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1989 J. Phys. D: Appl. Phys. 22 1558

(http://iopscience.iop.org/0022-3727/22/10/025)

J. Phys. D: Appl. Phys. **22** (1989) 1558–1561. Printed in the UK

LETTER TO THE EDITOR

Time evolution of Nd:YAG laser-induced plasma from $GdBa_2Cu_3O_7$ high-T_c superconductor

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Received 1 June 1989, in final form 24 July 1989

Abstract. In order to characterise the laser ablation process from high-T_c superconductors, the time evolution of plasma produced by a Q-switched Nd:YAG laser from a $GdBa_2Cu_3O_7$ superconducting sample has been studied using spectroscopic and ion-probe techniques. It has been observed that there is a fairly large delay for the onset of the emission from oxide species in comparison with those from atoms and ions of the constituent elements present in the plasma. Faster decay occurs for emission from oxides and ions compared with that from neutral atoms. These observations support the view that oxides are not directly produced from the target, but are formed by the recombination process while the plasma cools down. Plasma parameters such as temperature and velocity are also evaluated.

Most of the spectroscopic studies of laser-induced plasma from high-T_c superconductors do not clearly reveal the presence of CuO and Cu^+ (Geyer and Weimer 1988, Auciello *et al* 1988, Weimer 1988, Dyer *et al* 1988). Geyer and Weimer (1988) observed the presence of YO in the plasma generated from a $YBa_2Cu_3O_7$ target. Existence of oxides and ions in the plasma is important to obtain good quality superconducting thin films. Weimer (1988) and Wu *et al* (1989) have observed the presence of oxides of Ba and Cu in the excimer-laser-induced plasma from $YBa_2Cu_3O_7$ targets. Recently, we have also observed the characteristic spectral emissions of GdO, BaO, CuO and Cu^+ along with lines of neutral atoms and ions in the laser-induced plasma from a $GdBa_2Cu_3O_7$ superconducting sample using a Q-switched Nd:YAG laser (Padmaja *et al* 1989). In the earlier studies, oxides and ions might have escaped detection due to the fast decay of emission from these species as a result of the recombination processes and plasma cooling. Time-resolved studies of the laser-induced plasma can therefore yield a greater amount of information regarding the complex ablation and transport processes (Wu *et al* 1989). The dynamic measurements of Wu *et al* (1989) are limited due to wavelength selection using optical filters ($\Delta\lambda \simeq 100$ Å) which makes it nearly impossible to study unambiguously the time evolution of the line and band emissions from individual species. In this Letter, we report our results on time-resolved measurements of the evolution process in the laser-induced plasma from a typical rare-earth based, high-T_c superconductor, $GdBa_2Cu_3O_7$ ($T_c = 93$ K), using spectroscopic and ion-probe techniques. Important parameters such as temperature and velocity are also evaluated from the present study.

Plasma was generated by laser ablation of a $GdBa_2Cu_3O_7$ target using a 1.06 μm laser beam from a Q-switched Nd:YAG laser (10 ns pulse width at 10 Hz repetition rate). The pulsed Nd:YAG laser system used in this experiment (Quanta-Ray DCR-11) has an unstable diffraction-coupled resonator. It gives uniphase, nearly diffraction limited output having a line width <1 cm^{-1} with 220 MHz spacing between the longitudinal modes. The specimen was mounted in a stainless steel vacuum chamber equipped with quartz windows so that the target can be irradiated at normal incidence and the plasma ejected from the surface can be viewed at right angles. The laser beam was focused (power density $\simeq 10^{13}$ W cm^{-2}) onto the target using a quartz lens. A part of the plasma plume at about 1.5 cm away from the target surface was focused onto the slit of the monochromator (Jarrel-Ash, 0.5 m) coupled to a PMT and a CRO/Boxcar averager. Since we have used a 0.5 m monochromator for wavelength separation ($\Delta\lambda < 1$ Å), the line selection is much more accurate than in the work of Wu *et al* (1989). Also, the spectra

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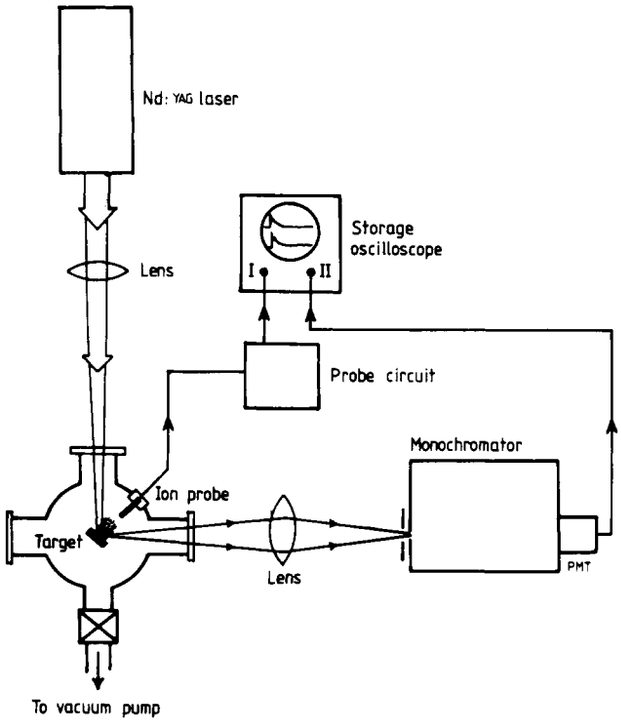

Figure 1. Schematic diagram of the experimental set-up.

were recorded photographically using a three-prism glass spectrograph (Carl-Zeiss) and the various atomic and molecular species in the plasma were identified. In order to study the time evolution of the species produced by laser irradiation, the characteristic lines were selected using the monochromator and the PMT output was fed to a 100 MHz storage oscilloscope (Tektronix Model 466) with a 50 Ω termination (figure 1).

In the ion-probe technique, a variable bias voltage (0–30 V) was applied between the probe and the body of the vacuum chamber. The electrons in the plasma were collected by the probe (3 cm length and 1.6 mm diameter) kept at about 1.5 cm away from the target surface (figure 1). The voltage pulse developed was measured across a 50 Ω load resistance on a 100 MHz storage oscilloscope. The probe current was studied as a function of probe voltage and from the *I–V* characteristics thus obtained, plasma temperature and plasma velocity were evaluated. Experiments were carried out at various laser power levels.

Detailed spectroscopic analysis of the plasma has been reported elsewhere (Padmaja *et al* 1989). Some of the major lines identified are given in table 1. Figure 2 is a typical CRO trace of the PMT response due to the line ($\lambda = 455.5$ nm) from the emission of copper ions. The response in this case has a time delay of 140 μs with respect to the laser pulse. This time delay was found to vary for different species (table 1). From the table, it can be seen that the oxide emission has a greater time delay compared with that of neutral atoms and ions. Initially, the plasma temperature is so high that oxide species apparently cannot exist. As the plasma cools down, recombination processes may give

Table 1. Time evolution of the spectral emission corresponding to various species (laser energy = 185 mJ/pulse).

Species	Wavelength λ (nm)	Time delay Δt (ms)	Decay constants b_1	Decay constants b_2
Cu	612.7	0.10	0.30	1.67
Cu^+	455.5	0.14	0.35	1.70
CuO	616.3	0.54	0.46	1.70
Ba	413.2	0.08	0.27	0.80
Ba^+	416.7	0.12	0.20	1.00
BaO	586.0	0.40	0.53	0.88
Gd	493.4	0.06	0.22	0.96
Gd^+	509.8	0.04	0.29	1.19
GdO	566.4	0.42	0.38	1.40

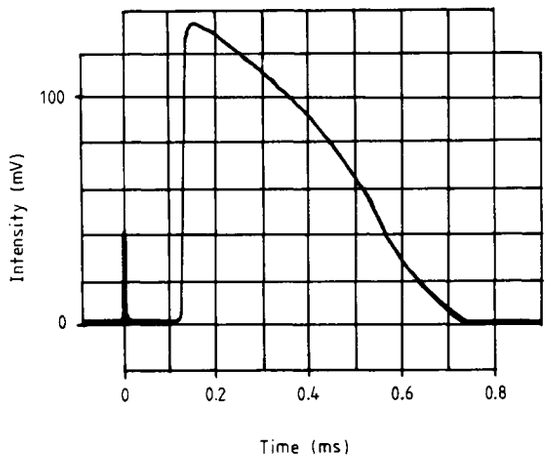

Figure 2. Typical CRO trace of the PMT response due to the emission line ($\lambda = 455.5$ nm) of copper ions.

rise to the formation of more oxides. A log–log plot of the time dependence of the emission intensities of all the species reveals an initial period of slow decay followed by a comparatively faster decay. Figure 3 shows such typical plots for the plasma emission lines of Cu, Cu^+ and CuO. The power law can therefore be expressed as

$$I(t) \simeq H(t_1 - t)t^{-b_1} + H(t - t_1)t^{-b_2} \qquad (1)$$

where $H(\tau)$ is the Heaviside function so that $H(\tau) = 1$ for $\tau \geqslant 0$, and 0 for $\tau < 0$. Decay constants b_1 and b_2 for various species are given in table 1. A careful analysis of these magnitudes will give some of the valuable information required for plasma diagnosis. The two time-periods evidently represent the 'hot' and 'cold' phases of the plasma. It is worth noting that in the hot plasma

$$|b_1|_{GdO} < |b_1|_{CuO} < |b_1|_{BaO}$$

and in the cold plasma

$$|b_2|_{CuO} > |b_2|_{GdO} > |b_2|_{BaO}.$$

This shows that the emission from CuO molecules dies down rather quickly.

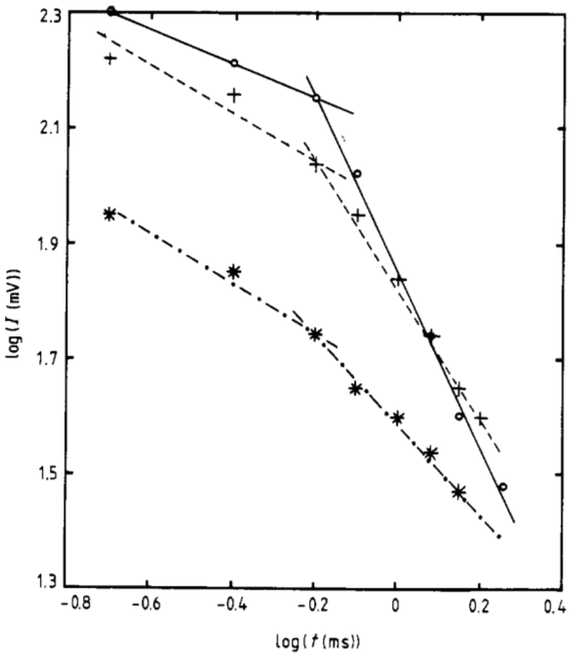

Figure 3. Plot of log I against log t for emission of Cu, Cu^+ and CuO: ○, Cu (λ = 612.7 nm); +, Cu^+ (λ = 455.5 nm); *, CuO (λ = 616.3 nm).

From the time delays observed, it is evident that the oxide species are formed only when the plasma temperature begins to fall. Under this condition, the absence of a continued excitation process required for the emission from the oxide species may cause a rapid reduction in the intensities of such bands. This aspect also lends support to the view that the oxide species may not be originating from the target material as such but are formed as a result of recombination processes as the hot plasma cools down. The oxygen deficiency, which is a critical parameter for the superconductivity in high-T_c ceramics, can thus be controlled by adjusting the partial pressure of oxygen in the plasma chamber during the process of thin-film deposition using the laser ablation method.

Figure 4 shows the time-evolution characteristics of the plasma recorded using a Langmuir probe at a laser energy of 185 mJ/pulse. From the slope of the I–V plot, the plasma temperature is calculated using the equation

$$e/kT_e = S \tag{2}$$

where S is the slope of the I–V curve ($S = 0.02$). The temperature of the plasma was calculated to be 5.8×10^5 K. The plasma (electron) velocity is given by

$$v_e = (8kT_e/\pi m_e)^{1/2} \tag{3}$$

where m_e is the mass of the electron. The velocity of the negative ions in the plasma was calculated to be 4.5×10^8 cm s^{-1}. For positive ions in the plasma, the velocity is given by

$$v_+ = (8kT_e/\pi m_+)^{1/2} \tag{4}$$

where m_+ is the mass of the positive ions in the plasma.

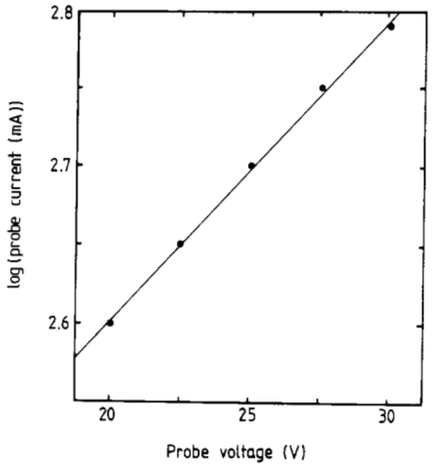

Figure 4. Plot of log (probe current) against probe voltage of the Langmuir-probe signal at a laser energy of 185 mJ/pulse. Slope = 0.02.

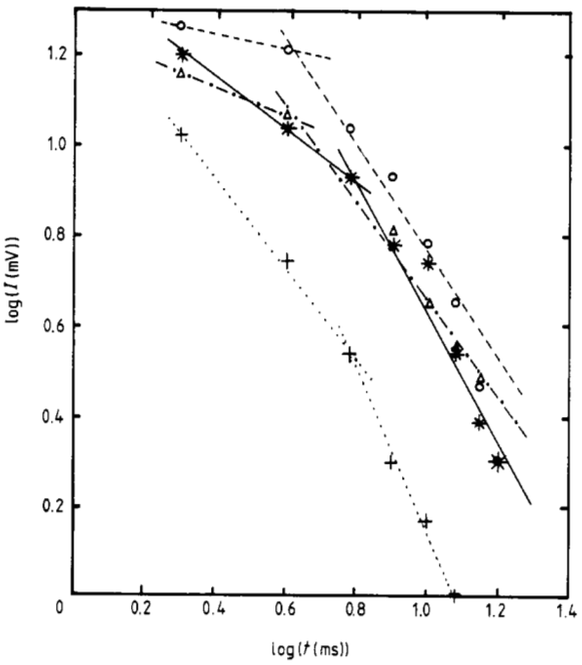

Figure 5. Plots of log I against log t of the laser-produced plasma from the high-T_c $GdBa_2Cu_3O_7$ plasma at various probe voltages: Laser energy = 230 mJ/pulse. ○, 27.5 V; *, 25 V; +, 22.5 V; △, 20 V.

The velocity of the positive ions in the plasma was calculated to be 1.06×10^6 cm s^{-1} (for an average value of the positive ion mass in the plasma). These values for the particle velocities prove conclusively that the observed delays for the emission from various atomic and molecular species are not due to a time-of-flight phenomenon as suggested by Dyer *et al* (1988). While plasma expansion velocities can bring about a small delay, the major part of the observed delays does seem to arise from the recombination process. The log–log plot (figure 5) of the temporal decay of the ion-probe current has two slopes S_1 and S_2 so that, as in the case

Table 2. Time evolution of Langmuir-probe pulse for various probe voltages and two values of laser energy.

Probe voltage (V)	Decay constants			
	230 mJ/pulse		185 mJ/pulse	
	S_1	S_2	S_1	S_2
20.0	0.84	1.67	0.82	1.93
22.5	0.94	1.44	0.40	1.38
25.0	0.53	1.31	0.13	0.80
27.5	0.17	1.15	—	—

of plasma intensity variation, the probe current $I(t)$ can be written as

$$I(t) \simeq H(t_1 - t)t^{-S_1} + H(t - t_1)t^{-S_2}. \qquad (5)$$

Decay constants, in this case, depend on the probe voltage and are given in table 2. The electrons produced during laser ablation develop as a sheath around the probe which causes an initial slow decay of the pulse. The decay becomes faster when the probe potential breaks the plasma sheath. Some control over the stoichiometry and composition of the film obtained can therefore be effected by creating an electric field near the substrate during the laser-induced plasma-deposition process of high-T_c materials.

In conclusion, we have studied the time evolution of the spectral emission from the laser-ablated plasma from a high-T_c ceramic material. Emission from the oxide species is found to take place after a significant time delay. Diatomic oxides are apparently not formed directly from the target material but seem to be generated by ion–oxygen recombination when the plasma begins to cool down. An external electric field can affect the recombination rates and, thus, the composition, of the high-T_c superconducting thin film deposited on a substrate can be controlled to some extent when the laser-ablation method is used for this purpose.

The authors wish to thank the Department of Science and Technology, Government of India and the University Grants Commission, New Delhi for financial assistance. Support from the Ministry of Human Resource Development, Government of India, is also gratefully acknowledged.

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