Inverse magnetoresistance in chromium-dioxide-based magnetic tunnel junctions

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(Received 11 December 2000; accepted for publication 26 January 2001)

Magnetic tunnel junctions have been fabricated using half-metallic chromium-dioxide (CrO_2) epitaxial film with a Co counterelectrode. The native insulating layer formed on the surface of CrO_2 after air exposure is used as the tunneling barrier. These junctions exhibit nonlinear current–voltage characteristics, and the changes in junction resistance with applied field correspond to the coercivities of the two magnetic layers. The maximum observed magnetoresistance (MR) is about 8% at 4.2 K and has a negative sign, i.e., the resistance of the junction with parallel alignment of the electrodes is higher than with antiparallel alignment. This is opposite of what is normally observed with transition-metal electrodes and an Al_2O_3 barrier. Possible reasons for the inverse MR are discussed based on previous results on manganite/Co junctions. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1356726]

Magnetic tunnel junctions, consisting of two ferromagnetic electrodes separated by an insulating barrier, have attracted much attention in recent years because they exhibit large magnetoresistance (MR) at relatively low fields.[1,2] In the simplest case, the magnitude of the MR is related to the spin polarization P of the individual ferromagnetic electrodes by the Jullière model:[1] $(R_{ap}-R_p)/R_p=2P_1P_2/(1-P_1P_2)$, where R_{ap} and R_p are the resistance of the tunnel junction corresponding to the antiparallel and parallel alignment of the ferromagnetic electrodes. Most of the studies thus far have focused on using transition-metal ferromagnets and their alloys—typically, with spin polarization values of less than 50%—where the maximum observed MR is usually limited to ~30%–40% at room temperature.[2–4] There is obvious interest in further enhancing the MR by using materials with a higher degree of spin polarization.[5] In particular, half-metallic systems, which contain a gap in one spin band at the Fermi level and no gap in the other spin band, are predicted to have a spin-polarization value approaching 100% at least at low temperatures.

Band-structure calculations have shown that the well-known magnetic-oxide material chromium dioxide (CrO_2) is a half-metallic system.[6] Spin-polarized photoemission data have confirmed the presence of nearly complete spin polarization at ~2 eV binding energy.[7] However, no spectral weight is observed for both spin electrons at the Fermi energy. This is rather surprising considering the metallic nature of CrO_2. More consistent with band-structure calculations, superconducting point-contact measurements have provided evidence of a high degree of spin polarization of CrO_2.[8,9] Ji *et al.*[9] have recently made Andreev reflection measurements using Pb/CrO_2 point contact and obtained a value of 0.96 ± 0.01 for P, which is very close to the theoretical limit. Observations of a relatively large low-field MR in polycrystalline films[10] and powder compacts[11] of CrO_2 also provide indirect evidence of a high degree of spin polarization in this material.

In this letter, we report on the fabrication and low-field MR properties of magnetic tunnel junctions using epitaxial CrO_2 as one of the ferromagnetic electrodes and polycrystalline Co as the other electrode material. We have used the native insulating layer formed on the air-exposed surface of the CrO_2 films as the tunneling barrier for these junctions. Reproducible tunneling characteristics have been observed, and the junctions exhibit low-field MR with resistance changes corresponding to the switching fields of the two electrodes. The maximum observed MR is about 8% at 4.2 K and has a negative sign, i.e., the resistance of the junction with parallel alignment of the electrodes is higher than with antiparallel alignment. This is opposite of what is normally observed with transition-metal electrodes and an Al_2O_3 barrier.[3,4] We have also observed negative MR in CrO_2 junctions with permalloy ($Ni_{81}Fe_{19}$) as the counterelectrode material.

Figure 1 illustrates the patterned growth of CrO_2 and the subsequent fabrication steps of micron-scale tunnel junctions. The CrO_2-based electrode (~1500 Å thick) is grown epitaxially on (100)-oriented TiO_2 substrates by chemical-vapor deposition (CVD).[12] Prior to the growth, a 1000-Å-thick layer of SiO_2 is deposited by sputtering on the TiO_2 substrate and is patterned to form parallel stripes using conventional lithography and lift-off. The CrO_2 nucleates and grows selectively within the stripe window openings on TiO_2, but not on the adjoining SiO_2 surface.[13] The length of the window openings is chosen to be along the crystallographic c-axis direction of the TiO_2 substrate so as to have the magnetocrystalline easy axis of the deposited CrO_2 (c axis) aligned in this direction. Following the growth of CrO_2, a lift-off mask is used to deposit a second patterned layer of SiO_2 for isolation and defining the junction areas. Finally, the patterned top electrode (500–1000 Å of Co) and Au metal-

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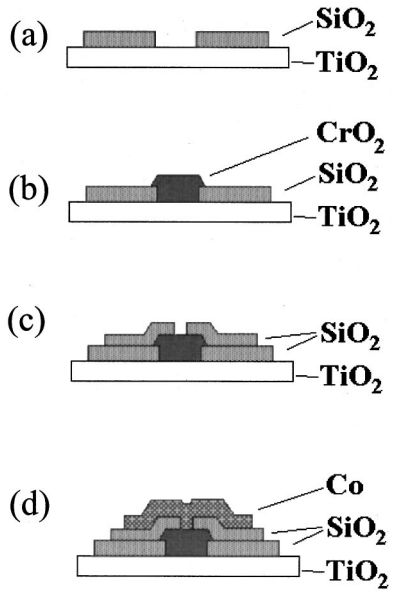

FIG. 1. Schematic drawing of the different process steps involved in the fabrication of CrO_2/natural barrier/Co magnetic tunnel junctions: (a) patterned deposition of SiO_2 on a (100) TiO_2 substrate; (b) selective growth of CrO_2 within the stripe window openings using CVD; (c) deposition of a second SiO_2 layer for isolation and definition of the junction area; and (d) patterned deposition of the Co top electrode by evaporation or sputtering.

lization layers are deposited by evaporation or sputtering using a separate lift-off mask. Prior to deposition of the Co layer, the surface of the exposed CrO_2 is cleaned in oxygen plasma. A reduced oxide layer, which acts as the barrier for the junction, is formed on the CrO_2 film surface soon after exposure to air. The plasma treatment helps in removing any organic residue on the surface prior to deposition of the top electrode.

Figure 2 shows the field dependence of the tunneling resistance (R) and the MR ratio ($\Delta R/R_p$) at 5 K for a CrO_2/natural barrier/Co tunnel junction fabricated using the above procedure. Here, R is measured at zero bias, and R_p is the resistance in the parallel orientation. The junction has a rectangular top contact of area $20\times 4\ \mu m^2$ and the magnetic field is applied along the easy axis of the rectangle. The magnetocrystalline easy axis of the selectively grown CrO_2 bottom electrode stripe also lies in this direction.[12] The dynamic conductance of the junction as a function of bias voltage (not shown) is parabolic at low bias voltages, indicative of electron tunneling. The sharp changes that are observed in R are associated with the moment reversals of the two electrodes. The switching fields for the increase and decrease in R correspond closely with the magnetic coercivities of the top and bottom electrodes, with the lower- and higher-field values corresponding to switching of the Co and CrO_2 electrodes, respectively. It is interesting to note that at high fields, when the moments of the two electrodes are aligned along the field direction, R attains a high value. On the other hand, a minimum for R is obtained with antiparallel orientation. This is *opposite* of what is normally observed in tunnel junctions consisting of magnetic transition-metal electrodes with an Al_2O_3 barrier. The MR for the CrO_2/natural barrier/Co junction is about -8% and decreases to about -1.5% at 150 K. For comparison, the MR of the CrO_2 bottom electrode is negligible ($<0.1\%$) over the measured field range. We have also fabricated CrO_2-based junctions using a $Ni_{81}Fe_{19}$ counterelectrode in place of Co. Similar resistance hysteresis characteristics have been observed in these junctions with maximum MR of about -2.3% at 5 K, but with significantly lower junction resistance. The lower junction resistance could possibly result from partial reduction of the natural barrier.

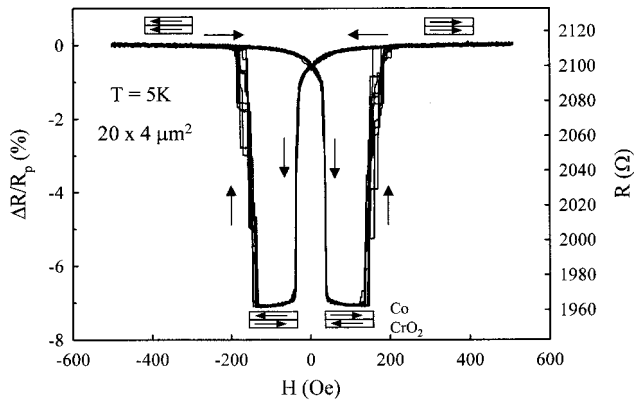

FIG. 2. Resistance and magnetoresistance ($\Delta R/R_p$) vs magnetic field, measured at 5 K, for a CrO_2/natural barrier/Co junction with a rectangular $20\times 4\ \mu m^2$ top electrode. The magnetic-field sweep directions and the field ranges for parallel and antiparallel alignment of the top and bottom electrodes are schematically indicated by arrows.

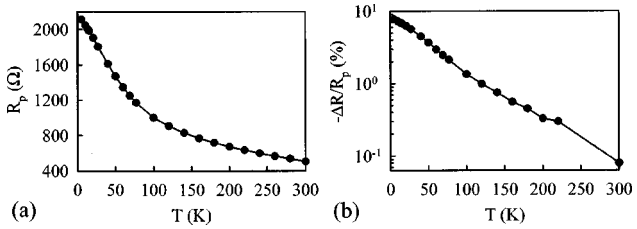

FIG. 3. (a) Resistance and (b) magnetoresistance ($\Delta R/R_p\%$) as a function of temperature for the tunnel junction whose hysteresis characteristics are shown in Fig. 2.

The temperature dependence of the CrO_2/natural barrier/Co junction resistance and MR are plotted in Figs. 3(a) and 3(b), respectively. Unlike metallic tunnel junctions, which exhibit only a weak temperature dependence,[2] the junction resistance here increases by about a factor of 4 in going down from room temperature to 5 K [Fig. 3(a)]. Nevertheless, the activated behavior is less pronounced than in $La_{1-x}Sr_xMnO_3$ tunnel junctions with a $SrTiO_3$ barrier.[5] The junctions also exhibit a rapid decrease in MR with increasing temperature, as seen in Fig. 3(b). The drop-off behavior is remarkably similar to that observed in polycrystalline thin films and powder compacts of CrO_2,[10,11] suggestive of similar spin–flip scattering processes operating at higher temperatures in all cases. This may be related to the similar nature of the natural barrier in our junctions and the intergrain-tunneling barrier in the polycrystalline samples.

Inverse (negative) MR has also been recently observed by De Teresa *et al.* in $La_{0.7}Sr_{0.3}MnO_3$ (LSMO)/I/Co tunnel junctions, when $SrTiO_3$ is used as the insulating barrier I.[14] However, when Al_2O_3 is used as a barrier, the MR is normal (positive) and with a very different bias dependence. The authors have concluded that the electronic structure of the barrier and the barrier–electrode interface has a strong influence on the spin polarization of electrons. Photoemission ex-

periments by Park suggest that the spin polarization of LSMO is positive with a value close to 100%.[15] With a positive spin polarization for LSMO, the inverse MR of Co/STO/LMSO junctions implies that, with the STO barrier, the polarization of Co is negative. This is in contrast to what is found with the Al_2O_3 barrier, but is in agreement with the spin polarization of the *d*-band density of states of Co at the Fermi level. Inverse MR has also been reported in NiFe/Al_2O_3/Ta_2O_5/NiFe composite barrier junctions[16] and in Fe_3O_4/STO/LSMO heterostructures.[17]

Assuming 96% spin polarization for CrO_2 and -42% for Co,[4,9] under ideal tunneling conditions one would expect a MR value of -57% using the Julliè re model.[1] This is significantly higher than the maximum value of -8% we have obtained in our junctions. At present, we can only speculate about possible causes for the reduction. Since magnetotunneling is an interface effect, spin–flip processes at the interface would certainly have a deleterious effect on the MR. A less-than-ideal insulating barrier containing magnetic impurities and defects would also lead to spin scattering. The native reduced oxide on the CrO_2 surface used as the tunneling barrier has been determined to have a composition close to Cr_2O_3 using photoemission spectroscopy.[18] Since Cr_2O_3 is antiferromagnetic at temperatures below 300 K, it could possibly lead to a large decrease in the polarization of the conduction electrons. Efforts are underway to fabricate CrO_2 tunnel junctions using other barrier materials, including Al_2O_3 and heteroepitaxial TiO_2.

The authors are grateful to J. Slonczewski, W. J. Gallagher, J. Z. Sun, and S. P. Parkin for useful discussions. This work is partially supported by NSF Grant Nos. DMR-0071770 and DMR-0080031.

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