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Giant magnetoresistive structures based on CrO_2 with epitaxial RuO_2 as the spacer layer

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Epitaxial ruthenium dioxide (RuO_2)/chromium dioxide(CrO_2) thin film heterostructures have been grown on (100)-TiO_2 substrates by chemical vapor deposition. Both current-in-plane (CIP) and current-perpendicular-to-plane (CPP) giant magnetoresistive stacks were fabricated with either Co or another epitaxial CrO_2 layer as the top electrode. The Cr_2O_3 barrier, which forms naturally on CrO_2 surfaces, is no longer present after the RuO_2 deposition, resulting in a highly conductive interface that has a resistance at least four orders of magnitude lower. However, only very limited magnetoresistance (MR) was observed. Such low MR is due to the appearance of a chemically and magnetically disordered layer at the CrO_2 and RuO_2 interfaces when Cr_2O_3 is transformed into rutile structures during its intermixing with RuO_2. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1855532]

I. INTRODUCTION

Half metals constitute a class of ferromagnetic materials with only one spin channel near the Fermi level. As a result, they have 100% spin polarization at the Fermi level and are supposed to be the ideal choice for spintronics. Chromium dioxide (CrO_2) is one of the few experimentally proven half metals and possesses the largest spin polarization so far reported.[1,2] Much effort has been devoted recently to TMR in CrO_2 containing structures.[3–5] On the other hand, ruthenium dioxide (RuO_2) is a metallic oxide ($\rho \sim 35\ \mu\Omega$ cm at RT) with a tetragonal rutile structure ($a=b=4.499$ Å, $c=3.107$ Å), and is closely lattice matched with CrO_2 ($a=b=4.421$ Å, $c=2.916$ Å).[6] In the area of microelectronics, RuO_2 has been proposed for use as an interdiffusion barrier between Si and Al and also as a precision resistor element.[7–9] Recent studies have also demonstrated its utility as a contact electrode material in ferroelectric random access memory devices that offer superior polarization fatigue properties with very low leakage current.[10–12] Band structure calculations suggest that heterostructures fabricated with $CrO_2/RuO_2/CrO_2$ can possibly exhibit significantly enhanced magnetoresistance (MR) resulting from the near complete spin polarizations of CrO_2.[13] In addition, our results demonstrate that the subsequent RuO_2 deposition on top of CrO_2 removes the Cr_2O_3 insulating barrier, resulting in a highly conductive interface. This makes RuO_2 an ideal contact material for the half-metallic oxide CrO_2.

II. EXPERIMENTAL DETAILS

Epitaxial RuO_2 and CrO_2 films are grown on (100)-oriented TiO_2 substrates by the thermal decomposition of tris(2,2,6,6-tetramethyl-3,5-heptanedionato) ruthenium [$Ru(TMHD)_3$, 99%, STREM Chemicals, Inc.] and chromium oxide [CrO_3, 98%+, Alfa Aesar] under atmospheric conditions in a 1 in. diameter quartz chemical vapor deposition (CVD) reactor tube placed inside a two-zone furnace. Details of CrO_2 deposition were published elsewhere.[3] Since CrO_2 is a metastable phase and it irreversibly decomposes into Cr_2O_3 at high temperatures, low temperature deposition of RuO_2 is favored. We have achieved epitaxial growth of RuO_2 films, with good uniformity, at substrate temperatures as low as 300 °C, while the source temperature was maintained at 130 °C. CIP transport measurements were performed on sandwich samples patterned into Hall bars by ion milling, and CPP measurements were performed on samples fabricated as in Ref. 14, the standard four probe method was used in all tests. In the case of the CPP configuration, the connection resistances turns out to be at least one order of magnitude larger than that of the junctions, so our measurement actually only showed a lower limit for the giant magnetoresistance (GMR).

III. RESULTS AND DISCUSSION

TEM images (Fig. 1) show that CrO_2 and RuO_2 can grow epitaxially on top of each other, enabling us to make different combinations with these two materials. The as-grown RuO_2 films have a resistivity of 40 $\mu\Omega$ cm at room temperature. The detailed transport properties and surface morphology of as-grown RuO_2 films will be published elsewhere.[15] It is commonly known that a natural Cr_2O_3 barrier will occur on the CrO_2 surface immediately after the film growth because this is a much more stable phase than CrO_2.

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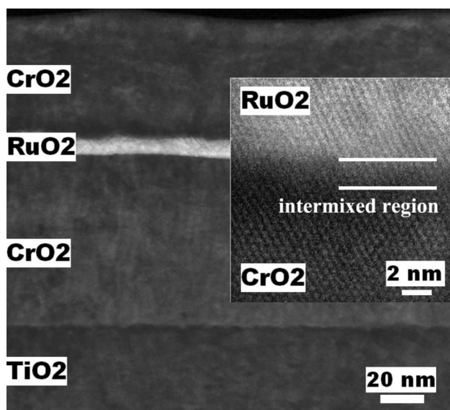

FIG. 1. Cross-section TEM images of an 80 nm CrO_2/15 nm RuO_2/50 nm CrO_2 heterostructure.

This barrier is insulating, and was successfully used as a tunneling barrier between CrO_2 and Co.[14] We have found that this natural barrier is eliminated during the deposition of RuO_2 on CrO_2 surface, which is evidenced by the very low resistance observed across the RuO_2 barrier. In two similarly fabricated junctions, the one with a 2 nm RuO_2 sandwiched between CrO_2 and Co has an RA value about four orders of magnitude lower than that without the RuO_2 layer (Fig. 2). Because of the low resistance of these junctions, the standard four probe measurements are no longer valid, most of the MR signals observed are contributions coming from the contact electrodes (Fig. 2 inset). Therefore, the resistance we recorded on CPP GMR junctions only defines an upper limit of the actual junction resistance. On the other hand, the HRTEM and the electron diffraction at and around the CrO_2/RuO_2 interface showed a 2 nm highly intermixed region with its lattice parameters between those of CrO_2 and RuO_2. Such a region is a direct result of the transforming

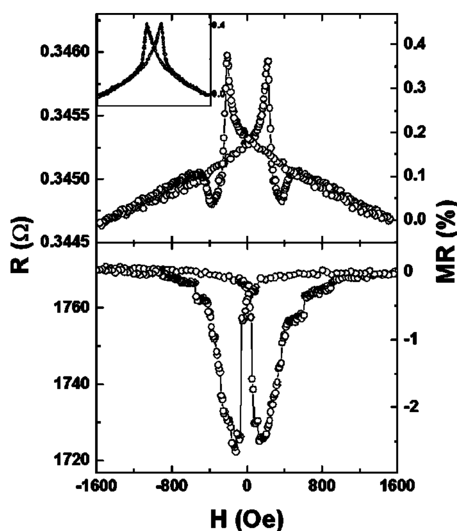

FIG. 2. Magnetoresistance at 78 K for a 100 nm CrO_2/2 nm RuO_2/50 nm Co junction in the CPP configuration. The result of a similarly made junction but without the RuO_2 layer is also shown for comparison. Both junction areas are $12.5 \times 2.5\ \mu m^2$. Inset shows the AMR signal measured on the CrO_2 bottom electrode.

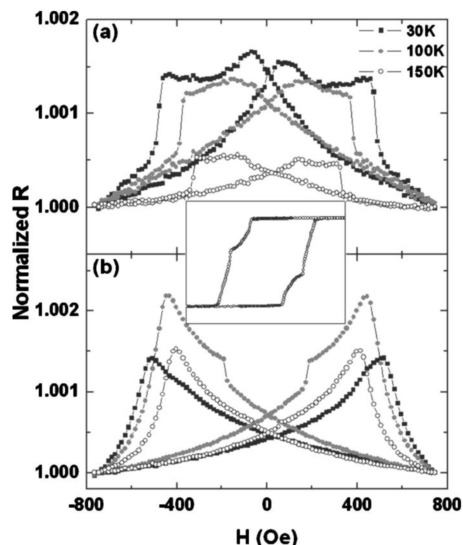

FIG. 3. Magnetoresistance in the CIP configurations at 78 K for (a) 10 nm CrO_2/3 nm RuO_2/10 nm CrO_2/TiO_2 (substrate); (b) 5 nm Co/2 nm RuO_2/10 nm CrO_2/TiO_2 (substrate), inset shows a typical hysteresis loops at room temperature for a sandwich of 40 nm and 30 nm CrO_2 layers separated by 2 nm RuO_2 layer. The applied field is along the *c* direction.

from the hexagonal corundum structure (Cr_2O_3 natural barrier) into the rutile structure (CrO_2/RuO_2 mixture).

We have fabricated dozens of $CrO_2/RuO_2/CrO_2$ sandwiches and studied their magnetic properties. A typical hysteresis loop is shown in Fig. 3, inset. About 2 nm is the minimum RuO_2 thickness needed in order to magnetically decouple the top and bottom CrO_2 films. This is partially due to the fact that RuO_2 can only form a continuous layer after passing the intermixed region. The different strain anisotropy induced by TiO_2 and RuO_2, or both, determines the different switching fields for each individual top and bottom CrO_2 layers.

The CIP transport measurements on these spin valve stacks only showed very low MR signals (Fig. 3). There exists some plateaulike part between the two switching fields of the top and bottom layers. However, the expected anisotropic magneto resistance (AMR) signals from the top and bottom magnetic layers are about the same magnitude at the applied fields, and this makes it hard to determine whether our observed signals are real GMR or only artifacts from AMR. But the results provide an upper limit (0.2% at 1 kOe) for GMR in such structures. This is much lower than we would expect from a spintronic device containing two half-metallic electrodes. We believe that the reason for the low observed MR is the occurrence of the intermixed layer, which is not only magnetic but also disordered. If there are loose Cr^{4+} spins in the mixed layer they may introduce strong spin-flip scatterings.

We believe that at least part of the reason for the low observed MR may lie in the presence of noncollinear spins in the intermixed region that separates the RuO_2 and the CrO_2. Preliminary first-principles calculations were performed for supercells of composition $Cr_2Ru_2O_8$ with the Cr and Ru occupying alternate layers along the (100) direction of the rutile structure. In this configuration each oxygen atom coordinates three nearest neighbor cations. In all cases one is Cr

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and the other two (at a slightly larger distance) are Ru or vice versa. In this configuration the calculations show that the moments of the two Cr atoms prefer to align at an angle of $\approx 150°$ while the Ru atoms develop a small moment that aligns opposite to that of the sum of the two Cr atoms. Such noncollinear spin arrangements which will depend on the details of the occupation of the disordered rutile structure lattice by Cr and Ru are expected to cause mixing of the spin channels and drastically reduce the GMR effect. We verified that the moments are collinear when all cations are Cr and that there are no moments when the cations are all Ru.

In summary, we have successfully deposited epitaxial $CrO_2/RuO_2/CrO_2$ sandwiches on (100)-TiO_2 substrates using chemical vapor deposition (CVD). Magnetic and transport properties have been studied on GMR structures using either sputtered Co or another epitaxial CrO_2 film as counterelectrodes, and epitaxial RuO_2 as the spacer. We attribute the observed low MR to the intermixing between CrO_2 and RuO_2 in the CVD growth.

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