

High resolution transmission electron microscopy and Raman scattering studies of room temperature ferromagnetic Ni-doped ZnO nanocrystals

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Ni-doped ZnO nanocrystals have been synthesized by a wet chemical reaction. The nanocrystals have been investigated carefully by high resolution transmission electron microscopy and all the particles are found to be the known wurtzite ZnO. X-ray photoelectron spectroscopy and Raman spectra results provide the evidence that Ni²⁺ is incorporated into the ZnO lattice at Zn²⁺ site. Magnetic property measurements reveal that the as-grown Zn_{1-x}Ni_xO nanocrystals exhibit room temperature ferromagnetic behaviors with saturation magnetization of 0.01 emu/g and Curie temperature above 340 K for Ni concentration of ~1% in atomic ratio. © 2007 American Institute of Physics. [DOI: 10.1063/1.2435606]

As one of the various candidate materials for realizing spintronic devices, Ni-doped ZnO has attracted intense interest. Wakno *et al.* reported the observation of ferromagnetism at 2 K for the Ni-doped ZnO films,¹ while above 30 K, superparamagnetic behavior was observed.² Yin *et al.* reported the paramagnetism in the Ni-doped ZnO films.³ On the other hand, ferromagnetism was observed at room temperature in Ni-doped ZnO nanorods,⁴ films,⁵ and nanowires arrays.⁶ Ni-doped ZnO quantum dots are formed to robust ferromagnetism with Curie temperature (T_C) up to 350 K.^{7,8} A number of studies indicate that the room temperature ferromagnetism in transition metal doped oxides may come from precipitation of magnetic clusters² or other secondary magnetic phases.⁹ On the other hand, there have many reports that support intrinsic ferromagnetism. Even so, the origin of ferromagnetism in diluted magnetic semiconductors (DMSs) remains in debate.

In this letter, Ni-doped ZnO nanocrystals were prepared in a round-bottom flask at low temperature. Zinc acetate dehydrated, nickel acetate, and tetramethylammonium hydroxide (25% in water) were used as precursors and distilled water as solvent. In a typical synthesis process of Zn_{1-x}Ni_xO, 0.5 ml tetramethylammonium hydroxide was added to 140 ml distilled water and heated by water heater firstly. Then 20 ml 0.25M metal acetate (Zn²⁺:Ni²⁺=9:1) were slowly injected into the flask and heated to 85 °C. The reaction was kept at 85 °C for 2 h with vigorous stirring. The condensed powders were washed by ethanol and water for several times to wipe off the possibly produced Ni(OH)₂. The as-grown Ni-doped ZnO nanocrystals were characterized using transmission electron microscopy (TEM, Tecnai 20ST), energy dispersive x-ray spectrometer (EDS), electron energy loss spectroscopy (EELS), x-ray Diffraction (XRD), x-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. Their magnetic properties were studied by a physical property measurement system (PPMS, Quantum Design).

Figure 1(a) shows the XRD patterns of the Zn_{1-x}Ni_xO powder (i) and standard ZnO (ii). All of the diffraction peaks for Zn_{1-x}Ni_xO can be indexed as those from the known wurtzite ZnO. But we can not exclude the possibility of information of other precipitates or clusters small enough not to be detected in XRD measurement. According to EDS spectra, as shown in Fig. 1(b), there are Zn, Ni, and O peaks in the sample besides Cu and C peaks from carbon coated TEM grid. The Ni atomic ratio is estimated to be ~1%. The inset in Fig. 1(b) is a low-magnification TEM image of the Zn_{1-x}Ni_xO powder. There are two different kinds image in shape, the bigger rodlike particles (~50 nm in diameter and

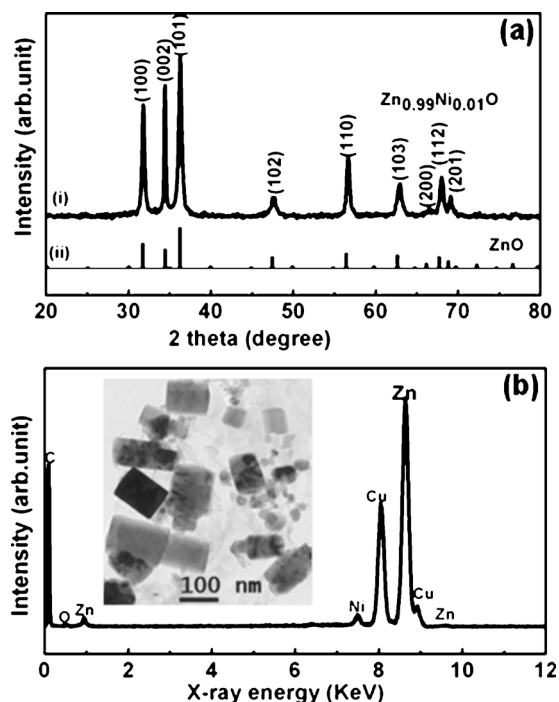


FIG. 1. (a) XRD patterns of the Zn_{1-x}Ni_xO powder and standard ZnO as indicated. (b) EDS spectrum for the Zn_{1-x}Ni_xO powder; inset is the typical TEM image.

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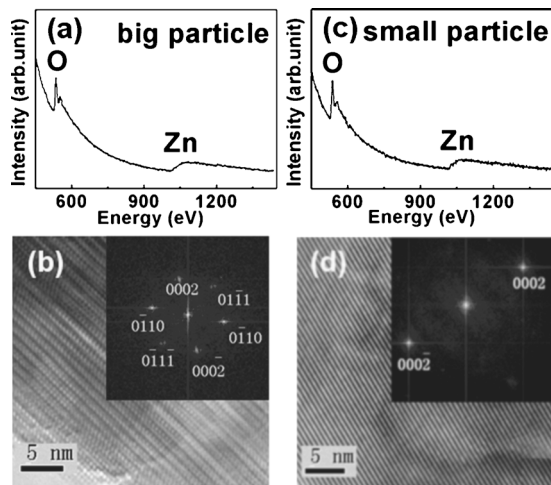


FIG. 2. (a) EELS spectrum of a typical big particle. (b) HRTEM image of a big particle; inset is the corresponding FFT. (c) EELS spectrum of a typical small particle. (d) HRTEM image of a small particle; inset is the corresponding FFT.

150–200 nm in length) and the smaller particles (~ 20 nm in diameter).

In order to discern whether any second phases exist in the powder, the two different kinds of particle have been analyzed, respectively. Figures 2(a) and 2(b) are from a typical bigger particle, and Figs. 2(c) and 2(d) are from a typical smaller one. As shown in Figs. 2(a) and 2(c), the EELS peak edges in the big particle are 528.5 eV (O edge), 547.0 eV (O edge), and 1017.5 eV (Zn edge), while in the small one are 529.5 eV (O edge), 548.2 eV (O edge), and 1018.7 eV (Zn edge); the average peak edge shift of about 1.1 eV between the big particle and the small one is due to the equipment itself, indicating that they have the same composition. On account of the low concentration, Ni is not able to be detected in a single particle by EELS. Figure 2(b) is a high resolution TEM (HRTEM) micrograph of a typical bigger particle; the inset is the corresponding fast Fourier transformation (FFT). The lattice spacing of 0.52 nm corresponds to the d spacing of (001) ZnO crystal planes, confirming that the $\text{Zn}_{1-x}\text{Ni}_x\text{O}$ nanocrystals are single crystals. Meanwhile, all d spacings estimated from the FFT are close to ZnO. The same results can also be observed from Fig. 2(d). So, we conclude that both the rodlike and the particlelike $\text{Zn}_{1-x}\text{Ni}_x\text{O}$ nanocrystals are with the same crystalline structure.

Ni concentration of ~ 1 at. % in ZnO is also suggested by XPS, which discloses the binding state of the compositional elements. As shown in Fig. 3, the Ni $2p_{3/2}$ peak is observed at ~ 855.46 eV and a satellite peak at ~ 861.56 eV, suggesting the oxidized state of Ni atom in the particles since the metallic Ni $2p_{3/2}$ peak should be at 852.7 eV. The Ni $2p_{3/2}$ peak position is quite from that of Ni and Ni_2O_3 , while close to NiO.³ This indicates that Ni ions in the products may have a valence of 2+, but the absence of NiO can be inferred by other features. Raman spectrum of $\text{Zn}_{0.99}\text{Ni}_{0.01}\text{O}$ nanocrystals is presented in the inset of Fig. 3. For pure ZnO, the 330 cm^{-1} frequency is the second-order vibration mode and the 379 cm^{-1} is A_1 (TO) mode. The phonon frequency of E_2 (high) and E_1 (LO) modes are 436 and 578 cm^{-1} .¹⁰ Compared with those of pure ZnO, $\text{Zn}_{0.99}\text{Ni}_{0.01}\text{O}$ have the classical Raman modes at 330, 379, 437, 573 cm^{-1} , and an additional mode at 670 cm^{-1} . Up to now, there are many reports of similar additional vibration modes in ZnO. The vibration

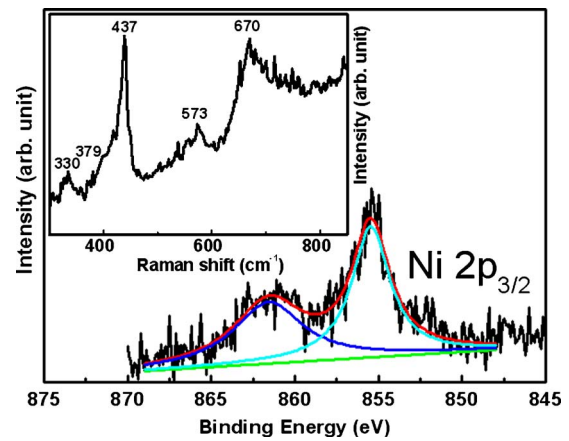


FIG. 3. (Color online) XPS spectrum of Ni $2p_{3/2}$ band of the $\text{Zn}_{0.99}\text{Ni}_{0.01}\text{O}$ powder; the inset is room temperature Raman scattering spectrum.

modes at $650\text{--}665\text{ cm}^{-1}$ are related to Mn-doped ZnO and attributed to the Mn based compounds.¹¹ Yang *et al.* proposed the additional mode at 660 cm^{-1} in Mn-doped ZnO related to intrinsic host-lattice defects.¹² In our experiment, the additional mode appears after doping, which maybe due to Ni^{2+} occupation at Zn^{2+} sites or defects in the nanocrystals.

Figure 4 shows the magnetic hysteresis (M - H) loop of $\text{Zn}_{0.99}\text{Ni}_{0.01}\text{O}$ measured at 305 K. The saturation magnetization of the products is about 0.01 emu/g ($0.14\ \mu_B/\text{Ni}^{2+}$) and the coercivity is about 100 Oe. Since ZnO is diamagnetic, the magnetization decreased at the tail end. The spontaneous moment was also found to be in the same small order in $\text{Zn}_{1-x}\text{Ni}_x\text{O}$ quantum dots⁷ and films,⁵ indicating that only a minority fraction of the Ni^{2+} ions is magnetically ordered. The temperature dependence of magnetization of the $\text{Zn}_{0.99}\text{Ni}_{0.01}\text{O}$ nanocrystals under the field-cooled (FC) and zero-field-cooled (ZFC) conditions are shown in the inset. The ferromagnetic ordering is maintained at temperatures beyond 340 K, i.e., T_C is above 340 K.

The ferromagnetism of these nanocrystals could arise from a number of possible sources. The first possibility is the precipitation of metallic Ni. But Ni is an unlikely source, because the $\text{Zn}_{1-x}\text{Ni}_x\text{O}$ nanocrystals are synthesized in air where metal Ni is unable to exist. In addition, NiO is also an unlikely candidate because of its antiferromagnetism with a Neél temperature of 520 K⁸ and NiO nanocrystals show supermagnetic behavior at room temperature.¹³ Another possibility have not been mentioned in previous studies yet may

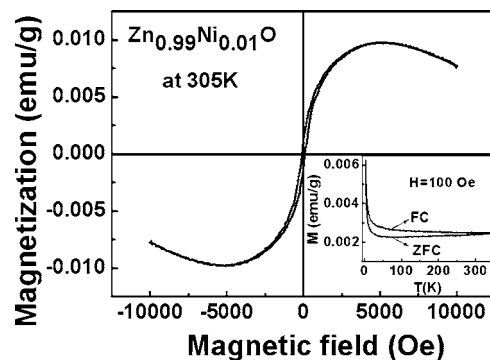


FIG. 4. Magnetic hysteresis loop of the as-grown $\text{Zn}_{0.99}\text{Ni}_{0.01}\text{O}$ powder at 305 K. The inset is temperature dependence of magnetization under the FC and ZFC conditions.

be the precipitation of Zn doped cubic NiO as determined by HRTEM in the samples annealed in air, which show strong room temperature ferromagnetic behavior (to be published elsewhere, see supplemental material). However, in the present as-grown sample, XRD and HRTEM analyses have not shown any of this phase. In the carrier-mediated exchange mechanism pertinent to ferromagnetism in oxide DMSs,^{5,14} defects are important to the ferromagnetism. As native point defects such as O vacancy are very common in ZnO and Ni doping may increase O vacancy concentration due to the radius of Ni ions being slightly bigger than Zn ions, they are likely to contribute to the observed ferromagnetism in the $\text{Zn}_{1-x}\text{Ni}_x\text{O}$ nanocrystals.

In summary, nanocrystalline $\text{Zn}_{0.99}\text{Ni}_{0.01}\text{O}$ has been synthesized by a simple solution approach. Microstructure analysis shows that the nanoparticles are single crystalline ZnO. XRD, HRTEM, EDS, XPS, Raman spectrum, and PPMS measurements indicate that Ni^{2+} substitute into ZnO lattice at Zn^{2+} site, instead of impurity compound or nickel oxide. The exchange interactions between Ni^{2+} ions mediated by carriers contribute to the ferromagnetism at room temperature.

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