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Chain oxygen disorder in deoxygenated $YBa_2Cu_3O_{7-\delta}$ thin films induced by light ion irradiation

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Abstract

We report on the effects of light ion (He^+) irradiation on the superconducting properties of epitaxial $YBa_2Cu_3O_{7-\delta}$ thin films. Films were grown by a pure oxygen dc sputtering system operated at high pressure (3.4 mbar). Irradiation at 80 keV and doses ranging between 10^{14} and 10^{15} cm^{-2} shows a systematic degradation of the superconducting transition temperature. We have studied the effects of annealing on the recovery of the superconducting properties of films irradiated at different fluences. Two sets of irradiated samples were evaluated, fully oxidized and deoxygenated samples. Irradiated fresh samples do not show significant recovery upon room temperature annealing for times as long as 6 months. Irradiated deoxygenated samples, however, show an up to 10 K increase in the critical temperature after 2 months room temperature annealing. The different behavior is discussed in terms of the two effects caused by irradiation: oxygen displacements from the CuO chains into stable interstitial positions along the *a*-axis, and oxygen disorder in the deoxygenated samples.

Keywords: High T_c superconductors; Thin films; Electronic transport

1. Introduction

Irradiation of high temperature superconductors has been extensively investigated for technological applications and for basic studies. It has been explored as a procedure to increase critical currents by the controlled introduction of pinning effective defects, and on the other hand, it offers a procedure to modify the vortex phase diagram, allowing a better understanding of the complex mechanisms governing vortex dynamics. It is well known that heavy ion irradiation at high energies (in the MeV range), and at low doses (10^{11} cm^{-2}) produces amorphization along nanometric tracks. This tracks are a source of correlated disorder and have shown to confine vortices, significantly enhancing the critical current [1]. Low energy electron or ion irradiation, on the other hand, has been reported to create mainly point defects related to atomic displacements. Although point disorder is not effective for enhancing the critical current, it has been reported to promote vortex meandering and entanglement [2] strongly depressing the cross over magnetic field to a disordered vortex solid in $YBa_2Cu_3O_{7-\delta}$ (YBCO) single crystals [3]. At high levels of disorder (high irradiation doses), point defects are known to depress the critical temperature, and, although considerable effort has been devoted to the study of the mechanisms involved in the T_c degradation under irradiation [4–8], a clear picture has not emerged yet.

In this paper, we report on irradiation of $YBa_2Cu_3O_{7-\delta}$ (YBCO) with light ions (He^+) at low energies (80 keV). We show that irradiation depresses the critical temperature, and increases the residual resistivity, but it does not significantly affect the carrier density. We show that irradiation mainly affects the oxygen in the Cu–O chains, the most loosely bound species in the structure. We present irradiation experiments of oxygen-depleted samples and results of long-term room temperature annealing to support these points.

2. Experiment

The samples for this study were high quality YBCO samples epitaxially grown c-oriented on STO by a high pressure (3.4 mbar) dc sputtering system in pure oxygen atmosphere. Substrate temperature was 900°C, and film thickness was 500 Å. Critical temperature of fresh samples was 91 K and transition widths smaller than 0.3 K.

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Samples were deoxygenated in situ, adjusting the oxygen content following a stability line of the pressure–temperature phase diagram during sample cool down [9,10]. These samples had also sharp superconducting transitions and small residual resistivity, pointing to a high degree of oxygen order. Samples were irradiated at room temperature using a commercial ion implanter for microelectronic applications. Beam currents were smaller than 2 μA cm^{-2} to minimize heating effects. Samples were tilted 7° away from the beam direction to avoid channeling. Energy was 80 keV, and doses were varied between 10^{14} and 10^{15} cm^{-2}. The projected ion range calculated using the SRIM 96 software was larger than 3000 Å in all cases, ensuring that He^+ ions go through the film and embed in the substrate. Structure (X-rays) and resistivity (four probe with evaporated silver pads, at current densities lower than 100 A/cm^2) were measured immediately after irradiation to minimize the influence of the defect annealing at room temperature.

3. Results and discussion

Fig. 1 shows the resistivity curves of a series of fully oxygenated YBCO samples irradiated with 80 keV He^+ ions at doses ranging between 10^{14} and 10^{15} cm^{-2}. Normal state resistivity characteristics are essentially linear and remain parallel up to doses of 8×10^{14} cm^{-2}. At higher levels of disorder resistivity anomalies characteristic of the oxygen-depleted samples are observed, as well as distortions related to the proximity of the metal insulator transition. Since, in the parallel regime, the slope of the resistance curves is inversely proportional to the carrier concentration, this suggests that, up to doses of 8×10^{14} cm^{-2}, carrier concentration is preserved. The residual resistivity, ρ_0, obtained from the low temperature extrapolation of the normal resistivity increases upon irradiation. The systematic increase of the resistivity along with the reduction of the critical temperature, point to irradiation-induced scattering centers. An analysis of the irradiated samples by X-ray diffraction showed that structure is essentially preserved, since there are no signs of peak broadening and the width of the rocking curves (0.15–0.35°) remained unchanged. An increase of the c lattice parameter was observed, which correlated with the decrease in the critical temperature: fresh samples (T_c=91 K) had c=11.65 Å, whilst irradiated samples with T_c=20 K showed c=11.71 Å. A similar increase is observed in oxygen-depleted samples. However, c lattice expansion can arise from stress associated to atomic displacements and should not be directly ascribed to changes in the carrier concentration [11]. Low temperature annealing in nitrogen (200°C 1 h) produced a substantial recovery of the critical temperature (more than 10 K for an YBCO sample irradiated with a dose of 6×10^{14} cm^{-2}), strongly pointing to irradiation-generated defects located at the CuO chains. A temperature of 200°C is a much too low to activate the diffusion of defects in the CuO_2 planes with higher binding energies than the chains. Since for fully oxidized samples there are no vacant sites along the chains, oxygen displacements into the vacant O(5) positions along the a axis are the most plausible defects [4]. This defect seems to be quite stable since no significant changes of the critical temperature were observed with room temperature annealing over several months.

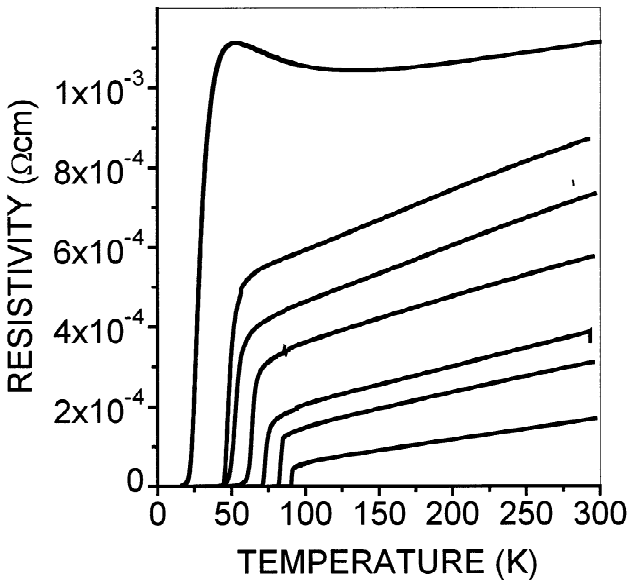

Fig. 1. Effect of ion irradiation at an energy of 80 keV and doses of 9, 7, 6, 5, 4 and 3.5×10^{14} cm^{-2} from up to down. The resistance curve with the highest T_c corresponds to a fresh sample.

In order to further investigate this point, we have grown oxygen deficient samples. For a given irradiation dose, a more pronounced relative T_c depression was observed the more oxygen depleted were the samples. For example, while a fully oxygenated sample irradiated with a dose of 4×10^{14} cm^{-2}, showed a $\Delta T_c/T_c$ change of 30%, an oxygen-depleted sample with $7-\delta=6.58$, irradiated with the same dose, showed a 54% change. Fig. 2 shows the resistivity curves of a non-irradiated sample with oxygen content $7-\delta=6.58$ (curve a) and irradiated with a dose of 4×10^{14} cm^{-2} (curve b). The same figure shows the evolution of the resistance curves with room temperature annealing in 2 months steps (curves c–f). It can be observed that the shape of the normal state resistivity is not deeply modified by the irradiation. In fact, the temperature derivative of the normal state resistivity shows maxima at the same temperature T_0=160 K in all cases. The inset of Fig. 2 shows this maxima before irradiation (a), immediately after irradiation (b) and after 8 months (f). This temperature is associated with the T^* for opening a spin gap in the spectrum of low energy excitations, and is closely related to the number of carriers, i.e., reduced carrier densities result in higher values of T^* [12]. It has

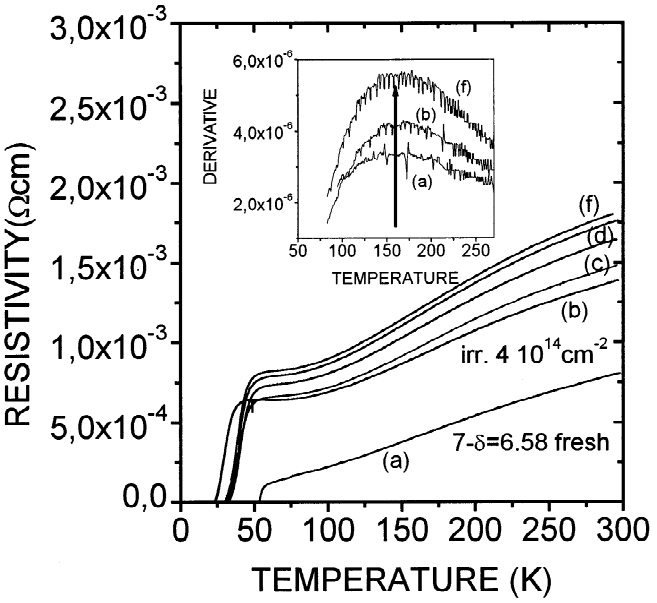

Fig. 2. Resistance curves of a sample with an oxygen content $7-\delta=6.58$: non-irradiated (a), and after irradiation with an energy of 80 keV and at a dose of 4×10^{14} cm^{-2} (b). Time evolution of the resistance curves in 2-month steps of room temperature annealing (c–f). Inset: derivative of the resistance curves of samples (a), (b) and (f). Arrows show the temperature, T_0, of the maxima.

been proposed that T^* is twice the temperature, T_0, of the maximum of the derivative of the resistance curves [13]. The fact that T_0 does not change upon irradiation strongly supports the point that irradiation does not modify the carrier concentration. For comparison, we show in Fig. 3 (curve (a)), an oxygen-depleted sample ($7-\delta=6.4$) with the same T_c of an irradiated sample (curve (b)) of Fig. 2. The inset shows a T_0 value close to 200 K, significantly higher than the value obtained for the irradiated sample, despite both samples have the same T_c. Fig. 3 shows also the behavior of the resistance curves after 9 months. T_c improves significantly more than the irradiated sample as a result of chain oxygen reordering [14]. The higher T_0 values of the non-irradiated oxygen-depleted samples ($7-\delta=6.4$) compared with the irradiated sample with a higher oxygen content ($7-\delta=6.58$), shows the effect of a reduced charge concentration. Moreover, since low temperature annealing in nitrogen (200°C 1 h) produced a substantial recovery of the critical temperature, this strongly points to defect centers generated by ion-irradiation being related to chain oxygen displacements. Thus, the effect of irradiation is the displacement of chain oxygen atoms, most likely into O(5) vacant positions along the *a*-axis. This defects does not modify the carrier concentration significantly for long enough chains, but constitute a scattering center which provides a plausible explanation for the reduction of T_c in terms of pair breaking [15].

4. Conclusions

In summary, we have shown that He^+ irradiation of epitaxial YBCO films causes oxygen displacements from the Cu–O chains, which are responsible for a significant increase of the residual resistivity, while the carrier concentration is preserved. Defect centers, probably oxygen atoms displaced from the chains into vacant positions along the *a*-axis, cause significant scattering of the charge carriers in the planes and result in pair breaking.

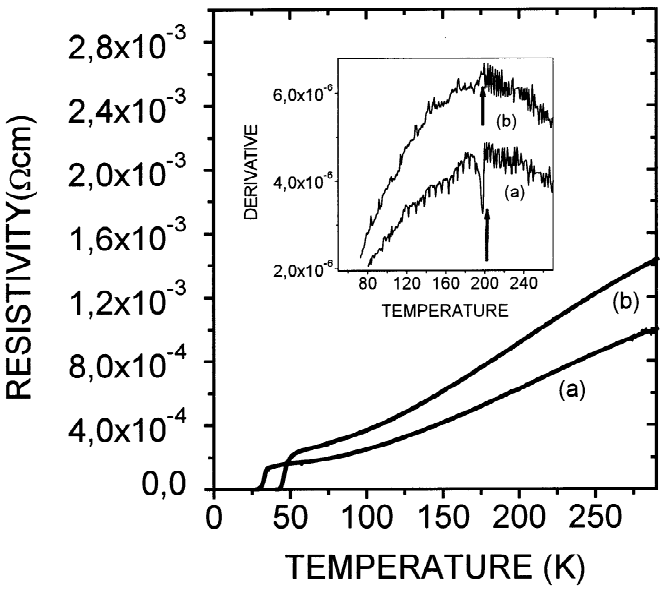

Fig. 3. Resistance curves of a sample with an oxygen content $7-\delta=6.4$ immediately after growth (a), and after 9 months (b). Inset: derivative of the resistance curves of samples (a) and (b). Arrows show the temperature, T_0, of the maxima.

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