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Effects of CD Doping on Structural, Optical and Photoconductive Properties of ZnO Nano Particles

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Abstract: ***ZnO nanoparticles were doped with Cd in various proportions 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 polycrystaline. Two new peaks were observed in XRD pattern of a few samples. The height of new peaks was increasing with the increase of amount of Cd in ZnO. SEM micrograph confirm the formation of nanoparticle and EDS study shows the success of doping ZnO with Cd. Optical properties like photoluminescence emission showed a blueshift in peak wavelength. General conductivity and photoconductivity was found increasing as the amount of Cd was increasing.***

Keywords: Cd doped ZnO nanoparticles, Chemical method, XRD, SEM, EDS, PL and Photoconductivity.

1. Introduction

Zinc Oxide has attracted a lot of research interest due to its enormous potential for application in a variety of optoelectronic 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 [1]. ZnO can be prepared by easy and cheap chemical method. It is nonpoisonous so can be used widely. ZnO normally forms in the hexagonal (wurtzite) crystal structure with a=3.25 A and c=5.12 A [2]. 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 band gap, 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. An overview of theoretical models describing the binding of excitons to isoelectronic impurities has been given by Zhang [5]. The replacement of host atom on cation site has been reported in many journals. Preparation and characterization of alloys like (Zn-Cd)O are important for 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 [7,8, 9]. Covalent radii of Zn and Cd are 122 and 144 pm respectively. Similarly ionic radii of Zn and Cd are 88 and 109 pm respectively [4]. Cd having larger radii can set in place of Zn in ZnO lattice structure with few deformations. ZnO and CdO both are used as transparent conducting oxides [6], their alloys will have modified properties.

2. Objective of Research

A number of results have been reported on doping ZnO with dopant such as Cadmium (Vijaylaxmi et al., 2008: Tabet-Derraz et al., 2002: Vinodkumar et al., 2010) [7,8,9] but no work is reported so far to the best of our knowledge on doping of ZnO with Cadmium from 0 % to 10 % by chemical method and to study its photoconductive and photoluminescence properties. Our effort is to find certain proportion of dopant like Cd in ZnO nanopowder which will increase substantially the conducting behavior of ZnO and enhance other properties.

3. Experimental

3.1 Synthesis

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 [10]. 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^{o}c for 2 hours. Dried samples were annealed at 600 C for half an hour. Next for doping with Cd, its nitrates was mixed with Zinc Nitrate in the ratio such that the number of atoms of Zn and that of Cd was in the ratio of 90:10, 92:8, 94:6, 96:4, and 98:2 . The percentage of Cd can be expressed by equation as $Zn_{1-x}Cd_xO$, where x = 0, 0.02, 0.04, 0.06, 0.08 and 0.1. Each sample was dried and then annealed at 600 C.

3.2 Sample Details

Table 3.1

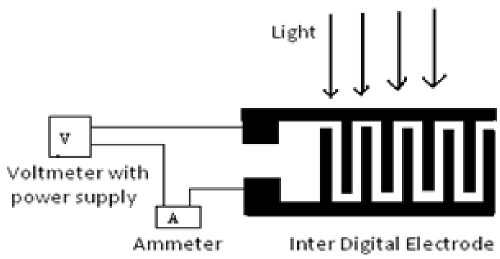
Sample name	*Chemical formula*	*Percentage ratio of Zn & Cd atoms*
ZnO-4.1	Zn_1Cd_0O	100:0
ZnO-4.2	$Zn_{0.98}Cd_{0.02}O$	98:2
ZnO-4.3	$Zn_{0.96}Cd_{0.04}O$	96:4
ZnO-4.4	$Zn_{0.94}Cd_{0.06}O$	94:6
ZnO-4.5	$Zn_{0.92}Cd_{0.08}O$	92:8
ZnO-4.6	$Zn_{0.9}Cd_{0.1}O$	90:10

3.3 Characterization

The XRD patterns of these samples were obtained by Rigaku Miniflex 2 X-ray Diffractometer with Cu Kα x-radiation of wavelength 1.5406 Angstron. Morphological study of one sample [ZnO-4.6] of this series was done by SEM at accelerating voltage of 10 kV and magnification of 50k and 80k. The detection and 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].

3.4 Photoconductive Studies

The photoconductive studies was done by pressing ZnO nanopowders on self designed inter digital electrode 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 were 40 Lx, 332 Lx, and 1640 Lx respectively [figure-3.1]. 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 0.15 x 7 + 3.6 x 0.5 = 4.32 cm^2] and 0.15 cm respectively by measuring the dimension of elctrode .



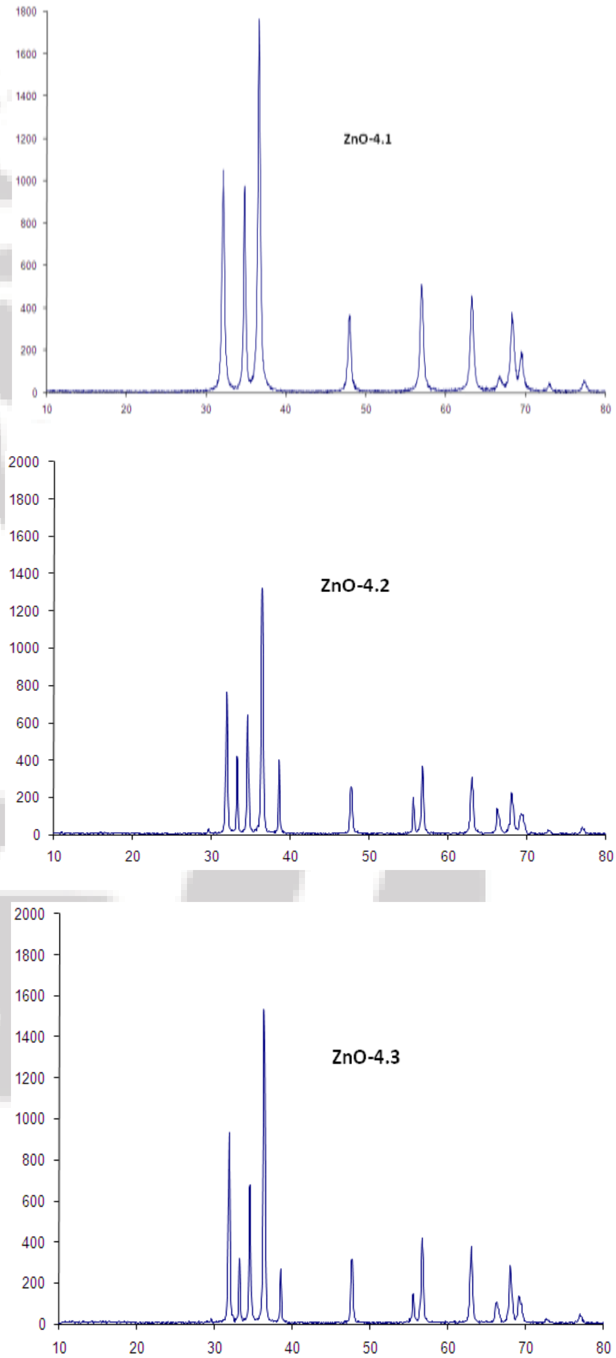
Circuit for photoconductivity measurement

Figure 3.1

4. Results and Discussions

4.1 XRD Results

XRD patterns of Pure Zinc Oxide showed that formation was polycrystalline. The doping of ZnO with Cd such that the numbers of doped atoms are upto 10% of the number of Zn atoms forms the new substance. There are formation of few new phases in sample ZnO-4.2, ZnO-4.3 and ZnO-4.4. The height of two new peaks decreases as the amount of Cd increases. 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 Angstron, 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 i.e. ZnO-4.1, ZnO-4.2, ZnO-4.3, ZnO-4.4, ZnO-4.5 and ZnO-4.6 as found are shown below in order [figure-4.1].



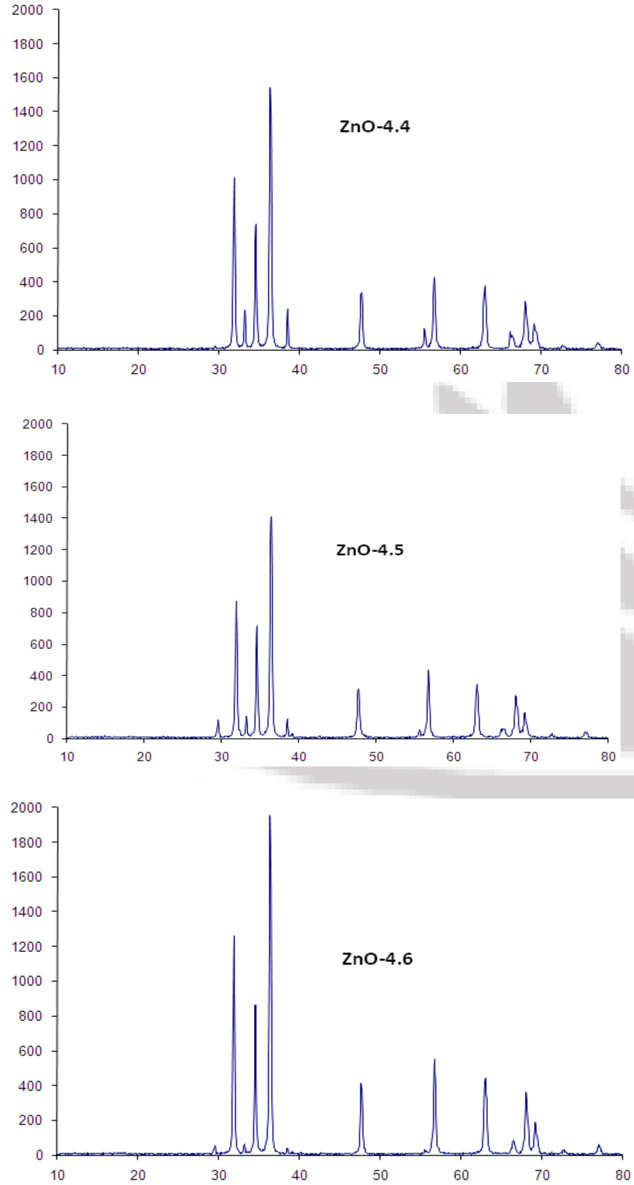
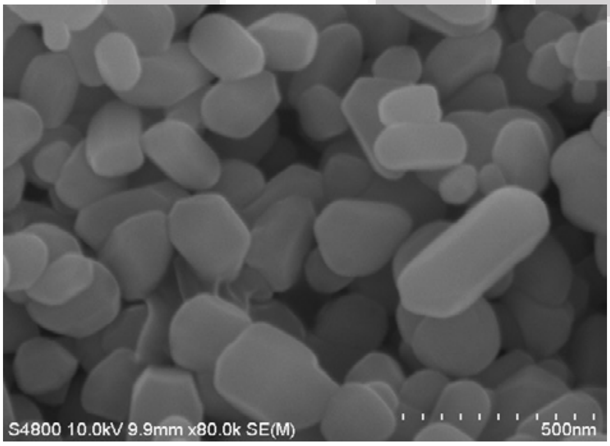


Figure 4.1

4.2 SEM and EDS analysis

SEM micrograph shows that ZnO powder was with small grain of size in micrometer range showing that each grain was made of hundreds of small crystallites in nanometer range. The structure of grain was like hexagonal flat stones. The picture is given below [figure-4.2].



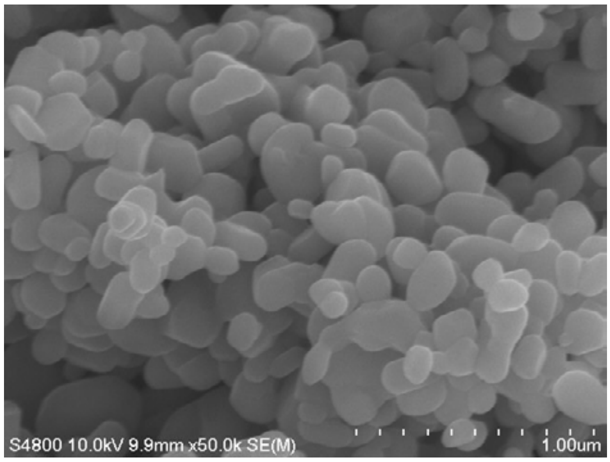


Figure 4.2

SEM micrograph of $Zn_{0.9}Cd_{0.1}O$ [ZnO - 4.6]

The spectrum obtained by EDS study of $Zn_{0.9}Cd_{0.1}O$ [ZnO - 4.6] is given below [figure-4.3].

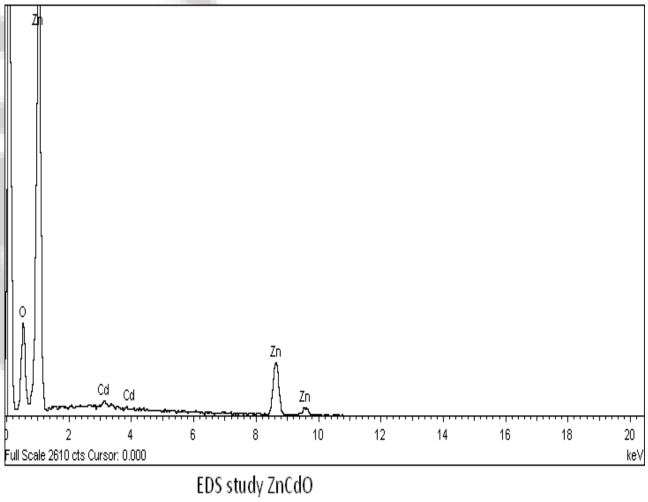


Figure 4.3

The atomic percentage of all elements as studied by help of EDS of Zn0.9Cd0.1O [ZnO - 4.6] are as follows [Table-4.1].

Table 4.1

	O	Zn	Cd
Atomic percentage	53.7 %	45.7 %	0.73 %

EDS study confirms the presence of doped element Cd in ZnO. The amount of doped elements Cd is found less than the actual amount intended to dope in ZnO. This may be due to inhomogeneity of sample. No impurity was found. The amount of Oxygen atoms in our samples is found more than 50 % shows the samples are rich in Oxygen. The site of Zn and Cd may be replaced by Oxygen.

4.3 Photoluminescence studies

PL measurement of doped Zinc Oxide was done at excitation wavelength 254 nm. The following figure-4.4 represents 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 sharp peaks in case of Cd doped samples at room temperature. The exciton emission [in UV range] is found in case of pure and doped ZnO [380 nm to 385.5 nm] but without peak. The first peak in case of Pure ZnO is at 414 nm while in case of doped are from 413-418 nm [Violet range]. The second peak is only in case of pure ZnO at 429 nm. Third peaks are in 480.5-482.5 nm [Blue range] blue shifted from 491.5 nm for pure ZnO, fourth peaks are in 525-528.5 nm [Green range] blue shifted from 534.5 nm due to more electrons contributed by the dopant . Fifth peak is only in case of pure ZnO at 614 nm [Red range]. The radiations 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 depends on the amount of oxygen present in the atmosphere during annealing of samples.

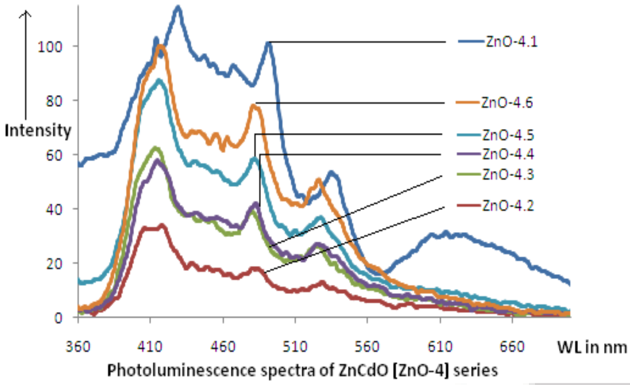


Figure-4.4

4.4 Photoconductive studies

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 high in case of doped ZnO i.e. more than 0.7 µA for pure ZnO and goes up to 3500 µA. The amount of current is enormously high in case of the sample ZnO-4.5 and ZnO-4.6 i.e. it goes up to 20 mA. The certain proportion of Cd i.e. [more than 8%] in ZnO shows very high presence of charge carriers causing large current. This result is in agreement with the fact that doping with Cd increase the conductivity of ZnO [8,9]. The least resistivity of doped ZnO [i.e. $Zn_{0.9}Cd_{0.1}O$] was found to be 2.98425 x 10^{-2} Ω-Cm which is very small in comparison with that of pure ZnO [i.e. 976.27118 Ω-Cm]. The least resistivity is still higher than that of doped ZnO found by other researcher. This is due to the less compactness of powder in comparison to that of film. The graphs of current [in µA] verses potential difference [in V] at different light intensities are shown below [figure-4.5].

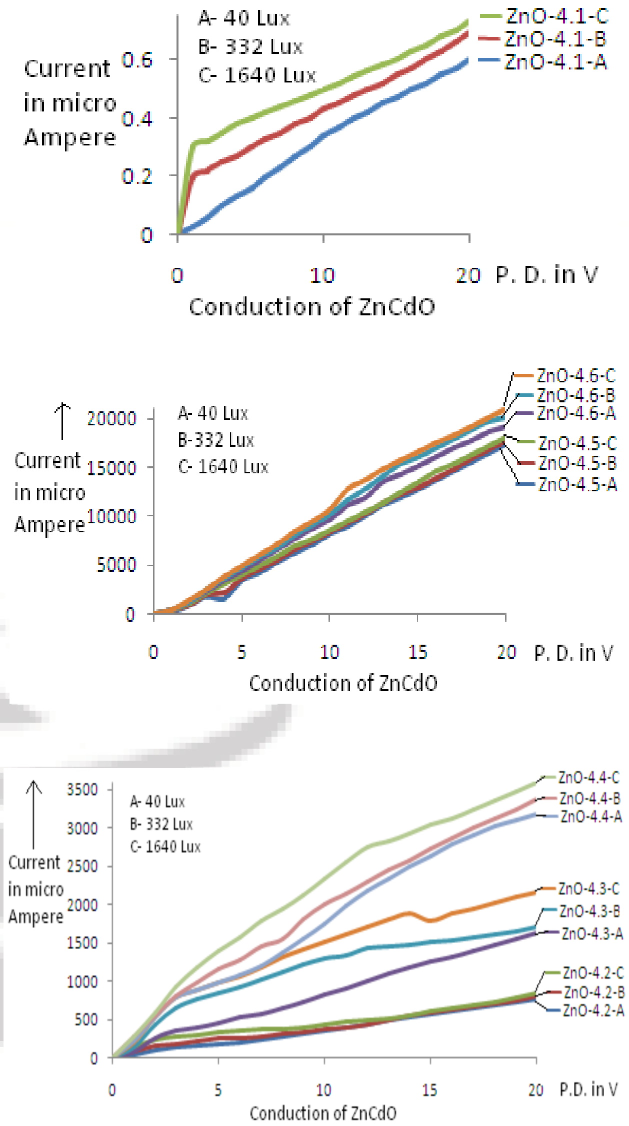


Figure 4.5

4.5 Summary of observed data

The data of particle size, interplanar distance , average resistance and resistivity can be tabulated as shown below [table-4.2].

Table-4.2

Sample name	*Particle size in [101] direction in (nm)*	*Interplanar distance [d] in Angstrom*	*Average resistance (ΔV/ΔI) in MΩ*	*Resistivity (ρ = RA/L) in Ω-Cm*
ZnO-4.1	25.5	2.4545	33.333333	976.27118
ZnO-4.2	37.3	2.4678	0.0261438	0.7529184
ZnO-4.3	36.9	2.4715	0.0122324	0.3522931
ZnO-4.4	35.1	2.4707	0.0062893	0.1811318
ZnO-4.5	32.7	2.4688	0.0011494	0.0331027
ZnO-4.6	41.1	2.4704	0.0010362	0.0298425

5. Conclusion

ZnO was doped successfully by very simple chemical method. XRD pattern shows its high crystalinity. Two new peaks are found in case of ZnO-4.2, ZnO-4.3, ZnO-4.4, ZnO-4.5 and ZnO-4.6. The height of new peaks decreases as the amount of Cd increases. The SEM micrograph shows the formation of nanoparticles of ZnO. EDS study shows the success of doping ZnO with Cd. EDS study also showed that the samples were rich in Oxygen. PL study shows blue shift of few peaks for Cd doped ZnO. Photoconductive study reveal that conductivity of ZnO nanopowder increases as the amount of Cd doping in ZnO increase. This result is in agreement with the result of other [7,8,9].

References

[1] U. Ozgur, Ya. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Dogan, V. Avrutin, S.J. Cho and H. Morkoçd, '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' Institute of Physics Publishing, Journal of Physics, Condensed Matter, 16 (2004) R829–R858.
[3] Parmanand Sharmaa) and K. Sreenivas, 'Analysis of ultraviolet photoconductivity in ZnO films prepared by unbalanced magnetron sputtering' Journal of Applied Physics, Volume 93, Number 71, April 2003.
[4] D Banerjee, J Y Lao, D Z Wang, J Y Huang, D Steeves, B Kimball and Z F Ren, 'Synthesis and photoluminescence studies on ZnO nanowires' Institute of Physics Publishing, Nanotechnology 15 (2004) 404–409 .
[5] Th. Agne, M.Dietrich, J.Hamann, S.Lany, H.Wolf and Th. Wichert, 'Optical properties of the isoelectronic trap Hg in ZnO' Applied Physics Letters Vol.-82, N.-20, May 2003.
[6] M. Godlewski, 'Zinc oxide for electronic, photovoltaic and optoelectronic applications,' Low Temperature Physics, Volume 37, Number 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(2008)245403(7pp).
[8] H. Tabet-Derraz, N, Benramdane, D. Nacer, A. Bouzidi, Investigations on $Zn_xCd_{1-x}O$thin films obtained by spray pyrolysis' ELSEVIER, 73 (2002), 249-259.
[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 (2010) 406-413.
[10] N. Daneshvar, S. Aber, M. S. Seyed Dorraji, A. R. Khataee, and M. H. Rasoulifard, 'Preparation and Investigation of Photocatalytic Properties of ZnO Nanocrystals: Effect of Operational Parameters and Kinetic Study' PROCEEDINGS OF WORLD ACADEMY OF SCIENCE, ENGINEERING AND TECHNOLOGY VOLUME 23 AUGUST 2007.
[11] MA De-Wei, YE 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. Vol. 20, No. 6 (2003) 942.

Authors Profile

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