Structural and Photoluminescence Study of Zinc Oxide Thin Films Grown by Laser Induced Plasma

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Abstract

The structural, compositional and optical properties of thin films grown by laser-induced plasma (LIP) were studied as a function of post-deposition annealing. Nanocrystalline powder of ZnO was prepared through a wet chemical method using zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) and potassium hydroxide (KOH) as precursors. The X-ray diffraction (XRD) spectra showed the improved crystalline quality at elevated temperatures with a temperature-dependent variation in lattice parameters, pointing the activation of zinc and oxygen related point defects at various annealing temperatures. X-ray photoelectron spectroscopy (XPS) of Auger Zn $L_3M_{4,5}M_{4,5}$ and O 1s peaks revealed the reversion of zinc interstitials to crystal lattice as zinc lattice sites at different annealing temperatures leading to strong Zn-O bonding. The origins of near band edge (NBE) and deep level emission (DLE) in room temperature photoluminescence (PL) spectra, pointing out the activation of temperature-dependent intrinsic defects states are briefly discussed. Among all the thin films under investigation, ZnO thin films annealed at 700 °C were found to have strong Zn-O bonding with maximum contribution of oxygen interstitials that is favorable to form un-doped p-type ZnO essential for optoelectronic and spintronic devices.

Key Words: ZnO, Laser induced plasma (LIP), Wet chemical method.

1. Introduction

ZnO is a promising material for various technological applications by virtue of its unique combination of piezoelectric, electrical and optical properties. It has attracted a lot of research interest due to its exciton binding energy (60meV) that is 2.4 times the binding energy of GaN (25meV) and having a band gap of 3.37eV which is useful in various fields such as transparent conductive films, solar cells, photoconductors and luminescence devices [1]. There are many studies on the growth of ZnO layers by sputtering[2], laser induced plasma (LIP) [3], metal organic chemical vapor deposition (CVD) [4] and molecular beam epitaxy (MBE) [5]. However, in consideration of low cost and wider application, relatively simple method to deposit ZnO thin films at relatively low temperature is expected. The main advantage of LIP is its ability to create high energy source particles which is expected to reduce the temperature for film growth as the film precursors ablated from the target might impinge on the substrate with high kinetic energies [6] compared with the other techniques. Because of its advantage of simple hardware,

the deposition can be controlled by adjusting the laser energy density, the pulse duration and pulse repetition rate [7]. In general, high purity ZnO target has been widely used to grow ZnO thin films by LIP [8].

It is well known that the properties of ZnO layers are strongly affected not only by growth but also by post annealing conditions. Annealing has a large effect on crystallinity of layers in terms of grain size, residual strain and the defect density [9]. The quality of a bulk ZnO crystal continuously increased up to 1100 °C [10], while 600-800 °C was usually reported to be the optimum annealing temperature for ZnO layers grown on Si substrates [11].

Many articles have demonstrated that the deep level emission (DLE) from PL spectra of ZnO thin films is caused by defects such as oxygen vacancies, zinc vacancies, interstitial zinc and interstitial oxygen among others [12, 13]. Some workers have investigated the luminescence characteristics of ZnO thin films based on the analysis of XPS [14], emphasizing the relationship between UV emission and stoichiometry of the film. Therefore, identification of the possible origins of DLE in ZnO thin films is essential.

In the present work, we report the influence of post-deposition annealing on structural, compositional and optical properties of ZnO thin films using LIP. Our experimental results reveal that beside the range of annealing temperatures investigated in this paper, 700 °C has been observed to be an optimum annealing temperature at which ZnO shows strong Zn-O bonding with maximum concentration of oxygen interstitials (acceptor impurity) making it favorable to develope a p-type material. The study further examines the contribution of zinc interstitials by studying the Auger Zn $L_3M_{4,5}M_{4,5}$ peak using XPS measurements of ZnO thin films at different post-deposition annealing temperatures.

2. Experimentation

Nanosrystalline ZnO powder with wurtzite structure was synthesized through a wet chemical method. The solution was continuously stirred and allowed to cool at room temperature for 24 hrs. Precipitates, formed after aging, were washed several times with distilled water to get rid of K completely from the solution. The precipitates were dried at 325 K in air to get solid powder. The powder obtained was palletized and sintered at 1275 K for 12 hrs in air. The sintered pellets of ZnO were ablated by second harmonic Nd:YAG laser (532 nm, 26 mJ) at pulse repetition rate of 10 Hz. The substrate holder was set to rotate with speed of about 33 rev/min to accomplish uniform thin films. The thin films were deposited on Si substrate for a constant ablation duration of 90 min in ultra high vacuum of 10^{-6} Torr. Si (001) substrates were sequentially cleaned in ultrasonic bath with ethanol, acetone and de-ionized water separately at 45 °C for 15 min each, before being mounted to the substrate holder in the LIP chamber. Post-deposition annealing was carried out at different temperatures ranging from 500 to 800 °C for 4 hrs in air.

The crystalline phase of thin films was analyzed by SIEMENS D5005 Cu Kα (1.504 Å) X-ray Diffractometer. Surface stoichiometry and elemental oxidation states were identified by X-ray Photoelectron Spectroscopy (XPS) with Kratos Axis-Ultra Spectrometer equipped with a focused monochromatic Al-Kα X-ray beam at room temperature for bulk and thin film samples.

Furthermore, near band edge (NBE) and DLE energy transitions from Photoluminescence (PL) spectra, measured using He-Ne (325 nm, 3 mW), were used to study the changes in the optical properties of thin films.

3. Results and Discussion

3.1 XRD Analysis

XRD spectra of post annealed ZnO thin films grown by LIP, are shown in Figure 1. The XRD spectra obtained, are matched well with the space group of $P_6 3mc$ (186) and no diffraction peak from other products has been detected. Higher peak intensity revealing the crystallinity of ZnO crystal was continuously improved by post-deposition annealing (refer Table 1) without any degradation of crystal quality as reported in literature [11].

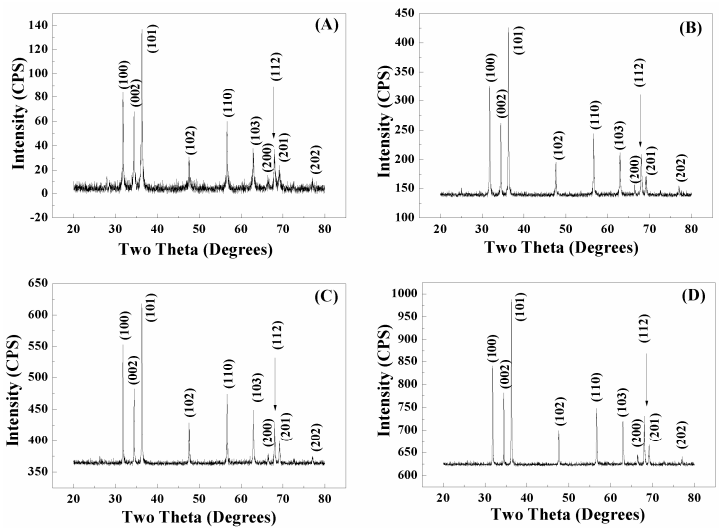

Figure 1: XRD spectra of ZnO thin films annealed at (A) 500 °C, (B) 600 °C, (C) 700 °C and (D) 800 °C.

Kim et al [15] investigated the annealing effect on the crystalline quality of ZnO thin films in 600-1050 °C and reported a continuous increase in peak intensity with an increase in annealing temperature that is also evident from our XRD results shown in Figure 1. The crystallite size estimated from the Full Width at Half Maximum (FWHM) of (101) diffraction peak by using the Sherrer equation was increased from 18.21 nm to 26.6 nm with increase in annealing temperature from 500 to 800 °C (refer Table 1), illustrating improved crystalline quality [16].

The defect concentration has been verified by change in lattice parameters as a function of annealing temperature. The lattice parameters a and c, calculated by using diffraction data of 101 and 002 peaks, were higher than those reported in literature (a = 3.2427 Å and c = 5.1948 Å) for ZnO [16]. Table 1 shows the variation of lattice constants with post-deposition annealing showing temperature dependent behavior. This might be attributed to the variation in tensile/compressive stresses of ZnO coated silicon wafer due to the activation of certain point defects at different annealing temperatures. The detailed analysis of temperature dependent

behavior of lattice parameters in terms of point defects such as zinc and oxygen interstitials has been discussed in XPS and PL section.

TABLE 1: CRYSTALLITE SIZE AND LATTICE PARAMETERS OF ZnO THIN FILMS ESTIMATED XRD PATTERNS.

Annealing Temperature	Center of the Peak	Max. Intensity	Crystallite Size (nm)	d-Spacing (Å)	Lattice Parameter a (Å)	Lattice Parameter c (Å)
500 °C	34.457	68.665	18.31	5.077	3.2458	5.205
600 °C	34.462	129.164	22.68	5.077	3.2458	5.2051
700 °C	34.476	123.988	24.86	5.075	3.2449	5.2048
800 °C	34.480	164.437	26.89	5.074	3.2452	5.205

3.2 XPS Analysis

XPS analysis of ZnO thin films was carried out by the investigation of the Zn $L_3M_{4,5}M_{4,5}$ and O 1s core level spectra. The photoelectron peaks of all the spectra were calibrated by adventitious C 1s peak centered at 284.6 eV. Zn LMM Auger peak analysis is often used to identify the chemical states of the zinc species because a single Auger transition involves three electrons and many body effects [17].

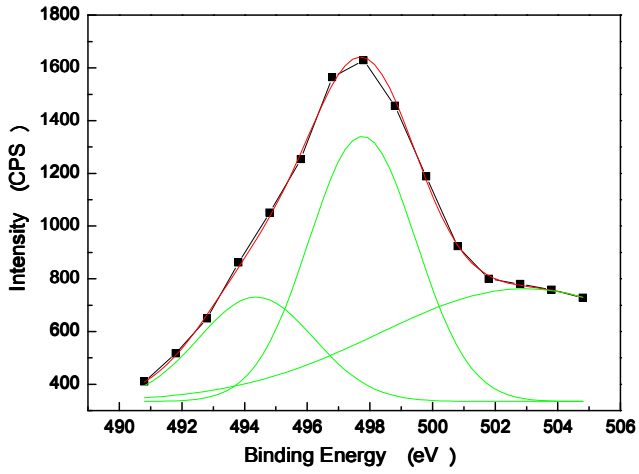

Figure 2: Gaussian fit Zn LMM spectrum of ZnO thin films annealed at 700 °C

Figure 2 shows the Auger Zn $L_3M_{4,5}M_{4,5}$ spectra of the ZnO thin films annealed at 700 °C. Two Auger peaks centered at about 494.5 and 497.8 eV are attributed to the interstitial zinc (Zn_i) and Zn-O bonds respectively [18]. By fitting the Zn Auger peak with Gaussian profile, the concentration of the Zn_i was estimated at different post-deoposition annealing temperatures and is shown in Figure 3. It is well known that there are Zn_i atoms in as-grown ZnO thin films, which usually locate between O^{2-} and Zn^{2+} layers resulting an increase in lattice constants [18]. During annealing, Zn_i are reported to obtain enough energy to revert back to crystal lattice sites after recombination with zinc vacancies resulting in strong Zn-O bonding[19] as is evident from Figure 3.

Figure 3: Variation in Zni and Zn-O bonds with annealing temperature

The concentration of Zn_i first decreases having minimum concentration at 700 °C and then increases when annealed to 800 °C. This variation in Zn_i is responsible for the expansion/contraction of crystal lattice at different annealing temperatures. The minimum value of Zn_i at 700 °C is responsible for the contraction of lattice at this temperature resulting in reduced lattice parameters as is evident from Table 1. Since the Zn_i is donor impurity, so the reduced concentration of Zn_i at 700 °C is favorable to form un-doped p-type ZnO useful for optoelectronic applications.

The asymmetric O 1s peak in the surface was deconvoluted with resolved peaks at 530.2, 530.9 and 532.1 eV respectively for the thin film annealed at 600 °C as shown in Figure 4. The results are almost similar to Chen et al and Wang et al [20, 21] who attributed 530.2 eV peak to the O^{2-} ions on the wurtzite structure of the hexagonal Zn^{2+} ion array Therefore, the lower energy peak of oxygen spectrum is attributed to Zn-O bonds. The higher binding energy (532.1 eV) is usually attributed to chemisorbed or dissociated oxygen or hydroxyl (OH^-) species on the surface of the ZnO thin film [10]. The component of binding energy centered at 530.9 eV is associated with the O^{2-} ions that are in oxygen deficient regions within the ZnO matrix. As a result, changes in the intensity of this component may be in connection with the variation in the concentration of the oxygen vacancies [22].

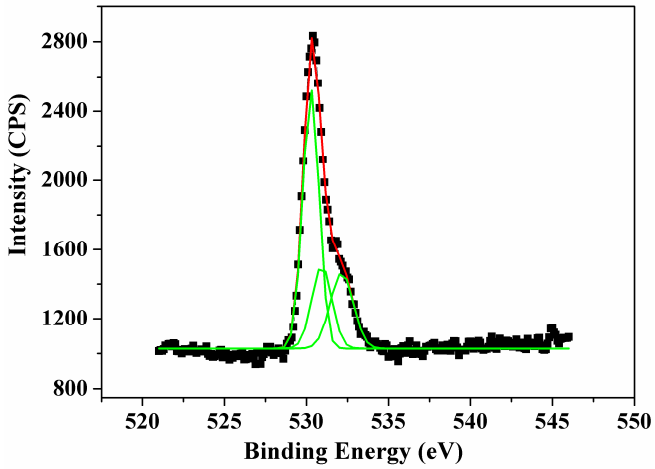

Figure 4: XPS core level spectrum around O1s of ZnO thin film annealed at 600 °C

3.3 Photoluminescence (PL) Analysis

Figure 5 shows the room temperature PL spectra of ZnO thin films annealed at 600 °C exhibiting UV and defect (green) emission. UV band emission centered at about 382.50 nm, is originated from the exciton recombination of the wide band gap ZnO taking place through an exciton-exciton collision process at room temperature [23].

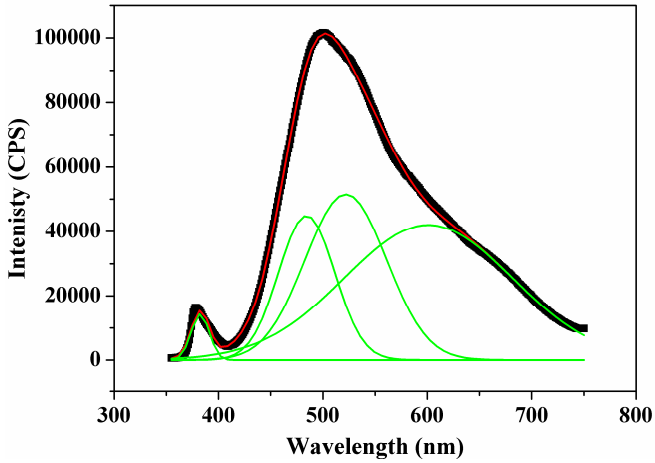

Figure 5: PL spectrum of ZnO thin films annealed at 600 °C

The DLE in green and yellow emission spectrum is relative to the variation in intrinsic defects of ZnO thin films, such as zinc vacancy, oxygen vacancy, interstitial zinc and interstitial oxygen. The DLE spectra was deconvoluted with four peaks centered at about 382.50 (3.24 eV), 484.48 (2.55 eV), 521.99 (2.37 eV) and 601.09 nm (2.06 eV) nm respectively. The energy related to 2.06 eV exhibits the signatures of yellow emission that is taking place due to the oxygen interstitials in ZnO thin films [24]. The evaluated energy of singly ionized Zn interstitial is 2.55 eV that is attributed to the transition from energy level of singly ionized Zn interstitial to Zn vacancy while 2.37 eV is related to oxygen vacancies from the bottom of conduction band to local defect energy level. It is believed that zinc interstitials/oxygen vacancies are donor impurities and oxygen interstitials/zinc vacancies are acceptor levels in ZnO thin films.

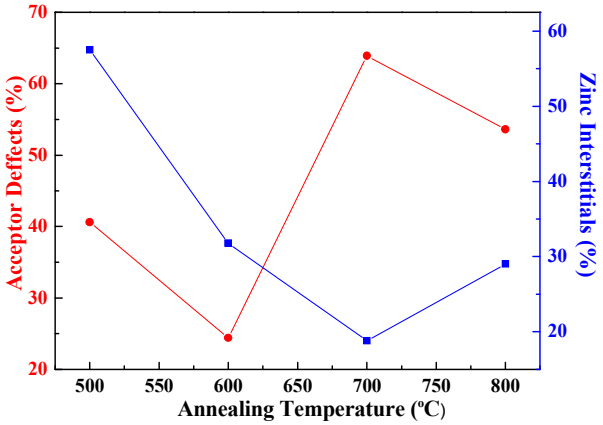

Figure 6: Variation in defect Concentration with annealing temperature in ZnO thin films

Figure 6 shows that donor defect levels related to zinc interstitials and oxygen vacancies are dominant at lower temperatures (500 and 600 °C) while the acceptor defects related to oxygen interstitials are dominant at elevated temperatures (700 and 800 °C). The concentration of acceptor defects is maximum in thin film annealed at 700 °C, leading to the formation of p-type ZnO thin film at this temperature.

4. Conclusion

We have investigated the influence of post-deposition annealing on structural, compositional and optical properties of ZnO thin films. Nanocrystalline ZnO powder was prepared by simple inexpensive wet chemical method using zinc acetate and potassium hydroxide as precursors. The XRD spectra showed improved crystalline quality of the thin films, with a consistent increase in crystallite size, at elevated annealing temperatures without any degradation in the wurtzite structure of ZnO. Temperature-dependent variation in lattice parameters was estimated to be minimum at annealing temperature of 700 °C exhibiting maximum reversion of zinc interstitials to crystal lattice as zinc lattice sites. The detailed XPS analysis of Auger Zn $L_3M_{4,5}M_{4,5}$ peaks reveals a continuous decrease in zinc interstitials (recombination with zinc vacancy) suggesting strong Zn-O bonding at 700 °C. Furthermore, the maximum contribution of oxygen interstitials in PL spectra, annealed at elevated temperatures, is favorable to form un-doped p-type ZnO thin films.

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