Electronic structure of HgBa₂CaCu₂O₆+δ epitaxial films measured by x-ray photoemission

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The electronic structure and chemical states of HgBa$_2$CaCu$_2$O$_{6+\delta}$ epitaxial films have been studied with x-ray photoelectron spectroscopy. Signals from the superconducting phase dominate all the core-level spectra, and a clear Fermi edge is observed in the valence-band region. The Ba, Ca, Cu, and O core levels are similar to those of Ti$_2$Ba$_2$CaCu$_2$O$_{8+\delta}$ but distinct differences are observed in the valence bands which are consistent with differences in the calculated densities of states.

Interest in Hg cuprate high-temperature superconductors (HTS), HgBa$_2$Ca$_n$Cu$_{2n+2}$O$_{2n}$ (Hg-1201, Hg-1212, and Hg-1223 for $n=1$, 2, and 3, respectively), has been stimulated by the higher superconducting transition temperatures, $T_c$, compared to other HTS cuprates ($T_c \sim 95$ K for Hg-1201, $T_c \sim 125$ K for Hg-1212, and $T_c \sim 135$ K for Hg-1223 at ambient pressure).$^{12}$ $T_c$ can be increased to over 150 K when these materials are subjected to quasihydrostatic pressure.$^7$ The recent growth of high-quality Hg-1212 epitaxial thin films$^3$ and the fabrication of these films into superconducting quantum interference devices$^5$ which operate at temperatures in excess of 110 K demonstrates the potential technological importance of these materials.

X-ray photoelectron spectroscopy (XPS) has been widely utilized to characterize the chemical states and electronic structure of HTS materials.$^8$ Results of these studies include a set of well-defined spectral features which are characteristic of high-quality surfaces:$^7,8$ a high binding energy Cu$^{+2}$ satellite in the Cu 2$p$ region, low binding energy O 1$s$ and alkaline earth core-level signals, and a clear Fermi edge in the valence band. These earlier studies on HTS materials should provide valid guidelines for assessing XPS measurements on the chemically and structurally similar Hg cuprates.

XPS measurements on Hg-1212 and Hg-1223 (Ref. 9) and on Hg-1201 (Ref. 10) polycrystalline pellets have previously been reported. In one study only Cu 2$p$ and Hg 4$f$ core-level measurements were presented,$^{10}$ so that it is not possible to ascertain the surface quality. In the other study,$^9$ a complete set of core-level measurements was presented. Chemical inhomogeneities and differential charging were reported, and the spectra included prominent, or even dominant, signals which were attributed to grain-boundary impurities. Both of these previous studies$^9,10$ mentioned valence-band measurements, including a report of a weak Fermi edge,$^{10}$ which were not presented. XPS measurements of Hg cuprates with higher surface quality are clearly desirable.

In this work, XPS measurements are reported for high-quality Hg-1212 epitaxial films, rather than the polycrystalline pellets used in earlier studies. Core-level measurements are presented which are dominated by signals attributable to the superconducting phase, and are compared to those of Ti$_2$Ba$_2$CaCu$_2$O$_{8+\delta}$ (TI-2212), which is chemically and structurally most similar to Hg-1212. Measurements of the Hg-1212 valence band, which exhibits a clear Fermi edge, are presented and compared to the TI-2212 valence band$^{11}$ and to the densities of states reported in Hg-1212 and TI-2212 band-structure calculations.$^{12,13}$

Two Hg-1212 films ~3000 Å thick were grown epitaxially on SrTiO$_3$ (100) substrates by laser ablation. Details of the film growth and characterization are described elsewhere.$^4$ The films exhibit zero resistance at 120 and 123 K. Both films were prepared in a nitrogen atmosphere for transport to the XPS spectrometer, one in an evacuated quartz ampoule, and the other in a polypropylene wafer container sealed with dessicant in a plastic bag, both of which were unsealed in the ultrahigh purity nitrogen atmosphere of a dry box which encloses the XPS load lock. The films are cleaned with a nonaqueous etchant consisting of 0.2% Br$_2$ in absolute ethanol, rinsed in ethanol, blown dry with nitrogen, and loaded into the XPS chamber with no air exposure. This procedure has yielded high-quality surfaces for other HTS materials.$^8$ The etchant forms reaction products (HgBr$_2$, BaBr$_2$, CaBr$_2$, CuBr$_2$) which are soluble in ethanol, and the etch rate is ~400–600 Å/min. The XPS spectra are accumulated on a Surface Science Instruments SSX-501 spectrometer with monochromatized Al $K\alpha$ x-rays (1486.6 eV) and a base pressure of $5 \times 10^{-10}$ Torr. The x-ray beam diameter is 150 μm for the core-level measurements and 300 μm for the valence-band measurements. The pass energy of the electron energy analyzer is 25 eV, yielding a peak full width at half maximum (FWHM) of 0.7 eV for a Au 4$f_{7/2}$ signal. The photoemission is normal to the film surface unless specified otherwise. Measurements of the ac susceptibility show that the films remain superconducting after transport, etching, and vacuum exposure.

Prior to etching, the XPS spectra exhibit differential charging, as determined by varying the filament current on an electron flood gun. No charging is observed after etching, indicating the removal of insulating impurities. Small SrTiO$_3$ substrate signals are observed prior to etching, indicating voids, and increase in intensity with etching, but ac-
count for $<8\%$ of the O $1s$ and $<1\%$ of the valence-band signals for the data presented here. Both films yield comparable XPS data, the data presented are from the film with $T_c = 123$ K etched for 90 s. The surface stoichiometry after etching is Hg:Ba:Ca:Cu:O$_{0.7:2.4:1:2:8}$. The Hg deficiency is likely due to the volatility of Hg, while the excess O and Ba are related to impurities, as discussed and shown in the spectra below, although some preferential etching cannot definitively be ruled out at this time.

The O $1s$ spectrum, which is commonly used to assess surface cleanliness, for Hg-1212 is shown in Fig. 1. The dominant peak near 528 eV is consistent with measurements from other HTS materials, and is therefore assigned to Hg-1212. The peak near 531.5 eV is enhanced for more surface-sensitive photoemission from normal, is dominant in a previous study of Hg cuprates and in this work prior to etching, and has been determined to originate from surface or grain-boundary impurities in studies of other HTS materials. The O $1s$ signal of Tl-2212 (Ref. 14) is also shown in Fig. 1 for comparison. Components at 527.8 and 528.8 eV can be resolved in the second derivatives, as shown in the inset of Fig. 1, and by least-squares fitting for both Hg-1212 and Tl-2212, and are assigned to Cu-O planes and Hg-O or Tl-O bonding, respectively. These assignments are consistent with studies of other HTS cuprates in which signals near 528.0 eV were assigned to Cu-O planes. The difference in line shapes evident in Fig. 1 is due to the difference in the relative intensities of the two components, since O in Cu-O planes accounts for 50\% of the O in Tl-2212 and 67\% in Hg-1212. For photoemission from normal, the O $1s$ signal associated with Hg-O bonding is enhanced relative to the Cu-O signal, indicating that Hg-O bonds occur closer to the surface and Cu-O planes occur deeper in the bulk.

The Hg $4f$ and Ba $4d$ spectra are shown in Fig. 2 together with the results of least-squares fitting. The Hg $4f$ spectrum can be seen in Fig. 2 to be well represented by a single doublet even neglecting energy losses from the Ba $4d$ signal. The small excess intensity between the two Hg $4f$ components, often an indication of additional chemical states, is eliminated when the Ba $4d$ signal of YBa$_2$Cu$_3$O$_{7}$ is shifted to the same binding energy as that of Hg-1212, scaled to the same integrated intensity and subtracted. The binding energy of the Hg $4f_{7/2}$ component is 100.6 eV (1.5 eV FWHM), close to the value of 100.8 eV reported for HgO. The Hg $5d$ signal can also be fit with a single doublet with a $5d_{5/2}$ component at 8.7 eV (1.1 eV FWHM). These results are in contrast to earlier studies in which higher binding energy signals were prominent and were attributed either to impurities and differential sample charging, or to Hg$^{+3}$, the existence of which would be unprecedented in an isolable chemical compound. In this work Hg is found to occur in a single chemical state consistent with Hg$^{+2}$, thereby excluding the possibility of Hg$^{+3}$.

The Ba $4d$ spectrum, shown in Fig. 2 together with the results of least-squares fitting, consists of a dominant doublet assigned to Hg-1212 with a $4d_{5/2}$ component at 87.8 eV (1.1 eV FWHM), and a much less intense signal at higher binding energy. The higher binding energy signal is dominant prior to etching and is enhanced for more surface-sensitive photoemission from normal, and is therefore assigned to impurities. Similar observations are made for other Ba core levels, with the dominant Ba $3d_{5/2}$ signal at 778.2 eV (1.45 eV FWHM) and the dominant Ba $5p_{3/2}$ signal at 12.6 eV (1.2 eV FWHM). The Ca $2p$ spectrum, shown in Fig. 3 together
with the results of least-squares fitting, consists of two prominent doublets with $2p_{3/2}$ components at 344.5 eV (1.1 eV FWHM) and 345.6 eV (1.2 eV FWHM), both assigned to Hg-1212. The prominent Ca $2p_{3/2}$ signal prior to etching (and therefore associated with impurities) is near 347 eV, but is not detectable after etching. These findings contradict the interpretation in an earlier study, in which dominant high binding energy Ba $3d$ and Ca $2p$ signals were assigned to the superconductor based on the questionable assumption that the surface stoichiometry reflected that of the bulk. The spectra in Figs. 2 and 3 are very similar to the Ba $4d$ and Ca $2p$ spectra of TI-2212. These signals occur at significantly lower binding energies than those of Ba and Ca metals, as is also the case for other HTS materials, which has been interpreted as due to initial state electrostatic effects. Two Ca $2p$ doublets have also been observed for TI-2212 and Bi$_2$Sr$_2$CaCu$_2$O$_{8+*}$, and have been interpreted as originating from occupation of inequivalent lattice sites due to cation disorder. For Hg-1212, the Ca $2p_{3/2}$ signal at 344.5 eV is reduced in intensity relative to the $345.6$ eV signal for photoemission from normal and can therefore be assigned to the site between Cu-O planes, consistent with the interpretation of the O $1s$ spectrum discussed above.

The Cu $2p_{3/2}$ spectrum of Hg-1212, shown in Fig. 4, is typical of Cu$^{2+}$ compounds, with a prominent multiplet at high binding energy corresponding to $2p^53d^9L$ final states, where $L$ denotes the oxygen ligand and underscoring denotes a hole. The more intense peak at 933 eV corresponds to well-screened $2p^53d^{10}L$ states resulting from ligand-to-metal charge transfer. The Cu $2p_{3/2}$ spectrum in Fig. 4 is similar to measurements of other HTS cuprates, though the $d^9/d^{10}$ intensity ratio of 0.36±0.02 is lower than the value of 0.45 observed for TI-2212. This difference may reflect differences in electron correlation in these similar materials, as discussed elsewhere. In an earlier study of Hg-1201 scraped in vacuum, no $d^9$ signal was detected, which may be an artifact of scrape-induced surface damage since for other HTS materials scraping results in loss of $d^9$ intensity due to reduction of Cu$^{2+}$ to Cu$^{+}$. The same study also concluded that Cu occurred in multiple oxidation states based on the complex line shape of the $d^{10}$ signal, which actually reflects a multiplet of final states, as discussed elsewhere.

Figure 5 shows the Hg $5d$ and Ba $5p$ shallow core levels and the valence band of Hg-1212, which consists primarily of hybridized Cu $3d$ and O $2p$ states. For the photon energy used here, the Cu $3d$ character is dominant (90% of the spectral weight assuming ideal stoichiometry) due to a higher photoelectric cross section. Shown below the valence band is the Cu $3d$ partial density of states from Hg-1212 band-structure calculations, shifted by 2 eV to approximately match the envelope of the valence band. Similar shifts have been found necessary for other HTS materials, and have been attributed to electron correlation effects which are inadequately treated in calculations. For comparison, the Cu $3d$ partial density of states of TI-2212 (Ref. 13) is shown below that of Hg-1212. As observed for high-quality surfaces of other HTS materials, a clear Fermi edge, shown more clearly in the inset in Fig. 5, verifies the high quality of the Hg-1212 surface.

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The above data show that the core levels of Hg-1212 are similar to those of other HTS cuprates, particularly those of Ti-2212. However, despite these similarities and the chemical and structural similarities, the valence bands of Hg-1212 and Ti-2212 exhibit distinct differences, as shown in Fig. 6. Hg-1212 exhibits a lower Fermi-level density of states despite its higher $T_c$, and a relatively higher density of states near 6 eV. The Hg-1212 and Ti-2212 Cu 3d partial densities of states are very similar (see Fig. 5), and do not appear to be sufficiently different to account for the data near 6 eV. The most notable differences occur for the apical oxygen 2p partial densities of states, shown below the valence bands in Fig. 6, which are qualitatively consistent with the differences in the valence bands. Both of the calculated spectra have been shifted by the 2 eV necessary to align the Cu 3d partial densities of states with the valence bands. Differences in the Cu-O plane oxygen partial densities of states are less prominent, but contribute twice the spectral weight of the apical oxygens and are also consistent with the observed differences in the valence bands. Differing contributions of the TI 6s/5d (Refs. 13, 22) and Hg 5d states, with lower partial densities of states in the energy range 0–8 eV but higher photoionization cross sections than the O 2p states, may be more important and are also consistent with the valence-band measurements.

In summary, XPS has been used to characterize epitaxial films of Hg-1212. Signals attributable to the superconducting phase dominate all the core-level spectra. Hg is found to be in a single chemical state consistent with Hg$^{2+}$, contrary to a previous report based on measurements from polycrystalline pellets. The Ba, Ca, Cu, and O core levels are similar to those measured from other HTS cuprates, particularly those of Ti-2212, which is chemically and structurally most similar to Hg-1212. Two O 1s signals assigned to Cu-O planes and Hg-O bonds are distinguishable, as are two Ca 2p signals which may indicate cation disorder. Despite the similarities in the core-level spectra, distinct differences are observed in the valence bands of Hg-1212 and Ti-2212 which are consistent with differences in the calculated densities of states. A clear Fermi edge is observed in the valence-band region.

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6. For recent reviews, see the special issue on high temperature superconductors in J. Electron Spectrosc. Relat. Phenom. 66, Nos. 3 & 4 (1994).