The effects of YBa$_2$Cu$_3$O$_{7-\delta}$ overlayers on the magnetic and electronic properties of La$_{0.7}$Sr$_{0.3}$MnO$_3$

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The effects of YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) cap layers on the magnetic and electronic properties of La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) underlayers was determined by x-ray magnetic circular dichroism and x-ray absorption spectroscopy techniques. The YBCO caps alter the LSMO in a way that effectively decreases the concentration of La at the LSMO/YBCO interface. © *2000 American Institute of Physics.* [S0021-8979(00)62908-0]

The colossal magnetoresistance[1–6] and extremely high degree of spin polarization,[7–10] which is important in applications exploiting spin-polarized electron transport, makes manganese perovskites preferential candidates for technological applications. Devices utilizing high T_c cuprate/manganite heterostructures that exhibit an enhanced breaking of Cooper pairs via spin-polarized quasiparticle injection have been demonstrated.[11,12]

It is reasonable to assume that, for such applications, the magnetic and electronic structure at the interface between the La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) and its overlayer strongly determines the overall transport characteristics of the structure.[13] Noble metals can be used as capping materials, but their poor lattice match with LSMO prohibits the deposition of high quality epitaxial overlayers, excluding them from being used as interlayer materials in epitaxial heterostructures. It was hypothesized that a capping layer or interlayer composed of a conducting oxide, with an oxygen content and lattice constant close to that of the underlying LSMO, would be less likely to affect the interface stoichiometry, and thus be less likely to affect the desired electronic and magnetic properties of the LSMO. One such conducting oxide that meets the above mentioned requirements is YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO). However, even though the structural characteristics of the YBCO/LSMO superlattices are very good, the resulting transport characteristics are far from the anticipated values, suggesting that the YBCO modifies the LSMO underlayer.

In order to acquire information about the magnetic properties and electronic structure of such a buried interface a technique with magnetic contrast which discriminates between the elemental constituents of the underlayer is required. Soft x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) are techniques that provide element-specific information regarding the local electronic structure and magnetic properties, respectively, of the constituent atomic species of complex materials. In this article we report the results of XAS and XMCD measurements at the Mn $L_{2,3}$ absorption edge of LSMO capped with Al, Au, and varying thickness of YBCO. By using the XMCD and XAS techniques, we can monitor the changes created near the cap/LSMO interface generated by the capping procedure.

The XAS and XMCD spectra were measured at the NRL-NSLS Magnetic Circular Dichroism facility located at beamline U4B at the National Synchrotron Light Source. The monochromator spans an energy range of 10–1350 eV and, by accepting radiation from above (or below) the plane of the orbit of the synchrotron ring, is capable of supplying circularly polarized light of variable polarization (in this case, 75%). The monochromator was set to an energy resolution of 0.15 eV at the Mn $L_{2,3}$ absorption edge. The details of the U4B beamline have been published elsewhere.[14]

For each XAS and XMCD spectrum two electron yield spectra were recorded, one with the incident light helicity (circular polarization) oriented parallel to the remnant magnetization and one antiparallel. The XAS is the average of the two spectra while the XMCD is the difference between the two. The remnant magnetization was switched by reversing a magnetic field that was applied in the plane of the sample while the incident light helicity was held constant. The XMCD spectra have been altered to compensate for the incomplete photon polarization (75%) and the 45° sample-plane orientation with respect to the incoming beam. With this sample orientation, the electron yield measurements are sensitive to the first 50–100 Å of the LSMO film. The additional YBCO overlayer increases the sensitivity of the measurements to the YBCO/LSMO interfacial region and decreases the signal intensity. Measurements were also taken at very grazing angles of incidence which increases the sensitivity to the interfacial region. No significant differences were observed between the spectra taken at normal incidence and those taken at grazing angles less than 15°. This indicates that the variations in our spectra, as a function of YBCO cap layer thickness, are not due to differences in the probing depth. The spectra were collected at pressures less than 5×10^{-10} Torr and were normalized to the incident flux via the current measured through a gold mesh that was placed in the beam in front of the sample.

Pulsed laser deposition (PLD) methods were used to prepare the LSMO and YBCO films.[15,16] The thick (1000 Å)

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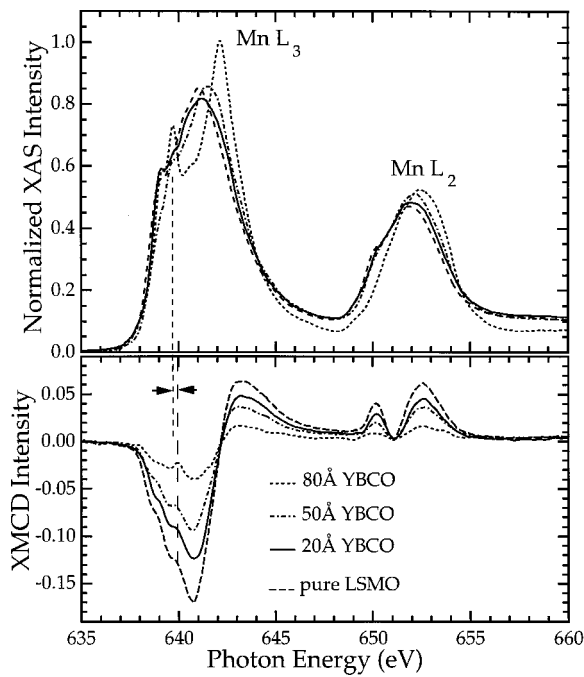
FIG. 1. Mn $L_{2,3}$ XAS and XMCD spectra for LSMO capped with various thicknesses of YBCO.

FIG. 2. Scaled $L_{2,3}$ XMCD of YBCO capped LSMO.

$La_{0.7}Sr_{0.3}MnO_3$ (LSMO) films were grown in an oxygen ambient of 400 mTorr on a $SrTiO_3$ (STO) substrate at a temperature of 800 °C. The Al and Au films were deposited by plasma sputtering with the substrate held at room temperature.

The Mn $L_{2,3}$ XAS and XMCD spectra for YBCO(t)/LSMO (1000 Å)/STO with thicknesses $t=0$, 20, 50, and 80 Å are shown in Fig. 1. The XAS spectra were normalized so that their respective integrated areas were equal. The changes in the spectral weight distributions represent electronic structure variations occurring at the buried YBCO/LSMO interface. The changes in the XMCD spectra are related to the magnetic behavior at the interface. It is clear that the deposition of the YBCO strongly affects the electronic and magnetic properties of the LSMO in the interface region, revealing the source of the poor spin-polarized transport properties observed for these structures.

The XAS spectra of Fig. 1 exhibit three distinct changes as the YBCO overlayer thickness is increased from $t=0$ to $t=80$ Å: the development of a second feature in the L_3 distribution at a fixed lower binding energy, the continuous energy shift of the L_3 maximum to higher energies, and the narrowing of the L_3 distribution. The XMCD spectra exhibit a decrease in magnitude with increasing overlayer thickness. The XAS spectral variations are very similar to results obtained for the Mn $L_{2,3}$ XAS of $La_{1-x}Sr_xMnO_3$ as a function of changing Sr concentration.[17,18] Abbate *et al.*,[17] have reported Mn $L_{2,3}$ XAS spectra that exhibit precisely the same spectral changes (narrowing, doubling, and continuous energy shift) as the concentration x varies from 0.3 to 0.9 as our Mn $L_{2,3}$ spectra do for increasing YBCO coverages. This strongly suggests that the deposition of the YBCO overlayer facilitates a cation displacement or exchange whose net effect is the out-diffusion of La (interchange of La with Ba) or
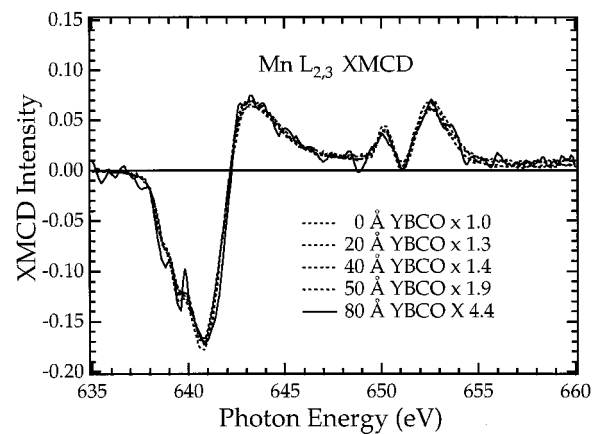
by exchange of Sr from deeper in the bulk of LSMO with La at the YBCO/LSMO interface. The latter mechanism is supported by the fact that, as the concentration x changes in favor of Sr, the unit cell volume of $La_{1-x}Sr_xMnO_3$ decreases and becomes a better match with the overlying YBCO lattice.[19,20]

Additional evidence for this conclusion is the observed decrease in the dichroism intensity as a function of increasing YBCO thickness. Whereas $La_{1-x}Sr_xMnO_3$ is ferromagnetic for concentrations in the range $0.2<x<0.6$,[17,21] the material becomes antiferromagnetic AF as the Sr concentration is increased.[22–25] As more interfacial Mn is transformed into the antiferromagnetic state the XMCD signal will diminish, but will not change in shape, as is indeed observed. In addition to the simple diminishing of the XMCD intensity, a new peak appears at high YBCO coverages, occurring at a slightly higher energy (640 eV) than the second (lower binding energy) peak in the XAS spectra. The source of this peak in the XMCD and its shift in energy with respect to the XAS peak is not known.

To confirm the similarity in each of the XMCD spectra, the spectra were scaled so that all of the spectra overlap (Fig. 2). The strong similarity in each of the spectra, in comparison to the distinct changes in the XAS spectra, demonstrates that although the Mn is in multiple chemical sites, it exists in only a single ferromagnetic site. Furthermore, the scaling factors are quantitative measures of the relative concentration of the ferromagnetic Mn phase present in this sample. This demonstrates the utility of XMCD to separate the spectra of a magnetic phase from coexisting nonmagnetic or, in this case, antiferromagnetic ones. If the Mn was present in only two phases (ferromagnetic and antiferromagnetic), then these scaling factors could be used to extract what the XAS spectrum of Mn in the antiferromagnetic phase would look like. By subtracting the contribution of the ferromagnetic Mn XAS spectra (represented by appropriately scaling the pure LSMO spectra) from the measured spectra, the remaining spectra should represent the XAS spectra of the antiferromagnetic Mn phase. For a two-phase system, each of these remaining spectra should be similar and represent the concentration of the AF phase. This procedure yielded only extraneous results, suggesting that the assumption that the XAS
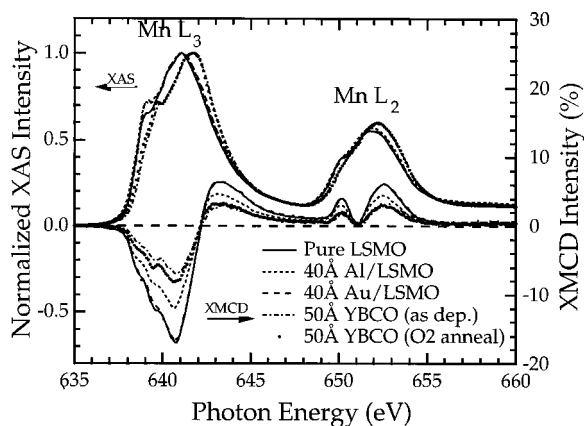
FIG. 3. Mn $L_{2,3}$ XAS and XMCD spectra for uncapped LSMO, LSMO capped with 40 Å of Al 40 Å of Au and 50 Å YBCO as deposited and annealed in O_2.

spectra is a simple summation of spectra for a system with only two phases (ferromagnetic and antiferromagnetic) is not appropriate. Finally, we found no variation in the La *M*-edge absorption spectra with YBCO coverage, a result which is consistent with another study of the effect on La *M*-edge absorption spectra of La compounds.[26]

The existence of oxygen vacancies also influences the transport properties of LSMO by reducing the hole concentration.[27] We considered the possibility that the variations in our XAS spectra were due to the oxygen depletion of LSMO at the YBCO/LSMO interface. To explore this possibility we have attempted to artificially change the oxygen stoichiometry at the interface.

The first method was to deposit an Al cap on the LSMO, which is known to alter the oxygen stoichiometry at the interface. In Fig. 3 the XAS and MCD of uncapped and of Al and Au capped LSMO are shown. The Al cap is expected to extract oxygen from the interface upon oxidation, whereas the Au cap is expected to prevent oxygen from leaving the interface. Other than the decrease in XMCD intensity for the Al capped sample (which is expected), the XAS and MCD spectra show few variations.

The second method we used was to anneal one of the YBCO capped samples in oxygen. It is known that oxygen readily diffuses through YBCO under annealing conditions.[28,29] A YBCO (50 Å)/LSMO/STO sample was annealed in 500 Torr of O_2 at 400 °C for 1 h to replenish the oxygen stoichiometry at the interface. The Mn $L_{2,3}$ XAS and XMCD spectra for the normal and annealed samples are shown in Fig. 3 where we find no differences between the spectra. We conclude from this, and the results of the Al capping, that the variations in our XAS and MCD spectra are not due to oxygen deficiency at the YBCO/LSMO interface.

In conclusion, we have shown that the effect of depositing YBCO as a cap layer on LSMO is to modify the electronic and magnetic properties of the LSMO interfacial region by effectively changing the Mn ground state configuration from ferromagnetic to antiferromagnetic as the cap layer thickness is increased. The mechanism is most likely a cation exchange where Ba from YBCO replaces La at the interface, thus modifying the relative concentration of

Sr to La, which is similar to that observed by Guo *et al.*,[30] for YBCO deposited on $LaAlO_3$ where a thin interfacial transition layer of $Ba_3Al_2O_6$ was observed.

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