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Metastable phase formation in the Au-Si system via ultrafast nanocalorimetry

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We have investigated the stability and solidification of nanometer size Au-Si droplets using an ultrafast heating/cooling nanocalorimetry and in situ growth techniques. The liquid can be supercooled to very low temperatures for both Au-rich (ΔT ~ 95 K) and Si-rich (ΔT ~ 220 K) samples. Solidification of a unique metastable phase δ1 is observed with a composition of 74 ± 4 at. % Au and a b-centered orthorhombic structure (a = 0.92, b = 0.72, and c = 1.35 nm; body-center in the a-c plane), which grows heteroepitaxially to Au. Its melting temperature Tm is 305 ± 5 °C. There is competition during formation between the eutectic and δ1 phases but δ1 is the only metastable alloy observed. For small size droplets, both the δ1 and eutectic phases show considerable depression of the melting point (size-dependent melting). © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4712342]

I. INTRODUCTION

Au was the first metallization used for Si or Ge based microelectronics. Au/Ge contacts formed the first transistor1,2 and the first solid state particle detector.3 Reactions of Au/Si are the earliest silicide contacts explored.4 Today, this system is particularly relevant since Si and Ge nanowires,5 interface layered liquid, the integrated thickness of the thickness of the 2-D layer, top-surface and bottom-surface.

The Au-Si system easily forms metastable crystalline and glassy phases. It also has one of the deepest relative eutectic points (T closely related to a low glass transition temperature (Tg ~ 273 K).6) Supercooled liquid (Au-Si)1 can obtain via rapid quenching ushered in the first studies of metallic glass.10,11 All Au-Si crystal alloys are metastable but can be easily made. The unusual aspects of Au-Si stem from the nature of the supercooled (Au-Si)1 liquid. It is an extremely fragile liquid15 and thus unusually stable due to strong local short-range ordering in the liquid. Recent studies16–19 show that there is additional enhanced ordering at the liquid/solid interface and surface.

There are four levels of ordering in the (Au-Si)1 liquid: (1) intrinsic ordering20 as indicated by the large anomalies (ΔCp > 60%) specific heat as compared to the vibrational Cp.21 (2) 2-D solid layer (surface freezing),16 (3) vertical layering (sheets) of atoms extending up to 10 layers (2.5 nm) into the liquid from the top surface,16 and (4) vertical layering extending from the bottom solid/liquid Au/(Au-Si)1 interface as in the Al/Al2O3 case.18,19 When combining the thicknesses of the 2-D layer, top-surface and bottom-interface layered liquid, the integrated thickness of the ordered liquid is in the order of 5–10 nm, a thickness which is accessible for heat capacity measurements using the ultra-sensitive nanocalorimeter device.

Size-dependent melting in the Au-Si system is also of interest and is significant at the 0–10 nm size-scale. It has been previously observed in pure elements22–25 compound materials,26 and eutectic alloys.27,28 The size of the Au droplets is important for determining practical growth temperatures of nanowires. Size-dependent properties have been studied in our previous nanocalorimetry work on magic-size clusters,29 glassy polymers,30 and single layers of alkanethiolate.31

In this paper, we explore the supercooling and solidification properties of (Au-Si)1 liquid using nanocalorimetry, which is sensitive enough to sample the liquid and solids throughout the thickness range of 0–10 nm. At this thickness, size-effect melting is clearly observed in the solidification products. Moreover, the enhanced layer-ordering (sheets) extends throughout all of the liquid being sampled. A schematic diagram is shown in Fig. 1. We find that there is a large increase in the stability of the liquid and the formation of a unique alloy δ1, which has a well-defined melting peak. We identify the formation path of δ1, establish the composition boundaries using in situ Cp(T) during deposition and then discuss the results in terms of ordered liquid and the interface energy. Our work shows in addition to structure, the stoichiometric, melting, solidification, and stability characteristics of the liquid phase.

II. EXPERIMENT

The operation,32,33 fabrication,34 and calibration33,35 of the nanocalorimeter have been discussed in detail in previous work. In brief, nanocalorimetry is an ultrasensitive thin-film differential scanning calorimetry technique consists of a thin
50 nm Si-N membrane supported by a Si frame. Samples are deposited on one side of the membrane and a thin (50 nm) metal heater strip is deposited on the other side. By inducing a short pulse of current through it, the heater serves both to heat the membrane/sample and to measure its temperature. The values of voltage and current across the heater are used for power and temperature calculations, and finally, for the calculation of $C_p(T)$. Very fast heating rate varied from 20 000 to 200 000 K/s allows the nanocalorimeter to operate in nearly adiabatic conditions.

Deposition and $C_p$ measurements are done using a dedicated UHV system with a base pressure of $2 \times 10^{-10}$ Torr and a Si deposition pressure of $<2 \times 10^{-9}$ Torr in order to abate oxidation effects due to the aggressive nature of metal induced oxidation process. The Au-Si $\delta_1$ (Ref. 38) alloy is formed in this study by rapidly cooling ($10^3$ °C/s) Au-rich, Au-Si samples deposited onto an electron-transparent nanocalorimeter device shown in Fig. 2(a). Using the high heating rate of nanocalorimetry, we reach 450 °C in 10 ms. The average passive cooling rate of $10^4$ °C/s is slower than $10^5$ °C/s which can induce glass formation but fast enough to form $\delta_1$. The resulting crystals of $\delta_1$ do not change during the short-time for air-transfer required for ex situ transmission electron microscopy (TEM) analysis. The stability of $\delta_1$ to ambient air exposure is tested in an experiment where a sample that has already undergone calorimetry measurement is then transferred to another vacuum chamber with an ambient air exposure of 15 min. The second calorimetry measurement shows that the melting peak height of $\delta_1$ was within 10% of the first calorimetry result. This result is in stark contrast to samples exposed to ambient for 2 months or more. In this case, there is no melting peak observed which is expected since all of the Si will be removed from the alloy due to metal induced oxidation.

III. RESULTS AND DISCUSSION

Using electron diffraction (ED), a $\delta_1$ single crystal was analyzed in multiple directions and tilted from [001] to [011] and from [001] to [101] diffraction zone axes. Selected diffraction patterns are presented in Fig. 3(a). Simulation of the ED patterns shows that $\delta_1$ is b-centered orthorhombic ($a = 0.92$, $b = 0.72$, and $c = 1.35 = 2 \times 0.675$ nm) with the body-center in the a-c plane. The ED patterns have regular spots at $h + l = 2n$ and extinctions at $h + l = 2n + 1$, where $n$ is an integer. Notice the different extinctions between the first and the second Laue zones, showing a b-center in the a-c plane. These values are close to those reported for the orthorhombic and surface structures in other studies after correction for thermal expansion (see Table I). The data reported by Shpyrko for 2D surface freezing on liquid Au-Si alloy were obtained at 360 °C; thus, adjustment for
The surface of the Au grain prior to solidification. The heat of melting of this microstructure does not depend on the amount of excess Au, suggesting very low solubility of Si in Au (<1 at. %).\(^\text{44}\)

The melting of $\delta_1$ in a Au-rich sample with Au$_x$ present is shown in the calorimetric curve in Fig. 2(b). Only a single melting peak (305 ± 5 °C) is observed and it is well below the eutectic point (363 °C). Since there is only one peak, we deduce that all of the liquid solidifies into $\delta_1$. The melting enthalpy $H_m$ (6.8 ± 1.1 J/mol-atom) is similar to the reported $\gamma$-Au-Si (6.6 J/mol-atom).\(^\text{20}\) The measured entropy $S_m$ (11.8 ± 1.9 J/mol-atom-K) is reasonable compared to other metal-rich silicides (e.g., 10.5 J/mol-atom-K for Ni$_2$Si), parent Au$_x$ phase (9.5 J/mol-atom-K), and other FCC metals (8–12 J/mol-atom-K).\(^\text{35}\) The results are summarized in Table II. The reported uncertainty in the temperature is a measure of the full width at half maximum of the melting peak of $\delta_1$. This uncertainty is larger than the instrumental error of ±2 °C determined from the calibration of the nanocalorimeter device against a standard class A 100 °C Pt resistance temperature detector and multiple experiments using the melting point of bulk indium as the standard temperature. The uncertainty in the heat of fusion is calculated from the errors in the determination of the enthalpy of melting and the number of moles. The enthalpy of melting is obtained from the integrated area under the melting peak using Origin™ peak analysis function. The error in the peak area measurement is 1.5% (20.8 ± 0.3 μJ) when comparing different scans taken over 2 days shown in Fig. 2(b). The number of moles of silicon is calculated from the shift in the heat capacity due to silicon divided by its specific heat. The estimated error is 3.6% (0.79 ± 0.03 nmol). In the formation of $\delta_1$ starting with excess gold, the deposited silicon will be fully consumed. The atomic percentage of silicon in $\delta_1$ is obtained from the energy dispersive spectroscopy (EDS) result and the average of the range of composition for the initial formation of $\delta_1$ as discussed below. The error is 15% (0.26 ± 0.04). The calculated error in the molar heat of fusion is 16% (6.8 ± 1.1 kJ/mol) with details of the calculation given below.

$$H_m = \frac{\Delta H}{\text{moles Au} + \text{moles Si}} = \frac{\Delta H}{\text{moles Si}} \times (1 - F),$$

where $F$ is the atomic % of Au obtained from EDS and the range of composition for the initial formation of $\delta_1$. Thus, $H_m = 20.8 ± 0.3$ μJ × (1 – 0.74) ± 0.04/0.79 ± 0.03

The thermal expansion is necessary to obtain values at room temperature using a thermal expansion coefficient of 15 ppm/°C which is typical for silicides.

$\delta_1$ forms as a crystalline shell around the Au$_x$ core. The ED pattern (Fig. 3(b)) shows that $\delta_1$ has a shared (epitaxial) orientation with Au$_x$: Au [111]//4 $\delta_1$ [001]. This result is consistent with a previous study of bi-layers of polycrystalline Au and amorphous-Si,\(^\text{43}\) although the crystal structure was not clear from that work. The uniform morphology of the core-shell structure suggests that the liquid easily wets

**TABLE I. Comparison of lattice constants.**

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Volume (Å³)</th>
<th>Δ Volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baumann(^a)</td>
<td>9.71</td>
<td>7.68</td>
<td>7.03</td>
<td>524</td>
<td>17</td>
</tr>
<tr>
<td>Gaigher(^b)</td>
<td>9.56</td>
<td>7.5</td>
<td>6.8</td>
<td>488</td>
<td>9</td>
</tr>
<tr>
<td>This work</td>
<td>9.2</td>
<td>7.2</td>
<td>6.75</td>
<td>447</td>
<td>0</td>
</tr>
<tr>
<td>Green(^c)</td>
<td>9.35</td>
<td>7.35</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shpyrkod(^d)</td>
<td>9.34</td>
<td>7.35</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shpyrkod(^e)</td>
<td>(9.39)</td>
<td>(7.39)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Reference 40. \(^b\)Reference 41. \(^c\)Reference 42. \(^d\)Reference 16. \(^e\)Reported values at 360 °C.

**TABLE II. Thermodynamic properties.**

<table>
<thead>
<tr>
<th>Phase</th>
<th>Tm (°C)</th>
<th>$H_m$ (kJ/mol-atom)</th>
<th>$S_m$ (J/mol-atom-K)</th>
<th>[Au] (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metastable(^a)</td>
<td>358</td>
<td>6.6 ± 0.6</td>
<td>10.5</td>
<td>81.4</td>
</tr>
<tr>
<td>Metastable(^b)</td>
<td>305 ± 5</td>
<td>6.8 ± 1.1</td>
<td>11.8 ± 1.9</td>
<td>74 ± 4</td>
</tr>
<tr>
<td>Eutectic(^a)</td>
<td>363</td>
<td>9.4 ± 0.3</td>
<td>14.8</td>
<td>80.5</td>
</tr>
<tr>
<td>Eutectic(^b)</td>
<td>363</td>
<td>9.8 ± 0.4</td>
<td>15.4</td>
<td>81.4</td>
</tr>
</tbody>
</table>

\(^a\)Reference 20. \(^b\)This work. \(^c\)Reference 52.
nmol = 6.8 ± 1.1 kJ/mol. The largest contribution to the error in \( H_m \) is the error in \((1 - F)\) which is 15%.

\( \delta_1 \) melts (305 °C) at a much lower temperature than the \( \gamma \)-Au-Si phase (358 °C). This is a rare case of the direct thermal analysis of a metastable alloy and to our knowledge the first direct measurement of alloy melting in the Au-Si system. Typically, Au-Si alloys decompose via solid-state processes into the eutectic components. As the temperature increases during the heating cycle, the liquid is a metastable supercooled liquid after \( \delta_1 \) has melted. Only after the temperature (during the heating-cycle) exceeds the melting point of the eutectic, the liquid is considered to be thermodynamically stable. Thus, both the liquid and the \( \delta_1 \) are kinetically trapped in the metastable states using this fast-scanning sequence. The cooling curve for this Au-rich (Au\(_x\) and \( \delta_1 \)) sample is also shown in Fig. 4.

The composition of \( \delta_1 \), which will be discussed later, obtained by EDS and the average of the range of composition which shows the initial formation \( \delta_1 \) when starting with either a Si-rich or a Au-rich sample is 74 ± 4 at. % Au, slightly less than the equilibrium, bulk eutectic point composition (81.4 at. % Au). For this analysis, the Si\(_x\)N\(_x\) support film was carefully removed by brief ion-milling so that partially supported large \( \delta_1 \) single crystals were studied. The magnitude of the error (±4 at. %) is comparable to the difference between Au-Si phases, e.g., Au\(_3\)Si has 75 at. % Au and Au\(_x\)Si has 80 at. % Au. \( \delta_1 \) may not be a line-compound since there is appreciable range in the reported lattice constants (see Table I) (a:5%, b:7%, c:4%) and their volume (\( \Delta V:17\% \)).

Given that the presence of Au is important to the formation of \( \delta_1 \), we explore the melting/solidification using heating/cooling data (Fig. 4) and the boundaries of \( \delta_1 \) formation over the entire composition range (Fig. 5). By performing nanocalorimetry during deposition, the evolution of the phases is tracked over a large range of average composition. Two separate experiments are done, the first starting with Si-rich conditions and then the reverse experiment with Au-rich conditions.

Results for the first experiment are shown in Fig. 5(a), where 3.7 nm of Si is initially deposited. Au is then slowly evaporated while simultaneously obtaining heating curves. The sample is heated to 450 °C and then cooled after each deposition step. In this way, the average composition is continuously changed with sub-monolayer increments from Si-rich to Au-rich. Only eutectic melting is observed during the early stages of Au deposition when the average composition is Si-rich and ranges from 0 to 55 at. % Au (0 to 4 nm).

Size-dependent melting of the eutectic is clearly present. The melting point of the eutectic (\( T_c \)) gradually increases from 260 °C to the bulk eutectic temperature 363 °C as the amount and size of Au\(_x\) crystals increase. TEM results

**FIG. 4.** The heat flow during heating (red) and cooling (blue) from measurement plotted as the time-derivative of the differential voltage, \( d(\Delta V)/dt \), versus temperature of Au-Si alloys. (Bottom) Au-rich, single-phase sample: Only one set of melting and solidification peaks are observed corresponding to \( \delta_1 \); (top) Si-rich, two-phase sample: Au-Si eutectic phase melting and solidification peaks can be found in addition to that from \( \delta_1 \). The supercooling of \( \delta_1 \) is ~30 °C, whereas the supercooling of Au-Si eutectic is much larger ~220 °C. The cooling rate is variable but on the order of \( 10^4 \) °C/s in both cases.

**FIG. 5.** Three dimensional (3D) \( C_p(T, t) \) caloric maps during (a) Au deposition with the sample initially Si-rich and (b) Si deposition with the sample initially Au-rich. Eutectic forms first in (a) followed by \( \delta_1 \) (Si-rich to Au-rich), whereas \( \delta_1 \) forms first in (b) followed by the eutectic (Au-rich to Si-rich). Both \( \delta_1 \) and eutectic are present in Si-rich samples beyond the thickness range shown in (b). Inset in (a) shows TEM lattice images of a 5 nm Au\(_x\) (2.34 Å) nanoparticle embedded in a Si\(_x\) (3.16 Å) matrix at the early stages of eutectic melting which exhibits melting point depression. Inset in (b) is a \( C_p(T) \) plot showing solidification (exothermic) of liquid after \( \delta_1 \) melts which occurs in the presence of Au(s) and Si(s).
confirm that the terminal phases are present with large Si plates in contact with nm-size Au particles (Fig. 6(a)). Each (Au-Si)\(_L\) droplet produces a single crystal Au precipitate of roughly 80% the same size. A small Au precipitate on a large Si plate will have a decrease in melting point. The melting point of the eutectic is 100 K below the bulk T\(_c\) which corresponds to nm size Au\(_s\) particles using the melting point depression data of Buffat and Borel.\(^47\)

At the composition 55 at. % Au (4 nm), an additional peak due to \(\delta_1\) begins to appear at 270 °C. It also exhibits an increase in its melting temperature with increasing thickness and sample volume and in the shape of small 3D particles. With further increases in composition, up to 80 at. % Au (\(~11.5\) nm) and thereafter, only the \(\delta_1\) melting peak exists in the caloric curves, consistent with our TEM results. At this final point, the sample is Au-rich with large core-shell particles of Au\(_s\) and \(\delta_1\) (Fig. 6(a)).

In the second experiment (Fig. 5(b)), the reverse compositional sequence of phase formation is performed by starting with a large amount of Au (12 nm) and then depositing Si and \(\delta_1\) is the first and major phase formed. After the average composition becomes Si-rich (\(<70\) at. % Au), the eutectic phase begins to dominate. Unlike the Au deposition case where the eutectic phase disappears when excess Au is supplied, as the Si deposition proceeds, \(\delta_1\) continues to persist even with excess Si. A convolution of endothermic (melting of \(\delta_1\)) and exothermic (re-solidification) processes occurs simultaneously in this temperature region (inset Fig. 5(b)). The \(C_p(T)\) below the solid heat capacity line indicates that an exothermic process occurs. This exothermic process is the re-solidification of the liquid (from \(\delta_1\)) to the eutectic.

Note, in this case we do not observe a significant shift in the melting peak temperature of \(\delta_1\). This lack of size effects is due to the impact of geometry and interface energy. In this case, small amounts of (Au-Si)\(_L\) solidify as a thin-shell (platelets)\(^48,49\) of \(\delta_1\) covering a very large-radius Au-core. Compare this to that of an ensemble of small spherical particles/droplets of (Au-Si)\(_L\) in contact with Si\(_s\) as is the case of the first experiment. Size-effects on spherical particle systems are much larger (\(3\times\)) than for platelet systems\(^48,49\) for the same size scales when comparing the ratio of surface area to volume. The underlying dissymmetry of the two growth sequence is due to the wetting phenomenon: (Au-Si)\(_L\) wets Au\(_s\) but (Au-Si)\(_L\) does not wet Si\(_s\) as shown in Fig. 6(a).

We summarize these experiments by evaluating the \(\delta_1\) fraction of the total heat of melting as shown in Fig. 6(b). The two curves overlay each other at the critical boundary near 73 at. % Au. We find that \(\delta_1\) is the only solidification product in the compositional range of 100-75 at. % Au and corresponds to a two phase (Au\(_s\) + \(\delta_1\)) region. The melting point of \(\delta_1\) is invariant (305 °C) over the range of Au-rich composition.

\[
\text{Au}_s + (\text{Au} - \text{Si})_L \xrightleftharpoons{\text{Heat}} \quad \text{Au}_s + \delta_1. \quad (1)
\]

The Au-Si system is analogous to the eutectic Pb-Sn system, which also has a metastable (\(x_1\)) alloy (50 at. % Sn). In this system, the formation of \(x_1\) is linked to the close lattice constant match between \(x_1\) and the parent Pb(\(x\)) phase.\(^50\) Similarly, there is a close lattice match between \(\delta_1\) and Au\(_s\).

\[
\text{Pb}_s + (\text{Pb} - \text{Sn})_L \xrightleftharpoons{\text{Heat}} \quad \text{Pb}_s + x_1. \quad (2)
\]

We estimate the stoichiometry (73% ± 6% Au) of the \(\delta_1\) phase using the data in Fig. 6(b). This provides an additional value for stoichiometry which is independent of EDS analysis. We use the criterion that only \(\delta_1\) occurs in Au-rich samples. Then, the stoichiometry of \(\delta_1\) should be equal to the average stoichiometry at the minimum Au concentration when only \(\delta_1 + \text{Au}_s\) are present. We obtain a value of 79% when the deposition sequence is from Si-rich to Au-rich and 67% in the reverse sequence. We speculate that the difference in these values stems from the variation in local stoichiometry of particles due to the distribution of shapes and sizes between the two sequences.

Solidification and the degree of supercooling can be investigated using heating/cooling data in Fig. 4. (Au-Si)\(_L\) liquid is extraordinarily stable when in contact with a Si\(_s\) reservoir (seed) without Au\(_s\) present. It can be supercooled to \(T = 513 \text{ K} (\Delta T = 125 \text{ K})\) as shown recently by Schülli et al.\(^17\) when cooled at slow rates and to extraordinary low values \(T = 418 \text{ K} (\Delta T = 220 \text{ K})\) when using faster rates and smaller length scales shown in this work (Fig. 4). (Au-Si)\(_L\) liquid is also extraordinarily stable when in contact with a Au\(_s\) reservoir without Si\(_s\) present. As shown in Fig. 4, the liquid can be supercooled to \(T = 578 \text{ K} (\Delta T = 95 \text{ K})\) before solidification.
During the cooling cycle (365–275°C), the composition of supercooled (Au-Si)\textsubscript{L} liquid remains unchanged when only Si\textsubscript{L} (not Au\textsubscript{L}) is present. Considering only thermodynamic arguments, all of the Si in (Au-Si)\textsubscript{L} could deposit onto the Si\textsubscript{L} since nucleation is not an impediment for Si growth, and thus reduce the remnant liquid to an Au\textsubscript{L} concentrate. However, experimentally the ordered liquid does not allow either Si or Au to be extracted nor nucleation (Au\textsubscript{L}) or growth (Si\textsubscript{L}) to occur. We conclude that the two possible barriers—growth (small) and nucleation (large)—are not independent but coupled in such a way that both Au\textsubscript{L} and Si\textsubscript{L} need to be present for eutectic solidification. Similarly, in the case of Au-rich samples (Au\textsubscript{L} present and Si\textsubscript{L} absent) neither nucleation (Si\textsubscript{L}) nor growth (Au\textsubscript{L}) occurs. Eutectic solidification occurs at this temperature only when both Au\textsubscript{L} and Si\textsubscript{L} are present (Fig. 4).

In discussing the details of the initial formation of δ\textsubscript{1} as opposed to that of γ\textsubscript{1}, we suggest that this process maybe due to the collective influence of the ordered liquid coupled with the low barrier nucleation sites of the Au\textsubscript{L} interface and Au-Si surface layer. The ordered liquid has the same average (and perhaps local) composition as does the δ\textsubscript{1} alloy. Unlike eutectic solidification, formation of δ\textsubscript{1} does not need significant molecular transport or rearrangement on the atomic length scale. In essence, the δ\textsubscript{1} solid is a frozen 3-D version of the ordered liquid. Because of the enhanced ordering by the surface and interface of the confined liquid it is expected to be an even weaker liquid (higher fragility) than the bulk (Au-Si)\textsubscript{L}.

Heteroepitaxial nucleation of δ\textsubscript{1} can occur at either (1) the interface of (Au-Si)\textsubscript{L} with the 2D surface lattice (a = 7.4, b = 9.4) or (2) the interface of (Au-Si)\textsubscript{L} with Au\textsubscript{L}. The lattice of the 2D surface and Au\textsubscript{L} closely matches two of the lattice parameters of δ\textsubscript{1}. Only a small nucleation barrier should exist in both cases since (Au-Si)\textsubscript{L} wets both the Au\textsubscript{L} and 2D surface. However, we suggest that the latter (2) process dominates since δ\textsubscript{1} crystal does not easily form without Au\textsubscript{L} present and since the orientation of the δ\textsubscript{1} crystal aligns with Au\textsubscript{L} lattice. However, the 2D layer may be inherently aligned with the underlying Au\textsubscript{L} surface since they are in close (nm) proximity to each other.

We did not observe the melting (T\textsubscript{m} = 371°C) of this surface layer using the nanocalorimetry instrument, perhaps a different experimental design is needed. Assuming that the melting enthalpy scales with that of bulk δ\textsubscript{1}, then one layer melting enthalpy would be in the order of ΔH = 140 nJ. This value of heat should be accessible to the nanocalorimeter since we have previously measured single peaks with ΔH = 10 nJ for single crystal polyethylene\textsuperscript{51} and ΔH = 2.5 nJ for magic number sized indium clusters.\textsuperscript{29}

When considering the governing criteria for the phase-segregation of δ\textsubscript{1} over other possible Au-Si alloys (e.g., γ\textsuperscript{1}), we do not consider that the cooling rate is a key parameter, since δ\textsubscript{1} forms at a variety of quenching rates ranging from (1 K/s),\textsuperscript{40} (10\textsuperscript{3} K/s)\textsuperscript{30} to (10\textsuperscript{5} K/s) the rates used in this work. This is the same range of quench rates used to form other alloys (e.g., γ\textsuperscript{1}).\textsuperscript{29}

Perhaps a more important selection factor is the small size (nanometer scale) of the liquid and solidification products. Most other Au-Si alloys (e.g., γ (Ref. 20)) form by quenching large bulk liquid samples yielding large particles ~40 000 nm. In contrast, all the previous work\textsuperscript{30,41} for δ\textsubscript{1} and work here show small sample sizes in the 15–100 nm range. It is possible that δ\textsubscript{1} is actually the first phase formed for all alloys but it goes undetected because of the miniscule amounts present at the initial stages of solidification—δ\textsubscript{1} may act as the nucleation seed for subsequent formation of other alloys.

IV. CONCLUSION

In summary, we have investigated the stability and solidification of nanometer size Au-Si droplets using an ultrafast heating and cooling nanocalorimetry technique. The liquid can be supercooled and is stable to very low temperatures for both Au-rich and Si-rich samples. Solidification of a unique metastable phase δ\textsubscript{1} is observed. Competition between the eutectic and a metastable phase has been observed but δ\textsubscript{1} is the only metastable alloy observed after rapid cooling of the melt to room temperature at the rate of 10\textsuperscript{4} C/s. TEM data show it to have a b-centered orthorhombic structure with lattice parameters which are closely matched to Au\textsubscript{L}. For small size droplets, both the metastable and eutectic phases show considerable depression of the melting point (size-dependent melting).

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