Resistivity changes and defect mobility in ion-irradiated $YBa_2Cu_3O_{7-x}$

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In situ measurements during MeV ion bombardment at room temperature are used to study the superlinear increase of resistivity with fluence which occurs in irradiated $YBa_2Cu_3O_{7-x}$. The functional form of the resistivity increase is found to be exactly exponential for O and As ion irradiation, confirming previous results of lower precision. For low ion damage rates, we find deviations from the exponential dependence at low doses. We show that these are caused by an unidentified phase transformation, occurring during the irradiation, which lowers the resistivity of the samples. Annealing of resistivity increments caused by brief irradiations occurs at room temperature, indicating that radiation-induced defects are mobile. The rate of annealing is strongly sample dependent, but in all cases the transformation induced by a small dose of irradiation causes a reduction in the resistivity of the sample. We suggest that the reduction in resistivity may be due to ordering on the oxygen sublattice.

INTRODUCTION

Studies of irradiation-induced disorder in high-T_c superconductors are of interest for a number of reasons. First, the disorder affects the superconducting transition temperature, the critical current, and the normal-state resistivity. The detailed mechanisms of the changes are, for the most part, still obscure and need to be investigated further. Second, the damage and disorder produced by ion implantation, which is a potentially useful technique for processing high-T_c materials into devices, needs to be understood. Last, very little is known about point defects in these novel materials, and in the past irradiation studies have been found to be useful in the study of defects, especially in metals.

It is already known that very low concentrations of defects introduced by neutron irradiation can increase the critical current in ceramic samples of $YBa_2Cu_3O_{7-z}$,[1] while in thin films J_c is reduced by irradiation. Progressively higher fluences of ion bombardment applied to thin films cause degradation of their superconductivity[2-5] and a metal-insulator transition.[4,6-8] One feature of the metal-insulator transition is that the normal-state resistance of $YBa_2Cu_3O_{7-z}$ is a superlinear function of fluence. For neutron irradiation at 80 K,[8] the resistivity increase closely follows an *exponential* dependence on dose over 8 orders of magnitude from the point where superconductivity is destroyed. For ion bombardment at room temperature, earlier studies,[2,5,6] in which resistivity measurements on thin films were made with a four-point probe after irradiation, indicated that the resistivity followed a similar dependence on ion dose. Irradiation with GeV ions at 105 K also produces exponential increases.[9] Such a dependence is quite unusual, and warrants further study as it is not yet understood.

This paper reports two main observations. First, by detailed *in situ* measurements we establish that the dependence of resistivity on ion dose is exactly exponential at room temperature from the beginning of the irradiation, if the dose rate (expressed in terms of damage) is not too low. Secondly, we show that for low dose rates the resistivity change deviates from the exponential, but that this occurs because of annealing caused by a phase transformation that occurrs the irradiation. Instability of the radiation damage, as seen by resistivity changes, is also found after brief irradiations, which suggest that it is due to mobile irradiation-induced defects. Some of these data were summarized in an earlier publication.[10]

EXPERIMENT

$YBa_2Cu_3O_{7-z}$ films made in two different ways were used in this study, and the annealing of radiation-induced defects was found to be different in the two cases. Both types of films had relatively high room-temperature resistivities and degraded superconducting properties compared to higher quality material. The significance of this for the interpretation of the data is discussed later. Sputtered films 8700 Å thick were deposited on yttria-stabilized zirconia substrates using a two ion-beam system.[11] The resulting films were polycrystalline, with a grain size of about 1 μm. They showed an onset of superconductivity at 91 K and zero resistance at 65 K. Their room-temperature resistivity was around 3 mΩ cm. Electron-beam evaporated[12] films 5200 Å thick were deposited on $SrTiO_3$ substrates. Similar films normally grow epitaxially and have room-temperature resistivities well below 1 mΩ cm. The samples that we used came from a batch with high room-temperature resistivity ($\sim$7 mΩ cm). Their superconducting onset was at 85 K, with zero resistance occurring at 68 K. Electrical contacts to our films were made by evaporating silver through a mask to form rows of 0.8×3-mm pads on 2-mm centers. Before evaporation of the silver, the film was etched with an ion beam to ensure removal of any surface layer.

In this work the resistance of the samples was measured *in situ* during and after irradiation. Samples were mounted in an implantation end station for ion bombardment. Beams of 2-MeV B, 1-MeV O, or 2-MeV As ions were used. Electrical contacts to the silver pads were made

with spring clips. The ion beam was electrostatically scanned across the sample holder, but a slit-shaped silicon mask was used to ensure that only the area between two adjacent contact pads was irradiated. The film was scored to ensure that current could only pass through the irradiated area. The dc resistance of the irradiated area was measured using a standard four-terminal method, with constant currents in the range 1–3 mA. Accurate ion-beam dosimetry was achieved by surrounding the sample holder with a Faraday cup, to which the silicon slit assembly and the copper plate supporting the sample were connected. Only the beam current falling on the sample itself, amounting to less than 1% of the total entering the Faraday cup, was not measured. However, since the beam irradiated the sample holder uniformly, the flux falling on the sample was known. The uniformity of the beam is known from implantation experiments to be $\pm 3\%$. The irradiations and measurements were done at room temperature. The current density in the beam was kept below 20 nA/cm^2 (40 mW/cm^2) to minimize heating of the sample. The calculated temperature rise for the highest fluxes is less than 1°.

Two different types of measurement are reported here. In one, the sample was irradiated continuously, and the change in the sample's resistance was recorded with an automatic data collection system. In some early measurements, resistivity changes were measured as a function of dose by briefly interrupting the irradiation to make a measurement, then resuming for another increment of dose. In the second type of measurement, a small ion dose was administered and subsequent annealing of the resistance monitored as a function of time.

In previous studies of the irradiation of $YBa_2Cu_3O_{7-z}$ with different ions, the effectiveness of the ions in producing a number of different effects was found to correlate with the amount of damage they caused. Accordingly, we estimated the rate of damage production by the ions used in this study by calculating the number of atomic displacements produced in $YBa_2Cu_3O_{7-z}$ as a function of depth. The Monte Carlo code TRIM[13–15] was used to perform the calculation, with the displacement energy E_d taken to be 20 eV. The full development of the recoil collision cascades was taken into account in the calculation. The mean concentration of displaced atoms in the sample (averaged over depth) was used to characterize the irradiation. Solutions[16] of the linear Boltzmann equations governing the transport of energetic recoil atoms show that the density of displaced atoms n_d can be expressed in terms of the density of energy deposited into atomic collisions ϕF_D, where ϕ is the ion fluence and F_D is the damage energy deposited per unit depth per ion:

$$n_d = 0.8\phi F_D / 2E_d . \quad (1)$$

Values of F_D calculated by TRIM are shown in Table I. It is convenient to quote damage levels in terms of the deposited energy (eV/atom). As Eq. (1) shows, the density of displaced atoms ("displacements per atom," or dpa) is an equivalent measure. However, it should be noted that the actual defect concentration in a sample is determined by a number of processes that occur *after* the initial displacement; for example, clustering or loss to sinks. Thus, while the displacement concentration can be a useful measure of the amount of damage initially generated in a sample, it may not be an accurate guide to the actual defect concentration.

TABLE I. Calculated damage energy deposited by irradiating ions. Values are averaged through 8700-Å thickness.

Ion	Energy (MeV)	F_D (eV/Å)
B	2	1.1
O	1	11
As	2	98

RESULTS

We first present the evidence that for ion beams which produce damage at a high rate, the normal-state resistivity in irradiated $YBa_2Cu_3O_{7-x}$ increases exponentially with ion dose. Then we show that for lower dose rates there are deviations from the exponential in the form of a low-dose transient, whose form depends on the method of sample preparation. Finally, we present data which show that the origin of these transients are resistivity changes which take place during the irradiation and are caused by mobile irradiation-induced defects. Post irradiation measurements show the presence of several defect-mediated processes occurring at different rates.

Continuous ion irradiation

Figure 1 shows the normal-state (room-temperature) resistivity of two thin-film samples irradiated with heavy ions as a function of irradiation fluence. Both irradiations produce exponentially increasing resistivity. The oxygen ion data (discrete points) is for a sputter-deposited film 8700 Å thick, and was taken by interrupting the irradiation briefly each time the resistance of the sample was recorded. The straight line is a least-squares fit to the data. The As ion irradiation data are for an *e* beam deposited film 5200 Å thick and were taken by continuously recording the sample's resistance during the irradiation, using an automatic data collection system. This curve consists of a large number of individual data points; it is not a fit. Note the difference in the dose scales for the different irradiating ions, which is a consequence of the differing amount of damage they produce (Table I).

Figure 1, together with previously published information,[5,6,17] establishes the exponential increase in resistivity with irradiation dose for heavy-ion irradiations. Figure 2 shows a semilog plot of the low-dose region of these curves, and in addition shows data for irradiation with a lighter ion, boron. In this plot the sample resistivities are shown normalized to their initial values, and the abscissa is plotted as the energy deposited into atomic displacements, given in Table I, whose calculation has already been outlined. Also, for each curve the irradiation ion and the method of preparation of the sample are indicated on the plot. The figure shows that for O and As ions, the ex-

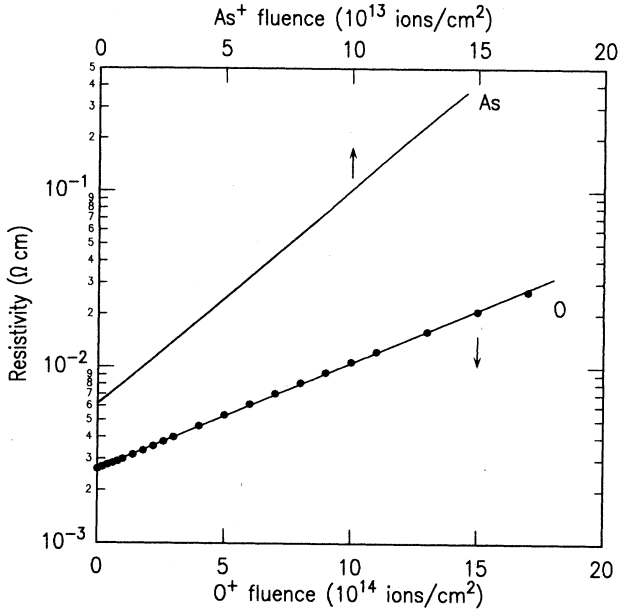

FIG. 1. The resistivity of ion-irradiation thin films of $YBa_2Cu_3O_{7-x}$ measured at room temperature as a function of ion fluence. Notice the different fluence scales for the O and As ions. The films were an 8700-Å-thick sputter-deposited film (O irradiation), and a 5200-Å-thick *e*-beam deposited film on $StTiO_3$ (As irradiation). In these irradiations, in which the damage rate is high, the resistivity rises exponentially with ion dose.

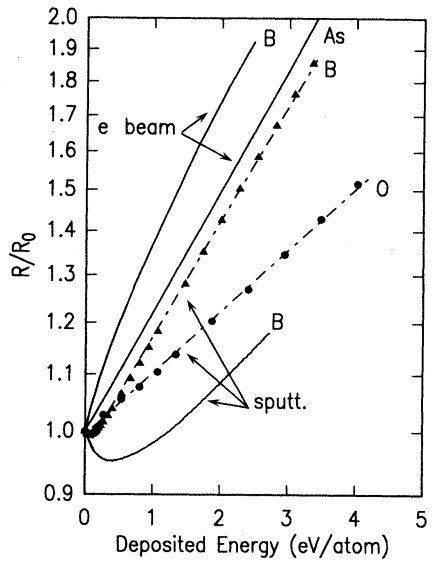

FIG. 2. Resistivity changes of $YBa_2Cu_3O_{7-z}$ samples irradiated with 2-MeV boron, oxygen, and arsenic ions as a function of the deposited damage energy density, calculated as described in the text. Data taken by interrupting the beam to measure the sample resistance are shown as individual points. The other curves were measured continuously during the irradiation. For all the irradiating ions the resistance increased exponentially with ion dose, except for boron ions for which there was an initial transient caused by point-defect motion during the irradiation, as discussed in the text. The curves are labeled with the method of preparation of the films used.

ponential dependence of the resistivity on fluence extends down to the lowest doses, but that for B ion irradiations there is a low-dose transient.

The form of the transient under boron irradiation was found to depend on how the sample was made: In sputtered samples it involved a reduction in resistance, followed by an exponential rise; in the *e*-beam deposited samples it took the form of a slightly increased initial rate of resistivity increase. In the next section we will present further information on the origin of these transients, showing that they are caused by defects which are mobile at the irradiation temperature, and which can cause phase transformations at rates which are fast enough to be seen during irradiation with B ions at a low damage rate, but are too slow to make themselves felt during irradiation with the heavier ions, whose damage rates for comparable fluxes are much higher (Table I).

With continued B ion irradiation, the resistivity of the samples continued to increase after the initial transient. In most cases, the size of the resistivity increase produced in reasonable irradiation times was too small to say definitely whether the increase was exponential with fluence. However, where the resistivity increase was large, and the period of the initial transient relatively short, as it was for the data for a sputtered sample represented by triangles in Fig. 2, the resistivity increase after the transient could be clearly seen to be exponential.

In a previous paper[6] it was concluded that the exponent in the resistivity increase with ion fluence for different ions was proportional to the energy deposited into displacements. If this were so, then the slopes of the straight-line segments of all the curves in Fig. 2 would be the same. They are not, but the transformation from fluence to deposited energy has removed almost all of the variation in slope which would result if we plotted against fluence. Thus we write the dependence of resistivity on ion fluence in the form

$$\rho \sim \exp(F_D \phi / N\eta) , \qquad (2)$$

where N is the atomic density, and η (eV/atom) is an energy density which can be derived from the slopes of the linear parts of the curves in Fig. 2. Values are shown in Table II from this and previous work. Some of the variation is probably due to sample-to-sample variability, par-

TABLE II. Energy densities characterizing the exponential increase of resistivity with dose.

Irradiating ion	Sample type	η (eV/atom)	Reference
B	sputtered	8.6	This work
B	sputtered	5.1	This work
O	sputtered	10.5	This work
As	epitaxial	4.8	This work
As	sputtered	2.6	Clark *et al.*[a]

[a] From Ref. 6, recalculated using the mean F_D from Table I instead of the peak value.

ticularly thickness variations which influence the mean values of F_D used in the calculation. Values of η lie in the range 5–10 eV/atom, which would therefore appear to be a characteristic damage level for the resistivity changes. This is also the order of magnitude of the damage level which causes a change from metallic to insulating behavior in the curve of resistance versus temperature, as reported in several papers.[3,7,17–19]

We find empirically that the resistivity transient in boron irradiated sputtered samples can be fitted by the sum of three exponential terms:

$$R = R_{01}\exp(-\alpha_1\phi) + R_{02}\exp(-\alpha_2\phi) + R_{03}\exp(\alpha_3\phi)\,. \tag{3}$$

The first two terms denote transient recovery processes which tend to *reduce* the resistance, and the third is an exponentially increasing term of the form of Eq. (2) (i.e., $\alpha_3 = F_D\phi/N\eta$) which dominates at high dose. A fit of Eq. (3) to some of the data is shown in Fig. 3, and the values of the fitting parameters are given in the caption. The good agreement confirms that this is an appropriate parametrization of the data, and, in particular, that the physical process represented by the third term is present from the lowest dose. This is a significant point: Despite the different form of the resistivity versus dose curves for sputtered films irradiated with B ions, the fit of Eq. (3) reveals the same underlying exponential increase of resistance with dose as is dominant for irradiation with the heavier ions. The values of the constants appearing in Eq. (3) are different for the two cases fitted, which indicates the presence of uncontrolled variables in the experiment. Nevertheless, the functional form of the equation suggests a physical interpretation of the data. The first two terms (which are absent or of negligible effect in O and As irradiation for reasons given later) must represent annealing or recovery processes which we tentatively identify with transformations occurring in the microstructure of the samples due to the effects of mobile irradiation-induced defects. The nature of the transformation is discussed later. The rates of the two processes differ by about an order of magnitude, and data to be described indicate that they are governed by complex kinetics, involving time dependence as well as dose dependence, which are strongly influenced by the microstructure of the sample.

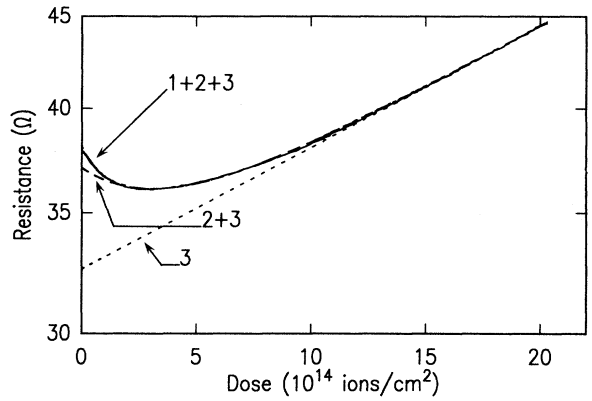

FIG. 3. Detail of the low-dose region in Fig. 2 for one of the B ion irradiations of a sputtered film, showing fits of Eq. (3) to the data. The data are shown as a solid line, and various combinations of terms in the fit are shown as dashed lines. A good fit is obtained when all three terms in Eq. (3) are included. This shows that the process described by the exponentially *increasing* term (the third term), is present from the beginning of the irradiation. The fitting parameters were $R_{0i} = \{1.05, 4.49, 32.58\}$, $\alpha_i = \{1.8\times10^{-14}, 2.8\times10^{-15}, 1.6\times10^{-16}\}$. An equally good fit was obtained for the other B irradiation shown in Fig. 2, with fitting parameters $R_{0i} = \{0.13, 0.61, 15.67\}$, $\alpha_i = \{3.5\times10^{-14}, 8.4\times10^{-15}, 2.7\times10^{-16}\}$.

Post-irradiation annealing: defect mobility

To gain more understanding of the initial transient under B irradiation, where the damage rate is very low, it is useful to consider a different type of measurement. Figure 4 [(a) and (b)] shows what happened to the resistivity of two different samples when they were exposed to a very small dose of 2-MeV As ions/cm^2 (10^{11} ions/cm^2, equivalent to 0.013 eV/atom, or 3×10^{-4} dpa). In both cases the irradiation, which took only a few seconds, was

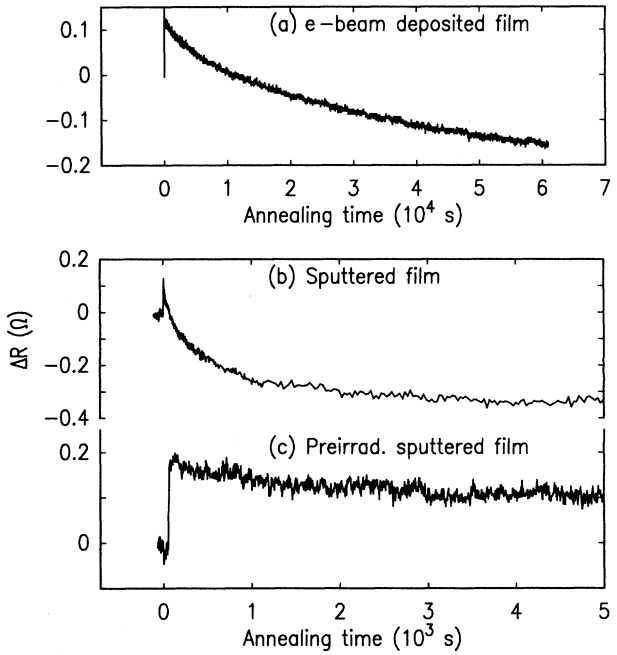

FIG. 4. Resistivity change of samples measured during and after a brief irradiation with 10^{11} 2-MeV As ions/cm^2. The sharp increase in resistivity is due to the production of defects by the irradiation. The subsequent decrease is attributed to the annealing of the defects. (a) Epitaxial (*e*-beam deposited) film; (b) sputter-deposited film; (c) sputter-deposited film after 2-MeV boron ion preirradiation to a dose of 1.77×10^{15}/cm^2. The process causing the resistance to be reduced below its starting value is tentatively proposed to be ordering on the oxygen sublattice. This is suppressed by irradiation [curve (c)]. Note the very different rates of annealing in the *e*-beam deposited film and the sputtered film.

accompanied by an immediate increase in resistance, followed after the irradiation ceased by a prolonged recovery in which the sample's resistance fell *below* its starting value. The occurrence of the annealing shows that radiation-induced defects are mobile at room temperature. However, the initial rate of annealing was very different in different samples. In sputtered films [Fig. 4(b)] the time taken for the resistance to fall back to its starting value was ~ 100 s, whereas for the *e*-beam deposited films [Fig. 4(a)] it was of order 10^4 s. This difference suggests that the kinetics of initial recovery depend strongly on the microstructure of the samples. However, after the initial fall, the resistance of the sputtered samples decreased more slowly, at a rate comparable with recovery in the *e*-beam deposited samples, perhaps indicating a common mechanism for this slower transformation.

These results not only show that defects are mobile at room temperature, but they reveal the existence of a process which causes the resistance of a sample to fall *below* its initial value. This can be understood if we recognize that the measured resistance is the sum of two components: first, the extra resistivity increment due to radiation-induced defects, whose magnitude can be seen from the initial resistivity increments in Fig. 4; second, a component reflecting the state of the bulk material. Any reduction in resistivity below the starting value must be due to the second component, i.e., a change in the state of the $YBa_2Cu_3O_{7-z}$ phase due to the action of mobile point defects. The nature of this change is discussed later. For the moment, it is enough to point out that it must be kinetically enabled by the presence of the mobile defects.

The differences in recovery kinetics between sputter-deposited and *e*-beam deposited films explain the differences seen during continuous boron ion irradiation. The samples which showed a pronounced reduction in resistance during the early stages of B irradiation (the sputtered samples) were those in which the recovery kinetics demonstrated in Fig. 4 were relatively rapid. On the other hand, where recovery kinetics were slower, as in the *e*-beam deposited samples, the resistance increased monotonically under B irradiation, with no initial decrease. Expressing this argument more quantitatively, the recovery time in sputtered samples (~ 100 s) was much less than the time needed to irradiate a sample to a damage energy density of 0.2 eV/atom (~ 2000 s), but the recovery time in *e*-beam deposited samples ($\sim 10^4$ s) was much longer. Thus the recovery rate in the sputtered samples was high enough to cause significant annealing during this irradiation, but in the *e*-beam deposited samples it was not. Instead, as we will see shortly, the most rapid process (~ 1000 s) in the B-irradiated *e*-beam deposited films was one which *increased* the sample's resistance.

This process was observed after a prolonged B ion irradiation. In most cases, after a prolonged ion irradiation the resistance increase recovered slightly over a period of time. However, in the case of 2-MeV B irradiation of an *e*-beam deposited film the resistance of the film continued to *rise* for some time (Fig. 5, upper plot, where the end of irradiation is marked by a vertical dotted line), before finally falling back (lower plot). The resistivity increase suggests that the damage configuration after the end of the B irradiation was unstable, and transformed into a higher resistivity form before being subject to the same recovery as in heavy-ion irradiated samples. Two points can be made about this result. First, it is quite consistent with the accelerated increase in resistance that occurred in the early stages of B irradiation of the *e*-beam deposited samples. Secondly, it implies the presence of two different defect reactions, one (with a short-time constant) which forms defect configurations which raise the resistance but which only operates in B-irradiated epitaxial material, and another with a longer time constant, which causes recovery in both types of material and for both B and As irradiations.

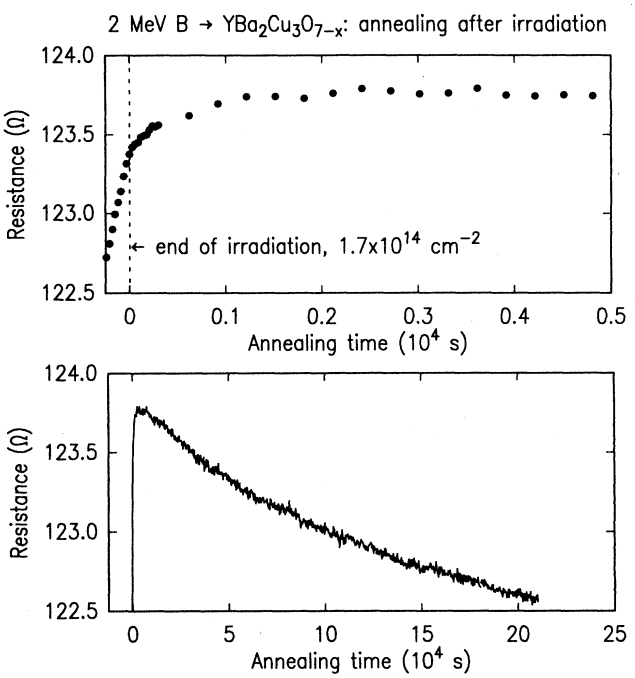

FIG. 5. Resistance changes in an *e*-beam deposited film at the end of an irradiation with 1.7×10^{14} 2-MeV B ions/cm^2. The upper plot shows the resistance increase *after* the end of the irradiation ($t=0$, marked with the vertical dotted line). The lower plot shows the partial recovery that occurred during a much longer anneal at room temperature.

The degree of recovery in preirradiated and unirradiated samples was compared using test doses of 10^{11} 2-MeV As ions/cm^2. Figure 4(c) shows a typical result for a sputtered sample preirradiated with 2.2×10^{15} 2-MeV B ions/cm^2. The recovery in this sample was much smaller than it was in unirradiated samples, and the resistivity did not fall below the starting value, as it did in unirradiated material. Results for a B-irradiated *e*-beam deposited film were similar. Thus, irradiation damage reduces the annealing of irradiation-induced defects, and suppresses the transformation that produces a low-resistance phase. These conclusions are consistent with the form of the empirical recovery terms in Eq. (2), which also show recovery that decreases with increasing dose.

In summary, then, we have identified *four* different kinetic processes in irradiated $YBa_2Cu_3O_{7-z}$: process I, which is the annealing of radiation-induced defects; process II, which reduces the resistivity of the sample and which we will argue is a microstructural transformation; process III, which is present only in B irradiated epitaxial material and may be a clustering reaction which raises the samples' resistance; and process IV, which is the exponential increase in resistivity with dose. The balance between the first three processes and the last is determined by the damage rate. At high damage rates, as in O or As irradiation, the recovery processes are too slow to have any effect during the irradiation. Only at low dose rate (B irradiation) can they make themselves felt, and even then only in the sputter-deposited films, in which the recovery kinetics were relatively rapid.

DISCUSSION

We have shown that, for the samples we have studied, deviations from exponentially increasing resistivity under irradiation can be traced to a defect-mediated processes occurring during this irradiation, some of which (i.e., those occurring in sputter-deposited samples) tend to reduce the resistivity of the sample and offset the irradiation-induced increase. However, these processes only make themselves felt at low dose rates, or during annealing after the irradiation. These observations are further evidence that defects are slowly mobile in $YBa_2Cu_3O_{7-z}$ at room temperature.

Our measurements confirm that the resistivity of ion irradiated samples of $YBa_2Cu_3O_{7-x}$ increases exponentially with ion dose from the beginning of irradiation. At room temperature, this conclusion holds good for samples with starting resistivities above 3 mΩ cm, such as we have studied, and for high dose rates. For low dose rates, the exponential increase is seen if defect mobility is suppressed by performing the irradiation at low temperature, as 80-K neutron irradiation data of Aleksashin *et al.*[8] show.

No theoretical model can as yet explain these striking experimental observations. The resistivity increase, accompanied by a metal-to-insulator transition, can be attributed in general terms to progressive localization of the charge carriers at low doses, culminating in trapping with thermally activated hopping at high doses.[5] The increase in resistivity seems to be caused mainly by a reduction in the mobility of the charge carriers, rather than a change in doping. Two pieces of evidence point to this conclusion. First, previous measurements have ruled out the possibility that irradiation changes the oxygen content, which would influence the doping.[20] Second, the Hall coefficient in irradiated material increases much more slowly than the resistivity,[21,22] which with a simple interpretation of the Hall coefficient (admittedly not a straightforward business for this material) implies that the mobility of the charge carriers is more affected by the irradiation than their density is.

The damage level at which the resistivity of $YBa_2Cu_3O_{7-x}$ is affected by irradiation suggests that the resistivity increase is caused by atomic-scale defects. The displaced atom concentration corresponding to a doubling of the normal-state resistivity can be estimated from the data in Fig. 2 which shows that a deposited energy density of 5 eV/atom is required. From Eq. (1), this corresponds to a displaced atom concentration of 10%. At this damage level each atom has a displaced atom as its first or second neighbor. The conclusion to be drawn is that the defects affecting the mobility of the charge carriers are of atomic size, i.e., point defects. It may be that the presence of a nearby point defect perturbs the Cu $3d$–O $2p$ hybridization which forms the bands in which holes move. The fact that the same exponential increase in resistivity is followed over a range of doses in which long-range order is destroyed[6] implies that the conductivity only depends on short-range order. The data rule out the possibility that the bulk resistivity might be changed by the formation of small insulating volumes by the irradiation, such as might be formed by collision cascades along the track of an ion. If this were the case, then at some critical dose one would expect to see percolation effects, i.e., a steeper increase in resistivity with dose, at a critical damage level where the insulating zones began to overlap. No such effects are observed.

From the foregoing discussion, we conclude that the irradiation-induced resistivity changes are caused by atomic-scale defects. We now turn to the effects of mobile defects at room temperature. The data presented above show that defects are indeed mobile at room temperature in $YBa_2Cu_3O_{7-z}$, but that the annealing they cause in irradiated material varies greatly from sample to sample. Furthermore, we have identified four different processes involving point-defect reactions from their characteristic time constants and differing effects on the resistivity of the sample.

The slow formation and growth of extended defects seen by Kirk *et al.* following electron irradiation of $YBa_2Cu_3O_{7-z}$ (Ref. 23) is consistent with the time scale of the annealing in the *e*-beam deposited films [see Fig. 4(a)], and suggests the hypothesis that part of the annealing of the resistivity is due to loss of radiation-induced defects to similar extended defects as they nucleate and grow in ion-irradiated material. On the other hand, electron microscopy has so far failed to show the existence of extended defects in ion-irradiated material.[17] An alternative idea would be that intrinsic fixed sinks play a role in absorbing the irradiation-produced defects. Grain boundaries and interfaces are a possible candidate for the sinks involved, but even in the sputtered films their density is hardly high enough to account for the rate of annealing. This can be seen if we estimate the defect diffusion coefficient necessary to traverse a grain of radius 1 μm in a time of order 100 s [Fig. 4(b)], which is 10^{-10} cm^2/s, a rather high value which is inconsistent with a recovery temperature of 200–300 K found in Ref. 4 if we assume an attempt frequency of 10^{13} s^{-1}. Thus, if sinks are important they must have a higher density than grain boundaries, even in the sputtered films.

No defect loss mechanism alone can account for the fall in the resistance of an irradiated sample *below* its initial value. The evidence points to this being due to ordering of excess oxygen vacancies in the basal plane. As is well

known, a fall in resistivity, and an increase in long-range order, is observed in partly ordered metallic alloys when they are irradiated,[24,25] because the introduction of mobile defects by irradiation allows atoms to diffuse at temperatures where an increase in order is normally forbidden. With increasing dose of heavy ions or neutrons, disordering becomes dominant because the radiation damage also generates sinks which in time absorb most of the defects, and then radiation-induced disordering becomes dominent. Ordered structures involving oxygen vacancies in the basal plane have been identified in orthorhombic $YBa_2Cu_3O_{7-z}$. There is evidence from electron microscopy, both from diffraction[26] and direct imaging,[27] that there is ordering of the excess vacancies in oxygen-deficient material. These vacancies lie predominantly in the basal plane, i.e., that which contains the Cu-O chains. Oxygen-vacancy ordering in the orthorhombic phase lowers the normal-state resistivity, and occurs in materials whose oxygen content leads to a T_c of order 55–60 K and a normal-state resistivity of a few mΩ cm,[26] i.e., similar to the sputter-deposited films used in the present study. Thus it is reasonable to ascribe the rapid resistivity reduction caused by irradiation of the sputtered films to the promotion of oxygen-vacancy ordering. In the extended Bragg-Williams-Dienes model of irradiation-enhanced ordering, the ordering rate falls with increasing order at high degrees of order.[25] We therefore suggest that the reason for the relatively slow kinetics exhibited by the *e*-beam deposited films is that they are initially more highly ordered than the sputter-deposited films.

Another possible explanation for the defect-promoted reduction in resistivity is the formation of a low-resistivity defect structure, namely the intercalated copper-oxygen layers[28] which when present in every unit cell give a "248" structure[29] whose resistivity is about half that of $YBa_2Cu_3O_{7-z}$. Interstitial-looplike defects, consisting of an intercalated layer in the basal plane bounded by partial dislocations, have been observed in electron irradiated material.[30] These loops can be expected to reduce the resistivity of the sample, but the proportion of transformed material required to cause a 5% drop in resistance (Fig. 2) would be around 10%, which seems high but should be easily checkable with TEM.

The nature of the defects which are mobile at room temperature is uncertain at present. They are presumably the same as those which cause an annealing stage at around 200 K.[4] It is interesting to note that the annealing of these defects manifests itself by a reversal of the irradiation-induced metal-insulator transition. This implies that these defects either lie in, or at least influence, the Cu-O planes in which the charge carriers are believed to move. More information about these defects might improve our understanding of the microscopic details of normal-state conduction in defective $YBa_2Cu_3O_{7-z}$, and would certainly shed more light on the nature of the metal-insulator transition.

CONCLUSIONS

By more precise measurements we have confirmed the conclusion of earlier work that the normal-state resistivity of MeV ion bombarded $YBa_2Cu_3O_{7-x}$ films increases exponentially with ion fluence, for high damage rate irradiations at room temperature. In addition, we have found that for such irradiations the exponential dependence is followed from the beginning of the irradiation where the resistivity change is small. For lower damage rates (boron ion irradiation) there are deviations from the exponential which we show to be caused by processes mediated by mobile point defects. The rate of these processes, as seen by resistivity changes, is different in films with different microstructures. In small-grained sputter-deposited films, irradiation-induced defects induce a transformation, tentatively proposed to be ordering of the oxygen atoms in the basal plane, which reduces the resistivity. A similar process occurs in *e*-beam deposited films, but more slowly. In such films a different process occurs during low damage rate irradiations, causing a transient in which the rate of resistivity increase with dose is increased for low doses.

From the data on the recovery and annealing of radiation-induced resistivity changes that we have presented, we conclude that some species of point defects introduced by irradiation are mobile at room temperature. The presence of these defects enables a transformation which reduces the resistivity of the sample while the defects anneal. The kinetics of this transformation are strongly sample dependent, and the process is suppressed by moderate levels of radiation damage. The dose dependence of the resistivity of $YBa_2Cu_3O_{7-z}$ ion irradiated at room temperature shows an exponential increase, in agreement with previous work, but for low damage rates in samples showing rapid annealing kinetics there are superimposed deviations from the exponential behavior due to annealing which takes place during this irradiation.

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