Nano-structured ZnO films by sol-gel process


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Received 7 June 2006; revised 28 December 2006; accepted 4 January 2007

Thin films of ZnO grown by sol-gel spin method using two different precursors viz. zinc nitrate and zinc acetate have been characterized for their crystalline nature and associated nanostructures. In some cases, the films consist of nanostructures in the form of nanocrystals and nanoneedles of dimensions in the range 15-60 nm. A comparison between the physical characterization and the nanostructures of the films grown by two different precursor materials has been presented and the results are discussed in terms of the fundamental considerations governing the growth kinetics of the ZnO films.

Keywords: ZnO films, Sol-gel, Scanning electron microscopy, XRD, Transmission electron microscopy, Nano-structured ZnO thin films

IPC Code: H01F41/30

1 Introduction

Thin films of ZnO have been an active area of research for nearly half a century due to the diverse technological applications of ZnO uniquely suited. It is an excellent material for a variety of photonic applications when doped with suitable dopant. Al or In, ZnO films are used as a transparent conducting electrode for display devices and amorphous silicon solar cells. Due to their piezoelectric and semiconducting properties, thin films of ZnO are extensively used in surface acoustic waves (SAW) components and various MEMS-based sensors. The properties of ZnO films depend upon the method of their preparation. Characterization of ZnO films becomes important in deciding their device worthiness in the light of the cost effectiveness, consistency and reliability of the sensor. It, thus, becomes important to investigate the crystalline features of these films for any preferred orientation during growth. Nanostructured zinc oxide materials are of current importance in electronic, optic and photonic applications and form the basis of nanotechnology applications in sensors and molecular electronics. The nanostructures exhibit novel electrical, mechanical, chemical and optical properties which are believed to be due to the surface confinement effects of nanostructures in one dimension (1 D). These 1 D objects are of great importance in understanding some basic physics related phenomena in the low dimension systems to form the basis of next generation high performance nanodevices. The current initiatives in nanotechnology research have led to discovery of a variety of nanostructures of ZnO such as nanorods, nanotubes, nanobelts, nanocombs, nanosaws, nanospings, nanospirals, nanorings etc. Wang has recently presented an excellent survey of the growth, properties and applications of a variety of nanostructures of zinc oxide. Nanowires of ZnO are a promising candidate as probe for AFM cantilever due to their high mechanical stability. However, a sharp needle shaped structure would still be a better option for the tip of the AFM probe.

The results on the thin films of ZnO grown by sol-gel method have been presented. This technique of film preparation is a low-cost process and is attractive as the film properties can be tailored conveniently for a given application. This process, thus, becomes a preferred option for exploratory studies where a large number of candidate materials require screening for their compositions and properties prior to their applications in devices. We have recently reported our limited investigations on ZnO thin films grown by sol-gel spin process and RF sputtering method. Using
sol-gel spin process, we found a smoother topography for the films grown by using zinc acetate than for the films grown by zinc nitrate. The films grown by RF sputtering besides being far more smoother in their topographical features, showed a lower value of refractive index than the films grown by sol-gel process. Scanning tunneling microscopy revealed that the films grown by zinc acetate as precursor show more uniform lattice than the RF sputtered films. Using the quartz substrate, the formation of ZnO phase ranging between 20-60 nm size has been reported. The formation of fine and nanostructured sharp needles (~15-20 nm sizes) during the growth of film on the Si wafer substrate having the similar finish (~2-3 µ) as the quartz substrate used in the earlier investigations has been reported.

2 Experimental Details
Sol-gel spin process was utilized by using 10% sol with zinc nitrate as the precursor material. Methods of preparation of thin films were essentially the same as described in earlier publications (Refs 2-5). These films were studied for their optical absorption, ellipsometry, XRD, SEM, EDS, TEM and STM. All these techniques confirmed that the films were primarily consisted of ZnO.

3 Results and Discussion
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. Calculations of $n.k.$ and $d$ were done using in-house developed software. The values of $n$ were found to be in close agreement with the reported values for ZnO. For obtaining workable thickness, repeated runs of spin coatings were performed. For ten coatings, a thickness of about 80-90Å was obtained. The films were crystalline in nature has been shown in the X-ray diffraction patterns of Figure 1 (A and B). Fig. 1(A) shows the XRD pattern for the film which was prepared using zinc nitrate as the precursor material. The diffractogram clearly resolved 100, 002, 101, 102, 110, 103 and 112 planes confirming the formation of zinc oxide phase (PDF#36-1451 zinc oxide hexagonal). The diffractogram indicates that the sol-gel derived films did not have preferred orientation. Unit cell parameters were calculated from the diffraction data by minimizing the sum of the squares of residuals of 2θ. The calculated values for zinc nitrate precursor film. are: $a = 0.3255(0.0004)$ nm and $c = 0.529(0.0008)$. These values are quite close to the reported data (PDF#36-1451): $a = 0.3250$ nm and $c = 0.5207$ nm. Fig. 1(B) shows the XRD diffractogram for the film grown by using zinc acetate as the precursor material. XRD measurements have shown that the films prepared by using zinc acetate as the precursor have larger crystalline size (~25 nm in c-axis direction) as compared to those prepared using zinc nitrate as the precursor material (~20 nm in c-axis direction).

Microstructural analysis of the ZnO films on Si substrates (Fig. 2) were carried out by using LEO-0440 SEM equipped with ISIS 300 Oxford

Fig. 1—X-ray diffractograms of thin films of ZnO prepared by sol-gel spin method, (A) Film prepared by using zinc nitrate as the precursor material and (B) zinc acetate as the precursor material
microanalysis system (EDS attachment). 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 such as shown in Fig. 2. Fig. 3 shows the surface morphology of the film using the same precursor on the amorphous quartz. It may be seen that the basic morphological features of agglomerations on the films are essentially the same as on the silicon substrate. On the other hand, the topographical features of the film grown by using zinc acetate as the precursor material, shown in Figure 4 exhibit a smooth surface.

Figure 5 shows the SEM micrograph of the surface of another film grown on an oxidized Si wafer using zinc nitrate. The films prepared showed a polycrystalline structure having two different morphologies. SEM micrographs delineated a dense networking of needle-shaped and island-shaped morphologies. At higher magnification, in general, the fine scale sharp needles converged to a tip is of the order of 15-20 nm, whereas the almost spherical shaped island appeared in two diameters of the range 5 to 10 µm and 0.5 to 1 µm. Importantly, the needles and island morphologies exhibited the homogeneous and uniform distribution over the entire film. Fig. 6 shows a magnified version of some selected area of the film. The two types of morphologies come from the same agglomerates. Fig. 7 shows a view at extended magnification. TEM investigations have shown that these features at high magnifications exhibited featureless growth within the individual island. Moreover, at the periphery, normally these islands are surrounded by ultra-fine dendrites type growth. Microstructures were investigated inside the needles. These needles are constituted of ultra-fine nanosized grains. An important observation resulted from the micrographs was that the surfaces of these needles was microscopically smooth throughout their length with uniform diameter except towards their tips.

From Figures 5-7, it may be noticed that, in general, two types of morphologies are produced. These micrographs suggest that the films prepared by
using zinc nitrate show a rapid and random crystallization. This is in contrast to the film prepared by using zinc acetate as the precursor material (Fig. 4) where the topographical features of the film were much smoother. We have investigated the quality of film grown by using zinc acetate as the precursor material using scanning tunneling microscopy. This is done by sensing corrugations in the electron density of the surface that arise from the positions of the surface atoms. Fig. 8 shows the atomic arrangement exhibiting an uniform lattice of the film. Fig. 9 shows a 3D view of the selected area at higher magnification.

The photoluminescence (PL) spectra of the sol-gel derived film was recorded using a Perkin-Elmer Spectrometer (model: LS-55) and a xenon flash lamp as the source of excitation. The PL spectra for the film on Si substrate, showed a broad peaks centering at ~650 and 520 nm, respectively, in addition to the UV peak at ~380 nm (Fig. 10).

The UV peak is attributed to the band-edge emission of ZnO, while the other two broad visible bands in the green and orange-red regions are generally attributed to deep-level defects in ZnO crystal, such as vacancies and interstitials of zinc and oxygen. The annealing treatment of the films in air atmosphere for about ½ hr showed that the defect peak at 520 nm does not change significantly, while the UV emission intensity has substantially decreased. This plays an important role in the PL process. When films of ZnO nanorods are annealed in air, more
oxygen vacancies and zinc interstitials are created, which increases the emission centers of green peak at 520 nm. At the same time, the free carrier density is also increased in ZnO and therefore reduces the width of depletion region and increases the volume of bulk region where radiative recombination occurs. Consequently, the intensity of the 520 nm peak increases significantly while the UV emission is suppressed due to large competition from the defect emission.

4 Conclusions

The present work compares the results of characterization of nanocrystalline features of ZnO thin films prepared by sol-gel spin method as well as RF-sputtering method. The results show some important features of the ZnO films. These include evidence of oxygen vacancies as shown by the photoluminescence measurements and surface topographs exhibiting the nanocrystalline nature of the material. STM measurements have shown the arrangements of atomic positions. Such characterization techniques would be helpful in assessing the quality of the films for practical applications such as use in MEMS based sensors.

Acknowledgement

This work has been done under the joint program of National Physical Laboratory (NPL), New Delhi and the Indian Institute of Technology, Delhi. The authors thank Dr Vikram Kumar, Director, NPL, New Delhi, for his encouragement and support.

References