Degradation of LaMnO$_{3-y}$ surface layer in LaMnO$_{3-y}$/metal interface

A. Plecenik and K. Fröhlich

_Institute of Electrical Engineering, Slovak Academy of Sciences, Dubravska cesta 9, 84239 Bratislava, Slovak Republic_

J.P. Espinós and J.P. Holgado

_Instituto de Ciencia de Materiales de Sevilla, Centro de Investigaciones Científicas "Isla de la Cartuja", C/ Americo Vespucio, s/n, 41092 Isla de la Cartuja, Sevilla, Spain_

A. Halabica and M. Pripko

_Institute of Electrical Engineering, Slovak Academy of Sciences, Dubravska cesta 9, 84239 Bratislava, Slovak Republic_

A. Gilabert

_University of Nice Sophia Antipolis, UMR CNRS 6622, Parc Valrose, 06108 Nice Cedex 2, France_

We report electrical measurements showing the degradation processes of LaMnO$_{3-y}$ (LaMnO) in LaMnO/normal metal interface in both point contact and planar-type junctions. Immediately after the preparation of the interface, the degradation process was followed by measuring the evolution of the junction resistance versus time. This process is characterized by the appearance of a second maximum in the resistance vs. temperature (R-T) dependence at temperatures lower than the Curie temperature $T_{\text{Curie}}$, which is the metal-insulator transition occurs in the bulk. These effects are explained in terms of the formation of a depleted interface layer in LaMnO caused by an out-diffusion of oxygen from the manganite surface to the normal metal. This assumption is confirmed by XPS measurement. Similar results on LaSrMnO$_{3-y}$ interfaces are also obtained.

The magnetoresistive rare earth perovskites La$_{1-x}$A$_x$MnO$_{3-y}$ (LaAMnO, A=Ca, Sr, Pb), which include LaMnO, have been in the research spotlight for a decade. Optimally doped LaAMnO exhibits a paramagnetic - insulating behavior above the Curie temperature $T_{\text{Curie}}$ and a ferromagnetic - metallic behavior below $T_{\text{Curie}}$. In the recent years, the giant magnetoresistance phenomenon (MR) has been intensively studied in these materials. However, till low-field, MR effects in granular films and tunneling of spin-polarized electrons through an insulating barrier in LaAMnO/Insulater/LaAMnO magnetic tunnel junctions (MTJ) gave promise to their technological applications like magnetic field sensor and nonvolatile magnetic random access memory. One can expect a near 100% value of tunneling magnetoresistance (TMR) in tunnel junctions based on half metallic LaAMnO ferromagnet. TMR depends on the quality of the magnetic state of the LaMnO surface, interface quality, surface roughness of the electrodes, etc. Anomalous tunneling behavior observed in MTJ could be explained by extrinsic factors playing a dominant role in the MTJ interfaces. This assumption has been made by several authors. Park et al. showed that even in a fully oxidized LaSrMnO sample, the magnetic properties at the surface boundary are significantly different from those of the bulk. In addition, several experiments indicated the creation of an oxygen depleted layer of LaAMnO interfaces. Mievile et al. studied the interface resistance and transport across conducting ferromagnetic oxide/metal interfaces. They measured a very high resistance of LaSrMnO/Al(Nb) junctions, which could be explained by the existence of a degraded surface layer of ferromagnetic oxide due to a loss of oxygen. Also de Teresa et al. observed a dependence of TMR on the type of tunneling barrier. The present work was stimulated by the above mentioned results, but mainly by the results published in our previous paper. LaMnO/Al$_2$O$_3$/Nb junctions were fabricated for the study of the influence of illumination on the electrical properties of MTJ. The Al$_2$O$_3$ insulating barrier was prepared using well-known thin films Nb technology. An aluminium thin film was sputtered on LaMnO, and then oxidized in an oxygen atmosphere. Finally a semi-transparent Nb upper electrode was sputtered on the top. Using the same technique with the same preparation parameters, the width of the barrier created on the LaMnO was about two times higher than that for Nb/Al$_2$O$_3$/Nb junctions.

In this paper we study the LaMnO surface properties in contact with Al, In, Au and Pb metals in order to explain the physical processes in the interface which give rise to an unusual behavior of MTJ. The LaMnO/normal metal point contact exhibits a change of resistance immediately after its preparation. In the planar junctions (more stable than point contact) the appearance of a second maximum in the R-T dependence was observed several hours after junction preparation. These effects are explained by an out-diffusion of oxygen from LaMnO, and they were confirmed by XPS spectroscopy.

200 nm thick LaMnO epitaxial thin films with $T_{\text{Curie}}=270$ K were deposited on single crystalline SrTiO$_3$ substrates by low pressure liquid source metal-organic chemical vapour deposition (MOCVD). LaMnO/metal point contacts were realized using a holder which exerted a constant pressure of the tip onto the sample. Bulk Au, Al, or Pb were used for the upper electrode. The shape
of the sharp point was prepared by mechanical sharpening. After the electrical measurements, a 200x200 μm² geometric area was evaluated for the Pb tip.

For the preparation of planar junctions, a 40 μm - wide and 260 μm - long LaMnO₃ base electrode was formed by wet etching through resist mask. After stripping the photoresist, the area for deposition of next layers by lift-off technique was defined in positive photoresist. Shortly before the deposition of the barrier and the upper electrodes, the surface of LaMnO₃ was etched to eliminate a contaminated and degraded upper layer. A 100 nm thick Al or In layer was deposited by thermal evaporation. Junctions with an area of 40x40 μm² were finalized after the removal of the photoresist.

The R-T and resistance vs. time (R-t) characteristics were measured by a computer controlled four point method.

XPS spectra were obtained in an ESCALAB 210 spectrometer that consisted of two separate independently-pumped chambers. Pressures in the range of 6x10⁻¹¹ mbar and 10⁻⁸ mbar were obtained in the analysis and preparation chambers, respectively. Al has been evaporated in the analysis chamber from a resistively heated filament made of Al wire wrapped around a thick tungsten wire. The power was maintained to give a reproducible evaporation rate of 1 monolayer of Al per minute. Control evaporation carried out onto a clean Au foil showed that under our experimental conditions, only metallic Al is evaporated, maintaining this oxidation state throughout all the acquisition time. A hemispherical electron energy analyser working in the pass energy constant mode was used. A hemispherical electron energy analyser working in the pass energy constant mode was used as the excitation source. Spectra were energy-calibrated by taking the La3d5/2 peak at 834.6 eV (BE). The spectra were acquired at 90 (normal) and 20 (grazing) degrees with respect to sample surface.

In Fig 1, the LaMnO/metal point contact resistance dependence versus time shows a significant increase at several hundred seconds after the preparation of the contact. These changes were observed even if noble metal (Au) was used as the upper electrode material. Similar results on high-Tc superconductors (HTS) were described in our previous work. The change of the point contact resistance was explained within an oxygen out-diffusion model.

The total point contact resistance with a tip made of nonreactive metal (e.g. Au) can be expressed as \( R = R_M + R_{\text{LaMnO}} + R_T \), where \( R_T \) is the tunneling resistance and \( R_M \) and \( R_{\text{LaMnO}} \) the contact resistances with metal and LaMnO, respectively. We suppose that \( R_M \) and \( R_T \) are constant in time for stable nonreactive metals, and the change of resistance \( R \) is then given by the change of \( R_{\text{LaMnO}} \). The creation of additional barriers from a LaMnO oxygen depleted layer as well as from the oxide of the upper metallic electrode (created from reactive metal like Al, Pb) creates a complex interface. But in all cases, the Curie temperature \( T_c \) in the LaMnO oxygen depleted region must be changed also.

In the next measurements the planar junctions were used because they were more stable than the point contact ones. Because Al is a very reactive metal with a very short time of interaction, indium as an upper electrode was used for the following measurements. The R-T characteristic measured on a LaMnO/In planar junction at different times (3, 5 and 23 hours) after preparation of the contacts is shown in Fig.2. We observed the classical maximum correlated with the I-M transition of the bulk material at \( T_c \) around 275 K of the bulk material. This maximum did not change very much with time. It means that the oxygen content in the bulk material does not change. After a long time (23 hours) a second maximum appears around \( T'_c \approx 185 \) K in the R-T characteristics. We know that in LaAMnO systems the \( T_c \) decreases with a decrease of the oxygen content, and it disappears for deoxygenated samples that exhibit semiconducting properties. This new maximum is related to the oxygen depleted interface, and it is broader due to a distribution of \( T_c \). This value of \( T'_c \approx 185 \) K corresponds to an average oxygen content at the interface of \( y \) around 0.1.

To confirm the occurrence of out-diffusion processes in the LaMnO surface layer, XPS measurements of LaMnO/Al interfaces were studied. Fig.3 shows spectra of the O1s, Mn2p, Al2p and La3d regions measured on clean (original) LaMnO surface (curves a) at the normal acquisition angle, after the deposition of around 1 monolayer of Al (curves b), at the normal acquisition angle, around 2 monolayers of Al, at the normal acquisition angle (curves c), and curves d were measured as curves c at a grazing acquisition angle. One can see the following features in the XPS spectra after the deposition of Al:

- two peaks correlated with Al and Al₂O₃,
- two peaks in the O1s spectra correlated with oxygen bonding in LaMnO₃ at 529.9 eV and Al₂O₃ at 531.6 eV,
- shift of the peaks in the Mn2p spectra due to the decreasing of Mn valency.

The deposition of the first monolayer of Al on the LaMnO surface provokes the oxidation of Al to Al³⁺, whose peak arises at about 75 eV (BE). This behaviour was tested by a simultaneous deposition of Al on Au. The detection of metallic Al during the whole experiment (more than 1 hour) exclude the oxidation of Al due to the residual O₂ partial pressure in the analytic chamber. In additional, when a second amount of Al was deposited (curve c in Fig.3a), most of it remained metallic (peak at 72.6 eV BE). Finally, when this situation is examined at the grazing acquisition angle (curve d in Fig.3a), the relative intensity of the peak from Al(0), in comparison with that from Al⁺³, increases substantially, indicating that metallic Al is located on the top of the Al₂O₃.

The oxidation of Al in the LaMnO₃/Al interface accompanying the appearence of two peaks in the O1s spectra is correlated with a change of binding energy due to the creation of Al₂O₃. The smooth second peak was measured also on clean LaMnO surface (curve a in Fig.3c) as well as after cleaning treatment. The origin of the second peak can be explained by the contamination of LaMnO.
by CO$_2$ species within the preparation procedure of the LaMnO thin film. Anyway, the intensity of the peak at the energy of 520.6 eV increase after the deposition of Al (curves b and c in Fig.3c) due to the arising of O$^=$ ions in Al$_2$O$_3$. The measurement at the grazing angle shows that Al$_2$O$_3$ is created on the LaMnO surface (the global intensity of Al2p signal grows and the Mn and La signals decrease). These facts also indicate the existence of metallic Al on the top of Al$_2$O$_3$.

A significant chemical shift of Mn2p peak from 642.5 eV before Al evaporation to 641.4 eV after Al evaporation strongly indicates a decrease of Mn valency to +3 state with a subsequent change of the Mn$^{3+}$/Mn$^{4+}$ ratio, typical for oxygen-deficient LaAMnO.

From XPS measurements described above, we can confirm the loss of oxygen from the LaMnO in the LaMnO/Al interface and the creation of a LaMnO/Al$_2$O$_3$/Al junction with a subsequent change in the Mn$^{3+}$/Mn$^{4+}$ ratio.

In conclusion, we presented R-T and R-t measurements on LaMnO/metal point contact and planar junctions. The time evolution of point contact junction resistance as well an arising of a second peak on the R-T characteristics were observed. These effects were explained in terms of the formation of a depleted interface layer in LaMnO$_{3-x}$ caused by the out-diffusion of oxygen from the manganite surface to the normal metal. This assumption was confirmed by XPS measurements. The similar results (XPS as well as time evolution of point contact resistance) on LaSrMnO magneto-resistive thin films were also obtained.

ACKNOWLEDGEMENT

This work was supported by the Slovak Grant Agency for Science (Grants No.2/7199/20 and 1/7072/20) and in part by the European Commission (project GRT-CT-2000-05001 MULTIMETOX)

1 J.-H.Park, E.Vescovo, H.-J.Kim, C.Kwon, R.Ramesh and T.Venkatesan 81, Phys.Rev.Lett. 81, 1953 (1998).
2 L.Mieville, D.Worledge, T.H.Geballe, R.Contreras and K.Char, Appl.Phys.Lett. 73, 1736 (1998).
3 J.M. de Teresa, A.Barthélémy, J.P.Contour and A.Fert, J.Magn.Magn.Mater. 211, 160 (2000).
4 A.Gilabert, A.Plecenik, K.Fröhlich, Š.Gaží, M.Pripko, Z.Mozolová, D.Machajdík, Š.Benáčka and M.G.Medici, Appl.Phys.Lett. 78, 1712 (2001).
5 M.Gurwitch, M.A.Washington and H.A.Huggins, Appl.Phys.Lett. 42, 472 (1983).
6 K. Fröhlich, J. Souc, D. Machajdík, A.P. Kobzev, F. Weiss, J. P. Senateur, K.H. Dahmen, Journ. de Physique IV C5, 533 (1995).
7 M.Grajcar, A.Plecenik, Š.Benáčka, Ju.Revenko, V.M.Svistunov, Physica C 218, 82 (1993).
8 A.M.De Leon-Guevara; P.Berthet; J.Berthon; F.Millot; R.Revcolevschi; A.Anane; C.Dupas; K.Le Dang; J.P.Renard; P.Veillet Phys.Rev. B 56, 6031(1997).
FIG. 3.
XPS spectra of the O1s, Mn2p, Al2p and La3d regions measured on the clean surface of LaMnO (curves a) after the deposition of one monolayer and two monolayers of Al, at the normal acquisition angle (curves b and c, respectively) and the same that curves c, at the grazing acquisition angle.