ESRF

ESRF	**Experiment title:** **In situ X-ray scattering investigations of the UHV-CVD growth of Si and Ge nanowires**	**Experiment number**: **32-03-704**
Beamline:	**Date of experiment**: from: 20/04/2011 to: 27/04/2011	**Date of report**: 29/02/2012
Shifts: 21	**Local contact(s)**: Gilles RENAUD	*Received at ESRF:*

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Report:

Objective & expected results :

The aim of the proposal was to perform the first *in situ* X-ray investigation on Si(Ge) nanowires (NW) using the new UHV-CVD injection system installed at IF-INS (BM32, ESRF). The installation of the system took 3 years and was completed by the end of February 2011. The system is attached to the beamline's existing UHV-MBE chamber and was at the time equipped with three gas precursors, silane(SiH_4), germane(GeH_4) and disilane (Si_2H_6).

We expected to follow *in situ* the growth of the Si(by silane) and Ge(by germane) NWs on Si(111) substrates, to extract information on strain relaxation, sidewall faceting, to conclude on size and temperature dependencies of various aspects, such as growth direction and growth rate, and finally to derive the optimal growth condition (defects, homogeneity) of the group IV NWs.

Results and the conclusions of the study:

The main objective of the experiement was not achieved.

We did observe evolution of strain relaxation once the injection began, and for one of the samples, signature of faceting near the bulk Bragg reflection (though quite weak). However, post-growth SEM measurements reveal that almost all Si NWs (grown with silane) were twisted (Fig. 1 a), and that the surface is covered with a very rough layer of Si deposition. We could not, as a result, conclude on the origin of the observed signals. Besides, intense signals indicating twinning stacking faults have also been recorded, both by X-ray diffraction and by RHEED.

In the case of Ge growth by germane, for injections at temperature below the T_e (Vapor Solid Solid process), the sample surface remains perfectly flat (SEM observation) even after hours of injection at maximum flux, whereas for injections at temperatures well above T_e (Vapor Liquid Solid process), we observe only features of direct Ge growth on Si substrates as if no catalyst is present (Fig. 1 b).

The failure of the experiment lies in the fact that the gas precursors used (silane, germane) in our experiment, though commonly used in the industries for the production of Si(Ge) NWs, show extremely low reactivity as their partial gas pressure are limited by our working condition (UHV, base pressure of the chamber should not exceed 5E-5 mbar). For germane, the decomposition of the gas precursor was even more limited when the substrate temperature is lowered (for the VSS process), thus explaining why nothing was observed in some case.
Although disilane is supposed to show adequate reactivity, the corresponding NWs growth was hindered by the conception of the old gas injector which tended to introduce turbulence at elevated gas flow, leading to the production of twisted NWs.

All these motivated the modification of our gas injection system right after the experiment.
We've abandoned the use the silane and germane as they were proved to be "not adequately reactive" under our working condition. In the mean time, a dedicated quartz capillary injector was put in place. The system has proved to be capable of producing Si NWs of excellent quality after optimal growth parameters were found in subsequent No-Beam Tests with disilane in late July.
Recently, (Dec 2011), we obtained 15 shifts of In House Research, and are finally able to resume our previous study (The one mentioned in this proposal) on the growth of Si NWs on Si(111) substrates with disilane.
In situ GIXD and GISAXS studies of these NWs during growth have revealed remarkable details on the NW morphology (Fig 3. a, b, c). The data is still under analysis, but the raw result is already exciting.
1. With the help of MAXIPIX Area Detector, we are able to precisely reconstruct the 3D profile of the sidewall sawtooth faceting.
2. Constant GISAXS measurements at the very first phase of growth show some mysterious change in faceting which then stabilized after about 10min of injection at 0.9sccm. The exact origin of the change is still under investigation.
3. Size modulation of the NWs was for the first time clearly observed in *in situ* X-ray investigation. (thanks to the relatively small dispersion in catalyst size)
4. Finally, thanks to the successful growth achieved at a variety of temperatures (from 440°C to 640°C), we were able to grow Si NWs with an average size (diameter) varying from 50nm to 250nm, thus providing insights into the size dependencies of various aspects (growth direction, crystalline quality-defects, growth rate, sidewall faceting, etc.).
We thus confirm that when optimal growth conditions are provided, the UHV-CVD system at IF-INS is capable of allowing us eventually complement the present understanding of the relations and differences between the VSS and the VLS process.

As the second part of the modification, precursor for Ge NW growth (digermane, Ge2H6) will be appended to the system during the long shutdown period (before May 2012) of the ESRF. This gas precursor, reported to be 100 times more reactive than the previously used germane, is reported to yeild successful growth of Ge NWs via VSS process ($T<T_e$) in various UHV installations.

Justification and comments about the use of beam time :

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. The progress on the study of Si(Ge) NWs (VLS/VSS) growth was delayed by the use of silane and germane which were later proved to be "not adequately reactive" under UHV conditions. The project recently took a big step forward thanks to the successful growth and measurements on disilane fueled Si NWs during Dec 2011's In House Research.

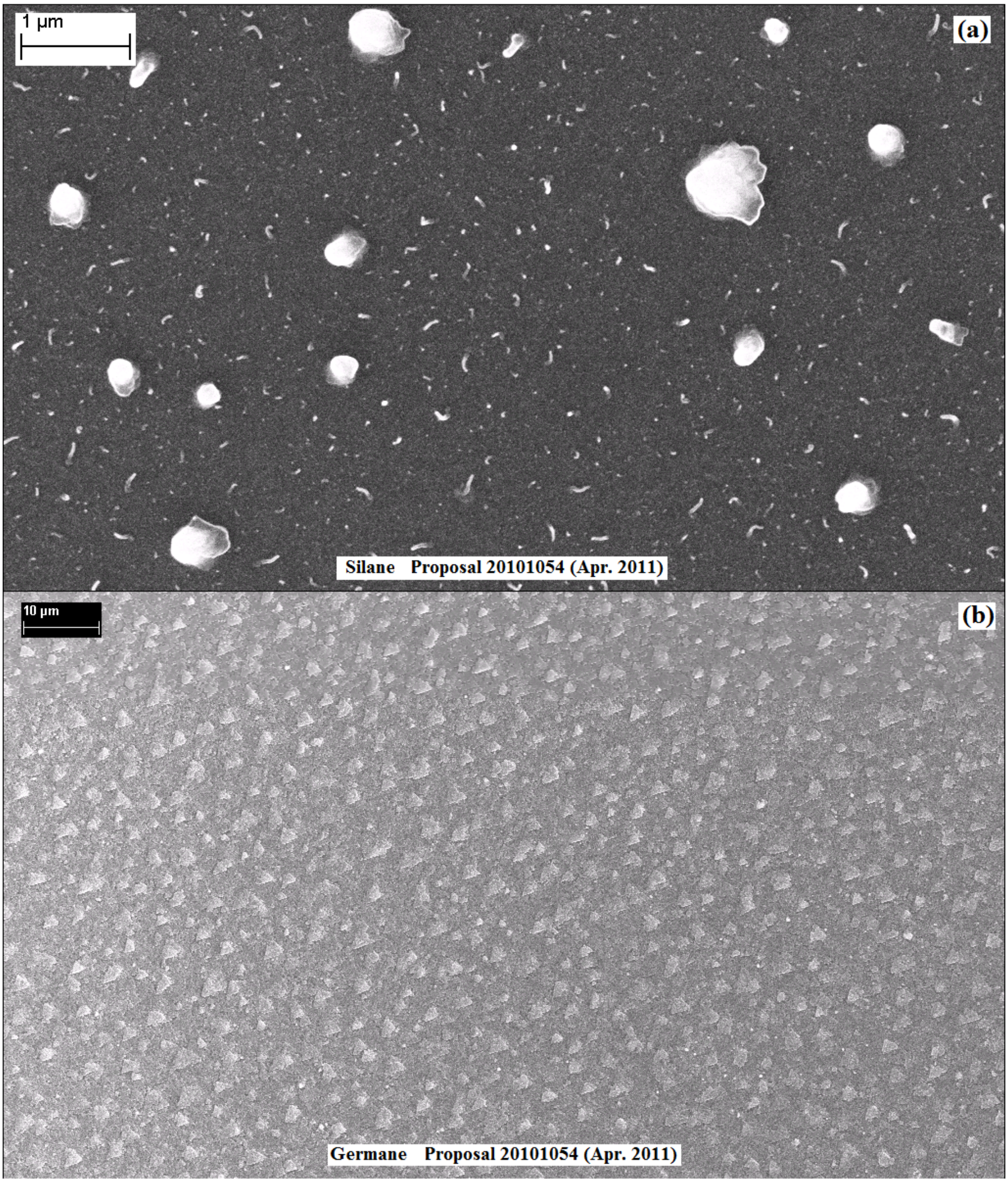

Fig. 1 (a) Top view of the surface of a Si(111) sample after 1H injection of silane at 0.9sccm The nanowires are twisted and are characterized by intense signal of stacking faults when subjected to X-ray investigation.

Fig. 1 (b) Top view of the surface of a Si(111) sample after 2H injection of germane at 0.7sccm Sample surfaces after injection at low temperatures (<Te) remain absolutely flat (not shown here) because of the extremely low reactivity of germane under the given conditions whereas sample surfaces after injection at high temperatures demonstrate only features of uncatalyzed growth of Ge on Si(111)

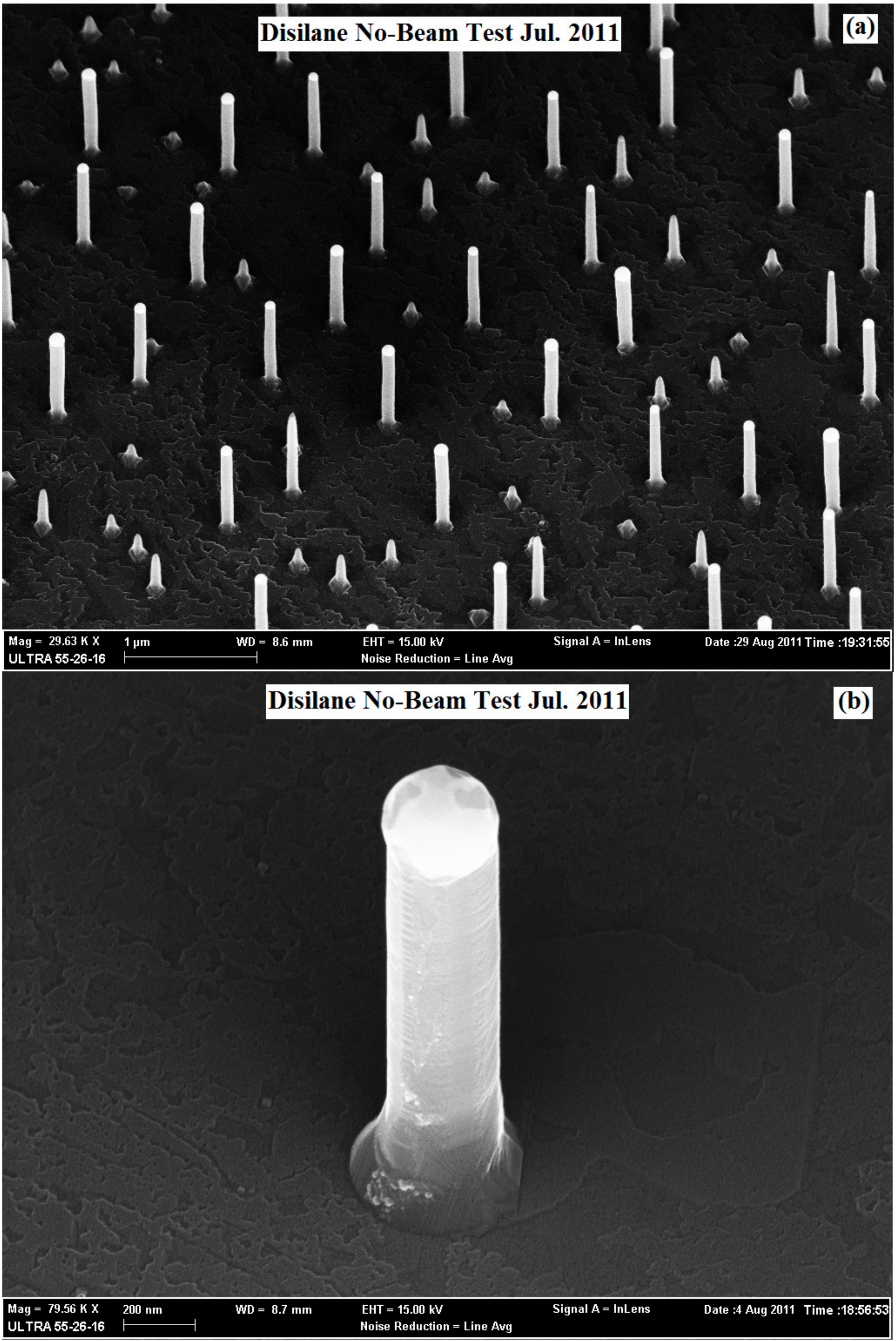

Fig 2. (a) : Perspective View of Si NWs on Si(111) substrate with disilane during one No-Beam Test in Jul. 2011. Most NWs follow the (111) growth direction while kinking has been generally avoided by optimizing the growth condition. Some NWs ceased to grow during the process because of catalyst out-diffusion which is characteristic of growth under ultra clean (or oxygen free) conditions (UHV in our case).

Fig 2. (b) : Perspective View of a Si NW grown with disilane during one No-Beam Test in Jul. 2011.

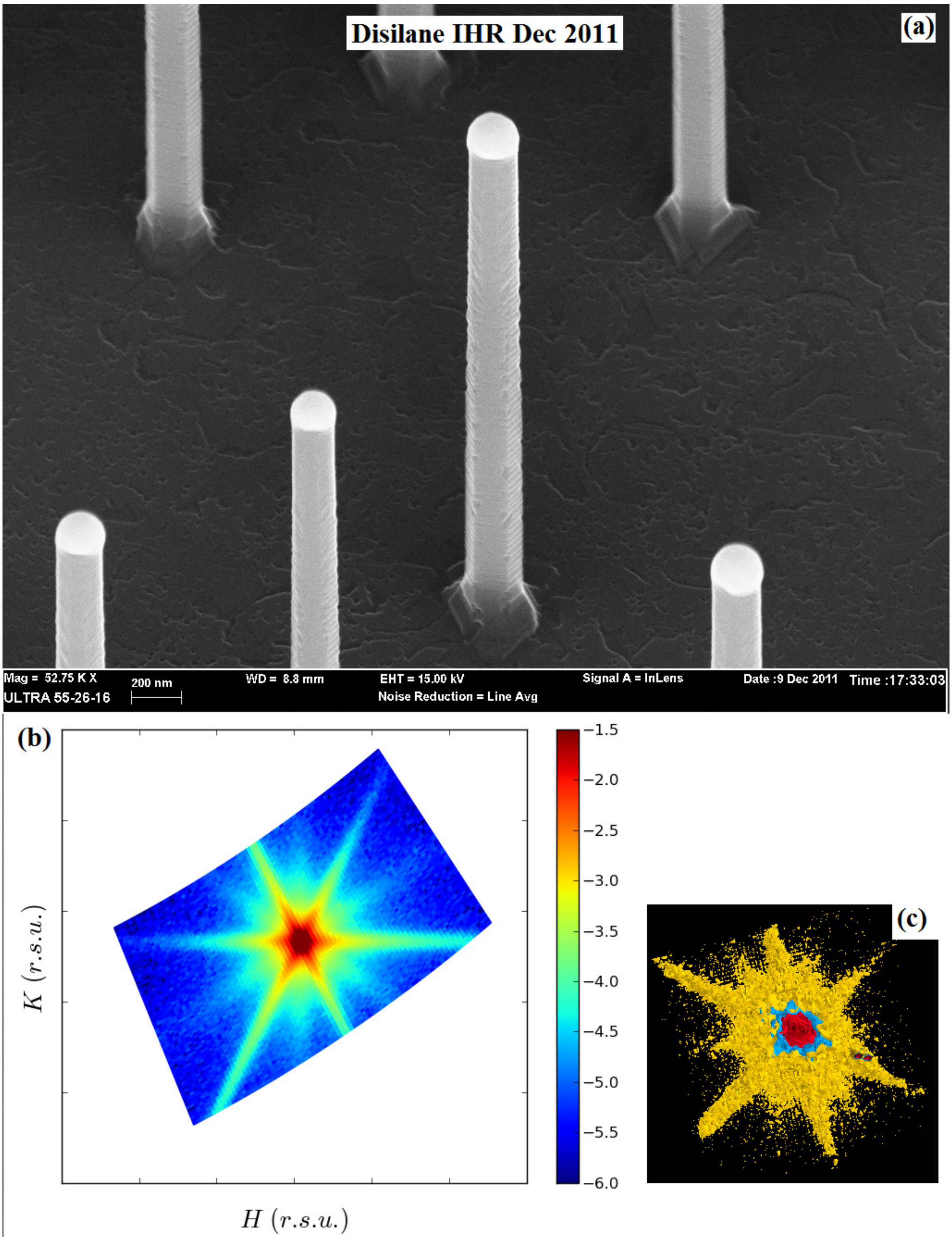

Fig 3 (a) : Perspective view of the Si NWs grown on Si(111) substrates after 2H30 injection of disilane at 0.9sccm

Fig 3 (b) : Reciprocal Space Map around the (111) reflection reveals distinct features of sidewall sawtooth faceting

Fig 3 (c) : A raw 3D plot of the data collected by MAXIPIX Area detector during the above mapping, precise orientation of the facets could then be extracted