Oxygen pressure and heat treatment effect on nanocrystalline ZnO films grown by pulsed laser deposition

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Nanocrystalline ZnO films with preferred c-axis orientation are grown under varying oxygen partial pressure. The crystalline quality decreases at lower oxygen partial pressure whereas the lattice constant increases. The optical band gap is determined to be ~3.27eV from the transmittance data. The ZnO films when subjected to repeat heating and cooling cycles at temperatures below the deposition temperature their properties get modified. Comparison between the diffraction peak position, interplanar spacing, lattice constant, FWHM, grain size, optical band gap and electrical resistivity before and after cyclic heat treatment of the films is done. The sharp absorption edge of the film deposited at higher oxygen pressure shows a small red shift after heat-treatment leading to a change of 0.04eV in the optical band gap. The resistivity of film deposited at higher oxygen partial pressure reduces to half whereas that of deposited at lower pressure reduces to one-fifth after the heat-treatment.

1. Introduction

Zinc oxide (ZnO) is a wide direct band gap material and has many attracting applications in varistors, transparent high power electronics, surface acoustic wave devices [1, 2] and gas sensors [3-7]. The exciton binding energy of ZnO (60eV) is larger than that of GaN (25eV) at room temperature. This is another advantage ZnO has over GaN for the exciton-related device applications [8-10]. ZnO film has been studied as a novel wide-band-gap semiconductor material for short-wavelength optoelectronics devices [11, 12], such as UV lasers, blue to UV light-emitting diodes and UV detectors [13], which have important applications in high density data storage system, solid state lighting, secure communication and bio-detection.

Transparent conducting oxide (TCO) films are currently of great commercial and scientific interest. A large variety of TCO, such as In_2O_3, ZnO, and SnO2, in doped and undoped state have been widely studied over the years [14-16]. Traditionally indium tin oxide has been the TCO of choice but it is expensive due to the low natural abundance of indium [17]. A number of studies have been devoted to improving the electrical conductivity of ZnO thin films grown by chemical vapor deposition [18-20] sputtering [21-23], atomic layer epitaxy (ALE) [24], vapor phase epitaxy [25] and molecular beam epitaxy (MBE) [26,27] in addition to pulsed laser deposition (PLD)[6,11, 16,28], spray pyrolysis[5], sol-gel [3]print and fire technology[4,7] etc. Pulsed laser deposition (PLD) has been realized to be more useful in growing high quality thin films of metal oxides compared with other techniques. The metal oxide films deposited by PLD in vacuum are typically metal rich due to re-

condensation of metal on the surface of target [29]. In this study, nanocrystalline ZnO thin films are grown by PLD in the varying atmosphere of oxygen and the influence of heat-treatment on the structural, optical and electrical properties of the films is investigated.

2. Experimental

In the present study, a single target pulsed laser deposition system is used to deposit highly oriented, transparent ZnO films on float glass substrate held at 400^0C. PLD is a good technique to produce quality crystalline and stoichiometric thin films. A critical step to getting high quality thin films is treatment of substrate surface. The float glass substrates were treated with hot chromic acid and cleaned with trichloroethylene, acetone, and methanol and dried. The zinc oxide powder taken from Aldrich Chemical Company Inc. is of 99.999% purity. ZnO powder is calcined to remove the water of hydration and carbon in the form of carbon dioxide from carbonates. The material is prepared by grinding it down to micron size. Polyvinyl alcohol is mixed with the ZnO powder which acts as organic binder in forming the pellet. The pelletization is done at room temperature, by using uniaxial die press. The density of formed pellet is increased by sintering. The zinc oxide pellet is loaded in the PLD chamber after polishing. The ZnO targets are ablated by third harmonic of Q switched Nd: YAG laser (Quantel YG 980). The wavelength of laser pulses is 355nm, repetition rate is 10Hz and pulse duration is 6ns.The fluence is $2J/cm^2$. The target is continuously

rotated during the ablation process for uniform ablation. Deposition chamber was initially evacuated up to 10^{-6} Torr. Reactive deposition in presence of oxygen gas is performed by introducing oxygen at a pressure of 10^{-3} Torr in the vacuum chamber during the growth. The deposition is carried out for 20 minutes at a deposition rate of nearly 2 A^0/second. Another film from the same target is deposited for same time duration at the same rate of deposition with oxygen partial pressure of 10^{-4} Torr. Here onwards films deposited at 10^{-3} and 10^{-4} Torr are named as samples 1 and 2 respectively.

The as-deposited films are subjected to four thermal cycles in presence of atmospheric air between room temperature and 150^0C. The XRD patterns of the films before and after heat-treatment are taken using X-ray powder diffractometer (SEIFERT ISO–DEBEYEFLEX2002) using wavelength Cu-K$_\alpha$1 (λ=1.54060A^0). The transmittance of the films is obtained in the wavelength range 200-900nm using UV-VIS spectrophotometer-108, Systronics. Electrical resistivity of the films is measured at room temperature by the Vander-Pauw four-point-probe technique.

3. Results and discussion

3.1 Structural properties

Fig. 1 shows XRD θ-2θ scans for samples 1 and 2 grown at same temperature 400^0C of glass substrate. XRD pattern has been recorded in the range 10 to 80^0 and is shown here for the relevant range as no other peak is occurring. It can be seen from the figure that the structure of the ZnO film deposited in partial pressure of 10^{-3} as

well as 10^{-4} Torr is single crystalline with a preferred c-axis orientation along (0002). The ZnO related reflection for the samples is obtained at 2θ = 34.445^0 and 34.350^0 respectively.

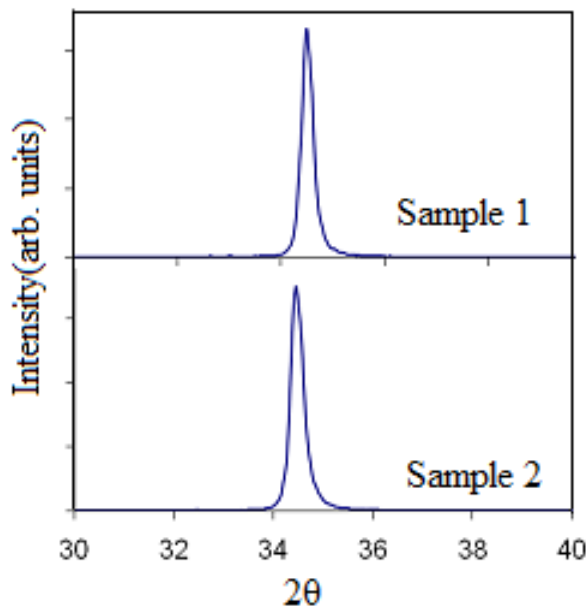*Fig. 1. θ-2θ XRD patterns of samples1 and 2 before heat-treatment.*

The structural parameters are summarized in Table 1. The FWHM is larger and therefore the grain size is smaller for sample 2 as compared to sample 1. Thus at lower oxygen partial pressure the crystalline quality decreases [22]. The lattice constant and interplanar spacing are comparatively larger for sample 2.

Table 1. Structural parameters of samples 1 and 2 before and after heat treatment.

Films	Peak position		FWHM		Grain size (nm)		Interplanar spacing		Lattice constant (c)	
	before	after	before	after	before	after	before	after	before	after
Sample 1	34.445	34.51	0.216	0.259	38.52	32.13	0.2602	0.2597	0.52030	0.51942
Sample 2	34.40	34.46	0.250	0.300	33.28	27.71	0.2608	0.2601	0.52172	0.52020

After heat treatment of both the samples 1 and 2 the ZnO related reflections in each pattern are obtained in (0002) plane (Fig. 2) thus retaining their strong c-axis orientation and single crystalline nature. For heat treated samples 1 and 2 the XRD peaks occur at 34.51^0 and 34.46^0 respectively. XRD peaks for the samples before heat-treatment are reproduced here for the purpose of comparison.

It can be clearly seen from Fig. 2 that the peak positions shift to higher θ-values after heat-treatment and therefore the c-lattice constant decreases. The grain size also decreases after heat treatment of the films, however, the crystalline quality remains better for higher oxygen partial pressure.
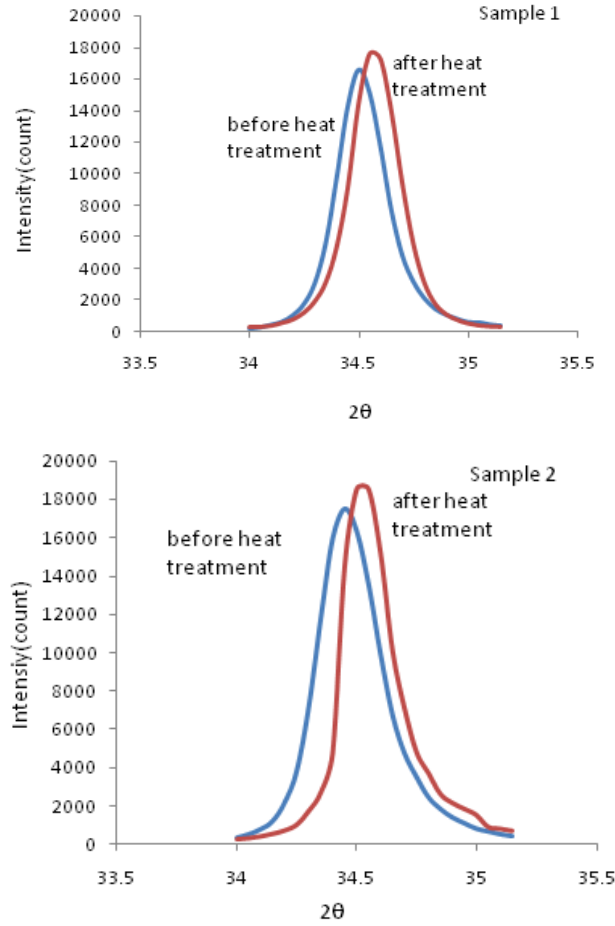
Fig. 2. XRD patterns of samples1 and 2 before and after heat-treatment. Diffraction peaks of Fig. 1 are reproduced here for the purpose of comparison.

Table 2. Optical and electrical properties of samples 1 and 2 before and after heat treatment.

Films	Average transmission in visible range		Optical band gap (eV)		Resistivity (ohm-cm)	
	before	after	before	after	before	after
Sample 1	70 %	65 %	3.27	3.23	0.030	0.014
Sample 2	66 %	60 %	3.24	3.23	0.091	0.018
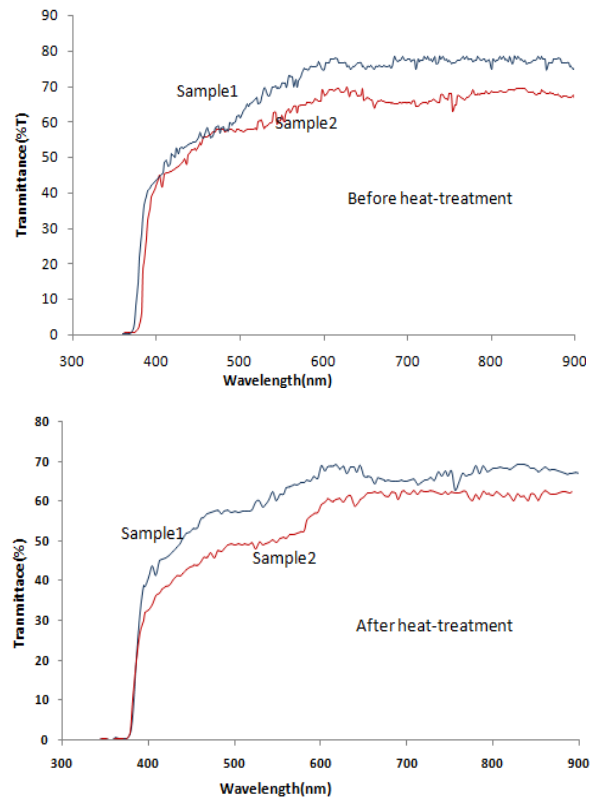
Fig. 3. Transmission spectra of samples1 and 2 before and after heat-treatment.

3.2 Optical properties

A complete scan over the wavelength range 200 to 900nm taking air as reference is carried out to obtain transmission spectra which are shown in Fig. 3. The films show an average transparency of 70 and 60% in the visible region, for samples 1 and 2, respectively. The sharp absorption edge occurs at 378 and 380 nm, respectively.

The optical absorption at absorption edge corresponds to the optical transition from valence band to conduction band, while the absorption in the visible region relates to some local energy levels caused by some intrinsic defects. Higher transmittance in visible region indicates that the film has less defects and better crystallinity. The optical band gap values for the two samples as determined are 3.27 and 3.2 5eV, respectively as shown in Table 2.

Heat treated film grown in oxygen partial pressure of 10^{-3} Torr shows an average transmission of nearly 65% between 450 to 900 nm i.e. in the visible and NIR region as shown in Fig. 3. Film of oxygen partial pressure of 10^{-4} Torr is lesser transparent. After heat-treatment, the sharp absorption edges for the two samples occur very close to each other and therefore the band gap for both the heat-treated samples films are obtained as 3.23 eV.

3.3 Electrical properties

The resistivity and Hall coefficient of films are determined by four probe Vander-Pauw method. Resistivity is found to be 0.03 and 0.09 $\Omega \cdot$ cm for samples 1 and 2, respectively, before heat treatment (Table 2).

The film shows n-type conductivity as determined from the signature of Hall-Coefficient. Zhao et.al.[30] reported the resistivity of undoped ZnO thin films deposited at 200 and 700^0C on quartz glass substrates by PLD to be 1.50 and 2.30 Ω-cm, respectively. The reasons for getting high resistivity might be the use of low energy density of the excimer laser. Jin et.al [31], reported the resistivity as 0.24 Ω-cm of ZnO thin film deposited at 400^0C on sapphire by PLD. Resistivity of heat treated films at room temperature is 0.014 and 0.018Ω-cm for samples 1 and 2, respectively and is shown in Table 2.The resistivity of undoped ZnO films obtained by us compares favorably well with Refs.30 and31.

4. Conclusions

Nanocrystalline ZnO films under varying oxygen partial pressures are grown. Films are single crystalline with a preferred c-axis orientation along (0002). It is seen that the crystalline quality decreases at lower oxygen partial pressure as the grain size decreases from ~38 nm (sample 1) to ~33 nm (sample 2) as the oxygen pressure decreases from 10^{-3} to 10^{-4} Torr. The optical band gap is determined to be 3.27and 3.24eV, respectively, from the transmittance data. The ZnO films when subjected to repeat. Heating and cooling at temperatures below the deposition temperature their properties - structural, optical and electrical - get modified. In some cases these properties get changed drastically. A comparison between the diffraction peak position, interplanar spacing, lattice constant, FWHM, grain size, optical band gap and electrical resistivity before and after cyclic heat treatment of the film samples 1 and 2 is done. Table1 summarizes the data for structural parameter and this facilitates a quantitative comparison between heat treated and as-deposited films. After heating, the XRD peaks shift to higher angles which lead to decrease in the interplanar spacing and the c-axis lattice constant. There is a small change in the transmittance of the heat-treated films. The sharp absorption edge for sample 1 shows a small red shift after heat-treatment leading to a change of 0.04eV in the optical band gap whereas the optical band gap for sample 2 remains practically unaffected. The resistivity of sample 1 reduces to half whereas that of sample 2 reduces to one-fifth after the heat-treatment.

Acknowledgements

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