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Research articles

Study of microstructure and magnetotransport properties of CrO_2 prepared under HTHP

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ABSTRACT

The microstructure of the CrO_2 particles prepared by high temperature and high pressure (HTHP) method was studied by HRTEM. It is found that the CrO_2 particles synthesized at 500 and 550 °C are covered by Cr_2O_3 surface layers of about 6 nm thick. However, the CrO_2 particles synthesized at 400 and 450 °C do not have Cr_2O_3 surface layers. The saturation magnetization of the CrO_2 particles synthesized at different temperatures is all very close to the theoretical value. The magnetoresistance (MR) of the CrO_2 particles synthesized at 500 and 550 °C is much larger than that of the CrO_2 particles synthesized at 400 and 450 °C, which should be due to the enhancement of tunneling magnetoresistance by insulating Cr_2O_3 surface layers. The tunneling MR of the CrO_2 particles can be fitted well by expression of $C_1(M/M_s)^2 + C_2(M/M_s)^4 + C_3(M/M_s)^6$. The proportion of the higher-order terms of $(M/M_s)^2$ in the expression is tightly related to the existence of the Cr_2O_3 surface layer.

1. Introduction

Chromium dioxide (CrO_2) has been an important research object for decades due to its potential applications in new spintronics devices. By the band structure calculation, Schwarz [1] has predicted that CrO_2 is a half-metallic ferromagnet whose conduction electrons at Fermi level are 100% spin polarized at 0 K. The half-metallic characteristic of CrO_2 has been actually demonstrated experimentally by different techniques, such as photoemission spectroscopy [2], point contact Andreev reflection [3] and Tedrow-Meservey experiment [4]. Due to nearly perfect spin polarization of CrO_2, it is an ideal candidate for magnetic tunnel junctions, where a high tunneling magnetoresistance (MR) effect is expected [5–7]. Large MR has been found at low temperature in CrO_2 powder compacts, which are made from commercial CrO_2 powders used for magnetic recording [8]. Many papers have reported that each commercial CrO_2 particle is enclosed by a 1–3 nm thick native Cr_2O_3 layer [9–11]. It is well known that the large MR of the CrO_2 powder compacts is mainly due to spin-dependent tunneling across the Cr_2O_3 layer at the grains boundaries [8–10,12–15]. The insulating Cr_2O_3 layer acts as the tunneling barrier and enhances the MR effect [16]. However, there have been still very limited reports about the microstructure of CrO_2 particles obtained by other methods [17]. The studies on the influence of the microstructure on the magnetotransport properties of CrO_2 particles obtained by other methods are also lacking.

In this paper, we have studied the microstructure of the CrO_2 particles prepared by a high temperature and high pressure (HTHP) method [18]. A Cr_2O_3 layer of about 6 nm thick was observed directly by HRTEM on the surface of the CrO_2 particles synthesized at 500 and 550 °C. However, the CrO_2 particles synthesized at 400 and 450 °C do not have the Cr_2O_3 surface layers. The influence of microstructure on the magnetotransport properties of the CrO_2 particles was studied, and the enhanced MR was found in the CrO_2 particles synthesized at 500 and 550 °C.

2. Experiments

The CrO_2 particles were prepared under high temperature and high pressure condition as described in our previous work [18]. Firstly, CrO_3 flakes were uniformly crushed down and shaped into a disk with diameter of 10 mm and thickness of 2 mm by cold pressing. Secondly, the disk was loaded in a cubic anvil high temperature and high pressure apparatus (SPD 6 × 800), and the synthesis was carried out at 1 GPa and different temperatures respectively for 30 min. Finally, the disk sample was cooled down to room temperature and then the 1 GPa was released, and the disk sample was took out from the cubic anvil high temperature and high pressure apparatus.

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The disk samples were composed of CrO_2 particles. The crystal structure of the CrO_2 particles was checked by X-ray diffraction (XRD) equipment with Cu K_α radiation. Scanning electron microscopy (SEM) was employed to characterize the morphology of the CrO_2 particles. High-resolution transmission electron microscopy (HRTEM) was used to investigate the microstructure of the CrO_2 particles. The magnetic and magnetotransport properties of the CrO_2 particles were measured on a Quantum Design physical properties measurements system (PPMS). In the transport measurements, the disk sample was processed into a bar with the length, width and height of about 10 mm, 2 mm and 1 mm, and four electrodes were made on the bar with conductive silver paste. Resistance was measured using a standard four-probe technique.

3. Results and discussion

Fig. 1 shows the XRD patterns of the CrO_2 particles synthesized at 1 GPa and different temperatures. As can be seen in Fig. 1, the observed peaks can be indexed to rutile phase CrO_2 (JCPDS card No. 84-1819) and other second phases are unobservable.

SEM micrographs of the CrO_2 particles synthesized at different temperatures are shown in Fig. 2. From the SEM micrographs, it can be seen that the CrO_2 particles synthesized at different temperatures mainly show rod-like morphology. In Fig. 2(a) and (b), the CrO_2 particles synthesized at 400 and 450 °C is mainly composed of thick rod-like grains besides a few very thin rod-like grain. The diameter of the thick rod-like grains ranges from 500 nm to 1 μm. From Fig. 2(c) and (d), it can be seen that the CrO_2 particles synthesized at 500 and 550 °C are also composed of rod-like grains, but the particles are smaller and more uniform than those synthesized at 400 and 450 °C. From Fig. 2, it is obvious that the size of the CrO_2 particles synthesized at different temperatures is much larger than that of the commercial CrO_2 powers which have lengths of about 400 nm and an aspect of about 9:1 [10,19].To further study the microstructure of the CrO_2 particles, HRTEM and fast Fourier transform (FFT) have been performed on the CrO_2 samples. Fig. 3 (a) shows a representative HRTEM image of the CrO_2 particles synthesized at 400 °C. The FFT pattern inserted in the upper right corner of Fig. 3(a) demonstrates that the sample is a single crystal CrO_2. In Fig. 3(a), the lattice fringes indicate that CrO_2 rod is well crystallized. The marked plane spacing is 0.243 nm and 0.221 nm, corresponding to the $(0\bar{1}1)$ and (0 2 0) lattice spacing of the rutile CrO_2, respectively. Furthermore, it is observed that the surface of CrO_2 rod is perfect and not covered by Cr_2O_3 layer. This is evidently different from the commercial CrO_2 powders [9–11], CrO_2 film [20,21] and CrO_2 rods reported by Bajpai [17] and Song [22]. The each CrO_2 particle mentioned above is enclosed by a 1–3 nm thick Cr_2O_3 layer. Fig. 3(b) shows a representative HRTEM image of the CrO_2 particles synthesized at 500 °C. On the surface of the CrO_2 particles, we can directly observe a Cr_2O_3 surface layer of about 6 nm thick on every CrO_2 particle. The insets of the Fig. 3 (b) show the FFT patterns of the surface Cr_2O_3 layer and rutile type CrO_2, respectively. This surface layer is found to be corundum-type Cr_2O_3. We can deduce that the $[1\bar{1}1]$ zone axis of the Cr_2O_3 layer is along the $[1\bar{2}1]$ zone axis of CrO_2. In HRTEM image of Fig. 3(b), the measured plane spacing in CrO_2 region is 0.243 nm, corresponding well to the $(\bar{1}01)$ lattice spacing of the tetragonal CrO_2 structure. The measured plane spacing in surface layer is 0.180 nm, corresponding to the (0 2 2) lattice spacing of the Cr_2O_3 structure. In short, the surface of the CrO_2 particles synthesized at 400 and 450 °C is perfect and not covered by Cr_2O_3 layers. However, the presence of continuous Cr_2O_3 layers was observed in the surface of each CrO_2 particles synthesized at 500 and 550 °C.

The magnetic properties of the CrO_2 particles are measured by PPMS. Fig. 4 shows magnetic hysteresis loops of the CrO_2 particles measured at 5 K. As shown in Fig. 4, the saturation magnetization (M_s) of the samples are 129.0, 130.0, 131.7 and 128.7 emu/g, corresponding to the CrO_2 particles synthesized at 400, 450, 500 and 550 °C, respectively. The M_s values of the CrO_2 particles synthesized at different temperatures are almost identical and very close to the theoretical value (i.e., 2 μ_B per formula unit). This illustrates that the volume content of the Cr_2O_3 surface layer in CrO_2 particles synthesized at 500 and 550 °C is very small and does not seem to affect the saturation magnetization. While the M_s value of the commercial CrO_2 powders is only about 110 emu/g, which is due to that Cr_2O_3 surface layers accounting for a larger proportion of the particle volume in commercial CrO_2 powders. The inset of Fig. 4 shows $M-T$ curve of a representative CrO_2 particles synthesized at 500 °C in an applied field of 500 Oe. By taking the first derivative dM/dT, the Curie temperature (T_C) of the CrO_2 particles is about 394 K, which is the same as the T_C of CrO_2 synthesized by other methods.

The magnetoresistance of the CrO_2 particles measured at 5 K are presented in Fig. 5(a). The magnetoresistance (MR) is defined as $MR = (R_H - R_0)/R_0$, where R_H and R_0 are resistance in external magnetic field (H) and in the initial $H = 0$ state, respectively. As shown in Fig. 5(a), the MR of the CrO_2 particles synthesized at 500 and 550 °C is much larger than that of the CrO_2 particles synthesized at 400–450 °C. The MR of all samples shows two well-defined regions. In the low-field region ($H < 10$ kOe), the MR displays a significantly sharp increase with magnetic field. However, in the high-field region the MR increases slowly and nearly linearly with magnetic field and its slope nearly does not change for all the CrO_2 particles. The low-field MR should originate from the tunneling magentoresistance. The Cr_2O_3 layers on the surface of the CrO_2 particles synthesized at 500 and 550 °C improve the tunneling effect and thus enhance the low-field MR. While the high-field MR might be the intrinsic nature of CrO_2. In order to further investigate the magnetic field response, Fig. 5(b) shows field sensitivity $d(-MR)/dH$ curves of the CrO_2 particles at 5 K. It is clear that the field sensitivity of all CrO_2 particles tends to a same small value in the high-field region. So the high-field MR is the same for all CrO_2 particles. The linear high-field MR is unrelated to the magnetization of CrO_2 because the magnetization of CrO_2 has been saturated at this point. These indicate that the high-field MR might be

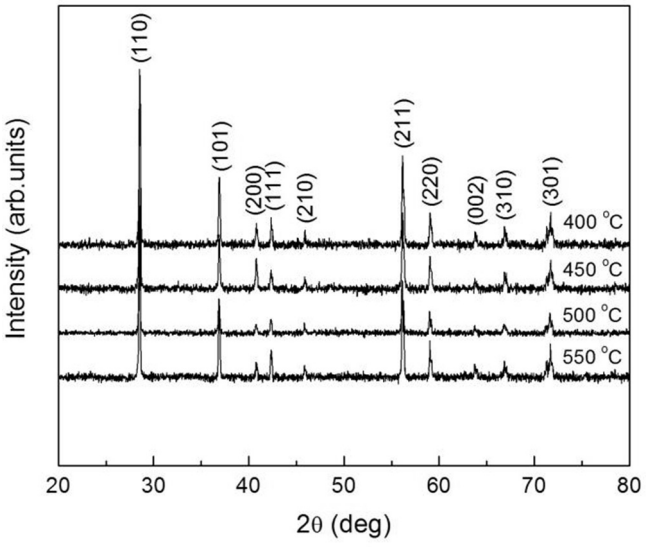

Fig. 1. XRD patterns of the CrO_2 particles synthesized at different temperatures.