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Influence of hot pressure on the magnetoresistance of CrO_2

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In this paper, we investigate the influence of high temperature and high pressure (hot pressure) on the magnetic and transport properties of polycrystalline CrO_2 samples compacted under high pressure and high temperature of up to 5 GPa and 600 °C, respectively. The magnetic moment increases with compacting temperature, and a metal-semiconductor transition is observed in hot-pressed samples, different from the cold-pressed samples. These results indicate that the formation of Cr_2O_3 at the grain boundaries of CrO_2 is suppressed by hot pressure. The magnitude of low field magnetoresistance of up to 1 T at 5 K is enhanced first with the increase of compacting temperature and then decreased under higher compacting temperature. This result can be well explained by the change of spin-dependent tunneling at the modulated grain boundaries of CrO_2 due to the transformation from Cr_2O_3 to CrO_2 under hot pressure. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2714272]

I. INTRODUCTION

As the simplest half-metallic oxide predicted by band structure calculation,[1] the magnetotransport properties of CrO_2 have drawn much attention because it has nearly perfect spin polarization (close to 100%) and higher Curie temperature T_C of 395 K, which are necessary for spintronic device applications.[2,3] The large low field magnetoresistance (MR) originating from the spin-dependent carrier tunneling at grain boundary has been observed in CrO_2 granular samples at low temperature,[3–9] but only a very small value of MR can be obtained in CrO_2 at high temperature.

Usually, there is a naturally grown Cr_2O_3 layer on the surface of CrO_2 particles,[3,7,10] in which the higher-order hopping of a carrier is considered to be one of the main reasons for the suppressed low field MR at high temperature.[9] It is obviously important to remove the Cr_2O_3 layer for understanding the intrinsic magnetotransport property of CrO_2. Unfortunately, Cr_2O_3 is more stable than CrO_2 at atmospheric pressure so it is hard to eliminate this native Cr_2O_3 layer from the surface of CrO_2 particles in air. It is well known that CrO_2 is stable under high pressure. In addition, a high-pressure chamber can offer an isolated environment for CrO_2 to avoid losing oxygen and transforming into Cr_2O_3.[11–13] Therefore, it is worthwhile to modulate the Cr_2O_3 layer by high temperature and high pressure (hot pressure), but clear experimental data on the influence of hot pressure on the magnetotransport property of CrO_2 are still lacking.

In this paper, we report some preliminary results of the magnetic and transport properties of CrO_2 samples compacted under hot pressure. Hot pressure not only prevents CrO_2 from transforming into Cr_2O_3 but also changes the original Cr_2O_3 to CrO_2. An enhanced low field MR and the conductance of polycrystalline CrO_2 can be obtained under suitable hot pressure conditions.

II. EXPERIMENTS

Nanosized CrO_2 powders were supplied by Dupont. They are needle-shaped particles with length of about 400 nm and an aspect ratio of about 9:1. These CrO_2 powders were pressed into a tablet and put into the chamber of a belt-type high-pressure apparatus, and compacted into bulk

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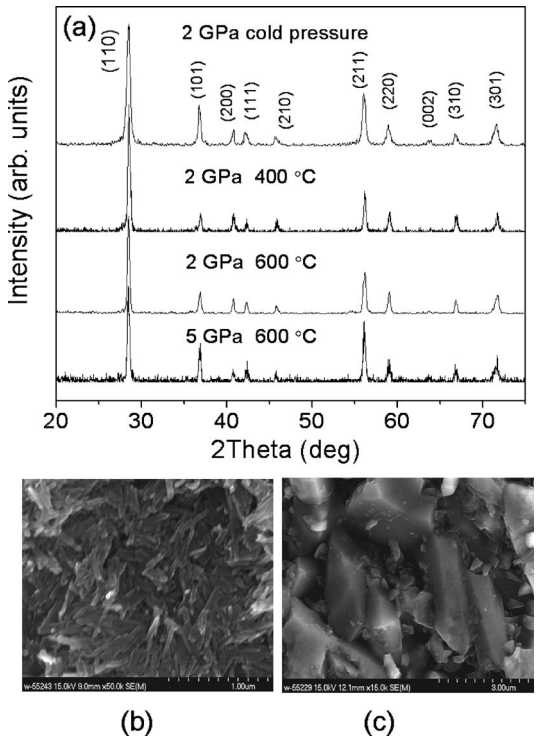

FIG. 1. (a) Room-temperature XRD patterns of CrO_2, (b) SEM of 2 GPa cold-pressed sample, and (c) SEM of the 2 GPa, 500 °C sample.

samples under different pressures and temperatures of up to 5 GPa and 600 °C, respectively. In the hot pressure procedure, the pressure was first increased to a desired value, followed by temperature. After holding the pressure and temperature for 30 min, the temperature was decreased to room temperature first, and then the pressure was released. The measurements of the pressure and temperature are described in Ref. 14.

X-ray diffraction (XRD) patterns were collected using a Bede D^1 XRD spectrometer with Ni-filtered Cu $K\alpha$ radiation. The surface morphology of the samples was obtained using a Hitachi S-4700 field emission scanning electron microscope. The magnetic and transport properties were measured by using the physical properties measurement system (PPMS) of Quantum Design.

III. RESULTS AND DISCUSSION

Figure 1(a) gives the room temperature XRD patterns of CrO_2 samples annealed under different pressures. Obviously, Cr_2O_3 may be introduced by annealing the CrO_2 in air at 400 °C for 20 min,[3,9] but there is not peak of Cr_2O_3 in all hot-pressed CrO_2 samples, indicating that high pressure can suppress the formation of Cr_2O_3 up to 600 °C. Figures 1(b) and 1(c) show the scanning electron microscopy (SEM) micrographs for the cold-pressed and hot-pressed CrO_2. The cold-pressed sample still has needle-shaped nanosized particles, but only large CrO_2 grains are seen in the hot-pressed sample due to the growth of CrO_2 particles under hot pressure. These results are consistent with the changes in the XRD patterns such that the peaks of annealed CrO_2 under high pressure are sharper than the cold-pressed samples.

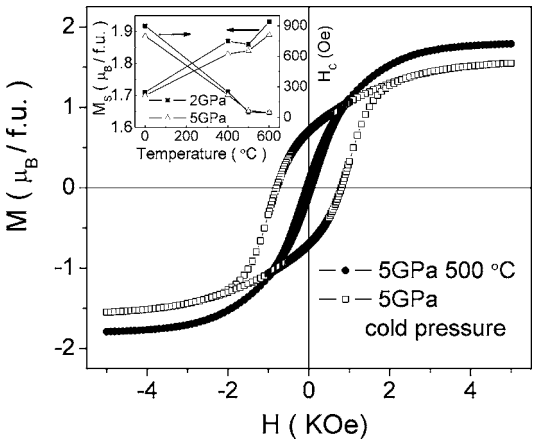

FIG. 2. Isothermal magnetization curves of CrO_2 at 5 K. Inset shows the variation of the M_S at 5 K and 5 T (left axes) and H_C (right axes).

Figure 2 shows the isothermal magnetization curves of CrO_2 at 5 K. The saturation moments per formula unit (M_S) and coercivity (H_C) of the cold-pressed sample are about $1.7\mu_B$ and 900 Oe, respectively, similar to the original CrO_2 powders.[15] However, the H_C of the hot-pressed CrO_2 at 5 K decreases rapidly from 900 to 40 Oe with increasing compacting temperature from room temperature to 600 °C, as shown in the inset of Fig. 2. This feature is mainly caused by the increase of grain size due to the growth of CrO_2 particles under hot pressure and is consistent with the results of XRD and SEM. The M_S value of the cold-pressed CrO_2 ($1.7\mu_B$) at 5 K and 5 T is much lower than the theoretical value of pure CrO_2 ($2\mu_B$), as reported in literatures. It means that there is a large amount of Cr_2O_3 on the surface of CrO_2 nanoparticles.[16] But it is obvious from the inset of Fig. 2 that M_S increases with increasing compacting temperature, and the highest value of M_S ($1.93\mu_B$), close to the theoretical value, can be obtained at 2 GPa and 600 °C. This remarkable increase of M_S should be attributed to the transformation from antiferromagnetic Cr_2O_3 to ferromagnetic CrO_2 on the grain surfaces. Because these data were measured in a high magnetic field of 5 T, the contribution due to the grain growth itself can be ignored. CrO_2 is more stable than Cr_2O_3 under high pressure, thus the Cr_2O_3 layer on the surface of the CrO_2 particles is eventually eliminated when they grow into larger particles under hot pressure. It should also be noticed that the values of M_S of 5 GPa hot-pressed samples are smaller than those at 2 GPa for the same compacting temperature, which suggests that the transformation from Cr_2O_3 to CrO_2 is difficult under higher pressure because the amount of oxygen in the high-pressure chamber, which is necessary for oxidizing Cr_2O_3 to form CrO_2, decreases with increasing pressure. This result also gives strong evidence that the increase in M_S arises from the transformation of Cr_2O_3 to CrO_2. If it were the change of grain size that is mainly responsible for the increase in M_S, the M_S of the 5 GPa samples would be larger than the 2 GPa samples at the same compacting temperature because the former should have larger particles than the latter.

The temperature dependence of the resistivity (ρ) of CrO_2 in zero field is displayed in Figs. 3(a) and 3(b). Here, ρ

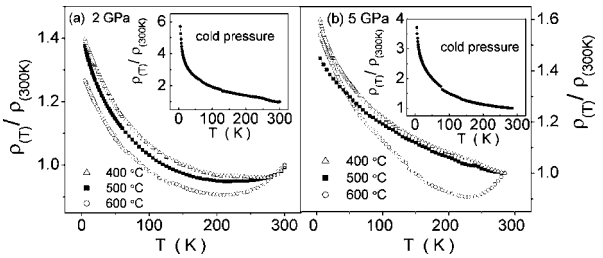

FIG. 3. Temperature dependence of the resistivity (ρ) at zero fields of hot-pressed CrO_2: (a) 2 GPa sample and (b) 5 GPa sample. The insets of (a) and (b) are the cold-pressed samples of 2 and 5 GPa, respectively.

is normalized to the value at 300 K. It is clear that the ρ vs T curves of all cold-pressed samples show a semiconductor behavior in the whole temperature range, which is similar to that of original CrO_2 powders.[9] However, the metal-semiconductor (*M-I*) transition occurs in hot-pressed samples, indicating that the resistance at the grain boundaries is weakened because much of the original intergranular barriers, such as the Cr_2O_3 layers, have been removed under hot pressure. It is interesting that the *M-I* transition can be found in all 2 GPa hot-pressed samples, but only observed in the 5 GPa hot-pressed sample at compacting temperature of 600 °C. We note that all samples showing the transition behavior have higher M_S over $1.85\mu_B$, and the 5 GPa samples have smaller M_S than the 2 GPa samples. It therefore suggests a strong correlation between the amount of Cr_2O_3 at the grain boundaries and the electrical conductance of the samples. Under a pressure of 2 GPa, there is enough oxygen in the high-pressure chamber for the transformation from Cr_2O_3 to CrO_2 to occur. The transition occurs at temperatures as low as 400 °C and is easier at higher temperatures. The *M-I* transition is observed in all hot-pressed samples at 2 GPa. Under higher pressure of 5 GPa, the transition from Cr_2O_3 to CrO_2 becomes more difficult and much higher temperature is needed to achieve the same. Therefore, the *M-I* transition only occurs in the 5 GPa hot-pressed sample at 600 °C.

Figure 4 shows the MR of 5 GPa samples as a function of magnetic field at 5 K, and the inset shows the variation of MR at 1 T and 5 K for all samples. Here, MR is defined as $\mathrm{MR}(\%)=[\rho_H-\rho_{\max}]/\rho_H$, where ρ_H and $\rho_{\max}$ are the resistivity of the sample in external field H and the highest resistivity value, respectively. With increasing compacting temperature, the low field MR increases remarkably first and then decreases, as shown in the inset of Fig. 4. It is well known that the low field MR of granular CrO_2 originates from the spin-dependent tunneling across the Cr_2O_3 layer at the grain boundaries.[3–8] As discussed earlier, because the amount of Cr_2O_3 in the 5 GPa hot-pressed samples is much more than that of the 2 GPa hot-pressed samples, the value of MR of the former is larger than that of the latter at the same compacting temperature. However, under lower compacting temperature, the Cr_2O_3 layer as tunneling barrier still exists at the grain boundaries in the hot-pressed samples, which may become more suitable for spin-dependent tunneling under optimum hot pressure conditions. The largest MR value of 42% is observed in the sample at 5 GPa and 400 °C. With

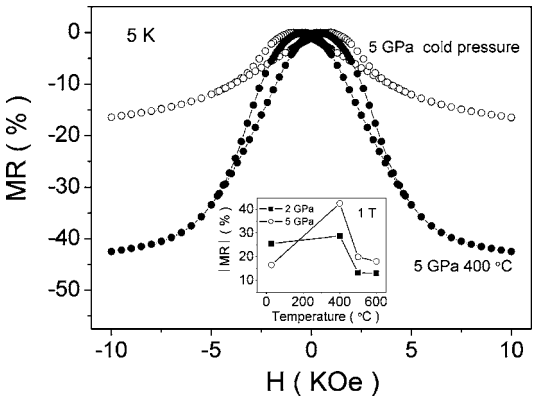

FIG. 4. The magnetic field dependence of MR at 5 K for the CrO_2 samples; the inset shows the MR data at 1 T and 5 K.

increasing compacting temperature, the amount of the Cr_2O_3 layer is reduced by the high pressure, and the low field MR is suppressed accordingly.

IV. CONCLUSIONS

In a high-pressure cell, not only the formation of Cr_2O_3 at high temperature is suppressed, but the original Cr_2O_3 layer on the CrO_2 particle surfaces has also been transformed to CrO_2. The change in the amount of Cr_2O_3 at the grain boundaries leads to the increase of magnetic moment and the appearance of the *M-I* transition in the hot-pressed CrO_2 samples, as well as changes in the magnetotransport properties of CrO_2. As a result, the low field MR is remarkably enhanced by the hot pressure, and a large MR value of 42% was observed in the sample hot-pressed at 5 GPa and 400 °C.

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