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Journal of Magnetism and Magnetic Materials



journal homepage: www.elsevier.com/locate/jmmm

Synthesis of Fe-doped NiO nanofibers using electrospinning method and their ferromagnetic properties

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ARTICLE INFO

Article history: Received 30 May 2011 Received in revised form 26 December 2011 Available online 22 February 2012 Keywords: Diluted magnetic semiconductor (DMS)

Diluted magnetic semiconductor (DMS Electrospinning Ni_{1-x}Fe_xO Ferromagnetism

1. Introduction

Diluted magnetic semiconductor (DMS) is a kind of novel semiconductors, which is formed using magnetic transition metal ions or rare earth metal ions to randomly replace the non-magnetic cations in semiconductors and to make the semiconductor show magnetic properties [1]. Such semiconductors are potential candidates for applications of spin-controlled devices. Unfortunately, most of the natural DMSs have relatively low Curie temperatures (T_c) , which hinder their wide applications. Since Dietl et al. [2] used average field theory to predict that adding a magnetic ion in wide band gap oxide semiconductor can cause it to become room temperature diluted magnetic semiconductor, the room temperature ferromagnetism in wide band gap semiconductors such as TiO₂ [3], ZnO [4], SnO₂ [5] by substituting magnetic transition metal (3d) ions have been discovered. The above mentioned DMS materials are known all as n-type DMS materials. For potential applications of spin-controlled devices, the p-type DMS systems are also needed. However, there are few reports about the detailed characteristics of p-type DMS.

Stoichiometric Nickel oxide NiO is known to show an antiferromagnetism that remains even at rather high temperatures T_N =523 K [6]. The measured band gap of NiO is about 4.0 eV, clearly indicating that it behaves as an insulator with roomtemperature conductivity less than 10⁻¹³ S/cm [7]. Although stoichiometric NiO is a Mott–Hubbard insulator at room temperature, after introduction of Ni²⁺ vacancies or doping with Li⁺, which can become a p-type semiconductor [8].

ABSTRACT

To make p-type diluted magnetic semiconductor (DMS), $Ni_{1-x}Fe_xO$ nanofibers with different Fe doping concentrations have been successfully synthesized by electrospinning method using polyvinyl alcohol (PVA) and Ni(CH₃COO)₂·4H₂O as starting materials. The nanofibers were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman spectroscopy, superconductivity quantum interference device (SQUID) and X-ray photoelectron spectroscopy (XPS) test. The results show that Fe doping has no influence on the diameter and surface morphology of NiO nanofibers, and the nanofibers are polycrystalline with NaCl structure. All Fe-doped samples show obvious ferromagnetic properties and the saturation magnetization is enhanced with increase of the doping concentration of Fe, which indicates that the doped Fe has been incorporated into the NiO host and results in room-temperature ferromagnetism in the $Ni_{1-x}Fe_xO$ nanofibers.

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One-dimensional nanostructured materials have gained increasing attention by virtue of their potential applications [9] due to their remarkable magnetic, optical, electric, and chemical properties. One-dimensional nanostructured magnetic material often shows a high degree of magnetic anisotropy due to its special size and structure. Therefore, compared with general ferromagnetic materials, the one-dimensional nanostructured magnetic materials have great value of spontaneous magnetization and coercivity. In case of dilute magnetic semiconductor, current researches are centered on film and bulk materials, the reports on one-dimensional nano-dilute magnetic semiconductor were few. Nanoparticles, nanorods, and films structure of NiO had been prepared by sol-gel techniques [10], hydrothermal route [11] and PLD [12]. Compared with other methods, electrospinning is a simple, versatile and convenient approach to manufacture one-dimensional nanomaterials with the characteristic of easy control and low cost [13].

In this paper, we report the successful fabrication of p-type DMS Fe-doped NiO nanofibers with diameters about 100 nm via electrospinning technique. In order to clarify the origin of ferromagnetism in these Fe-doped NiO nanofibers, the effects of Fe doping on the crystal structure, morphology and detailed temperature and fielddependent magnetization of the nanofibers were also investigated.

2. Experimental

2.1. Synthesis of NiO nanofibers

Pure NiO and Fe-doped NiO nanofibers with different doping concentrations were synthesized by electrospinning. In a typical

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^{0304-8853/\$ -} see front matter © 2012 Elsevier B.V. All rights reserved. doi:10.1016/j.jmmm.2012.02.017

procedure, the aqueous polyvinyl alcohol (PVA, Mw 80,000) solution (10 wt%) was prepared by dissolving 10 g PVA powder in 90 ml distilled water first. Then, 2 g Ni(CH₃COO)₂·4H₂O and the suitable amount of Fe(NO₃)₃·9H₂O with a different atomic ratios (Ni:Fe=100:0, 100:1, 50:1 and 20:1) respectively were added slowly into the aqueous PVA solution under vigorous stirring at 40 °C for 2 h, and then, 5 ml alcohol was dropped slowly into the solution with stirring. Ultimately, a lucid and viscous sol solution was obtained to prepare for electrospinning.

The precursor sol solution was loaded into a 20 ml plastic syringe with a syringe needle of which the internal diameter is 0.5 mm. The needle was connected to a DC high-voltage power supply. In our experiment, a voltage of 10 kV was applied between the cooper plate collector and the syringe needle with a distance of 12 cm. The PVA/Ni(CH₃COO)₂ · 4H₂O composite nanofibers were collected on the cooper plate during electrospinning processes. Pure NiO and Fe-doped NiO nanofibers were finally obtained by calcination at 650 °C for 3 h in air to remove PVA, completely.

2.2. Characterization methods

X-ray diffraction (XRD) was employed to investigate the crystal structure of nanofibers using Cu/K α radiation. And the morphologies of nanofibers were characterized by scanning electron microscope (SEM). Besides, Raman scattering spectroscopy with the Ar⁺ (514.5 nm) laser lines as the excitation sources was used to examine the vibrational modes of the nanofibers to identify the compositions in the nanofibers. The valence of the dopants was analyzed by X-ray photoelectron

spectroscopy (XPS) and magnetic properties of the samples was measured by superconductivity quantum interference device (SQUID).

To distinguish electric conduction type of the as-prepared samples, a Hot-Probe experiment was executed [14]. A certain amount of Ni_{0.98}Fe_{0.02}O nanofiber was molded by powder compression machine into the block of 1.0 mm \times 5 mm \times 5 mm and calcined at 1000 °C for 6 h, and then the electrically conductive Silver glue was brushed on the two opposite sides. A couple of cold probe and hot probe were attached to the two sides of the sample, the hot probe is connected to the positive terminal of the meter, while the cold probe is connected to the negative terminal.

3. Results and discussion

From the Hot-Probe experiment, a negative voltage is obtained for the as-prepared sample, so we can draw a conclusion that the Fe doped NiO nanofibers is a p-type semiconductor. The electrical resistivity of Ni_{0.98}Fe_{0.02}O is $\sim 8 \times 10^3 \,\Omega$ m obtained by a conventional ohmmeter.

Fig. 1 shows the SEM images of the nanofibers before and after calcination. Fig. 1(a) and (c) shows the SEM images of undoped NiO/PVA and Fe doped NiO/PVA composite nanofibers before calcination. It can be seen that the surface of composite fibers before calcination were smooth. They are several millimeters long with a diameter of approximately 300 nm. Furthermore, in contrast to undoped NiO/PVA composite nanofibers, Fe doped in NiO does not influence the morphologies of doped samples. After calcinations at 650 °C, due to the decomposition of PVA and the



Fig. 1. SEM images of the undoped NiO/PVA and Fe doped NiO/PVA composite nanofibers before and after calcinations.



Fig. 2. The XRD patterns of Ni_{1-x}Fe_xO(x=0, 0.01, 0.02, 0.05) nanofibers after sintering at 650 °C.

transformation from metal salts into metal oxides, the diameters of undoped and Fe-doped NiO nanofibers shrank drastically to 50–100 nm, as shown in Fig. 1(b) and (d).

Fig. 2 shows the XRD patterns of Ni_{1-x}Fe_xO(x=0, 0.01, 0.02, 0.05) nanofibers. It can be seen that five diffraction patterns at θ =37.2°, 43.4°, 62.9°, 75.2° and 79.4° correspond to (111), (200), (220), (311) and (222) characteristic peaks of cubic crystalline NiO. No impurity phase was observed with the sensitivity of XRD measurement, and the lattice constants of Fe doped NiO nanofibers hardly shifted with the increase of Fe content since the ionic radii of Ni²⁺(0.69 Å), Fe²⁺(0.74 Å), and Fe³⁺(0.64 Å) are quite close.

In order to further identify whether there is any trace amount of second phase in the $Ni_xFe_{1-x}O$ nanofibers, the room temperature Raman scattering of samples were examined. The room temperature Raman spectra of $Ni_xFe_{1-x}O$ nanofibers is shown in Fig. 3. For all samples with or without Fe doping, the Raman spectra are almost the same. Two Raman peaks are located at about 570 and 1100 cm⁻¹ in the range of 200–2000 cm⁻¹. The former peak can correspond to the one-phonon (1P) longitudinal optical (LO) phonon modes of NiO, and the latter peak can be assigned to two-phonon (2P) 2LO modes [15]. Stoichiometric NiO is in NaCl structure and is expected not to show first order Raman scattering. Therefore, the first-order Raman scattering peak centered at 570 cm⁻¹ is caused by nickel vacancies that break down selection rules, as in oxygen-rich or "black" NiO [16]. The firstorder Raman scattering peak of 570 cm^{-1} shown in the spectra was enhanced with the increases of Fe concentration, implying a high nickel vacancy concentration. Raman measurements show that both the undoped and Fe-doped NiO nanofibers have a good crystal guality with cubic crystalline NiO, and since a small amount of Fe doping will not change the structure of NiO. Fe doping neither caused a structural change nor induced a secondary phase. This is consistent with the XRD patterns.

Fig. 4 shows the hysteresis loops of undoped NiO and $Ni_xFe_{1-x}O$ samples measured at room temperature. For the undoped NiO samples, as shown in Fig. 4a, it can be seen that the extrinsic magnetic field dependence of magnetic moment is almost linear, which is a typical antiferromagnetic-like behavior, whereas all the $Ni_xFe_{1-x}O$ samples show ferromagnetic-like behaviors as shown in Fig. 4b. The magnetization of samples do not saturate up to 30,000 Oe, which indicates the coexistence of ferromagnetic phase and antiferromagnetic phase. The area of



Fig. 3. The room temperature Raman spectra of $Ni_xFe_{1-x}O$ nanofibers.

hysteresis loop of the samples increased with the concentration of dopant Fe indicated that the maximum values of magnetization and coercive field are increased, which is an identification of the increase of proportion of ferromagnetic phase with the concentration of dopant Fe. The presence of the hysteresis loops of $Ni_xFe_{1-x}O$ at room temperature indicates that the Curie temperature is above room temperature.

In order to explore the magnetized behavior of the samples, the magnetization curves of field cooling (FC) and zero field cooling (ZFC) were tested. As shown in Fig. 5, when extrinsic magnetic field H=100 Oe is applied, whether on undoped samples or on Fe doped samples, their field cooling (FC) and zero field cooling (ZFC) curves were bifurcate obviously at lower temperature range, while they overlapped nearby 300 K. As indicated in Fig. 5, the FC magnetization of Ni_{0.98}Fe_{0.02}O nanofibers rapidly increases with the decreasing temperature and becomes quite larger than the ZFC magnetization. Oppositely, for the ZFC-FC magnetization curves of undoped NiO nanofibers, the difference between FC magnetization and ZFC magnetization was tiny, and the value of FC magnetization or ZFC magnetization of these nanofibers was far lower than that of Ni_{0.98}Fe_{0.02}O nanofibers. The phenomenon indicates that Fe dopant NiO exhibits obviously ferromagnetic character in spite of the antiferromagnetism for undoped NiO. In the following we discuss the behavior of magnetic moments during FC or ZFC process. The ZFC magnetization curve is typically obtained by cooling in zero fields from a high temperature and measuring the magnetization at stepwise increasing temperatures in a small extrinsic magnetic field. The FC magnetization curve is typically obtained by measuring at stepwise-decreasing temperatures in the same small extrinsic magnetic field at each temperature. When the sample is cooled at non-zero field (FC), the spin moments are ordered almost parallel to the direction of applied field, the sample shows non-zero magnetization even if the extrinsic magnetic field decreases to zero. Thus, MFC (T) behavior is similar to the behavior of spontaneous magnetization, which can be easily explained by mean-field theory. When the sample is cooled at zero-field (ZFC), the spin moments are totally disordered. The sample shows zeromagnetization when the extrinsic magnetic field is zero. If a small extrinsic magnetic field is applied to the sample at low temperature, the spin moments rotate towards the extrinsic magnetic field direction, and the sample shows net magnetization. A large field and a large spontaneous magnetization (or MFC) give a large



Fig. 4. (a) The hysteresis loops of undoped NiO nanofibers and (b) $Ni_xFe_{1-x}O(x=0.01, 0.02, 0.05)$ nanofibers measured at 300 K.



Fig. 5. ZFC–FC magnetization curves of undoped NiO and $\rm Ni_{0.98}Fe_{0.02}O$ nanofibers.

ZFC magnetization. But the magnetic anisotropy (or coercive field) resists the rotation to extrinsic magnetic field direction.

For the undoped NiO sample, which is antiferromagnetic below the Neel temperature (573 K), as doped by Fe ions, the



Fig. 6. XPS spectra of Fe 2p, for the Ni_{0.98}Fe_{0.02}O nanofiber.

defects (e.g., Ni vacancy) could be introduced into NiO, which are randomly localized over the host lattice. Thus, this kind of disorder certainly breaks the translation symmetry of the system and the magnetic order in NiO grains would be interrupted, which causes relatively weak coupling between the sublattices and gives rise to ferromagnetism by interacting via a competing antiferromagnetic superexchange and ferromagnetic double-exchange coupling [12] through the introduced Fe ions and free charge carriers. As discussed earlier, the content of Ni vacancy is increased with Fe concentration, and Fe doping into NiO nanofibers neither caused a structural change nor induced a secondary phase, we believe that the room temperature ferromagnetism of $Ni_{v}Fe_{1-v}O$ nanofibers is intrinsic. As the concentration of dopant Fe increases, all Fe-doped samples can result in a significant enhanced saturation magnetic moment. This indicates that the doped Fe ions play an important role in mediating the magnetic interactions. In addition, as Yan et al. [17] propose that the Zn vacancy can induce the room-temperature ferromagnetism in Mn-doped ZnO by firstprinciples calculations, we can also believe that the Ni vacancy can also induce the room-temperature ferromagnetism in Fe-doped NiO; as illustrated in Fig. 3, the Raman scattering peak of 570 cm⁻¹ is enhanced with the increases in concentration of Fe, implying a high nickel vacancy concentration.

The valence of the Fe ions in the Ni_xFe_{1-x}O nanofiber is verified by the XPS measurements. As shown in Fig. 6, it can be seen that the spectra consist of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ peaks, which showed that the doped Fe in the Ni_{0.98}Fe_{0.02}O nanofiber exists as Fe²⁺, and no metallic Fe was observed in our samples. It can also indicate that the origin of ferromagnetism can be ruled out by the ferromagnetic secondary phase (e.g., metallic Fe).

4. Conclusions

Fe-doped NiO nanofibers with room-temperature ferromagnetism have been successfully synthesized by electrospinning method. We have studied the morphology and structures as well as the magnetic properties for different Fe doping concentrations. The results show that Fe doping has little influence on the diameter and surface morphology of NiO nanofibers, and the nanofibers exhibit the NaCl structure and no Fe-related secondary phases are formed in the samples. We believe that the room temperature ferromagnetism of Ni_xFe_{1-x}O nanofibers is intrinsic. All Fe-doped samples show obvious ferromagnetic properties and

as the concentration of dopant Fe increases, the saturation magnetization (Ms) is also correspondingly enhanced. We believe that the doped Fe has been incorporated into the NiO host, which induced Ni vacancy and excited the room-temperature ferromagnetism in the Ni_xFe_{1-x}O nanofibers.

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