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Structural, Optical and Magnetic Properties of Co Doped ZnO Thin Films

P.Thamaraiselvan[1], M.Venkatachalam[2], M.Saroja[2], P.Gowthaman[2], S.Ravikumar[3] S.Shankar[4]

[1]Department of Electronics &Comm, Selvamm Arts & Science College, Namakkal, India
[2]Thin film Centre, Erode Arts and Science College, Erode, India.
[3]Department of Electronics, Sengunthar Arts and Science College, Tiruchengode, India.

Abstract : The Co doped ZnO thin films were deposited on glass substrates by dip coating method. Characterization techniques of XRD, SEM, UV-visible spectra measurements and VSM were performed to investigate the structural, optical and magnetic properties. ZnO thin films were prepared with three different growth time of 3, 4 and 5 hours at 90°C. Cobalt (Co) was doped with the prepared ZnO thin film in three different growth layer concentrations (0.01, 0.02 and 0.03mol). In magnetic studies as cobalt concentration are increase and ferromagnetic behavior increase.

Key Words - ZnO thin film, Dip coating, VSM, Ferromagnetism and Cobalt.

Introduction

Cobalt is a transition metal, one of several elements found in rows 4 through 7 between groups 2 and 13 in the periodic table. The periodic table is a chart that shows how chemical elements are related to each other. Cobalt is located between iron and nickel and shares many chemical and physical properties with these two elements. Cobalt is a hard, gray metal that looks much like iron and nickel. It is ductile, but only moderately malleable. Cobalt is one of the three naturally occurring magnetic metals. The other two are iron and nickel. The magnetic properties of cobalt are even more obvious in alloys. An alloy is made by melting and mixing two or more metals. The mixture has properties different from those of the individual metals.

The melting point of cobalt metal is 1493°C (2719°F) and the boiling point is about 3100°C (5600°F). The density is 8.9 grams per cubic centimeter. Cobalt is a moderately reactive element. It combines slowly with oxygen in the air, but does not catch fire and burn unless it is in a powder form. It reacts with most acids to produce hydrogen gas. It does not react with water at room temperature. Another application of cobalt alloys is in the production of cemented carbides. In metallurgy, cementation is the process by which one metal is covered with a fine coating of a second metal. Cementation is used to make very hard, strong alloys, such as those used in drilling tools and dies.

The cobalt doped with some ceramics, films for improving their magnetic properties [1]. It is doped with suitable materials and then it will be used in fuel cells. Cobalt is doped with iron for improving their gas sensing applications [2].

Various dopants such as Co, Al, Mn, in and Ge can be doped with ZnO to get high quality doped samples. The dopants are added in order to improve the optical, magnetic and electrical properties of ZnO films. In case of ZnO with different dopant the orientation and morphology are modified either by thermal treatment or by the concentration variation and the type of dopants [3]. Cobalt nano-particles are of interest because of their unique optical, electronic and magnetic properties. They have an excellent chemical stability, therefore it is a promising choice for high density magnetic recording, bio-molecule separation, biomedical drug delivery, catalysis, magnetic resonance imaging, biocompatible magnetic nano-particles for magneto-optical devices [4].

In particular, [5] reported Curie temperatures above 300K for Co-doped ZnO, a key issue is the origin of magnetism. For Co-doped ZnO, there is some evidence that the observed ferromagnetism may be due to Co precipitates instead of carrier-mediated exchange in the ZnO matrix [6]. If the ferromagnetism reflects the formation of a dilute magnetic semiconductor, then it provides an excellent material system for investigating semiconductor-based spintronic device concepts. If the magnetic properties originate from Co nano precipitates, there may be opportunities to exploit these, particularly if the orientations of the hard and easy magnetic axes can be tailored as in the case of Co nanoparticles formed in single-crystal [7-10].

Transition metal doped ZnO is a promising candidate material for the field of spin-electronics. Spin-electronics (or spintronic) is based on concepts that utilize the quantum mechanical spin properties of carriers in addition to the carrier charge in realizing electronic functionality [11, 12]. Carrier spins are used to transport, store and process information in novel ways, providing both enhanced performance and new functionalities in traditional microelectronic devices. In recent years, most researches in material sciences have been focusing on semiconductor materials with wide band gap [13]. Dilute magnetic semiconductors (DMS)-semiconductors doped with a few percent of magnetic atoms are being actively investigated in the development of spintronic devices. The magnetic properties of DMS are intimately coupled to the carrier concentration and carrier type within the material through the s–d and p–d exchange integrals. This is beneficial in that as it allows external control over the magnetic properties by electronically or optically manipulating by the carriers in the DMS. ZnO is an interesting direct wide band gap semiconductor that is being explored for numerous applications [14], the motivation for studying semiconducting oxides [15, 16]. In recent years, a wide range of nanosized material have been synthesized to engineer desired properties such as chemical, electrical, mechanical and optical properties [17]. The present study gives experimental results of the structural, morphological, optical and magnetic properties of cobalt doped ZnO nanorods.

Experimental Technique

The seed and growth layer were prepared using sol-gel dip coating method. From literature It has also been observed that sol -gel method has several advantages because of low temperature (<100°C) processing, cheap, environment- friendly etc. Scientists synthesized ZnO Nanoparticles by solgel process [18]. The Co doped ZnO thin films were grown on ZnO seed coated glass substrates by hydrothermal technique. The magnetic property of the co doped ZnO was further characterized using VSM.

Hydrothermal technique

All chemicals applied were analytical grade and supplied by Merck Co.Ltd. ZnO growth layer was prepared by adding 10 ml of de-ionized water, 0.11gms of Zinc Nitrate $Zn(NO_3)_2$ and 0.56gms of hexamethylenetetramine $(CH_2)_6 N_4)$ are mixed well by magnetic stirrer for 1 hour. 0.01, 0.02 and 0.03 mol of Cobalt (Co) was added with 10ml of de - ionized water separately and stirred for 1 hour. The chemical composition was given in table1.

Table 1.Chemical composition of ZnO growth layer solution with Cobalt dopant.

Chemical Name	Chemical formula	Mole required	Material taken
Zinc Nitrate	$Zn(NO_3)_2$	0.02 mol	0.118988 grams
Hexamethylenetetramine	$(CH_2)_6 N_4$	0.2 mol	0.56076 grams
De-ionized water	H_2O	---	10 ml
Cobalt acetate	Co	0.01mol	0.049816 grams
		0.02mol	0.0996 grams
		0.03mol	0.14944 grams

ZnO growth layer solution (10 ml) was individually mixed into cobalt acetate solution and stirred for 2 hours. In the growth process the above solution was taken in a beaker with seed coated substrates and heated in hot air oven at 100°C for 5 hours. Which we optimized in the preparation of un doped ZnO nanorods. At the end of the growth period, the substrates were removed from the solution and immediately rinsed with de-ionized water to remove the residuals from the surface and dried in air at room temperature. Then the above films were annealed in muffle furnace at 500°C for 1 hour. The crystal structure and morphology of Co doped ZnO nanorods were investigated by X-ray diffraction (XRD) and Scanning Electron Microscope (SEM).The absorbance spectra have been recorded using a spectrophotometer JASCO V-570. The magnetic properties were studied using VSM.

Characterization of ZnO Nanorods with Cobalt

The structural surface morphology and Optical characterization of the thin films were carried out by XRD, Scanning Electron Microscope with EDX, UV–Vis spectrophotometer and magnetic properties of the Co doped ZnO thin films were measured using Vibrating Sample Magnetometer (VSM).

Results and Discussion

Structural Properties

XRD Analysis

The crystalline phase, arrangements of crystal atoms and structural characteristics of the ZnO thin films have been studied using X-ray Diffraction (XRD) with Cu-kα radiation with wavelength (λ)=1.54 Å. The data has been taken in 2θ, ranging from 20 to 40 degree. XRD patterns of the Cobalt doped ZnO with three different molar concentrations of 0.01,0.02 and 0.03 mol ware shown in figure 1.

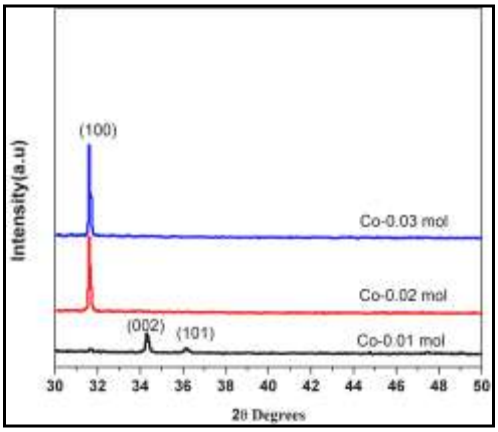


Figure 1.XRD patterns of cobalt doped ZnO thin films

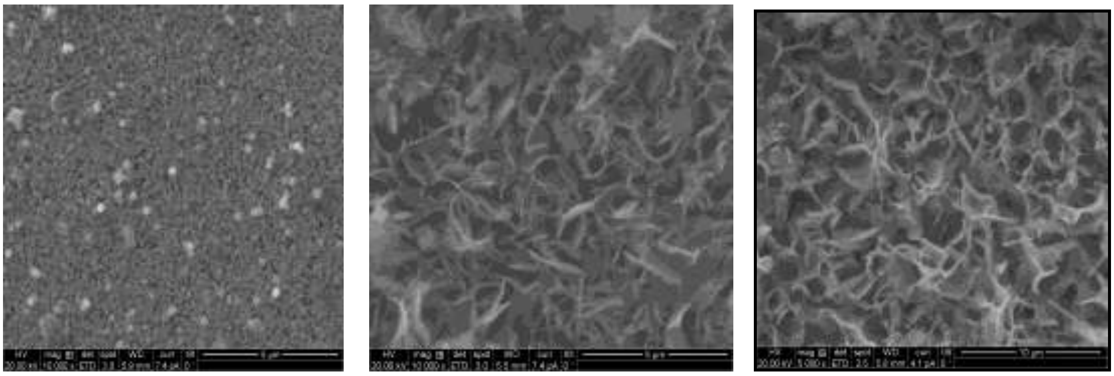
The result show three peaks corresponding to (100) (002) and (101) planes, as hexagonal quartzite structure ZnO with matches with the JCPDS card no (036-1451). From the XRD patterns it is clearly seen that, as the concentration of Cobalt increases from 0.01 to 0.03 mol the diffraction peaks were oriented strongly along the (100) peak. In 0.01 mol cobalt concentration, all three peaks (100), (002) and (101) were very low. As concentration increases from 0.01 to 0.02 mol, (101) and (002) peaks were suppressed and (100) peak appeared strong. As again cobalt concentration increased to 0.03 mol, only (100) peak is shown and it is very strong [19]. This is shown in fig.1. As the concentration of cobalt increases the development of crystal structure is not haphazard, it strongly relies on doping concentration and decreases in (002) peak and increase in (001) peak which indicates structural deformation [20].

Morphological Studies

Scanning Electron Microscopy (SEM)

The surface morphological studies of Co doped with ZnO films have been carried out using a scanning electron microscope. Figure 2 (a), (b) and (c) shows the SEM images of the Co doped ZnO films. SEM images of the ZnO incorporation with Co changed the surface morphology to a wrinkled network. As

Co concentration was increases, the morphology of the film changed to a network and this is in good agreement with the literature [21]. From the above SEM results the 0.01mol doped ZnO film shows better formation when compared to the 0.02 and 0.03 mol Co doped ZnO films. In all the doped ZnO films, the hexagonal wurtzite structure nanorods were suppressed and the structures of the nanorods were changed according to the dopant concentration. This is in good agreement with the obtained XRD results



a b c

Figure 2. (a) 0.01 mol Co (b) 0.02 mol Co and (c) 0.03 mol Co SEM spectrum of cobalt doped ZnO

Energy Dispersive Analysis of X-rays (EDX)

The EDX spectroscopy was used to know the percentage of the element present in the sample. The ZnO thin films were prepared using three (0.01, 0.02 and 0.03 mol) different concentration of Co. From the obtained data of EDX 0.01 mol Co shows that the Zn, O and Co present in the thin film were 66:08:26percentages respectively[18]. The EDX results of 0.02 mol Co shows that the Zn, O and Co present in the thin film were 73:06:21 percentages, the EDX results of 0.03 mol Co shows that the Zn, O and Co present in the thin film were 36:19:45 percentages respectively (fig. 3, Table 2).

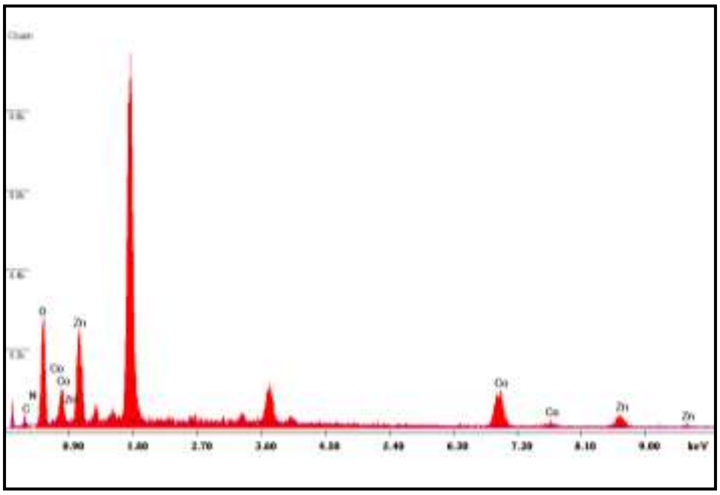


Figure 3. EDX spectrum of cobalt (0.03 mol) doped ZnO

Table 2.Data of EDX Spectrum of 0.03 mol Cobalt doped ZnO

Elem	Wt %	At %	K-Ratio	Z	A	F
C K	4.36	12.99	0.0093	1.1693	0.1832	1.0004
N K	0.00	0.00	0.0000	1.1574	0.2683	1.0012
O K	19.10	42.70	0.0945	1.1465	0.4311	1.0017
CoK	40.36	24.50	0.3999	0.9450	1.0009	1.0476
ZnK	36.18	19.80	0.3316	0.9306	0.9847	1.0000
Total	100.00	100.00				

Optical Properties

UV-Vis Absorbance and Transmittance

Figure 4 shows the absorption spectra of cobalt doped ZnO nanorods. The intensity of the optical absorption edge is very high at cobalt concentration at 0.01mol. When the concentration is increased to 0.02 mol, the intensity of the absorption has been suppressed to a very large extent. Again when the concentration of the cobalt is increased to 0.03mol, again the intensity gets decreased. From the results, as cobalt concentration is increased the intensity of the absorption gets decreased. This result is in accordance with XRD and SEM [22 - 24].

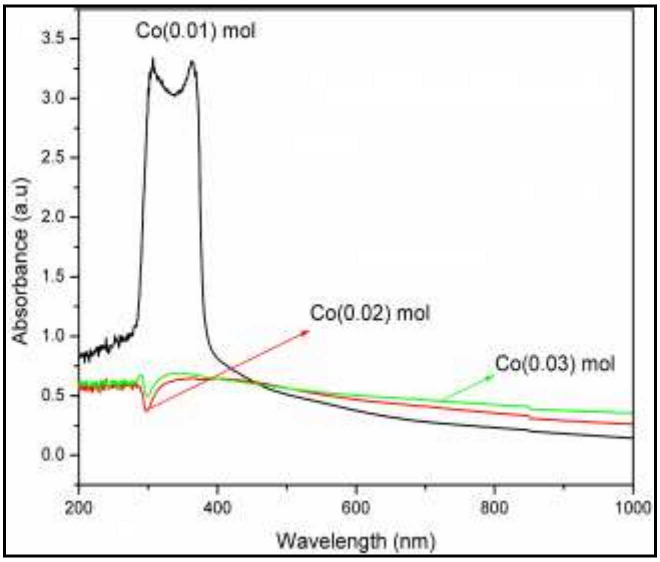


Figure 4.UV-Vis absorption spectra of Cobalt doped ZnO

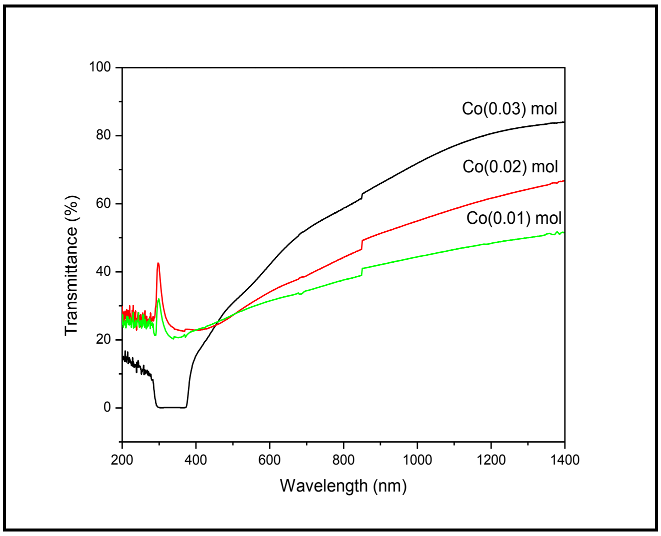


Figure 5. UV-Vis transmittance spectra of Cobalt doped ZnO

Figure 5 shows the optical transmittance spectra of samples with three different concentration of Cobalt. The transmittance spectra are in the visible range nearer to infrared wavelength region. The effect of change in the Cobalt concentration on the optical transmittance was investigated. A slight decrease in average transmission was observed with the increase of Cobalt molar concentration and was attributed to the increase of surface roughness. The optical transmittance of Cobalt doped ZnO films was found to decrease from 80%, 60% to 50% with the increase of cobalt concentration.

Magnetic Properties

Vibrating Sample Magnetometer (VSM)

All the M– H curves were obtained after subtracting the raw data from the back ground signal taken from bare silicon substrate to obtain the signal from thin films only. All the M–H curves reveal the strong dependence of magnetization on the ambient gas pressure. We can observe the typical ZnO peaks and presence of organic contents in 0.01 mol and 0.02 mol doped samples, but in 0.03 mol cobalt doped ZnO sample, some of the region of ZnO and Co bonding which again represents the presence of additional phases at higher concentration of doping.

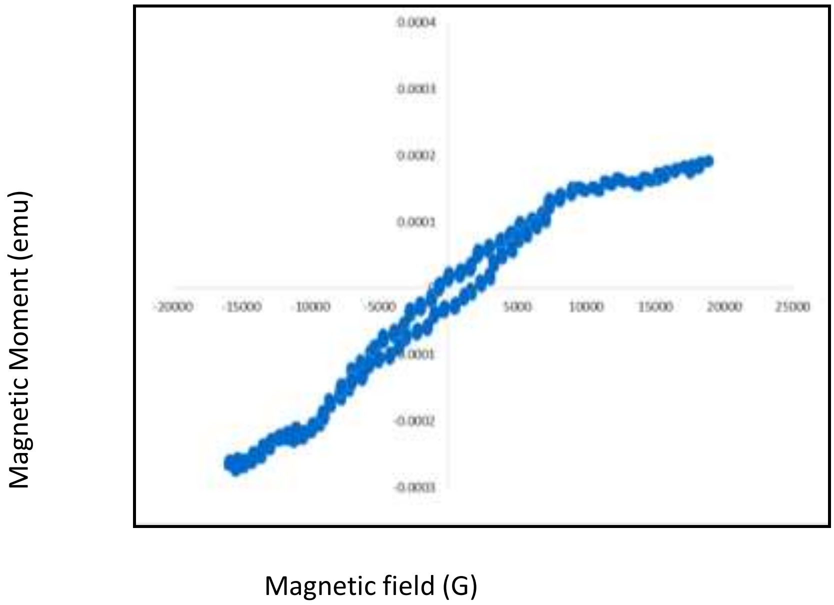


Figure 6.VSM profile of magnetic moment (emu) versus applied field (G) curve of 0.01 mol cobalt -doped ZnO

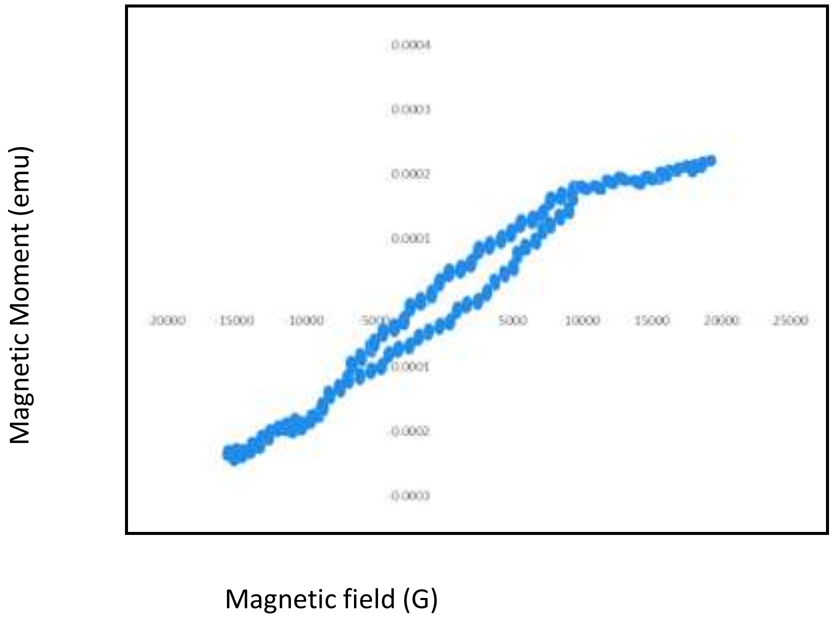


Figure 7.VSM profile of magnetic moment (emu) versus applied field (G) curve of 0.02 mol Cobalt-doped ZnO

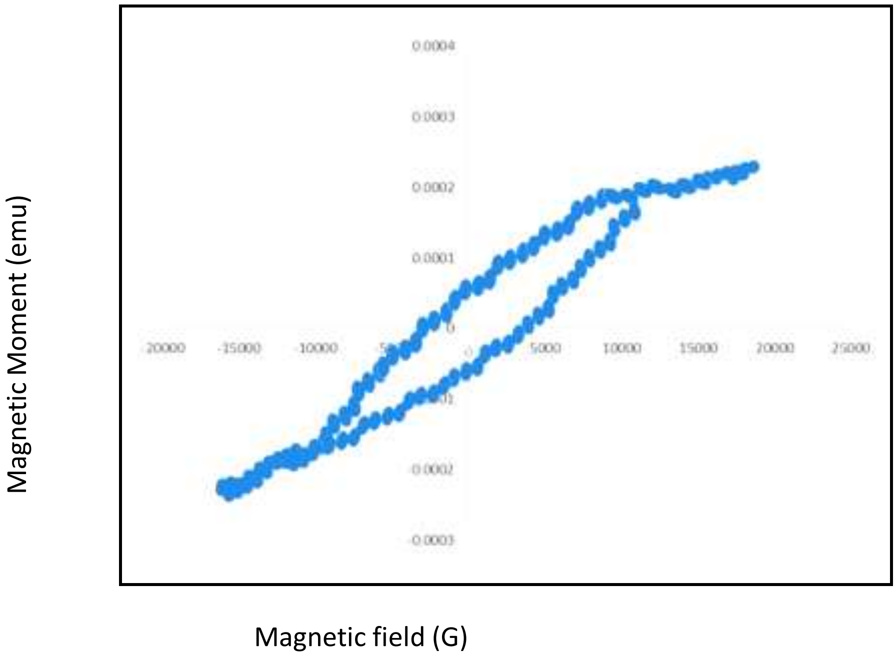


Figure 8.VSM profile of magnetic moment (emu) versus applied field (G) curve of 0.03 mol cobalt-doped ZnO.

We have done VSM analysis to observe magnetic characteristics. The given Figures 6, 7 and 8 represent VSM profiles of Co-doped ZnO sketched at room temperature. Obtained profile confirms the presence of ferromagnetic behavior at room temperature and hence a successful doping where the impurity magnetic atom has successfully replaced the atoms of host crystal lattice. Presence of magnetic behavior depicts the presence of magnetic atoms. The smaller width of loop for 0.01 mol magnetic doping shows that it is a soft magnet and 0.01 mol doped sample does not contain any cluster of atoms or segregation. So, we may deduce that presence of ferromagnetic behavior is due to intrinsic coupling between the atoms of doped materials but not due to the presence of secondary phase (segregation). We observed a proportional samples change in the shape and width of hysteresis loop, a stronger loop for 0.02 mol and 0.03 mol, as shown in Figures 7 and 8. These results were again contrasting, where some researchers observed ferromagnetic ordering at lower doping concentration but paramagnetic behavior for higher doping concentration. For iron doping, it was explained that paramagnetic behavior is due to antiferromagnetic coupling at higher doping concentration [25]. In our Cobalt-doped samples, as cobalt concentration is at 0.03 mol better ferromagnetic behavior is seen [26]. In our result, Cobalt proportional ferromagnetic strength was observed due to different electronic configurations of Cobalt and agglomeration of a little fraction of Cobalt atoms which prevents anti-ferromagnetic coupling.

Conclusion

ZnO nano rods had been successfully synthesized in a dip coating method at low growth temperature of 90°C for different growth periods and annealed at 500°C.The UV-Vis Absorption spectra also show that band gap of the grown rods decreases from 3.34 eV to 3.23 eV as growth time increases. The optical transmittance was found to decrease from 65%, 55%, to 52% with the increase of growth time. In cobalt-doped samples, a cobalt proportional ferromagnetic strength was observed due to different electronic configurations. The native point defects such as oxygen vacancies are very common in ZnO nano particles giving rise to ferromagnetic behavior.

References

1. Sakuma H, Watanabe Y, Aramaki K, Yun KS, Ishii K, Ikeda Y, and KondoH. Microstructure and magnetic properties of Co doped ZnO films deposited by gas flow sputtering, Materials Science and Engineering: B,2010, 173; 1-3, 7-10.
2. Neri G, Bonavita A, Galvagno S, Siciliano P, and Capone S. Co and NO_2 sensing properties of doped-Fe2O3 thin films prepared by LPD, Sensors and Actuators B,2002 , 82; 1, 40-47.

3. Sivakumar T,Venkatachalam M, Saroja M, Mahendran R. Characterization of the Magnetic Property of the Cobalt (Transition metal) doped with Zinc Oxide using Spin Coating Technique, Journal of NanoScience and Nano Technology (ISSN-2279-0381) 2014, 2, 1: 74 – 78.
4. Song Q, Zhang ZJ. Shape control and associated magnetic properties of spinel cobalt ferrite nanocrystals J. Amer. Chem. Soc.,2004, 126 (19), 6164.
5. Ingyu Xu, a Heidemarie Schmidt, Shengqiang Zhou, Kay Potzger, Manfred Helm, Holger Hochmuth,Michael Lorenz, ects Q Annette Setzer, Pablo Esquinazi. Room temperature ferromagnetism in ZnO films due to defects, Applied physics letter. 2008,92; 082508.
6. Ueda K, TabotaH, and Kamai T. Magnetic and electric properties of transition-metal-doped ZnO films. Appl. Phys. Lett. 2001,79; 988.
7. Lee HJ, Jeong SY, Cho CR, and CH. Study of diluted magnetic semiconductor: Co-doped ZnO, Park, Appl. Phys. Lett. 2002, 81; 4020.
8. Fitzgerald CB, Venkatesan M, Lunney JG, Dorneles LS, and Coey JMD. Cobalt-doped ZnO - a room temperature dilute magnetic semiconductor. Appl. Surf. Sci.,2005, 247(1-4);493-496.
9. Klimenkov M, von Borany J,Matz W, Eckert W, Wolf M, and KH Muller Structural and vibrational properties of Co nanoparticles formed by ion implantation, journal of applied physics Mater. Sci. Process.,2002, 74;571.
10. Sato M, Takada S, Kohiki S, Babasaki T, Deguchi H, OkuM, and Mitome M, Ferromagnetism in cobalt-implanted ZnO, Journal of applied physics. Lett. 2000, 77; 1194.
11. Wolf SA, Awschalom DD, Buhrman RA, Daughton JM, Von Molnar S, Roukes ML,Chtchelkanova AYandTreger DM.A spin-based electronics vision for the future Science. Spintronic 2001, 294;1488–95.
12. Pearton SJ, Norton DP, Frazier R, Han SY, Abernathy CR, and Zavada JM, Structure and magnetism of cobalt-doped ZnO thin film spintronic device concepts IEEE Proc. Circuits Devices Syst.2005,152; 312–22.
13. Balachander M, Saroja M, Venkatalachalam, M, Kumar V and Shankar S, Structural and Optical Properties of Zinc Sulfide Thin film prepared by sol-gel Spin Coating method, International Journal of Chemical Concepts, 2016, 02 (02) : 65-69.
14. PeartonSJ, Norton DP, Ip K, Heo YW, and T Steiner Recent progress in processing and properties of ZnO. Superlatt. Microstruct.2003,34; 3–32.
15. Jeong B S, Heo Y W, Norton D P, Kelly J G, Rairigh R, Hebard A F, Budai J D, and YD,Park,.Spatial distribution and electronic state of Coin epitaxial anatase $Co_xTi_{1-x}O_2$ thin films grown by reactive sputtering Appl. Phys. Lett.,2004,84; 2608–10.
16. Ivill M, Overberg M E, Abernathy C R, Norton D P, Hebard A F, Theodoropoulou N, and JD Budai. Properties of Mn-doped Cu_2O semiconducting thin films grown by pulsed-laser Deposition Solid-State Electronics.,2003,47; 2215–20.
17. Bari R H, Nanostructure pervoskite $ZnSnO_3$ thin films for H_2S gas sensor, International Journal of Chemical Concepts, 2015, 01(03):125-135.
18. Vanaja A, Ramaraju G V, Srinivasa Rao K, Role of NaOH concentration on Structural, Morphological and Optical Properties of ZnO Nanopowders Synthesized by Solgel process, International Journal of Techno Chem Research, 2016, 02 (02): 110-120.
19. Liu X, Shi E, Chen Z, Zhang H, Song L, Wang H and Yao S. Structural, optical and magnetic properties of Co-doped ZnO films. Journal of Crystal Growth 2006,296; 135–40.
20. Caffarena VD, Capitaneo JL: Preparation of electrodeposited cobalt nanowires. Mat. Res.,2006, 9(2); 205–208.
21. Liu XJ, Song C, Zeng F, and Pan F Donor defects enhanced ferromagnetism in Co:ZnO films. Thin Solid Films,2008, 516(23);8757-8761.
22. *M Basit, ShahN A, Ali S M and Zia A.* Cobalt Doping Effects on Zinc Oxide Transparent Conducting Thin Films, World Applied Sciences Journal., 2014, 32 (8);1664-1670.
23. NirmalaMurugesanand Anukaliani Achuthanunni, Structural and optical properties of undoped and co doped znonano structured thin films, Suranaree J. Sci. Technol., 2010, 18(1);81-88.
24. Kim KJ and Park YR. Spectroscopic ellipsometry study of optical transitions in $Zn_{1-x}Co_xO$ alloys Chromium-Doped ZnO Nanoparticles Synthesized by Co-Precipitation: Chromium Effects, Appl. Phys. Lett.2002, 81; 1420.
25. Sharma PK, RanukDK, Avinash PC: Effect of iron doping concentration on magnetic properties of ZnO nanoparticles J Magn. Magn. Mat.,2009, 321;2587–2591.

26. Muhammad Ahsan Shafique, Saqlain A Shah, Muhammad Nafees, Khalid Rasheed and Riaz Ahmad. Effect of doping concentration on absorbance, structural, and magnetic properties of cobalt-doped ZnOnano-crystallites, Shafique et al. International Nano Letters., 2012, 2;31.

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