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Local structure and magnetic properties of Co-doped 3C-SiC nanowires

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ABSTRACT

Co-doped 3C-SiC nanowires were synthesized using high-purity SiO, Co and carbon nanotubes as starting materials. The nanowires consist of cubic SiC with diameters ranging from 20 to 200 nm and lengths up to tens of micrometers, High resolution transmission electron microscopy reveals that the nanowires preferentially grew along the [111] direction. Extended X-ray absorption fine structure (EXAFS) reveals that the secondary phase of Co_3O_4 was formed in the Co-doped 3C-SiC sample. The nanowires exhibit the coexistence of paramagnetic response and weak ferromagnetic behavior. The influence of secondary phase Co_3O_4 on the magnetic properties in the Co-doped SiC nanowires has been briefly discussed.

1. Introduction

Diluted magnetic semiconductors (DMSs) generally achieved by doping transition metals (TMs) have attracted considerable interest for spintronic devices [1]. As a kind of the third generation semiconductor, SiC has huge potential due to high-power, high-temperature and high-frequency applications. While the magnetic properties of TMs-doped SiC without the formation of secondary phase are of great scientific interest [2], a mixed structure consisting of SiC and a precipitate can allow these systems to be exploited as magnetic field sensors [3]. In terms of Co-doped SiC, magnetic properties have been reported, but the precise determination of the local structure around Co atoms is still absent [4]. Moreover, magnetic properties of one-dimensional (1D) Co-doped SiC nanowires also have seldom been addressed so far.

In this work, the local structure around Co atoms in 1D Co-doped SiC nanowires has been investigated. The nanowires exhibit the coexistence of paramagnetism and weak ferromagnetism. The origin of the magnetic property has been briefly discussed.

2. Experimental

High purity SiO (99.99%), carbon nanotube (99.9%), and cobalt (99.999%) powders were used as starting materials. The homogenized mixture was placed in a graphite boat, covered with a smaller graphite boat, and then overlaid with high-purity graphite (99.99%) powders. The growth was performed at 1350 °C and kept for 3 h. The products were soaked in HF solution, rinsed using deionized water, and then gray-white SiC sample was obtained.

Phase identifications were performed on powder X-ray diffraction (XRD, DX-2700). Morphology and microstructure of nanowires were observed by scanning electron microscopy (SEM, JSM-5600LV) and high resolution transmission electron microscopy (HRTEM, JEM-2010), respectively. Magnetic measurement were carried out by superconducting quantum interference device (MPMS-7). Co K-edge extended X-ray absorption fine structure (EXAFS) data analyzed by the IFEFFIT package was measured at the BL14W1 beamline of Shanghai Synchrotron Radiation Facility operating at about 200 mA and 3.5 GeV.

3. Results and discussion

Fig. 1(a) shows the XRD pattern of Co-doped SiC nanowires. All of the strong diffraction peaks can be indexed to 3C-SiC with zinc blende structure (JCPDS Card No. 29-1129). The weak peak marked with 'SF' at $2\theta = 33.59^\circ$ is from stack faults [5]. A fluctation of kinetic growth conditon may cause a change in the stacking sequences, resulting in stacking faults. The stacking faults have a lower energy than that of 3C-SiC and thus are common feature in SiC materials [6]. It is clear that no other peaks of impurities such as Si, SiO_2, C, Co and Co-related compounds are detected within the resolution of the XRD diffractometer. The typical SEM image is shown in Fig. 1(b). It can be seen that the sample is mainly

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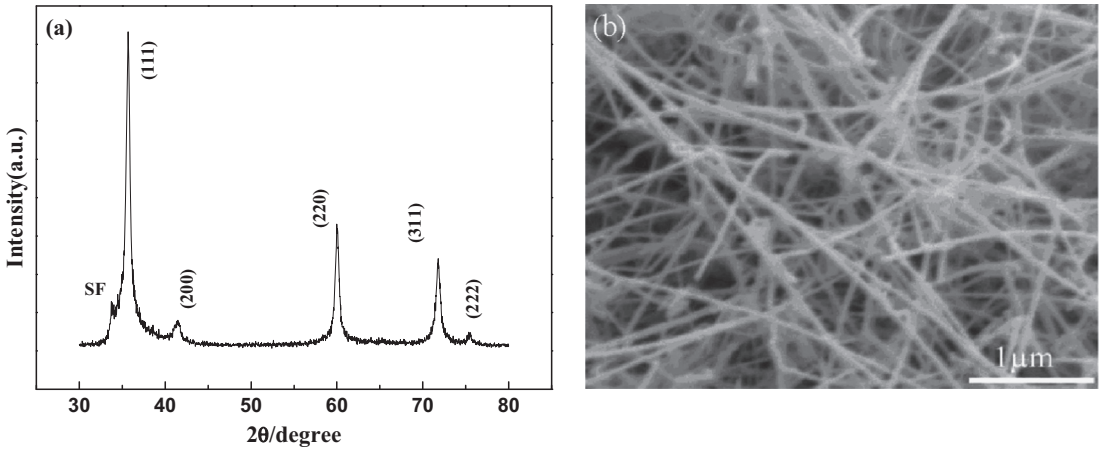

Fig. 1. (a) XRD pattern of Co-doped 3C-SiC nanowires sample and (b) a representative FESEM image of the sample.

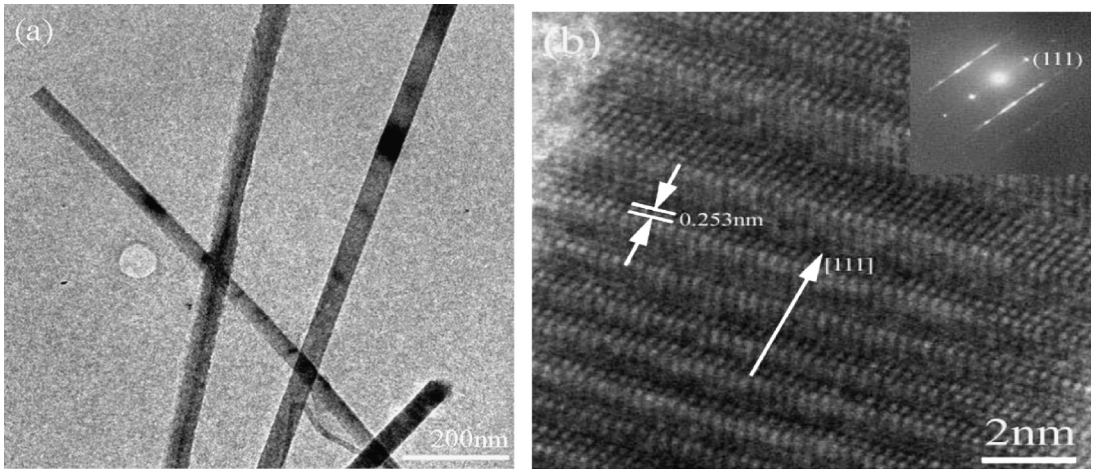

Fig. 2. Images of the Co-doped SiC nanowires: (a) low-magnification TEM image and (b) single nanowire, typical SAED pattern and HRTEM image.

nanowires with diameters ranging from 20 to 200 nm and length up to 10 μm.

Fig. 2(a) shows a typical low-magnification TEM image, clearly suggesting the surface of the nanowires are smooth and clean. The representative HRTEM image shown in Fig. 2(b) indicates that the nanowire is a 3C-SiC structure. The lattice fringes are about 0.253 nm corresponding to the (111) plane of 3C-SiC. Selected area electron diffraction (SAED) analysis (inset in Fig. 2(b)), recorded along the [110] zone axis, further confirms the 3C-SiC structure. The streaked spots in the SAED pattern along [11$\bar{2}$] imply the presence of stacking faults normal to [111] direction [7]. Moreover, both HRTEM and SAED reveal that the nanowire grew along the [111] direction, as marked by an arrow in Fig. 2(b).

EXAFS technique, with its sensitive to the low content and local structure around a selected element, has been successfully employed to identify Co-related clusters or precipitates in Co: ZnO DMSs [8]. Fig. 3 displays the Fourier transform (FT) of the Co *K*-edge EXAFS $k^3\chi(k)$ oscillation functions for the sample. As references, the Co *K*-edge functions of standard Co, CoO and Co_3O_4 are also plotted. Firstly, the existence of metallic Co clusters and CoO can be easily excluded by the evidently different characteristics of their FT with those of Co-doped 3C-SiC nanowires, in agreement with the XRD results. Moreover, it is astonishing that the overall FT EXAFS curve shapes of oscillation functions of the sample are very close to that of the Co_3O_4 powder since both the Co doped SiC and Co_3O_4 exhibited four FT peaks

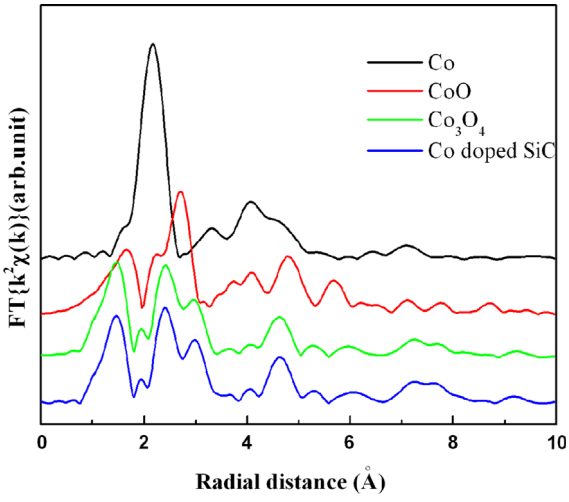

Fig. 3. FT curves of Co K-edge EXAFS oscillation functions $k^3\chi(k)$ for the Co-doped SiC sample and metallic Co, CoO and Co_3O_4, respectively.

located at about 1.5, 2.4, 3.0 and 4.6 Å, respectively. This demonstrates that the nanoscale Co_3O_4 formed although no Co_3O_4 was detected by the XRD technique because of either the nanoscale random orientation or its small size and volume-fraction. Actually, common XRD and HRTEM techniques have difficulty in detecting

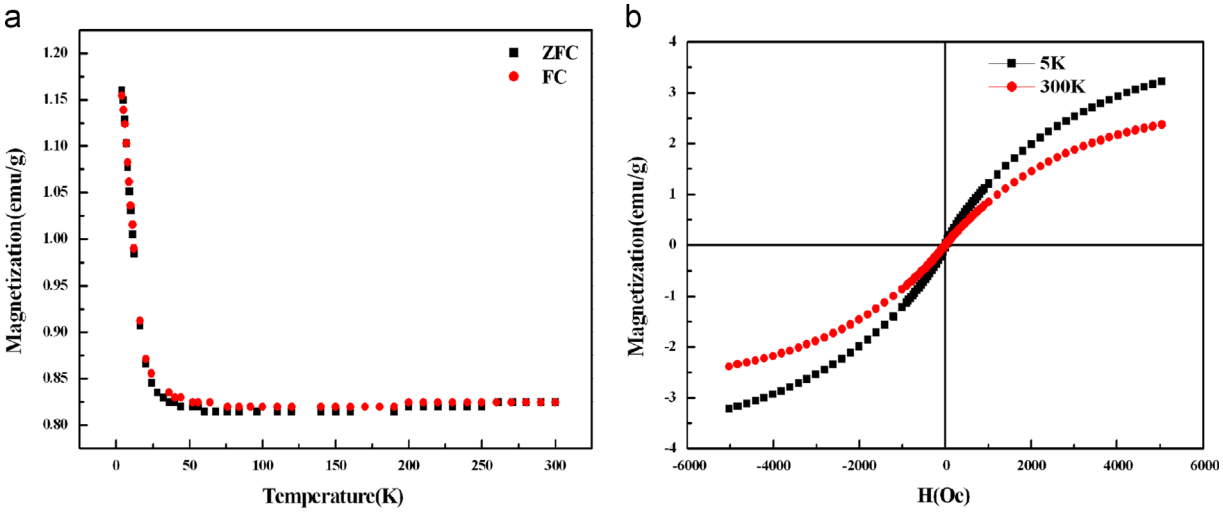

Fig. 4. (a) Temperature dependence of the magnetization $M(T)$ curves of the Co-doped SiC sample for ZFC and FC under 1000 Oe. M–H curves of the sample measured at 5 and 300 K, respectively.

the minor precipitates [8]. It is a big challenge to detect the phase separation in DMSs research. The miscibility gap between SiC and the incorporated Co makes it difficult to preserve the 'dilute' state. In this case, the existence of Co_3O_4 may result from the reaction of SiO with Co since the high background vacuum and continuous Ar gas protective atmosphere during the fabrication of the nanowires have excluded the possibility of Co being oxidized. The Co_3O_4 phase was also detected in cobalt-doped ZnO nanocomposites by EXAFS technique [9].

Fig. 4(a) shows the temperature dependence of magnetization (M–T) of the sample under zero-field-cooling (ZFC) and field-cooling (FC) mode with a magnetic field of 1000 Oe. From the ZFC curve, the absence of an obvious superparamagnetic transition was observed. In addition, the FC and ZFC curves nearly coincide, signifying a typical paramagnetic behavior. To further illustrate the magnetic behavior, magnetization (M) curves as functions of magnetic field (H) was recorded at 5 and 300 K, as shown in Fig. 4(b). It appears that the magnetization is the superimposition of an overwhelming paramagnetic component and a weak ferromagnetic component. The M–H curves are characterized by small coercivities (e.g. at T=300 K, H_C =11 Oe). Similar coexistence of paramagnetic and ferromagnetic phenomena has also been observed in Co, Fe or Ni doped ZnO systems [10]. It seems to be natural that the magnetic properties in the Co-doped SiC sample correlate with the Co_3O_4 secondary phase. Although the undoped SiC shows a paramagnetic behavior at 5 K, the magnetization is much smaller than that of the Co-doped 3C-SiC. Therefore, it is inferred that the paramagnetic contribution can be interpreted as the isolated Co ions in the Co_3O_4 secondary phase. Similarity, the enhancement of magnetic properties contributed by secondary Ga–Mn magnetic phases has been reported in (Mn+N)-implanted GaN systems [11]. As to the weak ferromagnetic signal, it can be expounded by the finite size effects resulting from the small dimensions of the Co_3O_4 nanoparticles. Moreover, FM may also derive from the uncompensated surface spins of Co cations. Magnetic secondary phases have been expected to play a significant role in explaining the magnetic behavior. The phase separated Co–O and CoZn are responsible for the superparamagnetism in Co doped ZnO [12].

4. Conclusions

Co-doped SiC nanowires with diameters ranging from 20 to 200 nm and lengths up to tens of micrometer were fabricated using high-purity SiO, carbon nanotubes and Co powders as staring materials. The magnetic behavior is not an intrinsic property but originates from Co_3O_4 secondary phase. It is possible to utilize DMSs composed of phase separated SiC as model systems of magnetic ensembles of nanowires.

Acknowledgments

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