PHYSICAL REVIEW B VOLUME 54, NUMBER 9 1 SEPTEMBER 1996-I

Electronic structure of $Tl_2Ba_2CuO_{6+\delta}$ epitaxial films measured by x-ray photoemission

R. P. Vasquez
Center for Space Microelectronics Technology, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109-8099

Z. F. Ren and J. H. Wang
Superconductive Materials Laboratory, Department of Chemistry and New York State Institute on Superconductivity, State University of New York at Buffalo, Buffalo, New York 14260-3000

(Received 22 April 1996)

The valence electronic structure and core levels of $Tl_2Ba_2CuO_{6+\delta}$ (Tl-2201) epitaxial films have been measured with x-ray photoelectron spectroscopy and are compared to those of $Tl_2Ba_2CaCu_2O_{8+\delta}$ (Tl-2212). Changes in the Tl-2201 core-level binding energies with oxygen doping are consistent with a change in the chemical potential. Differences between the Tl-2201 and Tl-2212 measured densities of states are consistent with the calculated Cu 3d and Tl 6s partial densities of states. [S0163-1829(96)08733-4]

The electronic structure of the $Tl_2Ba_2Ca_{n-1}Cu_nO_{4+2n+\delta}$ [Tl-22$(n-1)n$] family of superconducting cuprates is of interest because of the higher superconducting transition temperatures (T_c) which are obtainable relative to the more commonly studied $YBa_2Cu_3O_7$ and $Bi_2Sr_2CaCu_2O_8$. However, the difficulty in synthesizing high-quality materials due to the toxicity and volatility of Tl, combined with the well-known difficulty in obtaining clean cuprate surfaces due to the reactivity of the alkaline earth components, has limited photoemission studies of these materials. Additionally, the T_c of Tl-2201 depends sensitively on the oxygen doping,[1] varying continuously and reversibly from 85 to 0 K as δ varies from 0 to 0.1, thus requiring controlled annealing in an inert atmosphere to remove excess oxygen. Most x-ray photoelectron spectroscopy (XPS) studies of Tl-22$(n-1)n$ materials have consequently focused on Tl-2212 and Tl-2223, which have higher T_c's and do not require a final reducing anneal, and only a few[2–4] have included measurements on Tl-2201. Furthermore, these earlier studies have been on polycrystalline samples scraped in vacuum, which can yield surfaces with significant spectral contributions from nonsuperconducting grain boundary species and/or artifacts from scrape-induced damage,[5] such as reduction of Cu^{2+} to Cu^{+}. XPS measurements from higher-quality Tl-2201 surfaces are therefore desirable.

Recently, the growth of high-quality epitaxial films of Tl-2201 has been demonstrated.[6,7] Tricrystal ring magnetometry experiments utilizing these films have also provided strong evidence for d-wave pairing symmetry.[7] In this work, the results of XPS measurements on these films are presented and compared to earlier Tl-2201 measurements[2–4] and to results from Tl-2212 epitaxial films.[8] The valence band measurements are compared to the densities of states from Tl-2201 and Tl-2212 band structure calculations.[9,10] The influence of doping on the electronic structure of Tl-2201 is studied by comparing photoemission measurements from fully oxidized and reduced films with different oxygen contents and hence different T_c's.

5000-Å-thick epitaxial Tl-2201 films on $SrTiO_3$ (100) substrates are obtained by rf magnetron sputtering followed by a two-step annealing process. Details of the film growth, annealing, and characterization are described elsewhere.[6,7] Prior to the final argon anneal, which adjusts the oxygen content, the films typically exhibit zero resistance at 11–12 K, while zero resistance can be raised as high as ~80 K after argon annealing. Exposure of the films to reactive atmospheric gases, especially water vapor, was minimized during transport by use of dessicant in a Viton o-ring-sealed screw-top sample container. The sample container was unsealed only in the ultrahigh-purity nitrogen atmosphere of a glove box which encloses the XPS load lock. The films were cleaned with a nonaqueous etchant consisting of 0.1% Br_2 in absolute ethanol, rinsed in ethanol, and blown dry with nitrogen. This procedure has yielded high-quality surfaces for other cuprate superconductors,[5] including Tl-2212 (Ref. 8). The etch rate was found to be ~1000 Å/min, and a 15-s etch was found to be sufficient for obtaining XPS spectra characteristic of high-quality surfaces, using criteria described elsewhere.[5] The XPS spectra were accumulated on a Surface Science Spectra SSX-501 spectrometer with monochromatized Al $K\alpha$ x rays (1486.6 eV), photoemission normal to the film surface, and a base pressure of 5×10^{-10} Torr. The x-ray beam diameter was 150 μm for core-level measurements and 300 μm for the valence-band measurements. The pass energy of the electron energy analyzer was 25 eV, yielding a peak full width at half maximum (FWHM) of 0.7 eV for a Au $4f_{7/2}$ signal. One fully oxygenated and two annealed films were measured in this work, and ac susceptibility measurements of the annealed films following the XPS measurements showed onsets of the superconducting transition at 53 and 63 K with transition widths of ~2 K. Equivalent XPS spectra were obtained from both annealed films, the data presented here are from the film with $T_c = 63$ K.

The core-level binding energies and peak FWHM measured in this work from fully oxygenated and argon-annealed Tl-2201 epitaxial films are summarized in Table I, together with measurements previously reported[3,4,8] for Tl-2201 and Tl-2212. The O 1s spectrum, which is commonly used to assess surface cleanliness, measured from an annealed Tl-2201 film is compared in Fig. 1 to the corresponding spec-

TABLE I. Summary of core-level binding energies, peak full widths at half maximum (in parentheses), and Cu $2p_{3/2}$ d^9/d^{10} intensity ratios for fully oxygenated and argon-annealed Tl-2201 epitaxial films measured in this work, together with previously reported results for Tl-2201 and Tl-2212.

Material	Tl $4f_{7/2}$	Ba $3d_{5/2}$	Ba $4d_{5/2}$	Cu $2p_{3/2}$	d^9/d^{10}	O $1s$	Reference
Tl-2201							
oxygenated (T_c=11 K)	117.9 (1.2)	777.8 (1.5)	87.4 (1.0)	933.1 (3.2)	0.46	527.5(0.9),528.7(1.3)	this work
annealed (T_c=63 K)	118.1 (1.25)	777.9 (1.45)	87.5 (1.05)	933.1 (3.3)	0.46	527.6(1.0),528.9(1.3)	this work
(no T_c)	118.2	777.9	not reported	~933	0.45	~529	4
(T_c=88 K)	118.4	778.4 (2.4)	not reported	932.8 (2.4)	0.30	not reported	3
Tl-2212							
(T_c=102 K)	118.0 (1.25)	778.3 (1.55)	87.9 (1.15)	933.1 (3.1)	0.45	527.8(0.9),528.7(1.4)	8
(T_c=98 K)	118.1	779.6[a]	not reported	~933	0.39	~529	4
(T_c=102 K)	118.2	778.4 (2.6)	not reported	933.1 (3.0)	0.28	not reported	3

[a] The high binding energy is attributed in Ref. 4 to contaminant species.

trum from a Tl-2212 epitaxial film.[8] The peak near 531 eV is known to be associated with contaminants,[5] particularly alkaline-earth carbonates, while the lower-binding-energy manifold originates from the nonequivalent oxygen sites in the superconducting phase. O $1s$ spectra were not presented in one earlier study[3] of Tl-2201, making an assessment of the surface quality difficult, while another study[4] of Tl-based superconductors did present an O $1s$ spectrum from Tl-2223 which was stated to be typical and in which the contaminant signal was nearly equal in intensity to the signal from the superconductor. The dominance of the lower-binding-energy signals in Fig. 1 demonstrates the surface cleanliness obtained in this work. The lower-binding-energy signal consists of two components, as demonstrated more clearly in the second derivatives of the spectra shown in the inset of Fig. 1. The lower-binding-energy component is assigned to Cu-O planes, consistent with studies of other cuprate superconductors,[11–15] and the higher-binding-energy component is associated with Tl-O bonding. The difference in line shapes observed between the Tl-2201 and Tl-2212 O $1s$ spectra in Fig. 1 is primarily due to the difference in the energy separations of these two components.

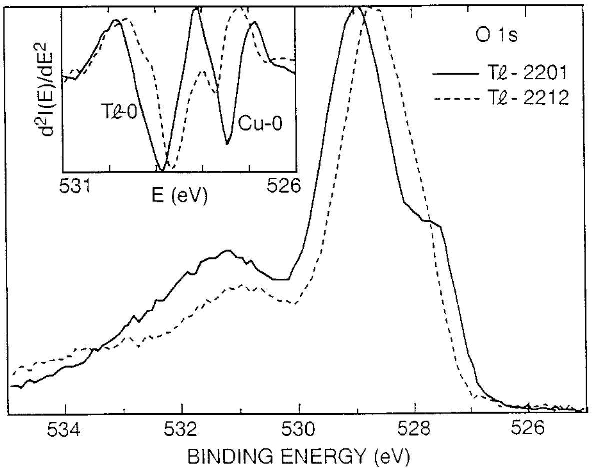

FIG. 1. O $1s$ spectra measured from chemically etched epitaxial films of Tl-2201 (this work) and Tl-2212 (Ref. 8). The inset shows the second derivatives of the spectra.

The Tl $4f$ and Ba $4d$ spectra are shown in Fig. 2 together with the results of a least-squares fitting. The Tl $4f$ spectrum can be seen in Fig. 2 to be well represented by a single doublet and is consistent with previous measurements from Tl cuprates.[3,4,8,16–19] The Ba $4d$ spectrum consists of a dominant doublet at low binding energy associated with the superconducting phase and a lower intensity doublet at 1.8 eV higher binding energy which is dominant prior to etching and is associated with contaminants. Similar observations are apparent in the Ba $3d$ spectrum (not shown). The Ba core levels occur at significantly lower binding energies than the corresponding signals from Ba metal, as is also the case for other superconducting cuprates, which has been interpreted as originating from initial-state electrostatic effects.[20] One earlier study[3] found a Ba $3d_{5/2}$ binding energy 0.5 eV higher than that measured in this work and cited the width of the signal (2.4 eV) as evidence of Ba occupancy of inequivalent sites. The lower binding energy measured in this work, in agreement with another earlier study,[4] and the significantly narrower peak width (1.45 eV) suggest that the earlier result is contaminant related, since the energy separation of the Ba $3d$ signals from the superconductor and contaminants is

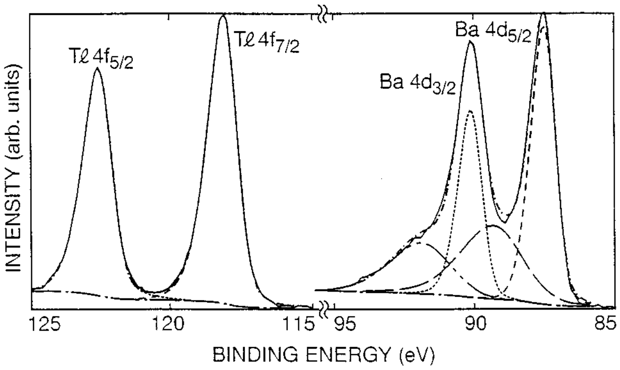

FIG. 2. Tl $4f$ and Ba $4d$ spectra measured from Tl-2201, together with the results of a least-squares fitting.

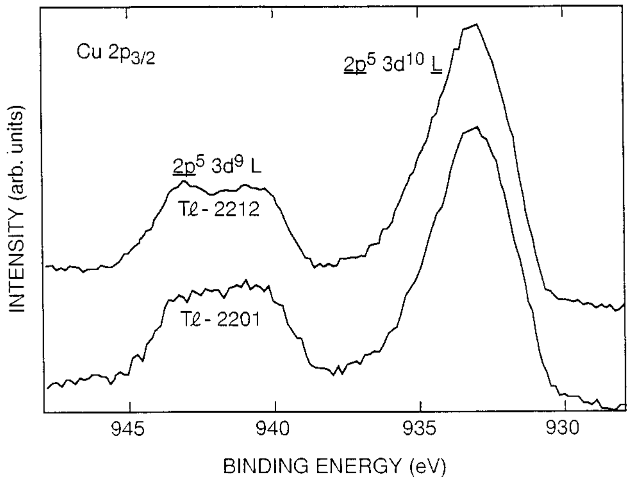

FIG. 3. Cu $2p_{3/2}$ spectra measured from Tl-2201 (this work) and Tl-2212 (Ref. 8).

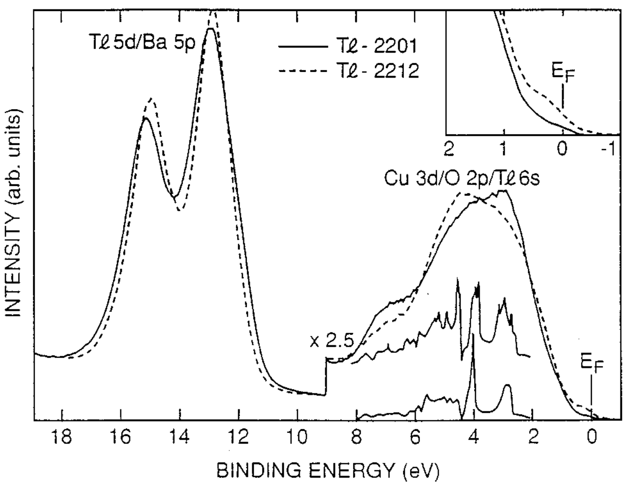

FIG. 4. Valence bands and Tl $5d$/Ba $5p$ shallow core-level spectra measured from Tl-2201 (this work) and Tl-2212 (Ref. 8). The inset shows the Fermi edges. Below the valence bands are the calculated Cu $3d$ partial densities of states of Tl-2201 (bottom) from Ref. 9 and Tl-2212 (top) from Ref. 10.

nearly the same as the peak width. The even narrower peak width observed in the Ba $4d$ spectrum (1.05 eV) provides further evidence against multiple Ba core-level signals originating from the superconductor.

The Cu $2p_{3/2}$ spectra measured from Tl-2201 and Tl-2212 are compared in Fig. 3 and are typical of Cu^{2+} compounds. The multiplet at higher binding energy corresponds to $\underline{2p}^5 3d^9 \underline{L}$ final states, where underscoring denotes a hole and L denotes the oxygen ligand, and the more prominent peak near 933 eV corresponds to well-screened $\underline{2p}^5 3d^{10} \underline{L}$ final states resulting from ligand-to-metal charge transfer. The relatively large width (>3 eV) of the d^{10} peak reflects a multiplet of final states.[21,22] The d^{10} binding energy and peak width and the d^9/d^{10} intensity ratio of 0.46 observed for Tl-2201 are similar to those of Tl-2212 and other cuprate superconductors.[5,21] These observations are in agreement with an earlier study[4] of Tl-2201, but differ significantly from another earlier study[3] in which a lower binding energy, narrower peak width (2.4 eV), and a lower d^9/d^{10} intensity ratio of 0.30 were reported. Such effects are consistent with the reduction of Cu^{2+} to Cu^{+} and have been demonstrated[5] to occur on surfaces damaged by scraping.

The core levels measured from argon-annealed Tl-2201 are observed at higher binding energies than those of the fully oxygenated sample. With the exception of the Cu $2p$ signal, for which small shifts are masked by the width of the signal, these binding energy shifts are in the range 0.12–0.24 eV for the $T_c=63$ K sample, and 0.15–0.28 eV for the $T_c=53$ K sample. Doping-induced changes in the core potentials caused by changes in effective charges or by changes in the Madelung potential (e.g., resulting from bond length changes) would be expected to have opposite effects on different sites. The fact that doping causes the core-level binding energies to shift in the same direction by nearly the same amount within experimental error suggests that these effects are small compared to the change in the chemical potential. Similar doping-induced changes in chemical potentials have been reported[23–27] for $La_{2-x}Sr_xCuO_4$, $Bi_2Sr_2CaCu_2O_{8+\delta}$, $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$, and $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$.

The Tl $5d$ and Ba $5p$ shallow core levels and valence bands, which consist primarily of Cu $3d$, O $2p$, and Tl $6s/5d$ states, of Tl-2201 and Tl-2212 are compared in Fig. 4. The spectra have been scaled to the same height in the valence-band region to facilitate comparison of line-shape differences. The Fermi edges are shown more clearly in the inset. The Cu and Tl states contribute most of the valence-band spectral weight for the photon energy used in this work.[28] The Cu $3d$ partial densities of states from band structure calculations[9,10] of Tl-2201 and Tl-2212 are shown below the valence bands, shifted by 2 eV to approximately match the envelopes of the valence bands. Similar shifts have been found necessary for other cuprate superconductors and have been attributed to electron correlation effects which are inadequately treated in the calculations. Distinct differences in the measured Tl-2201 and Tl-2212 densities of states are apparent in Fig. 4. In the region ~2–5 eV, the density of states of Tl-2201 increases towards the Fermi level, while that of Tl-2212 decreases. This is consistent with the calculations, in which Tl-2212 exhibits a larger Cu $3d$ partial density of states for binding energies larger than ~4.5 eV. The shoulder near 7 eV, which consists primarily of Tl $6s$ states,[9,10,28] is more prominent in the Tl-2201 spectrum, reflecting the larger Tl/Cu ratio relative to Tl-2212.

In summary, the valence electronic structure and core levels of Tl-2201 epitaxial films have been measured in this work with XPS. The core-level binding energies and spectral features are generally similar to those of Tl-2212 and other cuprate superconductors, and are more characteristic of clean surfaces than previously published spectra measured from polycrystalline pellets scraped in vacuum. Changes in the Tl-2201 core-level binding energies with oxygen doping are consistent with a change in the chemical potential, as previously observed in La-Sr-Cu-O and Bi-Sr-Ca-Cu-O materials with varying doping. Differences between the Tl-2201 and Tl-2212 measured densities of states are consistent with the calculated Cu $3d$ and Tl $6s$ partial densities of states.

Part of the work described in this paper was performed by the Center for Space Microelectronics Technology, Jet Propulsion Laboratory, California Institute of Technology, and was sponsored by the National Aeronautics and Space Administration, Office of Space Access and Technology. The work performed at the State University of New York at Buffalo was supported by the New York State Energy Research and Development Authority, Argonne National Laboratory, and Oak Ridge National Laboratory.

---

[1] Y. Kubo, Y. Shimakawa, T. Manako, and H. Igarishi, Phys. Rev. B **43**, 7875 (1991).

[2] S. Nakajima, M. Kikuchi, T. Oku, N. Kobayashi, T. Suzuki, K. Nagase, K. Hiraga, Y. Muto, and Y. Syono, Physica C **160**, 458 (1989).

[3] C. S. Gopinath, S. Subramanian, M. Paranthaman, and A. M. Hermann, Phys. Rev. B **48**, 15 999 (1993).

[4] Y. Fukuda, T. Suzuki, and M. Nagoshi, in *Thallium-Based High Temperature Superconductors*, edited by A. M. Hermann and J. V. Yakhmi (Dekker, New York, 1994), p. 511.

[5] R. P. Vasquez, J. Electron Spectrosc. Relat. Phenom. **66**, 209 (1994), and references therein.

[6] C. A. Wang, Z. F. Ren, J. H. Wang, D. K. Petrov, M. J. Naughton, W. Y. Yu, and A. Petrou, Physica C **262**, 98 (1996).

[7] C. C. Tsuei, J. R. Kirtley, M. Rupp, J. Z. Sun, A. Gupta, M. B. Ketchen, C. A. Wang, Z. F. Ren, J. H. Wang, and M. Bhushan, Science **271**, 329 (1996).

[8] R. P. Vasquez and W. L. Olson, Physica C **177**, 223 (1991).

[9] D. R. Hamann and L. F. Mattheiss, Phys. Rev. B **38**, 5138 (1988).

[10] J. Yu, S. Massidda, and A. J. Freeman, Physica C **152**, 273 (1988).

[11] J. H. Weaver, H. M. Meyer III, T. J. Wagener, D. M. Hill, Y. Gao, D. Peterson, Z. Fisk, and A. J. Arko, Phys. Rev. B **38**, 4668 (1988).

[12] H. M. Meyer III, D. M. Hill, J. H. Weaver, D. L. Nelson, and C. F. Gallo, Phys. Rev. B **38**, 7144 (1988).

[13] F. Parmigiani, Z. X. Shen, D. B. Mitzi, I. Lindau, W. E. Spicer, and A. Kapitulnick, Phys. Rev. B **43**, 3085 (1991).

[14] R. P. Vasquez, B. D. Hunt, M. C. Foote, L. J. Bajuk, and W. L. Olson, Physica C **190**, 249 (1992).

[15] R. P. Vasquez, M. Rupp, A. Gupta, and C. C. Tsuei, Phys. Rev. B **51**, 15 657 (1995).

[16] H. M. Meyer III, T. J. Wagener, J. H. Weaver, and D. S. Ginley, Phys. Rev. B **39**, 7343 (1989).

[17] A. E. Bocquet, J. F. Dobson, P. C. Healey, S. Myrha, and J. G. Thompson, Phys. Status Solidi B **152**, 519 (1989).

[18] T. Suzuki, M. Nagoshi, Y. Fukuda, Y. Syono, M. Kikuchi, N. Kobayashi, and M. Tachiki, Phys. Rev. B **40**, 5184 (1989).

[19] T. Suzuki, M. Nagoshi, Y. Fukuda, S. Nakajima, M. Kikuchi, Y. Syono, and M. Tachiki, Physica C **162–164**, 1387 (1989); Supercond. Sci. Technol. **7**, 817 (1994).

[20] R. P. Vasquez, J. Electron Spectrosc. Relat. Phenom. **66**, 241 (1994), and references therein.

[21] F. Parmigiani and L. Sangaletti, J. Electron Spectrosc. Relat. Phenom. **66**, 223 (1994), and references therein.

[22] M. A. van Veenendaal, H. Eskes, and G. A. Sawatzky, Phys. Rev. B **47**, 11 462 (1993).

[23] G. Rietveld, M. Glastra, and D. van der Marel, Physica C **241**, 257 (1995).

[24] Z.-X. Shen, D. S. Dessau, B. O. Wells, C. G. Olson, D. B. Mitzi, L. Lombardo, R. S. List, and R. J. Arko, Phys. Rev. B **44**, 12 098 (1991).

[25] M. A. van Veenendaal, R. Schlatmann, G. A. Sawatzky, and W. A. Groen, Phys. Rev. B **47**, 446 (1993).

[26] M. A. van Veenendaal, G. A. Sawatzky, and W. A. Groen, Phys. Rev. B **49**, 1407 (1994).

[27] G. Rietveld, S. J. Collocott, R. Driver, and D. van der Marel, Physica C **241**, 273 (1995).

[28] P. Marksteiner, J. Yu, S. Massidda, A. J. Freeman, J. Redinger, and P. Weinberger, Phys. Rev. B **39**, 2894 (1989).