PLASMA PLUME DYNAMICS AND YBaCuO SUPERCONDUCTING THIN FILM PREPARATION IN EXCIMER LASER ABLATION PROCESS

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ABSTRACT
Plasma plume dynamics and superconducting thin film preparation in an excimer laser ablation are studied. The plasma plume was generated by ablating YBaCuO superconducting bulk targets using a KrF(λ=248nm) excimer laser. Spectroscopic measurement showed that the plasma plume emits many spectral lines originated from Y, Ba, Cu, their ions and oxides. The YBaCuO thin films deposited at 710 °C have zero-resistivity critical temperature of 87.2 K and critical current density of $10^5$ A/cm$^2$.

INTRODUCTION
Pulsed laser deposition (PLD) has shown great promise in producing high temperature oxide superconducting thin films with good epitaxy, and high critical current density and transition temperatures. Although laser ablation dynamics in the oxide superconducting films has been studied by many researchers /1/, a further understanding of the PLD process is required to prepare high-quality superconducting films for electronic and power devices applications. Efforts to understand the laser beam-solid interaction during the deposition of superconducting thin films have concentrated mainly on characterizing the laser-induced plasma plume. Correlation between film quality and plasma plume properties have been made. The plasma plume during laser ablation has been studied using the spectroscopic method /2/-/5/ and mass spectrometric technique /6/,/7/.

In this paper, we present dynamics of the plasma plume and preparation of high-quality YBaCuO superconducting thin film by a KrF excimer laser ablation technique. The optical emission of the plasma plume during laser ablation of YBa$_2$Cu$_3$O$_{7-x}$ superconducting targets is analyzed to make clear appearance of excited species from the targets and formation of diatomic oxides. Effects of ambient O$_2$ pressure relevant to superconducting thin film growth are also discussed with optical emission spectroscopy. In addition, a plasma-assisted PLD process is attempted to prepare the films at lower process temperatures.

EXPERIMENTAL
Pulsed laser ablation technique has been used for fabrication of high-quality oxide superconducting thin films as a method for simple and reproducible preparation. Figure 1 shows a schematic diagram of a KrF excimer laser deposition system used here /8/,/9/. A Lambda Physik excimer laser (LPX 305icc: $\lambda = 248$ nm, pulse width = 30 ns, 1200 mJ max) was used to ablate the YBaCuO target in a deposition chamber.
Pure oxygen was introduced into the chamber and the total pressure during the film deposition was maintained at 100-300 mTorr. The laser beam was focused on the area (2x5 mm²) of the stoichiometric pellet rotated at 12 rpm. The laser energy density on the target surface was varied from 1 to 3 J/cm². The MgO (100) substrate placed at a distance 4-8 cm from the target was heated to 600-750 °C. Plasma plumes generated by the pulsed laser ablation were investigated by using a monochromator. The resulting films were characterized using x-ray diffraction, SEM, EPMA and the resistivity vs temperature measurements.

RESULTS AND DISCUSSION

In order to control the PLD process for high-quality superconducting thin films, it is of importance to understand the photophysical interaction between the pulsed laser and the target surface, the dynamics of the expanding plasma plume, its interaction with ambient gas and transient film growth on the substrate surface. Emission spectroscopy has been applied to understand the above complex phenomena of the plasma plume in the PLD process.

Figure 2 shows emission spectra of the YBaCuO plasma plume generated at a base pressure (about 10⁻⁵ Torr) and 200 mTorr O₂. The plasmas were produced using a laser fluence of 2 J/cm² with laser repetition rate of 5 Hz. The optical emission measurement was made at a distance d = 10 mm from the target surface. Prominent lines in the emission spectra have been assigned to neutral and ionic species such

![Diagram](image)

**Fig.1** A schematic diagram of the KrF excimer laser deposition system.

![Graphs](image)

**Fig.2** Emission spectra of the plasma plumes generated at the base pressure (top) and 200 mTorr (bottom); 2 J/cm², d=10mm.
as Y, Y⁺, Cu, Cu⁺, Ba, Ba⁺. In addition, the band emission originated from diatomic oxide species such as YO, BaO, and CuO have been detected. When the oxygen gas was introduced, spectral intensity for the diatomic oxides increases as evidence of formation of oxides in the plasma plume.

We studied the superconducting film growth mechanism by analyzing the temporal and spatial evolution of the plasma plume. The plume occurs when the laser power density is higher than the threshold value of about 10⁷ W/cm². Dyer et al. showed in the KrF excimer laser ablation that the threshold for ablation of the bulk YBaCuO target was 0.35-0.4 J/cm²/10/. It is well-known that when the laser pulse ablates the target, a burst of electrons and ions is emitted in addition to a copious amount of neutrals. The energized particles ejected from the targets surface collide with ambient gas (O₂).

Figure 3 shows the temporal evolution of spectral intensity of YI 412.830 nm at several values of distance d. It is found that the emission intensity decreases with the distance. Beyond a distance d = 30 mm, no significant emission was detected in the present experimental conditions. It is noticed that increase of distance d provides slow rise time of the intensity and large relaxation duration. It is also shown that the temporal location of the maximum emission intensity moves with the change of distance d.

Figure 4 shows the temporal evolution of emission bands of YO 613.210 and CuO 445.300 nm at d = 10 mm. The CuO band intensity has its peak at 1 μs but the YO band shows the peak at 2 μs. This result suggests that the oxide CuO is ejected in the molecule from the target but that the oxide YO subsequently is formed due to the collision with the excited oxygen in the plasma plume. The existence of gas phase reaction is considered to be essential for the production of high-quality as-grown superconducting films. This fact is also confirmed that when we increase the ambient pressure, the YO intensity increases proportionally to the O₂ pressure but that the CuO intensity shows only slightly increase of the intensity for the pressure increase.
Figure 5 shows the dependence of the spectral intensities (peak signals) for different oxide species on a distance $d$. The band emission originated from oxides species rapidly decreases with the distance and the emission from the $YO$ and $BaO$ species shows slow decay due to their gas phase formation. The ionization potentials are 6.378 eV for $Y$, 5.211 eV for $Ba$ and 7.726 eV for $Cu$, respectively. Higher ionization potential of $Cu$ atoms is estimated to suppress $CuO$ formation in the plasma plume. The excited oxygen atoms ($O^*$) in the plasma plume can collide with elements as following:

$$Y + O^* \rightarrow YO^*$$
$$Ba + O^* \rightarrow BaO^*.$$

These excited oxides can radiate their specified band emission on the way to the substrate.

Our experiments showed that the superconducting properties of the $YBaCuO$ films prepared by the present KrF excimer laser ablation technique change depending dominantly on the $O_2$ pressure and the substrate temperature. Figure 6 shows typical resistivity-temperature characteristics of the $YBaCuO$ thin film deposited at the substrate temperature of 710 °C and at the $O_2$ pressure of 200 mTorr. These are optimum conditions for our PLD process operated at a laser fluence of 2 J/cm². The film thickness was 0.3 μm. The film shows the superconducting transition with the zero resistivity critical temperature $T_c(\text{zero})$ of 87.2 K. The film has critical current density (at 77 K, zero magnetic field) of $10^5$ A/cm² and compositional ratios of $Ba/Y=1.58$ and $Cu/Y=4.0$.

A plasma-assisted laser ablation process has been developed to produce high-quality superconducting thin films at reduced substrate temperatures /2/./11/. We investigated the effect of the dc oxygen plasma on the deposited films. As illustrated in Fig.1, the dc oxygen plasma was generated by applying a dc positive voltage of 300 V to a ring electrode

**Fig.5** Distance dependency of the spectral intensities for different diatomic oxides.

**Fig.6** Typical resistivity vs temperature characteristics of the film deposited by the KrF excimer laser ablation at substrate temperature of 710 °C.
placed between the target and the substrate. Figure 7 shows the resistivity vs temperature curves of the films deposited at a low substrate temperature of 660°C. This result shows that the dc oxygen discharge improves the superconducting properties of the thin films prepared at low substrate temperature. Although the film deposited without the discharge has the critical temperature less than 77 K and higher normal resistivity, the plasma-assisted laser ablation technique provides the YBaCuO superconducting films with T_c(zero) of 87 K and the critical current density of 5x10^4 A/cm². This is due to the production of a copious amount of the excited oxygen species enhancing the transition from tetragonal structure to orthorhombic structure.

CONCLUSION

Plasma properties of a KrF excimer laser ablation for the preparation of high-temperature superconducting thin films are investigated by using the spectroscopic technique. It was shown that the ablation and the gas phase reaction of copper element and copper oxide are different from other elements and oxides. Reduction of the processing temperature could be realized by combining with the dc oxygen discharge plasma.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the extensive collaboration with Mr. K. Nakashima and Mr. H. Masunaga.

REFERENCES