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A Correlation between Optical and Structural Property of ZnO Nanocrystalline Films

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Abstract

ZnO thin film has been deposited using Sol-Gel technique. It is one of the most attractive methods to grow nanoparticles, because it is relatively easy to carry out and is less expensive method, as all the precursors are easily available. It also allows the production of a large quantity of material together which is highly pure in nature and homogeneous on the molecular level. With the increasing of dipping cycles, better crystallinity of the sample has been grown. In this method we have observed some interesting optical properties of nanocrystalline ZnO thin films, which will be discussed in due course. The wurtzite ZnO has been confirmed by X-ray diffraction (XRD) spectra and average distribution of the particle sizes varies from 17 nm to 35, confirmed by XRD and atomic force microscopy (AFM) analyses. The values of band gap have been determined by UV-VIS and photoluminescence spectra.

Key Words: *ZnO, Nanoparticles, Structural property, Optical property*

1. Introduction

The development of nanoscale materials with physical or chemical properties that are modified or enhanced relative to their bulk counterparts continues to offer enormous possibilities for novel applications in research, technology, and industry. However, several properties of nanomaterials justify particular cause for concern as to their biological interactions and human health impacts. Individual studies have shown that nanomaterials may be transported within organisms and into cells and exert toxic effects through unconventional mechanisms (Nel et al., 2006). Zinc Oxide is an important low-cost II-VI semiconductor material, which is being used considerably for its catalytic, electrical, optoelectronic and photo-electrochemical properties. Consequently, designing ZnO with novel morphology, well-defined anisotropy and preferred orientation is of significant importance for basic fundamental research as well as for various fields of industrial applications (Hara et al., 2000, Ginley et al., 2000, Mitra et al., 2001). It has been observed that optical properties of various typical morphologies show a morphology-dependent features induced by the crystal quality due to morphology variations. Such an abundant morphology world of ZnO provides better understanding of crystal nucleation and growth mechanism from various aspects and would provide possible candidates for nanodevice construction (Wang et al., 2004, Mandal et al., 2009). There is a substantial variation of optical band gap for nanocrystalline ZnO films with the particle size.

2. Objectives of the Study

A detailed knowledge of optical properties of ZnO film near the band edge is very important from the application point of view. The variability in the reported values of the band gap in the films can be rationalized on the basis of the existence of growth stresses and thermal expansion mismatch stresses. The band-gap values show size dependency, i.e. with the variation in particle size the band-gap value undergoes a variation. So, that we can easily tune the band- gap of the material and use it for various device applications.

3. Experimental

Zinc Acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) and 2-Propanol were taken as starting to coat ZnO thin films on glass substrates by sol-gel method. Initially 0.85mole/liter zinc acetate was dissolved into 2-propanol taken in a beaker. Since, zinc acetate has low solubility in 2-propanol, so diethanolamine (DEA) was added to obtain a transparent solution and to keep the solution stable for dip-coating. The amount of amine added was equimolar to that of metal cation. A second stabilizer can be added to the solution prepared with equimolar DEA for further stability. Of the second stabilizers examined, water was the best. Although lactic acid is effective against precipitation and gelation, it rendered the films opaque. Diethanolamine reduced the wettability of the solution on the substrate used. The solution prepared by adding equimolar DEA and double molar water was used as the dip solution. The pH of the solution was kept about 7.0. Then the solution was stirred in a constant temperature bath using a magnetic stirrer at a temperature 65^{o}C for 1 hour. During stirring 2-propanol was added drop by drop to the solution as and when required to maintain the definite proportion of all the components. Then the solution was aged for about half an hour so that the solution temperature came down to the room temperature also any unreacted component that might be left behind, was precipitated. After that the clear solution from the upper part of the beaker was taken in a separate beaker. This solution was used as the dipping solution. An ultrasonically cleaned glass substrate was dipped vertically into the solution and withdrawn at a uniform speed to coat the solution on the substrates. The coated substrate was dried at room temperature for 10 min and heated at 150^{o}C for 10 min in open atmosphere. This process was repeated for 5, 10 or 15 times for getting a thin film of different thickness. The microstructure and morphology of ZnO films were characterized by X-ray diffractometer (Philips X-Pert MRD) using CuKα radiation of wavelength 1.5418 Å at grazing incidence mode and Atomic Force microscopy (Nanoscope-IV) in tapping mode. Optical transmittance spectra were recorded by Perkin-Elmer Lamda 45 spectrophotometer in the wave length range of 300nm-1100 nm.

4. Results and Discussions

Figure 1. XRD pattern of ZnO films grown by varying dipping cycles

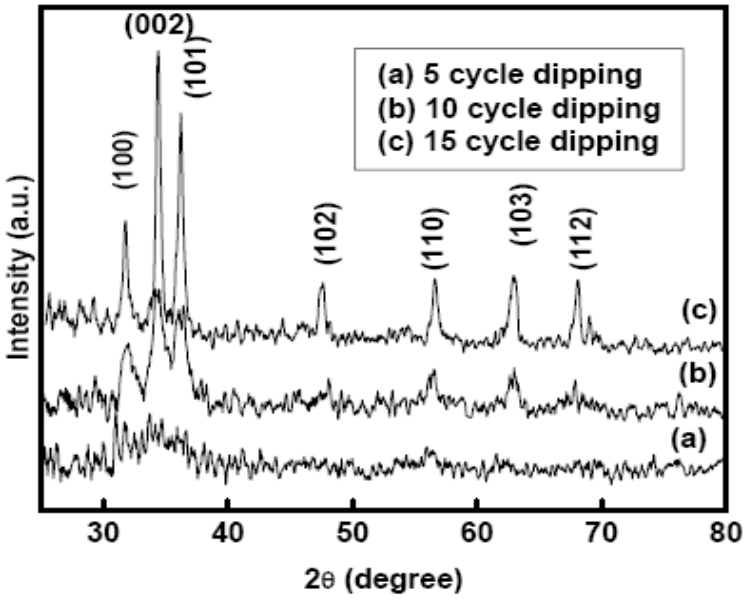


Figure 1 shows the XRD pattern of different films varying by dipping cycles from 5, 10 and 15. From the XRD pattern it is observed that initially (100), (002) and (101) peaks with nearly same intensity are predominant for the film deposited with 5 dipping cycles. It shows that the thin film is homogeneously grown in all peaks, and no preferential growth is observed. But, with increasing dipping cycle as the film thickness is increased, it is observed that the crystal growth along (100) plane falls to a certain extent, but the growth rate along (002) plane falls too drastically. Thereafter it continues to increase with the increase in dipping cycle for both the planes with the relative intensity of (101) plane being the strongest. Among all planes that are found to crystallize in ZnO thin films as function of various parameters , the most preferred is the (002) plane because of its most dense atomic packing and minimum surface energy. The degree of orientation normally follows the sequence (002)> (101)> (100). But in the present case the thin film was deposited on a glass substrate. It is non-crystalline in nature and hence possesses no long–range order. The inhomogeneity on the substrate surface might have acted as a deterrent to the preferred orientation of (002) plane of ZnO thin film (Christensen et al., 1990, Mandal et al., 2009). The films are mainly polycrystalline and exhibit (002), (100) and (101) peaks. The mean crystallite size can be determined from the integral width B according to Scherer's formula

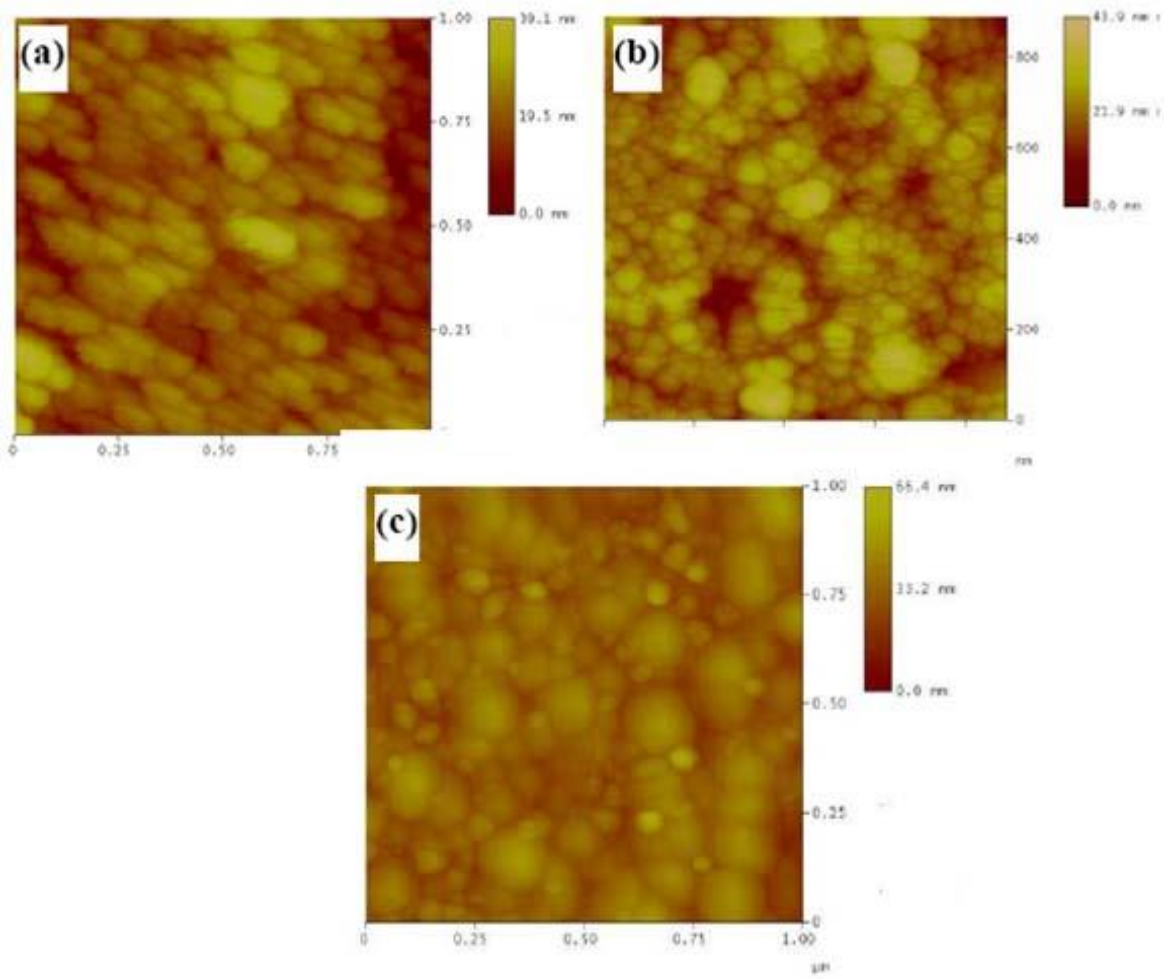
$$t = \frac{0.89\lambda}{B\cos\theta_B}$$

Where λ=0.15406 nm, wavelength of the CuK_α radiation, θ_B is the Bragg angle of diffraction with wavelength λ. It is observed that with the increase in dipping cycles, crystallite increases .So, we can conclude that at higher dipping cycles smaller particles cluster together to make larger particles resulting in the increase in crystallinity of the sample. The distribution of cluster size is depicted in Figure 2. It is also confirmed from the results obtained from AFM analysis. From the AFM analysis it was observed that the average surface roughness of the films gradually goes down as the dipping cycle is increased and average diameter of the particles also corroborates with the results, which is found from the XRD analysis. The details are given in the following table.

Table 1. Average roughness, diameter and crystallite size estimated from the XRD pattern and AFM analyses.

No. of Dipping Cycles	Average Roughness (nm)	Average Particle Diameter (nm) From AFM Analysis	Average Crystallite Size (nm) From XRD Analysis
5	6.3	17	-
10	5.5	24	27
15	5.1	40	41

Figure 2. Surface morphology of the ZnO thin films



The optical transmittance spectra of different ZnO thin films deposited on glass substrate with (a) 5 dipping cycles, (b) 10 dipping cycles and (c) 15 dipping cycles are shown in Figure 3. Dipping cycles is found to have a significant effect on the optical properties of ZnO thin films. By increasing the film thickness, the absorption edge becomes sharper. Also the average transmission of the film is increased to a certain extent. When the film thickness is increased, oxygen is absorbed throughout the bulk of the film, which produces a ZnO thin film with better stoichiometric ratio. So, an absorption edge is obtained. With more dipping cycles also there is possibility of increase in grain size. This decreases the surface roughness and hence reduces the optical scattering at the surface (Zhang et al., 1994, Meulenkamp, 1998). From the spectra it is observed that the films are highly transparent in the visible region (400 to 800 nm).Absorption coefficients (α) can be determined from the region of strong absorption of the transmittance data, by using the following relation, $\alpha(\lambda) = [2.303\log(1/T)]/d$, Where, T is the transmittance at a particular wavelength and d is the film thickness. The fundamental absorption, which corresponds to electron excitation from the valance band to conduction band, can be used to determine the nature and value of the optical band gap. As the films are crystalline in nature, the relation between the absorption coefficients (α) and the incident photon energy (hν) can be written as $(\alpha h\nu)^{1/n} = A_0 (h\nu - E_{opt})$, where A_0 is a constant and E_{opt} is the optical band gap of the material and exponent n depends on the type of transition (Natsume et al., 2000). For direct allowed transition, n =1/2, for indirect allowed transition, n

=2, and for direct forbidden transition, n =3/2. Since, Zinc Oxide is a direct band gap material in this case n=1/2. Hence we can write the equation as $(\alpha h\nu)^2 = A_0 (h\nu - E_{opt})$.

Figure 3. Transmittance spectra for different ZnO thin films

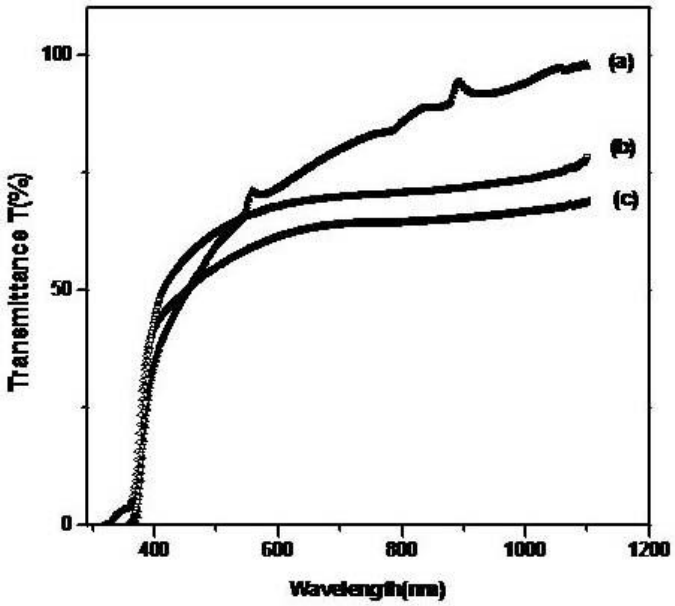
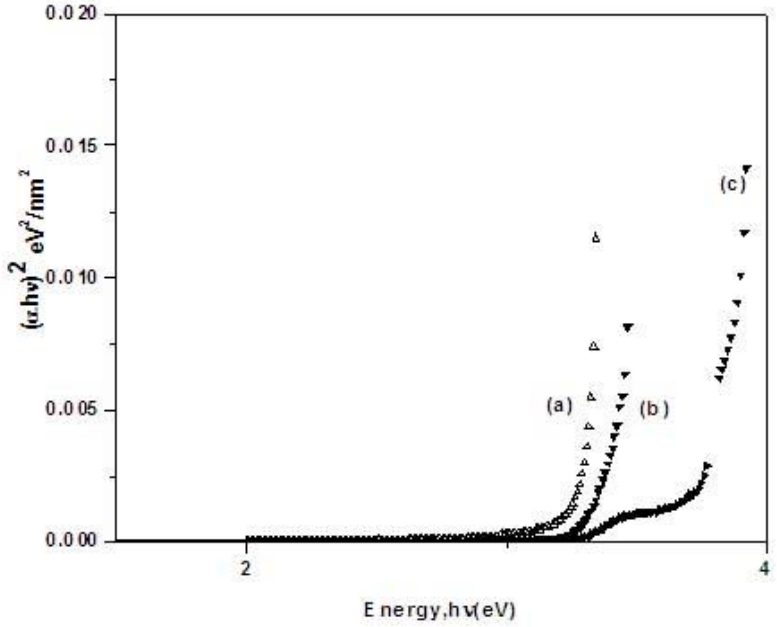


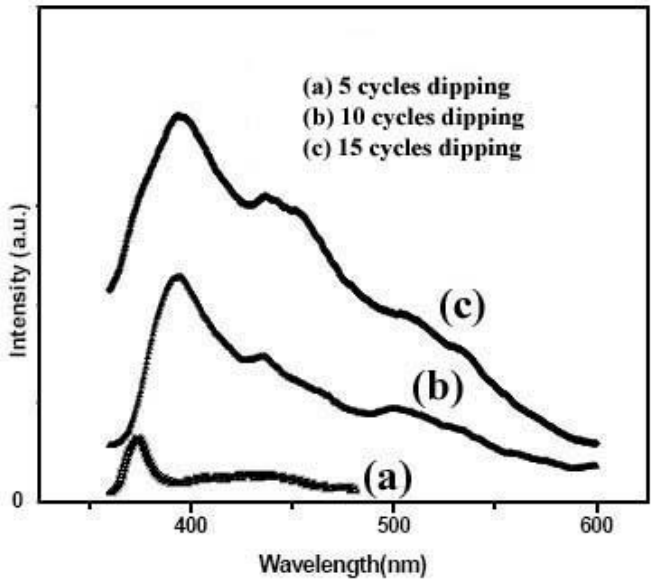
Figure 4. $(\alpha h\nu)^2$ vs. hv plots of ZnO thin films



Extrapolating the linear portion of the graphs in Figure 4 to the energy axis (**hv)** axis optical band gap values of ZnO deposited can be calculated from its intercept on the energy (**hv**) axis. For the ZnO films

deposited on glass substrates, the band gap values are 3.7 eV, 3.4 eV and 2.9 eV for dipping cycles 5, 10 and 15 respectively.

Figure 5. PL Spectra of ZnO thin films of different thickness



PL spectra of ZnO thin films of different thickness have been plotted in Figure 5. From the plot it is observed that each of the curves exhibits a band-edge emission in the UV region, which is due to transitions between different excitonic levels. Also a broad emission is observed with a weak peak in the wavelength range near 500nm, this may be duo to recombination of the photogenarated holes with singly ionized oxygen ion vacancies (Mandal et al., 2009). It is being observed that with the increase in film-thickness the emission peak shifts towards higher wavelengths as well as the peak becomes more prominent. This is due to the increase in particle size with increase in thickness of the film produced. Here, we can say that with the increase in thickness the film tends to show a bulk like behavior. Also deposition of larger particles on the film surface gives more prominent emission. Initially there was only a broad peak due to defect related transitions in a wavelength~450nm, but with the increase film thickness another broad peak appears at a wavelength ~ 495 nm.

5. Conclusions

We have successfully grown ZnO nanocrystalline thin films by low cost sol-gel method. The XRD pattern reveals the formation of wurtzite structure of ZnO. From AFM analysis it has been observed that with the increase in dipping cycles, the surface roughness has been decreased and at the same time the average diameter of particles has been increased which is in conformity with the XRD results. UV-absorption spectrum shows that the optical absorption edge for ZnO films shift towards longer wavelengths and the absorption edge become steeper with increase in dipping cycles, indicating the decrease in band gap values of the samples. From the PL spectrum of ZnO thin films it has been observed a near-band-edge (NBE) emission at around 385 nm also a broad emission is observed in the wavelength range near 500nm.

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References

Christensen, E., Gorczyca, I., Christtensen, O.B., Schmid, U., & Cardona, M. (1990). Band structure and heterojunctions of II VI materials, *Journal of Crystal Growth*, 101, 318-331

Ginley, D.S., & Bright, C. (2000). Transparent Conducting Oxides, Material *Research Bulletin*, 25, 15-18.

Hara, K., Horiguchi, T., Kinoshita, T., Sayama, K., Sugihara, H., & Arakawa, H. (2000). Highly efficient photon-to-electron conversion with mercurochrome-sensitized nanoporous oxide semiconductor, *Solid Energy Materials Solar Cells*, 64, 115-134

Mandal, S., Dhar. A., & Ray, S. K. (2009). Growth and photoluminescence characteristics of ZnO tripods, *Journal of Applied Physics*, 105, 033513-033518

Mandal, S., Sambasivarao. K., Dhar. A., & Ray, S. K. (2009). Photoluminescence and electrical transport characteristics of ZnO nanorods grown by vapor-solid technique, *Journal of Applied Physics*, 106, 024103-024110

Meulenkamp, E.A. (1998). Size Dependence of the Dissolution of ZnO Nanoparticles, *Journal of Physical Chemistry* B, 102, 7764–7769.

Mitra, A., Thareja, R.K., Ganesan, V., Gupta, A., Sahoo, P.K., & Kulkarni, V.N. (2001). Synthesis and characterization of ZnO thin films for UV laser, *Applied Surface Science*, 174, 232-239.

Natsume, Y., & Sakata, H. (2000). Zinc oxide films prepared by sol-gel spin-coating *Thin Solid Films*, 372, 30-36

Nel, A., Xia, T., Mädler, L., & Li, N., (2006). Toxic Potential of Materials at the Nanolevel, Science, 311, 622–627.

Wang, Z.L. (2004). Zinc oxide nanostructures: growth, properties and applications, *Journal of Physics: Condensed Matter*, 16, R829-R858.

Zhang, D.H., & Brodie, D.E. (1994). Effects of annealing ZnO films prepared by ion-beam-assisted reactive deposition, *Thin Solid Films*, 238, 95-100