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Ion-beam-induced destruction of superconducting phase coherence in $YBa_2Cu_3O_{7-\delta}$

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We have explored the effects of ion beam irradiation on the electrical and structural properties of superconducting thin films of $YBa_2Cu_3O_{7-\delta}$. Damage created by nuclear-energy loss processes degrades the superconducting transitions. Data from resistance measurements as well as from Rutherford backscattering and channeling measurements suggest that ion bombardment is not changing the volume fraction of superconducting material substantially. Instead, it appears that islands of good superconductor are becoming progressively decoupled, destroying the phase coherence.

Although the physical mechanisms leading to superconductivity in high-T_c oxide superconductors are not known, it has been demonstrated that some of the properties, such as the critical current, are governed by microstructure. Recent results, for example, suggest that thin films of these superconductors are capable of carrying higher currents than the polycrystalline ceramics or bulk single crystals.[1,2] Moreover, Clark, Marwick, Koch, and Laibowitz[3] have reported that the superconducting state is quite sensitive to defects created by ion bombardment. We have irradiated thin films of $YBa_2Cu_3O_{7-\delta}$ with MeV-energy ion beams and find that the electrical and structural changes produced in these films can be associated with loss of phase coherence. Similar ion bombardment studies were carried out in the $A15$ superconductors, the "high-T_c" material of the previous decade. Since then, we have learned much about the destruction of superconductivity by disorder. If the superconducting pair wave function is written as

$$\psi = \delta e^{i\phi} ,$$

where δ is the pair amplitude and ϕ is the phase, then it is clear that there are two ways to destroy the superconductivity: either reduce δ or destroy the coherence of ϕ. By varying the morphology of elemental superconductors, both of these regimes can be explored.[4] Films of Pb or Sn can be deposited to give either islanded films which show loss of phase coherence or highly disordered films of uniform thickness which show amplitude reduction.

It is now apparent that we can also probe both of these regimes by introducing disorder with an energetic ion beam: the response of the $A15$'s to ion damage can be thought of in the framework of amplitude (δ) reduction, while the behavior of $YBa_2Cu_3O_{7-\delta}$ is reminiscent of destruction of phase coherence (ϕ). For the $A15$'s, 2-MeV He irradiation in the range of 10^{16}–10^{17} ions/cm^2 causes the critical temperatures (T_c) to decrease steadily until they saturate at a level of damage (~0.06 eV/atom) which reduces the electron mean free path to an interatomic spacing.[5] The reduction in T_c results from a lowering of the electron density of states due to increased electron-defect scattering, i.e., amplitude reduction. Although the initially sharp transitions do broaden slightly in the middle of this fluence range, they become narrow again at the end. The broadening in this case is attributed to the slightly inhomogeneous nature of the damage (on the scale of the coherence length) at such low fluence levels.

We have studied radiation effects in $YBa_2Cu_3O_{7-\delta}$ films prepared by e-beam evaporation in three different chambers. High-energy ion beams were employed so that the rates of energy loss were approximately constant throughout the films and the ion ranges exceeded the film thickness. Calculated range, straggle, and nuclear energy loss and electronic energy loss values[6] for all the ions in this study are summarized in Table I. Irradiations were performed in a vacuum chamber at $<5\times10^{-6}$ Torr at low current densities (<40 nA/cm^2) to prevent significant heating of the samples. Resistances were measured in a four terminal configuration after each irradiation and $T(R=0)$ was accurately determined by reducing the measuring current by a factor of 50. Although the sample geometries were not well defined, each series of R vs T traces was taken without remaking the In solder contacts to the film, so relative resistance changes within a series are meaningful. Since these compounds can be degraded by water, we were extremely careful to avoid condensing water vapor on the films. For the initial runs, we measured an undamaged piece of the film to monitor the effect of temperature cycling alone on the R vs T traces, but no changes were found.

The phase diagram for $YBa_2Cu_3O_{7-\delta}$ is complicated, with the neighboring compounds being insulators and semiconductors rather than metals (as in the case of the $A15$'s). In particular, the compound is extremely sensitive to oxygen concentration.[7] One consequence of this was

TABLE I. Calculated (Ref. 6) ranges (R_p), straggles (ΔR_p), nuclear and electronic energy losses at the surface for the particular ion beams, and samples used in this experiment. Sample 3 is a 1.2 μm film of $YBa_2Cu_3O_{7-\delta}$ on $SrTiO_3$; sample 1 is a polycrystalline film of $YBa_2Cu_3O_{7-\delta}$, sandwiched between a 1 μm buffer layer of ZrO_2 on the sapphire substrate and a 0.5 μm ZrO_2 cap.

Ion	Sample 1 $R_p \pm \Delta R_p$	Sample 2 $R_p \pm \Delta R_p$	Sample 3 $R_p \pm \Delta R_p$	Nuclear energy loss (eV/Å)	Electronic energy loss (eV/Å)
3.5 MeV Be^+	3.5 ± 0.1 μm	4.30 ± 0.3 μm	4.0 ± 0.2 μm	0.22	110
0.8 MeV N^+		0.95 ± 0.1 μm		2.9	120
1.0 MeV Ne^+		0.90 ± 0.2 μm		6.3	150
2.0 MeV Ar^+		1.10 ± 0.1 μm		19	230

demonstrated dramatically by Cava *et al.*[8] who showed the large changes in the R vs T characteristics (from metallic to semiconducting) due to very small (~2%) reductions in the oxygen concentration. Furthermore, subtraction of only one oxygen per unit cell yields a semiconducting material.[9]

The behavior of all the films under irradiation was qualitatively similar, so we will present results from a typical case. This sample, no. 2, is a thin film (~1500 Å) on a single-crystal $SrTiO_3$ substrate.[2] The resistance has a metallic temperature dependence above the superconducting transition (which is less than 1 K wide) with $T(R=0)$ at 91 K. From Rutherford backscattering (RBS) and channeling, we know that the film is highly aligned with the substrate and x-ray measurements show that the c axis of the film is perpendicular to the plane of the substrate. RBS gives an average stoichiometry of $YBa_{1.4}Cu_{1.7}O_x$, so the film is not single phase; however, scanning Auger characterization of the surface of films fabricated the same way shows large (~5000 Å) grains of $YBa_2Cu_3O_{7-\delta}$.[10] Although the critical current of this particular film was not measured, similar films have shown critical current densities of $> 10^6$ A/cm^2 at 82 K.[2]

A sequence of resistive transitions for this film after irradiation with 1.0 MeV Ne ions is shown in Fig. 1. Note that the shape of the superconducting transition broadens continuously as a resistive tail develops and the room-temperature resistance of the sample initially increases linearly with fluence. These curves resemble the resistive transitions in the quench-condensed Pb and Sn films where grains are progressively decoupled to give loss of phase coherence.[4] Although bulk superconductivity in the film disappears at a fluence of $\sim 2\times10^{14}$/cm^2, the feature at T(onset) remains. We noticed that the drop in resistance (in ohms) at T(onset) in the R vs T characteristic for the highest fluence shown is the same magnitude as the resistance drop associated with the superconducting transition in the undamaged film (shown by the arrow). In addition, a hump develops in the transition region. This was also observed in pieces of this film that were irradiated with 3.5 MeV Be or 0.8 MeV N, but not those irradiated with 2.0 MeV Ar. (The difference between the Ne and Ar results may be due to the character of the damage from the much heavier mass Ar ions.)

These observations are difficult to understand unless we assume a model where the film consists of a series combination of regions of $YBa_2Cu_3O_x$ with slightly different oxygen compositions. In that case, as small amounts of the oxygen-deficient phases accumulate (perhaps at the grain boundaries as suggested by Clark *et al.*[11]), their resistance relative to the stoichiometric phase increases substantially, and the temperature dependence shows semiconducting behavior above the superconducting transition.[8] The sum of these resistance characteristics then gives rise to the drop at T(onset) which rides on top of the growing hump, as shown in the inset to Fig. 1. The magnitude of the resistance drop (R) can be associated with the volume of "good" superconductor by $R = \rho L/A$. If the volume were being reduced uniformly, the resistance drop would shrink, unless by some unlikely coincidence the ratio between the length (L) and area (A) remained exactly the same. Therefore, the fact that R is not changing much is strong evidence that the volume of superconducting material with T(onset) = 92 K is not being significantly altered by the irradiation. The development of the resistive tails is independent of this phenomenon, but it also implies that grains of good superconductor are being decoupled in these films.

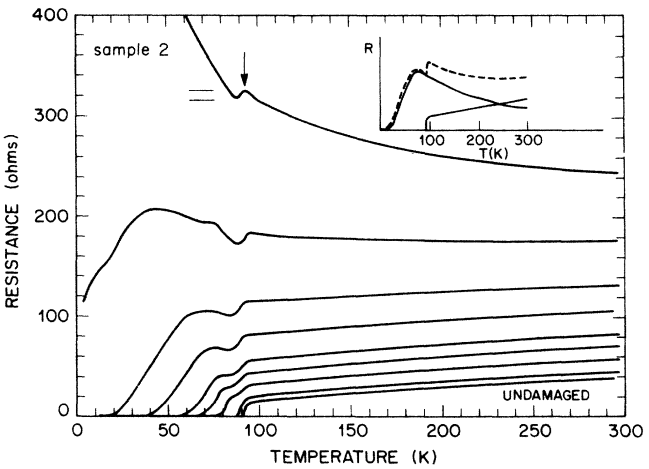

FIG. 1. R vs T characteristics for sample 2 after bombardment with 1.0 MeV Ne ions at fluences of 0 (undamaged), $0.1\times10^{+14}$, $0.4\times10^{+14}$, $0.7\times10^{+14}$, $1.0\times10^{+14}$, $1.4\times10^{+14}$, $1.8\times10^{+14}$, $2.2\times10^{+14}$, and $3.0\times10^{+14}$ ions/cm^2. Vertical arrow indicates T(onset) at ~92 K. Note that the R drop at 92 K in the undamaged films is the same magnitude as the R drop at 92 K in the most heavily damaged film (indicated by markers). The inset shows schematically how the "hump" below T(onset) might arise from a summation (dashed line) of the resistances from regions of different stoichiometry (solid lines).

Additional evidence for this model comes from structural information provided by RBS and channeling analyses on this sample. The results are presented in Fig. 2. In these spectra, the ratio between the channeled and random backscattered yield (χ_{min}) is a measure of the crystallinity of the sample. From the Ba part of the spectrum (1.6–1.8 MeV), we determine a χ_{min} of 33% in the undamaged film, indicating that ~67% of the film is crystalline with the same orientation as the substrate. After a fluence of $2.2\times10^{+14}$ Ne^+/cm^2 (~2 eV/atom), which is sufficient to destroy the superconducting properties of the sample, only a small rise in the backscattered yield in the channeling direction is measured, showing that the crystallinity of the film is hardly affected by the irradiation. Even after an additional fluence of $0.8\times10^{+14}$ Ne^+/cm^2, the χ_{min} has risen to 60%, so ~40% of the film is still crystalline and aligned with the substrate. When we used 2 MeV Ar irradiation to progressively damage the sample, similar results were achieved. In that case, we were able to completely disorder the film with a fluence of $5\times10^{+15}/cm^2$ which corresponds to a deposited nuclear energy of ~13 eV/atom.

Through the use of MeV beams in this experiment, it is possible to study damage mechanisms without complications due to chemistry or end-of-range damage. Therefore, we attempted to establish whether the dominant contribution to the destruction of superconductivity is due to ions colliding with the lattice atoms (nuclear energy loss) or to ions interacting with the electrons (electronic energy loss). Choosing $T(R=0)$ as the hallmark of superconductivity, we plotted the change in $T(R=0)$ as a function of the ion fluence in Fig. 3 for four separate irradiations of sample 2. These curves are linear in fluence at the lower fluences, but deviate at higher fluences as the number of superconducting paths diminishes and the exact temperature at which $R=0$ is somewhat more arbitrary. Nonetheless, the trends are as expected if nuclear energy loss processes dominate—larger fluences of the lighter

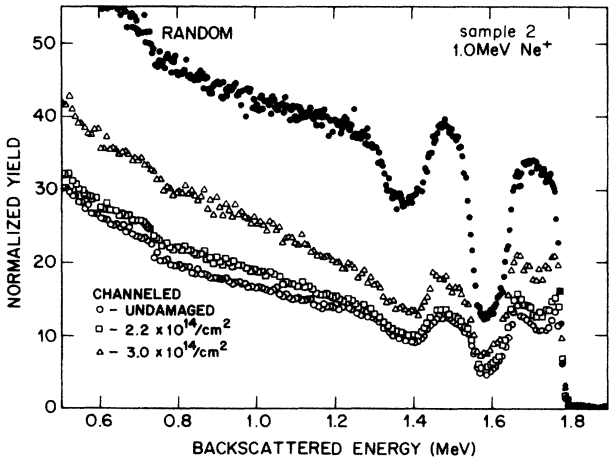

FIG. 2. RBS spectra for sample 2 comparing random and channeled backscattering yields (of 2 MeV He^+) for the undamaged sample to channeled yields for the sample after irradiation with 1.0 MeV Ne^+ at fluences of $2.2\times10^{+14}$ and $3.0\times10^{+14}$ ions/cm^2.

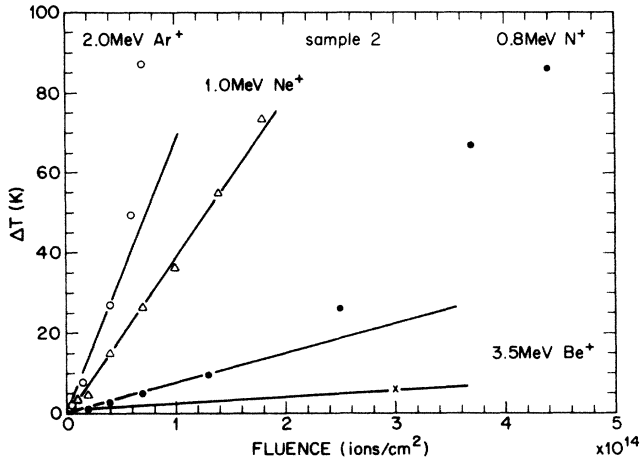

FIG. 3. ΔT_c, defined as $T(R=0$, undamaged film$)-T(R=0$, damaged film), for sample 2 after irradiation with a range of fluences of four ion beams. The slopes $[d(\Delta T_c)/d\Phi]$ of the linear portions of the curves (shown by the solid lines) show a linear dependence on nuclear energy loss.

ions are required to depress superconductivity. Furthermore, if the slope of the linear portion of each curve (low-fluence region) is compared with the corresponding nuclear and electronic energy loss for each ion, we find that they depend linearly on the nuclear component but there is no evidence for a linear dependence on the electronic component.

Clark *et al.*[11] present transmission electron microscope results that suggest that room-temperature ion bombardment stimulates the growth of an amorphous layer at the grain boundaries of the high-T_c films. The formation of such a layer, if insulating, can neatly explain the phase-decoupling behavior. A possible growth mechanism for that layer is diffusion of defects to the grain boundaries during ion irradiation. At low temperatures, diffusion will be reduced and growth of the phase decoupling layer will be inhibited; therefore, the films should be less sensitive to ion-induced damage. However, preliminary results from our low-temperature (<90 K) bombardment experiments in which *in situ* resistance measurements were performed show that the ion fluence required to destroy bulk superconductivity in the sample is lower than that at room temperature. We also observed that samples that are damaged at low temperatures "heal" on warming to room temperature. This annealing at room temperature has also been observed by Stritzker.[12] Although the room-temperature irradiation data are consistent with a radiation-enhanced growth of an insulating layer at grain boundaries, the low-temperature experiments indicate that other mechanisms are at work.

In conclusion, we have shown that the damage produced in thin films of $YBa_2Cu_3O_{7-\delta}$ by high-energy ion beams is dominated by nuclear collisions. These films exhibit resistive transitions which broaden with increasing fluence while the onset T remains the same. This is strong evidence that ion irradiation is destroying the superconducting phase coherence in these samples. Furthermore, the resistance drop at the superconducting transition in

the undamaged films is still apparent in the films which are no longer bulk superconductors. We interpret this as an indication that the volume of good superconducting material is not changing very much. RBS and channeling results on the oriented films show that bulk superconductivity disappears at fluences significantly below those required to disorder the crystal, corroborating this model. Although our results are consistent with destruction of phase coherence proceeding via diffusion of oxygen defects to grain boundaries, bombardments below 90 K showed that the films are actually more sensitive to damage at low temperatures where diffusion will be inhibited.

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