
Plasma phase oxidation during preparation of oxide superconducting and ferroelectric thin films using pulsed laser deposition

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Abstract

Plasma phase oxidation was investigated during preparation of Y–Ba–Cu–O (YBCO) superconducting and Pb–Zr–Ti–O (PZT) ferroelectric thin films using KrF pulsed laser deposition. The YBCO and PZT plasma plumes were produced at a laser fluence of 0.1 to 6 J/cm², a mixture ambient of oxygen and argon and a pressure range of 10⁻⁶–1 Torr. In the YBCO ablation, YO and BaO molecules are formed in the ablation plasma with different reactivities, while most of the CuO molecules are ejected from the target. In the PZT film preparation, TiO molecules are generated in the plasma phase. Plasma phase oxidation affects strongly the characteristics of oxide superconducting and ferroelectric thin films.

1. Introduction

Pulsed laser deposition (PLD) has been widely used to prepare thin films of various ceramic materials, especially high temperature superconducting (HTS) and ferroelectric films, because of its powerful advantages of reproducibility on film characteristics and high deposition rate. As for these oxide ceramic films, oxygen atoms incorporated in the films play an important role in the film characteristics such as chemical stoichiometry and crystallization. Therefore, in order to prepare high-quality thin films and to extract further potential from the PLD, it is required to control an interaction between a laser-produced plasma plume and ambient gas including oxygen. Although there are many publications describing the plasma plume dynamics using optical emission spectroscopy [1,2] and the laser-induced fluorescence method [3,4], only a few papers describe plasma phase oxidation during oxide film preparation [5].

Ferroelectric thin films offer applications such as non-volatile random access memories, surface acoustic wave devices [6], pyroelectric detectors [7] and piezoelectric vibrators [8]. HTS films have been regarded as a better electrode for ferroelectric memory devices than traditional Pt metal electrode. Furthermore, HTS-ferroelectric hybrid film is of great interest in the application to a superconducting field-effect transistor [9]. Specifically, a PbZr₄Ti₁₋ₓO₃ (PZT) ferroelectric thin film has drawn much attention in the device application, because of its high permittivity and ferroelectric switching properties.
We have investigated the oxidation in plasma phase during the preparation of YBa$_2$Cu$_3$O$_{7-x}$ (YBCO) HTS and PZT ferroelectric thin films using the PLD method [1,10]. Spectroscopic technique and Mach–Zehnder interferometry were used to measure the dynamics of the plasma plumes. In this paper, we investigate the plasma phase oxidation in YBCO and PZT plasma plumes produced by a KrF excimer laser, and describe the characteristics of the YBCO and the PZT films.

2. Experimental

Fig. 1 shows a schematic of the pulsed laser deposition system with a spectroscopic analyzing system. A KrF excimer laser (Lambda Physik LPX-305icc) was used to irradiate a target placed in the deposition chamber ($\geq 400 \times 500$ mm). We used a superconducting YBa$_2$Cu$_3$O$_{7-x}$ target and a ferroelectric PbZr$_{0.52}$Ti$_{0.48}$O$_3$ target. The laser beam was focused onto the target surface ($\geq 5$ mm) with an incident angle of 45°, and its fluence was varied from 0.1 to 6 J/cm$^2$. An ambient gas was a mixture of oxygen and argon, and a pressure range was $10^{-6}$–1 Torr. The YBCO and PZT thin films were deposited on MgO(100) substrates.

Optical emission from the plasma plume generated by the laser irradiation were imaged onto an entrance slit of the monochromator (Nikon P-250). The time-resolved emission spectra were detected by a photomultiplier (Hamamatsu R955). In order to improve a signal to noise ratio, those were averaged by the digitizing oscilloscope and data were transferred to the personal computer. Emission at several points away from the target surface were measured in various pressures.

3. Results and discussion

3.1. Plasma plume dynamics

Fig. 2 shows the time-resolved spectral intensities of (a) YO, (b) BaO and (c) CuO in the YBCO plume. It is clearly shown in Fig. 2(a) that spectral intensity of YO molecules decreases with increasing argon mixture ratio ($R_A$) and disappears without oxygen gas ($R_A = 100\%$).
Although the emission intensities of the BaO molecules decrease with increasing $R_{Ar}$, the oxide emission still remains at low oxygen mixture rate (Fig. 2(b)). On the other hand, the emission intensities of CuO show little change with $R_{Ar}$. Fig. 3 shows the spectral intensity changes of (a) YO and (b) CuO with $R_{Ar}$ which are normalized by the intensities at a base pressure of $10^{-6}$ Torr. The broken lines indicate the intensities of the base pressure. The emission intensity of YO molecules decreased with increasing of $R_{Ar}$ at a constant total pressure. These intensities of YO at the same oxygen partial pressure, for instance (i) 100 mTorr, $R_{Ar} = 0\%$, (ii) 200 mTorr, 50\% and (iii) 400 mTorr, 75\%, take the same value. Characteristic of BaO emission is similar to that of YO. On the other hand, intensities of CuO are almost constant at the different oxygen partial pressures. Otis et al. suggest that few CuO oxides are formed in the plasma phase [3].

These results suggest that YO and BaO molecules are mostly formed by the gas phase reaction with the oxygen, while most of CuO molecules are ejected from the target. The production rates of the oxides in the plasma plume depend on the deposition conditions. The optimum oxides production for the preparation of the high-quality HTS thin films by the PLD process can be controlled by the total pressure and the argon mixture ratio $R_{Ar}$.

Fig. 4. Spectral intensity evolution of Ti atoms and TiO molecules in the PZT plume.

We measured optical emissions from the PZT plumes generated under various conditions. Strong emissions from Pb, Pb\(^{+}\), Zr, Zr\(^{+}\), Ti, Ti\(^{+}\), O, PbO, ZrO and TiO were detected [10]. Fig. 4(a), (b) shows the spectral intensity evolution of Ti atoms and TiO molecules, respectively. The rise rate and the peak of Ti atoms decrease with increasing oxygen pressure. The emissions of TiO are observed in delay with that of Ti atoms and these intensities increase in the presence of oxygen. This is partly attributed to the plasma phase oxidation of Ti atoms:

\[
\text{Ti}^{+} + \text{O}_2 \rightarrow \text{TiO} + \text{O}.
\]  

Near the target surface, the peak intensities of Ti atoms were almost the same at different pressures. Therefore, it is suggested that the plasma phase oxidation of the ejected species is few at the target surface. The peak intensities of Ti at the base pressure are smaller than those in oxygen. Sakeek et al. reported a similar phenomenon on production of BaO and YO in the preparation of YBCO films [2]. This result is due to an excitation by electron impact and recombination. They showed that the excitation process would be enhanced as a result of cooling and confinement of the faster plasma species in the oxy-
The peak intensity dependence of Ti and Ti$^+$ as a function of the distance from the target surface is shown in Fig. 5. The peak intensities of Ti decrease linearly with the distance, but the intensity of Ti$^+$ decreases drastically near the target surface. It suggests that Ti ions recombine in the presence of oxygen and form the oxide:

$$\text{Ti}^+ + \text{O}_2 + e \rightarrow \text{TiO} + \text{O}.$$  \hspace{1cm} (2)

Other species, Pb and Zr atoms and their ions, showed similar dynamics to the Ti element. Formation of PbO and ZrO oxides was also found to occur in the oxygen atmosphere.

### 3.2. Film characteristics

The zero-resistivity temperature ($T_{\text{C0}}$) of the YBCO film is plotted in Fig. 6 as a function of total pressure. As concerning the films deposited at $R_{Ar} = 0\%$, the high-quality YBCO films with $T_{\text{C0}} > 80\,\text{K}$ are obtained only within narrow pressure range (150–300 mTorr). On the other hand, at $R_{Ar}$ of 20% and 50% the films with $T_{\text{C0}} > 80\,\text{K}$ are deposited at wider pressure range. Also, X-ray diffraction, surface morphology and critical current density measurements of the YBCO films suggested that the addition of argon gas enables relaxation of deposition conditions and lowering deposition temperature [1]. We consider that Ar atoms and/or ions excited/ionized by the plasma plume have important role to crystallize the film and to reduce the processing temperature. Metastable atoms of $4^1P_1\ (11.55 \text{ eV})$ and $4^3P_0\ (11.72 \text{ eV})$ of Ar might be able to contribute the interactions in gas phase and in the depositing film surface, because those atoms have a long life time over 1.3 s. These results clearly show that control of plasma phase oxidation dominates the superconducting properties of the oxide films prepared by the PLD.

### Table 1

<table>
<thead>
<tr>
<th>Oxygen pressure</th>
<th>Compositional ratio</th>
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<tbody>
<tr>
<td></td>
<td>(Pb : Zr : Ti)</td>
</tr>
<tr>
<td>Bulk target</td>
<td>1 : 0.52 : 0.48</td>
</tr>
<tr>
<td>Base pressure (10$^{-6}$ Torr)</td>
<td>1 : 11.7 : 12.1</td>
</tr>
<tr>
<td>100 mTorr</td>
<td>1 : 0.67 : 0.42</td>
</tr>
<tr>
<td>200 mTorr</td>
<td>1 : 0.48 : 0.39</td>
</tr>
<tr>
<td>400 mTorr</td>
<td>1 : 0.62 : 0.56</td>
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Compositional ratios of PZT films prepared at various oxygen pressures are listed in Table 1. As shown in Table 1, the films prepared at 100–400 mTorr have the near stoichiometric composition as the bulk target. At the base pressure, however, Pb composition ratio is extremely low in compared with Ti and Zr. It suggests that Pb atoms re-evaporate from a growing film surface because Pb has a higher vapor pressure than Ti and Zr. The oxygen pressure affects the atomic composition ratio and the crystallization of PZT film [10]. Introducing oxygen gas of optimum pressure enhances oxygen incorporation in the film as well as suppression of re-evaporation of Pb atoms from the deposited films.

### 4. Conclusion

We investigated plasma phase oxidation during preparation of YBCO superconducting and PZT fer-
roelectric thin films using the KrF-PLD. As for the YBCO, YO and BaO molecules are formed in plasma phase with different reactivities, while most CuO molecules are ejected from the target. In the PZT preparation, TiO molecules are almost generated in the plasma phase. Flux of oxides reaching the substrate affects strongly the characteristics of the thin films. It is suggested that the control of plasma phase oxidation is important to fabricate high-quality oxide superconducting and ferroelectric thin films.

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References