OXYGENATION AND POSSIBLE ETCHING OF HIGH T$_c$ SUPERCONDUCTING FILMS BY OXYGEN PLASMA

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ABSTRACT

The use of a radio frequency (RF) excited oxygen plasma for cleaning and oxygenation of high T$_c$ superconducting films at room temperature is studied by photoemission spectroscopy. Plasma oxidation at ~10 mT pressure, removes contaminants like carbon and causes the Ba 5p and 4d and the O 1s corelevels to shift to lower binding energy. Valence band spectra for an epitaxial $Y_2Ba_4Cu_8O_{16+x}$ film on $SrTiO_3(001)$ show a Fermi edge and resemble spectra presented by other groups for $YBa_2Cu_3O_7$ single crystals and epitaxial films. These films also show a sharp O 1s corelevel near 528 eV. Possible reactive ion etching of a degraded YBCO film surface is demonstrated in a series of spectra taken after successive oxygen plasma treatments. A surface contaminated with $BaCO_3$ becomes barium deficient after the initial plasma treatment but a second plasma treatment of a substrate biased to -200 V to promote sputtering produces photoemission features typical of an $YBa_2Cu_3O_7$ surface.

INTRODUCTION

The electronic properties and surface structure of $YBa_2Cu_3O_7$ and similar ceramic materials depend strongly on stoichiometry making control of surface composition and reduction of contamination during thin film growth and processing important.[1,2] For surface studies of high temperature superconductors, clean surfaces are prepared by cleaving single crystals in ultrahigh vacuum.[3] $YBa_2Cu_3O_7$ surfaces have degrees of stability in vacuum at room temperature depending, in part, on the structure and composition of the particular material.[4,5] $Bi_2Sr_2CaCu_2O_{8-x}$ is more stable and a true Fermi edge can be seen in materials maintained at 300 K.[6] Common techniques for preparing clean surfaces (e.g. Ar$^+$ bombardment, high temperature annealing, etc.) are known to fail because irreversible surface damage or compositional change occurs. For example, Lindberg et al.[6] examined $Bi_2Sr_2CaCu_2O_{8-x}$ films and found that these films are damaged by Argon bombardment. Unfortunately, cleaving can not be applied to films. Hence, the development of new methods to prepare and clean high T$_c$ film surfaces is necessary.

In this paper, surface sensitive photoemission spectroscopy is used to monitor the affect of an RF excited oxygen plasma on the surface of epitaxial $Y_2Ba_4Cu_8O_{16+x}$ films supported on $SrTiO_3$.

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Reactive plasmas are often used to remove organic materials like photoresists from semiconductor surfaces and etch semiconductors.[7] Oxygen plasmas are used in schemes designed to fabricate high T_c thin films requiring low temperature or no post-annealing step.[8,9] Bagley et al.[10] report that similar oxygen plasma treatments can restore superconductivity in thin films. Yoshida et al.[11] used an oxygen plasma to convert nonsuperconducting tetragonal $YBa_2Cu_3O_6$ to the orthorhombic superconducting phase at 160°C. Our photoemission data suggests that in addition to reoxygenating the high T_c material, the oxygen plasma chemically reacts with the surface and changes the surface composition. Increasing the kinetic energy of the incident oxygen ions (i.e. by applying an electric bias to the substrate) may cause sputtering, etching, or atomic mixing and leads to a surface resembling that obtained by Stoffel et al. for a cleaved 1-2-3 single crystal[3] or by Sakisaka et al.[12] for their in situ MBE grown and post annealed 1-2-3 thin film.

The oxygen plasma treatment and photoemission spectroscopy were done in a two compartment ultrahigh vacuum (UHV) chamber installed on the U7b PGM beam line at the Brookhaven National Laboratory National Synchrotron Light Source (NSLS). The epitaxial c-type $Y_2Ba_4Cu_8O_{16+x}$ films were grown on $SrTiO_3(100)$ substrates by co-evaporation of Cu, BaF_2 and Y. The post-annealing step included heating in flowing wet oxygen for 30 min at 835°C and slow cooling in flowing wet oxygen for 10 min and in dry oxygen for 20 min. X-ray diffraction and magnetization measurements were made to verify the structure and superconducting properties of the samples. The films show a sharp superconducting transition at 82.5 K and have large critical currents ($J_c > 10^6$) at 77 K. Oxygen plasma exposures were conducted on the thin film samples after the vacuum chamber in which they were placed was baked for 24 hrs at 130°C achieve an ultrahigh vacuum in the mid 10^{-10} Torr range. Plasma processing was done in the preparation chamber. An oxygen plasma containing O^+ ions was produced by an RF ion gun described in Ref. 13. Plasma was generated in the quartz tube by a 13.5 MHz RF field delivering 10 watts to the plasma. The plasma was directed onto the sample from a pinhole placed at the end of the quartz tube and the RF electrode was a helical coil wrapped around the quartz tube. The oxygen partial pressure in the preparation chamber was 12 mTorr. All plasma processing and photoemission work reported here were conducted at room temperature. The photoemission energy distribution curves (EDCs) were collected using a double-pass cylindrical mirror analyzer (CMA) operated at a pass energy of 25 eV with the superconducting film oriented with the sample normal 42° from the CMA axis. Monochromatic synchrotron radiation was incident on the sample at an angle of 48° from the sample normal. An x-ray source was added to the vacuum chamber to obtain EDCs of the O 1s corelevel.

RESULTS AND DISCUSSION

Figure 1 shows valence band photoemission spectra recorded for a contaminated "as is" $Y_2Ba_4Cu_8O_{16+x}$ thin film surface before exposure to the oxygen plasma; for the same surface after a 25 min oxygen

plasma exposure [curve (1)]; and for the same surface after a second 25 min exposure during which the thin film was negatively biased with 200 volts [curve (2)]. The spectra shown in Fig. 1 are taken at 105 eV photon energy to use 4d-5p giant resonance to enhance the intensity of the shallow Ba 5p corelevel. The valence band for the "as is" surface resembles spectra published by Schrott et al.[14] for bulk materials before a layer of contaminated surface material is removed. This surface is known to consist of oxides like CuO and Y_2O_3, carbonates like $BaCO_3$, hydroxides like $Ba(OH)_2$ and graphitic carbon. This nonsuperconducting surface layer is created by an incongruent chemical reaction with atmospheric gases[15] or remains after the post annealing step. The binding energy and sharp appearance of the Ba $5p^{3/2}$ (14.8 eV) corelevel suggests that Ba is found in a uniform surface environment and also suggests that the Ba compound is $BaCO_3$ or a similar compound.[16] The surface is not metallic because photoemission is not seen at the Fermi level (note: the Fermi level was located by evaporation of a thick Au film onto the sample).
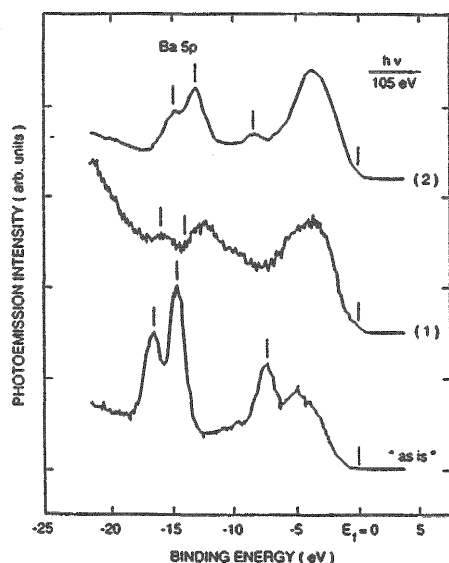

Fig. 1. Comparison of photo-emission spectra taken on the giant Ba 4d-5p resonance for (a) "as is" $Y_2Ba_4Cu_8O_{16+x}$ film before oxygen plasma exposure, (b) [curve (1)] the film after a 25 min oxygen plasma exposure with no bias applied, and (c) [curve (c)] the same film after a second oxygen plasma exposure during which a -200 V bias was applied to the sample.

After the first oxygen plasma exposure, Fig. 1, [curve (1)] the appearance of the valence band and the binding energy of the Ba 5p corelevel changes. The Ba 5p corelevel is less intense and the Ba $5p^{3/2}$ peak overlaps with a broad feature located between 10 and 15 eV which is not observed in the "as is" spectrum. The position of the Ba $5p^{1/2}$ peak is shifted 0.5 eV to lower binding energy. The 7.5 eV peak which is the strongest valence band feature in the "as is" EDC disappears after interaction with the oxygen plasma and the valence band becomes broader and its center of gravity moves about 0.5 eV closer to the Fermi level. The top of the valence band shows a Fermi edge indicating this surface is metallic. We believe the changes in the photoemission spectrum are due to a chemical reaction between O+ and the contaminated $Y_2Ba_4Cu_8O_{16+x}$ thin film surface. Exposure of the same surface to molecular oxygen gas did not produce a change. Interaction between the $Y_2Ba_4Cu_8O_{16+x}$ surface and the oxygen plasma modifies impurity phase containing barium. It is not clear from the data whether the Ba component is

removed from the surface or buried by a Ba-deficient oxide layer. We do not think sputtering is likely when no bias is applied to the substrate and are unaware of a suitable volatile Ba species. Carbon is removed from the surface and we speculate that O+ reacts with $BaCO_3$ or related compounds to form CO or CO_2. The resulting barium deficient surface is stable in the vacuum because spectra taken from this surface after it remained in the vacuum chamber overnight were unchanged.

Since the spectra taken after oxygen plasma treatment do not resemble those obtained for 1-2-3 surfaces, a negative 200 volt bias was applied to the sample to increase the kinetic energy of the incident oxygen ions to promote sputtering and remove the barium deficient oxide layer. The resulting spectrum for the 2-4-8 phase, Fig. 1, [curve (2)], is similar to spectra obtained for a $YBa_2Cu_3O_7$ surface produced by cleaving. The 5p corelevels are well resolved and the Ba $5p^{3/2}$ binding energy is at ~13 eV. There is also evidence from the shape of the Ba 5p peak of a Ba $5p^{3/2}$ component at ~12 eV. Stoffel et al.[3] report a value of ~13 eV for the binding energy of the Ba $5p^{3/2}$ of single crystal $YBa_2Cu_3O_7$. Fowler et al.[4] find that high quality 1-2-3 crystals have this feature at 12 eV. In the valence band spectra taken at 105 eV weak features are seen at 12 and 9.0 eV. The valence band peaks near 4 eV and photoemission is seen at Fermi level. Closer examination of the region near E_f shows a clear edge.

Figure 1 also shows a peak at 9 eV which grows in relative intensity (compared with the valence states) with decreasing photon energy. The interpretation of the 9 eV feature is complicated by the fact that surface contamination,[14] ion bombardment[6] or chemisorption[17,18] generates features near this binding energy. This feature is also seen for cleaved surfaces suggesting it may be an intrinsic feature of $YBa_2Cu_3O_7$.[19] However, other investigators[20] produced spectra showing weak or non-existent features at this binding energy. Sakisaka et al.[12] report that the 9 ev feature is largest for thin films showing obvious signs of surface disorder in their LEED patterns. Samples with sharp unreconstructed LEED patterns had no 9 eV feature. Like Tang et al.,[19] we find that the 9 eV feature seen for our film has an oxygen-like cross section suggesting it is oxygen related. Since XPS scans of the C 1s region show no trace of carbon, we conclude that the 9 eV feature is extrinsic and related to thin film defects or surface disorder.

In Figs. 2-4, we show spectra obtained after O_2 plasma exposure of a substrate biased at -200 V. The Ba 4d spectrum [Fig. 2(a)] is well-resolved and the oxygen plasma treatment causes the Ba 4d corelevel to shift 1.0 eV to lower binding energy. The 89.2 eV binding energy is close to that reported by Stoffel et al.[21] for a cleaved 1-2-3 crystal and the corelevel shift is smaller than that observed for the Ba 5p levels. Again, Fowler et al.[4] find this feature at a lower binding energy than Stoffel et al. The sharpness of the Ba 4d levels after oxygen exposure suggests that the Ba environment is homogeneous.
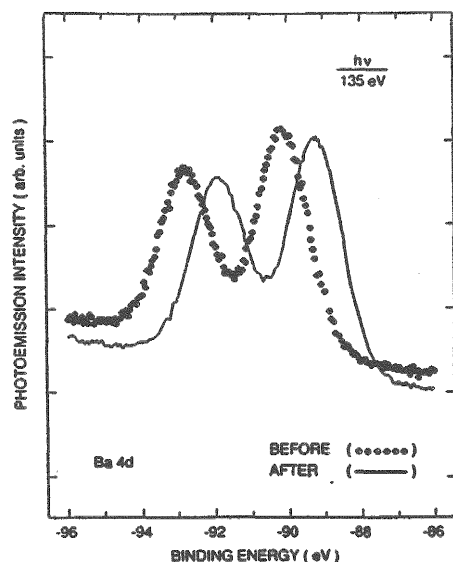
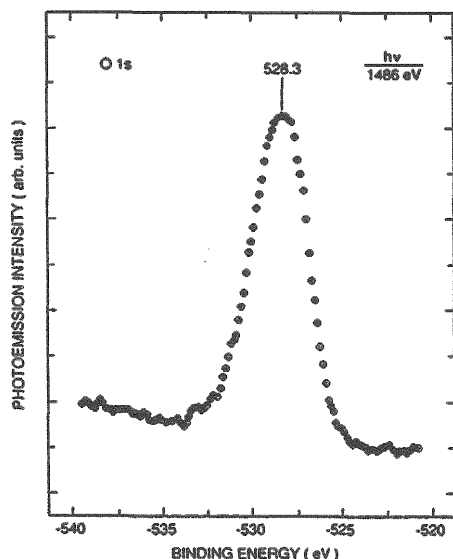Fig. 2(a). Comparison of Ba 4d corelevel spectra (hv = 135 eV) before (...) and after (——) oxygen plasma treatment.

Fig. 2(b). O 1s corelevel (hv = 1486 eV) for the plasma treated $Y_2Ba_4Cu_8O_{16+x}$ surface taken using Al K-α XPS source.

The O 1s corelevel shown in Fig. 2(b) is known to be sensitive to surface conditions and early results showed it had at least two or more components at 529 and 531 eV. Studies of high quality bulk material and single crystals conclusively showed that the O 1s has only one broad component between 528 and 529 eV and that the higher binding energy component is contamination related.[22] Our data for $Y_2Ba_4Cu_8O_{16+x}$ film after biased oxygen plasma treatment show a broad single peak (3 eV FWHM) with a maximum at 528.3 eV. Our experimental resolution of 1.2 eV broadens the peak and prevents resolution of O 1s into components from nonequivalent oxygen sites.[23] The appearance and binding energy of the O 1s corelevel strongly suggests that this thin film surface resembles the surfaces of high T_c superconductors produced by fracture, or cleaving.

Figures 3 and 4 show photoemission results for a less heavily contaminated 2-4-8 film before and after a biased oxygen plasma treatment. We believe these films lose oxygen during the bakeout needed to establish an ultrahigh vacuum and that the surface is oxygen deficient. Conard et al.[24] report that low temperature plasma oxidation can be used to restore materials like $YBa_2Cu_3O_7$ by replacing the lost oxygen. When 1-2-3 loses oxygen the Fermi edge disappears and the corelevels (e.g. Ba 4d or O 1s) or valence band features shift to higher binding energy. These changes are consistent with the surface material becoming non-metallic. Figure 3 shows that plasma oxidation increases the density of states at E_f, shifts the valence band towards the Fermi level and shifts the corelevels
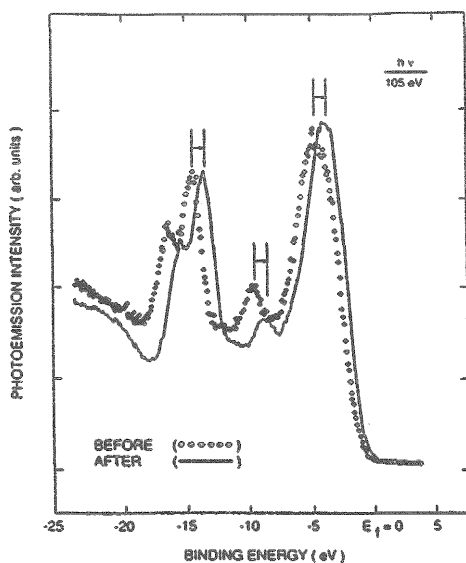
Fig. 3. Valence band spectra for oxygen deficient $Y_2Ba_4Cu_8O_{18+x}$ ($h\nu = 105$ eV) before and after reoxygenation at room temperature by the oxygen plasma.
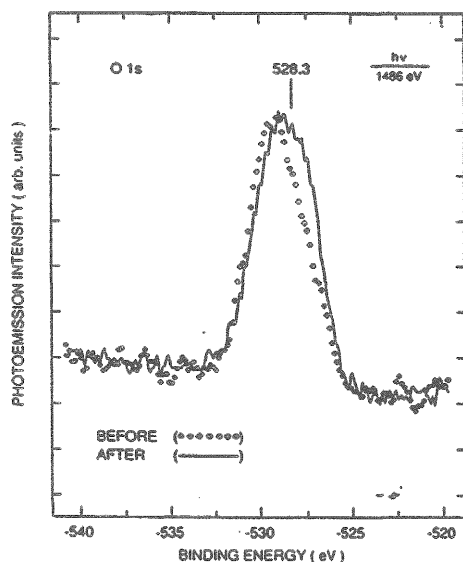

Fig. 4. O 1s corelevel for ($h\nu = 1486$ eV) oxygen deficient $YBa_2Cu_8O_{18+x}$ before and after reoxygenation by the oxygen plasma.

and "9 eV" peak to lower binding energy. The corelevel shifts are probably due to the improved screening of the core hole as the material becomes metallic. Figure 4 shows that plasma oxidation causes the O 1s corelevel to become less asymmetric and shift to lower binding energy. We believe the lower binding energy O 1s component near 528 eV is due to the "metallic" and presumed super-conducting phase of this material while the component near 529 eV is due to the non-metallic phase. Closer examination of the O 1s peak for the oxygen deficient 2-4-8 surface shows a small component at 528 eV which is probably due to photoemission from the superconducting phase which lies under the non-metallic surface layer.

CONCLUSIONS

Based on our photoemission data, we believe the oxygen plasma treatments produce a $Y_2Ba_4Cu_8O_{18+x}$ surface which is similar to surfaces of the $YBa_2Cu_3O_7$ prepared by several groups from crystals or films by other techniques. We have discussed valence band and corelevel photoemission results for a $Y_2Ba_4Cu_8O_{18+x}$ film supported on $SrTiO_3$ which was modified by interaction with an RF excited oxygen plasma. The oxygen plasma chemically reacts with the film surface and destroys impurity phases. We conclude that oxygen plasmas can be used to clean and possibly etch $Y_2Ba_4Cu_8O_{18+x}$ films without using mechanical means. Oxygen deficient surfaces can be modified by plasma oxidation. Such surfaces have a Fermi edge and can be distinguished on the basis of corelevel data from the non-metallic surface.

ACKNOWLEDGMENTS

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