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X-Ray Elastic Constants of ZnO Thin Films

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Abstract – Elastic constants of zinc oxide thin films have been determined using $\sin^2\psi$ method. Surface morphology and crystalline structure of zinc oxide were examined, using atomic force microscope (AFM) and field emission scanning electron microscope (FESEM). The different planes and lattice parameters of ZnO films were obtained by High Temperature X-Ray Diffraction (HT-XRD) method. The minimum stress and residual stress were found to be 1.27±4.88 Mpa and4.62±0.23 Mpa for (101) and (110) different atomic planes.

Keyword: ZnO films, Elastic Constants, $\text{Sin}^2\psi$ Technique, HT-XRD, Residual Stress

1. Introduction

Among all nanostructure semiconducting materials, ZnO is the richest family of them [1,2]. The average stress of ZnO thin films is dependent to the mechanical strain and stress. Internal stress will appear during the preparing of thin films. Internal stress can induce a variety of undesirable consequences including dislocations, permanent deformations and microstructural variations [3, 4]. However, the more researches are focused on fabrication method and the thermal, electrical and optical, structural properties of ZnO thin films, the less research are attended about the mechanical properties. In mechanical properties there are very different results [5-8]. It is clear that the two main properties extracted from peak width analysis are crystallite size and stress which are mechanical properties of thin films. The crystallite size is important parameter which concluding the mismatch and misfit between the film and substrate. The mismatch induces an increasing compressive stress state of the film as temperature increases [9]. These stresses arise because of the expansion mismatch between the coating and the substrate exposed to a temperature gradient (thermo mechanical stresses) and growth stresses. The role of residual stress in thin films comes into play when studying mechanical integrity of thin films. It has a significant influence on film strength, and thus on device reliability. If the stress is large enough, it could lead to substrate fractures, film or substrate/film interface.

However, the crystal quality of ZnO thin films strongly depends on the growth techniques, growth conditions and selected substrates. In this study stress, residual stress and X-Ray Elastic constant of ZnO thin films at different temperatures have been found and the morphology of substrate is shown at room temperature.

2. Experimental

The Zinc Oxide layer has been deposited on 1cm×1cm p-type Si(111) substrate by thermal evaporation method. Before deposition, the substrates cleaned in two steps. First used ethylic alcohol and acetone to remove impurity from the surfaces, then put them in 10% HF for one minute. The samples placed in a furnace at an oxygen flow with 300°C heat for 2 hours. After evacuation, the film thicknesses were measured by vibrating quartz system. The made crystal structure was analyzed by X-Ray Diffractometer (XRD) and in situ High-Temperature XRD(HT-XRD).To identify the crystalline structure and the residual stress of the deposited ZnO/Si films, X-ray diffractometer (Cu-Kα radiation, λ=0.15405 nm, Bragg-Brentano geometry, Philips PW3710 model) has been used. Zinc oxide with thickness of 240 nm was deposited on Si(111).The morphology, microstructure and the roughness of the surface were also studied using field emission scanning electron microscope (FESEM) and Atomic Force Microscope (AFM).

3. Results and Discussion

The ZnO thin film has a hexagonal structure and the basic parameters of structure are a=3.253 Å and c= 5.209Å. Figure1, showing the XRD and the in situ XRD, HT-XRD patterns of ZnO thin films from room temperature up to 500°C and vice versa to room temperature. Figure 2 reveals the reversible condition of ZnO thin films; it means that there are not any considerable changes in the curve.

The $\sin^2\psi$ method is used to determine the stress in ZnO thin films. The minimum stress is proportional directly to the slop in $\sin^2\psi$. The stress of ZnO thin films in this study is uniaxial stress which has a one direction in $\sin^2\psi$ curve and can calculate normal stress and shear stress. The lattice parameters are calculated at different tilt angles ψ [10]. In Figure 2, all of curves are nonlinear that shows the Bragg's angle in (35.4 degree) has a minimum value and in (36.6 degree) has a maximum value. There are considerable changes in different temperatures; therefore, it reveals the reversible condition of ZnO thin film.

(a)

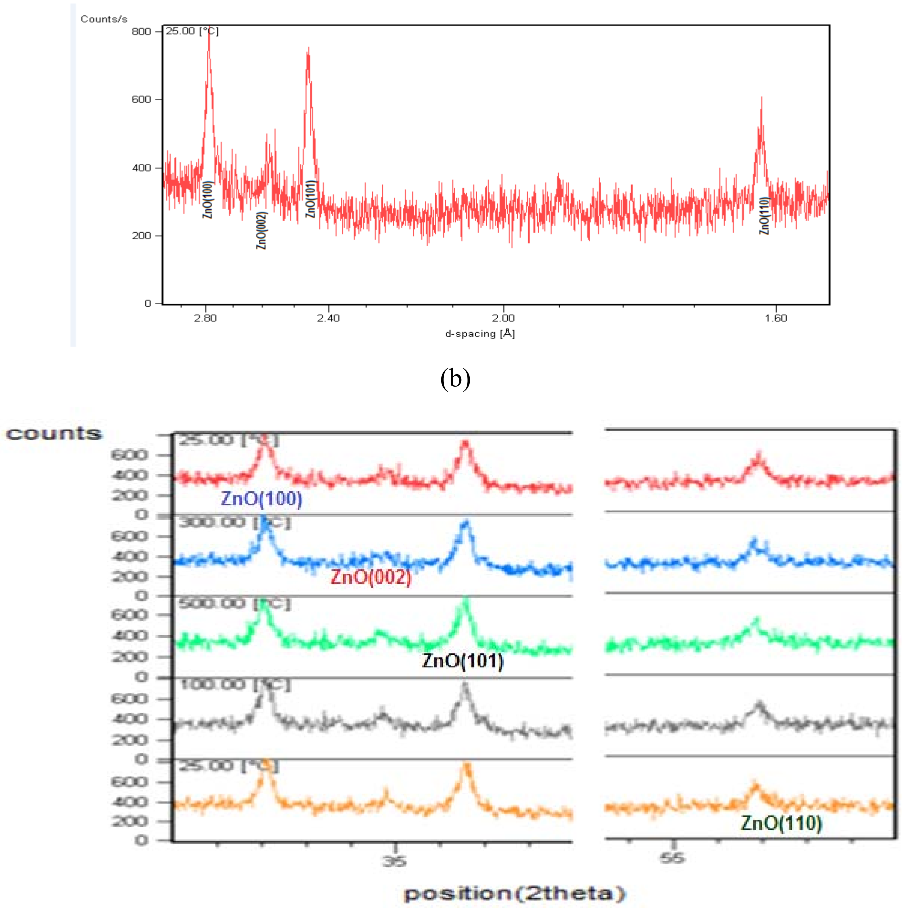

Figure 1: (a). XRD pattern of ZnO at room temperature

(b). In situ HT-XRD patterns of ZnO film on Si substrate.

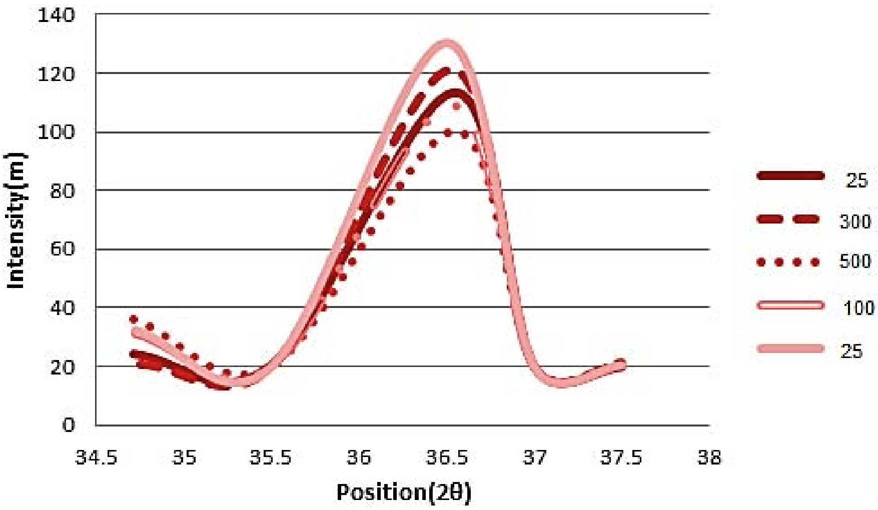

Figure 2: Intensity vs. Bragg angles at different temperatures.

For obtaining the X-Ray Elastic Constants (XEC), the single crystal elastic constant is critical; hence, it depends on the angle ψ and the plans with different atomic planes (hkl). The best plane in our study is (101) plane which has a zinc blend shape of ZnO thin film at 32, 34 and 56 position(2θ) and at 36 position(2θ) the shape of ZnO thin film is hexagonal.

The fundamental equation for X-ray stress measurement is:

$$\varepsilon = (S_2/2)\ {}^{i}_{\text{phase}} (\sigma_{11} \cos^2 \varphi + \sigma_{22} \sin^2\varphi - \sigma_{33}) \sin^2\psi + (S_2/2)\ \sigma_{33} + S_1(\sigma_{11}+\sigma_{22}+\sigma_{33})[], \qquad (1)$$

where $\varepsilon_{\varphi\psi}$ is a normal strain and σ_{ij} are stress components in the sample coordinate system. In the uniaxial mode ($\sigma_{11} = \sigma_{\varphi}$; $\sigma_{22} = 0$; $\sigma_{12} = 0$), S_1 and S_2 are the x-ray elastic constants and have the following relations to Young's modulus (E) and Poisons ratio (v) then $S_1 = -v/E$, $S_2/2 = 1+v/E$.

If $\varphi=0$ then $\sin^2\psi_{\textit{strain-free}} = \frac{-S_1}{\frac{1}{2}S_2}$, therefore $\sin^2\psi_{\textit{strain-free}}$ is determined to be equal to 0.2.

The Young's modulus (E_{hk}) is in direction normal to the set of crystal lattice plane (hkl). In a hexagonal crystal, ″E_{hk}″ is worked out them the single crystal elastic constant. The single crystal elastic constant for ZnO and Si are calculated using x'pert stress software version 2.2 and shown in table 1. The residual stress of ZnO thin films is found 4.62±0.23 (Mpa) at 56° Bragg angle and the other values of stress are shown in table 2.

Table 1: Single crystal elastic constants

Materials	S_{11}	S_{22}	S_{44}	S_{12}	S_{13}	C_{11}	C_{33}	C_{44}	C_{12}	C_{13}
Si	7.65	-	11.90	216	-	168	-	66	84	-
ZnO	$7.85(10^{-12})$	$6.24(10^{-12})$	$23.57(10^{-12})$	-	$2.20(10^{-12})$	-	-	-	-	-

Table 2: Mechanical properties of ZnO thin film.

Plane(hkl)	**Lattice parameter[Å]**	**Position (2θ)**	**Young Module (Gpa)**	S_1	$1/2S_2$	**Stress (Mpa)**
(101)	a:2.76	32	146.25	-2.43	9.17	4.41±4.42
(101)	a:3.39	34	117.80	-3.06	11.54	1.37±3.39
(101)	a:3.11 c:5.17	36	119.21	-3.02	11.41	1.27±4.88
(101)	a:3.91	56	122.83	-2.93	11.57	4.62±0.23

AFM technique has been used to study the roughness of the surface of these ZnO thin films. AFM 3-D image of ZnO thin films is shown in Figure 3 with 240 nm thickness in the 5×5 µm. This figure shows the topographic and phase trace at room temperature. The root-mean-square (rms) surface roughness is estimated 24 nm from the AFM image. FESEM images of nanostructured ZnO thin films deposited on Si substrate at temperatures 25^{o}C which is shown in Figure 4.

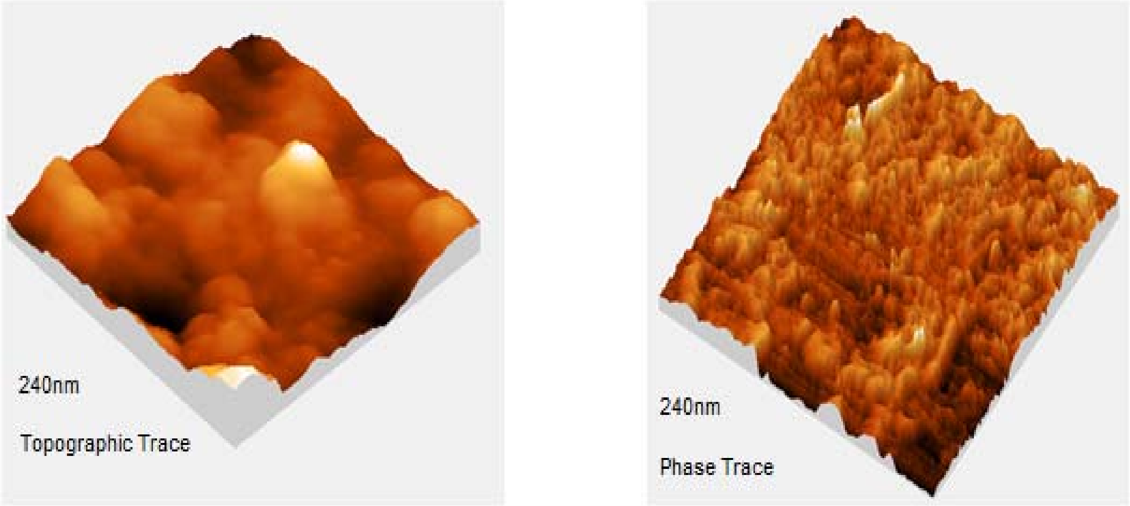

Figure3: AFM 3-Dimensional images of 5×5 μm scan of ZnO thin films with 240 nm thicknesses

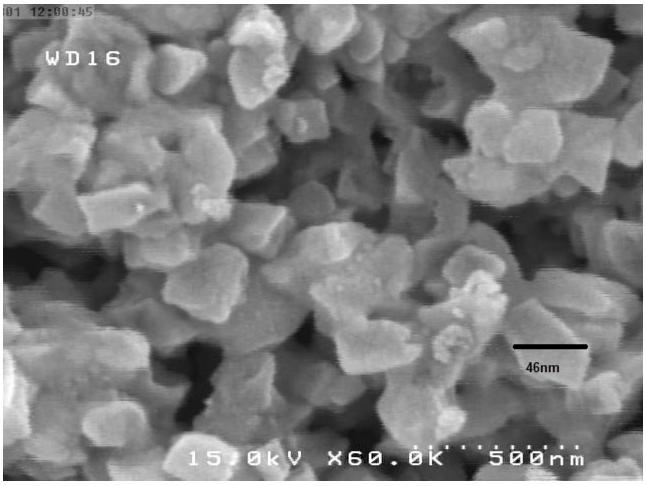

Figure 4: FESEM image of nanostructured ZnO thin film.

4. Conclusion

The structure of ZnO thin films has been identified by X-Ray Diffraction (XRD) and the different patterns of thin films is achieved by HT-XRD. The roughness of the surface is determined by AFM method: the root-mean-square (rms) is estimated 0.24 nm. The single crystal elastic constant is obtained by software and the Young's module is found which is so essential for calculation of stress and residual stress. The (101) direction is found to be the best plan which has a hexagonal structure and minimum uniaxial stress in ZnO thin film. The residual stress is taken out in 2θ=56^{o} because the stress is negative and the thin film is compressive. The nanostructured ZnO thin film is shown by FESEM.

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