Junction-like magnetoresistance of intergranular tunneling in field-aligned chromium dioxide powders

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The magnetic and magnetotransport properties of field-aligned half-metallic CrO_2 powders have been studied. Needle-shaped nanoparticles of CrO_2 have been aligned in a strong magnetic field. The aligned powder sample shows a strong anisotropy along the alignment direction. The conduction mechanism of the aligned CrO_2 powder sample has been examined and is consistent with the intergranular spin-dependent tunneling. Negative tunneling magnetoresistance of about 41% is achieved in a small field in the vicinity of the coercive field at 5 K. The magnetoresistance (MR) versus field curve shows two well-separated narrow peaks at the coercive fields and resembles that of a magnetic tunnel junction. This junctionlike MR results from the narrow switching field distribution of the aligned powders. Our results suggest that the aligned magnetic CrO_2 particles may find novel applications in spin-transport structures and devices.

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I. INTRODUCTION

Half-metallic oxide CrO_2 has long been of importance in magnetic recording and shows unique magnetic properties. In 1986, it was predicted to be half-metallic by Schwarz using band-structure calculation.[1] A number of experiments have been done, which suggest its half-metallicity, including photoemission experiments,[2] superconducting point-contact experiments,[3] and vacuum tunneling measurement.[4] It is suggested that half-metallic ferromagnets are ideal materials for the electrodes in spin-dependent tunneling devices, such as those described by Moodera *et al.*[5] Since the spin polarization is nearly 100% at the Fermi level, the tunneling junctions made of such materials would have an extremely large magnetoresistance (MR) and a very significant switching effect. It has been reported that polycrystalline CrO_2 thin films can have negative MR of about 13–25 % (Refs. 6 and 7) at low temperature. In 1998, Manoharan *et al.*[8] and Coey *et al.*[9] studied the cold-pressed powder samples and found that the MR of the pressed compacts can reach as high as 30–50 %. The conduction mechanism of these CrO_2 powder compacts arises from the spin-dependent intergranular tunneling influenced by the Coulomb gap.[9,10] We, and others, have studied the microstructure of the native barrier layer of the spin-dependent intergranular tunneling in CrO_2 powder samples.[11] Direct observation by transmission electron microscopy reveals that the barrier is a thin layer of dense and uniform crystalline Cr_2O_3 on the surface of the single-crystal CrO_2 powders. The composition and crystal structure of the native Cr_2O_3 layer is confirmed by x-ray-diffraction and x-ray photoelectron spectroscopy techniques. A CrO_2-I-Co magnetic tunneling junction using the native oxide barrier has also been recently reported but with a small MR of about 1%.[12]

In this paper, we use the needle-shaped CrO_2 single domain powders and align them along the direction of a strong applied magnetic field. It is found that our aligned powder sample is strongly anisotropic. The MR of the aligned powders exhibits a behavior bearing a resemblance to that of the magnetic tunneling junctions (MTJ) and shows a sharp switching effect at the coercive field of about 1000 Oe.

II. EXPERIMENTS

In our experiments, samples were made from pure commercial CrO_2 powders for magnetic recording supplied by DuPont. The ferromagnetic powders were characterized by x-ray diffraction and transmission electronic microscopy (TEM). The single domain CrO_2 particles are needle-shaped with an aspect ratio around 9:1. The easy magnetic axis is along the needle and the average length is about 400 nm as determined from TEM micrographs. The 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 CrO_2 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 CrO_2 powders 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 about 100 μm. Transport measurements were made using a Quantum Design physical properties measurement system (PPMS), which provides a platform for resistivity measurements in an applied magnetic field. The magnetization curves were measured by a superconducting quantum-interference device (SQUID) magnetometer. Figure

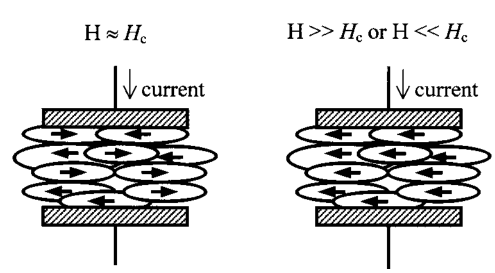

FIG. 1. Aligned magnetic moments of CrO_2 powders and the structure of transport measurement.

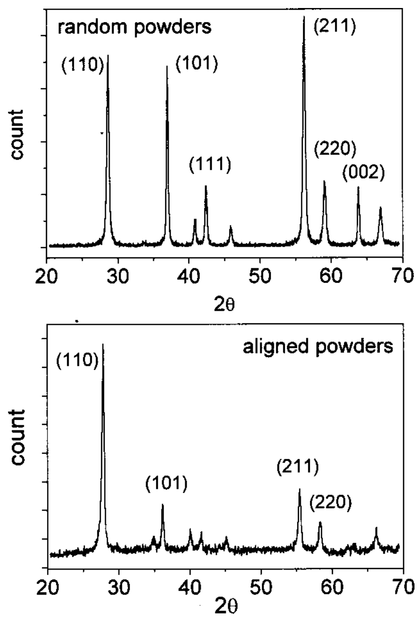

FIG. 2. X-ray-diffraction patterns of the random and aligned powders.

1 gives a schematic view of the alignment effect of CrO_2 nanopowders and the structure of transport measurement.

III. RESULTS AND DISCUSSION

Figure 2 shows the x-ray-diffraction patterns of the aligned powders in comparison with the random powders. One can see that the (110) plane shows strong diffraction and the intensities of (101), (111), and (211) are substantially suppressed. The (002) peak virtually disappears from the pattern of the aligned powders. The powders are aligned along the *c* axis and show an x-ray-diffraction pattern typical of textured materials. The dominant anisotropy here is the shape anisotropy and the easy axis is along the length of the particles, which is the *c* axis. Due to the high aspect ratio, the aligned CrO_2 powder sample exhibits strong anisotropy. Figure 3 gives the magnetization curves at 5 K of the aligned sample when the applied field is parallel to the easy axis. One can see that when the applied field is parallel and perpendicular to the easy axis (alignment direction), the hysteresis loop is close to a square with a high remanence and shows a coercivity of about 1000 Oe. The saturation magnetization M_s is about 110 emu/g. When the magnetic field is perpendicular to the easy axis, the hysteresis loop becomes more gradual and rounded with a much-reduced remanence as shown in Fig. 3. The coercivity is not so much changed for the perpendicular orientation, which may be due to imperfect alignment.

The magnetotransport measurements have been made on the aligned powder sample with the magnetic field applied along the easy axis. Figure 4 shows the MR versus field curve at 5 K. The MR ratio is defined as $(R-R_H)/R_H$, where R_H is the resistance at high field. The MR is about 41% at $T=5$ K and is characterized by two well-separated peaks near the coercive field $H\approx\pm 1000$ Oe. Unlike random

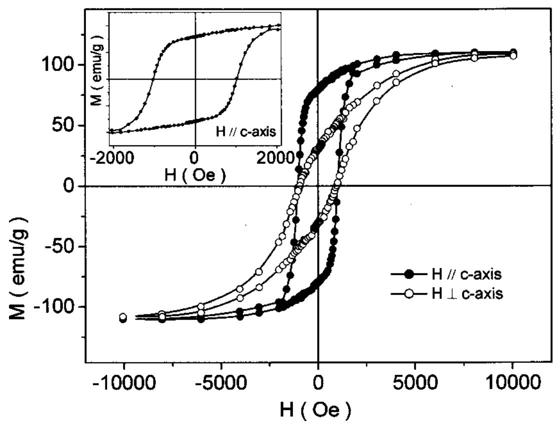

FIG. 3. The hysteresis loops of the aligned powders at $T=5$ K: field parallel to the easy axis (●) and perpendicular to the easy axis (○). Inset shows the hysteresis loop (field applied parallel to the easy axis) over the smaller field range.

powder compacts, whose MR curves are typically ''butterfly'' shaped, the aligned powders exhibit sharp switching of the resistance between high and low states in a small field region in the vicinity of the coercive field. The switching behavior is similar to that of a magnetic tunneling junction. This junctionlike MR is attributed to the fact that there is a narrow distribution of the switching field of the magnetic moments of the aligned powders as seen in Fig. 3. As the field is decreased to zero from the saturation, nearly all moments remain in the original direction and result in the low-resistance state near zero field. The situation is different for the random powders where a significant portion of the moments are already misaligned as soon as the field is reduced to near zero leading to a large increase in the resistance. The inset of Fig. 4 shows the MR over the same range of the applied field of a cold-pressed sample using the same CrO_2 powders but without the field alignment. One sees that both the low-field MR ratio and the sharpness of the switching

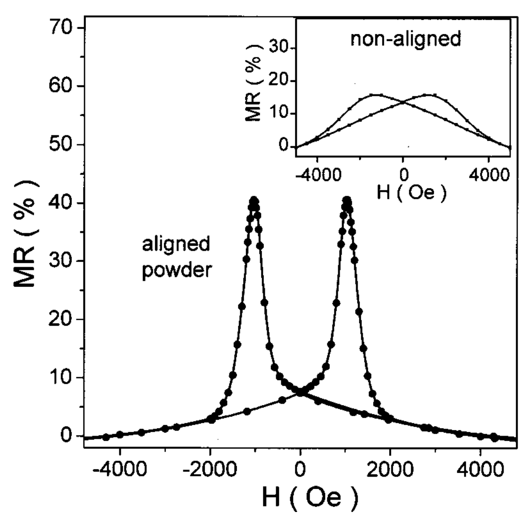

FIG. 4. TMR of the aligned powders at $T=5$ K. Inset shows the MR at 5 K of cold-pressed powders with random orientation, over the same field range.

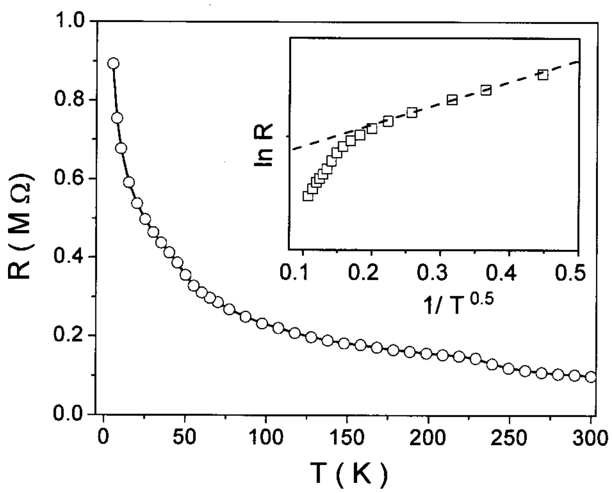

FIG. 5. Temperature dependence of the resistance R. Inset plots $\ln R$ as a function of $1/T^{1/2}$.

effect of the random powders are much lower than those of the aligned powders. There is no significant change of the MR when the direction of the current is changed from parallel to the easy axis to perpendicular to the easy axis.

The conduction mechanism of the CrO_2 powder compact has been analyzed by Coey *et al.*[9] and is associated with the spin-dependent intergranular tunneling across the grain boundaries. Figure 5 shows the temperature dependence of the resistance R, and the inset plots the $\ln R$ as a function of $1/T^{1/2}$. One can see that $\ln R$ is linear to $1/T^{1/2}$ when temperature is lower than 35 K, which is typical of intergranular tunneling associated with a Coulomb gap. The tunneling resistance as a function of temperature is usually given by[13–15]

$$R_{\text{tun}} \propto (1+P^2m^2)^{-1}\exp(\Delta/T)^{1/2}, \tag{1}$$

where P is the spin polarization, $m=M/Ms$ is the relative magnetization, and Δ is proportional to the Coulomb charging energy and barrier thickness. In our sample, Δ is about 5.5 K, which is determined from the slope of the linear region of the $\ln R \sim 1/T^{1/2}$ curve. This value is in reasonable agreement with that derived from the particle size and barrier thickness observed with TEM.[11] We have estimated the Δ value using the particle size ($\sim$400 nm), barrier thickness ($\sim$1 nm), dielectric constant of $\sim$10 for Cr_2O_3, and barrier height of $\sim$0.7 eV. The value for the barrier height was obtained from Ref. 12, which only provides a rough estimate of the true barrier height of our system. The Δ value thus derived is about 30 K, which is quite close to the value obtained from the transport data. The linear relationship between $\ln R$ and $1/T^{1/2}$ at $T<35$ K implies that the intergranular tunneling is the main contribution to the conductance at low temperatures. At high temperature a spin-independent conductance channel opens up due to higher-order inelastic hopping through the localized states in the barrier.[16]

The MR behavior is directly related to the switching of the magnetic moments of each single domain particle. The conductance of the aligned powder sample is through the intergranular tunneling between a pair of neighboring particles. Ideally, the magnetic moments are completely aligned in the same direction as the applied field when $H \gg H_c$. In this case the spin-dependent tunneling between neighboring particles has a high tunneling probability and the sample shows low resistance. When H is close to the coercivity field H_c, the magnetic moments of a portion of the particles are reversed, which causes antiparallel alignment of the moments of neighboring particles and reduces the tunneling conductance. The number of the antiparallel alignments peaks at H_c leading to the maximum value of the resistance. This corresponds to $m=0$ in Eq. (1), where the magnetic moments of one half of the particles are switched. When $H \gg H_c$ or $H \ll H_c$, the magnetic moments are aligned and the sample shows low resistance. The switching process of the magnetic moments in our aligned sample is also illustrated in Fig. 1. The uniqueness of the aligned powder sample is that there is a very narrow field region around H_c over which the moments reverse their directions. Therefore practically all moments are aligned, leading to the low resistance outside that region.

The tunneling process in the aligned powder sample can be approximately described as a network of many magnetic tunneling junctions, in which the boundary between each pair of neighboring particles is an individual junction. Considering the nearly 100% spin polarization of CrO_2, a tunneling path is either open or closed, and one can anticipate an extremely high MR of the MTJ network. However, in our system, at the coercive field, there are always those junctions where the two neighboring particles are aligned parallel (open) and those junctions that are in the closed states. Higher MR than the observed value here is possible if one can appropriately control the relative orientation of the neighboring particles.

The temperature dependence of MR of the aligned CrO_2 powders has also been studied. It is found that, at higher temperature, the MR ratio drops quickly. MR becomes less than 1% at room temperature. The decrease of MR at high temperature can be analyzed in terms of spin-independent conductance (and spin-flip effect), which become dominant with increasing temperature.[16,17] It is not clear at present how much the spin polarization of CrO_2 at the surface or in the bulk is suppressed at high temperatures, which may also reduce the MR.

There are several kinds of structures of CrO_2 that have been studied by different groups for the spin-dependent magnetotransport properties. Table I lists the experimental results of the MR of CrO_2 of different structures obtained from the literature. Comparing to those results, one can see that the aligned powders have a high MR value and a well-defined low switching field, which may be suitable for many applications. In addition, comparing to other thin-film structures, e.g., spin valves and magnetic tunneling junctions, the aligned powder structure is easy to make. The aligned CrO_2 magnetic particles and similar designs can find potential use in novel spin-transport devices and be useful for possible industrial applications provided the temperature characteristics are further improved.[17]

TABLE I. Magnetoresistance of CrO_2 of different structures.

Composition	Structure	MR	Field[a] Oe	Source
CrO_2	polycrystalline film (on $SiTrO_3$)	~13%	50 000	Ref. 6
$CrO_2+Cr_2O_3$	polycrystalline film (on $SiTiO_3$)	27% (22%)	50 000 (~5 000)	Ref. 6
CrO_2	crystal film (on ZnO_2)	~4%	20 000	Ref. 7
CrO_2	crystal film (on TiO_2)	~12%	70 000	Ref. 7
CrO_2	cold pressed	42% (~30%)	50 000 (10 000)	Ref. 8
CrO_2	cold pressed	~30% (23%)	50 000 (5 000)	Ref. 9
25% CrO_2, 75% Cr_2O_3	cold pressed	~50%	50 000	Ref. 9
CrO_2	aligned powders	~41%	1 000	this work
CrO_2-I-Co	tunneling junction	~1%	50	Ref. 11

[a]The magnetic field at which the indicated MR ratio is reached.

IV. CONCLUSIONS

We have studied the magnetic and transport properties of aligned needle-shaped CrO_2 powders. The powders are aligned to the same direction in a strong magnetic field and then affixed to a substrate. The sample is strongly anisotropic owning to the shape anisotropy of the particles. The spin-dependent intergranular tunneling is the major conduction mechanism of the CrO_2 aligned powders. A large negative MR of about 41% has been found at 5 K, and the magnetoresistance shows two well-separated peaks at the coercivity fields ($\pm$ 1000 Oe), which bears a resemblance to the behavior of the magnetic tunneling junctions. It is suggested that the described switching characteristics of the aligned particles may have useful applications.

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