2005). A number of sources like N2, N2O, NH3 and MMHy (monomethyl hydrazine) have been employed to dope N into ZnO.

Simultaneous codoping using acceptors and reactive donors can be expected to enhance the solubility of N in ZnO and give rise to a shallower N-acceptor level in the band gap (Yamamoto and Yoshida 1999). Investigations have shown that N solubility is facilitated greatly by the presence of Al in ZnO (Lu et al 2004 and Yuan et al 2005). The electrical properties of the deposited films were obtained by HALL measurement. The undoped ZnO thin films exhibited n-type conductivity with a carrier concentration of $9.22 \times 10^{13}$ cm$^{-3}$, resistivity of 1020 ohm cm and mobility of 66 cm$^2$V$^{-1}$s$^{-1}$. The carrier concentration, resistivity and mobility of the Al, N co-doped ZnO thin films were found to be $2.37 \times 10^{15}$, 937 ohm cm and 2.82 cm$^2$V$^{-1}$s$^{-1}$ respectively. Lu et al 2005 carried out XPS measurements to determine the chemical bonding of N or Al in ZnO. It was observed that the co-doping with N and Al induces the formation of N-Al bonds, as proposed by theoretical analysis, which is responsible for the p-type conduction of (Al, N) co-doped ZnO films. However, from the thermodynamic point of view, Al-O is a more stable phase than Al-N. at high temperature, good p-type conduction cannot
be realized because of the low incorporation of N due to Al-N dissociation. A relatively low temperature is preferred to enhance the incorporation of N for the formation of Al-N bonds.

5.8 CONCLUSIONS

Undoped and (Al, N) co-doped ZnO thin films were deposited on glass substrates using sol-gel spin coating method. The peak intensity of the (0002) plane is stronger in both the films indicating a preferential c-axis orientation of the grown films. Analysis of the UV-VIS spectra revealed a transmission of more than 80% in the visible region with a sharp fundamental absorption edge for the deposited films. The optical absorption edge has a blue shift to the region of higher photon energy in the (Al, N) co-doped ZnO thin films and is attributed to the Burstein Moss–effect. The room temperature PL spectra of the undoped and (Al, N) co-doped ZnO thin films showed the NBE and DL emission peaks. Doping Al and N in the ZnO thin films has been observed to suppress the DL emission indicating that the (Al, N) co-doped thin films are of good quality. The E2(High) mode which is the band characteristic of the wurtzite phase has been observed in the Raman spectroscopic studies of the deposited films. HALL effect measurements showed the n-type nature of the undoped ZnO thin films while the Al, N codoped ZnO thin films exhibited p-type conductivity.