Optical properties of Co doped ZnO thin films by chemical bath deposition technique

J. Yuvaloshini[1,*] and Ra. Shanmugavadivu[2]

[1]Department of Physics, Sree Sevugan Annamalai College, Devakottai-630303, Tamilnadu, India

[2]Department of Physics, Raja Doraisingam Goverment Arts College, Sivaganga-630561, Tamilnadu, India.

*Corresponding author: yuvaloshini15@gmail.com

Abstract

ZnO and Co doped ZnO thin films were prepared by chemical bath deposition method with the doping concentration of 0.01 M and 0.1 M of Co. The structural and optical properties of the as deposited films have been characterized using XRD, UV-Visible spectroscopy, photoluminescence spectra and FESEM. The XRD results revealed the polycrystalline nature of the film with the presence of hexagonal wurtzite structure. The average crystalline size was calculated using Scherrer's formula and it is found to be in the range of 27-54 nm, which were found to increase with increase in cobalt content. UV-Vis absorption and transmittance spectra showed that all the films are highly transparent in the visible region and in the case of doped ZnO thin films, d-d transition was observed in the violet region due to the existence of crystalline defects and grain boundaries. The energy band gap was found to decrease with increase in Co concentration with the range of 3.8-3.67 eV. The photoluminescence spectra of all the samples exhibited a broad emission in the visible range. The surface morphology of the thin films was investigated by FESEM and it revealed that they are homogeneously distributed. The energy dispersive X-ray analysis confirmed the stoichiometric composition of the Co doped ZnO thin films.

1. Introduction

ZnO is a wide band gap (~3.37 eV) material that has potential applications in the fabrication of devices such as ultraviolet (UV) light-emitters, varistors, transparent high-power electronics, piezoelectric transducers, gas-sensors, smart windows and solar cells [1]. It is one of the materials of the II–VI family of Semiconductors which have been studied extensively for many years [2]. Its electrical and optical properties could be modified thoroughly by thermal treatment with hydrogen or by an appropriate doping process either by cationic or anionic substitution [3]. Besides, ZnO doped with transition metals has been predicted theoretically to be very good candidates for room temperature ferromagnetism [4]. As a consequence, transitional metal doped Zinc Oxide has found potential applications in spintronics [5, 6]. Several studies described the growth processes of Co doped ZnO thin film and described the effect of cobalt doping on electrical, magnetic and magneto-optical properties [7-13]. In recent years, Co doped ZnO thin film has been deposited by Pulsed Laser Deposition (PLD), Molecular Beam Epitaxy and sputtering methods [14, 15]. In contrast, until now chemical bath deposition technique is rarely used as deposition technique although it represents a very simple and relatively cost-effective processing method (especially with regard to equipment costs) [16].

2. Materials and Methods.
2.1. Preparation of Co doped ZnO thin Films

ZnO and Co doped ZnO thin films were obtained by chemical bath deposition. All the reagents were of analytical grade and used without further purification. The entire process was carried out in distilled water for its inherent advantages of being simple and environment friendly. Glass substrate was previously cleaned by 24 hours immersion in chromosulphuric acid and rinsed with acetone and double distilled water. The ZnO thin films were prepared by dissolving 0.1 M of zinc sulphate heptahydrate in 80ml deionized water. To this homogenous solution, ammonia solution was added drop wise to maintain the pH of 10. Co doped

ZnO thin films were prepared by the solution contains 0.1 M zinc sulphate heptahydrate in 80ml deionized water. 0.01 M and 0.1 M of cobalt sulphate were added to two different solutions. A small amount of EDTA was added to the solution as a chelating agent. The mixture was maintained at pH of 10 using ammonia solution. The glass substrates were suspended vertically in the aqueous solution and kept in constant temperature bath of 80℃ for 1 h. After deposition, the thin films were annealed at 200⁰C in furnace for 2 h. Then the samples were used for further characterization.

2.2. Characterization

The structural characterization of deposited films was carried out by X-ray diffraction (XRD) technique on Bruker AXS D5005 diffractometer (monochromatic CuKa radiation, λ = 1.54 Å). The XRD patterns were recorded in 2θ interval from 20° up to 60° with the step 0.05°. The surface morphology was characterized by scanning electron microscopy (SEM). The room temperature optical studies were carried out using Perkin-Elmer Lambda 25 UV-VIS-NIR. The room temperature photoluminescence spectra were recorded in the wavelength range of 325 to 600 nm using Varian Cary Eclipse Fluorescence spectrophotometer. The surface morphology and chemical composition were studied using FESEM and EDX images recorded using Hitachi Model S-3000 H.

3. Results and discussions

X-ray diffraction patterns of ZnO and Co doped ZnO thin films are shown in Fig. 1 (a & b). All the peaks are in good agreement with the standard JCPDS-036-1451 card number and the corresponding structure of the sample is hexagonal wurtzite structure of ZnO [17, 18]. No other secondary phase such as Co clusters or cobalt oxides can be observed from the XRD pattern. The observed peaks for ZnO are at 22.4°, 24.9°, 29.4° indexed as (102), (110) and (200) respectively. It is also observed that the intensity of diffraction peak is decreased, for Co doped ZnO thin films, which indicates that the dopant Co^{2+} ions (ionic radius 0.58 Å) are successfully substituted in the inner lattice of Zn^{2+} ions (ionic radius 0.60 Å) [19]. The observation of small change in 2θ values of diffraction peaks and the peak broadening are due to the increase in micro-strain [20]. The structural change obtained from the diffraction peaks illustrate the incorporation of Co^{2+} ion into ZnO lattice which indicates that the crystal lattice undergoes obvious change by Co doping.

The average size (D) of ZnO and Co doped ZnO thin films was calculated using Debye- Scherrer formula, [21]

$$D = \frac{k\lambda}{\beta\cos\theta} \qquad (1)$$

Where, β is the full width at half maximum (FWHM), K is a dimensional number which is equal to 0.9, λ is the X-ray wavelength (1.54 Å for CuKα).
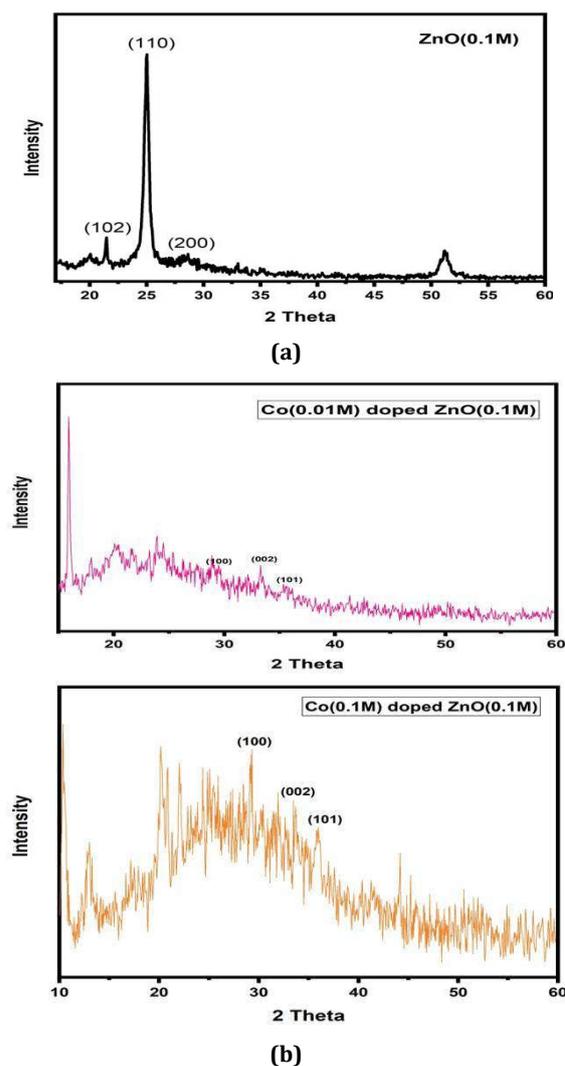

(a)

(b)

Fig. 2. *XRD pattern of (a) ZnO and (b) Co doped ZnO thin films.*

Table.1 *Grain size and dislocation density*

Sample	Grain Size (D, in nm)	Dislocation density
ZnO	27.08	13.63
0.01 M of Co doped ZnO	54.37	3.38
0.1 M of Co doped ZnO	54.66	3.34

Published 26 November 2019   **11**

The dislocation density is calculated using the formula,

$$\delta = \frac{1}{D^2} \qquad (2)$$

The grain sizes increase with increase in cobalt concentration and is given in Table 1. The crystallite size increases mainly due to the distortion in the host ZnO lattice by the Co^{2+} dopant ion which causes the increase in the nucleation growth rate of ZnO. The substitution of Co^{2+} in interstitial position of ZnO would affect the concentration of the interstitial Zn, O and Zn vacancies.

The UV-Vis absorption spectra of the thin films are shown in Fig. 2(a). It shows absorption edge of the thin films in the range of 310 nm which exhibits blue shift for the thin films. The blue shift in the absorption edge is due to the quantum confinement of the excitons present in the sample, resulting in a more discrete energy spectrum of the individual particles. The effect of the quantum confinement on impurity depends upon the size of the host crystal ZnO. As the size of the host crystal decreases, the degree of confinement and its effect increases [22]. As shown in Fig. 2(b), 0.01 M of Co doped ZnO thin film is relatively found to be highly transparent of about 85% in the visible and near infra-red regions and this makes them useful as a transparent window in solar cells whereas in 0.1 M of Co doped ZnO thin film, it is found to be transparent only 50% in the visible and near infra-red regions and this makes them useful as less window absorption loss in solar cells.
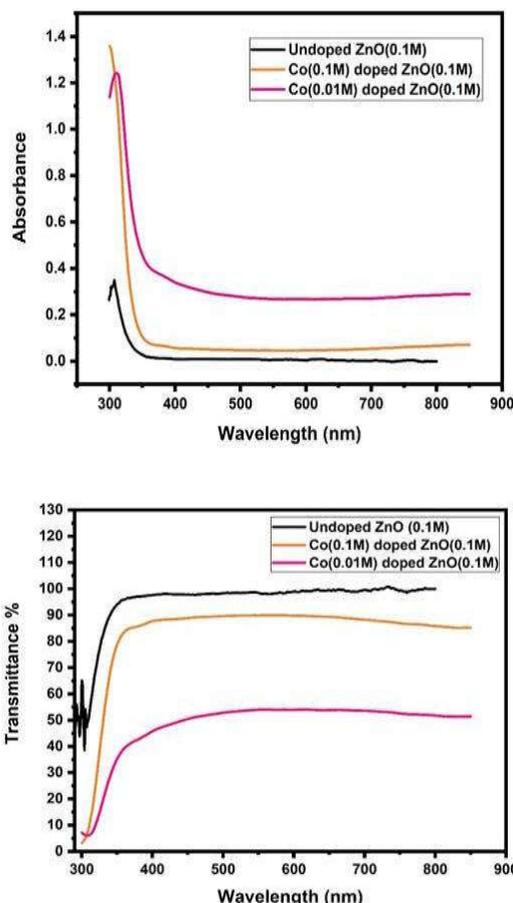

Fig. 2. *(Top) Absorption and (bottom) transmittance spectra of ZnO and Co doped ZnO thin films*
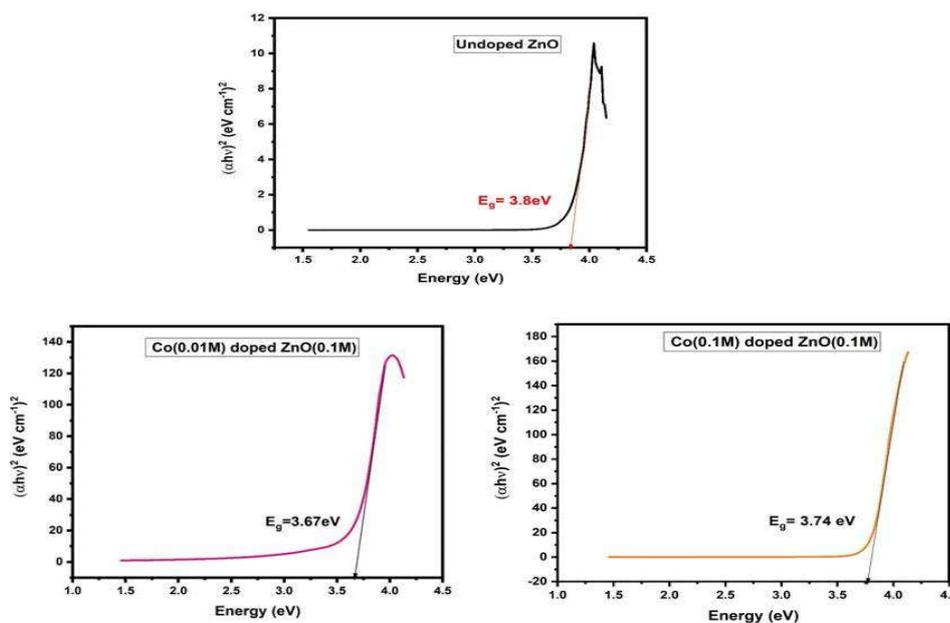

Fig. 3. *Plot of (αhν)² vs Energy for ZnO and Co doped ZnO thin films*

The optical band gap energy can be calculated using Tauc relation as given below

$$(\alpha h\upsilon)^2 = A(h\upsilon - E_g) \qquad (3)$$

Where α denotes the optical absorption coefficient, h is Planck's constant and ν is the frequency of the incident photon, E_g is the optical band gap and A is a constant. For pure and Co doped thin films, the estimated E_g values are ranging from 3.8 eV to 3.74 eV. Furthermore, for Co doped ZnO films E_g values decrease with the increase of Co molar concentration. However, the E_g value of low concentration of Co doped ZnO thin film is slightly higher than that of the E_g value of bulk ZnO.

In the present case, the observed reduction in E_g can be attributed to several factors, viz. defect/disorder induced band tailing, creation of impurity states, and grain size. Interaction of ions with matter, in the energy range under consideration, is dominated by nuclear energy loss caused by elastic collision between incident ions and target atoms. As a result, a dense collision cascade gets developed in a solid when energetic ions travel through it. Time evolution of such a collision cascade can be divided into different phases [23].

Fig. 4 shows the emission spectra of ZnO and Co doped ZnO thin films using an exciation wavelength of 325 nm. The photoluminescence emission observed for all samples covering from short wavelength of 365 nm to long wavelength of 550 nm. The UV emission peak of lowest wavelength is observed at 365 which correspond to the near-band emission of ZnO [24-26]. The peak observed at 488 nm corresponds to the blue emission, while the peak raised at 520 nm represents green emission. The emission peak observed at 488 nm can be attributed to the transition between oxygen vacancy and interstitial oxygen [27].
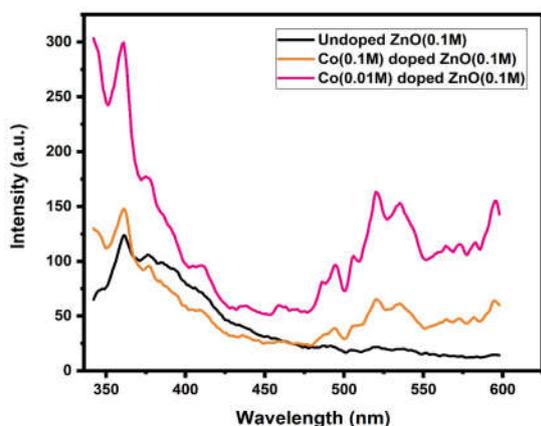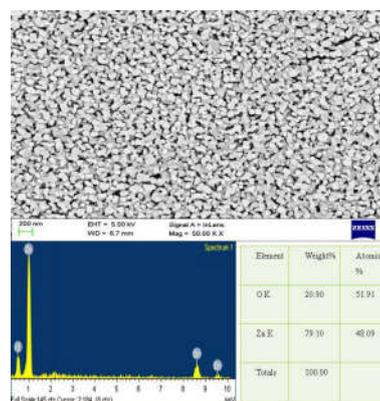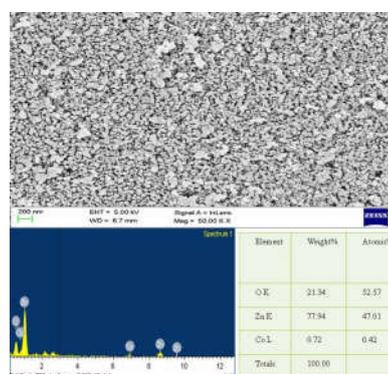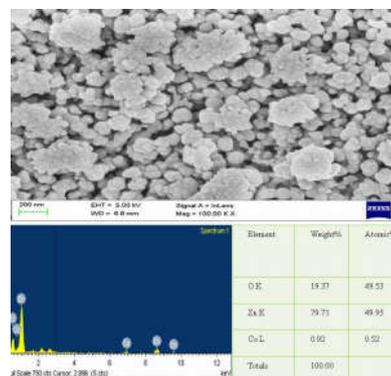

Fig. 4. *Photoluminscence spectra of ZnO and Co doped ZnO thin films*

(a)

(b)

(c)

Fig. 5. *FESEM image & EDX spectrum of (a) ZnO, (b) 0.01 M of Co doped ZnO and (c) 0.1 M of Co doped ZnO thin films*

The green emission peak at 520 nm is ascribing to the recombination of electrons in singly ionized oxygen vacancy with photo-excited holes in the valance band [28]. The green emission peak at 520 nm which has lowest intensity of emission in the spectrum coincides with the energy interval from the bottom of the conduction band (2.37 eV) [28]. It is interesting to note that an additional green emission peak appeared at 540 nm for the doped

samples and also the intensity of the green emission peaks gets increased with respect to the increasing doping level of Co^{2+}. It has been reported that green emission peaks are due to the oxygen vacancies and transition of a photo generated electrons from the conduction band to a deeply trapped hole [29].

Fig. 5 shows the FESEM micrographs of the pure and doped ZnO thin films with the magnification of 200 nm. It is observed that pure ZnO thin film spread over the surface throughout the film with spherical shape. The incorporation of Co ions in Zn lattice sites can influence the changes of the surface morphology into bounded grains. The small particles are agglomerated and are bound to uniformly and homogeneously, with the particles clustered together in the irregular shape. The quantitative analysis of the films was carried out by using the EDAX technique to study stoichiometry of the films. These spectra indicated the presence of only Zn, O and Co. The obtained thin films are made up of elements which show that the Co^{2+} ions substitute the Zn^{2+} ions in the Zn matrix. It confirms that the synthesized films are ZnO and Co doped ZnO thin films. The weight ratio and atomic ratio compositions of Zn, O and Co show that the amount of Zn element decreases with increasing Co content.

4. Conclusions

ZnO and Co doped ZnO thin films with different concentrations were successfully prepared on a glass substrate by chemical bath deposition method. The XRD pattern confirms the hexagonal wurtzite structure of ZnO for all the films. The nanocrystalline size is found to be increase with increase in Co dopant concentration and in the range of 27-54 nm. The optical spectra exhibit that all the films are highly transparent in the visible region. The estimated optical band gap energy was found to decrease with increase in Co concentration with the range of 3.8-3.67 eV. The photoluminescence spectra of all the samples showed two broad emission peaks in visible region. FESEM revealed homogeneous distribution of particles. The EDX studies confirmed the stoichiometric chemical composition of Zn, O and Co in the samples.

References:

[1]. A. Raidou, M. Aggour, A. Qachaou, L. Laanab, M. Fahoume, "Preparation and characterisation of ZnO thin films deposited by SILAR Method", M. J. Condensed Matter 12 (2010) 125.

[2]. T. A. Vijayan, R. Chandramohan, S. Valanarasu, J. Thirumalai, S. Venkateswaran, T. Mahalingam, S. R. Srikumar, "Optimization of growth conditions of ZnO nano thin films by chemical double dip technique", Sci. Technol. Adv. Mater. 9 (2008) 5.

[3]. M. Bedir, M. Oztas, A. N. Yazici, E. V. Kafadar, "Characterization of undoped and Cu-doped ZnO thin films deposited on glass substrates by spray cytolysis", Chin. Phys. Lett. 23 (2006) 939.

[4]. T. Dietl, H. Ohno, F. Matsukura, J. Cibert, D. Ferrand, "Zener Model Description of Ferromagnetism in Zinc-Blende Magnetic Semiconductors", Science 287 (2000) 1019.

[5]. Y. W. Heo, M. P. Ivill, K. Ip, D. P. Norton, S. J. Pearton, J. G. Kelly, R. Rairigh, A. F. Hebard, T. Steiner, "Effects of High-Dose Mn Implantation into ZnO Grown on Sapphire", Appl. Phys. Lett. 84 (2004) 2299.

[6]. S. Kolesnik, B. Dabrowski, J. Mais, "Structural and Magnetic Properties of Transition Metal Substituted ZnO", J. Appl. Phys. 95 (2004) 2582.

[7]. L. Yan, C. K. Ong, X. S. Rao, "Magnetic Order in Co-doped and (Mn, Co) Codoped ZnO Thin Films by Pulsed Laser Deposition", J. Appl. Phys. 96 (2004) 508.

[8]. M. S. Moreno, T. Kasama, R. E. Dunin Borkowski, D. Cooper, P. A. Midgley, L. B. Steren, S. Duhalde, M. F. Vignolo, "Local Study of the Magnetism of Co-doped ZnO Thin Films", J. Phys. D: Appl. Phys. 39 (2006) 1739.

[9]. L. H. Hoang, N. T. Khoi, N. H. Hai, W. Pacuski, I. Yang, "Magneto-Optical Properties of ZnO:Co Nanocrystalline Film", J. Kor. Phys. Soc., 52 (2008) 1621.

[10]. H. S. Hsu, C. P. Lin, H. Chou, J. C. A. Huang, "Room Temperature Anomalous Hall Effect in Co Doped ZnO Thin Films in the Semiconductor Regime", Appl. Phys. Let. 93 (2008) 142507.

[11]. M. Fonin, G. Mayer, E. Biegger, N. Janben, M. Beyer, T. Thomay, R. Bratschitsch, Y. S. Dedkov, U. R¨udiger, "Defect Induced Ferromagnetism in Co-doped ZnO Thin Films", J. Phys. Conf. Ser. 100 (2008) 042034.

[12]. S. Gautam, P. Thakur, K. H. Chae, G. S. Chang, M. Subramanain, R. Jayavel and K. Asokan, "Electronic Structure of Co-doped ZnO Thin Films by X-ray Absorption and Emission Spectroscopy", J. Kor. Phys. Soc. 55 (2009) 167.

[13]. A. A. Yousif, N. F. Habubi and A. A. Haidar, "Nanostructure Zinc Oxide with Cobalt Dopant by PLD for Gas Sensor Applications", J. Nano Elec. Phys. 4 (2012) 02007.

[14]. W. D. Song, M. H. Hong, T. Osipowicz, D. Y. Dai, S. I. Pang, Y. Z. Peng, J. F. Chong, C.W. An, Y. F. Liew, T. C. Chong, "Laser Synthesis of New Materials", Appl. Phys. A 79 (2004) 1349.

[15]. Y. Z. Peng, W. D. Song, C. W. An, J. J. Qiu, J. F. Chong, B. C. Lim, M. H. Hong, T. Liew, T. C. Chong, "Room Temperature Diluted Magnetic Semiconductor Synthesized by Dual Beam Laser Deposition", Appl. Phys. A, 80 (2005) 565.

[16]. F. Lianghuan, L. Jun, Z. Xinmin, C. Yaping, "Band offset, persistent photoconductivity and Temperature dependence of conductivity in c-Si: H/a-Si: H multilayers", Super lattice Microstruct. 13 (1992) 87.

[17]. G. K. Padam, S. U. M. Rao, "Preparation and characterization of chemically deposited CuInS2 thin films", Sol. Ener. Mater, 13 (1986) 297.

[18]. F. Bouaichia, H. Saidi, A. Attaf, M. Othmane, N. Lehraki, M. Nouadji, M. Poulain, S. Benramache, "The synthesis and characterization of sprayed ZnO thin films: As a function of solution molarity", Main Group Chem. 15 (2015) 57.

[19]. V. K. Sharma, M. Najim, A. K. Srivastava, G. D. Varma, "Structural and magnetic studies on transition metal (Mn, Co) doped ZnO nanoparticles", J. Magn. Magn. Mater. 324 (2012) 683.

[20]. S. Muthukumaran, R. Gopalkrishnan, "Structural, FTIR and photoluminescence studies of Cu doped ZnO nanopowders by co-precipitation method", Opt. Mater. 34 (2012) 1946.

[21]. S. Singhal, J. Kaur, Namgyal, R. Sharma, "Cu-Doped ZnO Nanoparticles: Synthesis, Structural and Electrical Properties", Physica B, 407 (2012) 1223.

[22]. S. Chakraborti, S. Sarwar, P.Chakrabarti, "The Effect of the Binding of ZnO Nanoparticle on the Structure and Stability of α-Lactalbumin: A Comparative Study", J. Phys. Chem. B 117 (2013) 13397.

[23]. S. Zhang, F. Hu, J. He, W. Cheng, Q. Liu, Y. Jiang, Z. Pan, W. Yan, Z. Sun, S. Wei, "Interplay between Occupation Sites of (Co, Cu) Codopants and Crystal Orientation of ZnO Matrix", J. Phys. Chem. C 117 (2013) 24913.

[24]. Y. W. Chen, Y. C. Lui, S. X. Lu, C. S. Xu, C. L. Shao, C. Wang, J. Y. Zhang, Y. M. Lu, D. Z. Shen, X. W. Fan, Optical properties of ZnO and ZnO:In nanorods assembled by sol-gel method**,** J. Chem. Phys. 123 (2005) 134701.

[25]. P. Li, S. Wang, J. Li, Y. Wei, "Structural and optical properties of Co-doped ZnO nanocrystallites prepared by a one-step solution route", J. Lumin. 132 (2012) 220.

[26]. A. A. Letailleur, S. Y. Grachev, E. Barthel, E. Sondergard, K. Nomenyo, C. Couteau, S. M. Murtry, G. Lerondel, E. Charlet, E. Peter, "High efficiency white luminescence of alumina doped ZnO", J. Lumin. 131 (2011) 2646.

[27]. S. Mahamuni, K. Borgohain, B. S. Bendre, "Spectroscopic and structural characterization of Electrochemically grown ZnO quantum dots," J. Appl. Phys. 85 (1999) 2861.

[28]. P. S. Xu, Y. M. Sun, C. S. Shi, F. Q .Xu, H. B. Pan, "Native point defect states in ZnO", Chinese Phys. Lett. 18 (2001) 1252.

[29]. D. Wu, Z. Huang. G. Yin, Y. Yao, X. Liao, D. Han, X. Huang, Preparation, structure and properties of Mn-doped ZnO rod arrays", J. Gu, Cryst. .Eng. Comm. 12 (2010) 192.