INFLUENCE OF Fe-DOPING CONCENTRATION ON MICRO STRUCTURAL AND MAGNETIC PROPERTIES OF Fe DOPED CdS THIN FILMS

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In this investigation, the influence of Fe-doping on the structural, elemental, micro structural and magnetic properties of the films has been studied. The structural properties of the films were investigated by using the X-ray diffraction (XRD). From the XRD analysis, it was observed that the doping concentration has a significant effect on crystalline quality and grain size of the films and all the films showed single phase with hexagonal structure. The composition analysis was determined by energy dispersive spectroscopy (EDS), and all the deposited films exhibited nearly stoichiometry. Evidence of nano crystalline nature of the films was observed from the investigation of surface morphology using atomic force microscopy (AFM). The films exhibited smooth fine grainy surface. The magnetic field dependence of the magnetizations was measured by VSM. Fe doping converts diamagnetic CdS into ferromagnetic and the results showed that the Fe doped CdS thin films can be employed in the fabrication of the nanoscale magnetic devices.

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1. Introduction

During the last few years, there has been much interest is focused on dilute magnetic semiconductors (DMS). DMS are II-VI, IV-VI or III-V compounds in which fraction of nonmagnetic cations has been substituted by magnetic transition metal (TM, e.g., Fe, Mn, Cr, Co, and Ni) or rare earth metal ions. DMS can manipulate both charge and spin degrees of freedom simultaneously in a single material. The main practical application of the DMSs material is the approach of ferromagnetism above room temperature to be compatible with junction temperature. The magnetic properties of II-VI compound semiconductors doped with TM, were found to be strongly dependent on the synthesis method, the concentration of TM atom, and the sample preparation condition. Extensive research has been done on the deposition and characterization of Cadmium sulfide (CdS) based dilute magnetic semiconductor thin films due to their potential application in the area of electronic, optoelectronic, spintronic devices, magneto-optical devices such as magnetic field sensors, isolators and magneto – optical switches, field emission displays, solar cells and gas sensors. CdS is a wide band gap semiconductor extensively studied under various configurations: bulk material, thin films, nanostructures as nanowires and tetrapod nano

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crystals, etc. Fe is a good ferromagnetic material with low coercivity and high Curie temperature. [1-19]

In the present work, the role of Fe-doping concentration on the micro-structural and magnetic properties of the electron beam evaporated CdS nanocrystalline thin films was investigated.

2. Experimental

Fe doped CdS polycrystalline alloy (Cd_{1-x}Fe_xS) with x=0.05, 0.1, 0.15, and 0.2 was synthesized by solid state reaction method. Stoichiometric amounts of high purity (99.999 %) analytical grade CdS and FeS powders (Sigma-Aldrich Co., USA) were mixed by grinding for about 8 hr. The mixed powders were pressed into a disk-shape pellet. Electron beam evaporation technique was employed for growing Cd_{1-x}Fe_xS thin films with x=0.05, 0.1, 0.15, and 0.2 at the substrate temperature 200^oC using high vacuum coating unit. The growth chamber was evacuated to a base pressure of 8.0×10^{-6} mbar and a working pressure of 6.0×10^{-4} mbar. The substrate to source distance was kept at 50 mm. The films were deposited on ultrasonically cleaned amorphous glass substrates maintained at 200^oC. The electron beam intensity and energy were fixed at 20 mA and 5 KeV respectively. During the deposition of the films, the substrate holder was rotated to improve the uniformity of the films.

The crystal structure of as-deposited films was studied by X-ray diffraction (XRD). The data was collected by-step-scan modes in a θ - 2θ range between 20^{0} and 80^{0} with step-size of 0.02^{0} and step time of 0.6 s. The X-ray diffractometer was operated at 40 KV and 30 mA with Cuk α_{1} radiation of wavelength 1.5406 Å. The elemental composition of the films was analyzed by using energy dispersive spectroscopy (EDS) unit interfaced with a scanning electron microscope, SEM, operating at an accelerating voltage of 30 KV which was used to study the morphology of the films. The grain size and root mean square (RMS) surface roughness of the films were obtained by atomic force microscopy (AFM). The magnetic properties of the films were studied by using Vibrating Sample Magnetometer (VSM).

3. Results and discussion

3.1. XRD results

XRD patterns of the as deposited $Cd_{1-x}Fe_xS$ thin films with x=0.05, 0.1, 0.15, and 0.2 are shown in Fig. 1. The observed XRD patterns showed a dominant peak at $2\theta \sim 26.56^{\circ}$ corresponds to the (002) plane, which was indexed on the basis of hexagonal CdS type structure (JCPDS No.41-1049). We observe a slight systematic shift of the main peak (002) towards higher values of diffraction angle 20 by increasing Fe concentration. The peaks are for x=0.1, $2\theta \sim$ 26.58° ; x=0.15, $2\theta \sim 26.62^{\circ}$; x=0.2, $2\theta \sim 26.66^{\circ}$. It suggests that the decrease in the lattice parameters due to the fact that substitution of larger ionic radius of Cd (0.97A^o) by smaller ionic radius of Fe (0.76A^o) requires a local contraction of the lattice to accommodate the Fe ion. The shifting of the peak position also confirms that the Fe is replaced in Cd atom positions and did not form any chemical reaction with sulphur to form new compounds.



Fig.1. X-ray diffraction patterns of the $Cd_{1-x}Fe_xS$ nanocrystalline films deposited at $200^{\circ} C(a) x = 0.05$, (b) x = 0.1, (c) x = 0.15, (d) x = 0.2

The average crystallite size was calculated from the full width at half maximum (FWHM) intensity of the XRD peaks using Scherrer's relation [20]

$$D_{hkl} = \frac{k\lambda}{\beta\cos\theta} \tag{1}$$

where k is a shape factor usually ~ 0.9, λ the wavelength of the X-ray diffraction used (1.5406 A⁰), β the full width at half maximum (FWHM) of the peak which has maximum intensity and θ the Bragg's angle. These average crystallite size values are found to be in the range of 22 nm to 45 nm. These crystallite values conforms the nanocrystalline nature of the Cd_{1-x}Fe_xS films.

3.2 EDS results

The elemental chemical composition was studied by Energy Dispersive X- ray analysis (Fig.2). The obtained results did not deviate much from the composition of starting precursor alloys. The ratio of Cd: Fe: S is observed to be about 44.58 at %: 4.49 at %: 50.93 at % for films with x = 0.05 which indicated that the composition was nearly stoichiometric. For x=0.15 it is 42.90 at %: 13.02 at %: 44.08 at %. Similarly, stoichiometry of all grown films has been also observed.



Fig.2 The EDAX spectrum of the $Cd_{1-x}Fe_xS$ nanocrystalline films deposited at 200^0 C with x = 0.05

3.3 AFM results

The quantitative information on microstructure properties of the thin films was studied using AFM. The average surface grain sizes were also calculated from AFM micrographs (Fig.3). The films exhibited smooth free grainy surface. These average grain size values were found to be in the range 28nm to 55nm. The RMS surface roughness decreased from 4.20 nm to 2.53 nm with increasing Fe content from x=0.05 to x=0.2. The surface relief clearly shows roughness and granular crystalline nature is evident from the figures.



Fig.3 3D AFM images of $Cd_{1-x}Fe_xS$ nanocrystalline films for (a) x = 0.05, (b) x = 0.15

3.4 VSM results

The magnetic field dependence of the magnetizations is measured by VSM. The VSM measurement of nanocrystalline $Cd_{1-x}Fe_xS$ (x=0.1 and x=0.2) thin films grown on glass substrates at 200^oC is represented in Fig.4.



Fig.4 The plot of magnetization as a function of magnetic filed of $Cd_{1-x}Fe_xS$ nanocrystalline films for x = 0.1 and x = 0.2

The magnetization curves (M-H) of the un-doped as deposited CdS films exhibited diamagnetic behavior which is in agreement with that reported in literature [21]. The films with lower Fe doping concentration (x=0.05) exhibited a paramagnetic like characteristic measured at 300 K. With further increase in Fe content in pure CdS, the M-H curves of the films showed a clear hysteresis loops, implying ferromagnetic behavior. The observed ferromagnetic behavior could be attributed to the substitution of Fe ions (Fe³⁺) for Cd ions in the CdS lattice. By increasing the Fe content, the ferromagnetic interaction becomes stronger (shorter Fe ions distance), so the magnetization is increased. The saturation magnetization for Cd_{1-x}Fe_xS system is found to increase with doping concentration (x). It is worth noting that several groups have reported ferromagnetism at and / or above RT for DMSs, compound doped with TM [22-27]

4. Conclusions

Fe doped CdS nano crystalline films were grown by electron beam evaporation method at different Fe-doping concentration. XRD studies showed a single phase with a hexagonal structure. Fe-doping concentration has a significant effect on crystalline quality and grain size of the films. The grain size evaluated from AFM is comparable with those obtained from XRD studies. Grain size increases as Fe doping concentration increases. Fe doping converts diamagnetic CdS into ferromagnetic and these results showed that the Fe doped CdS nanocrystalline films can be employed in the fabrication of the nanoscale magnetic devices.

References

- [1] J. K. Furdyna, J. Appl. Phys. 64, R29 (1988).
- [2] Y. H. Hwang, Y. H. Um, J. K. Furdyna, Semicond. Sci. Technol, 19, 565 (2004).
- [3] H. Ohno, Science **281**, 951 (1998).
- [4] H. Ohno, J. Magn. Magn. Mater. 200, 110 (1999)
- [5] H. Munekata, H. Ohno, S. von Molnar, A. Segmuller, L.L. Chang, L. Esaki, Phys. Rev. Lett. 63, 1849 (1989).
- [6] H. Ohno, A. Shen, F. Matsukura, A. Oiwa, A. Endo, Y. Iye, Appl. Phys. Lett. 69, 363 (1996).
- [7] A. Twardowski, T. Dietl, M. Demianiuk, Solid State Commun. 48, 845 (1983).
- [8] A. Twardowski, M.V. Ortenberg, M. Demianiuk, R. Pauthenet, Solid State Commun. 51, 849 (1984).
- [9] J.K. Furdyna, N. Samarth, J. Appl. Phys. 61, 3526 (1987).
- [10] T. Mina, S. Satyam, K.J. Prafulla, Phys. B: Condens. Matter 348, 235 (2004).
- [11] T. Miura, Y. Yamamoto, S. Itaya, K. Suga, K. Kindo, T. Takenobu, Y. Iwasa, H. Hori, Phys. B: Condens. Matter 346–347, 402 (2004).
- [12] V. Zayets, M.C. Debnath, K. Ando, Appl. Phys. Lett. 84, 565 (2004).
- [13] R. Rey-de-Castro, D. Wang, X. Zheng, A. Verevkin, R. Sobolewski, M. Mikulics, R. Adam, P. Kordos, A. Mycielski, Appl. Phys. Lett. 85, 3806 (2004).
- [14] B.Y. Geng, L.D. Zhang, G.Z. Wang, T. Xie, Y.G. Zhang, G.W. Meng, Appl. Phys. Lett. 84, 2157 (2004).
- [15] Y.Q. Chang, D.B. Wang, X.H. Luo, X.Y. Luo, X.Y. Xu, X.H. Chen, L. Li, C.P. Chen, R.M. Wang, J. Xu, D.P. Yu, Appl. Phys. Lett. 83, 4020 (2003).
- [16] M. Saleem, S.M.A. Durrani, N. Saheb, M.F. Al- Kuhaili, I.A. Bakhtiari, Applied Surface Science 320, 653 (2014)
- [17] Donguk kim, Young Park, Minha Kim, Youngkwan Choi, Yong Seob Park, Jaehyoeng Lee, Materials Research Bulletin MRB 8095 (2015)
- [18] J.H. Al-Zahrani, M. El-Hagary, A. El-Taher, Materials science in Semiconductor Processing 39, 74 (2015).
- [19] M. El-Hagary and S. Soltan, J.Appl.Phys.112, 043907 (2012)
- [20] B.D. Cullity, Elements of X-ray Diffraction, second ed., Addison Wesley, London.
- [21] S. Delikanli, S. He, Y. Qin, P. Zhang, H. Zeng, H. Zhang, and M. Swihart, Appl. Phys. Lett. 93, 132501 (2008)
- [22] J. Nogues, D.Lederman, T.J. Moran, and I.K. Schuller, Phys. Rev. Lett. 76, 4624 (1996)
- [23] A. Singhal, J.Alloys Compd. **507**, 312 (2010)
- [24] X. Y. Xu and C. B. Cao, J. Alloys Compd. 501, 265 (2010)
- [25] Z. Yang, W.P. Beyermann, M. B. Katz, O.K. Ezekoye, Z. Zuo, Y. Pu, J. Shi, X. Q. Wang, X. F. Liu, J. Appl. Phys. 105, 053708 (2009)
- [26] J.Iqbal, B. Q. Wang, X. F. Liu, D.P. Yu, B. He, and H. Yu, New J. Phys. 11, 063009 (2009)
- [27] C. Y. Lin, W. H. Wang, C. S. Lee, K.W. Sun, and Y.W. Suen, Appl. Phys. Lett. 94, 151909 (2009)