RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 39, NUMBER 4 1 FEBRUARY 1989

Reaction of Rb and oxygen overlayers with single-crystalline $Bi_2Sr_2CaCu_2O_{8+\delta}$ superconductors

P. A. P. Lindberg, Z.-X. Shen, B. O. Wells, and D. S. Dessau
Stanford Electronics Laboratories, Stanford University, Stanford, California 94305

D. B. Mitzi
Department of Applied Physics, Stanford University, Stanford, California 94305

I. Lindau and W. E. Spicer
Stanford Electronics Laboratories, Stanford University, Stanford, California 94305

A. Kapitulnik
Department of Applied Physics, Stanford University, Stanford, California 94305

(Received 19 September 1988)

Single crystals of $Bi_2Sr_2CaCu_2O_{8+\delta}$ superconductors, *in situ* cleaved and modified by Rb and oxygen overlayers, have been studied using ultraviolet and x-ray photoemission spectroscopy. The core-level results show that Rb strongly reacts with the Bi and O states, while the Cu and Sr states are left unchanged. This observation strongly indicates that the Bi-O plane forms the surface layer. Subsequent exposure to oxygen results in new oxygen states at the surface as monitored by the O 1*s* core-level data. For both Rb and oxygen overlayers the valence-band spectra are severely altered. In particular, new valence-band states, presumably of oxygen character, are formed.

The promising superconducting properties of Bi-Sr-Ca-Cu-O related compounds have stimulated a number of photoemission studies of this type of materials.[1-5] The results obtained firmly show a finite density of states at the Fermi energy, and a high stability in ultrahigh vacuum, thus showing promise for many important applications. So far, most of these studies have focused on the electronic structure of *in situ* cleaned surfaces of polycrystalline and single-crystalline samples. In this study, we instead concentrate on the interaction of $Bi_2Sr_2CaCu_2O_{8+\delta}$ with adsorbates of Rb and oxygen using photoelectron spectroscopy, thus complementing an earlier synchrotron radiation study.[6] With the use of both He II (40.8 eV) and Mg *Ka* (1253.6 eV) radiation the effects on both the valence band and the different core levels of the adsorbates were followed for a series of exposures. For Rb adsorbates, the valence-band spectrum is drastically changed, suggesting that new oxygen states are formed at the surface, presumable due to Rb pulling oxygen from the bulk. Moreover, the core-level data show that Rb strongly reacts with the Bi and O states by shifting the Bi 4*f* and O 1*s* core levels towards higher binding energy by about 0.5 eV. The Sr and Cu states, on the other hand, are basically unaffected by the deposition of Rb. Specifically, the Cu valency, as determined by the satellite to main-line intensity ratio, remains the same. Upon subsequent adsorption of O_2 a pronounced shoulder appears in the O 1*s* core-level spectra, while no change of the Bi, Cu, and Sr core levels can be observed. In addition, three prominent features, two of which have already been seen for the Rb adsorbate, come up in the valence-band spectra. The results imply that the Bi-O plane forms the surface layer of the crystal, in agreement with results using scanning tunneling microscopy (STM).[7]

The photoemission experiments were carried out in a Varian photoemission chamber operating at a base pressure of 1×10^{-10} torr. A helium lamp and an x-ray source providing, respectively, He II (40.8 eV) and Mg *Ka* (1253.6 eV) radiation were used for excitation. The photoemitted electrons were analyzed by a cylindrical mirror analyzer (CMA). The total energy resolution was 0.3 and 1.2 eV using He II (40.8 eV) and Mg *Ka* (1253.6 eV) radiation, respectively. Details of the preparation and characterization of the single crystals of $Bi_2Sr_2CaCu_2O_{8+\delta}$ are described elsewhere.[8] They exhibited a drop to zero resistance at 90 K according to magnetic-susceptibility measurements. The single crystals were transferred into the photoemission chamber using a transfer arm attached to it. The crystals were then cleaved *in situ*. Low-energy electron diffraction (LEED) showed sharp diffraction spots characteristic of a well-ordered single-crystalline surface.[8] The surface cleanliness was checked using XPS for both the *in situ* cleaved crystal and the Rb and O_2 exposed surfaces. In all these cases the surfaces were found to be free of carbon (within the experimental sensitivity). Rb was deposited onto the surface using a carefully outgassed getter.[9] The oxygen exposure was determined by reading off the pressure on the ion gauge.

Photoemission spectra were recorded using He II (40.8 ev) and Mg *Ka* (1253.6 eV) radiation for the following set of surfaces: (1) a cleaved single crystal of $Bi_2Sr_2CaCu_2O_{8+\delta}$, (2) after subsequent Rb deposition, (3) followed by first an exposure to 3×10^3 L (1 L = 10^{-6} torr s) of O_2, and (4) then a total O_2 exposure of 5×10^4 L of O_2. In the following, the same notation (labeling of the spectra) will be used throughout the paper, and all spectra within a figure have been normalized to have the same maximum intensity.

Figure 1 shows the valence-band spectra using He II radiation. The spectrum of the cleaved crystal is in agreement with previous results on single- and polycrystalline samples of $Bi_2Sr_2CaCu_2O_{8+\delta}$.[1-5] The principal feature in the valence band extends from about −7 to −1 eV with a centroid position around −4 eV. On either side of the centroid, shoulders are observed at about −2 and −6 eV, as indicated in the figure. Although the density of states (DOS) sharply drops as the Fermi level is approached, a clear Fermi-level cutoff has been observed.[2] The broad feature between −13 and −9 eV is believed to consist of two separate structures, of which at least one is due to a Cu d^8 satellite.[4]

Upon deposition of Rb onto the cleaved surface, profound changes of the valence-band features occur. The position and line shape of the main structure are severely altered. The shoulder at −2 eV is now clearly resolved. Presumably, this feature is due to states of $Bi_2Sr_2CaCu_2O_{8+\delta}$ that do not react with the Rb overlayer. The deposition of Rb also results in peaks at about −11.5, −9.5, and −8.5 eV which we attribute to new surface oxygen states, the formation of which is promoted by Rb on the surface (see the core-level data below). The presence of Rb on the surface is evident from the Rb 4*p* emission around −15 eV.

As the surface then is exposed to various amounts of oxygen, the peaks at −11.5 eV (*A*) and −9.5 eV (*B*) become more intense, while the feature at −8.5 eV completely disappears. Moreover, at −5 eV a prominent peak (*C*) is clearly discernible. We note that the position of the Rb 4*p* structure is unaltered, indicating that no significant change of the Rb states occurs. All these results are in agreement with a recent synchrotron radiation study of the Rb/$Bi_2Sr_2CaCu_2O_{8+\delta}$ interface that also showed additional features at −11.5, −9.5, and −5 eV, as well as a shift of the main structure, upon exposure to adsorbates of Rb.[6] Since the intensity of these features is drastically enhanced by the Rb deposition followed by exposure to oxygen, it is natural to associate them with oxygen-related states.[10] Further evidence for this assignment is given by the core-level spectra presented below.

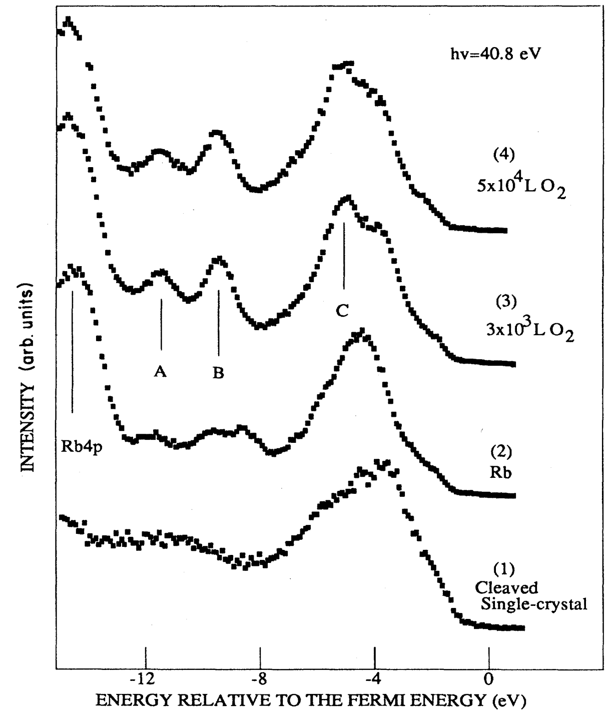

FIG. 1. Photoemission spectra using He II (40.8 eV) radiation of (1) a cleaved single crystal of $Bi_2Sr_2CaCu_2O_{8+\delta}$, and (2) after Rb deposition, (3) followed by exposure to 3×10^3 L (1 L = 10^6 torrs) of O_2, and (4) a total O_2 exposure of 5×10^4 L of O_2.

During the same series of adsorption experiments, core levels of the different constituents (apart from Ca, due to its low cross section) were also studied in order to gain further insight into the reaction of Rb and O_2 with the $Bi_2Sr_2CaCu_2O_{8+\delta}$ surface. In Fig. 2 we show the (a) Bi 4*f*, (b) O 1*s*, (c) Cu 2*p*, and (d) Sr 3*d* core-level spectra using the same notation as in Fig. 1. Concentrating first on the Bi 4*f* core level we note that the deposition of Rb results in a shift of 0.5 eV towards higher binding energy. A similar observation was previously found using synchrotron radiation.[6] This shift is tentatively attributed to a movement of the oxygen atoms away from the Bi atoms because of the Rb overlayer, which creates a more electropositive environment of the Bi ions at the surface. The subsequent exposure to oxygen, however, does not alter the position of the Bi 4*f* core level, suggesting that the Bi atoms are fairly stable in their new environment.

An even more drastic change occurs in the O 1*s* core level, as illustrated in Fig. 2(b). Again, the deposition of Rb causes a shift towards higher binding energy by about 0.5 eV. Moreover, the linewidth increases by approximately 30% from 2.2 to 2.8 eV [full width at half the maximum (FWHM)]. This increase in width suggests that the O 1*s* feature in curve (2) consists of two peaks, one attributed to unreacted oxygen at about −529 eV, and the other at about 1 eV higher binding energy (∼ −530 eV). As the surface is then exposed to oxygen [curves (3) and (4)], a prominent shoulder appears around −533 eV. It is clear that the appearance of this feature correlates with the observation of the 5-eV feature in the valence band shown in Fig. 1. Thus, we suggest that peak *C* and the higher binding energy shoulder in the O 1*s* core-level data are intimately related. The fact that both these peaks appear after exposure to O_2 points towards molecular oxygen species, such as O_2^{2-}, i.e., a peroxide ion as the origin. This assignment is supported by an earlier study on Bi-Sr-Ca-Cu-O superconductors as well as other perovskite-related materials, showing evidence of peroxides at the surface region.[11] We also note that the increased intensity of peaks *A* and *B* in the valence band correlates with the growth of the shoulder at about −533 in the O 1*s* core-level spectra. This finding points toward oxygen-related states as the origin of peaks *A* and *B* also. However, since peaks *A* and *B* already appear in the spectra from the Rb adsorbed surface, they, in contrast to peak *C*, do not require exposure to molecular oxygen for their existence.

In sharp contrast with the Bi 4*f* and O 1*s* data, are the

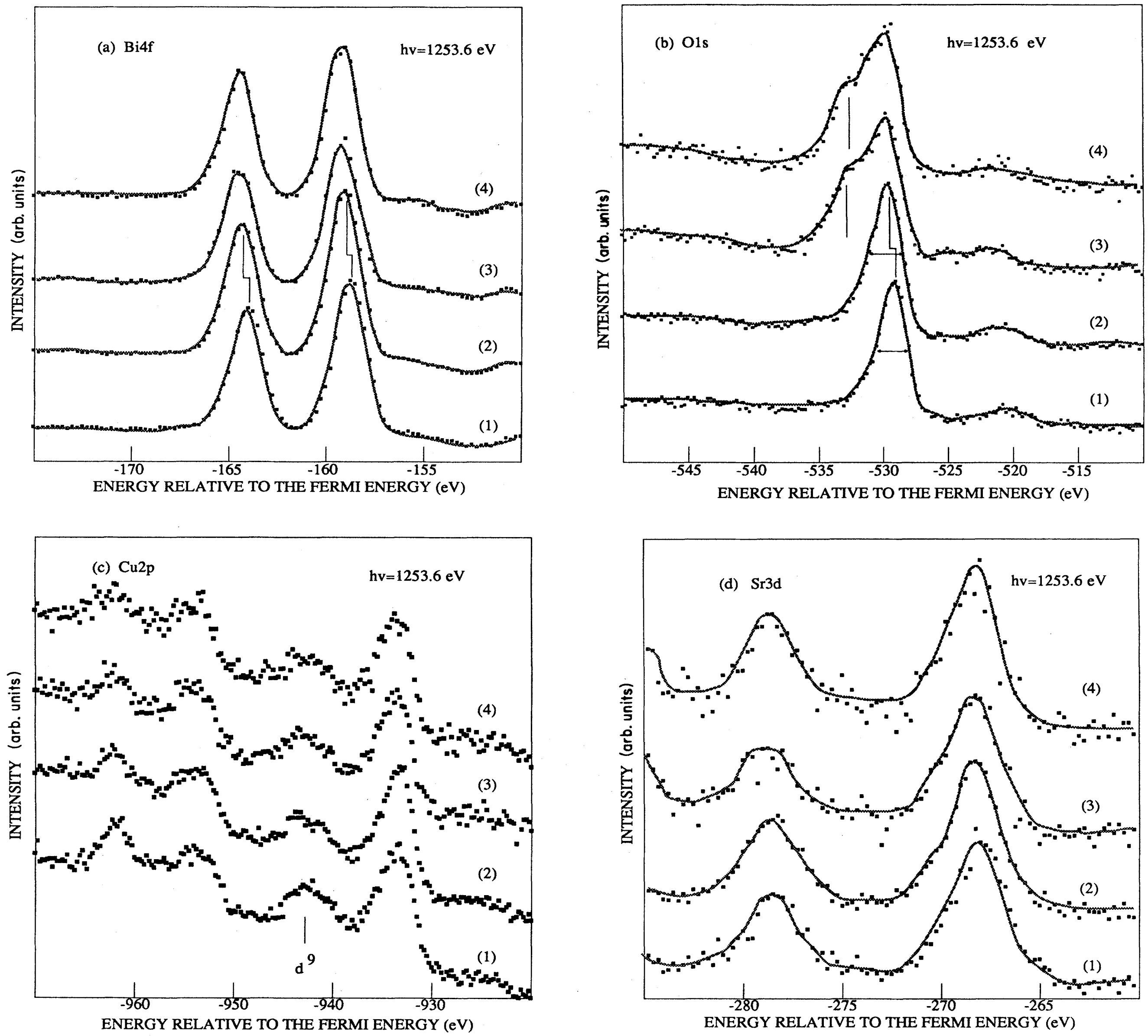

FIG. 2. Photoemission spectra using Mg $K\alpha$ (1253.6 eV) radiation of the (a) Bi $4f$, (b) O $1s$, (c) Cu $2p$, and (d) Sr $3d$ core levels. The notation of the different spectra is defined in the text and in Fig. 1.

Cu $2p$ and Sr $3d$ core levels, which hardly show any sign of reaction. Starting with the Cu $2p$ data shown in Fig. 2(b), we note that the Cu $2p$ core level is essentially unaffected by Rb deposition followed by coadsorption of O_2; the position as well as the linewidth remains the same. More important, hardly any change of the intensity ratio of the Cu d^9 satellite and the main line at about -933.5 eV, a ratio that is a measure of the Cu valency, can be observed. This is a most significant result, since other reactive metals, such as Al, In, Ti, and Fe,[12–15] as well as more inert metals as Cu and Ag,[13,16,17] have been shown to significantly reduce the Cu valency in similar materials. This might be due to the ability of these metals to penetrate into the substrate, an ability that large electropositive ions, such as Rb and Cs are lacking. Similarly, the Sr $3d$ spectra shown in Fig. 2(d) are essentially invariant upon deposition of Rb and oxygen onto the surface.

To this point, we have shown that while the Bi and O states of the superconductor are changed dramatically by reaction with Rb and oxygen, the Sr and Cu states are left basically unchanged. The origin of this may be traced back to the layered structure of this material.[18] A number of papers indicate that the most probable cleavage plane of this type of material is the one that is perpendicular to the c axis, i.e., the a-b plane.[7–8] Furthermore, because of the long bonding distance between the Bi-O planes, it is most plausible that the Bi-O a-b plane terminates the crystal at the solid-vacuum interface. Thus, since adsorbates almost invariably interact most strongly with the top atomic layer of a material, one would expect the Bi and O atoms in the surface layer to be those that are most strongly affected by the adsorbates. Since the core-level data indicate that a strong reaction occurs with the Bi and O states upon exposure to adsorbates of Rb and oxygen, while no change in the valency of either the Cu or the Sr states can be resolved, we infer that the effects of the adsorbates are confined to the top layer, which most probably consists of a Bi-O plane. Moreover, the results imply a fairly weak coupling between the different layers of the crystal structure.

To summarize, photoemission spectra from Rb and oxygen overlayers on single crystals of $Bi_2Sr_2CaCu_2O_{8+\delta}$ superconductors have been recorded in both the UPS and XPS regimes. The core-level data show evidence of strong interaction between the Rb adsorbates with the Bi and O states at the surface, while the Cu and Sr states are almost completely unaffected. This result suggests that the Bi-O plane of the cleaved crystal forms the surface layer. We have also shown that upon coadsorption with oxygen new oxygen species are formed at the surface of the superconductor as revealed by additional features in the UPS and XPS spectra.

Three of the authors would like to acknowledge support received from AT&T (D.B.M.), the Alfred P. Sloan Foundation and P.Y.I. (A.K.), and the National Science Foundation (D.S.D). Financial support from the U.S. National Science Foundation through the NSF-MRL program at the Center for Materials Research at Stanford University, and Air Force Contract No. AFSOR-87-0389 is gratefully acknowledged.

---

[1] M. Onellion, Ming Tang, Y. Chang, G. Margaritondo, J. M. Tarascon, P. A. Morris, W. A. Bonner, and N. G. Stoffel, Phys. Rev. B **38**, 881 (1988).

[2] Z.-X. Shen, P. A. P. Lindberg, B. O. Wells, D. B. Mitzi, I. Lindau, W. E. Spicer, and A. Kapitulnik, Phys. Rev. B **38**, 11 820 (1988).

[3] Z.-X. Shen, P. A. P. Lindberg, I. Lindau, W. E. Spicer, C. B. Eom, and T. H. Geballe, Phys. Rev . B **38**, 7152 (1988).

[4] Z.-X. Shen, P. A. P. Lindberg, P. Soukiassian, C. B. Eom, I. Lindau, W. E. Spicer, and T. H. Geballe, Phys. Rev. B **39**, 823 (1989).

[5] T. Takahashi, H. Matsuyama, H. Katayama-Yoshida, Y. Okabe, S. Hosoya, K. Seki, H. Fujimoto, M. Sato, and H. Inokuchi, Nature **334**, 691 (1988).

[6] P. A. P. Lindberg, P. Soukiassian, Z.-X. Shen, S. I. Shah, C. B. Eom, I. Lindau, W. E. Spicer, and T. H. Geballe, Appl. Phys. Lett. **53**, 1970 (1988).

[7] M. Kirk, C. B. Eom, B. Oh, S. R. Spielman, M. R. Beasley, A. Kapitulnik, T. H. Geballe, and C. F. Quate, Appl. Phys. Lett. **52**, 2071 (1988).

[8] P. A. P. Lindberg, Z.-X. Shen, B. O. Wells, D. B. Mitzi, I. Lindau, W. E. Spicer, and A. Kapitulnik, Appl. Phys. Lett. **53**, 2563 (1988).

[9] SAES Getter-Galileo Trademark, Milano, Italy and Colorado Springs, Colorado.

[10] P. Soukiassian, M. H. Bakshi, and Z. Hurych, J. Appl. Phys. **61**, 2679 (1987).

[11] Y. Dai, A. Manthiran, A. Campion, and J. B. Goodenough (unpublished).

[12] Y. Gao, I. M. Vitomirov, C. M. Aldao, T. J. Wagener, J. J. Joyce, C. Capasso, J. H. Weaver, and D. W. Capone II, Phys. Rev. B **37**, 3741 (1988).

[13] H. M. Meyer III, D. M. Hill, T. J. Wagener, Y. Gao, J. H. Weaver, D. W. Capone II, and K. C. Goretta, Phys. Rev. B **38**, 6500 (1988).

[14] D. M. Hill, H. M. Meyer, J. H. Weaver, B. Flandermeyer, and D. W. Capone II, Phys. Rev. B **36**, 3979 (1987).

[15] J. H. Weaver, Y. Gao, T. J. Wagener, B. Flandermeyer, and D. W. Capone II, Phys. Rev. B **36**, 3975 (1987).

[16] D. M. Hill, Y. Gao, H. M. Meyer III, T. J. Wagener, J. H. Weaver, and D. W. Capone II, Phys. Rev. B **37**, 511 (1988).

[17] P. A. P. Lindberg, Z.-X. Shen, I. Lindau, W. E. Spicer, C. B. Eom, and T. H. Geballe, Appl. Phys. Lett. **53**, 529 (1988).

[18] J. M. Tarascon, W. R. McKinnon, P. Barboux, D. M. Hwang, B. G. Bagely, L. H. Greene, G. Hull, Y. LePage, N. Stoffel, and M. Giroud (unpublished).