NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2016, 7 (3), P. 506–508

Effect of substrate temperature on microstructural, vibrational and electrical properties of ZnO nanostructured thin films

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PACS 81.07.-b, 81.15.Rs **DOI 10.17586/2220-8054-2016-7-3-506-508**

ZnO nanostructured thin films are synthesized by a simple spray pyrolysis technique using zinc acetyl acetonate precursor on Si substrates. The morphology control is achieved by varying the substrate temperature during deposition between 350 and 450 °C. The microstructural changes accompanying the changes in growth conditions are observed under the transmission electron microscopy. The vibrational properties of these films are studied using Raman spectroscopy and the differences in crystallinity are explained. The electrical properties are determined from I–V measurements.

Keywords: spray pyrolysis, ZnO nanostructured thin films, substrate effect, Raman.

Received: 31 January 2016

1. Introduction

Zinc oxide is a well-known semiconductor material with excellent optical and electronic properties. It has a wide direct band gap of 3.37 eV, a large exciton binding energy of 60 meV and a high melting temperature of 2248 K [1]. It crystallizes in hexagonal wurtzite structure and the presence of structural defects from growth process play an important role in varied applications such as solar cells, gas sensors, ultrasonic oscillators and transducers. Though ZnO has been synthesized in various shapes by different thin film deposition techniques, spray pyrolysis offers a simple yet versatile approach in controlling the properties through changes in processing parameters. ZnO has been synthesized by spray pyrolysis as early as 1995 as demonstrated by Krunks et al. [1] More recently, it has been shown to be a popular technique to synthesize nanostructures with various morphologies [2–5]. It is well known that c-axis orientation of the ZnO films increases as the deposition temperature or the annealing temperature is increased [6, 7]. The effect of substrate temperature on crystal structure, morphology and gas sensing of ZnO thin films grown by economic spray pyrolysis process has been previously reported [6]. In this paper, we discuss the effect of substrate temperature on grain size, vibrational and electrical properties of ZnO thin films grown by spray pyrolysis.

2. Experimental

Thin films of ZnO were grown on Si substrates by an ultrasonic spray pyrolysis technique. A solution of zinc acetate was prepared by dissolution in 3:1 ratio of ethanol and water. Acetic acid was added to keep the pH around 5.5. A static ultrasonic nebulizer with 1.7 MHz resonator was employed to generate aerosols having a fairly uniform size distribution in the range 1 – 3 μm. Films were synthesized at three different deposition temperatures 350 °C, 400 °C and 450 °C. The nozzle-substrate distance was maintained at 10 mm. Spraying time was optimized depending on the substrate temperature to obtain films of uniform thicknesses of around 400 $\sim$ 450 nm. The crystallite orientation, grain sizes and structure are confirmed using Zeiss Libra 200 FE high resolution transmission electron microscopy (HRTEM) operated at 200 kV assisted with selected area electron diffraction (SAED) studies. The vibrational properties are obtained from micro-Raman scattering studies using a inVia Renishaw spectrometer with 514.5 nm line of Ar^+ laser excitation ($<$ 1 mm laser spot at the sample surface) using 3000 gr mm^{-1} grating. Electrical properties were measured from I–V plots performed in 2-probe method.

3. Results and Discussion

The microstructure of the ZnO thin films are characterized using TEM. The morphology of the films deposited at 350 and 400 °C consisted mainly of nanoparticles which appeared similar. For the sake representation, the microstructure from deposited at 400 °C alone is shown. From Fig. 1a, it is observed that the size of ZnO nanoparticles are in the range of 6 – 10 nm. The SAED pattern shown in inset of Fig. 1a depicting fine rings is signature of the films nanocrystalline nature. These rings are indexed to wurtzite ZnO with the presence of characteristic (110) and (102) planes corresponding to the d spacing of 0.164 and 0.191 nm, respectively (JCPDS# 00-036-1451). Fig. 1b shows rod-like morphology for the films deposited at 450 °C. These nanorods are around 40 nm in diameter and several hundreds of nanometers in length. On closer observation, serrated features are observed on the nanorods which indicates the growth pattern in these stuctures. The appearance of discrete spots indicates the formation of larger grains at higher temperatures, as shown in the inset of Fig. 1b with [010] zone axis. These nanorods formed a part of the largely particle morphology as reported in our earlier studies [6]. The rod-like structures indicate the onset of preferred oriented growth.

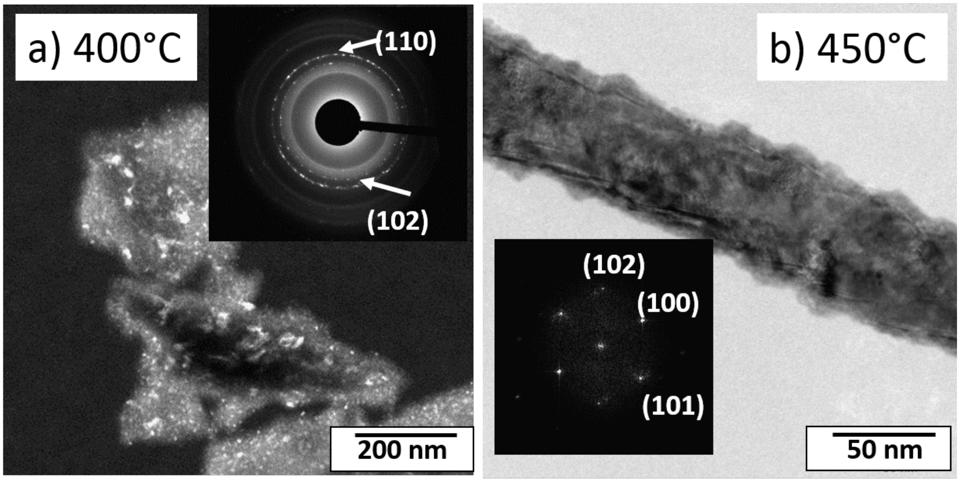

FIG. 1. a) Dark field TEM image showing nanocrystalline particles deposited at 400 °C Inset: SAED showing ring pattern; b) Bright field TEM image showing nano-rod like structures deposited at 450 °C Inset: SAED pattern showing spot pattern

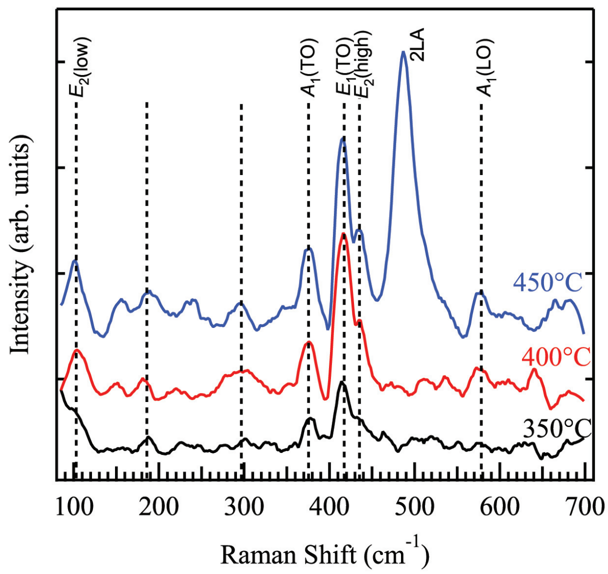

FIG. 2. Raman spectra of ZnO grown at different temperatures

The wurtzite-type lattice structure of ZnO shows 3 acoustic modes (1×LA, 2×TA) and 9 optical phonons (3×LO, 6×TO). At the zone-center (Γ-point of the Brillouin zone), the optical phonons have the irreducible representation $\Gamma_{opt} = A_1 + 2B_1 + E_1 + 2E_2$ [8], whereas the E modes are doubly degenerate. The B_1 modes are silent, i.e. IR and Raman inactive, and the E_2 branches are Raman-active only.

The vibrational spectra of ZnO thin films deposited at three different temperatures is shown in Fig. 2. The presence of triplet A_1(TO), E_1(TO) and E_2 (high) at 378, 410 and 438 cm^{-1} respectively confirms the presence

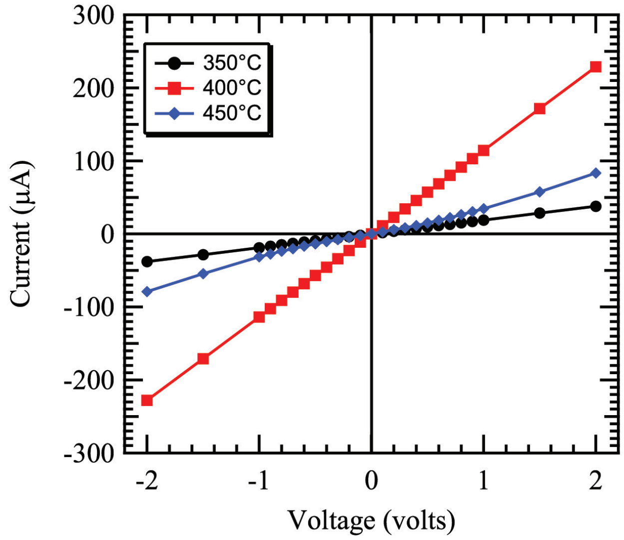

FIG. 3. $I-V$ Characteristics of ZnO grown at different temperatures

of wurtzite ZnO. This is more prominent at higher temperatures than at 350 °C. The presence of peak at 487 cm^{-1} for the thin film annealed at 450 °C is attributed to LA overtone (2LA) along $M-K$ Brillouin zone, belonging to A_1 symmetry as reported for high crystalline quality ZnO sample [9]. At the zone boundary, phonon dispersion is nearly flat and hence the phonon density of states is very high, showing a very strong intensity for the 2LA mode. Higher degree of crystallinity is observed for films grown at higher temperatures.

The electrical properties of the films shown in Fig. 3 reveals that the current increases linearly from -2 V to $+2$ V, which is indicative good ohmic behavior. Higher current is obtained for films deposited at 400 °C for a given applied voltage. This is due to lower dislocation densities in these films, as compared to other films as observed from earlier studies [6]. Hence, 400 °C is the optimum substrate temperature for better electrical applications.

4. Conclusion

ZnO thin films are grown on Si substrate using a simple yet versatile spray pyrolysis technique. By varying the substrate temperature during growth, films with varying grain sizes are obtained. Morphology is found to vary from nanocrystalline particles to nano-rod like particles as the temperature is increased. Raman study reveals differences arising due to phonon interactions in these films. Electrical charge carriers are also affected by this change in processing parameters.

Acknowledgements

AKP thanks Dr. Tom Mathews for help with synthesis and Dr. A. K. Tyagi for encouragement.

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