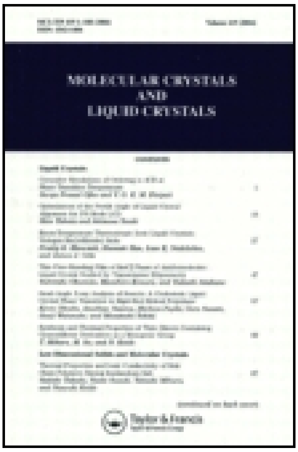

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CONDUCTIVE POLYMER/SUPERCONDUCTOR THIN FILM ASSEMBLIES

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Abstract Electrochemical procedures are utilized to deposit conductive polymer layers directly onto thin film samples of $YBa_2Cu_3O_{7-\delta}$ and to cycle the polymeric structures between their neutral (non-conductive) and oxidized (conductive) forms. Through changes in the polymer doping level, the superconducting properties of the high-T_c component can be modulated in a controllable fashion. In this regard, large changes in the superconducting critical temperature and critical current values are noted as a result of the doping of the polymer layer. This paper focuses on the role of superconductor weak link structures and how such features influence the magnitude of the modulation of the superconducting properties.

INTRODUCTION

A number of research groups, including our own, have initiated studies designed to explore the synthesis and characterization of conductive polymer/high-T_c structures.[1,2,3] We have found that high-temperature superconductors and conductive polymers can be used to form bilayer assemblies wherein the polymer can be used to control the electrical properties of the underlying superconductor thin film.[1] When the conductive polymer is in its doped state, the superconducting transition temperature can be reduced to values that are as much as 50 K less than that found for the bare superconductor film. Following the room temperature reduction of the polymer back to its non-conducting state, the transition temperature returns to a value very close to that found for the bare superconductor film.

One important factor which dramatically influences the magnitude of this effect is the morphology of the superconductor film. In this paper, the influence of the superconductor morphology, crystal orientation, film thickness and the presence of weak link structures on the properties of the polymer/superconductor bilayer structures will be explored.

SAMPLE PREPARATION

Thin films of $YBa_2Cu_3O_{7-\delta}$ (~200 to 5000 Å in thickness) were deposited onto single crystalline MgO (100) and $LaAlO_3$ (100) substrates using the pulsed laser ablation method.[4] After establishing a base vacuum of $\sim 10^{-6}$ torr, 150 mtorr of oxygen was introduced into the deposition chamber and the films were deposited with a substrate temperature of ~730°C using a KrF excimer laser operating at 248 nm to irradiate a ceramic target of $YBa_2Cu_3O_{7-\delta}$. Following their deposition, the thin films were cooled to ~450°C and 1 torr of oxygen gas was introduced for the annealing step which typically lasted about 15 minutes. High quality c-axis films were formed by using high density targets (~99% of the theoretical maximum density). Rough textured films were fabricated by using low density targets (~80% of the theoretical maximum density). Microbridges (~3 mm long and ~100 μm wide) were then created[5] from the $YBa_2Cu_3O_{7-\delta}$ film by scribing the superconductor with a diamond tip controlled by a micromanipulator or by using a laser etching technique.

Electrochemical procedures were then employed for the polymerization of pyrrole onto the superconductor microbridge surface and for doping of the polypyrrole film as reported previously.[1]

RESULTS AND DISCUSSION

The magnitude of the modulation of the superconducting properties in the conductive polymer/high-T_c superconductor bilayer structures is dependent on a number of factors including superconductor film thickness, crystal orientation and film morphology. Films with thickness values greater than 1000 Å, regardless of the film morphology, normally display little to no shift in T_c. Thin films of superconductor with rough morphologies show the greatest change in T_c, whereas the smooth films are influenced by the polymer only to a minor extent. Summarized in Table I for various thickness values and morphologies of the superconductor thin films are transition temperatures for the polymer/superconductor devices in both the neutral and oxidized forms. The first three sets of data are for cases where highly textured films of mixed a/c-axis were used, whereas the latter three sets correspond to smooth c-axis films.

There are a number of important differences between the rough and smooth films that may be responsible for the differences in the magnitude of the modulation of superconductivity. First, rough films possess regions which are much thinner than the average value. Locally, these weak structures possess critical current values that are much less than the remainder of the film and contribute to the enhanced sensitivity of such regions. Second, the polycrystalline films possess both a-axis and c-axis crystallographic orientations (vide infra). Since the coherence length along the c-axis ($\xi c \sim 1.5$-4 Å) is much shorter than that along the a-axis ($\xi ab \sim 20$-50 Å), the inclusion of an a-axis component into the device may serve to increase the sensitivity of the hybrid structure. Finally, the textured films possess polycrystalline film orientations which result in a large number of high angle grain boundaries that are highly sensitive to external stimuli.

Table I. Modulation of T_c for Polypyrrole / $YBa_2Cu_3O_{7-\delta}$ Thin Film Structures[a]

Superconductor Film Thickness/Å	*T_c (Neutral Polymer)/K*	*Tc (Oxidized Polymer)/K*	ΔT_c	*Film axis/ Morphology*
200[b]	74	≤ 24	≥ 50	a/c-axis/rough
500	84	70	14	a/c-axis/rough
1500	80	79	1	a/c-axis/rough
500	87.6	86.8	0.8	c-axis/smooth
900	87.6	87.0	0.6	c-axis/smooth
1200	87.0	87.0	0	c-axis/smooth

[a] Each superconductor device was coated with 2μm polypyrrole film.

[b] Reported thickness represents the estimated superconductor thickness over the step for a 800 Å film of $YBa_2Cu_3O_{7-\delta}$ that was deposited over a 1500 Å step edge.

Although deposition conditions for the preparation of $YBa_2Cu_3O_{7-\delta}$ films are often tailored to produce c-axis oriented films which exhibit high critical currents, polycrystalline films appear to be better suited for the fabrication of conductive polymer/superconductor structures. Figure 1 presents x-ray powder diffraction data obtained for a c-axis film on $LaAlO_3$ (100), an a-axis film on $LaAlO_3$ (100) and a polycrystalline film of $YBa_2Cu_3O_{7-\delta}$ prepared with the low density target. Although, the two films deposited on $LaAlO_3$ using the high density target exhibit almost exclusively c-axis and a-axis orientations, respectfully, the film fashioned with the low density target possesses mixed c- and a-axis orientations.

Low density targets appear to be effective for the deposition of rough high-Tc thin films. Such targets are not uniformly ablated on the atomic level, rather these targets produce plumes of ablated material that consist of particles of superconductor. The resulting superconductor thin films are more textured and have lower critical currents than the smooth films formed from high density targets. The weak link characteristics of these thin films are also enhanced by depositing the superconductor onto a cleaved MgO substrate. These substrates possess natural step

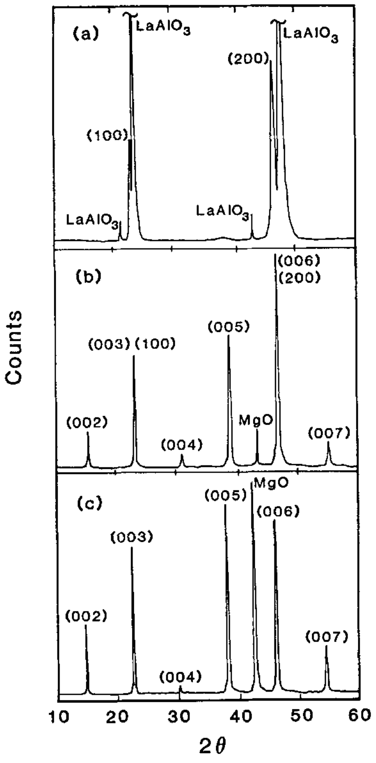

Figure 1. XRD powder patterns for the following samples: (a) $YB_2Cu_3O_{7-\delta}$ thin film a-axis orientation on $LaAlO_3$, (b) $YB_2Cu_3O_{7-\delta}$ thin film mixed orientation on MgO, (c) $YB_2Cu_3O_{7-\delta}$ thin film c-axis orientation on $LaAlO_3$.

edges and can be exploited to further disrupt the connection between selected superconductor grains. Figure 2 shows an image of a $YBa_2Cu_3O_{7-\delta}$ film created by laser ablation from a low density target. This specimen was utilized to create the superconductor/conductive polymer bilayer structure that displays the 50 K shift in T_c. The large grain size and rough texture of the superconductor element is readily apparent from the micrograph.

Similarly, Mannhart[6] et al. have prepared films rich with weak links for the purpose of making electric field effect devices which exhibit high sensitivities. To prepare such devices, the substrates were polished with 1 μm diamond paste prior to superconductor deposition. The diamond polishing procedure leads to the formation of a network of fine grooves on the substrate and induces the creation of grain boundaries in the film. Electric field devices fabricated from these weak link rich films have displayed large shifts in T_c.

While it is too early to identify the precise mechanism responsible for these observed shifts in T_c, it is possible that the modulation of superconductivity may be the result of a proximity effect.[7] The magnitude of the proximity effect observed for classical studies of metal/superconductor bilayer structures has been shown to be dependent on a number of factors such as the metal thickness, the superconductor thickness as well as the coherence length of the superconductor template.[8] The large shifts in T_c we have observed here are inordinately large based on the very small coherence length associated with $YBa_2Cu_3O_{7-\delta}$ and the relatively large average thickness values for the superconductor. However, these large shifts in T_c are only observed for polycrystalline films that possess a large number of weak links. Therefore, this mechanism can not be discounted. Although it seems plausible that the observed modulation of T_c may be the result of an electric field effect,[9,10], devices of this type normally yield ΔT_c changes which correlate with the changes in the normal state resistance, ΔR. Only minimal changes in ΔR are noted for our samples. Thus, our data seems to be inconsistent with the electric field effect explanation. A third possibility that must be considered is that reversible changes in the chemical structure (i.e. oxygen content) of the grain boundaries may play a role in the observed behavior.

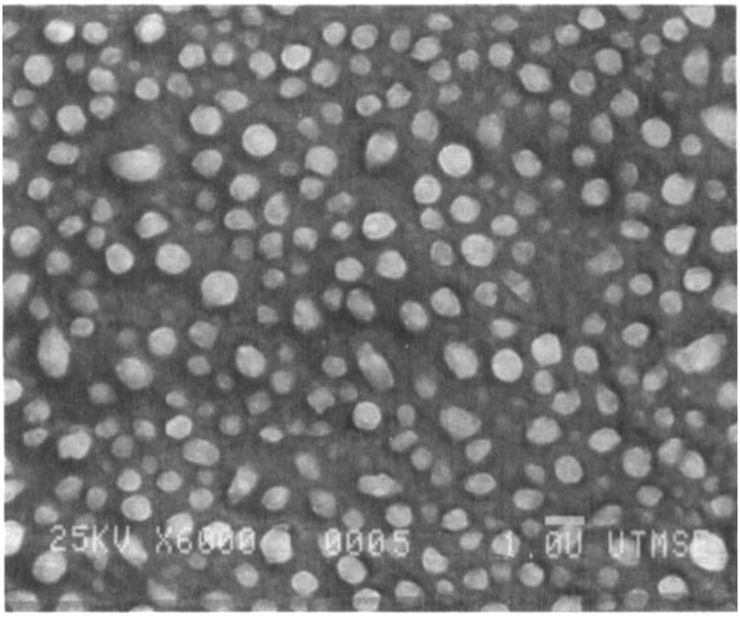

Figure 2. Scanning electron micrograph showing a ~800 Å thick film of $YBa_2Cu_3O_{7-\delta}$ that was deposited via laser ablation onto a cleaved MgO (100) substrate. Here, weakly coupled grains of superconductor regions form weak links.

Regardless of the explanation, however, we have demonstrated here strategies for tailoring the weak link rich films of high-T_C superconductor that can be used to prepare conductive polymer/superconductor bilayer structures which exhibit large reversible changes in T_C.

CONCLUSION

In summary, we have developed unique bilayer structures that form the basis for a new type of molecular switch for controlling superconductivity. The degree of modulation is highly dependent on the superconductor thickness as well as the morphology of the superconductor thin film. Rough films can be produced from low density targets and these films possess a large number of weak links as well as a mixture of both c- and a-axis orientations. While the exact mechanism for the suppression of T_C has yet to be determined definitively, we have shown that the conductive polymer layers can be used to modulate reversibly the transition temperature of a superconductor microbridge by as much as 50 K.

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