Large Scale Growth and Magnetic Properties of Fe and Fe_3O_4 Nanowires

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Fe and Fe$_3$O$_4$ nanowires have been synthesized by thermal decomposition of Fe(CO)$_5$, followed by heat treatments. The Fe wires are formed through the aggregation of nanoparticles generated by decomposition of Fe(CO)$_5$. A core-shell structure with an iron oxide shell and Fe core is observed for the as-prepared Fe wires. Annealing in air leads to the formation of Fe$_2$O$_3$/Fe$_3$O$_4$ wires, which after heat treatment in a N$_2$/alcohol atmosphere form Fe$_3$O$_4$ wires with a sharp Verwey [Nature (London) **144**, 327 (1939)] transition at 125 K. The Fe$_3$O$_4$ wires have coercivities of 261 and 735 Oe along the wire axis at RT and 5 K, respectively. The large increase of coercivity at 5 K as compared to RT is due to the increase of anisotropy resulting from the Verwey transition. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2172208]

Magnetic nanowires and their arrays have attracted intensive attention because of their potential applications in magnetic storage, gas sensor, spintronic devices, and biomedical treatments.[1–4] Especially, iron and its oxides are very important magnetic materials. Many efforts have been made to prepare nanowires and nanorods of iron and its oxides.[5–10] Most of the nanowires have been synthesized via template techniques, which have the limitation that the template has to be removed and large amounts of material cannot be produced. Fe$_3$O$_4$ wires have been made by a hydrothermal process.[10] The purity and morphology, however, are difficult to control. Recently, Lee *et al.*,[11] have fabricated Fe and Co nanocluster wires by thermally decomposing metal carbonyl vapors with a resistive heater under a magnetic field without templates. Since Fe$_3$O$_4$ has many potential applications in pigmentation, catalysis, magnetic storage, and biological sciences among others, we report herein results of studies on Fe and Fe$_3$O$_4$ nanowires synthesized without templates. The structure, morphology, composition, and the magnetic properties of the wires were studied using x-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Mössbauer, and magnetic measurements.

The Fe wires were prepared using a cylindrical glass reactor, as shown in Fig. 1. Glass or silicon substrates are placed on a heating plate. The heating plate is placed into the chamber between permanent magnet poles. The magnetic field is about 1000 Oe in the center of the magnetic poles. The entire system is evacuated to approximately 10 mTorr

before the deposition process. The temperature of the heating plate is maintained at 300–400 °C. The starting materials, Fe(CO)$_5$ vapors, are introduced into the reactor through a gas inlet. The Fe(CO)$_5$ is then decomposed into Fe atoms close to the heating plate where they form Fe nanoparticles (NPs). The NPs of Fe then form arrays of Fe wires on the substrate. These arrays of Fe wires, with diameters from 20 nm to 1 μm and lengths up to several centimeters, are obtained in the magnetic field using different deposition times and temperatures. Magnetite, Fe$_3$O$_4$, is prepared by the following heat treatment. First, the as-prepared Fe wires are annealed in air at 400 °C for 24 h and are then treated in a N$_2$/alcohol atmosphere for 1 h in order to remove the Fe$_2$O$_3$ phase. XRD with Cu $K\alpha$ radiation and ^{57}Fe Mössbauer spectroscopy were used to determine the phases and the compositions of the samples. The magnetizations of the samples were measured using a superconducting quantum interference device (SQUID) magnetometer in a field of up to 6 T from 1.5 to 300 K. The morphology was studied using SEM and TEM.

Figure 2 shows the XRD patterns of the as-prepared and post-treated samples. As evidenced in Fig. 2(a), the as-prepared sample is composed of single phase α-Fe. The XRD pattern exhibits much broader and less intensive peaks,
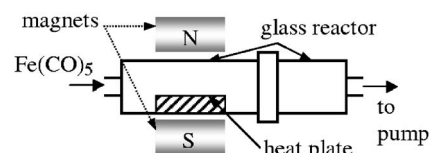

FIG. 1. The experimental setup for sample preparation.
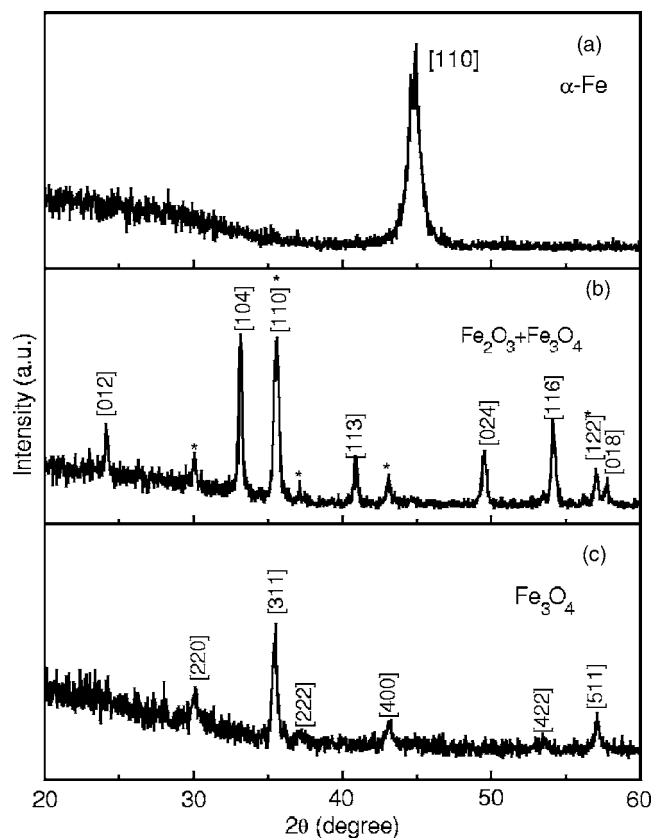
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FIG. 2. X-ray diffraction patterns of Fe (a), Fe oxide (b) wires (* indicates Fe_3O_4 peak), and Fe_3O_4 (c).
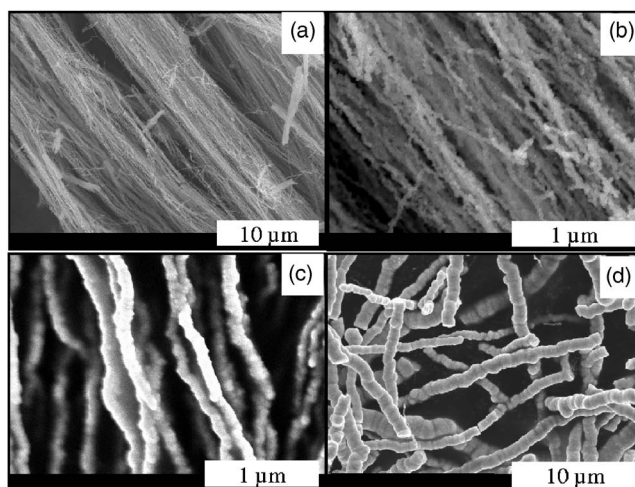

FIG. 3. The SEM images of the Fe and Fe oxides: (a) and (b) Fe nanowires grown under a magnetic field, (c) Fe_3O_4 wires, and (d) Fe wires prepared without an applied magnetic field.

due to the smaller grain size and the crystal defects in the sample. The mean size of the particles is about 25 nm as determined by the Scherrer formula using the width of the [110] peak from Fig. 2(a). After heating at 300–400 °C in air, Fe wires take on a rust color corresponding to a mixture of Fe_2O_3/Fe_3O_4 [Fig. 2(b)]. The Fe_2O_3/Fe_3O_4 mixture is then transformed to black Fe_3O_4 after heating at 350 °C in a N_2/alcohol atmosphere [Fig. 2(c)]. The phases and compositions were further confirmed by ^{57}Fe Mössbauer measurements. The Mössbauer spectra show that there is less than 3% Fe oxide in the Fe wires. This small amount of oxide is likely due to CO gas resulting from the decomposition of $Fe(CO)_5$, which plays a role as a reducing agent. Heat treatment of the Fe wires in air leads to a product consisting of an Fe core and an Fe_2O_3/Fe_3O_4 shell (as observed from x-ray and Mössbauer measurements) which subsequently forms pure Fe_3O_4 wires, as described above.

Figure 3 shows the SEM [(a)–(c)] images of the typical Fe and Fe_3O_4 nanowires obtained in an applied magnetic field. The Fe wires resemble a woolen yarn, consisting of bundles of small wires with an average diameter of 30 nm. Each wire consists of NPs of Fe [Figs. 3(a) and 3(b)]. It is evident that the homogeneity of the wires is not as good as those produced by templates.[8] Figure 3(c) shows the typical morphology of Fe_3O_4 wires obtained from the heat treatments. The diameter of an Fe_3O_4 wire is about 90 nm, suggesting that several Fe wires may bond together to form a Fe_3O_4 wire. It is interesting to note that the Fe wires can be formed without the applied magnetic field, except that the

diameter of the wires is much larger and they exhibit no orientation, as shown in Fig. 3(d). The suggested mechanism for the formation of Fe wires in the absence of a field is that the Fe NPs are formed first, and then self-assemble to form one dimensional wires. The decomposition of $Fe(CO)_5$ into Fe and CO with no magnetic field may give the NPs time to find energetically favorable lattice sites in this growing assembly.[12] The results of XRD and TEM studies indicate that no crystal orientation was observed in these wires, which is different from those Fe wires grown by templates. The wires are composed of fine particles with different crystalline orientations.

Figure 4 shows the zero field cooling (ZFC) and field cooling (FC) magnetization curves of Fe and Fe_3O_4 under a magnetic field of 50 Oe. The difference between the FC and ZFC magnetizations increases with decreasing temperature for Fe wires, resembling a spin glass behavior arising from
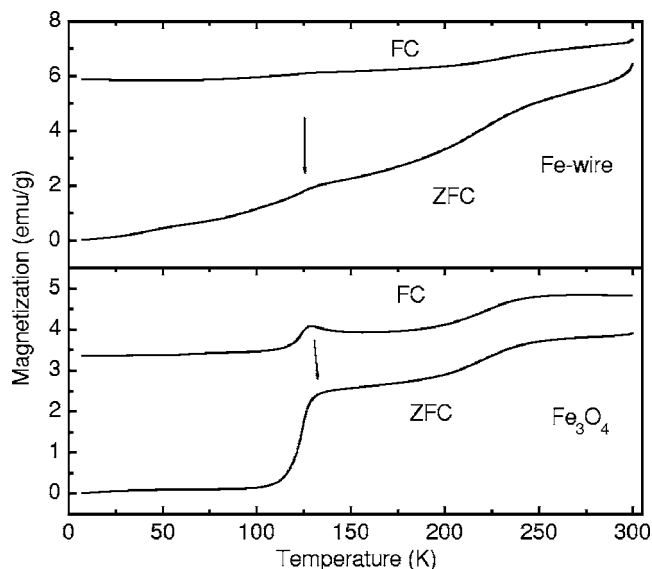

FIG. 4. The temperature dependence of the magnetization curves under zero field cooling (ZFC) and field cooling (FC) with a magnetic field of 50 Oe for Fe and Fe_3O_4 wires prepared with a magnetic field.
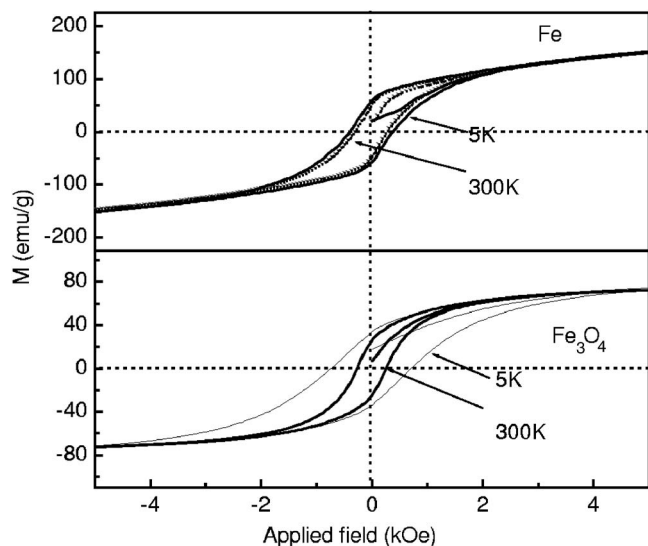
FIG. 5. The hysteresis loops of Fe and Fe_3O_4 wires prepared under a magnetic field along the wire axis at 300 and 5 K.

the local magnetic anisotropy of the individual grains. A small kink is observed at about 125 K in Fig. 4(a) corresponding to the Verwey transition temperature of Fe_3O_4.[13] This evidences that a trace of Fe_3O_4 is present in the Fe wires, even though it is not observed from x-ray and Mössbauer measurements. This suggests that a thin layer of Fe oxide was formed on the Fe wires and a core-shell structure of Fe/Fe oxide may be obtained. This was further confirmed by high resolution TEM images, which show a dark (core) and a light (shell) contrast (figure is not shown here). The steplike drop of magnetization at the ZFC curve for Fe_3O_4 [Fig. 4(b)] at temperature of 125 K is due to the Verwey transition,[13] which significantly changes the anisotropy of the Fe_3O_4 grains.[14] It is found that the transition temperature is similar to that of bulk materials,[13] but different from Fe_3O_4 wires prepared using a template.[8] A sharp Verwey transition in Fig. 4(b) indicates the formation of single phase Fe_3O_4. Figure 5 shows the hysteresis loops of samples measured at RT and 5 K. Coercivities of the 300 and 400 Oe have been observed for Fe nanowires along the axis of the wire at 300 and 5 K, respectively. The remanence ratios M_r/M_s are about 0.45 and 0.2 in the parallel and the perpendicular direction, respectively. This suggests that the magnetic moments of Fe atoms are not parallel to the axis of the wire. The coercivity of an Fe wire is lower than that of Fe nanowires prepared by templates[7] due to the larger grain size and smaller crystalline anisotropy. The Fe_3O_4 wires have coercivities of 261 and 735 Oe along the wire direction at RT and 5 K, respectively. The remanence ratios M_r/M_s are about 0.30 and 0.25 in the parallel and the perpendicular direction, respectively. A large increase of the coercivity at 5 K is due to the increase of anisotropy resulting from the Verwey transition.[15]

In summary, Fe wires are formed through the resulting aggregation of the nanoparticles generated by thermal decomposition of $Fe(CO)_5$. A core-shell structure with an iron oxide shell is observed for the as-prepared Fe wires. Single phase Fe_3O_4 wires are synthesized by heat treatment of Fe wires in varied atmospheres. Fe_3O_4 wires show a sharp Verwey transition at 125 K. Coercivities of 261 and 735 Oe are obtained for Fe_3O_4 wires at RT and 5 K, respectively. The large increase of the coercivity at 5 K is due to the increase of anisotropy resulting from the Verwey transition.

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