Supercond. Sci. Technol. 2 (1989) 279–283. Printed in the UK

Non-destructive preparation of thin-film $Bi_2(Sr,Ca)_3Cu_2O_{8+x}$ surfaces for photoemission studies by *in situ* oxygen annealing

D A Geeson†, M S Golden†, S J Golden‡ and W R Flavell†§

† Centre for High Temperature Superconductivity, Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, UK

‡ Department of Materials, School of Engineering, University of California at Santa Barbara, Santa Barbara, CA 93106, USA

Received 28 July 1989

Abstract. The non-destructive technique of *in situ* oxygen annealing is used to prepare clean surfaces of *c*-axis oriented $Bi_2(Sr,Ca)_3Cu_2O_{8+x}$ thin films. Core and valence level photoemission spectra are consistent with those previously obtained by the authors from ceramic samples. In particular, the density of states at the Fermi level is comparable to that observed from polycrystalline samples but is not consistent with one-electron band-structure calculations.

1. Introduction

A recurring problem in photoemission studies of high-temperature superconducting oxides has been inadequate surface characterisation. The photoelectron flux generated within the sample is attenuated as it leaves the sample in accordance with a Beer–Lambert-type law characterised by an electron mean free pathlength of only 10–15 Å [1]. Because of this there are several grounds for applying a degree of circumspection in the interpretation of photoemission results.

The first major problem is surface contamination, whether due to unreacted starting materials, secondary phases or arising from atmospheric degradation [2]. It is obviously necessary to find some means of removing this contamination before meaningful photoemission results can be obtained. This has been achieved by most authors by scraping ceramic samples [3] or cleaving ceramic bars [4] and single crystals [5] inside the UHV spectrometer. Whilst thin films of the BSCCO superconductors (~1000 Å thick) can be obtained by peeling them from single crystals with tape [6, 7], these techniques are all destructive and therefore inapplicable to the study of conventional thin films deposited onto a rigid substrate. There have thus been very few studies of superconducting thin films to date [8–11] although such studies are particularly valuable as most superconducting devices will probably be in thin-film form. Here we show that the technique of *in situ* oxygen annealing, which was first applied by our group to ceramic oxide superconductor surfaces [2, 12–16] may be used very successfully to produce contaminant-free surfaces on BSCCO thin films. A related technique has recently been applied with great success to thin film $YBa_2Cu_3O_{7-x}$ (001) by Sakisaka *et al* [8, 9].

A second problem in photoemission studies is that we have no reason to expect the DOS revealed by a technique with such a high surface sensitivity to be necessarily representative of the true bulk situation. The bulk termination represented by the surface can have quite a profound effect on electronic structure over the penetration depth of the technique, and can lead to *intrinsic* surface properties quite different from those of the bulk. We have commented on the nature of these effects in $YBa_2Cu_3O_{7-x}$ in a previous publication [15]. However, it is precisely because of these effects that surface studies are important, because in any working device, contacts and interfaces will have to be made to the superconductor surface, so the intrinsic surface properties of the materials will ultimately determine the scale of their application. When one takes into account the fact that the coherence length, ξ, in these materials (in the *ab* plane) is typically of the order of 25 Å [17], then studies on this depth range assume an added importance.

The third problem relating to surface characterisation is that ideally one would like to know which crystal face is under study. This is particularly important in these materials, not only because of the observed anisotropy in physical properties, but also because the unit cell length along the *c* axis is typically longer than

§ To whom correspondence should be addressed.

0953-2048/89/050279 + 05 $02.50 © 1989 IOP Publishing Ltd

the photoelectron mean free path (in the case of the (2212) phase of the BSCCO system by a factor of around two). Thus, even for *c*-axis oriented samples, we could expect the observed photoemission to depend to some extent on which layer of atoms is present at the bulk termination. Hence it is important to examine how far data obtained from ceramics are reproduced in experiments from good-quality single crystals and thin films. Here we show that data obtained from *c*-axis oriented thin films are essentially identical to those previously obtained by the authors from ceramic samples of the BSCCO superconductors [14], vindicating our conclusions drawn from experiments on ceramic samples and allowing us to draw some conclusions about the nature of the surface examined.

2. Experiment

Thin films of the '(2212)' phase of the BSCCO system were prepared by spin pyrolysis of 2-ethyl hexanoate precursors in proportions Bi:Sr:Ca:Cu of 2.3:1.3:1.0:2.0, using MgO (200) single crystals as substrates. The films were pyrolised at 400 °C, and then post-annealed at 830 °C for 10 h. XRD measurements revealed a considerable degree of *c*-axis orientation, together with a small amount (maximum 10%) of the '1-layer' $Bi_2Sr_2CuO_6$ phase. As a result, resistivity measurements showed the onset of superconductivity at 90 K, with the majority of the material becoming superconducting at 85 K, but there was a small tail below this temperature, due to the presence of the '1-layer' phase. SEM indicated a film thickness of ~10 000 Å. Using the starting solution composition given above, it was found to be possible to produce 85 K superconducting material over a wide temperature range (750–830 °C) [18]. (Using a starting composition of 2:2:1:2, a higher and more controlled temperature is required (880 ± 5 °C) to obtain the '2-layer' phase.) Completely single-phase '2-layer' material superconducting at 85 K has now been produced using this starting composition; results from these materials will be reviewed in a future publication [18]. Our major interest in the current work is the application of the *in situ* oxygen annealing technique to thin film BSCCO samples.

Photoemission studies were conducted in a VG Escalab Mark II spectrometer, equipped with a double-anode x-ray source (Mg Kα and Al Kα) and a noble-gas discharge lamp. The analyser resolution was set at 0.4 eV for x-ray measurements and at 0.1 eV for He I measurements. The position of the Fermi energy was established to an accuracy of ±0.025 eV from measurements on a cleaned Ni stub. In addition to the analysis chamber (base pressure 5×10^{-11} Torr), the spectrometer has a fast entry lock and preparation chamber.

Samples were mounted on platinum stubs and secured with platinum clips. Care was taken not to allow the clips to protrude onto the sample surface. Cleaning was effected by filling the preparation chamber with 1 atm pure oxygen and heating the platinum stub by coupling to the radio-frequency field provided by a water-cooled copper workcoil connected through a Leybold–Heraeus RF feedthrough to a Radyne 1.5 kW, 400 kHz power supply. The cleaning cycle was designed to mimic the conditions of sample preparation, and typically involved heating to around 600–700 °C for 1–2 h, followed by cooling to <400 °C over a period of several hours. After switching off the RF power, samples were allowed to cool to room temperature before evacuation of the preparation chamber. Spectra were typically recorded within 1 h of oxygen annealing.

3. Results and discussion

Uncleaned samples were invariably contaminated with both adventitious hydrocarbon and carbonate species, evidenced by the appearance of two components in the C 1s region of the XPS spectra. O 1s, Sr 3d and Ca 2p spectra were dominated by components to the high binding energy side of the peaks due to the superconductor. These increased in relative intensity on going from normal (90°) to 15° emission angle from the surface plane. This structure is similar to that observed by the authors from ceramic samples of the BSCCO superconductors [14, 16] and is similarly attributed to $SrCO_3$ and $CaCO_3$ resulting from atmospheric degradation. No peaks due to Mg from the substrate were observed before or after cleaning, indicating good coverage of the MgO substrate.

The effect of the oxygen annealing treatment on the thin-film sample is indicated in figure 1. This shows the Al Kα XPS in the O 1s region before cleaning (figure 1(*a*)) and after cleaning (figure 1(*b*)). Prior to cleaning, the dominant high binding energy component is due predominantly to carbonate contamination. Following oxygen annealing, the intrinsic peak shape of the superconductor is revealed. The high binding energy shoulder that remains after cleaning shows negligible enhancement at shallow offtake angles, and is too strong to be associated with any residual carbonate contamination. (Spectra in the C 1s region showed the surface carbonate to be reduced to vanishingly small levels.) Comparable shoulders, or at least some marked asymmetry in peak shape, have been observed in most studies of cleaned BSCCO polycrystalline surfaces [19–22] or cleaved single crystals [5, 7, 23–25]; we have observed essentially identical peak shapes from ceramic samples of both the (2212) phase [14] and the Pb-doped (2223) phase [16]. We have discussed the possible origins of this structure at length [16]; here we merely emphasise its similarity to our earlier data from ceramic samples, and add that we believe that the high binding energy component is due at least in part to the CuO_2-layer $|\underline{1s}^1 3d^9 \underline{L}^0\rangle$ satellite.

Figure 2 shows valence level photoemission spectra from cleaned thin-film (2212) phase samples. The valence band region revealed by He I UPS ($h\nu$ = 21.2 eV) consists of four different features at 1.5, 3.5, 4.8 and

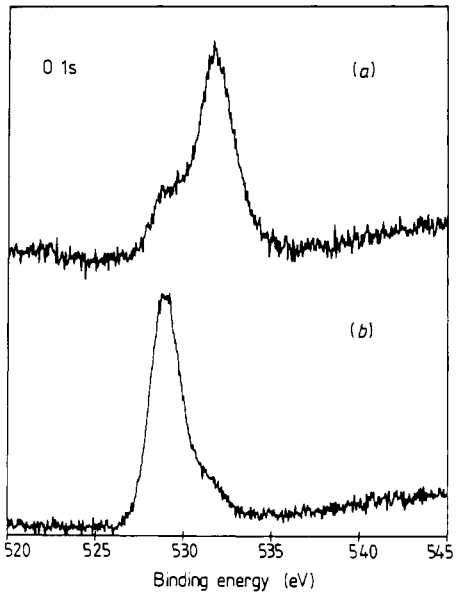

Figure 1. Comparison of Al Kα XPS O 1s profiles for (*a*) the *c*-axis oriented thin-film (2212) phase sample before cleaning by *in situ* oxygen annealing, and (*b*) as (*a*) after cleaning (see text), revealing the intrinsic peak shape due to the superconductor.

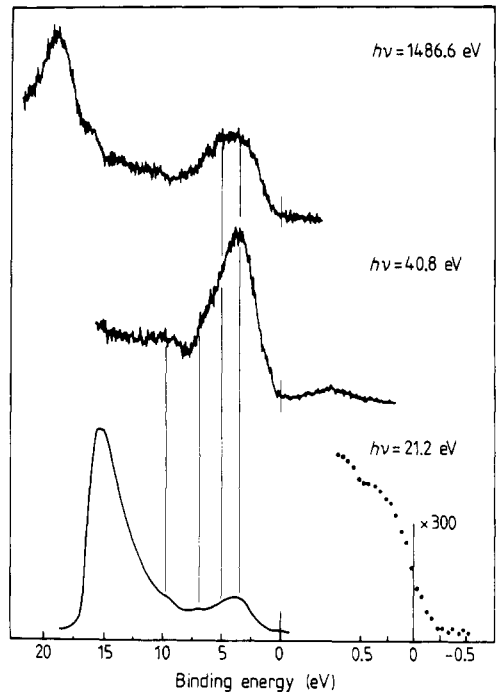

Figure 2. Valence region photoemission spectra of *c*-axis oriented thin-film (2212) phase material excited with Al Kα, He II and He I radiation. The Fermi level was established from measurements on a cleaned Ni stub. The expanded region around E_F in the He I spectrum has been stripped of contributions from He I β satellite radiation.

7.0 eV below the Fermi energy, E_F, energies identical to those observed in our earlier studies of (2212) phase ceramics [14]. The major part of the valence band intensity (to ~9 eV below E_F) is derived from strongly hybridised Cu 3d–O 2p states. The high degree of mixing of the orbitals is evidenced by the very small variation in the relative intensities of the valence band features on changing the incident photon energy and thus the O 2p:Cu 3d photoionisation cross section ratio [12, 14, 16]. The He I spectrum also shows a feature at 9.5 eV which has been widely attributed to a Cu satellite feature [14, 16]. A second satellite feature at ~12 eV merges into the secondary electron background beyond ~11 eV binding energy. For the present purposes, our main interest is in the density of states (DOS) at E_F, which is clearly apparent, although small (see inset, figure 2).

In order to compare our data with both band-structure calculations and our own work using ceramic samples, it is important to try to quantify this DOS, however roughly. We do this in the following way. Considering the valence band region of the spectrum, we may assume that the dominant contributions are from very strongly mixed Cu 3d–O 2p states (the contribution from these states is much larger than the Bi contribution in this region [26, 27]). Due to the strong mixing, we can ignore variation in ionisation matrix elements across the band, to a first approximation [13]. If we also assume that the density of final states available to ejected photoelectrons does not vary markedly with electron energy, then we can normalise the area of the valence band in He I photoemission to the total number of valence band states per $Bi_2Sr_2CaCu_2O_8$ or $(Bi_{1-x}Pb_x)_2Sr_2Ca_2Cu_3O_{10}$ unit cell, i.e. 66 and 87 states/cell respectively (both structures contain two formula units per cell). The assumption that the matrix elements and densities of final states do not vary much across the band is probably reasonable in the case of polycrystalline material, but it is conceivable that angle-resolved effects due to $\boldsymbol{k}$ conservation may arise in the case of the oriented thin film. However, experiments using cleaved single-crystal BSCCO materials have indicated that the appearance and relative intensities of the features in this part of the spectrum show only small changes with angle of offtake or photon energy, and band dispersion effects are very small [26, 27]. It is then possible to superimpose a vertical scale in units of states/eV cell on the observed photoemission. The result is shown in figure 3, which shows the DOS at E_F for three samples, all normalised to the scale of states/eV cell. Data for the thin film (2212) phase are shown by full circles. These are compared with previously obtained data from (2212) phase ceramics [14] (nominally $Bi_4Sr_3Ca_3Cu_4O_{16+x}$, open triangles) and a (2223) phase ceramic [16] (nominally $(Pb_{0.1}Bi_{0.9})_2Sr_2Ca_2Cu_3O_{10+x}$, open squares). Three points emerge from this analysis. Firstly, the DOS at E_F for the (2212) phase thin film is only around 0.15 states/eV cell, very much lower than estimates from band-structure calculations of around 3 states/eV cell [28–31]. Tight-binding calculations give an estimate of 2.4 states/eV cell [32]. Even allowing for the approximations involved in quantifying the photoemission data, the experimental results are clearly not consistent with one-electron band-structure calculations. Secondly, although there are some discrepancies away from E_F, the DOS at E_F from the (2212)

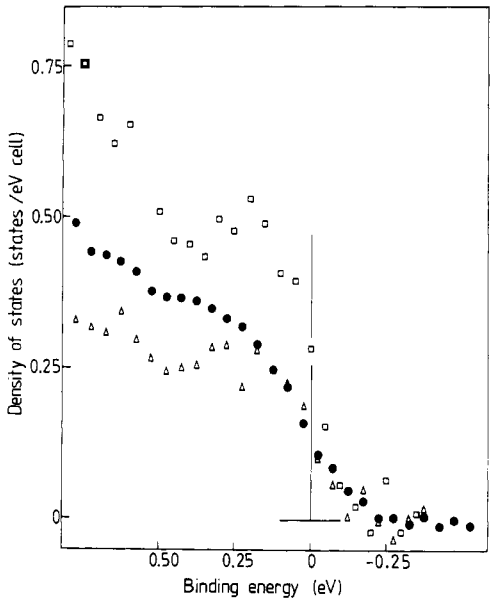

Figure 3. Densities of states, in states/eV cell, close to the Fermi energy for thin-film $Bi_{2.3}Sr_{1.3}Ca_{1.0}Cu_{2.0}O_x$ ((2212) phase, full circles), ceramic $Bi_4Sr_3Ca_3Cu_4O_{16+x}$ ((2212) phase, open triangles) and ceramic $(Pb_{0.1}Bi_{0.9})_2Sr_2Ca_2Cu_3O_{10+x}$ ((2223) phase, open squares), estimated from photoemission data (see text).

thin-film sample is identical to that from the ceramic sample of the same phase. Thirdly, as we have previously noted [16], the DOS at E_F from the Pb-doped (2223) phase is appreciably larger than that from the (2212) phase, as we would expect (note, however, that the numbers of valence band states/cell for the two structures are different).

The thin-film sample studied showed a high degree of *c*-axis orientation. This combined with the observation that the structure cleaves particularly easily between the Bi–O planes, perpendicular to the *c*-axis [33], means that the predominant plane forming the surface is likely to be a Bi–O layer. The close similarity between the thin film and ceramic data [14] for (2212) phase samples means that this assumption is probably also valid for the latter. If this is the case, then the 'topmost' Cu–O plane is buried ~4.5 Å into the surface [34]. As the photoelectron flux from the sample is attenuated by a Beer–Lambert-type law, then the observed photoemission will be unduly weighted by the contributions from the topmost few layers, in this case Bi–O (and to some extent Sr–O). Using the expression

$$I(x) = I_0(x)\exp(-d/\lambda)$$

where $I(x)$ is the emerging flux of photoelectrons and $I_0(x)$ is the flux of electrons of energy E originating at a depth d below the surface, and assuming a value for λ, the electron mean free pathlength of 10–15 Å [1], we easily arrive at the conclusion that the photoelectron flux from the Cu–O plane closest to the surface is attenuated to 64–74% of its absolute value on reaching the surface.

Parallel core and valence photoemission measurements on BSCCO and Pb-doped BSCCO materials [16] have previously led us to the conclusion (also reached by other groups [20, 22]) that the Bi–O planes make a contribution to the observed DOS at E_F in these materials. However, this is at variance with the recent work of Tanaka *et al* [35], who use a combination of photoemission and scanning tunnelling spectroscopy to conclude that the Bi–O planes are non-metallic. Band-structure calculations [28–31, 36, 37] indicate that there should be a Bi–O contribution at E_F, although its magnitude relative to the Cu–O plane contributions tends to vary from one calculation to another. However, all calculated values appear to be larger than our observed total DOS.

Whatever the possible magnitude of the Bi–O contribution, the absence of a Cu–O plane contribution to the DOS at E_F large enough to be consistent with band-structure calculations is striking. This is the case even when we take into account attenuation of the photoelectron flux from these planes discussed above. Thus, even though a metallic Fermi edge is easily observed in these materials, we cannot escape the conclusion that the Cu–O planes are strongly correlated as appears to be the case in $YBa_2Cu_3O_{7-x}$ [13, 15].

Acknowledgments

We thank Dr R G Egdell for several useful discussions. WRF is grateful to the Royal Society for the award of a 1983 University Research Fellowship.

References

[1] Seah M P and Dench W A 1979 *Surf. Interface Anal.* **1** 2
[2] Egdell R G, Flavell W R and Hollamby P C 1989 *J. Solid State Chem.* **79** 238
[3] see e.g. Shen Z-X, Lindberg P A P, Soukiassian P, Eom C B, Lindau I, Spicer W E and Geballe T H 1989 *Phys. Rev.* B **39** 823
[4] see e.g. Kurtz R L, Stockbauer R L, Mueller D, Shih A, Toth L E, Osofsky M and Wolf S A 1987 *Phys. Rev.* B **35** 8818
[5] see e.g. Lindberg P A P, Shen Z-X, Wells B O, Dessau D S, Mitzi D B, Lindau I, Spicer W E and Kapitulnik A 1989 *Phys. Rev.* B **39** 2890
[6] Nuecker N, Romberg H, Nakai S, Scheerer B, Fink J, Yan Y F and Zhao Z X 1989 *Phys. Rev.* B **39** 12379
[7] Nuecker N, Romberg H, Xi X X, Fink J, Gegenheimer B and Zhao Z X 1989 *Phys. Rev.* B **39** 6619
[8] Sakisaka Y *et al* 1989 *Phys. Rev.* B **39** 2304
[9] Sakisaka Y *et al* 1989 *Phys. Rev.* B **39** 9080
[10] Kohiki S, Hirochi K, Adachi H, Setsune K and Wasa K 1989 *Phys. Rev.* B **39** 4695
[11] Wagner G R Silver R M, Talvacchio J, Gavaler J R and Panson A J 1989 *Proc. 2nd Workshop on High-Temperature Superconducting Electron Devices (FED HiTcSc-ED), (Shikabe, Japan)*
[12] Flavell W R and Egdell R G 1988 *Supercond. Sci. Technol.* **1** 118
[13] Flavell W R and Egdell R G 1989 *Phys. Rev.* B **39** 231
[14] Flavell W R, Hampson J A, Neeson C and Tilley R J D 1989 *Supercond. Sci. Technol.* **1** 221
[15] Egdell R G and Flavell W R 1989 *Z. Phys.* B **74** 279
[16] Golden M S, Geeson D A, Male S E and Flavell W R 1989 *Supercond. Sci. Technol.* **2** 185

[17] see e.g. Wonltungton T R, Gallagher W J and Dinger T R 1987 *Phys. Rev. Lett.* **59** 1160
[18] Golden S J, Lange F F, Vaidya K J and Bloomer T E 1989 further work to be presented at the *MRS Fall Meeting, Boston*
[19] Steiner P, Huefner S, Jungmann A, Junk S, Kinsinger V, Sanders I, Thiele W R, Backes N and Politis C 1988 *Physica* C **156** 213
[20] Fujimori A, Takehawa S, Takayma-Muromachi E, Uchida Y, Ono A, Takahashi T, Okabe Y and Katayama-Yoshida H 1989 *Phys. Rev.* B **39** 2255
[21] Hillebrecht F U *et al* 1989 *Phys. Rev.* B **39** 236
[22] Shen Z-X, Lindberg P A P, Wells B O, Mitzi D B, Lindau I, Spicer W E and Kapitulnik A 1988 *Phys. Rev.* B **38** 11820
[23] Meyer H M III, Hill D M, Weaver J H, Nelson D L and Gallo C F 1988 *Phys. Rev.* B **38** 7144
[24] Hill D M, Meyer H M III, Weaver J H, Gallo C F and Goretta K C 1988 *Phys. Rev.* B **38** 11331
[25] Kishida S, Tokutaka H, Nakanishi S, Nishimori K, Ishihara N and Fijimoto H 1989 *Japan J. Appl. Phys.* **28** L406
[26] Minami F, Kimura T and Takekawa S 1989 *Phys Rev.* B **39** 4788
[27] Maeda F, Kawamura T, Oshima M, Hidaka Y and Yamaji A 1989 *Japan. J. Appl. Phys.* **28** L361
[28] Mattheiss L F and Hamann D R 1988 *Phys. Rev.* B **38** 5012
[29] Freeman A J Yu J and Massidda S 1988 *Physica* C **153–155** 1225
[30] Hybertsen M S and Mattheiss L F 1988 *Phys. Rev. Lett.* **60** 1661
[31] Krakauer H and Pickett W E 1988 *Phys. Rev. Lett.* **60** 1665
[32] Richert B A and Allen R E 1989 *Phys. Rev.* B submitted
[33] Nakanishi S, Fukuoka N, Nakahigashi K, Kogachi M, Sasakura H, Minamigawa S and Yanase A 1989 *Japan. J. Appl. Phys. Lett.* **28** 71
[34] see e.g. Tarascon J M, Le Page Y, Barboux P, Bagley B G, Greene L H, McKinnon W R, Hull G W, Giroud M and Hwang D M 1988 *Phys Rev.* B **37** 9382
[35] Tanaka M, Takahashi T, Katayama-Yoshida H, Yamazaki S, Fujinami M, Okabe Y, Mizutani W, Ono M and Kijimura K 1989 *Nature* **339** 691
[36] Herman F, Kasowski R V and Hsu W Y 1988 *Physica* C **153–155** 629
[37] Herman F, Kasowski R V and Hsu W Y 1988 *Phys Rev* B **38** 204