

# Surface Cleaning and Adsorbate Layer Formation: Dual Role of Alkylamines in the Formation of Self-Assembled Monolayers on Cuprate Superconductors

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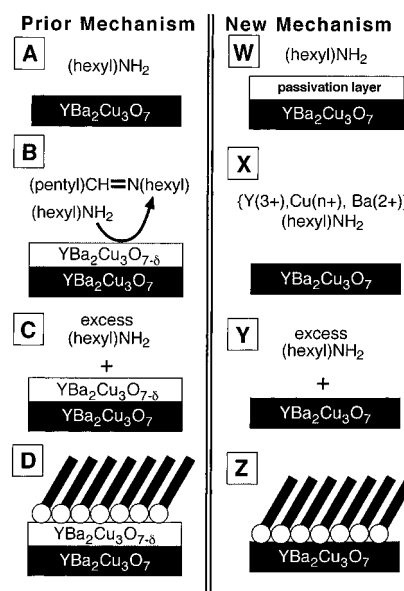
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The development of monolayer adsorption chemistry for superconductor surfaces is particularly important for a number of practical and fundamental reasons. As high- $T_C$  superconductors begin to approach the marketplace in areas of communications, power industries, medical applications, and scientific instrumentation, the development of new “soft chemistry” approaches for the surface modification of these technologically relevant electronic materials becomes increasingly important. Monolayer adsorption chemistry has been developed extensively for electronic materials such as metals, semiconductors, and insulators.<sup>1</sup> These methodologies have been expanded recently to include a variety of high-temperature superconductors (HTSCs).<sup>2–8</sup> Furthermore, the McDevitt group has shown in a recent publication that certain amine compounds foster the formation of monolayers that exhibit a high degree of conformational order on (001)-oriented samples of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ .<sup>2</sup> Arguably, these samples are, to date, the most complex substrate shown to support such organized self-assembled monolayer structures.

A recent study by Mirkin and co-workers makes an interesting hypothesis related to the surface interaction of amine monolayers with  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ .<sup>9</sup> According to this report, the alkylamine reagents become oxidized to alkylimines upon their exposure to HTSCs (Figure 1A,B). In addition, it is proposed that the surface region of the superconductor becomes reduced commensurate with the oxidation of alkylamines (Figure 1C). According to this model, the resulting oxygen-deficient exterior region supports the formation of an amine monolayer (Figure 1D).

Here, we describe a series of new X-ray photoelectron spectroscopy (XPS), four-point conductivity, critical current, atomic absorption spectroscopy (AAS), grazing angle infrared spectroscopy, and GC–MS experiments, which lead us to suggest that an entirely different mechanism is involved in the formation of HTSC-localized monolayers. According to our new model, the amine reagents serve two chemically distinct roles. In the initial



**Figure 1.** Schematic illustration showing the sequence of steps that are proposed to be involved in the formation of self-assembled monolayers atop the surface of the high- $T_C$  superconductor,  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . Steps A–D detail the adsorption scheme as proposed by in a recent paper Mirkin et al.<sup>9</sup> Steps W–Z summarize the new mechanism described herein.

phase, the degraded superconductor exterior is etched away with the help of the amine compounds, (Figure 1W). The etching process proceeds to the point where fresh  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is exposed, and only at this point do the amines adsorb and remain at the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  surface (Figure 1X,Y). As the adsorption process continues, there is an accumulation of an organized monolayer at the surface, which prevents further etching of the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  material (Figure 1Z).<sup>10</sup> The remainder of this paper describes the evidence we have acquired to support our alternative HTSC self-assembly mechanism.

Numerous studies of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and related compounds have shown that even short atmospheric exposures cause chemical damage to the surface of the HTSC samples.<sup>11–16</sup> Since the anchoring of adsorbate layers occurs at the surface, the most accurate description of the mechanism of superconductor monolayer adsorption must include a description of the influence of surface-localized degradation layers. From our XPS studies, we find that even short exposures of HTSC samples to the atmosphere (i.e., exposure times consistent with the transfer of samples from our thin-film deposition chamber or furnace to the XPS chamber) lead to the formation of a contamination layer. This layer (20–50 Å in thickness) contains the reduced “green phase” (i.e.,  $\text{Y}_2\text{BaCuO}_5$ ),  $\text{BaCO}_3$ , and  $\text{CuO}$ .

To explore the mechanistic details of alkylamine adsorption on  $\text{YBa}_2\text{Cu}_3\text{O}_7$  surfaces, we examined the XPS spectra of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  thin films taken directly from our deposition chamber to the XPS instrument (Figure 2, dashed curves). Even for samples that received atmospheric exposure for less than 2 min, the

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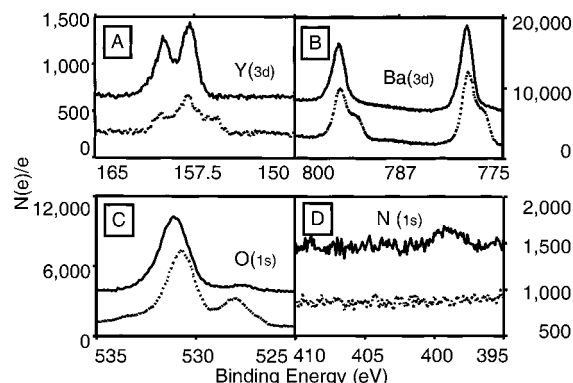
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**Figure 2.** Data for the XPS spectra of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  thin film (1500 Å thick, *c*-axis oriented on MgO) before and after exposure for ~12 h to a 2 mM dodecylamine solutions. The following spectral regions are shown: (A) the Y(3d); (B) Ba(3d  $5/2$ ); (C) O(1s); and (D) N(1s). In each panel, the lower/dashed curve shows data prior to any solution exposure. Similarly, the upper/solid curves show the spectral data obtained for the same set of films after their exposure to the amine solution.

acquired XPS signature is consistent with a degraded surface region. This degradation layer is characterized by a broad multiplet absorption in the Y(3d) region, the  $\text{BaCO}_3$  signature in the Ba(3d $5/2$ ) region (i.e., the lower energy humps on the main peaks), and a  $\text{CO}_3^{2-}$  signature in the O(1s) region (i.e., ~527 eV). These spectral signatures supports the presence of a degradation layer, in good agreement with the prior literature for similarly treated samples.<sup>17–19</sup> Quite interestingly, treatment of the “dirty”  $\text{YBa}_2\text{Cu}_3\text{O}_7$  samples with a 2 mM solution of octadecylamine, butylamine, or hexylamine for 12 h leads to a dramatic improvement in the XPS signature for the cuprate powder, film, and pellet samples (Figure 2, solid curves). The presence of a clean exterior is noted by the doublet-like feature in the Y(3d) region, matching closely the pristine case that was prepared and evaluated *in situ*.<sup>17–19</sup> In addition, the amine exposure serves, for the most part, to eliminate the  $\text{BaCO}_3$  surface layers, as evidenced by the clean Ba(3d $5/2$ ), Ba(3d $3/2$ ), and O(1s) transitions. Finally, the XPS signature of the adsorbed amine reagent is found in the N(1s) region of the spectra that was absent in the untreated samples. These results suggest that even carefully prepared  $\text{YBa}_2\text{Cu}_3\text{O}_7$  samples are initially coated with corrosion products, and that after exposure to the amine reagent the majority of the surface corrosion layer is removed.

To further support the occurrence of an initial etching step, we completed a series of atomic absorption spectroscopy (AAS) experiments to search for copper dissolution products. These experiments indicate that a significant amount of copper is dissolved into the solution during the initial few minutes of exposure.<sup>10</sup> The initially rapid copper dissolution is followed by a leveling off, where little additional etching is observed. The latter behavior appears to be consistent with the occurrence of an adsorbate-induced surface passivation that limits subsequent etching. From measurements of the dissolved Cu ion concentration, it is estimated that 20–50 Å of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is removed during this etching process. Similarly, from changes in resistivity of ~1000-Å-thick  $\text{YBa}_2\text{Cu}_3\text{O}_7$  films, we obtain an independent

estimate for the upper limit of the depth of etching of 50–100 Å for the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  thin-film specimen.<sup>10</sup> The resistivity measurements yield a slightly larger effective etching thickness due to a large sensitivity of the measurement to etching along the grain boundaries.

Although the above-described information strongly suggests the presence of a pre-etching step, these data do not exclude the possibility suggested by Mirkin and co-workers that the amine anchoring occurs with chemistry that results in the reduction of the exterior surface of the HTSC. While it is difficult to eliminate the possibility of ultrasmall amounts (<10 Å) of reduction to the HTSC surface, we note that previous publications have shown that ferrocenealkylamine adsorbed on  $\text{YBa}_2\text{Cu}_3\text{O}_{6.94}$  displays facile electron transfer, consistent with a conductive metallic electrode, and behavior reminiscent of an ideal surface-confined redox species is obtained.<sup>6,8,10,20</sup> In addition, we have shown in a previous publication that a very dramatic oxygen content dependence is observed for the electrochemical data acquired at  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  electrodes.<sup>21</sup> Although the above-mentioned studies do not exclude the possibility of an ultrasmall amount of surface reduction, they do question the presence of a systematically reduced exterior region with significant thickness.

While we do not challenge the formation of significant amounts of dialkylamine in the prior study, we do challenge its formation as being intrinsic to the monolayer formation process on superconductor surfaces. We completed a series of GC–MS experiments<sup>10</sup> analogous to those reported by Mirkin<sup>9</sup> for freshly prepared  $\text{YBa}_2\text{Cu}_3\text{O}_7$  powders. In hexanes solutions that are kept under an inert argon atmosphere, no increase in the concentration of the dialkylamine is noted.<sup>22</sup> For our particle size distribution, we calculate that conversion of one monolayer of hexylamine to dialkylamine would yield a change in the concentration of the dialkylamine contaminant that could be detected by GC–MS. We note that samples having thick degradation layers require longer exposure time before the etching process becomes complete. Furthermore, our grazing angle reflectance infrared measurements, and XPS studies have shown that it is possible to anchor amine adsorbate layers atop chemically damaged HTSC structures. The focus of our studies here has been placed on the evaluation of freshly prepared  $\text{YBa}_2\text{Cu}_3\text{O}_7$  samples, where degradation layer thickness is minimized. With these types of samples, no detectable changes in the amounts of oxidized amine compounds are noted for the amine/ $\text{YBa}_2\text{Cu}_3\text{O}_7$  exposure experiments.

In summary, a plausible new mechanism has been reported for the adsorption of alkylamine reagents on cuprate superconductor samples, in which the amine reagents serve two distinct roles. First, a variety of measurements provide convincing evidence that the alkylamines serve to remove the initially present degraded surface layer. Second, the amines are found to adsorb in a persistent manner on the high- $T_c$  surface. Once the amines are anchored to the cuprate surface, the etching process ceases, and the adsorbate layer is found to be anchored atop a highly conductive exterior region. Unlike the vast majority of the prior processing methods for the cuprate phases, the amine monolayer procedure described herein serves to create and preserve pristine interfacial chemistry. The self-termination and surface passivation methods described in this paper may find utility in the future for the processing/packaging of high- $T_c$  devices and conductors.

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**Supporting Information Available:** Three figures, showing the time dependence of the copper dissolution; two resistivity vs temperature curves for a single  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  thin film; and cyclic voltammetry for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  electrodes (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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