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EFFECT OF DIFFERENT SUBSTRATES ON STRUCTURAL AND OPTICAL PROPERTIES OF ZnO THIN FILMS PREPARED BY PULSED LASER DEPOSITION (PLD)

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ABSTRACT: ZnO thin films were deposited at 450°C on glass, Si(100) and Si-polycrystalline substrates by pulsed laser deposition (PLD) method. KrF excimer (248 nm, 25 ns, 5 Hz, 2 J/cm^2) was used as a laser source. The effect of different substrates on structural and optical properties of ZnO thin films had been investigated. The experimental results obtained using X-ray diffraction (XRD) technique show that ZnO films grow in hexagonal Wurtzite-type structure with a dominant peak at ~34° with (002) orientation. The mean roughness deduced from atomic force microscopy (AFM) is found to be between 6.4 and 15.6 nm. The average transmittance of ZnO thin films deposited on glass substrates in the wavelength range from 400 to 800 nm is 80 % with a band gap Eg=3.23 eV.

KEYWORDS: ZnO thin films, pulsed laser deposition (PLD), wurtzite, XRD, AFM, UV-vis

1. Introduction

Zinc oxide (ZnO) is a cheap optical material that has attention recently [1,2]. It is a II–VI semiconductor which is highly transparent in the visible region with a wide and direct band gap of about 3.37 eV at room temperature and a high exciton binding energy of 60 meV [3]. ZnO is a promising material because it could be applied in many fields such as transparent conductive contacts, solar cells, laser diodes, ultraviolet lasers, thin films transistors, optoelectronicnic and other [4,5]. Generally, undoped ZnO thin films typically exhibit n-type conduction and are transparent conducting oxides (TCO) with a background electron concentration as high as 1021 cm-3 [6]. A variety of methods were employed to grow ZnO thin films, such as RF sputtering [7], chemical-vapor deposition [8], molecular- beam epitaxy [9], and pulsed laser deposition (PLD) [10]. Among these techniques, PLD is widely used for its simplicity and experimental flexibility. We have prepared and investigated nominally undoped ZnO thin films deposited at 450°C on glass, Si(100) and Si-polycrystalline substrates by PLD method. KrF excimer (248 nm, 25 ns, 5 Hz, 2 J/cm2) was used as a laser source. In this paper, the morphological and optical property of prepared ZnO films was also discussed.

2. Experimental

Undoped ZnO thin films were grown onto glass, Si(100) and Si-polycrystalline substrates by the conventional pulsed laser deposition (PLD) method. The laser used was a KrF excimer LAMBDA physic (25 ns, 5 Hz and 248 nm), and an energy fluence of 2 J/cm^2. The ceramic pellets of undoped zinc oxide (ZnO) are prepared using conventional cold ceramic pressing technique using ZnO (99.0%) purity powder obtained from FLUKA Company, and then sintered at 500°C for 3h. Before deposition, the substrates were chemically cleaned using acetone and ethanol. The chamber was evacuated by a turbo pump to a pressure of 5×10^{-3} Pa, the oxygen gas was introduced into the chamber, with a pressure maintained at about 1 Pa. The distance between the substrate and target was kept fixed at 4 cm and the substrate temperature is maintained at ~ 450°C. The beam laser was incident on the rotating target at an angle of 45° with respect to the target normal. The resulting thickness of the films was about 370 nm. The crystal structure of the films was characterized by conventional X-ray diffraction (XRD) at (θ-2θ) configuration using CuKα radiation (λ = 0.154183 nm) from Bruker-AXS D8 diffractometer. Atomic force microscopy (AFM) (Pacific Nanotechnology) was used for the observation of surface morphology for ZnO films deposited on different substrates in a region of 2.34×2.34 μm^2 area. The optical properties of the ZnO thin films were characterized by UV-vis spectrometer Shimadzu (UV-3101 PC) in the wavelength range 300-800 nm. The thickness and compositional depth profile was studied by Rutherford Backscattering spectrometry (RBS) using a 2 MeV 4He+ ion beam. The recorded RBS spectra were processed by the RUMP simulation computer program [11].

3. Results and discussion

3.1. Structural properties

The (θ–2θ) XRD patterns of ZnO thin films deposited onto different substrates are shown in Figure. 1. The peaks in the spectra of ZnO thin films deposited on all substrates confirm the hexagonal wurtzite polycrystalline structure which is in good agreement with (JCPDS 36-1451) and has a preferred orientation with the c-axis perpendicular to the substrates [12].

The strongest peak appearing at ~ 34° is attributed to the (002) line of the hexagonal ZnO structure, and the other smaller peak at ~ 72° represents the (004) diffraction.

It is well known that the (002) orientation of ZnO wurtzite structure is generally observed, suggesting that the surface free energy of (002) plane is the lowest in ZnO films [13,14].

To calculate the average grain size of the samples, the Debye–Scherrer equation is used [15]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

where λ is the X-ray wavelength used, θ is half the angle between the incident and scattered X-ray and β is the FWHM. The values of grain sizes given in table I are found to be in the range from 22 to 38 nm. It is observed that the smallest one corresponds to the ZnO thin films deposited on Si-poly substrate.

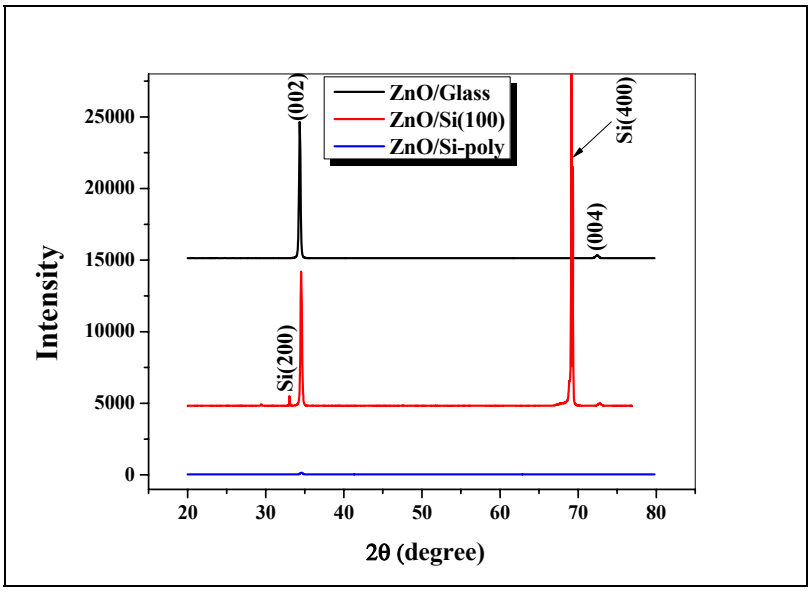

Figure. 1: XRD patterns of ZnO films grown on different substrates at 450° C.

Table 1:

Different structural parameters of ZnO thin films deposited on glass and silicon substrates.

ZnO film	Positions (002) (2θ°)	Crystallite size (nm)	d_{002} (nm)	stress (GPa)	*c*-lattice constant (nm)
ZnO/glass	34.36	37	0.2610	- 0.6709	0.5220
ZnO/Si(100)	34.54	38	0.2597	+ 0.4920	0.5194
ZnO/Si-poly	34.58	22	0.2594	+ 0.7603	0.5188

In order to additionally understand the effect of the substrate on the stress of ZnO thin films, the film stress σ_{film} can be calculated based by the following formula, which is valid for a hexagonal lattice [16,17].

$$\sigma_{film} = \frac{2c_{13}^2 - c_{33}(c_{11} + c_{12})}{2c_{13}} \times \frac{c_{film} - c_0}{c_0} \tag{2}$$

where c_{ij} (i,j = 1, 2, 3) stands for the elastic constants. c_0 (0.5205 nm) is the lattice constant of bulk ZnO and c_{film} is the lattice constant of fabricated ZnO films. c_{film} can be obtained by the following formula:

$$c_{film} = 2d_{002} = \frac{\lambda}{\sin\theta} \tag{3}$$

where θ is the Bragg diffraction angle. Substituting the values of c_{ij} (i,j = 1, 2, 3) in formula (2) with c_{11}=208.8, c_{33} = 213.8, c_{12} = 119.7, c_{13} =104.2 GPa [17]. We can obtain the residual stress σ_{film} in ZnO film by the following formula:

$$\sigma_{film} = -232.8 \times \varepsilon \tag{4}$$

where ε is the strain in the films in the direction of the c-axis:

$$\varepsilon = \frac{c_{film} - c_0}{c_0} \tag{5}$$

The films with values of c greater than the bulk value (0.5205 nm) have a positive or extensive strain in them whereas those with lower values have a negative or compressive strain [18].
The negative sign for the calculated stress for the ZnO thin films deposited on glass substrate indicate that the crystallites are in a state of compressive stress. For all the other films deposited on silicon substrates, the value of the stress is positive indicating that the films are under tensile stress.

3.2. RBS analysis.

RBS measurement was used to determine the composition and distribution of the Zn and O elements in the ZnO layers Figure. 2 shows the experimental (Random) and simulated RBS results deposited on Si (100) substrate. The thickness of the layer is about 370 nm. The composition obtained from RBS analyses are fixed at 42.2 at% O, 57.8 at% Zn.

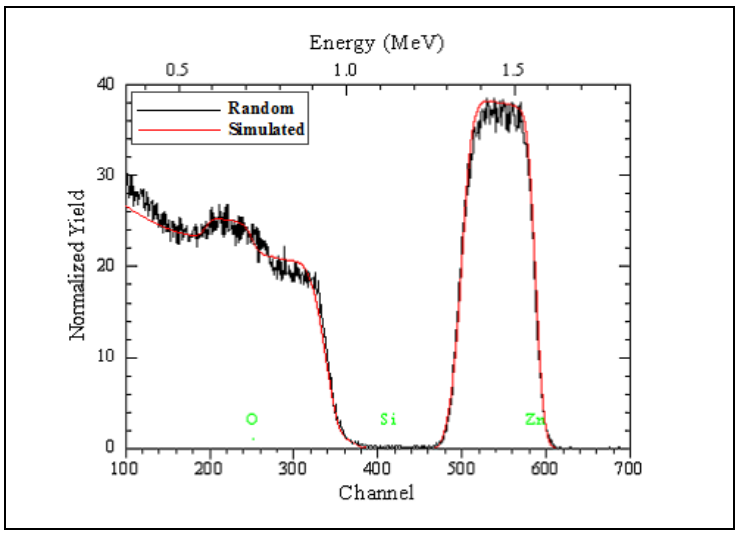

Figure. 2: Random and simulated RBS spectra of ZnO films deposited onto Si (100) substrate.

3.3. AFM analysis

Figure. 3 shows AFM topographies of the ZnO thin films deposited on glass, Si(100) and Si-poly substrates. The mean roughness (*Ra*) of the surfaces is calculated for a 5.51µm square scan area. It is found that the mean roughness significantly decreases from 15.6 to 6.4 nm of ZnO films deposited onto different substrates. It is known that the increase in surface roughness may cause deterioration of the electrical and optical properties [19]. However, these differences in mean roughness have a significant influence on optical properties of the films considered in this study.

These results, together with the XRD analysis, clearly indicate that the crystallinity is influenced by the substrates. This is in good agreement with other results [20].

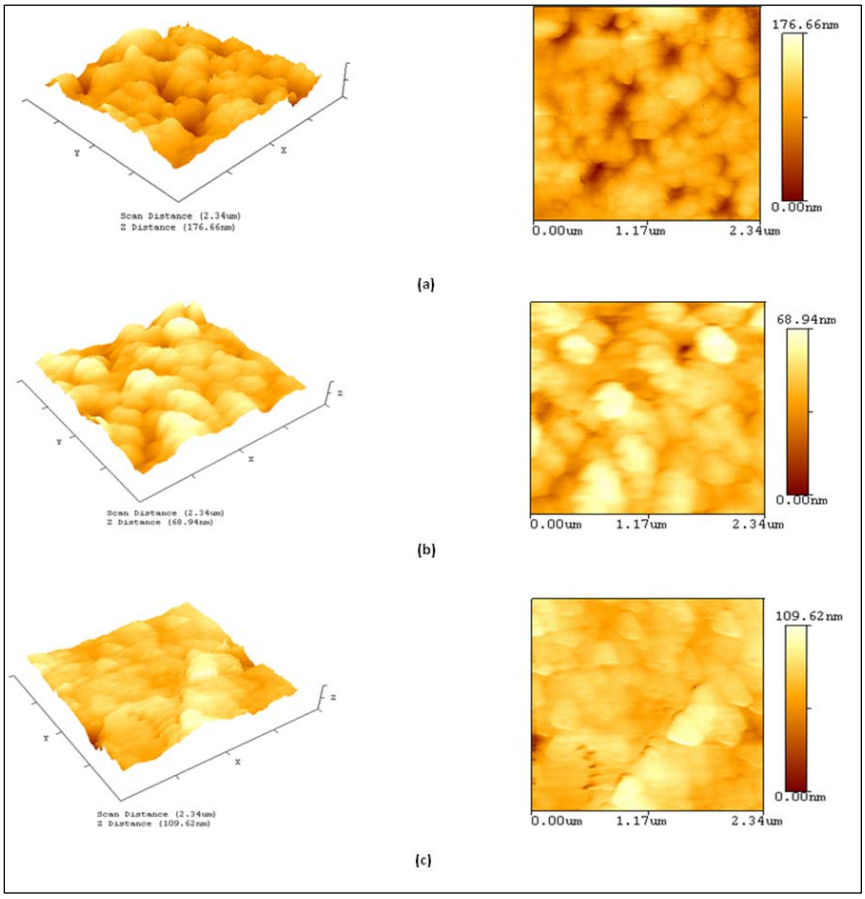

Figure. 3: AFM images of ZnO thin films deposited on glass (a), Si(100) (b) and Si-Poly (c) substrates.

3.4. UV–vis spectra analysis

Figure. 4 shows the transmission spectra of ZnO thin film deposited onto glass substrates in the wavelengths range of 300-800 nm. All the measurements are realized at room temperature.

As can be seen, the average optical transmittance of the samples in the visible range is amount 80%. In addition, it is important to notice that the films have a thickness 370 nm, leading to a good optical quality of the produced ZnO materials which is in good agreement with the literature reports [21, 22].

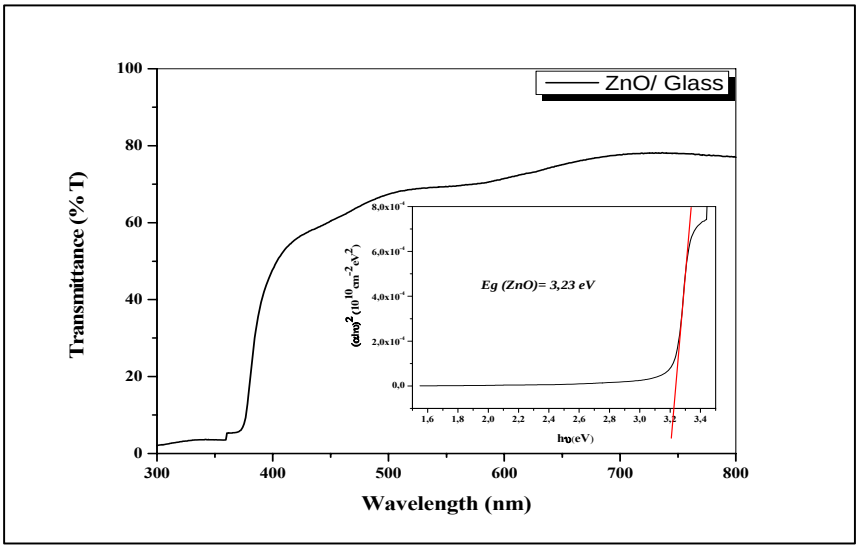

Figure. 4: Optical Transmittance spectra of ZnO thin films deposited on glass substrate by PLD(The inset shows plot of $(\alpha h\upsilon)^2$ versus hυ).

ZnO oxide has a direct band gap which has a close relationship with the absorption coefficient α and phonon energy, hυ [23],

$$\alpha^2 = A(h\nu - Eg) \tag{6}$$

where Eg is the optical band gap of the film, A is a constant. The absorption coefficient α could be calculated from the following equation [24],

$$\alpha = \frac{\ln 1/T}{d} \tag{7}$$

where T is the transmittance and d is the thickness of the film. The plot of the graph $(\alpha h\upsilon)^2$ vs $h\upsilon$ (see inset figure. 4) is accomplished using formula (7). The band gap value of the produced ZnO films, determined by the optical method, is obtained by extrapolating the linear portion of this graph to $(\alpha h\upsilon)^2 = 0$. As can be seen from the figure. 4, Eg is equal to 3.23 eV. The glass seems to be the most favorable substrate in the formation of strongly textured ZnO thin films.

4. Conclusions

The properties of ZnO thin films grown by PLD onto different substrates including glass, Si(100) and Si-Poly were investigated. It was observed that the substrate nature was a strong factor influencing the properties of ZnO films. All the films were polycrystalline with a hexagonal wurtzite structure and had highly (002) preferred orientations with a c-axis perpendicular to the substrates. The films ZnO deposited on glass and Si(100) showed the best crystallinity. The values of grain sizes vary from 22 to 38 nm and the mean roughness increases up to 15.6 nm in the case of the Si(100) substrate. The transmission of the ZnO films is about 80% and the deduced value of their optical band gap is 3.23 eV.

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