

# OPTICAL EMISSION STUDY OF THE LASER PLASMA PLUME PRODUCED DURING Y-B-C-O SUPERCONDUCTING AND Pb-Zr-Ti-O FERROELECTRIC FILM PREPARATION

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## ABSTRACT

We report the optical emission study of the pulsed plasmas generated by the excimer laser ablation while the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (Y-B-C-O) high temperature superconducting thin film and lead-zirconium titanate (PZT) ferroelectric film were deposited. In the preparation of the Y-B-C-O films the various atomic, ionic and molecular species were identified. It is shown that the deposited film-quality is dominated by the oxide formation in the gas phase reaction. During the PZT film preparation, optical emission originated in Pb,  $\text{Pb}^+$ , Zr, Ti, and  $\text{Ti}^+$  species were detected. The PZT film prepared on MgO substrate at  $600^\circ\text{C}$  showed the perovskite structure having the ( $n00$ ) orientations.

## 1. INTRODUCTION

The integration of high temperature oxide superconducting layers and a ferroelectric oxide layer has attracted much attention in the potential feasibility of the superconducting electronic devices. Recently, the investigation of novel three-terminal superconducting electronic devices has been of great interest due to the promise of high speed, high density and lower power consumption of devices [1-3]. In this device the transport properties of a  $\text{YB}_2\text{Cu}_3\text{O}_{7-x}$  (Y-B-C-O) film are modulated by application of great voltage across a dielectric layer and a consequent change of the charge carrier density in the superconductor. Lin *et. al.* reported a novel ferroelectric superconductor three-terminal device by replacing the dielectric gate with a ferroelectric such as  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  [PZT] film [3]. High temperature superconducting heterostructure consisted with PZT film can improve performance of the device, especially electric field

effect in the three-terminal superconducting device. This is due to the fact that PZT ferroelectric oxide is the perovskite oxide family with high permittivity, high emission current, piezoelectric, electro-optic, and pyroelectric phenomena.

PZT/Y-B-C-O heterostructures have been fabricated by the pulsed excimer laser ablation [4-6]. In this paper, we have investigated the optimal deposition conditions for PZT and Y-B-C-O thin film using the excimer laser ablation process. The nature of the laser generated plasma significantly influences superconducting properties of Y-B-C-O thin film and dielectric properties of PZT film. Optical emission spectroscopy can provide a convenient monitor for optimization of plasma conditions during the film deposition. Here, we identify various species and study the dynamics of the laser generated plasma plume.

## 2. EXPERIMENTAL

A schematic diagram of the experiment is shown in elsewhere [4-6]. A KrF excimer laser (Lambda Physik LPX305icc:  $\lambda=248$  m, pulse duration=25ns, max. energy= 850mJ) was used to ablate the targets in a deposition chamber ( $\phi 400 \times 500$ mm). We have used a stoichiometric bulk target of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  and  $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ . The laser beam with  $1.5\text{J}/\text{cm}^2$  was made incident on the small area ( $2 \times 5\text{mm}^2$ ) of the target at an angle of  $45^\circ$ . The target was rotated at 12 rpm to avoid texturing of its surface. A mixture of oxygen and argon was led into the chamber and total pressure was in the range of 100-300mTorr. Optical emission from the plasma plume was collected by a quartz lens and imaged onto an entrance slit of 0.25-m monochromator (Nikon P-250). Plasma emission spectra were obtained by temporally integrating over several consecutive laser shots at a repetition rate of 10 Hz. For time-resolved measurements, the emission intensity at the specified wavelength was accumulated and averaged 16 consecutive laser events using a fast photomultiplier (Hamamatsu R955).

The Y-B-C-O and PZT thin films were grown on MgO (100) substrates placed at a distance 4-8 cm from the target surface. The substrate was heated up to 600-750°C. The films were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), electron probe micro analysis (EPMA), and resistivity-temperature (R-T) measurements.

## 3. RESULTS AND DISCUSSION

### 3. 1 Wavelength identification and dynamics of Y-B-C-O plasma

The integrated plasma emission are shown in Fig. 1 for different mixture ratios  $R=\text{Ar}/(\text{Ar}+\text{O}_2)$ . In these spectra, strong emission are observed from atomic, ionic and diatomic oxide species [4]. At the base pressure of  $10^{-5}$ Torr, diatomic oxides such as YO, BaO, CuO are absent from the observed species. These molecular emission appears when oxygen gas is added to the ambient gas. This shows that diatomic oxides are formed by a chemical reaction in the plasma plume after the laser irradiation.

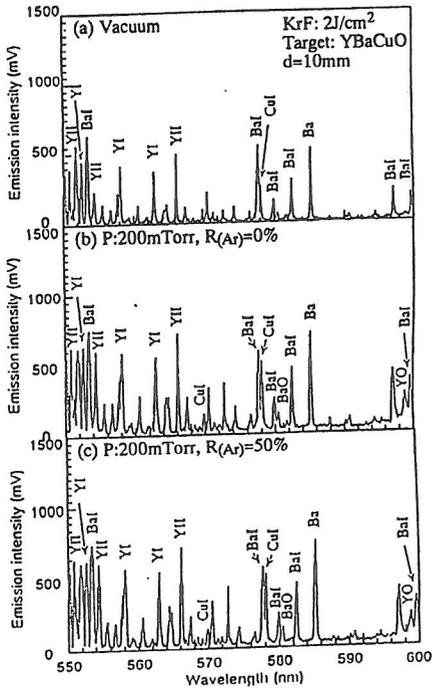


Fig. 1 Emission spectra of Y-B-C-O plume at different R.

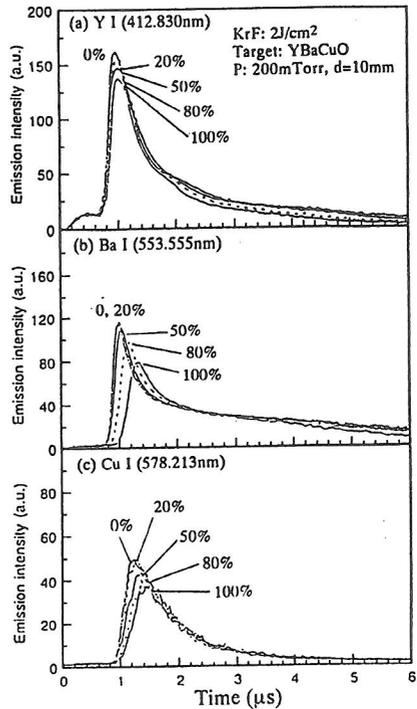


Fig. 2 Time-resolved spectral intensity of Y I, Ba I and Cu I.

Fig. 2 shows the temporal evolution of Y I (412.830nm), Ba I (553.555nm), and Cu I (578.213nm) emission at a distance from the target surface  $x=10\text{mm}$ . The plasmas were generated at various gas mixture ratios of total pressure 200mTorr. It is shown that, when oxygen content decreases, that is, argon ratio  $R$  increases, the atomic emission decreases and peak intensity appears after a few  $\mu\text{s}$  delay. Fig. 3 shows time-resolved spectral intensity originated in diatomic oxides: YO (613.210nm), BaO (580.500nm), CuO (445.300nm). The plasma was produced at 400mTorr and a laser fluence of  $2\text{J}/\text{cm}^2$  and the measurements were carried out at 10mm from the target surface. The molecular YO emission arises at  $0.7\mu\text{s}$  after the laser pulse. This result suggests that the YO molecule are formed in the plasma plume through the reaction:  $\text{Y} + \text{O}_2 \rightarrow \text{YO}^* + \text{O}$  [5]. The faster emission of BaO and CuO having their peaks at  $0.5\mu\text{s}$  is attributed to direct laser ablation from the target.

### 3. 2 Superconducting properties of Y-B-C-O

The relationship between the zero-resistivity temperature ( $T_{\text{C}}(\text{zero})$ ) and the total pressure is plotted in Fig. 4 at various argon mixture ratios  $R$ . As concerning the films

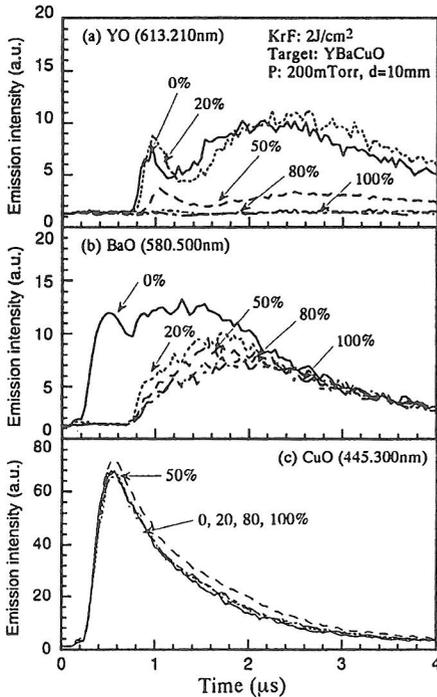


Fig. 3 Time-resolved spectral intensity of diatomic oxides of YO, BaO and CuO.

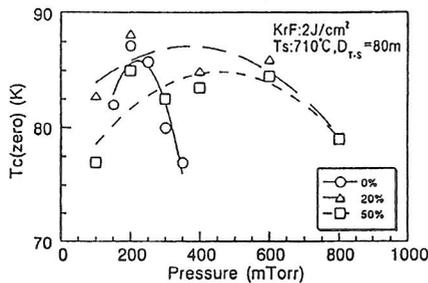


Fig. 4  $T_c(\text{zero})$  of Y-B-C-O film versus total pressure as a function of R.

deposited in pure oxygen, the  $T_c(\text{zero})$  changes drastically with the total pressure. However, using the mixture gas, the pressure requirement to prepare the high-quality Y-B-C-O film is relaxed. Also, the films deposited in the mixture gas are strongly oriented the  $c$ -axis. By using the mixture gas of oxygen and argon, the superconducting properties of the Y-B-C-O films are improved.

### 3. 3 Wavelength identification and dynamics of PZT plasma

Fig. 5 (a) and (b) show temporally integrated emission spectra from PZT plasma plume generated at the base pressure and the 200mTorr in oxygen, respectively. In these spectra, many strong emission from atoms and ions are observed, but no apparent emission from oxide species is detected.

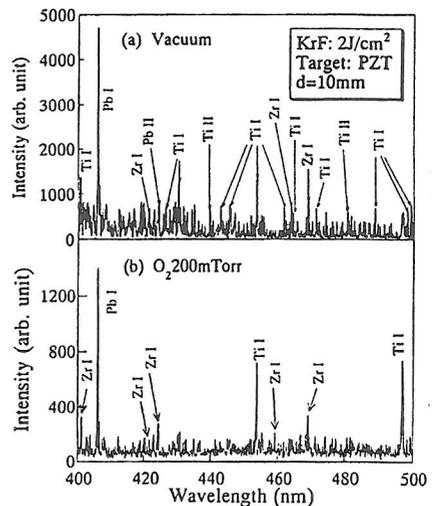


Fig. 5 Plasma emission spectra of PZT plume.

Table 1 Identified emission wavelength for PZT plasma plume.

Species	Identified wavelength (nm)											
Pb I	405.8	722.9										
Pb II	515.6											
Ti I	400.6	400.9	401.5	403.1	415.1	416.0	418.9	430.1	430.6	442.7	445.5	
	445.7	453.6	453.7	461.7	464.5	471.0	488.5	496.9	498.2	499.1	500.7	
	501.4	501.6	502.6	503.6	506.5	512.0	517.4	521.0	522.0	522.5	551.5	
	609.1	612.6	625.8	626.1	654.6	701.1	728.2	730.7	736.7	796.2		
Ti II	430.2	435.1	439.6	480.6								
Zr I	401.2	404.4	406.2	409.0	415.3	424.2	424.3	468.8	468.9	507.8	511.5	
	566.5	568.1	612.2	612.8	614.3							
Zr II	404.9	405.0	414.9									

Table 1 summarizes the identified atomic and ionic lines for the PZT plasma generated at the laser fluence of  $2\text{J}/\text{cm}^2$ . Fig. 6 show time-resolved emission intensities from Pb, Zr and Ti atoms, which were obtained at a distance of 10mm from the target surface. The PZT plasma plume was generated under the conditions of  $2\text{J}/\text{cm}^2$  and 200mTorr in oxygen. The emission intensities take a maximum value at  $3.0\mu\text{s}$  for Ti I,  $3.2\mu\text{s}$  for Pb I and  $3.5\mu\text{s}$  for Zr I delayed with the laser irradiation. The velocity of Ti, Pb and Zr atoms is  $3.3 \times 10^5\text{cm/s}$ ,  $3.1 \times 10^5\text{cm/s}$  and  $2.9 \times 10^5\text{cm/s}$ , respectively. The velocity difference between these atoms becomes larger when the pressure is increased.

### 3. 4 Film properties of PZT

We have prepared the PZT films on MgO (100) substrates under various substrate temperatures and pressures. From results of EPMA and SEM, the stoichiometric PZT films with smooth surface have been deposited at a substrate temperature ( $T_s$ ) of  $600^\circ\text{C}$ . The XRD spectra of the PZT films prepared at  $T_s=600^\circ\text{C}$  under various oxygen gas pressures are shown in Fig. 7. Closed and open triangles indicate the peaks for the pyrochlore and perovskite phase of PZT, respectively. As shown in Fig. 7, both peaks for pyrochlore and perovskite phase are observed in all samples. With the increase of oxygen gas pressure, however, the intensity of the perovskite phases diminish. At gas pressure above 100mTorr, the perovskite peak at

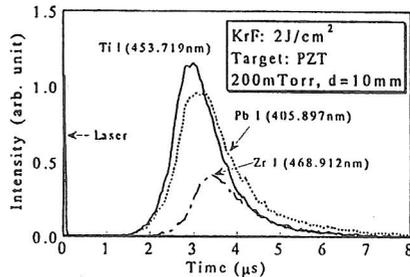


Fig. 6 Time-resolved spectral intensity of Ti I, Pb I and Zr I.

$2\theta=64^\circ$  disappears. All other peaks related to the perovskite phase are strong at 70mTorr.

#### 4. CONCLUSION

We described the properties of Y-B-C-O and PZT plasma plumes generated by a KrF excimer laser irradiation. In preparation of Y-B-C-O film, using argon and oxygen mixture as an ambient gas, we can control the flux of ablated species and improve the superconducting properties of the resulting Y-B-C-O films. In the investigation of PZT plasma plume, many atomic and ionic lines are identified. Also, we have shown that PZT films with a single perovskite phase can be grown on MgO (100) substrate using pulsed laser deposition technique. The authors wish to thank Mr. C. S. Choi and Mr. K. Shinohara for their help in experiments.

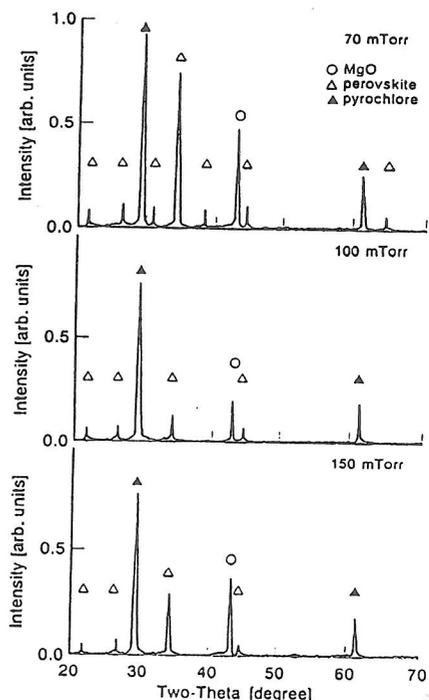


Fig. 7 XRD pattern for PZT films on MgO (100) at  $T_s=600^\circ\text{C}$ .

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