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Spin blockade effects in chromium oxide intergrain magnetoresistance

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CrO_2 thin films with crystallites of a significant size permit investigation of the thin intergrain conduction between a limited numbers of crystals. Phoemission techniques reveal that the CrO_2 films are covered by a 1–2-nm-thick Cr_2O_3 insulating barrier. The electronic band gap of the surface electrons is 3.4 eV at low temperatures, decreases sharply down to 2.8 eV at ambient. Electric transport though a few junctions in series shows a remarkable zero-bias anomaly, interpreted in terms of blockade effects. We show that the magnetoresistance is governed by low-bias blockade in these junctions. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1452240]

I. INTRODUCTION

Chromium oxide is among the best candidates for a high-spin polarization material.[1] Such a property, with one spin direction of the conduction electrons strongly dominant, is desirable for applications in spin electronics. CrO_2 pressed powders and CrO_2/Cr_2O_3 composites showed remarkable magnetoresistance (MR) of up to 50% at low temperature.[2–4] The results were explained in terms of intergrain tunneling, and the large MR values were attributed to the high degree of spin polarization of CrO_2. Evidence of the large spin polarization of CrO_2 has been suggested by the superconducting point contact spectroscopy method,[5] spin-polarized photoemission,[6] and vacuum tunneling,[7] but the interpretation of the results needs to take into account the limited wave vector sampling, strong surface effects, and differences in the definitions of spin polarization.[8] Discrepancies with the expected high spin polarization value are apparent in the small (1%) MR, found on CrO_2 tunnel junctions at 70 K,[9] or the small negative values (-8%) found at 4 K.[10]

We present a combination of photoemission and transport measurements demonstrating spin blockade effects in chromium oxide samples. Complementary photoemission and inverse photoemission studies confirm the presence of Cr_2O_3 insulating oxide at the surface, consistent with the studies of Dai *et al.*[11] on commercial CrO_2 powders. We show that the apparent density of states at the conduction band edge is strongly temperature dependent. The remarkable decrease of the conduction band edge energy at high temperatures can be related to low temperature anomalies in the $I-V$ curves of our junctions. A model of Coulomb blockade at the surface of the CrO_2 crystal allows us to explain both types of measurements. We show that the low-temperature magnetoresistance found in these samples decreases by a factor of 2 when the voltage bias is increased.

II. SAMPLE PREPARATION

Polycrystalline CrO_2 films were made by rf sputtering of CrO_3 onto $LaAlO_3$ substrates and annealing in a high-pressure cell. The sputtering was performed under of 10 mTorr argon and 2 mTorr oxygen pressure. The target was prepared by pressing CrO_3 powder and sintering at 150 °C. Thickness of CrO_2/CrO_3 films ranged between 0.1 and 1 μm. Annealing in about 100 atm of oxygen pressure at 390 °C leads to the formation of the stable CrO_2 phase.[2,12] X-ray diffraction confirmed the presence of CrO_2, with no detectable diffraction peaks from Cr_2O_3. The thinnest annealed films showed a grain density of about 10 crystals every 100 μm^2 area. The grains were of elongated shapes, typically 5 μm long and 0.5 μm wide.

III. RESULTS AND DISCUSSION

Appropriate surface preparation was established by x-ray photoemission (XPS), ultraviolet photoemission, and inverse photoemission. The surface composition was determined by angle-resolved XPS, using the Mg K_α line radiation (1253.6 eV). A negligible amount of C (less than 3% of a monolayer), was taken as a good indicator of a clean surface following sputtering and annealing. The binding energy of O 1s core level of 531.1 ± 0.2 eV and a significant shoulder around 529.5 ± 0.2 eV were found. This indicates a thin Cr_2O_3 layer formed on the surface of the samples, confirming other similar measurements.[11] Angle-resolved XPS was used to characterize the thickness of the Cr_2O_3 surface layer as has been undertaken for other oxide surfaces.[13] The ratio of Cr_2O_3 intensity to CrO_2 intensity for each emission angle was derived by decomposing every O 1s spectrum into two peaks, corresponding to the two oxide phases. We find that the thickness of the Cr_2O_3 layer is about twice the oxygen core level photoelectron mean free path, using a summation modeling analysis described elsewhere.[13] This corresponds to approximately 2 nm thickness.[14]

The energy distribution curves of the valence bands were acquired at normal emission, using a He I incident radiation source (21.2 eV). The inverse photoemission spectra were obtained by using variable energy electron and UV detector (a Geiger–Müller detector). The overall energy bandwidth was ~450 meV. The conduction band spectra were taken by changing the kinetic energy of the incidence electron energy from 5 to 19 eV. The Fermi level was established from tan-

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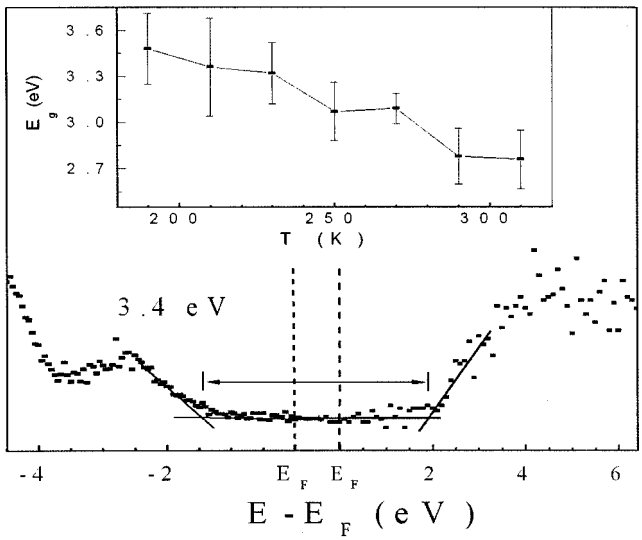

FIG. 1. The combined photoemission (left) and inverse photoemission (right) at several selected temperatures for Cr_2O_3 surface layers on CrO_2. The effective gap, uncorrected for instrumental resolution, is indicated. While the photoemission and inverse photoemission features are largely temperature independent, the density of states at the conduction band edge is strongly temperature dependent, resulting in an increasingly sharp conduction band edge at high energies with decreasing temperatures. The photoemission and inverse photoemission were obtained for normal emission and normal incidence, respectively.

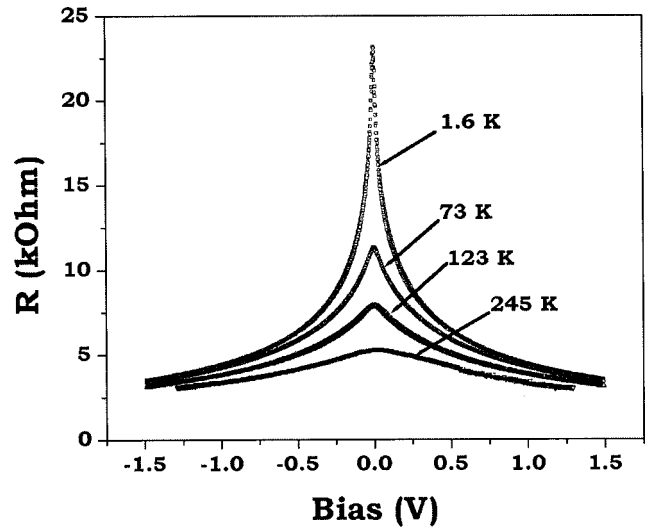

FIG. 2. Resistance vs bias at several temperatures. The sample corresponds to approximately 20 junctions in series.

talum in electrical contact with the sample for both photoemission and inverse photoemission, as has been undertaken on surface studies for other potential half-metallic systems.[15,16] Spectra of the density of states, near the Fermi level, of the Cr_2O_3 surface of the CrO_2 sample show temperature dependence much greater than $3\ k_BT$ (Fig. 1). At temperatures lower than 200 K, a gap of 3.5 ± 0.2 eV was found (or 3.8 ± 0.2 eV correcting for the combined instrumental line width), confirming that the Cr_2O_3 coverage of a CrO_2 grain provides a wide band gap tunnel barrier. Heating the sample to room temperature showed a remarkable decrease of the conduction band edge binding energy, without other significant changes in the spectra. An unambiguous temperature dependent change of the valence band conduction band gap by 0.7 eV with a nonsystematic error estimate of ±0.2 eV was found between 190 and 300 K. This change, much larger than k_BT, might be explained in terms of surface charging effects of the native oxide surface.[15] However, we did not find any noticeable band shifts in our spectra and the absence of any other significant changes in the spectrum, as well as the absence of a temperature discontinuity, make the hypothesis of surface phase transition very unlikely.

Electric transport measurements using two or four points ac or dc were undertaken, with electrical connections separated by less than 200 μm. With samples of resistance larger than a few hundreds of ohms, a strong nonlinear $I-V$ behavior was found, diminishing with increasing temperature (Fig. 2). This low-bias conductivity is strongly reminiscent of the so-called giant resistance peak observed by Rowell and Shen on Cr–I–Ag tunnel junctions.[17] This insulator "I" was fabricated by oxidation of a Cr film, and the anomaly attributed to the presence of magnetic CrO_2 and Cr_2O_3! We can directly superpose our resistance versus bias curve to the Rowell and Shen results if we scale down our bias voltage scale by a factor of 10. The half-width of the giant resistance peak at 3 K is around 50 mV, which is 10 times larger than Rowell and Shen results (Fig. 1 in Ref. 17). Explanations for the giant resistance peak were given by Giaver and Zeller in their seminal paper on Coulomb blockade in tunnel junctions,[18] where the low-bias peak corresponds to the current blocking due to the electrostatic charging energy of an island in the tunnel junction.

A magnetoresistance ratio, defined as $(R_{max}-R_{min})/R_{max}$, reached values of 30% at 1.6 K, consistent with previous studies (Fig. 3). The maximum of the resistance occurred at applied field values of 150 Oe, which is the coercive force of the CrO_2 films. For comparison, magnetoresistance curves for samples of low resistance values, obtained from thick films (several microns) of chromium oxide, showed similar ratios, but with more difficulty to reach saturation. The magnetoresistance decreases strongly with applied bias, on a voltage scale corresponding

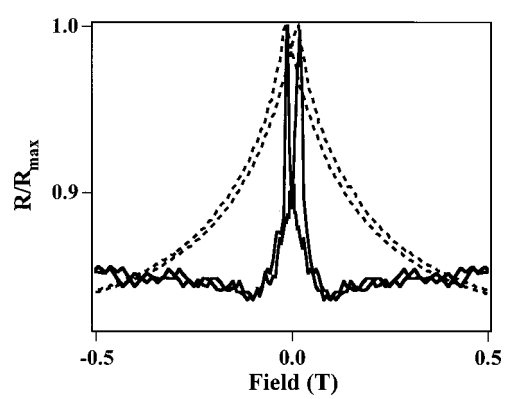

FIG. 3. Magnetoresistance curves of a chromium oxide powder. The full line curve corresponds to a sample made of a few crystallites with only a resistance of more than 10^5 Ω. The shaded line curve corresponds to a thick film sample (several microns), with a resistance of less than 10 Ω.

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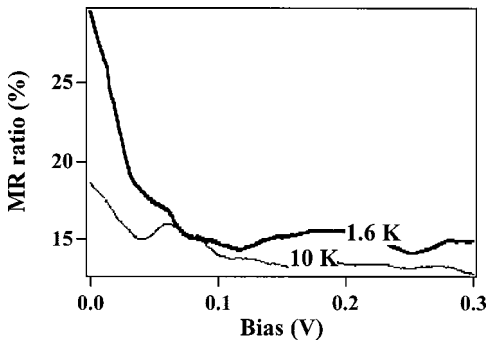

FIG. 4. Magnetoresistance of $CrO_2/Cr_2O_3/CrO_2$ junctions vs applied bias at low temperatures. The zero bias enhancement appears clearly at temperatures lower than 10 K.

to the occurrence of the zero-bias anomaly (Fig. 4). Such behavior is not observed for low resistance samples, where a large number of junctions are measured in series.

The interplay between Coulomb blockade and tunnel magnetoresistance (TMR) has recently attracted a lot of interest, mostly motivated by the perspective of the enhancement TMR by spin blockade effects. Theoretical models involving cotunneling[19] and spin accumulation[20,21] have been put forward. The magnetoresistance behavior in Fig. 4 corresponds to the predictions of Takahashi and Maekawa, using a model of enhancement of MR due to cotunneling effects.[19] At low-bias voltage values, the current flows though virtual states in the barrier.[22] The correlated hopping events lead to a squared magnetoresistance value, or a doubling of the magnetoresistance ratio. At higher bias, the magnetoresistance value saturates at half its zero-bias value. Data in Fig. 4 reproduces such a prediction remarkably well.

IV. CONCLUSIONS

Studies on samples made of a few crystals allowed us to characterize the nonlinear CrO_2 intergrain conductivity, which includes Cr_2O_3 barrier layers, without resorting to the investigation of the CrO_2/Cr_2O_3 composite system. Current–voltage measurements reveal the zero bias anomaly of these junctions, which is not observed when many junctions are measured in series. Angle-resolved XPS investigations performed on the same samples showed a Cr_2O_3 coverage to be more than 1 nm in thickness. This insulating surface oxide also plays the role of a thin barrier between adjacent crystallites. Combining photoemission data and current–voltage measurements, a picture of Coulomb blockade in these junctions emerges. It explains the high magnetoresistance values at low bias. Chromium oxide systems therefore show an enhancement of the magnetoresistance due to imperfections in the insulating barrier, playing the role of a blockade for electron flow.

ACKNOWLEDGMENTS

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