

Dynamics of laser-ablated particles from high T_c superconductor $\text{YBa}_2\text{Cu}_3\text{O}_y$

Osamu Eryu, Kouichi Murakami, and Kohzoh Masuda

Institute of Materials Science, University of Tsukuba, Tsukuba Academic City, Ibaraki 305, Japan

Atsuo Kasuya and Yuichirō Nishina

Institute for Materials Research, Tohoku University, Sendai, Miyagi 980, Japan

(Received 9 March 1989; accepted for publication 2 May 1989)

The dynamics of light-emitting particles produced by the excimer laser ablation of the high T_c superconductor $\text{YBa}_2\text{Cu}_3\text{O}_y$ has been investigated by means of space/time resolved optical measurements near the surface region with a space resolution of $100\ \mu\text{m}$ and a time resolution of $0.1\ \text{ns}$. Two distinct components of ablated particles were observed: one with high average velocities over $5 \times 10^6\ \text{cm/s}$ and the other with slow velocities, depending on laser energy density. The position of the maximum emission intensity in the slower component moved away from the surface and was further delayed from the time of maximum laser intensity as the laser energy density increased. If the incident laser was tilted from the normal of the target surface, the spatial distribution of the luminous plume inclined toward the incident laser beam. These results suggest that the slower component consists of light-emitting particles resulting from the fragmentation of clusters ejected from the surface.

Pulsed laser ablation and deposition have been employed for fabrication of high quality thin films of high T_c superconductors as a method for simple and reproducible preparation.¹⁻³ In particular, it has been reported that as-deposited films formed under suitable conditions at low substrate temperatures have a T_c of 85 K and a high critical current density J_c on the order of $10^5\ \text{A/cm}^2$ at 80 K without post-annealing.^{2,3}

Thin films of $\text{YBa}_2\text{Cu}_3\text{O}_y$, prepared using a Nd:YAG laser, show that their composition and crystallinity depend strongly upon laser energy density.⁴ This result suggests that particles in various forms and excited energy states are produced by laser ablation depending upon the laser energy density.

Recently, in an attempt to analyze the process of ablation, particles ejected from the $\text{YBa}_2\text{Cu}_3\text{O}_y$ surface by the irradiation of an excimer laser have been measured by mass and optical spectrometry.^{5,6} Though numerous investigators claim that the surface atoms evaporate thermally into monoatoms and their ions, several mass spectrometric measurements⁷ suggest that various cluster sizes are formed. These investigations suggest that in order to understand the laser ablation process for high T_c superconductors it is necessary to perform a transient analysis near the surface with high time/space resolution.

In this letter, we report the dynamical aspects of the laser ablation process deduced from space/time resolved measurements of the distribution of light-emitting particles near the target surface. Our measurements examine the transient behavior of the ablation process on a nanosecond time scale up to 100 ns. The results suggest that a surface layer is ablated in the form of clusters which eventually decompose into monoatoms and their ions. This interpretation is based on our simultaneous space/time resolved measurements which had not been carried out on these materials previously.

The block diagram of our experimental apparatus appears in Fig. 1. A Lambda-Physik EMG 50 KrF excimer

laser at the wavelength of 248 nm and a pulse width of 10 ns was used. The laser beam was focused on a stoichiometric $\text{YBa}_2\text{Cu}_3\text{O}_y$ pellet in a vacuum chamber with the base pressure lower than 10^{-5} Torr. The incident direction of the laser beam was normal (z direction) to the target surface, except for a measurement where the laser beam was tilted towards the tangential direction (y) to investigate the incident angle dependence of light emission. The light emission from the plume of ablated particles was detected by a television camera with a silicon intensified target (SIT) through a quartz window. Three different modes of measurement⁸ were used, i.e., (1) the space (z - y) mode, (2) time-space (t - z) mode, and (3) wavelength-space (λ - z) mode. The position of laser irradiation on the target was frequently changed to prevent damage affecting emission patterns. The streak

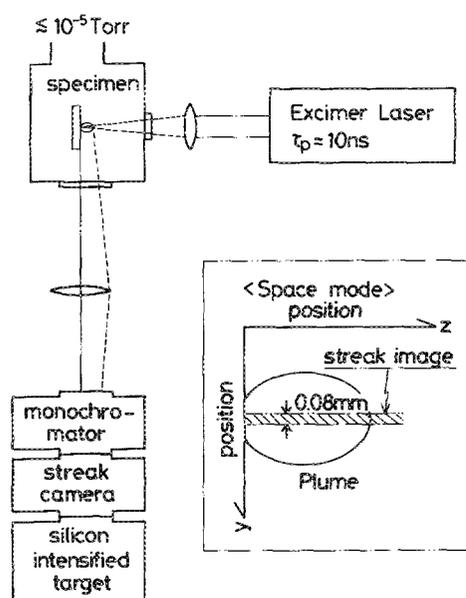


FIG. 1. Schematic diagram of the space/time resolved optical measurement system.

camera has a time resolution of 0.1 ns. The space resolution of emission pattern is estimated to be about 100 μm .

Figure 2 shows the streak pattern in the time-space mode of light emission from the plume of laser-ablated particles. Each pattern is recorded for one laser shot. The energy densities of the pulsed laser beam are (a) 0.14 J/cm², (b) 0.40 J/cm², and (c) 3.60 J/cm². In this measurement, the light emission from the plume was focused on the entrance slit of the streak camera, and the slit width in the direction y was set at 0.08 mm in order to obtain information concerning time-dependent light emission intensity at the center (shaded part) of the plume, as shown in the space mode in the inset of Fig. 1. The intensity distribution is represented by the tone of dotted patterns. The time t is measured from the peak of the laser pulse. Full width at half maximum of the laser pulse is indicated by the bar at the zero point of the abscissa. The vertical axis corresponds to the distance from the target surface as shown in Fig. 1. We changed the sensitivity of the streak camera to adjust the maximum intensity in the plume to a level nearly equal to the tone of the dotted patterns in each measurement. The intensity scale of the tone of (c) is higher by a factor of 16 compared to those of (a) and (b).

Figure 2(b) shows the presence of two distinct particle components, i.e., one slow moving, the other fast. Since the slope of the principal line of the time-space pattern represents the average expansion velocity of the light-emitting particles, the velocities are estimated to be 6×10^5 cm/s for the slow component and over 5×10^6 cm/s for the fast component.

As shown in Fig. 2(a), only the fast component pattern can be seen at lower energy densities. The intensity of light emission has a maximum in the area near the target surface at a time of 10 ns. The average expansion velocity is deduced to be over 5×10^6 cm/s. At higher energy densities, the slow component begins to appear and becomes dominant in the pattern as shown in Figs. 2(b) and 2(c). The expansion velocity of the slow component particles increases with in-

creasing laser energy density [e.g., 2×10^6 cm/s at 3.60 J/cm² in Fig. 2(c)]. Furthermore, with increase in laser energy density, the position of maximum emission intensity moves away from the surface and exhibits a greater delay in time.

We have also carried out measurements of the time-space mode for off-center portions ($y \neq 0$) of the plume for the energy density 1.5 J/cm². At $y = 0$, the time-space mode shows the presence of two distinct components at this laser energy density. At the edge of the plume, on the other hand, only the fast component was observed. This result suggests that the slow component of ablated particles expands with more forward direction in space than the fast component.

In order to examine the ablation process of luminous particles, we measured the changes in the space-mode pattern as the direction of the laser beam was tilted for angle θ from the z direction towards y . The angle $\Delta\theta$ corresponds to the angular deviation of the direction of the maximum emission intensity from the z direction. The inset shows the pattern in the space mode at $\theta = 60^\circ$ and at 0.26 J/cm². The result shows that the luminous plume inclines towards the laser beam as its incident angle θ is tilted from the normal of the target surface. Figure 3 also shows that for the same angle θ of measurements the $\Delta\theta$ decreases with increasing laser energy density.

The angular dependence in Fig. 3 applies only to those particles which emit light in the visible region. The angular dependence for the ablated particles including both radiative and nonradiative ones was measured by depositing them on a Si substrate in front of the target. Contrary to the distribution of radiative particles shown in Fig. 3, the θ dependence of the total deposited particles remains nearly the same regardless of the angle of the laser beam incidence. The results shown in Figs. 2 and 3 imply that those particles flying in the maximum intensity of laser beam mostly luminesce, as a result of their excitation in the plume.

In addition to the measurement of luminous particles, we measured the mass distribution of laser-induced YBa₂Cu₃O₇ fragments by means of time-of-flight measurements. For energy densities lower than 0.4 J/cm², no atomic mass peak of constituent elements was observed except for clusters lighter than 860 amu. With increasing laser energy density, atomic peaks and clusters heavier than 1500 amu appear in the spectrum.

From the above results, the directional dependence of the distribution of dense luminous particles may be explained by the ejection and subsequent decomposition of clusters,⁸ but cannot be explained only by the ordinary thermal evaporation of atoms. This conclusion is drawn from the two distinctive features of light emission found in our measurements shown in Figs. 2 and 3. Our space/time resolved analysis shows that particles ejected from the surface absorb laser energy after their ablation but exhibit a delay in their light emission from the peak of laser pulse at $t = 0$. These experimental facts cannot be explained by the desorption of surface atoms into atomic vapor. The inverse bremsstrahlung process of atomic absorption followed by prompt radiative recombination cannot explain our experimental results. The observed features suggest that the majority of particles

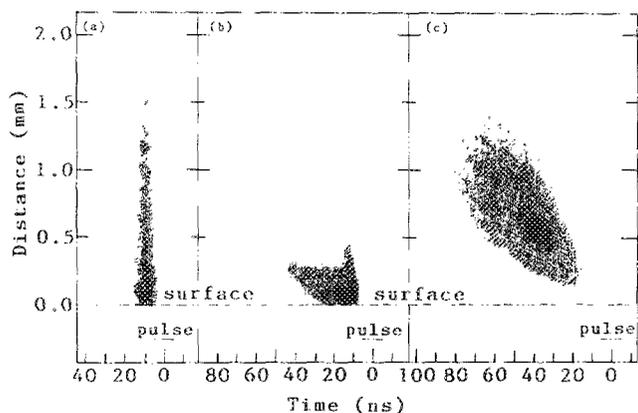


FIG. 2. Time-resolved measurements on intensity of the light emission from laser-ablated particles along the direction of laser incidence. Dotted line indicates the position of target surface. The densities of the pulsed laser beam are (a) 0.14 J/cm² (weak white color of emission), (b) 0.40 J/cm² (orange color of emission), and (c) 3.60 J/cm² (strong white color of emission), respectively.

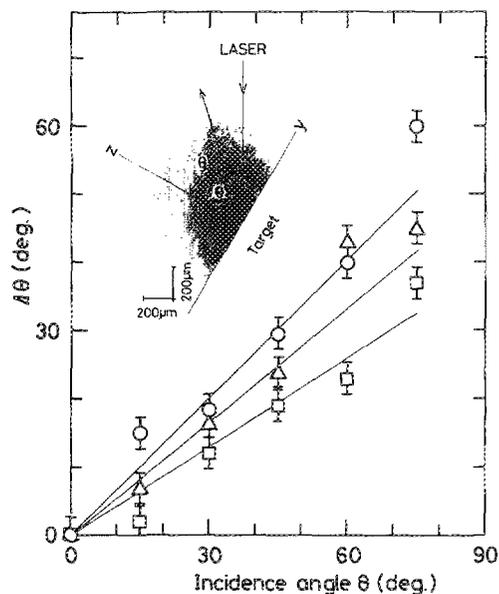


FIG. 3. Direction of the distribution dense luminous particles as a function of the direction of incident laser beam. Incident laser energy densities are (○) 0.14 J/cm^2 , (Δ) 0.26 J/cm^2 , and (□) 10.0 J/cm^2 , respectively, where only fast, fast and slow, and slow components are observed in the time-space mode measured, respectively.

ablated initially are neither atoms nor small particles, but clusters. Cluster sizes are thought to be below 1000 \AA in diameter.⁷ The absorption coefficient of these clusters is comparable to that of the solid, so that they are excited further by the latter part of laser pulse, as has been shown in the measurements shown in Figs. 2 and 3. The highly excited clusters eventually decompose by ejecting electronically excited atoms and their ions. With increasing laser energy density, the generation rate of atomic particles and plasma is enhanced due to the rapid decomposition of clusters. The atomic particles and plasma have smaller absorption coefficients compared to the clusters, so the degree of inclination decreases with the laser energy density as seen in our measurements shown in Fig. 3.

The position of maximal emission intensity in the time-space mode is further delayed with increasing laser energy

density [see Fig. 2(c)]. This may be caused by the production of a highly dense plasma by the inverse bremsstrahlung process. Hence, numerous highly ionized atoms and molecules are produced and their expansion velocity increases, so that the plasma recombination time becomes longer; i.e., the light emission is delayed.⁹ We believe that the direct cluster ejection from the surface is an essential mechanism for forming a film with stoichiometric composition, even though the clusters may decompose during the flight. The production mechanism of fast-component particles has not yet been clarified in detail at present.

In conclusion, the dynamics of the laser ablation process of $\text{YBa}_2\text{Cu}_3\text{O}_x$ oxide superconductor has been investigated by space/time resolved optical measurements. This experiment proves that there are two distinct components in produced particles, that is, the fast component and the slow component are ejected. Furthermore, it was found that the average velocity of the slower component particles increases with increasing laser energy density and the direction of the distribution of luminous particles inclines toward a laser incidence. These results, as well as the time-of-flight measurements, can be interpreted in terms of the ejection of clusters from the target surface followed by partial decomposition yielding light-emitting particles in a time scale of 1–100 ns after laser excitation.

- ¹B. Roas, L. Schlitz, and G. Endres, *Appl. Phys. Lett.* **53**, 1557 (1988).
- ²S. Witanachchi, H. S. Kwok, X. W. Wang, and D. T. Shaw, *Appl. Phys. Lett.* **53**, 234 (1988).
- ³A. Inam, M. S. Hegde, X. D. Wu, T. Venkatesan, P. England, P. E. Miceli, E. W. Chase, C. C. Chang, J. M. Tarascon, and J. B. Wachtman, *Appl. Phys. Lett.* **53**, 908 (1988).
- ⁴O. Eryu, K. Murakami, K. Takita, K. Masuda, H. Uwe, H. Kudo, and T. Sakudo, *Jpn. J. Appl. Phys.* **27**, L628 (1988).
- ⁵T. Venkatesan, W. D. Wu, A. Inam, Y. Jeon, M. Croft, E. W. Chase, C. C. Chang, J. B. Wachtman, R. W. Odom, F. Radicati di Brozolo, and C. A. Magee, *Appl. Phys. Lett.* **53**, 1431 (1988).
- ⁶P. E. Dyer, R. D. Greenough, A. Issa, and P. H. Key, *Appl. Phys. Lett.* **53**, 534 (1988).
- ⁷C. H. Becker and J. B. Palfix, *J. Appl. Phys.* **64**, 5152 (1988).
- ⁸A. Kasuya and Y. Nishina, in *Materials Research Society Symposium Proceedings, Boston 1988* (Materials Research Society, Pittsburgh, Pennsylvania, 1989).
- ⁹J. F. Ready, *Effects of High Power Laser Radiation* (Academic, New York, 1971), p. 171.