

Study of Concentration Effect on Synthesis ZnO Nanostructures

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Abstract: ZnO nanostructure with hexagonal structures were synthesized using spin coating and hydrothermal methods under variates concentration of seeding and grown solutions. Preferable structure of seeding layer have been choosing according to FESEM result with 0.6 Seeding sol gel concentration. Hexagonal structures of ZnO nanorods have recorded with 0.15g of zinc acetate dehydrate and hexamethylenetetramine. growth solution due to FESEM result. EDS data refer to high purity of synthesis materials which is supported by XRD result. In addition, crystal structure and orientation phase was investigated has agreement with EDS and FESEM results. Optical properties obtained by UV-VIS, to gain 3.72 eV band gap which is close to standard bulk ZnO. Concentration parameter has significant effect on synthesis of ZnO nanostructures

Keywords: ZnO , nanostructure, nanoparticle ,nanorods, spin coating, seeding layer

1. Introduction

Zinc Oxide is remarkable and attractive semiconductor due to optical and electrical properties. This unique properties represent in II-VI compound semiconductors, Direct band gap of 3.37 eV at room temperature and a large excitation binding energy (60 meV) made it candidate as a best semiconductor for fuel cell, optoelectronic and sensors application at room temperature[1]. ZnO with its fantastic physical and chemical properties, such as high chemical stability, high electrochemical coupling coefficient, broad range of radiation absorption and high photo stability, made it a multifunctional material [2].

A lot of structures of Zinc oxide have been successfully synthesis in different dimension such as one- (1D), two-(2D), and three-dimensional (3D) structures[3] in form of nanofiber, nanohelices nanorods, nanowires in term of (1D) form beside nanoplate, nanosheet nanopellets for (2D) form [4] , and for (3D) form example are flower, dandelion, snowflakes, coniferous urchin-like. Therefore, various physical and chemical techniques have been employed for synthesis ZnO nanostructures, such as spin coating b [5] , electrochemical , hydrothermal methods [6] chemical vapor deposition [7], sol-gel method [8], pulsed laser deposition [9] electrophoretic depositions , thermal decomposition [10], and combustion method [11] , gas expanding method [12], and vapor transportation method [13].

This work, include two synthesis method, firstly sol-gel spin coating method for seeding layer and secondly hydrothermal growth method for nanorods grow, was utilized to synthesis the ZnO nanostructure, crystal structure and emission characteristics of ZnO nanostructures.

2. Experimental Part

Zinc Oxide thin film seeding layer has been deposited on FTO glass substrate using spin coating method as a seeding layer to form ZnO nanoparticles. FTO glass coated substrate with 2*1*0.2mm dimensions was cleaned ultrasonically by distillate water, methanol, and acetone for 15min for each. In the mean time, four different concentration of sol-gel has prepared (0.6g, 0.8g, 1g, 1.2g) of zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O) was dissolved in 10ml of absolute ethanol with 2000rpm stirring and 60 oC temperature for all concentrations , meanwhile 0.3 ml Diethanolamine was added to solution slowly as a stabilizer .

Afterward, the resultant sol gel have been stirred for hour to yield a homogeneous clear transparent solution with constant temperature of 60oC. The prepared solution was stored to aging for 24 h, and then filtered to be subjected to spin coating on the FTO glass coated substrates. The aged solution was composited by VTC-200 vacuum spin coater on FTO glass substrate. Spin coating with 1000rpm for 30 sec at room temperature, for each concentration spritely. Subsequently, the coated samples ware dried at room temperature to anneal it later at 300 oC for 90 min to obtain ZnO nanoparticles as a seeding layer for each different concentrations . All seeded specimen has been investigated the surface topography by field emission scanning electron microscopy (FESEM) to exam the optimum ZnO nanoparticles seeding layer, for grow ZnO nanorods on only one of this specimen later. After choosing the optimum specimen according to FESEM result, hydrothermal technique was used to grow ZnO nanorods. The chosen specimen was immersed in four different concentrations of zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O) (1.5g, 2g, 2.5g, 3g) and same amount of hexamethylenetetramine((CH₂)₆N₄) were dissolved in 20ml distillate water at 95C temperature in the furnace for 3 hours. Thereafter, the specimens were rinsed thoroughly with

DI water to remove any residual reactants and then dried at room temperature. The resultant specimen were examined FESEM, energy-dispersive X-ray spectroscopy (EDS) which is attached to the FESEM, furthermore X-ray diffractometer (XRD) to identify the crystal structure and orientation of materials, and UV-VIS to investigate the absorption and band gap of ZnO nanostructure semiconductor.

3. Results and Discussion

FESEM micrographs result demonstrate a smooth homogenous surface of FTO coated glass substrate as a top view image (fig.1). The FESEM result of specimen (1,2,3,4) exhibited for seeding layer films in fig.2, it can be notes there are significant effect of concentration in shape, homogeneity and distribution of ZnO nanoparticle thin film on substrate surface. The increasing of concentration have been led to increase the defect on the surface films. Fig.1.a shows specimen 1, smooth homogenous distribution of ZnO nanostructure for all sides of specimen beside to absent defects have been recorded, as a result of suitable coated sol gel to employ it as a seeding layer. The specimen 2 exhibit a few defected such as small cracks cane recorded s result to increase the density of sol gel and less homogeneity of distribution of ZnO nanoparticles on the specimen surface. In addition, can easy observe the particle size become larger then before as a clue to lack of arengment of ZnO particles. Fig.2.c, demonstrate, surface morphorgy of specimen 3. High number of defect can be recorded easily, such as cracks, small aggregations, and unhomogeneity, as consequence of increasing the concentration of seeding sol gel due to in dissolve or may to evolute this aggregations during preparing seeding sol gel. This defects become greater and clearer in specimen 4(fig.2.d), because of rising of concentration and the ZnO got crowded to gain place on specimen, in addition white mass can be seen on the surface may be a residual reactants as result of increasing the coarseness of surface and could not remove it by rinsed in distillate water. According to surface invstigation above metions, specimen 1 with seeding sol gel concentration 0.6 g consider as a best or optimum specimen for grow ZnO nanorods because of growing nano rods need to smooth homogenous and stable distribution surface, which is really available in specimen 1.

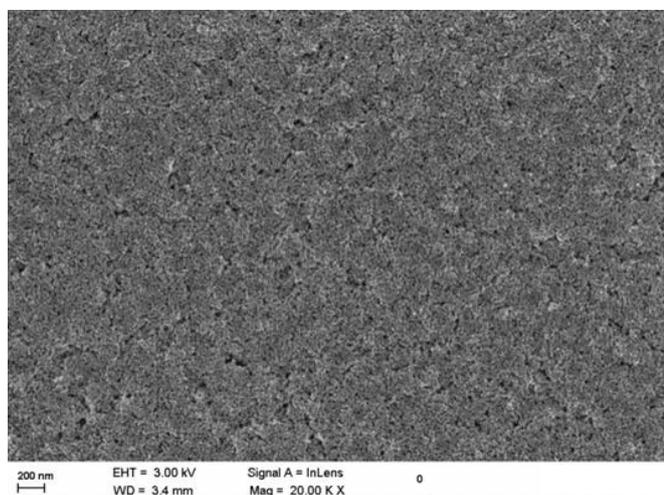


Figure 1: FESEM image of FTO glass coated substrate

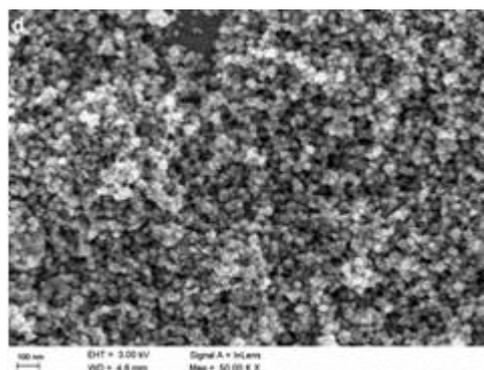
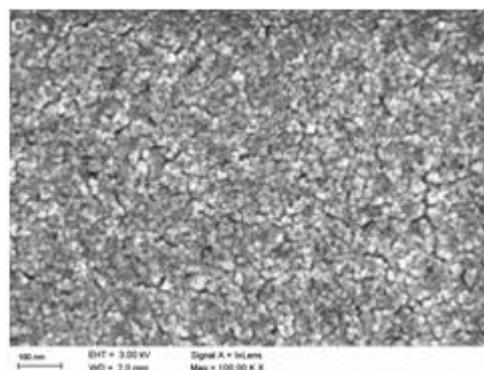
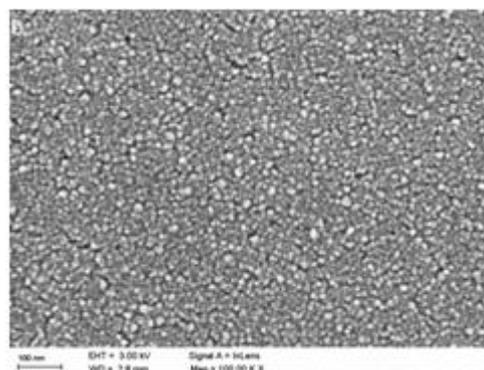
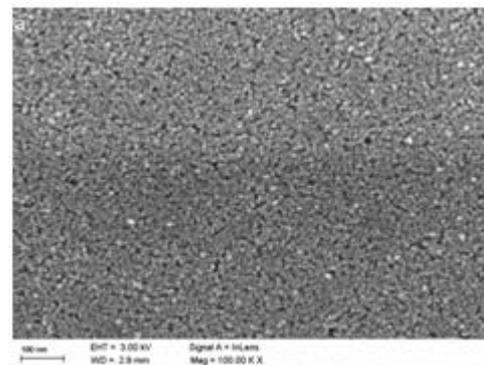


Figure 2: FESEM top view of ZnO seeding layer (a) Specimen 1, (b) Specimen 2, (c) Specimen 3 and (d) Specimen4

In like manner, whole ZnO nanorods samples have been examined by FESEM for top view and cross section. Figure 3.a exhibit top view of sharp hexagonal ZnO nanorods with suitable distribution of the nanorods which refer to stable growth occurred and the ZnO diameter was around 90-120 nm. Cross section of same specimen shown in fig.3.b, indicate to mostly vertical growth with approximate length

250nm. Significant change can be noticed in specimen 2 and specimen 3 as shown in fig 3 c,e. The nanorods can be clearly observed, but the sharpness of hexagonality of nanorods is absent. Besides the cross section demonstrates the nanorods have been grown but very compacted and crowded as a result of increasing concentrations of growth solution. Furthermore, aggregation on the nanorods looks like particles sticking to the rod, and can be noticed that it increases with increasing the concentration of the growth solution i.e., specimen 3 more than specimen 2 for the above-mentioned notice. Further little increasing the ZnO nanorods diameter to 140nm for specimen 2 and a little more for specimen 3. In the same manner for specimen 4, the nanorods length decreases and compacted with increasing the concentration of growth solution as shown in fig.3 g,h. In the meantime, the length of nanorods goes to decrease due to increasing the nanorods diameters and crowded which affects directly on growing the nanorods in vertical way.

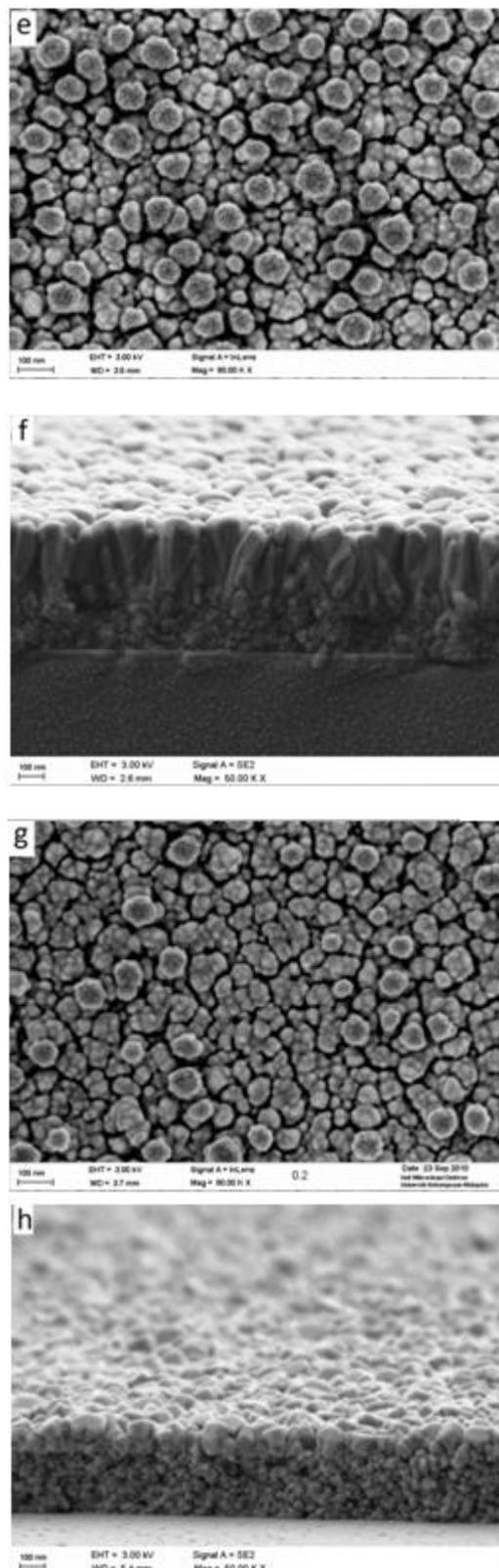
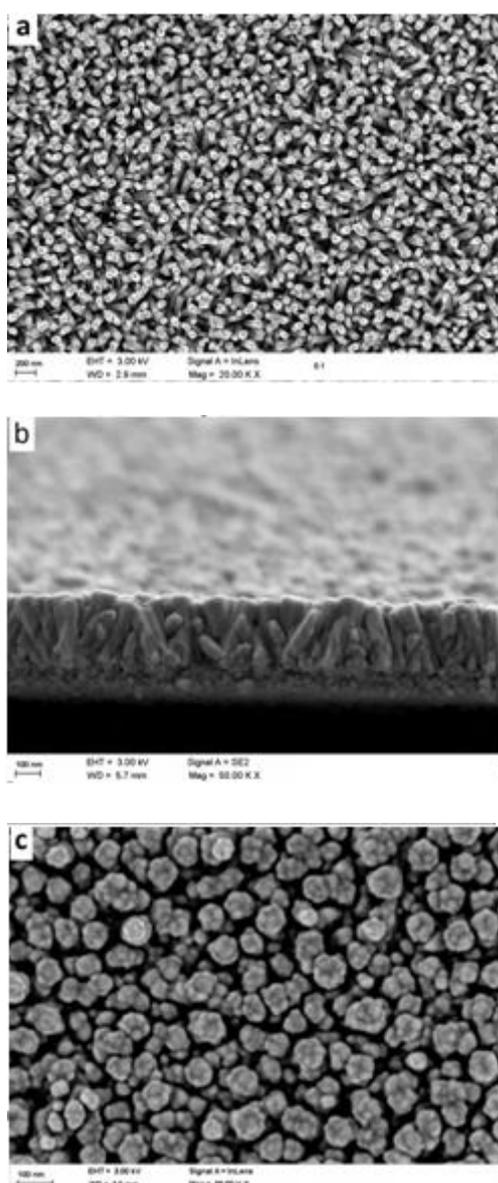


Figure 3: FESEM image of ZnO Nanorods: (a) top view of specimen 1, (b) cross section of specimen 1, (c) top view of specimen 2, (d) cross section of specimen 2, (e) top view of specimen 3, (f) cross section of specimen 3, (g) top view of specimen 4, and (h) cross section of specimen 4.

According to FESEM above information, can observe increasing the concentration of growth solution the diameter of nano rods is increasing, the length of nanorods is decreasing,

the distribution of nanorods going to get compact and more crowded and the crystallite due to shape of the nanorods.

Energy dispersive X-ray spectrometry (EDS) have been used to investigate the chemical materials composite for both chosen seeding layer specimen (fig.4.a) and best ZnO nanorods obtained (fig.4.b). There are three main peaks have been detected refer to zinc with dominate ratio, beside one peak of oxygen, and there are two peaks refer to silicon beside to smaller ratio of fluorine due to not covered edge of FTO glass substrate. On the other hand, the EDS result of ZnO nanorods indicate to high purity of materials have used. Likewise, three main peaks of zinc beside one peaks of oxygen. It can be notice that, absent peaks of silicon and fluorine as a evidence of whole coating of substrate by ZnO.

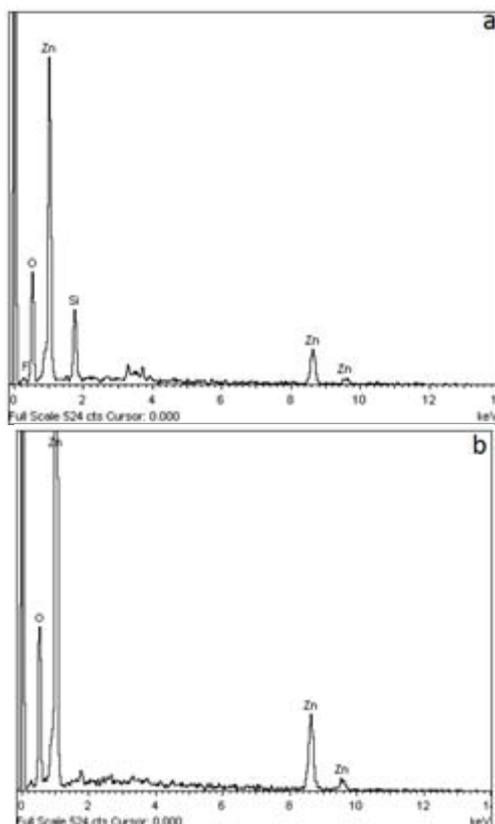


Figure 4: EDS spectrum of the (a) ZnO seeding layer and (b) ZnO nanorods

X-ray diffraction exam of ZnO nanostructure seeding layer composite on FTO glass coated substrate in (fig.5.a), have been carried out by (Bruker diffraction) X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406$ nm) (applied voltage 45 kV, current 40 mA) at a scanning rate of 0.025s⁻¹ in the 2 θ range from 2 θ to 60 θ . It shows a sharp diffraction peaks which correspond to the hexagonal wurtzite of ZnO, according to the standard spectrum of ZnO bulk crystal correlated with FESEM results as a clue of high crystallite structured where is clear with nanorods when formed in hexagonal shape. The average crystal size of ZnO nanostructure seeding layer 22.74 and 17.59nm for ZnO nanorods, which is obtained using Debye-Scherrer formula $D = K\lambda / (\beta \cos\theta)$ where K is the Scherrer constant, 0.89, λ is the X ray wavelength, 1.542 \AA , β is the peak width of halfmaximum, and θ is the Bragg diffraction angle. Since the width at half maximum (FWHM)

of the (002) diffraction peak are 34.471 $^\circ$ and 34.082. In compare with X-ray diffraction of seeding layer nanoparticles and nanorods can notice the crystal size of nano rods smaller then the crystal size of seeding layer, the reason perhaps becous of growth invrment of ech type of strycture, since the seeding layer formed under high temperature in time the nanorods formed in low temperature wich is agree with growth nanostructure mechanism

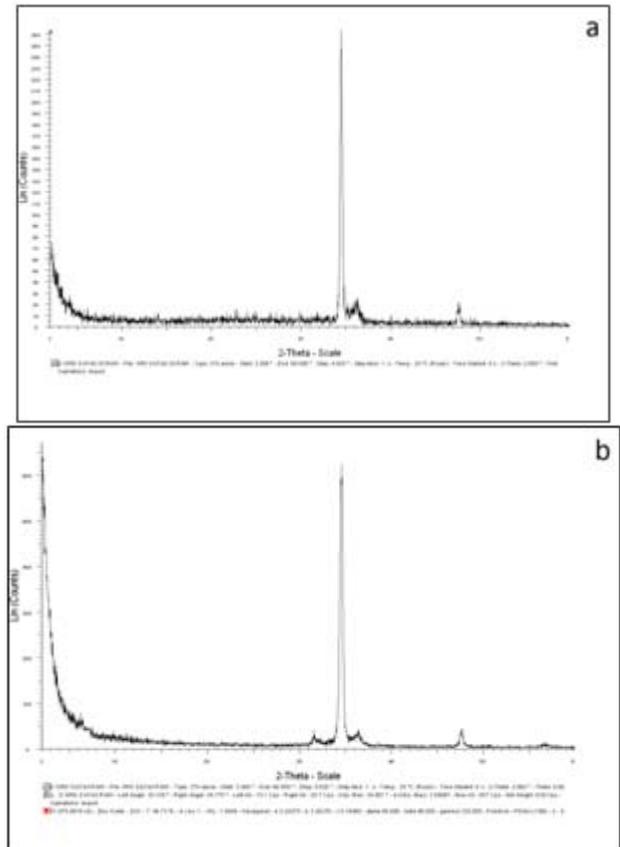


Figure 5: X-ray diffraction patterns of (a) ZnO seeding layer, and (b) ZnO nanorods

Band gap of ZnO nanostructure material has been investigated by UV-visible absorption spectra (shows in fig.6). Whole absorption spectra peaks exhibited in typical absorption peaks. Significant absorption at range 360–382 nm, due to a characteristic/standard peak of wurtzite hexagonal phase ZnO, which is refer to the synthesized products are pure ZnO. The obtained band gap is 3.72 eV wich is approximtly agrr with standard bulk ZnO (3.37 eV) via extrapolating the linear portion of the curve reveal that the absorption band of ZnO nanostructured is relative to the intrinsic transition between the valence band (VB) and the conduction band (CB)[14]. According to presence of a broad peak in the obtained UV-vis spectra, demonstrate a satisfied optical properties and containing wurtzite hexagonal phase.

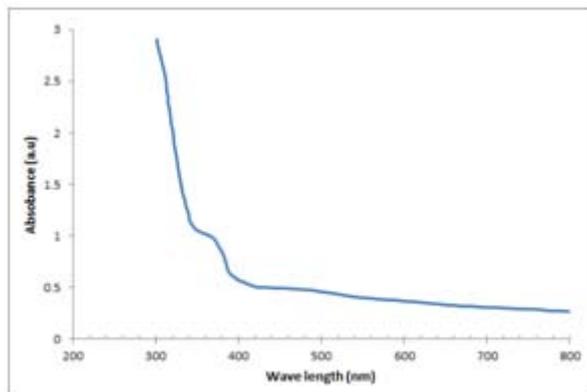


Figure 6: UV-Vis spectrum of ZnO

4. Conclusion

A systematic study of concentration variation using zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), Diethanolamine and hexamethylenetetramine ($(CH_2)_6N_4$) was successfully synthesized using spin coating technique and hydrothermal method. Best seeding layer have been selected according to FESEM result, to grow ZnO nanorods with different concentration of growth solutions later. Besides a sharp hexagonal ZnO nanorods at (0.1g) concentration which be examined later by X-ray diffraction to obtain hexagonal wurtzite phase for both, seeding nanoparticles and nanorods with high purity which is agreed with obtained EDS result. Moreover, good optical properties obtained by UV-VIS of ZnO nanostructure compeering with standard bulk ZnO. On the other hand, the core of study demonstrate a significant effect of concentrations on the ZnO nano structure growth.

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