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Preparation of ZnO nanoparticles on transparent and conductive In-doped ZnO thin film

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Abstract. Highly c-axis oriented transparent and conductive In-doped zinc oxide (ZnO:In) thin films were deposited on glass substrates by radio frequency (R.F) sputtering. The photoluminescence (PL) spectra were measured in the range of wavelength 350-750 nm at room temperature. The resistivity of the ZnO films doped 2 wt% indium was lowest and equal to $4.5\times10^{-4}\Omega$cm and a transmittance was of about 80 % in the visible range. Nanostructured ZnO materials have been synthesized from zinc acetate, sodium hydroxide (NaOH} and polyethylene glycol (PEG) by simple hydrothermal method. The results showed that the morphologies and sizes of ZnO nanomaterials depend on the temperature of creation, concentration of PEG, and the pH level of the solution. The ZnO nanopowders structure was characterized by X-ray powder diffraction (XRD). Raman scattering studies confirm that the as-synthesized nanomaterials on transparent and conductive ZnO:In thin films are of high crystalline quality. Photoluminescence have been observed. Nano ZnO/ZnO:In bilayer film was used in a dye-sensitized solar cell (DSSCs) as a working electrode and platinum electrode as a counter electrode.

Keywords: ZnO nanostructures;Transparent and conductive thin film;Hydrothermal method; SEM; Optical property.

1. Introduction

In recent years, great interests are focused on nanostructured zinc oxide (ZnO) because of its wide direct band gap, high exciton binding energy and promising applications for UV-lasers with low threshold [1], surficial acoustic devices [2], transistors and biosensors [3] in nanoscale. The stable structure of ZnO is wurtzite, in which four of oxygen atoms in tetrahedral coordination surround each atom of zinc.

Synthesis of ZnO nanomaterials is often accomplished by sputtering [8], chemical vapor deposition [4] and hydrothermal techniques [10].

In this paper, we report on the influence of the reaction temperature on the morphologies and sizes of ZnO nanoparticles prepared from zinc acetate, sodium hydroxide and polyethylene glycol at temperature in the range of 90-120^{o}C for four or eigh hours by simple hydrothermal method.

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2. Experimental

The ZnO:In films were deposited onto the glass substrates by radio frequency (R.F) magnetron sputtering. The target was a sintered oxide ceramic disk of ZnO (purity 99.9%) mixed with 2 wt% In_2O_3 (purity 99.99 %), 75 mm in diameter, and a density of 4.58 g/cm^3 [8]. Glass substrates were placed parallel to the target surface with a substrate to target distance of 7.5 cm. The film thickness was controlled by changing the sputtering time.

ZnO nanoparticles on transparent and conductive ZnO:In thin film were formed according to equation (1), the $Na(CH_3CO_2)$ was then removed by washing the sample with water.

$$Zn(CH_3CO_2)_2 + 2NaOH \rightarrow ZnO + 2Na(CH_3CO_2) + H_2O \quad (1)$$

For typical preparation, 1 mmol of zinc acetate dehydrate $Zn(CH_3CO_2)_2.2H_2O$ was dissolved in 80 ml of solvent in covered flask under vigorous stirring at 50^{o}C. After cooling to room temperature, 8 ml of the transparent zinc salt solution was added into 64 ml of the pure solvent. A 0.02 M NaOH solution was prepared by adding sodium hydroxide to the pure solvent in a covered flask under vigorous stirring at 60^{o}C. After cooling to room temperature, 8 ml of the sodium hydroxide solution was added into 20 ml of the pure solvent. The sodium hydroxide solution was then added into the zinc acetate solution under vigorous stirring to give a total volume of 100 ml with 0,1 mmol of zinc acetate and 0,16 mmol of NaOH. The initial layers were located on the teflon autoclave and then dipped in the aforementioned solution at temperature in the range of 90-120 ^{o}C for four or eigh hours.

The morphologies and structures of the products were investigated by SEM (JEOL-J8M5410 LV), TEM (JEOL JEM 1010, Japan), X-ray diffractometer (Bruker-AXSD5005). Raman scattering spectra at room temperature in the energy region between 100 and 1000 cm^{-1} were recorded by a micro-Raman spectrograph LABRAM-1B equipped with a He-Ne laser (λ = 632,817 nm) with a power of 11 mW. The photoluminescence (PL) at room temperature was excited on a 325 nm He-Cd laser. A UV-vis spectrophotometer (UV-2450PC Shimadzu) was used to record the UV-vis absorption spectra.

3. Results and discussion

The transparent and conductive ZnO:In film, exhibited columnar grain growth with a strong c-axis orientation perpendicular to the substrate surface. Fig.1 shows a typical X-ray diffraction pattern for the ZnO:In films. A strong diffraction line appears at 34.4 ^{o}, which is assigned to the (002) diffraction peak of hexagonal ZnO.

The lattice constants were calculated to be a = 0.3249 nm and c = 0.5212 nm utilizing the observed (002) diffraction peak, which is slightly larger than a reported value of a = 0.3248 nm and c = 0.5206 nm for bulk ZnO crystal. Consequently, it is obvious that the hexagonal ZnO films obtained in this work are of high crystalline quality.

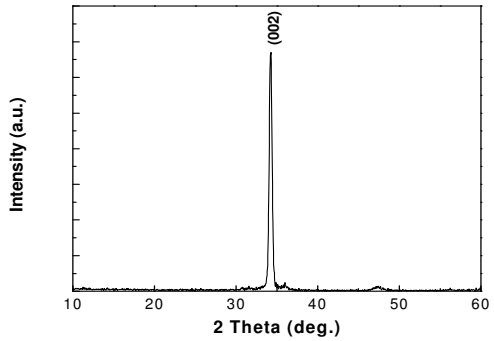

Fig. 1. XRD pattern of ZnO:In film deposited on a glass substrate

A typical SEM photograph of a resultant n-ZnO:In film is shown in Fig. 2. A thickness of the film was typically 1100 nm at a magnification of ×30.000 (Fig. 2a). The sharp clear edge indicates that the films are highly adherent to the substrates. A polycrystalline grain size of about 40 nm was observed under a magnification of ×100000 as shown in Fig.2b.

Hall effect measurement showed that the ZnO:In films are degenerately doped n-type semiconductor. The resistivity of the ZnO films doped with 2 wt% indium was lowest and equal to 1.5×10^{-3} Ωcm for the films deposited on glass substrate [8].

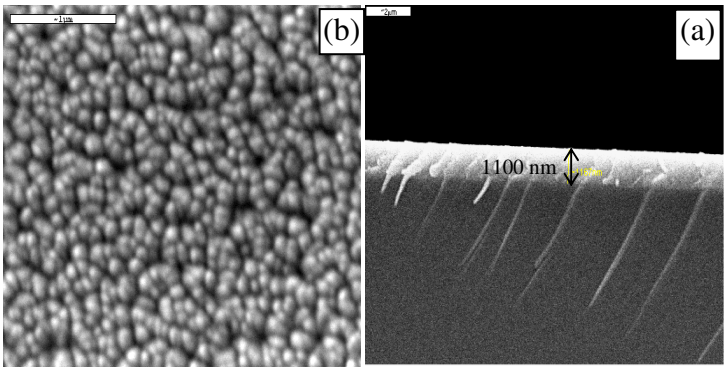

Fig.2. (a) SEM image cross-section and (b) surface image of a ZnO:In layer grown on a glass substrate at 150 ^{o}C.

The band gap of ZnO:In (E_g = 3.3 eV) [8] is larger than the energy value of visible photons ($\lambda \geq 400$ nm) and, therefore, it is transparent to the visible light. It is observed from the transmittance spectrum that the present ZnO:In films is highly transparent ($T \geq 90\%$) in the visible region [8].

The initial layers ZnO:In were located at vertical positions on the teflon bar and then dipped in the aforementioned solution. From different combinations of pH and reaction temperature, ZnO nanoparticles were synthesized by hydrothermal method with the pH value of 11 the reaction

temperature of 90-120 °C. It was found that the pH and the reaction temperature had a minor influence on the size and the morphology of the nanomaterials.

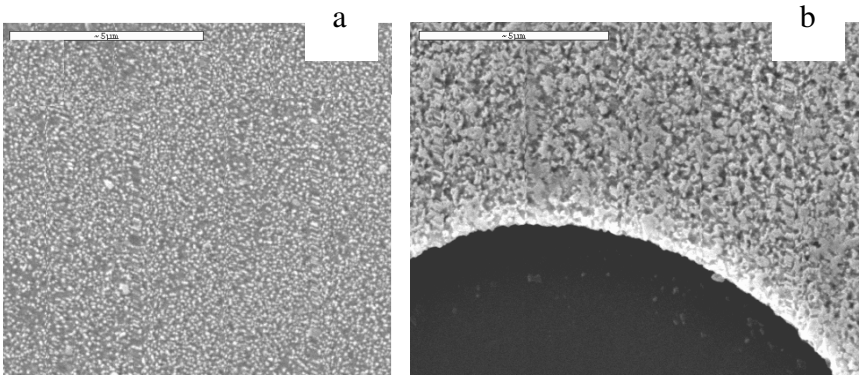

Fig.3. SEM images of nanoparticles prepared on the initial l ZnO:In ayers in the aforementioned solution at temperature of 90 °C for time of 6 hours (a-sample V_3) and for time of 9 hours (b-sample V_4)

When PEG was not used (at the reaction temperature 90 °C), the collected samples were ZnO nanoparticles with the Wurtzite hexagonal structure (Fig.3).

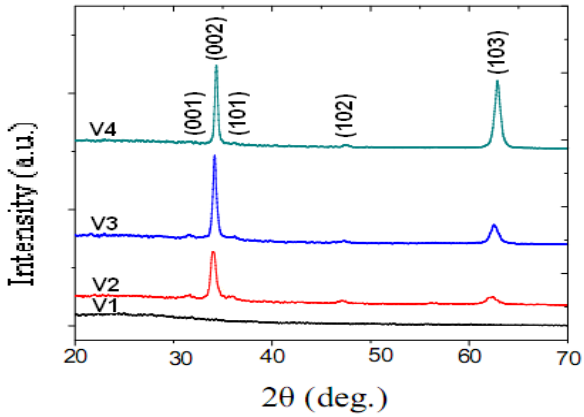

Fig. 4. XRD patterns of the samples (V_1-glass subrate, V_2-ZnO:In initial layer, V_3- ZnO:In initial layer and ZnO nanoparticles for time of 6 hours and V_4- ZnO:In initial layer and ZnO nanoparticles for time of 9 hours), ZnO nanoparticles prepared at the reaction temperature of 90 °C.

A typical XRD pattern of the products are shown in Fig. 4. It can be seen that there are two diffraction peaks corresponding to the (002) and (103) crystalline lattice planes. All the diffraction peaks can be indexed to the hexagonal structured ZnO. As indexed in the figure, all the diffraction peaks match those of wurtzite ZnO with lattice constants of a = 3.250 Å and c = 5.207 Å [5].

It can be seen that as the reaction temperature increases from 90 to 120 °C, the collected samples were ZnO nanorods with the wurtzite hexagonal structure (Fig.5). Figure shows that the sizes of the ZnO nanorods were rather small : 40-50 nm in diameter. These ZnO nanorods were found to grow with a high density and perpendicularly to the substrate.

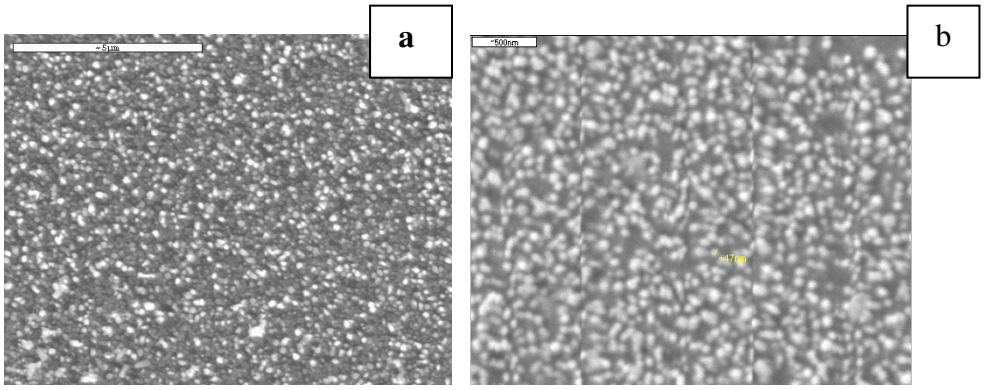

Fig.5. SEM images of nanorods prepared in the aforementioned solution at temperature of 120 °C for time of 6 hours (a-sample V_7) and for time of 9 hours (b-sample V_8)

The XRD patterns of the typical ZnO nanorods were shown in Fig.6. The figgure 6 shows that the nanorods were well oriented with the c-axis perpendicular to the substrates and have structure reconstitution of ZnO:In iniatial layer.

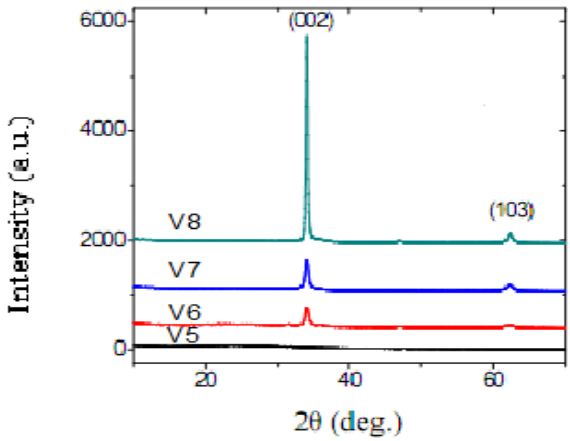

Fig.6. XRD patern of the samples (V_5-glass subrate, V_6-ZnO:In initial layer, V_7- ZnO:In initial layer and ZnO nanoparticles for time of 6 hours and V_8- ZnO:In initial layer and ZnO nanoparticles for time of 9 hours), ZnO nanorods prepared at the reaction temperature of 120 °C.

When PEG was used in the fabricating solution, its concentration was found to have considerable influence on the morphology of the samples.

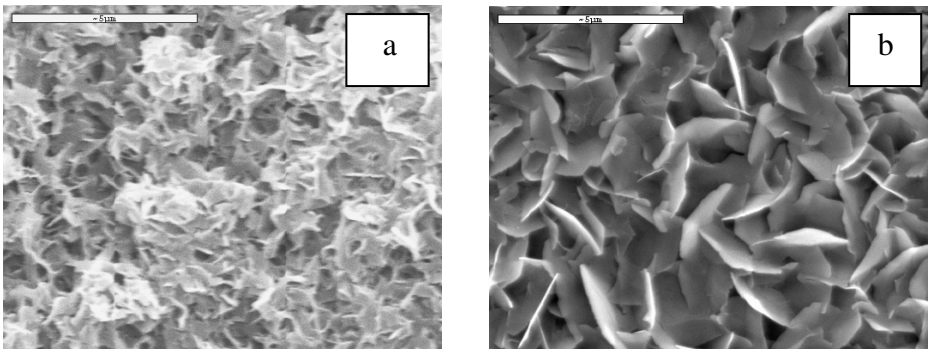

Fig.7. Influence of PEG concentration on the morphology of samples (a-PEG concentration of 0,001M, b- PEG concentration of 0.001M, prepared at the reaction temperature of 120 ^{o}C) for time of 8 hours

Further, Raman scattering, due to its sensitivity to the crystalization, structural disorder and defects in nanostructures, was measured for the ZnO nanoparticles. Figure 8a shows the Raman spectrum of ZnO nanoparticles. ZnO has a wurtzite crystal structure and belongs to C_{6v} group. According to group theory analysis, the $A_1+E_1+2E_2$ modes are Raman active. The two higher peaks at 103 and 438 cm^{-1} can be assigned to E_2 modes, characteristic of the wurtzite lattice. The much weaker peak at 379 cm^{-1} is attributed to the transverse optical modes of A_1. The other two weaker and broader peaks at 203 and 333 cm^{-1} can be assigned to the secondary Raman scattering arising from zero-boundary phonons 2-TA (M), and 2-E_2 (M), respectively [9]. The presence of the E_1 (LO, 580 cm^{-1}) mode of oxygen deficiency indicates that there are oxygen vacancies in our ZnO nanoparticles.

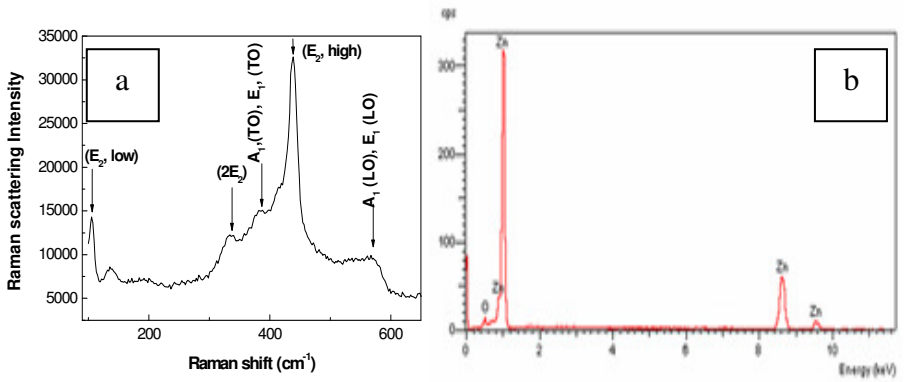

Fig. 8. (a) Room-temperature micro-Raman spectrum and (b) EDS spectrum of ZnO of the typical synthesized samples

The EDS elemental analysis is shown in Fig.8b. This result indicates that ZnO nanoparticles were only composed of zinc (Zn) and oxygen (O).

The transmittance and absorption spectra of typical ZnO nanoparticles are shown in Fig.9.

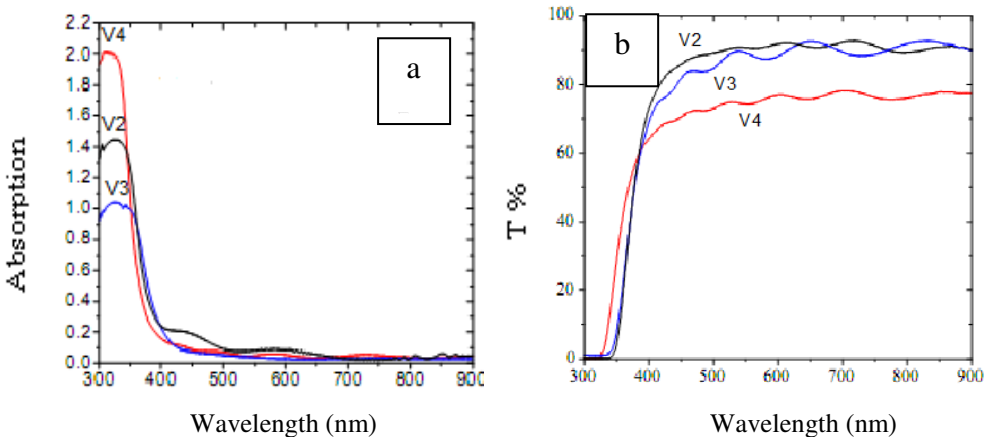

Fig. 9. The absorption (a) and transmittance (b) spectra of the samples (V_2-ZnO:In initial layer, V_3-ZnO:In initial layer and ZnO nanoparticles for time of 6 hours and V_4- ZnO:In initial layer and ZnO nanoparticles for time of 9 hours), ZnO nanoparticles prepared at the reaction temperature of 90 ^oC.

As a wide band gap semiconductor, photoluminescence (PL) is one of the most important properties of ZnO. The PL spectra of all samples, measured at room temperature, showed that there was one wide peak in the visble (VIS) band at 530-550 nm wavelengths (Fig.10). The green emission band is attributed to the radiative recombination of photogenerated holes with electrons belonging to singly ionized oxygen vacancies in the surface and subsurface. The observation of strong green band emission relative to bulk ZnO indicates the existence of oxygen vacancies concentrated on nanoparticles surface [10]. But the peak at 474-584 nm of ZnO:In initial layer (V_2) includes four subordinate peaks. We consider that it is possibly related with oxygen vacancies of zinc vacancies.

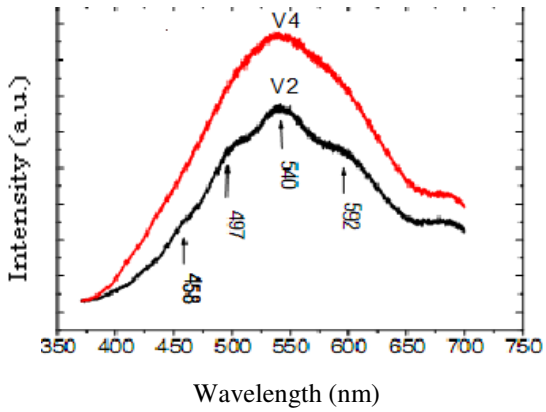

Fig.10. The PL spectra of ZnO:In initial layer (V_2) and ZnO nanoparticles (V_4)

4. Conclusion

Highly c-axis oriented ZnO:In films were deposited on glass substrates by R.F. magnetron sputtering. The lowest resistivity of In-doped ZnO film reached $4.5\times10^{-4}\Omega$cm and the carrier concentration was 2×10^{20} cm^{-3}. The transparency was 90% in the visible region.

ZnO nanomaterials were synthesized using the hydrothermal method. The ZnO nanomaterial are highly adherent to the ZnO:In initial layers. The influence of fabricating conditions on morphology and size of nanomaterials were also investigated. It was shown that the reaction temperature and polyethylene glycol (PEG) played the key role. Nanostructures of different morphologies were collected thanks to changes in the PEG concentration.

This would that ZnO macroporous structures on transparent and conductive In-doped ZnO thin film can be used as a working electrode to fabricate high efficiency dye-sensitized solar cell (DSSCs).

Acknowledgments

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