# INVESTIGATION of TERTIARY AMINES EFECTS ON STRUCTURAL, MORPHOLOGICAL AND OPTICAL PROPERTIES of NANOSTRUCTURED ZnO THIN FILM

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## ABSTRACT

Nanostructured ZnO thin film synthesized via sol-gel method. In this study, effects of stabilizer, as a vital part of sol with different molar ratios 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 500ºC. 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 change for different molar ratios of stabilizer to Zn. The images demonstrated 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 shown dependence of optical band gap to stabilizer's type and content.

**Key words:** ZnO thin film, sol-gel, stabilizer, nanostructure, optoelectronic properties

## 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. Oxygen vacancies as well as Zn interstitials make ZnO as an n-type semiconductor. Following properties caused ZnO widely used in various applications such as dye sensitized solar cells (DSSC) [1], light emitting diodes (LED) [2] and transparent conductive oxides (TCO) electrode [3].

Different methods are available for the synthesis of ZnO thin film such as sputtering [4], physical vapor deposition (PVD) [5], chemical vapor deposition

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(CVD) [6], and sol- gel method [7]. Sol-gel process is a liquid-based method that widely used to synthesis 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 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 investigated.

### *METHODS OF SAMPLE MANUFACTURING AND ANALYSIS*

Zinc acetate dehydrate ($Zn_2(CH_3COO)_2.2H_2O$) as a precursor, triethylamine ($N(C_2H_5)_3$) and triethanolamine ($N(C_2H_5O)_3$) as two main stabilizers and reactants and methanol ($CH_3OH$), ethanol ($CH_3CH_2OH$) and 1-propanol ($CH_3CH_2CH_2OH$) as solvents purchased from Merck Chemical.

Sol-gel method was carried out for synthesize of ZnO thin film. For the preparation of the first series sol, ZAD dissolved in methanol and then triethylamin (TeA) and triethanolamin (TEA) added to the solution in 0.25, 0.5, 1 and 2 molar ratio 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 consisted of 1 volumetric ratio of methanol-ethanol and methanol-1-propanol and triethanolamine in 0.5 molar ratio with Zn was added to the solution.

The thin films 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. To achieve thicker films, the spin coating process repeated for 6 times. 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 (λ=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.

### *RESULTS AND DISCUSSION*

*Fig.1* shows FESEM images of single layer ZnO thin films with different molar ratios of stabilizer/Zn for triethylamine and triethanolamine. In triethylamine specimens, increasing the content of stabilizer tends to the segregation of grains that is considerable in TeA 1 sample. The following phenomenon is due to the increasing of the polycondensation reaction in sol and severe situation for elimination of the organic compounds. In contrast with triethylamine samples, in triethanolamine specimens, thin films morphology is more compact and the grain sizes are smaller than triethylamin samples. The interesting point about

triethanolamine series is that in TEA 0.5 sample, hole shaped structures form on the surface of the film just like porous ZnO thin films that used PEG [9]. Boiling point difference between methanol and triethanolamine (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.

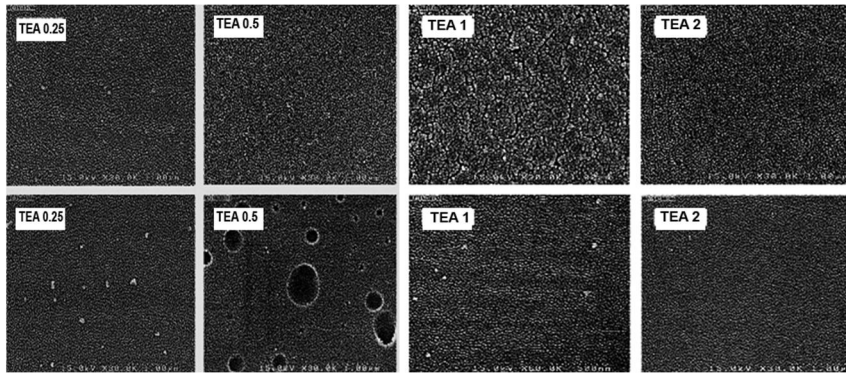


**Fig.1** – Sinle layer ZnO thin films with different molar ratios of triehylamine/Zn and triethanolamin/Zn

Making multilayer and increasing the boiling point of the solvent by addition of ethanol or 1-propanol, yield disappearing of the hole and formation of a uniform thin film (*Fig. 2*).

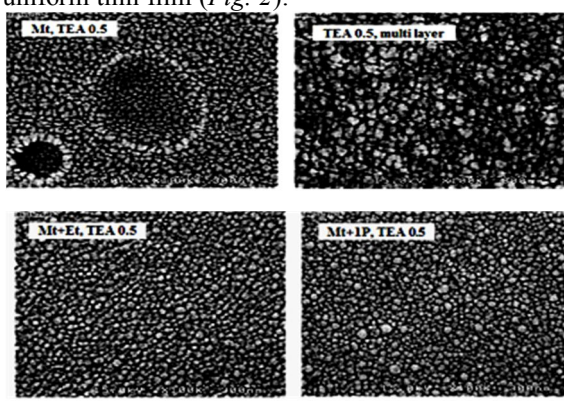


**Fig. 2** – Elimination of the holes in TEA 0.5 sample with making multi-layer and addition of ethanol and 1-propanol to the methanol in 1 volumetric ratio

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 in (002) direction (c-axis).

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 was calculated and has been brought in *Table.1*. The results confirm that increasing the content of triethylamine results the increasing of all structural parameters.

*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.

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

| Sample | c (Å) | a (Å) | c/a | I(101)/( I(101)+ I(002)+ I(100)) |
|---|---|---|---|---|
| TeA 1 | 3.2341 | 5.1741 | 1.5998 | 0.3539 |
| TeA 2 | 3.2618 | 5.2749 | 1.6018 | 0.3542 |

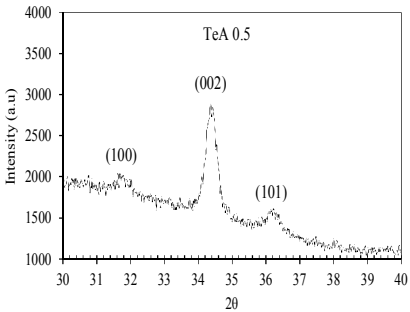


**Fig. 3** – XRD pattern of TeA 0.5 sample calcined at 500 °C

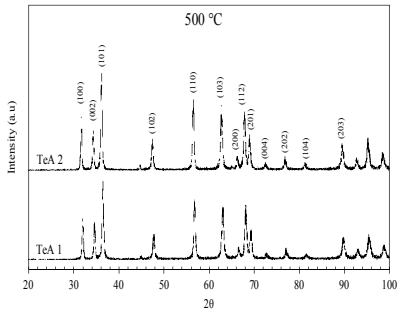


**Fig. 4** – XRD pattern of TeA 1 and TeA 2 powder samples calcined at 500 °C

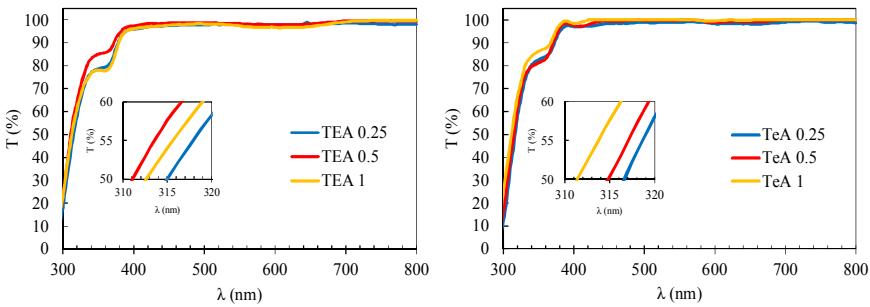


**Fig. 5** – XRD pattern of TeA 1 and TeA 2 powder samples calcined at 500 °C

The optical band gap of the semiconductors has been calculated by the following equation:

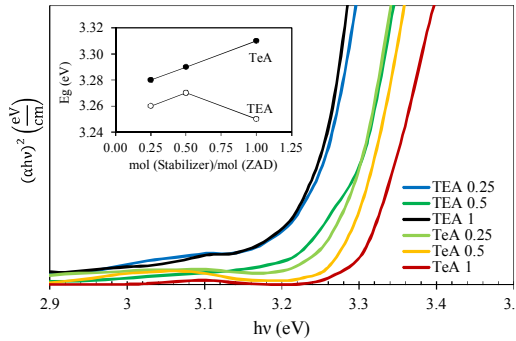


**Fig. 6** – Tauc plot for calculation of optical band gap

$$Ahv = A(hv - E_g)^n \quad (1)$$

where $\alpha$ is absorption coefficient, $hv$ is photon energy, $E_g$ is optical band gap, and $A$ is constant.

According to the band gap values (*Fig. 6*), the optical band gap of TeA samples are more than TEA ones that would be due to the remaining organic compound in TeA series. Moreover, ascending trend of band gap values in TeA specimens confirm this hypothesis.

## CONCLUSION

Increasing triethylamine 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 triethanolamine samples, an unusual behavior observed in TEA 0.5 with microscopic holes that is mainly due to the boiling point difference of TEA and methanol. 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 triethylamine results the increase in 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 grows by increasing stabilizers content and due to the remaining organic compounds in triethilamine samples, band gap values are more than triethanolamine specimens.

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