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| DUBBLE | **Experiment title:**<br>*In-situ* monitoring of the annealing process by synchrotron X-rays: $DyScO_3$ | **Experiment number:**<br>26-02-481 |
| **Beamline:**<br>BM26 | **Date(s) of experiment:**<br>From : 14-04-09<br>To : 19-04-09 | **Date of report:**<br>08-07-09 |
| **Shifts:**<br>15 | **Local contact(s):**<br>G. Portale | |

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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.
The preferred technique for the growth of these thin films is 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, PLD and surface diffraction is combined 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.
Previous experiments showed the possibility to study layer-by-layer growth of several complex oxides ($PbTiO_3$ on $DyScO_3$, $SrTiO_3$ on $DyScO_3$), using X-rays.
Earlier experiments of this project were 26-02-292, 309, 405 and 460.
During this experiment the surface structure of the substrate $DyScO_3$(110) (DSO) was investigated. The novel substrate DSO has special properties (e.g. a larger in-plane lattice constant) as compared to other commonly used substrates, creating the possibility to obtain, for example tensilely strained ferroelectric phases of extremely thin films. The crystal lattice of DSO consists of alternating DyO and $ScO_2$ layers: the typical perovskite pattern.
The thin films need to be grown at elevated temperature (550-850$^{o}$C). Previous measurements have shown that bare DSO substrates at these elevated temperatures do not have a simple bulk termination, neither DyO nor $ScO_2$ termination. The observed alteration of the surface from the regular bulk structure is maintained during film growth and incorporated into the system, the modification being ‘sealed in’ between the bulk substrate and the deposited film. This modification of the bare surface of DSO has consequences for the film growth process and the structure, thus properties of the thin film.
Therefore it is important to understand the surface behaviour and structure of DSO.
The first 3 shifts in this experiment were used to optimise the beam and to start-up and align the diffractometer.

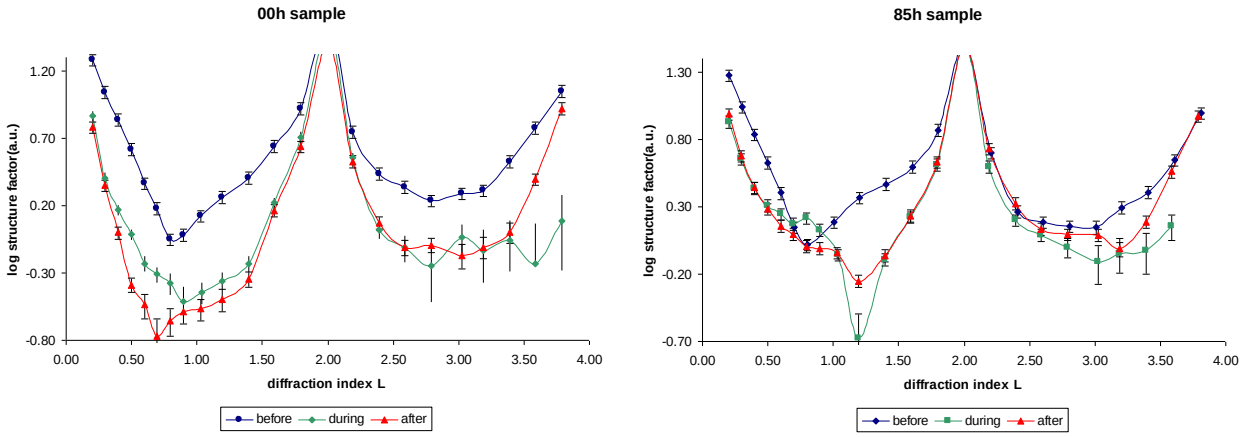


Figure 1: Specular rods of two DSO samples before (blue), during (green) at after the annealing stage (red) at $1000^0$ C Left:unannealed sample, right 85 hour pre-annealed sample.

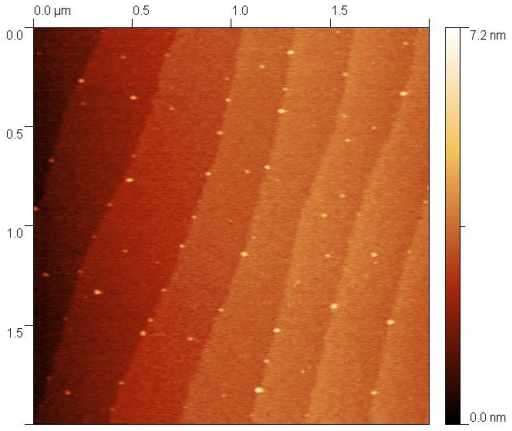


Figure 2 : AFM image of the 85h pre-annealed DSO surface. The terraces are one perovskite unit block high, meaning single termination.

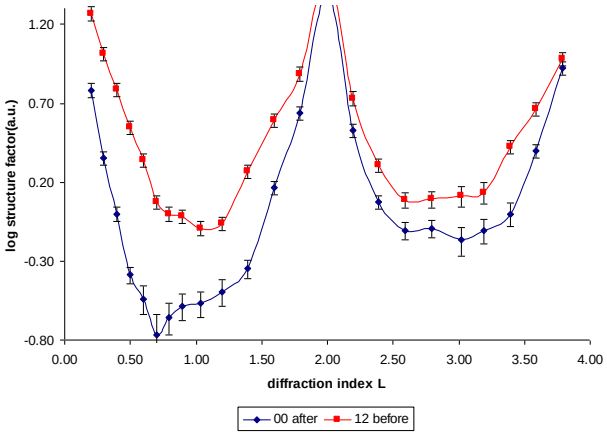


Figure 3 : Specular rods of the untreated DSO sample after annealing (blue) and the 12 hour pre-annealed sample (red).

Data for samples with different pre-annealing times where taken: no annealing, 12 and 85 hours at $1000^0$ C. The three samples where mounted on a heater simultaneously and measured before, during and after the annealing process. To remove all the water and other contaminations the substrates were first heated to 400 degrees Celsius (before measurement, figure 1). Next the substrates were heated to 1000 degrees Celsius in oxygen at atmospheric pressure (during measurement, figure 1). After annealing the substrates at $1000^0$ C for about 30 hours, they where cooled down again to $400^0$ C degrees (during measurement, figure 1).

The surface structure of the unannealed sample changes upon annealing (fig. 1, left). This change could be attributed to the formation of a single terminated surface with straight equidistant terraces (like fig. 2). The extensive 85h pre-annealing procedure should have placed the sample in an already stable state, single terminated surface with straight terraces (fig. 2). The difference upon annealing an additional "few" (30) hours was expected to be minimal. The surface structure of all the samples was expected to converge to a single state, but this is not the case. (figure 1, red curves are different). Also the unannealed sample was expected to be similar after annealing to the pre-annealed 12 hour sample before further annealing, for both samples have then had a similar treatment. Again there is a discrepancy between the expected and observed pattern (fig. 3).

The results of the experiment are not as clear-cut as we had hoped them to be. Through further investigation and modelling, together with the current and previous acquired data we strive to shed more light on the surface structure of DyScO.