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# Initial stages of degradation of superconductor surfaces: $O_2$, $H_2O$, $CO_2$, and CO chemisorption on $La_{2-x}Sr_xCuO_4$

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The initial stages of degradation of high-$T_c$ superconductor surfaces by interaction with atmospheric gases have been studied using ultraviolet photoelectron spectroscopy. $O_2$ has little effect, while $H_2O$ adsorbs dissociatively with an initial sticking coefficient $S_0 \sim 1$, and forms a surface hydroxide. $CO_2$ adsorbs forming a carbonatelike surface species with an initial sticking coefficient of $\sim 0.3$. CO is observed to result in similar adsorbed surface species with a much lower sticking coefficient of $\sim 3 \times 10^{-4}$.

Degradation of the surfaces of the new class of high-$T_c$ superconductors is a well-known problem, yet there have been no studies detailing the preliminary stages of the processes involved. The degradation is enhanced by exposure to atmosphere indicating that the process is a chemical interaction with specific contaminant molecules. We have found that $La_{2-x}Sr_xCuO_4$ is particularly susceptible to degradation upon atmospheric exposure, and sintered pellets have been observed to form a white powdery layer and crumble after only a few days exposure. Similar behavior is reported for $YBa_2Cu_3O_{7-x}$ with $H_2O$ implicated as being largely responsible for the degradation;[1] however, additional molecular interactions have been reported.[2] An understanding of the initial stages of the adsorption of a wide range of atmospheric gases would be invaluable in order to develop proper methods for handling these new ceramic materials. In this work, we describe the interaction of ultrahigh-vacuum (UHV) scraped surfaces of $La_{1.8}Sr_{0.2}CuO_4$ with four gases of interest: $O_2$, $H_2O$, $CO_2$, and CO. Similar effects have been observed in our laboratory in the initial stages of adsorption on scraped surfaces of bulk $YBa_2Cu_3O_{7-x}$.

The experiments were performed at the National Bureau of Standards SURF-II synchrotron light source using tunable radiation from a laminar-profile toroidal grating monochromator[3] (TGM). Bulk superconductors were prepared from mixtures of oxides and carbonates that were calcinined for 3 h at 925 °C followed by cold pressing and sintering in air for 6 h at 950 °C, and slowly cooled. Surfaces of $La_{1.8}Sr_{0.2}CuO_4$ were prepared by repeatedly scraping bulk sintered pellets in UHV using a stainless-steel blade; the chamber base pressure was $1 \times 10^{-10}$ Torr after bakeout to 100 °C. Direct evidence that scraping exposes clean surfaces is given by the rapid changes in surface chemistry of $La_{1.8}Sr_{0.2}CuO_4$ as it is dosed with certain gases; see below. Ultraviolet photoelectron spectra (UPS) were obtained with a double-pass cylindrical mirror analyzer operated in a constant pass-energy mode; the experimental configuration has been described elsewhere.[4] Photoelectron spectra obtained with $h\nu = 40$ eV are presented here. Gas doses were made by back filling the experimental chamber and the values quoted are for uncorrected ionization-gauge readings.

Figure 1 shows the effect of dosing a scraped $La_{1.8}Sr_{0.2}CuO_4$ surface with $O_2$. In this figure, the dashed curve is the spectrum obtained from the freshly scraped surface and the spectra obtained after $O_2$ doses of 0.1, 1.0, and 10 L (1 L = 1 langmuir = $10^{-6}$ Torr sec) are given by the solid curves. Larger exposures resulted in contamination due to displacement of other molecules from the chamber walls. This is a consequence of both the relatively low chamber bakeout temperature and the large sticking coefficients of the principal background gases compared with that of $O_2$, as shown below. The photoelectron spectra show no significant changes upon exposure to $O_2$ indicating that the scraped surface is not highly oxygen deficient. The change in the work function $\Delta\Phi$, obtained from the secondary-electron cutoff in the UPS data, is small after exposure to $O_2$, less than 0.04 eV (uncertainty ±0.02 eV).

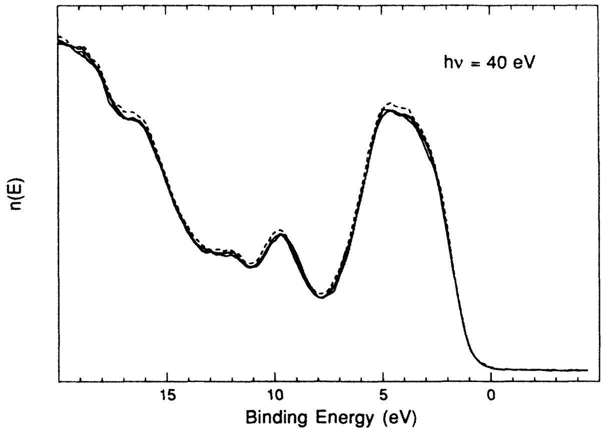

FIG. 1. Photoelectron spectra obtained from a UHV-scraped $La_{1.8}Sr_{0.2}CuO_4$ surface exposed to increasing amounts of $O_2$; $h\nu = 40$ eV. The $O_2$ doses are 0.1, 1, and 10 L and the dashed curve is the spectrum from the freshly scraped surface.

Figure 2(a) shows a series of UPS spectra taken with $h\nu = 40$ eV for a surface that has been scraped in UHV and dosed with increasing amounts of $H_2O$. For a dose of 0.1-L $H_2O$, little change is observed in the specrum, however, by 1 L, the valence-band feature near 2.5 eV is strongly attenuated and additional peaks rise near 5 and 9 eV. Saturation occurs at an exposure near 1 L implying that the initial sticking coefficient $S_0$ is $\sim 1$. For exposure greater than 1 L, the photoelectron spectra are not changed significantly. The change in the work function $\Delta\Phi$ is shown in the inset in Fig. 2(a). The work function initially decreases, dropping by 0.14 eV at 1-L $H_2O$ dose, and then rises for higher doses.

Additional information can be obtained from these data by generating difference spectra, produced by subtracting the spectrum of the clean surface from those of the $H_2O$-dosed surfaces. The resulting difference spectra are shown in Fig. 2(b). The depopulation of the top of the valence band is evident in the strong negative dip at 2.5 eV and the two additional features induced by the adsorbate are located at 5.2 and 8.8 eV. The separation of these two features is in good agreement with the splitting of the $3\sigma$ and the $1\pi$ levels of $OH^-$ adsorbed on other oxide surfaces.[5]

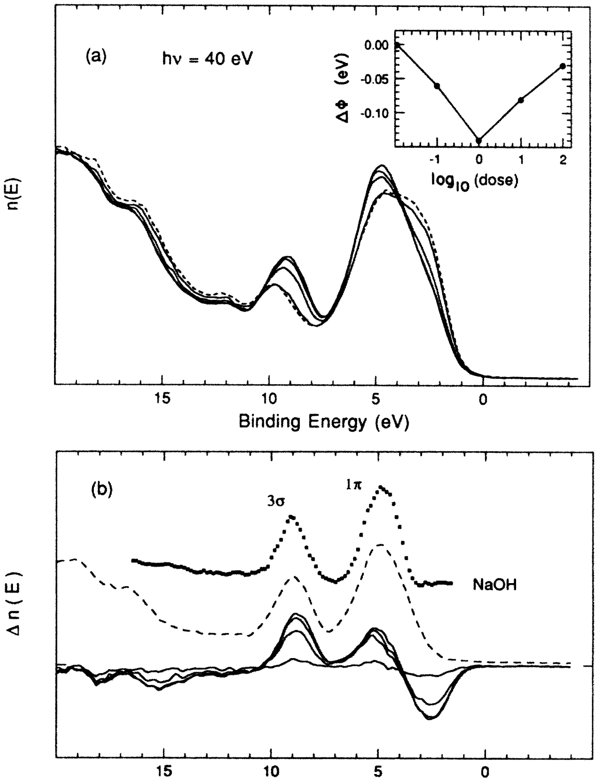

FIG. 2. (a) Photoelectron spectra obtained using $h\nu = 40$ eV from a UHV-scraped $La_{1.8}Sr_{0.2}CuO_4$ surface exposed to increasing amounts of $H_2O$. The change in the work function $\Delta\Phi$ vs the logarithm of the dose in langmuirs is given in the inset; (b) difference spectra obtained by subtracting the spectrum of the scraped surface from those that have been exposed to $H_2O$. The dashed curve is an alternative difference spectrum, produced as described in the text, and the dotted curve is the He II photoelectron spectrum obtained from solid NaOH (Ref. 6), shifted to lower binding energy by 3.4 eV.

Several explanations may be offered for the strong negative dip at 2.5 eV. This apparent depopulation of the upper edge of the valence band may indicate a charged transfer from the substrate to the adsorbate, consistent with the production of surface $OH^-$ species. In the presence of a charged surface species, one might expect the valence bands to be bent near the surface. However, the bottom edge of the valence band, shown in Fig. 2, is fixed in energy: the lack of a strong band-bending shift implies another possibility. The hydroxide could be simply an overlayer in which case it merely attenuates the 2.5-eV portion of the valence band. The difference spectra could then be obtained by scaling the clean surface spectrum by an attenuation factor that eliminates the negative dip at 2.5 eV. We have produced such a difference spectrum for the 100 L exposure and it is given by the dashed curve in Fig. 2(b). It shows the same two OH-related features (4.9 and 9.0 eV) with relative intensities and splittings similar to those that have been observed in photoemission from solid NaOH (Ref. 6), given by the dotted curve in Fig. 2(b).

Changes in the work function induced by molecular adsorbates can contain contributions from two effects: namely, the dipole moment (permanent or induced) of the adsorbed species and charge transfer between adsorbate and substrate. In Fig. 2(a), the work function is seen to decrease upon exposure to $H_2O$ and $\Delta\Phi$ remains slightly negative to high $H_2O$ doses. A similar drop in the work function of $Ti_2O_3$ and $V_2O_3$ surfaces is observed for the dissociative adsorption of $H_2O$.[5] In those cases, it was noted that the dipole moment of the adsorbed OH was partially canceled by a charge transfer from the surface to the adsorbed species that resulted in surface $OH^-$. This is likely to be the case here also. When a thicker hydroxide layer forms at higher coverages, the hydroxyl-induced dipole layer is destroyed, and the work function will reflect this change. This is consistent with the rise in the work function at exposures $> 1$ L, as indicated in the inset in Fig. 2(a).

The changes induced in the UPS spectra from freshly scraped $La_{1.8}Sr_{0.2}CuO_4$ upon dosing with $CO_2$ are shown in Fig. 3(a). In this case, saturation occurs for exposures somewhat greater than 1 L and we estimate that the initial sticking coefficient $S_0$ is $\sim \frac{1}{3}$. Again, we observe a strong depopulation of the valence-band feature near 2.5 eV but in this case three peaks arise with binding energies near 5.0, 9.3, and 11.4 eV. The work function rises dramatically and by 10 L $CO_2$ it has increased by more than 1 eV.

The difference spectra, presented in Fig. 3(b), show features at locations similar to those observed for the $H_2O$ adsorption [Fig. 2(b)]; however, there is an additional feature that is observed at 11.4 eV. As was the case for the $H_2O$ adsorption, the bottom edge of the valence band remains fixed. Difference spectra can be obtained, again, by scaling the clean surface spectrum, to result in a difference spectrum without the depopulation at 2.5 eV. Such a difference spectrum is shown for the 100 L $CO_2$

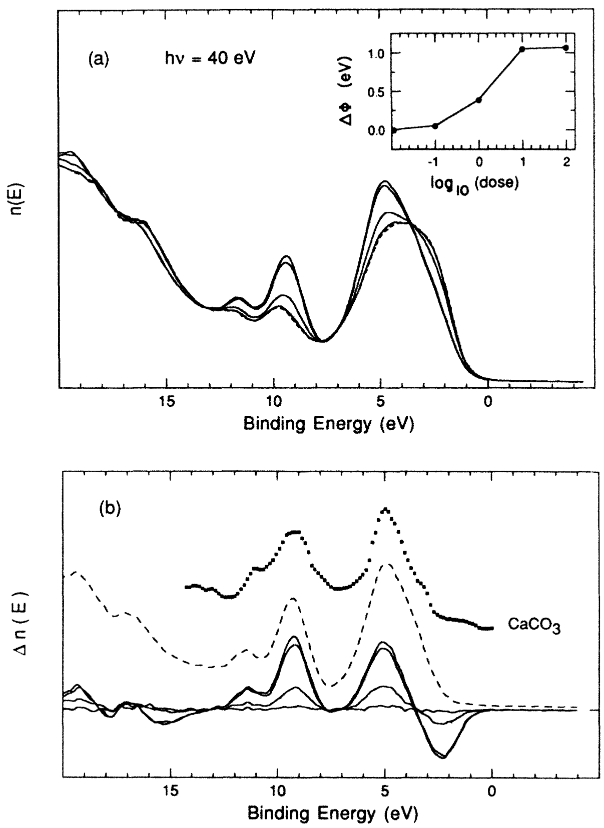

FIG. 3. (a) 40 eV photoelectron spectra from scraped $La_{1.8}Sr_{0.2}CuO_4$ exposed to increasing amounts of $CO_2$; the change in the work function $\Delta\Phi$ vs the logarithm of the dose is given in the inset. (b) Difference spectra are given by the solid curves, and the dashed curve is an alternative difference spectrum. The dotted curve is the He II photoelectron spectrum obtained from solid $CaCO_3$ (Ref. 9), shifted 0.5 eV towards $E_F$.

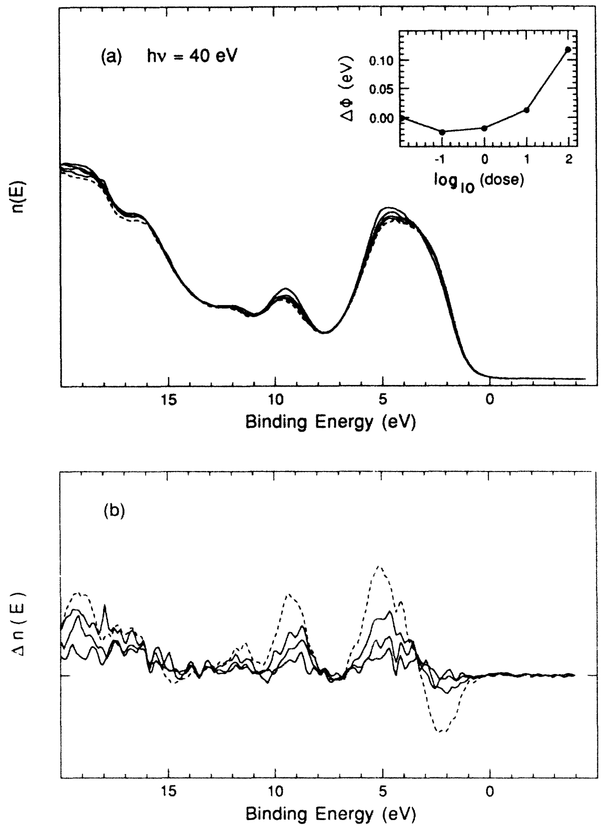

FIG. 4. (a) Photoelectron spectra with $h\nu = 40$ eV for scraped $La_{1.8}Sr_{0.2}CuO_4$ exposed to increasing amounts of CO; the change in the work function $\Delta\Phi$ vs the logarithm of the dose is given in the inset. (b) Difference spectra are given by the solid curves; the 100 L exposure difference spectrum is given by the dashed line. The intensity of these $\Delta n(E)$ data have been scaled up by a factor of 5.5 relative to Fig. 3(b).

exposure as the dashed curve in Fig. 3(b). In this case, the spectrum shows features that are only slightly shifted from the solid curves: The peaks are located at 4.9, 9.3, and 11.5 eV. By comparing these features with gas-phase photoelectron spectra of $CO_2$, one can associate the peak at 4.9 eV with the $1\pi_g$ molecular orbital, the 9.3 eV feature as an unresolved overlap of the $1\pi_u$, and the $3\sigma_u$ orbitals and the third peak at 11.5 eV as being due to the $4\sigma_g$ level.[7] However, the peak separations are slightly different in the two cases. By comparing the peaks in Fig. 3(b) with the features observed from bulk carbonate samples, e.g., $BaCO_3$, we find an excellent agreement with the peak separations in the difference spectra, though the bulk material gives features that are rigidly shifted by 2 eV to higher binding energy.[8] We can also compare these spectra to the $CO_3{}^{2-}$ features obtained in photoemission[9] from $CaCO_3$ shown as the dotted line in Fig. 3(b); again, we find excellent agreement with the observed difference spectra. This strongly suggests that $CO_2$ adsorption results in a surface carbonate species. Strong parallels can also be drawn by comparing the $CO_2$ chemisorption with CO chemisorption.

In Fig. 4, we show the photoelectron spectra and the corresponding difference spectra for CO chemisorption on scraped $La_{1.8}Sr_{0.2}CuO_4$. The changes that are introduced in the valence-band region are essentially identical to those produced by $CO_2$ chemisorption; however, the sticking coefficient for CO chemisorption is smaller than that for $CO_2$ by a factor of $10^{-3}$. Similar adsorbate-induced features are observed at identical binding energies to those in Fig. 3(b), implying that the resulting adsorbed species are similar, if not identical, in both cases. The work function change after a 100-L CO dose is positive relative to that of the clean surface. Both the photoelectron spectra and the $\Delta\Phi$ data are consistent with the formation of a carbonate species, but with lower surface concentration than seen for $CO_2$ exposure. Reaction of CO with the O ligand of an oxide surface has been observed previously. On cleaved NiO(100), CO is observed to abstract a surface O and desorb as $CO_2$, leaving behind a reactive defect site.[10] In the present case, a similar reaction may be responsible for forming a surface carbonate species.

These results show that additional information about the reactivity of these high-$T_c$ superconductors towards a wide range of contaminants is necessary in order to develop techniques for preventing degradation. Preliminary results from $YBa_2Cu_3O_{7-x}$ indicate that, in this exposure range, it too is unreactive towards $O_2$ but very reactive towards the adsorption of $H_2O$ and $CO_2$. Additional work is needed to assess the changes produced in these materials upon exposure at much higher pressures and temperatures.

In summary, we have observed the initial stages of decomposition of $La_{1.8}Sr_{0.2}CuO_4$ to form hydroxides and carbonates. Since oxides of both Sr and La are known to react with $H_2O$ and $CO_2$ to form hydroxides and carbonates, respectively,[11] we believe that the surface reaction products involve these elements. $O_2$ exposure has little effect on the spectra obtained from scraped surfaces while $H_2O$ is observed to adsorb dissociatively with a sticking coefficient ~1, resulting in the production of surface hydroxides. $CO_2$ reacts rapidly with freshly scraped surfaces to form carbonatelike species. The initial sticking coefficient is $\sim \frac{1}{3}$, indicating that during the initial stages of adsorption the surface is nearly as reactive toward $CO_2$ as it is toward $H_2O$. CO also reacts to form carbonates; however, it is much less reactive than $CO_2$. These results have important implications for the development of techniques for avoiding decomposition due to atmospheric exposure.

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