Angle-resolved photoemission spectroscopy study of $Bi_2Sr_2CaCu_2O_{8+\delta}$ thin films

D. S. Marshall, D. S. Dessau, D. M. King, C.-H. Park, A. Y. Matsuura, Z.-X. Shen, and W. E. Spicer
Stanford Electronics Laboratories, Stanford University, Stanford, California 94305

J. N. Eckstein and I. Bozovic
E. L. Ginzton Research Center, Varian Associates, Palo Alto, California 94304
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We report angle-resolved photoemission spectroscopy (ARPES) results from $Bi_2Sr_2CaCu_2O_{8+\delta}$ (2212) single-crystal thin films grown with atomic layer-by-layer molecular beam epitaxy (ALL-MBE). This was made possible by adapting the top-post cleaving technique to thin films of 2212. We have observed clear photoemission features from these films that disperse through the Fermi level. We have observed the superconducting energy gap with ARPES in thin films. Both the magnitude of the gap as well as its anisotropy are consistent with the results from bulk crystals. Furthermore, we observe the pile-up and dip in spectral weight associated with the gap. These results open possibilities for future research using thin-film samples in this materials system that take advantage of the ability to grow metastable materials with ALL-MBE.

Most studies of fundamental interest in the area of high-temperature superconductivity have been performed on bulk crystals due to the generally higher defect densities and wider superconducting transitions of thin films. However, issues such as the effect of a broad range of underdoped hole concentrations on the electronic structure in certain materials systems cannot easily be addressed with bulk crystals because the achievable stoichiometries are thermodynamically limited or there is no guarantee that substitutional ions will reside in the desired lattice locations. Using atomic layer-by-layer molecular beam epitaxy (ALL-MBE), metastable materials with a wide stoichiometric range can be synthesized with the vast majority of substitutional ions remaining on the desired site. However, before fundamental issues can be effectively addressed with thin films, comparable results to those of bulk crystals in known systems must be demonstrated. In this paper, we report results of angle-resolved photoemission spectroscopy (ARPES) on $Bi_2Sr_2CaCu_2O_{8+\delta}$ (2212) thin films grown by ALL-MBE that match those of bulk crystals.

Over the last five years, high-resolution angle-resolved photoemission has emerged as one of the most powerful experimental techniques for studying the electronic properties of high-temperature superconductors. However, virtually all the angle-resolved photoemission experiments that demonstrate clear energy dispersion, Fermi level crossings, and superconducting features were performed on bulk crystal samples.[1,2] The difficulty in performing photoemission experiments on thin-film samples hinges on two points: (1) Only single-phase films with a very low defect density and high degree of crystallinity will give good results, and (2) clean surfaces must be prepared for photoemission due to the surface sensitivity of the technique (approximately 15 Å). The ALL-MBE samples used in this experiment were single-crystal films without any second-phase precipitates. Previous attempts at preparing clean surfaces have included argon sputter cleaning,[3] oxygen annealing,[4,5] oxygen plasma exposure,[6] and most recently, atomic oxygen exposure.[7] The clarity of the dispersive photoemission features resulting from these techniques is mediocre. The cleaving technique, although proven for bulk 2212 crystals, has not been demonstrated successfully on thin films for UV ARPES. This is not trivial to accomplish due to the systematic defects (approximately every micrometer) present in the MBE material originating from steps on the vicinal substrates. These defects serve to strengthen the material in the third dimension, making them more difficult to cleave in a micaceous manner, but as anticipated, contribute to the photoemission in a minuscule way. The results reported in this paper were made possible by adapting the top-post cleaving technique to 2212 thin films. The essence of this technique is to mount the substrate with the film facing outward using electrically conductive epoxy to ground the sample. A top-post *with a thermal expansion coefficient matching that of the substrate* is then adhered to the face of the sample using epoxy. Once in ultrahigh vacuum (UHV) and cooled to cryogenic temperatures, the top post is knocked off the sample face by mechanical means, thus leaving behind a freshly cleaved surface. Great care must be taken to prevent shearing of the entire sample away from the substrate.

The films in this study were grown using ALL-MBE by exposing a heated substrate to shuttered sources of bismuth, strontium, copper, and calcium, all in the presence of ozone.[8] The shutter timing was accurately adjusted to deposit $Bi_{2.1}Sr_{1.95}Ca_{0.95}Cu_2O_{8+\delta}$; this composition is typical of the single-phase two-layer Bi compound. (We will refer to this as 2212 for brevity.) The shuttering sequence was repeated, atomic layer by layer, until approximately 1000 Å of material was deposited. The quality of the samples was quite high, showing single-phase growth (determined by x-ray diffraction and optical microscopy) and superconducting critical temperatures of 85 K (zero resistance temperature). The superconducting transitions for these thin films were 15 K wide (10%–90%) which is typical of 2212 thin films. The samples were mounted in air before insertion into the UHV photoemission chamber. The samples were cleaved in UHV where ARPES measurements were performed using 22.4 eV light from Beamline 5-3 of the Stanford Synchrotron Radiation Laboratory. Collection of the emitted electrons was accomplished with a hemispherical

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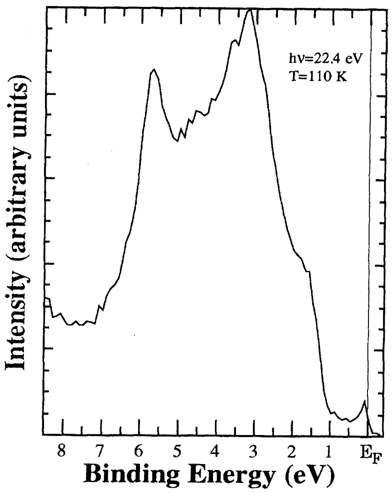

FIG. 1. Angle-resolved photoemission of the $Bi_2Sr_2CaCu_2O_{8+\delta}$ valence band showing a multiplicity of bands between 1 and 7 eV binding energy and the uppermost valence bands at the Fermi level.

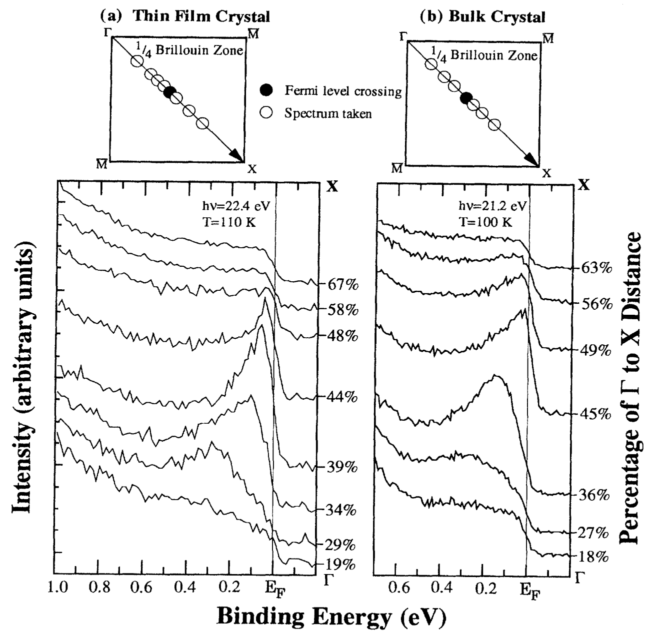

FIG. 2. Spectra of the uppermost valence bands from (a) a thin-film crystal and (b) a bulk crystal showing a clearly dispersive feature and a Fermi level crossing near 45% of the way from the Γ to X points of the Brillouin zone. Above each spectrum set is a depiction of $\frac{1}{4}$ of the Brillouin zone showing where in k space the spectra were taken.

electron analyzer under conditions that yielded a total experimental resolution of 45 meV (as measured on a gold Fermi edge) and having angular resolution of $\pm 1°$.

The photoemission spectra of these film samples were strikingly similar to those of bulk crystals in a number of aspects, including the general shape of the spectra, the normal-state dispersion of bands, the Fermi level crossings, and the symmetry of electronic states with respect to the polarization of the incident light. Figure 1 is a photoemission spectrum from a thin film of 2212. It has the hallmark characteristics of bulk 2212, with a multiplicity of bands between 1 and 7 eV binding energy and a small but measurable peak extending to the Fermi level.[9] The satellite feature at higher binding energies, although not shown in the figure, was also observed. Figure 2, panel (a), shows a series of spectra from a thin film in the normal (nonsuperconducting) state, and panel (b) shows a similar series from a bulk crystal also in the normal state. Each spectrum of the series is taken at a different collection angle and corresponds to a different point in k space. Figure 2 shows the dispersion of the uppermost valence bands (within 1 eV of the Fermi level) as they move toward and through the Fermi energy. The dispersions are very similar in both cases with no observable effect from the systematic defects in the thin film. In both panels, a Fermi level crossing is observed approximately 45% of the way from Γ to X. [As in ARPES of bulk crystals,[9] a Fermi level crossing is defined here as the point in k space where a dispersive feature moving toward the Fermi energy experiences a 50% intensity decrease and which has the midpoint of the leading edge at or above E_F ("negative" binding energy).] Figure 3 shows the first Brillouin zone, containing the Fermi surface as mapped by photoemission on bulk crystals[2] and thin films. The Fermi level crossings of the films agree well with bulk data within the error bars.[2] The Fermi level crossings were measured in both the x and y quadrants of the Brillouin zone and were identical within the error bars shown.

Other distinctive characteristics of photoemission from 2212 are the superconducting gap and dip structures in the spectra of the uppermost valence bands at the $\bar{M}$ point of the Brillouin zone [Fig. 4(a)] as the sample is cooled below the superconducting transition temperature.[10] Figure 4 shows a comparison of spectra from the uppermost valence bands taken at the $\bar{M}$ symmetry point and at the Γ-X Fermi level crossing for one thin film sample. Figure 4(a) shows that even quite sensitive features such as the gap and dip of the superconducting state which have been observed in bulk crystals can also be seen with these thin films. This confirms that the basic electronic structure and low-energy excitations in the films are very similar to those of bulk crystals, even though the films have higher defect densities and broader superconducting transitions. The anisotropy of the superconducting gap in k space is observed by comparing Figs. 4(a) and 4(b).[11] In bulk samples, the gap is widest (as wide as 25 meV in the best bulk samples) at the $\bar{M}$ symmetry point and has little or no gap at the Γ-X Fermi level crossing. The largest gap at $\bar{M}$ in the thin films under study was 17 meV and is shown in Fig. 4(a). The gap at the Γ-X Fermi level crossing [Fig. 4(b)] of this thin film is less than the experimental uncertainty of 4 meV. Such a large gap anisotropy is a unique feature of the high-T_c superconductors. This anisotropic gap is consistent with a novel form of the superconducting order parameter, the $d_{x^2-y^2}$ or "d-wave" model, which predicts a *zero* gap at the Γ-X Fermi level crossing[12] and is also consistent with an anisotropic form of the traditional superconducting order parameter or "s-wave" model that predicts a *diminishing* gap at the same point.[13] Thin-film ARPES can potentially provide superior experiments for de-

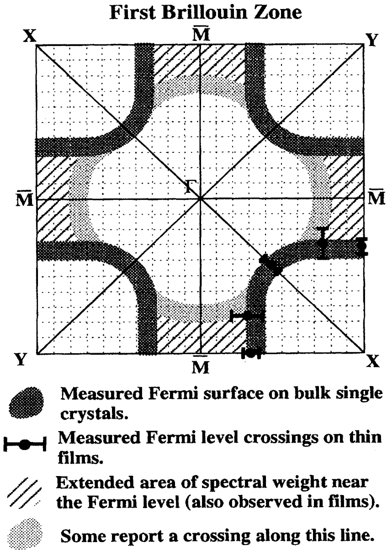

FIG. 3. First Brillouin zone indicating the Fermi level crossings of thin-film samples (with error bars) as well as the Fermi surface of bulk crystals (from Ref. 2). Each of the dashed lines represents one-tenth of the Γ to $\bar{M}$ distance.

termining the magnitude of the superconducting gap function at the Γ-X Fermi level crossing. This is because thin films, which are grown on flat, polished substrates, give the highest possible angular resolution for photoemission. Using this angular resolution along with improved experimental energy resolution, one could put a smaller upper limit on this important parameter.

In conclusion, we have shown that photoemission results comparable to bulk crystals can be obtained from high-quality 2212 thin films. We have found that both the gross features as well as the more sensitive features near the Fermi level are observed in thin films. In particular, the normal-state spectra show all the essential features of bulk 2212, having similar spectral intensities, band dispersion, and Fermi level crossings. The anisotropic superconducting energy gap and dip have been observed in thin films. These results represent a significant technical step forward and encourage further studies of ALL-MBE-grown thin films in this materials system such as cation-doped materials or metastable materials.

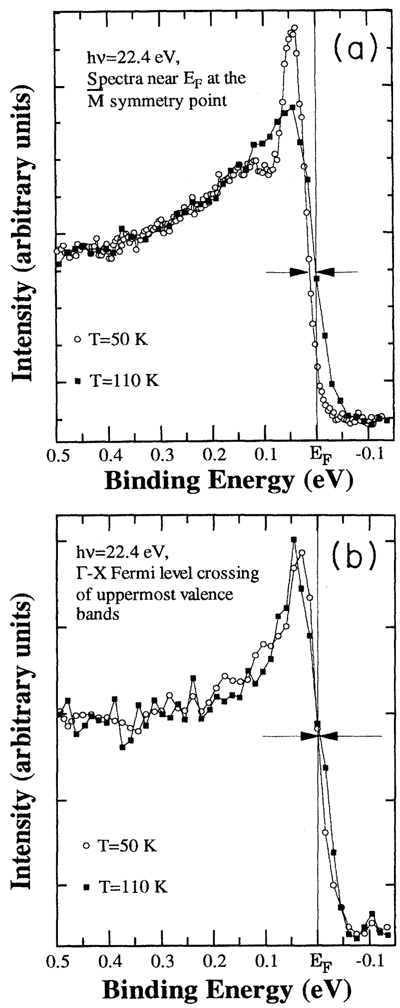

FIG. 4. Photoemission spectra taken above and below the superconducting transition temperature at (a) the $\bar{M}$ symmetry point and (b) the Γ-X Fermi level crossing. (a) clearly shows the superconducting pile up and dip as well as the superconducting energy gap of 17±4 meV in this sample. (b) shows that the gap in the Γ-X symmetry direction is within the experimental uncertainty of 4 meV.

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[1] C. G. Olson *et al.*, Phys. Rev. B **42**, 381 (1990); D. M. King *et al.*, Phys. Rev. B **70**, 3159, (1993); **73**, 3298 (1994); E. R. Ratner *et al.*, Phys. Rev. B **48** 10 482 (1993); R. Liu *et al.*, *ibid.* **45**, 5614 (1992); **46**, 11 056 (1992); J. G. Tobin *et al.*, *ibid.* **45**, 5563 (1992).

[2] D. S. Dessau *et al.*, Phys. Rev. Lett. **71**, 2781 (1993).

[3] P. A. P. Lindberg *et al.*, Appl. Phys. Lett. **53**, 1970 (1988).

[4] Y. Sakisaka *et al.*, Phys. Rev. B **39** 9080 (1989).

[5] D. A. Geeson *et al.*, Supercond. Sci. Technol. **2**, 279 (1989).

[6] M. W. Ruckman *et al.*, in *High T_c Superconducting Thin Films: Processing, Characterization, and Applications*, edited by Roger L. Stockbauer, S. V. Kvishnaswamy, and Richard L. Kurtz,

AIP Conf. Proc. No. 200 (AIP, New York, 1990), p. 114.
[7]N. Terada *et al.*, Appl. Phys. Lett. **64**, 2581 (1994).
[8]J. N. Eckstein *et al.*, Annu. Rev. Mater. Sci. **25**, 279 (1995); Mater. Res. Bull. **17**, 27 (1992); **19**, 44 (1994); Appl. Phys. Lett. **57**, 931 (1990); **57**, 1049 (1990).
[9]Z.-X. Shen *et al.*, Phys. Rev. B **38**, 11 820 (1988).
[10]Y. Hwu *et al.*, Phys. Rev. Lett. **67**, 2573 (1991); D. S. Dessau *et al.*, *ibid.* **66**, 2160 (1991); Phys. Rev. B **45**, 5095 (1992).
[11]B. O. Wells, *et al.*, Phys. Rev. B **46**, 11 830 (1992); Z.-X. Shen *et al.*, Phys. Rev. Lett. **70**, 1553 (1993); G. D. Mahan *et al.*, *ibid.* **71**, 4277 (1993).
[12]D. J. Scalapino, Phys. Rep. **250**, 329 (1995).
[13]S. Chakravarty *et al.*, Science **261**, 337 (1993).