Spontaneous Domain Switching during Phase Separation of Pb on Ge(111)

Y. Sato[1,2] and S. Chiang[1]

[1]*Department of Physics, University of California, Davis, California 95616, USA*
[2]*NCEM, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

N. C. Bartelt

Sandia National Laboratories, Livermore, California 94551, USA

(Received 23 April 2007; published 29 August 2007)

Using low-energy electron microscopy (LEEM), we have discovered a novel phase separation mechanism for Pb on Ge(111). When the low Pb coverage (1×1) phase coexists with the high coverage β phase, the surface consists of ~100 nm sized domains that spontaneously switch from one phase to the other. We argue this striking mechanism occurs because nanometer-scale domains can have density fluctuations comparable to the density difference between the two phases.

DOI: 10.1103/PhysRevLett.99.096103 PACS numbers: 68.35.Rh, 68.37.Nq, 68.47.Fg, 68.65.−k

Phase separation is often observed in epitaxial films on surfaces. Attractive interactions between adsorbed atoms cause dense, ordered phases to coalesce out of dilute disordered phases as adsorbate coverage is increased or temperature is decreased. The initial evolution with time of this phase separation process is usually well described by the familiar theories of nucleation and growth, or spinodal decomposition. At later stages, Ostwald ripening occurs caused by slow diffusion from small domains to large domains to minimize domain boundary length [1]. In this Letter, we present real time observations of a phase separation that occurs by a mechanism which is distinctly different from these processes. We find the $\beta \Leftrightarrow$ disordered (1×1) phase transition of Pb on Ge(111) to be dominated by thermal fluctuations that cause nanoscale switching between the two phases.

Usually, large thermal fluctuations are characteristic of critical points and second-order transitions. We will show, however, that the $\beta \Leftrightarrow (1 \times 1)$ phase transition is first order, with sharp boundaries between the phases. Pb on Ge(111) forms two stable $(\sqrt{3} \times \sqrt{3})R30°$ structures. A dilute structure that saturates at 0.33 ML is called the α phase, and a dense structure that saturates at 1.33 ML is called the β phase [2–4]. The high temperature (1×1) phase is a disordered phase. Based on the earlier studies [2,4–10], and work presented in this Letter, we propose the modified phase diagram shown in Fig. 1 [11]. To investigate the $\beta \Leftrightarrow (1 \times 1)$ phase transition, we have used low-energy electron microscopy (LEEM) to follow the phase transformation in real time and to measure the saturation coverage of the high temperature (1×1) structure. We find that the Pb atomic density difference between the β phase and the (1×1) phase is quite small (~3% of a monolayer), so that thermal fluctuations in the number of Pb atoms in a domain can easily cause a domain to flip its phase. A statistical mechanics analysis using quantities measured by LEEM shows that the observed domain fluctuations can indeed be explained by such thermal fluctuations.

The commercial ultrahigh vacuum (UHV) LEEM (Elmitec Gmbh) is connected to an analysis chamber equipped with an x-ray photoemission spectrometer (XPS) and Ar^+ ion sputter gun [12]. A resistively heated evaporator was used to deposit Pb at a rate of 0.25–0.4 ML/min, with the pressure in the LEEM main chamber $\leq 1.0 \times 10^{-9}$ torr at all deposition temperatures. The n-doped, 0.40 Ω cm, Ge(111) samples (Semiconductor Processing Company), were oriented within 0.2°. After sonicating in methanol, the Ge(111) samples were dipped into H_2O_2 for ~60 sec to form an oxide layer. *In situ* cleaning consisted of cycles of Ar^+ sputtering (250 eV, 5 μA) and annealing at 800 °C until no impurity was detectable by XPS.

As-deposited films just above the saturation coverage of the β structure (indicated by the dashed arrow in the phase

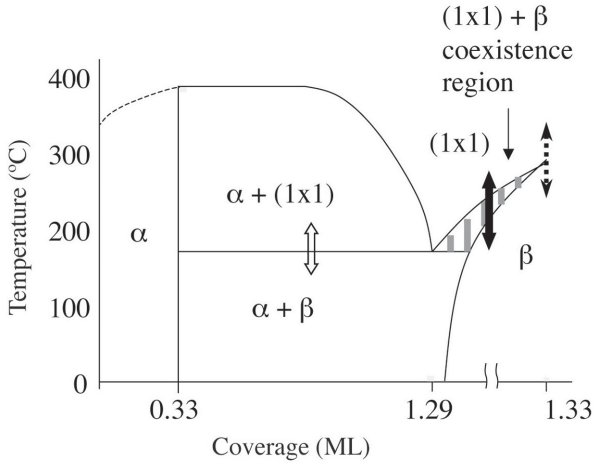

FIG. 1. Phase diagram of Pb/Ge(111). The dashed arrow on the right shows where a sharp first-order phase transition at ~295 °C is observed, and the solid arrow shows where the lower temperature transition with fluctuating domains is observed. The open arrow shows the transition which was measured to find the Pb saturation coverage of the (1×1) phase.

diagram shown in Fig. 1) show a simple first-order transition at 295 °C. When cooling through the transition temperature, the β phase nucleates and grows in a few seconds to cover the whole surface, as expected since there is no coexistence region (i.e., no density difference between the two phases) at this coverage [13]. When the coverage is lowered slightly and the coexistence region is entered, a dramatic change in the transformation process occurs, as shown in Fig. 2 [14]. In addition to a reduction in the transition temperature, the transformation process begins with the appearance of a few, isolated ~100 nm surface regions of the β phase [Fig. 2(b)]. As the temperature is lowered, the fraction of the surface in the β phase increases until the surface is completely converted to the β phase [Figs. 2(c)–2(f)]. The transformation reverses during the $\beta \Rightarrow (1 \times 1)$ transition upon heating.

The way in which the β phase grows is remarkable. Rather than continuously growing, these domains spontaneously revert back to the original phase and then switch between the two phases. This is shown in Fig. 3 by a sequence of LEEM images captured during the $(1 \times 1) \Rightarrow \beta$ phase transition at a fixed temperature of 189 °C [15]. Each domain of fixed shape constantly flips phase, frequently creating phase boundaries. Figure 3(d) shows the time dependence of the LEEM intensity of a fluctuating domain, showing that this domain fluctuated between two well-defined states. As the temperature is lowered further, the number of these fluctuating domains increases. Once a domain appears and starts to fluctuate, the fluctuation typically continues for a temperature range of about 5 K before it fluctuates into the new stable phase, until eventually the whole surface has transformed. The length scale of the fluctuating domains ranges from 50 to 150 nm. We attribute the pinning of domains to surface defects that cannot be resolved with the resolution of the LEEM (~10 nm). Although these defects pin the fluctuating domains, they are not responsible for the fluctuations as discussed below.

Often one interprets large fluctuations during a phase transformation as evidence of critical behavior near a second-order transition. It is important to note that the fluctuations we observe are not critical phenomena because LEEM images always show sharp phase boundaries between the two phases, not the diffuse boundaries which occur near second-order transitions. Furthermore, the average size of the fluctuating domains remains approximately the same throughout the transition region, rather than increasing as one would expect if approaching a critical point.

Each domain changes state on a time scale of less than 0.03 s. Because there is a density difference between the two phases at this coverage, it is a surprise that the transformation can occur apparently instantaneously because one might have thought that a large number of Pb atoms would need to diffuse towards or away from the fluctuating domain. Since domains of size 100 nm contain ~10^5 Pb

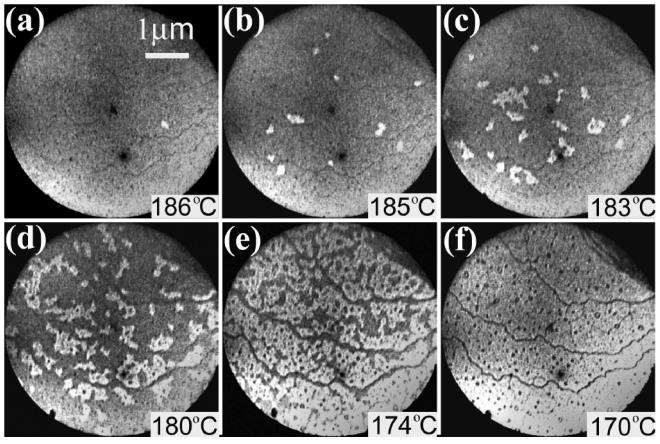

FIG. 2. A sequence of bright-field LEEM images captured during the $(1 \times 1) \Rightarrow \beta$ phase transition at a coverage of slightly below 1.33 ML. (See [14] for a LEEM movie of the same phase transition.) Steps, step bunches (in the upper right portion) are also observed. The black dot in the lower center of the images is a defect on the channel plate. The β phase areas appear brighter than the (1×1) phase areas due to the reflectivity difference for 6.1 eV electrons. (a) Initially, the surface is in (1×1) phase. (b) Several β domains appear and fluctuate. (c)–(e) More and more β domains appear and fluctuate. (f) The whole surface is transformed into the β phase. Ge adatom islands are apparent on terraces.

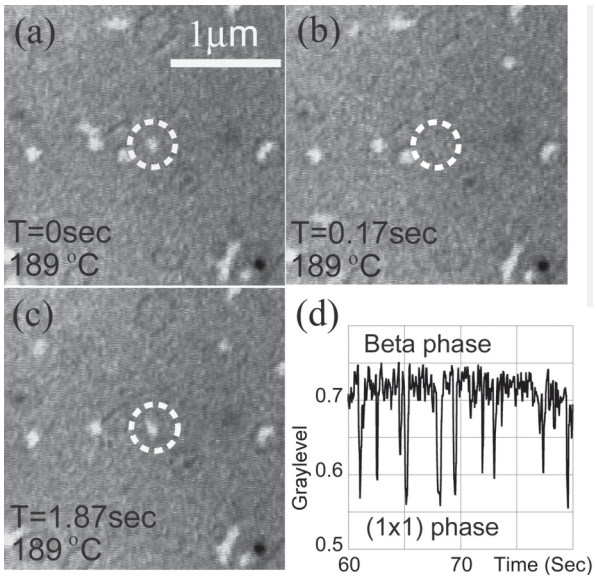

FIG. 3. A sequence of bright-field LEEM images captured during the $(1 \times 1) \Rightarrow \beta$ phase transition at a coverage of slightly below 1.33 ML. (See [15] for the LEEM movie from which the above movie stills were taken.) At an electron energy of 6.1 eV, the β phase appears bright, and the (1×1) phase appears dark. (a) A fluctuating β domain (circled) is observed. (b) The domain changed into the (1×1) phase. (c) It is in the β phase again. (d) Time dependence of the intensity of the circled domain at a constant temperature of 189 °C.

atoms, the required change in number of atoms to make the transformation could be extremely large. In normal situations, this flow of atoms is driven by the (slow) diffusion from small domains to large domains to minimize boundary length (i.e., by Ostwald ripening). There is no such driving force evident in our experiments. (In fact, the boundary length sometimes spontaneously increases.)

To explain this puzzle, we propose that thermal fluctuations in the local Pb density can cause the (1×1) phase to become unstable with respect to the formation of the β phase (and vice versa). Thermal fluctuations cause a small amount of mass transfer of Pb atoms in and out of a domain. This change in the local atom density subsequently allows a domain to spontaneously change its phase from one to another. During the short time of domain switching, there is very little Pb transfer; atoms arranged in one phase rearrange themselves into a new phase. A computed low activation barrier for Pb motion within the β unit cell is consistent with such quick rearrangements, as pointed out in [10].

To see if this explanation is plausible, we first estimate the variation in the number of Pb atoms one would expect from thermal fluctuations in the observed domains. We then compare these fluctuations with the measured density difference between the β and (1×1) phases.

Considering a surface in one phase, the thermal fluctuation in the local atom density within an area of a single domain can be calculated as follows. From the LEEM measurement, the area of a typical fluctuating domain is 8500 nm^2. The area of a $(\sqrt{3} \times \sqrt{3})R30°$ unit cell which contains 4 atoms in the β phase is 0.42 nm^2 on the Ge(111) surface, so that $n_{\text{unit cell}} = 8500\ \text{nm}^2/0.42\ \text{nm}^2 = 2.0 \times 10^4$ is the number of unit cells in a domain. From elementary statistical mechanics, $\Delta N_{\text{thermal}}$, the thermal fluctuation in the number of atoms for a domain with a mean number of atoms $\langle N \rangle$, can be expressed in terms of compressibility (κ) and $\langle N \rangle$ as follows. $\Delta N_{\text{thermal}} \equiv \sqrt{\langle N^2 \rangle - \langle N \rangle^2} = \sqrt{\kappa \langle N \rangle}$, where κ has been calculated to be on the order of 0.1 to 1 for the (1×1) or $(\sqrt{3} \times \sqrt{3})R30°$ phases [16]. This range of κ puts bounds on $\Delta N_{\text{thermal}}$.

To compute the mean number of atoms in a domain ($\langle N \rangle$), the Pb coverage was determined by desorbing measurable amounts of Pb from the saturated β phase at 1.33 ML [17]. For a sample in which the transformation is largely characterized by fluctuations of domains, the Pb coverage was thus estimated to be 1.30 ML. Presumably vacancies in the β phase allow it to exist for coverages below the saturation coverage of 1.33 ML. Then the density of the β phase will vary with the local vacancy concentration. The mean number of atoms in a domain is estimated to be $\langle N \rangle = n_{\text{unit cell}} \times (1.30/1.33) \times 4 = 7.8 \times 10^4$. Recalling the bounds on $\Delta N_{\text{thermal}}$, i.e., $\sqrt{\kappa_{\min} \langle N \rangle} \leq \Delta N_{\text{thermal}} \leq \sqrt{\kappa_{\max} \langle N \rangle}$, $\Delta N_{\text{thermal}}$ is then given by $90 \leq \Delta N_{\text{thermal}} \leq 280$. The above argument can be applied to the disordered (1×1) phase as well, giving a range of Pb atomic density for the (1×1) phase.

To determine if this change in the number of Pb atoms is sufficient to allow the β phase to convert to (1×1), we have measured the difference in the average density of the two phases at the saturation coverage. To do this, we have measured the saturation coverage of the (1×1) structure at the eutectic point, where the three phases, α, β and (1×1) coexist, by examining the $(\alpha + \beta) \Leftrightarrow \alpha + (1 \times 1)$ transitions at lower coverage (see open arrow in Fig. 1). A key feature of this first-order transition is that the dilute α structure acts as a sink of Pb atoms when the β phase transforms into the (1×1) phase and as a source when the transition is reversed. At this coverage, the local coverages of the α and β phases are 0.33 and 1.33 ML, respectively, from previous x-ray diffraction measurements [2]. The flux of Pb atoms in and out of the transforming region is observed as changes in the area of the α and the β or (1×1) regions. As the temperature increases above T_c, the area of the α phase decreases, and the area of the β phase increases as it transforms to the (1×1) phase. As the temperature decreases below T_c, the opposite happens. This change in area measured from the LEEM data is used to calculate the saturation coverage of the (1×1) phase using the following formula, $\Theta_{(1\times1)} = \{[\Theta_\beta \times (\text{area})_\beta] + [\Theta_\alpha \times \Delta(\text{area})_\alpha]\}/(\text{area})_{(1\times1)}$, where $\Theta_\alpha = 0.33$ ML and $\Theta_\beta = 1.33$ ML.

Figure 4 shows bright-field LEEM images of a 0.65 ML film of Pb deposited on Ge(111) at 275 °C, before, during, and after the $\alpha + \beta \Leftrightarrow \alpha + (1 \times 1)$ phase transition. Near 275 °C, bigger and fewer Ge adatom islands [18], around which the (1×1) phase preferentially starts to grow, nucleate on large (> 2–3 μm wide) terraces. Once the Pb

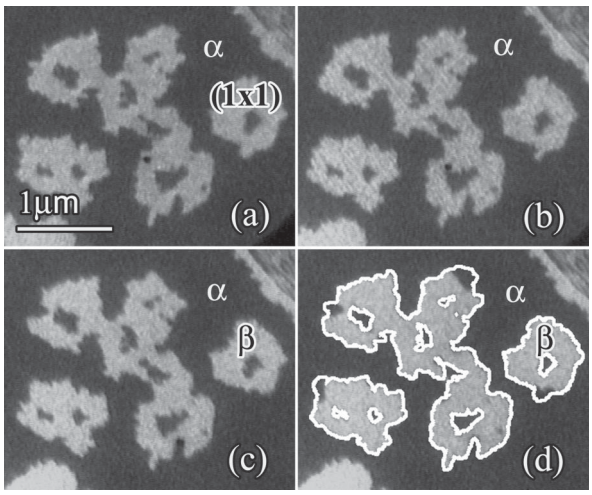

FIG. 4. 0.65 ML film of Pb on Ge(111) deposited at 275 °C, (a) before, (b) during, and (c) after the $\alpha + (1 \times 1) \Rightarrow \alpha + \beta$ phase transition. (d) Solid outlines of (1×1) phase are overlaid. Electron energy 11.2 eV. Temperature was changed from 187 °C to 163 °C ($T_c = 170$ °C).

film was deposited, the transformation was made to occur by quenching the sample temperature through the transition temperature, which was measured to be ~170 °C from earlier LEEM experiments [13], in good agreement with the published values [4,19].

In Fig. 4, the α phase areas appear dark, and the (1×1) and β phase areas appear bright due to the reflectivity difference for 11.2 eV electrons. Using the changes in the area of the phases [20], measured from images such as Fig. 4, in above formula, we find 1.29 ± 0.01 ML as the saturation coverage of the (1×1) phase at the eutectic point (see Fig. 1). The number density difference of Pb atoms between the two phases is actually very small, i.e., 0.04 ML. Based on this measurement, the difference between the number of atoms in a domain in the β phase and in the (1×1) phase can be determined as follows. The coverage of the β phase on a sample with fluctuating domains was estimated to be 1.30 ML, as described above, giving a difference in coverage from the (1×1) phase of 0.01 ML. Therefore, the difference between the number of atoms in a domain in the β phase and in the (1×1) phase is $\Delta N_{\text{experimental}} = n_{\text{unit cell}} \times (0.01\ \text{ML}/1.33\ \text{ML}) \times 4 = 600$.

That the values of ΔN_{expt} and $\Delta N_{\text{thermal}}$ have the same order of magnitude implies that there exists a significant probability that the density of a β domain will at times be low enough to convert to the (1×1) phase, and the reverse, i.e., that a (1×1) domain can occasionally have high enough density to convert to the β phase. This then explains our observations of spontaneous domain switching in the coexistence region. Note the actual value for ΔN_{expt} is likely to be smaller than that determined above, since the coverage of 1.29 ML for the (1×1) phase used in the calculation defines the lower limit of the coexistence region, and the actual density could be higher.

The above analysis also clarifies that the experimental and theoretical values of ΔN depend on the area of a fluctuating domain in different ways. ΔN_{expt} depends linearly on A, while $\Delta N_{\text{thermal}}$ depends on $\sqrt{A}$. Since these numbers are comparable only when A is small, the actual size of the nanometer-scale domains allows the manifestation of the thermal fluctuations as the transformation of the phase of domains on this surface.

In conclusion, we have evidence for a new phase separation mechanism within the coexistence region of the β and (1×1) phases on Pb/Ge(111), involving the phase fluctuations of domains, instead of nucleation and growth of a new phase. Rather than long-range atomic diffusion, thermal fluctuations in the density of atoms allow spontaneous domain switching to occur. The nanometer-scale size of the domains allows thermal fluctuations to cause this novel phase transformation.

We would like to thank Konrad Thürmer for his helpful comments. We acknowledge partial support from NSF No. CHE-0111671. The LEEM instrumentation was funded by NSF No. DMR 9512231. N. C. B. was supported by the Office of Basic Energy Sciences, Division of Materials Sciences of the U.S. DOE under Contract No. DE-AC-04-94AL85000.

[1] H. Ibach, *Physics of Surfaces and Interfaces* (Springer, New York, 2007).
[2] R. Feidenhans'l *et al.*, Surf. Sci. **178**, 927 (1986).
[3] H. Huang *et al.*, Phys. Rev. Lett. **62**, 559 (1989).
[4] S. A. de Vries, P. Goedtkindt, P. Steadman, and E. Vlieg, Phys. Rev. B **59**, 13 301 (1999).
[5] T. Ichikawa, Solid State Commun. **46**, 827 (1983).
[6] J. J. Metois and G. Le Lay, Surf. Sci. **133**, 422 (1983).
[7] F. Grey, Ph.D. thesis, Copenhagen University, 1988 (unpublished).
[8] L. Seehofer *et al.*, Phys. Rev. B **51**, 13 503 (1995).
[9] M. F. Reedijk, J. Arsic, D. Kaminski, P. Poodt, J. W. M. van Kessel, W. J. Szweryn, H. Knops, and E. Vlieg, Phys. Rev. Lett. **90**, 056104 (2003).
[10] F. Ancilotto, A. Selloni, and R. Car, Phys. Rev. Lett. **71**, 3685 (1993); Phys. Rev. B **50**, 15 158 (1994).
[11] Dotted line was used at lower coverage ($\Theta < 0.33$) where significant desorption of Pb was observed close to the transition temperature.
[12] C. L. H. Devlin, D. N. Futaba, A. Loui, J. D. Shine, and S. Chiang, Mater. Sci. Eng. B **96**, 215 (2002).
[13] Y. Sato and S. Chiang (to be published).
[14] See EPAPS Document No. E-PRLTAO-99-032730 for a LEEM movie of the same phase transition in a different experiment where the sample was quenched through the coexistence region. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
[15] See EPAPS Document No. E-PRLTAO-99-032730 for a LEEM movie of the experiment. Sample temperature was held constant at 189 °C throughout the movie. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
[16] J. Orban, A. Bellemans, J. Chem. Phys. **49**, 363 (1968).
[17] In a separate experiment, a film was deposited to form β phase (coverage 1.33 ML) and was subsequently annealed to desorb enough Pb at the same temperature as the above experiment until the surface consisted of the α phase (coverage 0.33 ML) and β phase when the temperature was lowered below T_c, i.e., coverage just below the eutectic point (1.29 ML). The annealing time to desorb a known amount of Pb is thus measured and used to compute the Pb coverage.
[18] According to the LEEM observation of Pb film growth on Ge(111), at a coverage close to 0.33 ML Ge adatom islands are formed from Ge adatoms on the reconstructed Ge $c(2 \times 8)$ surface as they are replaced by deposited Pb atoms during the initial stage of the deposition.
[19] I. S. Hwang and J. A. Golovchenko, Phys. Rev. B **50**, 18 535 (1994).
[20] The change in the areas of the α phase on the adatom islands, around which the β or (1×1) phase grew, is negligible. Therefore, we have assumed that Pb atom transfer only occurs between the β or (1×1) phase and the surrounding α phase but not between the β or (1×1) phase and the α phase on top of adatom islands.