LSMO Thin films deposited by PLD as electrodes for spintronic applications

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Spintronics research is focused on materials as well as on growth methods: In this respect, half-metals are optimal materials as sources of fully spin-polarized carriers and pulsed laser deposition (PLD) is one of the best-suited methods for growing complex material. The mixed-valence manganite La 0.7 Sr 0.3 Mn O_3 (LSMO) has been widely investigated due to its low carrier density (1021- 1022 cm^{-3}), high carrier spin-polarization, highest Curie temperature (Tc=370K in the bulk) among the mixed-valence manganites and colossal magnetoresistivity (CMR).

LSMO thin films were deposited by PLD technique using a Lambda Physics 305i ArF excimer laser (λ = 193 nm , τ= 20ns) to ablate sintered targets of La 0.7 Sr 0.3 Mn O_3. All of the films were grown on amorphous silica substrates. Prior to each deposition, the deposition chamber was evacuated down to a background pressure as low as $\sim 10^{-5}$ Pa. Then the oxygen background pressure was kept constant at 0.1 Pa, 0.5 Pa, 1 Pa, 5 Pa and 10 Pa during each film deposition. Laser energy density of 4 J/cm^2 was focused on the rotating targets. All depositions were carried out at a distance target-substrate of 45 mm. The ablation laser repetition rate was set to 10 Hz. Films were grown at a substrate temperature as high as 600^{o}C. The deposited LSMO samples will be referred to as (p_0, t) where p_0 and t denote, respectively, the deposition oxygen pressure in Pa and the film thickness in nm.

The temperature-dependent electrical resistivity curves of the deposited samples were measured by the four-point probe dc method in a cryostat allowing temperature ranging from 4K to 320 K. The film thicknesses, estimated by a stylus profilometer, were about 200 nm and 100 nm.

Figure 1 shows the measured UV-VIS-NIR film transmittance spectra normalized to bare substrateas a function of the deposition oxygen pressure and film thickness. The transparency drops as oxygen content is strongly reduced to at least 0.5 Pa. As expected, while preserving the oxygen pressure value, the transmittance increases for the halved film thickness. Two different film thicknesses are considered only for 0.5 Pa because just the LSMO films deposited at the lowest oxygen pressures (0.1 Pa and 0.5 Pa) show measurable resistivity at room temperature. Measurements based on the Van der Pawn method gave resistivity values at 300 K which amounts to nearly 4.8 Ω and 6.9 Ω for the 200 nm and 100 nm thick samples, respectively. Indeed, while high growth temperatures (at least 550^o C) are usually needed to stabilize LSMO structural and magnetic order and to assure maximum magneto-resistance, the real growth temperature was lower than the thermocouple reading, namely 600^o C. However, the measured resistivity values are not exaggeratedly high for LSMO polycrystalline samples deposited at relatively low temperature. As expected, the resistivity decreases as the film thickness increases. Whereas the de-

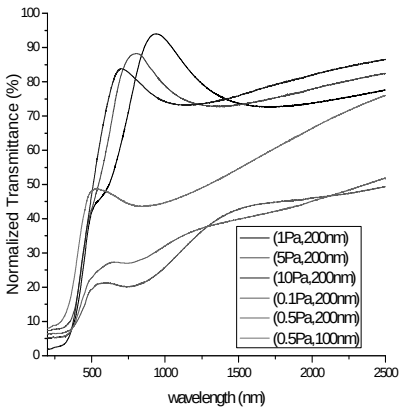

Figure 1 *Measured transmittance spectra normalized to the substrate.*

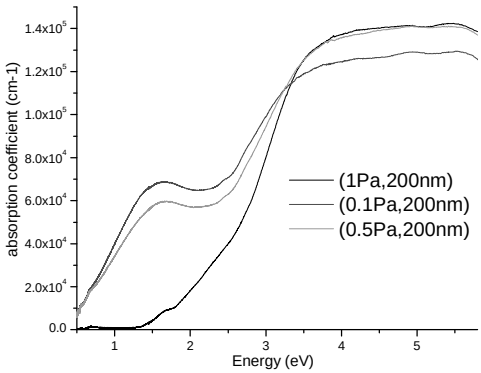

Figure 2 *Computed absorption curves of the LSMO films deposited at the lowest oxygen pressure.*

posited films with measurable resistivity value at room temperature exhibit reduced transparency, the obtained transmittance percentages in the visible ranges are good enough to be promising for spin-OLED applications after growth optimization.

Figure 2 compare the absorption curves of the deposited films calculated from the measured normalized transmittance and total reflectance spectra. As the deposition oxygen pressure decreases, a wide absorption band appears at 1.5 eV and its intensity increases as the oxygen content decreases. This result is fully consistent with the above discussion and demonstrates that the reduction of the oxygen content promotes the spontaneous JT effect through convertion of a number of Mn^{4+} ions to Mn^{3+}. The absorption observed at 1.5 eV just matches the expected energetic separation between the majority eg bands separated by the JT distortion of the oxygen octahedron surrounding each Mn3+ ion. Since the lowering of the crystal symmetry partially localizes carriers, all of this can also concur to explain the quite high resistivity values observed for the films under examination.

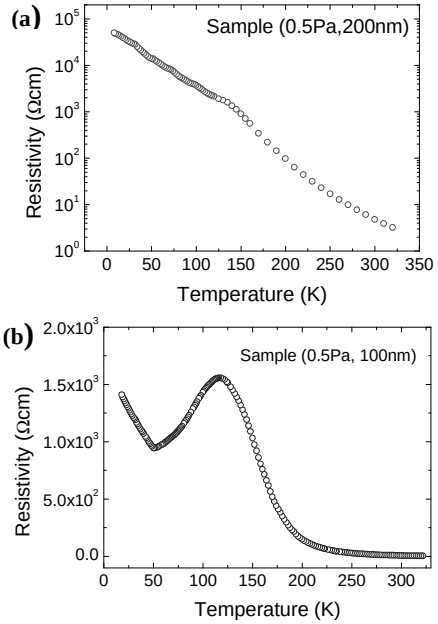

Figure 3 *Temperature-dependent resistivity in zero- magnetic field of the sample (a) (0.5 Pa, 200nm) and (b) (0.5 Pa, 100nm)*

The samples grown under the highest oxygen pressures show absorption features identical to the ones of the film (1 Pa, 200 nm). Both the absence of absorption feature at 1.5 eV and the very high resistivity at room temperature can be ascribed to the exceedingly high content of Mn 4+ ions compared to Mn^{3+} ions. Whereas Mn^{4+} ion isnt JT active, it provides holes, the content of which also can tune the carrier hopping along the Mn-O-Mn chains according to the double exchange (DE) model. Therefore, whatever magnetic phase is, oxygen excess also suppresses conduction through carrier trapping due to the lattice disorder induced by cation vacancies. Definitively our optical analysis successfully relates carrier localization to lattice and structural order, ratio Mn^{3+}/Mn^{4+} and density of the Mn^{3+} - O_2 - Mn^{4+} chains as induced by oxygen content.

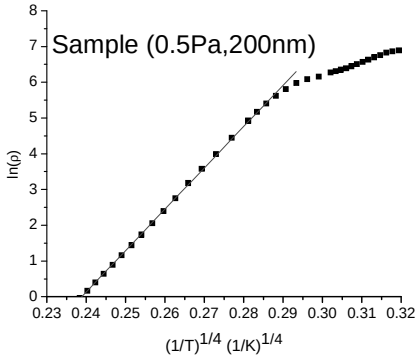

Figure 4 *The small polaron VRH conduction mechanism is satisfied above 150 K by the sample (0.5_Pa, 200_nm).*

In order to establish which mechanism rules the conduction regime of the deposited samples, their resistivity response vs. temperature has been measured in the range from 4 K to 320 K. Figures 3a and 3b show the obtained temperature-dependent zero-field resistivity of the conductive films (0.5 Pa, 200 nm) and (0.5Pa, 100 nm), respectively. The curve associated to the thicker sample shows a progressively decreasing resistivity as temperature increases. No peak that undoubtly could be ascribed to a transition metal-insulator is observable but the measured curve exhibits a knee around 150 K. Accounting that better structural ordering is favored by thicker films and more rapid oxygen desorption occurs by thinner growing films, our result is comparable to the one obtainable for a thicker film deposited by KrF ablation excimer laser and at higher deposition oxygen pressure. Therefore, ablation by ArF excimer laser effectively allows deposition at reduced oxygen pressure. Turning to the sample (0.5Pa, 100nm), a resistivity peak, namely the metal-insulator transition, occurs at nearly 150K and the high resistivity behavior at very low temperature is characteristic of polycrystalline films. The quoted low value of TMI is not surprising accounting for both ratio Mn^{3+}/Mn^{4+} differing from the optimal composition La 0.7 Sr 0.3 Mn O_3 the mismatch between the desired high growth temperature and the effective one which causes

non-optimal lattice order. While the former factor was deliberately tuned, the second was strictly linked to the substrate thermal properties.

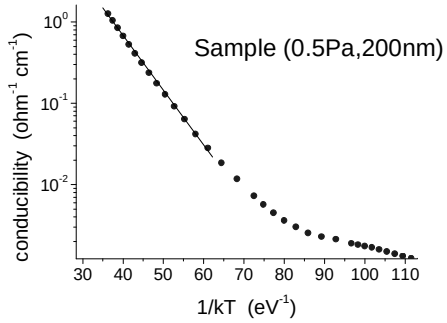

Figure 5 *The Arrhenius conduction mechanism is well satisfied above 150K by the sample (0.5_Pa, 200_nm).*

Concerning the conductivity regimes, for temperature slightly higher than 150 K the resistivity ro vs. temperature dependence of the (0.5Pa, 200nm) sample is well described by the small polaron variable range hopping (VRH) model, namely linear dependence of $\ln \rho$ vs. (1/T)1/4. In this respect, Fig. 4 shows that the plot of $\ln \rho$ vs. (1/T)1/4 in the range from 150K to 320 K is perfectly linear once the temperature is higher than the critical value 150 K and deviation from the linear trend occurs only at the highest temperatures. The SP transport mechanism was also tested but VRH was found to give better accordance with the corresponding theoretical law. This result is fully consistent with the disordered and /or polycrystalline nature of the examined film. Figure 5 shows the plot of the conducibility sigma vs. 1/kT for temperature ranging from 150 K to 320 K. In the temperature range where the small polaron VRH was found to fail, the sample exhibits thermally activated conductivity, that is the Arrhenius law is well satisfied with an activation energy Ea=0.154 eV.