



## Structural and Defect State analysis of ZnO nanoparticles

Surajit Mandal

Department of Physics,

Burdwan Raj College, Burdwan, (West Bengal), INDIA

(Corresponding author: Surajit Mandal)

(Received 14 September, 2017 accepted 02 October, 2017)

(Published by Research Trend, Website: [www.researchtrend.net](http://www.researchtrend.net))

**ABSTRACT:** Nanostructured ZnO films have been prepared by sol-gel method on Si substrate. The as-deposited film is amorphous in nature, and the crystallinity has been found to increase on post-deposition annealing. The effects of annealing temperature on the photoluminescence (PL) properties of the nanocrystalline ZnO films have been investigated. PL intensity is greatly improved with the increase in annealing temperature, and the band gap of ZnO films is red-shifted. The optical property has been investigated in detail. Heating in low oxygen pressure was found to enhance the UV emission substantially. The effects of heating temperature on blue and green emissions are also discussed.

**Keywords:** ZnO Nanostructures, Photoluminescence, Sol-Gel, Defect State

### I. INTRODUCTION

ZnO, a wide and direct band gap (3.3eV) semiconductor with large exciton binding energy (60 meV) at room temperature, is a promising material for optoelectronic applications [1]. The optical properties of ZnO make it one of the most promising materials for photonic devices in the ultraviolet range. Moreover, the binding energy of the exciton of ZnO (60 meV) is larger than its competitor GaN (25 meV) at room temperature making it attractive [2–4] for exciton-related device applications. Post-deposition annealing treatment is a conventional and effective technique to reduce intrinsic defects and to improve the crystallinity [5] in thin films. Stoichiometric zinc oxide is an insulator with the wurtzite structure. The structure contains large voids, which can easily accommodate interstitial atoms. Consequently, it is virtually impossible to prepare pure crystals; also, they tend to lose oxygen when heated to a very high temperature [6]. For these reasons, ZnO exhibits *n*-type semiconducting properties with inherent defects, such as the lack of O and the excess of Zn. In this regard, the study of the photoluminescence (PL) characteristics of ZnO is interesting because it can provide valuable information on the quality and purity of the materials. The effect of post-deposition annealing on the crystallinity, and the photoluminescence characteristics of nanocrystalline ZnO films grown by sol-gel technique on SiO<sub>2</sub>/Si substrates is reported.

### II. EXPERIMENTAL

Zinc acetate dihydrate (Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O) and 2-propanol were chosen as starting materials to coat ZnO films on SiO<sub>2</sub>/Si substrates by sol-gel method. Initially, zinc acetate was dissolved into 2-propanol. Since zinc acetate has low solubility in 2-propanol, diethanolamine (DEA) was added to obtain a transparent solution and to keep the solution stable. The particle size depends on the molar quantity of zinc acetate and diethanolamine (DEA). The molar ratio of zinc acetate and diethanolamine (DEA) was maintained at 1:1. The solution was stirred at a constant temperature 60°C for 1 hour followed by aging for about half an hour to make it cool and stable. Multilayer films were deposited on p-Si substrates by dip coating method. After each coating, the films were dried at 150°C for 5 minutes. The films thus formed were annealed at 400°C temperatures in oxygen environment. The properties of ZnO films annealed at an optimized temperature of 400°C were studied in detail. The microstructure and morphology of ZnO films were characterized by X-ray diffractometer (Philips X-Pert MRD) using CuK $\alpha$  radiation of wavelength 1.5418 Å at grazing incidence mode and a field emission scanning electron microscope (FE-SEM). Photoluminescence was measured using a He-Cd laser as an excitation source, operating at 325 nm with an output power of 50 mW and TRIAX 320 monochromator fitted with a cooled Hamamatsu R928 photomultiplier detector.

### III. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the as-deposited as well as nanocrystalline ZnO films annealed at temperature 400°C. The diffraction peaks match with the wurtzite structure of ZnO. The entire range of the XRD pattern shows three main peaks at  $2\theta=31.801^\circ$ ,  $34.544^\circ$  and  $36.334^\circ$ . By taking these three peaks I calculated lattice parameters are  $a=3.241\text{\AA}$  and  $c=5.187\text{\AA}$ , which is matched with the value of

$a=3.246\text{\AA}$  and  $c=5.187\text{\AA}$  (ICDD: Card no. 79-0250). XRD results demonstrate poor crystallinity of the samples annealed at low temperatures, while the crystallinity is improved with the increase in annealing temperature. The intensity of all diffraction peaks increase at higher annealing temperature, because higher temperature provides more energy to enhance the adatom mobility resulting in an improvement in the quality and crystallinity of the films.

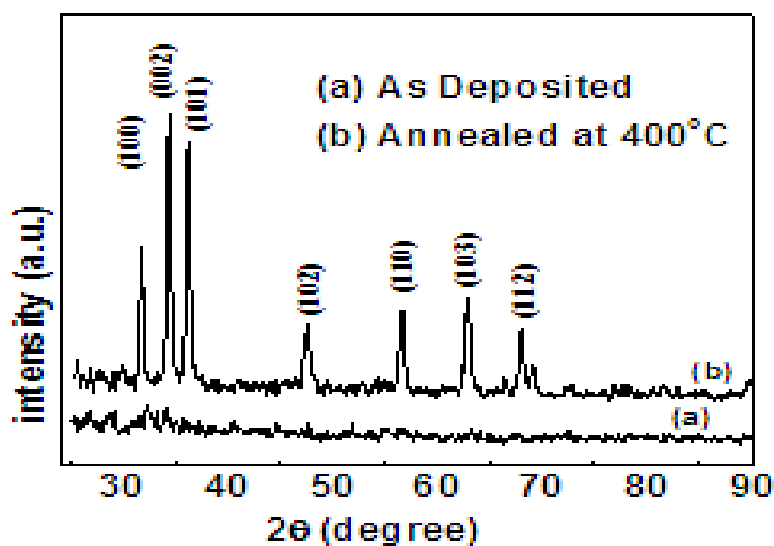


Fig. 1. XRD pattern of ZnO films (a) as grown and annealed at (b) 400°C.

FE-SEM image of sample annealed at 400° C shown in Fig. 2 indicate grain of average size 20 nm. The shape of the grains almost same and it is showing nearly spherical like structure.

Different reports have been published of visible emission due to vacancies and interstitial atoms, including cationic and anionic sites in ZnO [7]. The origin of the defect responsible for the green emission cannot yet be definitely determined only with the experimental results, because visible spectra were greatly affected by preparation methods, environmental conditions, and roles of the coordinating ligands [8]. In general, most defects are considered as a result of the surface states located in the band gap of the nanocrystals, which act as trapping states for the photogenerated carriers. A certain type of surface structure or surface reconstruction of thin films grown by the gas phase techniques can be accomplished by providing the system with a biased ratio of the precursors and annealing treatments. On the other hand,

the surface reconstruction in a solution reaction with a defined number of monomeric units takes place only for a short period of time due to the rapid variation in the concentrations of the monomers, the precursors, and ligands in the solution. The monomers on the surface of nanocrystals should collaborate and compete with the ligands to form stable crystallinity during the surface reconstruction and the growth. If the surface ligands could provide a good passivation for the surface states, some or all surface trapping states can be removed [9]. Consequently, the nature and density of the surface trapping states should depend on the surface structure of the nanocrystals and the surface ligands. At the surface of the ZnO nanoparticles, zinc atoms located at the surfaces with a help of polarized bonds between oxygen atoms reducing the surface defect densities [10]. On the other hand, the oxygen-related defects were not expected to be completely quenched by Zinc acetate dehydrate which suggested oxygen-related defects for the surface trapping states.

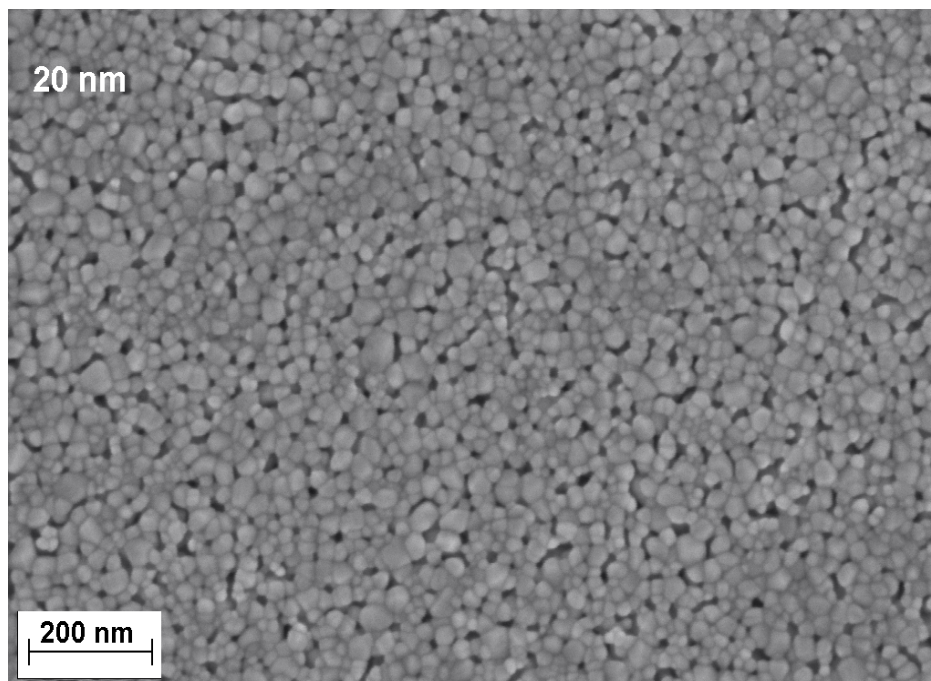


Fig. 2. SEM images of ZnO films annealed at 400°C.

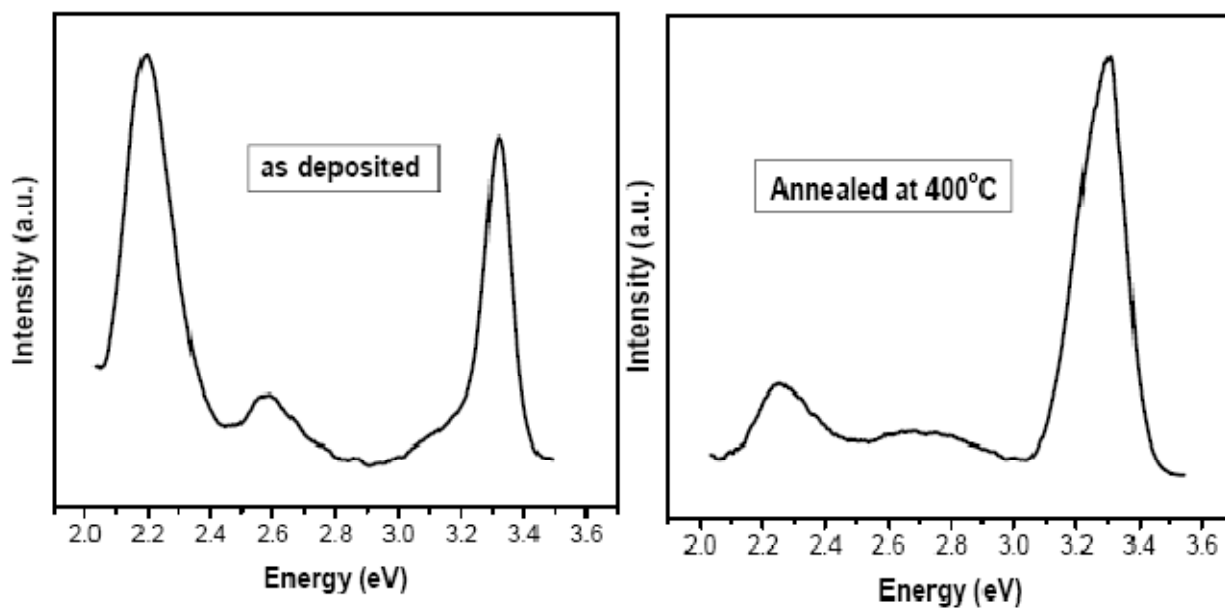


Fig. 3. Photoluminescence spectra of ZnO films (a) as grown and annealed at (b) 400°C.

Photoluminescence (PL) is an important property, which provides information on the optically active defects and relaxation pathways of excited states. The study is useful to identify the origin of sub-band-gap luminescence. Fig. 3 shows the room temperature photoluminescence characteristics of nanocrystalline ZnO films. The PL intensity is found to be enhanced

with increasing annealing temperature and the band emission energy is red shifted from 3.379 to 3.267 eV. The green emission due to a recombination between an electron in single positively charged oxygen vacancy and a hole in the valence band and oxygen vacancy was predicted to lie at 2.62-2.23 eV above the valence band.

It has been reported earlier that the intensity of green emission becomes stronger on post annealing treatment at 800 °C in oxygen ambient for 1 h, but annealing at low temperatures results in the suppression of green emission [11]. I emphasize my work on detail analysis of the luminescence characteristics of nanocrystalline ZnO film. ZnO has several defect states due to zinc interstitials or oxygen vacancies, which I want to, recover by annealing the film at an optimized temperature in oxygen environment. PL measurement shows that the defect energy state is negligible in comparison with band to band transition. It is noted that UV emission is not related with the defect states and a post-deposition annealing is essential to suppress the green band emission, which may appear due to zinc interstitial or oxygen vacancy defect states [12]. In amorphous phase, the extended localization in the conduction and valence bands results in the near band edge emission. The improvement of crystallinity of ZnO films leads to an increment in the intensity of band edge emission in comparison with the green band emission, because of annealing [13-14].

#### IV. CONCLUSIONS

Nanocrystalline ZnO films have been synthesized by sol-gel technique. XRD spectra revealed the formation of wurtzite structure ZnO. The band gap is red shifted and PL intensity is found to be enhanced with the increase in annealing temperature. A correlation between the structural and optical properties of ZnO films has been established.

The study shows the potential of simple sol-gel technique to synthesize a high quality nanocrystalline ZnO films useful for optoelectronics devices in the ultra-violet region. My study shows the potential of sol-gel technique to synthesize a high quality nanocrystalline ZnO films.

#### ACKNOWLEDGEMENT

I am grateful to Prof. S. K. Ray (IIT Kharagpur, Department of Physics and Meteorology) for giving me the opportunity to provide all the Laboratory facilities.

#### REFERENCES

- [1]. K. Hümmer, *Phys. Status Solidi B* **56**, (1973) 249.
- [2]. Y. R. Ryu, *J. Appl. Phys.* **88** (2000) 201.
- [3]. F. K. Shan, *J. Eur. Ceram. Soc.* **24** (2004) 1861.
- [4]. Y. F. Lu, *J. Appl. Phys.* **88** (2000) 498.
- [5]. K. Vanheusden et.al., *Appl. Phys. Lett.* **68**,(1996)403.
- [6]. L. V. Azaroff, *Introduction to Solids* (McGraw-Hill, New York, 1960), pp.371-372.
- [7]. D. S. Bohle and C. J. Spina, *J. Am. Chem. Soc.* **131**, (2009) 4397.
- [8]. S. Y. Kim, I. S. Lee, Y. S. Yeon, S. M. Park, and J. K. Song, *Bull. Korean Chem. Soc.* **29**,(2008) 1960.
- [9]. S. A. B. Djurišić, W. C. H. Choy, V. A. L. Roy, Y. H. Leung, C. Y. Kwong, K. W. Cheah, T. K. G. Rao, W. K. Chan, H. F. Lui, and C. Surya, *Adv. Funct. Mater.* **14**, (2004) 856.
- [10]. Y. Gong, T. Andelman, G. F. Neumark, S. O'Brien, and I. L. Kuskovsky, *Nanoscale Res. Lett.* **2**(2007). 297.
- [11]. H.S. Kang, *J. Appl. Phys.* **95** (2004) 1246.
- [12]. Y. Li, G. W. Meng, L. D. Zhang and F. Philli *Appl. Phys. Lett.* **76**(2000) 2011.
- [13]. S.T. Tan et.al, *J. Appl. Phys.* **98**, (2005) 013505.
- [14]. T. Matsumoto et.al. *Appl. Phys. Lett.* **81**, (2002)1231.