	<b>Experiment title:</b> Solid-liquid eutectic transition in catalysts for the growth of semiconductor nanowires	<b>Experiment number:</b> SI-1905
	<b>Beamline:</b> BM 32	<b>Date of experiment:</b> from: 15/04/2009 to:21/04/2009
	<b>Shifts:</b> 18	<b>Local contact(s):</b> Tobias U. Schüllli
<b>Date of report:</b>  <i>Received at ESRF:</i>		
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## Report:

Semiconductor (SM) nanowires (NWs) have been identified as important components for future electronic and sensor nanodevices. The way they are produced is known as the vapour-liquid-solid (VLS) mechanism [1] in which a low temperature semiconductor/metal eutectic is used to enable their nucleation and their growth. The heart of this mechanism is the liquid state of such eutectics conferring the catalytic properties even at low temperature: the vapor phase (SM) is incorporated in the liquid phase (SM+metal) and transported to the interface with the substrate (SM) to crystallise and grow. Even if such catalytic mechanisms are highly investigated, many fundamental questions in crystal-growth behaviour remain unanswered or/and controversial such as existence of a liquid catalyst below the eutectic temperature ( $T_e$ ) [2] or even growth via a vapour-solid-solid (VSS) mechanism [3-4]. As the state of the catalyst is of prime importance to control growth parameters (kinetic, orientation, morphology...) on which will later depend NMs properties, we need to investigate in details this mechanism and depict at the atomistic scale this intricate solid-liquid-solid transition.

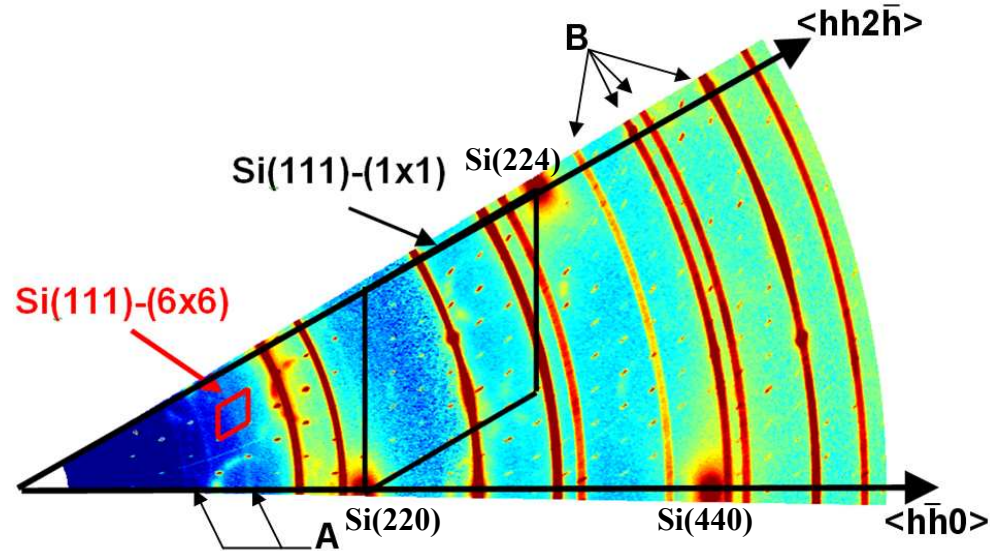
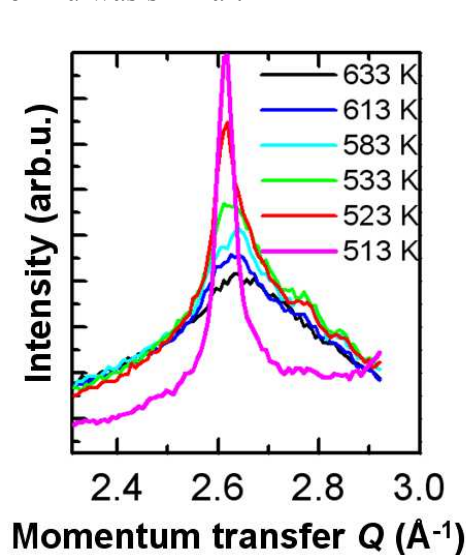
For that sake, we intensely investigated deposits of Au on Si substrates which is one of the most used metal-semiconductor eutectic ( $\text{Au}_{81}\text{Si}_{19}$ ) catalyst for the VLS growth of Si NWs. Special attention has been paid on the supercooling behaviour of this alloy and its potential correlation with the structure of the Si substrates. This requires a method to analyze *in situ* the local atomic structure as a function of temperature, in both liquid and solid states. We employed *in situ* Grazing Incidence X-ray Scattering (GIXS) in ultra-high vacuum (UHV) as a method of choice to study solid-liquid transitions on surfaces and nanostructures [5,6]. The experiment consisted in analyzing for different temperatures the atomic structure of the silicon surface, that of the liquid/solid Au(Si) islands, and that of the AuSi/Si(111) (or AuSi/Si(001)) interface and we are now able to depict the evolution of this system during gold deposit, heating and cooling steps.

Seven atomic layers of gold were deposited at room temperature (RT), forming a 1.6 nm thick film on the Si(111) which was previously deoxidized to form a well-defined Si(111)-(7×7) reconstruction. At low temperature, the Au film crystalline quality was found to be low but showed a clear preferential epitaxy with identical directions of the two cubic lattices:  $[100]\text{Au}(111) \parallel [100]\text{Si}(111)$ . When heating up to 623 K (still below the eutectic temperature  $T_e=636$  K) the Au film de-wets to form crystalline islands with a preferential in-plane epitaxy rotated by 19.2° with respect to the aligned epitaxy (i.e.  $[100]\text{Au}(111) \parallel [201]\text{Si}(111)$ ). *In situ* X-ray peak width analysis, *ex situ* High Resolution Secondary Electron

Microscopy (HR-SEM) and *ex situ* Atomic Force Microscopy (AFM) were performed and indicated that islands are 150 nm wide and 25 nm high on average.

Increasing the temperature, the islands are observed to melt exactly at the bulk eutectic temperature  $T_e$  suggesting that the Si substrate provided atoms to reach the adequate  $\text{Au}_{81}\text{Si}_{19}$  eutectic composition.

For annealing temperatures higher than 40K above  $T_e$  (673 K) and subsequent cooling below the eutectic point, more diffraction peaks appear, corresponding to a well defined Si(111)-(6×6) superstructure [7] but no Bragg peaks from solid Au re-appear: the islands stay liquid. Cooling down further reveals that solidification happens only at  $T_s=513$  K (Figure 1) which means that in this case the system is undercooled by more than 120 K, which is twice the amount of supercooling previously reported in this system [8]. After solidification, the (6×6) superstructure remains and Debye-Scherrer powder diffraction rings attributed to the fcc structure of Au islands with polycrystalline distribution can be observed (Figure 2 (B)). It has to be noticed here that this phase transition is found to be fully reproducible: when the temperature is cycled down and up, the above described solid-liquid-solid transition's behaviour remains: melting at  $T_e$  upon heating and solidification at  $T_s=T_e-120\text{K}$  upon cooling. Several samples were investigated with the procedure described above, all showing the same degree of supercooling during cyclic melting and solidification. In addition to these observations, powder diffraction rings very closed to the origin can be seen on Figure 2 (A), located exactly at the positions expected for the 2D Au-Si crystalline monolayers reported to form on the surface of the liquid eutectic by Shpyrko et al. [9]. When heating the sample just above  $T_e$ , which only yields a precursory  $(\sqrt{3}\times\sqrt{3})R30^\circ$  reconstruction, the measured value of undercooling is significantly smaller:  $\Delta T=70\text{K}$ . Proceeding alike on a Si(001) surface, on which no reconstruction coexists with the liquid, only yields  $\Delta T=60\text{K}$ . In all cases, peaks of the 2D AuSi surface crystallites were present and the deposited amount of Au was similar.



**Figure 1:** Evolution of the first maximum of the liquid. The initially very broad intensity distribution narrows progressively approaching the solidification temperature, below which it collapses to give rise to the Au(111) Bragg peak structure factor in the supercooling regime.

**Figure 2:** Reciprocal space map after unmixing and solidification of the supercooled liquid. Blue color corresponds to low intensities, and red to high intensities, the yellow one being intermediate. (A): powder diffraction rings from 2D Au-Si crystalline structures. (B): Diffraction rings from polycrystalline Au. The reciprocal lattice units of the Si(111) surface and of its (6×6) reconstruction are indicated.

## References:

- [1] R. S. Wagner, W. C. Ellis, Appl. Phys. Lett. **4**, 89–90 (1964).
- [2] J.C. Harmand et al, Appl. Phys. Lett. **87**, 203101 (2005).
- [3] S. Kodambaka, J. Tersoff, M. C. Reuter, F. M. Ross, Science **316**, 729 (2007).
- [4] E. Sutter, P. Sutter, Nano Letters **8**, **411** (2008).
- [5] H. Reichert, O. Klein, H. Dosch, M. Denk, V. Honkimaki, T. Lippmann, G. Reiter, Nature **408**, 839 (2000).
- [6] A. L. Pinardi, S. J. Leake, R. Felici, I. K. Robinson, Phys. Rev. B **79**, 045416 (2009).
- [7] D. Grozea, E. Landree, L.D. Marks, R. Feidenhans'l, M. Nielsen, R.L. Johnson, Surf. Sci. **418**, 1 (1998).
- [8] H. S. Chen, D. Turnbull, J. Appl. Phys. **38**, 3646 (1967).
- [9] O. G. Shpyrko et al., Science **313**, 77 (2006).

*Further results, interpretations and conclusion are described in the experimental report n° 32-03-687.*