

NANOSTRUCTURES IN THIN FILMS OF ZnO

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ABSTRACT

Structure property co-relationship of thin films of ZnO grown by sol-gel spin process using zinc acetate and RF magnetron sputtering method has been studied. The films were crystalline in nature. The crystallite size for the film grown by sol-gel spin method was found to be of the order of 20 nm and that of RF sputtered film was about 30 nm in the *c*-axis direction of the growth. TEM exhibited that the film with uniform microstructure consisted of distribution of nanosized grains of the order of 25 nm. Selected area electron diffraction patterns have shown the presence of different rings corresponding to different planes of hexagonal ZnO crystal structure. The RF sputtered films have shown the formation of nanorods of ZnO which were found to have uniform distribution of crystallites of the size ~10 nm. The results would find application in nanoelectronic piezoelectric sensors.

INTRODUCTION:

Synthesis and characterization of thin films of ZnO is an active area of research for nearly half a century. The primary interest for research in ZnO is due of its diverse technological applications. ZnO is a wide band gap semiconducting material and has piezoelectric properties as well. Characterization of piezoelectric thin films of ZnO forms an important part of our project of integrating such films into MEMS based acoustic sensors. It thus becomes important to investigate the crystalline features of these films for any preferred orientation during growth. It is known that ZnO has a wurtzite structure having a number of alternating planes composed of four fold coordinated O²⁻ and Zn²⁺ ions stacked alternatively along *c*-axis. It can thus be considered as two interpenetrating hexagonal closed-packed lattices of Zn and O. The preparation of ZnO thin films has been the subject of continuous research for a long time because the properties of ZnO films depend upon the method of preparation. Consequently, a wide variety of techniques have been reported in literature for growth of ZnO thin films. Doped with Al or In, zinc oxide is used as a transparent conducting electrode for display devices and amorphous silicon solar cells. It thus becomes an excellent material for various photonic applications in energy storage and conversion devices when doped with suitable dopant. Thin films of ZnO find application in various sensing devices because of the piezoelectric nature of the material. MEMS based sensors involve zinc oxide films for a number of applications in pressure transducers, accelerometers, acousto-optic devices, bulk and surface acoustic wave devices.

The characterization of ZnO thin films has been a subject of continuous research for a long time because the properties of ZnO films depend upon the method of preparation [1,2]. Consequently, a wide variety of techniques have been reported in literature for growth of ZnO thin films. Characterization of such films become important in deciding their device worthiness before integrating them in the device for the cost effectiveness, consistency and reliability of the sensor.

We present here a report of our study on investigations on nanostructures in thin films of ZnO. These films were deposited by RF sputtering and also grown by sol-gel spin process on Si

substrates. The characterization techniques used in the present work involve ellipsometry, X-ray diffraction, electron diffraction, scanning and transmission electron microscopy. Some of the recent work from our group has been published elsewhere [3-7].

EXPERIMENTAL

RF sputtered films were deposited on a 2 inch Si wafer in an RF (13.56 MHz) diode sputtering unit (Alcatel, France) using a 3 inch stoichiometric target of ZnO with various sputtering pressures ranging between 5-20 mTorr and RF power in the range of 100-300 W. The sol-gel derived films were prepared by spin method using zinc acetate as the precursor materials. Both types of the films were grown on silicon and fused quartz substrates. The growth procedure consisted of first making the surface of the silicon substrate hydrophilic by boiling the wafer in 70% HNO₃ followed by rinsing in de-ionized water and subsequent drying. This process oxidizes the Si surface to SiOH and improves its adhesion. The sol was prepared by dissolving 10 gm of zinc acetate [Zn(CH₃COO)₂ · 2H₂O] in 100 ml of boiling isopropyl alcohol at 84°C. This was followed by clarifying the turbid solution by adding a few drops of diethanolamine. For the film preparation, a Si wafer was mounted on a spinner and the sol was placed on top of it and the wafer was allowed to spin at the rate of 3000 – 4000 rpm. This step was followed by drying the coated wafer at 100°C and subsequent baking at 450°C for one hr. Multiple coatings were done to obtain the workable thickness of the film. X-ray diffraction measurements were carried out on a Bruker AXS D8 Advance diffractometer using Diffrac^{plus} software. Diffractograms were recorded in grazing incidence geometry. The incidence angle was fixed at 1.5° and 2θ was scanned in the required range. The radiation used was CuKα. The diffracted beam had a long soller slit and a LiF monochromator. The ellipsometric measurements were made on a Rudolph Research manual null-type ellipsometer, at a single wavelength of 546.1 nm, using angles of incidence in the range 50 - 75 degrees.

RESULTS AND DISCUSSION

The ellipsometric data show that for ten coatings, the film thickness was only of the order of 2000-2500 Å. The RF sputtered films showed thickness of about 1μ as measured by the our ellipsometer. Refractive index as measured by ellipsometric techniques was in the range of 1.92 to 2.03 which is in close agreement with the values reported in literature. That the films were crystalline in nature has been shown in the X-ray diffraction patterns of Figure 1 and 2 depict the XRD patterns for the films prepared using sol-gel spin method and RF sputtering method respectively. It may be seen that the film grown by RF sputtering method is highly c-axis oriented. Figures 3(a) represents asset of the surface topographical features of the ZnO films grown by sol-gel spin method using zinc acetate as the precursor material. Figure 3(b) depicts the surface topography of the ZnO film grown by RF sputtering method. It may be mentioned here that the topographical features represented in Figure 3b are identical with those obtained by Xiang et.al [8] who investigated ZnO films grown by RF sputtering and reported the formation of ZnO nanorods. Our results shown in Figure 4 exhibit the surface topograph and the cross sectional view. From the Figure, it is very clear that the formation of nanorods occur in the areas where the topographical features exhibit granular structure. The energy dispersive spectroscopy performed on the samples confirmed that the film material was ZnO. The main lines ZnKα (8.64 keV) and ZnKβ (9.57 keV) were not observable in the sol-gel derived film due to the small thickness of film. However, for the RF sputtered film, the EDS spectrum showed the ZnKα and ZnKβ lines very clearly. The peak for oxygen was also clearly seen. The optical absorption data for the films grown on quartz substrates confirmed that both types of films consisted of ZnO.

Figures 5 and 6 show the bright field TEM micrographs of the film grown by sol-gel process and RF sputtering method respectively. It may be observed from these Figures that both the types of the films grown by the sol-gel spin process and the RF sputtering show the formation of nanocrystallites. The crystallite size was estimated for both the types of films by using Scherrer formula [9]. Presently, in our system, Bruker AXS D8 Advance diffractometer, all this exercise is done by the inbuilt Diffrac^{plus} software. The crystallite size for the film grown by using zinc acetate on Si substrate was estimated to be about 25 nm in the *a*-axis and about 15-20 nm in the *c*-axis direction of the lattice. The films grown by RF sputtering method was found to have larger crystallite size of about 31 nm. Selected area electron diffraction patterns have shown the presence of different rings corresponding to different planes of hexagonal ZnO crystal structure.

SUMMARY AND CONCLUSIONS

Thin films of ZnO grown by sol-gel using zinc acetate as the precursor material, and RF sputtered deposition have been studied using ellipsometry, optical absorption, X-ray diffraction, scanning and transmission electron microscopy (SEM and TEM), measurements. The results of present investigations have shown that while the films grown by sol-gel route did not show any preferred orientation during growth, the RF sputtered films was highly *c*-axis oriented. SEM examination revealed the presence of some columnar-shaped grains at very high magnification corresponding to ZnO nano-rods formed during the deposition. The size of the nanocrystallites was larger in the RF sputtered films in comparison with the sol-gel derived films.

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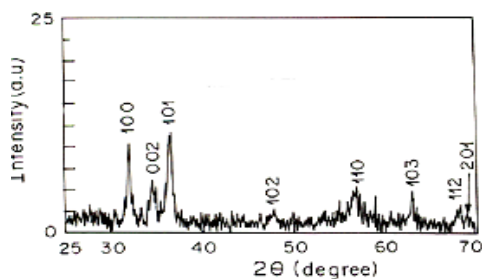


Figure 1. X-ray diffraction of ZnO thin film grown by sol-gel spin method using zinc acetate as the precursor material.

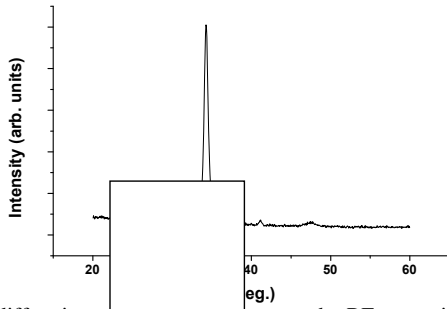


Figure 2. X-ray diffraction of ZnO film grown by RF sputtering method.

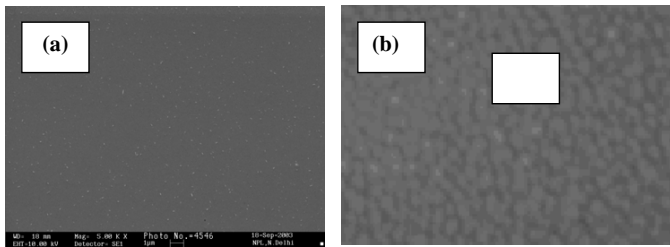


Figure 3. SEM micrograph of the ZnO films prepared by ; (a) sol-gel spin method and (b) RF Sputtering.

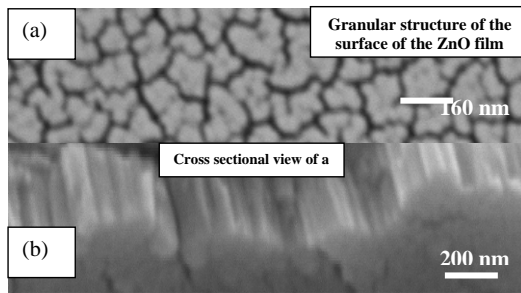


Figure 4. SEM micrographs of the RF sputtered films of ZnO. (a) showing grains of ZnO and (b) nanorods obtained at higher magnification than that of (a).

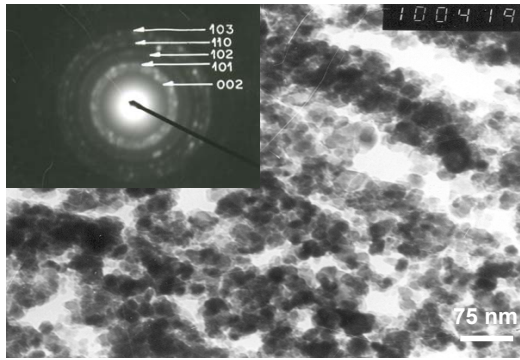


Figure 5. TEM bright field micrograph of the ZnO exhibiting the distribution of nanocrystallites of ZnO film grown by sol-gel spin method using zinc acetate. The electron diffraction is shown in the inset.

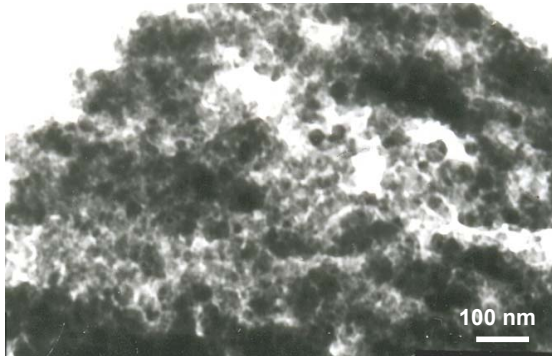


Figure 6. TEM bright field micrograph depicting the surface topographical features of a ZnO film grown by RF sputtering method.

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