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Studies on Zinc Oxide Nanorods Grown by Electron Beam Evaporation Technique

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Nanocrystalline zinc oxide-thin films have drawn the attention of researchers due to its attractive properties like transparency in visible region, abundance in nature and gas sensitivity. Nanostructured Zinc oxide (ZnO) thin films were grown on silicon, alumina and glass substrates at various substrate temperatures using a 6 kW electron beam evaporation technique. The effects of film thickness, growth temperature and substrate on the crystallinity of deposited ZnO films were investigated using X-ray diffraction, scanning electron microscopy, optical absorption and photoluminescence studies. Our studies show that good quality films are obtained for silicon substrate for a growth temperature of 250°C. Film thickness plays an important role on the evolution of the nanostructures. SEM studies combined with XRD analysis reveal that ultrathin nanorods are grown with (002), (101) and (102) orientations. All the ZnO films show room temperature photoluminescence emission bands at 394 nm and 468 nm. Optical absorption studies show strong absorption at 377 nm. Details of the structure and optical properties correlation will be presented and potential of a simple technique such as e-beam deposition to grown ZnO nanostructures suitable for optoelectronic application will be assessed.

Keywords zinc oxide, nanorods, XRD, SEM, electron beam evaporation technique

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INTRODUCTION

Nanocrystalline Zinc Oxide thin films have drawn the attention of researchers due to its attractive properties such as transparency in the visible region, abundance in nature, gas sensitivity, and high excitation binding energy.[1] With a direct band gap, slightly lower than that of GaN, (e. g., ZnO ~3.4eV at 2 K, ~3.3 eV at 300 K)[2,3] ZnO has generated

great interest for its potential for short wavelength applications. It has a wurtzite structure identical to that of GaN and lattice parameters[4] of a = 3.2417 Å and c = 5.1876 Å. This structure lends the material to the epitaxial growth for the lattice match band gap tuning on either the AlInGaN or MgCdZnO[3,5,6] alloy systems with a range of ~2.3 eV to 4.0 eV, with the perfect lattice match of ZnO substrates to $In_{0.22}Ga_{0.78}N$ for blue LEDs being an oft-cited fact.

The polycrystalline thin films have been used for more high-tech uses such as phosphors, piezoelectric transducers, varistors, and transparent conducting films.[7] However, the past decade's progress in developing single crystal bulk ZnO and the very recent results in growing p-type material have brought ZnO promise as a wide band gap semiconductor to the fore. The result is a renewed interest in a material providing unique opportunities for lattice-matched band gap tuning for optoelectronic applications, electronics applications ranging from high-power electronics to transparent thin film transistors,[8] solar cell, and even possible spintronic applications.[9]

Various chemical, electrochemical, and physical deposition techniques have been used to create ZnO nanostructures. Chemical Vapor Deposition,[10] Pulsed Laser Deposition,[11] sputtering,[12] and sol-gel methods[13] have been employed to prepare nanocrystalline ZnO films. However, the e-beam evaporation technique has not been reported for the preparation of ZnO thin films, as per our survey. In context of ease and simplicity of the technique, we have attempted this technique for the growth of nanocrystalline ZnO thin films. The present work is an effort to study and improve the morphologies and structural properties of ZnO thin films with a simpler growth technique.

RESULTS AND DISCUSSIONS

The crystallinity and orientation of ZnO nanostructures on different substrates were investigated by XRD.

Figure 1 shows the X-Ray Diffractometer trace of ZnO thin films grown at different substrate with different substrate temperature as specified in Table 1. The hexagonal Wurtzite structure of ZnO in accordance with JCPDS diffraction file

TABLE 1
Sample description of grown films

Sample no.	Thickness	Substrate temperature	Substrates
33 (H)	1000 Å	300°C	Si, Alumina and Glass
34 (H)	1000 Å	275°C	
35 (H)	1000 Å	250°C	
36	3000 Å	300°C	
37	3000 Å	275°C	
38	3000 Å	250°C	

No. 79-0205[4] is also shown in the figure for reference. As shown in the figure, the 2θ scan data shows dominant peaks at 33.24° corresponding to ZnO (002) reflection as compared with standard data in the samples grown on silicon and glass substrate at low vacuum (10^{-4} mbar). The (002) peak, seen in the ZnO films grown on Silicon and glass substrate indicate that the Zn and O atoms follow the columnar growth along the c-axis, which is the most favored orientation.[14] In the X-ray diffraction pattern for ZnO film deposited on silicon substrate also, a clear (002) orientation of ZnO islands is observed. Thus, the ZnO islands on Glass and silicon substrates show c-axis preferred orientation. However, on the Alumina substrate, only a low intensity peak is observed at 36.5°, which corresponds to (101) orientation. This is shown in Figure 1A. The (101) peak may be due to slightly tilted alignments of the structures with respect to the substrate normal.[15]

The surface morphology of ZnO thin films was studied by SEM. Figure 3 shows SEM images of ZnO thin films grown on silicon substrates at 250°C with 1000 Å, 2000 Å, and 3000 Å thicknesses.

As seen from Figure 2(A), at lower film thickness i.e., 1000 Å, ZnO islands are formed on the substrate with diameters around 400 to 600 nm. These islands are not densely

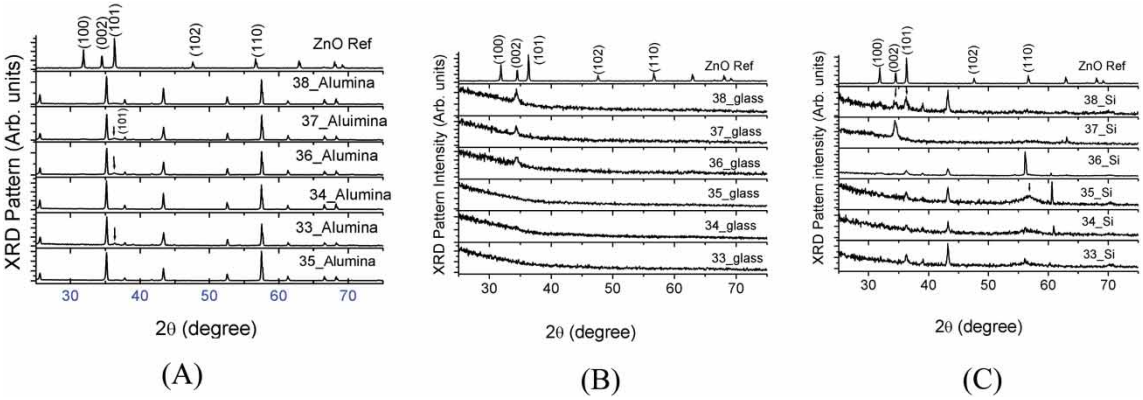

FIG. 1. X-ray diffractograms for films grown on (A) alumina, (B) glass, and (C) Si substrate for different substrate temperatures.

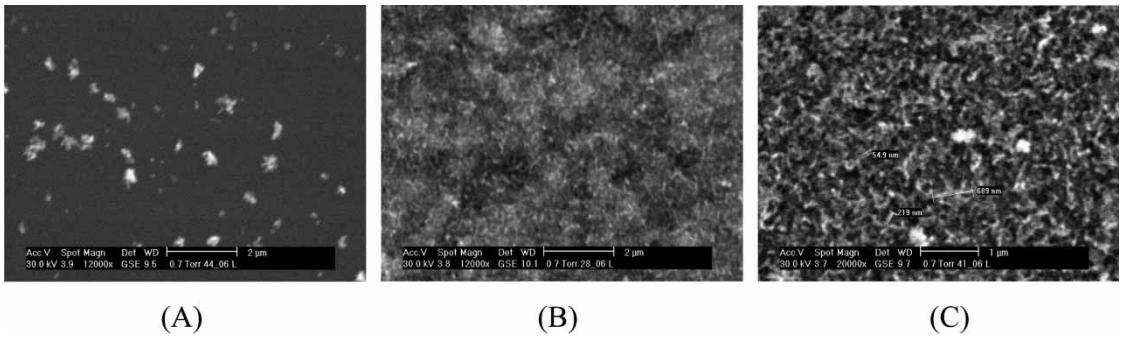

FIG. 2. SEM images of (A) 1000 Å (B) 2000 Å and (C) 3000 Å ZnO thin films deposited on Silicon substrate at 250°C.

populated. However, as thickness increases, a denser pattern evolves along the c-axis and the nano particles start forming in elongated shapes as shown in Figure 2B. Further increase in thickness leads to formation of nanorods-like structures with diameters of around 50–100 nm, oriented normal to the substrate [Figure 2C].

Figure 3 show SEM images of ZnO thin films with 1000 Å thickness, grown on silicon substrate temperatures of 250°C, 275°C, and 300°C.

As mentioned earlier, at 1000 Å, rod-like elongated nano structures are not observed. As the substrate temperature increased to 275°C, formation of clusters with the particle size of 400–600 nm was observed [Figure 3B]. However, at still higher substrate temperatures, more uniformly populated grains with smaller diameters of around 100 nm were found to develop [Figure 3C]. The SEM study revealed the formation of nanosized rod-like structures from an initial polycrystalline ZnO islands with increase in film thickness. But, when the substrate temperature was increased for a constant ZnO film thickness, the SEM study revealed the development of polycrystalline morphology with granular structure having a grain diameter around 100 nm. The shape and size of the

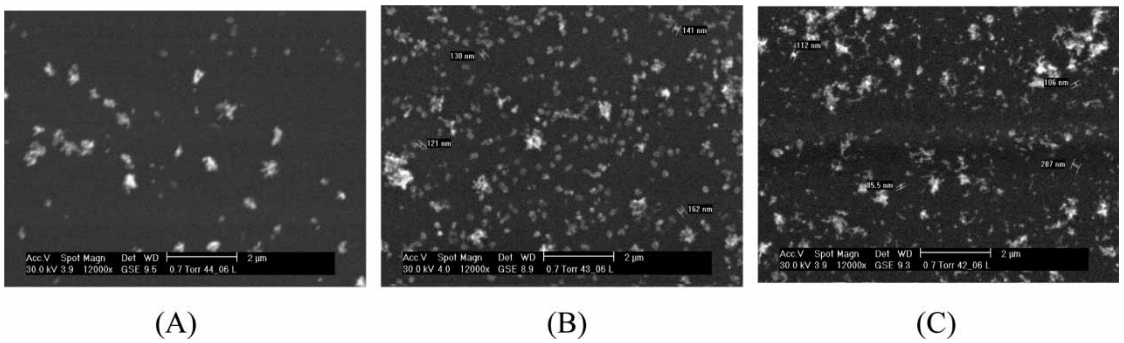

FIG. 3. SEM images of 1000 Å ZnO thin films deposited on Silicon substrate at (A) 250°C; (B) 275°C; and (C) 300°C.

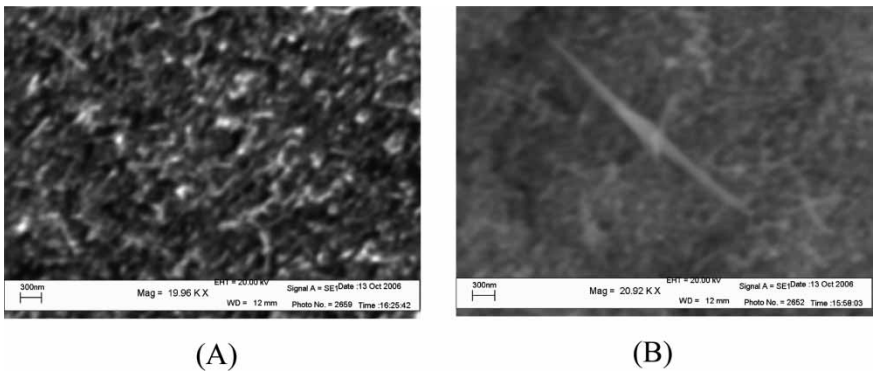

FIG. 4. SEM image of ZnO nanorods grown at (A) 250°C and (B) 275°C substrate temperatures.

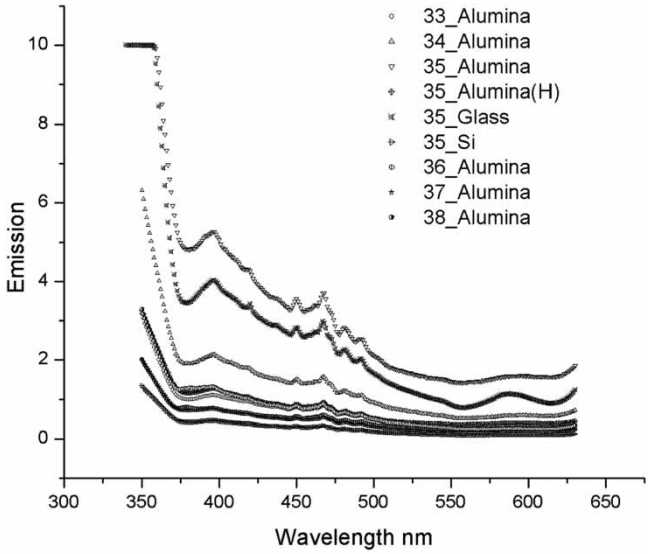

FIG. 5. Photoluminescence Spectra of ZnO films grown on different substrate with different substrate temperature.

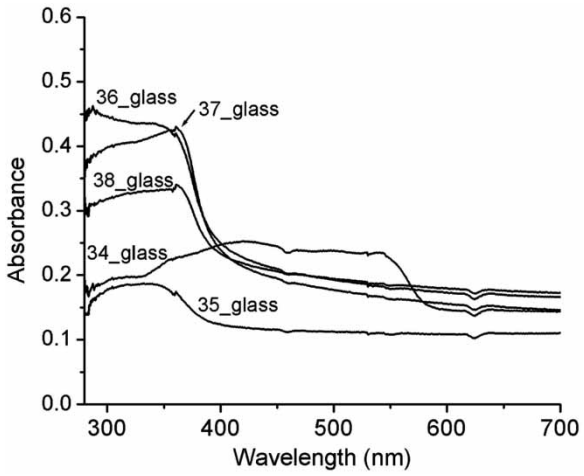

FIG. 6. UV/VS Absorbance spectra of ZnO thin film grown on glass substrate at 250°C, 275°C, and 300°C substrate temperature.

development of nanoparticles from the initial island like behavior was thus found different with film thickness vis-à-vis substrate temperature. Figure 4A shows SEM image of ZnO nanorods of film grown at a substrate temperature of 250°C. A magnified image of single nanorod having a base diameter of around 250 nm is shown in Figure 4B.

Figure 5 shows emission spectra of films, revealing that all samples of ZnO films emission bands at 394 nm and 468 nm at room temperature. The PL intensity is high for the sample grown at 250°C for Alumina and glass substrate, as substrate temperature increase in the photoluminescence intensity start decreasing. Similarly, as thickness increases from 1000 Å to 3000 Å PL intensity decreasing.

Figure 6 shows the absorption spectra of ZnO thin films deposited on Glass substrate at different substrate temperatures. A strong absorption at 377 nm is observed in all the samples that correspond to the direct band gap of ZnO (3.29 eV). This confirms the growth of good quality ZnO nanostructures. The band edge becomes sharper on increasing the substrate temperature. This can be partly related to the decrease in defects in the thin film.

The AFM image in Figure 7 displays the surface morphology of ZnO thin film deposited at different substrate temperatures having different film thicknesses. The AFM characterization revealed polycrystalline morphology with columnar nano-structures of ZnO. The height, width, and roughness of the nano-columnar structures were found to be dependent on film thickness as well as substrate temperature. Further work is in progress to use the three dimensional nature of the AFM images to find out the exact changes in the nanostructural parameters of ZnO film with the changes in the deposition parameters.

EXPERIMENTAL

ZnO thin films were deposited on Silicon substrates in high vacuum coating unit using 6 kW e-beam evaporator. ZnO powder (99.9%, Sigma-Aldrich Chemie GmbH, Germany) was dye-pressed to obtain the tablets. These tablets were

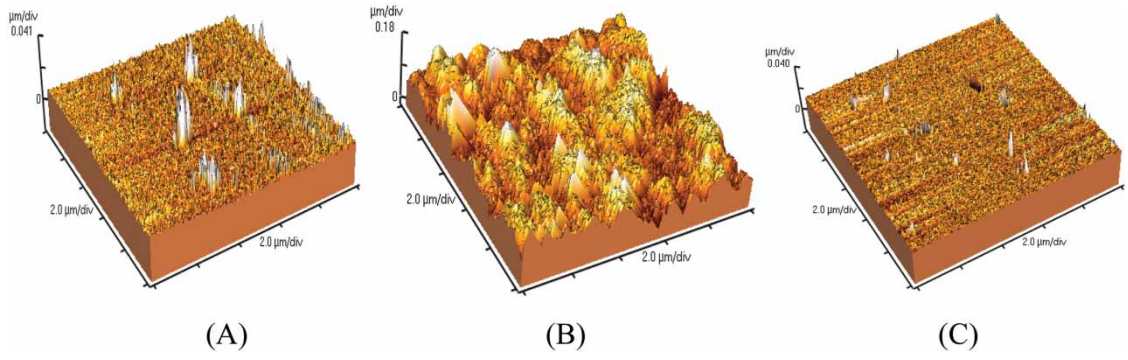

FIG. 7. AFM images of (A) 1000 Å (B) 2000 Å and (C) 3000 Å ZnO thin films deposited on Silicon substrate at 300°C, 250°C, and 275°C respectively.

placed in a copper hearth crucible. The substrates were heated and maintained at desired temperatures using a radiant heater. The e-beam evaporation system is interfaced with Sigma SQC-122c Thin Film Deposition Controller in order to monitor and control the thickness and deposition rate of the thin film precisely. The ZnO thin films with different thicknesses viz. 1000 Å, 2000 Å and 3000 Å were deposited at a deposition rate of 8 Å/sec by varying the substrate temperature. The films were deposited at 250°C, 275°C, and 300°C.

The structural properties of deposited thin films were examined by Atomic Force Microscope (AFM-VECCO CP II, USA), X-Ray Diffraction (XRD-Philips Xpertpro), and Scanning Electron Microscope (SEM-Phillips XL 30 ESEM, GERMANY and Jeol JSM 5610 LV), UV/VIS Spectroscopy and Photoluminescence. The diffraction profiles were obtained using a Cu target at a scan speed of 3 degree/min. within the 2θ range of 0 to 60 degree using solid state zirconium detector.

CONCLUSIONS

We have grown nanocrystalline ZnO thin films on silicon substrates using electron beam evaporation technique. ZnO thin films of different thicknesses were grown at various substrate temperatures and effect of these parameters on nanostructures were examined. Absorption spectra reveal the growth of ZnO nanostructures with absorption peak at 377 nm. XRD and SEM confirmed the growth of rod-like ZnO nanostructures on the substrate with (002) orientation. The present study has demonstrated the applications of simpler Physical Vapor Deposition technique such as e-beam evaporation for the growth of ZnO nanostructures.

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