Int. J. Chem. Sci.: 7(4), 2009, 2463-2469

EFFECT OF pH ON SILAR DEPOSITED ZnO THIN FILMS

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ABSTRACT

Zinc oxide thin films were deposited by successive ionic adsorption and reaction (SILAR) method using a zinc sulphate and sodium bath on glass substrate. The effect of pH, though one of the important factors, which determine the quality of films, is usually ignored. The present work explores the effect of pH of solution on the structural, morphological and optical properties of thin films. X-ray diffractograms and scanning electron microscopy reveal that the grain size is increased with the increase in pH of the precursor solution. The optical studies show that the band gap decreases from 3.29 to 3.09 eV with increase in pH.

Key words: ZnO thin film, Structural, Morphological, Optical.

INTRODUCTION

Zinc oxide (ZnO) is a versatile material of compound semiconductors with excellent properties and has extensive applications in electronics, photoelectronics, sensors, and catalyst. ZnO thin films have attracted considerable attention because they can be tailored to possess high electrical conductivity, high infrared reflectance, and high visible transmittance by different coating techniques. The remarkable properties of ZnO are due to its wide direct band gap of 3.37 eV[1,2].

The properties of zinc oxide films strongly depend on the deposition method. Many deposition techniques have been employed to prepare zinc oxide films, such as sol–gel, chemical vapor deposition, pulsed laser deposition, thermal evaporation and magnetron sputtering. The SILAR deposition offers many advantages for the fabrication of thin films, including excellent control of the stoichiometry of precursor solution, ease of compositional modification, customizable microstructure, ease of introducing various functional groups, relatively low annealing temperatures, feasibility of deposition on large-area substrates and

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inexpensive equipments. The variation of pH in the precursor sol affects the hydrolysis and condensation behavior of the solution, which, in turn, influences the structure of the resultant film. The pH of sol has been observed to be a very critical process controlling parameter that determines the phase formation, particle size and morphology of the final film. This, in turn, affects the structural, morphological and optical behavior of the films. In this paper, the effect of pH on the microstructure, surface morphology and optical properties of zinc oxide transparent films prepared by SILAR deposition method is investigated

EXPERIMENTAL

The details of ZnO film deposition on glass substrates (microscope slides) by alternate dipping into sodium zincate bath (Na_2ZnO_2) kept at room temperature and hot water maintained at boiling point were reported earlier[3-7]. Zinc sulphate ($ZnSO_4.7H_2O$) was used as source of zinc and an aqueous sodium hydroxide solution was added without stirring. Initially, the solution became milky-turbid due to the formation of $Zn(OH)_2$, which was dissolved by further addition of NaOH; thus, forming the Na_2ZnO_2 bath. The pH of the prepared solution was measured and found to be 10. Sulphuric acid or sodium hydroxide was then mixed drop by drop until the pH values reached 8.5, 9.0, 9.5 and 10.5. Films produced with more acidic solution (pH< 8.0) and more basic solution (pH >11.0) show poor quality after deposition.

The glass substrate was cleaned, before deposition, by chromic acid followed by distilled water rinse and ultrasonic cleaning with acetone and alcohol. The cleaned substrate was held tightly in a holder so that only a requisite area for film deposition was exposed. Thus, the film deposition area could be easily varied by adjusting the holder. The cleaned substrate was immersed first in the sodium zincate and then in hot water. This cycle was repeated several times in order to increase the overall film thickness of ZnO. In this way, the substrate was covered with a thin layer of the complex solution, which decomposed to ZnO when placed in boiling water according to the reaction:

$$Na_2ZnO_2 + H_2O \rightarrow ZnO + 2\ NaOH \qquad ...(1)$$

Part of the ZnO so formed was deposited onto the substrate as a strongly adherent film and the remainder formed a precipitate. The deposited film was subsequently annealed in air at 200 °C for 30 min.

The film thickness was determined by the weight gain method using the formula-

$$t = \frac{m}{A\rho} \qquad ...(2)$$

where 't' is the thickness of the film, 'm' is the weight gain, A is the area of the coated film and ρ is the density of ZnO (5.6 gcm^{-3}). The film thickness was estimated to be approximately 0.97, 1.21, 1.39, 1.62 and 1.77 μm for solution pH of 8.5, 9.0, 10.0, 10.5 and 11.0, respectively.

The crystalline structure was determined by X-ray diffraction using X'pert PRO (PANalytical) diffractometer with CuKα radiation (λ = 0.15405 nm) and employing a scanning rate of 5° min^{-1}. The particle size and morphology was examined using scanning electron microscope (SEM) Hitachi S-3000H model. For SEM studies, the samples are pre-coated with Au sputtering using fine coat ion sputter JFC-1100 model instrument. Optical transmittance was measured by Perkin Elmer Lambda 35 UV-vis spectrometer. All the measurements were performed at room temperature.

RESULTS AND DISCUSSION

Structural properties

The crystallization behavior of ZnO films deposited on glass substrate was examined by X-ray diffraction (XRD) measurements. Fig. 1 shows XRD patterns of ZnO films with different pH of solution.

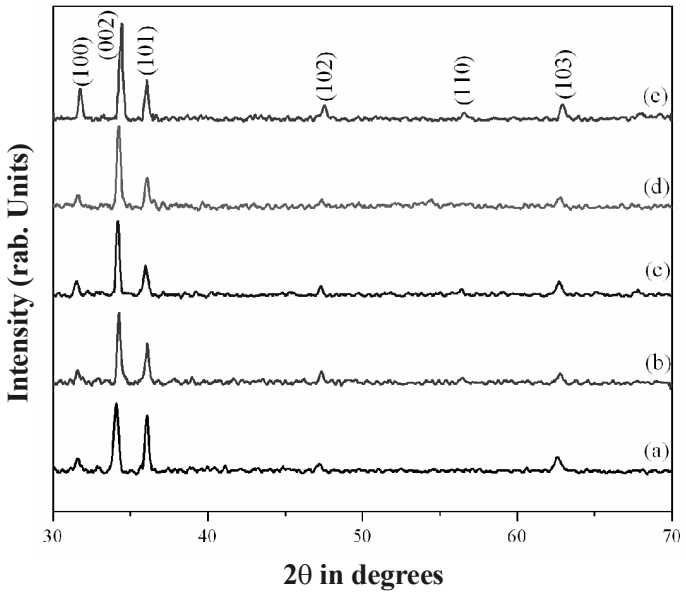
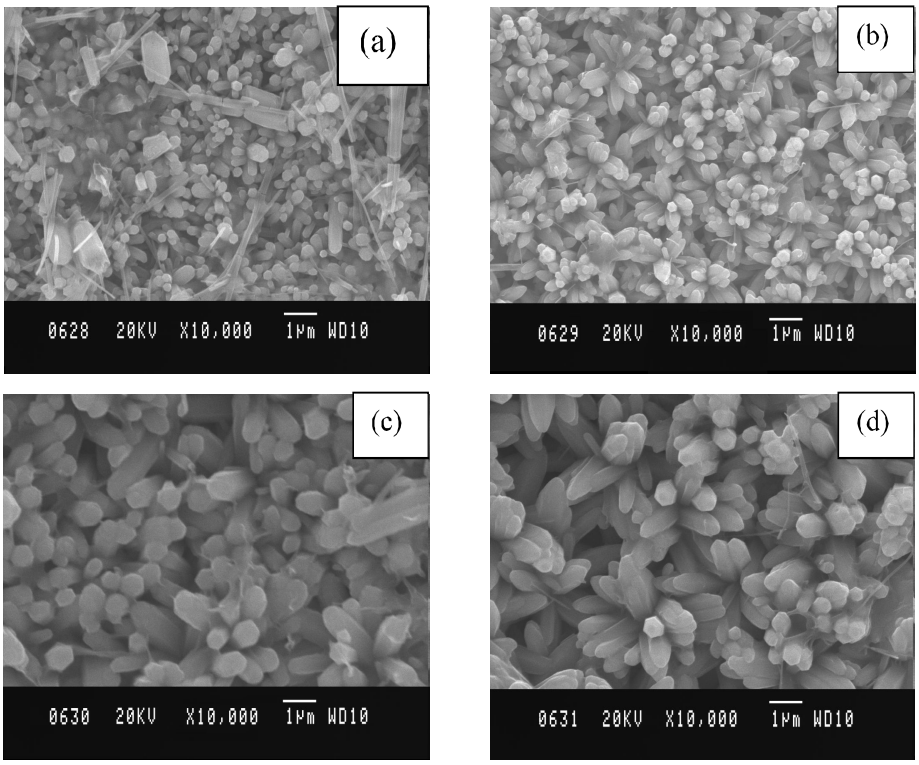


Fig. 1: X-ray diffractograms of ZnO thin films prepared at various pH of precursor solution

The XRD pattern clearly showed that all the samples are polycrystalline in nature and exhibit single-phase ZnO hexagonal wurtzite structure[8] whose c-axis was preferentially oriented normal to the glass substrate. The intensity of (002) plane increased, which reveal that the degree of crystallinity increases as the films deposit from solution of higher pH. This means that the film deposited from the solution of higher pH has more grain growth as compared to the film deposited from the sol of lower pH.

Morphological studies

Fig. 2 (a-e) shows the scanning electron micrograph (SEM) of ZnO films deposited at (a) pH = 8.5, (b) 9.0, (c) 9.5, (d) 10.0 and (e) 10.5, respectively. The SEM micrographs show that the grain size increases with increase in solution pH. The grains of the film deposited from solution with pH of 8.5 show somehow aggregated with non-uniform nature. Flower like structures appeared as solution pH was increased to 9.0. When the solution pH was further increased from 9.0 to 9.5, corresponding morphology of the film shows the grains with nano rods with hexagonal structure. The size of the nano rods increased as solution pH was further increased to 10.0. For the film prepared at 10.5 pH, the morphology shows well elongated nano rods sticking with one another.



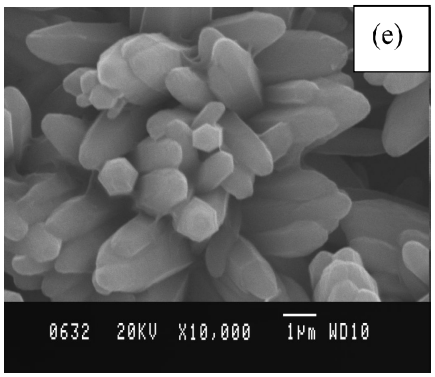


Fig. 2: SEM images of ZnO thin films prepared at (a) pH = 8.5, (b) 9.0, (c) 9.5, (d) 10.0 and (e) 10.5

Optical studies

The variation of optical transmittance with wavelength for ZnO thin film coated at different solution pH are shown in Fig. 3(a). It is observed that the transmittance decreases with increase in solution pH. The optical band gap of the films is calculated from the transmittance spectra employing Faue's plot. The absorption coefficient (α) is calculated using the equation[9] -

$$\alpha = In\left(\frac{1}{T}\right)/d \qquad \ldots(3)$$

where T is transmittance and d is film thickness. The absorption cofficient (α) and the incident photon energy ($h\nu$) is related by the following equation[10] -

$$(\alpha h\nu)^2 = A(h\nu - E_g) \qquad \ldots(4)$$

where A and E_g are constant and optical band gap, respectively. The E_g can be determined by extrapolation of the linear portion of the curve to the $h\nu$ axis. The Fig. 3(b) shows the curves of $(\alpha h\nu)^2$ versus photon energy. The calculated value for obtained E_g of the obtained ZnO thin films prepared by solution pH 8.5, 9.0, 9.5, 10.0 and 10.5 are 3.29, 3.27, 3.23, 3.16 and 3.09 eV, respectively. These values are little higher than those reported in literature[11,12]. This may be due to smaller film thickness used in the present study and the shift of the band gap towards shorter wavelength. The band gap energy, a constant value of the materials for bulk samples, is known to vary in thin films due to particle size effect. It has been reported that the band gap energy can be modulated by changing the particle or grain size in the films[13]. The decrease in the optical band gap of the films with increase in

the pH of precursor sol could be attributed to the grain size enhancement.

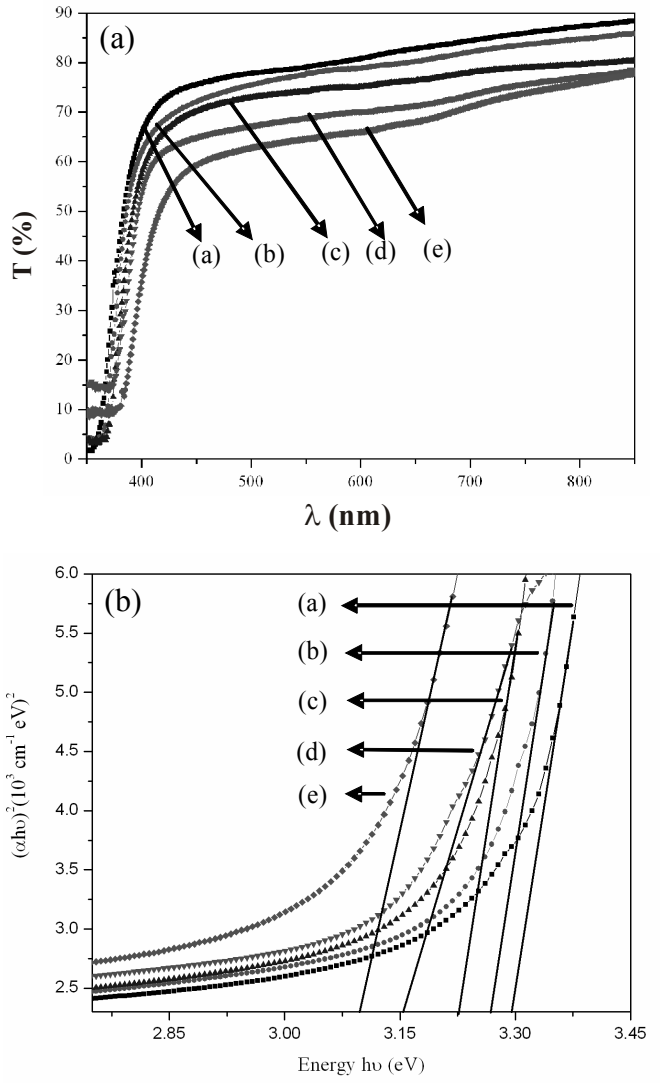


Fig. 3: (a) Optical transmittance spectra of ZnO thin films prepared from different pH of precursor solution (b) Plot of hν versus $(\alpha h\nu)^2$ for ZnO thin films coated on glass substrate

CONCLUSION

The variation of pH of the precursor solution is found to have pronounced effect on

the structure, morphology and optical properties of SILAR deposited ZnO thin films. X-ray diffractograms show film crystallinity enhancement, when pH of the precursor solution is increased from 8.5 to 10.5. The SEM micrographs also reveal that with increase in pH, the average grain size increases. Optical transmittance spectra of ZnO film decreases with increase in solution pH. The optical studies show that with increase in the pH of precursor solution, the band gap decreases from 3.29 to 3.09 eV.

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Accepted : 04.09.2009