RAPID COMMUNICATIONS

PHYSICAL REVIEW B **75**, 140512(R) (2007)

Interface hole doping in cuprate-titanate superlattices

N. Pavlenko,[1,*] I. Elfimov,[2] T. Kopp,[1] and G. A. Sawatzky[2]
[1]*Center for Electronic Correlations and Magnetism, Universität Augsburg, 86135 Augsburg, Germany*
[2]*Department of Physics and Astronomy, University of British Columbia, Vancouver, Canada V6T 1Z1*
(Received 28 March 2007; published 24 April 2007)

The electronic structure of interfaces between $YBa_2Cu_3O_6$ and $SrTiO_3$ is studied using local spin density approximation (LSDA) with intra-atomic Coulomb repulsion (LSDA+U). We find a metallic state in cuprate-titanate heterostructures with the hole carriers concentrated substantially in the CuO_2 layers and in the first interface TiO_2 and SrO planes. This effective interface doping appears due to the polarity of interfaces, caused by the first incomplete copper oxide unit cell. Interface-induced high predoping of CuO_2 layers is a key mechanism controlling the superconducting properties in engineered field-effect devices realized on the basis of cuprate-titanate superlattices.

DOI: 10.1103/PhysRevB.75.140512 PACS number(s): 74.78.Bz, 74.78.Fk, 73.20.At, 71.15.−m

In complex thin-film oxide heterostructures of structurally compatible but physically dissimilar compounds, interface phenomena can substantially affect the charge properties. A prominent example[1] is the titanate superlattice composed of insulating layers of $SrTiO_3$ and $LaTiO_3$, where the mixed valence $(+3/+4)$ of Ti leads to an interface-driven electronic redistribution and to metallic conductivity. Moreover, when one of the superlattice compounds is a copper oxide film, where the high-T_c properties can be tuned by doping, the behavior is even more intriguing. Such heterostructures consisting of $YBa_2Cu_3O_{7-\delta}$ films grown on $SrTiO_3$ layers are of essential importance due to their applications in superconducting field-effect devices.[2] It is well established that external electrostatic fields can significantly affect the superconducting transition temperature (T_c) in these layered materials, which is often understood in terms of electrostatic doping [the more charge is field injected into the film, the larger T_c].[2,3] Despite capturing a key mechanism of charge modulation in the field effect, this concept does not include a detailed consideration of the microstructure of the $YBa_2Cu_3O_{7-\delta}$ film near the interface, assuming that the latter remains unaffected by the adjacent $SrTiO_3$ interface layer.

Several experimental facts, however, indicate an interface-related change of the electronic states in the cuprate-perovskite oxide heterostructures. First, recent studies on underdoped cuprate films produced a T_c shift of about 5–15 K, whereas in the overdoped films no shifts were observed, a fact that cannot be explained satisfactorily by field doping.[2] Furthermore, studies of hole mobility in the CuO_2 planes of $SrTiO_3$-cuprate superlattices suggest a substantial localization of injected holes even above the hole-density level necessary for a bulk superconductor-insulator transition.[4,5] However, little is known about the electronic properties of the interfaces between the copper and titanium oxides. This is even more surprising considering the fact that, despite the different physical properties, the structural compatibility of the cubic $SrTiO_3$ and $YBa_2Cu_3O_{7-\delta}$ makes them good candidates to assemble heterostructures and study interfacial phenomena. The electronic band insulating state of bulk $SrTiO_3$ with a wide gap of about 3 eV between the valence O $2p$ band and empty Ti $3d$ bands is reasonably well described within an LSDA approach. In contrast, the standard band theory calculations fail to describe the antiferromagnetic Mott insulating state of strongly underdoped or undoped cuprates such as $YBa_2Cu_3O_6$. Instead, the band properties of $YBa_2Cu_3O_6$ with a gap of about 1.5 eV determined by Cu $3d$ and oxygen $2p$ electrons can be satisfactorily treated by introducing the intra-atomic orbital dependent Coulomb repulsion for the electrons in Cu $3d$ orbitals.

To provide deeper insight into the interface physics of such heterostructures, we present and interpret results of electronic structure calculations for the superlattice based on insulating $YBa_2Cu_3O_6$ films and $SrTiO_3$. As $SrTiO_3$ consists of an alternating sequence of electrostatically neutral (001) layers, one can expect that in such heterostructures, the chemical bonding at the (001) interface with $YBa_2Cu_3O_6$ will be determined by the first termination layer, which can be either SrO or TiO_2. It is worth pointing out that, if the first unit cell of a $YBa_2Cu_3O_6$ film were completely grown on the surface of $SrTiO_3$, the interface would be electrostatically neutral. In this case, our LSDA+U calculations performed for the antiferromagnetic arrangement in CuO_2 planes produce an insulating state with an energy gap of 1.2 eV between the Cu $d_{x^2-y^2}$ and O p_x and p_y orbitals, similar to the bulk $YBa_2Cu_3O_6$. Then the direct influence of the interface would be reduced essentially to the small change in the band structure of $YBa_2Cu_3O_6$, originating from the mismatch of the lattice constants ($a=3.9$ Å in cubic $SrTiO_3$ versus $a=3.86$ Å in $YBa_2Cu_3O_6$). However, recent x-ray studies of the interface arrangement[6,7] give clear indications of incompletely grown unit cells of the cuprate film at the $SrTiO_3$ substrate, which may drastically change the interfacial electronic properties.

In this case the interface between polar layers, formed with the anisotropic $YBa_2Cu_3O_6$-crystal structure, and nonpolar $SrTiO_3$ (001) planes would result in the so-called "polar catastrophe" which appears on account of the divergent electrical potential.[8] The electronic compensation of the divergence can be achieved by a redistribution of the extra charge carriers near the interface, which leads to a dramatic change of the electronic states in such a heterostructure. The possibility of such an electronic reconstruction has been demonstrated by Hesper *et al.* for a polar (111) surface of K_3C_{60}.[9]

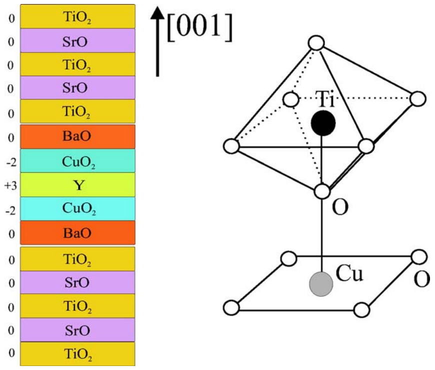

FIG. 1. (Color online) Scheme of a YBaCuO/$SrTiO_3$ sandwich where the polar interfaces appear due to the incomplete $YBa_2Cu_2O_6$-unit cell with an interface structural configuration shown in detail on the right.

To illustrate the resulting electronic properties, we consider first a superlattice formed on the basis of a sandwich-type supercell. The YBaCuO/SrTiO supercell shown in Fig. 1 consists of an incomplete copper oxide unit cell $YBa_2Cu_2O_6$ shared between two layers, each containing two unit cells of $SrTiO_3$. Effectively, the interface bonding here appears by a "substitution" of the CuO chains, terminating a full $YBa_2Cu_3O_{7-\delta}$ cell, with the TiO_2 planes that is illustrated in the right panel of Fig. 1. Our choice of interface bonding is strongly motivated by recent TEM studies of the $YBa_2Cu_3O_{7-\delta}$ films and similar compounds grown on $SrTiO_3$ with pulsed laser deposition technique.[6] In the case when the substrate of $SrTiO_3$ is terminated by a TiO_2 layer, the determined interface bonding arrangement is typically a stack of $\ldots/SrO/TiO_2/BaO/CuO_2/Y/CuO_2/BaO/CuO/\ldots$ layers. Such structural stacks suggest an interface chemical bonding Ti-O-Cu with the oxygen of the BaO layers shared between the CuO_2 and TiO_2 planes. From the electrostatical point of view, the initial "bulk-type" electronic charging of the constituent layers indicated in the left panel of Fig. 1 would result in one extra hole, which is needed in order to compensate the polarity. From the point of view of symmetry, this compensation leads to a doping of each block $\ldots/SrO/TiO_2/BaO/CuO_2$ by 0.5 holes.

To understand the redistribution of the extra charge density, which would appear near the interface, we calculated the densities of states of a $YBa_2Cu_2O_6/SrTiO_3$ sandwich using the linearized augmented plane wave method (LAPW) implemented in the WIEN2K package.[10] Technical details include the SIC variant of the LSDA+U method[11] on a $9\times 9\times 1$ $\boldsymbol{k}$-point grid with $U=8$ eV and $J=0.8$ eV on the Cu 3d orbitals. The lattice constants $a=b=3.8984$ Å are fixed to the structural values of $SrTiO_3$, whereas the optimized interface distance $\Delta=1.85$ Å between the apical oxygens of BaO layers and TiO_2 planes has been found by the minimization of the total energy, which corresponds to $c=27.53$ Å.

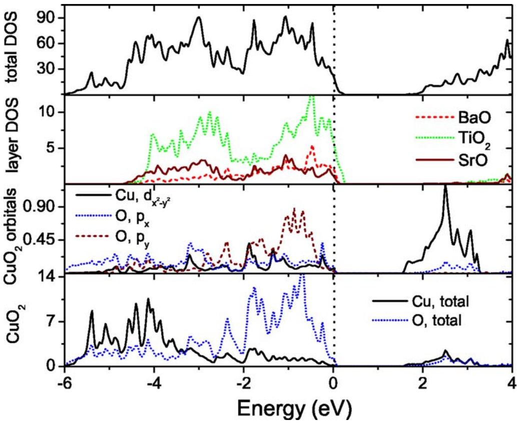

FIG. 2. (Color online) Density of states of the $SrTiO_3/YBa_2Cu_2O_6/SrTiO_3$ sandwich calculated within the LSDA+U approach with $U=8$ eV and $J=0.8$ eV for the electrons in Cu 3d orbitals. The zero of energy is at the Fermi level.

Figure 2 shows the calculated density of states where the position of the Fermi level E_F is indicated by dots. One can immediately identify the metallic state with hole carriers in the superlattice from the total density of states as originating from the oxygen p states. We note that, similar to bulk $YBa_2Cu_2O_6$, the Cu $d_{x^2-y^2}$ states are empty and separated by a gap of 1.34 eV from oxygen 2p whereas Cu $d_{3z^2-r^2}$ and t_{2g} bands remain below the Fermi level. As one can see from Fig. 2, a substantial amount of charge-compensating hole density is distributed over the CuO_2 planes. However, we find that also BaO layers as well as the first interface TiO_2 and SrO planes are doped. The upper boundaries of the O p bands of the more distant SrO and TiO_2 planes (with respect to the interface) remain almost on the same level with E_F, which implies that the charge is confined essentially in the interface block of $SrO/TiO_2/BaO/CuO_2$ layers. Figure 3 shows the distribution of hole density, spatially resolved along the z ([001]) direction within this interface block and calculated for optimized ($\Delta=1.85$ Å) and unrelaxed ($\Delta=1.94$ Å) sandwiches. To obtain this quantity, we have generated the charge density in the energy interval between the Fermi level and the top of the valence band. Specifically, we obtain that, although approximately 5% of the hole density is located in the CuO_2 planes, the major part is concentrated within the BaO ($\approx 25\%$) and the first TiO_2 (48%) and SrO (12%) layers. This suggests a finite metallic conductivity in the titanate, BaO, and copper oxide planes. Furthermore, while the relaxation of the structure leads to a reduction of the hole density in the BaO plane and to its redistribution within the interface SrO and more distant planes, the hole density in the CuO_2 planes remains almost unaffected.

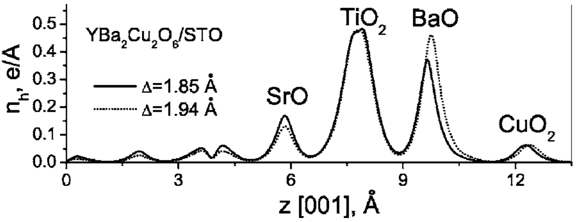

FIG. 3. Hole-density distribution near the $YBa_2Cu_2O_6/SrTiO_3$ interface for optimized ($\Delta=1.85$ Å) and unrelaxed ($\Delta=1.94$ Å) cases. The position $z=0$ is at the bottom TiO_2 plane of the $SrTiO_3/YBa_2Cu_2O_6/SrTiO_3$ sandwich.

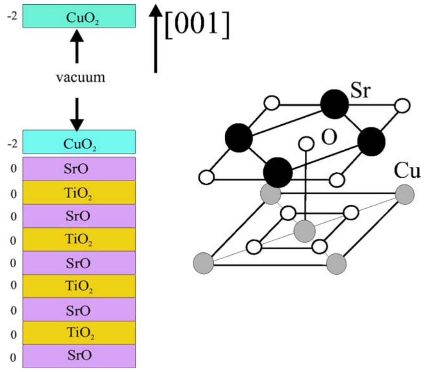

FIG. 4. (Color online) Scheme of a polar $CuO_2/SrTiO_3$ superlattice where a STO layer is terminated by a SrO plane. The right side shows a structural configuration, which appears at the interface.

Our results for the hole charge in the copper oxide planes of cuprate-titanate heterostructures clearly demonstrate that, apart from chemical doping, the interface polarity is another important mechanism that modulates the doping level in the cuprate films. We refer to this charge density as *predoped hole density* when we consider field-effect devices. In superconducting field-effect devices, operated by electrostatic charging, an initial predoped hole density, caused by the interface, may have striking consequences for their performance. The most important feature is the T_c shift with electrostatic doping. It may be directly affected by the considered predoping ($x=0.025$) of the copper oxide film. Moreover, it appears that much higher hole-doping levels including strong overdoping at the interfaces can be obtained in other interface configurations when the first unit cell of $YBa_2Cu_3O_{7-\delta}$ at the interface remains incomplete.

To demonstrate such a structurally induced overdoping, we consider a case in which a copper oxide plane is directly deposited on a $SrTiO_3$ substrate terminated by SrO (Fig. 4). The direct deposition of the single $Cu^{2+}O_2^{4-}$ plane on the nonpolar titanate layer would require two extra holes to maintain the overall charge neutrality. To achieve such an extremely high doping level, interface electronic reconstruction is inevitably required. The importance of electronic reconstruction is strongly supported by a significant smoothing of interference fringes observed with anomalous x-ray scattering in doped $La_2CuO_{4+\delta}$ films—an effect explained by the mobile carrier depletion in cuprate films near the $SrTiO_3$ substrate.[7] Apart from the electronic mechanism, other forms of interface reconstruction could modify the chemical composition. For example, the ionic compensation due to the cation intermixing and oxygen vacancies (oxygens missing in CuO_2 during the growth) will be a competing mechanism to compensate the polarity.[8] However, it is still instructive to enforce atomically flat and stochiometric surfaces in order to investigate comprehensively the electronic mechanism.[12]

In our theoretical studies, in order to focus on the effect of electronic reconstruction, we have introduced a decoupling vacuum layer of 13 Å thickness between the CuO_2 surfaces in the superlattice of the same slab geometry, as shown in Fig. 4. Furthermore, we have optimized the superlattice structure with a relaxed distance $\Delta=1.83$ Å between the interface CuO_2 and SrO which corresponds to a total energy minimum. The electronic density of states calculated from LSDA+U is shown in Fig. 5. Here we see that the effect of hole doping is more pronounced than in the case of the $YBa_2Cu_2O_6/SrTiO_3$ sandwich: the energy gap between O p and Cu d states basically disappears and the Fermi level is located well below the top of the valence band that characterizes a metallic state with hole carriers. The hole charge is present in the CuO_2 planes, where it is hybridized between the oxygen p_x and p_y, and Cu d orbitals. Also, there is clear evidence for holes in the first SrO layer and in the next TiO_2 layer of $SrTiO_3$. In these layers, E_F is also located below the top of the O p bands.

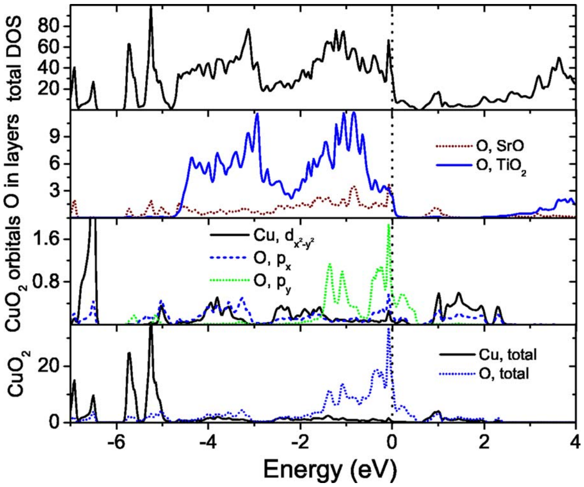

FIG. 5. (Color online) Density of states of the superlattice with CuO_2 deposited on $SrTiO_3$, terminated by SrO (LSDA+U studies). The zero of energy is at the Fermi level.

How is the hole charge redistributed near the interface? To provide more details, we have calculated the density of holes in the planes nearest to the interface. The results in Fig. 6 show that most of the charge (about 80%) is confined to the CuO_2 plane and a substantial amount of hole density is located in the first SrO plane (about 11%) and more distant TiO_2 (8%) plane. Consequently, such heavy overdoping of CuO_2 should completely exclude any possibility for a superconducting state in the interface unit cells of the cuprate films.

As the crystal structure of $YBa_2Cu_3O_{7-\delta}$ is closely compatible with the perovskite $SrTiO_3$, all possible basic polar interface configurations can be effectively reduced to the dis-

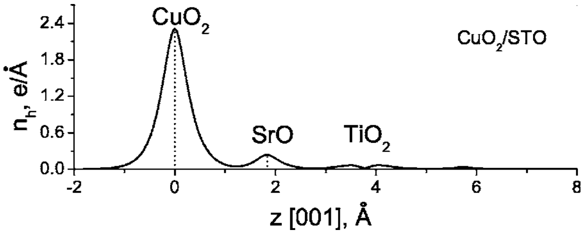

FIG. 6. Hole-density distribution in the interface planes of the $CuO_2/SrTiO_3$ superlattice. Here $z=0$ corresponds to the location of the lower CuO_2 plane.

cussed two cases. In the first case (A) with $\mathrm{TiO_2}$ termination of $\mathrm{SrTiO_3}$, the first interface layer in the incomplete cell of $\mathrm{YBa_2Cu_3O_{7-\delta}}$ is expected to be BaO in order not to disturb the perovskite stacking. In the second case (B) with SrO termination of $\mathrm{SrTiO_3}$, the $\mathrm{CuO_2}$ layer is the most compatible for a continuous stacking (cf. Fig. 4). In both of these situations, the interface polarity leads to a hole density in $\mathrm{CuO_2}$ ranging from ~ 0.05 [case (A)] to ~ 1.6 [case (B)] holes per interface. In addition, due to steps and different stacking modes at the interfaces,[6] one expects rather a combination of cases (A) and (B). In fact, the latter implies the formation of weak links with either connected or disconnected underdoped and heavily overdoped regions. For such possible interface configurations, the direct consequence of the deduced predoping is a strong suppression of the T_c shift related to the electrostatic hole injection—or even a complete suppression of the superconductivity in cuprate films of unit cell thickness.

Up to now, the growth of high-quality $\mathrm{YBa_2Cu_3O_{7-\delta}}$ films terminated by complete unit cells remains a challenging task due to their roughness caused by ionic compensation of the interface polarities. In order to make a step towards perfect interfaces, where the hole injection would completely determine the superconducting dome, we need to consider other superconducting cuprates as possible candidates for nonpolar interfaces. In this context, a proposal for field-effect experiments is to grow $\mathrm{Sr_2CuO_2Cl_2}$ (SCOC) or $\mathrm{Ca_2CuO_2Cl_2}$ (CCOC) on $\mathrm{SrTiO_3}$. These systems can be perfectly cleaved between SrCl(CaCl) layers, and the deposition on $\mathrm{SrTiO_3}$ terminated by $\mathrm{TiO_2}$ would result in a nonpolar interface stack $\ldots\mathrm{TiO_2/SrCl/CuO_2/SrCl/SrCl/}\ldots$ (for CCOC a similar stack with Ca → Sr). Our LSDA calculations for such superlattices suggest an insulating state. The lattice constants' mismatch ($a=b=3.96$ Å in SCOC) results in a slight increase ($V_{pd}/V_{pd}^{\mathrm{bulk}}=1.074$) of the p-d hybridization integral V_{pd}.[13] Assuming the on-site Hubbard coupling not to be affected by strains, the direct interface effect in $\mathrm{SCOC/SrTiO_3}$ is a renormalization of the parameters of the effective t–J model[14] ($t/t_{\mathrm{bulk}}=1.15$, $J/J_{\mathrm{bulk}}=1.33$) which would only increase T_c, without changing the doping level. Such superlattices, where the combination of chemical doping by Na and electrostatic hole injection should not be affected by interface predoping, would be ideal candidates to probe the electrostatic field effect.

This work was supported through the DFG Grant No. SFB-484, BMBF Grant No. 13N6918A, DAAD Grant No. D/03/36760, and by the Canadian funding agencies NSERC and CIAR. The research was performed with infrastructure funded by CFI and British Columbia Knowledge Development Fund (a parallel computer for compact-object physics). Grants of computer time from the Leibniz-Rechenzentrum München are gratefully acknowledged.

---

*Also at the Institute for Condensed Matter Physics, 79011 Lviv, Ukraine.

[1] A. Ohtomo, D. A. Muller, J. L. Grazul, and H. Yu. Hwang, Nature (London) **419**, 378 (2002); S. Okamoto and A. J. Millis, *ibid.* **428**, 630 (2004).

[2] J. Mannhart, D. G. Schlom, J. G. Bednorz, and K. A. Muller, Phys. Rev. Lett. **67**, 2099 (1991); C. H. Ahn, S. Gariglio, P. Paruch, T. Tybell, L. Antognazza, and J.-M. Triscone, Science **284**, 1152 (1999).

[3] G. Yu. Logvenov, A. Sawa, C. W. Schneider, and J. Mannhart, Appl. Phys. Lett. **83**, 3528 (2003); A. Cassinese, G. M. De Luca, A. Prigiobbo, M. Salluzzo, and R. Vaglio, *ibid.* **84**, 3933 (2004).

[4] S. Oh, M. Warusawithana, and J. N. Eckstein, Phys. Rev. B **70**, 064509 (2004); J. N. Eckstein and I. Bozovic, Annu. Rev. Mater. Sci. **25**, 679 (1995).

[5] N. Pavlenko and T. Kopp, Phys. Rev. B **72**, 174516 (2005).

[6] J. G. Wen, C. Traeholt, and H. W. Zandberger, Physica C **205**, 354 (1993); S. Bals, G. Rijnders, D. H. A. Blank, and G. Van Tendeloo, *ibid.* **355**, 225 (2001).

[7] P. Abbamonte, L. Venema, A. Rusydi, G. A. Sawatzky, G. Logvenov, and I. Bozovic, Science **297**, 581 (2002).

[8] D. Wolf, Phys. Rev. Lett. **68**, 3315 (1992); M. Kiguchi, S. Entani, K. Saiki, T. Goto, and A. Koma, Phys. Rev. B **68**, 115402 (2003); C. Noguera, F. Finocchi, and J. Goniakowski, J. Phys.: Condens. Matter **16**, S2509 (2004).

[9] R. Hesper, L. H. Tjeng, A. Heeres, and G. A. Sawatzky, Phys. Rev. B **62**, 16046 (2000).

[10] P. Blaha *et al.*, *WIEN2K, An Augmented Plane Wave+Local Orbitals Program for Calculating Crystal Properties*, ISBN 3-9501031-1-2 (TU Wien, Austria, 2001).

[11] V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyzyk, and G. A. Sawatzky, Phys. Rev. B **48**, 16929 (1993).

[12] In the more general case when a multiplanar YBaCuO layer terminated by $\mathrm{CuO_2}$ is deposited on $\mathrm{SrTiO_3}$, one extra hole is required to compensate the polarity. Despite the high doping level, such a structure will be more stable than a single $\mathrm{CuO_2}$ layer due to the compensating microscopic fields.

[13] Here we use Harrison's estimate $V_{pd}\sim a^{-4}$; see W. A. Harrison, *Elementary Electronic Structure* (World Scientific, Singapore, 2004).

[14] F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988); A. Macridin, M. Jarrell, T. Maier, and G. A. Sawatzky, Phys. Rev. B **71**, 134527 (2005).