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Magnetoresistance characteristics in individual Fe₃O₄ single crystal nanowire

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We report on the magnetoresistance (MR) and electron transport measurements observed on a single crystal magnetite nanowire prepared using a hydrothermal synthesis method. High-resolution electron microscopy revealed the single crystal magnetite nanowires with 80–120 nm thickness and up to 8 μm in length. Magnetic measurements showed the typical Verwey transition around 120 K with a 100 Oe room temperature coercivity and 45 emu/g saturation magnetization, which are comparable to bulk magnetite. Electrical resistance measurements in 5–300 K temperature range were performed by scanning gate voltage and varying applied magnetic field. Electrical resistivity of the nanowire was found to be around 5 × 10⁻³Ω m, slightly higher than the bulk and has activation energy of 0.07 eV. A negative MR of about 0.7% is observed for as-synthesized nanowires at 0.3 T applied field. MR scaled with increasing applied magnetic field representing the field-induced alignment of magnetic domain. These results are attributed to the spin-polarized electron transport across the antiphase boundaries, which implicate promising applications for nanowires in magnetoelectronics. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4914535]
Single crystal Fe₃O₄ nanowires were prepared by a simple hydrothermal method. In a typical process, FeSO₄, Na₂S₂O₃, and NaOH are mixed in 2:1:25 molar ratio and ground thoroughly. The mixture is then transferred to a Teflon lined autoclave containing polyethylene glycol (molecular weight—4000) in water (3:1). The autoclave is subjected to heat treatment at 160°C for 24 h and cooled to room temperature naturally. The contents are washed with water and ethanol to remove the polymer residue and vacuum dried. The samples were probed with X-ray diffractometer (Sintag XDS 2000), scanning electron microscopy (Sirion), high resolution transmission electron microscopy (Tecnai 200KV), and Quantum design SQUID magnetometer (0–7 T, 5–300 K). A solution containing Fe₃O₄ nanowires in ethanol is dropped onto a 500 nm SiO₂/Si substrate wafer and allowed it to dry under inert atmosphere. Fe₃O₄ nanowire (120 nm thickness) device with 3 μm channel length was fabricated using electron beam lithography and a 5 nm/100 nm thick Ti/Au electrodes were deposited using electron beam deposition.

X-ray diffraction data collected on as synthesized nanowire powder confirmed cubic magnetite (Fe₃O₄) pharse purity matching the JCPDS index card 79-0416 (not shown here). A small degree of a polymer residue and a second cubic magnetite phase is observed in XRD spectra. Electron microscopy analyses were performed to understand morphology, microstructure, and crystalline phase of the nanowires. Scanning electron microscopy image, Figure 1(a), shows representative Fe₃O₄ nanowires with 80–120 nm thickness and lengths up to 8 μm with uniform morphology. A small percentage of Fe₃O₄ discs and polymer remainder were also observed along with the nanowires. Selected area electron diffraction (SAED) pattern showed the discs to be of cubic Fe₃O₄ phase (JCPDS index card 88-0866). High resolution transmission electron microscopy images in Figures 1(b) and 1(c) reveal morphology and highly crystalline microstructure of as prepared nanowires. SAED pattern inset, Figure 1(c), collected on few nanowires can be indexed to the cubic magnetite phase. It can be seen that SAED pattern of nanowires conforms well to that of XRD pattern. HRTEM image in Figure 1(d) collected from 80 nm wide single nanowire shows single crystalline nature of nanowire and possibly shows growth defects that can be related to antiphase boundaries. It can be realized that the core and surface of nanowire are well preserved and a Fast Fourier Transform (FFT) analysis shown in Figure 1(d) inset reveals the diffraction planes for single crystal magnetite nanowire. The analyzed zone axis for electron diffraction pattern for nanowire is [−121] and the diffraction spots were indexed to (220), (311), and (111) lattice planes of Fe₃O₄. Electron microscopy results show a very low percentage of defects and clearly establish the single crystallinity of the Fe₃O₄ nanowires.

Magnetic properties of single crystal Fe₃O₄ nanowires were evaluated using a SQUIID magnetometer. Room temperature magnetic hysteresis was collected on nanowire powder sample without any preferred orientation of magnetic field. A saturation magnetization (Mₛ) of about 45 emu/g, 100 Oe coercivity, and a remanence magnetization (Mᵣ) of 6.2 emu/g were observed for randomly oriented single crystal nanowire samples, as shown in Figure 2(a) indicating room temperature ferromagnetism. Figure 2(a) inset shows clear coercivity and remanent magnetization confirming ferromagnetism. The observed saturation magnetization is comparable to that of bulk and higher than other Fe₃O₄ nanocrystalline samples. Orientation of nanocrystallites, crystallinity, shape anisotropy, defects, and magnetostatic coupling are the key factors influencing saturation magnetization and other magnetic properties. Magnetic susceptibility measurements were carried out on the Fe₃O₄ nanowires to study possible phase transitions associated with temperature (5–300 K) and magnetic field dependence. Figure 2(b) shows zero-field cooled (ZFC) and field cooled (FC) magnetization for Fe₃O₄ nanowires with a 100 Oe applied magnetic field. With increasing temperature, the magnetization reaches a maximum value around 120 K for ZFC/FC measurements, which is defined as blocking temperature Tₐ in bulk Fe₃O₄, where the thermal energy becomes comparable to the anisotropy energy barrier. Below Tₐ, magnetization of the nanowires aligns with the easy axis and anisotropy energy barriers would minimize magnetic moment with decreasing temperature. Above Tₐ, thermal energy overcomes the anisotropy and magnetic moments are aligned in the direction of external field. Blocking temperature is widely dependent on the magnetic interactions, morphology, and external agents. Above Tₐ, such “superparamagnetic” particles are expected to display zero coercivity and the FC and ZFC magnetizations will become identical. The clearly open hysteresis loops observed in our samples at T > Tₐ (see data at 300 K shown in Fig. 2) and the continued divergence of FC and ZFC magnetizations for T > Tₐ region suggest that 120 K is not a blocking temperature. The observed

![FIG. 1. Electron microscopy images showing Fe₃O₄ nanowires. (a) SEM image of Fe₃O₄ nanowires and discs morphology, (b) TEM images showing clean Fe₃O₄ nanowires, (inset) SAED pattern corresponding to Fe₃O₄, (c) TEM image of single nanowire, (inset) high resolution image without any defects, collected from the red circle region, (d) high resolution micrograph showing clean Fe₃O₄ without any surface reconstruction or impurities, (inset) FFT image showing zone axis [−121].]
magnetization change at 120 K can be explained with Verwey transition. According to Verwey transition, Fe₃O₄ undergoes a charge ordering and structural ordering in the crystal lattice with crystallographic phase changing from cubic inverse spinel to monoclinic and the electrical properties display a metal-insulator transition as the temperature drops below 120 K. Verwey transition has profound effect on electrical properties of the Fe₃O₄, which is discussed in the later section.

Figure 3 inset shows SEM image of Fe₃O₄ nanowire device fabricated using e-beam lithography. Electrical measurements performed in ambient conditions on the nanowire yielded a typical linear I-V curve showing Ohmic behavior for device. Figure 3 shows resistance from a single nanowire as a function of temperature in the 5–300 K regime at a constant voltage bias. The circles represent resistance (R) data points acquired from original I-V scans and the line represents best fit. Electrical resistance of single Fe₃O₄ nanowire at room temperature is around $5 \times 10^{-4}$ Ω m, which is comparable to epitaxial thin films and higher than bulk single crystal Fe₃O₄. Electrical resistance below 120 K is almost 2 orders of magnitude higher compared to room temperature. Above 120 K, the resistance decreased, which is in accordance with the Verwey transition. Above 120 K, Arrhenius plot shows linear relation, signifying thermally activated carrier transport mechanism at higher temperature. Activation energy (ln R vs 1000/T) deducted from Figure 3 is around 0.07 eV. This value is in close agreement with similar morphology Fe₃O₄ nanowire/nanotube studies as well as bulk Fe₃O₄.

Figure 4 shows 300 K MR measurements on a single crystal Fe₃O₄ nanowire device. Magnetic field is swept parallel to the nanowire from 0 to 0.3 T, keeping a constant voltage bias at a selected temperature. MR is calculated using equation, $MR = (R(H) - R(0))/R(0)$, where $R(0)$ and $R(H)$ are resistance at zero field and at an applied field H, respectively. A total of 3 devices were tested and the value varied from −0.2% to −0.7% at a 0.3 T applied field. MR of Fe₃O₄ nanowires increased with applied magnetic field and did not show any saturation. A linear background is subtracted from measurement, as the actual MR signal was small. MR studies
in single crystal Fe$_3$O$_4$ are quite inconsistent compared to that of bulk. Liao et al.\textsuperscript{16} reported anomalous positive MR \(\sim 7.5\%\) in single crystal Fe$_3$O$_4$ nanowire, while Coey et al.\textsuperscript{2} did not see any measurable MR in a single crystal Fe$_3$O$_4$. On the contrary, a negative MR is observed in this work. MR in the polycrystalline Fe$_3$O$_4$ is credited to magnetization in ferromagnetic grains, which are exchange-decoupled, or antiphase domains.\textsuperscript{2} Considering the fact that the single crystal Fe$_3$O$_4$ nanowire is 120 nm thick there is a strong possibility for huge density of antiphase domain walls to be present. HRTEM (Figure 1(d)) possibly shows the antiphase domains present in the nanowire. The resulting magnetic coupling between antiphase boundaries is antiferromagnetic.\textsuperscript{28–30} When an external magnetic field is applied, neighboring antiphase boundary magnetic moment aligns in the direction of the field, resulting in reduced resistance. The absence of resistance saturation in Fe$_3$O$_4$ nanowire indicates the strong antiferromagnetic coupling of antiphase boundaries. Spin-polarized transport across antiphase boundaries in single crystal is analogous to epitaxial films, resulting in MR.

In summary, we demonstrated single crystal Fe$_3$O$_4$ nanowire showing a small but definite negative magnetoresistance at room temperature and attributed to the spin-polarized current resulting from antiphase domains. Nanowires were synthesized by a hydrothermal method and high resolution electron microscopy revealed cubic single crystalline magnetite. Room temperature electrical measurements have shown a resistance of \(\sim 5 \times 10^{-4}\) \(\Omega\) m on single nanowire and activation energy of 0.07 eV. Magnetic saturation and coercivity of Fe$_3$O$_4$ were found to be 45 emu/g and 100 Oe, respectively, at 300 K consistent with reported values for bulk Fe$_3$O$_4$. Inconsistent magnetoresistance properties from Fe$_3$O$_4$ single crystal nanowire are still debatable and needs further research attention. Our work demonstrates the experimental evidence of negative MR in Fe$_3$O$_4$ single crystal nanowires suggesting that spin based device integration can be realized.


\textsuperscript{23}E. J. W. Vervey, “Electronic conduction of magnetite (Fe3O4) and its transition point at low temperatures,” Nature 144, 327–328 (1939).


\textsuperscript{27}A. Kozłowski et al., “Electrical-conduction in single-crystal Fe3-Ytio4 (0 less-than Y less-than 0.9),” Phys. Rev. B 48(4), 2057–2062 (1993).

