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Growth Pathways in Ultralow Temperature Ge Nucleation from Au

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ABSTRACT: Device integration on flexible or low-cost substrates has driven interest in the low-temperature growth of semiconductor nanostructures. Using in situ electron microscopy, we examine the Au-catalyzed growth of crystalline Ge at temperatures as low as 150 °C. For this materials system, the model for low temperature growth of nanowires, we find three distinct reaction pathways. The lowest temperature reactions are distinguished by the absence of any purely liquid state. From measurements of reaction rates and parameters such as supersaturation, we explain the sequence of pathways as arising from a kinetic competition between the imposed time scale for Ge addition and the inherent time scale for Ge nucleation. This enables an understanding of the conditions under which catalytic Ge growth can occur at very low temperatures, with implications for nanostructure formation on temperature-sensitive substrates.

KEYWORDS: Catalytic growth, chemical vapor deposition, germanium, low temperature growth, vapor–liquid–solid growth, vapor–solid–solid growth

Many applications of semiconductor nanostructures would benefit from the ability to grow functional structures on substrates such as plastics that cannot tolerate high temperatures. As a result, there is great interest in the growth of semiconductor nanostructures at low temperatures and in the fundamental mechanisms and limits of low-temperature growth. Catalytic growth of nanowires provides an ideal way to study these issues. The process is accessible through in situ microscopy, and the use of suitable catalysts can facilitate low-temperature growth. Nanowires have already displayed exciting applications in electronics, optoelectronics, thermoelectrics, sensing, energy conversion and storage,1–8 and the ability to grow nanowires on temperature-sensitive substrates such as plastics or materials with pre-existing metallization and dielectric layers9 would greatly expand the range of potential applications.

Semiconductor nanowires typically grow via a liquid droplet formed by eutectic reaction between the semiconductor and a metal such as Au [the vapor–liquid–solid (VLS) process, ref 10]. But the possibility of nanowire growth at low temperatures, well below the eutectic temperature (T_e), is already well-established.11,12 In particular, Ge nanowires have been grown from Au via chemical vapor deposition (CVD)9,13–20 at temperatures as low as 200 °C (T_e is 363 °C for Ge–Au). This growth below T_e is still VLS: the solid Au first reacts completely to form liquid eutectic AuGe, crystalline Ge nucleates from the liquid, and the catalyst remains in a stable, supersaturated, and supercooled state as the nanowires grow.13,17,21,22 But a vapor–solid–solid (VSS) mechanism is also possible at these temperatures.13,21–23 Here, the solid catalyst forms by phase separation of the liquid into solid Au + Ge, spontaneously or on lowering temperature or pressure; nucleation of Ge directly from solid Au has not been observed. The Ge/Au system has therefore been key for studying low-temperature nanowire formation, and observations made in this system at even lower temperatures have the potential to help us understand the general principles of very low temperature growth. We have therefore used in situ transmission electron microscopy (TEM) to examine the formation of the initial Ge nucleus at temperatures down to 150 °C. Novel and unexpected pathways emerge as we go deeper into the low temperature regime, differing in whether visible liquid and/or solid Au are present at the time of Ge nucleation. To understand the sequence of pathways, we develop a model that considers the rate of Ge nucleation and the evolution of each phase prior to nucleation. These reaction pathways show the complexity possible in even a simple binary eutectic system controlled by both kinetic and thermodynamic effects, while also suggesting the promise of catalytic growth for creating semiconductor nanostructures at low temperatures.

The experiments consist of exposing an array of Au nanocrystals, heated on a noninteracting substrate, to Ge supplied from the precursor gas digermane (Ge_2H_6). Gas dosing was carried out in an ultra-high vacuum (UHV) TEM (base pressure 2 × 10^{-10} Torr).24 The reaction was followed as a function of substrate temperature, digermane pressure, and Au particle size, recording images at 30 frames per second. Bright-field (BF) or dark-field (DF) imaging was used to...
provide optimum kinetic information, due to the strong contrast difference between Ge nuclei and the AuGe liquid or solid Au. High resolution microscopy was not used due to the time required to align each randomly oriented nanocrystal for imaging. (We discuss below the possibilities of forming phases other than Ge, Au, and liquid AuGe.)

To obtain the most complete information on kinetics, two different types of catalyst were used. First, size-selected aerosol Au particles allowed us to follow reactions at a well-defined geometry and size. (Note that unlike colloidal Au particles, aerosol-derived particles do not have an organic surface layer.\(^{25}\)) 30 nm radius particles on SiN-covered Si substrates were imaged in a side-view geometry, as described in ref 26, to provide details of the reaction pathway in individual particles. Second, 5–25 nm radius Au polycrystals, formed by agglomerating a 2–3 nm Au film deposited on a SiN membrane,\(^{27}\) allowed us to obtain measurements as a function of Au radius. The agglomerated samples were formed by cleaning SiN membrane substrates resistively under UHV at \(\sim 900^\circ C\) for 2 h, then depositing Au (without deliberate heating) in an adjacent UHV chamber and agglomerating in the TEM at \(\sim 500^\circ C\) for 20 min. For these experiments, plan-view imaging was used, to obtain simultaneous information on an ensemble of particles, typically 30–40 particles in the 180 × 140 nm field of view.

The accuracy with which the sample temperature is known is an important aspect of the analysis, yet it can be a challenge for in situ TEM. Here, the heating current was calibrated before and after each experiment using an infrared pyrometer and checked after each experiment by removing the sample, mounting a thermocouple on the back surface and remeasuring. For greater accuracy at low \(T\), we controlled the current but also measured the voltage and calibrated with respect to the power dissipated in the sample. We estimate an accuracy of \(\pm 10^\circ C\) in the values quoted below.

Figure 1a–c shows three image sequences that track the progress of Ge nucleation from representative Au nanoparticles observed in plan-view at different temperatures and as a function of digermane exposure time. The Ge nucleation processes deduced from these and other sequences are shown schematically in Figure 1d.

It is clear that the reaction can proceed via different pathways. Figure 1a is consistent with the VLS process. The Au particle transforms fully to a liquid AuGe alloy via a reaction front that moves inward from the surface; some time after this reaction is completed, solid Ge starts to precipitate. We observe this regime from well above \(T_e\) to \(100^\circ C\) below \(T_e\). The presence of liquid AuGe below \(T_e\) is consistent with observations made during Ge nanowire growth,\(^{13,21–23}\) and the sequence of reactions during nucleation (Figure 1d) resembles previous observations for Si above \(T_e\)\(^{26,27}\) and Ge below \(T_e\)\(^{23}\).

As the temperature is reduced below \(\sim 270^\circ C\), the reaction pathway changes. From 270 to 200 \(^\circ C\) we find an unexpected “mixed regime,” as in Figure 1b. Solid Au starts to transform to liquid AuGe as a shell surrounding the Au. But before the Au has fully reacted, solid Ge nucleates. Nucleation appears to occur at a location within the liquid shell, judging by the final position of the solid Ge. All three phases coexist only briefly, and within the time resolution of the experiment (1/30 s) the liquid portion becomes solid, separating into solid Au and solid Ge (as indicated by faceting and the appearance of crystalline contrast) so that the resulting structure appears to be formed only of these two solid phases. Over the temperature range of the mixed regime, there is a change in the relative amount of Au remaining at the time of Ge nucleation. This is illustrated in more detail in Figure 2a–c and will be discussed below. The formation of solid Ge in the presence of both Au and AuGe is intriguing, since previous reports\(^{23}\) (at higher pressures and on a different substrate) show Ge nucleation only after complete transformation of solid Au into liquid AuGe.

At the lowest temperatures at which we see any reaction (200–150 °C), an apparent VLS process occurs (Figure 1c). Here, the Au particles maintain flat facets and diffraction contrast consistent with a solid structure, but after some time Ge nuclei form at the edges of the particles. No liquid phase is visible, although it is important to note that a thin (subnanometer) liquid film would not show clearly given the image resolution.

The range of conditions under which these plan-view experiments were carried out spans a temperature range of 480–150 °C (crossing \(T_e\)); a pressure range 1 × 10⁻⁷ to 3.3 × 10⁻⁶ Torr; and a range of Au radii of 6.5–24 nm. For each experiment, nucleation events were observed in each of the \(\sim 30\) particles in the field of view. (Only particles that coalesced with neighbors or that drifted out of view were excluded from analysis.) These data show that temperature is the main factor determining the reaction sequence. Even near the transition temperatures, most particles appear to follow the same

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**Figure 1.** (a–c) Three series of plan-view BF images showing the reaction pathways of representative Au nanocrystals from an agglomerated film on exposure to digermane. Au, Ge, and L indicate solid Au, solid Ge, and AuGe liquid eutectic, respectively. Experimental conditions were (a) 280 °C, 1 × 10⁻⁶ Torr, 19 nm radius Au; (b) 260 °C, 1 × 10⁻⁶ Torr, 11 nm radius; (c) 150 °C, 3.2 × 10⁻⁶ Torr, 7.6 nm radius. The scale bar for all images is 10 nm, and the number indicates the time in seconds of each image since digermane flow started. Au appears polycrystalline with varying gray levels, while Ge appears to form as a single crystal. (d) Schematic diagrams of the three reaction pathways showing terminology and temperature range.

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![Image](nanolett.12.5867-5872 figure1.png)
mechanism in a given experiment, apart from the few smallest ones (4–6 nm) which we discuss separately below. In particular, the lowest temperature at which we observed the VLS regime did not vary (within errors) for the pressures we explored. We speculate that a simple categorization of nucleation regime by temperature is possible since these experiments were all at low pressures (compared to refs 21–23); we cannot rule out some role of pressure under more conventional conditions.

Detailed measurements of reaction kinetics allow us to understand qualitatively the transition between the regimes and evaluate the parameters of each regime. In Figure 2, as the temperature decreases in the mixed regime, more Au remains (and less AuGe has formed) at the time Ge nucleates. The boundary between what we label as the VSS and the mixed regimes is the point where the amount of liquid AuGe formed becomes too small to detect. Similarly, the boundary between the mixed and VLS regimes is the point where solid Au has just disappeared at the time of Ge nucleation. We can thus understand why, in the VLS regime, the AuGe remains liquid, while in the mixed regime, Ge nucleation immediately leads to phase separation and solidification of the AuGe liquid. In ref 13, the rate-limiting process for solidification of Ge-enriched, supercooled AuGe was shown to be the formation of an Au nucleus. In the mixed regime, solid Au is present so there is no barrier to immediate phase separation. In the VLS regime, solid Au is not present, and the AuGe remains a supercooled liquid. Thus the presence or absence of solid Au at the time of Ge nucleation determines the future evolution of the system.

Figures 3a–d present kinetic measurements from each regime. In Figures 3a,b we show the two stages of the VLS regime, the transformation from solid Au to liquid AuGe and the nucleation of Ge. We analyze these two transformations using the framework developed in refs 26,27 for Au–Si. In the first stage, incoming Ge forms a surface layer of liquid AuGe that wets the Au, and the AuGe–Au boundary moves inward as the transformation continues. We find that the volume 

\[ R_{\text{AuGe}} \]

of solid Au decreases linearly with time, indicating (as expected) a constant rate of Ge addition, until a point (\(R_{\text{AuGe}} \sim 3.6 \text{ nm} \)) at which the solid shrinks more rapidly and disappears. This final rapid decrease reflects the energetic cost of the Au–AuGe interface which destabilizes small volumes of solid Au.

For the second stage, Figure 3b, the amount of solid Ge visible (\(R_{\text{AuGe}} \)) in the liquid AuGe remains zero for a relatively long time, jumps rapidly, and then grows at a lower rate. The rapid jump provides an estimate of the supersaturation of Ge in AuGe required for Ge nucleation. This is based on the idea that a high supersaturation is required to form a Ge nucleus, but once the nucleus forms it rapidly captures the excess Ge from the liquid, leaving a much lower supersaturation that is only just enough to maintain the slow Ge growth rate. The supersaturation for nucleation is thus the jump volume (\(R_{\text{AuGe}} \)) divided by the liquid volume (\(R_{\text{AuGe}} \)) at nucleation. In a simple model, this number should be independent of pressure and \(R_{\text{AuGe}} \). For Si, this approximation holds, and supersaturation values are relatively low (up to a few percent in ref 27). But for Ge we find a different situation. The measured supersaturation
is constant for particles above $R_{\text{AuGe}} \sim 6$ nm but is larger for the smallest particles (Figure 4a). It also increases with pressure (Figure 4b). If we average over the larger particles and work at constant pressure, we obtain the approximate supersaturation values indicated in Figure 3e for the VLS regime.

The supersaturation values derived in this way are typically much higher than those obtained for Si, for example, 15% for Ge at 480 °C and 1 $\times$ 10^{-6} Torr (Figure 3e) compared with 1.5% for Si\textsuperscript{27} under the same conditions. Since the model in ref 27 was developed for small supersaturations, the radius and pressure dependence seen for Ge may be related to these large absolute values. The values for Ge are strongly temperature-dependent. The red line in Figure 3e suggests that, although the temperature range is small, the values are consistent with an Arrhenius behavior, as was seen for Si in ref 27. Interestingly, the trend line crosses $T_e$ without apparent effect, consistent with the nonequilibrium character of the system.

We next discuss the kinetics of the “VSS” regime (Figure 3d). A similar analysis of jump volume shows that nucleation from solid Au also requires an appreciable supersaturation ($\sim 4\%$ from the data shown). The presence of this much Ge in solid Au would be surprising, given the low bulk solubility of Ge in Au at 150–200 °C (<0.2%)\textsuperscript{28} but cannot be ruled out: the solubility is set by equilibrium with solid Ge, so the large nucleation barrier for solid Ge would allow a high supersaturation. Nevertheless, we believe that a more likely scenario is that Ge nucleates from the thin liquid AuGe shell that initially wets the Au.\textsuperscript{23} The Ge nucleus could be accommodated in a liquid shell less than $\sim 0.3$ nm in thickness, which would be difficult to resolve in the images. The ability to nucleate crystalline Ge at temperatures as low as 150 °C is exciting and encouraging for low temperature processing.

In the mixed regime (Figure 3c) the initial reaction in which AuGe forms from Au proceeds similarly to the VLS regime. However, Ge nucleates before the reaction is complete. Once the nucleus forms, the simultaneous presence of Ge and Au solids destabilizes the liquid, and it phase-separates. Thus the observed Ge jump volume $R_{\text{Ge}}/R_{\text{AuGe}}$ is much larger (e.g., $\sim 10\%$ at 260 °C) than expected from extrapolations of the supersaturation in the VLS and VSS regimes, because it reflects not only the prior supersaturation, but also the Ge that would be released by decomposition even in equilibrium. (It is difficult to carry out a more detailed analysis because we cannot measure the actual volumes of solid and liquid, since relatively few particles show clear contrast immediately before Ge nucleation.)

We have implicitly assumed that the solid phases are pure Au and Ge. The equilibrium solubility of Au in Ge is extremely low at these temperatures,\textsuperscript{29} and even allowing for solute trapping, it seems safe for our purposes to neglect any Au dissolved in the solid Ge. The solubility of Ge in Au is higher,\textsuperscript{29} but still not nearly high enough to affect our conclusions. More significantly, metastable AuGe phases have been observed to form during isothermal growth at low temperatures, although their composition has not been measured.\textsuperscript{30} In our experiments, such phases might be indistinguishable from fcc Au. However, the formation of those phases requires large Ge supersaturation in the liquid and/or a barrier to Au nucleation. Here we begin with fcc Au, and it remains present during all the novel transitions discussed. Therefore, we do not expect the conditions for metastable phase formation to be satisfied.
To understand this unexpected sequence of novel regimes, we consider the thermodynamics of the Au–Ge liquid and the resulting kinetics of Ge nucleation. For our purposes here, it is sufficient to consider the liquid as being in equilibrium with the Au and to neglect size effects. Then at a given temperature \( T_e \), the liquid composition corresponds to the Au liquidus line in the phase diagram (or its metastable continuation below \( T_e \)) in Figure 5a. Above \( T_e \), the liquid is stable, but below \( T_e \), it is metastable—it is supersaturated with Ge, and nucleation of Ge is thermodynamically favorable.

To quantify the supersaturation, we assume that the liquid is in equilibrium with Au. Then we use a standard thermodynamic model for this system\(^{27}\) to evaluate the liquid composition \( c_{L(Au)} \) (the Au-liquidus line in Figure 5a) and Ge chemical potential \( \mu_{L(Ge)} \) in the liquid of the Au + liquid system. The chemical potential \( \mu_{L(Ge)} \) of crystalline Ge is equal to that of Ge in the liquid at the Ge-liquidus composition \( c_{L(Ge)} \), denoted \( \mu_{L(Ge)} \). The Ge supersaturation is the difference \( \mu_{L(Au)} - \mu_{L(Ge)} \). This supersaturation steadily increases with decreasing temperature, as shown in Figure 5b.

According to classic nucleation theory,\(^{31}\) the waiting time \( \tau_{Ge} \) for Ge nucleation is

\[
\tau_{Ge} \approx \tau_0 \exp \left( \frac{\gamma^3}{(\Delta \mu)^2 kT} \right)
\]

(1)

where \( \gamma \) is a geometrically weighted difference of interfacial energies, and \( \Delta \mu \) is the Ge supersaturation. We show the scale-free shape of this dependence in Figure 5c, in a manner that is independent of the values of \( \tau_0 \) and \( \gamma \). Also, as seen in Figure 5b, \( \Delta \mu \approx \beta(T_e - T) \), so for temperatures below \( T_e \), we can write

\[
\tau_{Ge} \approx \tau_0 \exp \left( \frac{\gamma^3}{\beta^2(T - T_e)^2 kT} \right)
\]

(2)

Neither \( \tau_0 \) nor \( \gamma \) are known even roughly for this system, and there are other temperature dependences, which we neglect here because they have no special structure near \( T_e \). Nevertheless, it is clear that the liquid lifetime diverges as \( T \) approaches \( T_e \) while becoming exponentially brief at low temperature because of rapid Ge nucleation.

We can now see that the different regimes of growth arise from the competition between two natural time scales. One is the time \( \tau_{Ge} \) for Ge nucleation in the Au + AuGe system. The other is the time \( \tau_{Au} \) needed to add enough Ge to dissolve all of the Au, \( \tau_{Au} \propto V^{1/3} \rho^{-1} \), where \( \rho \) is the digermene pressure and \( V \) is the initial Au volume.\(^{26,27}\)

Near \( T_e \), the divergence of \( \tau_{Ge} \) guarantees that \( \tau_{Au} \ll \tau_{Ge} \) so the Au is entirely dissolved long before Ge can nucleate. Only after the Au is gone can the liquid composition rise above the liquidus value, so that Ge nucleates within the experimental time frame. This regime corresponds to normal VLS.

However, \( \tau_{Ge} \) decreases rapidly with decreasing temperature. At sufficiently low temperature \( \tau_{Ge} < \tau_{Au} \) thus solid Au is still present when Ge nucleates from the liquid. This corresponds to the mixed regime, below ~280 °C. All three phases are present, but the liquid decomposes into Au and Ge too rapidly to capture in video-rate imaging.

Finally, if the temperature is low enough, \( \tau_{Ge} < \tau_{Au} \) then Ge nucleates when the liquid volume is negligible compared to the Au particle size. Because the liquid initially forms as a film wetting the Au,\(^{23,24}\) a small amount of liquid will not be visible in TEM. This gives a regime that appears in experiment as VSS, although within our model it is really the same as the mixed regime with an extremely thin liquid layer. (The subtleties of prewetting and atomically thin phases are beyond the scope of this discussion.) Thus, straightforward considerations of the Ge supersaturation in the liquid, and hence the time before Ge nucleation, can explain the three regimes, suggesting also that at sufficiently low temperature the VLS mechanism would involve a liquid layer so thin that it would be indistinguishable from VSS.

In conclusion, we have described the complex and interesting processes by which Ge nucleates from Au below the equilibrium eutectic temperature and at low pressure, explaining the three observed pathways, VLS, mixed, and “VSS”, through a model based on one key factor, the Ge nucleation rate. At the lowest temperatures the reaction appears to be through a VSS mode, but with an unexpectedly large solubility of Ge in solid Au. Our model suggests that this mode is still initiated by formation of a liquid AuGe layer in which more Ge can dissolve than would be expected in solid Au. The ability to grow single crystal Ge from the vapor phase at temperatures as low as 150 °C is encouraging for the integration of Ge with unconventional substrates such as plastics. This regime of primarily solid catalyst will also be important for the fabrication of complex nanowire-based structures. For example, it should enable growth of a Ge nanowire on a Si substrate with an abrupt compositional interface,\(^{32}\) since it avoids dissolution of a relatively large volume of substrate Si into the catalyst, as occurs at the start of VLS growth. In the other regimes we observe, we measure high supersaturations and solubilities of Ge in the catalytic particles. These observations show that the bulk phase diagram is a poor guide to the reaction pathways in these nanoscale systems; in situ observations allow us to quantify the conditions and kinetics that determine reaction pathways and therefore to understand and optimize the design and fabrication of complex nanoscale structures.

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