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Role of Ni Doping on Structural, Electronic and Transport Properties of ZnO Thin Films

Tanveer Ahmad Dar[1*], Arpana Agrawal[2] and Pratima Sen[3]

Laser Bhawan, School of Physics,
Devi Ahilaya University Takshashila Campus Khandwa Road Indore, India, 452001.
*email: tanveerphysics@gmail.com.

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Abstract. Nickel doped (Ni=0.05) and undoped Zinc Oxide (ZnO) thin films have been prepared by Pulsed laser deposition (PLD) technique. The structural analysis of the films was done by X-ray diffraction (XRD) studies which reveal absence of any secondary phase in the prepared samples. UV transmission spectra show that Ni doping reduces the transparency of the films. X-ray Photoelectron spectroscopy (XPS) shows the presence of metallic Ni is present in the sample. Low temperature magneto transport properties of the ZnO and NiZnO films are also discussed in view of Khosla fisher model. Ni doping in ZnO results in decrease in magnitude of negative MR.

Keywords: II–VI semiconductors, X-ray diffraction, X-ray photoelectron spectroscopy

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INTRODUCTION

It has now become a well established fact that transition metal doped II-VI semiconductors provide the opportunity to combine both magnetic as well as semiconducting functionality together. The presence of transition metal (TM) ions in the host semi- conductors leads to an exchange interaction between itinerant sp-band electrons or holes and the d-electron spins localized at the magnetic ions, resulting in versatile magnetic-field-induced functionalities. This unique combination has manifested in the design of the novel materials (Diluted Magnetic Semiconductors: DMSs) and explored new physical phenomena which make this class of materials exceptional. Transition metal (Fe, Cu, Co, Ni, etc.) doped ZnO [1, 2] is one such wide band gap material which has found time-honoured applications in the field of spintronics [3] and optoelectronics [4, 5]. The prediction of room temperature ferromagnetism in p-type Mn-doped ZnO [6] lead to the vast and exploring research in growing ZnO doped with transition metals to achieve room temperature ferromagnetism [7-9] for spintronic applications. Some groups have also observed a spin-glass or a paramagnetic behaviour in their samples [10].

In this paper we report the role of Ni doping on structural, optical, electronic and magneto transport properties of Ni doped ZnO thin films on glass substrate grown by PLD technique. Our investigations reveal polycrystalline single phase Ni doped ZnO thin films with a slight red shift in the optical band gap subsequent to Ni doping.

EXPERIMENTAL

Pure ZnO, $Ni_{0.05}Zn_{0.95}O$ films were deposited on glass substrate by PLD technique using an excimer (KrF) laser at 248 nm wavelength to ablate the target. Substrate was prewashed by methanol and then cleaned ultrasonically. The pulse duration of the laser was 20 ns with repetition rate of 10 Hz and the energy density was 2 J/cm^2. Deposition was carried out in a vacuum chamber pumped down to a base pressure of 4 nbar and oxygen gas was flown into the chamber at 1 nbar. The target-to-substrate distance was maintained at 5 cm with optimized substrate temperature of 400^{0}C. After deposition, substrate was cooled at 20^{0}C/minute in the same environment as used during deposition. X-ray photoelectron spectroscopy (XPS) measurements were performed using Angle Integrated Photo-electron Beamline on INDUS-1 Synchrotron radiation source at RRCAT, Indore while the valence band spectroscopy (VBS) measurements were performed by using He-II source for excitation under same conditions. To reduce the contamination effect, all the samples were subjected to a surface clean procedure by Ar^+ bombardment in the vacuum chamber equipped in the XPS instrument. The magnetic field dependent resistivity measurements were carried out using standard four probe technique. The magnetic field is applied parallel to the direction of applied current giving rise to the longitudinal magnetoresistance (MR). Longitudinal MR for both the films was measured at various constant temperatures upto 8 T magnetic field.

RESULTS AND DISCUSSION

The obtained XRD results (not shown here) show the dimensions of c in doped and undoped samples as 5.18 and 5.219Å respectively. The variation of lattice constant c is due to the difference in the ionic radii of Zn^{2+} and Ni^{2+}. The mean grain size (D) of the thin film samples calculated using the Scherrer equation to the (0 0 2) reflection for undoped and Ni-doped ZnO thin films are 40.740, and 24.35 Å, respectively. The results reveal that Ni doped ZnO thin films can reduce the average crystallite size. The increase in lattice constant c and decline in diffraction intensity due to Ni doping hints that crystalline quality of the films degenerates (See fig. 1). This possibly

may be due to the low solubility limit of Ni in ZnO matrix which is not detectable within XRD limits. It may be possible that the Ni doping in ZnO films may also tend to segregate to form nanoclusters of metallic nickel which can create strain in the films. This strain leads to the poor film quality leading to low transmission as seen from fig. 1.

UV-transmission spectra of the samples in the wavelength range 350-750 nm is shown in figure 2. The results reveal decrease in the band gap. The obtained values of the band gap are 3.25 and 3.14 eV for ZnO and $Ni_{0.05}Zn_{0.95}O$ films respectively. Decrease in the band gap is related to the sp-d exchange interaction mechanism [11, 12]. The inset of the figure 2 shows that Ni doping leads to low transmission which is relate to the crystalline quality, decrease in band gap and grain size of the films.

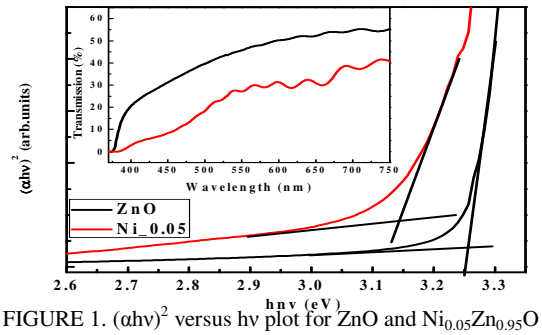

FIGURE 1. $(\alpha h\nu)^2$ versus hν plot for ZnO and $Ni_{0.05}Zn_{0.95}O$ films. Inset shows the transmission spectra for both the films

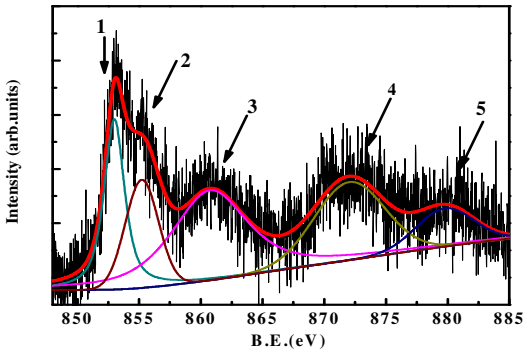

FIGURE: 2. Corelevel spectra of Ni 2p in $Ni_{0.05}Zn_{0.95}O$ film.

The valence state of the Ni in Ni doped ZnO thin film was investigated from XPS results which were calibrated with respect to C 1s peak (284.6 eV) for charging effects. The Ni $2p_{3/2}$ peak for $Ni_{0.05}Zn_{0.95}O$ occurs at around ~ 853.01 eV while as Ni $2p_{1/2}$ occurs at around ~ 872.95 eV. Corresponding satellite structures were clearly observed around 861 eV and 879 eV, respectively. From our analysis we found that the peak positions of Ni in $Ni_{0.05}Zn_{0.95}O$ film are quite close to that of metallic Ni [13]. Moreover the energy difference between Ni $2p3/2$ and $2p1/2$ peaks in $Ni_{0.05}Zn_{0.95}O$ is 16.812 eV which strikingly differs from 18.4 eV of NiO, indicating that Ni is in the metallic form instead of forming the phase of NiO.

Figure 3(a) and 3(b) shows magneto resistance (MR) data of ZnO and $Ni_{0.05}Zn_{0.95}O$ films taken at various temperatures from 0-8T magnetic field, respectively. The obtained results have been well fitted by using the empirical relation given by Khosla and fisher [Khosla and Fisher paper]. In Ni doped films, at 2K temperature, the MR first decreases with increasing field, attains a minima and then increases with increase in field. The field at which such change in the MR behavior was observed can be related to the temperature by an expression of the form H/T=constant. From the comparison of the curves taken at various elevated temperatures, it can be seen that the fields at which the MR behavior changes is temperature dependent and is shifted to higher fields with increasing the temperature. Furthermore the absolute value of the minimum in the MR also increases at low temperatures.

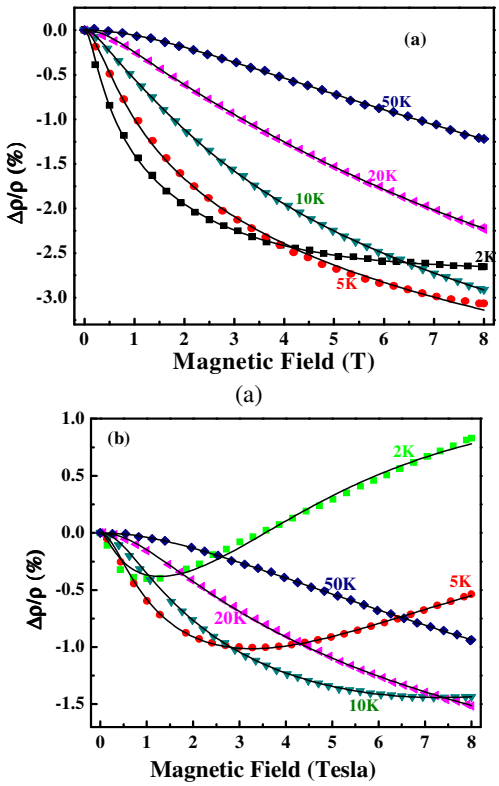

FIGURE 3: Magnetoresistance data of (a) ZnO and (b) $Ni_{0.05}Zn_{0.95}O$ films.

The presence of negative MR can be quantitatively explained on the basis of localized magnetic moment model proposed by Toyozawa [14] and further modified by Khosla and Fisher [15] by incorporating the third order term in the perturbation expansion of the exchange interaction. In the magnetic impurity atom, in the absence of any external magnetic field, the localized magnetic moments are random due to which the carriers get scattered by this localized magnetic moments. The application of external magnetic field orders these

localized magnetic moments which reduces the scattering of the carriers and thus results in a decrease in resistivity which causes negative MR. Positive MR can be attributed to the two band model where the two bands are attributed to the impurity band and valence band that is spin split due to the Zeeman Effect. The overall MR according to Khosla fisher model is given by the following equation:

$$\frac{\Delta\rho}{\rho} = -a^2 \ln\left(1 + b^2 B^2\right) + \frac{c^2 B^2}{(1 + d^2 B^2)}$$

Where first term on R.H.S contributes to the negative MR and second term contributes to the positive MR. a, b, c and d are the fitting parameters; B is the applied magnetic field. Negative contribution to MR in pure ZnO arises from the formation of Zn vacancies, which induce a high magnetic moment while in Ni doped ZnO films, this negative contribution arises due to 3d impurities which are related with spin dependent scattering due to sp-d exchange interaction and the positive contribution to MR is ascribed to the changes induced by the applied magnetic field in the relative populations in the two conduction bands with different conductivities. In conclusion we have studied the role of Ni doping in ZnO thin films. XRD studies confirm the polycrystalline nature of the films. Optical transmission spectra show that transmission of the films decreases on Ni doping with decrease in band gap. From XPS results it is found that Ni is in metallic state resulting in the poor quality of the film. MR measurements reveal overall negative behavior for ZnO. For NiZnO except at 2K, the MR is also negative but with small magnitude. The detailed study of Ni doping in ZnO can possibly lead to the successful use of NiZnO as a promising spintronic material.

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