Investigation of the room temperature ferromagnetism in transition metal doped ZnO thin films

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Abstract

In the present work, we have studied the ferromagnetic nature of the (Fe, Ni) co-doped $\text{Zn}_{1-x-y}\text{Ni}_y\text{Fe}_x\text{O}$ ($y = 0.01$ and $x = 0.01, 0.03, 0.05$) thin films fabricated through the RF magnetron sputtering on Silicon (400) substrate. Structural information of the deposited transition metal-doped ZnO thin films was studied through X-ray Diffraction (XRD) techniques. The surface roughness and average grain size of the thin films examine through Atomic Force Microscopy (AFM). The optical band gaps of the thin films have been analyzed through the UV-Vis spectroscopy and it was appropriate for the optoelectronic devices. Tau's Plots were used for the calculation of the band gap by extrapolating the $(\alpha h\nu) = 0$, the straight-line portion of the plot to zero absorption coefficient. The magnetic study of these thin films confirmed the ferromagnetic (FM) behavior. RT-FM in all the deposited thin films was discussed on the base of polaron percolation theory.

Introduction

Dilute Magnetic Semiconductor (DMS) in a nanometer size have been widely studied in the past few years, there has been particular interest in correlating their optical, magnetic and structural properties with the size and shape of the nanostructures [1, 2]. The fabrication of the DMSs thin films having room-temperature ferromagnetism (RTFM) leads to the development of multifunctional spintronic devices [3, 4]. Transition metals such as Fe, Ni-doped ZnO thin films were used scientifically in constructive optical, electronic and magnetic properties essential for spintronic materials [5]. The presence of the room temperature ferromagnetism (RTFM) behavior leads to another dimension towards the multiple applications of the material. The source of magnetism in “un-doped” and “doped” was believed to be powerfully reliant on deformities like Zn interstitials, Oxygen vacancies and other surface effects [6, 7]. The cause of presenting RT-FM in the uncontaminated and contaminated semiconductors is still ambiguous. Many reports were supporting the intrinsic magnetism in the diluted magnetic semiconductors and about the defect-induced magnetism. I. Lorite et al. [8] reported that Zn interstitials were primarily dependable for the magnetic ordering in ZnO based thin films. In contrast, a study by H. Hong et al. [9] revealed that deformity can lead to ferromagnetic behavior or the excess of oxygen could destroy the magnetic arrangements. A few years ago, ZnO based thin films were fabricated by metal-organic Chemical Vapor Deposition (CVD) technique, Pulsed Laser Deposition (PLD), Sol-Gel, Molecular Beam Epitaxial (MBE), etc. [10-12]. In the middle of these, we make use of the Radio Frequency magnetron sputtering deposition method, which has quite a few benefits such as thickness as well as surface roughness has controlled by adjusting the rate of the deposition. In this article, we have studied the room temperature ferromagnetism (RTFM) of Fe, Ni co-doped ZnO thin films by RF Magnetron sputtering, which have not reported until now.

Experiment

In the experimental part, Synthesis of Dilute Magnetic Semiconductors (DMS) thin films were same, as we have discussed in our previous article [2]. The Crystal Structure of the Dilute Magnetic

Semiconductors thin films was taken in the range of 25° - 80° through X-ray Diffractometer (XRD) (XPRT-PRO diffractometer) with Cu-K α radiation with the wavelength ($\lambda = 1.54 \text{ \AA}$). The (Perkin Elmer Lambda-750) spectrophotometer was used for the optical properties of the thin films with the range of wavelengths 200-800 nm. The NTEGRA based AFM was used for the surface roughness and surface morphology of the thin films. The Alpha Bruker model carried FTIR studies; Perkin Elmer LS 55 Fluorescence Spectrophotometer carried Photoluminescence study. A “Microsense” Vibrating Sample Magnetometer (VSM) was used for the room temperature magnetic studies with the applied magnetic field of 1 Tesla and the 14TPPMS Vibrating Sample Magnetometer performed the Low-temperature magnetic study with the applied magnetic field of 7 Tesla.

Results And Discussion

X-RAY DIFFRACTION

The X-Ray diffraction arrays of the Ni, Fe co-doped DMS thin films deposited on the Si (400) substrate having the various microscopic element of “dopant” ion $\text{Zn}_{1-x-y}\text{Ni}_y\text{Fe}_x\text{O}$ ($y=0.01$, $x=0.01$, 0.03 & 0.05) and denoted as NZF1, NZF3, NZF5 respectively [18]. The particle sizes calculated by using the Debye Scherrer method were found in the range of the 30-40 nm. The crystallite size calculated from the significant changes in the lattice constant. This indicates that the doped Fe and Ni atoms substitute Zn atoms.

The presence of all the Bragg diffraction in NZF1, NZF3 and NZF5 confirms the formation of the hexagonal wurtzite structure. The diffraction patterns of the thin film samples were diverse, this represents that the evolution of ZnO in several planes is dissimilar and the evolution is anisotropic. This shows the crystalline nature of transition metal-doped ZnO based thin films was significantly enhanced through changing the Fe ion with constant Ni concentrations. The crystalline size of all thin films has calculated by the Debye–Scherrer formula by considering the most intense peak (002) of each thin film.

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

Where k (~ 0.9) is the shape factor, λ is the x-ray wavelength of Cu K α radiation ($\lambda = 1.54059 \text{ \AA}$) , β is the full width at half maximum (FWHM) , θ is the Bragg diffraction angle of the respective diffraction peak. The larger the half-peak width, the smaller the grain size, i.e. more small grains are produced, indicating that a certain amount of Fe and Ni can inhibit the grain growth of zinc oxide thin films. Then predictable crystallite sizes were 40, 36 and 30 nm for the thin films NZF1, NZF3, and NZF5 respectively. The particle size decrease with the increase in the Fe concentration, in whole XRD pattern with the presence of the substrate peaks, marked as Si, no supplementary diffraction peaks not detected. This confirms the “doping” of Fe and Ni were not affecting the original wurtzite geometry of prepared thin films.

AFM ANALYSIS

The average grain size and surface morphology of the thin films has calculated by AFM analysis. The particles have equally distributed throughout the surface. Overall, the surfaces of all the samples were very smooth. The result shows that doping concentration plays an important role in the surface morphological nature of the thin film. One % of the Fe, Ni co-doped ZnO thin film has the largest surface roughness. The roughness of the thin films decreases, with an increase in Fe concentration. The results also confirm that the morphological variations maintained by the concentration of Fe, Ni in the film. The variations on the surface roughness were due to the decrease in grain size with a decrease in the absorbency of the films. Linhua Xu [13] reported a similar

result earlier. The large surface roughness of the thin films leads to the gas sensor for commercial applications [14]. Fig. 2 shows two-dimensional (2D) AFM surface height morphologies of Fe, Ni co-doped ZnO thin film scanning area with a dimension of $2 \times 2 \mu\text{m}^2$. The 3D replicated morphology of the thin film describe the growth along the C-axis and this result resemble with the preferred (002) plane orientation through X-ray diffraction results. In present study, the decrease in grain size also due to micro-densification effect. In that case, the number of nuclei of metal increases as an effect of increasing precursor concentration [15], which leads to the formation of a denser and compact structure of the ZnO thin film on the substrate surface. The low surface Ni-doped thin film also used as a NO_2 Sensor [16]

SEM ANALYSIS

The thicknesses of the thin film were examined by the cross-section image through scanning electron microscopy (SEM). Electrons emitted from the thin film which was surfaces facing the detector. In scanning electron microscope (SEM) electrons were collected and appear brighter in the image. If it was not like that, than the ejected electrons have difficulty in reaching the detector and the corresponding spot appears as dark.

Fig. 3 shows the SEM image recorded by secondary electron mode for the nano-structured dilute magnetic semiconductor (DMS) over the silicon substrate deposited by RF magnetron sputtering. The thicknesses of the thin films were of 150-170 nm as measured by the scanning electron microscopy (SEM).

OPTICAL STUDIES

Fig. 4 (a) shows the optical absorbance properties of the $\text{Zn}_{1-x-y}\text{Ni}_y\text{Fe}_x\text{O}$ ($y=0.01$, $x = 0.01, 0.03$ and 0.05) thin films deposited on Si (400) substrate. The $\text{Tau}'c$ plot was used for calculation of the energy “band gap” E_g of the prepared thin films. The absorption spectrum of DMS thin films shows sinusoidal behavior, which is due to, the covered structure of thin films. ZnO is a direct band transitions material and the absorption coefficient, which has been denoted by α expressed by the equation. (2)

$$(\alpha h\nu) = A (h\nu - E_g)^r \quad (2)$$

Where, A is the constant, E_g is the allowed energy gap, $h\nu$ is the photon energy. In our case, we have direct band transition so the value of $r = 1/2$.

Fig. 4(b) shows the absorption coefficient (α) and the two defined regions separated by the peak of the derivative of the absorption coefficient. The Urbach's area shows the structural and thermal chaos present in the thin film. The occurrence of an only incline in the plot indicates that the thin films have directed an acceptable transition. The tangent was taken by considering a common point for both the axis and extrapolating the $(\alpha h\nu) = 0$, the straight-line portion of the plot to zero absorption coefficient. The band gap E_g of thin films varies from 2.6 to 3.5 eV. The cause for the enhancement in the band gap is a blue shift, which arises due to the Moss–Burstein band-filling result in which the Fermi level lies in the conduction band [17-18]. This variation in “band gap” is due to the “quantum confinement” of the nano-crystal.

PHOTOLUMINESCENCE (PL) STUDY

Photoluminescence (PL) spectroscopy is an important tool to characterize the optical properties of dilute magnetic semiconductors. The intensity of the Photoluminescence spectrum varies directly to the imperfection concentration present in the fluorescent material. It was apparent that all ZnO thin films with various Fe and Ni co-doping concentrations revealed one violet

emission peak with a wavelength of about 338 nm moreover emission peak also was found. The absence of extra emission peaks is an indication of less number of defects in the thin films.

Fig. 5 shows the room temperature Photoluminescence spectrum of different ZnO thin films with various concentrations of Fe and Ni co-dopant. A comprehensible decrease in the intensity of this band is seen in the sample NZF3 in contrast with NZF1 and NZF5 indicating the successful assimilation of the dopants in the ZnO matrix. The slight change in the peak site also observed in the spectrum, and the shift can be attributed to the change in the band gap of thin films [19].

FTIR STUDY

FTIR spectroscopy provides the information regarding the functional groups, types of molecular interactions present in the compounds. We have employed FTIR spectroscopy to collect vibrational bands' information and to study the vibrational level changes after the addition of the dopants. The FTIR spectrums for prepared thin films have been revealing in Fig. 6.

The absorption peak at 1400cm^{-1} indicates the sulphate group present in the material, which approves the outcomes from XRD. The peak at 484cm^{-1} in all the spectra gave the Zn–O vibration while the peak at 614 cm^{-1} , found for Fe-doped materials are characteristic of a Fe–O stretch [20, 21]. So that we consider that Fe ions were replaced by Zn ions and fused into the crystal lattice of ZnO.

MAGNETIC PROPERTIES

To explore the magnetic properties of prepared thin films, hysteresis curves were recorded using a Vibrating Sample Magnetometer (VSM). Fig. 7(a) presents hysteresis curve for $\text{Zn}_{1-x-y}\text{Ni}_y\text{Fe}_x\text{O}$ ($y=0.01$, $x=0.01$, 0.03 and 0.05) films measured under a magnetic field up to 1 Tesla, at room temperature. It can be seen from the curve that they exhibit room-temperature ferromagnetism. Here, few probable descriptions for RT saturated the hysteresis loop. One is extrinsic was found by P.Dhiman et al and another one is intrinsic magnetism by D. Karmakar et al [22-23]. However, XRD has revealed the absence of any type of impurity or clusters present in the thin films. There is a decrease in the magnetization with the increase in the Fe but keeping the Ni concentration constant in the thin films. This is clear evidence that merely, Ni and Fe or Ni, Fe clusters have not contributed to the RT-FM behaviour of the prepared thin films. Therefore, it was a high possibility of existing several interaction mechanisms between Ni and Fe spins, which have resulted in room temperature ferromagnetism. We have also recorded M-H curves for thin films at 5K [Fig. 7(b)], which also shows the ferromagnetic nature of the samples with greater magnetization values. We were taken the low-temperature magnetic investigator by Field cooled (FC) and zero fields cooled (ZFC) measurements on prepared thin films to investigate the causes of the room-temperature magnetism. The observed magnetization and coercivity at 5K temperatures were depicted in Table 1.

Fig.9 shows FC-ZFC curves of $\text{Fe}_{0.01}$ and $\text{Ni}_{0.01}$ doped ZnO thin films taken from 5 K to 300 K. ZFC curve was found by primarily cooling the thin films from 300 K to 5 K in the nonappearance of an applied magnetic field and warming up in 7 Tesla field during the magnetization measurement. Both the FC mode and ZFC mode curves present unique behavior at very low temperatures. The FC curve shows a decrease in magnetization with an increase in temperature. However, the decrease is very prominent at low temperatures. However, by analyzing the ZFC curve we found that they're no blocking temperature that exists before 300 K.

Both FC and ZFC start following the same behavior after 290K. However, as there is a clear separation between the FC –ZFC curves close to room temperature, which implies the ferromagnetic behavior of the samples close to room temperature. The cause of

ferromagnetism may be attributed to the different mechanisms suggested by various authors [24-27], including bound magnetic polaron, defect induced, carrier-mediated and RKKY interactions, etc. by going through the previous reports, the curve of magnetization vs temperature was detected in a carrier-localized regime, which can be explained by the polaron-percolation-theory [28].

Along with this concept, the polaron percolation threshold (δ_p) and the cation percolation threshold (x_p) were the two main milestones which contribute to the magnetic phase diagram. If we have a large number of the magnetic cations in the samples then the ferromagnetic nature has been observed by satisfying the condition $\delta < \delta_p$ and $x < x_p$. In the case of cation threshold $x < x_p$, then the long-range ordering cannot lead to the antiferromagnetic superexchange interaction in the material. Now, by the concept of percolation theory, the distance between polaron – polaron is large enough for the generation of the strong ferromagnetic ordering. From all the characterizations, we can summarize that the detected RT-FM is not due to the defects or some other phase formation but only is the intrinsic one.

Conclusion

In conclusion, Fe, Ni co-doped thin films have been successfully deposited on Silicon (400) substrate and clearly show ferromagnetism at the room as well as at low temperatures. XRD revealed that there are no other impurities present in the thin film. The surface roughness of the prepared thin films reduced with the increment in Fe, Ni contents, which were explained by the micro-densification effect. Our X-ray diffraction studies also supported by the AFM data analysis of the thin film. From optical behavior, thin films were a suitable applicant for the opto-electronics devices. The variation of optical band gap energy on the carrier density explained by the Moss-Burstein effect and quantum confinement. Magnetic studies reveal the room temperature ferromagnetism in the thin film. A recent study shows that Ni-doped ZnO thin film uses as a NO₂ gas sensor.

Declarations

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Table

Table.1 The observed magnetization and coercivity at 5K temperatures are given in table.

Sample $Zn_{1-x-y}Ni_yFe_xO$	M (emu/cm ³)	H _c (Oe)
y=0.01, x=0.01	34.24	0.0075
y=0.01, x=0.03	54.63	0.0047
y=0.1, x=0.05	37.45	0.0061

Figures

Figure 1

(A) XRD of $\text{Zn}_{1-x-y}\text{Ni}_y\text{Fe}_x\text{O}$ ($y=0.01, x=0.01, 0.03$ and 0.05) thin films.

Figure 2

Surface morphology with the histogram of $\text{Zn}_{1-x-y}\text{Ni}_y\text{Fe}_x\text{O}$ ($y=0.01$ and $x=0.01, 0.03$ and 0.05) thin films.

Figure 3

SEM cross-sectional images of a Fe-Ni co-doped thin film.

Figure 4

The UV-Vis spectra (a) and energy band gap. (b) of the Zn_{1-x-y}Ni_yFe_xO (y=0.01, x=0.01, 0.03 and 0.05) thin films.

Figure 5

PL Spectra of $\text{Zn}_{1-x-y}\text{Ni}_y\text{Fe}_x\text{O}$ ($y=0.01$, $x=0.01$, 0.03 and 0.05) thin films.

Figure 6

Figure 7

(a). The magnetic hysteresis loops of the $\text{Zn}_{1-x-y}\text{Ni}_y\text{Fe}_x\text{O}$ ($y=0.01, x=0.01, 0.03$ and 0.05) thin films at 300 K, (b) at 5 K.

Figure 8

FC (Field-Cooled) and ZFC (Zero Field-Cooled) thermal variations of the saturation magnetization for NZF1 thin film under a magnetic field $H = 7\text{KOe}$.

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