

Metastable Crystalline AuGe Catalysts Formed During Isothermal Germanium Nanowire Growth

A. D. Gamalski,^{1,*} J. Tersoff,^{2,†} R. Sharma,³ C. Ducati,⁴ and S. Hofmann¹

¹*Department of Engineering, University of Cambridge, Cambridge CB3 0FA, United Kingdom*

²*IBM T. J. Watson Research Center, Yorktown Heights, New York 10598, USA*

³*Center for Nanoscale Science and Technology, National Institute of Standards and Technology, 100 Bureau Dr., Gaithersburg Maryland 20899-6203, USA*

⁴*Department of Materials Science and Metallurgy, University of Cambridge, Cambridge CB2 3QZ, United Kingdom*

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We observe the formation of metastable AuGe phases without quenching, during strictly isothermal nucleation and growth of Ge nanowires, using video-rate lattice-resolved environmental transmission electron microscopy. We explain the unexpected formation of these phases through a novel pathway involving changes in composition rather than temperature. The metastable catalyst has important implications for nanowire growth, and more broadly, the isothermal process provides both a new approach to growing and studying metastable phases, and a new perspective on their formation.

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Rapid thermal quenching has long been known to produce metastable phases [1]. Understanding and controlling the nucleation of such phases is crucial to a wide range of materials, from high-performance steels [2] to pharmaceuticals [3]. Here, we report a new pathway to the formation of metastable phases, which is radically different from conventional thermal quenching. We focus on the Au-catalyzed growth of Ge nanowires (NWs) as a model nanoscale system. Video-rate lattice-resolved environmental transmission electron microscopy (ETEM) allows us to directly observe the formation of metastable AuGe phases under strictly isothermal conditions, the opposite limit from thermal quenching. Both hexagonal closed packed (hcp) and body centered tetragonal (bct) phases of AuGe are observed. We propose that these metastable phases occur due to changes in composition during NW growth, and that the necessary conditions for metastable AuGe formation occur naturally during the NW growth process and reflect the large deviations from equilibrium achievable in nanoscale systems. We speculate that the high Ge solubility in these metastable AuGe crystalline phases [4–8] facilitates stable vapor-solid-solid (VSS) NW growth.

Figure 1 shows catalyst particles at the tip of Ge NWs growing at temperatures between 220 °C and 270 °C in He diluted digermane (Ge_2H_6). The images are part of video sequences [9] recorded in bright field imaging conditions at the rate of 9 frames per second by a modified Tecnai F20 ETEM [10] operated at 200 kV with a differential pumping system and a digital video camera. Temperatures are measured by a thermocouple on the TEM holder mini furnace. The electron dose was typical for high resolution imaging, and the electron beam was never focused onto the specimen in order to minimize the effects of electron-beam-induced damage, gas dissociation [11], and modification of the specimen. The Au catalyst was prepared by thermal

evaporation (nominal Au thickness <2 nm) onto perforated SiO_2 membranes or onto 2000 mesh Cu TEM grids coated with a holey carbon film and an approximately 30 nm sputtered SiO_x layer. The samples were transferred in air to the ETEM.

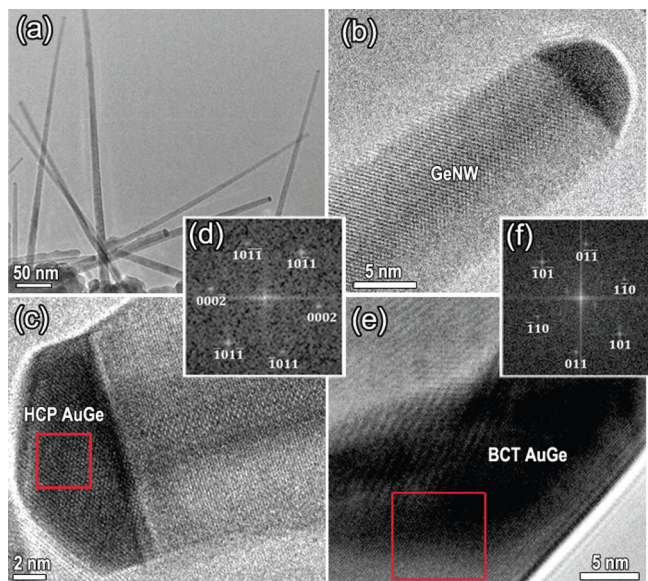


FIG. 1 (color online). Various high and low magnification bright field ETEM micrographs of Ge NWs growing from solid AuGe catalysts growing in (a) 6.0×10^{-1} Pa pure Ge_2H_6 at 273 °C, (b) 5.3×10^{-2} Pa Ge_2H_6 (30% mole fraction in He) at 272 °C, (c) 2.7×10^{-1} Pa (30% mole fraction in He) at 270 °C, and (e) 6.8×10^{-1} Pa Ge_2H_6 (30% mole fraction in He) at 224 °C. (d) Selected area FFT of the red boxed region of the catalyst particle in (c) which matches hcp β -AuGe viewed down the $[01\bar{1}0]_{\text{hcp}}^{(l)}$ axis. (f) Selected area FFT of the red boxed region of the catalyst particle in (e), which matches the spot pattern of bct γ -AuGe viewed down the $[\bar{1}\bar{1}1]_{\text{bct}}^{(l)}$ axis.

Prior to Ge_2H_6 exposure, the Au catalyst particles are crystalline with a face centered cubic (fcc) structure. Upon Ge_2H_6 exposure, the fcc Au nanoparticles transform into a AuGe eutectic liquid, even for isothermal growth at temperatures far below the AuGe bulk eutectic (361 °C) [12]. Upon Ge crystal nucleation and growth, the catalyst can remain liquid for seconds or minutes at the temperatures studied here. Eventually it solidifies and, as shown in Fig. 1, the system reaches a steady state where both catalyst and NW are in the solid phase, i.e., VSS growth.

The lattice-resolved ETEM data allow us to assign the crystal structures occurring during the entire process, in particular, during VSS growth. Figures 1(d) and 1(f) show the fast Fourier transforms (FFT) of the solid catalyst particles in Figs. 1(c) and 1(e), respectively. For the FFT assignment, we use published unit cell parameters [6,13,14] and calculate their theoretical electron diffraction spot patterns. The different crystal structures and cell parameters that best fit the FFTs are summarized in Table I.

Figure 1(d) shows the FFT of the catalyst particle in the high resolution image, Fig. 1(c). We find that the FFT is best matched to the known metastable hcp phase, denoted β , viewed down the $[01\bar{1}0]^{(I)}_{\text{hcp}}$ axis. Note that the superscript “(I)” indicates the imaging axis. Table II shows there is good agreement between the theoretical hcp unit cell and measured angles between reflections in Fig. 1(d). The closest possible match with fcc Au is viewed down $[101]^{(I)}_{\text{fcc}}$. The calculated values for FCC shown in Table II do not agree with the measured values for Fig. 1(d) shown in Table II. In addition to this, by comparing the ratios between reciprocal distances (measurements given in [15]) we find that the measured FFT deviates from the calculated β phase FFT by less than 2%.

Figure 1(f) shows the FFT of the catalyst particle imaged in Fig. 1(e). We find that the spot pattern in Fig. 1(f) is best fitted to the bct phase, denoted γ , viewed down the $[\bar{1}\bar{1}1]^{(I)}_{\text{bct}}$ axis. Table II shows that the angles between reflections for the theoretical bct unit cell are in good agreement with the measured reflection angles in Fig. 1(f). Again, by comparing the ratios between the reciprocal distances (measurements given in [15]) we find the measured FFT deviates from the calculated γ phase FFT by less than 4%. In contrast, we can rule out fcc—the closest match for fcc Au is viewed down $[101]^{(I)}_{\text{fcc}}$, which has calculated angles radically different from the values measured in Fig. 1(f).

TABLE I. Shown are the fcc Au, hcp β -AuGe [6], and bct γ -AuGe [13,14] unit cells used in this study.

Crystal structure	a (nm)	b (nm)	c (nm)
fcc Au, $Fm\bar{3}m$	0.408	0.408	0.408
bct γ -AuGe, $I4/mmm$	0.340	0.340	0.286
hcp β -AuGe, $P6_3/mmc$	0.289	0.289	0.474

In total we analyzed the FFTs of 17 lattice-resolved catalyst particles. We identified 4 catalyst particles that correspond to γ , eight cases of β , four which are either γ or β , and only one case of fcc Au, the equilibrium crystal structure. Of these 17 particles, 14 were imaged before cooling the sample to room temperature and removing it from the ETEM. During gas exposure and growth we observed two cases of γ , four cases of β , and two cases that are either β or γ . In other observations after turning off the source gas, but still in vacuum at the growth temperature, we observed one case of γ , two cases of β , one fcc Au, and two cases that were either γ or β . The remaining one case of γ and two cases of β were identified with *ex situ* high resolution TEM approximately 2 yr after the initial NW growth experiment, indicating that these metastable phases are very long-lived at room temperature.

The β and γ phases of AuGe are previously known to form by quenching liquid AuGe alloys [5,8,16,17]. Metastable phases have also been observed after the cooling of Ge NW catalysts [18–21], and attributed very reasonably to the rapid cooling of these nanoscale structures, or the suppression of diffusion at such low temperatures. Thus, it is quite surprising to find them forming at constant temperature, and moreover at a temperature high enough to sustain growth. One possible explanation would be if diffusion is too slow to allow separation of the liquid into Ge and Au phases, so that instead the liquid freezes into a crystal of the same composition [1,20,22–24]. This is appealing and consistent with the fact that the metastable crystal phases occur over a broad composition range [4]. However, as the catalyst solidifies into the metastable crystalline phase we observe rapid advancement of the interface with the Ge crystallite [25]. This indicates that formation of the γ and β phases involves considerable diffusive redistribution of Ge. We therefore sought an alternative to the occurrence of a diffusionless transformation as an explanation for our observations.

Here we propose a possible formation mechanism, which is novel but consistent with the known thermodynamics and kinetics of the Au-Ge system. We begin with the calculated [26–28] equilibrium Au-Ge phase diagram, Fig. 2. The red Au liquidus line is extended to show the boundary for equilibrium between Au and the metastable liquid below the eutectic. The metastable γ and β phases exist over a range of composition [4,5,8]. Since there is no detailed thermodynamic data, we take a crude but reasonable model for the free energy function $g_m(x, T)$:

$$g_m(x, T) = g_0(x, T) + h_{\text{mix}}(x) - s_{\text{mix}}(x)T. \quad (1)$$

This is the classic “regular solution” model [29], where x is the mole fraction of Ge in the $\text{Au}_{1-x}\text{Ge}_x$ alloy, T is temperature, $g_0(x, T) = (1-x)g^{\text{Au}}(T) + xg^{\text{Ge}}(T)$ is the free energy for unmixed Au and Ge in an hcp structure [26–28], $s_{\text{mix}}(x) = -k_B[(1-x)\ln(1-x) + x\ln(x)]$ is the molar entropy of mixing, and k_B is the Boltzmann constant.

TABLE II. The predicted and measured angles between the FFT reflections in Figs. 1(d) and 1(f). For comparison we include, for fcc Au, the calculated angles between the reflections viewed down the $[101]_{\text{fcc}}^{(l)}$ direction, which is the direction that gives the best match to the experimental FFTs. The measured angles are averaged over reflections with common symmetry. The error in the measured angles indicates 1 standard deviation in the measurement uncertainty.

FFT	Crystal structure and imaging axis	Family of reflections	Calculated angles between reflections	Measured angles between reflections
Figure 1(d)	hcp β -AuGe; $[01\bar{1}0]_{\text{hcp}}^{(l)}$	$\{\bar{1}01\bar{1}\}/\{\bar{1}011\}$ $\{0002\}/\{10\bar{1}1\}$	55.6° 62.2°	56.7° \pm 1.4° 62.1° \pm 1.4°
Figure 1(f)	bct γ -AuGe; $[\bar{1}\bar{1}1]_{\text{bct}}^{(l)}$	$\{101\}/\{011\}$ $\{\bar{1}\bar{1}0\}/\{101\}$	54.1° 63.0°	52.1° \pm 1.8° 64.1° \pm 1.8°
...	fcc Au; $[101]_{\text{fcc}}^{(l)}$	$\{020\}/\{11\bar{1}\}$ $\{\bar{1}\bar{1}\bar{1}\}/\{11\bar{1}\}$	54.7° 70.5°

The mixing enthalpy is $h_{\text{mix}}(x) = Cx(1-x)$, where the value $C = -12.5 \text{ kJ mol}^{-1}$ is chosen to give a plausible phase boundary for the present discussion (we expect that the liquidus curve for the γ phase will be similar to the β liquidus, so we do not distinguish between these here).

With Eq. (1), we can include on the phase diagram (Fig. 2) the calculated liquidus for the metastable AuGe phase. This is shown as an additional green dashed curve, calculated by the common tangent construction [2]. Although crude, the model illustrates two key properties that are important for understanding this system's behavior. The first is that the metastable liquidus curve has a smaller slope than the fcc Au liquidus. This occurs automatically for any reasonable value of C , reflecting the higher Ge composition of the metastable phase. The second is that the intersection of the stable and metastable liquidus curves must lie below the eutectic point. We know this

on physical grounds—otherwise the phase would occur in equilibrium—and it provides a constraint on the possible range of C .

Next we consider the system trajectory on the phase diagram during growth. The AuGe liquid can form at temperatures far below the equilibrium eutectic [12]. Then, due to the large barrier to nucleate solid Ge, during the growth process the liquid can become so highly supersaturated with Ge that nucleation of fcc Au is thermodynamically forbidden, despite the low T [30]. This corresponds to compositions to the right of the Au liquidus (including its extension into the metastable regime, shown dotted in Fig. 2). When solid Ge finally nucleates, the Ge particle grows rapidly due to the high supersaturation, and the liquid composition drops correspondingly, as suggested by the horizontal arrows from points a and b in Fig. 2. Once the composition crosses the Au liquidus, it becomes

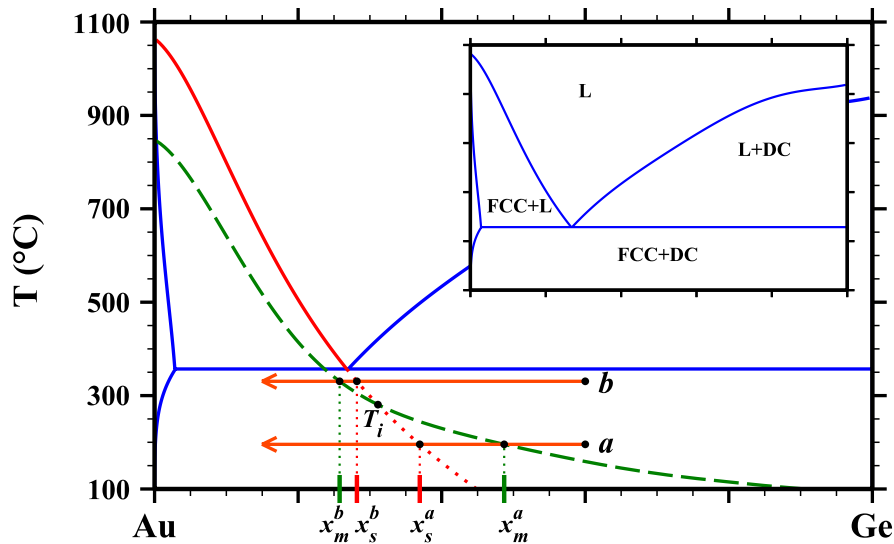


FIG. 2 (color online). Calculated [26–28] phase diagram for the Au-Ge system with the metastable AuGe liquidus curve. The solidus curves, diamond cubic (DC) liquidus curve, and eutectic temperature are given in blue. The red solid curve indicates the fcc Au liquidus line above the eutectic temperature with the extended subeutectic fcc Au liquidus indicated by the dotted red curve. The green broken line indicates the metastable AuGe liquidus. The temperature where the two liquidus lines intersect is indicated by T_i . The inset is the unaltered equilibrium Au-Ge phase diagram.

possible for fcc Au to nucleate. Similarly, the crystalline metastable AuGe phase can nucleate once the liquid composition crosses the dashed green line in Fig. 2.

The low- T regime, below the point where the two liquidus curves cross, is particularly interesting. For the case labeled “a” in Fig. 2, there is a range of compositions $x_s^a < x < x_m^a$ where metastable AuGe can nucleate, but fcc Au cannot. Even if the system evolves slowly, the thermodynamics would dictate the formation of a metastable AuGe catalyst particle. Therefore, we might expect that below T_i , all of the liquid AuGe particles will transform into solid metastable AuGe catalysts. If so, subsequent decomposition of the AuGe into fcc Au and Ge would require nucleation of fcc Au in the solid AuGe, and subsequent diffusion of material through solid AuGe, which will be extremely slow compared to diffusion through the liquid.

In the case labeled “b,” thermodynamics favors formation of a fcc structure after the composition of the liquid passes though the fcc liquidus line, while nucleation of the metastable phase is still not possible in the range $x_m^b < x < x_s^b$. Nevertheless, it may be possible to form a solid metastable AuGe catalyst in this temperature range. We expect that the interfacial energy between the metastable AuGe solid and the liquid is lower than between fcc Au and the AuGe liquid, since the former involves a much smaller discontinuity in composition. If so, solid AuGe may nucleate more readily than fcc Au. In process *b* (Fig. 2), if a large nucleation barrier prevents formation of fcc Au before the system passes the metastable liquidus line at x_m^b , the lower interfacial energy of metastable AuGe could cause this phase to nucleate first.

Metastable AuGe phase formation by rapid compositional variations during NW growth has intriguing similarities to thermal quenching. Just as we could expect different behavior at fixed T above or below the liquidus crossing point T_i , for quenching we could expect correspondingly different behavior for liquid composition to the left or right of this point, respectively. However, there are also important differences. The quenching of macroscopic systems typically gives a mixed-phase solid. In contrast, very rapid composition variation may be limited to nanoscale systems, where a pure single phase is virtually guaranteed. Also, rapid composition variation occurs naturally during the isothermal NW growth process, while rapid temperature variation would require disrupting the growth process.

The different kinetic pathways observed here are schematically illustrated in Fig. 3, with the various system states labeled (i–vi). States i–iii represent the transformation of the solid Au catalyst particle into Au-Ge liquid during Ge_2H_6 gas exposure. The metastable liquid becomes increasingly Ge rich until a Ge crystal seed nucleates, state iv. After nucleation, a brief period of solid Ge growth by the VLS mechanism occurs. The liquid

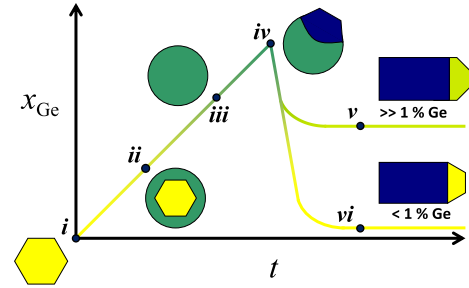


FIG. 3 (color online). A schematic plot illustrating the observed Au-Ge catalyst states plotted against the Ge composition in the catalyst x_{Ge} and time t (not drawn to scale). Yellow faceted shapes indicate fcc Au, solid Ge is given in blue, and metastable AuGe is given by the light green faceted solid. Liquid AuGe is indicated by the dark green circles. From quenching experiments, we expect that the metastable AuGe solid (state v) has composition $\approx 15\%$ – 50% Ge, while fcc Au has below 1% dissolved Ge [4–8].

catalyst particle can solidify into a metastable or stable phase, states v or vi. The thermodynamically favored end point is vi, the formation of fcc Au. Yet we almost never see this. Rather, we see the transition from iv to v, and much of the discussion above has focused on explaining this unexpected behavior.

In conclusion, we have observed the formation of solid AuGe metastable phases during isothermal Ge NW growth, and have proposed a mechanism to explain it. This process illustrates the striking new behavior that can occur in nanoscale systems, where very large supersaturations are readily achieved, opening kinetic pathways for solidification generally unavailable in the bulk. The small size also results in a single crystal, which facilitates characterization and minimizes extrinsic effects. We therefore believe that NWs and similar systems will provide a fruitful arena for the study of nonequilibrium phases.

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*adg40@cam.ac.uk

†tersoff@us.ibm.com

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- [10] Disclaimer: The full description of the procedures used in this paper requires the identification of certain commercial products and their suppliers. The inclusion of such information should in no way be construed as indicating that such products or suppliers are endorsed by NIST or are recommended by NIST or that they are necessarily the best materials, instruments, software, or suppliers for the purposes described.
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