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High- T_c superconducting thin films with composition control on a sub-unit cell level; the effect of the polar nature of the cuprates

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Abstract

Inspired by the work of Ohtomo and Hwang in 2004, we shed new light on thin films of layered cuprate high- T_c superconductors (HTS). In principle all HTS materials consist of charged perovskite-like layers which in thin films can lead to polar discontinuities at the interfaces of different materials. The resulting charge redistribution has to occur but we expect it to be far more complex than in the $\text{LaAlO}_3/\text{SrTiO}_3$ system since copper can be multivalent. This makes it hard to predict what will happen in terms of transport or even magnetic properties compared to the 'simple' insulator LaAlO_3 . Nevertheless, we point out that the picture of systems of charged layers is important and necessary to fully understand heterostructures of these complex materials.

1. Introduction

In their 1997 review, Triscone and Fischer discussed experiments regarding superlattices of various high- T_c superconductor (HTS) systems and related hybrid perovskite multilayer structures [1]. The research topics they addressed were T_c as a function of layer thickness and layer separation (separated by an insulating or metallic layer), vortex dynamics as a function of layer thickness, and tests of flux pinning models using superlattices. Many of the articles referred to in that overview demonstrated the feasibility of multi-layering in various cuprate systems. This includes the case of the so-called infinite layer system [2], in which superconducting multilayers were synthesized out of non-conducting blocks of CaCuO_2 , SrCuO_2 and/or BaCuO_2 .

Since then, various developments in oxide thin film technology have further advanced sub-unit cell control of HTS materials. A sensitive aspect of oxide growth is the presence of some oxidizing ambient, either pure oxygen or some activated form of oxygen (e.g. ozone, atomic oxygen, etc). To obtain a sufficient degree of oxygenation, deposition techniques such as sputtering and pulsed laser deposition (PLD) operate at relatively high ambient pressures. The catch is that most *in situ* analytical tools operate under ultra-high-vacuum conditions,

which defines the need for adaptive technology in the case of PLD and sputtering. In 1997 such adaptation became available for PLD in the form of high-pressure reflection high-energy electron diffraction (RHEED) [3], that allowed *in situ* monitoring at standard PLD conditions, (as opposed to earlier attempts to use RHEED, where the process itself was modified, e.g. [4]). At the same time, second generation oxide molecular beam epitaxy (MBE) tools were being developed, by combining a set of *in situ* analytical tools with the latest source technology [5].

Equally important has been the development of techniques to prepare single-terminated templates for thin film growth, most notably TiO_2 -terminated SrTiO_3 [6]. This has made possible the control of the stacking of subsequently grown thin films, whereby nature seems to favor a continuation of the AO and BO_2 stacking in ABO_3 .

Sub-unit cell control over the stacking sequence of HTS materials, however, now raises a different type of question, namely how to cope with the polar nature of the materials involved. A 2004 article by Ohtomo and Hwang was the onset of a flurry of research activity on the so-called polar discontinuity in the class of perovskite materials ABO_3 , of which the HTS materials are a sub-family and were at the center of attention [7, 8]. In the ideas presented, very much

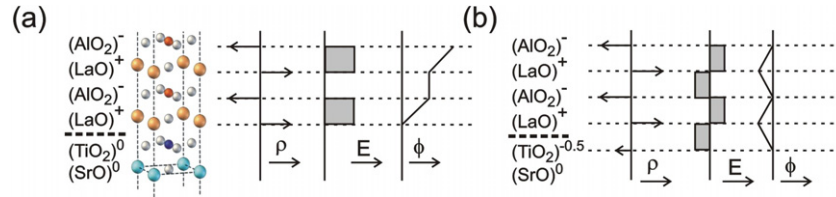


Figure 1. LaAlO₃ is a polar material with charged (ρ) layers that induce an electric field (E) within the material and a potential (ϕ) build-up. (a) The interface between LaAlO₃ on SrTiO₃ gives rise to a diverging potential. (b) It was shown by Nakagawa *et al* [26] how a transfer of half an electron per unit cell to the terminating TiO₂ plane provides a non-diverging potential and a stable interface.

(This figure is in colour only in the electronic version)

related to the observations of the polar interfaces between Ge and GaAs semiconductors [9, 10], one counts in its simplest form the formal charge on the AO and BO₂ layers, in the case of (001) oriented material. In figure 1, the example is given of LaAlO₃ grown on SrTiO₃. Ohtomo and Hwang showed that the alternation of charged layers causes a build-up of electric potential in the film, which cannot be sustained (figure 1(a)). This polar catastrophe drives an electronic reconstruction of the interface (figure 1(b)), either by charge transfer to the TiO₂ plane at the interface, by oxygen doping, or by structural deformations.

In analogy to the polar material LaAlO₃, HTS unit cells consist of layers that are not charge neutral. Therefore, electronic reconstruction at interfaces with changing polarity can be expected for HTS as well and the interface electronic reconstruction can now be used as an additional degree of freedom to distribute charge over the unit cell. The (super-)conducting properties of HTS are very sensitive to the amount of charge on the CuO₂ planes, whether intrinsic or induced by doping, so the interface effects are expected to be large.

In the following, we will illustrate the importance of interface electronic reconstruction for the case of the high- T_c cuprates, by giving two examples.

2. Electronic reconstruction at polar HTS interfaces

2.1. Single-layer sandwiched (La, Sr)₂CuO₄

A very important aspect of oxides and oxide electronics is the dependence of the electronic properties on the oxygen stoichiometry, which oftentimes determines the carrier doping level. The difficulty of studying this relationship is that the light oxygen atom, or lack thereof, is very hard to detect directly, although sensitivity has improved dramatically [11, 12]. A lot of research has been done in this respect and the role of oxygen has sometimes been clarified e.g. [13] and sometimes more questions have been raised, as is the case in the following examples.

The popular HTS compounds YBa₂Cu₃O_{7- δ} and La_{2- x} Sr _{x} CuO₄ are well known to have a variable oxygen stoichiometry, the former through the copper chain layer oxygen atoms as has been widely studied. Also for the latter compound, for which it is still unclear which oxygens are exactly involved, several groups have studied the role of oxygen doping [14–17] and its relation with superconducting properties. The variable oxygen stoichiometry is a curse on the one hand,

since it brings about uncertainties on homogeneity, etc. On the other hand, it is a blessing since it allows us to control properties, often reversibly. The latter is easiest to achieve when the surface to volume ratio is large, such as is the case in thin films. Also, kinetic control is preferable, which means that oxygen intake or reduction should take place at sufficiently low temperatures, where oxygen diffusion is possible but cation mobility is still very low, leaving the cation sublattice intact.

In figure 2(a), an example of such control is shown, where annealing of La₂CuO₄ and (La, Sr)₂CuO₄ films in various oxidizing ambient are compared. La₂CuO₄ is formally undoped and shows a striking variation of conductivity upon annealing. Coincidentally, a controversy [16, 18, 19] concerning the possibility of doping of this system through epitaxial strain was considered settled by these experiments.

To test whether an antiferromagnetic ground state and a superconducting ground state mix on significant length scales, Bozovic *et al* fabricated heterostructures of La₂CuO₄ sandwiched between (La, Sr)₂CuO₄ electrodes and the reciprocal structure (see figure 2(b) for a schematic drawing) [27]. They found that a single unit cell layer of La₂CuO₄ was able to block all supercurrent when insulating (see figure 2(c)) and sustain a supercurrent after ozone annealing. They concluded therefore that anti-ferromagnetism and superconductivity in the cuprates have such different energy scales and that a model for the mechanism of HTS should have no bearing on their respective mixing.

Now turning back to the original premise of the paper, insulating La₂CuO₄ is a polar material. Note that due to the double rock-salt layer there are several possibilities to start a stacking sequence. In order to see whether electronic reconstruction at La₂CuO₄ interfaces plays a role for the superconductivity, in figure 3, the possible initial stacking sequences of the insulating parent HTS compound La₂CuO₄ are investigated on a substrate of SrTiO₃. From the distribution of charges, the potential is shown not to diverge for any of the cases (a)–(d). In figures 3(a) and (c) there is no need for any electronic reconstruction and the interface is expected to be stable. However, in figure 3(b) a case is shown where electronic charge is transferred to the terminating TiO₂ layer in order to prevent a polar catastrophe. The necessary amount of transferred charge (one electron per unit cell) is larger than seen in figure 1(b) and also here conduction at the interface is expected. For a CuO₂ plane directly on an SrO-terminated SrTiO₃ substrate (figure 3(d)), electronic reconstruction is predicted to transfer electrons away from the CuO₂ plane. This

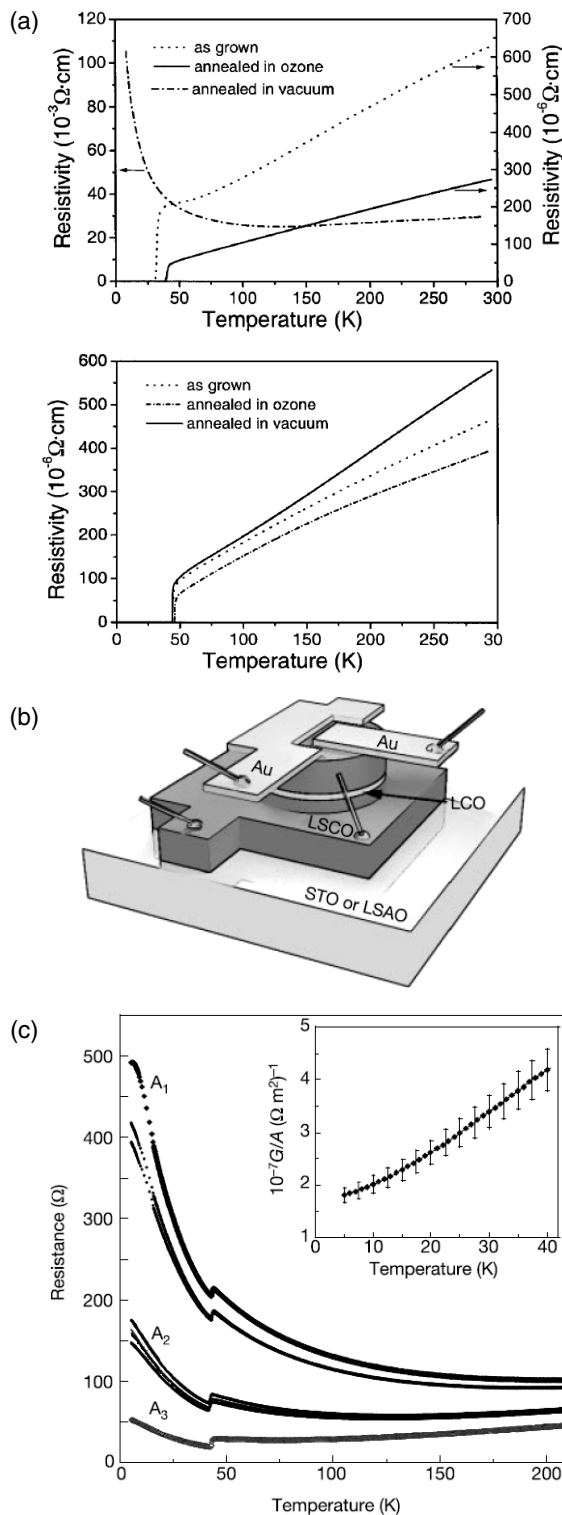


Figure 2. (a) Temperature dependence of resistivity of La_2CuO_4 film (top) and $(\text{La}, \text{Sr})_2\text{CuO}_4$ film (bottom) as-grown, annealed at 200°C in vacuum and annealed at 200°C in ozone, respectively. Taken from Bozovic *et al* [15]. (b) The structure of the SIS ‘sandwich’ $(\text{La}, \text{Sr})_2\text{CuO}_4/\text{La}_2\text{CuO}_4/(\text{La}, \text{Sr})_2\text{CuO}_4$ junctions studied by Bozovic *et al* [27]. (c) Transport in SIS junctions where the La_2CuO_4 barriers are one unit cell thick. The differences in absolute resistivity are caused by a variation in junction cross-section. The dip at 42 K corresponds to the $(\text{La}, \text{Sr})_2\text{CuO}_4$ electrodes becoming superconducting. Inset: average conductance per unit area, for $T < T_c$. Reprinted by permission from Macmillan Publishers Ltd: *Nature* [27], copyright 2003.

interface-induced form of hole-doping could perhaps even give rise to superconductivity in the first CuO_2 plane.

Whether interface-induced doping occurs or there is charge redistribution in the form of defects or oxygen vacancies remains an open question. However, it seems plausible that these effects influence the properties of these systems, especially since superconductivity, localized on one or a few CuO_2 layers, is still a rather large effect. Another possibility would be that the doping caused by oxygen vacancies is facilitated near the interface simply because of the large charge imbalance that needs to be restored somehow. In this light, previously obtained results should be reinterpreted.

Finally, on La_2CuO_4 , since we have two possibilities for every option of the substrate termination (resulting in a total of four options, see figure 3), the resulting reconstruction will also depend on whether a single option is present or whether a mix is at play. From a pure thin film growth perspective, why a single option would be the resulting situation is not trivial. However, the most plausible scenario would be the nucleation and growth of macroscopic crystallographic regions separated by grain boundaries. Since the planar size of these regions is likely to be much larger than the characteristic length scale of the polar instabilities, i.e. a few unit cells, these regions could be regarded as infinite and decoupled.

2.2. Multilayers consisting of separately deposited sub-unit cell blocks

For the system we discuss here, the infinite layer system, it is helpful to briefly review the experimental observations. For superlattices created by sequential deposition of SrCuO_2 and CaCuO_2 [20–22], no superconductivity was found. However, Norton *et al* have demonstrated superconducting artificial layered structures with BaCuO_2 and $(\text{Sr}_{1-x}, \text{Ca}_x)\text{CuO}_2$ by PLD [20], with a maximum T_c of ~ 70 K. The idea behind this is the fact that by periodically substituting layers containing smaller cations by larger ones; extra oxygen may be incorporated in the latter acting as charge reservoirs. They only observed superconductivity in structures with more than one BaCuO_2 block. Later, Balestrino *et al* found superconductivity ($T_{c,\text{max}} \sim 80$ K) using the same method, however, only the case of $x = 1$ [23], i.e. Sr-containing structures showed no trace of superconductivity. This was attributed to Ba/Sr inter-diffusion.

The relation between superconductivity and the structure is not clear yet, e.g. whether the relation found for the number of different layers with superconductivity [24] has a fundamental origin or is determined by the crystalline quality.

Structural analysis with x-ray diffraction (not shown) and high-resolution electron microscopy (see for latter figure 4) of the $\text{CaCuO}_2/\text{BaCuO}_2$ superlattices indicates first of all a high-quality structure, in both the overall crystallinity as well as in the imposed periodicity along the c -axis. Furthermore, the right estimate for the deposition rate per constituent was confirmed by the period of the superlattices. A systematic deviation turned out to be caused by the compressive stress in the film.

The studies on the $\text{CaCuO}_2/\text{BaCuO}_2$ superlattices made clear that almost true layer-by-layer growth does not

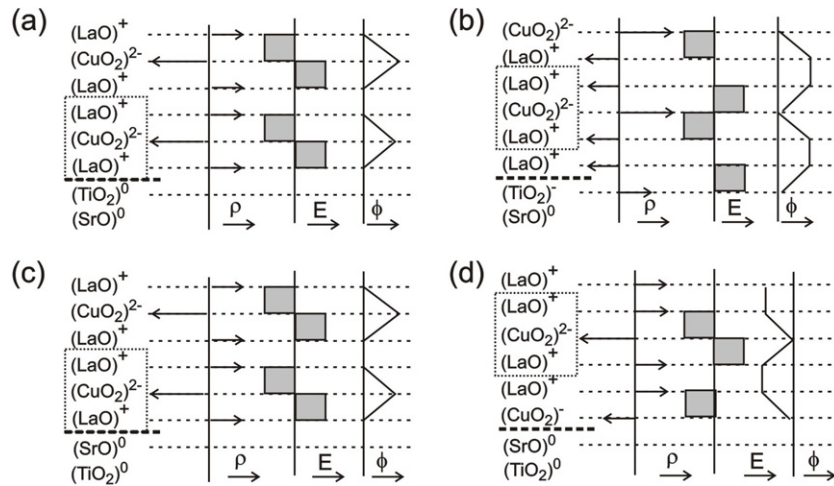


Figure 3. Possible stacking sequences for the deposition of La_2CuO_4 on SrTiO_3 that do not cause a polar catastrophe. The charge of each layer (ρ), the induced electric field (E) and the resulting potential build-up (ϕ) are given. (a) On TiO_2 -terminated SrTiO_3 , La_2CuO_4 can grow without the need for electronic reconstruction when a first LaO layer is followed by a CuO_2 plane. (b) Whenever the sequence of double LaO layers is maintained during the initial growth of La_2CuO_4 on TiO_2 -terminated SrTiO_3 , a stable interface can only be formed by electron transfer to the terminating TiO_2 plane. (c) On SrO -terminated SrTiO_3 , La_2CuO_4 can grow without the need for electronic reconstruction. (d) Whenever the initial growth of La_2CuO_4 starts with a CuO_2 plane on SrO , electronic reconstruction can take place by removal of electrons from the CuO_2 plane. The resulting doping with holes might result in superconductivity.

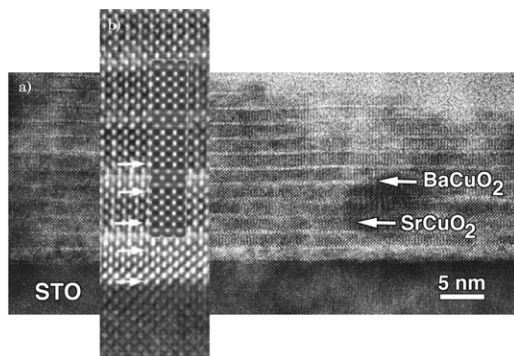


Figure 4. High-resolution electron microscopy image of a three times $(\text{Sr}, \text{Ca})\text{CuO}_2$ and two times BaCuO_2 structure; (b) enlargement including simulation, the arrows indicate the copper oxide planes. Reprinted with permission from [22].

necessarily lead to good superconducting properties, i.e. high- T_c s. The most perfect structures, e.g. $\text{SrCuO}_2/\text{BaCuO}_2$ superlattices, were never superconducting, whereas for the superconducting films, defects are expected to be present, although no systematic proof for this was found [22]. Most recently, the effects of oxidation conditions were studied in these systems [25], and the superconductivity ($T_{c,\text{onset}} \sim 55$ K) when films were deposited at pressures of 10^{-3} Torr for a mixture of oxygen and ozone and very low deposition rates were observed (10^{-2} unit cells per pulse).

As can be seen from figure 5, the infinite layer structure in the ionic limit is highly polar and as-deposited on neutral SrTiO_3 will result in a polar discontinuity. In contrast to the $\text{LaAlO}_3/\text{SrTiO}_3$ hetero-system, where essentially only Ti bands ($\text{Ti}^{3+}/\text{Ti}^{4+}$) are important, the infinite layer compound may respond in various ways, in particular because we now have multivalent Cu in the problem (e.g. Cu^+ and Cu^{2+}). Charge

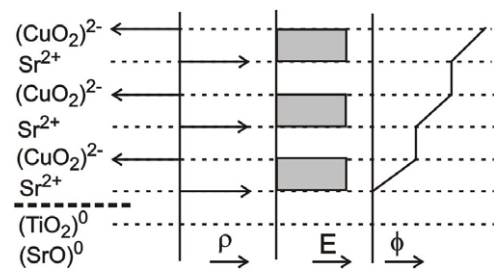


Figure 5. The interface between the polar infinite layer compound SrCuO_2 on SrTiO_3 gives rise to a diverging potential.

redistribution, random defects and oxygen vacancies are all possible on both sides of the interface. It is therefore hard to predict what exactly is going to happen but it is again not hard to imagine that the (superconducting) properties near the interface will be affected by the charge redistribution and also that the subsequent stacking of layers (see above; note that the interfaces created by subsequent superlattice layers should not contribute to any polar instability) will influence the outcome of transport measurements, especially in the case of superconductivity. This would explain the variation in success by different groups as well as the rather broad transitions that are typically observed in this system, with a word of caution that the latter still has to be checked in detail. Polar effects or free charge transfer from interstitials and other defects are not likely to be complementary, since ‘pre-existing’ free carriers will be detrimental to the potential build-up.

3. Outlook

In this article we have focused on the electronic properties of some HTS systems that generally are among the well-

controlled systems in terms of their growth. We very much agree with the observations and logic of Nakagawa *et al* [26] that the aforementioned polar discontinuities may also result in uncontrollable rough thin film growth; something has got to give. Our example in that respect would be the '123' system, which has always been a challenge to grow with atomically smooth surfaces and interfaces, depending on the substrate. For example, initial growth experiments in the DyBa₂Cu₃O_{7- δ} system, which were originally performed to control (minimize) the formation of anti-phase boundaries, may have indirectly been affected by polar discontinuities. We refer to the article of Blank *et al* in this issue for a more detailed discussion of growth-related issues.

From the perspective of electronic properties we argue that the polar discontinuity is at play in many HTS systems but the resulting measurable properties are hard to predict and therefore this problem needs attention from the oxide community. Fortunately, this picture leaves us also with opportunities in terms of controlling doping of HTS cuprates on the single-layer level.

Acknowledgments

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