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Direct Observation of Ni Metal Impurities in Lightly Doped Ferromagnetic Polycrystalline (ZnNi)O

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Diluted magnetic semiconductors (DMSs) in which magnetism and transport properties are combined in a single material offer potential technological applications such as in spintronics.[1] Carrier-induced ferromagnetism has been of considerable interest in III−V semiconductors doped with transition metal impurities. However, the Curie temperatures of such doped systems are much lower than room temperature (e.g., 160 K for (Ga,Mn)As,[2] 50 K for (In,Mn)As,[3] etc.). From the application point of view, it is essential that a DMS material should be ferromagnetic at or above room temperature to be used in spintronic devices. The large band gap II−VI semiconductor oxide (ZnO) doped with transition metal ions has been identified as a promising DMS material. Based on theoretical predictions, it has been proposed that ZnO doped with 3d transition metal atoms is a suitable candidate for ferromagnetic semiconductors.[4] Curie temperatures above 300 K have been predicted for Mn-doped ZnO.[5] Subsequent experimental results showed that ZnO doped with different transition metals such as Co, Mn, Ni, etc. is ferromagnetic at or above room temperature.[6−12] However, there are controversial reports on the origin of ferromagnetism in doped ZnO, especially in the case of Co- and Mn-doped materials. Some reports show the absence of ferromagnetism or the presence of secondary phases as the origin of ferromagnetism.[13−20] Bouloudenine et al. recently showed that $Zn_{1-x}Co_xO$ is antiferromagnetic, when synthesized by a wet chemical method.[21] Hence, after so many extensive studies on ZnO-based DMSs, the origin of ferromagnetism is still a big question.

Although there are many reports on the observation of ferromagnetism in Co- and Mn-doped ZnO, there are not many studies on Ni-doped ZnO. From the studies on different 3d transition metal-doped ZnO films, Ueda et al. found that their Ni-doped ZnO is not ferromagnetic.[6] Wakano et al. reported the observation of ferromagnetism at 2 K for the same system, which become superparamagnetic at 30 K and maintains it up to 300 K.[22] On the other hand, ferromagnetism is observed at room temperature in Ni/ZnO nanorods[23] and ZnO:Ni thin films.[24,25] There are further reports that $Zn_{1-x}Ni_xO$ quantum dots may be a good DMS material along with III−V system and that it is ferromagnetic up to 350 K.[26,27] However, from the observed saturation moments, it has been concluded that only a small fraction of the doped Ni^{2+} ions gives rise to ferromagnetism and that the majority of the material is paramagnetic or superparamagnetic. Magnetic measurements by Ando showed that some of the $Zn_{1-x}Ni_xO$ thin films are paramagnetic and that others are ferromagnetic.[20] However, from magneto-optical studies, it has been shown that ferromagnetic precipitations/secondary phases are responsible for the observed ferromagnetism in the films. Since small amounts of impurities cannot be detected by structural and magnetic studies, the author concluded that these measurements are not reliable for the characterization of DMS.

In this communication, we report the results on the studies of the structural, optical, and magnetic properties of nanocrystalline powder samples of Ni-doped ZnO synthesized by an auto-combustion method. Although optical absorption studies show the incorporation of Ni in the ZnO matrix, careful examination of X-ray and electron diffraction patterns showed the presence of Ni metal clusters, even in 2.5% Ni-doped sample, which is found to be ferromagnetic.

Polycrystalline $Zn_{1-x}Ni_xO$ ($x = 0, 0.025, 0.05$) powder samples were synthesized by an auto-combustion method from zinc nitrate, nickel nitrate, and glycine. Water solutions of zinc and nickel nitrates were mixed in the corresponding

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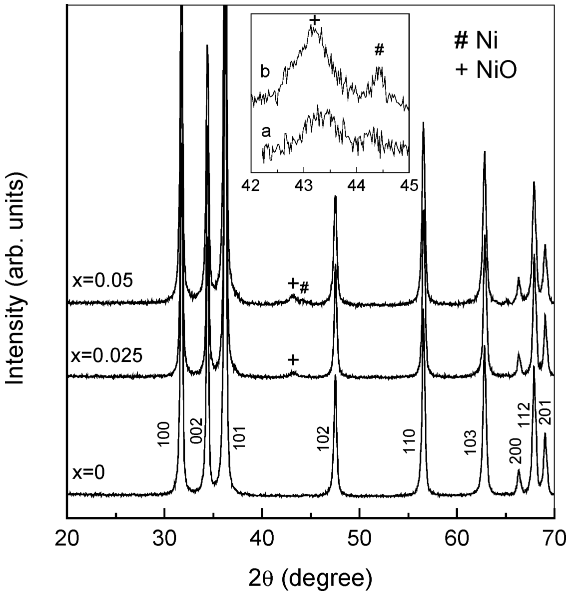

Figure 1. Powder XRD patterns of $Zn_{1-x}Ni_xO$. Inset: normal scan data of $x = 0.05$ (curve a) and slow scan data of $x = 0.025$ (curve b) in the region where most intense reflection from NiO and Ni metal is expected.

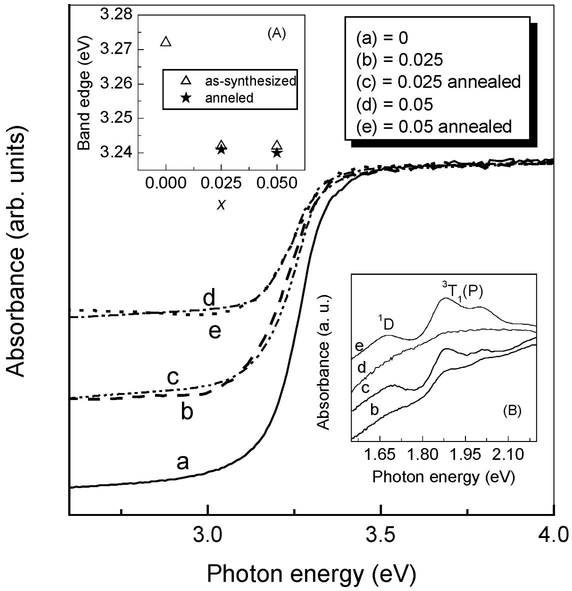

Figure 2. Room temperature optical absorption spectra of the as-synthesized and annealed $Zn_{1-x}Ni_xO$ powders, near the band edge. Insets: (A) band edge as a function of x; (B) the ligand field transitions of Ni^{2+} in tetrahedral symmetry for the as-synthesized and annealed samples of $x = 0.025$ and 0.05.

molar ratio of Zn and Ni in $Zn_{1-x}Ni_xO$. To the mixed solution of the metal nitrates, a water solution of glycine was added, taking 2 mol of glycine/mol of metal ion.[11] The final solution was evaporated on a hot plate kept at 200 °C until it formed a thick mass, which subsequently underwent auto-combustion giving a fine powder. Parts of the powder samples were annealed in air at 400 °C for 2 h to study the effect of heat treatment on different properties. All the powder samples were characterized by powder X-ray diffraction (Philips 1830, Cu Kα radiation). The particle morphology and selected area electron diffraction (SAED) patterns were obtained using a JEOL model 1200 EX transmission electron microscope. Magnetization measurements as a function of magnetic field were carried out using a vibration sample magnetometer (EG&G PAR 4500). Electronic absorption spectra were recorded on a JASCO V-570 and a Perkin-Elmer Lambda 650 spectrophotometers.

The powder X-ray diffraction (XRD) patterns of the as-synthesized samples of $Zn_{1-x}Ni_xO$ ($x = 0$, 0.025, and 0.05) are shown in Figure 1. For $x = 0$, the reflections correspond to the wurtzite structure of ZnO. The XRD patterns for $x > 0$ show that the ZnO structure is not disturbed on substitution. The average crystallite size of ZnO, calculated from X-ray line broadening using the Scherrer formula ($t = 0.9\lambda/\beta \cos \theta$) (where t is the crystallite size in Å, β is the half-maximum line width, and λ is the wavelength of X-rays) is obtained as ~30 nm for all compositions. An additional very low intense peak is observed at $2\theta = 43.2°$ for $x = 0.025$, which is the most intense peak of NiO. Apart from this peak with enhanced intensity, an additional weak reflection is observed for $x = 0.05$, close to the reflection from NiO. This weak extra peak in the XRD patterns is found to be due to Ni metal. Since Ni metal peak is detectable in the 5% doped sample, the XRD pattern of $x = 0.025$ sample is closely examined by recording the XRD pattern at a very slow scan rate, in the specific 2θ range where the most intense peak of Ni metal is expected. This procedure is known to be highly efficient in detecting very small quantities of impurity phases.[28] A weak reflection at $2\theta = 44.3°$ corresponding to Ni is obtained apart from that due to NiO, by this procedure. The normal scan data of the 5% doped sample (curve a) and the slow scan data of the 2.5% doped sample (curve b) in the 2θ region 42−45° are compared in the inset of Figure 1. Reflections from NiO and Ni metal can be clearly seen in both the samples. The approximate weight percentages of Ni and NiO were calculated from the least-squares refinement of the XRD patterns using the PowderCell program.[29] The fractions of NiO are obtained as 0.3% and 2.7%, and that of Ni is calculated as 0.15% and 0.3%, respectively, in the $x = 0.025$ and 0.05 samples. On the basis of the amounts of Ni and NiO in the $x = 0.025$ and 0.05 samples, the fractions of Ni^{2+} substituted for Zn^{2+} in the ZnO lattice are calculated as ~2.1% and ~2.6%, respectively. Thus the powder studies directly indicate the presence of Ni metal, apart from NiO, in the polycrystalline samples. Wakano et al. have observed the formation of NiO impurities when the substrate temperature is above 500 °C during the fabrication of Ni-doped ZnO films.[22]

Figure 2 shows the variation of optical absorbance with photon energy, near the band edge for the as-synthesized and annealed samples. The band gap transition for the undoped compound is observed at 3.272 eV, comparable to the value reported in the literature.[5] The band edge (band edge is obtained from the position of the maximum in the derivative of the absorption curve) is shifted to the lower energy side for the Ni-doped samples, as shown in the inset A of Figure 2. However, for both the $x = 0.025$ and 0.05 samples, the band edge is obtained as 3.242 eV. The decrease in the band edge, shown as inset A of Figure 2, is a clear indication for the incorporation of Ni inside the ZnO lattice.

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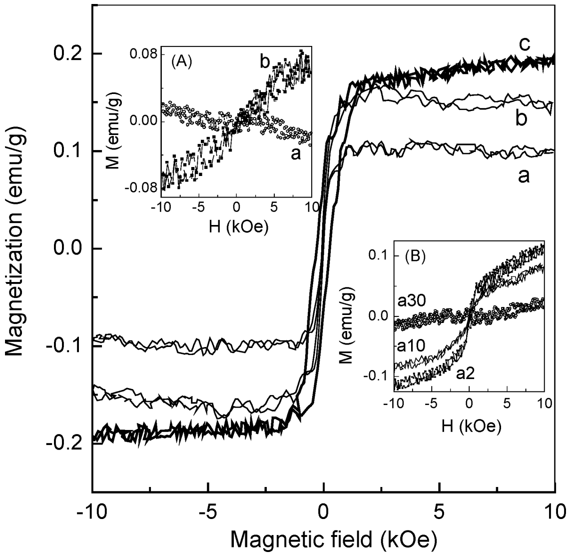

Figure 3. Magnetization as a function of field, measured at 300 K, for $Zn_{1-x}Ni_xO$; (a) $x = 0.025$ and (b) $x = 0.05$; (c) $x = 0.05$ measured at 12 K. Insets: (A) M−H curves of the samples annealed at 673 K for 2 h; (B) M−H curves of the $x = 0.025$ sample annealed at 800 K for 2 min (a2), 10 min (a10), and 30 min (a30).

There is not much variation in the band edge after annealing the Ni-doped samples. The red shift in the band edge is due to the increased sp−d exchange interactions between the band electrons and the localized d-electrons of the substituted Ni^{2+} ions.[30] It has been reported that the band edge becomes constant for the mole percentages of Ni > 2% and Co > 4%, respectively, for $Zn_{1-x}Ni_xO$ and $Zn_{1-x}Co_xO$,[31] and the present results are in agreement with the reported values. Inset B in Figure 2 shows the spin−orbit split $^3T_1(F) \rightarrow {}^3T_1(P)$ ligand field transitions of Ni^{2+} in tetrahedral symmetry, for the as-synthesized and annealed samples of $x = 0.025$ and 0.05. The electronic transitions are observed in all cases (the absorptions are partially masked in the as-synthesized samples, due to the residual carbon present), indicating that Ni^{2+} is substituted in the tetrahedral Zn^{2+} site and is in a stable environment.[26,27,32] The decrease in the band edge and the observation of the electronic transition of Ni^{2+} are clear indications for the incorporation of Ni inside the ZnO lattice, as observed in the case of Co-doped ZnO.[19] This shows that a small fraction of Zn is substituted by Ni in the ZnO lattice. Since the band edge remains the same for both the doped samples, the degree of substitution of Ni for Zn is likely to be the same in both samples.

The Ni-doped samples are found to be ferromagnetic at room temperature. Variation of the magnetization of the 2.5 and 5% Ni-doped samples as a function of magnetic field, measured at room temperature, is shown in Figure 3. Weak ferromagnetism (0.1 and 0.15 emu/g for $x = 0.025$ and 0.05, respectively), which is saturated just above 1 kOe, is observed at 300 K. For the $x = 0.05$ sample, the magnetization measured at 12 K is also shown in the figure. There is not much variation in the magnetization at 12 K when compared to the room temperature values. For $x = 0.025$ and 0.05, magnetization at 12 K is obtained as 0.12 and 0.19 emu/g, respectively. Since Ni metal and NiO are observed as impurities present in the as-synthesized samples, it can be assumed that magnetic contribution comes mainly from these two phases. Bulk NiO is antiferromagnetic with a Neel temperature of 520 K.[33] However, in the nanocrystalline form, NiO shows weak ferromagnetic or superparamagnetic behavior at low temperatures.[34,35] The fraction of NiO in the $x = 0.025$ sample is very small and is not likely to contribute much toward the observed ferromagnetism. For the $x = 0.05$ sample also, the antiferromagnetic (linear M−H variation) or weak ferromagnetic contribution will be much less than that expected from Ni metal. Assuming that the contribution to ferromagnetism comes from the Ni metal impurities only, the weight percentage of Ni metal present in the two different compositions is calculated based on the low-temperature saturation magnetization of Ni metal (57.65 emu/g).[36] The calculated values are 0.21 and 0.33%, respectively, for $x = 0.025$ and 0.05. The weight percentages of Ni metal impurity calculated from the magnetization data are almost comparable to that obtained from XRD data (0.15 and 0.3%), indicating that ferromagnetic contributions are mainly coming from the Ni secondary phase present in the samples.

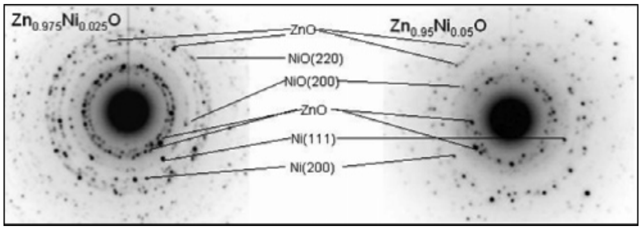

Figure 4. Comparison of selected area electron diffraction patterns of $Zn_{0.975}Ni_{0.025}O$ and $Zn_{0.95}Ni_{0.05}O$.

Further evidence for the presence of Ni metal and its oxides in the doped samples is obtained from electron diffraction studies. The selected area diffraction patterns of the $x = 0.025$ and 0.05 samples are compared in Figure 4. Many additional diffraction spots and rings, apart from those from the ZnO lattice, are observed in both the patterns. The additional spots and rings in the electron diffraction patterns are identified as those from fcc Ni and cubic NiO.

The next question is, if a small fraction of Ni is substituted for Zn as evidenced from the optical studies, is there a contribution to ferromagnetism from the doped sample? Since Ni metal will be oxidized to NiO at elevated temperatures when heated in air, it is expected that annealing of the samples in air will lead to complete conversion of ferromagnetic Ni metal impurities to antiferromagnetic NiO. If there is a contribution to ferromagnetism from the doped material also, this is expected to be retained after such heat treatment. To investigate this, both Ni-doped samples have been annealed at 673 K (above the T_C of Ni metal, which is 627 K[33]) for 2 h in air in a furnace, and the magnetization was measured after cooling the samples to room temperature.

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The M−H curves of the annealed $x = 0.025$ and 0.05 samples are shown in the inset A of Figure 3 (magnetization values corrected by subtracting the contribution from diamagnetic ZnO). Both the compositions are found to be nonferromagnetic after annealing at 673 K. The amounts of NiO in the 673 K annealed $x = 0.025$ and 0.05 samples is calculated from the XRD data as 0.4% and 2.7%, respectively. The negligible magnetization of the $x = 0.025$ sample and the linear variation of magnetization for the $x = 0.05$ sample after annealing is likely to be due to the antiferromagnetic nature of the NiO impurity (the Neel temperature of NiO is 520 K,[33] much above room temperature so that only a small linear variation is expected). Schwartz et al. had annealed their thin film samples at 800 K for 2 min and still the film showed ferromagnetic behavior at 350 K.[27] The ferromagnetic $x = 0.025$ sample also is annealed under these conditions and found that ferromagnetism at 300 K is almost retained when annealed for 2 min (inset B of Figure 3). On increasing the annealing time, it was found that magnetization decreases and that no ferromagnetism was observed after annealing for 30 min. It is already known that the oxidation of Ni in air is a very slow process; therefore, long annealing time is required for the complete oxidation of Ni metal impurities if present. The presence of Ni^{2+} in the ZnO lattice, as evidenced by the optical studies, and the absence of ferromagnetism in the annealed samples give evidence to the fact that the observed ferromagnetism is not intrinsic in case of Ni-doped ZnO.

Thus, based on the present results on the studies on polycrystalline samples of $Zn_{1-x}Ni_xO$, it can be concluded that ferromagnetism observed at room temperature in the powder samples is due to presence of Ni metal clusters as a secondary phase in the samples. XRD and electron diffraction studies give direct evidence for the presence of Ni metal in the 2.5% and 5% Ni-doped samples. Optical absorption studies show the incorporation of Ni in the ZnO lattice, and only a small fraction is likely to be incorporated as the rest of the Ni added is converted to Ni and NiO. The disappearance of ferromagnetism after annealing at 673 K indicates that the Ni-doped ZnO is not ferromagnetic.

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