Pulsed laser ablation and deposition of complex oxides

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Abstract
The pulsed laser ablation and deposition (PLD) processes of SrTiO3 were studied as a model system for developing a technique for the growth of structurally bulk-equivalent epitaxial thin films of typical complex oxides. Deposition rate vs. laser fluence measurements showed that there is a second critical fluence value above the ablation threshold. Below the critical value, both the ablation and deposition rates are linear functions of the fluence and independent of the ablation spot area. Above the critical value, the deposition rate per unit ablation area depends strongly on the ablation spot area. Homoepitaxial SrTiO3 films possessed the exact bulk lattice constant value only when the films were grown at the critical fluence, whereas larger lattice constants were obtained if the fluence was either higher or lower. Composition analysis revealed that the enlargement of the lattice constant was related to cationic unbalance. This critical laser fluence is essential for the growth of bulk-equivalent epitaxial films, and therefore accurate measurement of laser energy and ablation area is vital for reproducible film growth.

1. Introduction
In recent years, pulsed laser deposition (PLD) has evolved into one of the most versatile methods for growing high-quality functional oxide thin films containing materials with high congruent and incongruent melting points. Although PLD is widely used in the world, the basic mechanisms of oxide ablation and deposition processes are not well understood.

Related to this, a common problem with many PLD systems is limited experimental reproducibility of thin film properties. Thin film growth conditions typically need to be re-optimized for each deposition system and it is difficult to rely on the particular numerical parameters provided in literature. The main reason for this is the difficulty of reproducing accurately the ablation laser conditions in contrast with other growth parameters, like substrate temperature, ambient oxygen pressure, etc. There are a number of publications that discuss the effect of laser fluence on the asymmetric composition transfer from a target to a growing film, providing helpful information for selecting suitable ablation conditions [1-5].

In this paper, the fluence effect is re-examined in addition to the ablation area dependence in terms of film deposition rate, material ablation rate, film composition, as well as, more practically, crystal
quality of epitaxially-grown films. In order to focus on the thin film growth process, homoepitaxy of relatively simple SrTiO$_3$ was chosen as a prototypical example.

2. Experimental setup

To control accurately the relevant laser ablation conditions, a specially-designed PLD system was constructed (Pascal Co.). The details of this system can be found in our previous paper [6]. Briefly, this system includes a KrF excimer laser (248 nm) with a fast energy pulse rise time, excellent pulse-to-pulse energy stability, a fairly homogeneous beam profile, and a very small beam divergence (ThinFilmStar, TUI LASER) [7]. A through-chamber laser energy measurement feature allows us to determine the true laser energy at the ablation target surface, independent of transmission loss at the laser entrance viewport due to unwanted film coating. Reflection-type variable attenuator system was used to control the laser beam energy without changing the charging high voltage of the excimer laser, which can cause a considerable change in the laser ablation spot area on the target surface, since a higher voltage results in a larger beam divergence [6]. A slit for obtaining a sharp beam profile edge and precise positioning of the focusing lens allowed us to define and control the ablation spot area. Additionally, a fluorescent target in the chamber was used to measure the spot area accurately in situ. The incident angle of the laser on the target surface was 45 °, and the target substrate distance was fixed at 44 mm unless otherwise specified.

In the course of experiments, a non-doped and a 0.05 wt% Nb-doped SrTiO$_3$ single crystal were used as ablation targets to assure stoichiometric composition, as well as high mass density and to guarantee an absence of grain boundaries, both of which may affect the material ablation behavior. The targets were raster scanned on an x-y stage during ablation, instead of commonly-used target spinning to avoid denting of the target surface, which causes ablation plume tilting upon long-time deposition.

Laser ablation and deposition were carried out at various laser energies and ablation areas. The laser pulse rate was set at 2 Hz unless otherwise noted. Sufficient pre-ablation was performed before actual deposition to make sure that the target surface reached a steady state for each combination of laser beam parameters. The substrate temperature was kept constant at 700 °C for homoepitaxial growth. Most of the depositions were performed under an oxygen pressure of 1.3 x 10$^{-4}$ Pa while the chamber base pressure was ~4.0 x10$^{-7}$ Pa.

Reflection high-energy electron diffraction (RHEED) was used in situ for real time observation of the diffraction pattern, and the intensity of the specular spot in a [010] RHEED pattern was monitored for the detection of intensity oscillations during epitaxy to measure the deposition rate and to control the deposited film thickness. For the measurement of film thickness and line depth profiling of ablated target surfaces, a stylus profilometer was employed. A confocal ultraviolet laser scanning microscope (Keyence, VK-9500) was used for 3-dimensional depth profiling of ablated target surfaces. Epitaxial film crystallinity was examined by a conventional X-ray diffractometer with $\omega$-2$\theta$ scans, and the composition was evaluated with energy dispersive X-ray spectroscopy (EDS) during cross-sectional transmission electron microscopy (TEM) observations, as well as with X-ray fluorescent analysis (XRF) of films deposited on Si substrates.

3. Results and discussions

3.1.1. Film deposition rate

SrTiO$_3$ is a typical cubic perovskite with a lattice constant of 0.3905 nm. Homoeptaxy of SrTiO$_3$ can be done quite easily in layer-by-layer fashion up to almost infinite thickness under relatively wide range of growth conditions if the substrate surfaces are well defined [8]. It is known that one RHEED intensity oscillation corresponds to the growth of one unit cell thick SrTiO$_3$ (0.3905 nm) layer. To confirm this, films were deposited until 256 (= 100 nm /0.3905 nm) oscillations were counted, and the film thickness was ex-situ measured with the profilometer after unloading the sample, resulting in an average thickness of 100 nm within an error of +/- 5% for all samples. This error may be caused by imperfect uniformity of the film thickness and the difference of measured position between RHEED
Typical RHEED intensity oscillations during homoepitaxy at various beam spot areas and laser energies. (centre of the sample) and profilometer (sample edge). This result suggests that counting RHEED intensity oscillations can be used as an accurate and real time film thickness monitor or, as in this work, a deposition rate monitor of the crystal surface during epitaxy with unit cell resolution.

The RHEED intensity oscillations were monitored at various combinations of laser energy and ablation spot area while using a Nb-doped SrTiO3 target, as shown in Figure 1. As can be clearly seen, the oscillation period, which directly corresponds to deposition rate, varied systematically with changing laser energy and ablation spot area. Figure 2 shows the film deposition rate per pulse, calculated from the period of RHEED oscillations, as a function of laser fluence. The deposition rate is normalized by ablation area so that the ablation area difference can be compared at the same laser fluence.

This plot includes several interesting features. First, the ablation threshold fluence is clearly visible at about 0.1 J/cm². The film deposition starts above this fluence and the deposition rate per unit area increases almost linearly with increasing fluence regardless of the ablation spot area. The second point of interest is the spot area dependence of deposition rate at higher fluence. The data points corresponding to each spot size lie on respective linear lines but all of these extrapolations intersect at a single point, at an energy density of 0.3 J/cm². This unique fluence value, as well as the ablation threshold of 0.1 J/cm², could be accurately reproduced under higher oxygen pressures of 1.3 x 10⁻³ and 1.3 x 10⁻² Pa as well as at shorter (34 mm) and longer (54 mm) sample-target distances (not shown). We can conclude that 0.3 J/cm² is a “critical” laser fluence for SrTiO3 deposition. At a certain fluence above the critical value, e.g. at 0.5 J/cm², the deposition rate per unit ablation area decreased with reducing spot size, as can be seen in Fig 2. This clearly reveals the effect of larger divergence of the plume caused by a smaller ablation area.
3.2. Material ablation rate

It is quite important to know the behavior of material ablation from a target as well as film deposition on a substrate, because we can get the useful information, i.e., what ratio of ablated material is transferred to the substrate.

To do this, we used a mirror-polished 15 mm x 15 mm x 0.5 mm non-doped SrTiO$_3$ single crystal substrate as an ablation target. The surface was ablated at various combinations of laser energy and beam spot area. The ablation conditions are summarized in Table 1. By using the target scanning feature, a different region of the target surface was ablated at each set of ablation conditions. In each region, 40,000 laser pulses were fired at a frequency of 20 Hz at pre-selected spot size and laser energy while raster scanning the target in rectangular shape.

Figure 3 (a) shows a picture of the resultant target surface. The ablated material was deposited on 10 x 10 mm$^2$ Si substrates during the last 20,000 pulses at room temperature and the thickness and uniformity of the films were evaluated. It was found that the measured single-pulse deposition rate per unit ablation area on the Si substrates was almost identical to the one obtained with the above described RHEED intensity oscillation measurements at the same laser energy and ablation spot area, although the films grown here were not crystallized and the pulse rate of the laser was 10 times higher. This is likely due to the close packed crystal structure of perovskite SrTiO$_3$.

In order to estimate the ablated volume from the target surface, 3-dimensional depth profiles were measured by confocal laser microscopy. Figure 3 (b) shows a typical depth profile image, which is combined with a corresponding optical picture. The converted single-pulse ablation rate per unit ablation area was plotted in Fig. 4 as a function of laser fluence.

The ablation rate had simple linear correlation with the fluence and it was independent of the ablation area or sample-target distance. This result also demonstrates the measurement accuracy of the ablation area and laser energy. The ablation threshold was visible at around 0.1 J/cm$^2$, which agreed with the results of deposition rate experiments. However, it should be noted that there exists neither a “critical” fluence at 0.3 J/cm$^2$ nor an ablation spot area dependence in Figure 4, in contrast to the

![Figure 3](image_url)

**Figure 3.** 40,000 pulse ablated SrTiO$_3$ single crystal surface. (a) Optical microscope image and (b) 3-D depth profile.

![Figure 4](image_url)

**Figure 4.** Ablation rate per pulse, normalized by ablation spot area as a function of laser fluence. The S-T distance was either 44 mm (open circles) or 29 mm (closed circles).
deposition rate experiments shown in Figure 2. These facts reveal that the “critical” fluence is only related to the deposition process, and probably the ablation spot area plays an important role for film deposition since it affects the plume divergence, as described in the deposition experiment. The material transfer ratio calculated from the volume of ablated material and actual deposited amount is summarized in Table 1.

It is surprising that we are utilizing only around 8% of ablated material, although the value varies with laser fluence and sample-target distance, as well as laser spot area at a constant fluence, e.g. 0.3 J/cm² with different ablation spot area.

Table 1. Summarized ablation conditions and volume of ablated (40,000 pulses) and deposited (20,000 pulses) material, as well as material transfer ratio.

| Energy (x 10⁻³ J) | Spot area (x 10⁻² cm²) | Fluence (J/cm²) | S-T distance (mm) |Raster size (mm x mm) | Ablated vol. (x 10⁻³ cm³) | Deposited vol. (x 10⁻⁶ cm³) | Transfer ratio (%) |
|-------------------|------------------------|-----------------|-------------------|----------------------|---------------------------|---------------------------|-------------------|
| 1 3.4              | 1.1                    | 0.31            | 44                | 3 x 2                | 22                        | 7                         | 6.8               |
| 2 9.3              | 3.1                    | 0.30            | 44                | 3 x 2                | 67                        | 24                        | 7.1               |
| 3 12.7             | 1.1                    | 1.16            | 44                | 3 x 2                | 88                        | 18                        | 4.2               |
| 4 21.3             | 6.0                    | 0.36            | 44                | 3 x 2                | 138                       | 58                        | 8.4               |
| 5 25.4             | 6.0                    | 0.42            | 44                | 3 x 3                | 175                       | 75                        | 8.6               |
| 6 7.5              | 0.9                    | 0.83            | 29                | 3 x 2                | 62                        | 32                        | 10.4              |
| 7 12.3             | 6.1                    | 0.20            | 44                | 3 x 2                | 64                        | 21                        | 6.6               |
| 8 14.8             | 6.0                    | 0.25            | 44                | 3 x 2                | 84                        | 29                        | 7.0               |
| 9 18.3             | 6.0                    | 0.30            | 44                | 3 x 2                | 116                       | 45                        | 7.8               |

3.3. Lattice constant and composition of the homoepitaxial films

More than 100 homoepitaxial films were grown one by one at various combinations of laser conditions for the evaluation of crystal quality. The film thickness was fixed at 100 nm and measured by RHEED monitoring. The required deposition time varied considerably, from 9 min to 4 h, depending on the deposition rate.

The out-of-plane lattice constant of the films was characterized by XRD. Even though SrTiO₃ films were grown homoepitaxially, the film peaks were not overlapping with the substrate peak. The film peaks were always found on the larger lattice spacing side of the substrate peak in ω-2θ scan. Detailed lattice constant analysis of the grown films can be found elsewhere [9]. Similar results have been reported previously by various other groups [10,11]. According to the previously reported asymmetric composition transfer depending on laser fluence [1-5], the lattice expansion from bulk value is plotted as a function of laser fluence in figure 5. It is obvious that the lattice value of homoepitaxial films can be tuned widely by changing the ablation laser conditions at a fixed oxygen pressure and growth temperature. Again, we see that there is a unique laser fluence at 0.3 J/cm², where we obtain the expected bulk lattice constant. Even a slight deviation by, say 0.1 J/cm², to either side leads to considerable lattice expansion. We could not obtain any films at fluences below 0.1 J/cm² since no material ablation occurred. Multiple data points with identical fluence values resulted from experiments where the laser spot area on the target surface was changed at a constant fluence. A larger
spot area generally resulted in smaller lattice expansion for each laser fluence value. This appears to be caused by a change in the ablation plume shape.

An outstanding finding here is that the critical fluence, 0.3 J/cm\(^2\), which gives a bulk equivalent lattice parameter, is identical to the critical fluence found in the deposition rate experiments. On the other hand, in the ablation experiment this type of specific fluence was not observed, meaning that the lattice constant change is strongly correlated with the film deposition process, rather than the target ablation process.

EDX analysis was performed for cationic composition measurement during cross-sectional TEM observation on 3 homoepitaxial thin films grown at various laser conditions: 0.21 J/cm\(^2\) & 0.10 cm\(^2\), 0.30 J/cm\(^2\) & 0.06 cm\(^2\), and 1.90 J/cm\(^2\) & 0.01 cm\(^2\), using the substrate as a composition standard [9]. The lattice constants of these films were 0.4034 nm, 0.3909 nm, and 0.3955 nm, respectively. The resultant composition of the films, defined as Sr/(Sr+Ti) %, were 54.9 \(+0.8/-0.6\) %, 50.2 \(+1.7/-1.5\) %, and 48.9 \(+0.1/-0.3\) %, respectively. It is clear that the composition is strongly pushed to the Sr rich side at fluences below the critical value, which supported the results found in literature [4]. The composition of films grown at the critical fluence was stoichiometric within the measurement errors. In contrast, at fluences higher than the critical value, a small but significant deficiency of Sr was detected. Results of XRF analysis for the non-crystallized films on Si substrates, which were deposited during the ablation experiments, also supported the asymmetric composition transfer.

We conclude that the expansion of the lattice constant reflects the cationic unbalance, and bulk-equivalent stoichiometric films can only be grown only at the critical fluence.

4. Conclusion
In the PLD process, it was found that stoichiometric transfer of a complex oxide from an ablation target to a substrate surface could only be obtained at a single well-defined laser fluence under molecular beam epitaxy conditions. Either higher or lower fluence values resulted in a nonstoichiometric transfer. These effects appear to correlate with the process of material deposition as well as the ablation process. In case of SrTiO\(_3\) homoepitaxy, the critical fluence where epitaxial films reproduced the bulk lattice constant was 0.3 J/cm\(^2\). Accurate measurement of laser energy and ablation spot area is therefore universally vital for repeatable and reliable PLD film growth.

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