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Hydrothermal Growth of ZnO Nanostructures on Seed Layer Coated Substrates and their Characterization

Shrisha B. V., Shashidhara Bhat., Parvathy Venu M., K Gopalakrishna Naik.
Department of Studies in Physics, Mangalore University, Mangalagangotri – 574199, India

Abstract : Zinc Oxide (ZnO) nanostructures were grown on ZnO seed layer deposited glass, ITO coated glass, quartz and p-silicon (p-Si) substrates by hydrothermal method. The structural, morphological and optical properties of the grown ZnO nanostructures were characterized by XRD, FESEM and UV-visible spectroscopy. The elemental compositions of the samples were investigated by EDS.
Keywords: *ZnO, Nanostructures, Spincoat, Hydrothermal.*

I. Introduction

Nanostructured materials have received a special attention in many fields because of its unique physical, chemical and electrical properties which furnish them suitable for potential applications in optoelectronic devices, optics, photonics, medicine, and other fields [1]. When the size of a material reduces to the nanoscale, change in size dependent properties are often observed. This is mainly due to: (i) large fraction of surface atoms; (ii) high surface energy; (iii) spatial confinement of the carriers; (iv) reduction of imperfections in the nanometer size materials [2]. Among the various semiconductor nanostructure materials, the studies on ZnO nanostructures find special interest due to their applications in nanoelectronics and optoelectronics. ZnO has a bulk band gap of about 3.37 eV and large exciton binding energy of 60 meV at room temperature also find potential applications like in gas sensors, biosensors, solar cells, piezoelectric devices etc. [3]. The methods such as pulsed laser deposition, molecular beam epitaxy, metal organic chemical vapor deposition, hydrothermal, and electrochemical method have been used for growth of ZnO nanostructures [4]. Among these methods, hydrothermal technique has become a promising option because of its simplicity, low cost, environment friendly and high efficiency [5].

In the present work, ZnO nanostructures were grown on ZnO seed layer coated glass, ITO coated glass, quartz and p-Si substrates by hydrothermal method. The ZnO seed layers were deposited on the above substrates by sol-gel spin coat method.

II. Experimental

The growth of ZnO nanostructures on glass, quartz, ITO coated glass and p-Si substrates was carried out in two steps. In the first step, the ZnO seed layers were deposited on glass, quartz, ITO coated glass and p-Si substrates by a sol-gel spincoat method. Prior to deposition, the substrates were rinsed in distilled water and cleaned ultrasonically in ethanol and then in acetone for removing organic impurities. Zinc acetate dihydrate [$Zn(CH_3COO)_2.2H_2O$] was dissolved in a mixture of 2-methoxyethanol ($C_3H_8O_2$) and monoethanolamine (MEA, C_2H_7NO) which served as the solvent and stabilizer, respectively. The concentration of zinc acetate was maintained at 1 M and the molar ratio of MEA to zinc acetate was maintained at 1.0. The resultant solution was stirred at 60 ˚C for 4 h and then aged for 48 h. The prepared solution was then deposited on the substrates using the spin-coating technique at 3000 rpm for 30 s. The as-deposited films were immediately placed in a furnace which is maintained at 300 ˚C and kept for 10 min. The deposition and preheating processes were repeated for 4 times in order to get ZnO seed layer of desired thickness. Thereafter, the ZnO seed layer coated substrates were heated at 400 ˚C in ambient condition using a furnace for 1 h and then cooled to room temperature. This thermal treatment process is necessary to in order to improve the adhesion of the seeded ZnO particles with the substrate. Higher the temperature, larger the size of the ZnO seed crystal which results in the formation of ZnO nanostructures with bigger size. Therefore thickness and crystal size of the ZnO seed layers will affect the quality of the grown ZnO nanostructures.

After preparing the ZnO seed layers, a typical hydrothermal synthesis of ZnO nanostructures was carried out by immersing the ZnO seed layer coated substrates in equi molar solution (0.1 M) of zinc nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$] and hexamethylenetetramine (HMT, $C_6H_{12}N_4$,) taken in a teflon-lined stainless steel autoclave of 60 mL capacity. HMT is the most commonly used reagent which acts as a pH buffer reagent. The growth was carried out at 90 ˚C for 6 h. After that autoclave was allowed to cool to room temperature, the samples were removed, rinsed in distilled water and dried in air. The structural and morphological properties of the as grown ZnO nanostructures were investigated using X-ray diffraction (RIGAKU smart lab X-ray

diffractometer) and field emission scanning electron microscopy (FESEM ULTRA 55 Karl Zeiss), respectively. The optical properties were investigated by UV-visible spectroscopy (Shimadzu 2600).

III. Results And Discussion

Fig.1(a) to 1(d) show the of XRD patterns of ZnO nanostructures grown by hydrothermal method on: a) glass, b) quartz, c) ITO coated glass and d) p-Si substrates. The observed XRD spectra match with the hexagonal wurtzite structure of ZnO (JCPDS data card number 36–1451) and are dominated by (002) peak indicating the preferential growth direction is along c-axis in all the samples.

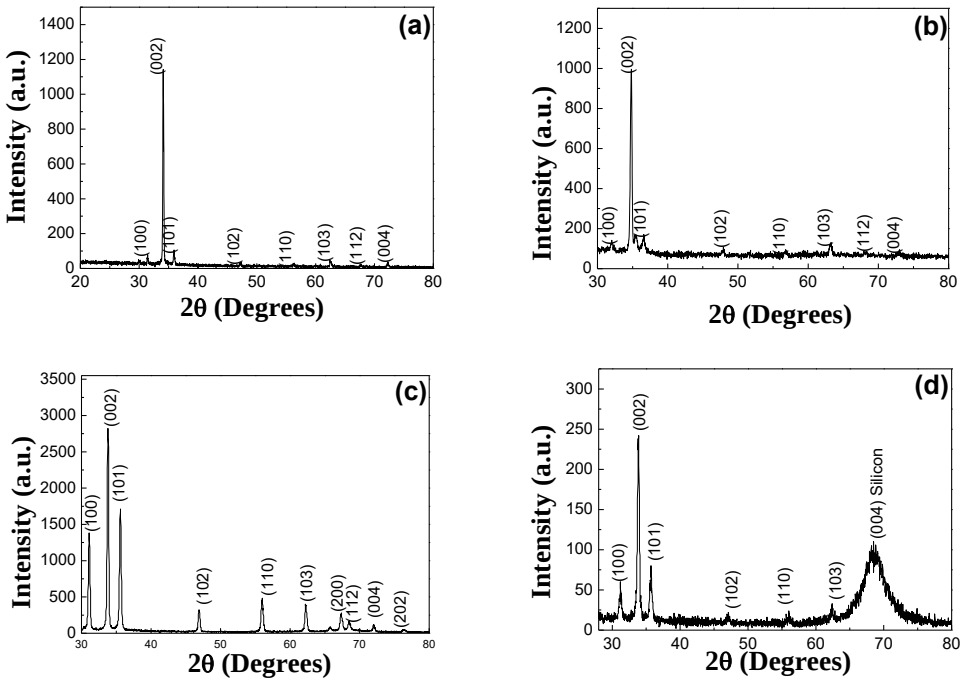
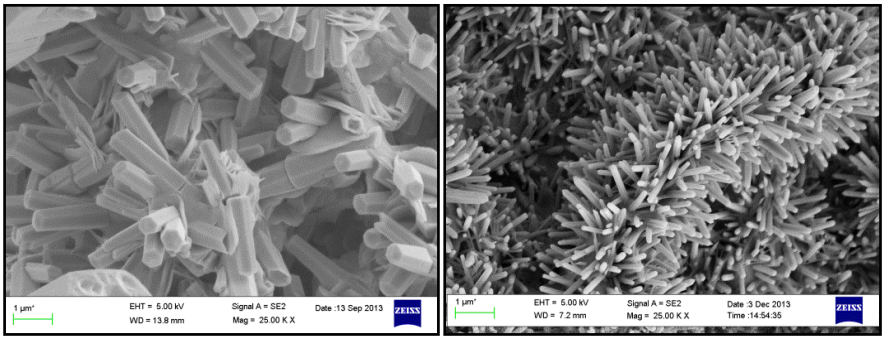


Fig.1: XRD patterns of ZnO nanostructures synthesized on a) glass, b) quartz, c) ITO coated glass and d) p-Si substrates.

In Fig. 2(a)-2(d), the FESEM images shows the formation of ZnO nanostructures on glass, ITO coated glass, quartz and p-Si substrates, respectively. Fig. 2(a) shows the formation of hexagonal shaped ZnO nanorods on glass substrates. The formation of ZnO nanowire array with caterpillar like structure was observed on ITO coated glass substrate, shown in Fig. 2(b). The formations of hexagonal dumbbell shaped ZnO nanostructures were observed on quartz substrate, shown in Fig. 2(c). Flower shaped ZnO nanorods was observed on p-Si substrate, shown in Fig. 2(d). Fig. 3(a) to 3(d) show the EDS spectra of ZnO nanostructures synthesized on a) glass, b) quartz, c) ITO coated glass and d) p-Si substrates, respectively. EDS spectra indicate that Zn and O atomic percentage is nearly stoichiometric in all the samples.



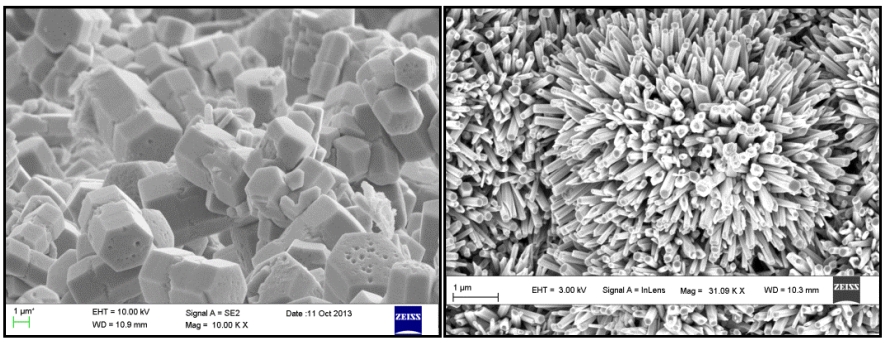


Fig.2: FESEM images of ZnO nanostructures synthesized on a) glass, b) ITO coated glass, c) quartz and d) p-Si substrates.

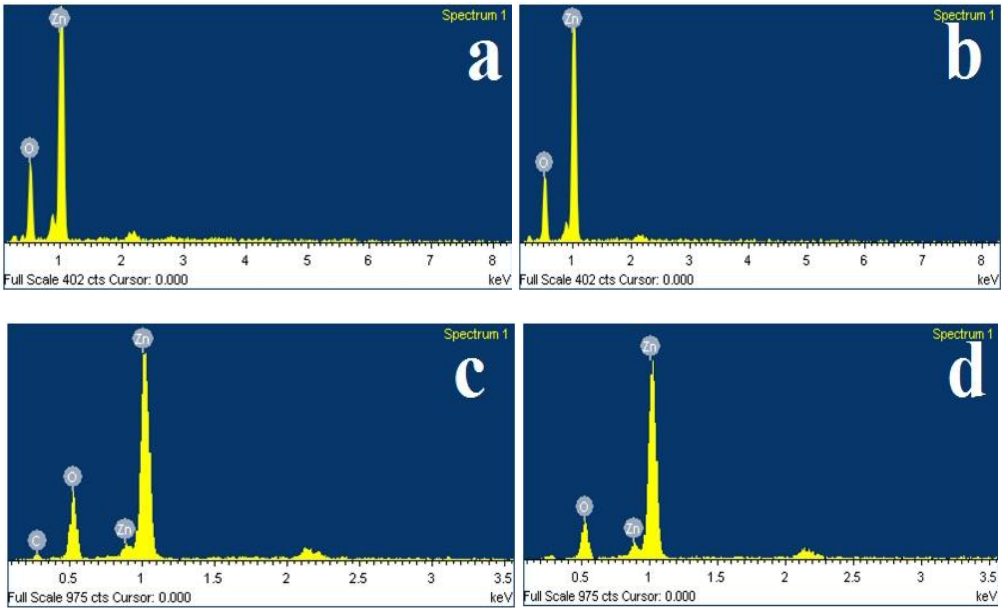


Fig.3: EDS images of ZnO nanostructures synthesized on a) glass, b) quartz, c) ITO coated glass and d) p-Si substrates.

The Fig. 4(a) shows the UV-Vis absorption spectra of ZnO nanostructures synthesized on a) glass, b) quartz and c) ITO coated glass substrates.The UV-visible absorption spectra show a strong exciton absorption peak in the UV region [6].

Fig. 4(b) shows the plot of $(ahv)^2$ versus hν of ZnO nanostructures synthesized on a) glass, b) quartz and c) ITO coated glass substrates. The energy gap (E_g) can thus be estimated by the relation [7]

$$(\alpha h\nu)^2 = A(h\nu - E_g) \qquad (1)$$

The band gap is determined by extrapolating the linear portion of the $(\alpha hv)^2$ against hν plot to intersect the energy axis. The obtained values of the optical band gap are 3.14 eV, 3.21 eV and 3.28 eV for ZnO nanostructures synthesized on a) glass, b) quartz and c) ITO coated glass substrates, respectively.

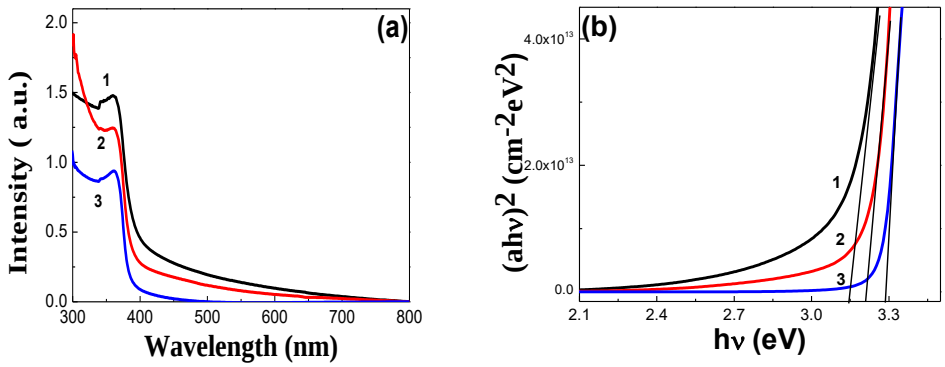


Fig.4: (a) UV-Vis absorption spectra and (b) $(\alpha h\nu)^2$ versus hν plots of ZnO nanostructures synthesized on 1) glass, 2) quartz and 3) ITO coated glass substrates.

IV. Conclusion

ZnO nanostructures are synthesized on glass, ITO coated glass, quartz and p-Si substrates by hydrothermal method. The XRD studies show that the grown ZnO nanostructures have hexagonal wurtzite structure. The UV-visible absorption spectrum indicates a strong exciton absorption peak in the UV region. The FESEM images show the formation of ZnO nanorods and ZnO nanowires array with caterpillar like structure on glass and ITO coated glass substrates. The dumbbell shaped ZnO nanostructures and flower shaped ZnO nanorods were observed on quartz and p-Si substrates. The Zn and O atomic percentage obtained from EDS indicates that the synthesized ZnO nanostructures were nearly stoichiometric.

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