Effect of Tertiary Amines on Structural, Morphological and Optical Properties of Nanostructured ZnO Thin Film

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Nanostructured ZnO thin film has been synthesized via sol-gel method. In this study, effect of stabilizer, as a vital part of sol with different molar ratios of stabilizer to Zn (stabilizer/Zn = 0.25, 0.5, 1, 2), on structural, morphological and optoelectronic properties of ZnO thin film has been investigated. Triehtylamine (TeA) and triethanolamine (TEA), as two important tertiary amines for synthesize of ZnO, has been used. Spin coating technique performed to deposition of sol on glass substrate and after deposition process, the samples clacined at 500 °C. X-ray diffraction method conducted in order to find structural properties of the films. The results showed the formation of hexagonal wurtzite ZnO as well as increasing the unit cell parameters by increasing TeA content. Field emission scanning electron microscopy (FESEM) used in order to see morphological changes for different molar ratios of stabilizer to Zn. The images demonstrate grain segregation in TeA samples by increasing TeA molar ratio. Also, in TEA samples, formation of micro holes in TEA/Zn = 0.5 and smaller grain size for higher TEA ratios has been observed. UV-Vis spectroscopy was employed to obtain optoelectronic properties and the results have shown dependence of optical band gap to stabilizer's type and content.

Keywords: ZnO thin film, Sol-gel, Stabilizer, Nanostructure, Optoelectronic properties.

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1. INTRODUCTION

As a promising wide band gap semiconductor, ZnO received great deals of attentions due to the unique properties such as non-toxicity, high surface activity and great sustainability. ZnO is a non-stoichiometric II-VI compound semiconductor with direct optical band gap of 3.37 eV and exciton binding energy of 60 meV at ambient temperature [1]. Oxygen vacancies as well as Zn interstitials make ZnO a n-type semiconductor. Following properties caused ZnO be widely used in various applications such as dye sensitized solar cells (DSSC) [2], light emitting diodes (LED) [3], transparent conductive oxides (TCO) electrode [4], and various sensors [5].

Different methods are available for the synthesis of ZnO thin film such as sputtering [6], physical vapor deposition (PVD) [7], chemical vapor deposition (CVD) [8], and sol- gel method [9, 10, 11]. Sol-gel process is a liquid-based method that has been widely used to synthesize thin films due to the excellent compositional control, atomic and molecular homogeneity, simple and controllable parameters, lower crystallization temperature, and good control on the microstructure.

In the present study, ZnO thin film is synthesized via sol-gel method by the use of spin coating technique and effects of stabilizers, as an important part of the sol, on structural, morphological and optoelectronic properties of the single and multi-layer ZnO thin film has been investigated.

2. DESCRIPTION OF THE OBJECTS AND INVESTIGATION METHODS

Zinc acetate dehydrate $(Zn_2(CH_3COO)_2.2H_2O\text{-}ZAD)$ as a precursor, triethylamine $(N(C_2H_5)_3\text{-eA})$ and triethanolamine $(N(C_2H_5O)_3\text{-TEA})$ as two main stabilizers and reactants and methanol $(CH_3OH\text{-MeOH})$, ethanol $(CH_3CH_2OH\text{-EtOH})$ and 1-propanol $(CH_3CH_2CH_2OH\text{-}nPrOH)$ as solvents have been purchased from Merck Chemical.

Sol-gel method was carried out for synthesis of ZnO thin film. For preparation of the first series of sols, ZAD dissolved in Mt and then TeA and TEA added to the solution in 0.25, 0.5, 1 and 2 molar ratios of stabilizer/Zn and let the sol stirred for 30 min in order to obtain a clear and transparent sol. In the second series of sols, the solvent consists of one volumetric ratio of Mt/Et or Mt/1P and TEA was added to the solution in TEA/Zn = 0.5 molar ratio.

Thin films were spin coated on glass slides substrates. The substrates cleaned and washed with detergent and deionized water and also acetone, in order to remove greasy substances. The sol dropped on a substrate rotated at 3000 rpm for 30 seconds and then films dried at 120 °C for 10 min. Finally, the films calcined at 500°C for 1 hr.

X-ray diffraction (XRD) measurements with scanning speed of 1.5°/min were performed on a Philips PW1730 X-ray diffractometer using Cu Kα radiation ($\lambda = 1.5405$ Å, 40kV, 30mA). The size and morphologies of the resultant nanocomposites were observed by Hitachi S4160 field emission scanning electron microscope (FESEM). UV-Vis spectroscopy was used to obtain optoelectronic properties of thin films.

3. RESULTS AND DISCUSSION

Fig. 1 shows FESEM images of single layer ZnO thin films with different molar ratios of stabilizer/Zn for TeA and TEA. In TeA specimens, increasing the content of stabilizer tends to the segregation of grains that is considerable in TeA 1 sample. This phenomenon is due to the increasing of the polycondensation reaction in sol and difficult situation for elimination of the

organic compounds. In contrast, thin films morphology is more compact and the grain sizes are smaller in TEA samples compare to the TeA ones. The interesting point about TEA series is that in TEA 0.5 sample, hole shaped structure form on the surface of the film just like porous ZnO thin films that used PEG [12]. Boiling point difference between methanol and TEA (about 100 °C) as well as aggregation of solvent in micro holes during the film deposition are the main reasons of the formation of the following structure.
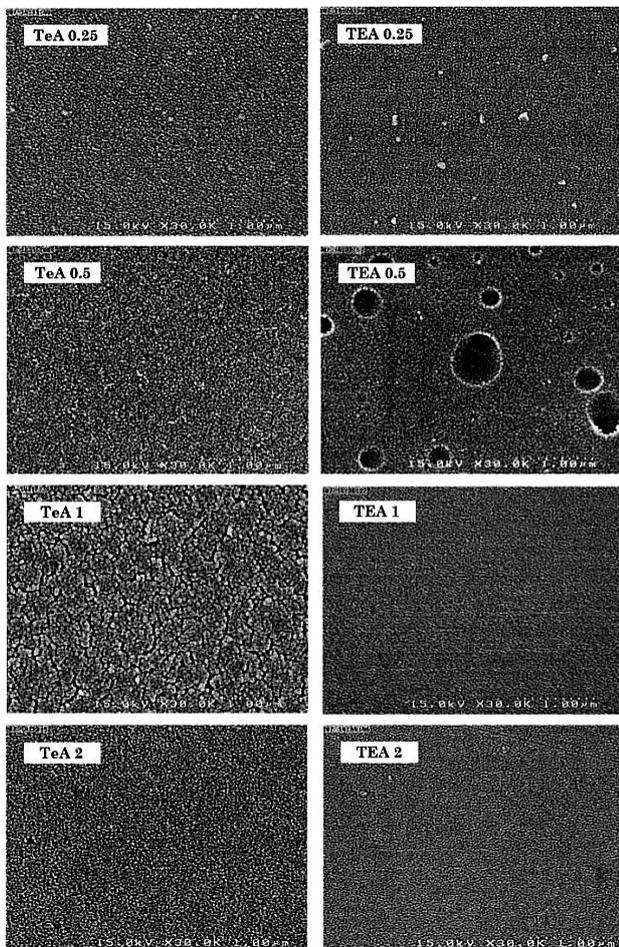

Fig. 1 – Single layer ZnO thin films with different molar ratios of TeA/Zn (TeA 0.25, 0.5, 1, 2) and TEA/Zn (TEA 0.25, 0.5, 1, 2)

Some methods has been implemented in order to prohibit the formation of the holes on TEA 0.5 sample (Fig. 2). At first, multilayer thin film of the TEA 0.5 sample was made. Homogeneous nucleation and growth is the most important phenomenon that encourages by making thicker film [13]. Increasing the thickness of the deposited film enhance the probability of homogeneous nucleation in various region of the film through thickness and surface. As a matter of fact, separation of stabilizer from media will be declined because the system becomes more homogeneous and there would not be any hole on the surface.

Second solution is changing the major factor of creating the mentioned hole. Increasing the boiling point of the solvent leads to the decreasing of boiling point difference between solvent and stabilizer. This results a homogeneous media without any separations such as holes

(Fig. 2). Substitution of half of methanol with ethanol and 1-propanol with boiling point of 78 and 98 ºC subsequently, results disappearing of the holes.
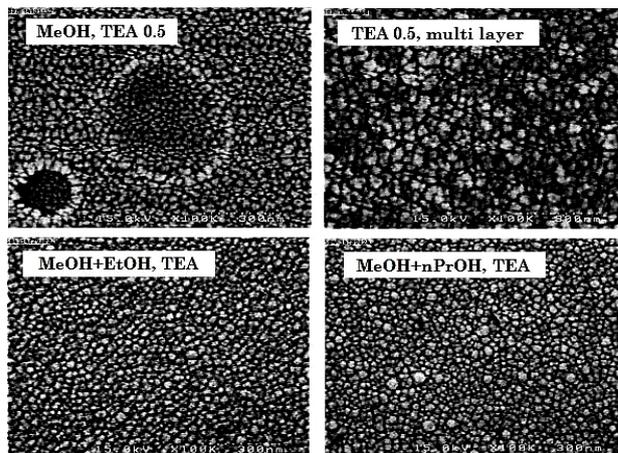

Fig. 2 – Elimination of the holes in TEA 0.5 sample with making multi-layer (TEA0.5, multilayer), and addition of ethanol and 1-propanol to the methanol in 1 volumetric ratio (MeOH+nPrOH, EtOH+nPrOH)

X-ray diffraction method performed to obtain structural properties of ZnO thin films. Fig. 3 demonstrate X-ray diffraction pattern of TeA 0.5 sample. The pattern confirms hexagonal wurtzite structure for ZnO and also shows preferred orientation structure through (002) direction (c-axis).
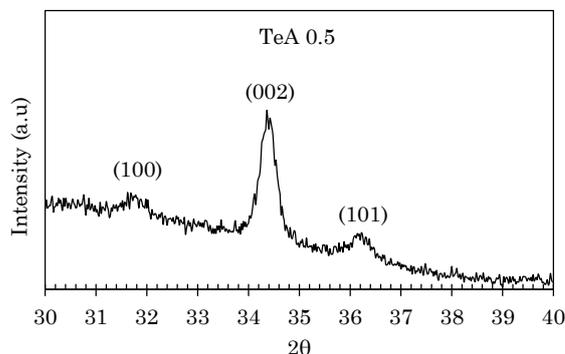

Fig. 3 – XRD pattern of TeA 0.5 sample calcined at 500 °C

In order to investigate structural parameters of ZnO precisely, XRD pattern of TeA 1 and TeA 2 nano powder samples was considered (Fig. 4). According to the crystallographic relationship for hexagonal structure, unit cell parameters such as a, c and c/a were calculated and shown in Table.1. The results confirm that increasing the content of TeA causes the increasing of all structural parameters. The main reason might be due to the remaining of the organic compounds such as stabilizers that distort crystal structure.

Table 1 – Structural parameters of TeA 1 and TeA 2 samples

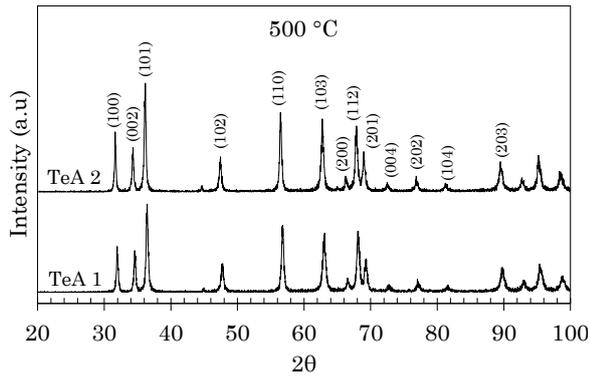| Sample	c (Å)	a (Å)	c/a	*I_R
TeA 1	3.2341	5.1741	1.5998	0.3539
TeA 2	3.2618	5.2749	1.6018	0.3542

* $I_{(101)}/(I_{(101)} + I_{(002)} + I_{(100)})$

Fig. 4 – XRD pattern of TeA 1 and TeA 2 powder samples calcined at 500 °C

Fig. 5 represents transmittance spectra of TeA and TEA samples. All samples are transparent in visible region ($T > 95\%$) and have shoulder in band gap wavelength.
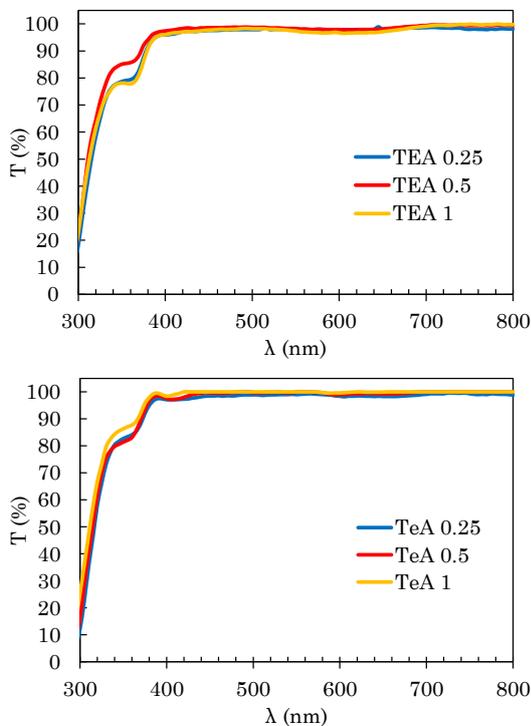

Fig. 5 – Transmittance spectra of TEA and TeA thin film series

The optical band gap of the semiconductors has been calculated by the following equation (Tauc) [15]:

$$\alpha h\nu = A(h\nu - E_g)^n \qquad (3.1)$$

where α is absorption coefficient, $h\nu$ is photon energy, E_g is optical band gap, and A is constant. Extrapolation of $(\alpha h\nu)^2$ vs. $h\nu$ for direct band gap and $(\alpha h\nu)^{0.5}$ vs. $h\nu$ for indirect band gap semiconductors to $\alpha = 0$, get the optical band gap (E_g).

According to the band gap values (Fig. 6), the optical band gap of TeA samples are higher than TEA ones. It is estimated that attaching of hydrogen and acetate
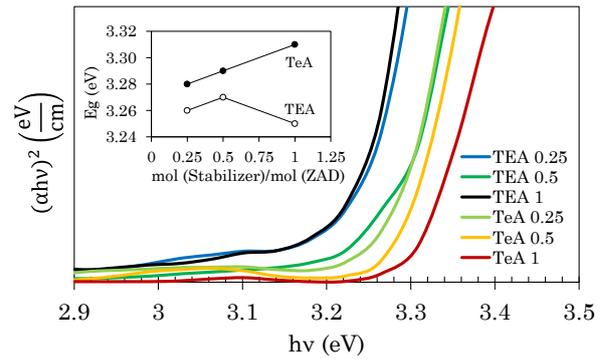

Fig. 6 – Tauc plot for calculation of optical band gap

to the TeA, produces TeA complexes [14] that gather together and make a milky sol and finally form a translucent gel. On the other hand in TEA sol, the reaction occurs by ligand exchange mechanism [16], and the complexes are not as sophisticated as TeA. Accordingly, elimination of TEA complexes might be easier than the TeA ones. So, the more complex remnant organic compound in TeA samples leads to increasing of optical band gap compare to the TEA samples.

Moreover, ascending trend of band gap values in TeA and TEA specimens by increasing the stabilizer's content reinforces the organic remnant hypothesis but, such trend breaks in TEA 0.5 to TEA 1 samples. It is speculated that in TEA 0.25 and TEA0.5 samples there are pure TEA and TEA complexes together simultaneously while in TEA1 there are only TEA complexes. As TEA has a great boiling point temperature, its elimination condition would be so hard and complete substitution of TEA complexes in TEA1 facilitate the organic compound elimination and drop the band gap value. Due to the low boiling temperature of TeA, remnant pure TeA does not have the same influence as TEA.

4. CONCLUSION

Increasing TeA content tends to the segregation of the grains that is considerable in TeA 1 sample with separated islands and similar situation arise in TeA 2 sample for individual grains. In TEA samples, an unusual behavior observed in TEA 0.5, microscopic holes, that is mainly due to the boiling point difference of TEA and methanol. Making multilayer and adding solvents with greater boiling point instead of methanol, leads to the disappearing of the holes. Furthermore, TEA samples have smaller grain size than TeA ones. XRD results confirm the formation of ZnO hexagonal wurtzite and also preferred orientation along c-axis for TeA 0.5. Increasing the quantity of TeA, results increasing of a, c, c/a as well as increasing the crystallinity of ZnO. UV-Vis spectroscopy confirms that ZnO thin film samples are transparent in visible region. Optical band gap shifted to higher energies by increasing the stabilizers content and TeA samples has greater optical band gap than TEA ones due to the remaining organic compounds and different nature of chemical complexes.

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