Structure versus properties in $\alpha$-Fe$_2$O$_3$ nanowires and nanoblades

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Abstract

We report structure/property relationships in bicrystalline $\alpha$-Fe$_2$O$_3$ nanowires (NWs) and nanoblades (NBs), synthesized by thermal oxidation of iron foils with different surface roughness. The electrical properties of individual nanostructures were studied by in situ transmission electron microscopy. Current–voltage ($I$–$V$) measurements using gold electrodes showed that a Schottky contact forms between $\alpha$-Fe$_2$O$_3$ NWs whereas an ohmic contact forms between $\alpha$-Fe$_2$O$_3$ NBs. The difference in transport properties is attributed to the existence of oxygen vacancies in the coincidence-site-lattice boundary region of $\alpha$-Fe$_2$O$_3$ NBs. Magnetic measurements indicate that the temperature-dependent zero-field-cooled magnetization rises more rapidly near the Morin transition temperature for $\alpha$-Fe$_2$O$_3$ NBs than that for NWs. The distinct magnetic properties of the NBs are ascribed to the enhanced magnetic order induced by the structural order in the two-dimensional NBs. These $\alpha$-Fe$_2$O$_3$ NBs are promising building blocks for electronic and magnetic devices since their 2D geometries facilitate integration into devices with realistic pathways to manufacturing. In addition, our study shows that boundary engineering is an effective approach for tailoring the physical properties of nanomaterials.

Keywords: one-dimensional Fe$_2$O$_3$ nanowires, two-dimensional Fe$_2$O$_3$ nanoblades, grain boundary, electrical properties, magnetic properties

(Some figures may appear in colour only in the online journal)

1. Introduction

The physical and chemical properties of nanomaterials strongly depend on their size, shape, and dimensionality [1, 2]. In addition to the atomic scale structure, crystal defects such as atomic vacancies and grain boundaries also have a great impact on the properties of nanomaterials [3–5]. Material scientists usually prefer defect-free structures in their pursuit to make predictable devices with high performance. Defects are thus perceived as material imperfections which could adversely affect device performance. However, because of the limited size of nanomaterials, the presence of defects can in fact be effectively used to regulate their local properties and achieve new functionalities towards the realization of novel devices. In bulk materials, defects such as grain boundaries have been extensively studied for many decades, especially in the contexts of mechanical strength and ductility of metals [6, 7]. However, because grain boundaries in small volume nanomaterials are scarce and the corresponding property measurements are challenging, limited studies have been reported so far.
Hematite (α-Fe₂O₃) has been widely studied because of its nontoxicity, low cost, high stability under ambient conditions, and multifunctionality [8]. Hematite has been intensively investigated for applications in lithium-ion batteries [9, 10], sensors [11, 12], catalysts [13] and magnetic devices [14]. The performance of α-Fe₂O₃ is greatly influenced by its dimensionality, morphology, and microstructure. In our previous studies, different types of α-Fe₂O₃ nanostructures including bicrystalline 1D α-Fe₂O₃ nanowires (NWs)⁸ and 2D nanobelts (NBs)⁹ were synthesized, and their optical properties were also investigated. It is found that the optical properties show a clear dependence on the growth morphologies of the nanostructured hematite.

Here we study structure versus properties in α-Fe₂O₃ nanostructures, comparing NWs and NBs. We focus on the investigation of electrical and magnetic properties and find that there are significant changes associated with different nanoscale structures. The measured I–V curve from the α-Fe₂O₃ NW is nonlinear and almost symmetrical, leading to a Schottky contact at the interfaces between semiconducting foils, then ultrasonicating them in ethanol for two minutes and electron microscopy (nanosheets). The order induced by the structural order in the two-dimensional properties of the NBs are ascribed to the enhanced magnetic fields-cooled magnetization rises more rapidly for α-Fe₂O₃ NBs than that for NWs. The distinct magnetic properties of the NBs are ascribed to the enhanced magnetic order induced by the structural order in the two-dimensional nanosheets.

2. Experimental section

The detailed synthesis procedure of α-Fe₂O₃ NWs and NBs was reported elsewhere [15, 16]. Specimens for transmission electron microscopy (TEM) observations were prepared by peeling off the black products from the surface of oxidized Fe foils, then ultrasonically etching them in ethanol for two minutes and dispersing a drop onto a holey-carbon-film-coated copper grid. Bright field (BF), selected-area electron diffraction (SAED), high-resolution TEM (HRTEM) and electron energy-loss spectroscopy (EELS) were carried out using field-emission TEMs (JEOL JEM 2100F or FEI Tecnai F20) operated at 200 kV. All EELS spectra were acquired in image mode with an electron beam probe size of 1 to 2 nm and a half collection angle of ~16 mrad with an acquisition time of 2 s.

The electrical properties of individual NWs and NBs were investigated using an in situ TEM sample holder (FM200E HA300) purchased from Sweden Nanofactory Company, specially designed to measure the electrical properties of nanomaterials. Specimens were dispersed onto the tip of a gold rod on the holder that was moved to touch an atomic force microscopy cantilever, also made of gold, using a piezo-driven manipulator inside the TEM. The applied bias voltage ranged from −5.0 V to 5.0 V. A schematic diagram for in situ measurement of electrical properties is shown in figure 1. The magnetic properties of NWs and NBs were studied using a Quantum Design superconducting quantum interference device (SQUID, Quantum Design, MPMS VSM). The temperature-dependent magnetization was measured under an applied magnetic field of 0.01 T. For the measurements of magnetic properties, α-Fe₂O₃ NWs and NBs were first peeled off from Fe substrates and then attached to the outer surface of a glass rod in the MPMS apparatus.

3. Results and discussion

Figures 2(a) and (b) are typical cross-sectional SEM and TEM images of the oxidized products, showing that α-Fe₂O₃ NWs cover the entire surface of the oxidized Fe foil. Figure 2(c) is a representative BF TEM image of an individual bicrystalline α-Fe₂O₃ nanowire (NW) with a diameter of ~43 nm. The inset in figure 2(c) shows that the bicrystal interface is parallel to its length direction. A twin boundary is clearly visible in the HRTEM image (figure 2(d)). From the analysis of the associated SAED pattern (figure 2(e)) two sets of diffraction spots can be identified, one being the [0001] zone-axis labeled by red lines, and the other being the [1101] zone-axis marked by yellow lines.

Figure 3(a) shows a typical cross-sectional SEM image of α-Fe₂O₃ NBs. These NBs are formed through the coalescence of two nanoscale islands during the oxidation process, possessing a bicrystal structure. Figure 3(b) shows cross-sectional TEM image of the NBs with dimensions of about 1 μm long and 500 nm wide. Figure 3(c) displays a BF TEM image of an individual α-Fe₂O₃ NB. Careful examination of the NB edge in the inset of figure 3(c) shows that it is not a single layer, but rather a double-layered structure. In figure 3(d) we report a typical [0001] zone-axis HRTEM image from the α-Fe₂O₃ NB edge. The image shows two parts, the lower part being a single-layered lattice image of α-Fe₂O₃, and the upper part being Moiré fringe contrast formed by the overlap of double-layered α-Fe₂O₃ crystal lattices.
Figure 3 is a SAED pattern taken from the α-Fe₂O₃ NB in figure 3(c), containing two sets of [0001] zone-axis diffraction spots which can be indexed using the lattice parameters of α-Fe₂O₃. These two sets of diffraction spots are rotated with respect to each other by an angle of 21.79°, indicating this is a typical coincidence-site-lattice (CSL) boundary [17, 18]. Comparison with the literature [17, 18] shows that this CSL boundary has a Σ value of 13. Both α-Fe₂O₃ NWs and NBs have a bicrystalline structure. However, their interfaces are intrinsically different. Bicrystalline NWs have a twinning structure which generates a coherent boundary with few defects, while bicrystalline NBs exhibit a large-angle twist boundary. Such dissimilar interfacial configurations may lead to different electronic structures.

To analyze the electronic structure of the α-Fe₂O₃ NWs and NBs, we carried out extensive EELS experiments.
vacancies exist in NBs than in NWs. NB, respectively. Thus, it can be concluded that more oxygen NW, however chemical shifts of L3 line of about 0.4 eV for intensity and position of individual L3 and L2 edges, ionization status of metal cations by determining the relative NWs. In addition, the Fe-L edges can provide us with the Fe-L2,3 edges for an relevant experimental result, more than 10 individual α-Fe2O3 NWs and NBs were examined. Under TEM inspection the nanomanipulator probe electrode was carefully adjusted to touch the samples, as shown in figures 5(a) and (c). A metal-semiconductor contact can be either a Schottky contact or an ohmic contact depending on the Fermi surface alignment between the metal electrode and the semiconductor [21, 22]. Figure 5(b) reports the measured I–V curve from the α-Fe2O3 NW, which is nonlinear and almost symmetrical. No current is detected between bias voltages from −0.8 V to 0.8 V, and a rapid current increase appears beyond this bias range. Such threshold effect may be ascribed to two Schottky contacts formed at the interfaces of the semiconducting NW and two gold electrodes [23, 24]. However, the measured I–V curve for the α-Fe2O3 NB in figure 5(d) exhibits an obviously linear I–V relation, indicating that an ohmic contact forms between the α-Fe2O3 NB and gold electrodes. The resistance of α-Fe2O3 NB can be estimated directly from the linear I–V curve, whereas the resistance of α-Fe2O3 NW can only be obtained from the large bias region in the I–V curve since the total voltage at the low bias is mainly controlled by the two Schottky barriers [23]. The resistivity of α-Fe2O3 NB and NW can be determined by

$$\rho = \frac{SR}{L},$$

where R is the resistance, and S and L are the cross-sectional area and length of the sample, respectively. We found that the resistivity of the NB is \(\sim 6.9 \times 10^{-3} \Omega \text{ m, smaller by three orders of magnitude than that of the NW (} \sim 4.1 \Omega \text{ m).}

The α-Fe2O3 NWs synthesized in oxidative ambient at high temperature are p-type semiconductors [25]. The work function of Au (\(\phi_M = 5.1 \text{ eV}) is slightly smaller than that of α-Fe2O3 NWs (\(\phi_B = 5.4 \text{ eV}) [26]. In the schematic band diagram shown in figure 6(a), the Fermi level of α-Fe2O3 is lower than that of Au, leading to band bending when Au contacts α-Fe2O3. Therefore, a Schottky barrier will form

Figure 4 shows typical EELS spectra of oxygen K-edges and Fe-L2,3 edges for an α-Fe2O3 NW and NB, respectively. For α-Fe2O3 NB, the spectra are collected from the central regions of the sample. In figure 4(a), three peaks (labeled a–c) can be identified in the oxygen K-edge energy-loss near-edge fine structure. Quantification of the EELS spectra in figure 4(a) shows that the intensities of peaks a and b for the NB are lower than those for the NW. It was previously demonstrated that the decreased intensities of these peaks are associated with oxygen vacancies inside the nanostructures [19, 20]. Thus, the lower the peak intensities in the EELS spectra, the higher the content of oxygen vacancies in α-Fe2O3. Then, it can be deduced that the content of oxygen vacancies is higher in the α-Fe2O3 NBs than in the α-Fe2O3 NWs. In addition, the Fe-L edges can provide us with the ionization status of metal cations by determining the relative intensity and position of individual L3 and L2 edges, respectively [20]. The Fe L2,3 edges spectra for α-Fe2O3 NW and NB are shown in figure 4(b). The quantification of the EELS spectra in figure 4(b) shows that the intensity ratio I(L3)/I(L2) is 5.1 ± 0.3 for the α-Fe2O3 NW and 4.2 ± 0.3 for the α-Fe2O3 NBs. In addition, the separation between the L2 and L3 lines remains constant (\(\sim 12.6 \text{ eV}) for the α-Fe2O3 NW, however, chemical shifts of L3 line of about 0.4 eV for the NB are detected. It was reported that the intensity ratio I(L3)/I(L2) and the position of the L3 line are sensitive to the valence states of the transition metal oxides [11]. As a result, the significant decrease in the intensity ratio I(L3)/I(L2) and chemical shifts for the L3 lines indicate a change in the partial oxidation states from Fe^{3+} to Fe^{2+}, consistent with other reports [11]. In addition, quantification of the EELS spectra shows that the atomic ratios of Fe and O are 2:(3.00 ± 0.03) for the α-Fe2O3 NW, and 2:(2.92 ± 0.02) for the α-Fe2O3 NB, respectively. Thus, it can be concluded that more oxygen vacancies exist in NBs than in NWs.

To investigate the influence of boundary configurations on the electrical properties of the α-Fe2O3 nanostructures, the electrical behavior of individual α-Fe2O3 NW and NB was studied by in situ TEM. To obtain a reliable and statistically relevant experimental result, more than 10 individual α-Fe2O3 NWs and NBs were examined. Under TEM inspection the nanomanipulator probe electrode was carefully adjusted to touch the samples, as shown in figures 5(a) and (c). A metal-semiconductor contact can be either a Schottky contact or an ohmic contact depending on the Fermi surface alignment between the metal electrode and the semiconductor [21, 22]. Figure 5(b) reports the measured I–V curve from the α-Fe2O3 NW, which is nonlinear and almost symmetrical. No current is detected between bias voltages from −0.8 V to 0.8 V, and a rapid current increase appears beyond this bias range. Such threshold effect may be ascribed to two Schottky contacts formed at the interfaces of the semiconducting NW and two gold electrodes [23, 24]. However, the measured I–V curve for the α-Fe2O3 NB in figure 5(d) exhibits an obviously linear I–V relation, indicating that an ohmic contact forms between the α-Fe2O3 NB and gold electrodes. The resistance of α-Fe2O3 NB can be estimated directly from the linear I–V curve, whereas the resistance of α-Fe2O3 NW can only be obtained from the large bias region in the I–V curve since the total voltage at the low bias is mainly controlled by the two Schottky barriers [23]. The resistivity of α-Fe2O3 NB and NW can be determined by

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between Au and α-Fe₂O₃ NWs. It has been demonstrated that α-Fe₂O₃ undergoes a peculiar transition from p-type to n-type under certain conditions due to its small bandgap \(E_g = 2.2\) eV [26]. The α-Fe₂O₃ NBs examined by in situ TEM have an n-type nature as a result of oxygen deficiencies in the CSL boundary region. The oxygen vacancies in the CSL boundary region of the α-Fe₂O₃ NB may result in a change in the work function. The Fermi level of the Fe₂O₃ NB shifts readily towards the conduction band \(E_c\) (figure 6(b)), and thus the work function of the Fe₂O₃ NB decreases to be smaller than that of Fe₂O₃ NW. In the schematic band diagram (figure 6(b)), the Fermi levels of Fe₂O₃ NB and Au are aligned, yielding an ohmic contact. Therefore, the \(I-V\) characteristic of α-Fe₂O₃ NB exhibits a linear relation. In addition, the oxygen vacancies increase the carrier concentration in the n-type semiconductor, which enhances the electrical performance of the α-Fe₂O₃ NBs.

A magnetic phase transition from a canted ferromagnetic phase to an antiferromagnetically ordered state at \(~264\) K has been reported for bulk hematite [27]. This transition is characterized by a sharp decrease in the zero-field cooling (ZFC) and field cooling (FC) magnetization curves called a Morin transition. Figure 7 shows the temperature dependence of ZFC and FC magnetization for α-Fe₂O₃ NWs and NBs. Both the NWs and the NBs exhibit a well-defined peak at 122 K, which corresponds to the Morin transition. The Morin
temperature of the \( \alpha \)-Fe\(_2\)O\(_3\) nanostructure decreases with decreasing size. The magnetic behavior of our \( \alpha \)-Fe\(_2\)O\(_3\) NWs is consistent with the expected behavior of hematite [28]. However, the \( \alpha \)-Fe\(_2\)O\(_3\) NBs show an obviously different magnetic behavior. The magnetization curve of the NBs rises more sharply than that of NWs near this Morin transition temperature. Since no secondary phases are detected in our samples, the magnetic behavior observed here is ascribed to an intrinsic property.

Considering the dimensionality and orientation relationship change of these \( \alpha \)-Fe\(_2\)O\(_3\) nanostructures, we ascribe their different magnetic behaviors to an enhanced magnetic ordering accompanied by the interfacial structural order in the 2D \( \alpha \)-Fe\(_2\)O\(_3\) NBs. Above the Morin temperature, \( \alpha \)-Fe\(_2\)O\(_3\) is a canted antiferromagnet with spins perpendicular to the \( c \)-axis except for a slight canting about 1 min of arc out of the basal plane [29]. When the temperature is decreased to 122 K, \( \alpha \)-Fe\(_2\)O\(_3\) is a uniaxial antiferromagnet with spins lying along the \( c \)-axis and the magnetic moments in \( \alpha \)-Fe\(_2\)O\(_3\) are frozen or blocked [30]. In our experiment, bicrystalline \( \alpha \)-Fe\(_2\)O\(_3\) NBs have a unified direction of the \( c \)-axis as shown in figure 3(d), while the direction of the \( c \)-axis in bicrystalline \( \alpha \)-Fe\(_2\)O\(_3\) NW is not uniform as shown in figure 2(d). Below 122 K, the magnetic moments in the 2D \( \alpha \)-Fe\(_2\)O\(_3\) NBs are more ordered than those in the 1D \( \alpha \)-Fe\(_2\)O\(_3\) NWs (figure 8). Therefore, compared with the magnetization curve of \( \alpha \)-Fe\(_2\)O\(_3\) NW, the ZFC magnetization curve of \( \alpha \)-Fe\(_2\)O\(_3\) NB shows more drastic changes.

4. Conclusions and perspectives

In summary, bicrystalline 1D \( \alpha \)-Fe\(_2\)O\(_3\) NWs and 2D \( \alpha \)-Fe\(_2\)O\(_3\) NBs were synthesized by thermal oxidation of Fe foils. The measured \( I-V \) curves show that a Schottky contact forms between \( \alpha \)-Fe\(_2\)O\(_3\) NW and gold electrodes, whereas an Ohmic contact was created between \( \alpha \)-Fe\(_2\)O\(_3\) NB and gold electrodes. Such transformation is caused by the special CSL boundary in the \( \alpha \)-Fe\(_2\)O\(_3\) NB. The magnetic measurements demonstrate that the ZFC magnetization curve of the NBs rises more rapidly near the Morin transition temperature than that of the NWs. Such distinct differences are ascribed to the fact that the magnetic moments in the 2D \( \alpha \)-Fe\(_2\)O\(_3\) NBs are more ordered than those in the 1D \( \alpha \)-Fe\(_2\)O\(_3\) NWs. The presence of grain boundaries opens new possibilities in the case of nanostructures since their properties are related to the reduced dimensionality. Understanding and controlling boundary properties in low-dimensional structures will pave the way for tailoring nanomaterial properties in the future.

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