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Electronic structure of the gold/Bi$_2$Sr$_2$CaCu$_2$O$_8$ and gold/EuBa$_2$Cu$_3$O$_{7-\delta}$ interfaces as studied by photoemission spectroscopy

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High-resolution photoemission has been used to probe the electronic structure of the gold/Bi$_2$Sr$_2$CaCu$_2$O$_8$ and gold/EuBa$_2$Cu$_3$O$_{7-\delta}$ interface formed by a low-temperature (20 K) gold evaporation on cleaved high quality single crystals. We find that the metallicity of the EuBa$_2$Cu$_3$O$_{7-\delta}$ substrate in the near surface region ($\sim$5 Å) is essentially destroyed by the gold deposition, while the near surface region of Bi$_2$Sr$_2$CaCu$_2$O$_8$ remains metallic. This has potentially wide ranging consequences for the applicability of the different types of superconductors in real devices.

A key requirement in both utilizing and understanding the high-temperature superconductors is the fabrication of very high quality materials. With the advent of high quality single crystals and films, this requirement is at least now partly fulfilled. One very important next step is a knowledge of the properties of interfaces of these materials with others. Photoemission spectroscopy is a natural tool to probe the interfacial region because of its surface sensitivity (in the range of 3–100 Å) and ability to detect changes in the local chemical environment of an atom. It has already been very successfully applied to the study of the interfacial chemistry of a wide variety of adatoms on the different types of high T_c substrates.[1-4] Typically, the effects of the adatoms on the Cu 2p and O 1s line shapes were emphasized most strongly, since the Cu-O planes are thought to be crucial to the superconductivity. In particular, a single O 1s peak centered at a binding energy of around $-$529 eV and a strong Cu 2p satellite/main line intensity ratio are thought to be especially important. Higher binding energy O 1s components are usually associated with the formation of some oxide while the disappearance of the Cu 2p satellite signals a decrease of the Cu valency from 2 + to 1 +. These earlier experiments showed that gold formed the cleanest interfaces with each of the cuprate superconductors; it goes down smoothly with no evidence for islanding and does not adversely affect the Cu 2p or O 1s line shapes.[1,2] Other noble metals such as Ag, Pd, and Cu did not tend to fare as well.[3,4]

This letter addresses primarily the states at the Fermi level, and how they are affected by the application of gold adatoms. This is a more sensitive and direct test of the interfacial region than the core level line shape studies for a number of reasons. First, we are considering those states that are directly responsible for the superconductivity. Second, we have used higher resolution (200 meV) than is possible with x-ray photoemission spectroscopy (XPS)

core level studies, and, since the photoelectron kinetic energies are lower, we are more surface sensitive (escape depths on the order of 3–10 Å as opposed to 5–50 Å for XPS).[5] This surface sensitivity is actually very crucial because of the very short superconducting coherence lengths of these materials, particularly along the c axis ($\sim$3 Å).[6] The coherence length is greater along the a or b axes, but surfaces for a- or b-axis junctions are much more difficult to prepare. Also, chemical intuition tells us that we are not as likely to have as clean an interface along the a or b axes as along the c axis. Our junctions were formed on crystals cleaved normal to the c axis (the easy cleavage direction).

The experiments were performed at the Mark II grasshopper monochromator at the Synchrotron Radiation Center in Stoughton, WI in an angle-resolved vacuum science workshop (VSW) chamber with base pressure in the 10^{-11} Torr regime. During the gold evaporations, the chamber pressure never rose above 2×10^{-10} Torr. All experiments were performed at normal emission, although we will interpret the spectra in this letter as if they were essentially angle integrated. This is because the photon energies are relatively high, which makes the uncertainty in the momentum k high, and because the cleaves of our single crystals were not perfect over a distance the size of the photon beam—about 3 square mm. The incident angle of the photon beam was 75° from normal, and the combined energy resolution of the photon source and spectrometer was held constant at 200 meV.

High quality single crystals of Bi$_2$Sr$_2$CaCu$_2$O$_8$ and EuBa$_2$Cu$_3$O$_{7-\delta}$, of transition temperatures of $\sim$90 K each, were cooled to 20 K before being cleaved in the ultrahigh vacuum environment, and were maintained at that temperature for the full duration (including the gold deposition) of the experiments. The low temperature is important for a number of reasons. It had been shown to be necessary for getting accurate spectra for the 123's, partic-
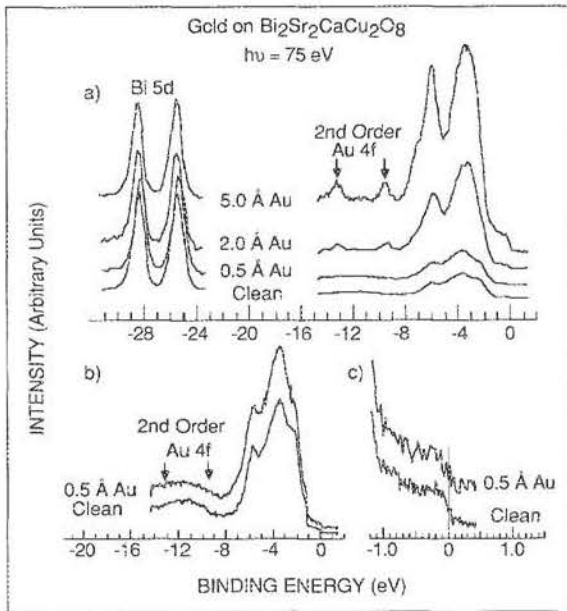
FIG. 1. (a) Valence bands and Bi 5d core levels of $Bi_2Sr_2CaCu_2O_8$ for different gold coverages. Spectra were normalized to give equal Bi 5d core level intensity. Blowups of (b) the valence bands and (c) the near Fermi level region of $Bi_2Sr_2CaCu_2O_8$ are shown for gold coverages of 0.0 Å and 0.5 Å, with the same normalization as in (a).

FIG. 2. (a) Valence bands of $EuBa_2Cu_3O_{7-\delta}$ for different gold coverages, normalized to the Ba 4d core level intensity. (b) Blowups of the near Fermi level region of $EuBa_2Cu_3O_{7-\delta}$.

ularly in the near Fermi surface regime.[7] Although the $Bi_2Sr_2CaCu_2O_8$ samples appear much more stable at room temperature[8] and there are recent reports showing high quality spectra from 123's cleaved at room temperature,[9] we elected to perform all of our measurements at low temperature for safety and consistency. The low-temperature evaporation is also superior for a number of reasons. Interfacial processes such as chemical reactions and the creation of defects will be greatly inhibited. In addition, the decreased surface mobility of the adatoms at low-temperature favors Frank–van der Merwe or layer-by-layer growth, instead of the Volmer–Weber growth mode, where the deposited atoms aggregate to form clusters or islands on the substrate surface. Examination of the spectra shows very uniform exponential decay of the Bi 5d core level intensity with gold coverage, implying true layer-by-layer growth. The very short escape depth of 3 Å in the gold layer confirms that no intermixing or alloying of the gold with the substrate surface has occurred.

Figure 1 shows the valence bands and Bi 5d core levels of $Bi_2Sr_2CaCu_2O_8$ for different gold coverages. As depicted in the figure, the spectra were all normalized to give equal Bi 5d core level intensity. Thus the contribution to the valence band from the $Bi_2Sr_2CaCu_2O_8$ states should to first order be essentially the same in each of the spectra presented, since the signal from the underlying states should fall off as a simple exponential with distance, governed by the photoelectron escape depth through the gold. Thus we see that with even as little as 2.0 Å of gold on the surface (approximately one monolayer), the valence band signal is almost completely dominated by the gold states. This is because of the extreme surface sensitivity of the spectroscopy.
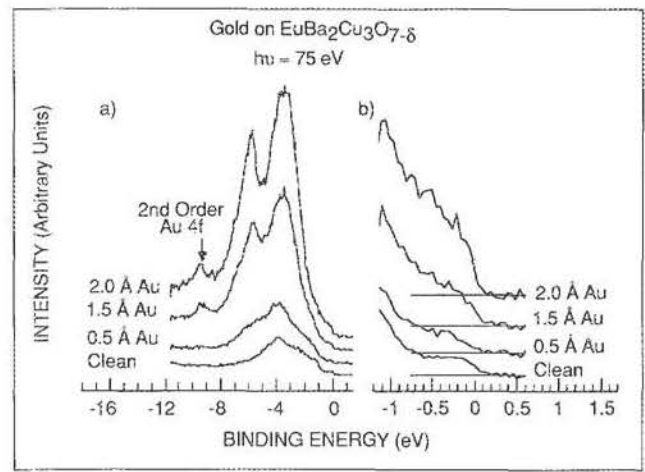
The detailed effects that the gold adatoms have on the superconducting substrate are best seen for low gold coverages (below one monolayer). For these coverages, the gold overlayer will not yet have reached its full "metallicity," which in cases where the substrate is nonmetallic, is easily discernable by the lack of a Fermi edge. Other signals of a film that have not yet reached metallicity are (adatom) core levels that are broader and at higher binding energy than those of the bulk material. The behavior of our core levels confirms that the 0.5-Å-thick gold films are not metallic. Blowups of the valence band and near Fermi level region of just the 0.0 and 0.5 Å gold coverages on $Bi_2Sr_2CaCu_2O_8$ are shown in Figs. 1(b) and 1(c), with the same normalization as in Fig. 1(a). A clear Fermi edge is observed for both the clean substrate and the substrate with the 0.5 Å gold overlayer.[10] Since the Fermi edges could not have been derived from the gold overlayers, it is clear that the surface of $Bi_2Sr_2CaCu_2O_8$ remains metallic, which is of course a prerequisite for the superconductivity. Thus we can conclude that there is very little chemical reaction between the gold and the $Bi_2Sr_2CaCu_2O_8$ substrate, and that the $Bi_2Sr_2CaCu_2O_8$ derived density of states at the Fermi level is essentially unaltered by the gold deposition, at least within the scale of our energy resolution (~ 200 meV). Ultrahigh resolution (~ 35 meV) angle-resolved measurements have recently been completed in our lab, and have in fact shown that there is some alteration of the BiO states (in the cleavage plane) at the Fermi level from a deposition of gold. The states which originate from the CuO planes, which are a few angstroms below the surface, are essentially unaltered.[11]

The gold/$EuBa_2Cu_3O_{7-\delta}$ interface is unfortunately not quite so nice, as is shown in Fig. 2, which presents the valence bands of a single cleaved crystal of $EuBa_2Cu_3O_{7-\delta}$ for different gold coverages. The normalization was performed in a similar way as done earlier on $Bi_2Sr_2CaCu_2O_8$, except that the Ba 4d core levels were used instead of the Bi 5d's. The crucial piece of information is obtained from the blowups of the near Fermi level region in Fig. 2(b). We

note a clear Fermi edge for the clean $EuBa_2Cu_3O_{7-\delta}$ substrate which disappears with 0.5 Å of gold coverage. (There is a sloping density of states that does just cut the Fermi level in the 0.5 Å spectrum, although it is much broader than the system resolution of 200 meV and the midpoint is pushed at least 100 meV below the Fermi energy). As the gold overlayer becomes metallic at larger coverages, a gold-derived Fermi edge appears. Thus we can conclude that the gold deposition alters the states near the Fermi level in the near surface region of the $EuBa_2Cu_3O_{7-\delta}$ substrate and renders it nonmetallic. Since we formed the interface under the ideal conditions of very low temperature and ultrahigh vacuum, with the most inert of overlayers, this is potentially hazardous for any device on these materials (particularly c-axis films) that intends to make use of the proximity or Josephson effects. Better choices may be to make the junctions along the a or b axes, where the superconducting coherence length is much greater,[6] or to use the $Bi_2Sr_2CaCu_2O_8$ material, which appears to be much less affected by the gold deposition.

In conclusion, low-temperature evaporations of gold, which should form the cleanest and most abrupt junctions with the high T_c cuprates, appear to alter the near Fermi level states of $EuBa_2Cu_3O_{7-\delta}$ at the interface enough to render the surface essentially nonmetallic, making the feasibility of 123/gold junctions along the c axis questionable at best. The situation with $Bi_2Sr_2CaCu_2O_8$/gold junctions is much more favorable, as the $Bi_2Sr_2CaCu_2O_8$ substrate remains metallic in the near surface region, making the feasibility of devices relying on the Josephson or proximity effects quite real.

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[10] We note that LDA band theory predicts that in our angle-resolved photoemission experiment along normal emission we should not observe any intensity at E_f. Recent ultrahigh-resolution photoemission experiments seem to support this prediction (C. G. Olson et al. preprint). The reasons why we do observe intensity there are not exactly clear, although they may be due to the fact that we are effectively sampling a large portion of the Brillioun zone because of the relatively high kinetic energies (and hence high k uncertainty) and the imperfections in the crystal surface, which scatter electrons with different k into the acceptance cone of the analyzer. For our purposes here though, the exact reason is not important, as we are only looking at the changes in the spectra as a result of the gold evaporation.

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