Spectroscopic study of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ablation plasma plume: crossover from the “blast” to the “drag” regime

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Abstract

In order to clarify fundamental mechanism of pulsed laser deposition (PLD) process, Mach–Zehnder interferometry and laser scattering spectroscopy were applied to $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ablation plasma plume in atmospheric pressure. At the early stage (< 10 μs), the KrF-laser ablation plume expands in agreement with the blast wave model, but later comes closer to the drag model. It is suggested that the yield of particulates in the ablation plume, which corresponds to the surface roughness of deposited film, increases with the laser energy density and the laser wavelength increase.

Keywords: $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$; Pulsed laser deposition; Mach–Zehnder interferometry; Laser scattering spectroscopy

1. Introduction

Pulsed laser deposition (PLD) has been regarded as a leading technique for the preparation of high-quality oxide thin films, especially high temperature superconductive (HTS) and ferroelectric thin films [1]. It has the advantages of high deposition rate, preparation of epitaxial and stoichiometric film, and high reproducibility of film characteristics compared with other deposition techniques. However, particulate deposition in the films, which is inherent to the PLD technique, remains a problem in the fabrication of multilayer structures and fine line patterning for many kinds of electronic applications. Although some reports [2,3] claim a reduction in particulate deposition, complete removal of the particulate has yet to be accomplished. The interaction of a pulsed laser beam with a target directly affects the properties of the ablation plume including clusters and droplets, and dominates the characteristics of the deposited film.

Although there are many publications that describe ablation plume dynamics using optical emission spectroscopy [4], laser-induced fluorescence [5] and Michelson interferometry [6], the PLD process is not sufficiently understood. Therefore, in order to prepare high-quality thin films without particulate deposition and to improve the potential of PLD, clarification and active control of the interactions of the laser–target and the plasma–ambient are required strongly.

In this work, $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) HTS and $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT) ferroelectric thin films were prepared using the PLD technique [7,8], and the relationships between the properties of YBCO and PZT ablation plumes and the characteristics of these deposited films were partially clarified [9,10]. In order to study ablation plume dynamics, optical emission spectroscopy, laser scattering and Mach–Zehnder interferometry were used. Previous investigations suggest that it is necessary to perform a transient analysis with high temporal and spatial resolutions near the target surface to understand the PLD process. In this paper, the dynamics of YBCO ablation plasma plume using transient Mach–Zehnder interferometry and
laser scattering spectroscopy were investigated. These techniques were utilized to observe the dynamics of nonradiative atomic fragments including clusters and droplets. The nature of the YBCO plume near the target surface and the mechanism of KrF- and Nd:YAG-laser ablations are described.

2. Experimental

Fig. 1 shows a schematic of the experimental setup for the Mach–Zehnder interferometry used to diagnose the dynamics of the ablation plasma plume. A KrF excimer laser (Lambda Physik LPX-305icc, \(\lambda = 248\) nm, pulse duration of 25 ns) was used to irradiate a sintered YBCO superconducting target. The diameter and the mass density of the target are 30 mm and 9.9 g/cm\(^3\), respectively. The laser beam was focused perpendicular to the target surface, and the laser energy density was varied from 0.1 to 6 J/cm\(^2\). The laser repetition rate was set at 1 Hz and the target was rotated at a rate of about 2 rev./min to avoid pitting by frequent laser irradiation. YBCO ablation plume is generated by the laser irradiation and expands normally to the target surface. A Nd:YAG laser (Quanta-Ray GCR-130-10, \(\lambda = 533\) nm, pulse duration of 6 ns) was used as the light source for the interferometry. The probe beam passed through the YBCO ablation plume at right angles to the normal of the target. The probe beam and the reference beam were combined by a half mirror, then passed through a band pass filter to remove the effect of plasma emission on the interference signal. The interference fringe was detected by a CCD camera and the data were transferred to a personal computer.

3. Results and discussion

Fig. 2a–c show the Mach–Zehnder interferograms of YBCO ablation plume obtained at 0.01, 10 and 20 \(\mu\)s after the KrF excimer laser irradiation, respectively. These YBCO ablation plume was produced in atmospheric air by the KrF excimer laser at the laser energy density of 2 J/cm\(^2\). The degree and the direction of the fringe shift on interferogram corresponds to a line-integrated density of the plume. A shock wave can be seen in Fig. 2 as a border around the ablation plume, and expands symmetrically into atmospheric air from the target surface. As Fig. 2b, c indicates, the direction of fringe shift near the target surface is opposite compared with that near the shock wave. It suggests that the pressure is low inside the shock wave, especially at the target surface irradiated by laser. Normal positions of the shock wave front from the target surface are plotted in Fig. 3 as a function of time. Two theoretical curves based on a classical drag force model and a blast wave model [11] are also drawn for comparison. During the initial stages of expansion (< 10 \(\mu\)s), the experimental data show better agreement with the blast wave model than the drag model. After that, the shock wave grows faster than the blast wave model predicts and gradually comes closer to that given by the drag model. This crossover from the “blast” to the “drag” regime suggests that another force accelerates the shock wave after 10 \(\mu\)s in this experimental condition.

In order to investigate the initial stage dynamics of the ablation plume, laser scattering spectroscopy was used. Under all measurement conditions used here, the transmittance of the He–Ne laser through the YBCO ablation plume was also measured. The laser beam passed parallel and close to the target surface (about 1 mm), and the beam waist was about 1.8 mm. Transmittance signal was measured by using a narrow-band pass filter and a fast pin-photodiode. In order to improve signal-to-noise ratio, those signals were averaged by a digitizing oscilloscope (HP 54504A) and the data were transferred to a personal computer.
Fig. 2. Mach–Zehnder interferogram of YBCO ablation plume at (a) 0.01 µs, (b) 10 µs and (c) 20 µs after the KrF excimer laser irradiation (2 J/cm²).

It has been demonstrated that Mach–Zehnder interferometry and laser scattering measurements can addition to that caused by the refraction. It is the authors’ view that these broad peaks are caused by scattering of the probe laser beam due to clusters and droplets ejected from the target. At the laser energy density of 1 J/cm², there are four peaks before 50 µs, and no decrease of the transmittance is observed after that time. As laser energy density increases (2 J/cm² and 4 J/cm²), the transmittance decreases and the broad peaks come closer to $t = 0$. Also, a weak decrease of the transmittance can be observed even after 50 µs. These results suggest that the yield of particulates increases with the laser energy density increase. Fig. 5 shows the time-resolved transmittance of the He–Ne laser for the YBCO ablation plumes produced by the KrF- and the Nd:YAG-laser irradiations. Those ablation plumes were produced at a laser energy density of 1 J/cm² in atmospheric air. As can be seen in Fig. 5, very slow and broad components caused by the ablated particles appear around 50 µs for the Nd:YAG-laser (533 nm) ablation. Also the transmittance is much lower than that of the KrF-laser (248 nm) ablation. A large amount of particulates are ejected from the target by Nd:YAG-laser ablation compared with KrF-laser ablation. Koren et al. have presented the particulates on the YBCO films deposited by the PLD with different laser wavelengths [12]. In this paper, it is showed that the density of the particulates is lower and their average size is smaller as the wavelength becomes shorter. A decrease in ablated particulates results in the smoothing of the film surface. This is one of reasons why the excimer laser (UV) has advantages for the preparation of performance thin oxide films with excellent surface morphology.

4. Conclusions

It has been demonstrated that Mach–Zehnder interferometry and laser scattering measurements can
Fig. 5. Difference of time-resolved transmittance between the KrF- and the Nd:YAG-laser ablation plumes.

provide useful information on dynamics of ablation plasma plume. The shock wave originating from the KrF-laser ablation expands in agreement with the blast wave model at the early stage (< 10 μs), then deviates from the theoretical curve after that time. It is postulated that another force drives the shock wave after 10 μs in this experimental condition. From laser transmittance measurements, it is suggested that the yield of particulates in the ablation plume increases as the laser energy density increases, and that a large amount of particulates are ejected from the target by Nd:YAG-laser ablation compared with KrF-laser ablation.

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