DUBBLE	**Experiment title:** **Towards *in-situ* monitoring of the PLD process by synchrotron X-rays** ***In-situ monitoring of the PLD process by synchrotron X-rays Study of the formation of thin layers by interface diffraction methods.***	**Experiment number**: **26-02-271**
Beamline: BM26	**Date(s) of experiment**: From: 09-06-2005 To: 14-06-2005	**Date of report**: 21-06-2005
Shifts: 15	**Local contact(s)**: W. Bras, F. Meneau	

Names and affiliations of applicants (* indicates experimentalists):

V.Vonk[1*] , S. Harkema[1*], H. Graafsma[2], A.J.H.M. Rijnders[1], D.H.A. Blank[1] and H. Rogalla[1]
K.Driessen[1#], M.Huijben[1#], P. Tinnemans [2#]
[1]Low Temperature Division and MESA+ Research Institute, University of Twente, POB 217, 7500AE, Enschede, The Netherlands
[2]European Synchrotron Radiation Facility, Grenoble, France
[#] experimentalists, non-applicants

Report:

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 ferromagnets, 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.

$SrTiO_3$ (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.

The first steps of this project were taken in experiments 26-02-129,157, 224 and 248.

In our previous runs, we have succesfully tested and implemented the sample chamber, which is designed especially for use on the Dubble interface diffractometer. Intensity oscillations in the specularly reflected X-ray beam were observed, which indicates that with the present set-up it is possible to grow and study layer-by-layer growth of complex oxides. In the present proposal the main aim was to stop deposition at a well defined coverage and collect data in the form of several crystal truncation rods (CTR's), in order to solve the interfacial atomic structure. The high-Tc superconductor $YBa_2Cu_3O_{7-x}$ (YBCO) on a $SrTiO_3$ (001) substrate was chosen as system, because although studied extensively and used in a variety of applications, the exact nature of growth and interface structure are not completely solved yet.

During the first two buffer days the set up was completed and the optics were aligned to obtain a suitable X-ray beam at the sample position. We obtained a positionally very stable 1x1 mm^2 beam, with a flux of about $5x10^{10}$ photons/s. Although the specifications of the optics should provide sufficient higher harmonic

suppression, we still found non-negligible contamination of $\lambda/3$ and $\lambda/4$ in the diffracted signal. This is quite a nuisance when searching for fractional order reflections, and a systematic investigation of the cause of this problem seems to be in order.

With the final set-up, several deposition runs using different substrates were carried out. The first step was to measure several CTR's of the bare STO substrate close to deposition conditions (T=780 °C p=10^{-4} mbar), in order to be able to compare this structure with the one obtained after depositing 2/3 monolayer YBCO. A first attempt to fit a model to these data indicate that the STO(001) surface consists of a TiO_2 layer which is completeley covered by oxygens. This is a surprising result, because in an earlier run, we studied the same surface at room temperature in air. The outcome of that experiment was the same: a TiO_2 terminated crystal completely covered with oxygens, which most likely are water molecules, bonded to the ionic surface. The new result seems to indicate that the oxygen layer is still present at 780 °C and P=10^{-4} mbar, and the question arises whether it can really be water.

By carefully monitoring the specular intensity during deposition, it is possible to stop after a fully closed layer has been grown. Figure 1 shows the intensity of the reciprocal point (0,0,0.18) during the initial deposition. From previous experiments it is expected that the maximum corresponds to approximately 2/3 monolayer YBCO. This very thin layer of YBCO seemed not to be stable for periods of more than a few hours at deposition conditions. This is conluded from the appearence of diffraction peaks, belonging to a so far not identified phase. Nevertheless, the specular rod shown in figure 2, which was measured within one hour after deposition of the thin film, can be used for further analysis. A drastic change in the specular rod between before and after depositing the thin layer is observed, which is shown in figure 2. The exact atomic structure of this monolayer of YBCO is presently being worked out.

Two other samples were used to measure specular rods at different thicknesses, which could be done much faster than when collecting a whole data set. This will allow us for detailed analysis of the influence of adding one or half a unit cell layer to the already grown thin film on the diffracted intensities.

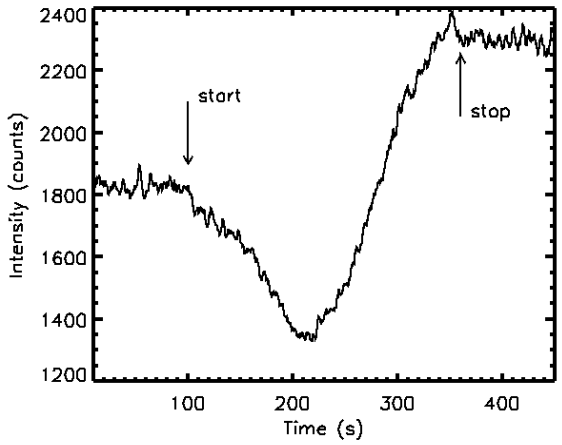

Fig.1 The intensity of the reciprocal point (0,0,0.18) during depostion of the first completely closed layer of YBCO. After starting the laser for deposition, due to roughening the intensity decreases, and finally upon completion of the layer the surface is smooth again, hence a maximum.

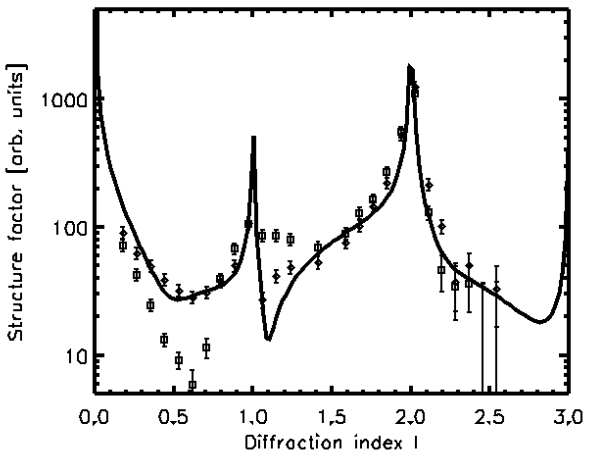

Fig. 2 The specular rods at 780 ºC of the bare STO(001) (circles) and of that surface covered by approximately 2/3 monolayer YBCO. The solid line is a fit to the bare substrate using a model consisting of a TiO2 terminated surface, completely covered by oxygens.

In conclusion, we have succeeded in obtaining surface crystallographic data sets of the interface structure of the YBCO/STO system for different layer thicknesses. Since a YBCO film thinner than a unit cell proved not to be stable during the whole data collection time, not all the data can be used. Nevertheless part of this particular dataset, which was taken within two hours after completing the deposition, will be very helpfull for clearifying the unknown atomic structure.