EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

# Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office via the User Portal:
*https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do*

## Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

### Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report")*,
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

## Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

### Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

| ESRF | **Experiment title:** In-plane and out-of-plane structural analysis of epitaxial 2D $MoS_2$ thin films MOCVD-grown on distinct $Al_2O_3$(0001) surfaces | **Experiment number**: HC-4981 |
|---|---|---|
| **Beamline**: BM32 | **Date of experiment**: from: Set 5, 2022 to: Set 12, 2022 | **Date of report**: 03/10/2022 |
| **Shifts:** 18 | **Local contact(s)**: Lucio Martinelli | *Received at ESRF:* |


**Names and affiliations of applicants** (* indicates experimentalists):

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**Report:**

The main part of the experiment consisted in a detailed grazing incidence X-ray diffraction (GIXRD) analysis of two samples of sub-monolayer domain coverage $MoS_2$ films grown by MOCVD on $Al_2O_3$(0001) single crystal substrates pre-annealed at 1200ºC under either an $O_2$ atmosphere, or a $H_2$-enriched atmosphere, resulting in predominantly $(1 \times 1)$ or $(\sqrt{31} \times \sqrt{31})R9°$Al-terminated surface reconstructions, respectively.

<u>GIXRD in-plane reciprocal space maps of as-deposited samples:</u>

Beam energy was first set to 18 keV, but then 11.19 keV was found optimal to obtain the best film to substrate peak intensity ratio. The in-plane reciprocal space maps covered a large area ($\Delta\omega$ = 80º) including several *h00* and *hk0* reflections from film and substrate. The measured maps are shown in Figure 1. The main difference between the samples is that the in-plane orientation of the $MoS_2$ domains on $O_2$-treated sapphire consists of about 97% of the so-called R0º orientation (basically a 3 x $MoS_2$ unit cell on 2 x $Al_2O_3$ unit cell), while on $H_2$-treated sapphire the $MoS_2$ grows as a combination of about 75% R0º and 25% R30º (30º degrees in-plane rotated domains). For a more quantitative exploration of the film domain orientation we measured accurate radial scans (combinaton of δ

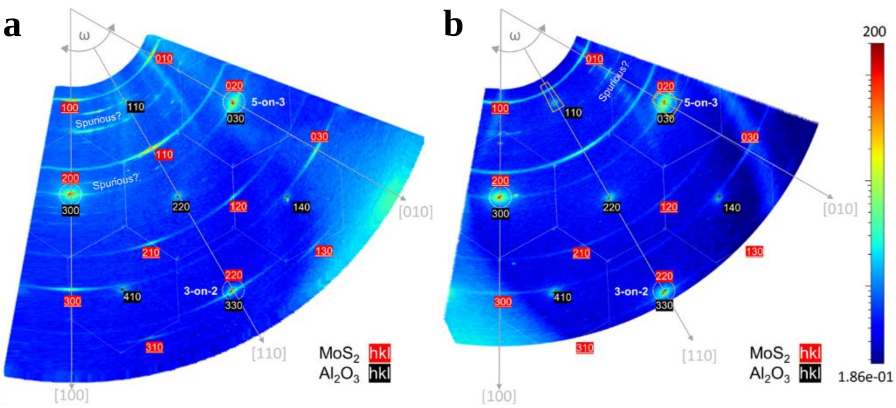


**Fig.1** In-plane reciprocal space maps measured for as-grown $MoS_2/Al_2O_3(0001)$ on (a) $O_2$-annealed $(1 \times 1)$ and (b) $H_2$-annealed $(\sqrt{31} \times \sqrt{31})R9°$ reconstructed surfaces.

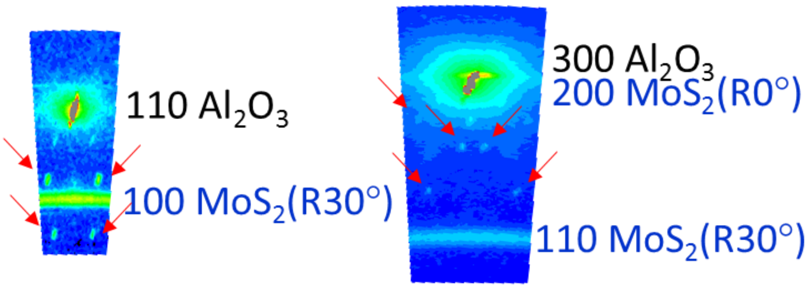


**Fig.2** Detailed maps, as marked in Fig. 1b, showing the surface reconstruction of the 1200°C, $H_2$-annealed $Al_2O_3$ substrate along with $MoS_2$ peaks.

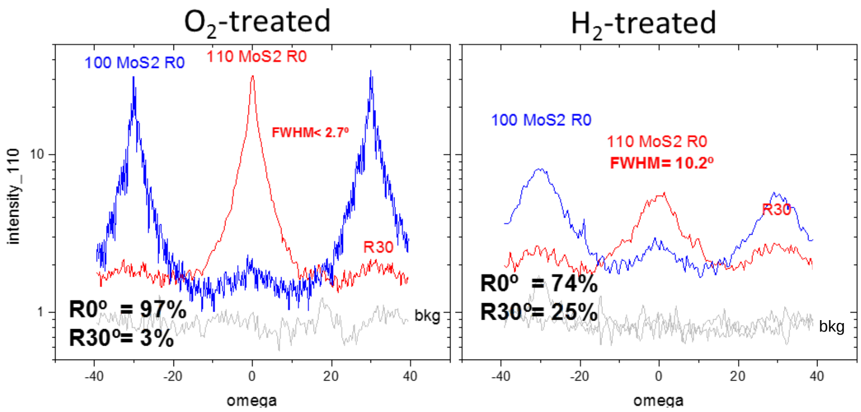


**Fig.3** Azimuthal scans around 100 and 110 $MoS_2$ in-plane reflections.

and ω goniometrer angles) along the main crystallographic directions of the samples: //[010],[110],[100], as well as azimuthal scans (ω scans) of the (110) $MoS_2$ reflections. One of the most striking results was the observation of the persistence of the $(\sqrt{31} \times \sqrt{31})R9°$ reconstruction of the Al-rich sapphire surface after $MoS_2$ growth, as evidenced by the presence of multiple spots (marked with red arrows in Fig. 2), which seems to be responsible for the loss of the R0° epitaxial arrangement of $MoS_2$ domains in favour of R30° orientation. The difference in the domain arrangement is also depicted in the omega scans (Fig. 3) of 100 and 110 $MoS_2$ in-plane reflections of the as-deposited samples with an in-plane dispersion (mosaic spread) measured by the FWMH of about 2-3° and 10° for the $O_2$- and $H_2$-treated samples, respectively.

<u>*In situ* high temperature annealing under $H_2S$ atmosphere:</u>

The second part of the experiment was devoted to the analysis of the same crystallographic features (in-plane maps, radial and azimuthal linear scans) after having exposed the samples for 45 min at 600°C and $H_2S$ atmosphere (0.025sccm, 1.8 $10^{-5}$ mbar). No substantial differences were observed for the in-plane domain arrangement of $MoS_2$, neither in radial nor azimuthal scans.

<u>*In situ* high Temperature vacuum annealing:</u>

Further annealing at 600°C under UHV conditions (1.8 $10^{-9}$ mbar) was performed to account for possible desorption/de-intercalation of species and/or subtle reconstruction of the $Al_2O_3$ surface or $MoS_2$ islands.

<u>X-ray reflectivity (XRR) analysis</u>

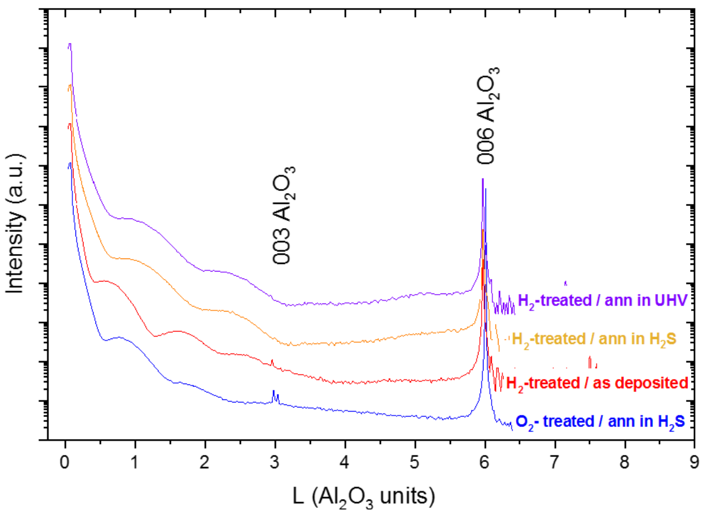


**Fig.4** XRR curves of the $MoS_2/Al_2O_3$ samples under different *in situ* annealing conditions, as indicated.

This experiment took advantage to carry out XRR analysis of the two different films as-deposited, as well as after $H_2S$ and vacuum annealing, in an attempt to explore the out-of-plane arrangement of atomic planes and distances between the S-Mo-S trilayer sheet to the outermost Al layer of $Al_2O_3$ (i.e. van der Waals gap). As observed in the XRR scans in Fig. 4 the films on $O_2$- and $H_2$-treated substrates show different behaviour. In the $H_2$-treated substrates there is a variation between as deposited and after $H_2S$ annealing, while subsequent annealing in UHV left this sample unchanged. An atomic layer model is necessary to extract any information about interlayer distances at the $MoS_2/Al_2O_3$ interface.

<u>Crystal-truncation rod analysis</u>

Similarly, we acquired *L*-scans at different *HK* postions of $MoS_2$ film (R0° domains) either along the rods and left and right background *L*-scans. Rods analysed: 10*L*, 20*L* (overlapped with 30*L* $Al_2O_3$ position), 30*L*, 11*L* and 22*L* (overlapped with 33*L* $Al_2O_3$ position).