Conductance of perovskite oxide thin films and interfaces

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Introduction

The physics of metallic oxides has been an area of intense research ever since the discovery of high temperature superconductivity by Bednorz and Müller in 1986. In that case, the oxide was $(La,Ba)_2CuO_4$, which, as we would now describe it, consisted of a parent compound La_2CuO_4 in which the trivalent La was partly replaced by divalent Ba. As a consequence, the Cu takes on a mixed valence character and can be Cu^{2+} or Cu^{3+}. The material in question is a perovskite, which can be thought of as containing Cu-O planes, and the Ba doping leads to hole doping of these Cu-O planes. Here, all the ingredients which makes the correlated electron (metallic) oxides so interesting, come together. The parent compound is a Mott insulator, in which the Cu d electrons cannot form a band because of the strong Coulomb interactions. It is also magnetic, because the Cu has a half-integer spin ($S = 1/2$). Doping then brings in holes, bands start to form, and the magnetism changes its character. Within the family of perovskite oxides, all of the $3d$ elements can be accommodated in the structure, and all yield different properties. In particular the Mn-based materials have their own interesting niche. The parent compound $LaMnO_3$ (a perovskite variant with a somewhat different structure than the 2-1-4 compound discussed above) is also an antiferromagnetic insulator, with the magnetism coming from the trivalent manganese with spin $S = 2$. Doping with divalent ions such as Ca or Sr also here leads to metallicity, and also the antiferromagnetism is replaced by ferromagnetism. Since the electronic band formation forces the electron spins to be parallel in this case, transitions can be found from a paramagnetic insulating phase to a ferromagnet metallic (FM) one. This is the basis of the so-called Colossal magnetoresistance effect, which was (re)discovered in 1991. More phases are possible than the FM one, and in particular static ordering of the charges, or also ordering of the directions of directed d-orbitals, leads to a multitude of physical phenomena.

Although the research questions are mostly curiosity-driven, a possible interest from an applications point of view is that in going from a Mott insulating state to a metallic state, large numbers of electrons become available for conduction, and this might offer alternative scenario's for transistor-like devices. Next to research on bulk materials, it is therefore of interest to study the behavior of these materials in thin film form. This also leads to other particular questions. Films have to be grown on substrates, high quality films should have small amounts of defects, and an epitaxial relation with the substrate is therefore strongly desired. Even then, lattice parameters will usually not match, and the films will be under tensile or compressive strain, which also has consequences for the out-of-plane lattice parameter. Since the properties of the perovskites are strongly linked to their structure, consisting of deformable cages of oxygens surrounding the metal ions, strain will lead to different properties, and strain engineering becomes a possibility. Working in the direction of devices, there are then two important questions, which also have strong fundamental coloring. One is how thin a film can be made on a given substrate and still show uniform and homogeneous properties (which may still be different from the bulk because of the strain). In other words, what is the possible influence of the interface and the various discontinuities presented by the interface. The other is whether the charge carrier density can be influenced by an electric field, and therefore is switchable. Here, the field offers a bonus in the sense that one of the most used substrates for perovskites growth, $SrTiO_3$ (a Ti-based 1-1-3 perovskite itself) has a very high dielectric constant, and is therefore very suitable for applying electric fields. This Thesis concentrates on the first question posed above, about the conducting properties of very thin films and interfaces, but it opens the door to the second question by using $SrTiO_3$ as the preferred substrate.

In the first part, we study two different manganites which have been doped into the metallic regime, $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) and $La_{0.7}Sr_{0.3}MnO_3$ (LSMO). When grown on various substrates, in particular on $SrTiO_3$ (STO), it is known that the strain leads to a change of the temperature of the combined paramagnetic-to-ferromagnetic and insulator-to-metal transition, which is most pronounced in LCMO. There, the bulk transition temperature of about 270 K goes down to 110 K for very thin films on STO. This is connected to subtle changes in the structure and the electronic bandwidth, but there is also the question whether the carrier concentration or the basics of the band structure are changing. This is investigated by measuring the Hall effect in various combinations of manganites and substrates. The data indicate that, quite generically, the electrical conductance of the films are due to the combined effect of the strained material, and a relatively thick layer extending from the interface with non- or badly conducting properties. This layer is of the order of 5 nm and therefore relatively thick. We also investigate what happens with the properties of such films when they are structured into bridges of micron- or submicron width. Here we concentrate on LSMO, and find that structuring down to 1 μm does not change the basic conducting properties, but going down to 300 nm does : the conductance becomes non-Ohmic, which is probably due to loss of oxygen, or oxygen-based inhomogeneities.

In the second part, we go to a slightly different subject, and study the properties of the interface between two simple perovskite band insulators, $LaAlO_3$ (LAO) and $SrTiO_3$. The interest here lies in the fact that the discontinuity in the charge variation which occurs when stacked layers of ionic AlO and LaO_2 give way to neutral SrO and TiO_2 is believed to lead to a conducting interface. This has been a much investigated topic in the last ten years. The conductance is (quasi-) 2-dimensional, which is of interest in itself, while gating can be applied when the substrate is STO on which a thin film of LAO is grown. It has become clear over time, that not only electronic reconstruction (moving charges to the interface to compensate for the discontinuity) plays a role, but also intermixing effects, oxygen vacancies, and even possibly stoichiometry. Almost all of the published research has been performed on samples grown with the process of pulsed laser deposition (PLD), and it is well documented that the interface properties, including the amount of conductance, are correlated with the oxygen background pressure which is used in the process, and which should not be too high. The interfaces studied in this thesis are grown by sputtering in a high background pressure of oxygen (typically 10^3 higher than in PLD), and they are found to be insulating, and also non-magnetic. Investigations by transmission electron microscopy show them to be of high quality, and it seems the high oxygen pressure is the important factor in rendering the interface non-conducting, although the afore-mentioned issue of stoichiometry also plays a role. This leads to a different perspective on the formation of the conducting layer.

Outline of thesis

Following this Introduction, in **chapter 2** we discuss the fundamental physics of manganese perovskite oxides. The phase diagram, electrical transport phenomena and the effects of strain are discussed there. In **chapter 3**, the deposition technique of sputtering in a high oxygen pressure atmosphere is presented, and details are given of the techniques used to characterize the thin films which are grown in this way. In **chapter 4**, measurements of the ordinary and anomalous Hall effect are presented and used to discuss the transport properties of very thin films of LCMO and LSMO. In **chapter 5**, the transport properties of LSMO thin films are studied further, now by structuring them down to mesoscopic length scales by electron beam lithography. In **chapter 6**, the results are presented of the fabrication of interfaces between LAO and STO by reactive radiofrequency sputtering, which are found to be non-conducting. Since the possibility of magnetism at the interfaces also is under discussion, magnetic properties are measured as well, and an estimate is given for the upper boundary of the amount of magnetism present at these sputtered interfaces.