

## Direct measurements of room-temperature oxygen diffusion in $\text{YBa}_2\text{Cu}_3\text{O}_x$

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We have investigated the room-temperature oxygen depletion in the near-surface region of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  samples kept under high vacuum. Results obtained from secondary-ion-mass-spectroscopy and four-probe-conductivity measurements are presented. The depletion process is limited by oxygen out diffusion in the samples with diffusion coefficients of  $10^{-18}$ – $10^{-19}$   $\text{cm}^2/\text{s}$ . The reverse oxygen in-diffusion process occurs in oxygen atmosphere. The oxygen out-diffusion process can be accelerated by direct ultraviolet light (UV) irradiation of the samples in vacuum. The in-diffusion process is accelerated if UV light is used in oxygen atmosphere to produce ozone and atomic oxygen.

It is well known that oxygen stoichiometry plays a crucial role in  $\text{YBa}_2\text{Cu}_3\text{O}_x$  (YBCO) superconductors. The crystalline structure of YBCO changes from orthorhombic to tetragonal with the decrease of oxygen content. The transition temperature  $T_c$  and the superconducting properties in the orthorhombic phase are also very sensitive to the oxygen concentration.<sup>1–3</sup> It has been shown<sup>4–8</sup> that the surface of the YBCO samples is very unstable if they are kept in ultrahigh vacuum (UHV). From a photoemission study,<sup>4</sup> it was found that at low temperature a very distinct and stable Fermi edge exists in  $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$  single crystals cleaved in vacuum and that this Fermi edge rapidly disappeared after heating the crystals above  $\sim 50$  K. This result was interpreted in terms of oxygen loss in the near-surface area. The same conclusion was reached from scanning tunneling microscopy studies at room temperature of YBCO single- and polycrystals.<sup>5,6</sup> These authors found that the surface of the samples kept at UHV had very low conductivity<sup>5</sup> or became nonconducting.<sup>6</sup> Tunneling current appeared only after the tip was moved about 20 nm (Ref. 6) or about 100 nm (Ref. 5) into the samples. Raman scattering experiments<sup>6</sup> made *in situ* have shown that the characteristic peak at  $590\text{ cm}^{-1}$  for the high-temperature superconducting (HTS) YBCO phase disappeared if samples were annealed in UHV at room temperature and this peak reversibly appeared if the crystals were heated to  $100^\circ\text{C}$  in an oxygen atmosphere. The authors concluded that these reversible changes in the Raman spectra were caused by the diffusion of oxygen from and to the near-surface area. However, direct measurements of the oxygen concentration in the near-surface area and the dynamics of the oxygen depletion affected by UHV exposure have never been previously performed. Only high-

temperature oxygen diffusion measurements were carried out.<sup>9–11</sup> It has been shown that the typical value for the oxygen diffusion coefficient is about  $10^{-13}$   $\text{cm}^2/\text{s}$  for the lowest measured temperature (573 K) at atmospheric pressure and that the activation energy is about 1.0–1.3 eV.<sup>9,10</sup>

Veal *et al.*<sup>12,13</sup> have shown that intrinsic oxygen in oxygen-depleted YBCO samples is very mobile even at room temperature and this oxygen motion can lead to internal ordering with time and to an increase of up to 27 K (Ref. 14) in the transition temperature. Light irradiation of HTS samples can also affect their properties.<sup>15–18</sup> Recent work by Kudinov *et al.*<sup>15</sup> shows evidence of persistent photoconductivity and metastable, photoinduced superconductivity for initially oxygen deficient HTS thin-film samples measured at temperatures below 270 K. These samples also showed evidence of superconductivity enhancement photoinduced by laser irradiation.<sup>16,17</sup> Kawasaki *et al.*<sup>18</sup> have shown a reversible change of  $T_c$  of the order of 20 K in YBCO and Bi-Sr-Ca-Cu-O exposed to UV irradiation in oxygen atmosphere at elevated ( $\sim 700$  K) temperatures. They explained these results as oxygen incorporation into the films caused by irradiation.

In this paper we present experimental results obtained at room temperature which indicate that in UHV an oxygen out-diffusion process occurs, while an oxygen in-diffusion process occurs in an oxygen atmosphere. These oxygen diffusion processes are reversible and can be accelerated by UV light. Two independent experimental techniques were employed: direct measurements of near-surface oxygen concentration using secondary ion mass spectrometry and four-probe conductivity measurements. These methods have been successfully used to study oxygen diffusion processes in ceramic materi-

als.<sup>10,19,20</sup> Both methods give reproducible and consistent results. YBCO samples show significant oxygen loss even after five minutes under UHV at room temperature. The oxygen depletion process is limited by oxygen out diffusion in the samples. The diffusion coefficients calculated from the data obtained by the two independent methods are both in the range  $10^{-18}$ – $10^{-19}$   $\text{cm}^2/\text{s}$ .

Polycrystalline samples with different oxygen concentration and fully *c*-axis-oriented  $\text{YBa}_2\text{Cu}_3\text{O}_x$  thin films have been used for this study. The bulk polycrystalline samples were sintered in a regular solid-state diffusion process. High purity  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$ , and  $\text{CuO}$  were used as starting components. The samples were calcined several times with intermediate grinding. X-ray and magnetic measurements showed a single-phase Y-1:2:3 structure. Fully *c*-axis-oriented  $\text{YBa}_2\text{Cu}_3\text{O}_x$  thin films were grown by pulsed metalorganic chemical vapor phase epitaxy. A detailed description of this method can be found in a previous paper.<sup>21</sup> The quality of these thin-film samples was tested by x-ray diffraction and resistivity measurements. They were about 100 nm thick with only (00L) diffraction peaks present and superconducting transition temperatures above 90 K.

Two bulk, polycrystalline samples with starting compositions  $\text{YBa}_2\text{Cu}_3\text{O}_{6.93}$  and  $\text{YBa}_2\text{Cu}_3\text{O}_{6.38}$  and superconducting transition temperatures 92 and 35 K, respectively, were studied. These samples were polished and mounted on an aluminum sample holder for study using the University of Chicago Scanning Ion Microprobe (UC SIM).<sup>22,23</sup> This instrument makes use of a 40 KeV  $\text{Ga}^+$  primary ion beam, focused to a spot  $\sim 50$  nm wide to sputter ions from a solid surface. The ejected ions are collected and analyzed by a secondary ion mass spectrometer (SIMS) system. For this analysis, the primary ion beam was rastered over an area of  $20 \times 20 \mu\text{m}^2$  or  $40 \times 40 \mu\text{m}^2$ , depending on the sample. During a scan the gallium beam sputtered the surface, continually exposing deeper and deeper layers for SIMS analysis (depth profiling). In the so-called "peak-switching" mode<sup>22</sup> we were able to simultaneously gather the depth profile of up to four secondary ion species. The erosion depth was calculated from the primary ion current, the average density of YBCO, the duration and the area of the scan and a secondary particle sputter yield.<sup>24</sup> The latter was determined from data obtained for YBCO thin films of known thickness.

After the samples were inserted into the UC SIM UHV chamber ( $10^{-9}$  Torr) at room temperature, we sputtered the surface of the samples with the  $\text{Ga}^+$  ion beam until a constant  $\text{O}^-$  signal was observed. This signal intensity was interpreted as corresponding to the bulk oxygen concentration. Then the samples were kept in the same UC SIM UHV chamber at room temperature turning the  $\text{Ga}^+$  ion beam off for different time intervals (5 min, 1 h, etc.) and depth profiles of near surface oxygen distributions were again measured after each time interval until the bulk concentration was reached.

Resistivity measurements were carried out on thin-film samples. Samples initially  $1 \text{ cm} \times 1 \text{ cm}$  in size were cut by diamond saw into stripes with a width of 1 mm and partially coated with Ag by thermal evaporation to make

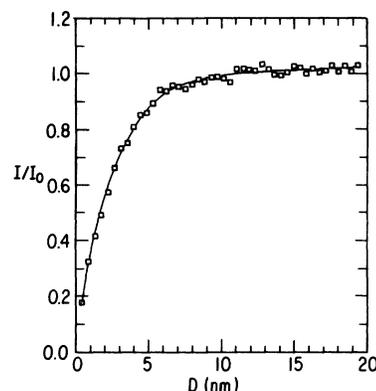


FIG. 1. SIMS depth profile of the near-surface oxygen distribution for the bulk  $\text{YBa}_2\text{Cu}_3\text{O}_{6.93}$  sample exposed for 5 min to UHV at room temperature.

contact pads for conductivity measurements under high vacuum. The high vacuum chamber was equipped with a UV light source ( $\lambda = 253.7$  nm) and a magnetically operated shutter whose combined action allowed either direct UV illumination of the sample in vacuum or ozone production in oxygen atmosphere without direct illumination. At these conditions the photon flux was about  $1.28 \times 10^{17} \text{ s}^{-1} \text{ cm}^{-2}$ . The four-probe dc conductivity measurements were carried out with a current of 10  $\mu\text{A}$  ( $j = 0.17 \text{ A/cm}^2$ ) at room temperature. The superconducting temperature was checked by the same four-probe method. During the measurements the contact resistance was always smaller than 1% of the sample resistance.

In Fig. 1 we present a typical and reproducible depth

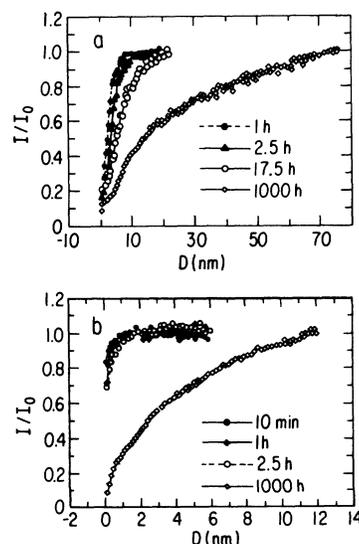


FIG. 2. SIMS depth profile measurements of the depth dependence of the near surface oxygen concentration for different UHV exposure times: (a) YBCO sample with initial oxygen concentration  $x = 6.93$ ,  $T_c = 93$  K; (b) sample with initial oxygen concentration  $x = 6.38$ ,  $T_c = 35$  K.

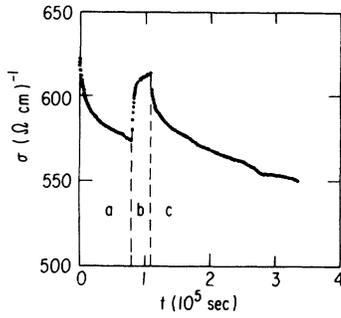


FIG. 3. Conductivity of a YBCO thin film as a function of exposure time at room temperature: (a) under UV illumination in  $10^{-6}$  Torr atmosphere; (b) under UV illumination in 600 Torr oxygen atmosphere; (c) same as case (a).

profile for oxygen in the bulk sample  $\text{YBa}_2\text{Cu}_3\text{O}_{6.93}$  which was exposed to UHV for 5 min. These measurements were done by the SIMS technique as described above. Even for this short period of UHV exposure, the oxygen depleted area can reach a depth of about 9 nm. No significant changes in the oxygen concentration were observed for the sample with  $x = 6.38$  kept for the same time in UHV.

As the time the samples were kept in UHV was increased, the thickness of the depleted area also significantly increased (Fig. 2) to reach about 70 and 12 nm for the samples with  $x = 6.93$  and 6.38, respectively, for UHV exposure of up to 1000 h. The out-diffusion processes in the sample with bulk oxygen concentration  $x = 6.38$  are much slower than for the one with concentration  $x = 6.93$ . The depth profile obtained at room temperature and illustrated in Fig. 1 can be fitted to the solution of the diffusion equation of the form:<sup>25</sup>

$$C(x, t) = A_1 \text{erfc}(-Bx),$$

where  $A_1$  is a constant and  $B = (4Dt)^{-1/2}$ ,  $D$  is the diffusion coefficient. The best fitting was obtained with  $D$  about  $1.0 \times 10^{-19} \text{ cm}^2/\text{s}$ .

It is known that the normal-state conductivity  $\sigma$  of the YBCO is very sensitive to the oxygen concentration.<sup>10</sup> In Fig. 3 we show how the room temperature dc conductivity of one of the thin-film samples changes due to the effect of high vacuum and oxygen environments. When the sample was exposed to high vacuum with direct UV illumination, the conductivity dramatically decreased [Fig. 3(a)]. In view of the SIMS results above, we must attribute this decrease to the loss of oxygen from the near-surface area. Following that, we introduced 600 Torr of pure oxygen in the chamber and again turned on the UV lamp but shielded the sample from it [Fig. 3(b)]. The UV light in the oxygen atmosphere produced ozone and atomic oxygen which stimulated the reverse oxidation of the reduced sample as evidenced by the increase of the room-temperature conductivity back to the initial value. That procedure was completely reversible and could be repeated many times at room temperature [Fig. 3(c)].

In Fig. 4 we show the oxidation-reduction curve for another thin-film sample. Compared with the sample in

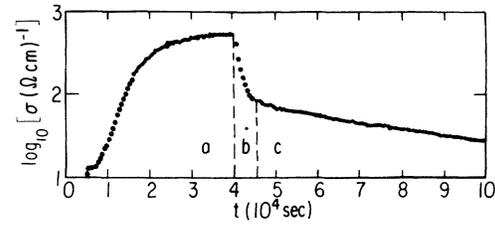


FIG. 4. Conductivity of YBCO thin film as a function of exposure time in 600 Torr oxygen atmosphere (a) and under UV illumination at  $10^{-6}$  Torr [(b) and (c)].

Fig. 3, this sample starts from a much lower value of the room-temperature conductivity, but the conductivity increase during oxidation is much faster and spans almost 2 orders of magnitude [Fig. 4(a)]. The decrease of the conductivity during reduction [Fig. 4(b)] is also faster than that in Fig. 3. This emphasizes the surface nature of the process: the changes in the conductivity follow the oxygen diffusion process and proceed from the sample surface into the bulk. As a result, the conductivity of a sample which is initially highly conducting changes only by a small amount because the conducting bulk short circuits the oxygen-sensitive surface layer. And vice versa, the conductivity of a sample whose bulk is less conducting (as is the case with the sample in Fig. 4), will increase abruptly and by a large amount once its surface is made more conducting by oxidation because it is the surface layer that now short circuits the bulk and controls the overall conductivity. Only in this second case is the actually measured sample conductivity directly related to the oxygen in- or out-diffusion process and that is why we used the curve shown in Fig. 4 to calculate the oxygen diffusion coefficient. Assuming that the conductivity of the sample is proportional to the oxygen concentration and using the general solution of the diffusion equation<sup>26</sup> we have

$$c_{\text{ox}} = \frac{1}{h} \int_0^{2h} \left[ c_0 \sin \left( \frac{\pi x}{2h} \right) dx \right] \exp \left[ -\frac{\pi^2 d_{\text{ox}} t}{4h^2} \right] \sin \left( \frac{\pi x}{2h} \right),$$

where  $c_0$  is the initial oxygen concentration on the sample surface,  $c_{\text{ox}}$  is the oxygen concentration,  $d_{\text{ox}}$  is the oxygen diffusion coefficient,  $t$  is the time, and  $h$  the film thickness.

The time dependence of the sample conductivity  $\sigma$  during reduction (out-diffusion) is obtained as

$$\sigma(t) = \frac{8}{\pi^2} \sigma_0 \exp \left[ -\frac{\pi^2 d_{\text{ox}} t}{4h^2} \right]$$

where  $\sigma_0$  is the initial conductivity of the sample (prior to reduction).

The calculated oxygen diffusion coefficient from the region of slower conductivity decay [Fig. 4(c)] is  $1.0 \times 10^{-18} \text{ cm}^2/\text{s}$  which is in a reasonable agreement with the diffusion coefficient  $D$  obtained from the direct measurements using the SIMS method.

After the samples were exposed to high vacuum with UV irradiation for 3 days, the superconducting transition temperature  $T_c$  defined as the midpoint of the transition,

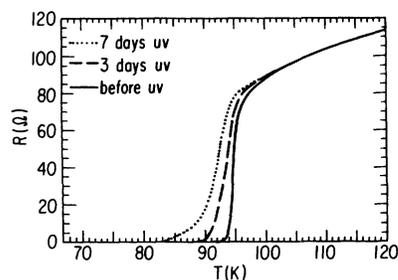


FIG. 5. Resistance as a function of temperature for a YBCO thin-film sample before exposure (solid line), and exposed to UV irradiation under high vacuum 3 days (dashed line) and 7 days (dotted line). The resistivity of the samples at 100 K is about  $3.8 \times 10^{-4} \Omega \text{ cm}$ .

decreased due to the out diffusion of oxygen from an initial value of 94 to 92.5 K (Fig. 5). Then the same sample was kept in high vacuum at room temperature for an additional 7 days (Fig. 5, dotted line).  $T_c$  dropped to the lowest value of  $\sim 91.5$  K and the zero resistance temper-

ature decreased by about  $10^\circ$ . We note that the UV irradiation and low-temperature resistivity measurements were not done *in situ*, so that some oxygen restoration could have taken place during the transport of the samples. The decrease of  $T_c$  indicates that oxygen is depleted throughout the film, while the broadening of the transition profile can be explained by the oxygen concentration profile obtained from the SIMS measurements.

We have presented results on the effect of high-vacuum room-temperature annealing on the near-surface oxygen concentration in YBCO samples. Based on two different methods, we have shown that the near-surface area experiences fast oxygen depletion and that the process is limited by oxygen diffusion with diffusion coefficients in the range  $10^{-18}$ – $10^{-19} \text{ cm}^2/\text{s}$ . Work to measure the anisotropy of oxygen out diffusion in high vacuum in the temperature range  $30$ – $150^\circ \text{ C}$  is in progress.

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