PHYSICAL REVIEW B VOLUME 37, NUMBER 1 1 JANUARY 1988

Cu-induced surface disruption of $La_{1.85}Sr_{0.15}CuO_4$

D. M. Hill, Y. Gao, H. M. Meyer III, T. J. Wagener, and J. H. Weaver
Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455

D. W. Capone II
Materials Science Division, Building 223, Argonne National Laboratory, Argonne, Illinois 60439

(Received 14 September 1987)

Interface reactions for vapor-deposited Cu on $La_{1.85}Sr_{0.15}CuO_4$ were investigated with x-ray photoemission and inverse photoemission. Strong Cu—O reactions indicate oxygen removal and the Cu $2p_{3/2}$ emission shows conversion of the superconductor Cu^{2+} configuration to Cu^{1+} within 40–50 Å of the surface. Valence-band results show a loss of the Cu $3d_{x^2-y^2}$–O $2p_{x,y}$ electronic states near the Fermi level, and we conclude that the surface layer is not superconducting. Changes in the occupied and empty electronic states of La at low Cu coverages provide additional evidence of Cu-induced reaction. A metallic overlayer begins to form at ~2 Å nominal Cu coverage as these surface reactions become diffusion limited at room temperature.

The recently discovered high-T_c superconductors $La_{1.85}Sr_{0.15}CuO_4$ and $YBa_2Cu_3O_{7-x}$ hold the promise of a technological revolution.[1,2] Much of the work of the past several months has emphasized the crystal structure,[3] the electronic structure,[4] and the composition dependence of T_c.[5] Relatively little is known about how these materials interact with their environment[6] although applications will depend critically on those interactions. Of particular interest is interaction with overlayers of their constituent elements. If there is intermixing or reaction at the interface, one would expect that changes in the oxygen stoichiometry would adversely affect the superconducting properties at the interface and introduce high-resistance patches of unknown dimension. In investigations of constituent-element-overlayers on high-T_c materials, Cu is an important starting point since Cu—O bonding plays a critical role in superconductivity. Moreover, the pervasiveness of Cu as an electrical conductor implies that Cu-high-T_c interactions might be important for future applications.

In this paper, we discuss the room-temperature evolution of the Cu/$La_{1.85}Sr_{0.15}CuO_4$ interface. High-resolution x-ray photoemission (XPS) and inverse photoemission (IPES) have been used to measure changes in the chemical states for Cu layers grown by *in situ* deposition onto clean polycrystalline $La_{1.85}Sr_{0.15}CuO_4$. Reactions were determined from shifts in the energies of the occupied and unoccupied electronic states and by changes in the emission intensities from each element. We will show that Cu adatoms induce the removal of O from the superconductor on a scale much larger than the nominal overlayer thickness and the electronic states of all species in the substrate are affected. These reactions notwithstanding, a metallic Cu overlayer grows after Cu—O reactions become diffusion limited.

XPS measurements were done with a Surface Science Instruments SSX-100-3 spectrometer using a 300 μm diameter monochromatized Al K_α x-ray beam. The photoelectrons were energy analyzed with a multichannel hemispherical analyzer operated at a pass energy of 50 eV. The angle of emission relative to the normal of the sample surface was nominally 60°, and the cone of acceptance of the analyzer was 30°.[7] IPES measurements were performed by directing a collimated monoenergetic electron beam onto the sample surface and measuring the distribution of emitted photons that result when the incident electrons radiatively decay to empty states. Measurements were taken at incident electron energies of 20.25 and 28.25 eV relative to the Fermi level of the sample and the beam current was ~20 μA.[6] The probe depth ranged from ~12 Å in IPES to ~50 Å in XPS.

$La_{1.85}Sr_{0.15}CuO_4$ samples in the form of posts were cut from high-density (>90%), single-phase polycrystalline disks with a transition temperature of ~35 K.[8] The clean surfaces were obtained by fracturing the posts *in situ* at pressures better than 6×10^{-11} Torr. Previous studies have shown that surfaces prepared in this manner are reproducible and stable with respect to x-ray and low-energy electron bombardment over the times needed for XPS and IPES measurements.[6,9] Cu was evaporated from W baskets at rates of ~0.5 Å/min, as measured by quartz oscillators. Thicknesses reported are nominal values for a uniform overlayer. 1 Å would correspond to 8.5×10^{14} atoms/cm^2 or 0.56 ML of the close packed plane of Cu. Evaporations were done at pressures $\leq 2\times10^{-10}$ Torr. Measurements were made for coverages of 0.25, 0.5, 1, 2, 4, 8, 16, 30, 50, 80, and 100 Å with both instruments but only representative spectra are shown for visual clarity.

In Fig. 1 we show core-level energy-distribution curves (EDC) for Cu $2p_{3/2}$ for coverages of 0–100 Å. The peak heights are normalized to emphasize changes in the peak shape. The Cu $2p_{3/2}$ emission for the clean surface demonstrates that the dominant oxidation state of Cu is nominally 2^+. The Cu $2p$ spectral features have been analyzed by van der Laan, Westra, Haas, and Sawatsky[10] for divalent Cu systems and are made up of a main line and highter binding energy satellites. The main line reflects final-state screening of the $2p_{3/2}$ core hole by a $3d^{10}$ configuration and a suitably symmetrized ligand p

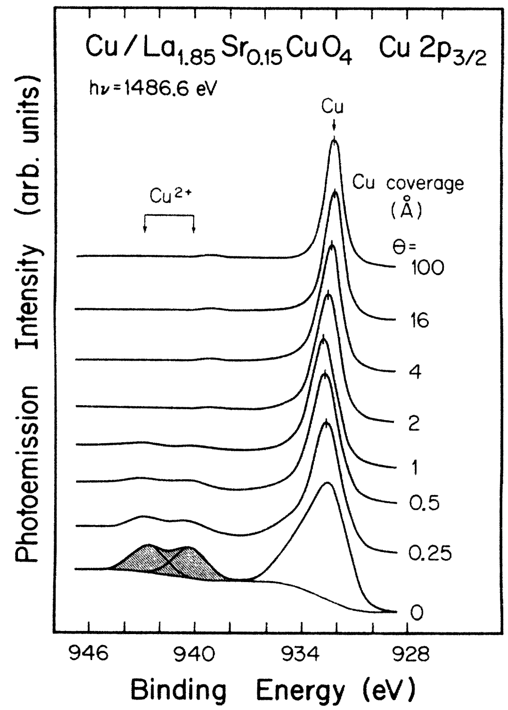

FIG. 1. Core-level EDC's showing the Cu $2p_{3/2}$ emission for the Cu/La$_{1.85}$Sr$_{0.15}$CuO$_4$ interface. The peak heights are normalized for visual clarity. The clean surface spectrum (bottom curve) shows the characteristic behavior of the Cu^{2+} oxidation state, but these are rapidly lost as Cu^{2+} is converted to Cu^{1+}. Ultimately, the EDC's converge to Cu metal as interface reactions become diffusion limited.

hole, denoted $\underline{2p_{3/2}3d^{10}L}$. The satellites represent the envelope of eight multiplet states derived from the $2p_{3/2}3d^9$ configuration. The main line is clearly asymmetric and this asymmetry led us to erroneous lineshape decompositions and the conclusion of mixed Cu^{1+} and Cu^{2+} valence. As shown in Fig. 1, the deposition of Cu greatly decreases the Cu^{2+} emission as the dominant configuration is converted to Cu^{1+}. Indeed, the Cu^{2+} states become undetectable within the 50 Å XPS probe depth by ~48 Å nominal Cu coverage. The full width at half maximum (FWHM) of the Cu $2p_{3/2}$ peak decreases from 1.5 eV at 4 Å coverage to 1.2 eV at 16 Å, and remains constant thereafter. Detailed examination of the Cu $2p_{3/2}$ lineshapes shows two general trends. For coverages from 0.25 to 1 Å, the main $2p_{3/2}$ peak narrows as the high-binding-energy shoulder associated with Cu^{2+} is lost and shifts 0.4 eV toward higher binding energy. For coverages greater than 1 Å, the peak shifts 0.6 eV back toward lower binding energy, reaching a constant value for coverages greater than 8 Å. The net Cu $2p$ emission intensity for coverages below ~2 Å changes only by the amount of added Cu, indicating that the Cu in the Cu^{2+} in the superconductor was reduced to a Cu^{1+} state. There is no indication of the formation of CuO during interface reaction, but Cu$_2$O is likely. Attenuation of the substrate signals for these coverages is insignificant. Thus, the disappearance of the Cu^{2+} emission indicates that the Cu adatoms have a profound impact on the stoichiometry of the superconductor surface region. The Cu—O bonding configuration at the surface appears to be more favorable than that in the bulk ceramic. Although surprising, it is not inconsistent with the high mobility of O and the variable stoichiometry encountered in this system.

It is difficult to distinguish elemental Cu from the Cu^{1+} oxidation state of disrupted La$_{1.85}$Sr$_{0.15}$CuO$_4$ because of the slight variation in Cu $2p_{3/2}$ binding energy. Although the coverage at which metallic Cu begins to nucleate cannot be identified from the Cu emission alone, it can be determined from other measurements, as shown below. The final energy of the Cu $2p_{3/2}$ state lies 0.2 eV to lower binding energy than the maximum of the main peak for the superconductor. As shown in Fig. 1, there is also a satellite feature associated with this structure, shifted 6.7 eV, and the metallic $2p$ core line is much sharper than for the superconductor (1.15 eV FWHM for Cu vs ~2.8 eV).

Figure 2 shows valence band EDC's for the clean surface and for representative coverages of Cu to illustrate the evolution of the interface from La$_{1.85}$Sr$_{0.15}$CuO$_4$ through an intermediate, nonmetallic system to a final overlayer of metallic Cu. The clean surface spectrum shows a broad band of states derived from Cu $3d$–O $2p$ hybrid extending from ~1 to ~8 eV below E_F and a low density of states immediately below E_F. These states at E_F have been shown to be derived from the antibonding Cu $3d_{x^2-y^2}$–O $2p_{x,y}$ orbitals.[4] The most important changes induced by Cu adatoms correspond to a loss in emission within ~1.5 eV of E_F and are identified with the arrow of Fig. 1. Although the emission did not go to zero, as has been observed when reactive transition-metal over-

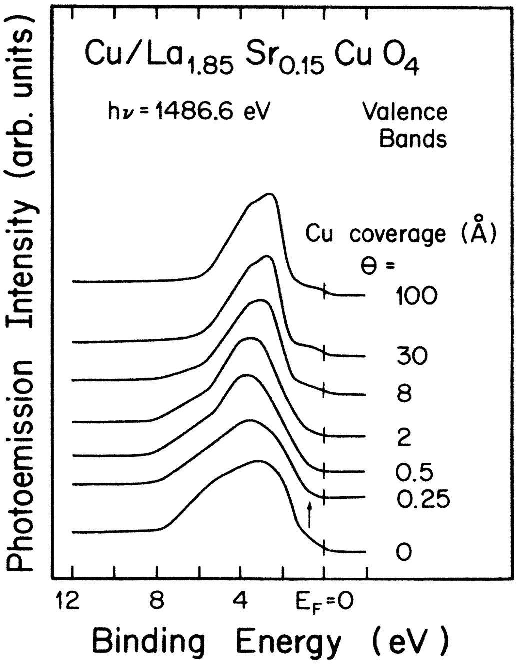

FIG. 2. XPS valence-band spectra for Cu/La$_{1.85}$Sr$_{0.15}$CuO$_4$. The arrow points to the region where Cu $d_{x^2-y^2}$—O $P_{x,y}$ emission is lost due to the deposition of Cu. Emission at the Fermi level reappears when Cu metal starts to nucleate at ~2 Å coverage.

layers are grown on these ceramic superconductors,[6,9] the valence-band spectrum for 0.5 Å shows an extremely low state density near E_F. At higher coverages, the emission from this region increases so that the characteristic emission for the Cu 4*sp*-derived bands was evident by 8 Å coverage. By 30 Å coverage the valence-band emission was essentially that of pure Cu. (The d^8 final-state satellite that appears 12.4 eV below E_F for $La_{1.85}Sr_{0.15}CuO_4$ is not observed in XPS, but the evolution from satellites characteristic of d^8 to those of metallic Cu has been observed in synchrotron radiation photoemission studies of Cu/$YBa_2Cu_3O_{6.9}$.)

Complementary conduction-band information can be obtained from IPES measurements, as summarized in Fig. 3 for incident electron energies of 28.25 eV. The photon distribution curve (PDC) for the clean cleaved surface (top curve) shows very low emission to ~3.5 eV above E_F. Well-defined features appear at 5.8 and 8.7 eV above E_F and these correspond to empty La 5*d* and 4*f* levels, as reported elsewhere.[6,9] The deposition of Cu adatoms causes significant losses of emission within ~1.5 eV of E_F for $\Theta \leq 1$ Å, consistent with Fig. 2. A shift to lower binding energy by 0.4 eV for the La 5*d* and 4*f* features was observed for $\Theta \leq 1$ Å, but these changes stabilized by 2 Å deposition. Analysis of the integrated intensity of the La 4*f*- and 5*d*-derived states shows exponential attenuation as a function of Cu overlayer thickness. This implies that continued interactions are diffusion limited.

XPS measurements of the La occupied core levels provide additional information about the changing chemical environment of La. The clean surface La EDC shown in Fig. 4 is similar to that of La_2O_3 where the higher binding energy feature is a final-state satellite.[11] The deposition of 2 Å of Cu induces a shift toward higher binding energy of 0.4 eV for both components, but there are no further chemical effects for higher coverages of Cu. The shift for the La–O emission is consistent with the chemical state of the La becoming more like metallic La and parallels the shifts seen in the the empty 4*f* levels (Fig. 3). Analysis of the changing intensities for the La $3d_{5/2}$ core level and the empty La 4*f* level showed an exponential decrease as a function of Cu coverage, suggesting that there is minimal intermixing of La and the Cu overlayer. The Sr 3*d* results mirror those for La.

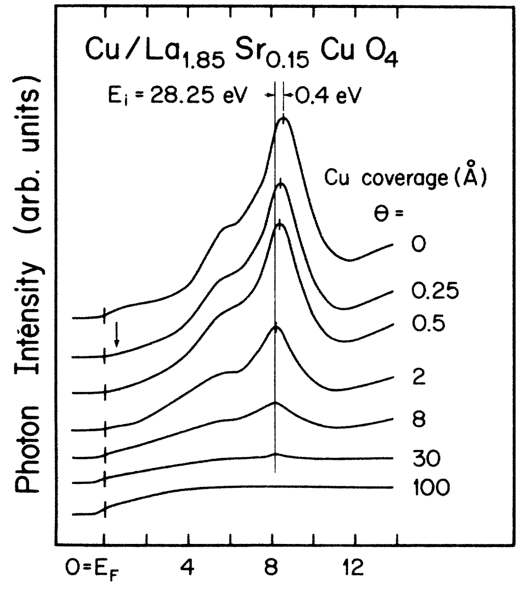

FIG. 3. Inverse photoemission spectra of the empty states within 13 eV of E_F for the Cu/$La_{1.85}Sr_{0.15}CuO_4$ interface. The features at 5.8 and 8.7 eV are the La 5*d* and La 4*f* states, respectively; changes in the La 4*f* emission results from the chemical modification of the local environment around the La atoms as oxygen is withdrawn. Again, the arrow indicates the loss of states near E_F. At high coverage, the spectra are indistinguishable from pure Cu.

Finally, the O 1*s* core level EDC's (not shown) reveal a total shift of 0.6 eV toward higher binding energy when 1 Å of Cu is deposited, and that this does not change at higher coverage. The O 1*s* FWHM increases from 1.7 eV for the clean surface to 2 eV at 1 Å Cu coverage, but decreases to 1.5 eV at 100 Å coverage. The intensity attenuation rate for the O 1*s* emission is slower than that for the La and Sr signals and O 1*s* emission remains after emission from other substrate species has vanished. Hence, O liberated from the superconductor forms a Cu–O phase at low coverage but O atoms which are not chemically trapped near the interface can diffuse into the Cu overlayer.

This study suggests that the Cu/$La_{1.85}Sr_{0.15}CuO_4$ interface formation occurs in two stages. At low coverages, ≤ 1 Å, Cu adatoms react with O from the superconductor, disrupting the substrate crystal structure and forming a metastable, nonstoichiometric Cu–O phase. This Cu–

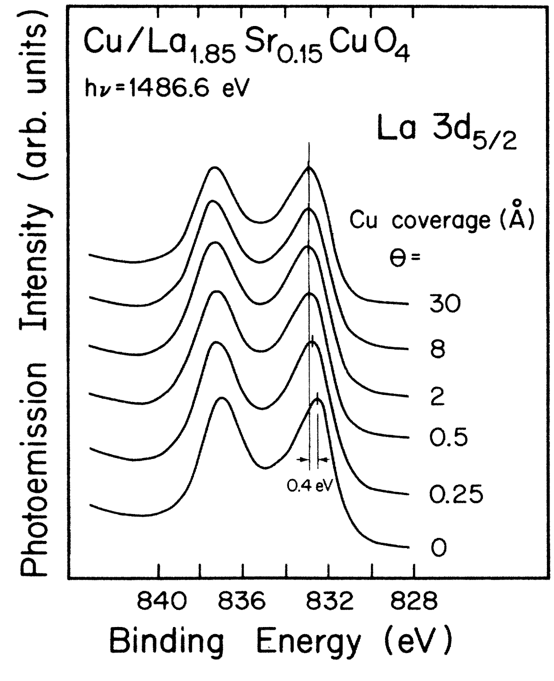

FIG. 4. La $3d_{5/2}$ core-level EDC's showing the shift in binding energy at low Cu coverages, but minimal changes for $\Theta \geq 8$ Å.

O reaction product, together with the modified Cu configurations of the substrate, shifts the Cu $2p_{3/2}$ emission centroid to higher binding energy for low Cu coverages. Changes in the La core levels and the antibonding Cu $3d_{x^2-y^2}$—O $2p_{x,y}$ orbitals near the Fermi level confirm the strong interaction of the Cu overlayer with O from the superconductor. This suggests disruption of the planar Cu—O bonds to form more energetically favorable bonds with Cu in the overlayer. The rapid attenuation of emission characteristic of Cu^{2+} implies disruption of the superconductor on a scale much larger than the overlayer thickness for these coverages. At this point it is impossible to unambiguously describe the distribution of atoms and the microscopic metallic/semiconducting/insulating character of the interface. The second stage occurs when the complex Cu—O layer acts as a buffer to reduce further interaction with the substrate. At this stage, there is O diffusion into the overlayer, similar to selective anion segregation at reactive metal/ III-V semiconductor interfaces.[12] The shift of the Cu $2p_{3/2}$ emission to lower binding energy reflects the growth of metallic Cu on the reacted region. This results in increased emission at the Cu-to-Cu^{1+} energy and simultaneously attenuates the emission from the reacted region. The valence bands also show convergence to Cu metal.

In this paper we have shown that the Cu/$La_{1.85}Sr_{0.15}CuO_4$ interface is not passive and that Cu enrichment is likely to lead to undesirable properties in the superconductor. This system is most likely metastable, and reaction of the Cu overlayer with the superconductor is diffusion limited. These Cu-induced disruptions of the superconductor must be controlled if Cu is to be used as an electrical contact or passivating layer.

The work at the University of Minnesota was supported by the Office of Naval Research under Grant No. ONR-N00014-87-K-0029 and that at Argonne National Laboratory was supported by the Department of Energy under W-31-109-ENG-38.

---

[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2] C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and Y. Q. Wang, Phys. Rev. Lett. **58**, 405 (1987).

[3] See, for example, R. J. Cava, A. Santoro, D. W. Johnson, Jr., and W. W. Rhodes, Phys. Rev. B **35**, 6717 (1987); T. Seigrist, S. Sunshine, D. W. Murphy, R. J. Cava, and S. M. Zahurak, *ibid.* **35**, 7137 (1987).

[4] Band calculations have been reported by many groups, including L. F. Mattheiss, Phys. Rev. Lett. **58**, 1028 (1987); J. Yu, A. J. Freeman, and J. -H. Xu, *ibid.* **58**, 1035 (1987); W. E. Pickett, H. Krakauer, D. A. Papaconstantopoulos, and L. Boyer, Phys. Rev. B **35**, 7252 (1987); F. Herman, R. V. Kasowski, and W. Y. Hsu, *ibid.* **36**, 6904 (1987).

[5] R. B. van Dover, R. J. Cava, B. Batlogg, and E. A. Rietman, Phys. Rev. B **35**, 5337 (1987).

[6] D. M. Hill, H. M. Meyer III, J. H. Weaver, B. Flandermeyer, and D. W. Capone II, Phys. Rev. B **36**, 3979 (1987); J. H. Weaver, Y. Gao, T. J. Wagener, B. Flandermeyer, and D. W. Capone II, *ibid.* **36**, 3975 (1987); Y. Gao, T. J. Wagener, J. H. Weaver, B. Flandermeyer, and D. W. Capone II, Appl. Phys. Lett. **51**, 7032 (1987); H. M. Meyer III, T. J. Wagener, D. M. Hill, Y. Gao, S. G. Anderson, S. D. Krahn, J. H. Weaver, B. Flandermeyer, and D. W. Capone II, *ibid.* **51**, 1118 (1987).

[7] S. A. Chambers, D. M. Hill, F. Xu, and J. H. Weaver, Phys. Rev. B **3**, 634 (1987).

[8] J. D. Jorgensen, H. B. Schuttler, D. G. Hinks, D. W. Capone II, K. Zhang, M. B. Brodsky, and D. J. Scalapino, Phys. Rev. Lett. **58**, 1024 (1987).

[9] Y. Gao, T. J. Wagener, J. H. Weaver, A. J. Arko, B. Flandermeyer, and D. W. Capone II, Phys. Rev. B **36**, 3471 (1987).

[10] G. van der Laan, C. Westra, C. Haas, and G. A. Sawatsky, Phys. Rev. B **23**, 4369 (1981), and references therein.

[11] R. Kumar, M. H. Mintz, and J. W. Rabalais, Surf. Sci. **147**, 37 (1984).

[12] Zhangda Lin, F. Xu, and J. H. Weaver, Phys. Rev. B **36**, 5777 (1987), and references therein.