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Effects of Ni concentration on structural, magnetic and optical properties of Ni-doped ZnO nanoparticles

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ABSTRACT

Ni-doped zinc oxide ($Zn_{1-x}Ni_xO$, $0 \leqslant x \leqslant 0.08$) diluted magnetic semiconductors have been synthesized by the using a sol–gel method. Structural, magnetic and optical properties of the samples have been studied. The results of X-ray diffraction (XRD), transmission electron microscope (TEM) and X-ray absorption fine structure (XAFS) indicated that Ni ions were substitutionally incorporated into the crystal lattice of ZnO. With Ni concentration increasing up to 2 at.%, all diffraction peaks corresponded to wurtzite structure of ZnO, but for $Zn_{0.97}Ni_{0.03}O$, secondary phase of NiO emerged. Based on the results of X-ray photoelectron spectroscopy (XPS), Ni incorporated into the ZnO lattice as Ni^{2+}. The produced samples showed good high-Tc (Curie temperature) ferromagnetism. The results of vibrating sample magnetometer (VSM) and photoluminescence (PL) showed that ferromagnetism (FM) of the Ni-doped ZnO nanoparticles originated from the presence of the O vacancy.

1. Introduction

Diluted magnetic semiconductors (DMSs) have been arousing wide interest due to the possibility to control spin and charge properties at the same time for future applications of spintronics [1–3]. However, the requirement of high Curie temperatures for ferromagnetic ordering has hindered the development of DMSs [4–6]. Since Dietl et al. [7] predicted the existence of room temperature ferromagnetism in transitional metal doped ZnO, the system has been extensively studied [8–10].

Ni-doped ZnO DMSs have been extensively studied [11–15]. However, it is always under debate on the existence and origin of the ferromagnetism of Ni-doped ZnO DMS materials. Some researchers held the negative opinion, because they did not observe ferromagnetism in their samples. For example, Wakano and colleagues used pulsed laser deposition (PLD) method to produce Ni-doped ZnO film on sapphire substrate [16]. However the ferromagnetism in the film was only observed at 2 K, which vanished at temperatures above 30 K. In contrast, there are still others who have positive opinion. They insisted that significant room temperature ferromagnetism did exist in single phase of Ni-doped ZnO based DMSs. For instance, Elilarassi et al. synthesized Ni-doped ZnO nanoparticles by using a low temperature sol–gel method which exhibited room temperature ferromagnetism [17]. Photoluminescence (PL), Fourier transform infrared spectroscopy (FTIR) and other characterization methods were employed to prove that the ferromagnetism was induced by the d–d exchange interaction between Ni^{2+} ion magnetic moment. Thereafter, on one hand the magnetism of Ni-doped ZnO based DMSs is dramatically dependent on the preparation methods or experiment parameters. On the other hand, even with the same preparation method whether there is magnetism or not is still highly controversial.

In this paper, we used sol–gel method to prepare $Zn_{1-x}Ni_xO$ with different Ni doping concentrations [18]. We studied their structural, magnetic and optical properties in order to investigate the possible origin of the ferromagnetism.

2. Experimental details

Zinc nitrate hexahydrate [$Zn(NO_3)_2{\cdot}6H_2O$] and the appropriate amounts of nickel nitrate hexahydrate [$Ni(NO_3)_3{\cdot}6H_2O$] were dissolved into citric acid monohydrate ($C_6H_8O_7{\cdot}H_2O$) with stirring to form sols. Then, the mixture was polymerized to form gels. We sintered the gels at 500 °C in Ar atmosphere to form the Ni-doped ZnO nanoparticles.

Structure characterization of $Zn_{1-x}Ni_xO$ was performed by XRD on D/max-2500 copper rotating-anode X-ray diffractometer with Cu Kα radiation (40 kV, 200 mA). Morphology, interplanar distance and energy dispersive spectroscopy (EDS) were

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investigated by using a TEM (200 keV, JEM-2100HR, Japan). Valence state of Ni was analyzed by using XPS (VG ESCALAB Mark II). XAFS measurements for the Ni K-edge were performed in fluorescence mode at room temperature on an XAFS station of the U7C beam line of the National Synchrotron Radiation Laboratory (NSRL, Hefei, China). Magnetic hysteresis loops of the $Zn_{1-x}Ni_xO$ NPs were measured by using a Lake Shore 7407 vibrating sample magnetometer (VSM). PL measurement was performed on an HR800 Labram Infinity Spectrophotometer, excited by a continuous He–Cd laser at a wavelength of 325 nm and a power of 50 mW.

3. Results and discussion

Fig. 1 shows XRD patterns of the $Zn_{1-x}Ni_xO$ ($x = 0$, 0.01, 0.02, 0.03, 0.05, 0.08) nanoparticles. When $x \leqslant 0.02$, all samples show only single phase wurtzite structure. When doping concentration is higher than 0.03, the NiO (200) diffraction peak is observed. Its intensity increases with increasing doping concentration. Therefore, the saturated solubility of Ni in ZnO is 2%. Crystalline particle sizes of the six samples are 31.8, 31.2, 30.5, 28.7, 26.3 and 24.4 nm. The particle size decreases with increasing doping concentration, which is the result of surface reaction competition [19]. Because the Ni–O bond energy is higher than Zn–O bond energy, the reaction mobility to raise growth surface will decrease with increasing doping concentration. Unit cell constants of the $Zn_{1-x}Ni_xO$ against Ni concentration are plotted in Fig. 2. The lattice constant c decreases with increasing doping concentration when the concentration is lower than 2%. This is because Ni^{2+} radius (0.069 nm) is smaller than that of Zn^{2+} (0.074 nm) [20,21]. This proves that Ni^{2+} has been incorporated into ZnO. However, c axis increases at higher concentration. This is probably because some Ni^{2+} ions have taken interstitial sites in ZnO.

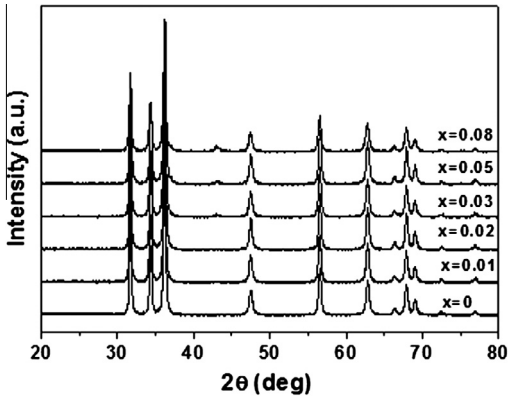

Fig. 1. XRD patterns of the $Zn_{1-x}Ni_xO$ nanoparticles annealed at 500 °C in Ar.

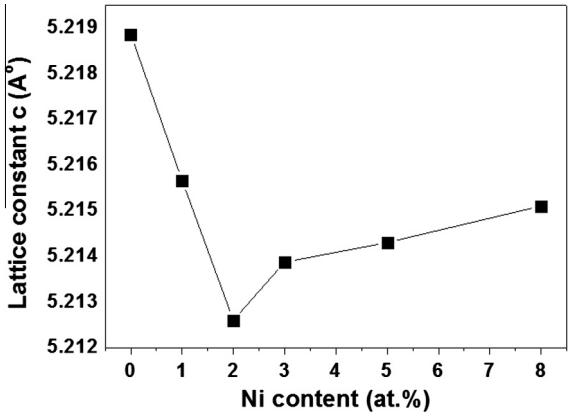

Fig. 2. Unit cell constant *c* of ZnO as a function of Ni doping concentrations.

Fig. 3 shows low magnification TEM images of $Zn_{0.98}Ni_{0.02}O$ and $Zn_{0.92}Ni_{0.08}O$. Both samples show spherical morphology, without obvious aggregation. Their average sizes are 30 and 25 nm,

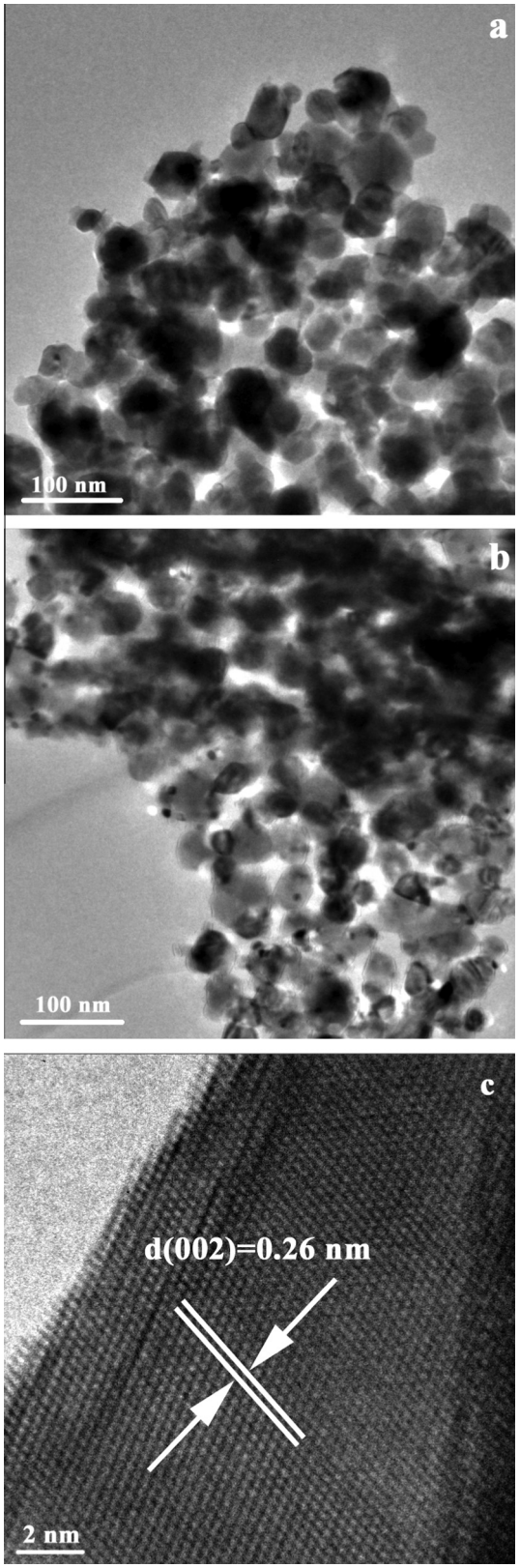

Fig. 3. TEM images of the $Zn_{0.98}Ni_{0.02}O$ (a) and $Zn_{0.92}Ni_{0.08}O$ (b) nanoparticles; HRTEM image of the $Zn_{0.98}Ni_{0.02}O$ nanoparticles (c).