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Radiation damages and flux pinning in $YBa_2Cu_3O_7$ thin films

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We were able to increase the critical current density (J_c) and implicitly, enhance the flux pinning in high quality epitaxial YBCO thin films by 200 keV proton irradiation. The critical temperature (T_c) of the film does not change until radiation-induced localized defects begin to overlap over distances to the extent of a coherence length. The point defect induced by radiation damage or the radiation induced weak center (RWC) is believed to be responsible for the observed flux pinning enhancement. The self-field of the transport current transforms the RWCs into pinning centers. Compared to the bulk materials, the much lower J_c enhancement factor observed after irradiation of the thin films is due to the already very strong pinning force of the pinning defects in thin films. The extra pinning force of radiation defects is just a small perturbation on top of a large background.

The large increase of critical current density (J_c) in single crystals of $Y_1Ba_2Cu_3O_7$ (YBCO) after being irradiated with fast neutrons [1] or MeV protons [2–4] indicates that radiation defects in HTS materials can be very good pinning centers. However, very few studies have been reported on flux pinning modification of YBCO thin films which already have very strong pinning centers. Schindler et al. [5] showed that the J_c of epitaxial YBCO thin films can still be increased by neutron irradiation, which implies that the flux pinning in these films is not yet optimized and can still be improved upon. 3 MeV proton irradiation has been shown to be able to enhance the J_c of the YBCO thin film slightly [6]. Even so, no study has shown that, by few hundred keV ion irradiation, the already very high J_c of YBCO thin films can be improved. Xiong et al. have studied the transition-temperature-dependence on ion radiation dose [7–8], and have proposed some models to explain the observed results, but the mechanism for T_c reduction is still controversial.

In this paper, a first observation of transport J_c enhancement in epitaxial YBCO thin films, with a high starting J_c at 77 K of about 3×10^6 A/cm^2, using low energy, 200 keV, proton irradiation, will be reported. A weak center concept will be used to explain the pinning enhancement.

Epitaxial YBCO thin films with a thickness of 0.2 μm were deposited onto (100) $LaAlO_3$ substrates by an optimized laser ablation process. Briefly, the films were deposited at a substrate temperature of 770°C in O_2 at 200 mTorr pressure. The excimer laser was operated with KrF at 248 nm with a repetition rate of 25 Hz. The peak energy density was 2 J/cm^2, re-

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sulting in a deposition rate of 0.1 nm/pulse. The *c*-axis orientation was confirmed by X-ray diffraction. $T_c(\rho=0)$ ranged between 85 and 89 K. J_c was generally around 2 to 4×10^6 A/cm^2 at 77 K. For transport measurements, standard photolithography with negative photoresist (Olin Hunt HNR 120 process) and Ar ion milling were used to pattern the thin films into 5 μm lines to create a four point probe pattern. Large thin film samples were cut into smaller pieces with area around 3×3 mm^2 for magnetic measurement (*M–H* loops).

Patterned thin film bridges were irradiated with 200 keV protons at room temperature. Under such conditions, minor damage is annealed away automatically during implantation [9]. This is helpful in keeping the size of the damage structure small. Beam current was limited to 0.2 μA over a 1.29 cm^2 area to avoid sample heating. The microbridges were irradiated by 200 keV protons at a range of fluxes accumulatively, from 5×10^{13} H$^+$/cm^2 to about 1×10^{16} H$^+$/cm^2. T_c and J_c after each radiation were measured with the sample taken out of the implantation target chamber. The same irradiation conditions have been used for the unpatterned samples used for the magnetic studies. Irradiation dosage ranged between 8×10^{13} and 5×10^{15} H$^+$/cm^2 for this case.

A four point probe technique was used in the transport study. An APD cryogenic DE202 close cycle cryostat was used to cool down the sample. The temperature of the sample was controlled by a scientific instrument temperature controller within an accuracy of 0.1 K. Analog output of the temperature controller (T) and four wire AC resistance bridge (R) were connected to an X–Y recorder to plot the R–T curves, and then T_c is determined by the onset of zero resistance. The J_c measurement was done by superimposing a small AC signal over a DC bias current passing through the bridge, and the differential resistance ($\mathrm{d}V/\mathrm{d}I$) at current I was measured by a lock in technique. Numerical integration was then used to derive the *V–I* relationship.

The correlation of the flux pinning enhancement with the magnetic field has been studied using an inductive technique. Magnetic hysteresis loops of unpatterned epitaxial thin films were measured by an LDJ vibrating sample magnetometer (VSM) in a field of up to 1 T at 77 K before and after 200 keV H$^+$ irradiation.

Clearly, enhancement of flux pinning by 200 keV proton irradiation has been achieved, as shown in fig. 1. Here, flux pinning refers to the magnetic field of the critical current itself, in a transport measurement [10] under zero applied magnetic field. In order to overcome, partially, the arbitrariness associated with the electric field criterion in the determination of transport J_c, we show the entire family of *V–I* curves with proton irradiation as a parameter. The J_c enhancement at an irradiation dose of 8×10^{13} H$^+$/cm^2, using a 1 μ*V*/mm electric field criterion, is about 14% at 70 K or 12% at 77 K ($H_{\mathrm{ext}}=0$). Further increase of the dose to 1.2×10^{14} H$^+$/cm^2 results in a decrease in J_c. The cross over of the *V–I* curve at 77 K at a dose of 1.2×10^{14} H$^+$/cm^2, but not at 70 K, might indicate the temperature independence of the superconducting cross section shrinkage. A detectability limit of 10 nV in the *V–I* measurements and the 2% reproducibility of the results preclude the possibility of an increase of J_c of this amount being due to inaccuracy, which will be confirmed in a magnetic study.

Figure 2 shows the development of the magnetic hysteresis loop with H$^+$ irradiation dose as a parameter. The enhancement rate characterized by the ratio of ΔM or the magnetization difference between

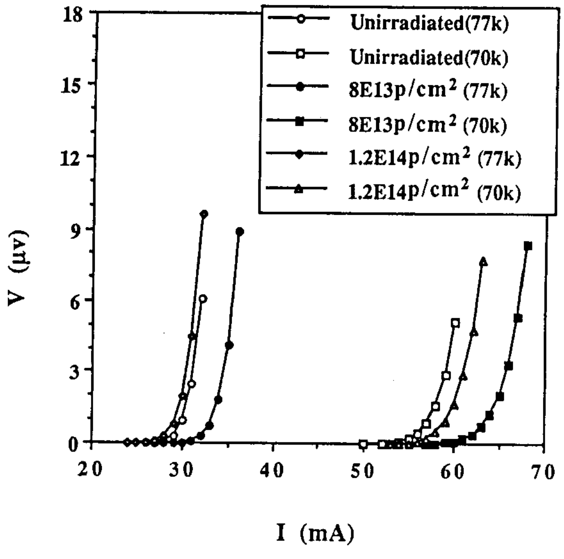

Fig. 1. *V–I* curves of a 5 μm bridge at 70 and 77 K before and after two doses of 200 keV proton irradiation. About 14% J_c enhancement can be observed at 70 K after 8×10^{13} H$^+$/cm^2.

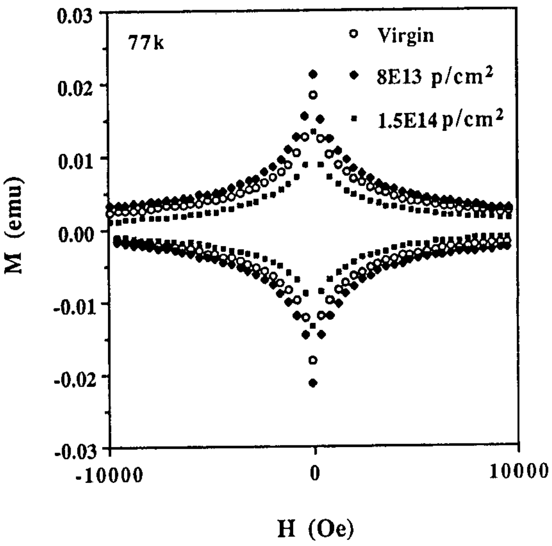

Fig. 2. Inductive measurements of pinning change before and after 200 keV proton irradiation. M–H loops include that for unirradiated sample, the one for 8×10^{13} H^+/cm^2, and the one for 1.5×10^{14} H^+/cm^2 irradiation.

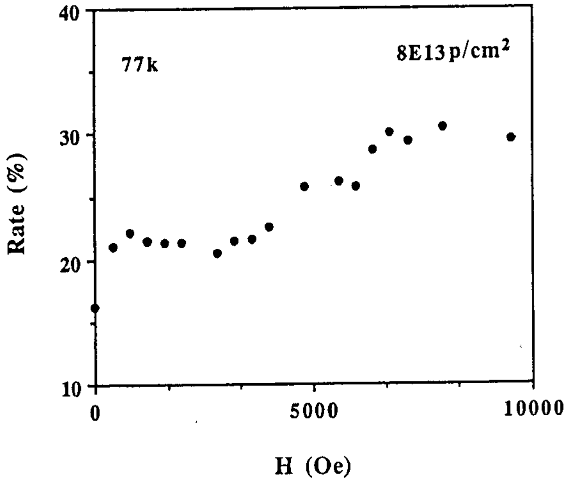

Fig. 3. Magnetic J_c enhancement rate vs. field at 77 K. The largest J_c enhancement is around 30% at 1 T.

the upper and lower branches of the M–H loop at the same field, which is proportional to J_c according to the Bean model, is about 16% ($H_{ext}=0$) and 30% ($H_{ext}=1$ T) for 8×10^{13} H^+/cm^2 (fig. 3). This is in good agreement with the transport results.

The field induced state transformation of the radiation caused weak center (RWC) [4] generate extra pinning centers in the thin film, which contribute to the flux pinning or J_c enhancement. Self-field of the transport current is responsible for the state transformation in our zero external field transport measurements. The self-field in the direction parallel to the c-axis, $H_{s\parallel}$, can be derived from Ampere's law $4\pi Jw\delta/10=H_{s\parallel}\times2\delta+H_{s\perp}\times2w$ in practical units, and perpendicular to the c-axis the component $H_{s\perp}=(2J/5)[\delta/2\,\ln(1+w^2/\delta^2)+w\times\tan^{-1}(\delta/w)]$ by straightforward integration [10], with w as bridge width, δ as film thickness. For a 5 μm wide 2000 Å thick thin film microbridge, the self-field of a transport current [10] of 3×10^6 A/cm² at 77 K is roughly 190 Oe for the $H_{s\parallel}$ component or 96 Oe for the $H_{s\perp}$ component. At 70 K, this self-field of the transport current, at a critical density of 5×10^6 A/cm², is going to be larger than 300 Oe for the $H_{s\parallel}$ component and 150 Oe for the $H_{s\perp}$ component. Both are larger than the upper critical field of the RWCs at 70 K, which is around 150 Oe [4]. So even at zero external field, the RWCs will be transformed into the normal state by the self-field of the transport current and become effective pinning centers [4]. This in turn leads to the above observed pinning enhancement.

Pinning enhancement at much lower proton doses in an epitaxial thin film, compared to the case of single crystals [2–4], is a direct consequence of the strong pinning defects existing before proton irradiation. The pinning strength of a radiation weak center is much weaker than that of intrinsic pinning defects, for instance, the dislocations, in epitaxial films [11]. With a high concentration of these radiation defects at large irradiation doses, the distortion of the flux line lattice by these isolated point defects is believed to cancel out part of the pinning effect of those strong pinning defects, just like the case in proton irradiated single crystal YBCO [3] where the point defects of radiation damage also decrease the density of states near the Fermi energy, which then decrease the transition temperature at a certain concentration level of the defects.

A reduction in the critical temperature of conventional superconductors [12], as measured from transport properties, was found to be caused by one of the two mechanisms. First, the introduction of microscopic scattering defects either during the fabrication or by radiation-induced displaced atoms, changes the density of states (DOS) at the Fermi en-

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ergy, $N(E_f)$, thereby causing a uniform depression of T_c [13]. Second, T_c reduction can come about from the isolation of individual grains of materials by complex film preparation techniques or by amorphous phase formation at the grain boundaries caused by radiation damage [14]. Since no grain boundary is present in the epitaxial YBCO thin films, the first mechanism of T_c reduction is the more plausible, i.e. by decrease of DOS by densely distributed point defects.

Figure 4 shows T_c as a function of the radiation dose. The drop of T_c starting at a dose of 2×10^{15} H^+/cm^2 is caused by suppression of the DOS. As Monte Carlo simulation [15] (Trim89) shows, the distance between the localized defects approaches 20 Å at that dose, which is comparable to the superconducting coherence length [4,10]. Before this, the electron can pass around the radiation defects without being scattered. So, no pair breaking or DOS decrease, i.e. the T_c drop will not happen. Incidentally, the T_c increase around 1×10^{14} H^+/cm^2 as shown in fig. 4 is not quite understood.

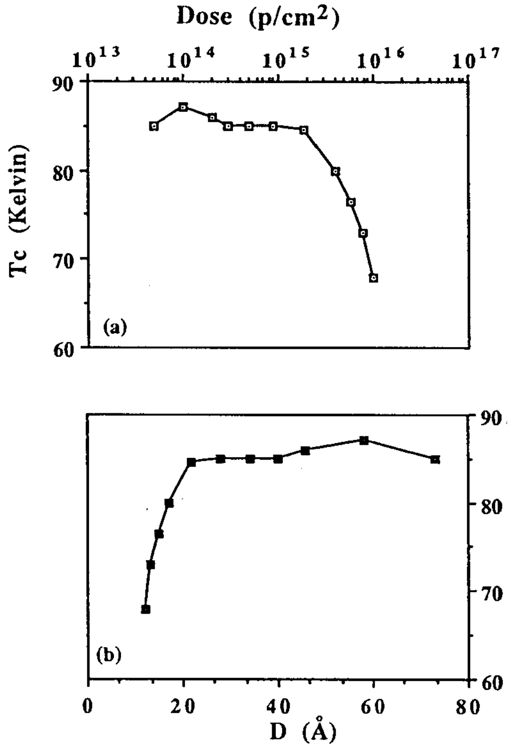

Fig. 4. (a) T_c vs. proton dose; (b) T_c vs. distance between the point defect of displacement calculated from Trim simulation. A clear T_c drop happens at 2×10^{15} H^+/cm^2 or when the defect distance is around 20 Å or close to the coherence length.

In the R–T transition curves, as shown in fig. 5, no obvious broadening has been observed as the irradiation dose increases, not even after T_c has dropped about 10 degrees. The parallel shift of the transition curve up to a dose of 9.9×10^{15} H^+/cm^2 from around 9×10^{14} H^+/cm^2 is characteristic of the high quality of YBCO thin film growth and absence of any superconducting decoupling between the grains which is characteristic of the polycrystalline films [14].

From the X-ray results of ref. [16], the c-lattice parameter of GBCO thin films increases from 11.68 Å to 11.70 Å at a dose of 2×10^{16} p/cm^2 under 300 keV proton irradiation. This result may be extrapolated to YBCO. However, this lattice parameter change ordinarily takes place with a change of composition from $Y_1Ba_2Cu_3O_7$ to $Y_1Ba_2Cu_3O_{6.8}$ [17], which is equivalent to an oxygen sublattice damage of 0.03 dpa. On the other hand, from Monte Carlo simulation, a 300 keV proton can only generate a displacement of 0.01 dpa at a dose of 2×10^{16} H^+/cm^2. If, however, a smaller binding energy of oxygen

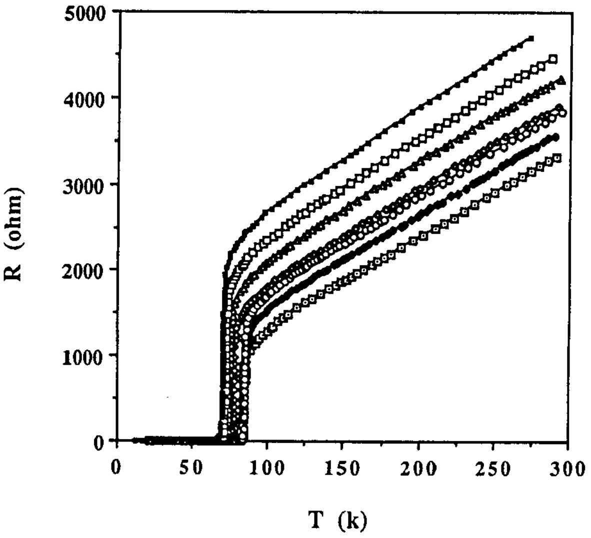

Fig. 5. Resistance vs. temperature measurements after 200 keV proton irradiation at various doses. Irradiation doses are 9×10^{14}, 1.9×10^{15}, 3.9×10^{15}, 5.9×10^{15}, 7.9×10^{15}, 9.9×10^{15} H^+/cm^2, respectively, T_c decreases with radiation dose. No broadening of resistive transition has been observed, indicating no phase transition, which is typical of epitaxial thin film.

atoms, for instance, is assumed, the displacement could have been larger, which will then be in good agreement with the X-ray diffraction study. This supports the hypothesis of phase change during ion irradiation. Further experiments are needed to clarify the nature of the point defects, i.e. the oxygen displacement or cationic displacement or both.

In our own X-ray study (fig. 6), the *c*-lattice parameter increases from 11.695 to 11.730 Å as the proton dose is increased to 1×10^{15} H^+/cm^2, and then saturates as the dose is further increased. This is in good agreement with the result of ref. [16].

In summary, we have found that it is possible to increase the transport J_c of epitaxial YBCO thin films by low energy (200 keV) proton irradiation. Although the relative amount of J_c increase is only a few percent, the absolute J_c increase is still significant considering the very high J_c initial value. The point defects from radiation damage behave as point defects or electron scattering centers in a *R–T* transport study, when the field including both the external- and self-field is very low compared to the upper critical field of the RWCs. However, during the transport J_c measurement, the self-field of the transport current is high enough to turn RWCs into the normal state or pinning centers. This enhances the total J_c. We believe that the localized point defects including the oxygen displacement serve as the electron scattering centers which reduce the DOS in the superconductor, when the point defect concentration reaches a level that the distance between them becomes smaller than the coherence length. This is responsible for a T_c depression.

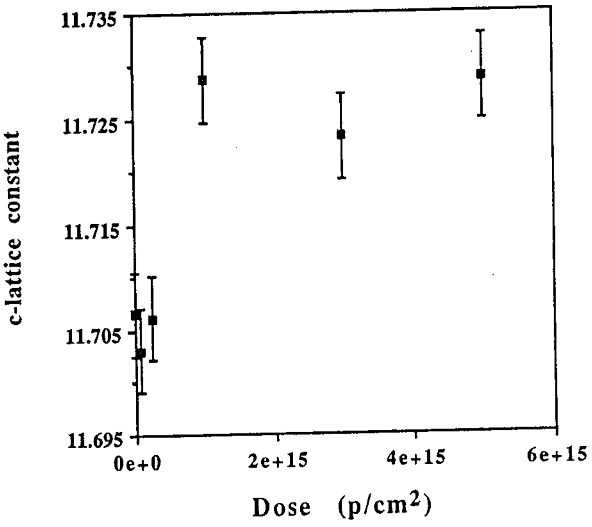

Fig. 6. *c*-lattice parameter in Å of YBCO thin film measured by X-ray diffraction after different doses of 200 keV proton irradiation.

References

[1] R.B. van Dover, E.M. Gyorgy, L.F. Schneemeyer, J.W. Michell, K.V. Rao and R. Puzniak, Nature 342 (1989) 55.
[2] R.B. van Dover, E.M. Gyorgy, A.E. White, L.F. Schneemeyer, R.J. Felder and J. V. Waszczak, Appl. Phys. Lett. 56 (1990) 2681.
[3] L. Civale, A.D. Marwick, M.W. McElfresh, T.K. Worthington, A.P. Malozemoff, F.H. Holtzberg, J.R. Thompson and M.A. Kirk, Phys. Rev. Lett. 65 (1990) 1164.
[4] Y.J. Zhao, J.R. Liu and W.K. Chu, to be published.
[5] W. Schindler, B. Roas, G. Saemann-Ischenko, L. Schultz and H. Gerstenberg, Physica C 169 (1990) 117.
[6] D. Christen et al., AIP Conf. Proc. 219 (1991) 336.
[7] G.C. Xiong et al., Phys. Rev. B 38 (1988) 240.
[8] G.C. Xiong et al., Physica C 153–155 (1988) 1447.
[9] B. Egner, J. Geerk, H.C. Li, G. Linker, O. Meyer and B. Strehlau, Jpn. J. Appl. Phys. 26 (1987) Suppl. 26-3.
[10] Y.J. Zhao, W.K. Chu, M. Davis, J.C. Wolfe, S. Deshmukh and D. Economou, presented at the 1990 MRS Fall Meeting at Boston (H9.10).
[11] Y.J. Zhao, Ph. D. thesis, University of Houston.
[12] G.P. Summers, E.A. Burke, D.B. Chrisey, M. Nastasi and J.R. Tesmer, Appl. Phys. Lett. 55 (1989) 1469, and the references therein.
[13] R. Viswanathan and R. Caton, Phys. Rev. B 18 (1978) 15.
[14] Alice E. White, K.T. Short, D.C. Jacobson, J.M. Poate, R.C. Dynes, P.M. Mankiewich, W.J. Skocpol, R.E. Howard, M. Anzlowar, K.W. Baldwin, A.F.J. Levi, J.R. Kwo, T. Hsieh and M. Hong, Phys. Rev. B 37 (1988) 3755.
[15] J.F. Ziegler, J.P. Biersack and U. Littmark, The Stopping and Range of Ions in Solids, vol. 1, (Pergamon, New York, 1985) p. 109.
[16] G. Linker, J. Geerk, T. Kroener, O. Meyer, J. Remmel, R. Smithey, B. Strehlau and X.X. Xi, submitted to IBMM90, preprint.
[17] JCPDS-ICDD Powder Diffraction File (NIST X-ray standard data book) (1989).