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Full Length Article

## Improved thin film growth using Slow Kinetics Intermittent Sputtering

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## ABSTRACT

Radio-frequency off-axis magnetron sputtering is a well established technique to produce high quality epitaxial thin films of complex oxides. It has been successfully used for over two decades to grow thin films, superlattices and even solid solutions. The main drawback is the common lack of in situ monitoring of the growth, which can significantly slow down the optimisation of the many growth parameters. However, once the optimal parameters are found, they are usually very stable in time, leading to consistently high quality thin films. One of the main growth parameters is the growth temperature, with typical optimal ranges as narrow as 20 °C. Here, using the prototypical ferroelectric PbTiO<sub>3</sub> as a model system, we show that by periodically interrupting the deposition process to allow the deposited material to relax, we can significantly increase the temperature range over which we obtain atomically flat surfaces to more than 50 °C. Moreover, the overall crystalline quality is greatly improved, as shown by X-ray diffraction. Finally, we demonstrate the applicability of this method to other materials.

## 1. Introduction

To take advantage of the multitude of functional properties complex oxide offer for miniaturised applications [1–3], cheap and scalable methods are needed for their deposition. More fundamentally, extended defects such as grain boundaries and dislocations, as well as dopants and stoichiometry variations can be to a large extent eliminated or relatively precisely engineered in monocrystalline, epitaxial thin films. This makes them a great system to study the intrinsic properties of these materials. To obtain such high quality thin films, physical vapour deposition techniques are the method of choice. Of the three main such techniques - molecular beam epitaxy, pulsed laser deposition, and radio-frequency (RF) magnetron sputtering - the latter is by far the cheapest to implement, since it requires neither ultra-high vacuum nor expensive laser equipment. RF magnetron sputtering has been very successfully applied for many oxide systems, and in particular ferroelectrics, producing extremely high quality thin films [4–6] and superlattices [7–9] with atomically sharp interfaces, and more recently, solid solutions whose properties can be continuously tuned via their stoichiometry [10].

Despite the great success of this technique in producing ultra-thin films and superlattices, growing films thicker than approximately 10 unit cells can be challenging for certain materials. Many different

growth parameters need to be optimised to obtain good quality films, a task which is slowed down by the fact that sputtering usually does not allow for in situ monitoring of the growth by reflection high energy electron diffraction (RHEED), routinely used during pulsed laser deposition or molecular beam epitaxy. However, once the optimal parameters are determined, they are usually very stable in time, and lead to consistently high quality films. One of the key optimisation parameters is the growth temperature, which can moreover be used to control the functional properties of the thin films via defect gradient engineering [11] or strain relaxation [12,13]. However, moving this parameter outside the optimal growth window can be detrimental to the crystalline quality of the films, thus limiting its applicability. Here, we present a technique that allows us to increase the temperature range over which the samples present a consistently high crystalline quality, opening the possibility to use temperature as a tuning parameter for the functional properties of the sample. We demonstrate this technique in 50 nm films of lead titanate (PbTiO<sub>3</sub>), which is a prototypical tetragonal ferroelectric, and which has been grown by sputtering for more than two decades [4–9].

Recent studies [10] have looked at solid solutions of lead titanate and strontium titanate, grown by depositing alternating sub unit cell amounts of materials from two targets, up to a total thickness between 20 and 100 nm. Inspired by the high quality of these solid solutions, and

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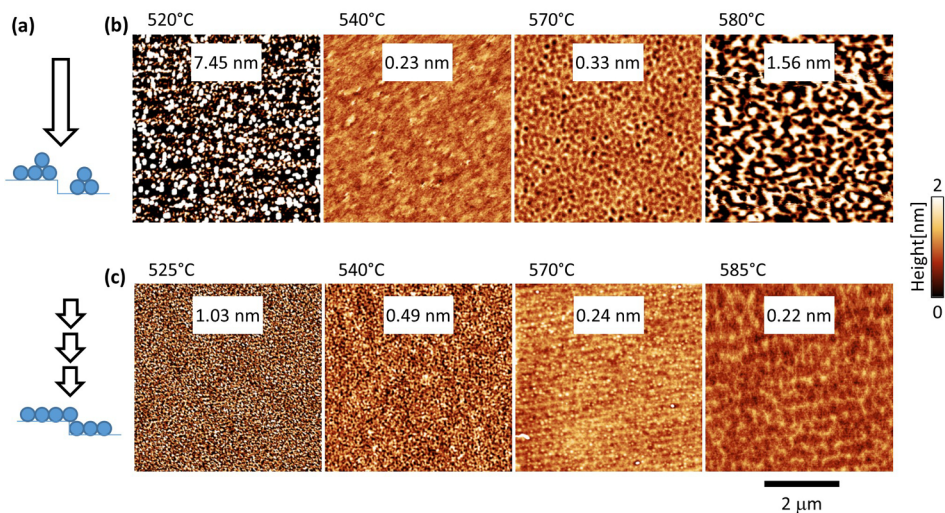
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**Fig. 1.** Growth temperature range for high surface quality (a) Schematic representation of our method: instead of depositing all the material continuously (top), we intermittently sputter and wait, to allow the adatoms to relax and rearrange on the surface (bottom). Surface topographies for a series of samples grown at different temperatures using (b) the continuous mode and (c) the SKIS mode. All images are represented on the same 2 nm colour scale, and the RMS roughness is indicated on each image. We can see that for samples grown continuously outside the range of 540–570 °C, the surface roughness increases dramatically, whereas the SKIS-grown samples are much more homogeneous over the entire temperature range investigated, with sub-unit-cell roughnesses up to the highest temperatures.

by similar approaches for pulsed laser deposition [14], where the target material is deposited via intermittent pulses alternating with waiting periods of several seconds, we decided to modify our deposition technique to allow more time for the realisation of slow kinetic processes at the surface of the growing film, resulting in Slow Kinetics Intermittent Sputtering (SKIS). In this technique, the RF gun is turned on for approximately one minute, a quarter of the time needed to deposit a full unit cell. The gun is then switched off completely for approximately 20 s, to allow the newly deposited adatoms to relax and optimise their position on the surface, similarly to what is shown by in situ RHEED in Ref. [14], and the process is repeated until the desired thickness of material is deposited (Fig. 1(a)). We found that longer relaxation times did not change the sample characteristics, and shorter relaxation times were hard to obtain with our experimental set up. Routine diffraction experiments revealed no extra phases in either continuous or SKIS grown lead titanate, see [supplementary Fig. S1](#).

## 2. Experimental methods

The samples in this study were grown epitaxially using off-axis radio frequency magnetron sputtering. All samples were grown on TiO<sub>2</sub> terminated, (001)-oriented, undoped SrTiO<sub>3</sub>. PbTiO<sub>3</sub> thin films were deposited between 520 °C and 580 °C, in 180 mTorr of a 20:29 O<sub>2</sub>/Ar mixture using a power of 60 W, with a LaNiO<sub>3</sub> back-electrode deposited in situ at the same temperature as the PbTiO<sub>3</sub> in 180 mTorr of a 10:35 O<sub>2</sub>/Ar mixture using a power of 50 W. The SrTiO<sub>3</sub> thin films were deposited at 540 °C in 180 mTorr of a 29:20 O<sub>2</sub>/Ar mixture using a power of 60 W. BiFeO<sub>3</sub> thin films were deposited at 650°, in 100 mTorr of a 25:75 O<sub>2</sub>/Ar mixture using a power of 40 W, with a LaNiO<sub>3</sub> back-electrode deposited in situ at 550 °C in 100 mTorr of a 30:70 O<sub>2</sub>/Ar mixture using a power of 50 W. The LaFeO<sub>3</sub> thin films were deposited at 650 °C, in 100 mTorr of a 25:75 O<sub>2</sub>/Ar mixture using a power of 50 W. PbTiO<sub>3</sub> and SrTiO<sub>3</sub> were grown in one growth chamber, while BiFeO<sub>3</sub> and LaFeO<sub>3</sub> were grown in another. *Hüttinger PFG 300* RF power supplies were used in power control mode for all materials and all chambers. The sample holders were grounded during deposition, but the sample surface was left floating. Pb<sub>1.1</sub>TiO<sub>3</sub> and Bi<sub>1.1</sub>FeO<sub>3</sub> targets had a 10 % excess of Pb and Bi respectively to compensate for the volatility of these species, while stoichiometric targets were used for all other materials.

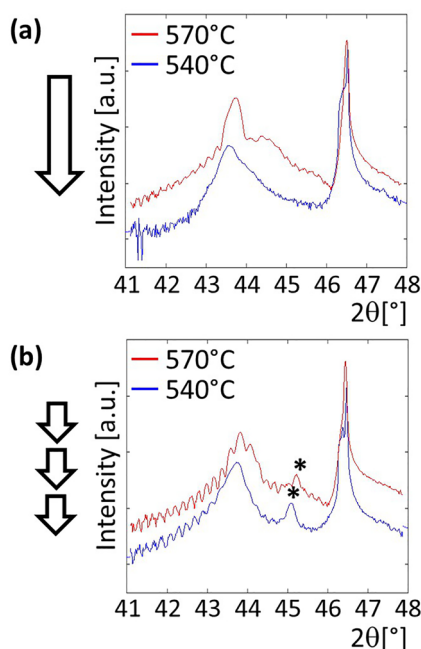
For the SKIS deposition, the plasma was turned on and off at regular intervals by starting and stopping the power supply while keeping the process atmosphere constant. No transient behaviour could be observed, and the plasma appeared and disappeared immediately upon switching the power supply. A shutter was placed in front of the target after the plasma was turned off.

The surface morphology of our samples was characterised using an *Asylum Research Cypher* atomic force microscope in tapping mode, using *Bruker TESPA* tips. To assess the crystalline quality of our samples, X-ray diffraction measurements were performed using a *Panalytical X'Pert* diffractometer equipped with a monochromator and a triple axis detector.

## 3. Results and discussion

We first applied our SKIS deposition technique to produce bilayers consisting of 50 nm thick ferroelectric PbTiO<sub>3</sub> films on top of a lanthanum nickelate (LaNiO<sub>3</sub>) bottom electrode, grown on (001)-oriented strontium titanate (SrTiO<sub>3</sub>) substrates. Fig. 1(b) shows the surface topographies of four samples in a series grown in continuous mode to optimise the growth temperature, all on the same 2 nm colour scale. We can see that outside the optimal growth range of 540–570 °C, where the RMS roughness is less than one unit cell, the surface morphology greatly deteriorates, with holes and pillars appearing. In contrast when SKIS mode is used (Fig. 1(c)), while the RMS roughness remains higher for very low growth temperature, all the samples through the same temperature range show far more homogeneous morphology and remain extremely flat, even for very high growth temperatures. Similar roughness values were observed in different regions and for different length scales, see [supplementary Fig. S2](#). This observation demonstrates that the SKIS technique allows us to grow high quality samples in a broader temperature range than the conventional continuous sputtering deposition approach.

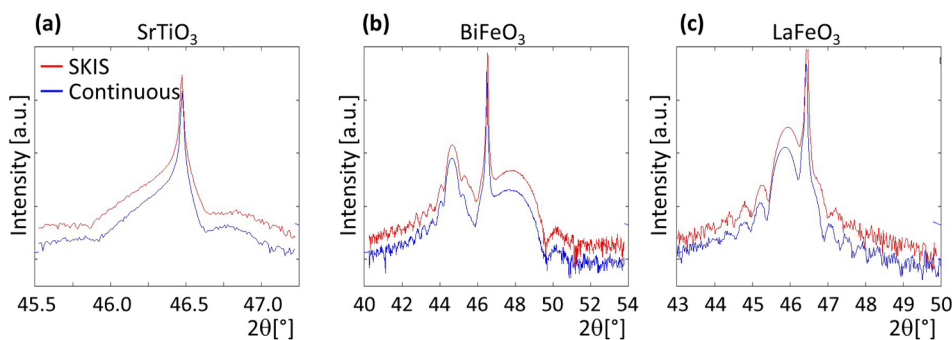
We now focus on two pairs of samples, again all at 50 nm thickness, grown one immediately after the other, one at each end of the optimal temperature range for surface quality in the continuous mode, and two samples grown at the same temperatures in SKIS mode. The X-ray diffractograms around the (002) Bragg peaks for both the sample and the substrate are shown in Fig. 2(a) for the two samples grown in continuous mode. We can see that, although the sample grown at 570 °C shows some finite size oscillations, these are not very marked, and the sample peaks for both films are quite broad, indicating some loss of coherence and therefore less than optimal crystalline quality. The same measurement for the SKIS-grown samples (Fig. 2(b)), on the other hand, show very clear finite size oscillations and sharper peaks, both of which are indicative of higher crystalline quality. The diffractograms of these films even present an additional peak (indicated with a \* in Fig. 2(b)) between the film and the substrate, in the position where a double diffraction peak is expected when the films are coherent enough to allow double diffraction [15,16], and which we rarely observe with the continuous sputtering approach. The diffractograms around the (001) Bragg peaks show the same trend (see [supplementary Fig. S3](#)). This



**Fig. 2.** X-ray diffraction patterns Comparison of the X-ray diffractograms around the (002) reflection of the film and the substrate of samples grown at two different growth temperatures in the continuous mode (a) and in the SKIS mode (b) in immediate succession. For both growth temperatures, SKIS-grown samples show significantly higher crystalline quality, as evidenced by the more pronounced finite size oscillations and the appearance of a double diffraction peak (indicated with a \*) signalling high coherence [15–17].

comparison further shows that, where the growth temperature has a strong impact on the quality of the thin films for continuous growth, SKIS mode allows us to grow high crystalline quality films over a broad temperature range, in addition to producing a more coherent structure at all growth temperatures.

To test how well this approach works for other systems, we applied the SKIS deposition technique to a range of materials with different crystal symmetries. All the samples were grown on the same substrate as the  $\text{PbTiO}_3$  thin films, (001)-oriented  $\text{SrTiO}_3$ . The materials we selected were homoepitaxial cubic  $\text{SrTiO}_3$ , rhombohedral  $\text{BiFeO}_3$  with a  $\text{LaNiO}_3$  bottom electrode, and orthorhombic  $\text{LaFeO}_3$ . In each case, two samples were grown in immediate succession, one in continuous mode, one in SKIS mode. The growth parameters used were the ones that had been previously optimised using continuous deposition for each of the materials. Comparison between the X-ray diffractograms around the (002) reflection are shown in Fig. 3. For  $\text{SrTiO}_3$  (Fig. 3(a)), the shape of the peaks for both samples corresponds to a film about 20 nm thick, with a c-axis of 3.911 Å, slightly higher than the expected 3.905 Å,



**Fig. 3.** Materials with different symmetries Comparison of the diffractograms around the (002) reflection of the film and the substrate for materials with different symmetries than tetragonal  $\text{PbTiO}_3$ : (a) cubic  $\text{SrTiO}_3$  (homoepitaxial) (b) rhombohedral  $\text{BiFeO}_3$  on  $\text{SrTiO}_3$ , with a  $\text{LaNiO}_3$  back-electrode and (c) orthorhombic  $\text{LaFeO}_3$  on  $\text{SrTiO}_3$ . For all these materials, since the growth conditions were already highly optimised, the change in deposition mode had no visible impact on the (very high) crystalline quality of the samples.

which is also the lattice parameter of the substrate, thus showing a slight off-stoichiometry of both films. For  $\text{BiFeO}_3$  and  $\text{LaFeO}_3$  (Fig. 3(b)-(c)), both samples show very well defined peaks and finite size oscillations, indicating very high crystalline quality. All three materials show virtually identical diffraction patterns for both the continuous and the SKIS grown samples. Note that the  $\text{BiFeO}_3$  and  $\text{LaFeO}_3$  were grown in a different growth chamber from the  $\text{PbTiO}_3$  and  $\text{SrTiO}_3$ , which excludes a system specific effect. These observations indicate that when growth conditions are fully optimised, SKIS works just as well as continuous growth, i.e. the waiting time does not destroy order that would otherwise be present.

#### 4. Conclusion

To summarise, we have shown a very easy-to-implement adaptation that has allowed us to significantly increase the growth window that produces high quality  $\text{PbTiO}_3$  thin films using RF magnetron sputtering. We have also shown that although this approach does not have any additional benefits for highly optimised growth conditions, it also does not seem to disturb the order already present in films grown under these conditions. We hope our observations will inspire other groups to try this approach on materials they might have a hard time optimising the growth conditions for, and that this technique will expand the range of materials available to RF magnetron sputtered thin films. Furthermore, the ability to change the growth temperature without deteriorating the film quality will lead to more possibilities to tailor functional properties to one's needs. Industrial application will undoubtedly greatly benefit from a wider pool of available materials and a larger range of available tuning parameters in a cost effective and scalable deposition technique.

#### Declaration of data availability

The data that support the findings of this study are openly available in Yareta at <http://doi.org/10.26037/yareta:wdmelj7tcrghkc4eina32jl2e>.

#### CRediT authorship contribution statement

**Christian Weymann:** Conceptualization, Investigation, Writing - original draft. **Céline Lichtensteiger:** Supervision, Writing - original draft. **Stéphanie Fernandez-Peña:** Investigation, Writing - review & editing. **Kumara Cordero-Eduards:** Investigation, Writing - review & editing. **Patrycja Paruch:** Supervision, Writing - original draft, Funding acquisition.

#### 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 material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.apsusc.2020.146077>.

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