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Characterization of the natural barriers of intergranular tunnel junctions: Cr$_2$O$_3$ surface layers on CrO$_2$ nanoparticles
Low field intergranular tunneling effect in CrO₂ nanoparticles and characterization of the barriers

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The magnetoresistance (MR) and microstructures of half-metallic CrO₂ nanoparticle systems were studied. Using field alignment, the needle-shaped CrO₂ single domain particles were aligned in the same orientation. The MR of this structure showed a magnetic junction-like behavior with two well-separated peaks in the MR at coercivity fields and the MR of the aligned CrO₂ particles reached >41% at a relatively low field of about 1000 Oe. The magnetotransport mechanism was analyzed in terms of spin dependent tunneling between CrO₂ nanoparticles. Using transmission electron microscopy, x-ray diffraction, and x-ray photoelectron spectroscopy techniques, the intergranular tunneling barrier was characterized to be a very thin Cr₂O₃ interface layer between the CrO₂ particles. Temperature dependence of MR and conductivity in cold-pressed CrO₂ nanopowders were studied. The MR significantly decreased with increasing temperature and the spin independent hopping conduction is suggested to be responsible for the suppression of MR at high temperature.

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I. INTRODUCTION

Chromium dioxide (CrO₂) has been predicted to be a half-metallic material by Schwarz using band structure calculation in 1986. The high spin polarization close to 100% of CrO₂ has been demonstrated by different experiments, including photoemission experiment, superconducting point contact experiment, and vacuum tunneling measurement. The nearly perfect spin polarization of CrO₂ suggests that it would be ideal for applications in a ferromagnetic tunneling junction device, where a large magnetoresistance (MR) ratio is expected. It has been reported by Huang et al. and Suzuki et al. that CrO₂ thin films can have negative MR of about 13%–25% at low temperature. In 1998, Manoharan et al. and Coey et al. studied the cold-pressed CrO₂ powder samples and found that the MR of the pressed compacts can reach as high as 30%–50% at a magnetic field of about several tesla. The conduction mechanism of these CrO₂ powder compacts is due to the spin dependent intergranular tunneling influenced by the Coulomb gap. A CrO₂–I–Co tunneling junction using a native oxide barrier has also been reported with a small MR of about 1%, and so far no large MR in single magnetic junction made with CrO₂ has been reported.

In this work we studied magnetic transport between nano-sized CrO₂ single domain particles. Cold-pressed CrO₂ nanopowders show a significant MR at low temperature. The transport mechanism has been understood as the intergranular tunneling. Using transmission electron microscopy (TEM), x-ray diffraction (XRD), and x-ray photoelectron spectroscopy (XPS), the tunneling barrier has been characterized to be a Cr₂O₃ native oxide layer on the CrO₂ particle surface. In order to enhance the magnetotransport behavior of the tunneling effect between CrO₂ particles, needle-shaped CrO₂ particles have been aligned using a strong magnetic field. The field-aligned particles show junction-like MR behavior with two well-separated peaks and the switching magnetic field is about 1000 Oe which is much lower than that of the cold-pressed powders.

II. EXPERIMENTS AND DISCUSSIONS

A. MR of cold-pressed CrO₂ nanopowders

Cold-pressed CrO₂ powder compacts were made with the nano-sized powders supplied by DuPont. The powders were analyzed by XRD and TEM. They are single crystal needle-shaped particles with lengths of about 400 nm and an aspect ratio of about 9:1. The coercivity is about 600 Oe at room temperature and about 1000 Oe at T = 5 K. Using a hardened-steel die, the cold-pressed compacts were made under a pressure of 5 × 10⁸ N/m². The magnetization was measured with a superconducting quantum interference device magnetometer and the electron magnetotransport properties were measured with a Quantum Design physical properties measurement system (PPMS). The two-terminal method was used in the transport measurements and electrodes were made with silver print. The cold-pressed sample shows a resistivity of about 0.1 Ω cm at room temperature.

Figure 1 shows the negative MR of the cold-pressed CrO₂ sample at T = 5 K, where the MR is defined as (R_H − R_H=0)/R_H=0. It reaches about 28% in a field of 5 T. The inset of Fig. 1 shows the MR over the low field range together with the magnetic hysteresis loop. One can see that the resistance reaches its maximum values coordinating to the reversing of the magnetic moments. The mechanism of this MR effect is understood to be a result of the electron spin dependent tunneling between neighboring CrO₂ particles.

B. MR of aligned CrO₂ nanopowders

From Fig. 1 one can see that the switching field (the magnetic field at which significant MR ratio has been

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reached) of the cold-pressed powder is quite large. Normally the switching field for the powder compacts and polycrystalline films is larger than 1 T, which is too large for many applications. Basically, the value of the switching field corresponds to the external field at which the magnetic moments of particles (grains) are reversed. It is obvious that random orientation of moments may cause the overall switching field to become much larger than the coercivity of a single particle. This problem can be solved by finding a way to align the CrO₂ single crystalline particles to the same orientation. The switching field can be reduced theoretically to the coercivity field of a single particle.

In our experiment, since the magnetic moments of the needle-shaped CrO₂ single crystalline particles were along the easy axes (c axes), the particles can be reoriented by applying a strong magnetic field. The CrO₂ powders were added to ethanol with a 1:200 ratio, and an ultrasonic shaker was used to break the aggregates for uniform distribution of the CrO₂ particles in the suspension. The suspension was dropped onto a polymer substrate at room temperature in a magnetic field of 1 T. After drying, the needle-shaped CrO₂ particles became affixed to the substrate and were aligned along the direction of the magnetic field. Two electrode contacts were made by silver paste. The size of the measured samples was approximately 100 µm, and the resistance was around 0.1 MΩ at room temperature, which was much larger than that of the cold-pressed powders. Figure 2 illustrates the aligned particles and the transport measurement.

The aligned needle-shaped CrO₂ particles express a very interesting MR effect with two well-separated peaks, like a single magnetic tunneling junction, as shown in Fig. 3. Comparing to the cold-pressed powders in which the particles have random orientations, the junction-like MR of the aligned powders is about 41% at T = 5 K, and the switching field significantly decreases to about ±1000 Oe. Notice that the resistance change is less than 5% for the random-orientated pressed powders over the same range of magnetic field. One can see that by using alignment technique, a much larger MR ratio can be reached over a low field range (0–±1000 Oe), which shows a much better switching behavior than that of the random-oriented powder compacts.

Temperature dependence of the MR and resistivity R of the aligned CrO₂ particles were measured and results are shown in Fig. 4 and its inset, respectively. One sees that the ln R is proportional to 1/T^1/2 at low temperature (<50 K), which is typical in the intergranular tunneling. It is known that the temperature dependence of intergranular tunneling resistance follows 12–14

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**PICTURE 1**

**FIG. 1.** MR of cold-pressed CrO₂ powder compact, measured at T = 5 K. Inset shows the low field MR together with the magnetization curve.

**FIG. 2.** Illustration of the field-aligned needle-shaped CrO₂ particles and the measurement of magnetotransport.

**FIG. 3.** MR of the field-aligned CrO₂ particles which shows a junction-like behavior with a low switching field of about ±1000 Oe.

**FIG. 4.** Temperature dependence of the MR of the aligned CrO₂ powders. The inset shows the logarithmic resistance ln R as a function of 1/T^1/2, the resistance is 99.4 kΩ at 300 K and increases to 893 kΩ at 5 K.
\[ R \sim \exp(\Delta/T)^{1/2} \tag{1} \]

where \( \Delta \) is proportional to the Coulomb charging energy and barrier thickness. The Fig. 4 inset shows that the \( \ln R \) is linear to \( 1/T^{1/2} \) and indicates that the intergranular tunneling is the major conducting mechanism at low temperature. With increasing temperature, the resistance decreases faster than Eq. (1), which implies that some other conducting channels become larger. MR also decreases quickly with increasing temperature as Fig. 4 shows. This phenomenon can be correlated to the spin-flip effects, which becomes significant at high temperature, and suppresses the spin dependent conduction. Several spin-flip mechanisms have been introduced.\(^9\,15,16\) It is found in our work that the spin dependent tunneling MR between CrO\(_2\) particles can be relatively suppressed by an spin independent conducting channel, which is due to the high-order inelastic hopping. The details about inelastic hopping is discussed in another article.\(^{17}\)

C. Microstructure of the intergranular tunneling barrier

For the intergranular tunneling systems of CrO\(_2\) powder compacts or polycrystalline films, the role of the tunneling barrier was suggested to be played by the grain boundary.\(^8,9\) and the barrier material was expected to be composed of Cr\(_2\)O\(_3\) since it is the most stable phase of chromium oxides.\(^2,11,18\) In our experiments performed using TEM, XRD, and XPS, etc., hard evidence of the existence of the Cr\(_2\)O\(_3\) boundary layer were found, and intergranular tunneling barrier was well-characterized.

Using TEM, we directly observed a 1–3 nm thick native oxide layer on the surface of the CrO\(_2\) single crystal particles. Figure 5(a) shows the TEM image of the CrO\(_2\) single crystal particles which has a needle shape and a diameter of about 50 nm. Figure 5(b) is the high-resolution lattice image of the CrO\(_2\) particle with an [001] axis along its length, showing clearly the thin layer on the surface of the single crystal CrO\(_2\). This layer was observed on every particle.

XPS measurement was performed, and the results suggested that the Cr\(^{3+}\) dominated in the near surface region (~10 monolayers) of the CrO\(_2\) particles. One should notice that XPS is sensitive within 10–20 Å into the particle surface. Our result indicated that the 1–3 nm thick surface layer on the CrO\(_2\) particles was not CrO\(_2\) but a Cr\(^{3+}\) compound. The result confirmed the expectation that a Cr\(_2\)O\(_3\) native oxide layer existed on the CrO\(_2\) surface.\(^8,9\,11\) and this insulator layer played the role of the tunneling barrier. This result was also supported by a very slow scan of XRD experiment, which showed that a small amount (5%–10%) of crystalline Cr\(_2\)O\(_3\) existed in the “pure” CrO\(_2\) powders.

III. SUMMARY AND CONCLUSIONS

We have studied the magnetic properties and magnetotransport of cold-pressed CrO\(_2\) nanopowders; the large MR ratio corresponded to the spin dependent intergranular tunneling effect. By using field-introduced order, the needle-shaped CrO\(_2\) nanoparticles were aligned along the same direction and exhibited texture structure. The magnetotransport of the aligned CrO\(_2\) nanoparticles showed a junction-like MR behavior with a low switching field of about 1000 Oe. It also showed a large MR ratio of about 41% at \( T = 5 \) K. The MR ratio decreased with the increasing of temperature, which was due to the spin independent conduction becoming dominant at high temperature. The microstructure of the intergranular tunneling system was analyzed using TEM together with XPS and XRD. A very thin layer of Cr\(_2\)O\(_3\) was observed and characterized on the surface of the CrO\(_2\) particles, which confirmed that the role of the intergranular tunneling barrier was played by Cr\(_2\)O\(_3\).

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