Investigation of the Pb depletion in single and dual pulsed laser deposited epitaxial PZT thin films and their structural characterization

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ABSTRACT

We have investigated the Pb depletion in laser ablated PZT ($PbZr_{1-x}Ti_xO_3$) films through a systematic study of PZT target-laser interactions for both single laser and dual-laser ablation methods. The study includes films deposited from a stoichiometric and an excess PbO PZT targets. The films were deposited on single crystal $SrTiO_3$ [100] substrates at 550˚C with a background oxygen pressure of 500 mT. Single laser deposited films at a laser fluence of $5J/cm^2$ produced the highest Pb content while dual-laser ablated films where an excimer and a CO_2 pulsed lasers were synchronized for ablation produced high Pb content for an excimer laser fluence of less than $2J/cm^2$. This enabled the growth of particulate-free PZT films with high Pb content. ICCD imaging of the plasma plumes showed variations in the expansion profiles at different laser fluencies that correlated well with the Pb content observed in the deposited films.

INTRODUCTION

Pulsed laser deposition (PLD) technique offers unique advantages in the growth of thin films of multi-component ferroelectric materials such as PZT. The most promising characteristics of the PLD technique is the stoichiometric transfer of materials from the target to the substrate. However, for oxides such as PZT which involve volatile elements like Pb, ablation of stoichiometric PZT targets causes preferential evaporation of Pb from the target at low laser fluences. In addition, Pb depletion in films was observed for typical growth temperatures of 500˚C to 600˚C necessary for getting crystalline films [1]. This Pb deficiency is responsible for the coexistence of a pyrochlore phase with the perovskite PZT phase, degrading the ferroelectric properties of the films. To compensate for the Pb loss it is a general practice to add excess PbO during the preparation of the dense ceramic PZT targets. Our investigations have shown that the preferential evaporation of Pb from target is suppressed at high laser fluences, but with the undesirable increase in the particulate density. On the other hand the advantages of growth of multi-component materials using dual laser ablation had been demonstrated earlier [2]. In this work we report the effectiveness of the dual laser ablation technique in producing particulate free high Pb content PZT films. Not only have the films grown by dual laser ablation retained the crystalline quality and high Pb content like the high excimer fluence single laser ablated films but also there has been a reduction in particulates on film surface.

EXPERIMENTAL DETAILS

The dual laser ablation system used in our experiments has been described in detail elsewhere [3]. Briefly, a 20-ns FWHM KrF laser pulse at 248 nm overlapped a 200-ns FWHM CO_2 laser pulse of wavelength 10.6 μm at the target. Two targets, namely a stoichiometric PZT

target and a PZT target with 30 at. % excess PbO were prepared by standard ceramic procedures. First, the prepared targets were irradiated by 1000 laser pulses for various fluences with a background oxygen pressure of 500 mT using both single and dual laser ablation. After ablation, the surface morphologies and the compositions of the laser target interaction sites were examined by scanning electron microscopy (SEM) and X-ray energy dispersive spectroscopy (EDS). Time gated intensified charge-coupled detector (ICCD) images of the generated plasma plumes during ablation were captured for both ablation processes at the various laser fluences. The plume emission was collected normal to the propagation direction. The films were deposited on single crystal $SrTiO_3$ [100] substrates at 550˚C with a background oxygen pressure of 500 mT. The prepared thin films were measured by X-ray diffraction (XRD) for crystal structure. All XRD measurements were carried out with Cu Kα radiation using Bruker D8 Focus X-ray Diffractometer. The film surfaces were studied using Digital Instruments D 3100 atomic force microscope (AFM).

RESULTS AND DISCUSSION

Figure 1 shows the XRD scans for the two PZT targets. Both the scans match the tetragonal $PbZr_{1-x}Ti_xO_3$ phase with $x \geq 0.48$ with no other observed impurity phases besides PbO.
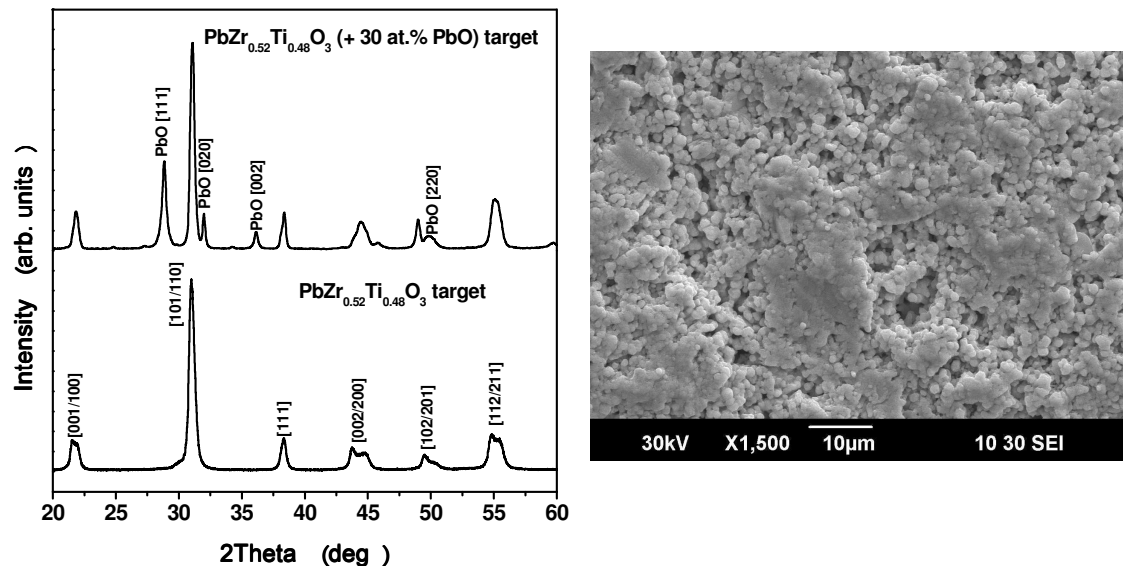

Figure 1. (Left) XRD data for stoichiometric PZT target and PZT target with 30 at. % excess PbO (right) SEM image of typical PZT target before irradiation by excimer laser.

Laser-target interactions

Figure 2 shows the SEM images of single laser target interaction sites on the PZT (30 at. % excess PbO) target surface after irradiation by 1000 pulses of the excimer laser with a range of laser fluences from 1-5 J/cm^2. We observed severe surface melting and formation of columnar structures. Two kinds of cones can be identified: one type with well defined cone tip and body with all cones having same orientation formed at low excimer fluence of 1 J/cm^2 and the other type having only a cone tip with different orientations formed at high fluences. Such conical structures are indicative of preferential removal of highly volatile Pb during ablation. Also the

higher ambient O_2 gas pressure favored the surface melt by confining the plasma expansion and facilitating the plasma absorption.
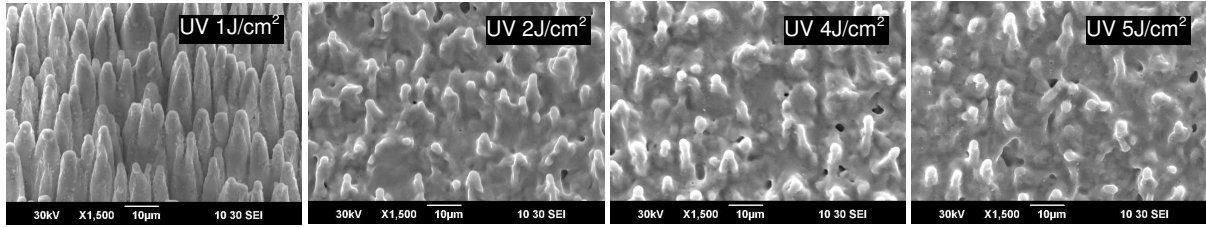

Figure 2. SEM images of PZT (30 at. % excess PbO) target surface after irradiation by 1000 pulses of a KrF laser beam in 500 mT O_2 ambient at various UV laser fluences.

Figure 3 shows the chemical compositions measured using EDS of the laser target interaction sites for the stoichiometric PZT and the PZT (+30 at. % PbO) targets. For both the targets the lead content i.e. atomic % Pb/(Zr+Ti) increased with higher excimer fluences although the Zr and Ti content remained almost constant for the same range of fluences.
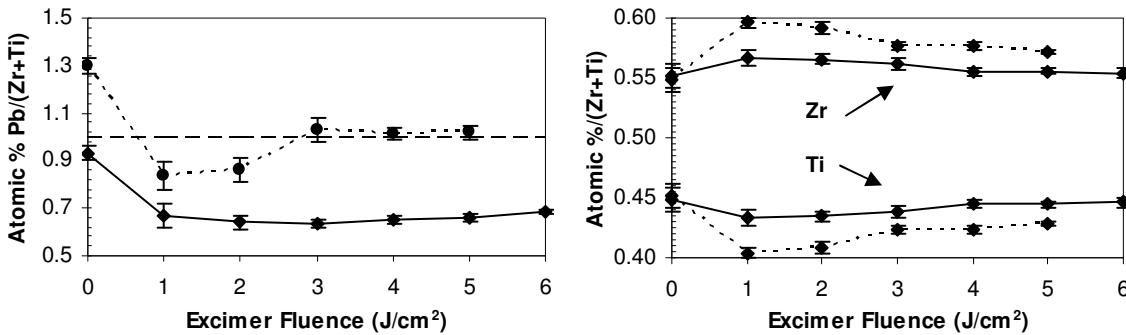

Figure 3. Chemical compositions using EDS analysis of the ablated target surfaces versus excimer fluence for stoichiometric PZT (solid line) and PZT (30 at.% PbO) target (dotted line).

Initial studies using dual laser ablation showed that a temporal peak to peak interpulse delay of 100 ns was ideal for the efficient coupling of the CO_2 laser energy into the KrF laser ablated plasma plume [5]. Figure 4 shows SEM images of dual laser target interaction sites using a CO_2 laser fluence of 2J/cm^2 and varying the KrF laser fluence in the range 1-4 J/cm^2. Surface morphologies were similar as observed in single laser ablation.
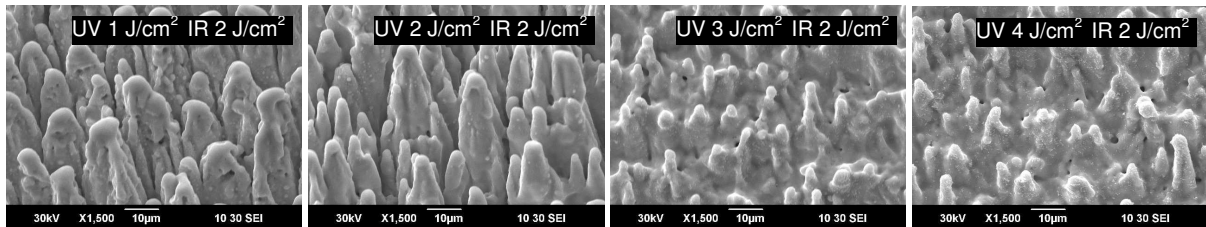

Figure 4. SEM images of PZT (30 at.% excess PbO) target surface after irradiation by 1000 pulses of dual laser ablation using CO_2 laser fluence 2 J/cm^2 and varying excimer fluence from 1 to 4 J/cm^2 with 100 ns peak to peak interpulse delay in 500 mT O_2 ambient.

However, EDS analysis of the laser-target interaction sites showed that the amount of preferential Pb loss is lesser in dual laser ablation although the Zr and Ti contents were same in both cases as is evident in figure 5. This happens because of the CO_2 laser energy gets absorbed into the initial excimer laser ablated plasma which causes increase in plasma temperature which increases the temperature of target surface facilitating the stoichiometric removal of materials by ablation [6].
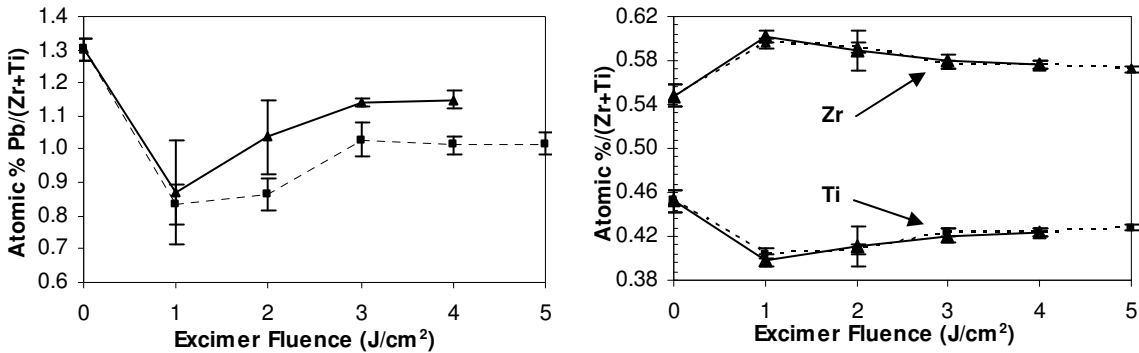

Figure 5. Chemical compositions using EDS analysis of the ablated target surfaces versus excimer fluences for PZT (30 at.% PbO) target using single laser ablation (dotted line) and dual laser ablation (solid line) using CO_2 fluence of 2J/cm^2 and 100 ns peak to peak interpulse delay.

Plume-optical diagonostics

ICCD images of the plasma plumes using the detector with zero gain showed that the visible plumes lasted for about 11 μs. Thus, in order to capture the complete visible emission a 20 μs gate was used.
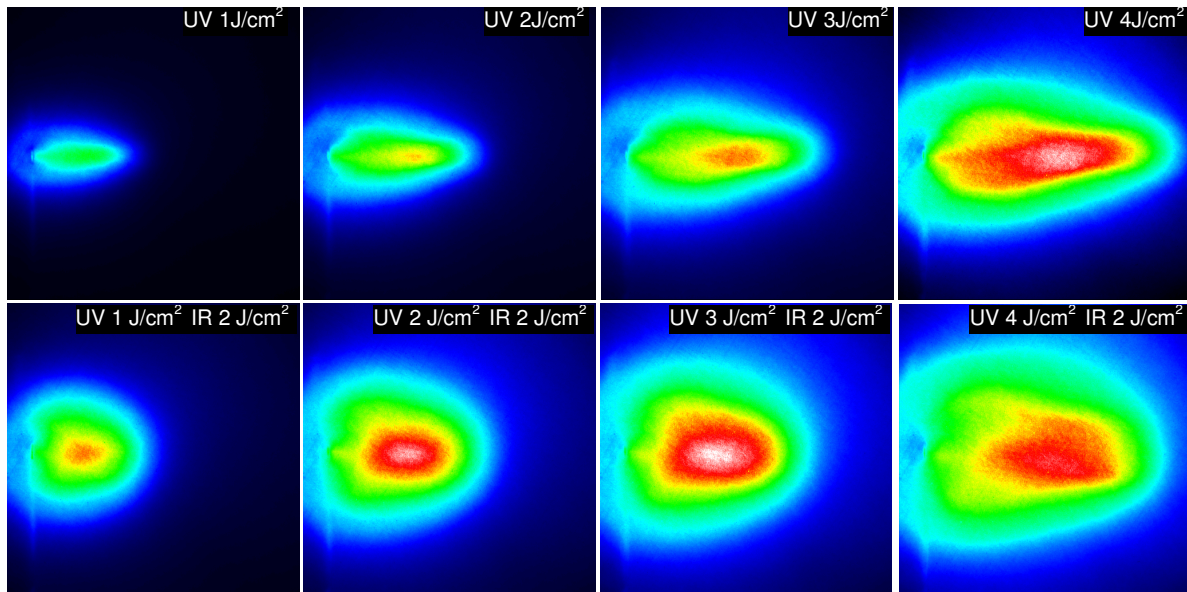

Figure 6. ICCD images of total visible emission spectra of single laser plumes (top row) varying the excimer (UV) fluences from 1 to 4 J/cm^2 and dual laser plumes (bottom row) varying excimer fluences keeping 2 J/cm^2 CO_2 (IR) fluence and 100 ns peak to peak interpulse delay.

Figure 6 shows the ICCD images for the total visible emission spectra of the single and dual laser plumes at various fluences. The enhanced plume expansion in dual laser ablation showed the efficient coupling of CO_2 laser energy to the excimer laser ablated plume.

Thin film properties

The films were grown epitaxially on single crystal $SrTiO_3$ (100) substrates at 550˚C with a background oxygen pressure of 500 mT from excess PbO PZT target. Initial studies indicated that the films grown from stoichiometric PZT target were Pb deficient which showed up as a pyrochlore impurity phase in XRD scans. A high O_2 pressure of 500 mT was used during growth to minimize the desorption of the high vapor pressure Pb from the film surface at 550 ˚C. Figure 7 shows the XRD scans of three films all deposited at 550˚C under 500 mT O_2 pressure, two using single laser ablation named as *S2J/cm^2* and *S5J/cm^2* i.e. using excimer fluences 2 J/cm^2 and 5 J/cm^2 respectively and one using dual laser ablation named *D1J/cm^{2}UV2J/cm^{2}IR* i.e. using KrF laser fluence 1J/cm^2 and CO_2 laser fluence 2J/cm^2 with 100 ns peak to peak interpulse delay. The films were highly textured with no observed peaks from secondary phase formation within the resolution limits of XRD. The log-scale for intensity was used to exaggerate the low intensity peaks so that if secondary phases are present, they can be identified easily. Figure 7 also shows the rocking scans about the PZT (200) plane for the single laser high fluence *S5J/cm^2* and dual laser *D1J/cm^{2}UV2J/cm^{2}IR* films both films having same thickness of about 350 nm. Both films have excellent in plane epitaxy indicated by the narrow full width half maxima of the rocking curves.
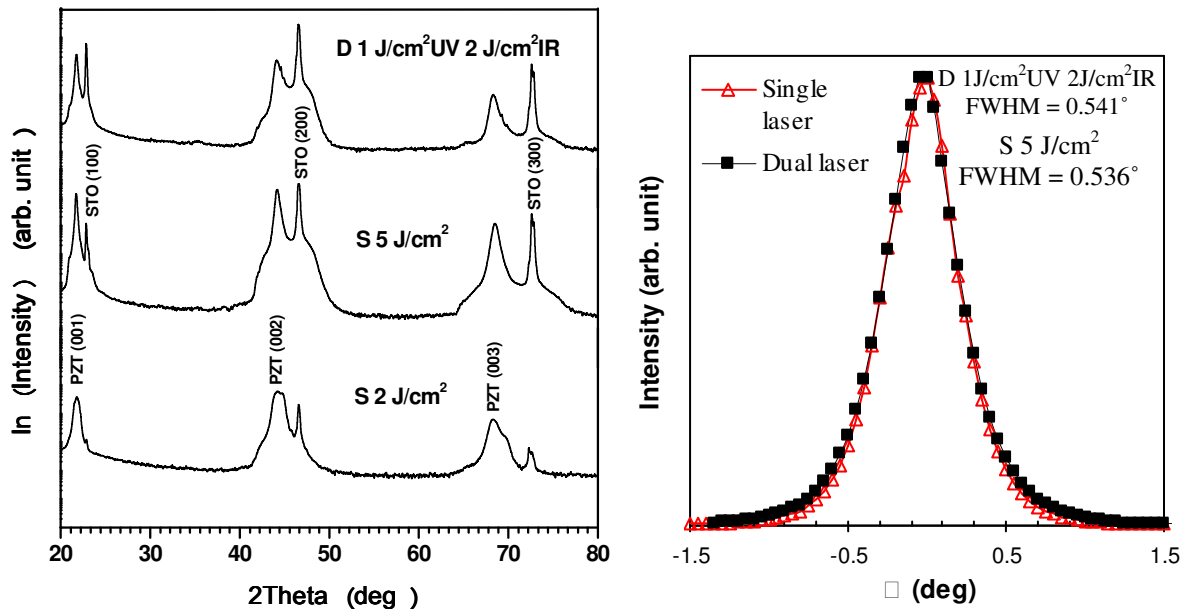

Figure 7. (Left) XRD data for PZT films deposited on SrTiO3 (STO) substrates using single laser ablation with excimer fluences of 2 J/cm^2 (S 2J/cm^2) and 5 J/cm^2 (S 5J/cm^2) and dual laser ablation with excimer fluence of 1 J/cm^2 and CO_2 fluence 2 J/cm^2 (D 1J/cm^{2}UV2J/cm^{2}IR). (Right) Rocking curves about PZT (200) plane for films S 5 J/cm^2 and D 1J/cm^{2}UV2J/cm^{2}IR.

EDS analysis of the films revealed that the atomic lead content Pb/(Zr+Ti) of single laser ablated film *S 2J/cm²* was 0.39 and that for *S 5J/cm²* was 0.85 respectively. However the dual laser ablated film *D1J/cm²UV2J/cm²IR* had high Pb content of 0.84 showing the effectiveness of the method. Figure 8 shows the AFM surface images of the films under given conditions. A reduction in particulate density and surface roughness is observed in dual laser deposited film.
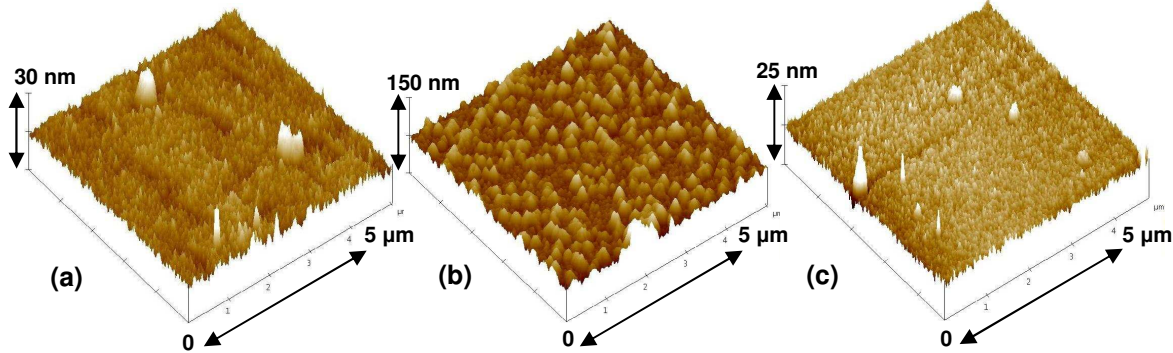

Figure 8. AFM images of PZT films deposited using single laser ablation **(a)** *S 2J/cm²* **(b)** *S 5J/cm²* and **(c)** dual laser ablation *D1J/cm²UV2J/cm²IR*. All scan areas are 5x5 μm. Surface roughnesses for **(a)**, **(b)** and **(c)** are 3 nm, 12 nm and 2 nm respectively.

CONCLUSIONS

In conclusion, using a dual laser ablation process we have successfully grown high Pb content, particulate free and smooth PZT films with the desired perovskite structure and no impurity phases. This technique could be generalized to all multi-component thin film growth where high volatility of one of the elements leads to non-stoichiometric transfer of materials in the PLD process.

ACKNOWLEDGMENTS

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