ESRF	**Experiment title:** ***In-situ*** **X-ray diffraction studies of the homo-epitaxial growing modes of Ge and Si by Chemical Vapour Deposition (CVD) on Ge(111) and Si(111)**	**Experiment number:** 32-3-699
Beamline: BM32	**Date of experiment:** from: 25/01/2011 to: 31/01/2011	**Date of report:** 10/03/2011
Shifts: 21	**Local contact(s): Gilles Renaud**	*Received at ESRF:*

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Report :

Nanoscale one-dimensional materials have been stimulating great interest thanks to their unique mechanical[1], thermoelectrical[2], and optical properties relative to their bulk counterparts. NWs are usually grown by chemical vapour deposition (CVD) following the vapour–liquid–solid (VLS) mechanism, first proposed in 1964 for larger (micrometer-scale) 'whiskers'[3], in which NWs spring up from catalyst-substrate eutectic droplets (AuSi - AuGe) under flux of Si / Ge provided by the decomposition of precursor gases. Heterostructures such as Si/Ge NWs are grown by changing the source gas [4]. A catalyst that is in the solid rather than liquid state can also be used, leading to a vapor–solid–solid (VSS) growth mode.

Many aspects of the VLS growth are still not well understood because phenomenological considerations are extracted mainly by *ex situ* investigations, *i. e.* once the VLS process stopped and at RT. Experimental methods that follow growth dynamics and extract quantitative parameters remain a challenge requiring instruments of unique performance. A deep understanding of the crystallographic characteristics and morphology evolution as a function of the growing parameters is an essential step to control the NWs formation. X-ray scattering investigation methods, GISAXS and GIXD, are applicable under gas-atmospheres and can non-destructively probe the structural properties of nanostructures during growth and the evolution of surfaces, providing a very valuable information as they average over millions of nanostructures. GISAXS grants access in a statistical manner to the morphological information (size, spacing, and faceting) [5-7] and GIXD provides in addition an unparalleled view on the structural properties such as stress/strain, atomic composition, and defects [7-9].

All these considerations motivated few years ago the launch of a priority program of our laboratory, supported by the Nanoscience Foundation, to develop UHV-CVD capabilities on the existing UHV-INS chamber (In situ Nanostructure growth on Surfaces - operated by CEA and CNRS), with associated Post-Doc and PhD funding. From the end of August 2010, the INS instrument is equipped with UHV-CVD gas injection system for hydride semiconductor gas precursors up to a working pressure 5×10^{-4} mbar. The flexibility of this growth system allows working at base pressures of 10^{-11}-10^{-10} mbar for ultra clean surface preparations, MBE growth of the metal catalyst and a quick change to UHV-CVD conditions avoiding surface contaminations.

Figure 1 gives a graphical overview of the installed gas injection system. Ultra pure gas precursors (Silane (SiH_4) as Silicon source, pyrophoric installed

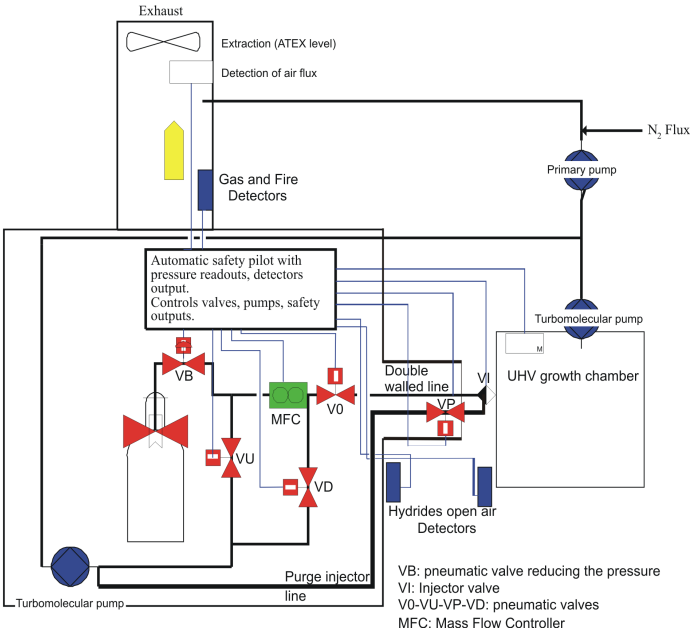

Figure 1: Drawing of the gas injection system, representing one gas injection line.

on August 31st 2010; Disilane (Si_2H_6) as Silicon source, pyrophoric installed on January 18th 2011 and Germane (GeH_4) as Germanium source, highly toxic and pyrophoric installed on January 21st 2011) are injected at very low pressure and flow rate (down to 0.02 sccm), causing a jet of molecules that is well oriented by a quartz guiding cone (final inner diameter: 0.5 mm, length 444 mm) to the sample surface, provoking a local pressure increase without strongly affecting the average pressure in the chamber. In this way, additional analysis tools such as RHEED and Auger electron spectrometry can be used to monitor the CVD process.

Due to the dangerousness of the employed gases, this installation, designed according to the ESRF safety regulations, is equipped of three hydrides detectors, two for ambience and one for the exhaust: a simultaneous alarm of 0.3 ppm of the two hydride open air detectors will cause the evacuation of the whole ESRF experimental hall. Whatever operation with the gas distribution system must be previously approved by the ESRF safety group and at least two authorized operators from the beam-line staff must be present at all time during the experiments. All pressure and flow readouts, as well as gas and heat detectors are connected to a central automated controller that automatically regulates the closing/opening of the valves, the pumps and the exhaust, reducing the human intervention to the operation of the gas mass flow controller.

The extension of the existing UHV-MBE system to CVD compatibility offers a promising tool of a unique flexibility for sample growth, which can respond to fundamental questions concerning structural parameters still under discussion in theoretical and applied research.

Preliminary studies

The gas sources of Silane and Disilane have been investigated by exploring the Si – Au phase diagram around the eutectic temperature.

In the first case Au was deposited by MBE on a sapphire substrate (Al_2O_3) in order to prevent the substrate to supply Silicon to the Au droplet. At a constant temperature a long exposition to Silane constant flux of 0.6 sccm allowed to obtain the complete disappearing of the crystalline signal of 50 Å of Au after about 6 hours (figure 2).

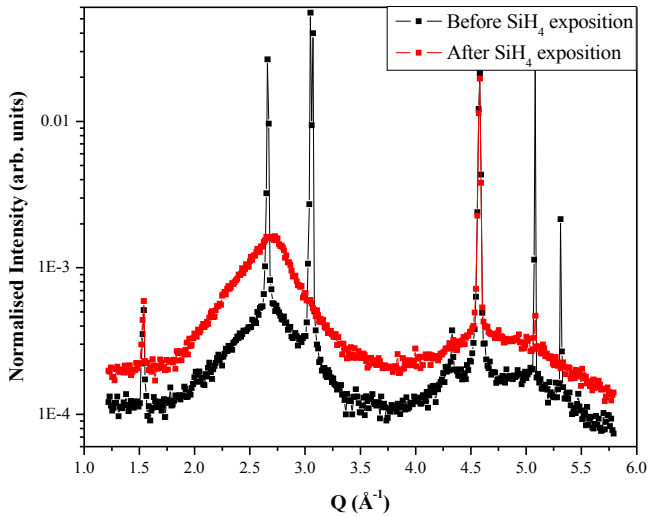

Figure 2: Au deposited on sapphire: the Au droplet melt because of exposition to SiH_4.

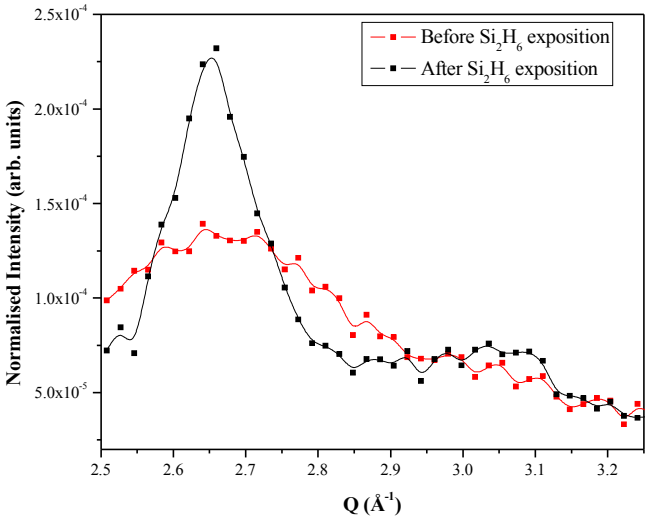

Figure 3: Au deposited on sapphire: the Au droplet melt because of exposition to Si_2H_6.

For comparison, in figure 3 is reported the fusion of 16 Å of MBE deposited Gold on SiO_2 substrate at 370°C as a consequence of 120 s of exposition to the Si_2H_6 source at 0.03 sccm.

This experiment clearly evidence the much higher reactivity of Disilane if compared with Silane. Moreover from by successive rapid scan around the (220) Au signal is possible to monitor the state change of the Au nanoclusters even in a fast regime reaction as with Disilane, usually applied to investigate NW growth at pressure in the order of 10^{-5} mbar.

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