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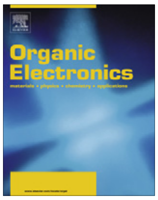

Letter

Manganite/Alq3 interfaces investigated by impedance spectroscopy technique

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ABSTRACT

With the general objective of studying interfaces between ferromagnetic materials and organic semiconductors, we report *ac* impedance investigations on $La_{0.7}Sr_{0.3}MnO_3$ (LSMO)/tris(8-hydroxyquinoline)aluminum (Alq3)/Al and Indium Tin Oxide (ITO)/Alq3/Al heterostructures, in the frequency range between 20 Hz and 1 MHz. The comparison of the equivalent circuits deduced to fit the experimental ac responses allows isolating a specific RC contribution which can be attributed to the LSMO/Alq3 interface region. Using the information obtained from our ac measurements, we propose a model which fits the temperature dependence of the magnetoresistance in spin valves combining LSMO electrodes and Alq3 layers.

Devices based on the combination of the highly spin polarized manganite LSMO and organic semiconductors have recently become the object of great interest and intense research [1,2]. Multilayer structures, where an organic thin film is sandwiched between LSMO and another ferromagnetic electrode (usually Cobalt), exhibit a spin valve effect as a function of the electrode magnetization orientation. At cryogenic temperatures and for low magnetic fields, magnetoresistance (MR) values up to some tens per cent have been demonstrated [2–6]. Room temperature magnetoresistive responses have been also reported [6]. Furthermore, under the application of high magnetic field (>1 Tesla), large negative MR effects have been found in LSMO based organic diodes, even when a non ferromagnetic metal (i.e. Al) is used as top electrode [2,7]. This effect was suggested to be basically related to the carrier injection process from LSMO to the organic layer. Finally, first evidences of electrically addressable non volatile memory effects in LSMO based organic spin valves have been reported [8], opening the perspective to the design of multifunctional devices based on the occurrence of two distinct and non-related physical phenomena. Commonly, most of these interesting features are believed to be strongly affected by the unusual and still not well understood properties of the interface between LSMO and organic layers, where both charge and spin injection occur. Nevertheless, so far, very few studies on the nature of this type of interface have been performed [9].

In this letter, complex impedance spectra of LSMO/Alq3/Al and ITO/Alq3/Al structures from 20 Hz to 1 MHz and in the temperature range between 293 K and 35 K

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are reported. In recent years, impedance spectroscopy has showed to be a powerful tool to investigate the behavior of multilayer devices, disclosing the contributions of the different layers and the related interfaces [10,11]. The structure of the investigated devices is depicted in Fig. 1a. Glass substrates covered with 120 nm thick ITO patterned strips were used for ITO based devices. LSMO films (40 nm thick) were grown by pulsed electron deposition (pulsed plasma enhanced configuration – PPD) on $SrTiO_3$ substrates, through a shadow mask with a width of approximately 1 mm. LSMO films grown by PPD have been extensively investigated [9,12], showing typical room temperature conductivity of 10^2 S/cm and Curie T_c temperatures of about 340 K. Magnetic properties of LSMO films were checked by Magneto-Optical Kerr Effect (MOKE) and found to be in accordance with the existing literature. For any evaporation run, one ITO and one LSMO sample were introduced together in the chamber after a rinse in acetone and isopropanol ultrasonic bath. Before the deposition, the samples were annealed following the procedures established by XPS investigations [12], in order to remove the surface carbon contamination and to restore the surface oxygen stoichiometry in LSMO films. Then, 80 nm thick Alq3 (SIGMA–ALDRICH) films were deposited on ITO and LSMO substrates at room temperature, by sublimation from a Knudsen cell at 10^{-8} to 10^{-9} mbar and growth rate of 0.1–0.2 Å/s. Finally, Al films (~60 nm thick) were evaporated on the top of Alq3 by using a shadow mask to obtain the final crossbar structure. The device area was 1 mm^2 and, hence, all the reported magnitudes are referred to this value.

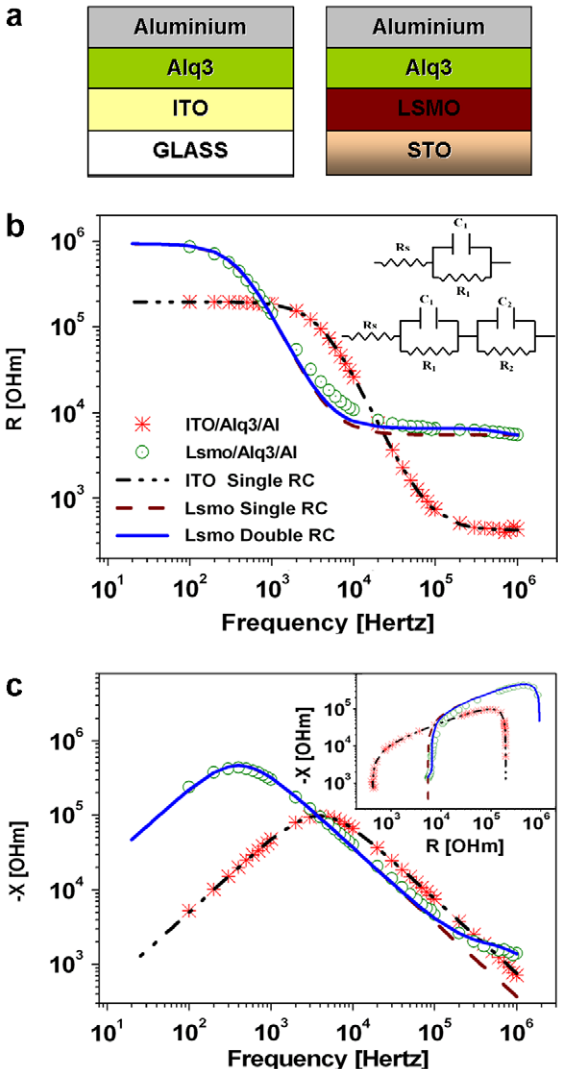

Fig. 1. (a) Structure of the investigated devices, (b) real and (c) imaginary parts of the complex impedance of ITO/Alq3/Al and LSMO/Alq3/Al devices, compared with the fitting curves obtained by the equivalent circuits in the inset in Fig. 1b. In the inset in Fig. 1c, the impedance spectra are reported in a log–log Nyqvist plot.

Impedance spectra were collected in vacuum by an Agilent LCR meter, mounting the samples in a cryogenic probe station or in a closed cycle cryo-generator equipped with RF probes [13,14]. The oscillating voltage in measuring process was fixed at 100 mV, in order to test the device response in the injection limited current regime where MR phenomena are usually investigated [8]. We have focused on Alq3, since, so far, the combination LSMO/Alq3 showed to provide the most interesting results in organic spintronics, even if an exhaustive explanation for this occurrence is still lacking. Furthermore, the widely investigated behaviour of ITO/Alq3/Al devices, which were used in many cases to analyze the Alq3 intrinsic electrical parameters, represents a reliable reference to evidence the features related to the LSMO/Alq3 interface [11,15–18].

Room temperature real and imaginary parts of the complex impedance, $Z(f) = R(f)+jX(f)$ for two typical ITO/Alq3/Al and LSMO/ALq3/Al structures are shown in Fig. 1b and c, respectively. The inset in Fig. 1c represents the same curves in a log–log Nyqvist plot. For both structures, $R(f)$ spectra stay constant in the low frequency range even if at different values. Then, $R(f)$ begin to decrease rapidly as frequency is increased. The corresponding −3 dB cut-off frequencies are 400 Hz and 3.5 KHz for LSMO and ITO based devices, respectively. These differences are also reflected in the position of local maxima in $-X(f)$ spectra. The non zero values of $R(f)$ in the upper frequency edge reveal a limiting resistance Rs, which has been estimated to be 300 Ohm for ITO structures and about 5 KOhm for LSMO ones. For comparison, it is clear that the distinguishing features of the LSMO/Alq3/Al device can only be ascribed to the peculiar properties due to the combination between LSMO and Alq3.

With the aim to better address this fundamental issue, the equivalent circuits in the inset in Fig. 1b have been considered to fit the experimental impedance measurements. The fitting curves are also reported in Fig. 1b and c. As shown, the ITO device ac response is well fitted by a single circuit, involving a parallel resistor R_1 and a capacitor C_1, with the Rs in series. This description is in agreement with previous studies, where the ITO/Alq3/Al response has been investigated also as function of temperature and applied bias voltages [15–18]. In our case, R_1 (coinciding with $R(f)$ value at low frequencies) is about 200 KOhm and the extracted equivalent conductivity (4×10^{-9} S/cm) is very close to the data reported in Ref. [15].