

Parametric study of barium titanate gradient thin films via off-center pulsed laser deposition

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ABSTRACT

The deposition parameters used in complex oxide thin film growth are typically tuned to optimize functional properties with minimized heterogeneity, for instance in composition and crystalline structure. However, in pulsed laser deposition (PLD), gradients in film thickness and stoichiometry can be created deliberately by taking advantage of the anisotropic expansion of the plasma plume. Here, we use PLD with an off-center alignment to study barium titanate (BTO) thin films grown with a fluence sweep at constant pressure, and a pressure sweep at constant fluence. First, reflection high energy electron diffraction (RHEED) is used to distinguish between 2D layer-by-layer, multi-level, and 3D island growth by observing both diffraction patterns and positional RHEED scans. Next, X-ray diffraction (XRD) reveals that the out-of-plane lattice parameter increases with higher fluence values and decreases with higher pressure. Lastly, X-ray photoelectron spectroscopy (XPS) shows that Ba-rich phases can form either at low fluence conditions or within the pressure range greater than 0.02 mbar but less than 0.2 mbar. This study highlights the potential of off-center PLD as an efficient way to study the effect of compositional gradients on the material properties of BTO and other multi-cation functional oxides.

1. Introduction

Pulsed laser deposition (PLD) is a thin film deposition technique which first gained attention as a method for producing high T_c superconducting oxide thin films. Since then, it has been applied for the fabrication of thin films in fields such as multiferroics, energy storage, catalysis, and resistive switching. One feature that sets PLD apart from the other physical vapor deposition techniques is that the target material is transferred to the substrate via a so-called transient plasma plume which expands anisotropically away from the target. Parameters such as laser fluence [1,2,3,4,5], background gas pressure [6,7,8], target-to-substrate distance [4,9], and spot size [10] control the energetic and chemical state of particles upon arrival at the substrate surface during deposition, and in turn affect the film composition and crystallinity and therefore functional properties.

An uneven deposition rate [11] is one consequence of the anisotropic plasma plume expansion. For conventional laboratory-scale PLDs without a scanning plasma plume, there is a narrow range within which the thicknesses are reasonably homogeneous. This is why square substrates with a side length of 5 mm or 10 mm are the standard sizes used

for this technique. But within this range it is still possible to obtain a thickness gradient of few unit cells (uc) using specific settings of the laser beam on the target. Demonstrations were reported for LaAlO₃ grown on SrTiO₃ with an abrupt thickness-dependent metal-to-insulator transition [12]. The induced thickness variations can be measured as a function of distance from the point on the substrate directly perpendicular to the center of the plasma plume. The resulting gradients have been used in the past as a platform to study conductivity behavior in oxide thin films [12,13].

The stoichiometry of films grown by PLD is another property affected by the plasma plume dynamics. The background gas molecules function as scattering centers which are more effective at changing the trajectory of lighter ions, whereas the laser fluence not only influences the target ablation mechanism but also the kinetic energy of the rapidly moving ablated species [14]. Off-stoichiometry caused by suboptimal parameter selection produces defects that can alter material properties such as surface morphology and resistivity.

In this study, we have chosen barium titanate BaTiO₃ (BTO) – one of the earliest discovered perovskites and the prototypical ferroelectric oxide with applications in energy storage, computing memory, and

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photonics – as our model material. The effect of cation stoichiometry and film thickness on the polarization behavior of BTO has been widely discussed in other studies [1,2,3,6]. Furthermore, the cations in BTO are non-volatile at the typical PLD growth conditions in literature which allows for the study of stoichiometry without the influence of growth temperature, unlike the case for Pb, Bi, or alkali metal-containing ferroelectric oxides. All the films in this study were grown on SrTiO₃ (STO), which has a 2.3 % in-plane compressive lattice mismatch with BTO. We deposited films below 5 nm thickness with the intention of obtaining out-of-plane-oriented BTO with minimal relaxation.

Gradients are made possible using an off-center alignment of the substrate with respect to the plasma plume central axis, taking advantage of the asymmetric expansion of the plume. While conventional film growth treats individual samples as singular data points by averaging measurements over the entire sample, understanding the interplay between these growth parameters and material properties along the sample length allows for the treatment of PLD-grown films as data surfaces with position-dependent properties.

2. Experimental methods

The samples were grown using a KrF excimer laser (248 nm) on (100) oriented STO single crystal substrates (Crystrac GmbH) with miscut tolerance of 0.1–0.2° and dimensions of 5 mm × 10 mm. Prior to growth, the substrates were chemically etched in buffered hydrofluoric acid followed by annealing for 90 min at 950 °C under 150 L/h O₂ flow in order to get atomically-flat TiO₂ terminated terraces on the substrate surface. A sintered BaTiO₃ target (SurfaceNet GmbH) was used for the deposition, and the laser spot size was 1 mm × 1.76 mm. The substrate was aligned in such a way that the ablation spot is directly facing the bottom edge of the sample. A sketch of the substrate-target geometry and is depicted in Fig. 1 and is described in more detail in [12]. For the local measurements along the sample length, we describe the data as a function of lateral distance, which we define as the distance between the substrate edge aligned with the central axis of the plasma plume during growth and a given point along the translation axis.

Under a constant background gas of 0.02 mbar O₂, samples were grown with laser fluence values of 0.7 J/cm², 1.5 J/cm², 1.9 J/cm², 2.3

J/cm², 2.7 J/cm², and 3.5 J/cm²; these are collectively referred to as the fluence sweep series in this study. Using a constant 1.9 J/cm² laser fluence, samples were grown at 0.005 mbar O₂, 0.02 mbar O₂, 0.05 mbar O₂, 0.1 mbar O₂, 0.2 mbar O₂, and at 0.1 mbar absolute pressure with 20 % O₂ and 80 % Ar mixture; these samples shall be referred to as the pressure sweep series. A single sample grown at 0.02 mbar O₂ and 1.9 J/cm² was included in both the fluence sweep and pressure sweep series.

All the BTO films were deposited at a set point of 700 °C, as measured by a pyrometer on the back side of the sample holder and using a repetition rate of 1 Hz. The samples were then cooled at a rate of 20 °C/min immediately after growth without changing the pressure in the chamber. Growth was monitored *in situ* using a reflection high energy electron diffraction (RHEED) beam at 30 keV and 1.4–1.5 mA. Before taking the sample out of the chamber, the entire sample length was scanned with the RHEED beam along the z-axis indicated in Fig. 1, producing an intensity-versus-lateral distance plot and this technique is also referred to as positional RHEED in the text to distinguish it from the RHEED intensity-versus-time plots used for growth monitoring. The samples were grown with a desired thickness of approximately 11 monolayers at the 0 mm lateral distance position which was estimated by counting the number of pulses per RHEED oscillation, whereas the 0.2 mbar sample which exhibited no oscillations was grown with the same number of pulses used for the 0.1 mbar sample.

The samples were characterized in ambient conditions with atomic force microscopy (AFM) in tapping mode using a TESPA-V2 tip with a spring constant of 37 N/m and radius 7 nm on a Bruker Dimension Icon system. X-ray diffraction (XRD) was performed using a Bruker D8 Discover diffractometer. A collimator diameter of 0.5 mm was used to perform local measurements on the sample. Measurement spots were taken at 1 mm, 3 mm, 5 mm, 7 mm, and 9 mm away from one edge. X-ray photoelectron spectroscopy (XPS) was performed *ex situ* using a PHI Quantex scanning microprobe. An Al K α source was used, and the beam diameter was set to 0.2 mm. Like the XRD, measurements were also performed at 2 mm intervals along the length of the sample. A 45° XPS photoemission angle was used for all BTO films.

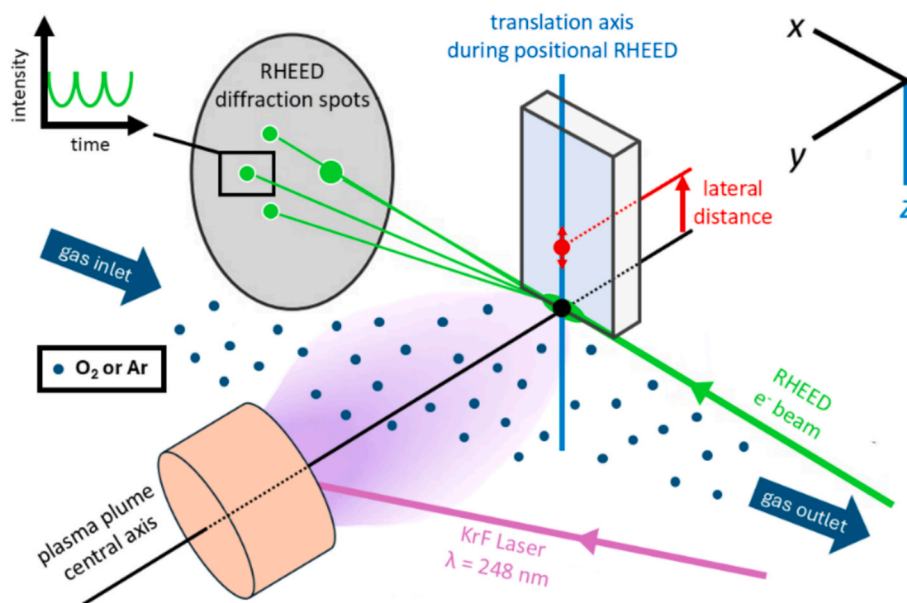


Fig. 1. Schematic of substrate-plume off-center alignment during deposition along with the position of the RHEED beam. The y-axis is the direction at which the substrate-target distance is measured while the z-axis is the translation direction when obtaining RHEED intensity-versus-position plots. During growth, the RHEED beam is focused on the sample edge and aligned with the central axis of the plasma plume. The target and the substrate are not drawn to scale. Gas molecules are only shown along the plume path for better visibility of the substrate and RHEED of the figure.

3. Results

RHEED is a technique which provides information on surface structure and morphology using an electron beam hitting a surface at a grazing incidence and is often used as an *in situ* monitoring tool for physical vapor deposition at pressures below 1 mbar [15,16]. Fig. 2a shows the RHEED diffraction patterns of the BTO films before being taken out of the chamber. For the fluence sweep samples, the (00), (10), and (−10) reflections were singular spots at 1.9–3.5 J/cm² indicating a 2D surface, whereas the 0.7 J/cm² sample shows multiple transmission spots indicating 3D islands. whereas For the pressure sweep samples, a 2D pattern can be observed for 0.005 mbar to 0.02 mbar, whereas the 0.1 mbar and 0.2 mbar samples are 3D. Additionally the 1.5 J/cm² fluence and the 0.05 mbar sample shows a 2D pattern with surface roughening, since the (00) spot is diminished in intensity compared to the (10) and (−10) spots. The surface morphologies estimated from diffraction patterns are confirmed using AFM data shown in Fig. 2b.

To characterize the surface roughness of the films across the entire length, RHEED intensity-versus-lateral distance plots were created by

moving the sample along the z-axis (as described in Fig. 1) with the results compiled in Fig. 2c and 2d, and these were compared to the *in situ* time-dependent RHEED specular intensity plots. There were samples that exhibited a 2D layer-by-layer growth mode in which the *in situ* RHEED oscillations recover close to 100 % of their initial intensity as shown in Fig. 2e – these samples produced regularly-spaced positional RHEED oscillations that persisted throughout the length of the sample, and the oscillations are shown to correspond to roughness variations that can be observed with AFM (see Fig. S1). Several samples exhibited a multi-level mode during growth in which there is damping of the oscillation intensity, as demonstrated by Fig. 2f. Interestingly, the samples which underwent multi-level growth also showed positional RHEED oscillations, but only at lateral distances more than 5 mm away from the plume center. Lastly, the samples grown at 0.1 mbar (with pure O₂ and O₂-Ar) and 0.2 mbar showed a steady, non-oscillating RHEED intensity at the latter part of the deposition and a transmission pattern indicating 3D island growth as in Fig. 2g, and shows a flat positional RHEED intensity plot. Table 1 summarizes the observed growth modes for all samples.

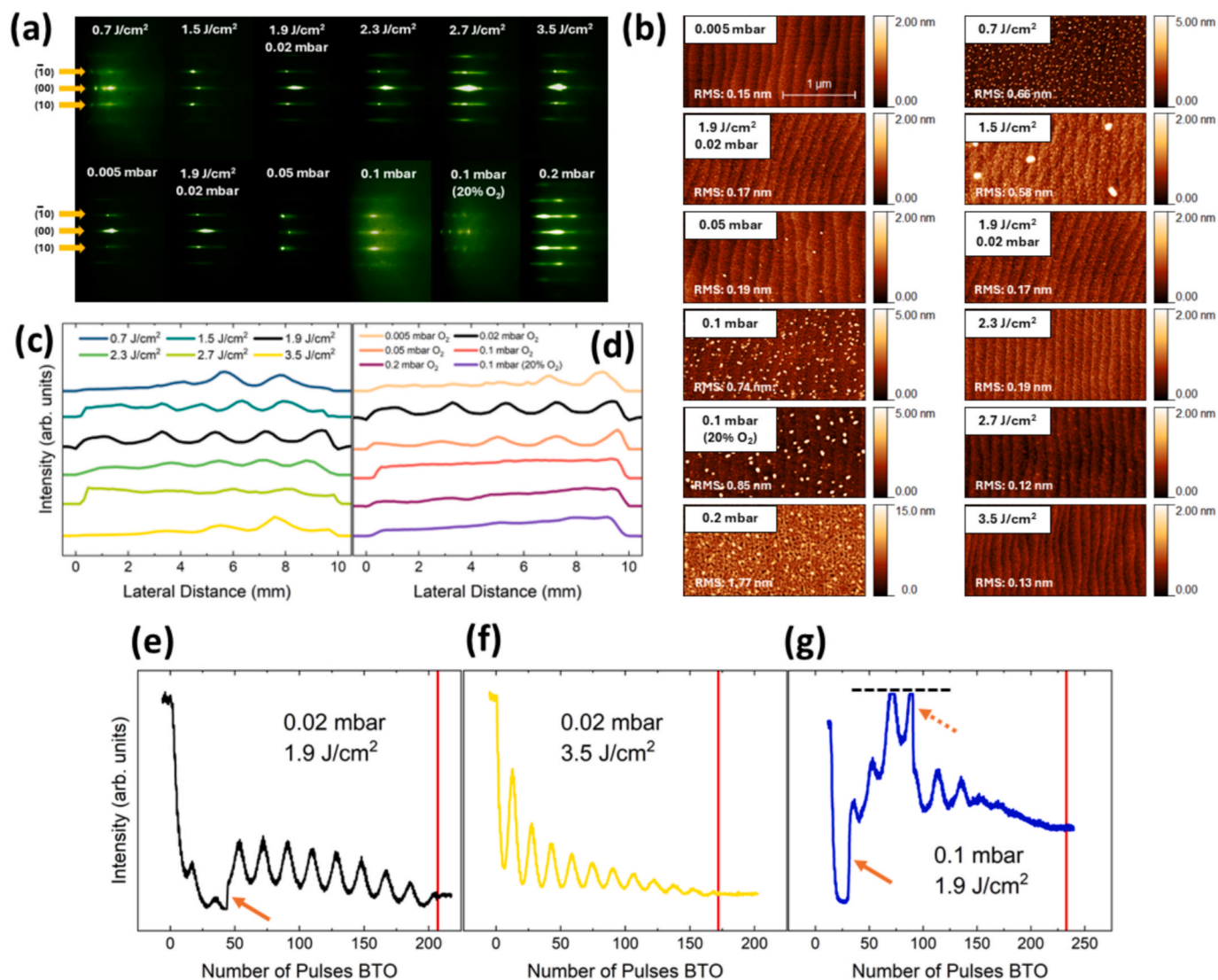


Fig. 2. RHEED surface diffraction images in the 01 direction at the 0 mm lateral distance position (a). Atomic force microscopy scans (b) of size 2.5 $\mu\text{m} \times 1.25 \mu\text{m}$ of the films were taken at approximately 1 mm lateral distance for validation of the RHEED diffraction data. Positional RHEED intensity-versus-lateral distance scans of the fluence sweep (c) and pressure sweep (d) were taken *in situ* at $< 100^\circ\text{C}$ and at $< 10^{-6}$ mbar pressure before the samples were taken out of the PLD chamber. *In situ* RHEED monitoring shows intensity as a function of the number of pulses of BTO in which the growth is completed on a 2D layer-by-layer (e), multi-level (f), and 3D island (g) mode, with red lines marking the endpoint. In (e) and (g), a manual increase (decrease) of the RHEED current is represented by a solid (dotted) arrow. The dashed line in (g) indicates the threshold at which the RHEED intensity exceeded the measurable range.

Table 1

Classification of samples according to growth mode observed with RHEED.

Mode during end of growth	2D layer-by-layer	Multi-level	3D island
Fluence Sweep	1.5–2.3 J/cm ²	0.7, 2.7–3.5 J/cm ²	–
Pressure Sweep	0.02–0.05 mbar	0.005 mbar	0.1–0.2 mbar

The X-ray symmetrical scans of all samples were fitted with the Stepanov X-ray server GID SL program [17], which uses a dynamical model describing all interactions between the incident wave and the lattice planes. The dynamical approach uses the Debye-Waller factor, a quantity that represents the attenuation of X-ray photons due to thermal vibrations [18] of which values can vary from 0 (indicating an amorphous film) to 1 (indicating a perfect crystal). The BTO films were treated as monolayers when performing the fittings except for the case of the sample grown at 0.2 mbar, which is treated as two layers with the initial layer having a lower crystallinity than the succeeding layer. The measured data and fittings are shown in Fig. 3 with the fitting parameters listed in Table 2. All the samples are strained to the STO substrate as shown by XRD reciprocal space mapping (Fig. S3) thus the changes in the unit cell volume can be quantified solely with the BTO out-of-plane lattice parameter c_{BTO} .

For the fluence sweep series, the BTO film thickness as a function of

Table 2

Values used in the XRD fittings for the entire dataset.

Parameter	0.2 mbar BTO film	Rest of films
STO Roughness	2 Å	2 Å
BTO Roughness	1 Å (1st layer), 4 Å (2nd layer)	2–3.5 Å
BTO Debye-Waller Factor	0.425 (1st layer), 0.7 (2nd layer)	0.7

lateral distance along the STO substrate is shown in Fig. 4a. All samples had a similar thickness at a lateral distance of 1 mm except the sample grown at 0.7 J/cm². Furthermore, films grown at low fluences had a greater decrease in film thicknesses from 1 mm to 9 mm along the sample compared to those grown at higher fluences. The film grown at 3.5 J/cm² shows minimal thickness loss and was treated with the same fitting conditions from 1 mm to 5 mm lateral distance.

Fig. 4b highlights the change in c_{BTO} with respect to the lateral distance along the substrate. Two general trends were observed. First, at every measurement point along the STO substrate, higher fluences led to a larger c_{BTO} . The exception is for the film grown at the highest fluence of 3.5 J/cm² where c_{BTO} was almost constant up to 5 mm before decreasing at larger values of lateral distance. Second, there was a decrease in c_{BTO} with respect to normal. Fig. 4c presents the change in the c_{BTO} from 1 mm to 9 mm at different fluences. As expected, an increasing trend is seen except for the sample grown at the highest fluence, where the difference in the out-of-plane parameter is closest to

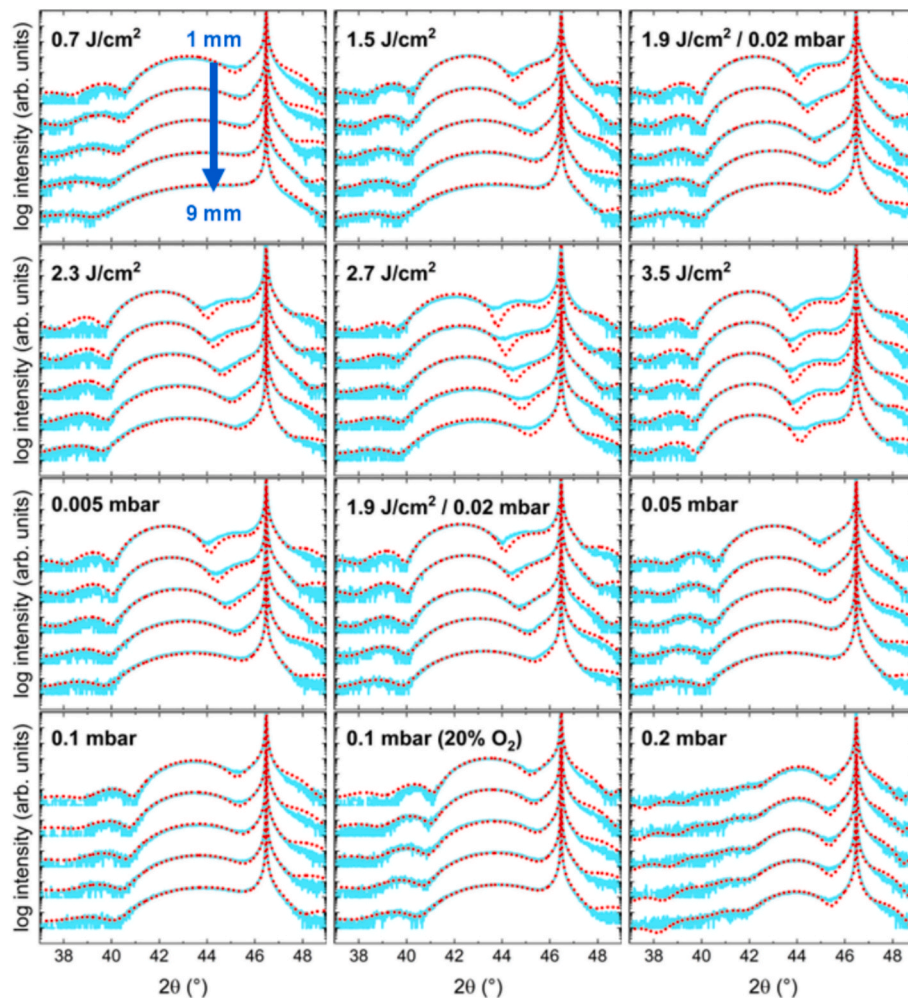


Fig. 3. Experimental (cyan) XRD measurements which are fitted (red) for simultaneous extraction of both the out-of-plane parameter and the film thickness. For each fluence/pressure condition the plots are arranged from top to bottom with increasing lateral distance from 1 mm to 9 mm, as shown by the blue arrow inset in the 0.7 J/cm² plots.

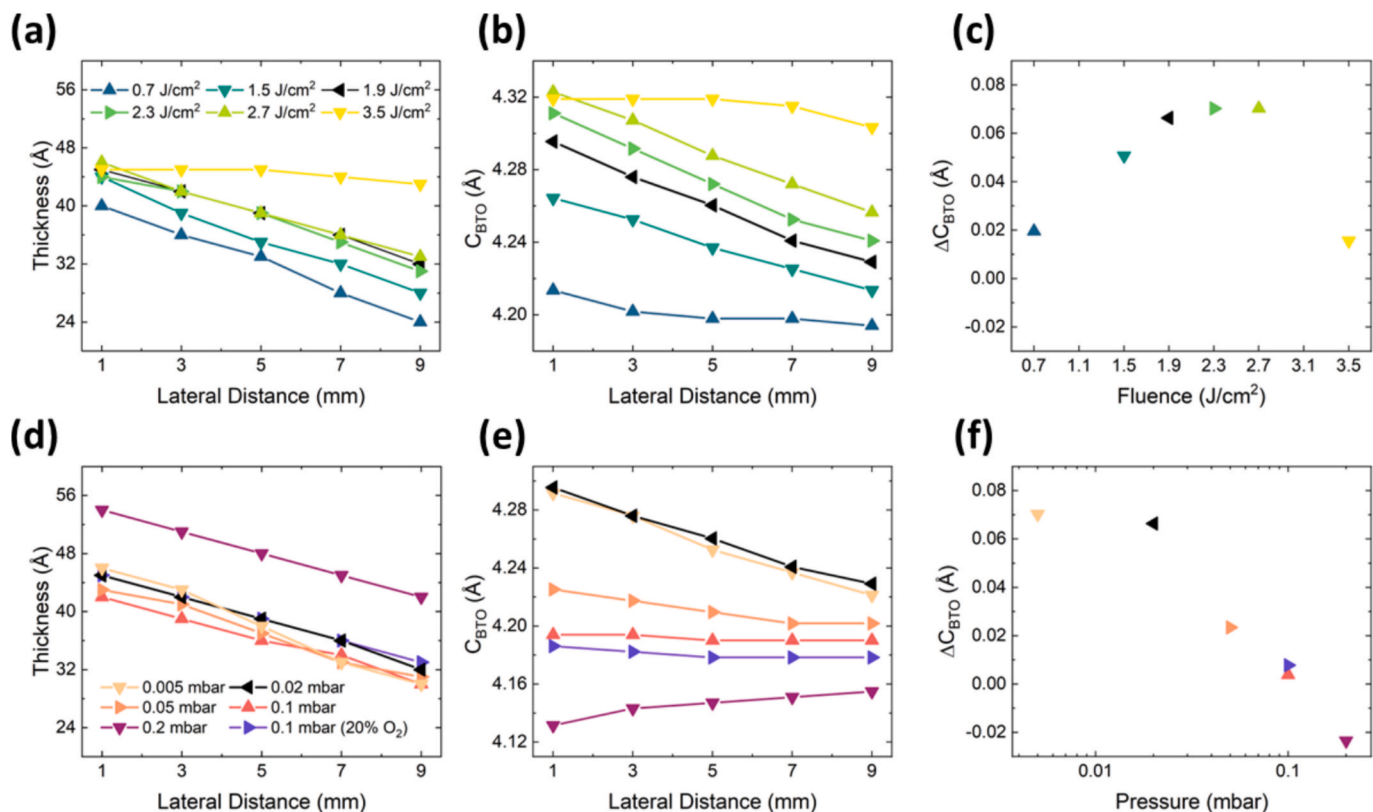


Fig. 4. For the fluence sweep series, the thickness (a) and out-of-plane parameter (b) were extracted from the fits generated by Stepanov X-ray server. The extraction was also performed for the thickness (d) and out-of-plane parameter (e) of the pressure sweep series. The change in c_{BTO} between position 1 mm and position at 9 mm laterally as a function of fluence (c) and pressure (f). Note that the films are fitted as single BTO layers except for the 0.2 mbar sample, with additional details in Fig. S2.

zero.

For the pressure sweep series, the same study of thickness as a function of lateral distance from the plume is shown in Fig. 4d. There is a thickness difference of approximately 3 monolayers for all samples when going from 1 mm to 9 mm. Fig. 4e shows that there is a significant decrease in the out-of-plane lattice parameter with increased lateral distance for the lower range of pressures used for this study, quite like the behavior we noticed in samples grown at intermediate fluences.

Fig. 4f shows the change in c_{BTO} over lateral distance as a function of pressure. Samples grown at pressures of 0.005 mbar and 0.02 mbar had a constant total change in c_{BTO} . At 0.05 mbar to 0.1 mbar, the change in out-of-plane parameter is still positive but close to zero. At 0.2 mbar the opposite trend is observed, with an increase in the c_{BTO} at higher distances.

To further get some information on stoichiometry changes in the films, presumably responsible for the unit cell volume changes, we performed XPS measurements. XPS provides information about the ratio of cations for a given probing depth of approximately 6 nm for Al K α . For experimental measurements and comparison of the cation ratios we use the Ba fraction F_{Ba} which in the current study is calculated using the normalized areas under the Ba 3d peaks $\tilde{I}_{Ba}$ and the Ti 2p peaks $\tilde{I}_{Ti}$ shown in Eq. (1).

$$F_{Ba} = \frac{\tilde{I}_{Ba}}{\tilde{I}_{Ba} + \tilde{I}_{Ti}} \quad (1)$$

The Ba 3d_{5/2} and Ti 2p spectra measured at 1 mm lateral distance are shown in Fig. S4 and Fig. S5 of the supporting information. Since the samples were taken out of vacuum and stored in ambient conditions prior to the *ex situ* XPS measurements, we forego the analysis of the oxygen spectra which is highly affected by adsorbates such as

hydroxides and carbonates forming on the surface in a time-dependent manner.

It is important to distinguish between termination-related cation ratios as compared to off-stoichiometry in the film, and this is possible with the F_{Ba} . To estimate the effect of termination changes in the measured F_{Ba} , we simulate the intensity ratios for 100 % TiO₂ and 100 % BaO, following a similar approach used by Baeumer et al [19] which is explained in detail in the ‘Ba Fraction Calibration’ section in the supporting information. Even for perfect film stoichiometry (i.e., a Ba/Ti ratio of 1), surface termination leads to deviations in the measured F_{Ba} . An F_{Ba} of 0.527 corresponding to 100 % BaO termination and 0.449 corresponding to 100 % TiO₂ termination for perfect film stoichiometry are marked with dashed lines in Fig. 5a–5b as a visual guide for interpreting the experimental F_{Ba} data. The measured F_{Ba} for stoichiometric films is expected to fall in this range.

Fig. 5a shows that the 0.7 J/cm² and 1.5 J/cm² samples contains excess Ba relative to the samples grown at higher fluences probably due to preferential ablation of BaO from the BaTiO₃ [14,20]. This is supported by the AFM images in Fig. 2 showing an island-rich surface for the samples grown with the lowest fluence, which are possibly Ba-rich phases. Next, the sample grown at 1.5 J/cm² is slightly below the F_{Ba} threshold, however the RHEED patterns and AFM in Fig. 2a and 2b show the presence of islands albeit with a lower density than that of the 0.7 J/cm² sample, indicating that the F_{Ba} being close to the threshold is likely due to the Ba-rich islands rather than having full BaO termination of the surface. The Ba excess in the 0.7 J/cm² and 1.5 J/cm² samples also seems to be more pronounced at values of lateral distance closer to 0 mm, indicating the Ba distribution in the plasma plume is inhomogeneous at low fluences across a lateral distance of 10 mm. Increasing the fluence further from 1.9 J/cm² to 3.5 J/cm² produces films which fall within the threshold F_{Ba} values which are free of islands, indicating that

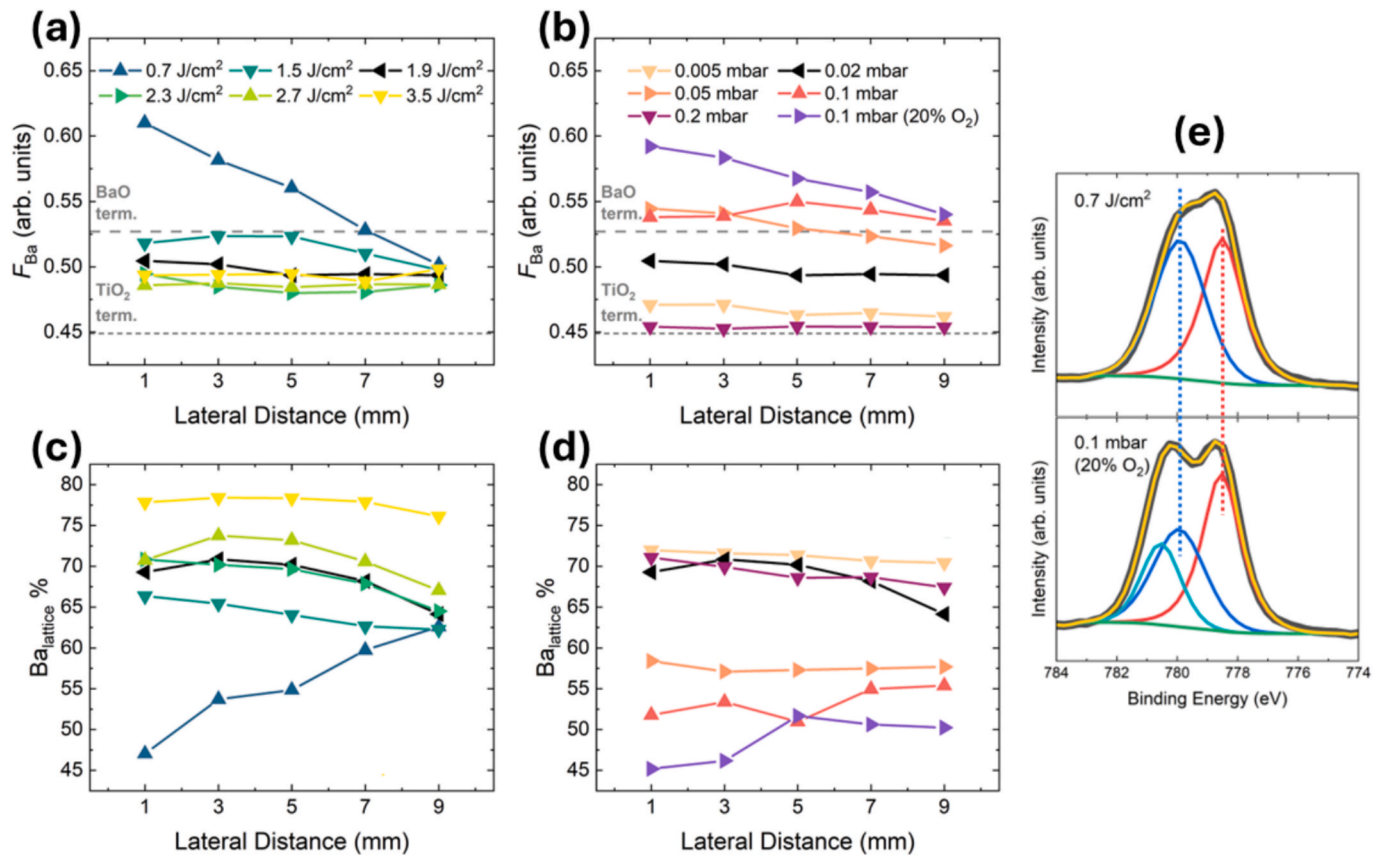


Fig. 5. F_{Ba} values as a function of lateral distance of the fluence sweep (a) and pressure sweep (b) samples measured at 45 degrees emission angle. The region in between the gray dashed lines represents the range of F_{Ba} values which are possible for stoichiometric BTO films with varying surface termination. The percentage of the Ba 3d peak corresponding to lattice Ba was shown for both sweeps (c-d). The black line at 1.9 J/cm² for the fluence sweep is the same sample as the data with 0.02 mbar for the pressure sweep. The highest F_{Ba} values obtained were at 0.7 J/cm² and 0.1 mbar (20 % O₂) for the fluence sweep and pressure sweep, respectively and shown in (e). The Ba 3d_{5/2} peaks of the two Ba-rich samples were compared with the red line indicating the lattice Ba, the blue line indicating the + 1.4 eV surface peak, and the cyan line for the + 2.0 eV surface peak. The raw data, sum of the fittings, and the background are the black, yellow, and green lines, respectively.

these films are likely to be stoichiometric with mixed termination.

Next, the effect of growth pressure on the cation ratio as measured by XPS is shown in Fig. 5b. Both the 0.005 mbar and 0.02 mbar samples fall within the expected F_{Ba} values for stoichiometric films, with the lower value of the 0.005 mbar sample indicating higher TiO₂ coverage for this sample. The samples at 0.05 mbar to 0.1 mbar growth pressure are mostly above the F_{Ba} threshold indicating Ba excess. Lastly, even though the 0.2 mbar sample seems to fall within the stoichiometric F_{Ba} values, the topography of this film in Fig. 2c is shown to be highly defective and thus additional probing of the surface would be necessary to conclude on the stoichiometry of this film. The excess Ba in the samples grown at 0.1 mbar for both pure O₂ and O₂-Ar gas had a higher Ba fraction at lower lateral distances, but the decrease in the F_{Ba} across the sample length is not as drastic as that observed in the 0.7 J/cm² sample from the fluence sweep series.

We attempted to find a fitting model for the Ba surface peak at a fixed position with respect to the BaO lattice peak at 778.5 eV. For the fluence sweep series, all the samples can be fit with a surface hydroxide/carbonate component at + 1.4 eV binding energy, which is close to reported literature values [21,22]. The + 1.4 eV peak was also a sufficient fit for all the pressure sweep samples with the exception of the samples grown at 0.1 mbar, which required an additional surface peak at + 2.0 eV binding energy in order to match the raw data as shown in Fig. 5e.

The Ba 3d_{5/2} peak of the 0.1 mbar sample grown with mixed O₂-Ar has an extended shoulder on the higher binding energy side compared to the sample grown at 0.7 J/cm². Furthermore, this + 2.0 eV peak is shown to decrease when moving away from the center of the plasma

plume, as shown in Fig. S6. Along with the F_{Ba} results, Fig. 5c and Fig. 5d illustrate the percentage of the Ba 3d peaks associated with the lattice Ba peak, with the peak model shown in Fig. 5e. It is noted that the films with Ba excess in Fig. 5a and Fig. 5b also had the lowest percentage of lattice barium, indicating that the excess Ba accumulates on the surface of the films and not in the bulk.

4. Discussion

We discuss the overall results of the fluence sweep series, which is summarized in Fig. 6. The BaO-TiO₂ phase diagram shows a congruent melting point for BaTiO₃ at 1625 °C [23], indicating that the Ba excess in the films comes from preferential vaporization of BaO from the molten BaTiO₃ on the target surface, similar to what was observed with SrTiO₃ ablation at low fluence conditions [20]. The excess BaO produces Ba-rich phases which accumulate on the film surface as islands, with the islands decreasing in quantity with further distance from the plume center. Upon reaching the threshold fluence value of 1.9 J/cm² the islands are no longer present, and we obtain a stepped surface with 2D growth and minimal roughness. Within the 1.9–2.7 J/cm² fluence range we obtain films with the same surface stoichiometry, Δ_{CBTO} , and thickness distribution with respect to lateral distance. At a fluence of 3.5 J/cm² we get the most homogeneous film of the series having a minimal Δ_{CBTO} and thickness loss along the sample length, which suggests greater lateral expansion and homogenization of the plasma plume at this condition.

One important observation with the fluence sweep series is the

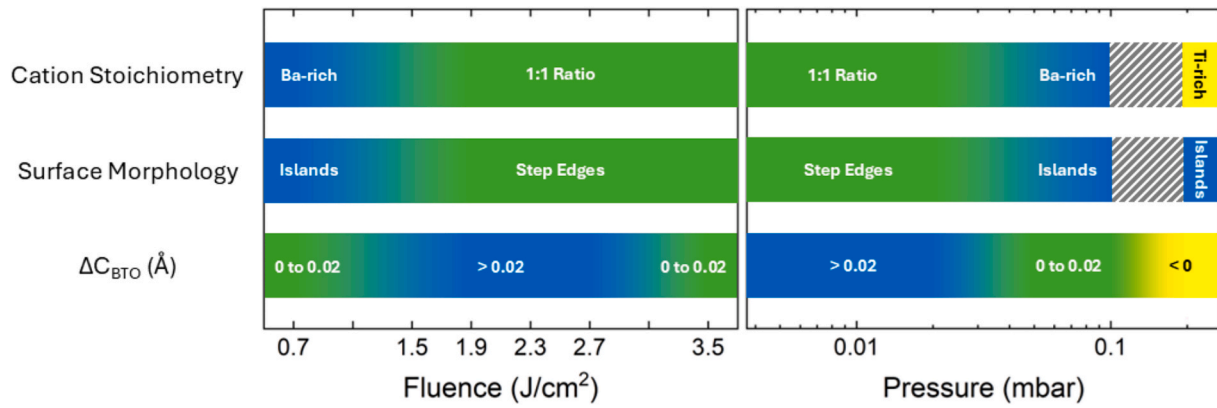


Fig. 6. Graphical summary of the findings from the fluence sweep and pressure sweep experiments. The shaded region for cation stoichiometry and surface morphology at 0.1–0.2 mbar represents parameters not explored in this study which could potentially show abrupt property transitions.

decoupling of the cation stoichiometry from the c_{BTO} . For the samples grown at the 1.9–3.5 J/cm² fluence range, c_{BTO} at 1 mm lateral distance is greater than the c_{BTO} at the 9 mm position even though the measured Ba fraction of the films remain constant all throughout. A previous study using optical emission spectroscopy suggests that TiO₂ ablated at < 0.05 mbar pressure creates a plume in which the Ti oxidation state increases proportionally to the lateral distance from the center [24], and this may result in an oxygen vacancy gradient along the deposited film. The trend of decreasing c_{BTO} with increasing lateral distance is also visible in the 0.7 J/cm² albeit with a value close to zero. Although Fig. 5a and 5c shows that most of the excess Ba accumulates on the surface at this low fluence, it is difficult to rule out cation off-stoichiometry in the film without using techniques such as transmission electron microscopy which can detect Ba-rich phases in the oxide lattice.

One aspect to take note of for studying BTO stoichiometry as a function of fluence is that the results vary based on the growth pressure used. Two studies from the same set of authors indicate that a fluence sweep at 2.67×10^{-2} mbar produces films that exhibit approximately 1:1 ratio of Ba/Ti once a threshold fluence value is exceeded [2], whereas a fluence sweep at 5.33×10^{-2} mbar produces greater Ti excess with increasing fluence [3]. The fluence sweep in the current paper closely matches the conditions in the former as well as those in [1], even though those studies were performed using GdScO₃ substrates. We expect that Δc_{BTO} due to oxygen vacancies are diminished at higher pressures, but the effect of cation off-stoichiometry on Δc_{BTO} along the sample at different growth pressures would be an interesting point of exploration for future studies.

For the pressure sweep series (also shown in Fig. 6), we observe a change in the Ba fraction within 0.005 mbar to 0.02 mbar going towards higher F_{Ba} with increased pressure. At 0.05 mbar the formation of a Ba-rich Island phase starts to occur, and the quantity of these phases increase further at 0.1 mbar. We have shown that this Ba-rich phase has an additional Ba 3d_{5/2} surface peak with binding energy which is + 0.06 eV higher than the surface peak at 779.9 eV which is present in all the samples. The higher-energy Ba peak is absent in the Ba spectra of the 0.7 J/cm² sample shown in Fig. 5e – this implies that the excess Ba with + 2.0 eV binding energy created at 0.1 mbar growth pressure has a different origin than the excess Ba that forms under low fluence conditions due to preferential vaporization of BaO from the target melt. Interestingly there is a reversal of surface stoichiometry between 0.1 mbar and 0.2 mbar growth pressure, going from a highly Ba-rich to a Ti-rich surface which has also been observed in previous studies [6]. Notably, the change in F_{Ba} of the 0.1 mbar samples along the sample length is not as drastic as the change in the sample grown at 0.7 J/cm² indicating that higher pressure homogenizes the amount of Ba being deposited throughout the length of the samples.

Our study confirms that decreased growth pressure causes the

elongation of the out-of-plane parameter for BTO films due to oxygen vacancies, which have been shown extensively not only with BTO but also several PLD-grown perovskite oxides [4,25]. By measuring c_{BTO} as a function of lateral distance, we see that decreasing the growth pressure below 0.05 mbar creates positive Δc_{BTO} values greater than 0.02 Å. This is likely caused by an increase in the Ti oxidation state in the plasma plume with increased lateral distance from the plume center during deposition. The Ti oxidation state as the sample arrives on the substrate in turn affects the oxygen vacancy concentration at different points in the deposited BTO films.

Assuming a stoichiometric BTO film is perfectly strained on STO and assuming a Poisson's ratio of 0.35 [26], the out-of-plane parameter should be 4.17 Å – this theoretical value is lower than the c_{BTO} of all the samples except for the one grown at 0.2 mbar. BTO out-of-plane lattice parameter values above 4.30 Å are not typically observed for films with more than 10 nm thickness because highly defective initial layers induce abrupt relaxation of succeeding layers [27,28]. This relaxation seems to occur at a critical thickness less than 2 nm when the growth pressure is 0.2 mbar, as shown in Fig. S2, and likely will occur for the other samples in this study if greater thicknesses had been explored. Studies on ferroelectric thin films in which functional properties are modified through the manipulation of a highly strained initial layer have been performed not only on BTO but also in BiFeO₃ [9] and Pb(Zr,Ti)O₃ [29].

When comparing the 0.1 mbar sample grown in pure O₂ and the 0.1 mbar sample grown at 20:80 O₂:Ar ratio, we arrive at two observations: first, that the c_{BTO} is mainly affected by the absolute pressure and not the partial oxygen pressure during growth; and second, that the c_{BTO} is not further affected by the amount of oxygen during cooldown within the 0.02–0.1 mbar range. Moreover, when comparing the 0.1 mbar sample with pure O₂ background and 0.1 mbar with 20:80 ratio of O₂ and Ar in Fig. 5b, it is shown that Ar causes a more drastic increase of the Ba fraction in the resulting film. One hypothesis could be that Ar has a greater atomic mass and thus is more effective at deflecting the lighter Ti ions compared to both molecular O₂ and O which are present in the chamber, but further study needs to be performed to confirm this.

Another knowledge gap is the drastic transition in sample stoichiometry from 0.1 mbar to 0.2 mbar where the BTO films transition from Ba excess towards a Ti-rich surface, and a lack of understanding of how the morphology changes during this transition. We do not expect a drastic transition in the out-of-plane lattice parameter between 0.1 mbar and 0.2 mbar because we have already established that large positive Δc_{BTO} values are caused by an inhomogeneous distribution of oxygen vacancies at lower growth pressures.

5. Conclusion and outlook

The study demonstrates the use of an off-center alignment during

PLD to look at film characteristics as a function of lateral distance from the plasma plume center, showing that heterogeneity of certain properties along the sample length can be minimized or maximized by tuning the growth conditions.

First, the effect of laser fluence was explored at a fixed growth pressure of 0.02 mbar O₂. Low fluence produces Ba-rich islands which are constrained within the area directly aligned with the plasma plume. Using an off-center alignment at low fluence produced films which are highly uneven in terms of roughness and stoichiometry. Once the fluence is past the threshold of 1.9 J/cm², stepped surfaces of mixed termination and no visible islands are obtained. Although the cation ratios past the threshold are approximately 1:1, the amount of oxygen vacancies start to increase proportionally with the laser fluence as demonstrated by the increasing out-of-plane parameter. Furthermore, the c_{BTO} decreases along the length of the sample in the direction away from the plasma plume, which can be attributed to the heterogeneous Ti oxidation state of the plume during BTO deposition creating an oxygen vacancy gradient on the film. It is important to note that these results are highly dependent on the growth pressure and that a fluence sweep at a different starting pressure may produce dissimilar results.

Next, the effect of growth pressure was studied at a fixed fluence of 1.9 J/cm². At low pressure conditions, the films are proportional in terms of cation ratio and show a stepped topography which is TiO₂ terminated at 0.005 mbar and mixed terminated at 0.02 mbar. The film at 0.005 mbar also shows Δc_{BTO} values within a similar range as those observed in the fluence sweep series at 0.02 mbar from 1.9–2.7 J/cm². Once the threshold pressure of 0.05 mbar is reached, Ba-rich islands are observed on the surface and persist up to 0.1 mbar pressure. Unlike the localized island density in low fluence conditions, the pressure-induced islands are more evenly distributed along the film length as evidenced by the positional RHEED and position-dependent XPS data. Following this, there is a sharp transition between 0.1 mbar and 0.2 mbar growth pressure in which the stoichiometry goes from Ba-rich to Ti-rich. XRD measurements also indicate the formation of a low crystallinity interfacial layer at 0.2 mbar pressure which produces the highest degree of relaxation of c_{BTO} out of all samples.

The results of the study indicate that for the two growth parameters tested on BTO, the growth pressure has the most significant effect in the morphology, unit cell volume, and stoichiometry of the samples over the entire sample length. Not only is there a critical pressure below which oxygen vacancy gradients form, there are also drastic changes in the Ba fraction within the 0.1–0.2 mbar range which are not yet fully understood in literature. Despite this, the fluence calibration is also important because decreasing this parameter past a certain point produces localized Ba-rich phases on the sample surface. Aside from this, increasing fluence is a viable option in exploring functional properties that favor higher concentrations of oxygen vacancies in BTO. The significance of fluence and pressure may be of a different priority according to the material used as well as the parameters used in controlling the expansion of the plasma plume, such as the laser spot size and substrate-target distance.

CRediT authorship contribution statement

Romar Angelo Avila: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Ellen Kiens:** Investigation. **Yorick Birkhölzer:** Investigation. **Ojas Shanker:** Investigation. **Tom Coolman:** Investigation. **Menno Struik:** Investigation. **Yibin Bu:** Investigation, Formal analysis. **Christoph Baeumer:** Writing – review & editing, Supervision, Conceptualization. **Guus Rijnders:** Writing – review & editing, Supervision, Conceptualization. **Gertjan Koster:** Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcrysgro.2025.128313>.

Data availability

Data will be made available on request.

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