1. Supplementary Methods:

**Experimental set-up**
The sample preparation and the x-ray experiments have been carried out at the synchrotron beamline for *in situ* nanostructure growth (BM32) at the ESRF (European Synchrotron Radiation Facility, Grenoble, France) (A description of the ESRF and of the BM32 beamline can be found on [http://www.esrf.eu/UsersAndScience/Experiments/CRG/BM32/Beamline/SUV/index.html](http://www.esrf.eu/UsersAndScience/Experiments/CRG/BM32/Beamline/SUV/index.html)), using an X-ray energy of 11 keV. Grazing incidence X-ray scattering (GIXS) and Surface X-Ray Diffraction (SXRD) were performed with the incident beam fixed at the critical angle (0.163°) for total external reflection, in order to be sensitive to the sample surface. The different Si-samples where outgassed at 500 K for 24 hours in a preparation chamber before being transferred under ultra high vacuum (UHV) into the growth chamber of the beamline. This UHV chamber [R. Baudoing-Savois, G. Renaud, et al., Nucl. Inst. and Meth. In Phys. Res. B. 159, 120 (1999)], which is equipped with a large cylindrical beryllium window for x-ray transparency, was operated at a base pressure of ~$1 \times 10^{-10}$ mbar. In addition to x-ray scattering it is possible to perform reflection high energy electron diffraction (RHEED) measurements, especially useful for sample preparation. The Au deposition has been calibrated using a quartz microbalance, as well as *in situ* x-ray reflectivity.

**Temperature control**
The temperature of the sample surface was measured with two IRCON infrared pyrometers through a special sapphire window. Together they cover a temperature range from 470 to 2200 K. A calibration in the critical temperature regime for the present study has been done at the melting point of ultra pure lead at 600 K, confirming the accuracy based on earlier calibrations using bulk Al$_{80}$Si$_{11}$ eutectic with a melting point of 850 K. The calibration was further confirmed during each experiment since we always found the melting temperature of AuSi eutectic exactly at the expected temperature of 636 K. The temperature accuracy is evaluated to ± 5 K.

**Sample preparation and island formation**
The silicon surface was first deoxidized at 1300 K at a base pressure of $10^{-10}$ mbar. *In situ* RHEED and GIXS/SXRD both showed the formation of a well-defined Si(111)-(7×7) reconstruction, which is characteristic of a clean surface. After cooling down to room temperature, our standard procedure was to deposit 7 monolayers (ML) of Au (1.65 nm) (2, 10 and 30 ML were also done). A preferential (111) orientation, with low crystalline quality and a tendency to aligned epitaxy with the underlying substrate was observed. After melting, supercooling and solidification, HR-SEM images of the islands reveal that some islands show marble-like structures similar to those shown in [N. Ferralis, R. Maboudian, C Carraro, J. Am. Chem. Soc. 130, 2681 (2008)] with bulk Au crystals coexisting with Si crystals, whereas others seem to be of homogeneous nature. Upon heating the sample from room temperature, a Au-induced Si(111)-($\sqrt{3}\times\sqrt{3}$)R30° reconstruction first appears around 400 K. It remains stable while improving in quality upon further heating. If the temperature of 673 K is not exceeded, only this reconstruction is observed. When heating above 673 K, and then cooling down, a Au-induced Si(111)-($6\times6$) reconstruction (which is closely linked to the ($\sqrt{3}\times\sqrt{3}$)R30°) takes over and then remains at all
temperatures below 673 K. The higher the annealing temperature, the better the quality of the final (6×6) structure below 673 K. The phase diagram for the determination of the eutectic point and the supercooling was taken from Okamoto, H. and Massalski, T.B. *Phase Diagrams of binary gold alloys*, ASM International Metals Park, USA (1987).

**Ab initio molecular dynamics simulations:**
For the *ab initio* molecular dynamics simulations, canonical NVT (constant number, volume, temperature) ensembles were used using the Vienna *ab initio* simulation package. Projected augmented plane waves (PAWs) with the Perdew-Wang exchange-correlation potentials have been adopted. The valence state of each element has been previously defined in the provided PAW potentials. The temperature was controlled using a Nose thermostat [D.J Evans, B.L Holian, J. Chem. Phys. 83, 4069 (1985)]. A number of 256 atoms at the desired composition are arranged in a cubic box with periodic boundary composition. Only the Γ-point sampling was considered to sample the supercell Brillouin zone. Three temperatures were considered, namely T=700, 600 and 500K, the two latter being in the supercooled regime. For each temperature the typical durations of the runs are 30 ps with a time step of 3fs. The individual motion of the atoms can be followed by using the mean-square displacement: $<r^2(t)>$.

**Neighbor analysis of the simulated liquid eutectic**
The detailed three-dimensional picture of the local structure was extracted by common-neighbor analysis performed on inherent structures in which atoms are brought to local minima of the potential energy surface by applying a conjugated gradient technique. This method is able to distinguish between various local structures like fcc, hcp, bcc and icosahedral environments, describing them with the nomenclature composed of the four Honeycutt-Andersen indices: the first integer indicates whether or not atoms composing the pair studied are near-neighbors, the second one corresponds to the number of common nearest neighbors shared by the reference pair, the third one is the number of bonds between common nearest neighbors and the last one is used to distinguish structures with the same first three indices but differing from their topology. Considering this, the fcc structure is described by pairs with 1421 indices whereas 1661 and 1441 pairs are typical bcc configurations. Pairs with 1551, 1541, and 1431 indices are five fold symmetry indicators, the 1551 pair describing a perfect fivefold ring and the two last pairs being formed when the perfect fivefold structure is deformed.
Supplementary Figure 1:

Melting and solidification cycles of AuSi islands on different Si surfaces – influence of the interface structure.

**a.** Solid-Liquid transition of the Au-Si islands on a Si(111)-(6×6) reconstructed surface. The numbers 1 to 5 refer to successive experimental steps. The blue (yellow) color indicates solid (liquid) islands. The islands are solid (steps 1,2) below the eutectic point at 636 K where melting sets in. Heating up to 673 K (step 3) prior to cooling leads to a preservation of the liquid phase down to 513 K (step 4), where phase separation and solidification occurs (step 5).

**b.** Solid-Liquid transition of the Au-Si islands on a Si(001) substrate (or a -(√3×√3)R30° reconstructed Si(111) surface). The liquid phase is only preserved down to 560-570 K.

**c.** The pentagonal sites present on the Si(111)-(6×6) reconstructed surface may serve as seeds for icosahedral clusters and induce lateral order stabilisation of the liquid phase inside a AuSi droplet.
Supplementary Figure 2:

a. Sketch of different characterization scans that were performed to follow the evolution of the Au crystal structure during annealing.

b. Scan along the surface normal of the film, crossing the (3 \bar{1} 1)_{Au} Bragg point. Its half width is inversely proportional to the thickness of the regarded crystallites. After deposition at room temperature size oscillations confirm the film thickness to be \( \sim 1.6 \) nm, as calibrated. Upon annealing at 620 K, 20 nm high crystalline Au islands form. At 640 K all crystalline signals disappear.

c. The crystallographic orientation in the plane was studied by rocking scans on the Au(2 2 0) peak, proving that the [1 \bar{1} 0] axis of Au is oriented preferentially along the Si[1 \bar{1} 0] direction. Upon annealing, an in-plane rotation of 19.2° is found, to the preferred epitaxy [1 \bar{1} 0]Au(111)||[2 \bar{3} 1]Si(111), as well as a growth of these crystallites in size. At the eutectic temperature of 636 K, the islands “melt” via the formation of the Au_{81}Si_{19} eutectic.

d. Graphical representation of the different annealing steps followed in (b) and (c). The formation of islands happens prior to melting.
Supplementary Figure 3:

Melting, supercooling and solidification of the AuSi eutectic melt on the Si(111)-(6×6) (a) and Si(001) (b) surfaces.

a, Radial scans through the Au(2 2 0) Bragg peak for Au-islands on a Si(111)-(6×6) surface. The dashed lines describe the intensity during heating: the islands are still solid at 623 K. After melting at $T_m=636$ K and annealing at $T>673$ K, the islands stay liquid down to 513 K, where the crystalline signal reappears. The broad background that reduces significantly for $T<513$ K is the diffuse scattering by the liquid.

b, The same scenario as in (a) but on a Si(001) surface. Melting occurs for $T>636$ K, solidification sets in at 578 K.
Supplementary Figure 4:

a, Sketch of the measurement of an extended in-plane reciprocal space map (RSM) of a symmetry equivalent section of the Si(111) surface. The incident and exit x-ray beams are

b, In-plane extended reciprocal space maps at room-temperature on 7ML of Au on the Si(111)-(6×6) (b), the Si(111)- (\sqrt{3}×\sqrt{3})R30° (c) and Si(001) (d) surfaces.

In-plane extended reciprocal space maps at room-temperature on 7ML of Au on the Si(111)-(6×6) (b), the Si(111)- (\sqrt{3}×\sqrt{3})R30° (c) and Si(001) (d) surfaces.

a, Sketch of the measurement of an extended in plane reciprocal space map (RSM) of a symmetry equivalent section of the Si(111) surface. The incident and exit x-ray beams are
kept grazing with respect to the surface to ensure surface sensitivity. The in-plane momentum transfer $Q$ is varied (yellow arrow) by changing the scattering angle $2\theta$. At each $Q$-value, a rocking scan (blue arrow) is performed through a rotation $\omega$ of the sample around its surface normal by more than 30°. Bulk Bragg peak positions are indicated by blue dots, together with two high-symmetry directions.

b. 35° angular section of in-plane RSM after unmixing and solidification of the supercooled liquid on a (6×6) reconstructed Si(111) surface. Blue color corresponds to low intensity, and red to high intensities, the yellow one being intermediate. Three bulk Bragg peaks are visible, together with a mesh of smaller peaks arising from a surface/interface periodic superstructure. The reciprocal lattice units of the Si(111) surface and of its (6×6) reconstruction are indicated. Diffraction rings from polycrystalline Au are observed.

c. Cooling down the sample right after obtaining a eutectic melt at 636 K (not exceeding a sample temperature of 673 K) leaves a Si(111) surface with a ($\sqrt{3}$×$\sqrt{3}$)R30° reconstruction induced by the Au deposit, instead of the (6×6) that forms only after annealing at higher temperatures followed by cooling below 673 K. Here a section of 32° of an in-plane RSM is shown. The in-plane reciprocal unit cell of the Si(111)-($\sqrt{3}$×$\sqrt{3}$)R30° reconstruction is indicated. The powder diffraction rings corresponding to the Au(111) and Au(200) lattice spacing are visible.

b. Following similar procedures on Si(001) leaves an unreconstructed surface. The Au crystals are in a cube on cube epitaxy with the underlying Si substrate.

**Supplementary Figure 5:**

Surface diffraction analysis of the Si(111)-(6×6) reconstruction.

In-plane diffraction rods have been quantitatively measured to solve the atomic structure of the Si(111)-(6×6) reconstruction. The measurement covers 120° with p6mm symmetry (systematic error ~4.5%) and thus 4 symmetry relevant fractions. The black half disks area (resp. radii) are proportional to the experimental Bragg intensities (resp. structure factors), whereas the white half disks area are representative of the simulated intensities from the fitted structure model. Some reconstruction rods have also been quantitatively measured, along the
surface normal. One is presented to the right as a function of perpendicular momentum transfer. They reveal a thickness of the order of 2-3 Å showing that the structure is of mono-atomic thickness. The final model found is nearly identical to that published by Grozea et al. If only the top gold monolayer is included (model shown in Fig. 4), the final $\chi^2$ is already 2.8. Including the underlying silicon bilayer improves the fit down to a $\chi^2$ of 1.

**Supplementary Figure 6:**

Mean structure factor extraction from the Si(111)-(6×6) reconstruction.
In order to be able to compare the intensity distribution of the liquid with the mean intensity distribution of the Si(111)-(6×6) reconstruction, and thus to show the similarity in local atomic structures, the intensity of all measured (6×6) diffraction peaks was sorted as a function of momentum transfer Q and summed up in intervals of 0.05 Å$^{-1}$ throughout the whole experimentally accessible range of 8.45 Å$^{-1}$ resulting in the black crosses. For every interval this sum was normalized taking into account the surface integration element in two-dimensional q-space. To smoothen the discrete characteristics of this curve and keep its representative nature of a one dimensional intensity distribution in reciprocal space, a fast Fourier transform convolution was used to filter out the higher frequency components. The function used consisted in a parabola having its maximum 1 at the origin and falling to zero at 0.5 Å$^{-1}$. This treatment was performed using the ORIGIN software (http://www.OriginLab.com). The resulting smoothened curve is plotted in red and serves to see where the main maxima are located. It can serve as a guide to the eye for a comparison with a liquid structure factor.
Supplementary Figure 7:

Solidification hysteresis for a deposit of 30 ML Au on Si(111). The influence of the Si(111)-6×6 surface structure is as well present for a 30 ML deposit but the solidification temperature is higher than for the 7 ML deposit. This can be attributed to bigger AuSi islands and thus to a decrease of the interface/volume ratio.
Supplementary figure 8:

Silicon regrowth on a Si(111) surface with a Si(111)-6×6 reconstructed Au-layer.

a, sketch of reciprocal space of a Si(111) surface. Along the <11\bar{2}> in plane direction one crosses the crystal truncation rod (CTR) at the \( \frac{1 1 2}{3 3 3} \) position. The observed intensity at this point oscillates during Si-deposition.

b, the intensity oscillates as a function of Si-deposition at T=626 K. These intensity oscillations are a proof for layer-by-layer growth on the Si(111) (see e.g. P. H. Fuoss et al., Phys. Rev. Lett. 63, 2389-2392, (1989)).

c, Reconstruction peaks of the 6×6 structure and first maximum of the liquid AuSi structure factor show no changes before and after the Si layer-by-layer growth.
Supplementary Figure 9:

The mean-square displacement $\langle r^2(t) \rangle$ as deduced from MDS is drawn for the three temperatures (T=700K, 600K, and 500K), revealing three distinctive regimes: a ballistic motion of the atom seen at very short times, in which the atoms motion amplitude evolves as $t^2$, is followed by a crossover region, called the cage effect, where the slope of $\langle r^2(t) \rangle$ weakens. The latter is interpreted as a slowing down of the motion of the atoms as they encounter their first neighbors, forming coordination polyhedra whose characteristics are examined below. Finally, at longer times, the atoms enter a diffusive regime in which the mean-square displacement grows linearly with time.
Supplementary Figure 10:

Evolution of the quantity of the different icosahedral signature pairs with temperature. Red, green and blue lines correspond to 1551, 1541 and 1431 clusters respectively, referring to the left axis with typical topology for each one shown on insets. The black line represents the evolution of the total proportion of the five-fold symmetry clusters cited above (1551+1541+1431) referring to the right axis.
3. Supplementary Table
Self-diffusion coefficients estimated in the stable liquid (T=700K) as well as in the supercooled region (T=600K and 500K) from the corresponding velocity auto-correlation functions showing a diffusive regime during the time of the simulations as displayed in Fig. S4, and therefore prove a liquid behavior for the three temperatures.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Self-diffusion coefficients (Å².ps⁻¹)</th>
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<tbody>
<tr>
<td>700</td>
<td>0.075</td>
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<tr>
<td>600</td>
<td>0.046</td>
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<tr>
<td>500</td>
<td>0.020</td>
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