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Study of the physical properties of PLD grown cobalt doped nanocrystalline $Zn_{0.9}Cd_{0.1}S$ thin films

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ABSTRACT

We report a systematic study of structural, optical, and magnetic measurements on $Zn_{0.9}Cd_{0.1}S$:yCo films in the concentration range of $0.005 \leq y \leq 0.05$ M using pulsed laser deposition technique. Structure, composition analysis, and optical measurements revealed that Cobalt is incorporated into the lattice, as Co^{2+} substituting Zn^{2+} ions, forming a solid solution with cubic structure instead of Cobalt precipitates. Low temperature magnetization measurements reveal a paramagnetic behavior. UV–vis measurements showed a red shift with respect to undoped sample in the energy band gap with increasing Cobalt concentration. Photoluminescence measurements shows ~300 times increase in intensity by Cobalt doping in $Zn_{0.9}Cd_{0.1}S$ matrix.

1. Introduction

In recent years, extensive studies have been carried out to modify the properties of zinc sulfide for different applications [1, 2]. The introduction of magnetic transition metals (TM) into nonmagnetic semiconductors provides further possibilities for the generation of diluted magnetic semiconductors (DMS) [3, 4]. Recent studies of Mn-doped ZnS nanoparticles revealed significant increase in luminescence intensity. The increase of luminescence intensity is attributed to the strong interaction of Mn^{2+} d electrons with s–p electrons of the host nanocrystalline ZnS [5-7]. The sp–d exchange interactions in Co^{2+} doped II–VI semiconductors have been found to be much larger than those in the Mn^{2+} doped counterparts [6, 7].

The interest in Zn based ternaries is also particularly concerned with increasing demand for materials useful for the production of flat panel display, high efficiency electroluminescent and field emission devices [8-10]. When deposited as thin films, these alloys give the possibility of tailoring devices showing band gap engineering [8, 11]. In semiconductors the systematic tuning of their band gap can also be controlled by alloy formation as well as the size variation. Undoped ternary semiconductors, whose bandgap is tuned as a function of their composition, were reported including $Zn_{1-x}Cd_xSe$ [12-14] and $CdSe_{1-x}Te_x$ [15]. II–VI semiconductor material, $Zn_{1-x}Cd_xS$ is also considered to be a promising host material [16-18]. Furthermore, their electronic band structure and wide range of band gap together with a low refractive index allow intense light transmission and also effective electron transport at high electric field. Nevertheless, they show a lower crystallinity, with respect to other semiconducting compounds; therefore they are highly defective and their structural properties are mainly linked to the growth processes used for thin film deposition [19]. Nicolau et al. synthesized the $Zn_{1-x}Cd_xS$ films by the successive ionic layer adsorption and reaction process [20]. The pure zincblende phase was obtained from $x = 0$ to x 0.75 and the pure wrutzite phase from x 0.75 to $x = 1$. Their results however suffer from lack of stoichiometry. Sebastian and Ocampo used the screen printing for the preparation of $Zn_{1-x}Cd_xS$ *thick films* from a paste containing CdS and $ZnCl_2$ pigments [21]. Presence of $CdCl_2$ and $ZnCl_2$ phases along with ZnS were found in the screen printed films. Ex-situ heat treatment of these films at about 500 °C transformed them into $Zn_{1-x}Cd_xS$ films. Gunasekaran and Ichimura studied the effect of precursor concentration on the growth of $Zn_{1-x}Cd_xS$ films prepared by a photochemical technique for x ranging from 0 to 1. A change in surface morphology with zinc content in the alloy was observed [22]. Their experiments with Auger electron spectroscopy (AES) indicate the presence of oxygen along with sulfur, cadmium and zinc. Structure of the films was found to be a mixed phase of $Zn_{1-x}Cd_xS$ and ZnO.

Most of the reports for the deposition of $Zn_{1-x}Cd_xS$ films involve the chemical route. The need for a post-annealing or calcination step — commonly required in most wet chemical techniques, usually leads to coarsening of particle size, and broadening of the size distribution, in addition to undesirable chemical reactions. Among the new and up to date techniques used for thin film deposition, pulsed laser deposition (PLD) is one of the most versatile methods to obtain films of several materials that can be processed into a pellet target. One of the important features of this method is based on the possibility of maintaining the stoichiometry of the ablated target in the

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deposited films [23-25]. The target ablated by laser can create a highly energetic growth precursor, leading to non equilibrium growth conditions. Therefore high quality films can be obtained at a fairly low substrate temperature. With this aim, in the current work, we have tried to investigate the effect of doping concentration on the structural, optical and magnetic properties of Co doped $Zn_{0.9}Cd_{0.1}S$ thin films.

2. Experimental

In the present work $Zn_{1-x}Cd_xS$: yCo, where mole fraction x is 0.1, films were deposited on corning 1737 glass substrates by ablating stoichiometric home-made targets using pulse laser deposition technique. Targets for laser ablation were obtained by applying uniaxial pressure (18–20 tons) on the $Zn_{0.9}Cd_{0.1}S$: yCo powders prepared by a conventional co precipitation method. Value of mole fraction ($x = 0.1$) in the target material has been controlled by taking appropriate molar amount of salts containing Cadmium and Zinc. Cobalt concentration (y) in the target material has been varied by varying the molar Cobalt concentration from 0.005, 0.01, 0.015, 0.025, and 0.05 M. Nanocrystalline thin films were deposited with a KrF excimer laser (Lambda Physik) operating at 248 nm. Substrate and target were placed in a custom designed vacuum chamber (Excel Instruments, India) and were maintained at base vacuum of 6.6×10^{-4} Pa with the aid of rotary and turbo molecular pump. The distance between the target and the substrate was maintained at 30 mm. The target was rotated at 20 rpm to preclude pit formation on the target surface and to ensure uniform ablation of the target. Pulsed laser used for ablation was set with a pulse width of 25 ns and with a repetition rate of 10 Hz. Deposition temperature, and laser energy were kept at 400 °C, and 400 mJ respectively. The value of Laser fluence was 3.33 J/cm^2 during the sample preparation.

X-ray analysis was performed by using a Bruker D8 Advance diffractometer using CuK$_\alpha$ ($\lambda = 1.54$ Å) radiation. Room temperature absorbance spectra were measured in the spectral range from 200 to 800 nm using a UV–vis-NIR spectrophotometer (Varian Cary 5000). Photoluminescence (PL) emission spectra were recorded at room temperature with a luminescence spectrometer (Perkins Elmer LS55). The particle size, morphology, and electron diffraction were determined by transmission electron microscope (FEI TECNAI-G^2). EPMA studies were carried out by using Cameca SX 100. Magnetic measurements were taken with superconducting quantum interference device (SQUID) magnetometer. (QD MPMS-XL). Thicknesses of the deposited film were measured by using surface profilometer (Ambius Technology XP 200).

3. Results and discussions

Fig. 1 shows the XRD patterns of the $Zn_{0.9}Cd_{0.1}S$: yCo nanocrystalline thin films along with the undoped sample. It can be seen that all the samples exhibited a cubic structure, which was consistent with the result reporting that ZnS exists in cubic structure at low temperature [20]. However the diffraction peak (111) shifted to a lower angle from 28.6 to 28.52° from the standard Cubic structure of ZnS [26]. This shift toward lower angle is believed to result from the incorporation of Cd ions into the ZnS lattice, and the larger ionic radius of Cd^{2+} as compared to that of Zn^{2+} (Cd^{2+}: 0.97 Å, Zn^{2+}: 0.74 Å) [27]. Grain sizes (L) of the deposited films were estimated from the full width at half maximum of the major XRD peak using the Scherrer's relation [28].

Semiconductor ternaries have been proposed to obey Vegard's law [29], revealing the linear relationship between the lattice constant and composition as follows:

$$a^0_{A_{1-x}B_xC}(x) = (1-x)a^0_{AC} + xa^0_{BC} \qquad (1)$$

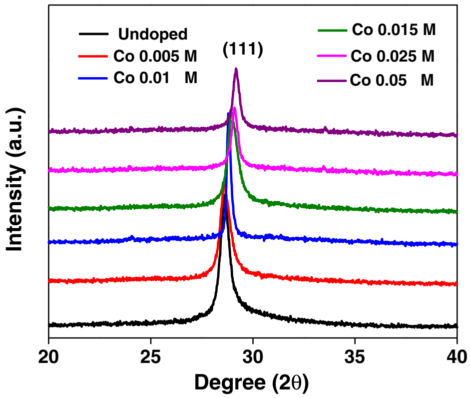

Fig. 1. X-ray diffraction patterns of $Zn_{0.9}Cd_{0.1}S$: yCo (y = 0.0, 0.005, 0.01, 0.015, 0.025, and 0.05 M) nanocrystalline thin films deposited at 400 °C.

where $a^0_{A_{1-x}BxC}$ is the natural constant of the ternary form $A_{1-x}B_xC$ and a^0_{AC} & a^0_{BC} are the natural constants of the binaries AC and BC respectively, and x is the mole fraction of binary BC. In the case of Cubic $Zn_{0.9}Cd_{0.1}S$ nanocrystalline thin films, the ideal lattice constant obtained by using Eq. (1) with x = 0.1 is 5.392 Å, where cubic $a^0_{ZnS} = 5.345$ Å (PDF # 80-0020) and $a^0_{CdS} = 5.820$ Å (PDF # 01-0647). Lattice constants have also been calculated by XRD patterns. The lattice constant for undoped sample is found as 5.404 Å, which is comparable to the lattice constant obtained by Vegard's law (5.392 Å). From Fig. 1, it can also be seen that there is a slight shift in the XRD peak position to higher angles with increase in Cobalt concentration resulting in variation in the lattice constant. In Fig. 2 we showed variation in lattice constants of $Zn_{0.9}Cd_{0.1}S$: yCo nanocrystalline films with Cobalt concentrations. From Fig. 2 it is also observed that the lattice constant of doped nanocrystalline films varies from 5.4 to 5.294 Å with Cobalt variation from 0.005 to 0.05 M. Similar dependence of the lattice constant on Cobalt concentration is also observed in the reported results [30]. Moreover, this also reflects that Co^{2+} ions were substituted without changing the cubic structure. This is quite expected as the ionic radii of the Co^{2+} (0.72 Å) in the tetrahedral coordination are nearly the same as that of Zn^{2+} site (0.74 Å) [30, 31]. As a result the unit cell parameters do not vary significantly with increase in the doping concentration.

Dislocation densities in the films have been calculated in order to investigate the effect of Cobalt incorporation on the host lattice. The

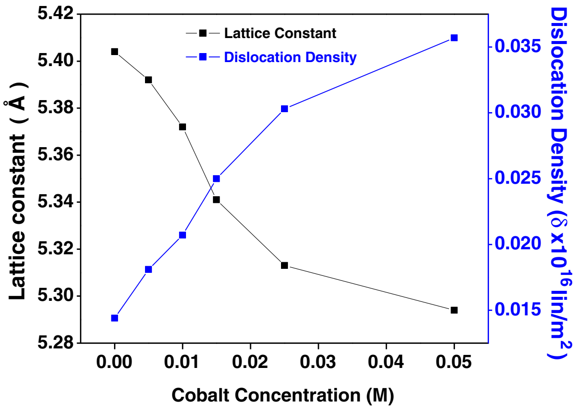

Fig. 2. Variation in lattice constant and dislocation density in $Zn_{0.9}Cd_{0.1}S$: yCo nanocrystalline films deposited at 400 °C, with Cobalt concentration (0.0, 0.005, 0.01, 0.015, 0.025, and 0.05 M).