Effect of Zn/O contents ratio on the structural, optical and electrical properties of MBE grown ZnO

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Abstract. In this study, the strong dependence of structural, optical and electrical properties of ZnO on the concentration of Zn/O has been observed. Four samples of ZnO with Zn/O-ratio of 1.08, 1.12, 1.17 and 1.22 were grown by molecular beam epitaxy. The x-ray diffraction (XRD) pattern demonstrates that intensity of (002) peak and crystallite size decreases as the Zn/O ratio increases in the samples, suggesting that the crystallinity of the samples degraded. In Raman spectra the E²(high) mode shifts towards higher frequency with increasing the concentration of Zn in films. According to electrical measurements, the Vₒ-Zni act as donor defects in ZnO because the carrier concentration increases and resistivity decreases with increasing the Zn/O ratio in the samples.

1. Introduction
ZnO has potential applications in electronic and optical devices due to its wide band gap (3.37) and rich chemistry of intrinsic defects [1-3]. To enhance the performance of such devices, the basic understanding of defect chemistry of ZnO is essential. ZnO has two type of intrinsic defects; donors and acceptors. O vacancies (VO), Zn antisites and Zn interstitials (Zni) are considered to be donor levels and Zn vacancies (ZnO), O-interstitials act as acceptor levels [4]. Therefore control of density of intrinsic defects in ZnO has fundamental importance. Different methods and growth techniques are used to modulate the density of intrinsic in the grown films. MBE is very versatile and ultra high vacuum technique for the control growth of semiconductor materials. Literature suggested that one can precisely control the concentration of source materials by using MBE. On the other hand the structural, optical and electrical properties of ZnO are strongly depends upon the concentration of intrinsic defects. For example intrinsic n-type of conductivity of ZnO is related to intrinsic donors like Vₒ, Zni and Znₒ-Vₒ donor complex [5-7]. Similarly the defect luminescence from ZnO is also related with intrinsic defects but its origin is still controversial [8, 9]. The roots of hurdles in the way of p-type conductivity of ZnO are also supposed to be compensation effect of intrinsic donor defects. Therefore a detailed study of intrinsic defects in ZnO would be very interesting and can provide better understanding of film quality and its optical and electrical properties.

In this paper, the effects of Zn/O ratio on the structural, optical and electrical properties of ZnO grown by molecular beam epitaxy, have been investigated by Energy dispersive x-ray spectroscopy, X-ray diffraction, Raman spectroscopy and Hall measurements. The crystal quality of films degrades with increasing Zn/O ratio in the samples. Furthermore Zn_i-V_o complex is the major source of carrier concentration.
2. Experimental

Four layers of bulk ZnO each having Zn/O ratio 1.08, 1.12, 1.17 and 1.22 (hereafter referred as D, C, B and A) were grown on 3 inch diameter p-type silicon (111) wafers by means of molecular beam epitaxy (MBE). The detail can be found in reference [6]. Characterization of ZnO films were carried out by the following equipment: XRD by PANALytical X’pert, SEM/EDAX by JEOL, Hall measurements by Ecopia 3000 and Raman/PL spectroscopy by Horiba using He-Cd laser of excitation wavelength 325 nm. All the measurements were performed at room temperature.

3. Results and Discussion

XRD patterns of the as grown samples A, B, C and D confirmed hexagonal structure of ZnO (see Figure 1). Three distinct peaks were observed at angles (2θ) 34.47°, 36.20° and 72.40° from all samples associated with the (002), (101) and (004) planes of ZnO, respectively [10]. Peak (002) being the dominant among the others, indicates that the preferable direction of the growth is along this plane i.e. c-plane.

![Figure 1. Typical XRD pattern of MBE grown samples with different Zn/O ratio](image)

The position of (002) peak remains constant for all the samples but the intensity of (002) peak decreases with increasing Zn/O ratio in the samples. The lattice constants ‘a’ and ‘c’ of the wurtzite structure of ZnO can be calculated using relations given below [11].

\[
a = \frac{1}{3 \sin \theta} \frac{\lambda}{\beta \\
c = \frac{\lambda}{\sin \theta}
\]

For (002) plane calculated values are a= 3.12 and c= 5.15 Å which agree with JCPDS data. The crystallite size was calculated by using Scherer’s formula [1];

\[
D = \frac{0.9 \lambda}{\beta \cos \theta}
\]

Where D is crystallite size, λ is wavelength of x-ray, β is full width at half maximum of (002) peak.
Figure 2. Effect of Zn/O ratio on FWHM of (002) peak and crystalline size of MBE grown samples

Figure 2 shows the relation of FWHM and crystallite size with Zn/O ratio in the samples. The FWHM of ZnO (002) peak for samples A, B, C and D is 0.35°, 0.32°, 0.30° and 0.28° respectively, showing the good crystallinity of films. We observed that with increasing the Zn/O ratio in the samples, the FWHM of samples increases and crystallite size decreases.

Figure 3. Typical Raman spectra of MBE grown samples with different Zn/O ratio. Inset shows the shifting of E2\text{high} mode towards higher frequencies of ZnO with Zn/O ratio

This means that the crystalline quality degrades with the increase of Zn/O ratio in the samples. The degradation of crystalline quality probably related with stress in the films with increasing the density of Zn\text{-}V_0 complex defects due to increase of Zn/O ratio. The presence of Zn\text{-}V_0 defects in the samples is confirmed from the Raman spectroscopy measurements.

To support the presence of complex donor defects, we performed Raman spectroscopy as well. The ZnO crystal structure belongs to the space group C46v, and the group theory analysis predicts the zone-center optical modes; A1 + 2B1 + E1 +2E2. The A1, E1 and the two E2 modes are Raman active, while the B1 modes are forbidden in Raman scattering. Furthermore, the A1 and E1 modes are polar: their vibrations polarize the unit cell, which results in the creation of a long-range electrostatic
field. This field results in the splitting of A1 and E1 modes into longitudinal optical (LO) and transverse optical (TO) components, thus creating the A1 (LO, TO) and E1 (LO, TO) modes.

Figure 3 displays the typical Raman spectra of MBE grown samples with different Zn/O ratio. The inset of figure 3 shows the effect of Zn/O on the $E_{2}^{\text{high}}$ Raman mode of ZnO for samples A, B, C and D. The spectrum shows a non-polar optical phonon mode $E_{2}^{\text{high}}$ for all samples [12]. The theoretical calculations by Tsuboi and Wada [13] predicted the frequency of $E_{2}^{\text{high}}$ mode of pure ZnO to be 433 cm$^{-1}$. We observed this mode at 436 cm$^{-1}$, 437 cm$^{-1}$, 439 cm$^{-1}$ and 440 cm$^{-1}$ for samples D, C, B and A respectively. The shift of $E_{2}^{\text{high}}$ phonon frequency is directly related to the stress in film. Huang et al. [14] pointed out that under a compressive stress the $E_{2}^{\text{high}}$ shifts up. We observed an up shift of 3 cm$^{-1}$, 4 cm$^{-1}$, 6 cm$^{-1}$ and 7 cm$^{-1}$ for sample D, C, B and A, respectively. This up shift indicates a compressive stress in the film. The reason of this stress may be the formation of Zn$_{i}$-V$_{O}$ complex defects in the films with increasing II/VI ratio.

Table 1: Effect of Zn/O ratio on FWHM, Crystalline size, intensity of $E_{2}^{\text{high}}$ mode, carrier concentration and resistivity

| Zn/O Ratio | FWHM (Degree) | Crystalline Size (nm) | Position of $E_{2}^{\text{high}}$ mode (cm$^{-1}$) | Carrier concentration (cm$^{-3}$) | Resistivity (Ohm-cm) |
|------------|---------------|----------------------|--------------------------------------------------|----------------------------------|---------------------|
| 1.08       | 0.28          | 65                   | 436                                              | $5 \times 10^{16}$              | 1.44                |
| 1.12       | 0.30          | 60                   | 437                                              | $3 \times 10^{18}$              | 0.9                 |
| 1.17       | 0.32          | 48                   | 439                                              | $4 \times 10^{17}$              | 0.08                |
| 1.22       | 0.35          | 44                   | 440                                              | $2.2 \times 10^{19}$            | 0.009               |

Figure 4. The plot shows the dependence of carrier concentration and resistivity on Zn/O ratio. The graph is evident that with increasing Zn/O ratio, the carrier concentration increases and resistivity decreases.

Figure 4 shows the effect of Zn/O ratio on carrier concentration and resistivity of samples. With increasing Zn/O ratio in the samples the carrier concentration increases and resistivity of samples
decreases. The carrier concentration increased from $5.0 \times 10^{16}$ cm$^{-3}$ to $2.2 \times 10^{19}$ cm$^{-3}$ and resistivity decreased from 1.44 $\Omega$ cm to 0.009 $\Omega$ cm for samples with increasing Zn/O ratio from 1.08 to 1.22 respectively. The detail of carrier concentration and resistivity can be shown in table 1. The carrier mobility was also calculated and shows that mobility decreased from 7.5 to 1.4 cm$^2$/V.Sec as the Zn/O ratio increased from 1.08 to 1.22. As ZnO has hexagonal structure with half of the tetrahedral sites are occupied by Zn atom whereas all the octahedral sites are empty, hence there are a plenty of sites for ZnO to accommodate intrinsic (Zn-interstitials, O-vacancy and/or Zn-antisite) [15] and extrinsic defects. Therefore with increasing Zn/O ratio, the densities of both donor defects (Zn$_i$ and V$_O$) might be increased. Therefore Zn$_i$ form a complex with V$_O$ vacancy which is donor complex in ZnO also demonstrated by Asghar et al [7]. Therefore the increased of carrier concentration with increasing Zn/O ratio is understandable.

4. Conclusion

We have deposited four samples with Zn-concentration of 52%, 53%, 54% and 55% by molecular beam epitaxy. The structural, optical and electrical properties of grown films are strongly depending on contents ratio of Zn/O. It is concluded that structural and optical properties degrades with increasing Zn/O ratio because the density of V$_O$-Zn$_i$ donor complex increased.

5. References

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