High temperature growth of Ag phases on Ge(111)

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The growth of the (3 × 1) and ($\sqrt{3} \times \sqrt{3}$)R30° phases of Ag on Ge(111) on substrates at temperatures from 540 to 660 °C is characterized with low energy electron microscopy (LEEM) and low energy electron diffraction (LEED). From 540 °C to the Ag desorption temperature of 575 °C, LEEM images show that growth of the (3 × 1) phase begins at step edges. Upon completion of the (3 × 1) phase, the ($\sqrt{3} \times \sqrt{3}$)R30° phase is observed with a dendritic growth morphology that is not much affected by steps. For sufficiently high deposition rates, Ag accumulates on the sample above the desorption temperature. From 575 to 640 °C, the growth proceeded in a manner similar to that at lower temperatures, with growth of the (3 × 1) phase to completion, followed by growth of the ($\sqrt{3} \times \sqrt{3}$)R30° phase. Increasing the substrate temperature to 660 °C resulted in only (3 × 1) growth. In addition, for samples with Ag coverage less than 0.375ML, LEEM and LEED images were used to follow a reversible phase transformation near 575 °C, between a mixed high coverage phase of [(4 × 4) + (3 × 1)] and the high temperature, lower coverage (3 × 1) phase. © *2013 American Vacuum Society*. [http://dx.doi.org/10.1116/1.4772623]

I. INTRODUCTION

Ge(111) and Si(111) are well understood surfaces that have been studied extensively as substrates for growth. Nevertheless, additional experiments using numerous surface science techniques continue to reveal new phenomena. The growth of Ag on Ge(111), in particular, has received much attention, due in part to the complexity of its phase diagram, which includes at least eight different phases, some of which have novel, nonequilibrium coexistence regions in the phase diagram.[1] Eight Ag phases have been reported for submonolayer coverages on Ge(111): (4 × 4), ($\sqrt{3} \times \sqrt{3}$)R30°, (3 × 1),[2–4] (1 × 1), (5 × 1),[3] ($12\sqrt{3} \times 12\sqrt{3}$)R30°,[5] (6 × 6),[6,7] ($\sqrt{39} \times \sqrt{39}$);[6] however, the latter four phases are observed under special preparation conditions and are not located on the proposed phase diagram.[1]

The Ag (3 × 1) phase on Ge(111) has received less attention than the Ag (4 × 4) and ($\sqrt{3} \times \sqrt{3}$)R30° (abbreviated here as $\sqrt{3}$) phases, the two dominant phases in the phase diagram,[1] but the structures of all three phases are fairly well understood. The (3 × 1) structure is the “honeycomb chain channel” reconstruction with a Ag surface coverage of ∼1/3 monolayer (ML), similar to the Ag (3 × 1) structure on Si(111).[2,8] In contrast to the (3 × 1) phase observed on Si(111), only one previous study has observed large regions of (3 × 1) on Ge(111).[2] All other Ag studies report observations of the (3 × 1) phase only as small domains bordering domains of (4 × 4) and Ge. The (4 × 4) structure is a missing top layer reconstruction with Ag surface coverage of 0.375 ML.[3,4,9] The $\sqrt{3}$ structure is referred to as a “honeycomb chained trimer” reconstruction with a Ag surface coverage of 1.00 ML,[3,7,10] similar to the $\sqrt{3}$ reconstruction of Ag on Si(111).[11,12]

We have found interesting features in the growth of Ag on Ge(111) substrates held at high temperatures, between 540 and 660 °C. Low energy electron microscopy (LEEM) and diffraction (LEED) are used to examine the structure of the various phases as they grow on the surface as a function of temperature and coverage. For high temperature growth, we observe substantial regions with (3 × 1) structure, in addition to the better known and more studied $\sqrt{3}$ and (4 × 4) phases. In addition, we find that dosing Ag at high deposition rate onto substrates held at temperatures above the desorption temperature of ∼575 °C can yield samples with both (3 × 1) and $\sqrt{3}$ regions, with the (3 × 1) phase occurring exclusively for higher temperatures. In addition, LEEM and LEED images were used to follow the progress of a reversible structural phase transition occurring near the desorption temperature.

II. EXPERIMENT

Measurements were performed in an ultrahigh vacuum (UHV) system composed of three connected chambers housing several commercial instruments, including a low energy electron microscope (LEEM) (Elmitec GmbH), STM (Oxford Instruments), and x-ray photoemission spectrometer (Vacuum Generators).[13] Ge(111) samples were cut from commercial 2-in. diameter, Sb-doped wafers. All wafers had a reported miscut from (111) of <0.5°. Samples were cleaned with alternating cycles of Ar^+ sputtering (250 eV, 5 μA) and annealing (800–830 °C) until a sharp Ge(111) c(2 × 8) low energy electron diffraction (LEED) pattern was observed at room temperature. The sample temperature was controlled with radiant and electron beam heating from a tungsten filament located behind the sample. A thermocouple in contact with the edge of the sample was used to measure the sample temperature, after calibrating to readings from an infrared pyrometer that measured the temperature at the center of the sample.

Ag was deposited via direct evaporation from a resistively heated evaporator. During Ag deposition the pressure in the LEEM chamber did not rise above 1.0×10^{-9} Torr. The dosing rate was periodically calibrated to the evaporator

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filament current by monitoring the growth in LEEM of the (4 × 4) and $\sqrt{3}$ phases of Ag on Ge(111) for substrates held at temperatures below 300 °C. Differences between calibrating the dosing rate to the completion of the (4 × 4) phase at 0.375 ML or the $\sqrt{3}$ phase at 1.00 ML were typically within 5% and often within 2%. Ag coverages in this work are reported in monolayers, referenced to the atomic surface density of the unreconstructed Ge(111) substrate at 300 K, 7.22×10^{14} atoms/cm^2. The evaporator was generally calibrated at several dosing rates, which ranged from 0.005 ML/min to 1.5 ML/min, referenced to the Ge(111) surface.

III. RESULTS AND DISCUSSION

The growth of Ag phases on the Ge(111) surface was imaged with LEEM and LEED between 540 and 660 °C. Growth of the Ag (3 × 1) and $\sqrt{3}$ phases was observed up to the Ag desorption temperature of 575 °C. For sufficiently high deposition rates, the incident Ag flux overcomes the desorption of Ag from the surface, resulting in Ag accumulation on the surface above the desorption temperature. Above the desorption temperature, the $\sqrt{3}$ phase was observed up to 640 °C, and the (3 × 1) phase up to at least 660 °C.

A. Growth of (3 × 1) and $\sqrt{3}$ phases for Ag on Ge(111) substrates between 540 and 575 °C

Note that the well-known clean Ge(111) c(2 × 8) structure observed at room temperature has been previously observed to transform to a (2 × 1) reconstruction at 300 °C, with some hysteresis.[14] In addition, heating Ge(111) above 400 °C results in the observation of only (1 × 1) LEED spots, with cooling below 200 °C yielding the c(2 × 8) structure again; and the subsequent phase transformations between these two structures are reversible.[15] Our observations of the LEED patterns of the clean Ge(111) surface as a function of temperature are consistent with these previously reported results.

Figure 1 presents a sequence of LEED images taken as Ag was deposited at 540 °C. Before deposition, the LEED pattern shows only the first-order spots of the clean Ge(111) surface [Fig. 1(a)], as expected for this elevated temperature. As Ag is deposited, the first Ag LEED spots observed are consistent with three rotational domains of Ag (3 × 1) [Fig. 1(b)]. Up to at least 0.2 ML, the Ag grows exclusively in the (3 × 1) phase [Fig. 1(b)]. Between 0.3 and 0.5 ML, sharp $\sqrt{3}$ spots appear [Fig. 1(c)]. As the $\sqrt{3}$ layer completes, the $\sqrt{3}$ spots become stronger while the (3 × 1) spots become weaker. As the coverage approaches 1 ML, the $\sqrt{3}$ spots increase in intensity, and the (3 × 1) spots are extinguished. Additional Ag deposition above 1 ML does not result in a substantial change in the LEED pattern, with $\sqrt{3}$ spots remaining [Fig. 1(d)].

In a matter of several seconds, it is possible to switch back and forth between viewing the sample in LEEM and LEED modes. In doing so, LEED patterns, such as those shown in Fig. 1, can be associated with corresponding real space LEEM images of the surface. Although LEEM images were measured between the LEED patterns shown in Figs. 1(c) and 1(d), they are not shown here because similar growth features were identified for substrates held at higher temperatures (Fig. 2).

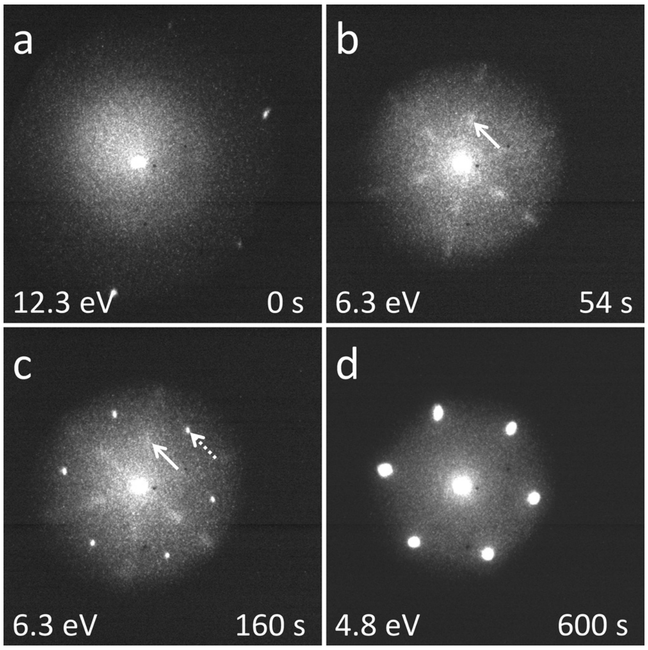
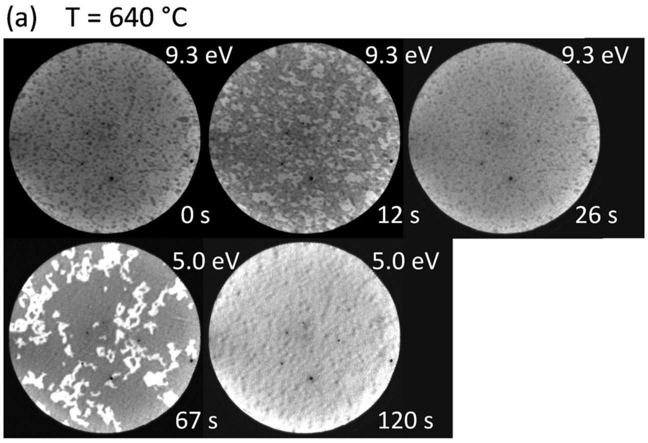


FIG. 1. LEED patterns measured during deposition of Ag on Ge(111) at 540 °C. Time given is seconds of deposition, at a deposition rate of 0.2 ML/min. (a) Clean Ge(111) before deposition. At this temperature and electron energy, only the Ge(111) first-order spots are visible (four of the first-order spots are visible, with the remaining two off screen). (b) (3 × 1) Ag. A solid arrow points to one 1/3rd-order (3 × 1) diffraction spot. The Ge(111) first order spots are not visible at this energy. (c) (3 × 1) Ag + $\sqrt{3}$ Ag. The solid arrow points to one (3 × 1) diffraction spot, and the dotted arrow to a $\sqrt{3}$ spot. (d) $\sqrt{3}$ Ag. The completion of the first $\sqrt{3}$ layer and the beginning of multilayer island growth beyond 1 ML coverage were observed by LEEM (images not shown here), between the LEED images in (c) and (d).

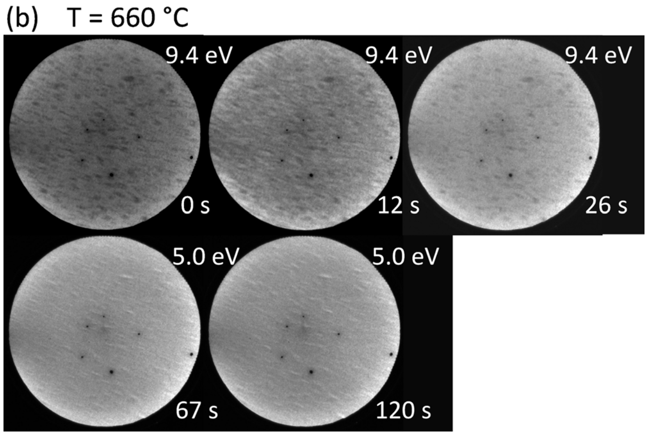
B. Growth of Ag on Ge(111) on substrates above 575 °C

Figure 2(a) shows a sequence of LEEM images taken as Ag was deposited onto a Ge(111) substrate held at 640 °C, corresponding to the same growth sequence, Ge → Ag (3 × 1) → Ag $\sqrt{3}$, as the LEED images for a substrate held at 540 °C (Fig. 1). Growth of the Ag (3 × 1) phase (imaged as bright phase contrast) is first observed at step edges in the Ge(111) substrate, at 9.3 eV incident electron energy after 12 s of Ag deposition [Fig. 2(a)]. The (3 × 1) phase spreads out from step edges until the surface is covered with this phase, which occurs before 26 s of Ag deposition [Fig. 2(a)]. Upon the completion of the (3 × 1) phase, Ag $\sqrt{3}$ is observed with intense bright phase contrast at 5.0 eV [$t = 67$ s in Fig. 2(a)]. The same growth sequence was measured in both LEEM and LEED images for substrates held at several temperatures between 540 and 640 °C.

The morphology of $\sqrt{3}$ growth at these temperatures is dendritic and not hindered by steps, suggesting that the growth mechanism of the $\sqrt{3}$ layer could be explained by diffusion limited aggregation,[16,17] as previously observed for



(a) T = 640 °C



(b) T = 660 °C

FIG. 2. LEEM images of deposition of Ag on Ge(111) at (a) 640 °C and (b) 660 °C. Although the deposition rate was not calibrated, it is the same for both temperatures. The contrast in the LEEM images taken at 0 s, before deposition, is due to defects in the clean Ge(111) substrate accumulated over many Ar^+ ion sputtering (cleaning) cycles. (a) A (3×1) overlayer, bright contrast in the image measured at 12 s, completely covers the surface before t = 26 s. Following completion of the (3×1) layer, a $\sqrt{3}$ phase forms with very bright contrast evident in the 67 s image. The $\sqrt{3}$ phase completes by 120 s. Additional deposition up to 330 s (data not shown) does not cause a change in the LEEM image shown for 120 s deposition, indicating that additional Ag beyond 1ML does not stick. (b) A (3×1) overlayer (bright contrast in 12 s images) completes at $t < 26$ s of deposition, as seen for the $T = 640$ °C case. Additional deposition up to 540 s (data not shown) does not produce any change in the LEEM image, suggesting that no further Ag sticks to the surface. Identification of the surface phases was accomplished with LEED. The contrast and resolution in (b) are worse than in (a) because of poorer adjustment of the LEEM lenses.

several systems of metal adsorption on metals, such as Ag on Pt(111),[18] Au on Ru(0001),[19] and Ag on Au(111).[20] Suppose impinging Ag atoms stick preferentially to other Ag atoms which have already nucleated at step edges and defects. If these incident Ag atoms diffuse rapidly compared with atoms diffusing along step edges, then statistical fluctuations in the growth front could be amplified because the protruding arms are more likely to attract additional impinging Ag atoms, leading to fingerlike-growth.

Interestingly, a $\sqrt{3}$ layer did not form at 660 °C [Fig. 2(b)] when the sample was exposed to Ag at the same dosing rate that formed such a layer at $T \leq 640$ °C [Fig. 2(a)], whereas a complete (3×1) layer did form at both temperatures. At both 640 °C and 660 °C, the (3×1) phase completed within 26 s. As discussed above, at 640 °C, continued deposition results in the growth and completion of the $\sqrt{3}$ phase. On the other hand, at 660 °C, continued deposition up to 540 s did not result in $\sqrt{3}$ growth or any change in the LEEM image. After the completion of the (3×1) phase on the higher temperature sample, additional Ag does not stick to the surface, and the lower density (3×1) phase is energetically preferred at these higher temperatures.

LEED images were used to determine the identity of the (3×1) growth observed in LEEM images for samples held at 540–660 °C during the Ag dosing. The resolution of LEEM ($\sim 10\,\mu$m) combined with this identification method leaves open the possibility that the phase that we have been calling "(3×1)" in LEEM images may be composed of a mixture of small domains of both (3×1) and the so-called "(1×1)" phase or disordered Ag. Additional structural information, possibly from high resolution microscopy, would be necessary to remove the possibility of having some disordered Ag in the "(3×1)" phase described here.

For all substrate temperatures between 575 °C and 640 °C and for Ag deposition rates of ~0.5–1.5 ML/min, we did not observe Ag island growth after the completion of the Ag $\sqrt{3}$ layer, indicating that the first layer Ag atoms are bound more strongly to the surface than subsequent Ag layers. For temperatures of both 640 and 660 °C, when the Ag deposition is stopped, Ag begins to desorb slowly from the surface. Note that the vapor pressure of pure Ag is significant at temperatures above the Ag/Ge(111) desorption temperature, 10^{-8} Torr at 574 °C and 10^{-6} Torr at 685 °C.[21]

C. Reversible structural phase transition: $[(3 \times 1) + (4 \times 4)] \leftrightarrow (3 \times 1)$

A reversible phase transition, $[(3 \times 1) + (4 \times 4)] \leftrightarrow (3 \times 1)$, was observed with LEEM and LEED at coverages less than 0.375 ML. The phase transition was observed near the 575 °C Ag desorption temperature.

Above 575 °C, the (3×1) phase is also energetically preferred over the (4×4) phase. Below 575 °C, we found that the (3×1) phase can coexist with the $\sqrt{3}$ phrase, the (4×4) phase, or both, depending upon coverage, temperature, and annealing history of the sample. Figure 3(a) shows the LEED pattern of a surface at 560 °C, which clearly has a superposition of (3×1) and (4×4) diffraction spots. Heating this surface beyond the desorption temperature reveals that the (3×1) phase persists longer than the (4×4) phase. After raising the temperature briefly to 590 °C, the (4×4) LEED spots disappear, while strong (3×1) spots persist, even as Ag is desorbing from the surface [Fig. 3(b)]. If the temperature is lowered to 560 °C, before all the Ag has desorbed, the (4×4) spots return. Although the critical temperature, T_c, for this structural phase transition between the $[(3 \times 1) + (4 \times 4)]$ and (3×1) phases is close to the 575 °C desorption temperature, our observations show that the transition occurs between 550 and 590 °C. One can go back and forth through this phase transition between $[(4 \times 4) + (3 \times 1)]$ below T_c and only (3×1) above T_c multiple times.

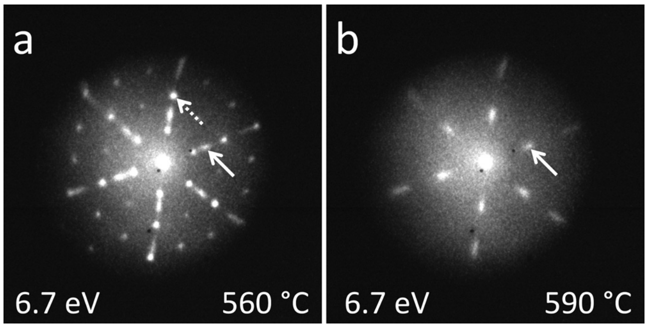


FIG. 3. LEED images of the phase transformation, $[(4\times4)+(3\times1)]\rightarrow(3\times1)$, upon increasing sample temperature. (a) The surface was prepared by deposition of 0.3 ML Ag at 170 °C and later annealed to 560 °C. The LEED pattern shows superposition of the (4×4) (dotted arrow) and (3×1) (solid arrow) diffraction patterns. (b) (3×1) (solid arrow). When heating, the (4×4) spots disappear before the (3×1) spots, but they return as soon as the temperature drops again. One can go back and forth between "a" and "b" multiple times, with additional Ag desorbing each time, as seen by the gradual strengthening of the Ge (2×1) spots and weakening of Ag (3×1) and (4×4) spots.

If the temperature is held at 590 °C, the (3×1) spots weaken and eventually disappear as the Ag on the surface is depleted. That the (3×1) phase persists above the desorption temperature longer than the (4×4) phase indicates its relatively greater stability at this coverage and temperature.

While the LEED images in Fig. 3 showed the phase transition from $[(4\times4)+(3\times1)]\rightarrow(3\times1)$ as a function of increasing temperature, the reverse transition as a function of decreasing temperature was viewed with LEEM. Figure 4 shows LEEM images of the $(3\times1)\rightarrow[(4\times4)+(3\times1)]$ transition as 0.1 ML of Ag on Ge(111) is cooled from 580 to 540 °C. The phase change is apparent in the LEEM image as a change in relative contrast between the Ag phase [bright in Figs. 4(a) and 4(b)] and the Ge substrate [dark contrast in Figs. 4(a) and 4(b)]. As the sample is cooled, the (3×1) phase [Fig. 4(a)] transforms to the (4×4) phase [Fig. 4(b)] and becomes brighter relative to the Ge surface. The lower density of the (3×1) phase is evident from the reduced areas of high contrast, corresponding to Ag, in the LEEM images after the transition at lower temperature to the higher density $[(4\times4)+(3\times1)]$ phase [Fig. 4(b)]. This is consistent with previous studies of the structure of the (3×1) phase,[2,8] with coverage close to 1/3 ML, and the (4×4) phase,[3,4,9] with coverage of 0.375ML. Again, we observe that the relatively less dense (3×1) phase is preferred over the relatively more dense (4×4) phase at higher temperatures.

After the LEEM image in Fig. 4(b) was measured, the sample was cooled to obtain sharper diffraction spots in the LEED pattern [Fig. 4(c)]. No evidence for any additional phase changes was observed between the measurements of Figs. 4(b) and 4(c). The pattern shows strong (4×4) spots and some faint (3×1) spots. Although domains of (3×1) structure should be present in the LEEM image at 540 °C [Fig. 4(b)], they are not readily apparent, either because they are too small to resolve or the intermediate LEEM intensity of the 3×1 phase is difficult to distinguish between that of the (4×4) phase and the contrast of the steps on the surface.

IV. CONCLUSIONS

Ag was deposited onto Ge(111) at high temperature, both below and above the nominal desorption temperature of 575 °C. A similar pattern of growth occurred for substrates at temperatures from 540 to 640 °C, with (3×1) growth occurring first until a completion of a layer of this structure, followed by the growth of a layer of the $\sqrt{3}$ phase. No multilayer islands stick to the surface, however. For Ag growth on a substrate at the higher temperature of 660 °C, only the (3×1) phase was observed, even for long deposition times, and no additional Ag seemed to stick to the surface after completion of the (3×1) layer. Thus, Ag does not form the higher coverage (4×4) or $\sqrt{3}$ phases at high temperature. The (3×1) phase is the lowest coverage of the well-known phases of Ag on Ge(111), and it appears to be the most stable at high temperature, suggesting stronger binding of the Ag atoms to the Ge substrate for this structure. At all temperatures above the desorption temperature, additional Ag accumulation after completion of the $\sqrt{3}$ phase was not observed, and the amount of Ag on the surface began to decrease as soon as deposition was stopped.

A reversible phase transition, $[(3\times1)+(4\times4)]\leftrightarrow(3\times1)$, was observed with LEEM and LEED at Ag coverages less than 0.375 ML. T_c for this structural phase transition was close to the Ag desorption temperature. The observations of the phase transition demonstrate again that

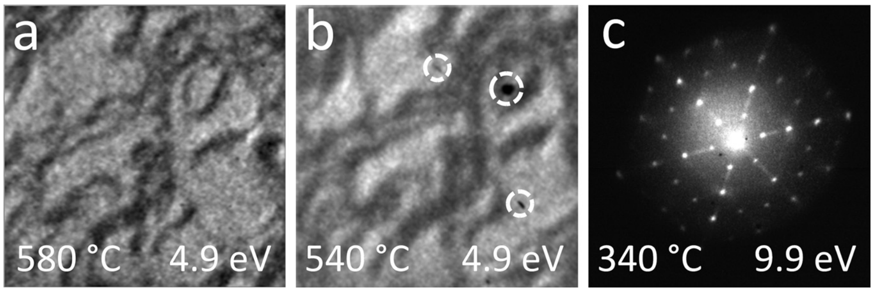


FIG. 4. Transformation of 0.1 ML Ag (3×1), deposited onto Ge(111) at 580 °C, to Ag $[(4\times4)+(3\times1)]$ upon decreasing sample temperature. The field of view (FOV) in the LEEM images in (a) and (b) is 2.0 μm, masked from original images with 10 μm FOV. (a) Ag (3×1) (bright) on Ge (dark) after deposition at 580 °C. (b) Image measured 18 s later shows Ag (4×4) (bright) on Ge (dark) at 540 °C. The decrease in surface area of the Ag phase upon transformation from $(3\times1)\rightarrow[(4\times4)+(3\times1)]$ reflects the slightly larger density of the (4×4) phase. The change in phase is indicated in LEEM images by the increased (4×4) Ag-Ge contrast compared to (3×1) Ag-Ge contrast, as well as the change in the LEED pattern, shown in (c) after the sample has cooled further. Defects in the image due to burns of the LEEM channel plate are indicated with dotted circles. (c) Cooling surface shown in (b) results in LEED pattern with sharper diffraction spots. The primary LEED pattern is (4×4), with some very faint (3×1) spots.

the lower coverage (3 × 1) phase is particularly stable at high temperatures.

The experiments described here give detailed information on a higher temperature region of the phase diagram of the Ag/Ge(111) system[1] than had previously been explored. The observed (3 × 1) and $\sqrt{3}$ phases at high temperatures are certainly consistent with the previously observed coverage ranges for these phases at low temperatures. The surface structures measured during continuous Ag deposition at temperatures above the Ag desorption temperature, however, are likely not to be equilibrium structures, as the Ag is observed to desorb from the surface at both 640 and 660 °C after the deposition is stopped. Nevertheless, with care, additional information on the structural phases of Ag on Ge(111) from these studies could be used to develop a more comprehensive version of the phase diagram for this prototypical metal on semiconductor system.

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