The importance of pressure and mass ratios when depositing multi-element oxide thin films by pulsed laser deposition

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Angle-resolved thickness and compositional analyses of BaTiO₃, CaTiO₃, La_{0.4}Ca_{0.6}MnO₃, EuAlO₃, and LiMn₂O₄ were performed to study the influence of the background gas pressure when depositing multi-elemental oxide materials. With increasing gas pressure the typical forward directed deposition changes to a constant thickness at all angles. Compositional changes with respect to the target show dependencies on (in order of influence): target material, deposition pressure, and angular location (substrate size). A linear relationship was found between target mass-ratios and compositional deviations. This can lead to compositional deviations of up to 70% for large mass-ratios in certain pressure regimes.

Keywords: Angular distribution; Perovskites; Pulsed laser deposition; Stoichiometric transfer; Congruent transfer;

1. Introduction

The apparent ease to prepare thin films with a complex stoichiometry and for a wide range of materials is one of the reasons for the widespread use of pulsed laser deposition (PLD) [1]. However, the congruent transfer using PLD does not always take place and depends on many process parameters [2]. For instance, the use of a background gas, either inert or reactive [1, 3-6], has important effects on the final film composition as well as on its thickness [2, 7, 8]. In [7] it is shown that for BiFeO_3 the Bi/Fe ratio decreases with oxygen pressure during the deposition, which negatively affects the pursued ferroelectric properties of the films. For LiCoO_2 , Ohnishi *et al.* [9] show that in relatively high oxygen background pressures, where the mean free path (MFP) becomes shorter than the target-to-substrate distance, Li may be preferentially scattered leading to Li deficient films. This is also shown by Dumont *et al.* when producing LiMn_2O_4 electrodes by PLD [10] where high background gas pressures have a strong influence on the Li content of the film and the electrochemical activity. An analytical model based on elastic collisions for $\text{Li}_{1.3}\text{Mn}_2\text{O}_4$ is described in [11] to visualize the effect of the deposition pressure on the cation compositional deviations. Furthermore, Canulescu *et al.* [12] report such an effect experimentally by using time resolved plume imaging to analyse the expansion of LiMn_2O_4 for different oxygen background pressures. This leads to the conclusion that the ablation of materials containing a combination of light and heavy elements are prone to be deficient with respect to the light element in as-grown films for certain pressure regimes. Sambri *et al.* [13] reach the same conclusion with a similar imaging approach for LaGaO_3 , finding a cation off-stoichiometry at the forefront of the plume. Nevertheless, imaging shows only a distribution of selected plume species evolving with time. What matters, however, is the final composition of the film. It is not necessary that this corresponds to the composition of the film, as there are other processes involved in the deposition that can strongly alter the composition (i.e.: bouncing reactions, sputtering or evaporation to name a few).

It has also been reported that at laser fluences slightly above the ablation threshold the film composition may deviate considerably, either towards stoichiometric values (e.g.: LiCoO_2 [9] or SrTiO_3 [14]) or not, as in the case of BaTiO_3 [15], where stoichiometric films are mostly obtained at fluences much higher than the threshold fluences.

It is rather a combination of many interdependent depositing parameters (e.g.: target composition, fluence, background pressure, background gas element, target-to-substrate distance, spot size, or substrate temperature) that may enable the PLD user to deposit a film with the desired composition. Although very often and for practical reasons one must fix some of those process parameters (i.e.: for geometrical reasons) and vary the remaining ones. It would be therefore very valuable to have some guidelines on how much a film composition can deviate, if it is more pronounced or not in certain material combinations and which process parameters to vary to adjust the composition. This would not only raise awareness among PLD users that a congruent transfer is not guaranteed, but also open the door to on-demand composition variations.

In this work we focus on the interdependence between background gas pressure, elemental mass ratios and substrate angular location. In a previous paper [16], we have shown that for $\text{La}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ the film composition could be changed up to 16% with respect to the ablated target depending on the deposition pressure. We proposed that the masses of the participating elements play an important role in the compositional deviations due to the collisional interactions with the background gas. We now investigate this assumption further by selecting four additional target materials based on their elemental mass ratios: BaTiO_3 , CaTiO_3 , EuAlO_3 and LiMn_2O_4 . These targets range from very similar cation masses (ratio of 1:1.17 for Ca:Ti) to very dissimilar ones (ratio of 1:5.6 for Al:Eu and

1:8 for Li:Mn) and a mass ratio similar to the original that initiated the investigation $\text{La}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ (1:2.9 for Ti/Ba vs. 1:2.5 for Mn/La).

We performed depositions at different background gas pressures and analysed the composition and thickness of the deposited films at different angular locations using Rutherford backscattering spectrometry (RBS: with 2-4MeV ^4He ions) or Elastic Recoil Detection Analysis (ERDA) depending on the target material. Software from the Ion Beam Physics group at ETH Zurich and RUMP software were used for data analysis.

2. Materials and methods

Five cylindrical ceramic targets of BaTiO_3 , CaTiO_3 , $\text{La}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$, EuAlO_3 and LiMn_2O_4 were used for the deposition with a diameter of 10-12mm, a length of 10-40mm and their compositions were verified by RBS or ERDA (for LiMn_2O_4). BaTiO_3 and $\text{La}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ had the expected composition, while CaTiO_3 and LiMn_2O_4 had compositions of $\text{Ca}_{1.1}\text{Ti}_{0.9}\text{O}_{2.9}$ and $\text{Li}_{0.7}\text{Mn}_2\text{O}_{3.8}$ respectively and are presented as such hereafter. EuAlO_3 due to the much higher scattering cross-section of Eu vs. Al had an uncertainty of ~7%.

All the depositions were performed in a UHV chamber (base pressure of 1×10^{-9} mbar) at room temperature using a KrF excimer laser (Lambda Physik LPX 300, 20ns, $\lambda = 248\text{nm}$) with a laser fluence of $2\text{J}/\text{cm}^2$ and a repetition rate of 3Hz for 40 min (except for LiMn_2O_4 where 60min were used to prepare thicker films for ERDA measurements). The laser pulses arrived at the target with a 45° angle with respect to the target-to-substrate axis and in the same horizontal plane. A mask was used to obtain a flat-top beam profile and a rectangular laser spot with dimensions of 1mm x 1.4mm was imaged on the target. With the purpose of avoiding cratering, the targets were continuously rotated and displaced along their main axes. The depositions for each target material were performed at four different Ar background pressures: vacuum (1×10^{-6} mbar), 1×10^{-3} mbar, 1×10^{-2} mbar and

1×10^{-1} mbar. Ar was used to study the effect of inelastic scattering during the expansion of the plasma while avoiding chemical interactions with the background gas. Although its mass and volume are slightly higher than molecular oxygen, the general tendencies should be similar.

All films, except for EuAlO_3 , were deposited onto $20 \mu\text{m}$ thick aluminium foils (99.999% purity), which allowed a straightforward RBS/ERDA measurement and avoided channelling effects that would affect the accuracy of the measurements. In the case of EuAlO_3 , a conductive carbon tape was used to avoid the overlapping of both Al signals on the RBS spectra (thin film and substrate). All foils/tapes were placed on a “semi-sphere” holder that allows to study the angular deposition profile (up to $\pm 86^\circ$) while keeping a constant target-to-substrate distance of 40 mm due to its intrinsic geometry, as described in detail in [16].

Except vacuum, the other three pressures were chosen to capture the evolution from a free expansion of the plasma plume (1×10^{-3} mbar), with very limited interactions with the background gas, to very significant interaction with the background gas (1×10^{-1} mbar). The mean free paths (MFP) of the different species for Ar at such pressures and at room temperature are shown in Table 1 and are given by the formula:

$$\lambda = \frac{k_B \cdot T}{\sqrt{2} \cdot P \cdot \pi \cdot d_m^2} \quad (1)$$

where T is the temperature of the gas, P the pressure and $d_m = (d_{\text{Ar}} + d_{\text{species}})/2$.

Element	Mass (amu)	Radius (pm)	MFP (mm) at different Ar pressures			
			1×10^{-6} mbar	1×10^{-3} mbar	1×10^{-2} mbar	1×10^{-1} mbar
Li	6.94	145	198478	198	20	2.0
O	16	60	539606	540	54	5.4
Al	27	125	241065	241	24.1	2.4
Ca	40	180	146985	147	15	1.5
Ti	47.9	140	207996	208	21	2.1
Mn	54.9	140	207996	208	21	2.1
Ba	137.3	215	113211	113	11	1.1

La	138.9	195	130875	131	13	1.3
Eu	152	185	141308	141	14.1	1.4

Table 1. Mean free path values for the different species in Ar gas calculated for the four pressures used in the depositions. The average target-to-substrate distance was 40mm, which means that the mean free path of the ablated species becomes shorter than the target-to-substrate distance at pressures above 1×10^{-3} mbar Ar (dashed line)

The angular composition and thickness profiles of the deposited films were subsequently obtained by RBS and ERDA. Both techniques directly yield ratios between elements in the material and for each target material the corresponding elemental ratios were obtained (e.g.: Mn/La and Ca/La or Ti/Ba). The collection for each RBS/ERDA data point took 3-10 min to guarantee the same counting statistics for all film thickness measured depending on the substrate's deposition angle and deposition pressure (see also ref. [17]).

3. Results and discussion

3.1 Film thickness variation with background gas pressure

The angular thickness profiles obtained by RBS/ERDA measurements are shown in Fig.1. In all graphs, the centre position of the plasma plume is marked with a dashed line at 0° , while the typical deposition area for most PLD users (1 cm^2) is highlighted by a grey rectangle ($\pm 10^\circ$ for a target to substrate distance of 40mm). The thickness values are given in units of the areal density with $1 \times 10^{15} \text{ at/cm}^2$. This is the natural thickness unit for RBS. Distance units such as nm require a conversion to the areal density via an estimated atomic density, which may vary as a function of thickness and increase the uncertainty.

The film thickness profiles of all five target materials show a consistent picture on the effect of pressure on the deposition with the characteristic strong forward directed deposition of PLD. Such a thickness profile is maintained for most deposition pressures (vacuum, 1×10^{-3} mbar and 1×10^{-2} mbar) and only changes at the relative high pressure of

1×10^{-1} mbar to a quasi-constant thickness for the entire angular range. Vacuum and 1×10^{-3} mbar show very similar profiles consistent with a MFP larger than the target-to-substrate distance, while at 1×10^{-2} mbar there is a slight reduction in thickness at the peak location (0°). The exception is $\text{Li}_{0.7}\text{Mn}_2\text{O}_{3.8}$ where such a reduction is larger, since the MFP is already shorter than the target-to-substrate distance and one scattering event with the Ar gas will scatter the much lighter Li and Mn species (Fig.1d). The mentioned behaviour for the four pressures is observed for all deposited materials, although with noticeable differences in the amount of deposited material.

Fig.1. Angle resolved film thickness profiles of BaTiO₃ (a), Ca_{1.1}Ti_{0.9}O_{2.9} (b), La_{0.4}Ca_{0.6}MnO₃ (c), EuAlO₃ (d) and Li_{0.7}Mn₂O_{3.8} (e) for four different Ar background gas pressures.
Note: ERDA results are presented in normalized units instead of at/cm² as the RBS results

A comparison of the deposited material (as percentage of maximum for each material) is shown on Fig.2 to highlight the considerable material loss when depositing at 1x10⁻¹ mbar. The deposited amount is reduced by ~50% compared to the vacuum deposition for most target materials (Fig.2a). This represents a remarkable loss of deposition efficiency. Furthermore, the typical angular range covered in a PLD deposition for a substrate of 1cm² at a distance of 40mm is ±10°. In this case, the loss of material is a significant ~70% (Fig.2b). The reason is that at this pressure the deposition is no longer forward peaked but spherical (redistribution of material due to strong scattering), and due to geometrical limitations the substrate holder fails to capture it (Fig.3). The aluminium/carbon substrate has a finite area that covers most of the central part of the plume, but only a reduced portion at high angles (red areas in Fig.3b).

Fig.2. Percentage bar charts of deposited material for the different materials and deposition pressures. The percentages were calculated with respect to the maximum amount (vacuum) either for (a) the entire angular range or (b) for $\pm 10^\circ$.

Fig.3. Schematic view of the substrate holder with the rod target (a) and frontal view explaining the limitations of the holder when having a fully scattered plume (b) red 3D areas are not captured

3.1.1 Estimation of the average scattering angle from the thickness data

From the thickness data it is possible to obtain an estimate of the average scattering angle of the species with the background gas. The convolution of the vacuum profile with a Gaussian distribution gives the non-vacuum profile, in which the width of the best fitting Gaussian corresponds to the average scattering angle. An example for BaTiO₃ is shown in Fig.4, in which an average scattering angle of 13.5° (σ) is estimated at 1×10^{-2} mbar Ar.

Fig.4. Example for BaTiO_3 in which the original vacuum signal and a Gaussian signal are convoluted to fit the measured film thickness at 1×10^{-2} mbar Ar and estimate the average scattering angle (in this case 13.5°)

The results for the different target materials at a pressure of 1×10^{-2} mbar are shown in Table 2. They show an inverse relationship between the average scattering angle and the average mass of the species involved. This is expected from simple scattering laws since the heavier particles undergo a smaller momentum change [6]. We are aware that the use of such average amu of the unit cell is not ideal, but it provides a rough estimate. The calculations were only performed for this pressure as in vacuum and 1×10^{-3} mbar no scattering with the background gas is expected and at 1×10^{-1} mbar the plume is fully scattered. Nonetheless, it would be interesting to explore the trend of the average scattering angle between 1×10^{-3} mbar and 1×10^{-1} mbar with further experiments.

Material	Average mass [amu]	Average scattering angle at 1×10^{-2} mbar Ar
BaTiO_3	46.6	13.5°
EuAlO_3	45.4	14.5°
$\text{La}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$	36.5	16.2°
$\text{Ca}_{1.1}\text{Ti}_{0.9}\text{O}_{2.9}$	27.3	19.0°
$\text{Li}_{0.7}\text{Mn}_2\text{O}_{3.8}$	25.8	55.5°

Table 2. Average scattering angle values for the different target materials at an Ar background gas pressure of 1×10^{-2} mbar. Ordered in decreasing average amu of unit cell and obtained by convoluting the thickness data

3.2 Film cation composition variation with background gas pressure

In addition to thickness information, the RBS/ERDA measurements also provide accurate composition profiles. The results are plotted in Fig.5 for the RBS analyses of BaTiO_3 , $\text{Ca}_{1.1}\text{Ti}_{0.9}\text{O}_{2.9}$, $\text{La}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ and EuAlO_3 , and in Fig.6 the ERDA composition results for $\text{Li}_{0.7}\text{Mn}_2\text{O}_{3.8}$ (as RBS is limited in accuracy when measuring light elements such as Li or O). In all graphs, the horizontal black lines represent the composition of the target material. An initial overview of all target materials is provided hereafter, while the material specific analyses are given in separate sections.

Overall, the compositional profiles exhibit noticeable variations showing that consistent congruent transfer by PLD is not necessarily the case. The variations are dependent on target material, pressure, and also angular location. In terms of pressure, vacuum and 1×10^{-3} mbar show very similar profiles for most materials, comparable to what was seen in the thickness profiles (Fig.1). While at 1×10^{-2} mbar the highest compositional changes take place (green line in Fig.5 and Fig.6). This is very relevant as the biggest compositional changes at this pressure are often seen at the typical PLD angular range of $\pm 10^\circ$. Finally, at 1×10^{-1} mbar the film composition becomes uniform throughout the angular range in a similar way as with the thickness profiles (Fig.1). Although not necessarily with the same composition as the target material.

Fig.5. Angle-resolved film composition for $\text{Ca}_{1.1}\text{Ti}_{0.9}\text{O}_{2.9}$ (a), BaTiO_3 (b), $\text{La}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ (c and d) and EuAlO_3 (e) at four different Ar background-gas pressures. Composition was obtained by RBS. The horizontal black lines represent the target composition (verified by RBS). The composition of EuAlO_3 had an uncertainty of 7% and is represented by the additional grey lines. The grey box

represents the typical PLD deposition range. Note: error bars are smaller than the symbols.

3.2.1 Material BaTiO₃ (mass ratio of 1:2.9)

In the particular case of BaTiO₃ (mass ratio of 1:2.9), the film elemental ratio is close to the target composition for most pressures and angles except for 1x10⁻²mbar Fig.5a. The composition profiles for vacuum and 1x10⁻³mbar are nearly identical with a deviation at angles above 65° which highlight either an increase in Ba or a decrease of Ti. At 1x10⁻²mbar and in contrast with the thickness profiles, a marked deviation takes place with a decrease in Ti/Ba of ~15% (~10% in ±10° region). The film composition returns to the original target values at 1x10⁻¹mbar and is uniform throughout the angular range.

3.2.2 Material Ca_{1.1}Ti_{0.9}O_{2.9} (mass ratio of 1:1.2)

As for Ca_{1.1}Ti_{0.9}O_{2.9} (mass-ratio of 1:1.2 Ca:Ti) the behaviour with pressure is analogous (Fig.5b). Vacuum and 1x10⁻³mbar have similar profiles, and 1x10⁻²mbar shows the strongest deviation with pressure, although in this case it is mostly at 0° (~10%).

3.2.3 Material La_{0.4}Ca_{0.6}MnO₃ (mass ratios of 1:2.5 and 1:3.5)

With similar mass-ratios as BaTiO₃ (1:2.5 for Mn:La and 1:3.5 for Ca/La), La_{0.4}Ca_{0.6}MnO₃ also exhibits comparable behaviour (Fig.5c and d). Composition profiles for vacuum and 1x10⁻³mbar are alike for each particular elemental ratio. The increase in deviation at high angles also takes place for Mn/La (towards Mn increase). In both cases, the strongest compositional deviations occur at 1x10⁻²mbar and 0° angular location with a decrease in the lightest element: 13% for Mn/La (Fig.5c) and 16% for Ca/La (Fig.5d) respectively. At 1x10⁻¹mbar the composition becomes uniform like for BaTiO₃, but not identical to the target composition.

3.2.4 Material EuAlO₃ (mass ratio of 1:5.6)

The particular case of EuAlO₃ (Fig.5e) is very relevant as it possesses a high mass-ratio and participating cations which are still measurable by RBS (1:5.6 for Al/Eu). The

composition profiles for vacuum and 1×10^{-3} mbar follow surprisingly matching patterns. Again, it is at 1×10^{-2} mbar where the strongest change in the composition can be seen with a deviation of $\sim 33\%$ and mainly in the central location where thin films by PLD are typically produced ($\pm 20^\circ$ region). At 1×10^{-1} mbar the composition becomes uniform throughout the entire angular range, as with the other materials, but it is below the target composition.

3.2.5 Material $\text{Li}_{0.7}\text{Mn}_2\text{O}_{3.8}$ (mass ratio of 1:8)

There is a strong general loss of lithium at all pressures and a strong angular variability. Vacuum and 1×10^{-3} mbar do not share similar angular profiles. The pressure that yields the strongest changes in composition ($\sim 70\%$) is in fact 1×10^{-3} mbar and not 1×10^{-2} mbar. The reasoning is that Li has a much smaller mass than the background gas Ar ($A \approx 7$ vs. $A = 40$), meaning that solely one collisional interaction event with Ar is sufficient to scatter these light elements. Even at 1×10^{-3} mbar, where the MFP has a similar order of magnitude as the target-to-substrate distance, the light elements might already be stopped with one scattering event.

At 1×10^{-2} mbar the compositional deviations are reduced, possibly due to the stopping of the Mn by the background gas (inferred from $\text{La}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ composition profiles in Fig.5c). At 1×10^{-1} mbar the deviations increase again getting close to values seen at 1×10^{-3} mbar. This change in composition is not yet understood.

Fig.6. Angle-resolved film composition for $\text{Li}_{0.7}\text{Mn}_2\text{O}_{3.8}$ at four different Ar background-gas pressures. Composition was obtained by ERDA. The horizontal black line represents the target composition (verified by ERDA). The grey box represents the typical PLD deposition range.

3.2.6 General discussion

The general observation from all results is that when depositing multi-element oxide films by PLD it is very likely to have a different composition compared to the original target material (cation wise). Such variations can be strong and seem dependent on (in order of influence): target composition, pressure and angular location of the substrate.

With respect to the influence of pressure, the results show that the composition profiles for vacuum and 1×10^{-3} mbar are very similar for most materials with the exception of $\text{Li}_{0.7}\text{Mn}_2\text{O}_{3.8}$.

Furthermore, at such pressures two mass ratios exhibit an interesting variation at high angles. In vacuum and 1×10^{-3} mbar, Ti/Ba (Fig.5 a) and Mn/La (Fig.5 c) both show deviations at angles above 65° towards the element with the lower sublimation energy. This is, an increase of the Ba and Mn content vs. Ti and La, respectively. This has been suggested in [18, 19], where a linear relationship was found between sublimation energies (vapour pressure) and broadness of the angular distributions for metals. However, in our case we have oxides and the explanation is not yet clear. The sublimation energy values

are tabulated in Table 3, and for Mn and Ba the behaviour seems independent of mass. This dependence on the sublimation energy was not noted in the case of Ca/Ti (Fig.5 b) and Ca/La (Fig.5 d) and alternatively, at 1×10^{-2} mbar the enrichment behaviour is reversed at high angles.

Element	Mass (amu)	Sublimation energy at 25°C (KJ/mol)
Li	7	161
Ca	40	176
Eu	152	177.8
Ba	137.3	192
Mn	54.9	291
Al	27	321.9
La	138.9	430
Ti	47.9	470

Table 3. Mass and sublimation energies of elements in ascending order of sublimation energy (from Ref.[20, 21])

Nevertheless, the main compositional deviations appear at a pressure of 1×10^{-2} mbar for BaTiO_3 , $\text{Ca}_{1.1}\text{Ti}_{0.9}\text{O}_{2.9}$, $\text{La}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ and EuAlO_3 . With variations of (ordered with increasing mass-ratios): ~10% for Ca/Ti, ~13% for Mn/La, ~15% for Ti/Ba, ~16% for Ca/La and ~33% for Al/Eu. At this pressure the MFP is ~25% of the target-to-substrate distance (Table 1) and some collisions are expected. These interactions with the background gas have stronger effects on the lighter elements and are sufficient to stop or scatter them, while heavier species continue to arrive (preferential scattering). In the particular case of $\text{Li}_{0.7}\text{Mn}_2\text{O}_{3.8}$ the loss of the Li is seen at an even lower Ar pressure of 1×10^{-3} mbar, but this is caused by a different process. The pressure dependence of Li is difficult to assess due to its light nature and volatility: at very low pressures Li has a tendency of being re-sputtered or bounces off a surface as a consequence of the high arrival energies [22, 23], while at elevated pressures it is very easily scattered towards high angles.

Based on the presented data, we conclude that there is a strong enhancement of the compositional deviations with increasing mass-ratios. This is presented in Fig.7 where the compositional deviations are plotted against the mass-ratios. As an anchor point,

$Y/Zr \approx 1.025$ is used from [24]. There is an almost linear dependence between the compositional deviations and the mass ratios, which implies that a congruent transfer from a multi-element target with high mass ratios is difficult and probably requires additional strategies to achieve it.

Fig.7. Maximum compositional deviations mostly at PLD relevant angular areas ($\pm 10^\circ$) vs. mass-ratios, mostly for 1×10^{-2} mbar. Except for O/Mn and Li/Mn in which the maximum deviations already appear at 1×10^{-3} mbar. Symbols ■ are for RBS measurements, ▲ for ERDA measurements and ● for data from [24]. Note: O/Mn deviation has a high uncertainty due to the suspicion of ambient water trapping by the amorphous film as described in the “anion composition” section. Error bars are smaller than the symbols except for EuAlO_3

3.3 Film anion composition variation with pressure

Both, RBS and ERDA measurements also provide the oxygen concentration of the films. ERDA measurements should provide a higher accuracy than RBS, as for RBS due to background and detection efficiency issues these values have an uncertainty of around 5 to 7 percent. Though, the main concern is not the accuracy of the measurements, but the source of the apparent oxygen of the film.

The results for all measured target materials are plotted in Fig.8 with the exception of EuAlO_3 in which due to the use of the carbon tape as substrate, the oxygen content could not be obtained properly. The oxygen concentration appears mostly above the oxygen concentration of the target material. There is a clear dependency of the oxygen

concentration with film thickness. The thinner the film, the higher the oxygen concentration as can be seen at high angular locations as well as the films deposited at 1×10^{-1} mbar. We suspect that the amorphous nature of the films (deposited at room temperature) makes them prone to capture ambient water.

Fig.8. Angle-resolved oxygen concentration of films deposited at four different Ar background-gas pressures and using four different target materials: BaTiO_3 (a), $\text{Ca}_{1.1}\text{Ti}_{0.9}\text{O}_{2.9}$ (b), $\text{La}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ (c) and $\text{Li}_{0.7}\text{Mn}_2\text{O}_{3.8}$ (d) measured by RBS (a,b and c)/ERDA(d). The horizontal black line represents the target composition. The grey box represents the typical PLD deposition range.

In order to verify the potential trapping of ambient water, ERDA measurements with a 2 MeV He beam using the absorber foil technique to detect the hydrogen content were performed for all materials (except for EuAlO_3 on carbon tape). Only those films which had a strong oxygen enrichment and dissimilar angular profiles have been investigated in detail (vacuum and 1×10^{-1} mbar Ar). The films were measured at three different locations (0° ,

~45° and ~85°) using an ion beam of 4mm diameter at a glancing angle of 15° for the incidence beam and also for the detector.

The results are shown in Table 4 and confirm that thinner films have a higher hydrogen concentration (i.e.: in the form of H₂O), with those located at high angles (85°) often having the highest concentrations compared to the central and intermediate locations (0° and 45°, respectively). In most cases, 1x10⁻¹mbar films (thinnest films) have a higher hydrogen concentration than those deposited in vacuum. This does not have to be directly linked to the thickness itself, but thickness might be an indication of the mass transport mechanism [25, 26] which could preferentially form porous films prone to ambient water trapping. This is the case for La_{0.4}Ca_{0.6}MnO₃ as reported in [16].

Moreover, the smallest ambient water/hydrogen concentration can be found in the Li_{0.7}Mn₂O_{3.8} films, which were the only films that showed smaller oxygen concentrations than the target material Fig.8d. Alternatively, the Ca_{1.1}Ti_{0.9}O_{2.9} films show the highest hydrogen concentrations, in line with the oxygen results seen in Fig.8b.

ERDA measurements of film hydrogen content [at%]				
Material	Pressure	Angular location		
		0°	45°	85°
BaTiO ₃	Vacuum	16	20.2	20.5
	1x10 ⁻¹ mbar	12.6	15.2	16.7
La _{0.4} Ca _{0.6} MnO ₃	Vacuum	8.7	12.3	12
	1x10 ⁻¹ mbar	19.3	16.4	23.4
Ca _{1.1} Ti _{0.9} O _{2.9}	Vacuum	9	12.1	14.7
	1x10 ⁻¹ mbar	22.3	19.9	20.9
Li _{0.7} Mn ₂ O _{3.8}	Vacuum	3.2	4.3	7.9
	1x10 ⁻¹ mbar	11.6	11	11.6

Table 4. Hydrogen content of the different films in at%. They reflect the ambient water trapping by the amorphous films, with the thinner films often showing the highest concentrations (45° and 85° locations for those films deposited at 1x10⁻¹mbar Ar).

Is the ambient water being trapped at the surface or does it penetrate the entire film? The results, some of them plotted exemplarily in Fig.9 for CaTiO₃, show that the detected

hydrogen was present through the entire films and not only at their surfaces. The thickness of the hydrogen profiles matches the thickness of the films (with vacuum at 0° being the thickest and 85° the thinnest).

Fig.9. Depth profiles of H concentration vs. nm of CaTiO₃ films (black) with suspected trapping of ambient water. The plotted charts correspond to vacuum deposition conditions and at 0°, ~45° and ~85° angular locations respectively.

With these data a rough estimate of the oxygen addition to the film from ambient water can be calculated. For instance, a 15% H content could mean a composition of CaTiO₃+0.5H₂O making the oxygen content circa 3.5. This is a considerable oxygen enrichment which is even underestimated due to sample geometry and the measuring technique. We suspect that we might be underestimating the hydrogen content because of the signal being shadowed by the wrinkles on the thin Al foil substrate combined with the glancing incidence angle. The beam shape is an ellipse with axes of 1x4 mm. The ellipse was perpendicular to the foil, i.e. precision in “angular” position is 1 mm and the measurement averages over 4 mm of the foil along the same angle. The hydrogen signal was very sensitive to slight variations of the measured location.

In summary, it is not possible to assess the effect of pressure on oxygen concentration using the current depositing approach. Deposition of epitaxial films on suitable substrates and with heating is therefore needed.

4. Conclusions

The deposition of five different multi-element oxides by PLD has shown the influence of background gas pressure on the angular distribution of film thickness and composition.

With respect to film thickness, the selected pressure might reduce or cancel the strong forward deposition character of PLD and bring in exchange a loss in material deposition efficiency of ~70%. Although a constant angular thickness distribution might still be interesting for industrial applications.

In terms of film composition, the conclusions are numerous. Overall, compositional deviations with respect to target composition are common. The reported results show the dependency on target composition, background pressure and angular location, as these were the parameters explored in these experiments.

The background gas can have a strong influence on the composition. An influence that increases with higher mass-ratios of the participating elements for a certain pressure regime. At 1×10^{-2} mbar the deviations for Ca/Ti were ~10% while for Ca/La it was ~16% and for Al/Eu ~33%. Whilst for 1×10^{-3} mbar, Li/Mn showed a deviation of ~70%. The assumption is that at precise pressure windows the number of scattering events with the background gas are sufficient to preferentially stop the light elements from reaching the substrate, while the heavier ones still arrive. As a consequence a compositional deviation is detected. However, once the pressure is high enough to also affect the heavy elements, the compositional deviations are reduced, with the composition becoming uniform throughout the angular range, but not necessarily the same as the target. The anion compositional deviations could not be evaluated due to the detected large ambient water trapping by the amorphous films.

In addition, the results for the given pressures are for room temperatures conditions and it is therefore expected that the use of a higher deposition temperature will cause a shift of the regimes to higher pressure values [27].

Nevertheless, the main finding is that when depositing multi-element materials with high mass-ratios the selection of background gas pressure is critical.

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