Characterization of ZnO Thin Films

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ABSTRACT

ZnO is a strategic material for various photonic applications. We present our results on characterization of thin films of ZnO grown by sol-gel spin and RF sputtering methods. The characterization techniques involved ellipsometry, scanning electron microscopy with energy dispersive analysis, X-ray diffraction and scanning tunneling microscopy. Microstructural characterization of the films using zinc nitrate precursor has delineated many interesting features These morphologies are homogeneous and uniformly distributed on the entire film. The energy dispersive spectroscopic measurements carried out on the both types of morphologies, island and needles, have confirmed that the film composition is ZnO and preserve the crystal symmetry. After the nucleation, the growth lead to preferred crystallographic axes.

INTRODUCTION:

ZnO is a material of wide ranging application. Not only it finds application in various photonic associated technologies but because of its piezoelectric nature, it can be used effectively as a sensor in various MEMS related devices. We aim at developing MEMS based acoustic sensor using thin films of ZnO. Characterization of ZnO films thus becomes an important part of our project. In this paper, we report results of our characterization studies on the polycrystalline thin films of ZnO prepared by RF-sputtering and sol-gel processes. The characterization techniques involved ellipsometry, scanning electron microscopy with energy dispersive analysis, X-ray diffraction and scanning tunneling microscopy. The techniques of film growth have been described elsewhere [1-3].

RESULTS AND DISCUSSION

Optical absorption data on the deposited films was measured using Shimadzu UV3101 PC spectrophotometer. For measurements in the UV and optical region, the films were coated onto a substrate of amorphous quartz. Figure 1 depicts the representative optical absorption of the films using zinc nitrate precursor. In both the cases, the absorption band around 372 nm is characteristic of ZnO. The band gap corresponding to the absorption is 3.3 eV. That the films were crystalline in nature has been shown in the X-ray diffraction pattern of Figure 2.

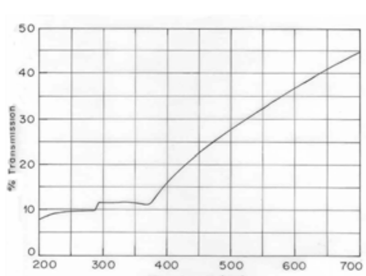


Figure 1

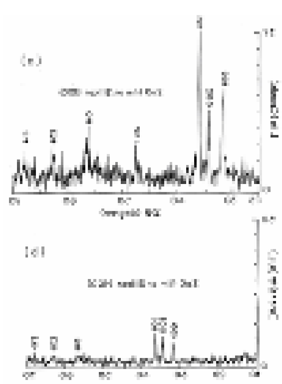


Figure 2

Ellipsometric Measurements

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 deg. Measurements were made at three angles of incidence and the best, most consistent results for refractive index, extinction coefficient and thickness of the thin film sample were calculated using in-house developed software. Calculations of *n. k.* and *d* were done using in-house developed software. Using the measured values of the ellipsometric angles Θ and) at each of the three different angles of incidence, and searching in specified range of values for *n* and *k*, the value of *d* is calculated for each pair (*n*,*k*) and a common value (or small range of values) for *d* for all three angles of incidence is searched for. Once such a value (or small range of values) for *d* is found, this *d* and the corresponding (*n*,*k*) values are taken as solution for *(n,k,d)* of the film. Table (I) shows the results for different film samples using zinc nitrate and zinc acetate precursors on both quartz and silicon substrates. It may be mentioned here that the ellipsometric measurements on the film grown on silicon wafer by using zinc acetate precursor could not be performed with our manual single wavelength ellipsometer, due to the fact that film was highly absorbing and nonuniform.

TABLE - (I)

Ellipsometric data of *n, k* and *d* for the sol-gel grown thin films of ZnO

Precursor	Substrate	Refractive index (*n*)	Extinction coeff. (*k*)	Film thickness (*d*)
$[Zn(NO_3)_2 . 6H_2O]$	Silicon wafer	1.83 ± 0.03	0.47 ± 0.02	227 ± 15 nm
$[Zn(CH_3COO)_2 . 2H_2O]$	Silicon wafer	....	....	....
$[Zn(NO_3)_2 . 6H_2O]$	Fused quartz	1.63 ± 0.02	0.085 ± 0.005	200 ± 2 nm
$[Zn(CH_3COO)_2 . 2H_2O]$	Fused quartz	1.64 ± 0.01	0.16 ± 0.03	275 ± 15 nm

Scanning Tunneling Microscopy

The scanning tunneling microscopy provides a picture of the atomic arrangement of a surface by sensing corrugations in the electron density of the surface that arise from the positions of the surface atoms. Figure 3 depicts a representative surface topographical features of the film grown by using zinc acetate precursor. The results show that the film with an average roughness of 0.45 nm and the standard deviation of 0.07. A 2D lattice of the film is shown in Figure 4. Figures 5 and 6 show the nanograph for a film grown by RF sputtering method. In this case, although, the overall lattice structure showed an uniform distribution it may be observed that the lattice was disturbed. Perhaps this was due to the fact that the films after the deposition were not thermally annealed.

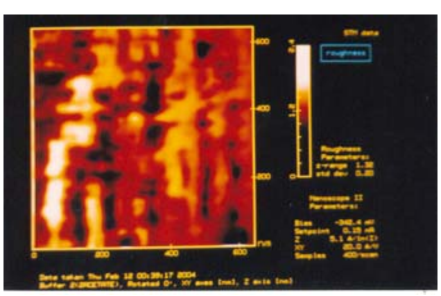


Figure 3

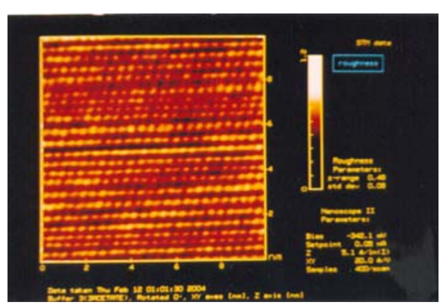
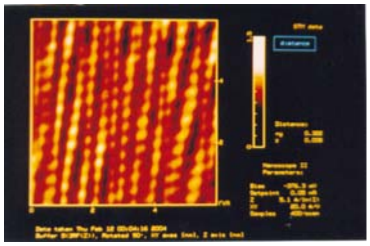


Figure 4



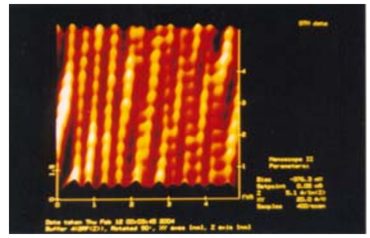


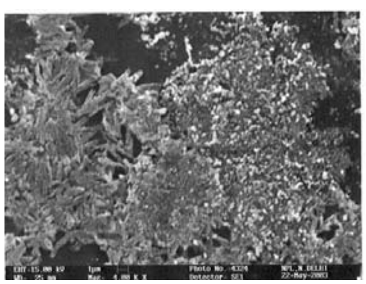
Figure 5 **Figure 6**

ELECTRON MICROSCOPIC STUDIES

Microstructural analysis of the sol-gel grown ZnO films on Si substrates were carried out by using LEO-0440 SEM equipped with ISIS 300 Oxford microanalysis system (EDS attachment). The specimens were mounted on a 15 mm diameter stub and a thin layer of gold was sputtered onto it. The stubs were then fixed on the viewing stage of the SEM having a *xyz* movement as well as rotation and tilt facility. The specimen was scanned thoroughly at a lower magnification in order to see the uniformity of the film.

The film prepared by zinc nitrate precursor showed a polycrystalline structure having dendrite growth with agglomeration of dendrites in some areas as shown in Figure 7. Figure 8 shows the microstructure of the film grown by using zinc acetate precursor. The films so prepared have shown uniform structure with needle shaped particles distributed throughout the area scanned. The micrographs suggest that the films prepared by using zinc nitrate show a rapid and random crystallization compared to that using zinc acetate.

Bright field transmission electron microscopic investigations of the films revealed many interesting features. Nano-structured fine grains with the size of about 20-60 nm with clear surface boundaries were observed. These micrographs are shown in Fig.9 for the film grown on fused quartz substrate using zinc nitrate precursor. The individual grains show a distinguished contrast on the surface. In some cases, different facets with sharp edges may also be seen. A non-spherical shape and faceted morphology of these grains may be attributed to their crystallographic symmetry of the wurtzite ZnO and a preferred growth direction during deposition.



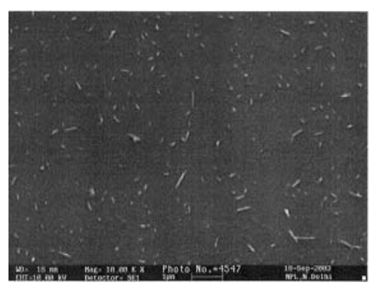


Figure 7 **Figure 8**

A selected area electron diffraction pattern recorded on one of films (Fig. 10) for which the XRD pattern is shown in Figure 1(a) clearly demonstrated three important planes of hexagonal structure (100, 002, 202) in the form of continuous rings in the reciprocal space. It shows that the film is polycrystalline in nature with a random distribution of nano-grained ZnO in it. However, the absence of certain important reflections of hexagonal ZnO in the electron diffraction pattern elucidates that the film has certain texture with preferred growth direction.

SUMMARY:

Zno thin films grown by sol-gel spin and RF sputtering methods have been characterized by using a variety of techniques. The results show that the films although consisted primarily of ZnO were not of high quality for use in MEMS-based sensors. Work is continued in this area to grow high quality oriented films.

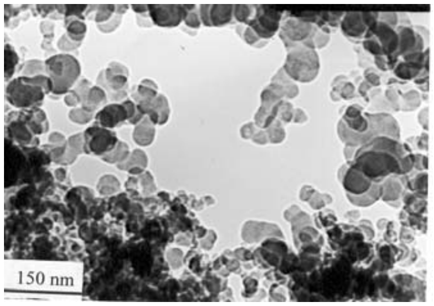


Figure 9

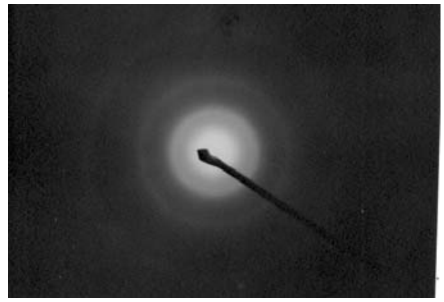


Figure 10

Figure Captions:

Figure 1. Optical absorption of a ZnO thin film grown on quartz substrate.

Figure 2. XRD patterns for the ZnO films grown by using zinc nitrate and zinc acetate as precursor material.

Figure 3. Scanning tunneling micrograph of the Zno film showing the surface undulations.

Figure 4. Scanning tunneling micrograph of the Zno film showing the lattice structure.

Figure 5. Scanning tunneling micrograph of the Zno film grown by RF sputtering showing the lattice.

Figure 6. Scanning tunneling micrograph of the Zno film grown by RF sputtering showing the lattice structure at a different surface location other than the one shown in Figure 5.

Figure 7. Scanning electron micrograph of the ZnO film exhibiting dendrites grown by using zinc nitrate as precursor material.

Figure 8. Scanning electron micrograph of the ZnO film grown by using zinc acetate as precursor material.

Figure 9 Bright field TEM micrograph of the ZnO film exhibiting formation of nanocrystalline phases of ZnO.

Figure 10. Electron diffraction from a selected area of the film showing the crystalline nature of the film.

ACKNOWLEDGMENTS

This work was done as a collaborative research between the National Physical Laboratory (NPL) and the Indian Institute of Technology, Delhi under their academic exchange program. The authors thank Dr. Vikram Kumar, Director, NPL for his encouragement and support in the present work.

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