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A Review on the Optical Properties of ZnO Nanostructures for Optoelectronic Device Application

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Abstract

The theoretical and the experimental aspect of ZnO nanoparticles for application in thin film optoelectronic device are well explained in this work. Different synthesis procedures for ZnO nanoparticles are discussed. The optical properties of versatile ZnO nanostructures and the influence of various synthesis methods on the absorption and luminescence properties are discussed. The comparative study of optical properties of ZnO nanoparticles reveals the potential application for improving the performance of thin film optoelectronic device by light capture enhancement.

Keywords: *ZnO nanoparticles, Quantum Tunneling, Absorption, Luminescence.*

1. Introduction

ZnO nanostructures had attracted the attention of new researcher because of their potential applications in device electronics, photovoltaic cells, solar cell and sensors [1-5]. It is a direct band gap semiconductor with energy gap of 3.37 eV and the exiton binding energy of 60 meV at room temperature [6-10].

These ZnO nanoparticles are becoming a suitable material for photovoltaic application [8] and they are more efficiently used for designing new hybrid structure of smart sensor at a reduced cost. Now a days, different methods have been employed for the synthesis of ZnO nanostructures [1-15] and the optoelectronic properties of these nanostructures were studied with respect to the synthesis procedure for application in high efficient optoelectronic device and sensors. The optical properties of ZnO nanoparticles were reviewed in correlation with their synthesis procedures.

2. Synthesis of ZnO nanoparticles

Zhong Lin Wang in his review paper explained a solid vapor process for the synthesis of ZnO nanoparticles [1-5] . He explained the thermal evaporation process as a very sensitive method to control the concentration of oxygen in the growth system. Actually oxygen influenced the volatility of the source material as well as the stoichiometry of the vapor phase [5].

In case of the growth of ZnO, the highest growth was observed along the fixed axis (c – axis) [1-5]. Therefore, the growth behavior of ZnO nanostructure could be altered by controlling the growth kinetics.

Again, G. Vijaya Prakash et al. Proposed two novel methods for preparation of ZnO nanostructures namely, chemical synthesis and electrochemical deposition [6-10]. They have optimized the growth parameters by measuring various properties like optical, structural and electrical properties [7-9]. ZnO nanostructures were synthesized by the hydrolysis of zinc acetate dehydrate with dietylene glycol. The electrochemical synthesis was performed by using two kinds of electrolytes namely, aqueous mixture of zinc chloride and potassium chloride and zinc nitrate solution maintaining the potentiostatic condition [8-9]. The ITO coated glass was used as a conductive substrate. In Electrochemical deposition method both bare and zinc hydroxide was annealed at 400^0C for 12 hours in order to obtain crystalline ZnO nanostructures [6-7].

Edgar Mosquera et al studied the effect of Ag content on the properties of ZnO nanoparticles by various characterization techniques. They adopted the sol–gel process to prepare ZnO and ZnO: Ag nanoparticles [11]. The zinc nitrate and silver nitrate were dissolved in deionized water and ethanol solution and then PVA were added to obtain gel solution. The ZnO nanoparticles were prepared by dissolving zinc nitrate and PVA in ethanol-water mixture [11-15] and stirred at 80^0C, then the gels of ZnO and ZnO: Ag was heated at 600^0C for 8 hours.

3. Structural and optical properties

The optical properties of ZnO nanostructures were studied by Zhong Lin Wang in reference to their growth mechanism. In the synthesis of ZnO nanostructure the solid vapor process was employed for the growth of ZnO nanorods [1]. In that work the author explained about the nano wire growth direction and also defined the diameter of the nano wires. The SEM image of ZnO nano rods is reproduced in the figure (1).

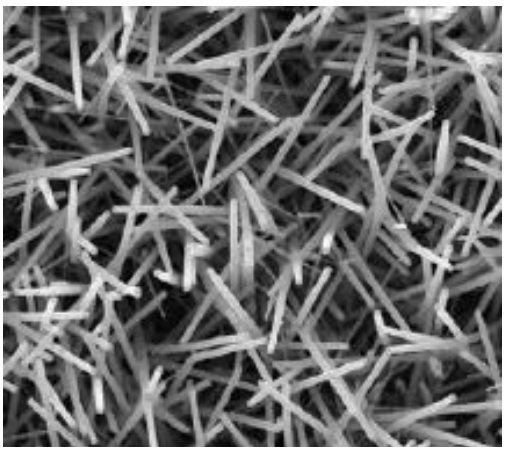

Figure 1. ZnO nanorods grown using gold as a catalyst (Reproduced from Reference No. 1).

Again the optical or photoluminescence properties of the as prepared ZnO nanostructures were found to be the function of doping level of Ga [1-5]. The photoluminescence intensity could be tuned by varying the doping level. The peak shift of 14 nm was observed in between the average width of 200nm and 6nm nanobelts. These are attributed to the size reduced quantum effect of the ZnO nanostructures. The reproduced curve is given in the figure 2.

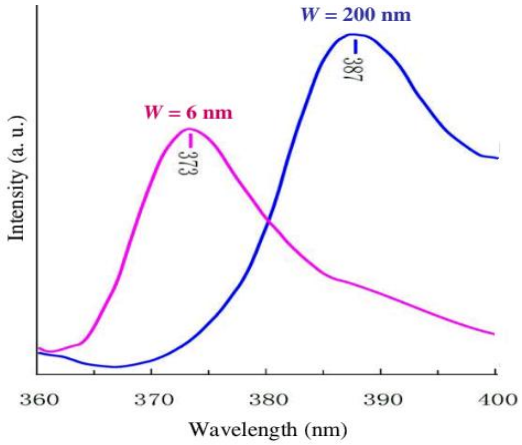

Figure 2. Photoluminescence spectra recorded from ZnO nanobelts with widths of 200 nm and 6 nm, respectively, showing a blue-shift with a reduction in nanobelt size (Reproduced from Ref.No.1)

In G. Vijaya Prakash et al the TEM analysis for ZnO nanostructures obtained by two step chemical synthesis were ranged between 5nm to 13 nm average radius [6]. The figure 3 shows the reproduced TEM image of ZnO nanostructures.

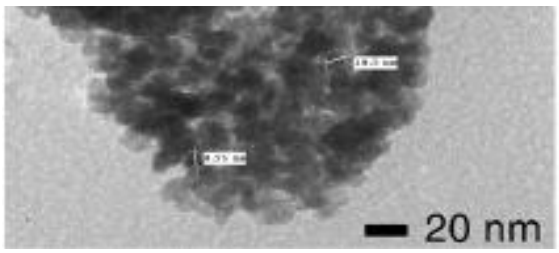

Figure 3. TEM image of ZnO nanostructures (Reproduced from Ref. No. 2).

The X-ray Diffraction of ZnO for electrodeposited thin film deposited at −0.75 and −1.1 V deposition potentials [((i) and (ii)] and for synthesized nanoparticles (iii) are given in the figure 4. XRD images of these ZnO nanospheres are shown to be high quality wurtzite crystalline structure [1-5].

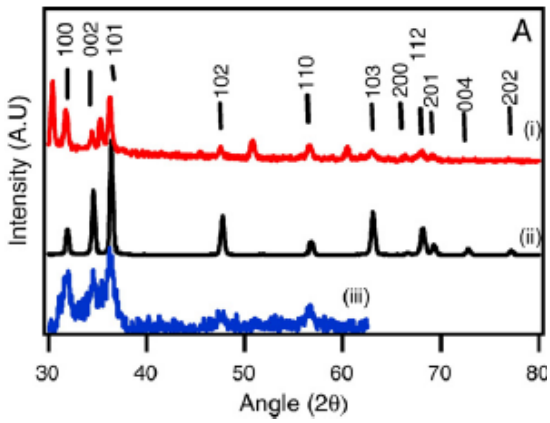

Figure 4. XRD images of ZnO nanospheres (Reproduced from Ref. No. 2)

The optical absorption and emission peak of the as prepared ZnO nanostructures revealed the blue shift with decrease in size [1-15]. The reproduced curve of optical absorption spectra of electrodeposited thin film at -0.75 and 1.1 V is given in figure 5.

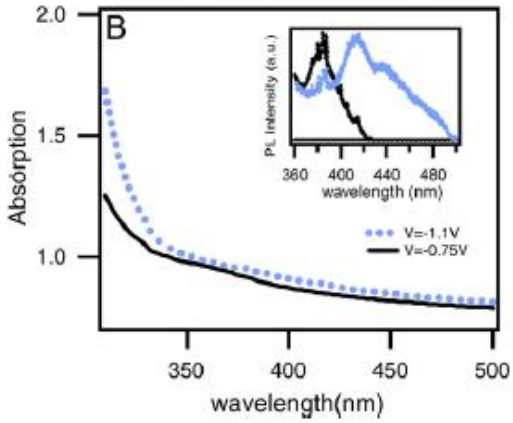

Figure 5. Optical absorption spectra (reproduced from Ref. No. 2)

In Edgar Mosquera et al the XRD patterns of undoped ZnO showed the characteristics peaks of hexagonal wurtzite structure [11]. The XRD patterns for the low percentage of silver doping (0.6% Ag) showed the light intensity diffraction peaks at 2θ values of 38.08^0, 44.27^0 and 64.38^0 showing the presence of Ag besides the ZnO diffraction peaks. The XRD patterns for higher doping percentage of Ag contain four additional peaks at 2θ values of 38.08^0, 44.27^0, 64.38^0 and 77.33^0 assigned to pure Ag. These results suggested that as-prepared ZnO: Ag nanostructures showed the formation of elemental Ag as a second phase [11-15]. The XRD patterns of ZnO and ZnO: Ag nanostructures synthesized by PVA based sol gel method is given in the figure 6.

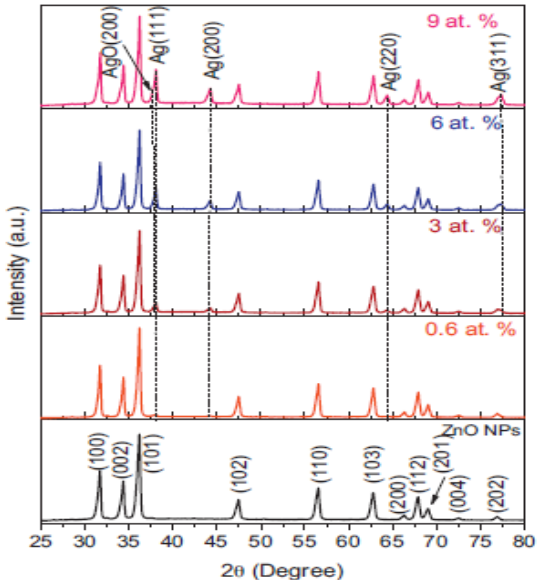

Figure 6. XRD patterns of ZnO and ZnO: Ag nanostructures (Reproduced from Ref. No. 3)

Fig. 7 shows the SEM images of the Ag doped ZnO nanoparticles obtained with different contents of Ag percentage. The nano composites revealed the formation of spheroidal particles with the size ranging from 28 nm to 35 nm [11-15] (Fig.7 (a)–(d))

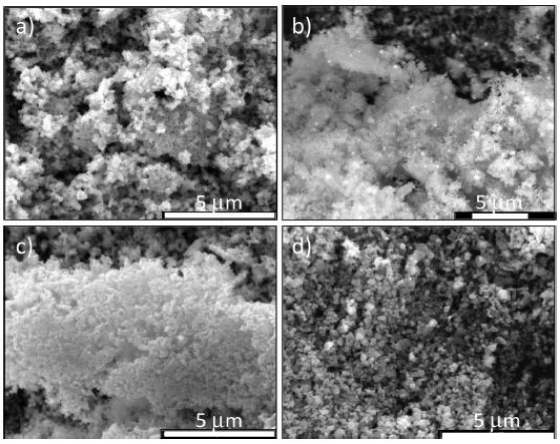

Figure 7. SEM micrographs of ZnO: Ag with different Ag content ((a) 0.6 %, (b) 3 %, (c) 6 %, and (d) 9 % Ag). (Reproduced from Ref. no. 3)

The prominent absorption peak at 374 nm (3.32 eV) or 378 nm (3.28 eV) for ZnO and ZnO:Ag nanoparticles, respectively were obtained in the room temperature UV–visible absorption spectra.

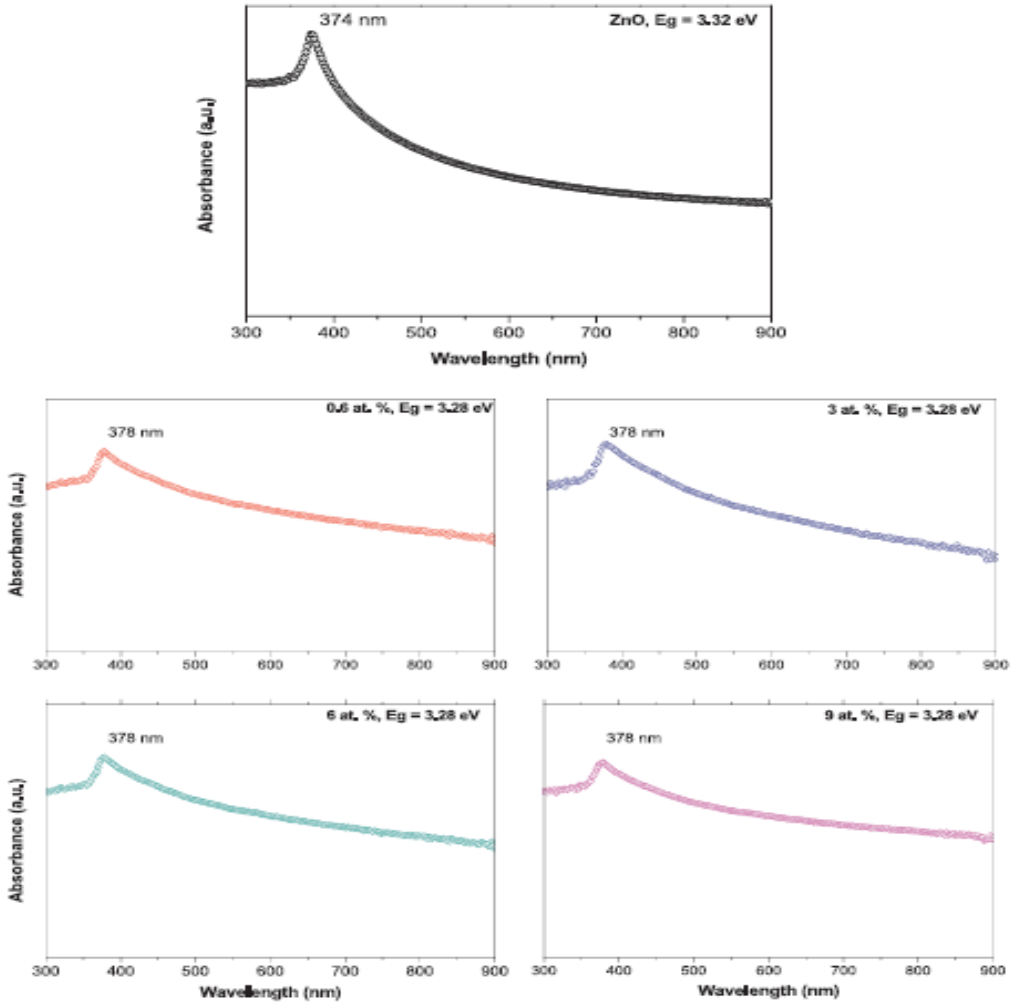

Figure 8. Room temperature UV–visible absorption spectra of samples. (Reproduced from Ref. No. 3)

These peaks are obtained due to the excitonic absorption peak of ZnO nanoparticles [11]. The surface Plasmon resonance (SPR) peak around 400 nm –500 nm were not observed here, which is due to strong inter-facial coupling between ZnO and Ag [13]. The shift of 0.04 eV showed due to the energy band gap of ZnO: Ag nanoparticles had less than that of bare ZnO nanoparticles. The room temperature UV–visible absorption spectra of ZnO and ZnO: Ag nanoparticles are shown in the figure 8.

The room temperature photoluminescence (PL) spectra showed a strong blue emission peak at 488 nm (2.54 eV) and 426 nm (2.91 eV) along with a green emission peak of relatively lower intensity located at 530 nm (2.34 eV) [12].The green emission at 530 nm were due to recombination of photo-generated hole and singly ionized oxygen. The origin of the blue emission at 426 nm and 488 nm were attributed to the transition from Zn interstitials to the valence band, and the peak at 426 nm were the result of the singly ionized oxygen vacancy [14]. A blue emission peak positioned at 469 nm (2.65 eV) was observed in all samples, and its relative intensity decreased with increasing Ag content. In addition to it, a weak violet peak at 407.5 nm (3.04 eV) was observed in bare ZnO nanoparticles. However, the intensity of this peak increased as the Ag content in the nanoparticles was increased. After doping it shifted down to around 398 nm (3.12 eV, E = 0.08 eV, at. 9 % Ag) in ZnO: Ag samples. The blue shift of the UV emission peak from 407.5 nm to about 398 nm after Ag doping was due to the variation of the energy band gap of ZnO nanoparticles. The blue emission peak centered at 488 nm was shifted up to about 491 nm (2.53 eV, E = 0.01 eV) with the Ag doping. As the Ag-doping increased, the association of Ag atoms may compensate the Zn vacancies. The room temperature PL spectra are shown in figure 9.

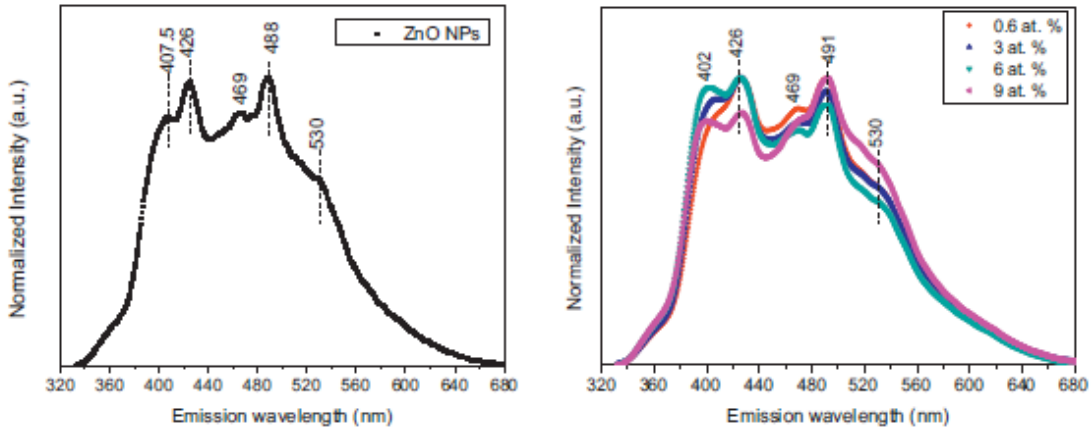

Figure 9. Room temperature photoluminescence spectra of ZnO and ZnO: Ag nanoparticles (Reproduced from Ref. No. 3)

4. Discussion

The different synthesis methods for the preparation of ZnO nanostructures were discussed and structural as well as optical properties of these nanoparticles were explained. The growth mechanism for the preparation of ZnO by using a solid vapor process was established by Zhong Lin Wang [1]. He explained the stoichiometry of the prepared nanoparticles and concluded that the highest growth of ZnO nanostructures was observed along the particular axis (c - axis). Therefore, the growth kinetics of ZnO nanostructures can be controlled by the synthesis procedure. The growth of ZnO nanostructures were studied by Zhong Lin Wang and they have found rod like and wire like structures of ZnO as shown in the figure (1). The reference PL spectra of the ZnO nanorods were also studied and the stokes shift of 14 nm was observed in the luminescence spectra of these nano rods [1-5]. The blue shift of the ZnO nanostructures in the spectra was the clear indication of the formation of ZnO nanorods.

On the other hand, G. Vijaya Prakash et al depicted chemical synthesis method and electro chemical deposition method for the growth of ZnO nanoparticles. The dependence of optical and structural properties of ZnO nanoparticles on the growth parameters have been discussed by them. They have used the hydrolysis of zinc acetate dehydrate with dietylene glycol for the preparation of ZnO nanostructures. In case of electrochemical synthesis, they have used the aqueous mixture of zinc chloride, potassium chloride and zinc nitrate solution for optimizing the controlled growth [6-10]. The structural characterization was carried out by employing TEM and the particles of 5 nm to 13 nm of average radii were obtained. The TEM results were supported by the XRD spectra and high quality wurtzite crystalline structure of ZnO nanospheres were observed. The blue shift was observed in the absorption spectra and the formation of ZnO nanospheres were also confirmed from their optical properties characterization.

The effect of silver doping on the optical and structural properties of ZnO nanoparticles was explained by Edgar Mosquera et al. They have published the sol gel method as one of the best method for the preparation of ZnO and silver doped ZnO nanoparticles. The PVA was used to obtain the gel solution and zinc nitrate, silver nitrate were dissolved in de ionized water and ethanol solution prior to the addition of PVA [11]. The ZnO nanoparticles were prepared by stirring the solution at 80^0C. The structural characterization of the prepared ZnO nanostructures were examined by the XRD diffraction pattern. In this work, the variation of silver doping was carried out from 0.6% to 9% in the solution. At low concentration (0.6% Ag), the ZnO nanoparticles were count to be at 100,002,101,102,110 and 103 planes respectively. Again at the higher concentration of silver (9%), the following planes were found. The plane of ZnO at 100, silver oxide at 200, silver at 111,200,220 and 311 respectively [12]. Therefore it is clear that as per the enhancement of the doping percentage of silver the planes of silver oxide and silver were found more in the sample. Therefore, optical properties were also varied in accordance with the doping percentage of Ag: ZnO nanoparticles. They have found the green emission at 530 nm in the emission spectra due to photo generated holes and ionized oxygen. With increasing the doping percentage of Ag content in the sample, the intensity of blue emission peak positioned at 469 nm was decreased [11-15]. Again a blue shift of the UV emission peak was also observed due to variation of band gap of ZnO nanoparticles because of Ag doping. Thus Zn vacancies could be compensated by the Ag atoms in higher percentage of Ag doping.

5. Conclusion

The structural and optical properties of ZnO nanostructures were studied and the physics behind the optical spectra observed for ZnO nanostructures were explained. The shape dependent of ZnO nanostructures on the growth mechanism of the nanoparticles were reported by the various workers. In this work, we have reviewed the different growth mechanism and their effect on structural and optical properties of the nanoparticles. Again, the variation of structural and optical properties of nanostructures depending upon the percentage of Ag doping was also revealed in this work [11].

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