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INFLUENCES OF ANNEALING TEMPERATURE ON THE ELECTRICAL AND OPTICAL PROPERTIES OF Na DOPED ZnO THIN FILMS

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ABSTRACT

This paper reports on the electrical and optical properties of natrium doped zinc oxide thin films. Transparent Na doped ZnO thin films have been prepared by sol-gel method using zinc acetate dihydrate as a starting material, 2-methoxyethanol as solvent and diethanolamine (DEA) as sol stabilizer. Then followed by mixing with the doping solution, natrium. Film deposition was performed by spin coating technique at spin rate of 3000rpm on quartz substrates. Then the films were annealed at 400°C, 500°C, 600°C, 700°C and 800°C for 60 minutes in hydrogen. The sheet resistance of the layers decreased from 1.4 x 10^4 Ω/ to 1.1 x 10^4 Ω/ as the annealing temperature increased from 400 to 800°C. The average optical transmittance values of the annealed films were more than 85% in the visible range. The energy band gap calculated from the transmittance spectra is about 3.25 – 4.30 eV.

INTRODUCTION

ZnO is a well known semiconductor [1,2] and has a broad range of applications in optoelectronics, acoustic devices and light-emitting diodes. As a semiconducting oxide material with low resistivity, high transmittance down to UV spectral range, and good chemical stability under strong reducing environments, ZnO is thus a promising transparent conductive oxide (TCO) and a possible alternative to tin oxide and indium oxide to be used as a transparent electrode for photovoltaic solar cells and electrodes on flat panel displays [3]. Till now, metal elements like Al [4,5], Ga [6,7], Ba [8], Fe [9] and In [9,10], which substitute for Zn, have been widely used. To our knowledge, there are no data in the literature for natrium doping of ZnO. In this paper we investigate the effect of natrium doping on electrical and optical properties of ZnO using sol-gel method.

EXPERIMENTAL

The Na doped ZnO thin films was prepared from zinc acetate dehydrate ($Zn(CH_3COO)_2.2H_2O$), 2-methoxyethanol, diethanolamine and metal sodium, refluxed at 70°C for about 2 h. The molarity of the solution was chosen to be 0.5M. The solution must free from water to avoid turbidity and obtain a clear solution.

The quartz substrate were cleaned with methanol and acetone for 15 min each in ultrasonic. Then rinsed with distilled water and dried in nitrogen. Deposition of films

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was carried out using spin coating process with spinning speed, 3000rpm for 30s. The thin films was then dried at 150°C for 10 min. After that, the resulting films were annealed in hydrogen at different temperatures (400, 500, 600, 700 and 800°C) for 60 min. The thickness of the films was approximately 120 nm and the area of the films was 2.5cm x 2.5cm.

The sheet resistance and optical transmittance of the films were studied using four-point probe and UV-Vis-NIR spectrometer (Perkin Elmer, Lambda 900), respectively.

RESULTS AND DISCUSSION

Figure 1 shows the sheet resistance for all of the films as a function of annealing temperature. Annealing the film at 400°C increased the sheet resistance value. However as the temperature was increased up to 500°C, the sheet resistance decreased and become almost constant as we further increased the temperature. The decreasing of the sheet resistance could be due to the generation of oxygen vacancies in Zn sites [11]. Mizuta *et al*. [11] has reported that the value of sheet resistance of their ZnO thin films is in the range of 10^2-10^5. Their thin films were annealed at 100-500°C.

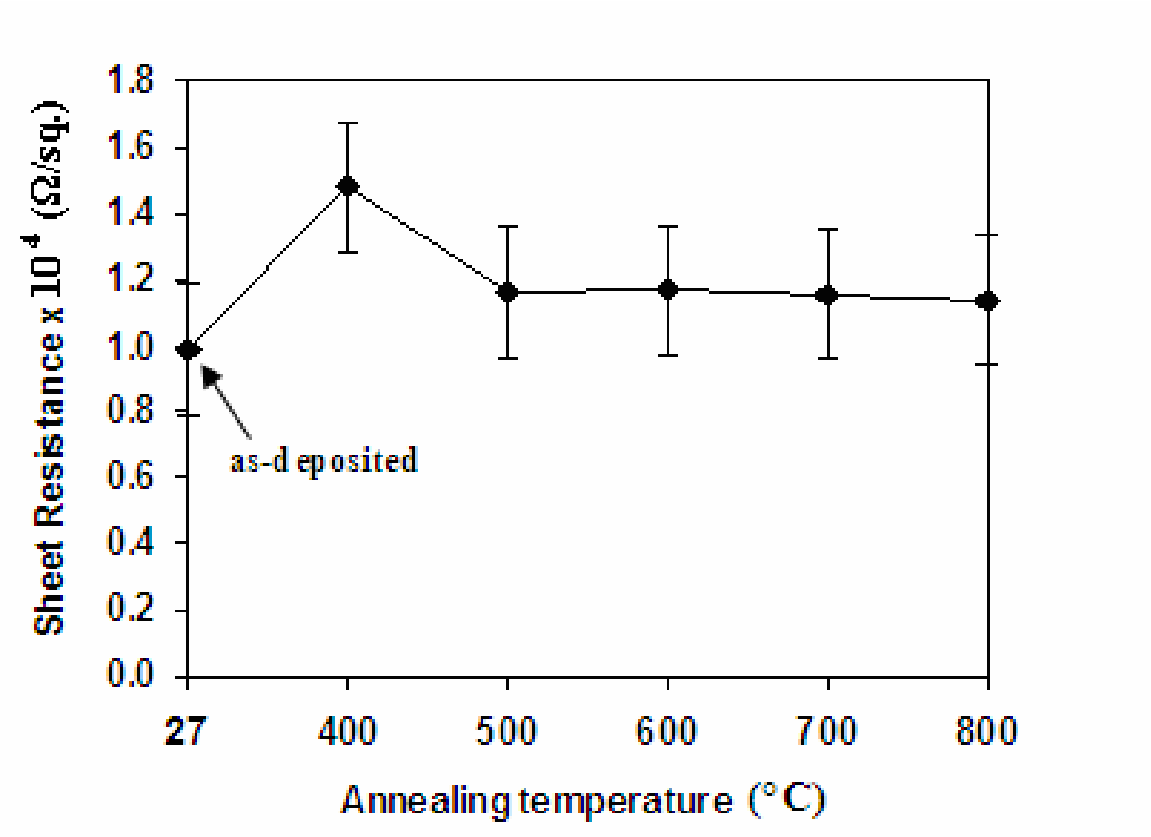

Figure 1: Sheet resistance of Na doped ZnO as afunction of annealing temperature.

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The thin films optical properties were studied using UV-ViS-NIR spectrometer. Figure 2 shows the results. The transmittance spectra show that all of the films exhibit a transmittance higher than 85% in the visible region.

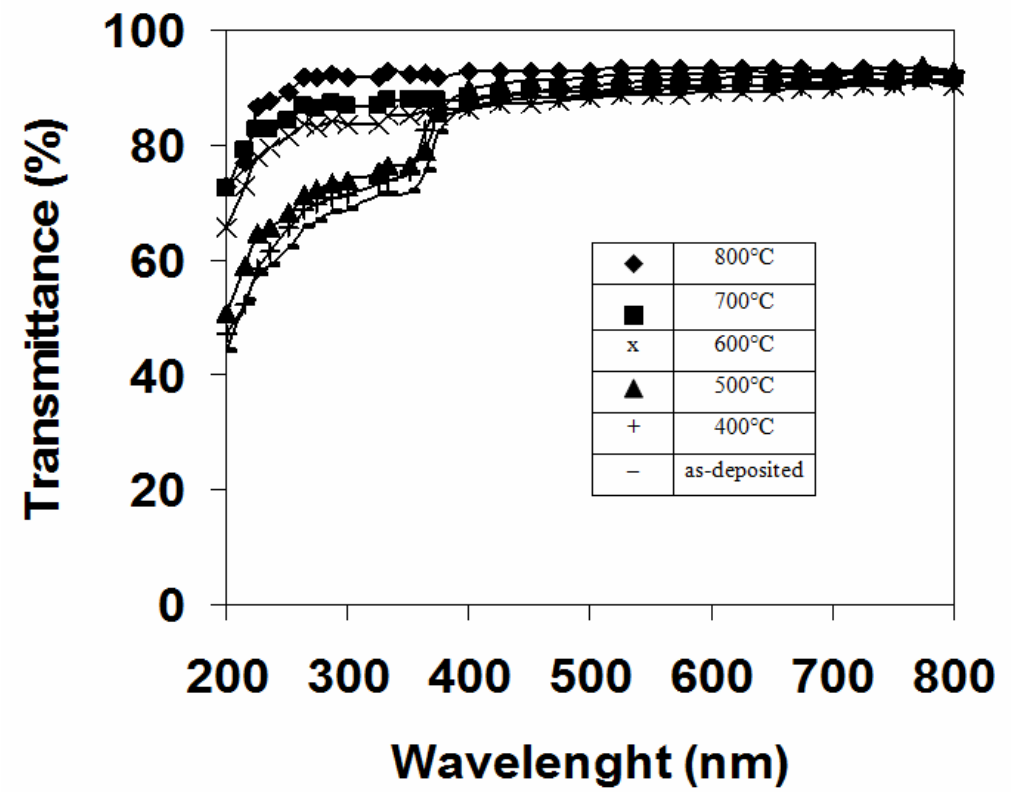

Figure 2: Transmittance curves of Na doped ZnO films at different annealing temperatures.

To estimate the optical band gap, absorption coefficient α was first calculated from the relation :

$$T = A \exp(-\alpha d) \qquad (1)$$

Where T is the transmittance of the film, A is the constant, and d is the film thickness. The constant A is approximately unity. The optical band gap of the films are determined by applying the Tauc model [12], and the Davis and Mott model [13], in the high absorbance region:

$$\alpha h\nu = D\,(h\nu - E_g)^n \qquad (2)$$

where $h\nu$ is the photon energy, E_g is the optical band gap, and D is the constant. For n = ½ the transition data provide the best linear curve in the band edge region, implying the transition is direct in nature. The band gap of the films have been calculated using Tauc's plot by plotting $(\alpha h\nu)^2$ versus $h\nu$ (see Figure 3 and Figure 4) and by

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extrapolating the linear portion of the absorption edge to find the intercept with energy axis [14].

The measured optical band gap values are 3.25eV and 3.27eV for 400°C and 500°C, respectively (figure 3), which were in the range of band gap values of intrinsic ZnO (3.2 – 3.3 eV) measured by previous researchers [15]. But for 600, 700 and 800°C, obviously the band gap values are increased to 4.0, 4.2 and 4.3 eV respectively (figure 4).

It has been reported by Oral et al. that based on the Burstein-Moss effect [16], doping the ZnO film above the Mott critical density can broaden the energy band [17]. At high doping level, the carriers may be degenerate and for n-type semiconductor, the Fermi energy may lie within the conduction band while for p-type semiconductor, it may lie within the valence band. However in our case the shifting of the Fermi level could be due to the high annealing temperature, which in turn shifts the absorption edge to higher energies (blue shift) thus broaden the energy band. Using equation:

$$\Delta E_g = \frac{h^2}{8m^*}\left(\frac{3}{\pi}\right)^{2/3}\eta_e^{2/3} \qquad (3)$$

where h is the Plank's constant, m^* the electron effective mass in conduction band and η_e is the carrier concentration, Oral et al. suggested that the increment of the carrier concentration in the Li-doped ZnO films are due to the energy band broadening which shows that most of the Li ions must be incorporated as interstitial donors in the ZnO structure rather than substitution acceptors. Our results are similar with them hence the Na ions must also acts as the interstitial donors.

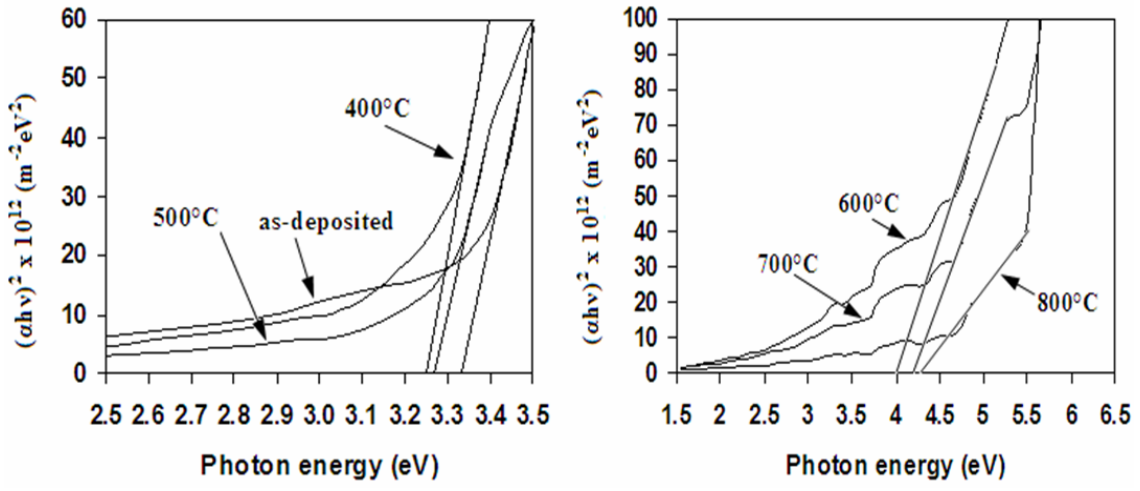

Figure 3: Variation of optical band gap with annealing temperature.

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CONCLUSIONS

The effect of annealing temperature on the electrical and optical properties of natrium doped ZnO thin films has been examined. The sheet resistance of the layers decreased from 1.4 x 10^4 Ω/ to 1.1 x 10^4 Ω/ as the annealing temperature increased from 400 to 800°C. All of the films exhibit a high transmittance (>85%) in the visible region. The bandgap values of the natrium doped ZnO films are found to be from 3.25 to 4.30 eV.

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