Synthesis and temperature Effect of ZnO nanoparticle seeding layer and nanorods

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Abstract:
Zinc oxide nanostructured with different seeding layer annealing temperature have been synthesized by drop casting technique on FTO coated glass substrate. The optimized seeding layer have employed to synthesis ZnO nanorods were growth aqueous solutions method of zinc nitrate and HML as precursors with different growth temperatures.

FESEM supported by EDS results showed significant information of ZnO topographic surface. X-Ray diffraction scan demonstrate a hexagonal wurtzite structure with c-axis orientation of the ZnO nanorods. Strong ultraviolet (UV) emission of ZnO nanorods has detected by UV visible measurement. The obtained results have analyzed optimize annealing temperature of ZnO seeding layer and suitable growth temperature of ZnO nanorods, with crystal hexagonal ZnO nanorods and homogenous distribution with 95°C growth temperature.

Key words: ZnO, nanostructure, nanorods, seeding, sol-gel

Introduction:

One of excellent electronic, optical and photocatalytic materials properties is (ZnO) Zinc oxide [1]. It is unique and fascinating properties of II-VI compound semiconductors have triggered tremendous motivation among the scientists to explore the possibilities of using them in industrial applications. ZnO with its unique physical and chemical properties, such as high chemical stability, high electrochemical coupling coefficient, broad range of radiation absorption and high photo stability, is a multifunctional material [2]. 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 optoelectronic and sensor application at room temperature [3].

A variety structure of Zinc oxide have been successfully synthesis in different dimension such as one- (1D), two- (2D), and three-dimensional (3D) structures[6.
zinc] in form of nanohelixes nanorods, nanowires in term of (1D) form beside nanoplate, nanosheet nanopellets for (2D) form , 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, for instance {pulsed laser deposition [4], electrochemical deposition hydrothermal methods [5] chemical vapor deposition [6], sol-gel method [7], electrochemical depositions [8], thermal decomposition [9], and combustion method [10] , gas expanding method [11], and vapor transportation method [12].

In this work, drop casting method and aqueous solutions growth method have been employed investigate the morphology, crystal structure and emission characteristics of ZnO nanostructures.

**Experimental Part:**

Zinc Oxide seeding nanoparticles were synthesis using drop method as a seeding layer as a thin film to form Zinc oxide nanorods later. Firstly, 1 g Zinc nitrate was dissolved in 20ml of absolute ethanol with stirring at 70 °C, 3 drops of Diethanolamine was added to solution slowly.

The resultant solution was stirred for one hour to yield a homogeneous clear transparent solution. Then, the prepared solution was stored to aging for 24 h, and then filtered to be subjected to drop casting the FTO glass substrates. The aged solution was on FTO coated glass substrate which is cleaned before, by distillate water, methanol, and acetone ultrasonically for 15 min each. Room temperature drop casting to obtain homogenies distribution of solution. Then, the samples ware dried at 80C temperature to followed annealing at three different temperature (250,350,450) °C for 120 min to obtain ZnO nanoparticles as a seeding layer for each. Afterword the obtained samples chantries using field emission scanning electron microscopy (FESEM) to investigate the optimum seeding layer to utilize later to growth nanorods.
The optimum sample have used to grow ZnO nanorods using aqueous method. The ZnO seeded sample was immersed vertically in growth solution contain of 0.2gm zinc nitrate and same amount of hexamethylenetetramine with 20 ml distillate water at various growth temperatures (50,70,90)°C in oven for 4 hours. Finally, the substrates were rinsed thoroughly with DI water to remove any residual reactants and dried in room temperature.

The surface morphology and structured of coated glass ZnO nanorods substrates were examined using field emission scanning electron microscopy FESEM with energy-dispersive X-ray spectroscopy (EDS) which is attached to the FESEM, besides X-ray diffractometer (XRD) was used for phase identifications (Bruker diffraction).

**Results and Discussion:**

Top view of FTO coated glass substrate by FE-SEM micrographs shows (Fig.1) a homogenous smooth surface which is suitable for ZnO nanoparticles deposition. Fig.2 demonstrate seeding layers of ZnO nanoparticles were investigated by FESEM as before sample. The top view of three samples with three different annealing temperature indicate to 250C (Fig.2a), 350C (Fig.2b), and 450C(Fig.2c). The 250C annealing temperature sample shows humongous distribution of ZnO nanoparticles but there is small holes have been recorded ma due to low annealing temperature which resulted reducing in crystallite of the ZnO nanostructure. The recorded defect in sample have disappear in sample 2 according increase annealing temperature to 350C, which demonstrate homogenous distribution of nanoparticles with flat surface. The increasing the annealing temperature have resulted a cracks and unhomogeny on the surface of ZnO nanostructure due to broking the bond of ZnO molecular to obtain the appeared cracks in figure 2c. According to above mentioned result, the ZnO nanostructured annealed at 350C temperature is a most suitable seeding layer for growth ZnO nanorods. Furthermore, previous studies [14], the introduction of a well-oriented ZnO seeding layer on the substrate is one of the effective factor in controlling the alignment of ZnO nanorods.[15,16]
Figure (1): FESEM top-view topography of FTO coated glass substrate.
Figure (2): FESEM topography result of ZnO seeding layer (a) annealed at 250°C, (b) annealed at 350°C, and (c) annealed at 450°C.

Aqueous method of ZnO nanorods samples investigated also using FESEM. All ZnO nanorods samples have been grown on samples that annealed at 350°C due to above evidences by FESEM, which made it as a preferable sample. Fig. 3a, demonstrate a top view of ZnO nanorods growth at 50°C, small nanorods have been noticed with high density and closed backing due to low rate of growth at 50°C. The increasing annealing temperature led to decreasing of density of nanorods and the nanorods could be noted clearly with approximate diameter 75 nm. Figure 3c, illustrate high very clear ZnO nanorods with acceptable distribution and the diameter around 85 nm. The third sample result refer to the growth of the ZnO nanorods have successfully achieved with nano diameter beside to prove the effect of temperature on the path of nanod growing. As result of decrease the temperature of solution cause a low number of nuclei have enough energy to adhesive and build a homogenous nanorods, beside that anisotropic building may be occur according to the decreasing of growth temperature which is led to directly influence on slow down the growth speed along of crystallization.
Figure (3): FESEM topography of ZnO nanorods result at (a) 50°C growth temperature, (b) 70°C growth temperature, (c) 90°C growth temperature.
ZnO nano particles as a seeding layer and ZnO nano rods were examined by energy dispersive X-ray (EDX) spectrometry to check the chemical composite. Three main peaks of zinc with oxygen peak could observe as result of pure chemical materials composite. Silicon and Indium have been detected as a clue of non covered edge of FTO coated glass substrate as shows in Fig.4a. EDX spectrometer result of ZnO nanorods (Fig.4b) refer to also three clear zinc peaks and one peak of oxygen with absent of silicon and Fluoride peaks which indicate to covering of whole substrate sample. Accordingly, ZnO nanorods deposited on ITO glass substrate is strongly provided with high degree of purity.

Figure (4): energy dispersive X-ray (EDX) spectrometry of (a)ZnO seeding layer, (b)ZnO nanorods.
Typical XRD pattern of ZnO nanostructure of seeding layer on FTO coated glass substrate beside ZnO nanorods (Fig.5 a, b) exhibit 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 evident of high crystallite structured. Full width at half maximum (FWHM) of the (002) diffraction peak are 34.593° and 34.089°, for ZnO single seeding layer and for ZnO nanorods sample respectively. Debye-Sherrer formula $D=K\lambda/(\beta\cos\theta)$ used to obtain crystal size, where $K$ is the Sherrer constant, 0.89; $\lambda$ is the X-ray wavelength, 1.54 Å; $\beta$ is the peak width of halfmaximum; $\theta$ is the Bragg diffraction angle. Resulted average value of crystal size is 27.97 nm for ZnO seeding layer and 19.21 for ZnO nanorods. The difference of grain size of seeding layer and nanorods consequence of temperature condition of growing which is lead to increasing the building unit (grain size). This increasing due to the change of growth rate between the different crystallographic planes of seeding layer nanoparticles and nanorods which as agree with previous study [17]. There is no characteristic diffraction peaks from other phases or impurities were detected which implies that pure ZnO was formed which is correlated with the EDX result. Higher intensity pecks have recorded with ZnO nanorods sample in compare with as a result of increasing the thickens of coated sample.

Fig.5b demonstrate the XRD patterns of the ZnO nanorods grown on the ZnO films of seeding layer is compared with that of the underlying ZnO seed layer in Fig.5a. Higher intensity peaks have recorded with UV-visible absorption spectra of ZnO nanostructure demonstrated in Fig.6. All the absorption spectra shows a typical absorption peak. Significant absorption at the band edge confirms the preparation on ZnO nanorodhs have a crystalline nature.
Figure (5): XRD pattern of (a)ZnO seeding layer, (b)ZnO nanorods.

The sharp shape of the UV edge and the strong absorption in the UV region at 380 nm wavelength with band gap of 3.38 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).
Figure (6): UV-visible absorption spectra of ZnO nanostructure.

ZnO nanoparticles (r) radius have been determined via the absorption onset of the UV spectra by use the following expression [18]:

\[ E^* = E_g^{bulk} + \frac{\hbar^2}{2e^2} \left( \frac{1}{m_e m_0} + \frac{1}{m_h m_0} \right) \]

where \( E^* \) is the real band gap of ZnO nanoparticles, \( E_g \) is the bulk band gap (eV), \( h \) represent the reduced Planck constant; \( m_0 \) is the electron rest mass (\( m_e = 0.26 \), \( m_h = 0.59 \)). \( m_e, m_h \) are the effective mass of the ZnO semiconductor band electron and the valence band hole. Combining above equation with the real band gap of ZnO nanoparticles determined from Fig.5, the crystalline size of nano-sized ZnO synthesized by a direct precipitation method could be worked out to be the smallest. These results have good agreement with those determined from the XRD data. [19]

**Conclusion:**

ZnO nanorods have been successfully synthesized using drop casting technique and queues method, with different annealing temperature and different growth temperature. The seeded layer in annealed sample at 350C is the preferred sample for previous reason. Furthermore the optimum growth temperature was 95C gained with sharp diameter of ZnO nanorods as showed with FESEM result. High purity ZnO...
nanostructured was recorded with EDX measurement, which is agreed strongly with X-Ray diffraction result, were demonstrate hexagonal wurtzite structure. Significant agreement between above result has noted. Optical properties were detected by UV visible test which referred to strong absorption at UV region at 380nm wavelength with band gap of 3.38ev.

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