

Intergranular coulomb blockade in thin films of magnetoresistive manganites

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The low temperature behavior of the resistance of polycrystalline thin films of magnetoresistive manganites has been investigated for grain sizes in the nanometric scale. We have optimized the dc-sputtering deposition and annealing procedures so as to meet the grain size requirements while keeping the basic features of the magnetic and electronic transport of the bulk material. A systematic upturn of the resistance at around 50 K is observed in all films (12nm-80nm grain diameter). These results point out the existence of a Coulomb blockade mechanism affecting the conduction of electrons at least in the smallest grain sizes explored. The evolution of this effect with the magnetic field is also investigated.

1. Introduction

The study of the low temperature electrical transport in granular metals and metal-insulator composites have been the focus of a great deal of studies since the pioneering works of Abeles and Sheng in the early seventies [1-3]. It is well established that the electrical conduction in granular metals results from the transport of electrons and holes from charged to neutral grains. A carrier has, therefore, to be created by removing one electron from a neutral grain and placing it in a neighboring neutral grain. This process involves an electrostatic energy, E_c . The charging energy E_c , can be written as $E_c = e^2/2C = e^2/4\pi\epsilon_0\epsilon_r d$, where e stands for the electronic charge and C is the capacitance of a grain, ϵ_0 and ϵ_r are the permeability of the vacuum and the relative permeability, and d is the grain diameter. From this equation it is obvious that E_c becomes very large for grain sizes very small (in the nanometer scale). Consequently, for small grains, as the temperature decreases it is increasingly difficult to activate the transport process and this situation may evolve to a point in which the transport could be effectively blocked. In this case an increase in the resistance, $R(T)$, of the system should be observed at low temperatures where the electron localization effects take place. This phenomenon has been reported for all granular metal films explored [2].

Recently, a similar behavior in the low temperature resistivity of some oxides has been observed [4-6]. This phenomenology has been explained either in terms of the existence of an intergranular Coulomb gap also in these materials or related to the divergent behavior reminiscent of a spin glass system [7]. In particular, Balcells et al report their measurements on a series of ball milled powdery compacts of $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO), annealed to different temperature so as to vary the grain size. They explain their observations as a result of a Coulomb blockade of the electronic transport at low temperatures.

However, for the smallest grain sizes samples the metallic behavior expected [8] for this system is missing in the reported temperature dependence of $R(T)$. In addition, the reported low temperature dependence of $R(T) = \exp(\Delta/T)^{1/2}$ instead of the usual $\exp(\Delta/T)$, predicted for a

CB, could point out the coexistence of more than one effect operating in the electronic transport properties of these materials. In this context, it seems in order to address the question as to whether a pure CB mechanism or, on the contrary, an actual change, of the electronic transport mechanism induced by connectivity and/or structural disorder are at the root of the reported divergences.

Therefore, our aim in this paper is to assess the nature of the enhancement of the low temperature resistance in magnetoresistive manganites.

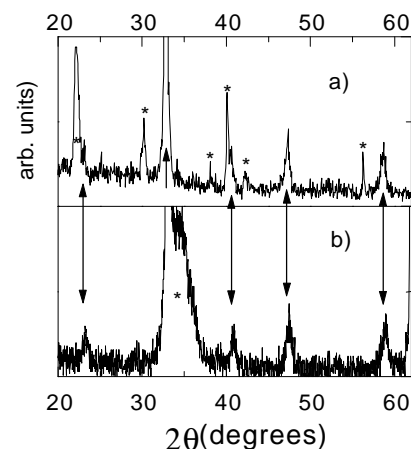


Fig 1. Xray diffraction pattern of a representative film a) grazing incidence and b) 0/20 sweep. Asterisks are spurious peaks due to Si wafers

2. Experiments and Results

From the experimental viewpoint, we only consider nanometric granular samples that basically reproduce the transport and magnetic properties of a bulk magnetoresistive manganite. To do so we have developed a protocol to grow $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ thin films whose grain size is basically controlled by the film thickness. We will also follow the dependence of the electronic transport on the applied magnetic field so that we can have some hints on the sort of processes that are involved. Following classical ceramic techniques $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ was prepared by mixing stoichiometric amounts of La_2O_3 , MnO_2 and

CaCO₃ followed by the annealing of the mixture for 72 hours at 1400C and quenching of the sample in air. In order to conform the target, the powder was subsequently pressed and sintered at 1200 for another 10 hours. No steps were taken to further densify the target which presents an average grain size of several μm. X-Ray diffractograms (Fig1), analyzed in terms of the pseudocubic structure, give a value for the lattice constant of 5.466(2) Å for the target implying an actual composition of La_{0.73}Ca_{0.27}MnO₃ [9].

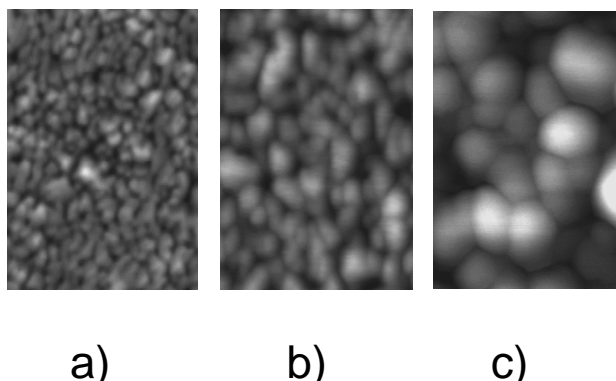


Fig. 2 AFM image of films with grain diameters d a) d=12 nm, b) d=20 nm c) d=45nm (scale 250 nm x 250 nm)

Thin films were deposited by dc-magnetron sputtering on (100) Si substrates at room temperature in a vacuum chamber allowing a base pressure of the order of 10⁻⁷ mbar. The sputtering process takes place at room temperature, so as to avoid crystal growth, in a mixed atmosphere of Ar and O₂ flowing at a ratio of 4:1 resulting in a total pressure of 5.4 10⁻³ mbar. The deposition rate was verified by small angle X-ray scattering to be linear in time and equal to 250 Å/hour. The as grown films were found to be amorphous and, in order to reproduce the properties found in the bulk material, they needed to be annealed to a polycrystalline form. We have tried several annealing sequences so as to approach the magnetic and transport properties of the bulk while minimizing the grain size. Best results were achieved for samples annealed under continuous O₂ flow at a temperature of 850 C for 10 minutes. It is worth mentioning that the exchange of O₂ by Ar during the thermal treatment hardly decreases the value of the ferromagnetic transition temperature (around T_{FM} = 240 K) for all samples or otherwise alter the electronic transport properties of the samples.

This observation can be explained if the annealing process is understood basically as a means to input energy to the system which reorganizes the broad distribution of Mn-O-Mn angles present in the as-grown film and not as a way to deeply vary the oxygen stoichiometry.

Fig 1 shows the X-Ray diffraction patterns whet it can be seen that there is not any preferential orientation of the manganite on Si (100). Atomic Force Microscopy (AFM) images of the films reveal the morphology of quite homogeneous samples consisting of spheres whose

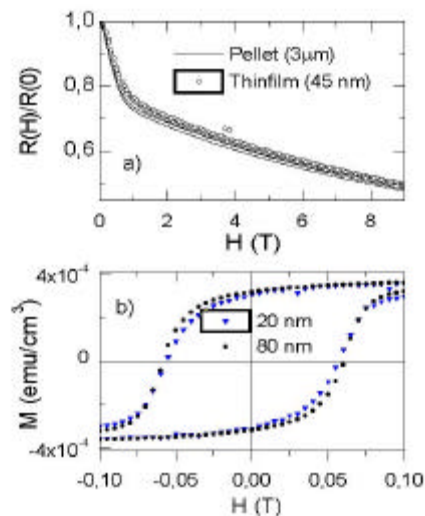


Fig. 3. (Upper) Magnetic field dependence of $R(H)/R(H=0)$ measured for two dissimilar samples: Compact with average grain size $d=3$ nm and a representative film with $d=45$ nm. (Lower) Histeresys cycles corresponding to two representative films with average diameters $d=80$ nm (triangles) and $d=20$ (circles)

average diameters range from 12 to 80 nm depending on the film thickness. Fig. 2 shows the AFM image of representative samples. A Quantum Design SQUID Magnetometer was used for magnetization measurements under a static field of 0.1T. The measured values for the magnetization of the manganite films also contain a diamagnetic contribution from the substrate. In order to scale the magnetization data we use the surface area of the films and their deposition time.

Fig 3b shows the histeresys cycles measured at T=5K for several representative films. The measured cycles are compatible with samples built out of single domain spheres with the magnetic field at a random distribution of angles to the easy axis [10]. Further, the Curie temperatures T_c , and the cohercive field values are also similar for all the films, which leads to the conclusion that from the magnetic point of view all of our films are very similar to each other. The electrical resistance and its field dependence were measured using a four probe method with a PPMS Quantum Design instrument.

Fig. 3a shows the high field magnetoresistance $R(H)/R(H=0)$ of a representative film as compared with a polycrystalline for which the high field magnetoresistance (MR). We have understood the observed behavior of the electronic transport [11] in terms of the existence of two kinds of conduction channels ("poorly" conducting and "good" conducting paths), connected in parallel, whose relative cross sections vary with field and temperature and do not depend on the grain size.

Our model allows the reproduction of the linear behavior of the high field MR ratios [12] under the assumption of a progressive opening of new productive

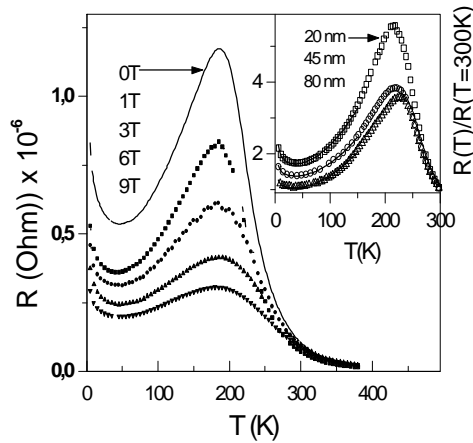


Fig 4. Resistance vs temperature for the smallest particle size explored (d=12nm) at several external magnetic. Inset resistance vs temperature for other representative films in the series as measured at 0T

conduction channels that were spin blocked before the corresponding external magnetic field is applied.

Fig 4 shows the resistance for different magnetic fields corresponding to our smallest grain size film (grain diameter d=12nm). The inset shows the resistance at zero field normalized to the room temperature value for the rest of the films in the set. All of them share the same features: a neat MI transition at a temperature, as expected for a bulky manganite, and an upturn of the resistance that starts to develop below 40 K, that is assigned to the existence of a Coulomb gap.

The latter being more prominent as the grain size diameter of the sample decreases. As expected, when the applied magnetic field increases a decrease of the resistance is observed.

We have analyzed the portion of the curves, up to T=150K, as the sum of two contributions $R(T) = A R_0 + B \exp(\Delta/T)^{1/2}$, where R_0 stands for the resistance of the bulky target, which does not present the upturn below 40K, and A is an amplitude factor. Regarding the exponential contribution, we mention that fits improve assuming a $T^{1/2}$ dependence in the argument of the exponential instead of the T^{-1} dependence postulated for a pure Coulomb blockade effect.

B is an amplitude factor and Δ is a fitting parameter related to the energy of some sort of activated process. The model fits the data nicely and indeed the calculated function lies within the symbols as it can be seen in the inset of Fig 4.

Fig 5a) shows the results for the parameter Δ corresponding to the best fit of our R(T) curves measured under an applied magnetic field of 0T and 9T versus the average grain diameter for each sample. Fig 5b) shows the dependence of the parameter Δ on the applied magnetic field for the sample with average grain diameter d=12nm.

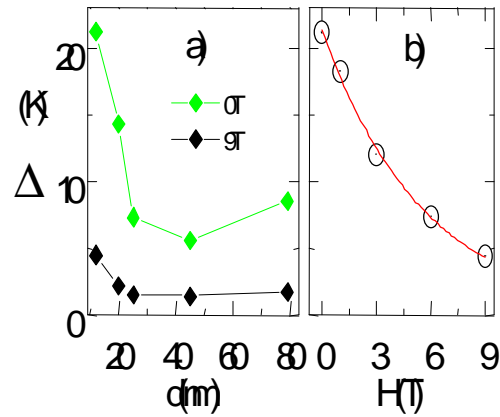


Fig. 5. A) Best fit results for the parameter Δ vs the average grain diameter of the measured films. b) Magnetic field dependence of Δ corresponding to the film with d=12 nm.

3. Discussion and Conclusions

A very strong variation of Δ with the applied field is readily seen in the inset and an exponential dependence is inferred. Notice that, for all samples, an approximate 80% decrease of the magnitude $\{\Delta(T,H=0T) - \Delta(T,H=9T)\} / \Delta(T,H=0T)$ is observed when an external magnetic field of 9 T is applied. This fact implies that, on top of the invoked Coulomb blockade, there is an underlying magnetoresistive mechanism contributing to the low temperature behavior of R(T).

This fact can be rationalized if one takes into account other variables, apart from pure charging effects, entering the problem of the electronic transport in granular manganites. Among them, the intergrain resistance has proved to be utterly important. Experiments [12] show that, at low fields, this magnitude depends basically on the relative alignment of the magnetization of neighboring grains and decreases very fast with the applied magnetic.

At high magnetic field, it continues linearly to decrease but now at a slower rate and this effect is related to the opening of new productive conduction channels across the grain boundaries [12].

From our results it can be concluded that the decrease in the intergrain resistivity leads to a suppression of the charging effects as it is apparent in Fig. 5b. In summary, the increase of the resistance observed at low temperatures could be ascribed to charging effects due to the small size of the grains in our films. However, these effects are probably modulated by the resistance of the intergrain contacts and that explains the observed dependence of Δ on the applied magnetic field [4].

Acknowledgments

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