Laser Ablation of $YBa_2Cu_3O_{7-\delta}$ as Probed by Laser-Induced Fluorescence Spectroscopy

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(Received 17 July 1991)

Ground-state populations of cationic and neutral Y, Ba, Cu, and neutral YO, BaO, and CuO are monitored by laser-induced fluorescence during laser ablation of $YBa_2Cu_3O_{7-\delta}$. 193-nm photons completely dissociate CuO allowing the observation of a subsequent reaction of the Cu atom with O_2 to form CuO. As a function of O_2 pressure, the CuO signal increases to a maximum at approximately 120 mTorr of O_2, presumably minimizing δ, and then falls to negligible levels by 400 mTorr. Ablation at 248 and 351 nm dissociates a smaller fraction of the CuO, i.e., nascent CuO is observed in the absence of O_2.

PACS numbers: 79.20.Ds, 74.70.Vy

The processing of high-T_c thin films by laser ablation has become a powerful method for the production of films with both high critical temperatures and critical currents [1-4]. Of the many parameters which affect the quality of the film, the concentration of atomic constituents and oxides present in the plume seems to play a major role [1,5-9]. Many spectroscopies have been used in an attempt to determine the relative concentrations of the plume constituents, including absorption and optical excitation methods [5,6,10], emission [7,9,11-17], as well as mass spectrometry [1,8,18-21]. The inclusion of oxygen in the deposition chamber has been shown [2,22,23] to be important in producing films with the correct stoichiometry, eliminating the need for *ex situ* postdeposition treatment. To date, no *direct* probe of the plume-oxygen reaction pathways has been reported. In this Letter, we report direct observation of metal-atom reaction with background oxygen and also report the pressures at which the maximum amount of diatomic oxide is present in the plume as it proceeds toward the substrate. Specifically, we have measured the O_2 pressure at which the number density of CuO peaks and have found that it is in very good agreement with those pressures which have been determined empirically to produce the films with the highest critical temperature [1,22].

Pulsed laser evaporation of a 2.5-cm-diam, 1-cm-thick target of $YBa_2Cu_3O_7$ (YBCO) was done with a Lambda Physik EMG 201 excimer laser at 193, 248, or 351 nm. The laser beam was focused on a translatable, rotating sintered $YBa_2Cu_3O_7$ pellet in a turbopumped vacuum chamber, as shown in Fig. 1. The laser-induced fluorescence (LIF) measurements are made some 1-100 μs after the ablation pulse and 1-2 cm above the ablated target, depending on the O_2 pressure. One significant advantage that LIF affords over most other techniques is its ability to provide quantitative results. In its most common form, tunable dye-laser pulses excite a specific transition of specific species, and emission from this excited-state population is monitored. As an example, to monitor the presence of CuO, the $M\,^2\Pi_{3/2} \leftarrow X\,^2\Pi_{3/2}$ transition at 418.2 nm [24] was pumped and fluorescence to the ground state was monitored. This transition was chosen since it is a relatively strong transition and provides a band with relatively few rotational branches (one *P* and one *R* branch), limiting the complexity of the rotational structure that occurs due to the two major isotopes of copper. Under these conditions a rotational temperature can be determined. Figure 2 shows a representative scan of this transition. While this transition is partially overlapped by the BaO $A\,^1\Sigma^+ \leftarrow X\,^1\Sigma^+$ (15,0) band, the very different lifetimes allowed gating on the longer CuO emission while ignoring the much faster BaO emission.

The use of 193-nm photons to ablate the $YBa_3CuO_3O_7$ produces copious amounts of BaO and YO, and we have recorded the spectra of several vibrational bands from the *B-X* and *A-X* transitions of both molecules, yielding translational, vibrational, and rotational energy distributions [25]. However, it was not possible to detect CuO via LIF with 193-nm ablation. The same applies when

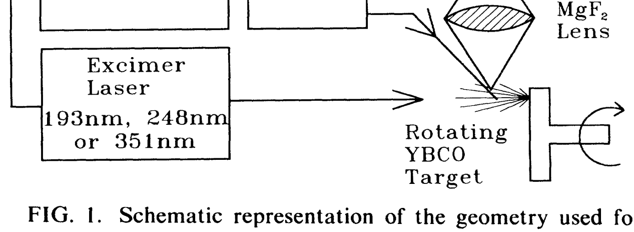

FIG. 1. Schematic representation of the geometry used for laser-induced fluorescence detection of neutral and ionic species produced in the excimer-laser deposition of YBCO.

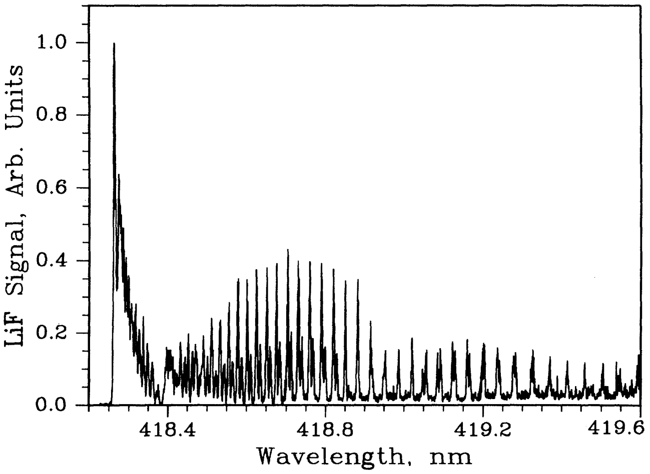

FIG. 2. Spectrum of the CuO $M\ ^2\Pi_{3/2} \leftarrow X\ ^2\Pi_{3/2}$ transition at 418.2 nm, recorded by laser-induced fluorescence after 248-nm ablation of YBCO. Rotational structure from the two isotopic species ^{63}Cu and ^{65}Cu is present. The drop in intensity of the P branch at 418.95 is reproducible, a result of a perturbation by a close-lying state whose symmetry is not known at present. This spectrum was recorded while ablating YBCO in 120 mTorr of O_2.

ablating a pellet of pure CuO. The dissociation energy of CuO is low (2.7 eV) and appears directly related to the absence of nascent CuO in the 193-nm ablation. However, 248- and 351-nm ablation produces large amounts of nascent CuO from the pure CuO pellet *and,* as shown in Fig. 3, the $YBa_2Cu_3O_7$ pellet; the relevant LIF spectra are readily obtainable in vacuo in these cases.

To observe the reactions of emitted atomic species with O_2, variable pressures (baratron capacitance monitor) of O_2 were maintained in the chamber. In the case of 193-nm ablation, where no CuO was detectable under high-vacuum conditions, introduction of O_2 provides a direct demonstration of the production of CuO. As mentioned previously, by pumping the bandhead of the M-X transition, we monitor the intensity of the CuO resonance fluorescence as a function of O_2 pressure, keeping the delay between the lasers such that the dye laser probes the peak of the velocity distribution. At pressures greater than about 100 mTorr, significant broadening and slowing in the velocity distributions are observed and correction for this is necessary. Figure 3(a) displays the result of this measurement. At a pressure of approximately 120 mTorr of O_2, the CuO signal (i.e., density) is seen to peak and then to decrease to much lower levels by 400–500 mTorr. While the reason for the falloff at high pressures is not clear, it is possibly a result of the reaction $Cu+O_2 \rightarrow CuO+O$ being endothermic and hence requiring significant kinetic energy input on the part of the Cu. This energy input would be restricted at high O_2 pressures. Another explanation could involve clustering to form Cu(metal)$_x$O$_y$ species. Constant fluorescence lifetimes observed above 1 Torr of O_2 indicate that pressure

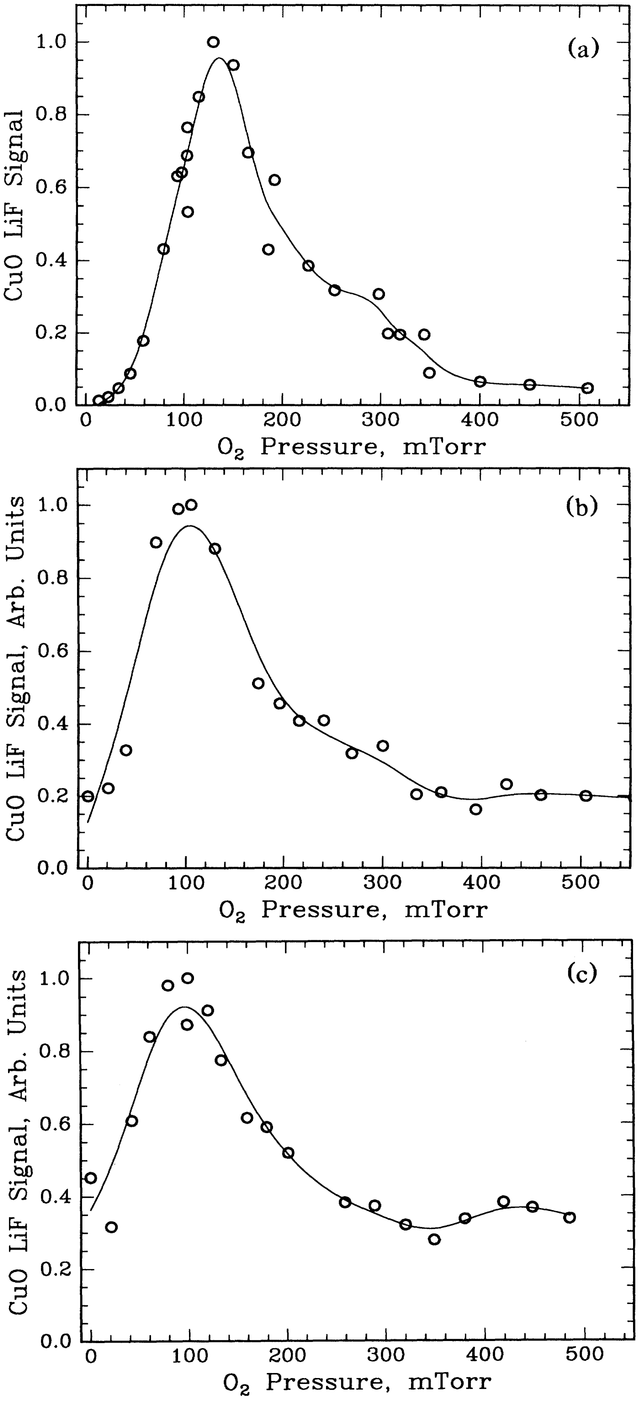

FIG. 3. The result of measuring the intensity of the CuO LIF signal as a function of O_2 pressure leaked into the deposition chamber. Because the time-of-flight distribution is perturbed significantly above 100 mTorr, the measurements were taken at the peak of the time-of-flight distribution for each point. Fluences used were (a) 160 mJ/cm^2 (193 nm), (b) 355 mJ/cm^2 (248 nm), and (c) 450 mJ/cm^2 (351 nm). Note that the high-pressure signal is similar to the no-O_2 signal in all cases and that this supports the concept that kinetic energy is important in the formation of the CuO; see text.

quenching of the CuO fluorescence is not responsible for this decrease. It is important to note that the measurements reported represent the number density during a particular point during the plume expansion. The transition from free flight to diffusional extraction will ultimately affect the measurement of the number density. Note that the final CuO density is similar to the no-O_2 level in Figs. 3(a)–3(c), which supports the idea of a minimum kinetic-energy requirement for reaction to occur.

Ablation of the $YBa_2Cu_3O_7$ target by 248- and 351-nm pulses produces similar results (Fig. 3) except that the background (high vacuum) level of CuO is not zero and represents a significant level of the total CuO produced in the ablation plume. These results are consistent with emission studies [16,17] where 193-nm ablation was used and emission from diatomic species other than CuO was observed. Emission and mass spectrometric studies at 248 and 351 nm [1,9] have shown that all three diatomic species are present even without the addition of O_2. A recent report by Nogar *et al.* [26], using emission spectroscopy as a diagnostic, has demonstrated that the reaction of ablated Y atoms with O_2 to form excited-state YO approaches a limiting value at approximately 400 mTorr of O_2. Direct comparisons between different metal-atom–oxygen reactions are difficult, however, because of the different cross sections for reaction of atomic copper [27] and yttrium [28] with molecular oxygen, the energy dependence of the collision cross section [29], etc. The data in Fig. 3 also show that the ratio of the LIF signal ($S_{120\,\mathrm{Torr}}/S_{0\,\mathrm{Torr}}$) decreases systematically in going from 193-nm ablation to 351-nm ablation. The presence of significant Rayleigh scattering from the probe beam when using 351 nm to ablate also signifies that an increasing portion of the plume constituents consists of larger particles whose size is reaching the half micron range. This was not observed under any fluence conditions at 193 nm.

We have also recorded LIF spectra from all the metal-atom constituents and their ions (Y, Y^+, Ba, Ba^+, Cu, Cu^+), as well as BaO, YO, and reported here, CuO, which result from the laser ablation of $YBa_2Cu_3O_7$. Some of the other interesting results directly obtained from the LIF measurements are as follows: The large number densities of nascent YO and BaO, even using 193-nm ablation, do not appear to increase, upon introduction of O_2, as dramatically as for CuO. The density of neutral Y atoms is increased while that for Y^+ is decreased by reactions with O_2, the Y^+ disappearing at O_2 pressures of $\sim 10^{-4}$ Torr. The increase in Y-atom number density could be due to gas dynamic effects (bunching of the plume constituents) although collisional dissociation of larger yttrium-containing species could also increase the ground-state Y-atom population transiently. No detectable signal from Cu_2 was observed, even for etching at the two longer wavelengths. Another metallic diatomic, YBa^+, has, however, been observed as a significant component of the plume in a very-high-resolution Fourier-transform mass spectrometric investigation of the ionic plume constituents [30]. Another feature is that the kinetic energies are highly superthermal, typically 1–20 eV for neutrals and as high as 50 eV for ions. This is typical for laser ablation and is primarily the result of plasma potential acceleration of ions and a high pressure (due to the inverse bremsstrahlung heated plume) gaseous expansion.

In summary, we have probed relative densities of reaction products in the ablation plume of $YBa_2Cu_3O_7$ by laser-induced fluorescence, which does not suffer from the limitation imposed by high vacuum, as multiphoton ionization does. Nevertheless, LIF retains the temporal and spectroscopic resolution of laser excitation. In overcoming the vacuum restrictions it has been possible to observe directly the short-wavelength dissociation of the CuO diatomic and its subsequent reformation at moderate (≈ 125 mTorr) pressure of oxygen. In contrast, the densities of YO and BaO do not increase comparably. The observation of a peak in the production of CuO as a function of O_2 pressure may point to the mechanism by which nearly stoichiometric films are produced under an oxygen atmosphere, even though this is an endothermic reaction. High kinetic energies and/or Cu^+ reactions are quite possibly involved as follows from the initial high kinetic energies and the high cross sections for ion+O_2 reactions.

The authors would like to thank R. Laibowitz (IBM Yorktown Heights) and R. Beckner (Naval Air Development Center, Warminister, PA) for valuable discussions during the course of this work and for providing us with initial samples of YBCO.

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