ESRF	**Experiment title:** Solid-liquid transition of Gold nanocatalysts for the growth of semiconductor nanowires	**Experiment number:** SI-1650
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Report:

The rapidly developing field of vertical Semiconductor nanowire growth makes use of metal catalysts combined with chemical vapour deposition. It is essentially the formation of low temperature eutectics between semiconductors and metal that drives the nucleation and growth of these structures. For Silicon nanowires, previously deposited metallic nanoparticles, Au as the most commonly used, serve as catalysts and offer unique growth conditions and restrictions due to their capacity of transporting Si even at low temperatures in the eutectic liquid $Au_{80}Si_{20}$.

We have studied the melting behavior and the liquid state of these AuSi droplets on a Si(111) surface by Grazing Incidence X-ray Scattering on the BM32 beamline. Au was deposited at room temperature on a 7x7 reconstructed Si(111) surface. The epitaxy shows frustration between various in-plane orientations, with a preference for (111)Au[110]||(111)Si[110]; *i.e.* with identical directions of the two cubic lattices. Upon annealing, the film roughens and forms islands that undergo a rotation of the in-plane epitaxy by 19.2°.

At the eutectic temperature of 636 K, these islands form liquid eutectic droplets, all Bragg peaks from fcc-Au dissappear in reciprocal space. Instead the liquid structure factor of the Au-Si melt can be observed. L-scans across the Au(113) reflection (Fig. 1b) allow to follow the formation of islands as well as the melting.

While cooling down, we observed significant supercooling of the eutectic melt, depending on thermal history: Cooling down directly after reaching the eutectic temperature T_E, led to a solidification around 573 K. After an annealing step of up to 60 K above T_E, the liquid was found to be stable down to 523 K, corresponding to a supercooling of 110 K.

Mapping out reciprocal space in the sample plane permitted to shed light on the principal differences, obtained by different thermal treatments: In the case of low temperature annealing the Si-Au interface corresponds to a $(\sqrt{3}\times\sqrt{3})R30°$ superstructure as published in [1]. For higher annealing, a 6×6 superstructure is formed. This surface seems to play an important role in the stabilization of the liquid alloy. We have analyzed this structure, measuring and integrating 983 Bragg peaks (corresponding to 234 non-equivalent reflections) and using the ROD software. The results are close to a structure published by Grozea at al [1]. We find Au atoms in pentagonal arrangement at the surface, with an interatomic distance close to what simulations obtain for an icosahedral Au13 or Au12Si molecule. The role of icosahedral complexes for the stability of liquids is discussed since the early works of Frank et al. , our x-ray measurements are the first observation of the "epitaxial" stabilization of such structures and their influence on the supercooling of liquids.

Our results show that it is of crucial importance to draw an atomistic picture of eutectic liquids in order to understand their catalytic function in semiconductor growth as well as their outstanding transport properties for Si atoms even at relatively low temperatures. Without doubt, recent observations by other groups in similar systems, can by attributed to such phenomena [2]. It shows the importance of in-situ x-ray diffraction in the field of catalytic nanostructure growth.

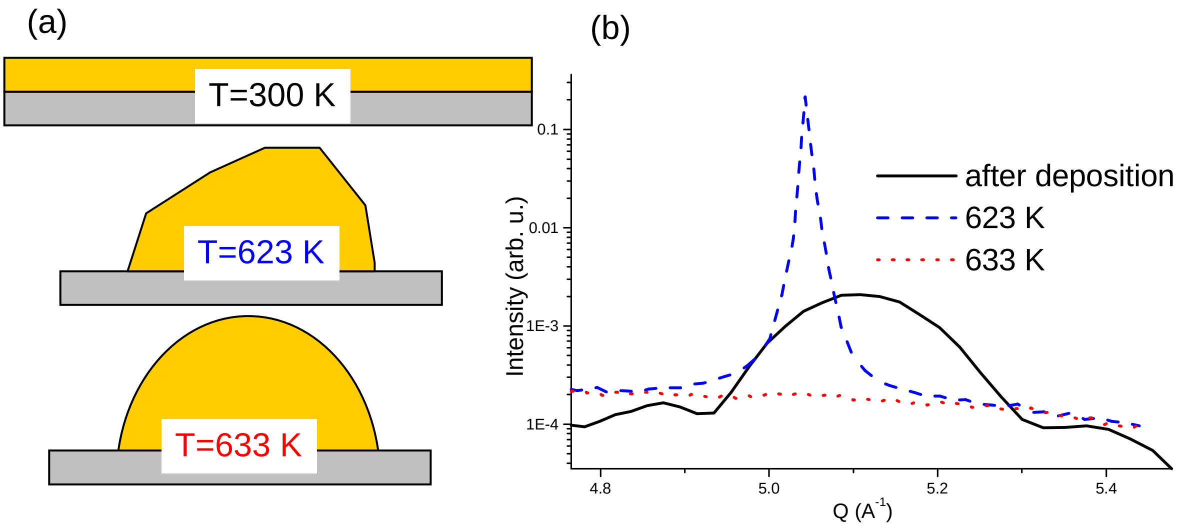

Fig.1Growth of eutectic catalysts, here for the system Au-Si. A 1.5 nm thin Au film is deposited in (a), the black curve in (b) shows its size oscillations corresponding to its thickness. Annealing at 623 K leads to islands (dashed blue curve in (b)). At 633 K the island transforms into a $Au_{82}Si_{18}$ liquid droplet.

References

[1] D. Grozea, E. Landree, L.D. Marks, R. Feidenhans'l, M. Nielsen, R.L. Johnson, Surf. Sci. 418, 32 (1998).
[2] S. Kodambaka J. Tersoff, M. C. Reuter, F. M. Ross Science **316,** 5825 (2007).