



Study of structural, optical and photoconductivity in ZnO nanoparticles codoped with Mg and Cd

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ABSTRACT

ZnO codoped with Mg and Cd in various proportions were prepared by chemical method and annealed at 600 C. The structural and optical properties of these oxide samples were systematically studied by XRD, SEM, EDS and PL spectrometer. XRD pattern shows a hexagonal wurtzite structure. The size of particle as shown by XRD machine and calculated by Scherer's formula are found in the nano range. The formation of particles showed that they were polycrystalline. Due to large ionic and covalent radii of Cadmium than those of Zinc a lattice deformation occurs with development of strain field. New phases were observed in XRD pattern of few samples. SEM micrograph show the formation of nanoparticles. EDS study confirm the codoping of ZnO with Mg and Cd. Optical properties like photoluminescence emission showed a blue shift in peak wavelength. General conductivity and photoconductivity was found high in sample containing certain proportion of Mg and Cd in comparison with pure ZnO.

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KEYWORDS

Codoping of ZnO with Mg and Cd;
Preparation of nanoparticles by chemical method;
XRD;
SEM;
EDS;
Photoluminescence emission;
Photoconductivity.

INTRODUCTION

Zinc Oxide has attracted a lot of research interest due to its enormous potential for application in a variety of optoelectronic and electronic device. The main advantages of ZnO for optoelectronic applications are its large exciton binding energy [60 meV], wide band gap energy of 3.2 eV at room temperature and the existence of well developed bulk and epitaxial growth processes. ZnO can be prepared by easy and cheap chemical method. It is nonpoisonous so can be used widely. ZnO thin films are used as transparent electrodes in photo-

voltaic cell in place of expensive Indium Tin Oxide^[1]. ZnO nanowires have also been investigated as gas sensors^[2,3]. ZnO is suitable for UV detection by using its photoconduction properties^[3]. ZnO normally forms in the hexagonal (wurtzite) crystal structure with $a=3.25$ Å and $c=5.12$ Å. The Zn atoms are tetrahedrally coordinated to four O atoms where the d-electrons of Zn hybridize with the p-electrons of O. Layers occupied by Zinc atoms alternate with layers occupied by Oxygen atoms. Presence of free electrons in undoped ZnO has been attributed to Zn interstitials and Oxygen vacancies^[4]. The intrinsic defect levels that lead to n-type

doping lie approximately 0.01 to 0.05 eV below the conduction band. The photoluminescence study of ZnO reflect the intrinsic direct bandgap, a strongly bound exciton state and the gap states due to point defects^[4]. Visible emissions in violet blue, green and red orange range in case of ZnO are due to transitions between self activated centers formed by doubly ionized Zinc Vacancy and an ionized interstitial Zn⁺, Oxygen vacancies, donor acceptor pair recombination involving an impurity acceptor^[4].

For the fabrication of optoelectronic devices, knowledge about the properties of impurities like donors, acceptor and isoelectronic impurities, is of essential interest. It is known that isoelectronic traps can enhance the efficiency of the radiative recombination of electrons and holes^[5]. Isoelectronic properties are generated by substituting a host atom by an atom from the same column of the periodic table. The binding mechanism can be described as a consequence of the lattice deformation due to atomic size difference between impurity and host atom. The replacement of host atom on cation site has been reported in many journals. Preparation and characterization of alloys like (Zn-Mg-Cd)O are important for band gap engineering, as p-n junction applications and creating a new combinations to form a substance of modified optical properties. Electrical conduction has been found to increase for higher concentration of Cd in ZnO^[8,9]. Covalent radii of Zn, Mg and Cd are 122, 141 and 144 pm respectively. Similarly ionic radii of Zn, Mg and Cd are 88, 86 and 109 pm respectively^[4]. Mg and Cd having larger radii can set in place of Zn in ZnO lattice structure with few deformation. Few work have been done on the doping ZnO with Cadmium but work on codoping ZnO with Mg and Cd has not been done. Our effort is to find certain proportion of dopant like Mg and Cd in ZnO which will increase the conductive behavior.

EXPERIMENTAL

The chemical route is simple and economical for preparing high quality nanomaterial like Zinc Oxide. Zinc Oxide nano particle can be prepared by treating Zinc Sulphate or Zinc Nitrate with Sodium Hydroxide in aqueous solution and then heating the white precipitate [Zinc Hydroxide] at a temperature greater than 100 C.

All chemicals used were of high purity taken from Merc India Ltd. To prepare pure Zinc Oxide nanomaterial Zinc Nitrate and Sodium Hydroxide were taken in stoichiometric ratio in aqueous solution and stirred for 12 hours. The white precipitate was washed with deionized water 8 times so that only Zinc Hydroxide precipitate remained. It was then dried at 100°C for 2 hours. Dried samples were annealed at 600 C for half an hour. Next for doping with Mg and Cd, their nitrates were mixed with Zinc Nitrate in the ratio such that the number of atoms of Zn and those of [Mg and Cd] were in the ratio of 90:10. The amount of Mg and Cd were varied to obtain samples containing the number of Mg and Cd in [0,10], [2,8], [4,6], [6,4], [8,2], [10,0] percent ratios. The percentage of Mg and Cd can be expressed by equation as Zn_{0.9}Mg_xCd_{0.1-x}O, where x = 0, 0.02, 0.04, 0.06, 0.08 and 0.1. Each sample was dried and then annealed at 600C. The XRD patterns of these samples were obtained by Rigaku Miniflex 2 X-ray Diffractometer with Cu K α x-radiation of wavelength 1.5406 Angstrom. Morphological study of one sample [ZnO-7.3] of this series was done by SEM at accelerating voltage of 10 kV and magnification of 30k and 70k. The detection of presence of doped element and base element was studied by EDS. Photoluminescence spectra of all samples were studied with excitation wavelengths of 254 nm by help of Fluorescence spectrometer [Perkin Elmer LS 55]. The photoconduction studies was done by pressing ZnO nanopowders on self designed inter digital electrode (figure 1) and covering it with glass cavity and illuminating it with visible light from general 100 W bulb kept at two heights such that the illuminance at the sample are 40 Lx, 332 Lx, and 1640 Lx respectively. The effective area of cross section (A) and effective length between two electrodes (L) for the calculation of resistivity were taken as [2.4 x

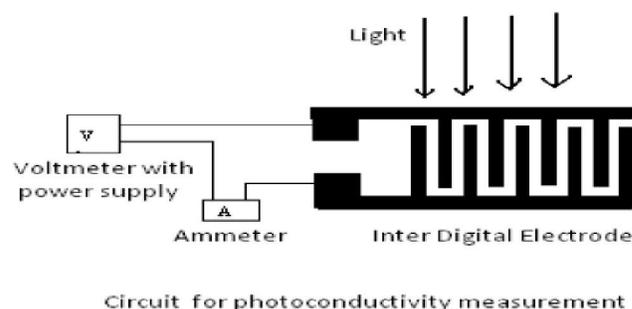


Figure 1

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0.15 x 7 + 3.6 x 0.5 = 4.32 cm²] and 0.15 cm respectively by measuring the dimension of electrode.

RESULTS AND DISCUSSIONS

The ZnO samples containing different proportion

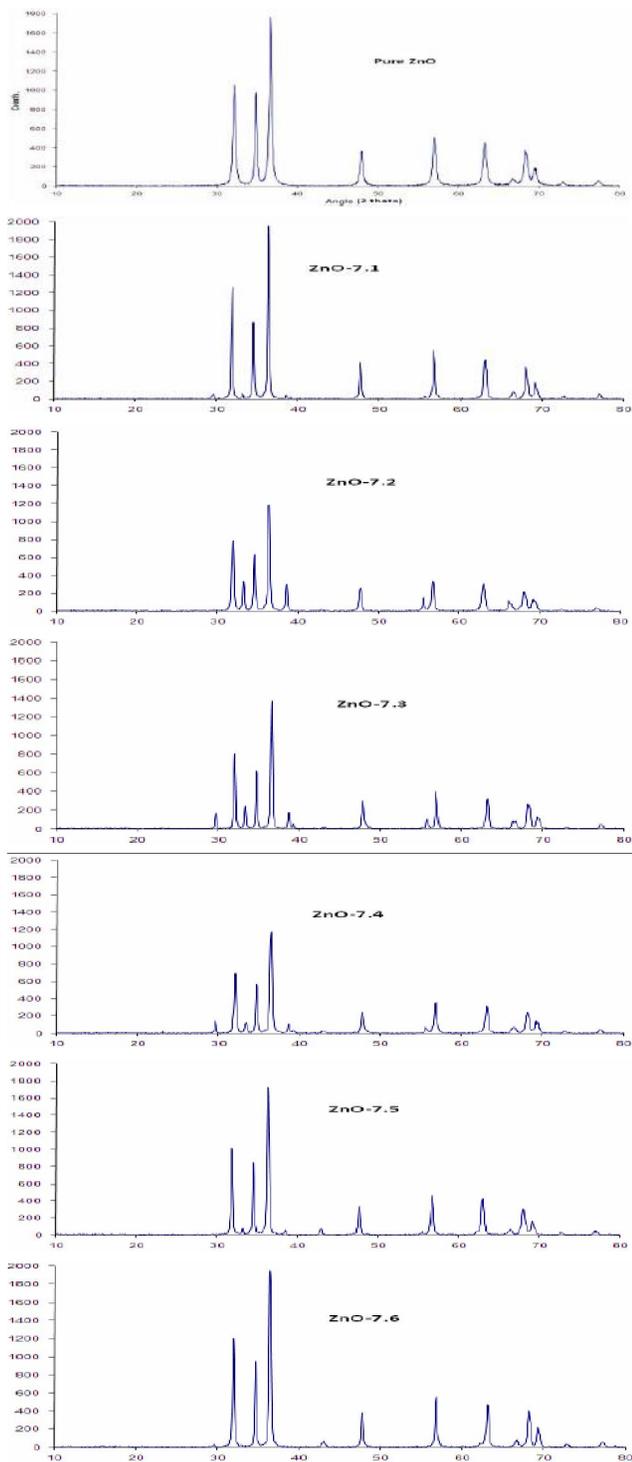
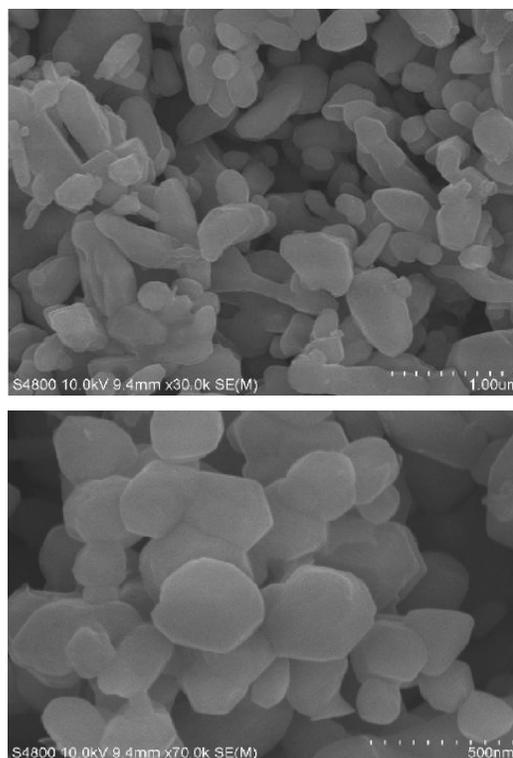


Figure 2

of Ca and Cd are coded as given below. $Zn_{0.9}Mg_{0.1}Cd_{0.01}O$:- ZnO - 7.1, $Zn_{0.9}Mg_{0.02}Cd_{0.08}O$:- ZnO - 7.2, $Zn_{0.9}Mg_{0.04}Cd_{0.06}O$:- ZnO - 7.3, $Zn_{0.9}Mg_{0.06}Cd_{0.04}O$:- ZnO - 7.4, $Zn_{0.9}Mg_{0.08}Cd_{0.02}O$:- ZnO - 7.5, $Zn_{0.9}Mg_{0.1}Cd_{0.0}O$:- ZnO - 7.6

XRD patterns (figure 2) of Pure Zinc Oxide showed that formation was polycrystalline. The doping of ZnO with Mg and Cd such that the number of doped atoms are upto 10% of the number of Zn atoms form the new substance. They have the same phases as that of ZnO except the formation of few new phases in sample number 7.2, 7.3 and 7.4 representing the presence of Cd and Mg. The size of nanoparticle was in the range of 20 nm to 50 nm. The peaks were found in basically 8 directions [100, 002, 101, 102, 110, 103, 112, 201] among which prominent peak was in third i.e. [101] direction. The distance between two planes of crystal and the size of nanoparticles were calculated by Rigaku software and by Scherrer equation, $\{D=0.9\lambda/\beta\cos\theta\}$ where D is the size of crystal, λ is the wavelength of X-ray 1.5406 Angstrom, β is the full width at half of maximum [FWHM] and θ is the angle of diffraction. The XRD pattern of all samples ZnO pure, ZnO-7.1, ZnO-7.2, ZnO-7.3, ZnO-7.4, ZnO-7.5 and ZnO-7.6 as



SEM micrograph of $Zn_{0.9}Mg_{0.04}Cd_{0.06}O$ [ZnO - 7.3]

Figure 3

found are shown below in order.

SEM micrograph (figure 3) shows that ZnO powder was with small grain of size in nanorange. The SEM study of samples were done one year after its preparation so the size of grain was increased comparing to that found by XRD machine which was smaller than 50 nm at the time of preparation. The structure of grain was like flat stones. The picture is given below.

The atomic percentage of all elements as studied by help of EDS of $Zn_{0.9}Mg_{0.04}Cd_{0.06}O$ [ZnO - 7.3] are as follows.

	O	Zn	Cd
Atomic percentage	60.2 %	37.16 %	2.64 %

EDS study confirm the presence of doped element Cd in ZnO. The amount of doped elements Cd are found less than the actual amount intended to dope in ZnO. The presence of Mg was also not seen. This may be due to inhomogeneity of sample.

The spectrum (figure 4) obtained by EDS study of $Zn_{0.9}Mg_{0.04}Cd_{0.06}O$ [ZnO - 7.3] is given below.

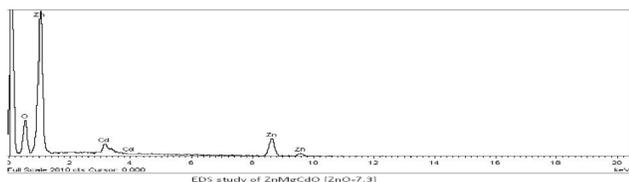


Figure 4

PL measurement of doped Zinc Oxide was done at excitation wavelength 254 nm. The following figure 5 represent the PL spectra of doped Zinc Oxide at excitation wavelength of 254 nm at room temperature. There are five sharp peaks in case of pure ZnO and three peaks in case of doped samples at room temperature. The exciton emission [in UV range] is found in case of pure and doped ZnO but peaks are not found. The first

peak in case of Pure ZnO is at 414 nm while in case of doped are from 413.5-417 nm [Violet range]. The second peak is found in case of pure ZnO at 429 nm but those are absent in doped ZnO. Third peaks are in 481-483 nm [Blue range] while for pure ZnO is 491.5 nm, fourth peaks are in 526-528 nm [Green range] while for pure ZnO 534.5 nm. Third and fourth peaks are little blue shifted due to more electrons contributed by the dopant and fifth peak is only in case of pure ZnO at 616-620 nm [Red range]. The radiation in visible range are due to recombination between point defects and oxygen vacancies. The intensities of peak are not in certain order because the number of defects depend on the amount of oxygen present in the atmosphere during annealing of samples.

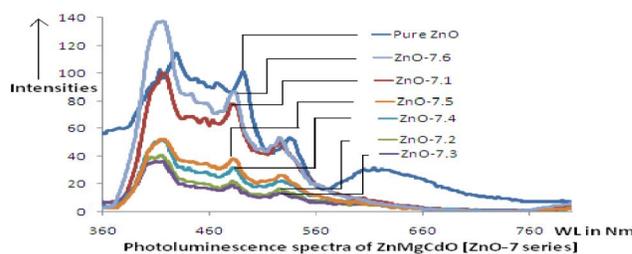
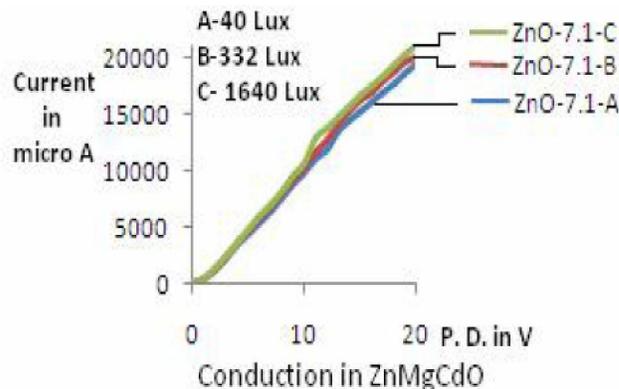
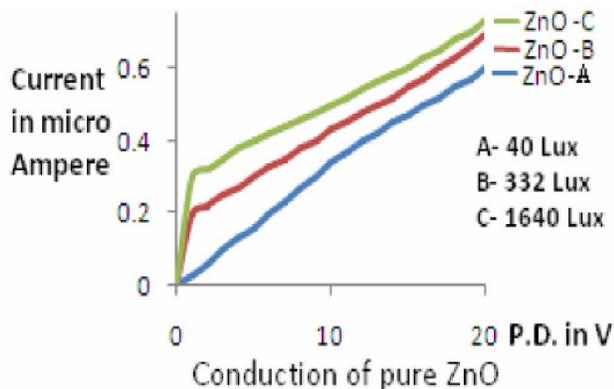


Figure 5

The study of photoconduction reveal that pure and doped ZnO are photosensitive. The amount of current increases as the light intensity falling on the sample surface is increased. The sample illuminated with light intensities 40 Lx, 332 Lx, and 1640 Lx are coded as A, B, and C respectively. The amount of current is very low in case of pure ZnO i.e less than 0.6 μA . The amount of current is enormously high in case of the sample ZnO-7.1 and in which amount of Cd is 10% and current is not uniformly increasing or decreasing according to the amount of Cd and Mg changes. The observed resistance and resistivity of all samples are given in the table



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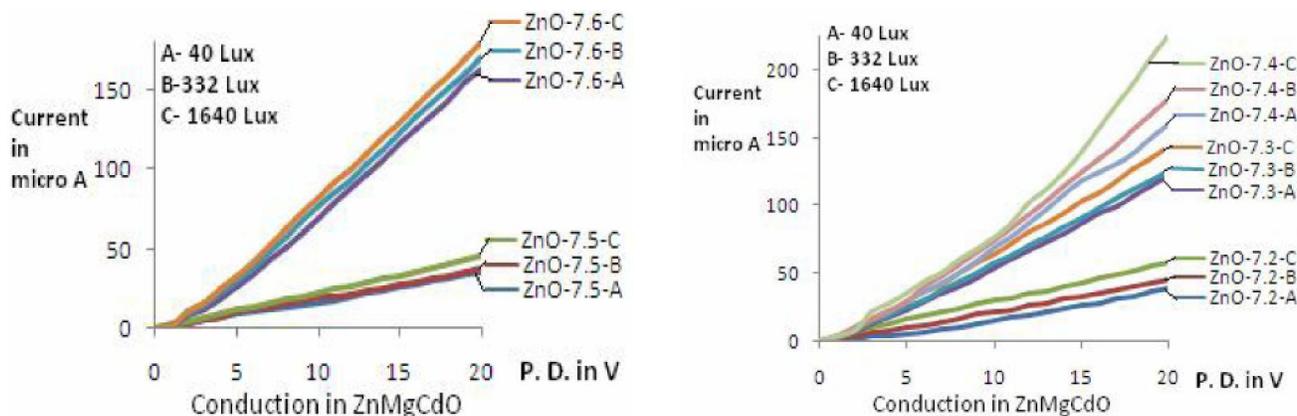


Figure 6

given before conclusion. The least resistivity of doped ZnO [i.e. $Zn_{0.9}Mg_0Cd_{0.1}O$] was found to be $2.984256 \times 10^{-2} \Omega\text{-Cm}$ which is very small in comparison with that of undoped ZnO [i.e. $976.27118 \Omega\text{-Cm}$]. The least resistivity is still higher than that of doped ZnO found by other researcher. This is due to the less compact-

ness of powder in comparison to that of film. The current [in μA] versus potential difference [in V] graph at different light intensities are shown below (figure 6).

The data of particle size, interplanar distance, average resistance and initial rate of decay of current can be tabulated as shown below.

Sample name	Particle size in [101] direction in (nm)	Interplanar distance [d] in Angstrom	Average resistance ($\Delta V/\Delta I$) in $M\Omega$	Resistivity ($\rho = RA/L$) in $\Omega\text{-Cm}$	Initial rate of decay of current in $\mu\text{A/S}$
Pure ZnO	26	2.4590	33.898305	976.271184	0
ZnO-7.1	41.1	2.4704	0.0010362	0.02984256	0
ZnO-7.2	33.5	2.4694	0.5025125	14.4723600	0
ZnO-7.3	41.4	2.4617	0.1640689	4.72518432	0
ZnO-7.4	29.6	2.4628	0.1250000	3.60000000	0
ZnO-7.5	35.5	2.4731	0.5649717	16.2711850	0
ZnO-7.6	37.7	2.4650	0.1226994	3.53374272	0

CONCLUSION

ZnO was doped successfully by very simple chemical method. XRD pattern shows its high crystallinity. New phases were obtained in few samples ZnO-7.2, ZnO-7.3, ZnO-7.4. The SEM micrograph shows the formation of nanoparticles of ZnO. EDS study shows the success of doping ZnO with Cd. PL study shows a little blue shift in the blue and green range emission due to codoping with Mg and Cd. Photoconductive study reveal that doping ZnO with both Mg and Cd increase its conductivity. For the sample ZnO-7.1 in which amount of Mg is 0% and that of Cd is 10% the conductance is very high. As the amount of Cd increases and that of Mg decreases the conductance fluctuate i.e. increase and decrease showing that certain proportion of Mg and Cd in ZnO high resistance and certain for low resistance.

REFERENCES

- [1] U.Ozgur, Ya.I.Alivov, C.Liu, A.Teke, M.A.Reshchikov, S.Dogan, V.Avrutin, S.J.Cho and H.Morkoç; A comprehensive review of ZnO materials and devices Journal of Applied Physics, **98**, 041301 (2005).
- [2] Zhong Lin Wang; Zinc oxide nanostructures: growth, properties and Applications J.Phys.: Condens. Matter, **16**, R829–R858 (2004).
- [3] Parmanand Sharma, K.Sreenivas; Analysis of ultraviolet photoconductivity in ZnO films prepared by unbalanced magnetron sputtering Journal of Applied Physics, **93**, 71 April (2003).
- [4] D.Banerjee, J.Y.Lao, D.Z.Wang, J.Y.Huang, D.Steeves, B.Kimball, Z.F.Ren; Synthesis and photoluminescence studies on ZnO nanowires Institute of Physics Publishing, Nanotechnology, **15**,

- 404–409 (2004).
- [5] Th.Agne, M.Dietrich, J.Hamann, S.Lany, H.Wolf, Th.Wichert; Optical properties of the isoelectronic trap Hg in ZnO Applied Physics Letters, **82**, 20 May (2003).
- [6] M.Godlewski; Zinc oxide for electronic, photovoltaic and optoelectronic applications, Low Temperature Physics, **37**, 3 March (2011).
- [7] S.Vijaylaxmi, S.Venkatraj, R.Jayavel; Characterization of cadmium doped zinc oxide (Cd : ZnO) thin films prepared by spray pyrolysis method, J.Phys. D:Applied Physics, **41**, 245403 (7pp) (2008).
- [8] H.Tabet-Derraz, N.Benramdane, D.Nacer, A.Bouzidi; Investigations on Zn_xCd_{1-x} thin films obtained by spray pyrolysis ELSEVIER, **73**, 249-259 (2002).
- [9] R.Vinodkumar, K.J.Lethy, P.R.Arunkumar, Renju R.Krishnan, N.Venugopalan Pillai, V.P.Mahadevan Pillai, Reji Philip, Effect of cadmium oxide incorporation on the microstructural and optical properties of pulsed laser deposited nanostructured zinc oxide thin films, Material Chemistry and Physics, **121**, 406-413 (2010).
- [10] Huang Wen-jun, Vincent JI; Strain and stress analysis on Zn multicrystal film by XRD method' Science Direct, **16**, s735-s738 (2006).
- [11] Zhong Lin Wang; Zinc oxide nanostructures: growth, properties and Applications' Institute of Physics Publishing, Journal of Physics, Condensed Matter, **16**, R829–R858 (2004).
- [12] J.H.He, P.H.Chang, C.Y.Chen, K.T.Tsai; Electrical and optoelectronic characterization of a ZnO nanowire contacted by focused-ion-beam-deposited Pt IOP PUBLISHING N, Nanotechnology, **20**, 135701 (5pp) (2009).
- [13] Harish Kumar Yadav, K.Sreenivas, Vinay Gupta; Persistent Photoconductivity due to trapping of induced charges in Sn/ZnO thin film based UV photodetector Applied Physics Letters, **96**, 223507 (2010).
- [14] Nicola R.S.Farley, Christofer R.Staddon; Lixia Zhao, A. Kevin, W.Edmonds, a Bryan L. Gallagera and Duncan H.Gregory, Sol-gel formation of ordered nanostructured doped ZnO films, Journal of Material Chemistry, (2004).
- [15] M.A.De-Wei, Y.E.Zhi-Zhen, Huang Jing-Yun, Zhao Bing-Hui, Wan Shou, Sun Xue-Hao, Wang Zhan-Guo; Structural and Optical Characterization of $Zn_{1-x}Cd_xO$ Thin Films Deposited by dc Reactive Magnetron Sputtering, Chin.Phys.Lett., **20(6)**, 942 (2003).
- [16] M.K.Yadav, M.Ghosh, Ranjit Biswas, Arup K.Raychaudhuri, Abhijit Mookerjee; Band-gap variation in Mg- and Cd-doped ZnO nanostructures and molecular clusters Physical Review, 2007, B, **76**, 195450 (2007).
- [17] K.A.Idriss, H.Sedaira, S.S.Ahmed; Determination of strontium and simultaneous determination of strontium oxide, magnesium oxide and calcium oxide content of Portland cement by derivative ratio spectrophotometry' Elsevier, Talanta, **78**, 81–87 (2009).
- [18] Niu Jie-xin, Chen Qiu-rong, Xu Nai-xin, Wei Zhongling; Effect of combinative addition of strontium and rare earth elements on corrosion resistance of AZ91D magnesium alloy Science Direct, Nonferrous Metal Society of China, **18**, 1058-1064 (2008).