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

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

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.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal 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 situ X-ray scattering investigations of the nanocatalyst-substrate eutectic system and subsequent VLS growth of Si(Ge) monodisperse and equally spaced NWs on patterned Si(111) substrates	**Experiment number**: 32-03-712
Beamline: BM32	**Date of experiment**: from: 13/06/2012 to: 19/06/2012	**Date of report**: 28/08/2012
Shifts: 21	**Local contact(s)**: Gilles RENAUD	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Objective & expected results :

The aim of the proposal was to provide :

1. Above all, the first *in situ* measurement in reciprocal space of the Si nanowire (NW) growth by UHV-CVD, from the very early stage of eutectic formation, to the end of the entire growth process.
2. We also planned to determine the NW size effect on various aspects (eutectic temperature, growth direction, etc.) with the use of E-beam patterned substrates.
3. And finally, the investigation of the influence of different growth parameters (flow rate, growth temperature, etc.)

We expected, with the combination of *in situ* GIXD (Grazing Incidence X-ray Diffaction) and GISAXS (Grazing Incidence X-ray Small Angle Scattering), to not only confirm what has been previously reported by TEM measurements, but also to find out what is missing, especially about what is happening in the early stage of growth, the duration of which is rather short thus making it impossible to be studied by any *ex situ* techniques.

Results and the conclusions of the study:

1. The main objective of the experiment has been achieved. As a matter of fact, not only were we able to follow the growth by applying alternatively the two techniques, we did manage to find something interesting in the early stage of growth (see Fig. 1).

With GISAXS, we first observed a sudden change in the aspect ratio (contact angle) of the liquid catalyst as soon as the precursor gas was introduced into the growth chamber. This is probably due to the increase of Si percentage in the liquid alloy during the supersaturation process.

The supersaturation process might be partially or solely responsible for the so called incubation time which manifests itself as a characteristic delay between the beginning of the injection and the onset of the NW growth. In our case, the incubation time, which varies from tens of seconds to several minutes depending on the growth condition, was measured by conducting the same diffraction scan on a Si Bragg peak or by a time scan at the foot of a peak.

Under appropriate growth condition, the size distribution of the NWs could be narrow enough to give rise to an observable NW size modulation during GIXD measurements. The result is a gradually decreasing value in direct space from 230nm to 150nm, which can be explained by the initial growth of the larger NW base and the subsequent growth of the smaller NW body.

Meanwhile, GISAXS measurements reveal some strange faceting feature during the formation of the NW base, which has to our knowledge never been reported before. A detailed explanation requires further analyse of the current data and more precise measurements in the future (next proposal).

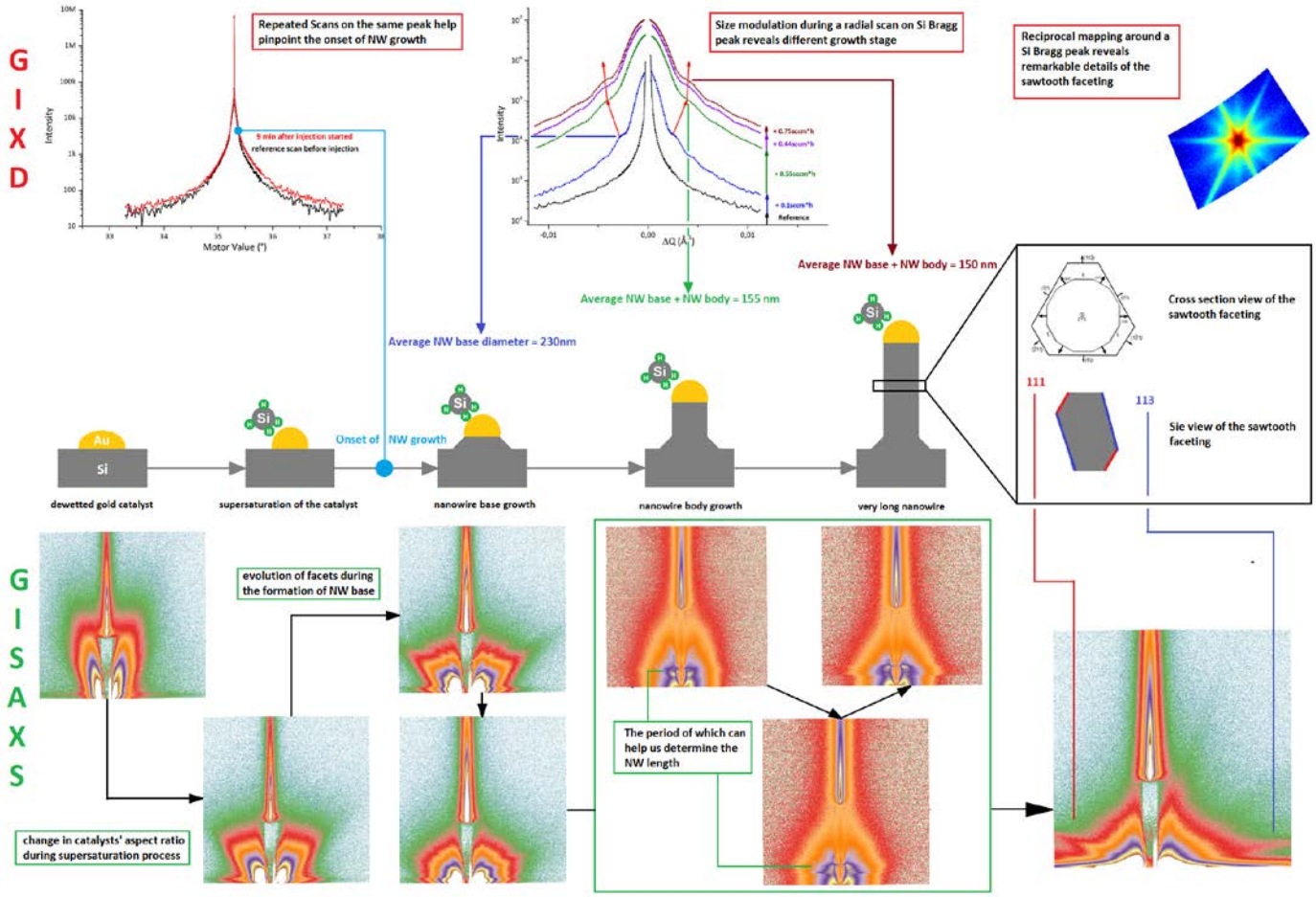

Figure 1 : GIXD and GISAXS measurements of the VLS growth of Si NWs on Si(111) substrate by UHV-CVD

Once the NW growth begins, the NW length can be tracked by analysing the length modulation in GISAXS measurements. This is, however, possible only until about 200 nm as the resolution of the GISAXS is limited by divergence of the beam perpendicular to the sample.
Finally, the well known sawtooth faceting was observed by both techniques, and has been reported by us in a previous experimental report already.

2. The use of E-beam patterned substates was, however, not successful as a result of various difficulties encountered during preparation of the sample (oxide free while not disturbing the pattern). We therefore switched back to the use of standard Si(111) substrate. Fig. 2 shows the result of a typical growth with different levels of magnification where we observe long straight and well faceted NWs grown on large surface area.
Future improvement will focus on
(i) A modified way of sample preparation to increase the yield after E-beam patterning.
(ii) Alternatively, we will try to apply the use of nano-colloidal gold as catalyst thanks to our new collaborators at the CEA laboratory (CEA/INAC/SiNaPs)

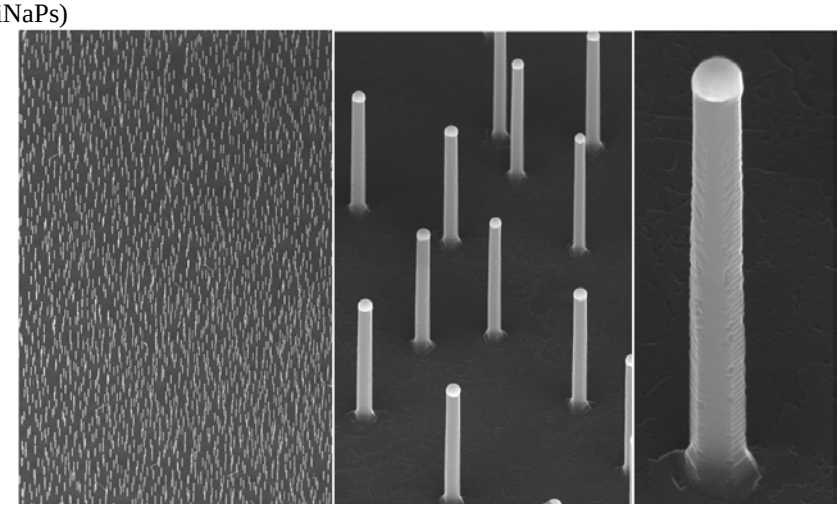

Figure 2 : SEM image of a typical Si NW growth at BM32

3. The third objective was also achieved.

Much as expected, changing the flow rate seems to affect only the growth speed while changing the growth temperature also affects the mean NW size as a result of increasing level of catalyst agglomeration at higher temperatures.
One final thing worth mentioning is the use of inert gas (Ar in our case) to suppress catalyst agglomeration. While it appears that lower pressure (1e-5 mbar) has no effect at all (catalyst diameter ~ 150nm after 10min annealing at 550°C), more elevated Ar pressure (>1e-4 mbar) seems to be capable of limiting the catalyst diameter to less than 50nm.
The use of elevated pressure to suppress surface diffusion is already known, but the resulted GIXD measurements is rather interesting (Fig. 3). We clearly distinguish two cases, the one with twin-tower shoulders and the one with just moderate modulation. In the former case, the maxima of the interference function is situated far away from the Bragg position as a result of small inter-NW distance. The steep interference function thus dominates when calculating the structure factor. In the latter case, the distance between NW sites are relatively large, the maxima of the interference function is therefore close to the Bragg position, leaving an almost constant tail aside thus rendering the entire size modulation in the form factor to be visible.
It is worth noting that when part of the small NWs ceased to grow later during the injection (confirmed by SEM images), which explains the disappearance of the twin-tower shoulders in the later stage of growth (black curve, case #1).

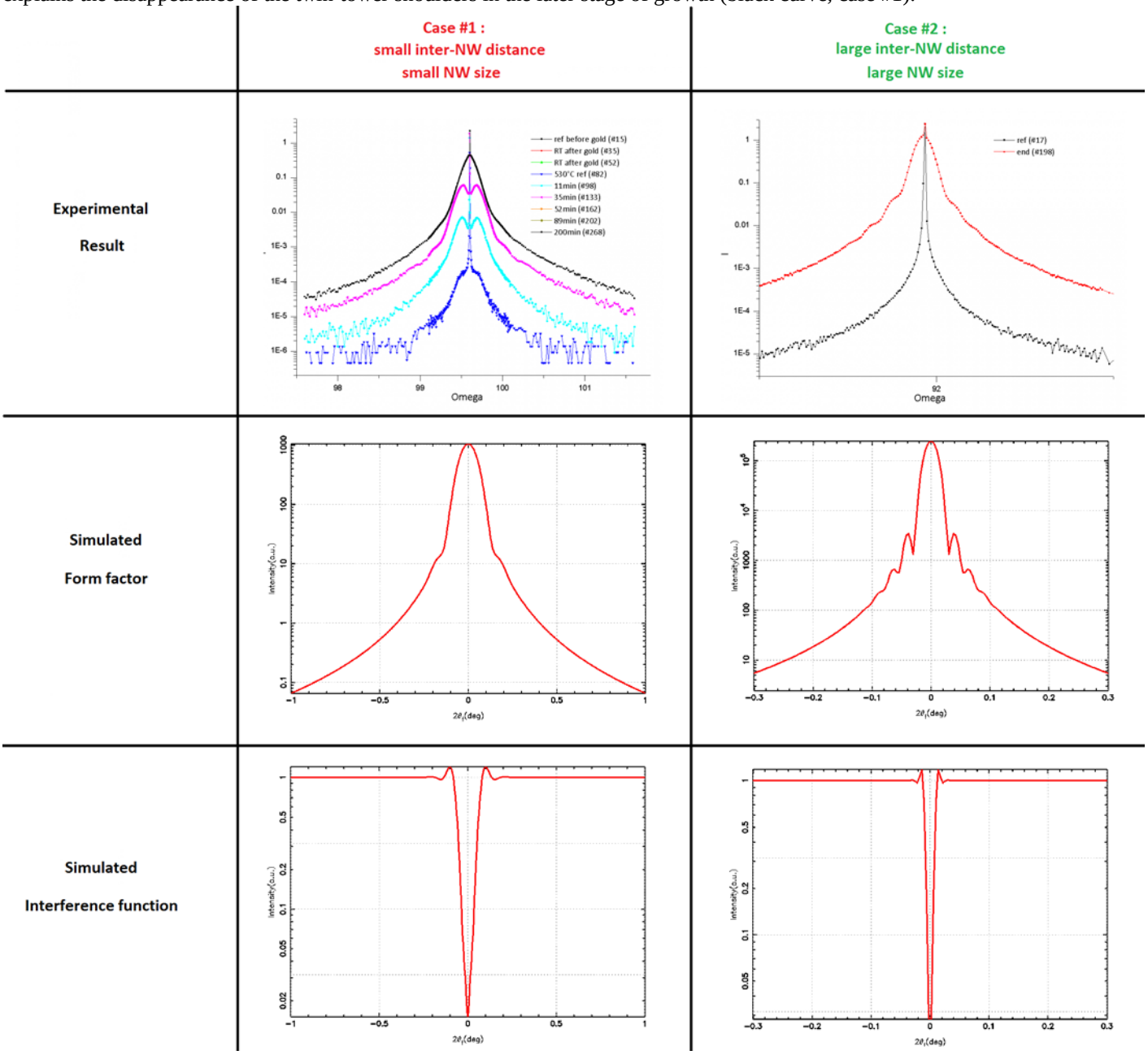

Figure 3 : GIXD measurements on samples with and without the presense of Ar (>1e-4 mbar)

Justification and comments about the use of beam time (5 lines max.):

IF-INS (BM32 ESRF) possesses, to our knowledge, the only system worldwide capable of delivering both CVD (group IV precursors) and MBE growth under UHV condition while performing *in situ* GIXD and GISAXS measurement at the same time.