DUBBLE	**Experiment title:** *In-situ* monitoring of the PLD process by synchrotron X-rays Study of the formation of thin PTO layers on STO by interface diffraction methods.	**Experiment number:** 26-02-309
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An important class of oxidic materials is formed by the perovskites: complex transition metal oxides. Depending on composition, this class of materials includes itinerant and local ferro-magnets, high Tc superconductors, ferroelectrics, insulators, semiconductors and half-metallic magnets. In view of the technological importance of these compounds and especially of thin layers of these materials, they are extensively studied in our group. SrTiO3 (001) substrates are widely used in thin film growth of related oxide materials by Pulsed Laser
Deposition (PLD). The PLD process can be monitored by high pressure Reflection High Energy Diffraction (RHEED). The RHEED method, however, only probes the topmost layers. Furthermore, due to the strong interaction, the theoretical interpretation of the result is complicated. When using (synchrotron) X-rays the periodicity is probed on a much larger scale, making the method less sensitive for contaminations. The theoretical interpretation (kinematical theory) is much simpler. Therefore, we started a project to combine PLD and
surface diffraction by means of synchrotron X-rays to in-situ monitor intensity oscillations during PLD and to study the thin (few unit cell) layers produced this way.
Earlier experiments of this project were 26-02-129,157, 224, 248, 271 and 292.

In our previous runs, the sample chamber, which is designed especially for use on the Dubble interface diffractometer, was successfully tested and implemented. Intensity oscillations in the specularly reflected X-ray beam were observed during the deposition of complex oxides, which indicates that with the present set-up it is possible to grow and study layer-by-layer growth. Systems used so far are $YBa_2Cu_3O_{7-x}$ on $SrTiO_3$ and $LaTiO_3$ on $SrTiO_3$.
In the present proposal, the main aim was to examine the structure of lead titanate ($PbTiO_3$) on strontium titanate ($SrTiO_3$). The final goal is to examine the structure of lead zirconium titanate ($PbZr_xTi_{1-x}O_3$) on $SrTiO_3$, but because this is a very complex system, first a good understanding of the growth of $PbTiO_3$ on $SrTiO_3$ is needed. Thin films with a different number of monolayers were deposited and the crystal structure examined.

The previous group (Shah *et al*) had aligned the diffractometer and the beam. A stable 20 keV beam (1.00x0.25 mm^2) was obtained, with an excellent flux of about $2.7x10^{11}$ photons/second. The advantage of a higher energy beam, compared with former experiments, is a more transparent aluminium chamber window. The suppression of higher harmonics at 20 keV was much better as compared to the 12 and 16 keV beam used before. Several old problems with the diffractometer seem to have been solved. The failure of the homing procedure of one of the pre-sample slits was not observed. The occasional sudden movements of the hexapod are did not occur.

The fist day the set-up was completed and the optics of the laser was aligned. During the run thin films of $PbTiO_3$, varying in thickness or deposited at different temperatures, were deposited on five substrates (TiO_2 terminated $SrTiO_3$).
An important deposition parameter, which was optimised, is temperature. The 550^{o}C substrate temperature used at the University of Twente is a bit to high when using the set-up of the ESRF. Lowering of the temperature to 500^{o}C proved to yield much better films.
Figure 1. shows the intensity at the reciprocal point (0,0,0.5) monitored during deposition. The first 100 seconds the laser is not yet turned on. After 100 seconds, the laser is put into operation. The signal drops a bit and the first oscillation starts. After the first oscillation, the signal continues to oscillate. In the maximum of each oscillation, a complete monolayer is grown on the substrate. The laser is stopped after 1250 seconds and the signal remains constant, indicating a stable thin film. After deposition of the three monolayers, crystal truncation rods were measured. Preliminary calculations indicate that the stacking at the interface is the expected bulk-PbO-TiO_2.
The measurement of a single monolayer of $PbTiO_3$ proved to be more difficult. It was seen that one monolayer of $PbTiO_3$ on $SrTiO_3$ at 500^{o}C is not stable for a longer period of time. Figure 2 shows again the intensity of the reciprocal point (0,0,0.5) during deposition; the laser turned on at 100 sec and stopped at the top of the peak (270 seconds). At this point one complete monolayer on $PbTiO_3$ is deposited and the substrate heating is turned off to stabilize the monolayer. However, it can be seen that in time the signal deceases indicating a transformation of the layer. Probably this is due to lead evaporating from the layer and preliminary data support this.

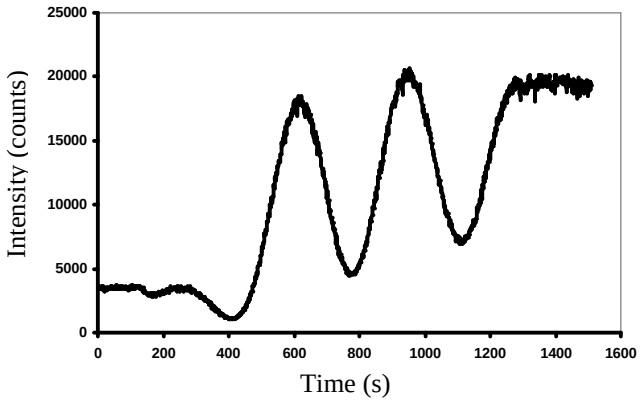

Fig. 1: The intensity of the reciprocal point (0,0,0.5) during l depostion of $PbTiO_3$ on $SrTiO_3$ at 500^{o}C. After starting the laser for deposition, due to roughening the intensity decreases, and finally upon completion of the layer the surface is smooth again, hence a maximum.

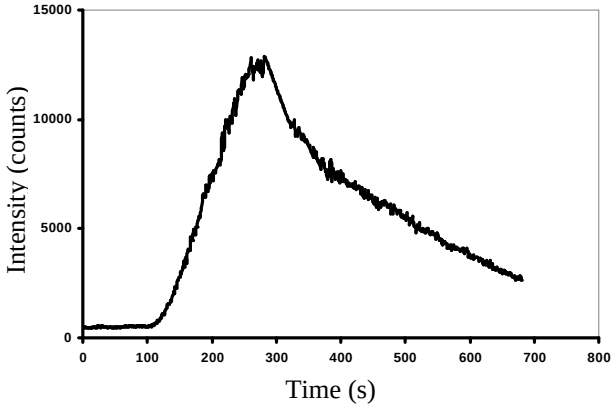

Fig.2: The intensity of the reciprocal point (0,0,0.5) during deposition. After starting the laser, the intensity increases but after the laser is turned off (270 sec.) the intensity drops because the layer is unstable.

In conclusion, structural information was obtained form the growth of $PbTiO_3$ thin films on $SrTiO_3$. Datasets (crystal truncation rods) for different thickness of film were collected. The data are presently being worked out.