

Growth and motion of liquid alloy droplets of Au on Ge(110)

B. H. Stenger, A. L. Dorsett,¹ J. H. Miller, E. M. Russell, C. A. Gabris,² S. Chiang³

Department of Physics
University of California Davis
1 Shields Avenue
Davis, CA 95616-5270, USA

Abstract

The growth of low-dimensional nanostructures of Au on Ge(110) and their temperature-induced motion were observed with Low Energy Electron Microscopy (LEEM). Ge(110) was dosed with 0.5–4 ML of Au and heated to 850°C. Above 500°C, liquid AuGe eutectic alloy islands grew on the surface. Islands were 0.3–3.0 μm in width, 1–10 μm in length, and elongated in the $[1\bar{1}0]$ direction. Above 600°C, islands began moving with speeds of 0.1–1.0 μm/s, absorbing smaller stationary islands upon collision and increasing in size to more than 100 μm in width. A temperature gradient of ~0.017 °C/μm across the sample results in a gradient in the Ge concentration across the islands, inducing their movement in the direction of increasing temperature. Optical microscopy confirmed that the large islands moved from the cooler edges of the sample towards its hotter center. The mechanism for motion of the droplets is discussed, and the island velocities fit well to a model for diffusion-driven motion of the liquid droplet. When the temperature was subsequently lowered, islands became supersaturated with Ge, which crystallized on the island edges.

¹ Present Address: Department of Physics, University of California, Santa Barbara.

² Present Address: Department of Electrical and Computer Engineering, Mississippi State University.

³ Corresponding Author, e-mail: chiang@physics.ucdavis.edu

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1. Introduction

Metal on semiconductor surfaces are systems of interest due to their importance in nanoscale technology, specifically metal contacts on semiconductor devices. The growth of 1-dimensional atomic chains has previously been observed for Au and Pt on Ge(001) [1-3] and Au on vicinal Si(111)[4, 5]. The Ge(110) and Si(110) surfaces have an anisotropic unit cell that has been shown to produce 1-dimensional structures in metal on semiconductor systems [6-9]. Monatomic nanowires were recently observed in an STM study of <1 ML of Au and Pt on Ge(110) [10]. Previously, we reported the growth of larger nanowires, ~100nm in width, in Ag/Ge(110) [11], and similar island growth was expected for Au/Ge(110). Instead of nanowire growth, however, we observed the formation of liquid eutectic alloy islands at high temperature, which were elongated due to the anisotropy of the substrate. The formation of 3D Au structures was also observed above a high temperature dewetting transition in the study of Au/Ge(001).[12]

Using low energy electron microscopy (LEEM), we observed movement of the eutectic alloy islands that is caused by a temperature gradient across the surface of the sample. Temperature gradient induced movement of liquid eutectic islands has been observed previously for Pt/Si(001) [13], Au/Si(110) [14], and Pt/Ge(110)[3]. These eutectic alloys are relevant to the vapor-liquid-solid (VLS) growth of Si and Ge nanowires.[15]. When VLS is used to fabricate Si nanowires, chemical vapor deposition of Si onto an alloy droplet of Au-Si results in supersaturation and nucleation of Si at the liquid-interface, leading to the growth of vertical nanowires. Understanding the dynamics of the island motion in the Au-Ge system discussed in this paper, which is closely related to the VLS

process, could be useful for controlling the arrangement of droplets that could catalyze nanowire growth in VLS.

2. Experimental

Measurements were performed with an ultrahigh vacuum (UHV) low energy electron microscope (LEEM, Elmitec GmbH). The LEEM is part of the Advanced Surface Microscopy Facility at the University of California at Davis, which consists of LEEM, a scanning tunneling microscope (STM, Oxford Instruments), and an x-ray photoemission spectrometer (XPS, Vacuum Generators) integrated together in a system of connected UHV chambers [16]. Samples of ~1 cm x 1 cm were cut from Sb-doped Ge(110) wafers (MTI Corporation) with a miscut of <5°. The Ge samples were cleaned in UHV with alternating cycles of Ar⁺ sputtering (450 eV, 5uA) for 15 minutes and annealing at 800°C for 10 minutes. Electron beam heating with a tungsten filament located 3mm beneath the sample was used to control the temperature of the sample. The temperature of the sample was measured with a type-K thermocouple beneath the edge of the sample and, for temperatures exceeding 500°C, with an infrared pyrometer with an emissivity setting of 0.42. We estimate the error in temperature measurement as ±20°C. Differences in temperature across the sample were measured in the XPS chamber, where the sample was placed in front of a large window for more precise measurement with the infrared pyrometer. At 800°C, the temperature at the center of the sample was ~60°C higher than the temperature at the edge of the sample, with the color difference between the center and the edges apparent to the naked eye. The reported temperatures in this

paper refer to the temperature at the center of the sample. LEEM and low energy
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electron diffraction (LEED) measurements were made between room temperature and 850°C. Au was deposited onto the sample using direct evaporation from a gold wire melted onto a resistively heated tungsten filament.

After deposition of Au, the XPS spectra of the sample were measured with Al K α x-rays. Using CasaXPS software [17], a Shirley background [18] was subtracted from the spectra, and the areas of the Ge 3d and Au 4f peaks were measured. To determine the Au coverage of the sample, the ratio of areas of the peaks was compared with the ratio of areas of peaks in simulated spectra produced with Simulation of Electron Spectra for Surface Analysis (SESSA) software [19]. The sample was not removed from the UHV system between the LEEM and XPS measurements.

Defects on the LEEM channel plate produce marks in the presented LEEM images. These marks, shown in figure 1, do not represent features on the sample surface.

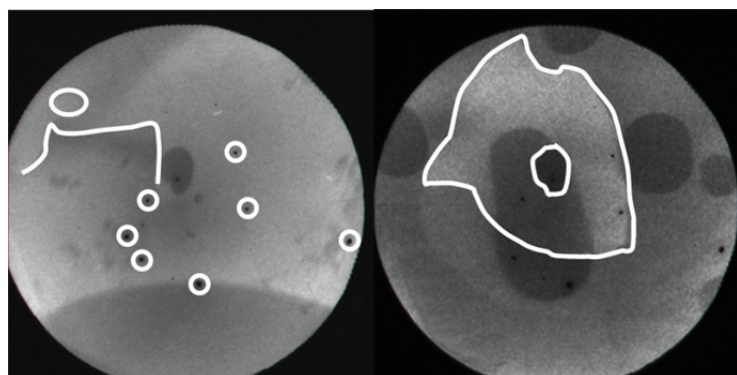


Figure 1: Several defects on the LEEM channel plate are outlined in white. These marks in the presented data do not represent surface features.

3. Results and discussion

Ge(110) samples at room temperature were dosed with 1–4 ML of Au. During deposition, LEED measurements show a change from the $c(8 \times 10)$ and (16×2) patterns characteristic of the clean Ge(110) surface to a diffuse (1×1) pattern, with no significant change in specular intensity.

After deposition, when the samples were heated above 500°C, liquid Au/Ge eutectic alloy islands began to nucleate and grow (Figure 2). Islands were elongated along the $[1\bar{1}0]$ direction and continued growing in both length and width until reaching a size of 1–10 μm in length and 0.3–2 μm in width. During growth, the length of the islands increased linearly with time, but the width would repeatedly cease growing and then later resume. Some smaller islands decreased in size and eventually vanished. Both the number and size of islands increased with coverage. When two islands came into contact during growth, they were observed to rapidly merge into a single island. The smaller of the two islands collapsed over a period of <0.5 seconds, accompanied by an increase in size of the larger island.

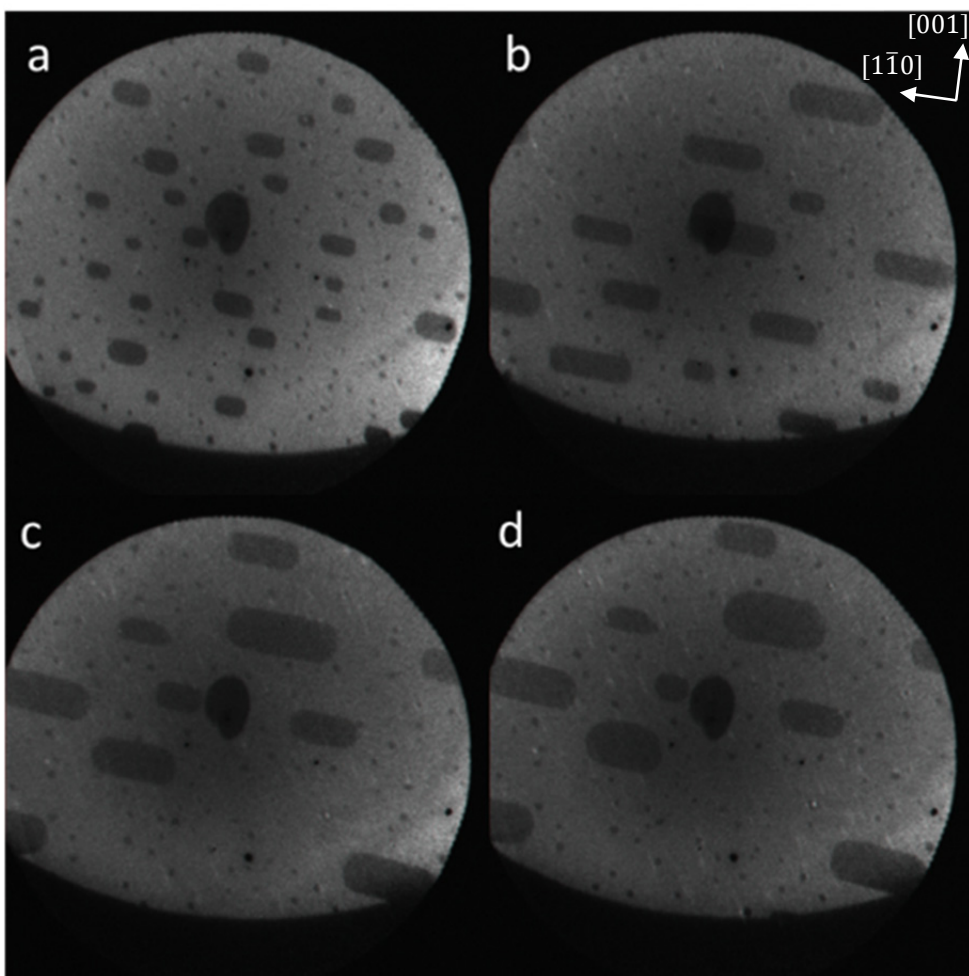


Figure 2: LEEM images of island growth after deposition of 4 ML Au on Ge(110) at room temperature, after annealing at 600° C for (a) 1 min, (b) 4 min, (c) 6 min, and (d) 7 min. 10 μ m field of view (FOV). E=10.3eV.

Island growth during deposition at 600°C is shown in Figure 3. Islands grew at similar rates during deposition at high temperature, compared to growth during heating after deposition at room temperature, but the final dimensions of the islands differed. After high temperature deposition, islands had lengths of 1–4 μm and widths of 0.5–3 μm, whereas typically longer and narrower islands formed after room temperature deposition and subsequent annealing.

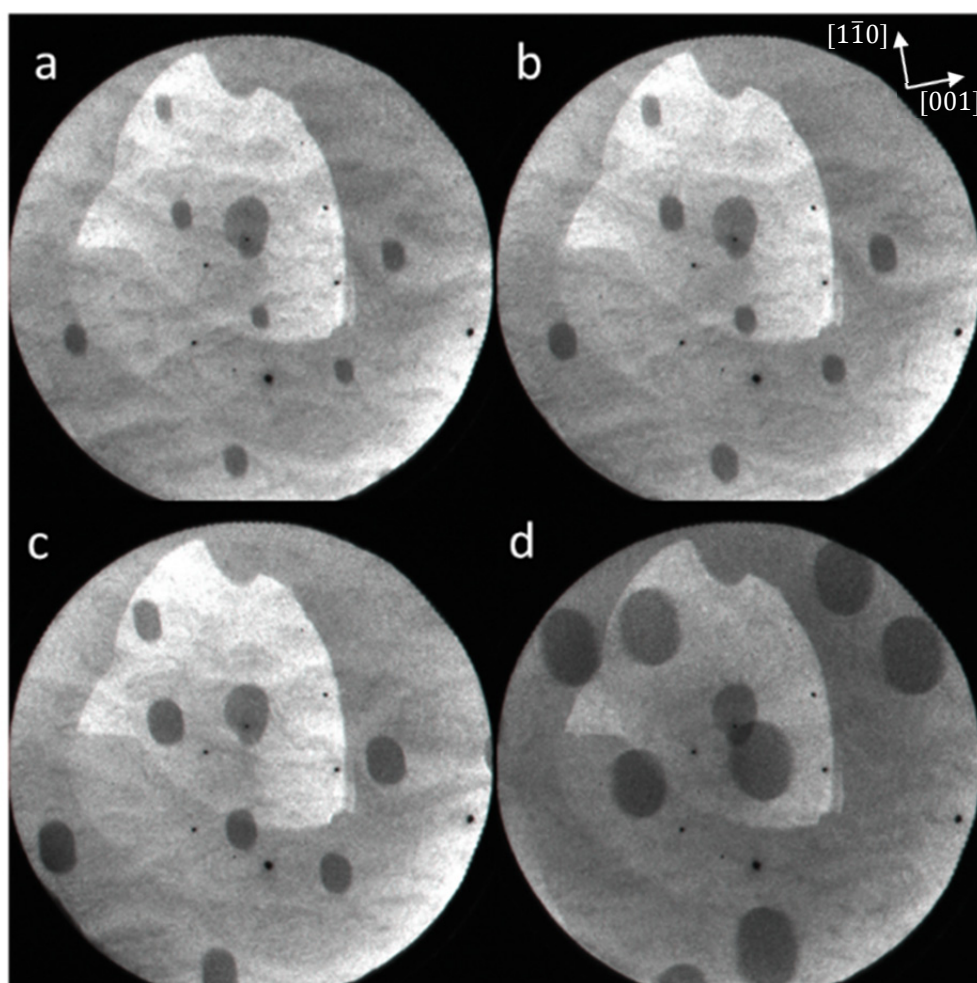


Figure 3: LEEM images of Au island growth on Ge(110) at 600° C after (a) 1 min, (b) 5 min, (c) 10 min, and (d) 20 min of Au deposition. The final coverage is 3 ML. 10 μm FOV. E=8.6 eV.

At temperatures above 600°C, islands were observed to begin moving spontaneously with velocities of 0.1–1 μm/s along the $[1\bar{1}0]$ direction. Islands appeared to initiate movement at random, with larger islands more likely to move than smaller islands. The movement of an island often occurred immediately after two smaller islands merged into a single larger island. More slowly moving islands (<0.3 μm/s) typically stopped moving after a few seconds. The island velocity increased with higher temperature, and reducing the temperature caused islands to stop. With the exception of collisions with other islands, the size and shape of islands did not change during movement. At particular electron energies, we could observe a trail that was left on the surface behind the islands as they moved. These, however, are not evident in the figures shown.

This spontaneous movement can be explained by a mechanism previously observed in Au/Si(110) [14], Au/Si(111) [20], and Pt/Si(001) [13]. An eutectic alloy of Au-Ge forms as Ge is dissolved into the deposited Au. From the Au-Ge bulk phase diagram, the equilibrium concentration of Ge in the Au-Ge alloy droplet depends on temperature, with a higher Ge concentration at higher temperature [21]. The temperature gradient across the sample ($\sim 0.017^\circ\text{C}/\mu\text{m}$) creates a gradient in the equilibrium Ge concentration across the Au-Ge island. Ge dissolves into the island at the higher temperature edge and crystallizes out of the island at the low temperature edge. Diffusion of Ge through the island, from high temperature to low temperature, maintains a uniform concentration. This diffusion of Ge causes movement of the island in the direction of increasing temperature. The crystallized Ge at the trailing edge of the islands leaves the observed trails following the path of the moving islands. Since such trails were determined to be Si nanowires formed by crystallization of Si behind the islands for the

system of Au/Si(110) [14], we assume that these correspond to crystallized Ge in our system.

While the mechanisms of island growth and movement are similar to those of previously studied systems, the details of the observed phenomena differ significantly. Islands grew with a lower aspect ratio than those observed for Au/Si(110), which had similar lengths but widths of 0.1–0.4 μm . The island movement for Au/Si(110) was observed close to the eutectic temperature of 360°C and had lower velocities of <2 nm/s. The study of Pt/Si(001) reported similar island velocities to those we have measured, but the dynamics of the movement differ due to the anisotropic nature of the Ge(110) surface, as discussed below.

No island growth was observed for temperatures less than 500°C, which is well above the Au-Ge eutectic temperature of 361°C [21]. Low energy electron diffraction (LEED) measurements from a 25 μm diameter area of the sample show a reversible phase transition at 500°C from a lower temperature (4x5) structure to a higher temperature (2x1) structure (Figure 4). The more diffuse LEED pattern for the (2x1) phase indicates less large scale ordering. In contrast, the lower temperature (4x5) phase appears to have more long range order. If that phase impedes the diffusion of Au, that could prevent the formation of islands below 500°C. Alternatively, at lower temperatures, the islands may be too small to observe in LEEM images.

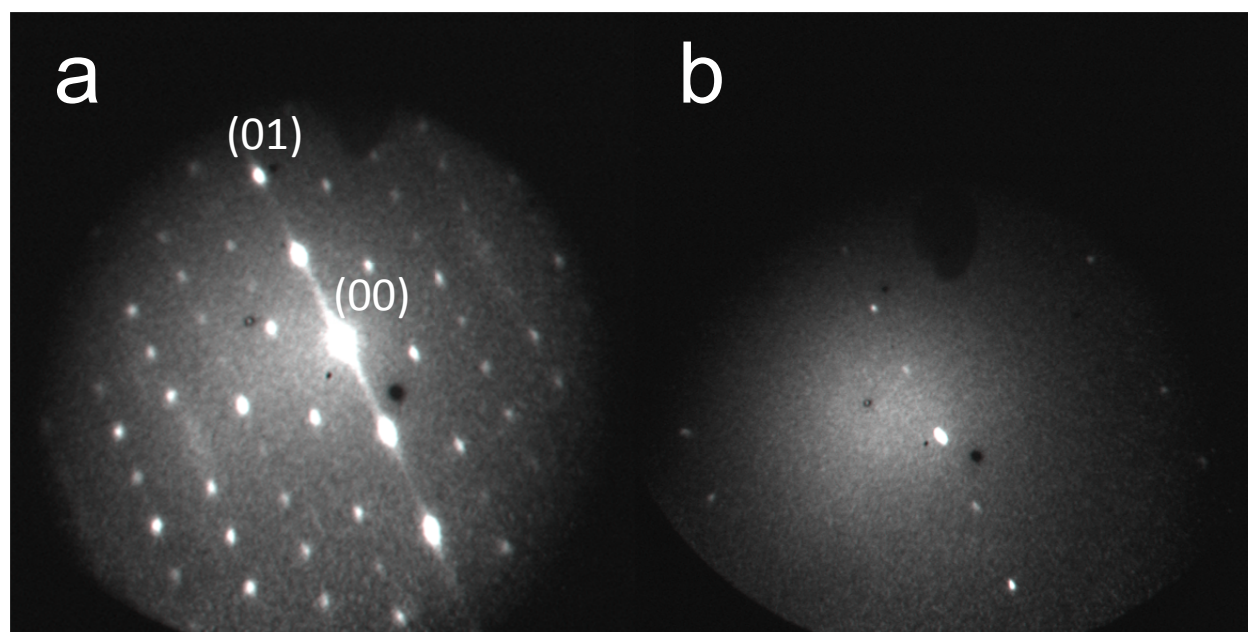


Figure 4: LEED of 4 ML Au on Ge (110). (a) The (4x5) structure at 410°C. $E = 8.3$ eV. The (00) and (01) spots are circled and labeled. The (10) and (11) spots are just outside of the field of view. (b) The (2x1) structure at 650°C. $E = 20$ eV.

Using a smaller electron beam diameter of 5 μm , LEED measurements can be taken either on top of islands or on the background regions between the islands. When clear LEED patterns are observed, they come from the crystalline structure of the surface between the islands. No LEED pattern was visible when the electron beam was placed on the islands themselves, giving evidence that they are liquid droplets.

The velocity of islands can either be limited from the rate of diffusion of Ge through the island, similar to the case of Au/Si(110), or from the rate of dissolution of Ge into the advancing front of the island, as is the case for Pt/Si(110). If the diffusion of Ge is the limiting factor, the rate of dissolving and crystallizing Ge at the high and low temperature ends of the island, respectively, must be equal and the island is expected to maintain a constant shape during movement. If the dissolution of Ge is the limiting factor, the rates

of dissolving and crystallizing may differ, resulting in a change in the size of the island

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during movement. The observed islands maintained a constant size and shape, indicating that the movement is diffusion-limited.

As the movement is diffusion-limited, we can use an equation for the migration of a liquid droplet through a solid by temperature gradient induced diffusion to estimate the expected velocity of the islands across the surface.

$$V = \frac{G}{(C_s - C_l)m} D$$

where D is the diffusion coefficient, G is the temperature gradient, m is the liquidus slope, and C_s and C_l are the atomic fraction concentrations of the solid medium and liquid droplet, respectively [13, 22, 23]. The diffusion coefficient, D , has a temperature dependence from the Arrhenius equation,

$$D = D_0 \exp\left(-\frac{E_D}{k_B T}\right)$$

where D_0 is the pre-exponential factor, E_D is the activation energy, k_B is the Boltzman constant, and T is the absolute temperature. Values of D_0 and E_D have been experimentally determined for diffusion of liquid AuGe by Tanimoto, et al [24].

$$D_0 = 5.34 \times 10^{-8} \text{ m}^2\text{s}^{-1}$$

$$E_D = 1.65 \times 10^{-1} \text{ eV}$$

The observed temperature gradient is 1.7×10^4 °C/m. C_s is assumed to be 1. C_l and m are temperature dependent and can be obtained from the Au-Ge phase diagram. With this model, the island velocity is dependent on temperature and independent of island size or shape. The calculated and measured dependences of velocity on temperature

are shown in Figure 5. They agree well for higher measured velocities ($>0.2 \mu\text{m/s}$). At lower velocities, the measured dependence on temperature diverges from the calculated dependence. These low island velocities all occurred shortly after islands began moving. Thus we can conclude that the diffusion limited model accurately describes the motion of islands once a constant velocity has been reached, but it is not an accurate model for the initial velocity, immediately after an island begins moving.

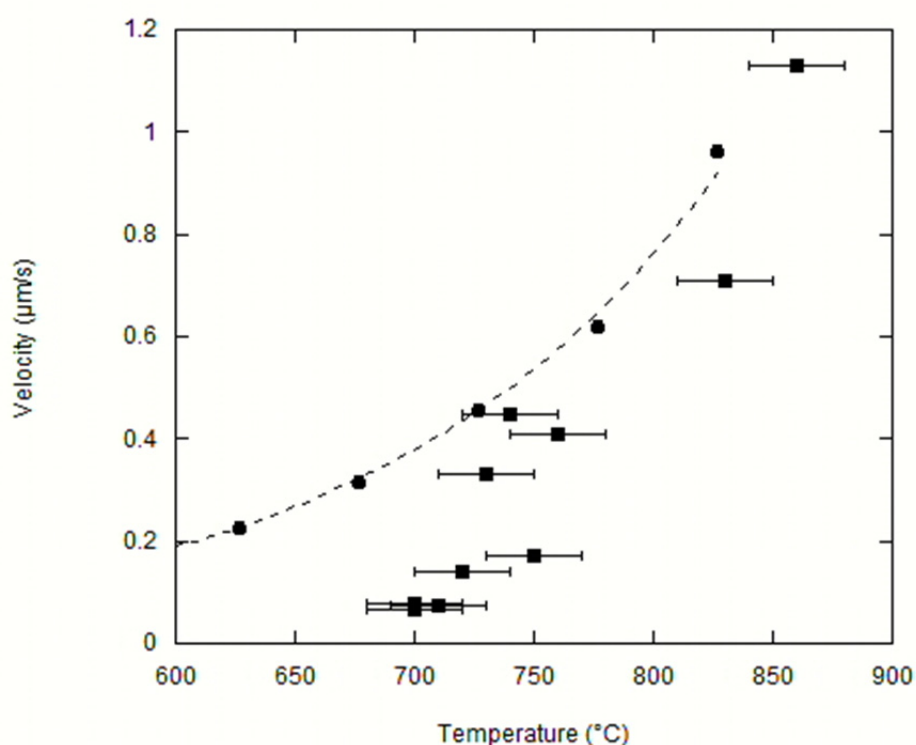


Figure 5: The temperature dependence of calculated island velocities (●) and measured island velocities (■). The dashed line is a guide to the eye from the calculated island velocities.

The shape of the islands, which is elongated along the $[1\bar{1}0]$ direction, is caused by an anisotropy in the dissolution rate of Ge. Etching of the Ge(100) surface has been shown to result in pits with sides formed by $\{111\}$ planes [25]. Due to the top layer of atoms of Ge(111) having three bonds each, in comparison to Ge(100) in which the top atoms have two bonds each, the dissolution rate of the Ge $\{111\}$ planes is slower than that for other planes. Ge in the surface beneath islands is dissolved as islands grow. The limited dissolution rate of the $\{111\}$ planes restricts growth perpendicular to the (100) direction, resulting in the formation of troughs with $\{111\}$ sides, extended in the $[1\bar{1}0]$ direction over which the islands grow.

The direction of the movement of the islands is also determined by the dissolution anisotropy of Ge. Dissolution of Ge occurred more rapidly at the ends of islands than at the sides of islands bordered by $\{111\}$ planes. While islands moved due to a temperature gradient, the direction of movement was generally restricted to the $[1\bar{1}0]$ direction, parallel to troughs formed during island growth. (Figure 6) Large islands ($>10\mu\text{m}$ is width) were observed moving in directions other than $[1\bar{1}0]$. At large scales, the effect of dissolution anisotropy on the direction of island movement likely became less significant than the effect of the temperature gradient on the island movement.

When larger islands began moving, islands below a threshold size remained stationary. The threshold size was temperature dependent and varied between samples. The model of diffusion driven motion of islands alone does not explain why this is the case. Islands may be pinned to defects, preventing motion. In addition, the difference in the direction of the temperature gradient driving the motion and the $[1\bar{1}0]$ direction in which the motion is constrained may also create a barrier to motion. Although the velocity of

islands is diffusion limited and independent of island size, for a stationary island the driving force to initiate movement should depend on the extent to which the high and low temperature ends of the islands are supersaturated and undersaturated with Ge. Therefore, the difference in temperature across the island, dependent on both temperature gradient and island size, will determine whether an island overcomes the barriers to island motion. Thus, a larger island, with a greater temperature difference between the ends of the island, will have a greater concentration difference and will begin moving before smaller islands.

When islands collided during movement, they would merge in the same manner as during island growth. After colliding with and absorbing a stationary island, the velocity of a moving island would briefly increase. Due to the high density of islands on samples with higher Au coverage, moving islands would frequently collide and absorb stationary islands. Repeated collisions over time caused islands to rapidly grow in size. Islands that were initially $\sim 1\ \mu\text{m}$ in width grew to widths of $>100\ \mu\text{m}$ (Figure 7).

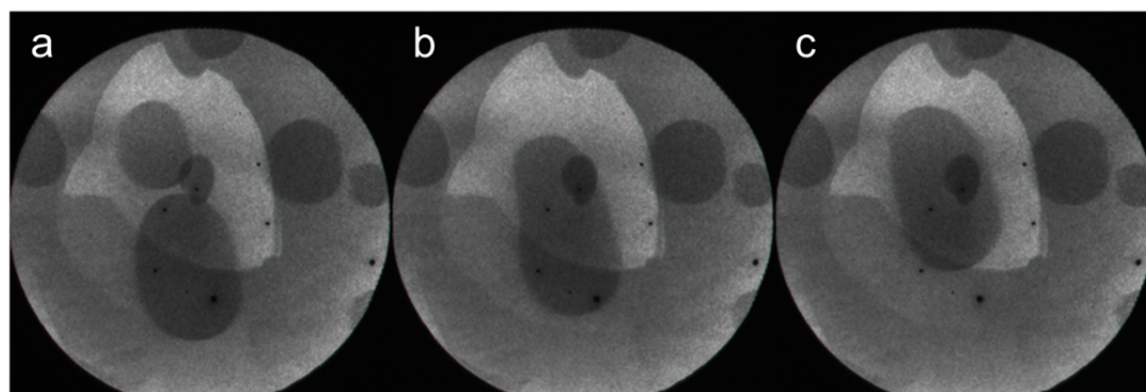


Figure 6: A moving island colliding with a stationary island and absorbing it. (b) and (c) are 4 and 7 seconds after (a). The Au islands are elongated along the $[1\bar{1}0]$ direction, and the island motion is along the same direction, as described in the text. Au coverage is 3 ML. The temperature is 760°C . $10\ \mu\text{m}$ FOV. $E=9.0\ \text{eV}$.

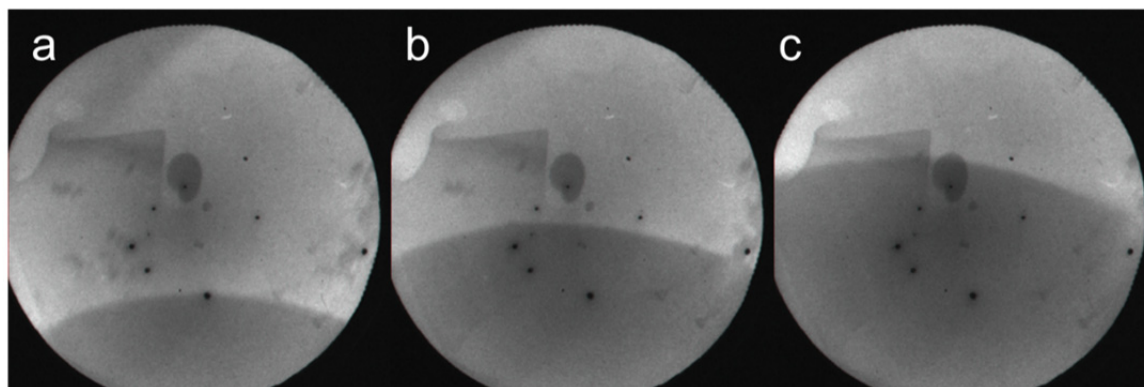


Figure 7: A large moving island after repeated merging of smaller islands. Au coverage is 2.5 ML. This island is large enough that the direction of motion is controlled by the temperature gradient instead of the dissolution anisotropy of Ge. (b) and (c) are 10 and 20 seconds after (a). The temperature is 800°C. 20 μm FOV. $E=10.0$ eV.

After removing the sample from the UHV system, the largest islands were observable with an optical microscope (Figure 8). The paths of travel of the islands, where all smaller islands had been absorbed, were also visible, revealing the path of movement over a larger scale than visible with LEEM. All paths showed movement from the lower temperature edge of the sample to the higher temperature center. The paths typically started along the $[1\bar{1}0]$ direction but curved as they approached the center of the sample, consistent with the LEEM observations of the motion of large islands.

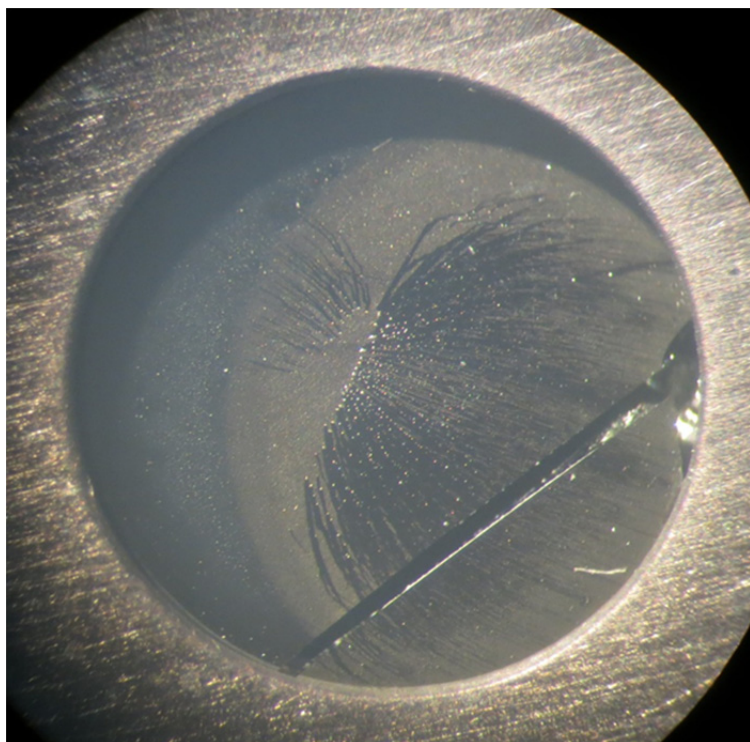


Figure 8: Photograph of Au-Ge alloy islands with trails on Ge(110) observed with optical microscope after the sample was removed from the UHV system; the crack in the sample occurred after the experiments. The circular area of the uncovered sample has a diameter of 7mm.

Referring to the phase diagram, the concentration of Ge in the eutectic alloy decreases with temperature. Therefore, as the temperature is lowered, we expect that the islands should become supersaturated with Ge, resulting in the crystallization of excess Ge.

After annealing above 600°C, the Ge samples were allowed to cool to room temperature. Immediately upon lowering temperature, the islands began to contract. An outline of the original extent of the island remained visible, as shown by the ovals in Figure 9b. This contraction is consistent with the crystallization of Ge, initially at the edges of the islands. The remaining outlines, left by Ge deposited during the crystallization of the islands, are similar to the trails behind moving islands, discussed

above. In the case of crystallizing during cooling, a larger quantity of Ge segregates from the island, because the change in temperature is significantly larger than the lateral temperature gradient during island motion. As a result, these outlines are more apparent than the trails observed previously.

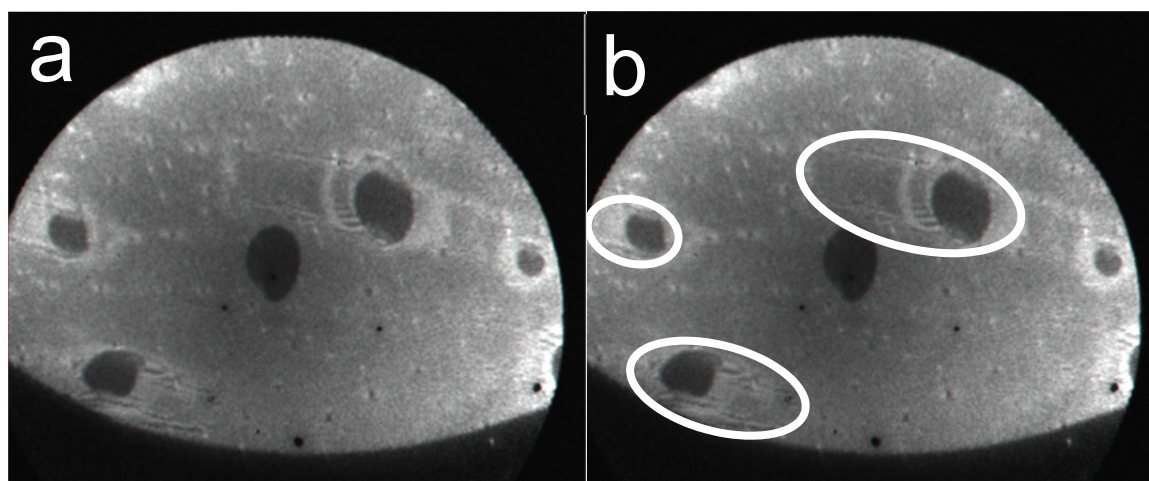


Figure 9: Crystallized Au-Ge islands during cooling from an initial temperature of 600°C. (a) and (b) show the same image with the original extent of the islands before crystallization indicated with circles in (b). The Au coverage is 4 ML. 10 μm FOV. $E = 6.4$ eV.

4. Conclusions

The behavior of liquid eutectic Au-Ge islands on Ge(110) was studied with LEEM. When heated above 500°C, the islands nucleated and grew to 0.5–3 μm in width. The islands were elongated in the $[1\bar{1}0]$ direction due to an anisotropy in the dissolution rate of Ge, but with a significantly lower aspect ratio than islands observed in the similar systems, Au/Si(110) and Ag/Ge(110). Above 600°C, a temperature gradient across the surface caused some islands to move with velocities of 0.1–1.0 $\mu\text{m}/\text{s}$. The island velocity increased with higher temperature, and the observed island velocities fit well to a simple

model of diffusion-driven motion of a liquid droplet. Upon collision, islands merged, forming islands of $>60\mu\text{m}$ in width after repeated collisions. For smaller islands, movement was restricted to the $[1\bar{1}0]$ direction as a result of the anisotropy in the dissolution rate of Ge planes, while larger islands moved in the direction of increasing temperature. When cooled, the islands become supersaturated with Ge, and excess Ge crystallizes along the island edge.

Our study of Au/Ge(110) has elucidated interesting details in the formation of the island shapes and sizes, as well as the velocities and directions of their motion at high temperature. Clearly, the physical properties of the alloy islands are closely related to the bulk alloy phase diagram and the local sample temperatures. The sample temperature gradient drives the diffusion-driven motion of the liquid alloy droplets. Understanding the processes of growth and motion of the islands may lead to improvements in catalytic growth of nanostructures in the future.

5. Acknowledgements

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Supplementary Information

M1. LEEM movie of a moving island during annealing at 760°C. Islands are elongated along $[1\bar{1}0]$ direction, and the moving island also travels along the $[1\bar{1}0]$ direction. The sample was moved during the movie to keep the island within the field of view. Au coverage is 3 ML. 10 μ m FOV. E=9.0eV. Movie is speeded up by factor of 20.

M2. LEEM movie of a large moving island during annealing at 860°C. For this large island, the direction of motion is controlled by the temperature gradient instead of the dissolution anisotropy of Ge. The sample was moved during the movie to keep the island within the field of view. Au coverage is 3 ML. 10 μ m FOV. E=9.8eV. Movie is speeded up by factor of 5.

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