Optimization of the epitaxial growth of ferroelectric PbTiO₃ films

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Abstract: In this work, I have grown ferroelectric PbTiO₃ films on SrTiO₃ single-crystal substrates by pulsed laser deposition. I have optimized the growth conditions, namely, the substrate temperature, the oxygen pressure, and the laser energy density to achieve high crystal quality films, stoichiometric and without any spurious phases in the Pb - Ti - O system, like TiO₂. These growth conditions are found to be very narrow making the growth of high quality PbTiO₃ films very elusive.

I. INTRODUCTION

Many devices, such as multilayer ceramic capacitors, actuators, sensors, piezoelectric ultrasound transductors, etc, are based in ferroelectric materials [1-3]. Ferroelectricity was discovered by Joseph Valasek in 1920 but had already predicted by Edwin Schrödinger in 1912 [1]. The nomenclature was adopted in recognition of the parallels between the behaviour of that phenomenon and the ferromagnetism, which was already known. The miniaturization of these materials, in particular in nanometric thin films, has been of great importance when it comes to developing new devices and enhancing their performance [2,3].

Ferroelectric materials display spontaneous polarization in the absence of an electric field. The direction of the polarization can be hysteretically reversed by applying an external electric field, analogous to the magnetization with the magnetic field in ferromagnetic materials. Moreover, they form ferroelectric domains (regions in the material with a particular orientation of the polarization) akin to the magnetic domains. They undergo a ferroelectric-to-paraelectric phase transition at the ferroelectric Curie temperature, above which the material stops being ferroelectric and behave as a regular dielectric.

In this work, I have focused on the epitaxial growth of thin films of the ferroelectric material PbTiO₃. The epitaxial growth consists of synthesizing a single crystal film onto a single crystal substrate, ideally by growing one monoatomic layer after another of the desired material, resulting in a film with the crystallographic axes (both out-of-plane and in-plane axis) oriented following those of the substrate (see appendix) [4]. When growing thin films on substrates that have similar in-plane lattice parameters, those of the film will deform to match those of the substrate (see appendix) [4, 5]. This is, the in-plane lattice parameters of the film are no longer that of the material in bulk form but adopt the value of the in-plane lattice parameters of the substrate (see appendix). In this scenario, the film is said to be grown fully strained [4, 5]. This strain can be compressive when the in-plane lattice parameter of the film is smaller than that of the bulk or tensile if it is larger than that of the bulk (see appendix). The strain is computed as follows:

$$f = \frac{a_{film} - a_{bulk}}{a_{bulk}} \quad (1)$$

where a_{film} is the in-plane lattice parameter of the film (which coincides with that of the substrate when it is fully strained) and a_{bulk} is the in-plane lattice parameter of material when it has a bulk form, that is, without strain.

Here I have grown PbTiO₃ films onto SrTiO₃ single crystal substrate by pulsed laser deposition (PLD) [the technique is explained in the experimental section]. Both oxides belong to the perovskite class of materials (ABO₃), with the cation A at the corners of the unit cell, the cation B at the centre of the unit cell, and the oxygens at the centre of the faces (see appendix). At room temperature the structure of PbTiO₃ is tetragonal with lattice parameters a =3.90 Å and c=4.15 Å [6], whereas the structure of SrTiO₃ is cubic, with lattice parameter a = 3.905. However, at the growth temperature of the films, which are between 500°C and 750°C (see Appendix), PbTiO₃ is cubic [7]. In order to determine the strain that PbTiO₃ will have when growing on SrTiO₃, a pseudocubic lattice parameter, a_c, is computed using the volume of the tetragonal unit cell at room temperature, V, and evaluating the cubic root:

$$V = a \cdot a \cdot c \quad \text{and} \quad a_c = \sqrt[3]{V} \quad (2)$$

where a and c will be the lattice parameters of tetragonal PbTiO₃ at room temperature. This yields a pesudocubic lattice parameter at room temperature: a_c = 3.98 Å. Then this parameter was used in equation (1) as the a_{bulk}. The in plane lattice of the film, a_{film}, is used that of the substrate (3.905 Å) since thin film is expected to grow fully strained, resulting in a compressive strain of -1.95%.

The aim of this work is to optimize the PLD growth conditions to obtain epitaxial PbTiO₃ thin films, with high crystal quality, and without any spurious phases, like TiO₂ or PbO₂, in the Pb-Ti-O ternary system.

II. EXPERIMENTAL SECTION

II.1 Pulsed Laser Deposition (PLD)

The PLD growth process consists of focusing a series of laser pulses on a target, which is inside a vacuum chamber.

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This target is a bulk piece, containing a mixture of oxides with the desired composition, in our case Pb - Ti - O mixture enriched with 50% of lead regarding the stoichiometric ratio ([Pb]/[Ti] = 1.5). The target are provided by the *Departament de Ciència de Materials i Química Física* (*UB*).

A 32 ns pulsed laser is used, that works with monochromatic radiation of 248 nm wavelength, in the ultraviolet range. The fluence (or the concentrated energy per unit area) drives the target material to be ejected towards the substrate which is placed in front of it [4] (Fig. 1). Pulse after pulse the film is gradually growing on top of the substrate. Depending on the number of pulses the film will be thicker or thinner. In our case, the thickness of the films is comprised between 25 and 40 nm. The thickness was determined by X-ray reflectivity [4] done by the technician Dr. Josep Bassas at Centres Científics i Tecnològics de la UB.
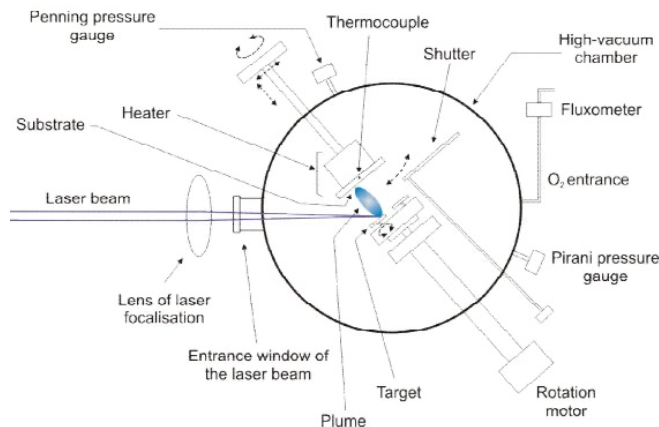

FIG. 1: Sketch of the pulsed laser deposition technique

The substrate is heated to provide the arriving ions from the target with the sufficient energy to move on the substrate and to find the equilibrium positions to form the PbTiO₃ compound. These equilibrium positions are created by the in-plane lattice of the substrate, which favour, thus, the formation of PbTiO₃.

This deposition is made in a partial oxygen pressure inside the vacuum chamber. This is typically needed for the formation of oxides to avoid a large amount of oxygen vacancies.

At the end of growth, the sample is cooled down, maintaining (or increasing) this oxygen pressure, in order to continue avoiding the desorption of volatile elements. In our case, the films are cooled down at 10^3 mbar of oxygen pressure.

In this work, I have explored the substrate temperature, the oxygen pressure, and the laser fluence to optimize the PLD growth conditions to form high crystal quality epitaxial PbTiO₃ films. More details about the other PLD parameters used for the growth of the films of this work are listed in the appendix. In total 13 samples were grown (see appendix).

II.2 X-ray diffraction (XRD)

X-ray diffraction consists of irradiating the sample with X-ray and obtaining measurements of its reflection and interferences with the atomic planes.

Incident X-rays are monochromatic and have a wavelength of 1.54056 Å (line $K_{\alpha 1}$ of Cu). The diffraction condition occurs when Bragg's law is fulfilled, this is:

$$2d_{hkl}\sin\frac{2\theta}{2} = n\lambda \quad (3)$$

Where hkl are Miller indices, d_{hkl} are the interplanar distance between hkl planes, 2θ is the angle between the incident beam and the diffracted beam (see Fig. 2), and λ is wavelength of the radiation.
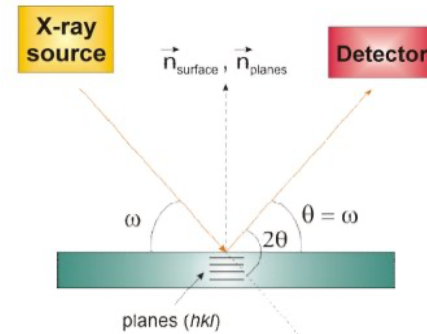

FIG. 2: Sketch of the 2θ-ω XRD scan.

In the XRD scans, the angle 2θ is swept coupled with the angle ω in such a way that $\omega = \theta$ in the whole scan (Fig. 2). In this kinds of scans, so-called 2θ-ω scan or $\theta/2\theta$ scans, only the atomic planes that are parallel to the surface of the film and substrate are going to be detected (Fig. 2). In our case, as the out-of-plane crystallographic axis of the SrTiO₃ substrate is the [001], only the 00*l* planes can be detected (this is, the 001, 002, 003, etc). When the Bragg's law is met, a diffraction peak appears. The out-of-plane lattice parameter, *c*, of the PbTiO₃ films can be computed by: $d_{00l} = c/l$. And the d_{00l} is computed by determining the 2θ value of the 00*l* XRD peaks of PbTiO₃ film in the $\theta/2\theta$ scans and using the Bragg's law (eq. 3).

The XRD measurements were performed by Dr. Josep Bassas at Centres Científics i Tecnològics de la UB. The raw data was analysed, plotted, and treated by myself with the supervision of my advisor Dr. Eric Langenberg.

III. RESULTS AND DISCUSSION

Three series of samples have been made regarding the PLD parameter that is explored: substrate temperature, oxygen pressure, and laser fluence.

For each sample of the series, 2 diffractograms were made: i) one with long range in 2θ (from 10° to 110°) to detect if there is the presence of any spurious phases in the film (apart from PbTiO₃) and ii) another with more statistics and resolution in a short range in 2θ (from 36° to 50°) close to the 002 XRD peak of the substrate and PbTiO₃ to better characterize the thin film crystal quality. The reason why this second diffractogram is around the XRD 002 peak is because this peak is much more intense than the others and it has sufficient angular separation from the substrate peak.
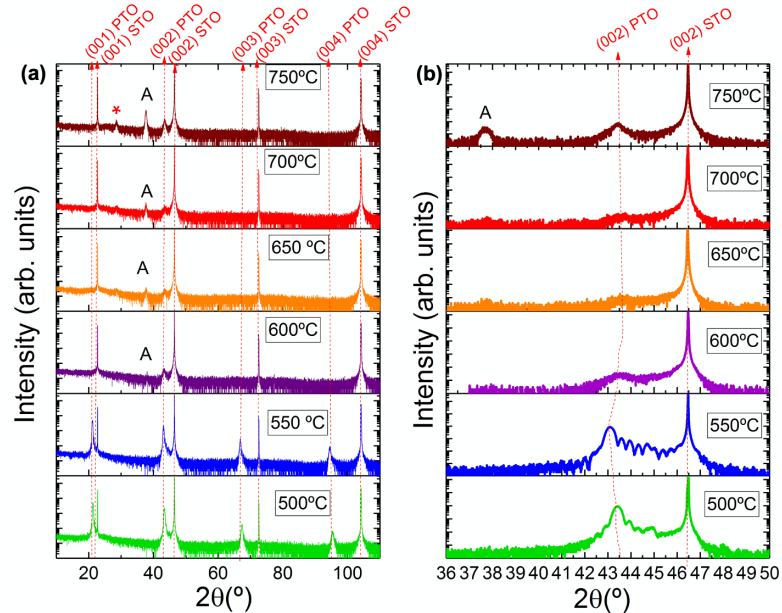
A. SUBSTRATE TEMPERATURE DEPENDENCE

FIG. 3: **Temperature dependence. (a)** Long range 2θ-ω XRD scan; **(b)** 2θ-ω XRD scan around the 002 reflection. The label A denotes the TiO₂ anatase. The label * corresponds to an unidentified phase, probably Ti-rich

The first case to be analysed was the series of samples taken at different temperatures. All the samples in the series are made with an oxygen pressure of 0.13 mbar and a fluence of approximately 1.66 J/cm². Fig. 3a and 3b show the diffractograms of the series.

Looking at the long 2θ range diffractogram (Fig. 3a), the sample growth at 550ºC only shows the 00l XRD peaks of the PbTiO₃ and the SrTiO₃ substrate. That is, there are no spurious phases of the Pb-Ti-O ternary system. The XRD peaks of the substrate are much more intense and narrower than those of the film because of the size: the film is a few tens of nanometres thick and the substrate is 0.5 mm. In addition, observing the more resolution 2θ scan around the 002 reflection (Fig. 3b) one can observe a sort of a series of oscillations around the 002 XRD peak of the film. These interference fringes (so-called Laue fringes) are constructive/destructive interference pattern due to the X-rays reflected in the surface of the film and in the interface between the film and the substrate. These are indicative of a very high single crystal quality, since the presence of dislocations, misarranged atomic planes, cation/anion defects and/or other crystallographic defects would destroy this constructive/destructive interference pattern [4].

At higher temperatures, an additional XRD peak is observed at ≈38º, which becomes more pronounced as the temperature increases (Fig. 3a). This peak corresponds to (TiO₂), in anatase phase [8]. Instead, the PbTiO₃ XRD peak significantly attenuates with increasing temperature (Fig. 3a) and the Laue fringes completely disappear (Fig. 3b). This is due to the high volatility of lead. As the growth temperature increases, more lead is desorbed on reaching the substrate during growth and the sample becomes more and more deficient in this element. When this occurs, the crystalline quality of PbTiO₃ greatly decreases and parasitic phases rich in titanium appear.

In the diffractogram of the sample made at 500ºC, spurious phases are not shown either (Fig. 3a), but the Laue fringes are less noticeable than in the case of 550ºC (Fig. 3b), which indicates a slightly deterioration of the crystal quality. In addition, the PbTiO₃ XRD peak has shifted towards higher 2θ values, which implies smaller out-of-plane lattice parameter value compared to the sample grown at 550°C (as explained in Section II.II). Some studies [9] show that the out-of-plane parameter of perovskites varies with the stoichiometry of the cations, reaching a maximum value when they have the correct stoichiometry and decreasing when there is a defect or excess of any of the two cations of the perovskite. With this criterion, the correct stoichiometry ([Pb]/[Ti] = 1) should occur at 550ºC which displays the largest out-of-plane lattice parameter, the samples grown at higher temperatures there is a deficit of lead, and it can be assumed that at 500ºC there is an excess of lead ions (remember that target is enriched in lead).

In particular, the PbTiO₃ 002 XRD peaks at temperatures of 500ºC, 550ºC and 600ºC are found in the angular positions 2θ: 43.42º, 43.08º and 43.56º, respectively. Using Bragg's law (3), c parameters are 4.17 Å, 4.20 Å, and 4.15 Å, respectively.

B. OXYGEN PRESSURE DEPENDENCE

The second case to be analyzed was the series of samples taken at different oxygen pressures. All the samples in the series are made with temperature of 550ºC and a fluence of approximately 1.66 J/cm². Fig. 4a and 4b show the diffractogram of the series.

The sample growth with 0.13 mbar shows the 00l XRD peaks of PbTiO₃ and SrTiO3 substrate (Fig. 4a), so there are no spurious phases, and the Laue fringes can be clear observed (Fig. 4b).

The sample growth with 0.3 mbar show the Laue fringes too (Fig. 4b), but they are less noticeable than in the case of
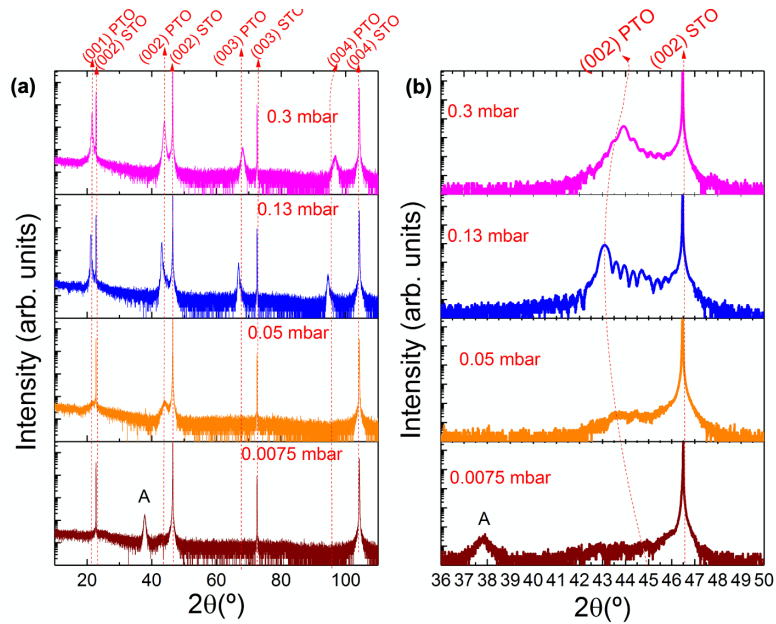
FIG. 4: **Oxygen dependence. (a)** Long range 2θ-ω XRD scan; **(b)** 2θ-ω XRD scan around the 002 reflection. The label A denotes the TiO₂ anatase.
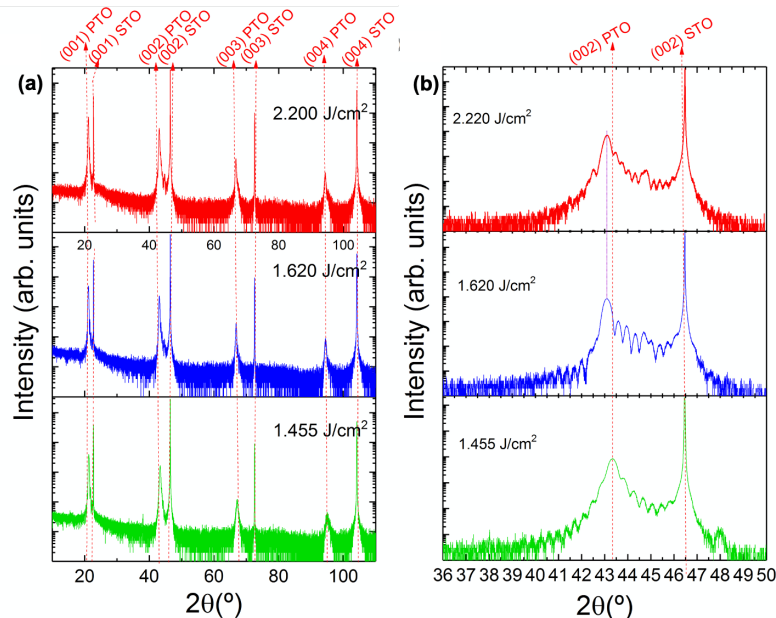

FIG. 5: **Fluence dependence. (a)** Long range 2θ-ω XRD scan; **(b)** 2θ-ω XRD scan around the 002 reflection

0.13 mbar, so a slight deterioration of the crystal quality occurs. We also observe that the PbTiO₃ 002 XRD peak is shifted to a higher 2θ value, which, with the same reasoning used before, implies a poorer stoichiometric composition and a worse crystal quality.

In the sample grown with 0.0075 mbar, an XRD peak appears again at ≈38º corresponding to the TiO₂ anatase phase. In addition, the XRD peak corresponding to PbTiO₃ is not observed, that is, the desired compound is not formed. So this sample has so large Pb deficient that only TiO₂ can be formed.

At the sample growth with 0.05 mbar is observed that the PbTiO₃ 002 XRD peak is displaced towards 2θ values higher than the high crystal quality sample of 0.13 mbar. Given the

lead deficit observed in the sample grown at 0.0075 mbar, we can assume that this sample is also Pb deficient but less than that at 0.0075 mbar since the PbTiO₃ XRD is at least formed. Yet no Laue fringes are observed, so the crystal quality is poor.

Therefore, the oxygen pressure prevents Pb from desorption when the film is growing. The lower the oxygen pressure the more deficiency in Pb and vice versa. Thus, the sample grown at 0.3 mbar should be Pb-rich and the samples grown at oxygen pressure lower than 0.13 mbar should be Pb-deficient.

In particular, the PbTiO₃ 002 XRD peaks at oxygen pressures of 0.05 mbar, 0.13 mbar and 0.3 mbar are found in the angular positions 2θ: 43.60º, 43.08º and 43.91º,

respectively. Using Bragg's law (3), c parameters are 4.15 Å, 4.20 Å, and 4.12 Å, respectively.

C. FLUENCE DEPENDENCE

The third case to be analyzed was the series of samples taken at different fluencies. The three samples in the series are made with temperature of 550ºC and an oxygen pressure of 0.13 mbar. Fig. 5a and 5b show the diffractograms of the series.

In all the three samples only the 00l XRD peaks of the PbTiO₃ film and SrTiO₃ substrate are observed (Fig. 5a). Hence, no spurious phases in the ternary Pb - Ti -O system are found. If we look at the 002 XRD peaks of the PbTiO₃ (Fig. 5b), we see that corresponding to the sample grown at 1.455 J/cm^2 fluence has a larger 2θ diffraction angle, that is, a smaller c lattice parameter compared to the other two samples grown at larger fluence values. Instead, the 002 XRD peaks of the PbTiO₃ films of the two samples grown at larger fluence values (1.62 J/cm^2 and 2.22 J/cm^2) lie at the same 2θ values and, thus, they have the same c lattice parameter. In addition, we observe that the peaks at a higher fluence are narrower, this is because a higher fluence has removed more material from the target and consequently a slightly thicker layer has been deposited. The width of the peaks is inversely proportional to the number of cells in the sample. As in the case of the temperature and oxygen pressure series, the fact that the sample grown at low fluence displays smaller out-of-plane lattice parameter indicates that it is slightly off-stochiometric ([Pb]/[Ti] ≠ 1). Yet it cannot be determined if it is Pb rich or Ti rich.

Therefore, there is a threshold in the fluence above which the material ablated from the target is stoichiometric and below which there is a deficiency in either of the two cations. This might be due to fact that in the pulsed laser deposition process, high fluence values are required to ablate the material stoichiometrically. For lower fluence values, the laser pulse -matter interaction, instead of ablating the material, it spreads the heat to a larger region and then a mix between ablation and evaporation occurs [4]. The evaporation will not be stoichiometric as each element (in our case Pb and Ti) has different vapour pressures.

In particular, the PbTiO₃ 002 XRD peaks at fluencies of 1.455 J/cm^2, 1.620 J/cm^2 and 2.220 J/cm^2 are found in the angular positions 2θ: 43.32º, 43.08º and 43.08º, respectively. Using Bragg's law (3), c parameters are 4.17 Å, 4.20 Å and 4.20 Å, respectively.

IV.   CONCLUSIONS

Based on this work, it can be concluded that growing PbTiO₃ thin films is an arduous task, especially due to the high volatility of Pb.
In this work, it has been possible to determine:
1) There is a narrow growth window in substrate temperature around 550ºC, increasing the substrate temperature by 50ºC shows that the PbTiO₃ thin film barely forms. If the temperature is lowered, the thin film does form, but not stoichiometrically.
2) There is a narrow growth window in oxygen preassure around 0.13 mbar. Increasing the oxygen pressure, the thin films grow non-stoichiometric and decreasing this parameter the PbTiO₃ compound simply does not form.
3) There is fluence threshold between 1.46 J/cm^2 and 1.62 J/cm^2, below which a lower fluence will give non-stoichiometric PbTiO₃ growth.

In particular, it can be concluded that PbTiO₃ grows ideally, with this target and equipment, at the substrate temperature of 550ºC, an oxygen pressure of 0.13 mbar, and a fluence over a threshold that should lie around 1.5 - 1.6 J/cm^2

V.   APPENDIX

In the Appendix the details of all the samples grown in this work are described together with the sketches of the epitaxial growth and the perovskite structure.

Acknowledgments

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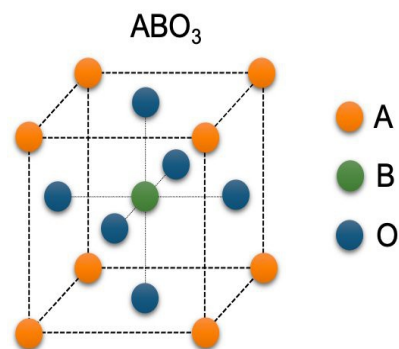
1. Epitaxial growth
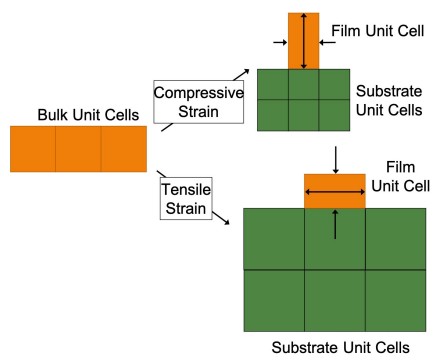
Sketch showing the effects of the epitaxial strain on the film unit cell.

2. Perovskite

Sketch of the perovskite structure

3. Table of samples growth

SAMPLE	RESIDUAL PREASURE	OXYGEN PREASURE	SUBSTRATE TEMPERATURE	NUMBER OF SHOTS	FLUENCY	RATE	OBSERVATIONS
PTO-01	$9 \cdot 10^{-6}$ mbar	$1.3 \cdot 10^{-1}$ mbar	600ºC	10000	0.900 J/cm^2	10Hz	The laser optics was misaligned and the window of the vacuum chamber was dirty. That is why the sample was grown badly.
PTO-02	$6.7 \cdot 10^{-6}$ mbar	$1.3 \cdot 10^{-1}$ mbar	600ºC	10000	1.670 J/cm^2	10Hz	
PTO-03	$6.7 \cdot 10^{-6}$ mbar	$1.3 \cdot 10^{-1}$ mbar	650ºC	10000	1.675 J/cm^2	10Hz	
PTO-04	$7 \cdot 10^{-6}$ mbar	$1.3 \cdot 10^{-1}$ mbar	700ºC	10000	1.670 J/cm^2	10Hz	
PTO-05	$6.7 \cdot 10^{-6}$ mbar	$1.3 \cdot 10^{-1}$ mbar	750ºC	10000	1.663 J/cm^2	10Hz	
PTO-06	$6 \cdot 10^{-6}$ mbar	$1.3 \cdot 10^{-1}$ mbar	700ºC	10000	1.660 J/cm^2	10Hz	
PTO-07	$6.4 \cdot 10^{-6}$ mbar	$1.3 \cdot 10^{-1}$ mbar	550ºC	6900	1.620 J/cm^2	10Hz	
PTO-08	$8 \cdot 10^{-6}$ mbar	$3 \cdot 10^{-1}$ mbar	550ºC	6900	1.650 J/cm^2	10Hz	
PTO-09	$8.8 \cdot 10^{-6}$ mbar	$5 \cdot 10^{-2}$ mbar	550ºC	6900	1.660 J/cm^2	10Hz	
PTO-10	$7.9 \cdot 10^{-6}$ mbar	$7.5 \cdot 10^{-3}$ mbar	550ºC	6900	1.660 J/cm^2	10Hz	
PTO-11	$6 \cdot 10^{-6}$ mbar	$1.3 \cdot 10^{-6}$ mbar	500ºC	6900	1.670 J/cm^2	10Hz	This sample belongs to the substrate temperature series
PTO-12	$5 \cdot 10^{-6}$ mbar	$1.3 \cdot 10^{-6}$ mbar	550ºC	6900	1.455 J/cm^2	10Hz	
PTO-13	$7.7 \cdot 10^{-6}$ mbar	$1.3 \cdot 10^{-6}$ mbar	550ºC	6900	2.200 J/cm^2	10Hz	