



	<b>Experiment title:</b> Solid-liquid eutectic transition in Au-Si and Au-Ge catalysts for the growth of semiconductor nanowires.	<b>Experiment number:</b> 32-03-687
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**Report:** *Introduction, experimental details and previous results are described in the experimental report SI-1905*

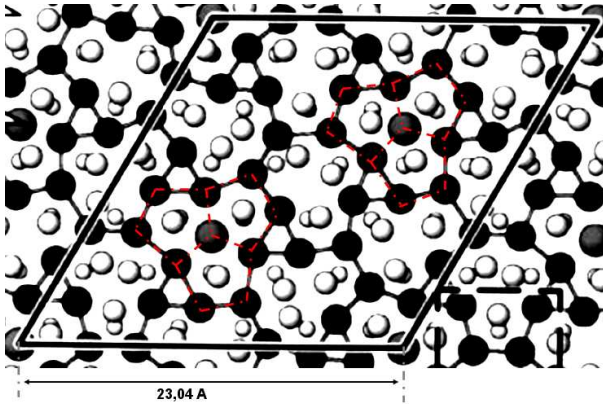
From experimental results (experimental report SI-1905) we observed that supercooling is always present in AuSi eutectic liquid islands on Si substrates, whatever the solid/liquid interface structure. The highest supercooling value previously reported in this system was  $\Delta T = 60$  K [1], for droplets included in fused silica, comparable with our observations on Si(001) or Si(111) ( $\sqrt{3} \times \sqrt{3}$ )R30° surfaces. Thus, the increase of this supercooling to  $\Delta T = 120$  K by a change of the surface reconstruction (i.e. the Au-induced Si(111)-(6×6) reconstruction) can not be explained by classical arguments like the absence of seeds for Au crystallization. This suggests that the specific atomic structure at the surface/interface favors peculiar ordering effects in the adjacent liquid layers, which inhibit the phase separation classically observed in the solid bulk system. Systems with important layering as Al droplets on Al<sub>2</sub>O<sub>3</sub> have shown significant supercooling [2,3] and the influence of a solid-liquid interface on the fivefold order inside the liquid has been discussed [4,5]. This underlines the importance of investigating the structure, both parallel and perpendicular to the interface, of these interfacial liquid layers.

In the present system, we have thus to spend particular attention to the structure of the Au-induced Si(111)-(6×6) reconstruction. To do so, 983 in-plane Bragg reflections from this superstructure were quantitatively measured and analyzed using the ROD software for surface structure analysis. The final model ( $\chi^2 = 2.8$  with only the Au atoms taken into account) is remarkably close to the model proposed in [6] for the (6×6) surface reconstruction. The real space structure in Fig. 1 consists of several trimers of deformed pentagons surrounding the three-fold axes. The nearest-neighbor distance in these pentagons is 2.86 Å at RT, denser than for gold in its bulk fcc structure (2.90 Å at 550 K). On the other hand this nearest-neighbor distance (2.86 Å) is close to the interatomic one (2.84 Å) in icosahedral Au-clusters in the supercooled liquid which has been deduced theoretically by *ab initio* molecular dynamics simulations. On the theoretical side, we also performed common-neighbor analysis [7] for AuSi eutectic, which allows distinguishing between various local structures like fcc, hcp, bcc and icosahedral environments. Our results indicate that the short-range order displays an appreciable proportion (46%) of pairs in local five-fold arrangement in the liquid state (T=700 K); the supercooled regime being characterized by an increased fraction of five-fold atomic ordering (51% at T=600K and 54% at T=500K). Thus, the (6×6) surface structure offers perfect sites to stabilize the five-fold clusters which themselves stabilize the supercooled metal. This is not the case of the intermediate ( $\sqrt{3} \times \sqrt{3}$ )R30° reconstruction which is based on Au trimer units and does not show five-fold order. Two additional observations reveal a clear link between the structure of this reconstruction and that of the liquid. Fig. 2 shows high resolution measurements of the scattered intensity performed along a symmetry direction of the Si(111)-surface, hence crossing its reconstruction peaks. The first and second orders of the liquid structure factor S(Q) both reveal a marked correlation between the appearance of the (6×6) reconstruction

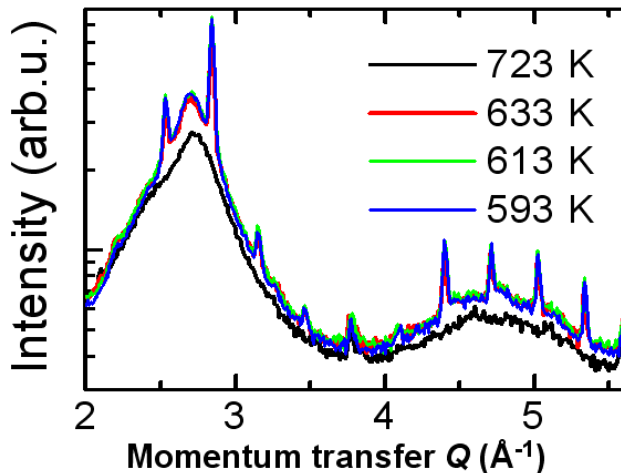
peaks and an increase in intensity in the maxima of  $S(Q)$ . In addition, the radial intensity distribution obtained by integration and convolution of all diffraction peaks measured from the  $(6\times 6)$  reconstruction compares well to the liquids' experimental and theoretical structure factor in Fig. 3, showing evident similarities of the main interatomic distances in the liquid and on the surface. These two results leave no doubt about a correlation between the internal structure of the liquid and that of the  $(6\times 6)$  reconstruction.

To better understand this surface enhanced supercooling one needs to compare the theoretical and experimental structure of the liquid with the atomic arrangement of the  $(6\times 6)$  reconstructed Si(111) surface. The observed interface induced phase stability in liquid AuSi droplets on Si(111) surfaces has significant importance for the understanding of technologically relevant processes as liquid phase epitaxy or the VLS process employed for the growth of semiconductor nanowires. This inertia against solidification of liquid metal-semiconductor phases may be the origin of the exceptional mobility of the semiconductor atoms, possibly also in the supersaturation regime, and hence of the unparalleled capabilities to induce the growth of nanowires even at low temperatures or high speed. The fundamental conclusions are even more far reaching: the much enhanced degree of supercooling of the liquid AuSi on the Si(111)- $(6\times 6)$  as compared to the  $(\sqrt{3}\times\sqrt{3})R30^\circ$  surface structures clearly shows the influence of a dense pentagonal atomic arrangement on the substrate's surface on the metastability of a liquid. The latest measurements let us think that the liquid becomes anisotropic: we found that the scattered intensity is more pronounced in the vicinity of the most intense peaks of the  $(6\times 6)$  reconstruction, assuming also a morphological similarity of the  $(6\times 6)$  structure and the adjacent liquid layers.

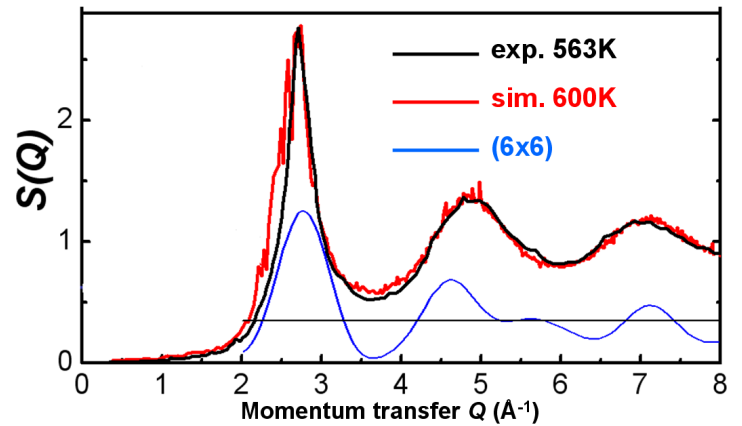
If the induced order presents a strong incompatibility with the crystal structure required for solidification, the solid liquid interface stabilizes the supercooled liquid instead of triggering heterogeneous nucleation. A solid with a particular (pentagonal) local surface structure can thus significantly affect a liquid in contact with it and then control its fluidity, which governs flow, diffusion and chemical reaction rate. The question remains of the generality of this argument, which calls for further investigations in different liquid/solid systems. We began to study the Au-Ge system with similar experimental procedures for comparison but more measurements are needed to depict it as accurately as we have already done for Au-Si.



**Fig. 1:** Unit cell of the complex  $(6\times 6)$  reconstruction (taken from [6]) formed at  $T < 673$  K after annealing temperatures  $T > 673$  K in our experiments. Au atoms are in black and Si ones are in white. Red lines depict the deformed pentagones.



**Fig. 2:** Liquid structure factor (logarithmic scale) along the  $\langle 1-10 \rangle$  crystallographic direction of the Si(111) surface, crossing the peaks of the  $(6\times 6)$  reconstruction. The strong influence of its appearance on the structure of the liquid is visible.



**Fig. 3:** Angular average of the experimental structure factor  $S(Q)$  of liquid  $\text{Au}_{81}\text{Si}_{19}$  at 563 K (black line) together with the theoretical structure factor extracted from Molecular Dynamics simulations at 600 K (red line). The blue line is the radial intensity distribution obtained by angular averaging, integration and convolution of all diffraction peaks measured from the  $(6\times 6)$  reconstruction.

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