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# Correlation between electrical transport, optical, and magnetic properties of transition metal ion doped ZnO

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We report on the transport and optical properties of transition metal ions, namely Ti, V, Fe, Co and Ni doped ZnO samples. Diffuse reflectance spectroscopy of doped ZnO showed the existence of absorption bands which were attributed to the *d-d* transitions of respective dopants. Resistivity was found to decrease in the case of Ti, V, Fe, and Ni dopings. Correlation between the electrical resistivity and magnetic properties of the samples has been explained on the basis of impurity *d*-band splitting model. © 2008 American Institute of Physics. [DOI: 10.1063/1.2834443]

## I. INTRODUCTION

Zinc oxide, which occurs naturally as the mineral zincite, finds wide applications in varistors, pigment in paints, and sunscreen for the prevention of sunburn due to its ability to absorb ultraviolet light. ZnO is an *n*-type degenerate semiconductor with high dielectric constant and exhibits activated conduction behavior. Realization of diluted magnetic semiconductors (DMS) behavior in such wide-band-gap materials provide an important insight into spin injection applications, such as in spin filters and spin transport media. In ZnO, the Zn *d* electrons hybridize with the oxygen *p* electrons. The interest in determining electrical and optical properties of doped bulk ZnO is motivated by the need to develop an understanding of the material response to impurities introduced by doping. ZnO doped with Ga or Al increases the carrier concentrations in ZnO.<sup>1,2</sup> ZnO nanomaterials doped or alloyed with Ga,<sup>3,4</sup> Co, Ni,<sup>5</sup> Cd,<sup>6</sup> and Mg (Ref. 7) have also been reported. There has been a great deal of attention on search for magnetism in transition metal (TM) ion doped ZnO.<sup>8–12</sup> Despite its technological importance, the electrical property of TM ion doped ZnO is not well understood and the resistivity data of bulk TM doped ZnO need to be investigated. In our recent work<sup>13</sup> on transport property of Ni doped ZnO, the resistivity of the Ni doped samples was found to decrease with increase in Ni concentration and this has been explained using the impurity *d*-band splitting model. Based on this result, we investigated further the influence of other TMs, namely, Ti, V, Cr, Mn, Fe, and Co dopants on the transport and optical properties of ZnO samples.

## II. EXPERIMENT

The samples for the present study were prepared using sol-gel technique. The single phase nature of the compounds was ascertained using x-Ray diffraction using PANalytical

Xpert-Pro-Philips diffractometer. Diffuse reflectance spectra (DRS) at normal incidence of powder samples were measured with a spectrophotometer (Ocean Optics USB 2000). Electrical resistivity was measured using linear four-probe technique. Room temperature magnetic measurements were carried out using superconducting quantum interference device (SQUID) magnetometer. Thin films of the above samples were grown using pulsed laser deposition technique.

## III. RESULTS AND DISCUSSIONS

From the XRD patterns of doped compounds (not shown here) the solubility limits of V, Fe, Co, Ni, and Ti in bulk ZnO were found to be 2, 1, 5, 2, and 2 mol %, respectively. Impurity peaks of respective oxides were observed for higher values of doping. For uniformity, we restricted our study to single phase compounds of 1 mol % doped ZnO for all the dopants. DRS of homogenized powdered samples were recorded by collecting scattered light from the bulk samples (Fig. 1). These spectra were recorded in the region from 350 to 650 nm using BaSO<sub>4</sub> powder compact (white in color) as a reference. Undoped ZnO sample showed the absorption edge around 380 nm. Doped ZnO samples exhibited absorptions in the visible region in addition to the absorption edge due to the bands originating from the crystal-field tran-

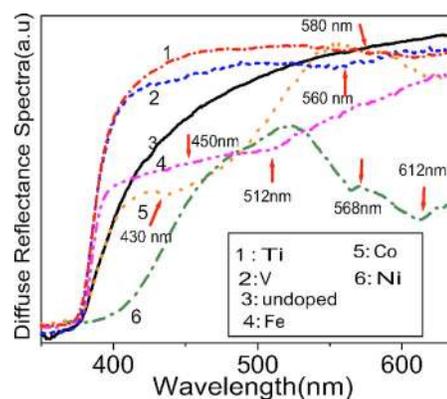


FIG. 1. (Color online) Diffuse reflectance spectra of bulk polycrystalline undoped and doped ZnO samples.

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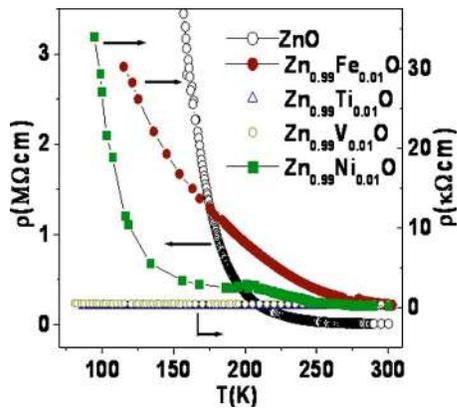


FIG. 2. (Color online)  $\rho$  (resistivity) vs  $T$  (temperature) of undoped and TM ion doped ZnO polycrystalline samples.

sitions of TM ions replacing Zn in tetrahedral coordination. In the case of Co doped ZnO, the absorption peaks are well separated from absorption edge and absorption peaks at 612 and 568 nm are attributed to as due to transition from the  ${}^4A_2$  ground state to the  ${}^4T_1(P)$  state for the tetrahedral Co(II). Absorption spectrum of  $\text{Ni}^{2+}$  doped ZnO shows mid-band-gap states appearing at about 430 and 580 nm corresponding to the  $d-d$  transition bands, which are characteristic of Ni(II) with tetrahedral symmetry.<sup>14</sup> Figure 1 also shows the  ${}^3T_1(F) \rightarrow {}^3T_1(P)$  ligand field transitions of  $\text{Ni}^{2+}$  ions in tetrahedral symmetry for the Ni doped samples. For Fe doped ZnO samples absorption band at 450 nm has been attributed to  $\text{Fe}^{3+}$  in tetrahedral coordination.<sup>15</sup> Grygar *et al.*<sup>16</sup> reported that the mid-band-gap state at 512 nm can be attributed to some form of tetrahedrally or octahedrally coordinated Fe(III) ions. No significant absorption corresponding to  $\text{Fe}^{2+}$  ions was observed and so determination of presence of tetrahedral  $\text{Fe}^{2+}$  by optical spectra was not possible. The absorption around 560 nm for V doped samples represents typical  $d-d$  transition of  $\text{V}^{2+}$  ions in a tetragonal crystal field.<sup>17</sup> Raman peaks were observed at  $663 \text{ cm}^{-1}$  [ $A_1(\text{LO}) + E_2(\text{low})$ ],  $538 \text{ cm}^{-1}$  (2LA mode),  $437 \text{ cm}^{-1}$  (attributed to ZnO nonpolar optical phonon  $E_2$  mode),  $407 \text{ cm}^{-1}$  [ $E_1(\text{TO})$  mode] and  $381 \text{ cm}^{-1}$  [ $A_1(\text{TO})$  mode] for all the samples. However, an anomalous mode at  $626 \text{ cm}^{-1}$  for the Fe doped sample alone was observed, possible reason of which is under study.

A decrease in resistivity for Ti, V, Fe, and Ni doped samples was observed with respect to the undoped sample (Fig. 2). Figure 3 shows the room temperature resistivity data and magnetic moment data on 1 mol % of TM doped samples. Figure 4 shows the carrier concentration data of the as prepared samples. The magnetic moment values have been obtained from the first quadrant of hysteresis loops for the respective samples and were normalized ( $\mu_3 \text{ T} / \mu_0 \text{ T}$ , ratio of magnetic moment at 3 T and magnetic moment at 0 T taken at room temperature) since we could not get the accurate weights of the samples taken. The conducting samples of Ti, V, Fe, and Ni have magnetic moment values of  $\sim 0.7$ , 2.94, 6.8, and 3.29 which are higher than the magnetic moment value of 0.12 for that of Co doped ZnO (having higher resistivity than undoped sample). These results suggest an

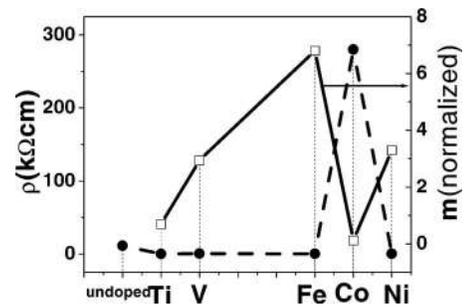


FIG. 3. Room temperature  $\rho$  of TM ion doped ZnO bulk polycrystalline samples and room temperature magnetic moment of TM ion doped ZnO bulk polycrystalline samples.

underlying magnetic exchange mechanism in these samples, which should involve the spin split defect states as well as the TM ion dopants present in the host. The decrease in resistivity of the isovalent TM ion doped samples can be explained as follows.

The magnetic impurity  $d$  states in DMS generally appear near the Fermi level (here TM ion is the magnetic impurity in ZnO).<sup>18</sup> These states may exhibit splitting, resulting in the high-spin configuration of  $d$  electrons. These impurity states undergo hybridization with valence  $p$  states of the host compound. For phase pure samples, TM ion replaces the  $\text{Zn}^{2+}$  ion which is at the center of the tetrahedron. The  $d$  states of a TM ion split under the influence of tetrahedral crystal field of ZnO, leading to lower doublet  $e_g$  state and a higher energy triplet  $t_{2g}$  state. The  $t_{2g}$  state hybridizes with  $p$  orbitals of the valence band further splitting into  $t_{\text{bonding}}$  and  $t_{\text{antibonding}}$  states. The  $t_{\text{bonding}}$  states participate in bonding and hence are localized. However, the antibonding states have higher energy level and contain itinerant electrons. The energy of the bonding state lies very close to the conduction band of ZnO and hence with the increase in temperature the electrons in this state can jump to the conduction band because of thermal activation. Thus we observe that the change in resistivity in these systems is due to the presence of defect/impurity states within the ZnO band gap. Coey *et al.*<sup>19</sup> explained the magnetism in  $d^0$  systems as due to that of an exchange that is mediated by a spin split impurity band derived from defect/impurity states. We have compared the nature of our resistivity data on 1 mol % of TM doped samples to that of magnetic moment data of 1 mol % of TM doping (Fig. 3). We

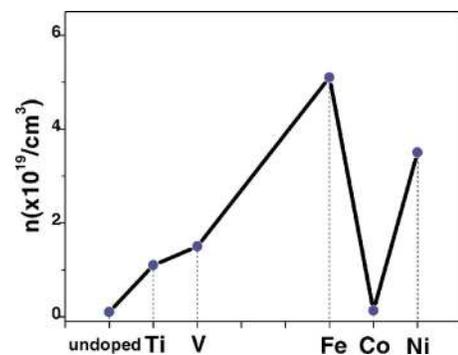


FIG. 4. (Color online) Carrier concentration of undoped and TM ion doped ZnO samples.

TABLE I. Comparison of  $\rho$  (resistivity) of doped and undoped ZnO (bulk) at room temperature (300 K). It also presents normalized magnetic moment ( $\mu_3 \text{ T} / \mu_0 \text{ T}$ ) at room temperature.

Dopant ion	Bulk 1 mol % doped ZnO $\rho$ (k $\Omega$ cm) (300 K)	Magnetic moment ( $\mu_3 \text{ T} / \mu_0 \text{ T}$ ) ( $10^2$ ) at (300 K)
Undoped	11.34	...
V	0.41	2.94
Fe	0.23	7.1
Co	Insulating	0.26
Ti	0.14	0.6
Ni	0.2	3.29

would like to point out here that, in the case of Fe, Ti, and V doped samples the presence of higher valence states cannot be completely ruled out. As, for example, the presence of Fe<sup>3+</sup> was corroborated by Mossbauer spectra as well as DRS spectra. Higher valency cations of these TM ions will introduce oxygen defects in the parent compound. The presence of oxygen defects on the other hand also contributes to lowering of resistivity. There are certain deviations observed with respect to doping of certain transition metal ions such as Co. Co doping in bulk polycrystalline ZnO was found to increase the resistivity of parent compound as against the decrease in resistivity for the other TM ions (Table I). The carrier concentration in Co doped ZnO samples was also seen to decrease with doping. This can be ascribed to the incorporation of Co atoms in the microcrystal boundaries and the resultant shrinkage of high carrier density regions.<sup>20</sup>

Though there is no unpaired  $d$  electron in Ti and V ions, the magnetic moment value in Fe, Ti, and V doped samples can be attributed to the exchange arising from spin split defect states<sup>19,21</sup> providing transfer from the impurity states to  $3d$  states of the TM ions. However, the correlation of appearance of magnetic moment of Ni doped sample along with the decrease in resistivity still remains to be addressed.

We have also compared our resistivity data on 1 mol % of TM doped thin films (Fig. 5) to that of magnetic data reported by Venkatesan *et al.*<sup>21</sup> on 5 mol % of TM doped thin films. The inset in Fig. 5 is the same data as in the main graph but without Cr and Mn on a log scale. It was observed that the dopants for which magnetic moment is low in the in Ref. 21 have higher resistivity (as compared to parent compound) in our work. Since the model proposed in Ref. 21 does not explain the above behavior, further studies are being carried out and will be addressed in future.

#### IV. CONCLUSION

We have systematically studied the electrical, magnetic, and optical properties of TM ion doped ZnO. The presence

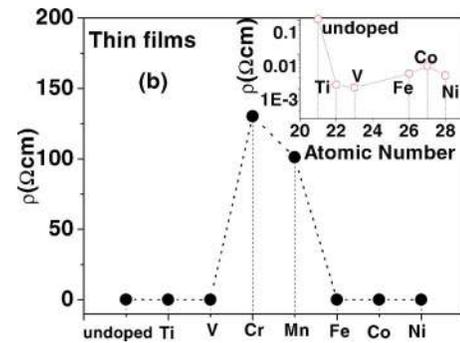


FIG. 5. (Color online) Room temperature  $\rho$  (resistivity) of undoped and TM doped ZnO thin film samples. The inset in Fig. 5 is the same data as in the main graph but without Cr and Mn on a log scale.

of TM ions in the host lattice was confirmed through optical studies. We have tried to explain between magnetic and electrical behaviors of the samples based on the presence of the defect/impurity states of the TM ion in the parent ZnO lattice.

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