ESRF	Experiment title: In situ GIXD and GISAXS investigations of growing self-organized Ge nanowires on patterned Si(111) via the Vapor-Solid-Solid process, using UHV-Chemical Vapour Deposition	**Experiment number**: SI-2572
Beamline: BM32	**Date of experiment**: from: 13/02/2013 to: 19/02/2013	**Date of report**: 27/02/2013
Shifts: 18	**Local contact(s)**: Gilles RENAUD	*Received at ESRF:*

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Objective

The original objective was to conclude on the parameter dependences of different phenomena observed during VSS (Vapor-Solid-Solid) growth of Ge nanowires (NWs) using patterned Si(111) substrates.

We didn’t follow the original objective as we have recently (Dec. 2012 – Jan. 2013) developed at BM32 (ESRF) the capability of growing SiGe radial (a.k.a. core-shell) and axial NW heterostructures (fig. 1). Compared to traditional heterostructure formed by growing epitaxial films, NW heterostructure is much more appealing to modern electronics and optoelectronics applications as it boasts not only its inherited properties of being an one-dimensional nanostructures, but also its tunable stacking period as the critical thickness (beyond which dislocations/structural change become imperative for stress relaxation) is theoretically unlimited.

The fundamental picture of the growth concerning group IV semiconductors is missing. To our knowledge, *in situ* observation with electron microscopy has only been reported on the so called substrate-NW heterostructures (i.e. growing NWs of one material directly on the substrate of another mateiral), and yet on neither radial nor axial NW heterostructures.

Difficulties encountered:

We have encountered a 2-day long breakdown of the beamline, which shortened our beamtime to only 12 shifts. Furthermore, since this was the first time for us to study *in situ* with X-ray these types of growth and since we had just enough time to measure one sample per growth type, the *in situ* measurements were (relatively) poorly designed as we had no idea where in the reciprocal space would the strained signal first emerge (i.e. will the subsequent grown material be fully relaxed, fully strained or in between?).

Despite all these difficulties, we were able to acquire fascinating results, which could shed light on the understanding of the evolution of stress relaxation / intermixing during growth, and would certainly serve as the guiding light for our future experiments.

NW Heterostructure Growth Current State:

We shall begin with the current state of the NW heterostructure growth at BM32.

We have previously reported *in situ* measurements on the growth of state-of-the-art Si (Ge respectively) NWs on Si(111) (Ge(111) respectively) substrates. The Si NWs are mostly (111) oriented and have dodecagon sawtooth faceted sidewall (fig.1, case 1). The Ge NWs also follow the (111) growth direction but are more tapered (fig.1 case 2).

By adjusting the growth conditions, we were able to synthesize three types of heterostructures:

1. Pure radial NW heterostructure with a Si core and a Ge shell. (fig.1 case 3)

2. Axial NW heterostructure consisting of a Si lower body and a Ge upper body with inevitable but small quantity ($v_{axial} > v_{radial}$) of radial growth. (fig.1 case 4).

3. Axial NW heterostructure consisting of a Ge lower body and a Si upper body with inevitable but negligible ($v_{axial} >> v_{radial}$) radial growth. (fig.1 case 5)

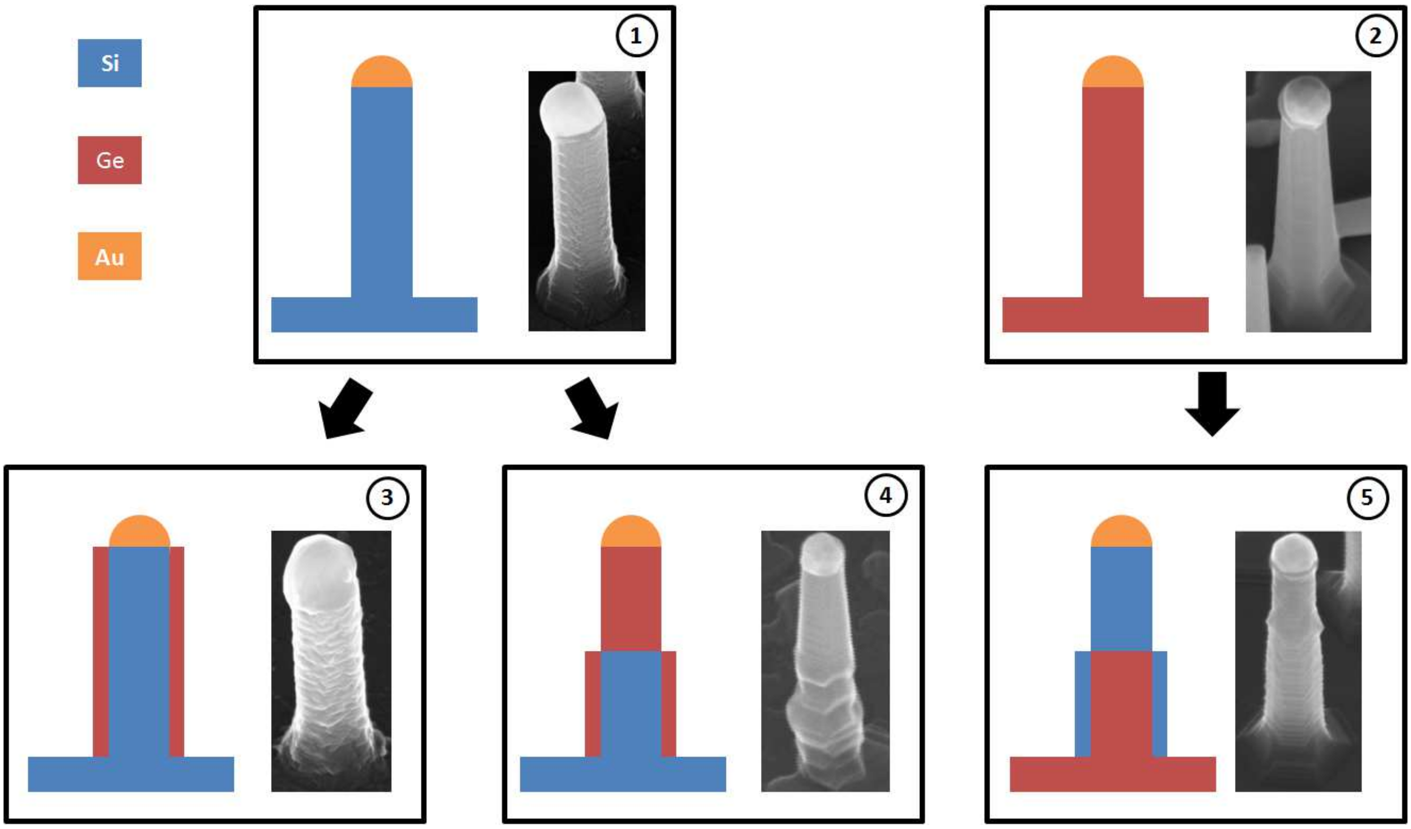

Figure 1 : Current State of NW heterostructure Growth at BM32. (Case 1) Previously reported growth of Si NW on Si substrates. (Case 2) Previously reported growth of Ge NWs on Ge substrates. (Case 3) Pure radial NW heterostructure with a Si core and a Ge shell grown on Si substrates. The Ge shell presents only irregular sidewall facets. (Case 4) Axial NW heterostructure consisting of a Si lower body and a Ge upper body grown on Si substrates. The grown Ge part is tapered and faceted, while the original Si facets are "killed" during the radial overgrowth. (Case 5) Axial NW heterostructure - Ge lower body and Si upper body- grown on Ge substrates. The grown Si part is nicely faceted while the original Ge facets are well preserved thanks to the negligible radial growth rate.

Experimental Results:

As the experiment was terminated only 2 weeks before the submission of this report. Only preliminary and qualitative results are presented here.

Case 3: For the growth of pure radial NW heterostructure with a Si core and a Ge shell, in plane radial scans (fig.2a) reveal that only (partially) strained Ge was grown in the beginning, and that even after 2h of exposure to digermane (the amount is equivalent to 600nm of axial growth, the radial growth thickness should be much smaller, the exact value of which awaits further TEM investigations), strained Ge signal still dwarfs its fully relaxed counterpart. Out-of-plane measurements (fig.2b) also show a partially relaxed Ge signal, which is much expected for this specific growth type under investigation. Before Ge overgrowth, the Si NWs were nicely faceted as shown by the strong dodecagon streaks observed by reciprocal space mapping (RSM) around a Si Bragg peak (fig. 2c). After Ge overgrowth, the faceting signal disappeared. However, this does not necessarily mean that the initial facets are destroyed during the process. Indeed, if from fig.1, we can infer that the Ge shell has irregular facets, given the low growth temperature (~300°C), intermixing between Si and Ge should be rather limited. In other words, the Si facets might as well be perfectly preserved, which is possibly the reason why sawtooth faceting signals are still observed with GISAXS measurements (fig.2d) after Ge overgrowth. Certainly, if the disappearance of the faceting signals with RSM (fig. 2c) is simply due to a large Ge Thermal Diffuse Scattering (TDS) nearby, we should be able to "uncover" the buried streaks with anomalous measurements near the Ge absorption edge. Unfortunately, quite significant amounts of Ge are deposited so that even with the aforementioned approach, the Ge TDS is still way higher than the original Si streaks. Improvements will be implemented in future experiments.

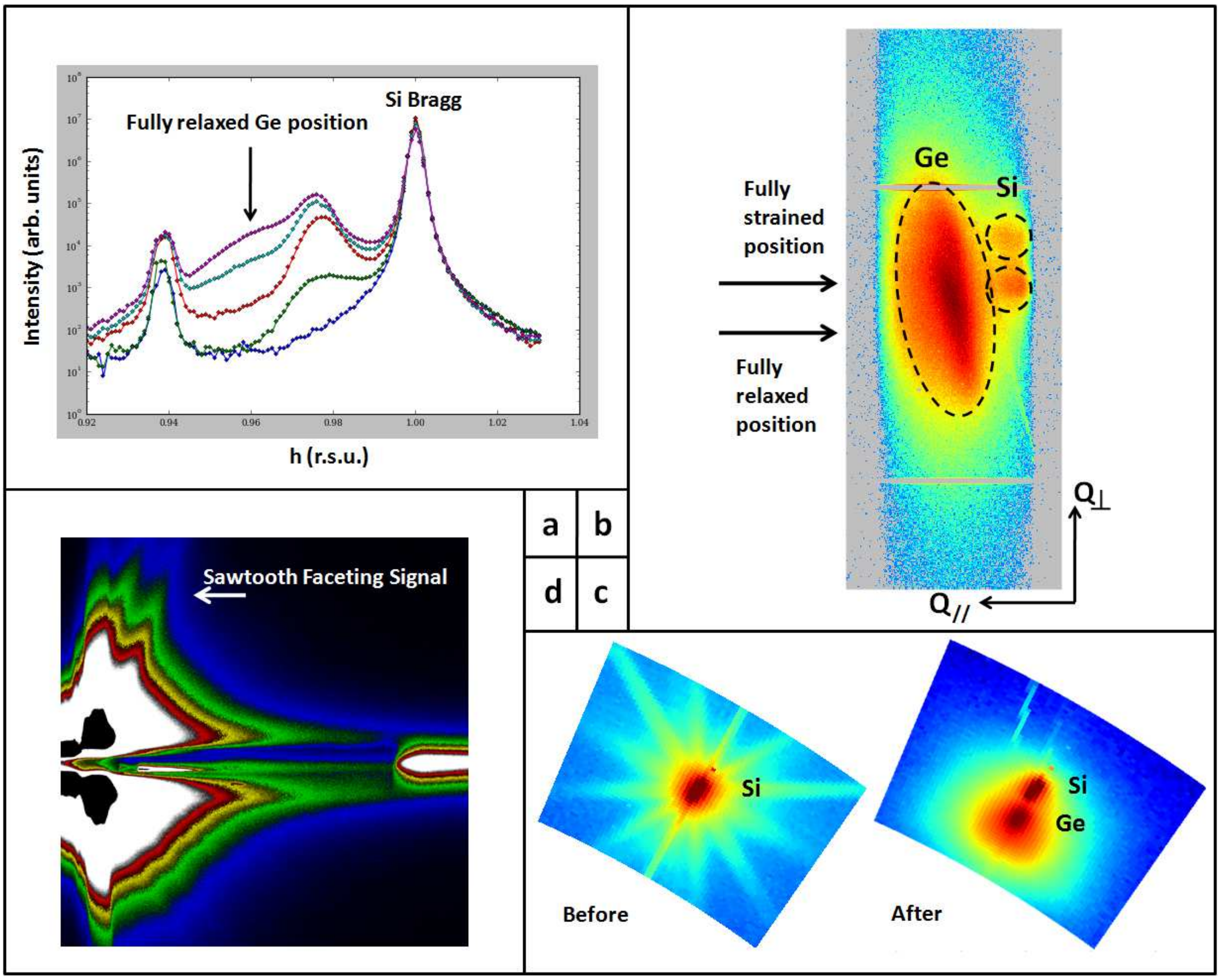

Figure 2 : (a) In plane radial scan from the fully relaxed Ge (Bragg) position to the Si bulk/NW Bragg position. (b) Out-of-plane snapshot with the 2D detector, the detector was centered on the partially strained Ge signal. The doubling of the Si peak can be explained by the DWBA while its weak intensity is the result of mis-alignment (i.e. the detector is not centered on the Si peak) (c) Reciprocal Space Mapping around a Si peak before and after Ge overgrowth. (d) GISAXS measurements after Ge overgrowth.

Case 4:

For the growth of Axial NW heterostructures consisting of a Si lower body and a Ge upper body, contrary to the previous case, a fully relaxed Ge signal (fig.3a) was observed from the beginning. By the end of the growth, the fully relaxed signal is of several orders of magnitudes larger than its partially relaxed counterpart, which is coherent with the picture of a large axial to radial growth ratio. The result of RSM (fig.3b) is also somewhat different from that of the previous case, but conclusions can be drawn only after further analysis of the 2D detector data acquired during the RSM. Out-of-plane measurements (fig. 3c) also indicate that the fully relaxed component is the dominant signal observed by diffraction.

We were able to achieve remarkably narrow NW size distribution on this sample which is evident from the modulation observed on GISAXS measurements (fig. 3d). After Ge overgrowth, the Si faceting signal can still be observed alongside the new Ge ones.

Case 5:

For the growth of Axial NW heterostructures consisting of a Ge lower body and a Si upper body, similarly to the previous case, a fully relaxed signal (this time, Si) was observed from the beginning and remained the dominating signal during the entire growth process for both the in-plane (fig.4a) and out-of-plane (fig.4b) measurements. GISAXS measurements (fig.4c) saw retraction of the characteristic Ge facet signal and enhancement of the sawtooth facet signal during Si overgrowth. Beautiful faceting signal from both elements have been observed during the RSM (fig. 4d). More quantitative results await further analysis. Meanwhile more dedicated experiments could be designed thanks to the knowledge we acquired during this measurement.

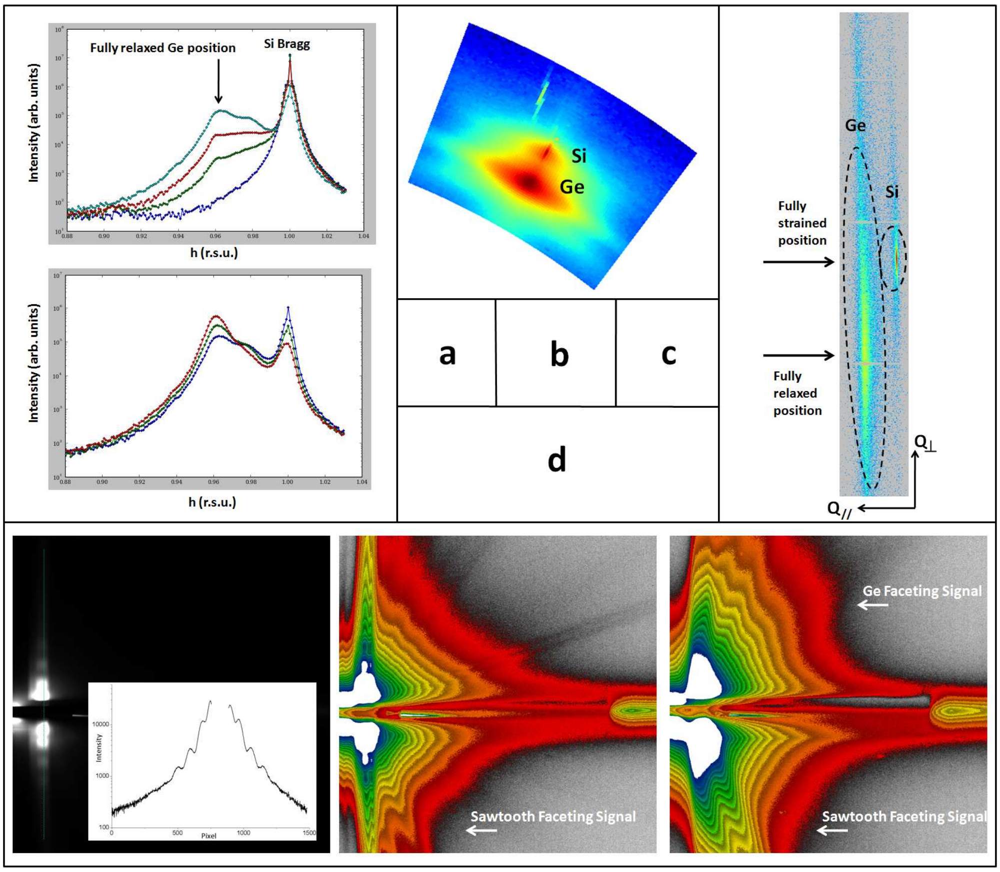

Figure 3 : (a) In plane radial scan from the fully relaxed Ge (Bragg) position to the Si bulk/NW Bragg position. (b) Reciprocal Space Mapping around a Si peak after Ge overgrowth. (c) Out-of-plane snapshot with the 2D detector, the detector was centered on the fully relaxed Ge signal. (d) left, size modulation observed after growth of the Si NWs, inset, linecut profile along the modulated direction, right, GISAXS measurements before and after Ge overgrowth.

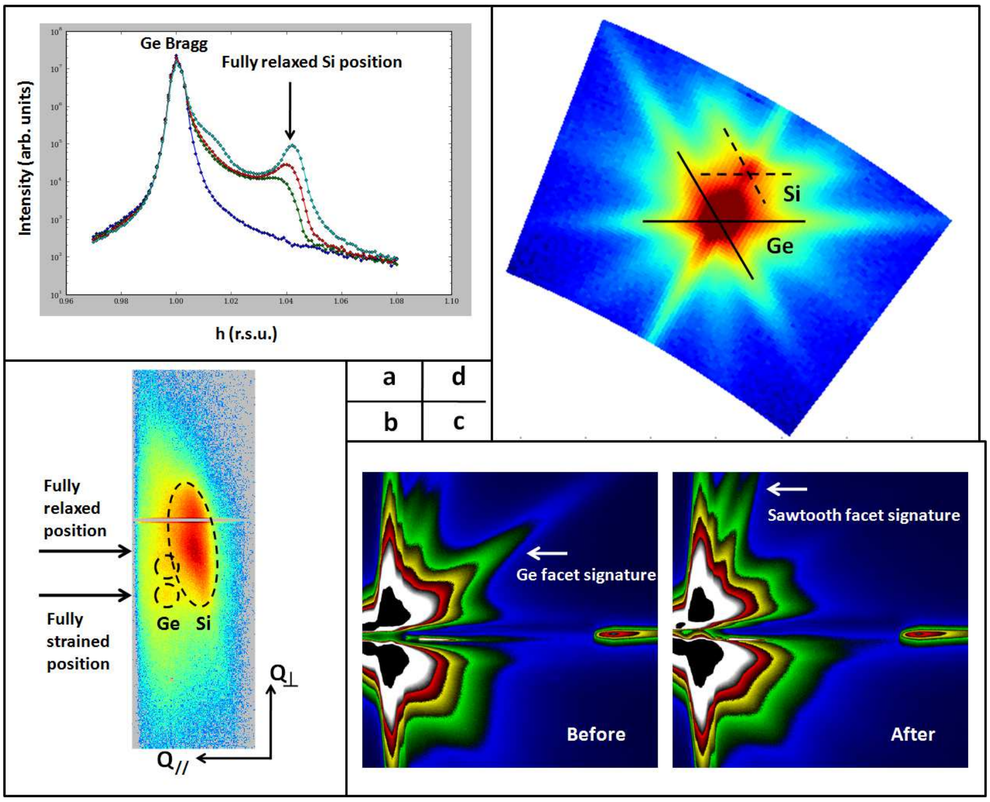

Figure 4 : (a) In plane radial scan from the Ge bulk/NW Bragg position to the fully relaxed Si (Bragg) position. (b) Out-of-plane snapshot with the 2D detector, the detector was centered on the fully relaxed Si signal. The doubling of the Ge peak can be explained by the DWBA while its weak intensity is the result of mis-alignment (i.e. the detector is not centered on the Ge peak) (c) GISAXS measurements before and after Si overgrowth. (d) Reciprocal Space Mapping around a Ge peak after Si overgrowth.