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Growth and characterization of ZnO thin films using XRD and AFM

FUNCTIONALIZATION OF MATERIAL SURFACES

Abstract

The zinc oxide (ZnO) films were deposited by RF sputtering from a ZnO:Al target on oriented p-type Si (111) substrates at RF power of 300W and 600W. The deposited films were post-growth annealed in a tube furnace in nitrogen atmosphere for 3 minutes at temperatures of 400 and 500 °C. The X-ray diffraction (XRD) and atomic force microscopy (AFM) were employed in order to investigate the effect of the process parameters and post-deposition annealing on the microstructure and the surface morphology of ZnO thin films. Changes due to different preparation conditions were recognized.

1. Introduction

Transparent conductive zinc oxide films have received much attention over the past few years because of their good electrical and optical properties, in combination with their large bandgap, abundance in nature and absence of toxicity [1]. ZnO has a wide range of properties that depend on doping, including a range of conductivity from metallic to insulating (including n-type and p-type conductivity), high transparency, piezoelectricity, room-temperature ferromagnetism and huge magnetooptic and chemical-sensing effects. It can be grown in many different nanoscale forms, thus allowing various novel devices to be achieved. Control of its defect chemistry is critical for controlling properties, which determine applications of ZnO thin films and ZnO nanostructures [2].

The properties exhibited by ZnO thin films depend on the non-stoichiometry of the films, resulting from the presence of oxygen vacancies and interstitial zinc. Moreover, aluminium-doped ZnO (AZO) films can be deposited at relatively low deposition temperature with good stability (in H_2 plasma). The electrical behaviour

of ZnO thin films could be improved by replacing Zn^{2+} species by elements with higher valence, such as In^{3+}, Al^{3+} or Ga^{3+} using the metal–organic chemical vapour deposition (MOCVD) method, the sol–gel method, spray pyrolysis, pulsed laser deposition or sputtering. The electrical and optical properties are generally dependent on the deposition and post-deposition conditions, because these properties change significantly with the absorption and desorption of oxygen that occurs during these processes. [1]

ZnO is on the borderline between a semiconductor and an ionic material. Under most growth conditions, ZnO is an n-type semiconductor, while p-type conductivity of ZnO has also been reported for growth under certain conditions. ZnO exhibits a wurzite structure (hexagonal symmetry) or rock salt structure (cubic symmetry). However, ZnO crystals most commonly stabilize with the wurzite structure (hexagonal symmetry), whereas the crystals exhibit the rock salt phase (cubic symmetry) at high pressure. The lattice parameters of ZnO are a = 0.32495 nm and c = 0.52069 nm at 300K, with a c/a ratio of 1.602, which is close to the 1.633 ratio of an ideal hexagonal close-packed structure. In the direction parallel to the c-axis, the Zn-O distance is 0.1992 nm, and it is 0.1973 nm in all other three directions of the tetrahedral arrangement of nearest neighbours [3].

It is well known that the structural properties and surface morphology of materials in thin film form depend on the deposition techniques, deposition conditions and post-deposition processing. These properties for metal oxide films have become of great interest in the last few years. In particular, the field of optoelectronics devices has benefited from the production of Transparent Conducting Oxides (TCO) materials characterized by a high transmittance due to high optical bandgap and low refractive index. The optical properties of Transparent Conducting Oxides are closely related to the material surface, its quality and the microstructure.

The microstructure determines how the light is transmitted through the layer. Compact and porous layer is rather different. Porous and texturized layers with granular surface tend to scatter the light whereas compact layers with homogeneous and flat geometric surface have higher reflection. Porous layers are therefore much viable.

In this paper, the effect of the process parameters and post-deposition annealing on the microstructure and the surface morphology of ZnO thin films is reported. Throughout these investigations, the aim was to find the correlation between process parameters and these physical properties.

2. Experimental

The ZnO films were prepared onto unheated p-type Si substrates with crystallographic orientation <111>, doped with boron. The ZnO films were deposited by RF sputtering from a ZnO:Al target with 2 wt.% Al. (10 cm in diameter, with 99.999% purity) at the Department of Microelectronics. Before deposition, the surface of the target was pre-sputtered for 10 minutes. The sputtering was done at RF power of 300W and 600W. The pressure of working atmosphere was 1,33 Pa. The distance between the target and the substrate was approximately 4cm. The sputtering conditions are listed in *Table 1*. The film thickness under the above conditions was ranged from 250 to 350 nm and was measured by a Talystep. After deposition, samples 1a400, 1a500, 2a500 were annealed in a tube furnace for 3 minutes in N_2 atmosphere at 400°C and 500°C, respectively (see the *Table 1*)

Table 1. List of samples:

sample no.	RF power	thickness	annealing temperature
1	600 W	350 nm	-
1a400	600 W	350 nm	400°C
1a500	600 W	350 nm	500°C
2	300 W	250 nm	-
2a500	300 W	250 nm	500°C

The crystal structure was identified with a Theta Theta Diffractometer D5000 with a Goebel mirror in Bragg-Brentano geometry and grazing incidence geometry with CuKα radiation. The structure refinement process was calculated using the software EVA Diffrac Plus.

The surface morphology was observed by atomic force microscopy (AFM) using Park Systems XE-100 under normal air conditions, operating in non-contact mode.

3. Results

3.1 XRD results

The XRD patterns of the ZnO films deposited at RF power of 600 W (samples no.1) and 300 W (samples no.2) are shown together with the annealed samples no. 1a400, 1a500, 2a500 in *Fig.1* (GID mode - grazing incidence diffraction) and *Fig. 2* (BB mode- Bragg-Brentano geometry). In XRD spectra, the dominance of (002) diffraction peak

showed that the ZnO thin films are polycrystalline with hexagonal structure and have a good c-axis orientation, corresponding to vertical growth with respect to the substrate. The values of the full-width at half-maximum (FWHM) are summarized in the *Table 2* and dependence of FWHM of the (002) diffraction peak on the annealing temperature is shown in *Fig. 3*.

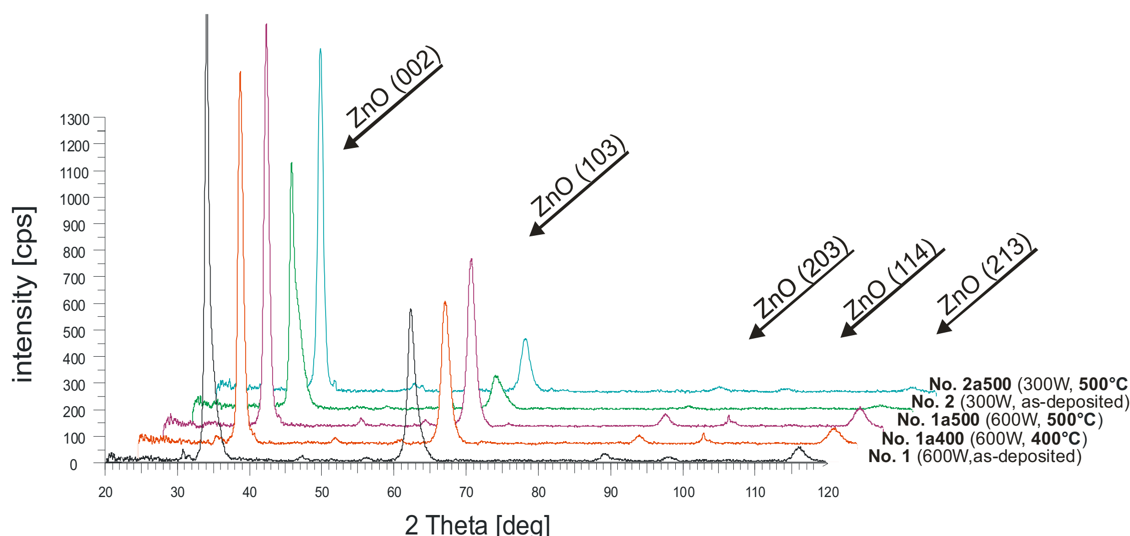

Fig. 1. XRD patterns of ZnO films (mode grazing incidence)

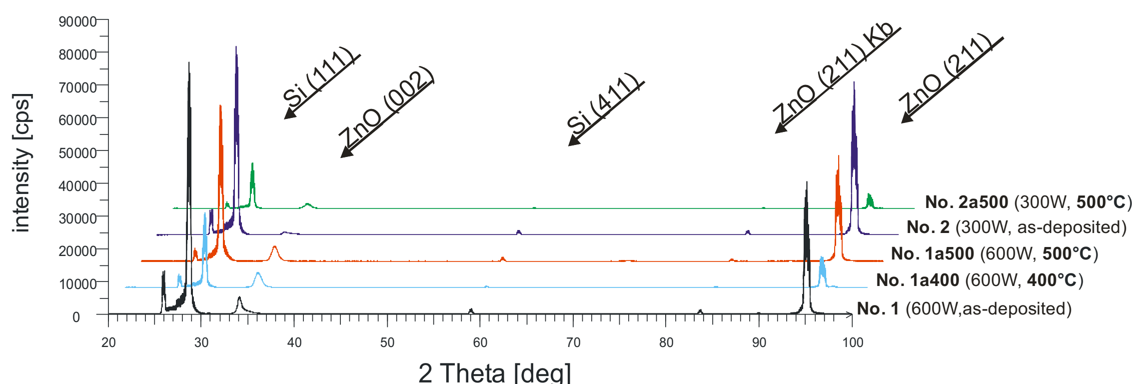

Fig. 2. XRD patterns of ZnO films (mode Bragg Brentano)

Grazing incidence geometry (GID mode) results

The full-width at half-maximum (FWHM) of the diffraction peak (002) of sample 1 (deposited at 600W) is 0.55, which is less in comparison to 0.82 of sample 2 (deposited at 300W). The value of FWHM is also lower for the diffraction peak (103) for sample 1. These results indicate that films deposited at RF power of 600 W have better crystalline

structure. Post-deposition thermal annealing has the effect of broadening the diffraction peak (002) for sample 1, indicating that the size of grains has been modified. On the other side, there is no change for sample 2 after annealing. Peak (103) has been broadened after annealing at 400 °C, but sample annealed at 500 °C has about the same FWHM as sample 1. In contrary, (103) peak narrows for sample 2.

Table 2. Full-width at half-maximum (FWHM) of the diffraction peaks

	FWHM [°]				
	mode grazing incidence (GID)		mode Brag Brentano (BB)		
sample no.	ZnO (002)	ZnO (103)	Si(111)	ZnO(002)	ZnO(211)
1	0.55	1.14	0.25	0.43	0.32
1a400	0.80	1.21	0.21	0.72	0.32
1a500	0.80	1.16	0.25	0.68	0.32
2	0.82	1.31	0.24	0.33	0.35
2a500	0.83	1.13	0.23	0.54	0.31

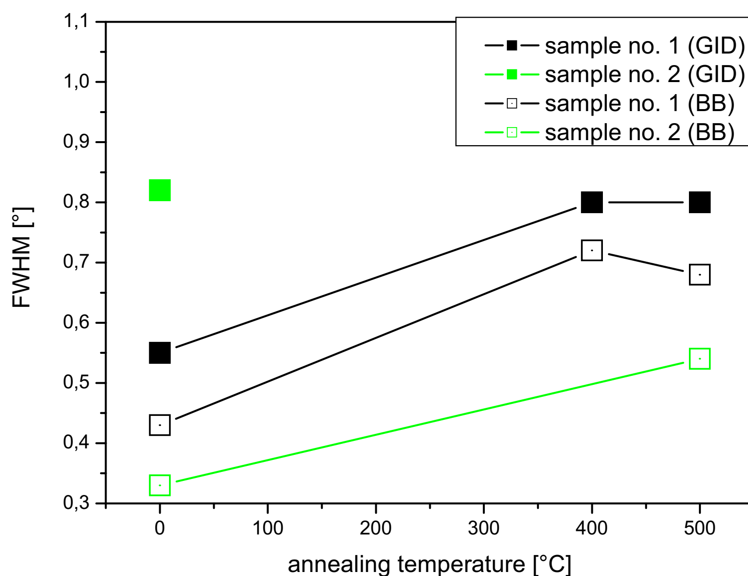

Fig. 3. The dependence of FWHM of the (002) diffraction peak on the annealing temperature (BB and GID mode).

The comparison of the relative intensities normalized to the highest peak is presented in *Fig. 4.* ,*Fig. 5.* and also *in Table 3.*

Table 3. Relative intensities of the diffraction peaks

	relative intensities of the diffraction peaks		
	mode grazing incidence (GID)		mode Brag Brentano (BB)
sample no.	ZnO (002) : ZnO (103)		Si(111) : ZnO(002) : ZnO (211)
1	1 : 0,33		1 : 0,07 : 0,53
1a400	1 : 0,39		1 : 0,19 : 0,42
1a500	1 : 0,42		1 : 0,09 : 0,68
2	1 : 0,15		1 : 0,02 : 0,80
2a500	1 : 0,17		1 : 0,13 : 0,31

<u>Bragg Brentano geometry (BB mode) results</u>

From XRD spectra of as-deposited ZnO films it was found that diffraction peaks from the (211) lattice plane of the ZnO lattice have the value of FWHM about the same for all samples. On the other hand, the value of FWHM of diffraction peaks from (002) lattice plane show increasing trend for annealed samples. Increasing value of FWHM indicates that the film has smaller grains and is rather amorphous than polycrystalline.

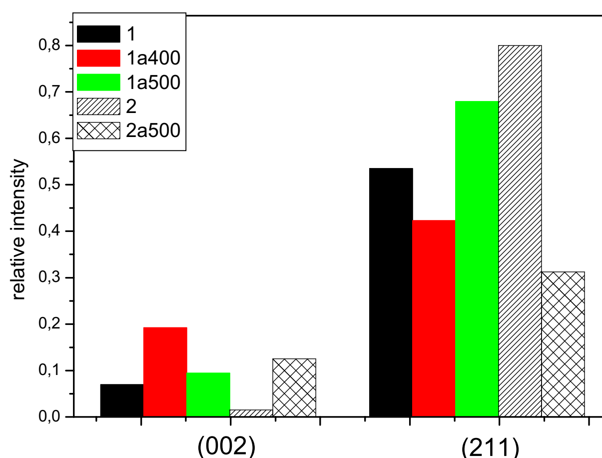

Fig. 4. Relative intensities of diffraction peaks (002) and (211) – mode BB

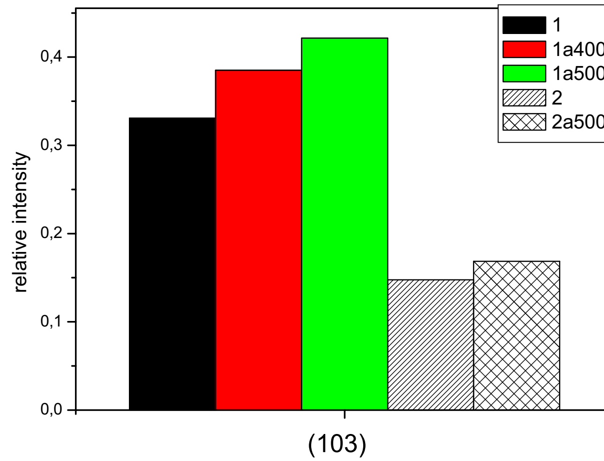

Fig. 5. Relative intensities of diffraction peak (103) – mode GID

The grain size of the films can be estimated by the Debye-Scherrer formula using FWHM value of the XRD diffraction peaks as follows:

$$D = 0.89\lambda / B \cos\theta$$

where D, λ, θ and B are the grain size, the X-ray wavelength of 0.15406 nm, Bragg diffraction angle and the FWHM of the diffraction peak of the (002) direction for ZnO films, respectively. The calculated grain sizes of the samples are presented in *Table 4*, indicating that grain size is larger for samples deposited at 600W in comparison to those deposited at 300W.

The position of (002) peak shifts to higher 2θ angle, from 33,895° to 34,535° in BB mode and in GID mode from 34,545° to 34,850°. According to the XRD data of the Joint Committee on the Powder Diffraction Standards (JCPDS) card [4], the 2θ angle for the bulk ZnO without stress is equal to 34.431°. This value best fits the sample 1a400.

Table 4. Calculated grain size.

sample no.	grain size [nm]
1	15.1304
1a400	10.4022
1a500	10.4022
2	10.1485
2a500	10.0262

3.2 AFM results

Fig 6.-10. show the surface morphology variations of the ZnO thin films over a scale of 2μm x 2μm. The AFM measurements of the ZnO films surface morphology shows similar results as measured by XRD. The surface morphology shows changes in grain size for deposition power of 600 W and 300 W as shown in the 3D pictures, respectively. After annealing the rearrangement of the polycrystalline structure as well as grain size is visible in Fig. 7., Fig. 8., Fig. 10. for ZnO films. AFM images indicate that larger clusters formations were formed after annealing. Most visible changes due to annealing occurred for samples no.2 prepared at lower RF power of 300 W. These changes of the morphology were proven also by statistical values of root mean square (RMS). The values of RMS were increased for annealed samples (*Table 5*).

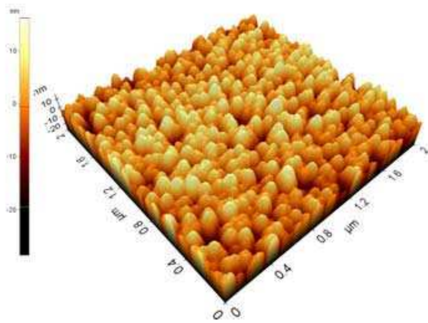

Fig. 6. AFM image of sample no. 1

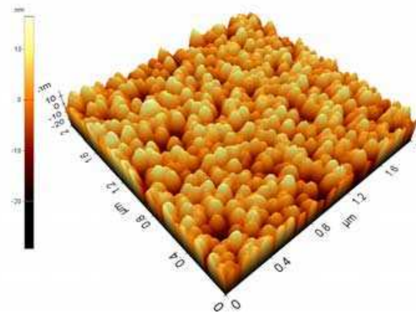

Fig. 7. AFM image of sample no. 1a400

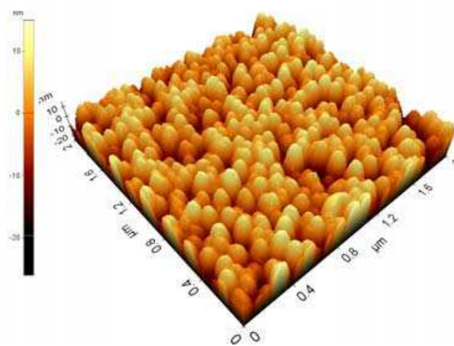

Fig. 8. AFM image of sample no. 1a500

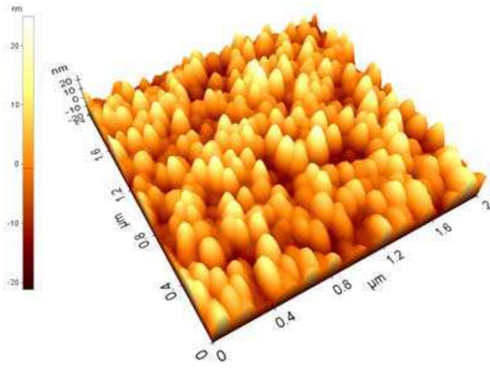

Fig. 9. AFM image of sample no. 2

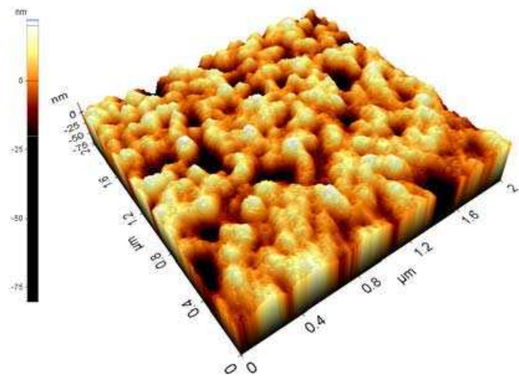

Fig. 10. AFM image of sample no. 2a500

Table 5. Quantitative roughness analysis

sample no.	RMS [nm]
1	5,68
1a400	5,87
1a500	5,90
2	4,61
2a500	7,91

4. Conclusion

In this paper, the effect of the process parameters and post-deposition annealing on the microstructure and the surface morphology of ZnO thin films is evaluated. In XRD spectra, the dominance of diffraction peak (002) was revealed, which shows that ZnO thin films are polycrystalline with hexagonal structure and have a good c-axis orientation, corresponding to vertical growth with respect to the substrate. The samples deposited at 300W have higher value of FWHM than those deposited at RF power of 600W, which implies that the film has smaller grains and is rather amorphous than polycrystalline. The process of post-deposition annealing did not improve the microstructure of the samples, because the annealed samples have higher value of FWHM in comparison to as-deposited. The AFM surface morphology images show similar features in dependence on deposition power and annealing temperature.

Acknowledgments

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