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Ruihua Cheng  
University of Nebraska-Lincoln

C.N. Borca  
University of Nebraska-Lincoln

N. Pilet  
University of Nebraska-Lincoln

Bo Xu  
University of Nebraska-Lincoln

Lu Yuan  
University of Nebraska-Lincoln, lyuan2@bigred.unl.edu

See next page for additional authors

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Oxidation of metals at the chromium oxide interface

Ruihua Cheng, C. N. Borca, N. Pilet, Bo Xu, L. Yuan, B. Doudin, S. H. Liou, and P. A. Dowben

Department of Physics and Astronomy and the Center for Materials Research and Analysis, Behlen Laboratory of Physics, University of Nebraska–Lincoln, Lincoln, Nebraska 68588-0111

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Metal thin-film deposition, over the Cr2O3 surface of CrO2 thin-film substrates, exhibits a redox reaction at the interface. The transition metal forms an oxide in combination with the reduction of the near-surface chromium oxide to Cr2O3. The insulating barrier layer Cr2O3 increases with the formation of Pb3O4 in Pb/Cr2O3/CrO2 and CoO in Co/Cr2O3/CrO2 junctions, respectively. © 2002 American Institute of Physics. [DOI: 10.1063/1.1506942]

Electric transport in ferromagnetic–insulating–ferromagnetic (FM–I–FM) systems has attracted a lot of attention since 1995.1,2 If the insulating layer is thin enough (less than 2 nm), the electron tunneling probability becomes significant. Changes of the resistance, typically 20% as a function of the applied field, have been observed in magnetic junctions, though values as high as 400% are known. Existing junction magnetoresistance data are mostly restricted to Al2O3 oxide as the insulating barrier layer, though a number of other oxide barrier layers,3 including Cr2O3,4,5 have been recently explored.

Chromium oxides have been seriously considered as spin-polarized electron injectors to spin-tunnel junctions.4–7 Nonetheless, Co oxidation at NiO–oxide interfaces is now fairly well established.8–10 This raises significant questions about the composition of insulating oxide barrier layers and the coupling of the ferromagnet at the barrier interface. Oxide magnetic/insulator superlattices consisting of Fe3O4/NiO,11–13 and NiO/CoO14–16 have been fabricated but superexchanges appear to be suppressed in the insulating systems and the interlayer coupling is confined primarily to the interface region and therefore sensitive to interface morphology.8–10 Because of the interest in both superconductor–insulating–ferromagnetic4 and FM–I–FM1–3 junctions, we have examined the reduction and oxidation reaction that accompanies the deposition of both a superconductor (Pb) and a transition metal ferromagnet (Co) on the stable Cr2O3 insulating surface of CrO2.

Cr2O3/CrO2 samples were made by two techniques. In one approach, samples were made of a thin Cr film (30 nm thick) sputtered on a clean Si wafer and oxidized in partial oxygen pressure. We reproduced the synthesis route of Rowell and Shen,17 with the samples heated 14 h at 470 K in 730 mbar oxygen partial pressure. The observed current–voltage curve of the resulting film was strongly reminiscent of the so-called “giant resistance peak” observed by Rowell and Shen on Cr–I–Ag tunnel junctions.17 The insulator “I” in their junctions was also fabricated by oxidation of a Cr film, and the anomaly attributed to the presence of magnetic CrO2 and Cr2O3. Angle-resolved x-ray photoemission (ARXPS) investigations of these films,18 allowed us to differentiate between CrO2 and Cr2O3. We find a mixture of these two oxides, being phase separated after longer annealing times, and becoming a superposition of CrO2 and Cr2O3 thin films after even longer annealing. The observed resistance per unit area down values of 500 kΩ/μm2 was surprisingly low for such thick barriers.19 Our measurements indicate that this thickness is more likely corresponding to a conducting thin (4–5 nm) CrO2 film covered by a thinner (1–2 nm) Cr2O3 insulating barrier.20 In our other approach to Cr2O3 thin-film fabrication, the Cr2O3 thin films were fabricated by epitaxial growth through chemical vapor deposition, with CrO3 as the molecular precursor, on single-crystal rutile TiO2 (100) substrates. Increasing temperature leads to decomposition of CrO3 but at 390 °C, the reaction leads to growth of a stable Cr2O3 phase. The x-ray diffraction data exhibits the sharp diffraction lines characteristic of high-quality epitaxial Cr2O3 thin films grown on TiO2 (100).

Prior to ARXPS studies, samples were cleaned by sputtering and annealing to remove surface contamination.5,18,20 From the outset, i.e., from the initial stages of surface preparation, the core-level binding energies indicated that the stable surfaces were Cr2O3. X-ray photoemission (XPS) measurements were obtained using the Mg Kα line radiation (1253.6 eV). Both the Cr 2p and O 1s core levels were investigated as a function of emission angle for the various thin film samples, along with the Pb 4f and Co 2p core levels following metal deposition. The emission angle is defined with respect to the surface normal, and binding energies are reported with respect to the Fermi level of the metal (Au, Co, Ta, and Pb) in intimate contact with the sample and compared with binding energies similarly assigned. Photoemission final state effects, similar to surface photovoltage effects, have been extensively characterized and eliminated.5 Valence-band spectra were obtained using He II (hν = 40.8 eV), at room temperature as well, and the photoelectrons were collected normal to the surface.

The ARXPS Cr 2p data for different Cr2O3/CrO2 samples, both following the preparation of the clean stable Cr2O3 surface oxide, and following the deposition of Pb and

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Footnotes:

1Present address: JILA, University of Colorado, Boulder, CO 80305-3328.
2Also at: Department of Physics, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland.
3Author to whom all correspondence should be addressed at: Department of Physics and Astronomy, 255 Behlen Laboratory of Physics, University of Nebraska, Lincoln, NE 68588-0111; electronic mail: pdowben@unl.edu
Co, are plotted in Fig. 1. Pb was evaporated on top of samples fabricated by the approach of Rowell and Shen, while the Co was evaporated on the epitaxial Cr$_2$O$_3$/CrO$_2$ samples on single-crystal TiO$_2$. As expected, Cr$_2$p core-level spectra show that the surface clean CrO$_2$ surface and the left-hand side upper panel is the XPS data for clean CrO$_2$ surface and the right-hand side lower panel shows the data for the Cr$_2$O$_3$ with Pb evaporated. Right-hand side upper panel also shows the data for clean CrO$_2$ surface and the right-hand side lower panel shows the data for the Cr$_2$O$_3$ with Co evaporated on top.

With transition metal deposition on the Cr$_2$O$_3$/CrO$_2$ samples, there are two obvious changes Cr$_2$2p$_{3/2}$ (and Cr$_2$2p$_{1/2}$): first, the shift of the Cr$_2$2p$_{3/2}$ peak to higher binding energies with thin Pb or Co deposition, and second, the full width at half maximum (FWHM) decreases with Pb or Co deposition (Fig. 1). This is very apparent for Co deposition on top of the Cr$_2$O$_3$/CrO$_2$ thin film. Before Co growth, the binding energy of Cr$_2$2p$_{3/2}$ is 576.3±0.2 eV but with a large FWHM, indicative of a thin layer of Cr$_2$O$_3$ residing atop of CrO$_2$. After deposition of the equivalent of 3 monolayers (ML) of Co, the Cr$_2$2p$_{3/2}$ binding energy increases to 576.7±0.2 eV with smaller a FWHM. This binding energy is more representative of the Cr$_2$O$_3$ phase and the smaller FWHM indicates a decreased amount of the CrO$_2$ phase superimposed in the spectra. This indicates that either some CrO$_2$ has been reduced to the native Cr$_2$O$_3$, increasing the amount of Cr$_2$O$_3$ or, because of the limited mean-free path, the deposition of Co or Pb diminished the sampling of the CrO$_2$ that lies below the native Cr$_2$O$_3$ oxide at the metal/oxide interface. A combination of both effects is also possible.

Both Pd and Co oxidize at the Cr$_2$O$_3$ interface, upon deposition. As seen in the left-hand side panel of Fig. 2, core-level photoemission of both Pb 4f$_{7/2}$ and 4f$_{5/2}$ show sharp peaks combined with a significant shoulder instead of the simple expected 4f doublet. The binding energy for the main core-level feature Pb 4f$_{7/2}$ is 131.1±0.2 eV corresponds to the accepted binding energy for Pb$_3$O$_4$ and the binding energy of the accompanying shoulder is 136.7±0.2 eV, which is the core-level binding energy expected for metallic Pb.

Evidence of CoO formation at the Co/Cr$_2$O$_3$ interface, for Cr$_2$O$_3$ epitaxial samples, is found after the deposition of 3 monolayer Co. The Co 2p$_{3/2}$ XPS spectra, for both normal emission angle (black) and 60° emission (red), plotted in Fig. 2, exhibit two strong overlapping features. The binding energy of Co 2p$_{3/2}$ major peak, at 776.8±0.2 eV, corresponds to the metallic Co binding energy. The 2p$_{3/2}$ core-level feature at 780.2±0.2 eV is generally associated with the binding energy of CoO$^{25}$ The relative intensities of these two features depends upon the emission angle, and as the emission angle increases and photoemission becomes more surface sensitive, the high binding energy Co 2p$_{3/2}$ core level decreases relative to the other Co 2p$_{3/2}$ core-level features. Since the Co 2p$_{3/2}$ core-level feature at 780.2±0.2 eV is suppressed at the large emission angles, it is clear that CoO resides below the metallic Co, or rather, Co oxidizes at the interface between Co and Cr$_2$O$_3$/CrO$_2$.

From Fig. 1, we conclude that Pb undergoes oxidation at Pb$_2$O$_3$ at the Pb/Cr$_2$O$_3$ interface while Co is oxidized into CoO at the interface between Co and Cr$_2$O$_3$/CrO$_2$. For both Pb/Cr$_2$O$_3$/CrO$_2$ and Co/Cr$_2$O$_3$/CrO$_2$ junctions, chemical mass balance require that the oxidation of the Pb or Co must be accompanied by either reduction of Cr$_2$O$_3$ to Cr$_2$O$_2$, with an associated increase in the Cr$_2$O$_3$ layer thickness and oxy-
gen transport to the interface, or reduction of the Cr$_2$O$_3$ to a suboxide. There is little evidence to support the latter redox reaction, but it can not be wholly excluded by the data presented here.

Although Pb and Co at the interfaces of Pb/Cr$_2$O$_3$/CrO$_2$ and Co/Cr$_2$O$_3$/CrO$_2$ junctions are oxidized, the surface of Pb or Co top layer is metallic if Pb or Co film deposition is sufficiently thick. The evolution of the valence-band ultraviolet photoelectron spectra, with different Co coverages on Cr$_2$O$_3$/CrO$_2$, is shown in Fig. 3. For a clean Cr$_2$O$_3$/CrO$_2$ surface (zero monolayers Co coverage), the spectrum is the typical Cr$_2$O$_3$/CrO$_2$ valence-band spectrum. With increasing Co coverage, the bands at 4 to 8 eV from Cr–O$_2$ hybridization bands, and the band at 2 eV binding energy dominated by the Cr 3d orbitals, are suppressed while a few bands dominate the region near the Fermi level.

In summary, we have used both ARXPS and ultraviolet photoemission to study the metal to chromium oxide interface. Both Pb and Co oxidize at the interface, and in the context of previous work investigating the Co/NiO interface, it must be now recognized that many metal to metal–oxide interfaces involve further oxidation and reduction making such interfaces very heterogeneous. The interpretation of junction magnetoresistance results must now assume that ferromagnetic metals will NOT generally form abrupt interfaces with transition metal oxide dielectric barriers.

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