

Gasphase oxidation of copper during laser ablation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in different oxidizing ambients

C. E. Otis, A. Gupta, and B. Braren

Citation: [Applied Physics Letters](#) **62**, 102 (1993); doi: 10.1063/1.108824

View online: <http://dx.doi.org/10.1063/1.108824>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/62/1?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Laser ablated copper plasmas in liquid and gas ambient](#)

Phys. Plasmas **20**, 053503 (2013); 10.1063/1.4807041

[Transport of YO molecules produced by ArF laser ablation of \$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\$ in ambient oxygen gas](#)

J. Appl. Phys. **74**, 7510 (1993); 10.1063/1.354976

[Gasphase oxidation chemistry during pulsed laser deposition of \$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\$ films](#)

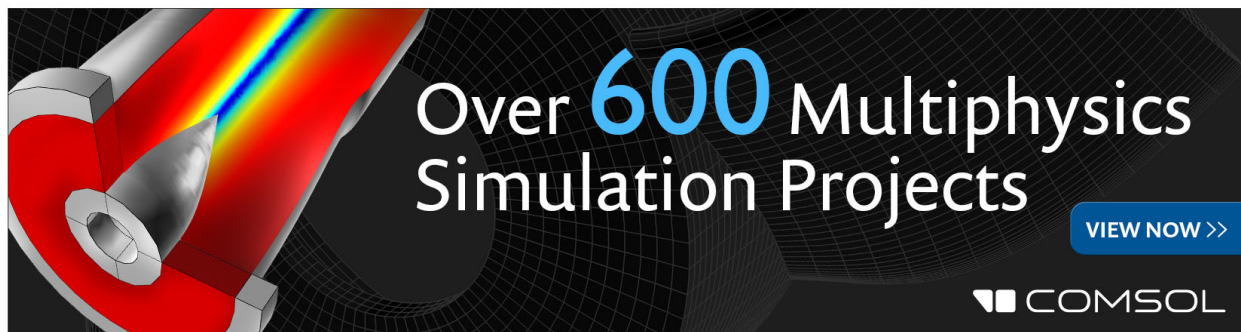
J. Appl. Phys. **73**, 7877 (1993); 10.1063/1.353939

[Direct imaging of the fragments produced during excimer laser ablation of \$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\$](#)

Appl. Phys. Lett. **59**, 1302 (1991); 10.1063/1.105481

[Defect formation caused by a transient decrease in the ambient oxygen concentration during growth of \$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\$ films](#)

Appl. Phys. Lett. **57**, 2365 (1990); 10.1063/1.104175

An advertisement for COMSOL Multiphysics simulation projects. It features a 3D cutaway view of a mechanical part with a red and yellow thermal stress distribution. The text 'Over 600 Multiphysics Simulation Projects' is prominently displayed in white and blue. A blue button with the text 'VIEW NOW >>' is located in the bottom right corner. The COMSOL logo is in the bottom right corner of the image area.

Over 600 Multiphysics Simulation Projects

VIEW NOW >>

COMSOL

Gas-phase oxidation of copper during laser ablation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in different oxidizing ambients

C. E. Otis, A. Gupta, and B. Braren

IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

(Received 29 July 1992; accepted for publication 21 October 1992)

The gas-phase production of CuO during ablation of a $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ target in the presence of three different oxidizer background gases: oxygen (O_2), nitrous oxide (N_2O), and nitrogen dioxide (NO_2), has been monitored using laser-induced fluorescence. The oxides of nitrogen are found to be much more efficient than oxygen in the production of CuO, with the order of reactivity being $\text{O}_2 < \text{N}_2\text{O} < \text{NO}_2$. In general for all the reactant gases, and independent of the ablation laser wavelength (193 and 308 nm), the CuO concentration has been observed to initially increase with increasing background gas pressure to reach a maximum before decreasing again to negligible levels at higher pressures. The rate of increase in the CuO concentration and its subsequent decrease with pressure, while being dependent on the nature of the oxidizer gas, is also very sensitive to the laser fluence used for ablation. The results are discussed in terms of the reaction energetics and the known dynamics of other gas-phase metal oxidation reactions.

Over the past few years the pulsed laser deposition (PLD) technique has emerged as one of the simplest and most versatile methods for the deposition of films of a wide variety of materials.¹ The stoichiometric removal of constituent species from the target during ablation, as well as the relatively few number of control parameters, makes the PLD technique particularly attractive for the growth of complex multicomponent systems like the high T_c copper oxides. For the *in situ* deposition of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO), and other superconducting oxides, the films have to be grown in an oxidizing environment to help form and stabilize the desired phase at the high growth temperature.^{2,3} For obvious practical reasons, most of the work related to *in situ* growth has been restricted to the use of molecular oxygen as the background oxidizer gas. While generally successful, the effectiveness of O_2 as an oxidizing agent is somewhat limited because of its low activity, which requires the use of relatively high pressures and deposition temperatures for the growth of good quality superconducting oxide films. Recently, a number of reactive oxygen sources, including nitrous oxide, nitrogen dioxide, and ozone, have been shown to be more effective than O_2 in reducing the temperature and pressure requirements for growth of good quality YBCO and other superconducting oxide films.³⁻⁶

Depending on the background gas pressure used during film growth, both gas phase and surface reactants will be important for oxidation. For typical oxygen pressures used during PLD, there will be significant interaction of the expanding cation species in the plume with the background gas leading to the formation of diatomic oxides. The oxidation reactions of Ba and Y, being highly exothermic, occur quite readily, with some of the oxide products also being produced in electronically excited states. Indeed, strong emission from excited YO and BaO has been observed during ablation of YBCO in an O_2 ambient.⁷ On the other hand, because of the low bond energy of CuO, the gas-phase oxidation of Cu is much less favorable. The reaction with O_2 is, in fact, substantially endothermic and

does not occur at normal collision energies. Nonetheless, the energetic Cu atoms in the plume can be effective in surmounting the substantial energy barrier and promote the formation of ground-state CuO, as has recently been observed by Otis and Dreyfus using laser-induced fluorescence (LIF).⁸

Energetically, the oxidation reactions of Cu with other oxidizer gases, like N_2O , NO_2 , O_3 , are much more favorable than with O_2 . It would, therefore, be interesting to compare the relative effectiveness of these gases to form gas phase CuO during ablation of YBCO and see whether it correlates with their enhanced oxidation capability as deduced from the superconducting properties of the films prepared using these gases. In this letter we report on the formation of CuO in the reactions of Cu with N_2O , NO_2 , and O_2 during laser ablation, as monitored by LIF. We find that NO_2 and N_2O are indeed more effective in the formation of gas phase CuO than O_2 , with the order of reactivity being $\text{O}_2 < \text{N}_2\text{O} < \text{NO}_2$.

A schematic diagram of the experimental setup is shown in Fig. 1, the details of which have been described in a previous publication.⁸ Briefly, either a XeCl (308 nm) or an ArF (193 nm) excimer laser (both Lambda Physik Model LPX 205) was used for ablation, with the laser beam being appropriately collimated and focused to provide a variable fluence in the range of 1–6 J/cm² on a rotating YBCO target placed inside a vacuum chamber. The ground state CuO products were detected by their characteristic excitation spectrum using a tunable pulsed dye laser as a probe. The $\text{CuO } M^2\Pi_{3/2} \leftarrow X^2\Pi_{3/2}$ excitation spectrum (418.2–419.6 nm) was pumped and the fluorescence to the ground state monitored as a function of wavelength. For a particular oxidizer gas, the variation in the concentration of the CuO produced as a function of background pressure was obtained from monitoring the intensity of the resonance fluorescence, through excitation of the band head of the $M-X$ transition, while the pressure in the chamber was slowly increased. After completion of measurements with a particular gas, the chamber was pumped

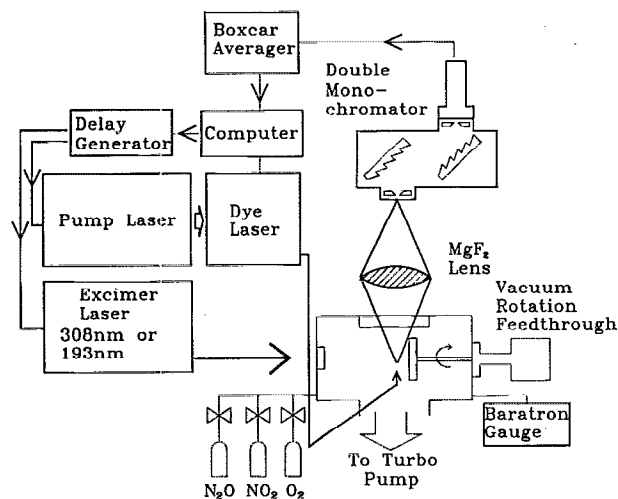


FIG. 1. Schematic diagram of the experimental setup for excimer laser ablation of YBCO with synchronized dye laser probe of gas-phase products by laser-induced fluorescence. The opening of the boxcar was delayed 30 ns from the firing of the dye laser, and the detection gate width was set to 100 ns for the CuO measurements.

out and the next gas introduced to continue measurements during the same experimental run. This ensured that the variations in the ablation and probe laser power were minimal during measurements with the different gases. For the results described in this letter, the LIF signal was collected at a distance of 1.5 cm from the target, with the dye laser probe delayed 40 μ s from the ablation pulse to reduce background signal from the plume luminescence.

The CuO signal observed as a function of background gas pressure for the three different oxidizer gases during 193 and 308 nm ablation are plotted in Figs. 2(a) and 2(b), respectively. The LIF signal is proportional to the number density of CuO molecules probed in the interaction zone at the preset delay, which in turn is directly related to the concentration of the reagents in the probed zone and the reaction cross section. At low pressures, NO₂ is observed to be at least an order of magnitude more effective than O₂ in promoting the formation of CuO at both laser wavelengths. The effectiveness of N₂O is intermediate, being a factor of about 4–5 times higher than O₂ when they are compared at their respective peak values. Note that the nascent CuO concentration, in the absence of an oxidizer gas, is very small and within the detection limit for the probe delay used for our measurements. For all the three gases one observes that with increasing background pressure the CuO signal increases almost linearly to a maximum in the range of 100–250 mTorr and then decreases by 400–500 mTorr to negligible levels. Moreover, in going from NO₂ to O₂, a systematic shift to slightly higher values is observed for the gas pressure at which the maximum CuO signal is achieved.

The most striking difference observed in the results presented in Figs. 2(a) and 2(b) is in the width of the distributions, i.e., the gas pressure range over which the CuO signals are observable at the two different wavelengths. We have found that the distribution width is very

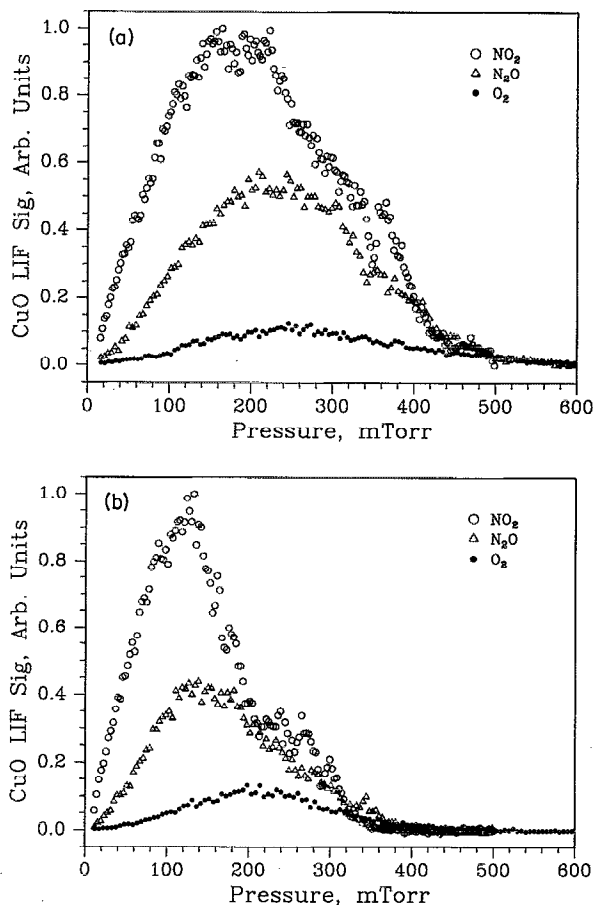


FIG. 2. Relative yields of CuO (as measured by LIF) as a function of background pressure of NO₂, N₂O, and O₂. The fluence used was 1.9 J/cm², 193 nm, (b) same as in (a) but using 1.5 J/cm², 308 nm.

sensitive to the laser fluence used for ablation. While photochemical effects may be partly responsible for the observed differences in the widths of Fig. 2, most of it can be attributed to the small difference in the fluence used at the two wavelengths—which was difficult to avoid with the use of two different lasers for the measurements. To illustrate the extreme sensitivity of the distribution width on the laser fluence, we plot in Fig. 3 the CuO signal observed as a function of NO₂ pressure for various laser fluences used for 248 nm ablation. While the CuO signal rises and falls rapidly for a laser fluence of 1.0 J/cm², at the highest fluence studied (6.0 J/cm²) the rise is much more gradual with the signal reaching a limiting value which remains essentially constant even for a NO₂ pressure as high as 1200 mTorr.

The reaction exothermicities for the formation of CuO from reaction with the different oxidizer gases increase in the order O₂ < NO₂ < N₂O (−2.36, −0.36, and +1.08 eV, respectively), corresponding to the decrease in bond dissociation energy of the molecule. Thus, for thermal energies, only the reaction with N₂O is exothermic and would proceed normally if there is no additional activation barrier to reaction. On the other hand, reactions with N₂O and O₂, particularly the latter, would require an additional input of energy to produce CuO because they are endothermic. Pro-

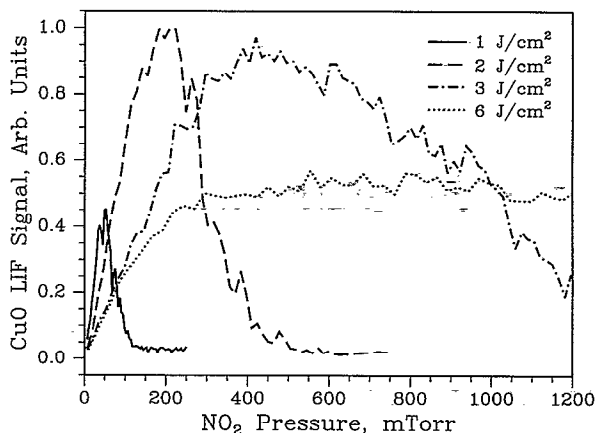


FIG. 3. Relative yields of CuO as a function of NO_2 pressure, for several incident fluences.

vided that sufficient energy is available for surmounting the reaction barrier, the increased reactivity observed with N_2O as compared to O_2 is consistent with its substantially lower bond energy. But the very high reaction rate with NO_2 cannot be explained on energetic grounds alone. Therefore, in addition to thermodynamic factors, the reaction dynamics has to be considered to explain the observed order of reactivity for the different gases.

It has generally been observed in molecular beam studies that the cross sections for the oxidation reactions with O_3 and NO_2 are substantially larger than those with O_2 and N_2O .⁹ The high reaction rates for these gases have been successfully explained in terms of the electron-jump (harpun) model.⁹⁻¹¹ In this model, the initial stage of the reaction involves transfer of the valence electron from the atom to the oxidant molecule as the two approach each other. The strongly attractive Coulombic force brings the two oppositely charged ions together and results in oxide formation. Thus an increase in reaction cross section would be expected with a decrease in the ionization potential of the metal atom and increase in the vertical electron affinity of the oxidant molecule. The high reactivity with NO_2 and O_3 can be attributed to the much higher vertical electron affinities for these molecules (2.36 and 2.5 eV, respectively) as compared to N_2O (-0.15 eV) and O_2 (0.44 eV)¹⁰ This helps explain the high reaction rate of Cu with NO_2 that we have observed during ablation of YBCO.

We finally consider the effect of the plume energy on the reaction, and also the influence of hydrodynamical effects which can cause substantial deceleration and attenuation of the plume species at high background gas pressures. The high collision energy and internal excitation of the plume species during PLD will undoubtedly influence the reaction cross section. For reactions without an activation barrier the reaction cross section usually decreases with increasing collision (translational) energy, whereas for reactions with a barrier the cross section initially increases in the post-threshold region before leveling off or

decreasing at much higher energies.¹¹ Thus for the endothermic reactions of Cu, the reaction cross sections would be expected to initially increase with collision energy. This is particularly valid during ablation in a relatively low pressure oxidant ambient, where the energy of the ablated neutrals is strongly dependent on the ablation laser fluence, and is typically in the range of 1-10 eV.

For gas pressures greater than about 10 mTorr, the ablated species undergo deceleration due to hydrodynamical effects, and show a continuous decrease in velocity with interaction distance.¹² The decrease in average collision energy due to deceleration may be partly responsible for the generally observed decrease in CuO concentration at higher pressures, as has also been suggested by Otis and Dreyfus.⁸ Moreover, the attenuation and broadening of the time-of-flight distribution of the plume species at higher pressures will also affect the measured concentration of CuO at a preset delay. In principle, a quantitative comparison would therefore require temporally integrated measurements of the CuO concentration for different background gas pressures. It should also be noted that the reduction in the CuO concentration discussed above can be partly compensated by the possibility of enhanced reactions at higher pressures because of the formation of a nonsteady shock wave. The shock wave will promote reaction between the ablated species and the shocked gas due to excitation and mixing in the high-temperature zone near the shock front.

In summary, we have monitored the gas-phase production of CuO during ablation of YBCO in different oxidizing ambients using LIF. We find that NO_2 and N_2O are much more effective than O_2 in the production of CuO, with the order of reactivity being $\text{O}_2 < \text{N}_2\text{O} < \text{NO}_2$. This suggests that, in addition to surface reactions, the enhanced gas-phase oxidation of Cu may be responsible for the increased effectiveness of NO_2 and N_2O as oxidizing agents during pulsed laser deposition.

¹ For example, see *Laser Ablation for Materials Synthesis*, edited by D. C. Paine and J. C. Bravman (Materials Research Society, Pittsburgh, PA, 1990), Vol. 191.

² R. Beyers and B. T. Ahn, *Ann. Rev. Mater. Sci.* **21**, 335 (1991).

³ A. Gupta and B. W. Hussey, *Appl. Phys. Lett.* **58**, 1211 (1991).

⁴ M. Kanai, T. Kawai, S. Kawai, and H. Tabata, *Appl. Phys. Lett.* **54**, 1802 (1989); G. Koren, A. Gupta, and R. J. Baseman, *ibid.* **54**, 1920 (1989).

⁵ S. Watanabe, M. Kawai, and T. Hanada, *Jpn. J. Appl. Phys.* **29**, L111 (1990); M. Kanai, K. Horiuchi, T. Kawai, and S. Kawai, *Appl. Phys. Lett.* **57**, 2716 (1990).

⁶ A. Gupta, B. W. Hussey, and M. Y. Chern, *Physica C* **200**, 263 (1992).

⁷ D. Fried, G. P. Reck, T. Kushida, and E. W. Rothe, *J. Appl. Phys.* **70**, 2337 (1991); R. C. Dye, R. E. Muenchausen, and N. S. Nogar, *Chem. Phys. Lett.* **181**, 531 (1991).

⁸ C. E. Otis and R. W. Dreyfus, *Phys. Rev. Lett.* **67**, 2102 (1991).

⁹ M. R. Levy, *Prog. Reaction Kinetics* **10**, 1 (1979).

¹⁰ J. W. Cox and P. J. Dagdigan, *J. Chem. Phys.* **79**, 5351 (1983); C. D. Jonah, R. N. Zare, and Ch. Ottinger, *J. Chem. Phys.* **56**, 263 (1972).

¹¹ R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics and Chemical Reactivity* (Oxford University, New York, 1987), pp. 26-206.

¹² D. B. Geohegan, *Mater. Res. Soc. Symp. Proc.* **201**, 557 (1991).