Anomalous Enrichment of Pb^+ Ions by Crossed Beam Scattering of a $Pb(Zr_xTi_{1-x})O_3$ Plume and an O_2 Jet

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A crossed beam scattering of a $Pb(Zr_xTi_{1-x})O_3$ plume and an oxygen jet was studied by using a time-of-flight quadrupole mass spectroscopy. Both simple collisions and reactive scatterings had significant effects on the transport and energetics of ions in the plume. Relative enrichment of metal and metal oxide ions was also changed with the oxygen pulse because of the differences in the mass and chemical properties of the ions. In particular, an anomalous increase of Pb^+ ions was observed as the oxygen jet crossed the plume at high laser fluences, while the signal magnitudes of all other ions were reduced. This originates from the fact that PbO^+ ions dissociate easily to liberate Pb^+ ions in the plume since the bond energy of PbO^+ is as low as 2.2 eV.

Introduction

Since the advent of lasers, there has been a growing interest in pulsed laser deposition (PLD) technique aiming at the growth of thin films of superconductors, ferroelectrics, metals, and refractory materials.[1] One of the major advantages of PLD is the stoichiometric transfer of multi-element target material to a substrate. For multi-element oxide targets like $YBa_2Cu_3O_{7-x}$ (YBCO) and $Pb(Zr_xTi_{1-x})O_3$ (PZT), however, the stoichiometries of the films deposited in vacuum often do not represent that of the bulk as far as oxygen is concerned, which results in a serious deficiency of oxygen in the films.

By adopting a reactive laser ablation in an oxygen atmosphere, such problem has been circumvented in a conventional PLD, where the optimal pressure of oxygen during film growth ranges from 0.1 to a few Torr. But this pressure is too high for *in situ* analysis and elaborate control of the film deposition by reflection high energy electron diffraction (RHEED), which is one of the most powerful and convenient techniques for monitoring of the film deposition. In this respect, use of synchronized pulsed jet of oxygen has been suggested by Gupta *et al.*[2] to deposit YBCO films at pressures below 10^{-3} Torr, which is low enough for RHEED. They also demonstrated that oxygen is effective in forming the YBCO phase only when it is provided during actual growth of the film. Recently, Willmott *et al.*[3] employed the reactive crossed beam PLD and reported successful growth of high quality GaN films using a pulsed nitrogen source. PLD is inherently a digital process and PLD combined with a pulsed source of reactive gas is expected to become an ideal technique for a digital laser epitaxy to grow more complicated multi-layered structures in ultrahigh vacuum systems.

In order to obtain optimal parameters of film deposition by using a pulsed reactive gas, a deep understanding of the physical and chemical interactions in the laser-induced plasma (plume) and the transport of the ablated species to the substrate is essential. For the last few years, diverse diagnostic techniques including optical emission,[4] imaging,[5] laser-induced fluorescence,[6] and probe beam deflection[7] have been employed to investigate the plume expansion dynamics and gas phase reactions in a static background gas. However, very little work has been done to elucidate the effects of synchronized pulsed jet on the elastic and inelastic scatterings in the plume.[8-10]

Here, we present experimental results on a scattering of a laser-induced PZT plume by a pulsed oxygen jet. By direct analysis of ions escaping from the plume by using a time-of-flight (TOF) quadrupole mass spectroscopy, we have examined the effects of simple collisions and chemical reactions in the plume caused by injection of the pulsed oxygen molecules with an attempt to provide critical information required to develop a reactive digital laser epitaxy technique. Significant changes in the relative enrichment of atomic metal and oxide ions and their mean kinetic energies were observed with the pulsed oxygen jet crossing the plume.

Experimental Methods

A schematic diagram of the experimental setup is shown in Figure 1. The apparatus consists of a target chamber and an analysis chamber, which are separated by a skimmer with an orifice diameter of 0.97 mm. Laser ablation and subsequent reactions occur in the target chamber, where a 25.4 mm dia. PZT target was rotated by a standard rotary motion feedthrough to avoid a target aging effect. The distance from the target to the orifice of the skimmer was 2.7 cm. The 266 nm radiation from a Nd : YAG laser (Spectra-Physics GCR150-10) was focused onto the target by using a 300 mm lens at an incident angle of 50°. The spot size of focused laser beam on the target was 1.1 mm^2.

To study the reactive scattering of ions with oxygen molecules, a pulsed valve (General Valve Series 9) was mounted inside the target chamber such that the propagation axis of the gas jet was perpendicular to the direction of plume expansion. The distance from the orifice of the valve to the axis of the plume was 1.7 cm. The backing pressure of the

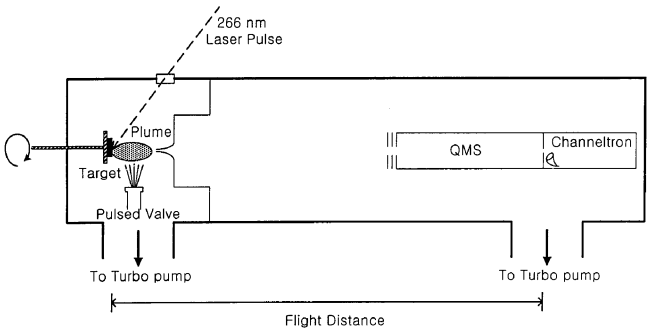

Figure 1. Schematic diagram of the experimental setup.

pulsed valve was held at 2 bar. A delay generator was used to vary the delay time between the laser pulse and the electric pulse to open the pulsed valve. The pulse width of the gas jet is quite close to the electrical pulse width applied to the valve.[11] The pulsed valve actually started to open at the electric pulse width of 170 μs.

The analysis chamber was equipped with a quadrupole mass spectrometer (VG SX300). A boxcar averager (SR250) was used to get laser-correlated ion mass spectra. Time-of-flight (TOF) spectra at fixed mass as well as the conventional mass spectra were obtained. The flight distance of ions, 48.7 cm, was defined as the length between the target and an entrance hole to a detector. The region between the target and the entrance to the quadrupole was field free. Ion optics in front of the quadrupole housing were grounded and the ionizer was turned off during the experiment to detect ions only. The small radial oscillation field in the quadrupole had negligible effect on the measured TOF spectra for the ion energies observed here.[9] One hundred laser shots were irradiated on the rotating target surface, each giving a TOF spectrum. These spectra were averaged into a single TOF spectrum by a storage oscilloscope (LeCroy 9361, 300 MHz). The typical equilibrium pressure of the target chamber with the laser impinging on the target was 8×10^{-6} Torr when the pulsed valve was open with a pulse width of 250 μs.

Results and Discussion

As the pulsed oxygen jet crossed the PZT plume, the signal magnitude of each ion was reduced significantly. Figure 2 shows normalized signal magnitudes of atomic and molecular ions as a function of the electric pulse width applied to the valve. The accurate local pressure near the target region as the oxygen jet was supplied was not measurable, but the momentum flux *vs.* width of the pulsed valve has been found to show a strong correlation.[11] The signal magnitudes of ions which are detected by the mass spectrometer are expected to be changed by elastic and inelastic scatterings in the plume as the pulsed valve is open. The intensities of the ions which pass through the skimmer will be changed by collisions with oxygen molecules in the plume. Since a substrate is in general mounted facing the target in PLD, the deflection of ions caused by collisions would certainly affect the transport of ions to the substrate and the film growth. In our experiment, the intensity of Ti^- ions which had relatively small kinetic energies compared with Zr^- and Pb^- ions as shown in Table 1 and Figure 2 was reduced remarkably by the oxygen pulse. Because the less energetic ions in the plume are perturbed more easily than those of more energetic ones, the mean kinetic energies of ions which ultimately reached the detector increased as the oxygen pulse was on.

In addition to the simple collisions, reactive scatterings of ions and oxygen molecules would certainly contribute to the relative enrichment of ions in the plume. Intensities of TiO^- and PbO^+ ions increased as the width of oxygen pulse increased from 190 to 250 μs although their concentrations in the plume were negligible. But they decreased slightly at pulse width longer than 250 μs presumably due to collisions. Unlike TiO^- and PbO^+ ions, a fair amount of ZrO^+ ions was detected in the plume even without the oxygen jet because ZrO^+ has larger dissociation energy than TiO^- and PbO^+ and may avoid dissociative collisions. The bond dissociation energies of TiO^-, ZrO^-, and PbO^+ ions[12] are 6.8 eV, 8.0 eV,

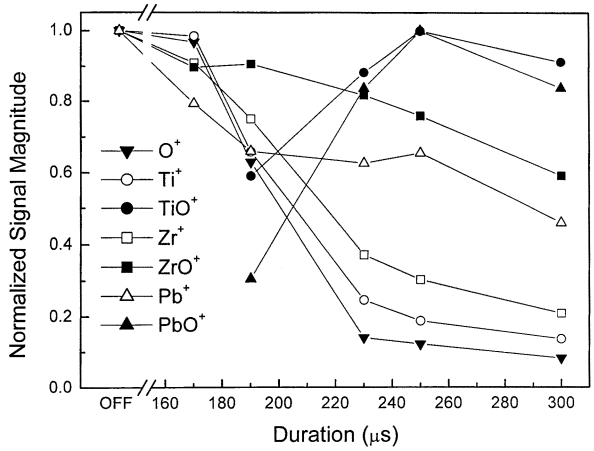

Figure 2. The normalized signal magnitudes of ions as a function of the width of the electric pulse applied to the pulsed valve. The pulsed valve starts to open at 170 μs. The laser fluence was 0.22 J/cm^2.

Table 1. Mean kinetic energies of the ions detected by quadrupole mass spectrometer (eV)

Laser fluence (J/cm^2)	Pulse width (ms)	O^+	Ti^+	Zr^+	Pb^-	TiO^+	ZrO^+	PbO^-
0.22	0	9.3	13.6	23.0	44.3	–	15.8	–
	250	15.3	18.0	26.3	48.4	11.9	19.8	47.7
0.35	0	22.5	24.9	29.4	44.9	–	14.0	–
	250	20.0	27.5	38.2	63.1	15.5	22.3	52.6

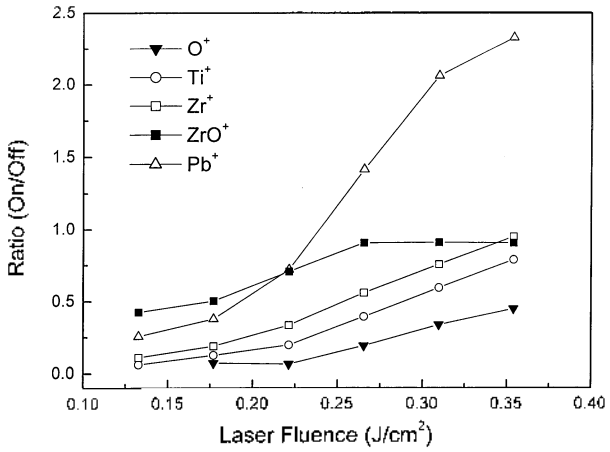

Figure 3. The ratio of the signal magnitudes of ions with the oxygen pulse on (250 μs) and off as a function of the laser fluence.

and 2.2 eV, respectively. The intensity of ZrO^+ ions decreased as the pulse width increased from 170 to 300 μs, which leads to a conclusion that the deflection of ZrO^- ions by the oxygen pulse is more significant than the formation of ZrO^- ions by chemical reactions between Zr^+ ions and oxygen molecules.

At low laser fluences near the ablation threshold, ions have small kinetic energies and are easily deflected by the oxygen pulse. The oxygen pulse became less effective on the signal magnitude of each ion as the laser fluence was increased, which is manifested in Figure 3. The ratio of signal magnitudes with the oxygen pulse on and off for O^-, Ti^+, Zr^-, and ZrO^+ converged to 1 as the laser fluence was increased from 0.13 to 0.35 J/cm^2. The intensity of Pb^+ ions, however, showed an anomalous enrichment as the oxygen jet was supplied to the plume at laser fluences above 0.27 J/cm^2. This indicates that a particular formation channel of Pb^+ ions which is aided by the oxygen pulse becomes overwhelming at high laser fluences.

Figure 4 illustrates TOF spectra of Pb^+ ions at a laser fluence of 0.35 J/cm^2. When the oxygen pulse was off, the TOF

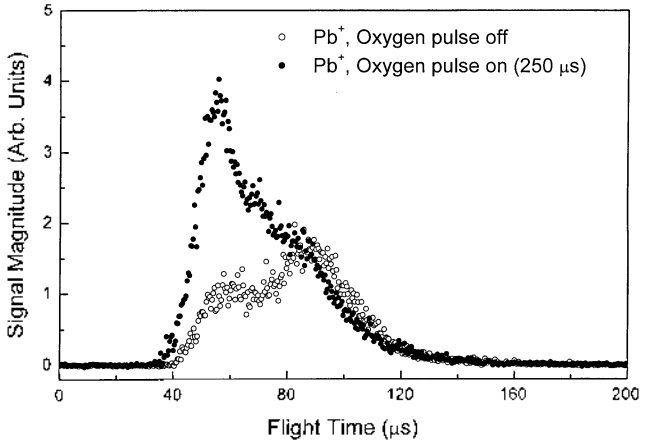

Figure 4. The time-of-flight spectra of Pb^+ ions with the oxygen pulse on (250 μs) and off at the laser fluence of 0.35 J/cm^2.

spectrum of Pb^+ ions showed a bimodal distribution. Similar peak splitting was reported in the laser ablation of ZnO by Leuchtner,[13] who proposed the possibility of formation of doubly charged metal ions and their recombination with electrons giving high-energy peak in the TOF spectra of Zn^+ ions. In our experimental conditions, however, the fast peak is believed to correspond to the Pb^+ ions produced by a direct laser ablation or dissociation of PbO^- ions. The ultimate arrival time of the ions would be affected not only by the formation mechanisms of the ions but also by the time and place of ionization in the plume. The ions formed at the initial stage of laser ablation are more accelerated by the local electric field in the plume produced by a space charge effect.[14] On the other hand, the slow peak originates presumably from the Pb^+ ions produced by ionization of Pb atoms. As the oxygen jet crossed the plume, the intensity of the fast peak was drastically increased while that of the slow peak remained almost unchanged. Also, PbO^- ions produced by the oxygen jet were slower than the fast Pb^- ions but they were faster than the slow Pb^- ions. This is suggestive of the following formation mechanism of Pb^+ ions when the oxygen jet is supplied to the plume:

$$Pb + O_2 \rightarrow PbO + O \quad (1)$$

$$Pb^+ + O_2 \rightarrow PbO^+ - O \quad (2)$$

$$PbO - M \rightarrow PbO^- - e^- + M \quad (3)$$

$$PbO^+ + M \rightarrow Pb^- + O + M, \quad (4)$$

where M represents collision partners like e$^-$, O_2, and other chemical species in the plume.

The increase in metal ion signal by the oxygen jet was observed only for Pb^+ ions as shown in Figure 3. Since the ionization potentials of Pb^+, Ti^+, and Zr^+ ions[15] are 15.0 eV, 13.5 eV, and 13.1 eV, respectively, it is unlikely that Pb^{2+} ions are formed preferably in the plume by collisional ionization. Also, no doubly charged ions were detected. The intensity of the fast peak would not increase by the oxygen jet if the fast peak in the TOF spectra of Pb^+ ions were responsible for the Pb^- ions formed by recombination of Pb^{2+} ions and electrons. The ionization potentials of Pb, Ti, and Zr atoms[15] are 7.4 eV, 6.8 eV, and 6.6 eV, respectively. So collisional ionization of Pb atoms by the oxygen jet in the plume is not expected to have contributed to the increase of the fast peak because the signal magnitudes of Ti^+ and Zr^+ ions decreased by the oxygen jet. Instead, the unusually small bond dissociation energy of PbO^+ ($D_0(PbO^+) - 2.2$ eV) is thought to have caused the growth of the fast peak.

The maximum available amount of energy, ΔE that can be transferred to a PbO^- ion as internal energy by an inelastic collision between a stationary O_2 molecule and a PbO^+ ion with initial kinetic energy of $E(PbO^+)$ is

$$\Delta E = \frac{m(O_2) \cdot E(PbO^+)}{m(O_2) + m(PbO^-)}$$

where $m(O_2)$ and $m(PbO^+)$ are mass of O_2 and PbO^-, respectively.[8] For example, we get ΔE = 6.6 eV for PbO^- if we just

use the mean kinetic energy value of PbO^+ ions at 0.35 J/cm^2 given in Table 1. Since the bond dissociation energy of PbO^+ is as small as 2.2 eV, most of PbO^- ions produced by reactive scatterings of Pb^- ions and oxygen jet are to be easily dissociated by collisions in the plume and ultimately contribute to the enrichment of the fast Pb^- ions.

Summary

Elastic and inelastic scatterings of the PZT plume and the oxygen jet had significant effects on the transport and energetics of ions. In particular, a fair amount of ions was deflected by the oxygen jet at low laser fluences. The kinetic energies of ions which passed through the skimmer increased when the oxygen pulse was on because slow ions are more vulnerable to collisions. Pb^+ ions showed an anomalous enrichment by the oxygen pulse because of the formation and subsequent dissociation of PbO^+ ions in the oxygen atmosphere. Dissociation of PbO^+ ions and other cluster ions containing oxygen produced by direct laser ablation also contributes to the enrichment of Pb^- ions as they collide with oxygen molecules. The amount of certain ions which arrive at the detector is determined by collisions and chemical reactions in the plume, which are largely dependent on the mass and chemical properties of the ions. Although we have focused on the ionic species in this work, we expect similar results for the neutrals. Therefore, a control of the flux and energetics of the chemical species which arrive at the substrate might be accomplished by adopting the pulsed oxygen source in a reactive pulsed laser deposition.

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