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Communications

Use of a Self-Assembled Monolayer for the Preparation of Crystalline Organic Superconductor/High-T_c Superconductor Structures

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Recent contact resistance, modulation of the transition temperature and critical current measurements in conductive polymer/superconductor bilayer structures as well as calculations of the superconducting coherence lengths have yielded the initial evidence consistent with the induction of superconductivity into conductive organic materials.[1−3] From theoretical studies, it has been determined that charge-transfer salts based on BEDT−TTF, such as β-(BEDT−TTF)$_2$I$_3$ (T_c = 1.5 K), are particularly attractive candidates to support superconductivity via the proximity effect at temperatures where the cuprate compounds alone are known to exhibit this phenomenon.[4] The potential for observing superconductivity at elevated temperatures in these organic systems makes the fabrication and analysis of organic superconductor/inorganic superconductor structures an important new area of research. In this communication, we describe the successful combination of organic superconductor and inorganic superconductor materials into a single hybrid structure and discuss methods for influencing the crystalline properties of the charge transfer salt.

Thin films of $YBa_2Cu_3O_{7-\delta}$ used in this study were deposited onto single-crystal MgO (100) substrates by the laser ablation method.[5,6] The organic superconductor/inorganic superconductor structures were fabricated through the vapor-phase deposition of (BEDT−TTF)$_2$I$_3$ onto the surface of $YBa_2Cu_3O_{7-\delta}$ films, according to a method similar to that used by Kawabata et al.[7−9] Accordingly, (BEDT−TTF)$_2$I$_3$ is sublimed with source and substrate temperatures of 225 and 70 °C, respectively. The (BEDT−TTF)$_2$I$_3$ films used in this study are ~1 μm thick and those of $YBa_2Cu_3O_{7-\delta}$ are ~1500 Å in all cases. Evidence that the (BEDT−TTF)$_2$I$_3$ is coating the $YBa_2Cu_3O_7$ comes from scanning electron microscopy, X-ray fluorescence, atomic force microscopy (AFM), and optical reflectivity studies of the hybrid structures.

Because 14 distinct crystallographic phases in the BEDT−TTF:polyiodide system have been identified previously, X-ray powder diffraction has proven to be an invaluable technique for analysis of the hybrid structures.[10] Exhaustive evaluations of over 100 thin films of α- and β-(BEDT−TTF)$_2$I$_3$ deposited onto substrates such as glass, Si, MgO, $LaAlO_3$, and Al_2O_3 have shown that nearly single phase purity, a high degree of crystallinity, and *c*-axis orientation are achieved when appropriate precautions are taken to control carefully the source and substrate temperatures. On the con-

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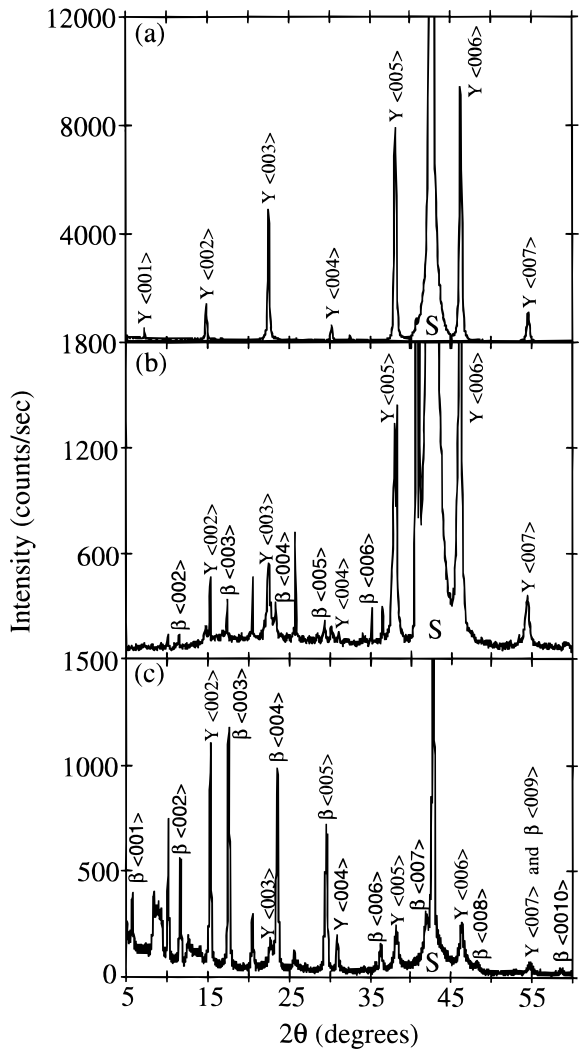

Figure 1. X-ray powder diffraction patterns (Cu Kα radiation, $\lambda = 1.5405$ Å) of (a) $(BEDT-TTF)_2I_3$ vapor phase deposited directly onto bare $YBa_2Cu_3O_{7-\delta}$, showing only reflections from the high-T_c cuprate material, (b) $(BEDT-TTF)_2I_3$ deposited onto a dodecylamine monolayer which has been adsorbed to $YBa_2Cu_3O_{7-\delta}$, and (c) $(BEDT-TTF)_2I_3$ deposited onto an octadecylamine monolayer which has been localized onto $YBa_2Cu_3O_{7-\delta}$. Reflections from both the inorganic and organic superconductor materials are readily identified in cases (b) and (c) where the cuprate surface is coated with the amine monolayers. Peaks assigned to the (00*l*) reflections of *β*-$(BEDT-TTF)_2I_3$ are labeled "*β*(00*l*)" and those associated with *c*-axis oriented $YBa_2Cu_3O_{7-\delta}$ are designated by "Y(00*l*)". The MgO (100) reflection is labeled "S". Unlabeled peaks correspond, in most cases, to the α-phase of $(BEDT-TTF)_2I_3$.

trary, $(BEDT-TTF)_2I_3$ films deposited onto bare $YBa_2Cu_3O_{7-\delta}$ show very little, if any, degree of order and crystallinity, as shown in Figure 1a. Here, only peaks for the (00*l*) reflections of $YBa_2Cu_3O_{7-\delta}$ are evident. This interesting, highly reproducible result suggests that poorly ordered deposition of $(BEDT-TTF)_2I_3$ onto $YBa_2Cu_3O_{7-\delta}$ is caused by a specific interaction between BEDT−TTF and $YBa_2Cu_3O_{7-\delta}$. Plausible chemical interactions that may be responsible for this unusual behavior include sulfur atom lone pairs binding to the ionic copper−oxide surface of the high-T_c material, as well as hydrogen−oxygen−iodine associations. The former binding mode is supported by recent crystallographic data of Cu−BEDT−TTF coordination complexes.[11−13] These interactions may provide sufficient cause for the $(BEDT-TTF)_2I_3$ to deposit in the described disordered fashion.

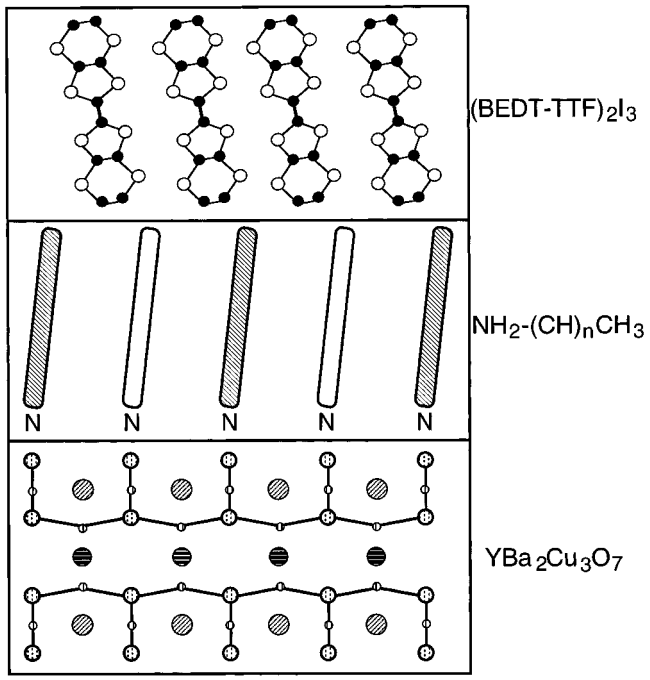

Figure 2. Schematic structural representation of an organic superconductor−insulator−inorganic superconductor trilayer structure consisting of a $(BEDT-TTF)_2I_3$ thin film supported on a dodecylamine monolayer that is adsorbed onto the Cu-O chain layer of $YBa_2Cu_3O_{7-\delta}$. The orientation of the BEDT−TTF stacks shown here is consistent with that which is observed from X-ray powder diffraction data. The adsorbed dodecylamine monolayer is shown to bind in a highly ordered, idealized manner (a feature which has yet to be shown from an experimental perspective). The lattice termination site for the $YBa_2Cu_3O_{7-\delta}$ layer depicted here is consistent with that expected based on recently reported studies.[18] Hydrogen atoms of the alkylamine monolayer and the BEDT−TTF donor molecule are not shown.

Through collaborative studies completed by the McDevitt and Mirkin research groups, methods have been developed through which long-chain alkylamines can be spontaneously adsorbed onto the surface of high-temperature superconducting materials, thus altering the interfacial properties of such compounds.[14] In an effort to control the chemical interactions at the interface between the $(BEDT-TTF)_2I_3$ and $YBa_2Cu_3O_{7-\delta}$ components, this self-assembly technique was employed to modify the cuprate superconductor surface and eliminate direct contact between the organic and inorganic superconductor materials, Figure 2. Trilayer assemblies incorporating an alkylamine buffer layer between the conductive organic and high-T_c materials were prepared in a three-step process. First, the $YBa_2Cu_3O_{7-\delta}$ was deposited onto MgO (100) via the laser ablation process.[5,6] Second, a self-assembled monolayer of dodecylamine or octadecylamine was formed on the surface of the cuprate compound using the previously reported

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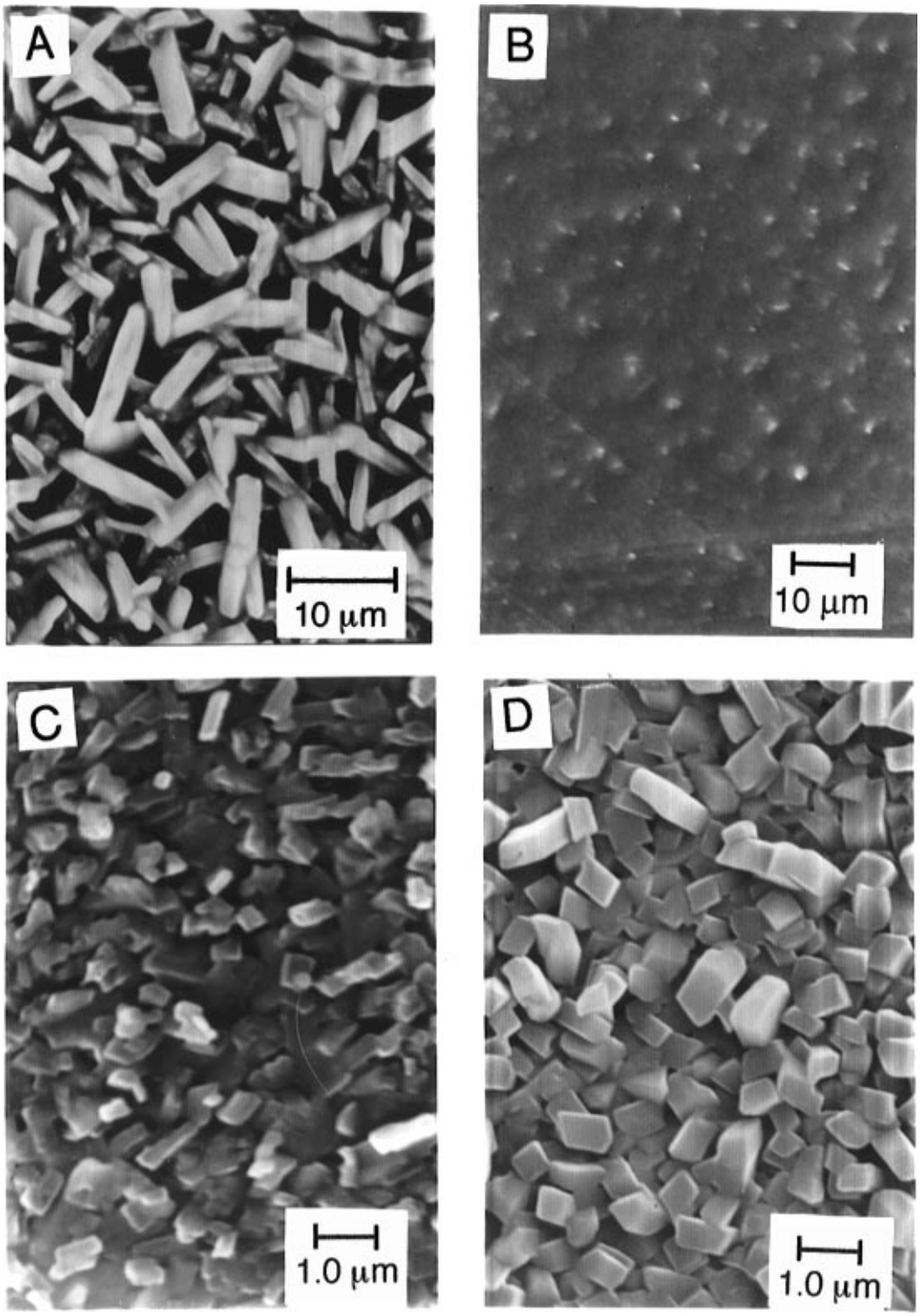

Figure 3. Scanning electron micrographs detailing the morphological features for $(BEDT-TTF)_2I_3$ thin films that were vapor phase deposited onto a variety of substrates. The organic superconductor films were prepared in each case with a source temperature of 225 °C and a substrate temperature of 70 °C. The $(BEDT-TTF)_2I_3$ layers are ~1 μm thick and the $YBa_2Cu_3O_{7-\delta}$ films are ~1500 Å in thickness. For these studies, the following substrates were exploited: (a) glass, (b) bare $YBa_2Cu_3O_{7-\delta}$, (c) $YBa_2Cu_3O_{7-\delta}$ coated with a monolayer of dodecylamine, and (d) $YBa_2Cu_3O_{7-\delta}$ coated with a monolayer of octadecylamine.

method.[14] Third, $(BEDT-TTF)_2I_3$ was sublimed onto the derivatized superconductor using the above-described vapor-phase procedure.[7-9]

Since $YBa_2Cu_3O_{7-\delta}$ has been shown previously to exhibit high chemical reactivity with the environment as well as strong oxidizing power, it is also possible that surface reactivity issues play some role in the observed phenomena. However, aged $YBa_2Cu_3O_{7-\delta}$ film samples yield more crystalline $(BEDT-TTF)_2I_3$ films as evaluated by SEM and XRD, than do pristine $YBa_2Cu_3O_{7-\delta}$ samples. Prior work has shown that such aged films become coated with decomposition layers rich in carbon (i.e., $BaCO_3$).[15] Although, the possibility of surface reactivity as being responsible for the observed effect

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cannot be eliminated completely, the described control experiments suggest that corrosion is not the dominant factor. For the work presented here, efforts were made to utilize only fresh $YBa_2Cu_3O_{7-\delta}$ thin films that were taken directly from the laser ablation chamber. Although corrosion reactions do not seem to be responsible for the unusual surface effect, the possibility of oxidative damage of the BEDT−TTF molecules at the interface between the two superconductors cannot be excluded.

Interestingly, the inclusion of a dodecylamine buffer layer fosters the crystalline growth of the organic material, as shown in Figure 1b. Here, a substantial degree of *c*-axis orientation for the deposited $(BEDT-TTF)_2I_3$ layer is observed. Evident from the X-ray powder diffraction patterns are peaks characteristic of a crystalline, *c*-axis oriented film of the superconductor, β-$(BEDT-TTF)_2I_3$ as well as those from the underlying $YBa_2Cu_3O_{7-\delta}$ substrate. Moreover, the longer octadecylamine molecule, when adsorbed to the cuprate superconductor, results in a further improvement in cation-radical salt thin-film crystallinity and orientation, as shown in Figure 1c. Tenth-order reflections from the now clearly present β-$(BEDT-TTF)_2I_3$ can be seen here, along with smaller reflections from the α-$(BEDT-TTF)_2I_3$ phase. Moreover, the inclusion of the monolayer buffer structure results in the appearance of more regular crystal facets in the SEM images, as expected for a more ordered sample. These features are absent in cases where $(BEDT-TTF)_2I_3$ is deposited directly onto the cuprate superconductor substrate. Clearly, the elimination of the direct contact between the two superconductor materials through incorporation of the self-assembled monolayer restores the crystallinity and order observed for the $(BEDT-TTF)_2I_3$ thin films.

Further evidence for the unusual interfacial interactions is obtained from scanning electron microscopy (SEM) and atomic force microscopy (AFM) studies. Features reminiscent of well-ordered crystals of $(BEDT-TTF)_2I_3$ are noted for those samples deposited onto glass as well as on $YBa_2Cu_3O_{7-\delta}$ that has been modified with an alkylamine reagent as shown by the SEM images of Figure 3. Such crystalline features are lacking for samples of $(BEDT-TTF)_2I_3$ that are deposited onto the bare $YBa_2Cu_3O_{7-\delta}$ surface. Likewise, AFM images show well-resolved facets for the $(BEDT-TTF)_2I_3$ crystals on all of the substrates examined except for bare $YBa_2Cu_3O_{7-\delta}$, where a noncrystalline blanket of the organic layer is noted.[19]

In summary, described in this report are composite organic superconductor/inorganic superconductor structures that were prepared with and without monolayer buffers. From this work, the following information has been acquired: (1) Methods for the preparation of hybrid organic superconductor/inorganic superconductor systems have been identified wherein chemical and physical damage to the components is minimized. (2) Although crystalline, *c*-axis oriented films of $(BEDT-TTF)_2I_3$ can be deposited onto substrates such as glass, Al_2O_3, Si, MgO, and $LaAlO_3$, the same material when deposited directly onto the high-temperature superconductor, $YBa_2Cu_3O_{7-\delta}$, yields poorly crystalline and predominantly disordered layers. (3) When the surface of the cuprate material is modified through the adsorption of an alkylamine monolayer, the crystalline properties of deposited $(BEDT-TTF)_2I_3$ films are obtained. (4) Lengthening of the alkylamine chain results in further improvement in $(BEDT-TTF)_2I_3$ film crystallinity. Studies are now in progress to explore the induction of superconductivity into the $(BEDT-TTF)_2I_3$ systems at elevated temperatures, to evaluate the prospects for creating organic superconductor−insulator−cuprate superconductor tunnel junctions as well as to examine by in situ electrochemical methods the growth characteristics of $(BEDT-TTF)_2I_3$ on $YBa_2Cu_3O_{7-\delta}$ surfaces.[16,17]

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Supporting Information Available: XRD and AFM images and contact resistance vs temperature curve (6 pages). Ordering information is given on any current masthead page.

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