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Room temperature ferromagnetism in hydrothermally grown Ni and Cu co-doped ZnO nanorods

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Abstract

The fabrication and magnetic characteristics of Ni and Cu co-doped ZnO nanorods are reported. The Ni and Cu co-doped ZnO nanorods are synthesized by a facile hydrothermal method. Structural characterizations reveal that Ni and Cu ions enter into ZnO lattices without any secondary phases. SEM images show that they are regular nanorods. Magnetic measurements indicate that the obtained rod arrays exhibit room-temperature ferromagnetic behaviors. The exchange interaction between free delocalized carriers (holes from valence band) and the localized d spins of Ni and Cu ions is considered as the cause of the room-temperature ferromagnetism.

Keywords: D. ZnO; Diluted magnetic semiconductors; Ferromagnetism; Nanorods

1. Introduction

In the past decade, diluted magnetic semiconductors (DMSs) have gained increasing interest due to their potential applications in spintronics devices, transparent electronics, piezoelectricity, optoelectronics, etc [1–5]. The main challenge for practical applications of the DMSs materials is the achievement of ferromagnetism (FM) above room temperature (RT). ZnO is known as ionic semiconductor with a wide band gap of about 3.36 eV at room temperature and a high excitation binding energy of 60 meV, which give rise to its outstanding properties and potential applications in diverse fields [6–12]. ZnO-based DMSs are appealing since they were predicted to have Curie temperature (T_C) above room temperature [13]. Among them, 3d transition metal (Fe, Co, Ni and Mn) doped ZnO DMSs have been extensively studied [14–17]. The introduction of 3d transition metal ions which contain local magnetic moments can lead to exchange interaction between itinerant sp-band electrons or holes and the d-electron spins localized at the magnetic ions, inducing high temperature ferromagnetism [18]. One-dimensional ZnO DMSs nanostructures are extremely interesting on account of their tunable magnetic, electronic and optoelectronic properties [18–21]. For example, one-dimensional nanostructures DMSs with ferromagnetism could restrict all spin rotations to a single axis, making them promising candidates for spin transistors [22]. In fact, there are different methods for fabricating ZnO nanorods, including chemical vapor deposition, electrochemical approach, pulsed laser deposition [23] and solid state reaction [24]. Hydrothermal route has the merit of one-step synthesis, powder reactivity and shape control. Hydrothermal process is an important and the very simple low-temperature method among wet chemistry, which has been used to fabricate one-dimensional ZnO nanorods in recent works [25]. Moreover, the hydrothermally grown ZnO nanorods is the very interesting system due to their high surface-to-volume ratios, strange surface-states and abundance defects. In particular, hydrothermal route can boost room-ferromagnetism on account of the presence of –OH

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ligands on the surface of the as-grown sample [26]. Unfortunately, few reports have been presented on synthesis of one-dimensional Ni and Cu co-doped ZnO nanorods using hydrothermal route. Here, the synthesis of high quality Ni and Cu co-doped ZnO nanorods have been fabricated by a facile hydrothermal route. Ferromangnetism above room temperature has been successfully achieved in these nanorods and the origin of ferromagnetism in ZnO DMSs has been discussed.

2. Experimental details

Ni and Cu co-doped ZnO nanorods were prepared by a hydrothermal method. 0.744 mmol of zinc acetate [$Zn(Ac)_2 \cdot 2H_2O$], and the desired amount of copper acetate [$Cu(Ac)_2 \cdot H_2O$] and nickel acetate [$Ni(Ac)_2 \cdot 4H_2O$] were firstly mixed and then dissolved in 20 ml absolute ethanol to form Solution A. Simultaneously, 6.4 mmol NaOH was dissolved in 8 ml absolute ethanol to form Solution B. Then the Solution B was added to Solution A under magnetic stirring, followed by adding 6.4 ml PEG-400. Finally, the mixture was transferred to a Teflon lined stainless steel autoclave of 50 ml capacity and heated at 140 °C for 24 h. After cooling to room temperature, the obtained products were collected and thoroughly washed with distilled water and absolute ethanol for several times, and then dried at 60 °C for 4 h.

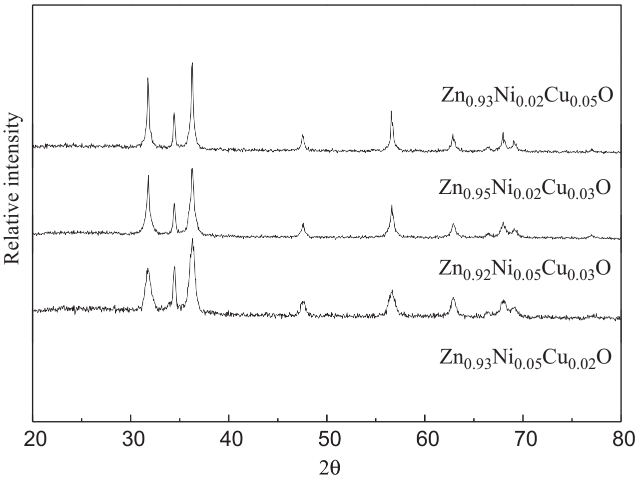

Fig. 1. XRD patterns of Ni and Cu co-doped ZnO samples.

Powder X-ray diffraction (XRD) with Cu Kα radiation was performed to check the structure and phase purity of all samples. The morphology of products was investigated by scanning electron microscopy (SEM). The magnetic measurements were carried out by a Quantum Design superconducting quantum interference device (SQUID). X-ray photoelectron spectroscopy (XPS) experiments were performed on a BSCALB MK-II spectrometer equipped with a monochromatized Al Kα X-ray source. The overall energy resolution was 0.6 eV.

3. Results and discussions

The XRD patterns of Ni and Cu co-doped ZnO nanorods are shown in Fig. 1. All the diffraction peaks can be indexed as pure ZnO phase with a hexagonal symmetry. The refined lattice parameters for these samples are given in Table 1. The lattice parameters decrease with the introduction of Ni and Co ions, which can be attributed to the larger ion radius of Zn^{2+} (0.97 Å) compared with that of Ni^{2+} (0.69 Å) and Cu^{2+} (0.72 Å). It is indicated that Ni and Co ions occupy the Zn sites in

Table 1
Lattice parameters *a* and *c* for Ni and Cu co-doped ZnO samples.

Sample	ZnO [27]	$Zn_{0.93}Ni_{0.05}Cu_{0.02}O$	$Zn_{0.92}Ni_{0.05}Cu_{0.03}O$	$Zn_{0.95}Ni_{0.02}Cu_{0.03}O$	$Zn_{0.93}Ni_{0.02}Cu_{0.05}O$
a (Å)	3.2554	3.252	3.2477	3.249	3.2517
c (Å)	5.2153	5.2055	5.2030	5.2011	5.2059

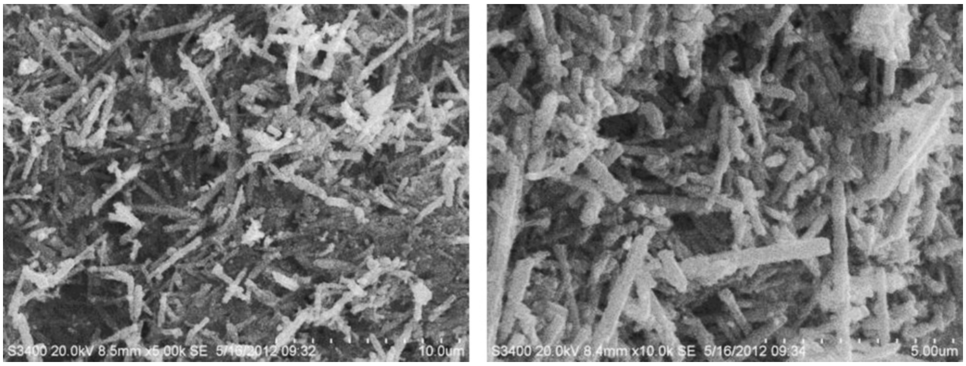

Fig. 2. SEM images of Ni and Cu co-doped ZnO nanorods.

the hexagonal wurtzite structure and no impurity phase can be detected. Fig. 2 shows SEM images of these samples. As shown in Fig. 2, Ni and Cu co-doped ZnO nanords can be produced after the hydrothermal treatment. The nanorods are about 200 nm in diameter and 1–5 μm in length.

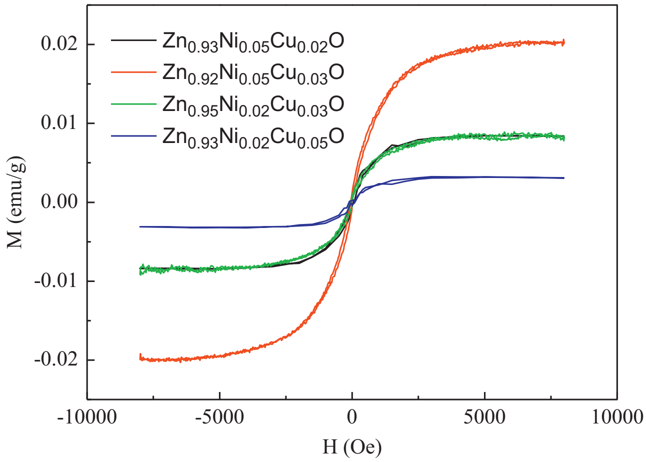

Fig. 3. $M-H$ curves for Ni and Cu co-doped ZnO nanorods detected at 300 K.

Table 2
The values of M_r, H_c and M_s for Ni and Cu co-doped ZnO samples.

Sample	M_r (emu/g)	H_c (Oe)	M_s (emu/g)
$Zn_{0.93}Ni_{0.05}Cu_{0.02}O$	9.25×10^{-4}	45	0.008
$Zn_{0.92}Ni_{0.05}Cu_{0.03}O$	1.45×10^{-3}	57	0.02
$Zn_{0.95}Ni_{0.02}Cu_{0.03}O$	9.37×10^{-4}	74	0.008
$Zn_{0.93}Ni_{0.02}Cu_{0.05}O$	2.02×10^{-4}	100	0.003

Magnetic properties of the Ni and Cu co-doped ZnO nanorods were investigated by SQUID. Fig. 3 shows the magnetic hysteresis ($M-H$) curves measured from −8000 to 8000 Oe at 300 K for the samples. The diamagnetic contribution from the sample holder has been subtracted. As shown in the magnetic curves, all the samples exhibit obvious ferromagnetic behaviors. Furthermore, the magnetization of the samples depends on the doping level of Ni and Cu. The values of remanence (M_r), coercive field (H_c) and saturation magnetization (M_s) for Ni and Cu co-doped ZnO samples are given in Table 2. The samples have different M_s, indicating that room temperature ferromagnetism is induced by the introduction of Ni and Cu. It is worthy to note that the sample $Zn_{0.92}Ni_{0.05}Cu_{0.03}O$ with a high Ni content has a large M_s up to 0.02 emu/g, which can be attributed to the enhanced ferromagnetic coupling after Ni substitution. There are several different explanations for the origin of ferromagnetism in 3d transition metal doped ZnO. A number of studies suggested that ferromagnetic ordering originated from magnetic precipitation or secondary magnetic phases [16]. Lee et al. argued that the origin of ferromagnetism could be ascribed to hydrogen contamination [28]. However, a free carrier mediated exchange mechanism was proposed to induce the intrinsic ferromagnetism in transition metal doped ZnO [29,30]. Based on our XRD analysis, magnetic precipitation and secondary magnetic phases can be ruled out. To clarify the origin of ferromagnetism, we also performed X-ray photoelectron spectroscopy (XPS) measurements on the samples. Fig. 4a shows Ni 2p XPS spectrum of $Zn_{0.92}Ni_{0.05}Cu_{0.03}O$ compound. The XPS peaks of Ni $2p_{3/2}$ and Ni $2p_{1/2}$ are located at

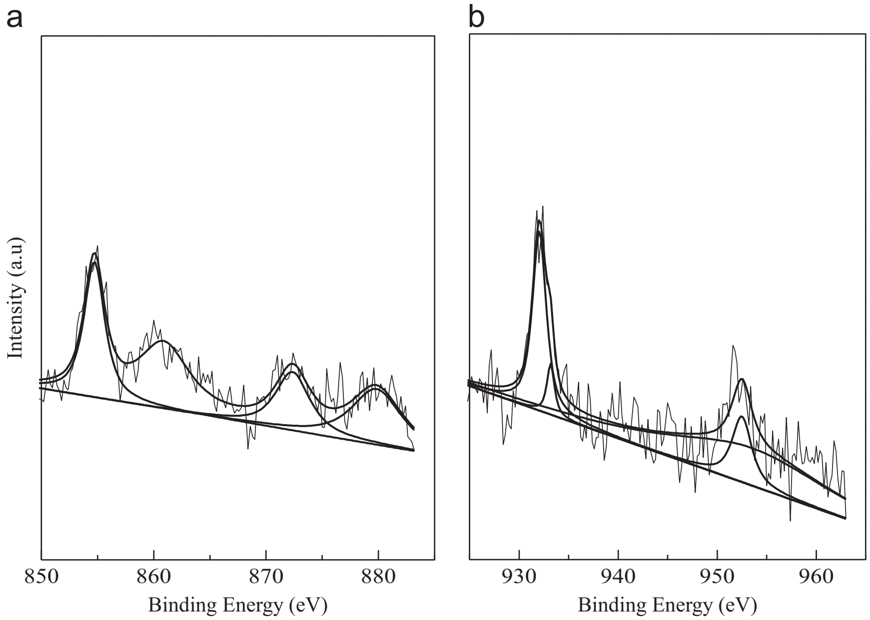

Fig. 4. XPS spectra for $Zn_{0.93}Ni_{0.02}Cu_{0.05}O$, (a) Ni 2p, (b) Cu 2p.

854.7 eV and 872.4 eV, respectively. The other peaks appear at 860.9 and 879.8 eV. All these peaks are very close to that of Ni^{2+} ions [31], which reveals that Ni^{2+} ions present in the ZnO lattices. Cu 2p XPS spectrum is given in Fig. 4b. The binding energies of Cu are determined as 932 eV (Cu^{1+} $2p_{3/2}$), 952.5 eV (Cu^{1+} $2p_{1/2}$), 933.2 eV (Cu^{2+} $2p_{3/2}$) and 953.5 eV (Cu^{2+} $2p_{1/2}$), suggesting that both Cu^{1+} and Cu^{2+} ions exist in the materials [32]. Therefore, we conclude that the simultaneous doping of Ni and Cu into ZnO increases carrier (hole) concentration of these materials. Free carriers play an important role in establishing the magnetic phase and hence the ferromagnetism in ZnO-based DMSs [7]. According to the RKKY exchange mechanism, the ferromagnetic interaction in DMS materials originates from the exchange interactions between local spin-polarized electrons and free carriers [33]. The presence of free carriers is considered as a compulsory condition for the appearance of ferromagnetism in the Ni and Cu co-doped ZnO nanorods. On the basis of XPS analysis, we can assign the electronic configurations of Ni^{2+} and Cu^{2+} to $3d^84s^0$ and $3d^94s^0$, respectively. This suggests that localized d spins present in these materials due to Ni and Cu introduction. As a result, we think that the observed room-temperature ferromagnetism originates from the exchange interaction between free delocalized carriers (holes from valence band) and the localized d spins of Ni and Cu ions. The substitution of Ni and Cu ions for the Zn sites is suggested as the main cause for the enhanced ferromagnetic properties.

4. Conclusions

Ni and Cu co-doped ZnO nanorods were synthesized by a facile hydrothermal method and their magnetic properties were investigated. Structural characterizations reveal that Ni and Cu ions enter into ZnO lattices without any secondary phases. The diameters of the nanorods are about 200 nm. The field dependence of magnetization (*M–H*) measured at 300 K exhibits obvious ferromagnetic characteristics. The observed room-temperature ferromagnetism could be induced by the exchange interaction between free delocalized carriers (holes from valence band) and the localized d spins of Ni and Cu ions.

Acknowledgments

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