

## Growth and Morphology of Pb Phases on Ge(111)

Y. Sato<sup>1</sup> and S. Chiang<sup>2,3</sup>

Department of Physics

University of California Davis

1 Shields Ave.

Davis, CA 95616-5270 USA

### Abstract

Using low energy electron microscopy (LEEM), we investigated how various phases of the Pb overlayer on Ge(111) grow as the Pb coverage increases in the submonolayer range, for substrate temperatures between 200°C and 300 °C during Pb deposition. We find that each of the three known Pb phases forms in a distinct manner. The low coverage  $(\sqrt{3}\times\sqrt{3})R30^\circ$  -  $\alpha$  phase forms small islands less than 10nm in size, which then coalesce and saturate the surface at 0.33ML. During the formation of the  $\alpha$  phase, Pb atoms replace Ge adatoms of the  $c(2\times 8)$  reconstructed structure of the Ge (111) substrate, and the released Ge atoms diffuse and form islands on terraces or attach to steps. We show that the size and density of the Ge islands can be controlled systematically by controlling the film deposition parameters. After the saturation of the  $\alpha$  phase, the  $(1\times 1)$  phase starts to grow preferentially at the lower side of the step edges. LEEM data provide direct evidence of the  $(1\times 1)$  phase being a disordered phase, rather than a Pb-terminated unreconstructed Ge(111) surface, resolving the previous controversy. The  $(\sqrt{3}\times\sqrt{3})R30^\circ$  -  $\beta$  phase forms in a dramatic first-order transition from the  $(1\times 1)$  phase, with spontaneous domain switching occurring in the coexistence region of the two phases.

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<sup>1</sup> Current address: Gatan, Inc., Pleasanton, CA 94588

<sup>2</sup> American Vacuum Society member

<sup>3</sup> Electronic mail: [chiang@physics.ucdavis.edu](mailto:chiang@physics.ucdavis.edu)

## I. INTRODUCTION

As a prototypical 2D metal-semiconductor interface, studies of the Pb/Ge(111) system have shed considerable light upon fundamental processes on semiconductor surfaces such as surface reconstruction,<sup>1</sup> atom diffusion,<sup>2,3</sup> and phase transitions.<sup>4,5</sup> The clean Ge(111) surface reconstructs into the c(2x8) structure, with the atomic model inferred from scanning tunneling microscopy (STM) data.<sup>1</sup> The addition of a small amount of Pb on this surface reduces the energy barriers for activated processes and excites metastable structures that involve concerted atomic motions between Ge adatoms and substitutional Pb atoms; the discovery of this mechanism provided important insight into atom diffusion on semiconductor surfaces.<sup>2</sup> In addition, the observed rate of atomic diffusion on the Pb/Ge(111) surface at low temperature was orders of magnitude slower than expected;<sup>6</sup> this was explained as the result of “orchestrated exchange,” a complicated motion involving many surface atoms which ensures that a minimal number of covalent bonds are broken during diffusion.<sup>3</sup> Structural phase transitions occurring on Pb/Ge(111) at low temperature have been studied more recently by STM,<sup>7,8</sup> reflection high energy positron diffraction (RHEPD),<sup>9</sup> and He atom scattering.<sup>10</sup> For high coverage multilayers of Pb, the system exhibits bilayer growth that is attributed to quantum size effects (QSE).<sup>11-13</sup>

The growth and phase diagram of this system have also been studied by many techniques,<sup>14-29</sup> The Pb film forms two ( $\sqrt{3}\times\sqrt{3}$ )R30° structures at room temperature, called the  $\alpha$  and  $\beta$  phases, with known atomic structures. Although there continues to be some disagreement in the literature about the structure of the  $\beta$  phase, between a close-packed model with coverage of 1.33ML<sup>14-23</sup> and a trimer model with coverage of 1.0 ML,<sup>25,26,29</sup> we will follow the majority of the papers and assume that the coverage of the  $\beta$  phase is 1.33ML in the following discussion. In addition, there exists a high temperature (1x1) phase whose structure has been a point of controversy. The main debate is whether the (1x1) phase is a 2D liquid, consisting of mobile

adatoms, or a bulk-terminated ordered phase. Because of the observed weak halos of diffuse scattering in the diffraction pattern, the early reflection high energy electron diffraction (RHEED) study by Ichikawa claimed that the (1x1) phase is a 2D liquid layer which is unperturbed by the Ge substrate.<sup>16, 17</sup> A similar ring of diffuse scattering was also observed in a surface x-ray diffraction study by Gray *et al.* for a film of  $1.25\text{ML} \pm 0.05\text{ML}$  at  $223^\circ\text{C}$ . They concluded that the (1x1) phase was a 2D liquid, weakly modulated by the substrate.<sup>28</sup> A low energy electron diffraction (LEED) study by Metois and Le Lay, however, argued that it was an ordered structure because the LEED pattern of the (1x1) structure was sharp.<sup>25</sup> Based on their STM images, Hwang and Golovchenko also concluded the (1x1) structure was a Pb-terminated unreconstructed Ge(111) surface and that the transition was order-order.<sup>26</sup> In another model, Dev *et al.* suggested that the (1x1) phase consists of small islands of  $\beta$  phase, based on their x-ray standing wave study.<sup>19</sup>

A novel phase separation mechanism was discovered in this system.<sup>4, 5</sup> When the low Pb coverage (1 x1) phase coexists with the high coverage  $\beta$  phase, the surface consists of  $\sim 100$  nm sized domains that spontaneously switch from one phase to the other. This novel mechanism occurs because the density difference between the  $\beta$  and (1x1) phases is actually so small ( $\sim 0.04\text{ML}$ ) that the nanometer-scale domains can have density fluctuations comparable to the density difference between the two phases.<sup>4, 5</sup>

Using the real-time imaging capability of the low energy electron microscope (LEEM) to follow the surface morphology, we show how various phases of the Pb overlayer on Ge(111) grow as the Pb coverage increases in the submonolayer range at deposition temperatures between  $200^\circ\text{C}$  and  $300^\circ\text{C}$ . Below  $200^\circ\text{C}$ , the growth features were smaller than the resolution of the LEEM ( $\sim 10\text{nm}$ ), and above  $300^\circ\text{C}$ , the desorption rate of Pb became significant. The LEEM has significant advantages in these studies because of two key capabilities: the comparison of sample

morphology over large areas (in the millimeter range) of the sample and the in-situ measurement of growth during deposition of the overlayer. We show that the islands that form during the early stage of Pb film growth consist of Ge adatoms released from the reconstructed Ge c(2x8) substrate and that the initial distribution of these islands determines the morphology of the film. We further show that the size and density of the islands can be systematically controlled using the deposition temperature. Finally, based on our LEEM observations, we conclude that the (1x1) phase is a disordered phase rather than a Pb-terminated unreconstructed Ge(111) surface, resolving the existing controversy.

## II. EXPERIMENTAL DETAILS

We present results from experiments using a commercial ultrahigh vacuum (UHV) LEEM built by Elmitec GmbH. The main chamber of the LEEM is connected to an analysis chamber equipped with an x-ray photoemission spectrometer, an ion sputter gun, and a mass spectrometer; the system also has a UHV STM which can measure the same samples as the LEEM.<sup>30</sup>

The Ge(111) substrates were cut from polished wafers purchased from the Semiconductor Processing Company. The wafers were n-doped with a resistivity of 0.40  $\Omega$ -cm, and the orientation was within  $\pm 0.2^\circ$  of the (111) direction. The Ge(111) substrate was first chemically treated *ex situ*. Initially, the substrate was degreased by sonicating in methanol. It was then dipped into H<sub>2</sub>O<sub>2</sub> for about 60 sec in order to remove carbon contamination from the Ge surface, leaving a thin oxide layer that can be easily removed by sputtering and annealing cycles in UHV.<sup>31</sup> The *in situ* cleaning in the analysis chamber consisted of cycles of Ar<sup>+</sup> sputtering (250eV, 5 $\mu$ A) and annealing at 800°C until no impurity was detectable in XPS spectra. The sample was heated from the back by electron bombardment. Its temperature was measured with a

W-5%Re/W-25%Re thermocouple mounted between a doughnut-shaped Ta foil and the back of the sample. Temperature calibration was performed with an infrared pyrometer.

The LEEM main chamber is equipped with a resistively heated evaporator that was used to deposit Pb on Ge(111) at a rate of 0.023 – 0.04 ML/minute. During deposition, the pressure in the LEEM main chamber was maintained at or below  $1.0 \times 10^{-9}$  torr. For each deposition experiment, the LEEM images were captured, and the percentages of bright ( $\alpha$  phase with the quoted saturation coverage of 0.33 ML<sup>18</sup>) and dark ((1x1) phase with the measured saturation coverage of 1.29 ML at the eutectic point<sup>4</sup>) areas were measured and used to determine the Pb coverage and subsequently the deposition rate.

### III. RESULTS AND DISCUSSION

The clean Ge(111) surface exhibited the characteristic c(2x8) LEED pattern, as shown in the inset of Fig. 1(a). LEEM images clearly distinguish the two  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structures and the high temperature (1x1) phase and show that each of the three phases grows in a distinct manner on this surface. As the Pb coverage was increased, observations from separate LEED experiments were used to identify the real space features with bright or dark LEEM contrast that correspond to particular LEED patterns, such as  $(\sqrt{3} \times \sqrt{3})R30^\circ$  or (1x1).

#### A. Growth of the $\alpha$ phase and the $\alpha \Rightarrow$ (1x1) phase transformation

Below 0.33ML, the bright-field LEEM image shows little change in surface features until the formation of Ge adatom islands are observed for Pb coverage close to 0.33ML. These Ge adatom islands are formed from Ge adatoms on the reconstructed Ge c(2x8) surface as they are replaced by deposited Pb atoms during the initial stage of the deposition. The adsorption of Pb onto the surface is recognized by a change in the image intensity due to a change in surface work

function. According to STM work by Seehofer *et al.*,<sup>21</sup> for 0.1ML Pb films deposited at room temperature and annealed for about 5min at 100 °C, most of the Pb atoms had replaced Ge in the adatom sites, and the  $\alpha$  phase started to nucleate where the local density of Pb atoms was higher.

The lack of observable growth features in the LEEM indicates that the initial nucleation of the  $\alpha$  phase over the surface happens on a length scale below the resolution of LEEM ( $\sim 10\text{nm}$ ); the Pb then coalesces to form an ordered  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure that saturates at 0.33ML. The displaced Ge c(2x8) adatoms diffuse over the surface to attach to step edges or form circular adatom islands on a terrace. Figure 1(a) shows a bright-field LEEM image of the surface before the deposition and (b) at close to 0.33ML. In the Fig. 1(b), the red (right) inset shows the magnification of an area where two Ge adatom islands are observed, while the blue (left) inset shows for comparison the image of the same area captured at the later growth stage shown in Fig. 1(g). In the latter, the contrast between the adatom islands in the  $\alpha$  phase and the surrounding area in the (1x1) phase helps to identify the profile of the adatom islands clearly. Although the contrast is weak in Fig. 1(b), the formation of adatom islands is clearly observed at this stage. From this point of the deposition process, the size and the distribution of these islands remain very close to the initial configuration. Only a little ripening is observed during the rest of the experimental process. This suggests that the diffusion of Ge atoms is significantly slowed down by the saturation of Pb atoms on the surface. The attachment of the Ge adatoms to the steps can be observed from the change in the step profile, since the clean Ge(111) c(2x8) surface has a smooth step profile, whereas a jagged step profile was often found on the samples with adsorbed Pb.

Fig. 1(c)-(h) show the transformation of the surface, measured in LEEM images at 11.6eV, from the dark  $\alpha$  phase to the bright (1x1) phase as the Pb coverage is increased from 0.35 to 1.39ML. Above 0.33ML, in contrast to the lattice gas formation of the  $\alpha$  phase over the

surface, the (1x1) phase starts to grow preferentially at the lower side of the step edges. In addition, the (1x1) phase preferentially grows around the above-mentioned adatom islands on terraces, as shown in Fig. 1(c) for a sample with Pb coverage of  $\sim 0.35\text{ML}$ . Saturation of the  $\alpha$  phase over the surface at this stage is confirmed by the dark-field LEEM image shown in Fig. 2. The LEED pattern in Fig. 2(a) shows the symmetry of the  $(\sqrt{3}\times\sqrt{3})R30^\circ$  structure of the  $\alpha$  phase, as well as the (1x1) spots. One of the  $\alpha$  phase LEED spots is used to obtain the dark-field LEEM image, and thus only the areas with  $\alpha$  phase show bright intensity in Fig. 2(b). The Ge islands have a bright intensity in this image, showing that, at this stage, the first layer of the surface, including these islands, is saturated by the  $\alpha$  phase. Note that the (1x1) phase, which appears dark in Fig. 2(b), starts to grow at step edges and around the Ge islands. This dark-field LEEM image confirms that only the  $\alpha$  phase grows below  $0.33\text{ML}$  coverage and that, upon saturation of the  $\alpha$  phase over the surface, additional deposition of Pb leads to the transformation of the  $\alpha$  phase into the (1x1) phase preferentially along the step edges and around the Ge adatom islands.

Fig. 1(d)-(e) clearly show the bright (1x1) phase forming at the step edges and surrounding the Ge adatom islands. One Ge adatom island, with the bright (1x1) phase forming around it, is circled in Fig. 1(c)-(h) so that it can more easily be followed through the progression of images showing the  $\alpha$  to (1x1) phase transformation. In 1(f), most of the terraces have transformed from the dark  $\alpha$  phase into the bright (1x1) phase. Fig. 1(g) shows that the Pb layer on top of the Ge adatom islands transforms last into the (1x1) phase, at close to  $1.29\text{ML}$ . The whole surface is in the (1x1) phase in Fig. 1(h).

Figure 3 shows a sequence of bright-field LEEM images captured during Pb monolayer deposition at  $257^\circ\text{C}$ . For the LEEM images of Fig. 3(b)-(k) at  $6.1\text{eV}$ , the low and high coverage  $(\sqrt{3}\times\sqrt{3})R30^\circ$  phase, i.e.,  $\alpha$  and  $\beta$  phase respectively, appear bright, and the (1x1) phase appears

dark. (Note that these are opposite from the dark  $\alpha$  phase and the bright (1x1) phase shown in the 11.6eV LEEM images in Fig. 1(c)-(h).)

Figs. 3(b)-(f) show the transformation from the bright  $\alpha$  phase to the dark (1x1) phase. As in Fig. 1, the  $\alpha$  to (1x1) transformation begins at step edges and adjacent to the Ge adatom islands (Figs. 3(b)-(c)) that form when Ge adatoms are released from the Ge(111) c(2x8) reconstruction upon Pb adsorption.<sup>21</sup> In Fig. 3(d), most of the terraces have transformed to the dark (1x1) phase. By the coverage shown in Fig. 3(e), Pb atoms arriving at random places on the surface travel over the terrace to transform the remaining bright  $\alpha$  phase on top of the Ge adatom islands. Fig. 3(f) is completely dark, showing the completion of the (1x1) phase.

Fig. 3(l) shows a plot of the percentage of the area occupied by Ge islands for samples grown at varying deposition temperature. Images such as those presented in Figure 4 were used for the data shown in the plot. Note that the c(2x8) Ge adatoms form a coverage of 1/4 ML on the Ge(111) substrate. Thus, the measurement clearly shows that, at a lower deposition temperature where the diffusion length is expected to be short, most adatoms nucleate and form islands on terraces. For example, at 218°C, over 20% of the area is covered by the islands, indicating that 80% of the displaced Ge adatoms nucleated on terraces. As the deposition temperature increases, more adatoms diffuse over the terrace and attach to step edges, resulting in the observed decrease in the percentage of the area occupied by Ge islands.

## **B. Transformation from (1x1) phase to $\beta$ phase with increasing coverage**

After the (1x1) phase saturates, neither the LEEM images nor the LEED patterns change significantly as the Pb coverage increases, until a transformation into the  $\beta$  phase occurs at higher coverage,  $\sim 1.39$ ML. Since the  $\beta$  phase is a denser phase than the (1x1) phase, the (1x1) phase must accommodate more and more atoms into its structure as the coverage increases.



Thus, the (1x1) phase must be a disordered phase which can accommodate a range of Pb coverage, instead of an ordered, Pb-terminated, unreconstructed Ge(111) surface, as concluded by Hwang and Golovchenko based on their STM images.<sup>26</sup>

As the coverage increases, the transformation of the (1x1) phase into the  $\beta$  phase near 1.33ML is a first-order phase transition involving spontaneous domain switching between the two phases (Fig. 3(g)-(j)).<sup>4,5</sup> When the Pb coverage reaches  $\sim 1.39$  ML, a few, isolated  $\sim 100$  nm sized domains start to switch from (1x1) phase to  $\beta$  phase (Fig. 3(g)).<sup>32</sup> These domains spontaneously revert back to the original phase and then switch between the two phases. Within a short amount of time ( $\sim 15$  seconds), more and more domains appear and show this spontaneous phase switching behavior until they become stable in the  $\beta$  phase. Eventually, the whole surface is transformed into the  $\beta$  phase (Fig. 3(k)). Note that these observations correspond to the phase transformation which occurs as the Pb coverage changes at fixed sample temperature, while in previous work, the occurrence of the phase transformation for fixed coverage in response to temperature change was discussed.<sup>4,5</sup> As the images in Fig. 3(g)-(k) show, the nature of the phase separation mechanism between the (1x1) and  $\beta$  phases which was observed during the deposition of the Pb monolayer is the same as what was previously reported.<sup>4,5</sup>

Finally, we show that by simply changing the deposition temperature, we are able to control the surface morphology of the film. Figure 4 shows images of samples deposited at varying temperature and at deposition rates of 0.02 to 0.036 ML/min. A film with small, dense islands can be achieved by simply lowering the deposition temperature. As shown in Figure 4(a), when deposited at 218°C, the adatom islands are small ( $\sim 15$  nm diameter) and dense (average spacing  $\sim 40$  nm). Raising the deposition temperature results in an increase in the size of the islands and a decrease in the density. At 278°C (Figure 4(c)), the islands become 160 nm in diameter, and their average spacing is  $\sim 500$  nm. The trend is clear in the plot shown in Fig. 4(d).

Although this behavior is expected from standard nucleation and growth theory,<sup>33</sup> we note that the ability to control the island size enabled us to perform the experiment that resulted in the measurement of the coverage of the (1x1) phase that was described in Ref. 4.

#### IV. CONCLUSIONS

The first real-time, real-space resolved LEEM data on the growth of a Pb monolayer on Ge(111) were presented here. According to the reported STM observations, Pb atoms initially replace Ge c(2x8) adatoms.<sup>21</sup> The displaced Ge adatoms diffuse over the surface and either form adatom islands on a terrace or attach to a step. LEEM observations of the formation of Ge islands before the saturation of the  $\alpha$  phase support this picture. With further deposition, the  $\alpha$  phase starts to nucleate over the surface and coalesces at 0.33ML. Above 0.33ML, the transformation of the  $\alpha$  phase to the (1x1) phase starts at step edges and in regions adjacent to the Ge adatom islands. It then proceeds until the surface saturates, i.e., the whole surface is in the (1x1) phase, and the  $\alpha$  phase is no longer observed. The (1x1) phase is a disordered phase and continues to accommodate more Pb atoms. When it is dense enough, the (1x1) phase transforms into the  $\beta$  phase, and the transformation is first-order, involving spontaneous domain switching between the two phases. This study provides a nanoscale picture of the growth process of this system and complements the previously reported studies, which focused on the atomic structures of the overlayer phases.

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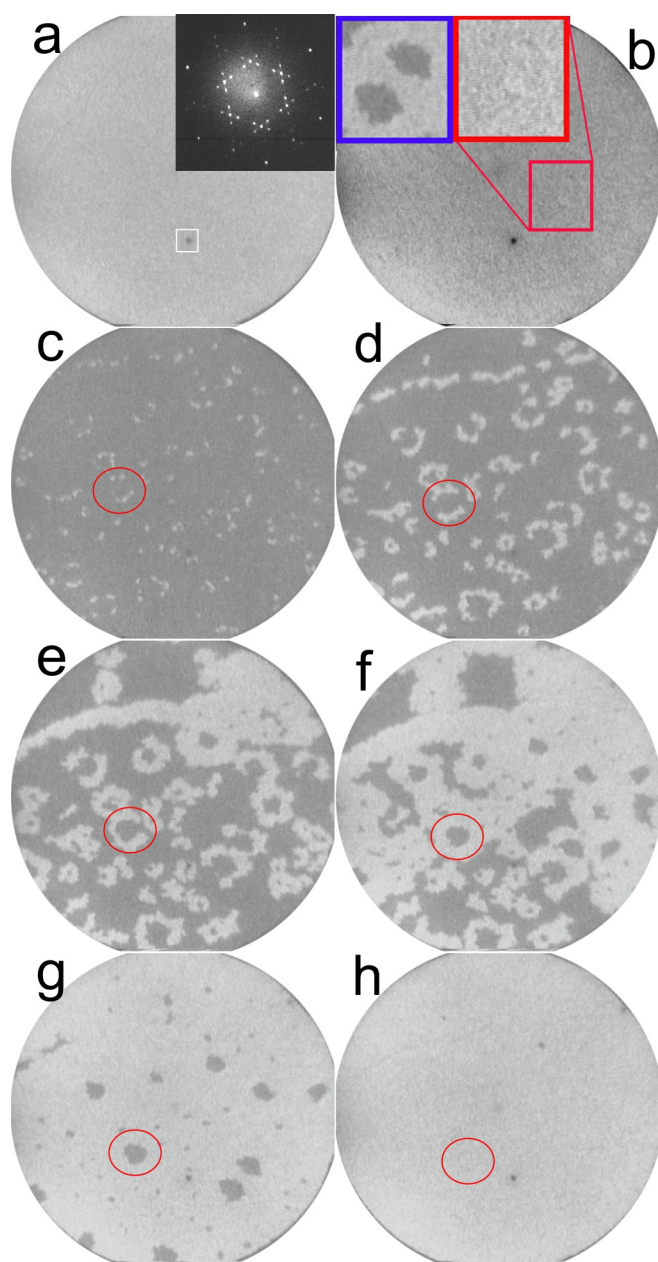


Fig. 1. A sequence of bright-field LEEM images captured during Pb deposition on Ge(111) at 300°C. 5 $\mu$ m Field of View (FOV). (a) Clean Ge(111) before deposition, 6.1 eV. The white square surrounds a channelplate defect, which appears in all LEEM images in this article. The inset shows the c(2x8) LEED pattern measured at 13.2 eV, with sharp 1/8<sup>th</sup> order spots indicating a clean surface, but 1/4 order spots are not visible at this energy. (b) Pb coverage close to 0.33 ML, 6.1 eV; although the contrast is weak, the formation of adatom islands is observed at this stage. See text for description of inset regions. (c) ~0.35 ML, 11.6 eV. At this energy, the  $\alpha$  phase appears dark, and the (1x1) phase appears bright. The dark  $\alpha$  phase saturates the surface at 0.33 ML, and small regions near the step edge and around the Ge adatom islands are beginning to transform to (1x1) phase. The dark gray (red online) oval borders the (1x1) phase surrounding a Ge adatom island in (c)-(h). (d) 0.48 ML, 11.6 eV. Additional regions near the step edge and around the Ge adatom islands have transformed from the dark  $\alpha$  phase into the bright (1x1) phase. (e) 0.70 ML, 11.6 eV. Additional regions of the surface are transforming from the dark  $\alpha$  phase to the bright (1x1) phase. (f) 0.84 ML, 11.6 eV. Most of the 2 terraces are now in the bright (1x1) phase. (g) 1.16 ML, 11.6 eV; the Pb layer on top of the Ge adatom islands is still dark and has not yet transformed to the (1x1) phase. (h) 1.39 ML, 11.6 eV. The whole surface is in the bright (1x1) phase.

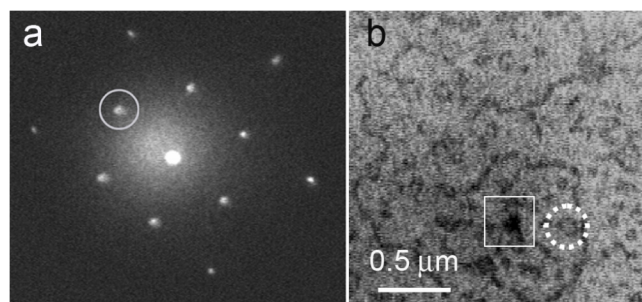


Fig.2. LEED pattern and a dark-field LEEM image of a sample at  $\sim 0.37\text{ML}$  during Pb deposition at  $261^\circ\text{C}$ . (a)  $\alpha$  phase ( $(\sqrt{3} \times \sqrt{3})R30^\circ$ ) and  $(1 \times 1)$  LEED pattern. One of the  $\alpha$  phase spots, indicated by a circle, was used to obtain the dark-field LEEM image in (b). (b)  $2\mu\text{m}$  FOV. In this dark-field LEEM image, only the areas in the  $\alpha$  phase show bright intensity. Note that the  $(1 \times 1)$  phase, which appears dark, starts to grow at step edges and around the Ge islands, one of which is identified by a dotted circle. This image confirms that the  $\alpha$  phase saturates the surface before the  $(1 \times 1)$  phase growth can begin. The white square surrounds a channelplate defect.



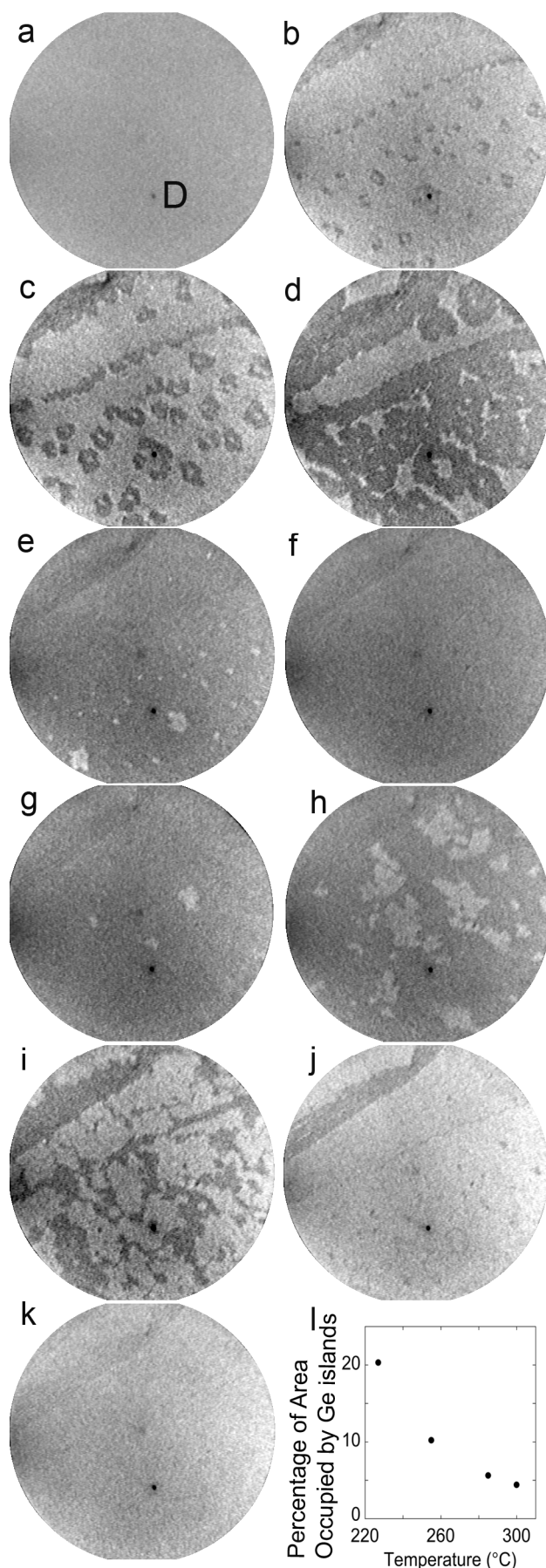


Fig. 3. A sequence of bright-field LEEM images captured during Pb deposition on Ge(111) at 257°C. 5μm FOV. For (b)-(k) at 6.1eV, the low and high coverage ( $\sqrt{3}\times\sqrt{3}$ )R30° phases, i.e., α and β phases respectively, appear bright, and the (1x1) phase appears dark. (a) Clean Ge(111) surface before deposition, 9.5eV. The letter D indicates a channelplate defect. (b) ~ 0.35ML. The regions near the step edges and around the Ge adatom islands begin to transform first from the bright α phase into the dark (1x1) phase. (c) 0.48ML. Additional regions along the step edge and surrounding the Ge adatom islands have transformed from the bright α phase into the dark (1x1) phase. (d) 0.84ML. Most of the terraces are now in the dark (1x1) phase. (e) 1.16ML. The remaining bright regions consist of α phase on top of the Ge islands; these regions are the last to transform to (1x1). (f) Complete (1x1) dark phase at 1.19ML (g) ~ (k) 1.39 ML; the low coverage (1x1) phase (dark region) coexists with the high coverage β phase (bright region) (g) A few ~ 100 nm sized domains start to spontaneously switch from the dark (1x1) phase to the bright β phase. (h) and (i) More domains appear and spontaneously switch between the two phases until they become stable in the bright β phase. (j) Most of the surface is in the bright β phase except the area in the upper left where the step density is high. (k) The whole surface is in the bright β phase. Note that the transformation from (g) to (k) occurs within a few seconds while the Pb coverage is nearly the same. (l) Percentage of area occupied by Ge islands for samples grown at varying deposition temperature. See text for explanation.

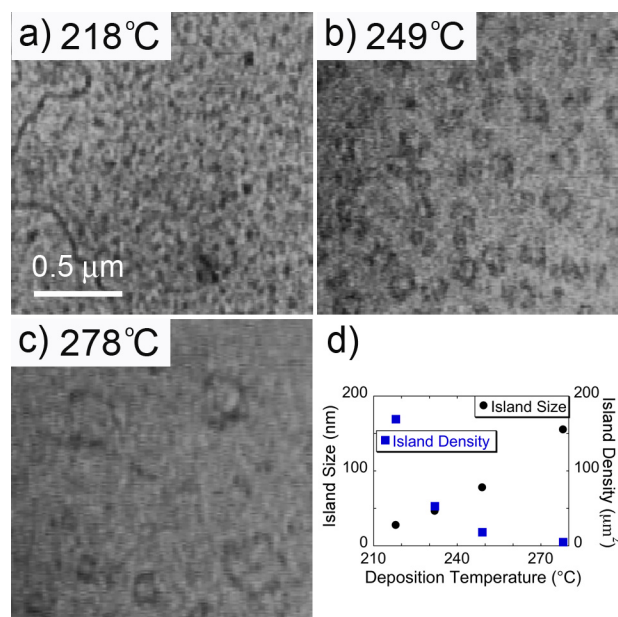


Figure 4 LEEM images of Pb/Ge (111) samples grown at a variety of substrate temperatures. Images were captured when the Pb coverage was  $\sim 0.35$  ML, just above the saturation of the  $\alpha$  phase. Electron energy is 6.1 eV. (a) The Ge islands are small ( $\sim 15$  nm diameter) and dense (average spacing between adatom islands is  $\sim 40$  nm). (b) Island size becomes bigger ( $\sim 80$  nm), as do the spacings ( $\sim 200$  nm). (c) Island size is  $\sim 160$  nm; spacing is  $\sim 500$  nm. (d) Island size increases with substrate temperature, whereas island density is inversely proportional to the temperature.