Existence of superconductivity in oxygen-disordered $YBa_2Cu_3O_{7-\delta}$

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Understanding the role of CuO_2 planes and Cu(1)-O(1) chains is critical to the mechanism for high-temperature superconductivity in $YBa_2Cu_3O_{7-\delta}$. By applying low-energy nanosecond excimer laser radiation on epitaxial single-crystal $YBa_2Cu_3O_7$ thin films on various substrates, we have shown that superconductivity can exist in these specimens even when the Cu(1)-O(1) chains are disordered. Raman results show that ultrarapid controlled laser heating and cooling rates ($\sim 10^9 - 10^{10}$ K/sec) result in selective disordering of the weakly bonded copper-oxygen chains without affecting the oxygen in the copper-oxygen planes. Microstructure-property correlations showed the existence of two regimes. In regime I, which exists below a certain laser-energy-density threshold, no degradation in the superconducting properties was observed even though the scattering efficiency of the Raman signal from the Cu(1)-O(4) vibrations is strongly diminished. The scattering efficiency of the Cu(1)-O(4) vibrations has been attributed to the Cu(1)-O(1) chains. Above the threshold laser fluence, regime II initiates, which is accompanied by concomitant degradation in the microstructure as well as in the superconducting properties. This regime has been correlated with the melting of near-surface regions in the film.

One of the most intriguing features of $YBa_2Cu_3O_{7-\delta}$ is the contribution of copper-oxygen planes and chains to the superconducting phenomena in these materials.[1-5] Extensive investigations on the structure and properties of $YBa_2Cu_3O_{7-\delta}$ have shown that a high degree of ordering in $Cu-O_2$ planes and Cu(1)-O(1) chains leads to superior superconducting properties. Although more recent studies indicate that the $Cu-O_2$ planes are primarily responsible for high-temperature superconductivity, there has been considerable speculation on the role of Cu-O chains in the superconducting process.[2] Figure 1 shows
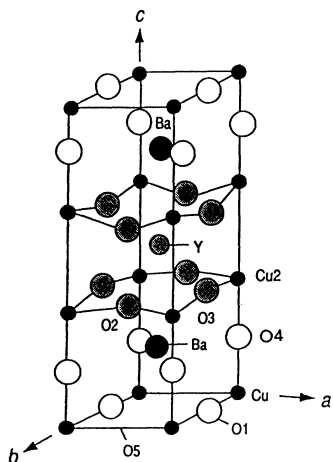

FIG. 1. Schematic diagram of the fully oxygenated superconducting $YBa_2Cu_3O_7$ unit cell (adapted from Ref. 20).

the positions of all the atoms of a fully oxygenated ($\delta = 0$) $YBa_2Cu_3O_{7-\delta}$ superconducting unit cell. For $\delta = 1$, $YBa_2Cu_3O_{7-\delta}$ is nonmetallic and nonsuperconducting, while for $\delta < 0.1$, a maximum T_c of ~ 93 K is observed. The transition from the superconducting to the nonsuperconducting state is accompanied by an orthogonal-to-tetragonal phase transition with the onset of antiferromagnetism. During this transformation a vacancy is created in the O(5) position in the unit cell, which leads to formation of Cu(1)-O(1) chains.[2-5] There has been considerable debate on the contribution of chain oxygen atoms to the superconducting mechanism. The disappearance of superconductivity with concomitant disordering of Cu(1)-O(1) chains in oxygen-deficient samples led to initial speculations that the ordered Cu(1)-O(1) chains were responsible for superconductivity. However, with the discovery of copper-oxygen-chain-free bismuth-based superconductors, researchers argued that the copper-oxygen planes and not the chains were primarily responsible for high-temperature superconductivity. Although the exact mechanism for the occurrence of superconductivity is still not clear, it is widely believed via indirect observations that the superconductivity in these compounds arises only due to the two-dimensional $Cu-O_2$ planes.[5] A direct correlation has been established between the hole concentration in the $Cu-O_2$ planes and T_c. In an insulating $YBa_2Cu_3O_6$ structure, the lack of oxygen atoms at the chains isolates the CuO_2 planes from the chains, rendering the sample nonsuperconducting, whereas in a fully oxygenated $YBa_2Cu_3O_7$ structure, the chains act as an electron reservoir for electron transfer from the planes to the chains.[2]

Till now it has not been possible to disorder the Cu(1)-O(1) chains selectively and still maintain superconductivity in the $YBa_2Cu_3O_7$ system. The Cu(1)-O(1) bond is relatively weak, which allows easy exchange and removal of oxygen during thermal processing. The mobility of the O(1) atom has also been confirmed by neutron diffraction measurements, which show unusually large and anisotropic temperature factors for the O(1) atom.[6] Thus, in principle, it should be possible to employ extremely rapid thermal treatments which can selectively disorder the chain oxygen atoms only. Nanosecond laser irradiation under controlled fluences represents an elegant method to introduce nonequilibrium changes in near-surface regions ($\sim 2000–5000$ Å) of materials in which the surface regions are heated and cooled at rates exceeding 10^{10} K/sec. These rates are many orders of magnitude higher than those which can be achieved by conventional means, such as quenching in liquid nitrogen, etc. In this paper, we provide evidence of planar superconductivity in a chain-disordered $YBa_2Cu_3O_{7-\delta}$ system. By employing low-energy nanosecond pulsed laser irradiation, the Cu(1)-O(1) chains in $YBa_2Cu_3O_{7-\delta}$ specimens were preferentially disordered without affecting the Cu-O$_2$ planes. Low-energy pulsed laser irradiation (below the melting threshold) causes rapid surface heating in the material without causing any phase change.[7,8] The rapid nonequilibrium heating only disorders the oxygen atoms in the copper-oxygen chains, which represent the most weakly bonded atoms in the system. The chain-disordered superconducting films still exhibit excellent electrical properties, thus providing evidence that superconductivity can exist in chain-disordered $YBa_2Cu_3O_7$ system.

To conduct the experiments, epitaxial $YBa_2Cu_3O_{7-\delta}$ superconducting thin films with thicknesses ranging from 1000 to 1500 Å were grown on (100) $LaAlO_3$ and yttria-stabilized zirconia (YSZ) substrates by the pulsed laser deposition technique. Standard deposition conditions (temperature of $\sim 650\,°C$ and pressure of 200 mtorr) were employed during the deposition.[8,9] These films exhibit excellent superconducting properties with T_c in the range of 90–92 K and resistive transition widths of less than 1 K. The critical current densities J_c (for an electrical field of 1 $\mu V/cm$) of the films were in the range of $(4–5) \times 10^6$ A/cm^2 at 77 K and zero magnetic field. These films were irradiated in air with a low-energy excimer laser (wavelength $\lambda = 308$ nm, pulse width $\tau = 45 \times 10^{-9}$ sec). The pulse energy density was varied from 40 to 400 mJ/cm^2; however, interesting results were observed below 50–150 mJ/cm^2. To determine the effect of the low-energy laser irradiation on the microstructure of the superconducting thin films, especially the modification in the copper-oxygen chains and planes, Raman spectroscopy and x-ray diffraction measurements were conducted and the results correlated with the superconducting properties.

The understanding of the nature of laser-solid interactions and the thickness of the laser-modified surface are critical in interpreting the Raman results and the superconducting properties of $YBa_2Cu_3O_{7-\delta}$. Nanosecond pulse lasers provide a controlled source of energy which

gives rise to transient thermal effects in the solid. The thermal history of the laser-irradiated regions can be determined by solving the heat-flow equation with appropriate boundary conditions. Figure 2(a) shows the temperature distributions across the $YBa_2Cu_3O_{7-\delta}/LaAlO_3$ sample at different times after irradiation with a 45-nsec excimer laser pulse with energy density of 350 mJ/cm^2. Although the absorption depth for the laser beam is approximately 350 Å, the thickness of the heat-affected regions is much larger, due to the thermal diffusion of the laser-deposited energy.[10] In these calculations, the thermal conductivity of the film and the $LaAlO_3$ substrate were assumed to be 0.02 and 0.1 W cm^{-1} K^{-1}, respectively, while the specific heat of the superconducting film was assumed to be 0.39 J g^{-1} K^{-1}.[11,12] The figure shows that the temperature profiles are discontinuous at the film/substrate interface primarily because of the large differences in thermal conductivity of the two materials. The heat-affected zone is approximately 5000 Å at 30 nsec and increases to approximately 1 μm at 100 nsec. Thus the whole thickness of the film is affected by the laser pulse. It should also be noted that the Raman measurements using laser radiation at 514.5 nm have a penetration depth of 1200 Å in $YBa_2Cu_3O_{7-\delta}$.[10] Thus these measurements are also expected to provide structural information from the whole film.
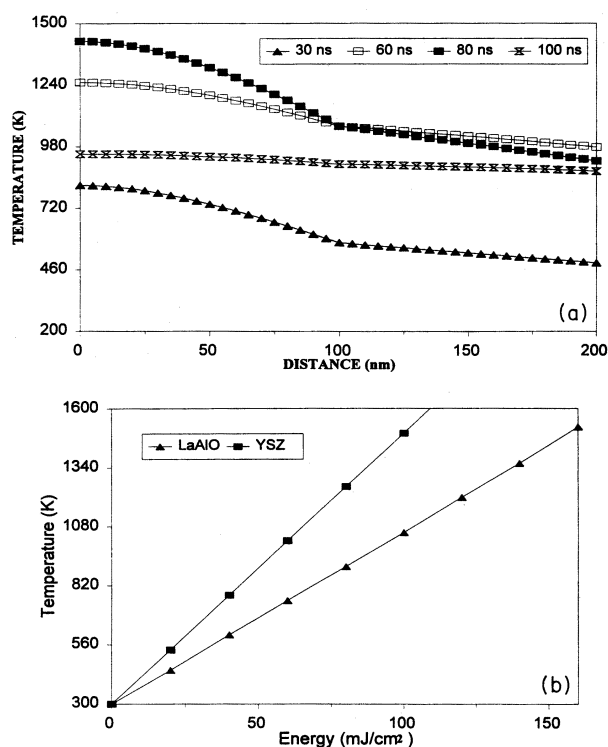

FIG. 2. (a) Simulated temperature profiles across the 1000-Å $YBa_2Cu_3O_{7-\delta}$ film on (100) $LaAlO_3$ at different times after irradiation with 45-nsec excimer laser pulse with energy density of 150 mJ/cm^2. (b) The maximum surface temperature expected for $YBa_2Cu_3O_7$ films on $LaAlO_3$ and YSZ substrates as a function of energy density.

Figure 2(b) shows the maximum temperature expected after laser irradiation as a function of energy density in superconducting thin films deposited on $LaAlO_3$ and YSZ substrates. Due to the lower thermal conductivity of YSZ (0.04 $W cm^{-1} K^{-1}$) in comparison to $LaAlO_3$, the maximum surface temperature in YSZ is higher than in $LaAlO_3$ for a fixed energy density. For example, at 80 mJ/cm^2, the maximum surface temperatures are approximately 750 and 1250 K, for $YBa_2Cu_3O_7$ films on $LaAlO_3$ and YSZ substrates, respectively. These calculations also show that, if the laser energy density on superconducting films on (100) $LaAlO_3$ substrates exceeds 150 mJ/cm^2, the surface temperature will exceed the melting point of $YBa_2Cu_3O_7$, thus initiating melting at the surface. From this graph the melt threshold has been calculated to be 90 and 160 mJ/cm^2 for 1000-$\overset{\circ}{A}$ superconducting films on YSZ and $LaAlO_3$ substrates, respectively. Calculations conducted on nanosecond laser melting of semiconductors and metals have shown that the maximum melt depth varies approximately linearly with the energy density.[13] Thus, if degradation in the superconducting properties is observed due to melting, the thickness of the degraded layer will be a function of pulse energy density.

Figure 3(a) shows the resistivity versus temperature curves of the $YBa_2Cu_3O_{7-\delta}$ film on (100) $LaAlO_3$ substrate irradiated at different energy densities. The resistivity curves show ideal metallic curves. Based on the resistivity and the critical current density data, two separate regimes are observed. In regime I, no distinct change in resistivity versus temperature curves is observed. Resistivity versus temperature measurements made in this regime show no change from the unirradiated data. As shown in the figure, the upper limit for the energy-density threshold for regime I is below 180 mJ/cm^2. This energy-density threshold was found to be dependent on the substrate material. For YSZ substrates, the laser energy threshold was approximately 90–100 mJ/cm^2. Regime II initiates above this laser fluence, when the room-temperature resistivity starts to increase. However, even in this regime, the resistivity curves show nearly perfect metallic behavior with sharp resistivity transitions near 90 K. Similar resistivity-temperature behavior was observed for laser-irradiated superconducting films on YSZ substrates. The sudden increase in resistivity correlates well with the thermal calculations, and is attributed to the partial deterioration of the film due to near-surface melting. This statement was further corroborated by the critical current density measurements on these films as shown in Fig. 3(b). The J_c values represent a more critical parameter because they are strongly dependent on the volume of superconducting material and the nature of intergranular current transport. The J_c of the unirradiated samples was approximately 5.0×10^6 A/cm^2 at 77 K at zero magnetic field for $LaAlO_3$ substrates. The high J_c value suggests that the films possess excellent epitaxial microstructure which is free of extended defects. As seen in the figure, the critical current densities of the film do not degrade in regime I. This suggests that no appreciable reorientation in the grain microstructure occurs in regime I. However, in re-
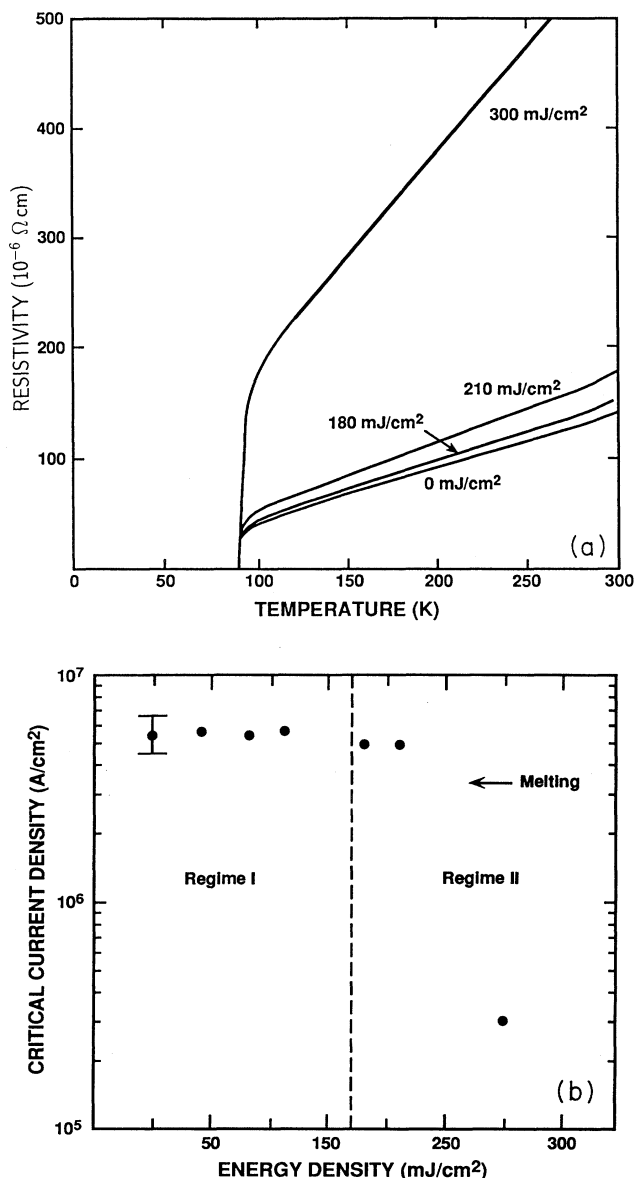

FIG. 3. (a) Resistivity as a function of temperature and (b) critical current density as a function of laser fluence for superconducting $YBa_2Cu_3O_7$ films on (100) $LaAlO_3$ substrates irradiated with a XeCl laser at different energy densities.

gime II, J_c values for the films decrease along with a concomitant increase in room-temperature resistivity as shown in Fig. 3(a). Surface observations of the film have shown that partial melting of the film takes place above the threshold energy-density value, causing a precipitous drop in the J_c value. Based on the superconducting measurements and the thermal calculations, regime II can be correlated with the melting of the surface.

The change in the microstructure and oxygen stoichiometry of $YBa_2Cu_3O_{7-\delta}$ films after laser irradiation was determined by Raman spectroscopy. Very few techniques are available to identify the exact location of

oxygen in the $YBa_2Cu_3O_7$ unit cell. Polarization experiments in Raman spectroscopy combined with lattice-dynamic calculations have been used to identify the location of the oxygen signal from a superconducting unit cell.[14-18] The dominant contribution to the Raman polarizability have been observed to come from the Cu-O and O-O interactions.[17] Figure 4 shows the Raman spectra obtained from $YBa_2Cu_3O_{7-\delta}$ films on (100) $LaAlO_3$ substrates which have been irradiated with different pulse energy densities (a) 0, (b) 90, (c) 150, (d) 250, and (e) 400 mJ/cm^2. The virgin film shows the characteristic Raman peaks at 116, 145, 230, 340, and 500 cm^{-1} corresponding to the A_g phonon vibrations of the $YBa_2Cu_3O_7$ phase.[14-17] We have determined that the peak at 110 cm^{-1} corresponds to plasma excitation of the sample. It has been established that the 230-, 340-, and 500-cm^{-1} lines in the Raman spectra are due to the oxygen vibrations, while the other two lines at 116 and 145 cm^{-1} represent Cu and Ba modes, respectively. The Raman peak at 145 cm^{-1} has been assigned to vibrations due to the symmetric stretching of the barium planes, while the 116-cm^{-1} peak arises due to Cu(2) vibrations along the c axis in the CuO_2 planes of the superconducting unit cell. The higher-frequency Raman modes have been assigned to different oxygen vibrations. The Raman peak at 340
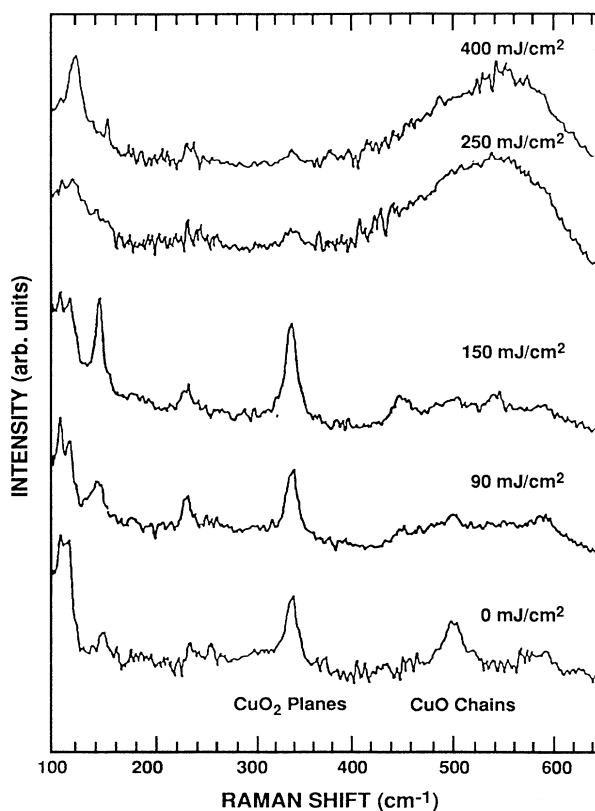
cm^{-1} has been unambiguously assigned to the in-phase bond bending of the O(2) and O(3) atoms in the CuO_2 planes, while the peak at 500 cm^{-1} has been assigned to axial symmetric stretching of Cu(1)-O(4) bonds as shown in Fig. 1. This assignment for the 500-cm^{-1} peak has been confirmed by varying the peak position as a function of oxygen composition in $YBa_2Cu_3O_6$.[16] The scattering efficiency of the Cu(1)-O(4) vibrations at 500 cm^{-1} has been attributed to the Cu(1)-O(1) chains.[17] Thus a weaker signal at 500 cm^{-1} directly relates to the disordering of the Cu(1)-O(1) bond. Experiments conducted with single-crystal untwinned samples have established that the 500-cm^{-1} peak is observed when the Raman beam is parallel to the c axis; however, its intensity is much larger when the Raman laser beam is perpendicular to the c axis.[14] Thus by observing the changes in intensity of the 340- and 500-cm^{-1} Raman peaks, information on the $Cu-O_2$ planes and Cu-O chains can be obtained.

Upon laser irradiation of the $YBa_2Cu_3O_7$ films at different energy densities, some distinct changes are clearly observed. The crystallinity of the films shows a distinct improvement until an energy density of 150 mJ/cm^2. This is shown by the stronger and cleaner low-frequency Raman peaks at 145, 230, and 340 cm^{-1}. The first two peaks correspond to the vibrations from the copper and barium atoms, while the stronger 340-cm^{-1} Raman peak shows an increased crystallinity in the oxygen atoms present in the copper-oxygen planes. The improvement in the crystallinity of the films and ordering of the oxygen atoms in the CuO_2 planes after low-intensity laser irradiation may lead to improvement in the superconducting properties. The stronger Raman signal from oxygen atoms in the copper-oxygen planes has been confirmed to be due to the removal of surface particles after controlled laser irradiation.[19] However, there is a deterioration and broadening of the high-frequency Raman peak at 500 cm^{-1} which suggests the disordering of the chain oxygen atoms with increasing pulse energy density. The 500-cm^{-1} peak completely disorders at low energy density without any deterioration in the vibrations corresponding to the $Cu-O_2$ planes. At larger energy-density values all the Raman peaks show a marked degradation, suggesting loss in crystallinity of the film. Thus a correlation of the Raman and electrical properties shows that $YBa_2Cu_3O_{7-\delta}$ films are superconducting even though the Cu(1)-O(1) chains have been disordered. It should be noted that all these measurements were carried out on different areas of the same substrate, thus eliminating misorientation effects in these experiments.

Similar microstructural changes were also obtained for laser-irradiated superconducting films on YSZ substrates. Figure 5 shows the Raman spectra obtained from $YBa_2Cu_3O_{7-\delta}$ films on (100) YSZ substrates which have been irradiated with different pulse energy densities (a) 0, (b) 50, (c) 90, and (d) 150 mJ/cm^2. This figure also shows that in regime I the signal strength of the 500-cm^{-1} peak diminishes strongly while the intensity of the 340-cm^{-1} peak does not change. However, in this case we observe that the threshold laser fluence for regime I is approximately 90–100 mJ/cm^2. The lower threshold energy

FIG. 4. Raman spectra of $YBa_2Cu_3O_7$ film on $LaAlO_3$ substrates after XeCl laser irradiation at different energy densities. Increased ordering in $Cu-O_2$ planes coincides with disordering in Cu-O chains for increasing energy density up to the melt threshold.
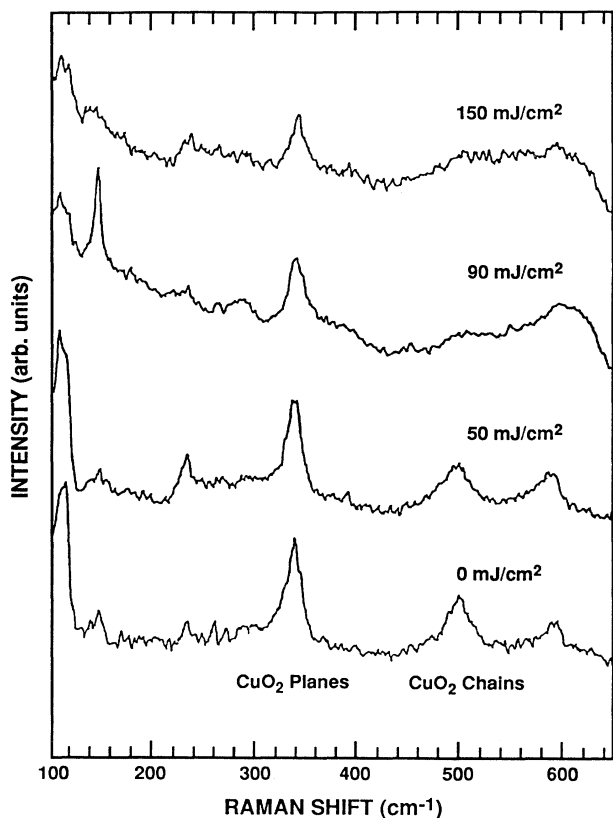
FIG. 5. Raman spectra for $YBa_2Cu_3O_7$ film on YSZ substrates irradiated with XeCl laser pulses at different energy densities (0, 50, 90, and 150 mJ/cm^2).

density is attributed to the lower thermal conductivity of the material, which results in a higher near-surface temperature under similar laser irradiation conditions. In regime II, all the Raman peaks broaden, suggesting deterioration of the sample. Thus these experiments confirm that under certain laser irradiation conditions it may be possible to selectively disorder the Cu(1)-O(1) chains.

X-ray diffraction measurement were also conducted to determine the oxygen location after low-energy laser radiation. When a unit cell of $YBa_2Cu_3O_{7-\delta}$ is altered in either size or lattice occupancy, the relative intensities as well as the position of the x-ray diffraction peaks shift. The relative intensities of the (001) peak, $l = 1, 2, 3, \ldots$, were found to change upon laser ir radiation in regime I conditions. The relative intensities of (001), (002), (003),

(004), (005), and (007) peaks were found to increase relative to the strength of the (006) peaks. Preliminary simulations showed that this can be linked to the removal of the oxygen atom from the chain position. However, it should be noted that unambiguous information cannot be obtained because the structure factor which controls the scattering intensity can also change, with possible change in the atomic positions of other atoms in the superconducting unit cell. It should, however, be noted that the c-axis lattice parameter was not altered by the laser irradiation process.

The selective disordering of copper-oxygen chains can be linked to the high mobility of the O(1) atoms in the superconducting unit cell.[6] The isotropic temperature factor of O(1) is more than a factor of 5 greater than that of the other oxygen atoms in the superconducting unit cell. Thus the O(1) atom can be selectively removed during rapid heating and cooling. The thermal calculations in Fig. 2(a) show that the films are at the elevated temperatures only for very short times (~ 100 nsec), thus freezing the thermodynamically favorable transformations and preventing the loss of superconductivity in the thin film. The threshold for partial melting of the film lies between 90 and 100 mJ/cm^2 for YSZ substrates, while it is approximately 160 mJ/cm^2 for LaAlO$_3$ substrates. Thus the initiation of regime II is in good agreement with the melt threshold. During melting, the structure of the superconductor is completely destroyed. In the resulting resolidification, new phases can be formed, which may explain the new Raman peaks observed in regime II conditions in Fig. 4. It should be noted that, even though the whole thickness of the film may be thermally affected, the diffusion of oxygen can be different. Oxygen can diffuse more easily from the near-surface regions than from the film/substrate interface. Even in this scenario, the conclusions remain the same. Because no change in J_c and concomitant Cu-O chain disordering is observed in regime I, we can still conclude that superconductivity exists in chain-disordered films. If not, there would be a drastic decrease in J_c in this regime.

In conclusion, we have observed that superconductivity can exist in metastable chain-disordered $YBa_2Cu_3O_{7-\delta}$ samples. This was accomplished by subjecting the superconducting samples to controlled nanosecond laser irradiation, which causes the highly mobile oxygen atom in the copper-oxygen chain to selectively disorder. No deterioration in the superconducting properties was observed under these conditions.

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