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Phase coexistence between the $(\sqrt{3} \times \sqrt{3})R30^\circ$ – β and (1×1) phases on Pb/Ge(1 1 1)

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ABSTRACT

We have characterized the phase transition between the (1×1) and $(\sqrt{3} \times \sqrt{3})R30^\circ$ – β phases on Pb/Ge(1 1 1) using low energy electron microscopy (LEEM). We show that the transition is first-order and that, in the coexistence region of the two phases, the dominant mechanism for phase separation changes critically with Pb coverage, from nucleation and growth at 1.33 ML (saturation coverage of the β phase) to spontaneous domain switching due to thermal fluctuations of the local Pb density for slightly smaller coverage. As the Pb coverage decreases, the concentration of vacancies in the β phase increases, making additional possible Pb adsorption sites available. The larger resulting local density fluctuation of Pb becomes comparable to the density difference of the two phases, manifesting itself in the observed domain switching.

1. Introduction

Phase coexistence is a universal phenomenon in surface phase transitions. Long-range interactions such as the elastic interactions between two phases with different surface stress or the electrostatic interactions due to work function differences can preclude a sharp first-order transition involving a latent heat and give rise to phase coexistence over a range of temperatures near T_c [1–4]. In epitaxial films, coexistence regions can exist over a range of film coverage, as well as temperature. Pb on Ge(1 1 1), for example, is a system that shows such coexistence of two phases, the low coverage (1×1) phase and the high coverage $(\sqrt{3} \times \sqrt{3})R30^\circ$ – β phase [5]. We have previously reported the discovery of a novel phase separation mechanism between these two phases [4]. When the Pb coverage is slightly reduced from the saturation coverage of the β phase, the transformation is dominated by spontaneous phase switching of nanoscale domains over the surface. This novel mechanism occurs because the density difference between the β and (1×1) phases is actually so small ($\sim$0.04 ML) that the nanometer-scale domains can have density fluctuations comparable to the density difference between the two phases. One important issue that has not been discussed previously is how the transformation process within the coexistence region evolves critically with Pb coverage. In this paper, we present real-time observations of how the phase transformation process changes from conventional nucleation and growth behavior at the saturation coverage of the β phase to the novel spontaneous domain switching at slightly reduced Pb coverage. Based on direct observations of the coexisting phases using time-resolved low energy electron microscopy (LEEM), we propose that this change in the transformation process is due to the change in the vacancy concentration of the ordered β phase, resulting in a large Pb density fluctuation.

Pb on Ge(1 1 1) forms two stable $(\sqrt{3} \times \sqrt{3})R30^\circ$ 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 [6–8]. The saturation coverage and the atomic structure of the dilute α phase were determined by Feidenhans'l et al. based on their surface X-ray diffraction measurements [6], and their results were later confirmed by others [9–11]. The structure and coverage of the β phase remained controversial. A model with a saturation coverage of 1.33 ML was proposed based on studies using reflection high energy electron diffraction (RHEED), X-ray scattering, and low energy electron diffraction (LEED), but other authors who used scanning tunneling microscopy (STM) and LEED have argued that the coverage is 1 ML. The 1 ML trimer model proposed by Hwang et al. based on STM images [8], however, was found to be unstable by first-principles calculations. Further, Seehofer et al. showed that interpretation of the STM images of the β phase is not straightforward [12]. They observed a varying number of protrusions per $(\sqrt{3} \times \sqrt{3})R30^\circ$ unit cell depending on the tunneling parameters. Based on their study, they ruled out the model proposed by Hwang. A review of the different structural models proposed for the β phase is given by Franklin et al. [13].

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Most experiments, including their X-ray standing wave results, give support to the saturation coverage of 1.33 ML. More recently, de Vries et al. confirmed the saturation coverage of 1.33 ML using the X-ray diffraction technique and proposed an atomic structural model that is consistent with other LEED and X-ray scattering studies [7]. Based on these reviews, we assumed the saturation coverage of 1.33 ML for the β phase and used this value in our phase diagram. The accepted structural model for the α phase was published in Ref. [6] and that for the β phase in Ref. [7].

The high temperature (1×1) phase is a disordered phase, which can accommodate a range of coverage [14]. Based on the LEEM data presented in this paper and elsewhere [14,15], we propose a phase diagram of this system (see Fig. 1, [4]), which is a modified version of the previously published phase diagrams [16–18]. The main differences from the most recently published diagram by Reedijk are the coexistence region of the (1×1) and β phases, the measurement of the Pb coverage of 1.29 ML at the eutectic point [4], and the presence of only the β structure at high coverage.

The main questions about the $\beta \Leftrightarrow (1 \times 1)$ phase transition are the order of the transition and the reason for a sharp increase in the transition temperature near the saturation coverage of the β phase. Based on the STM observation of "fluctuating" (1×1) structure just above the transition temperature of 180 °C, Hwang and Golovchenko suggested that the transition is second-order near the saturation coverage of the β phase [8]. Reedijk et al. experimentally determined the critical exponents of the transition using surface X-ray diffraction for a 1.28 ML sample with a transition temperature of 247 °C and reported a continuous (second-order) phase transition [19].

As for the sharp increase in the transition temperature, Hwang argued that, after the first layer saturates, further deposition leads to the formation of Pb islands as well as the modification of the profile of the step edges, causing the surface strain field to change, in turn causing the transition temperature to increase [8]. Based on their room temperature STM and RHEED studies [20], Seehofer concluded that the lower transition temperature of 180 °C corresponds to the commensurate β phase, while the higher transition temperature can be assigned to the striped incommensurate (SIC) phase.

Reedijk et al. [17], on the other hand, proposed that the increase in the transition temperature occurs before the saturation of the β phase and explained it in terms of vacancy-induced disordering as occurs in the N_2 adlayer on graphite, i.e., the melting temperature of the N_2 adlayer on graphite is reduced for coverages below the saturation coverage because the presence of vacancies facilitates melting [21]. They also proposed the existence of a new metastable phase, which they called the β' structure, that irreversibly transforms to the (1×1) phase at 330 °C, on as-deposited samples. Once the bulk Pb melting temperature (T_m = 327.5 °C) is reached, subsequent transformations of their β' structure occur at a lower temperature, and the structure can then be identified as the well-studied β phase.

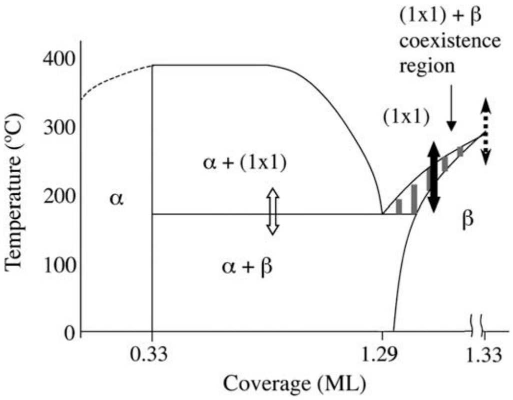

Fig. 1. Modified phase diagram for Pb/Ge(1 1 1) [4]. The dashed arrow on the right shows where a sharp first-order phase transition at ~295 °C is observed, and the solid arrow shows where the transition is dominated by fluctuating domains. The melting temperature of bulk Pb is 327 °C.

Our LEEM experiments give no evidence for an extra β' phase. In fact, LEEM data are consistent with the observation made by Reedijk et al. [17] if we assume their irreversible phase transition that occurred at higher temperature involves desorption of lead so that the subsequent phase transition occurs at lower coverage in the coexistence region. LEEM data clearly show that a slight reduction in the Pb coverage induces a dramatic change in the transformation process, causing a sharp change in the transition temperature near 1.33 ML. This could account for Reedijk's observations without invoking a model with two different structures, i.e., the β and β' phases. Our model of the increase in vacancy concentration explains the changes in the transformation behavior and temperature in the coexistence region by incorporating the novel phase separation mechanism recently found in this system [4], resolving existing controversies about this transition [8,12,16,17,19,22,23].

2. Experimental description

The commercial ultrahigh vacuum (UHV) LEEM is connected to an analysis chamber equipped with an X-ray photoemission spectrometer (XPS) and an Ar^+ ion sputter gun [24]. A resistively heated evaporator was used to deposit Pb at a rate of 0.25–0.4 ML/min, with pressure in the LEEM main chamber $\leqslant 1.0 \times 10^{-9}$ torr. The deposition rate measurement is based on the areas of different structures in the LEEM images during the deposition, using the quoted coverages of 0.33 ML for the α phase [6] and 1.29 ML for the (1×1) phase at the eutectic point [4]. The n-doped, 0.40 Ω-cm, Ge(1 1 1) samples, were oriented within 0.2°. After sonicating in methanol, the Ge(1 1 1) samples were dipped into H_2O_2 for ~60 s to form an oxide layer. *In situ* cleaning consisted of cycles of Ar^+ sputtering (250 eV, 5μA) and annealing at 800 °C until no impurity was detectable by XPS. The sample was heated from the rear by electron bombardment. Its temperature was measured with a W-5%Re/W-25%Re thermocouple mounted between a donut-shaped Ta foil and the back of the sample. To account for the temperature gradient between the imaged area over the center of the substrate and the edge where the thermocouple is located, a temperature calibration was done using an optical pyrometer. In addition, the melting temperature of the Ge crystal (937 °C) was compared with the thermocouple reading. The critical temperature for the $\beta \Leftrightarrow (1 \times 1)$ transition at 0.65 ML Pb coverage was measured to be 170 °C in this study, 5–10 °C below the reported values [7,8].

Lead was deposited onto the clean Ge(1 1 1) substrate held at 300 °C, with coverage at or close to the saturation of the β phase (1.33 ML). All of the features of the transformation process discussed in this paper were reproducible on samples on which Pb had been deposited at varying temperatures between 200 and 300 °C. The formation of the β phase was confirmed by the observation of the $(1 \times 1) \Rightarrow \beta$ transformation during the deposition. To make samples with slightly different coverage, the Pb coverage was decreased by annealing at 350 °C to desorb Pb. The coverage of an annealed sample was then determined by comparing the total annealing time with the time needed to desorb a known amount of Pb at the same temperature. The saturation coverage of Pb for the β phase is known to be 1.33 ML, and the coverage of Pb at the eutectic point was measured to be 1.29±0.01 ML [4]. At a temperature of 350 °C, the annealing time required to go between these two states, which differ in coverage by 0.04 ML, was measured to be 30 min. Assuming a linear relationship between the amount of desorbed Pb and the annealing time, we have estimated the Pb coverage. Note that a relatively small change in annealing time, corresponding to a small coverage change, results in a dramatic difference in the behavior of the phases near the transition temperature, as observed directly in the LEEM images. Therefore, in the discussion of the following data, we give an additional digit on the coverage to give the reader an indication of the monotonic decreases in coverage, even though the additional digit is not significant.

3. Results and discussion

3.1. β ⇔ (1 × 1) phase transition at 1.33 ML

Fig. 2 shows a sequence of bright-field LEEM images captured during the (1 × 1) to β phase transition at 1.33 ML. The phase transition at this coverage is marked by nucleation and quick growth of the new stable phase at the specific temperature of 295 °C. This is an expected behavior for a first-order phase transition occurring at the entrance of the coexistence region. At this point of the phase diagram, where there is no difference in the density of the two phases, the transformation should be sharp and should occur at a fixed temperature. Distinct contrast between the β and (1 × 1) phases, and the absence of intermediate states between the two phases also indicate that this is a first-order phase transition rather than a continuous (second-order) phase transition. When the film coverage is reduced, the densities of the two phases become different, giving rise to the phase coexistence, as we discuss in detail below.

The dark islands visible on the surface are formed from Ge adatoms of the clean, reconstructed Ge(1 1 1) c(2 × 8) surface structure. During the initial stage of Pb deposition, Pb atoms replace the Ge adatoms in the reconstructed sites, and the Ge adatoms which are released from the surface then diffuse and form islands on the surface [15]. Further Pb deposition results in the formation of a Pb film over the whole surface, including on top of the Ge islands. The transition temperature of the (1 × 1) phase on the Ge islands is about 10 °C lower than on the rest of the surface (see Fig. 2(c) and (d)), with the phase transition occurring suddenly, as on the rest of the surface. Note that the phase diagram shown in Fig. 1 is based on the transition temperatures measured for the Pb layer on the Ge surface excluding the top of the Ge islands, as the transition temperature of the phase of the Pb layer on top of the Ge islands is always ∼10 °C lower than on the rest of the surface.

3.2. Coverage dependence of the β ⇔ (1 × 1) phase transition

When the coverage of the Pb is slightly decreased by desorbing Pb through annealing, dramatic changes occur in the transformation process. Fig. 3 shows a sequence of bright-field LEEM images of the (1 × 1) to β phase transition after the sample in Fig. 3 was annealed at 350 °C for 1 min. The estimated Pb coverage is 1.329 ML. While the images look similar to those from the previous

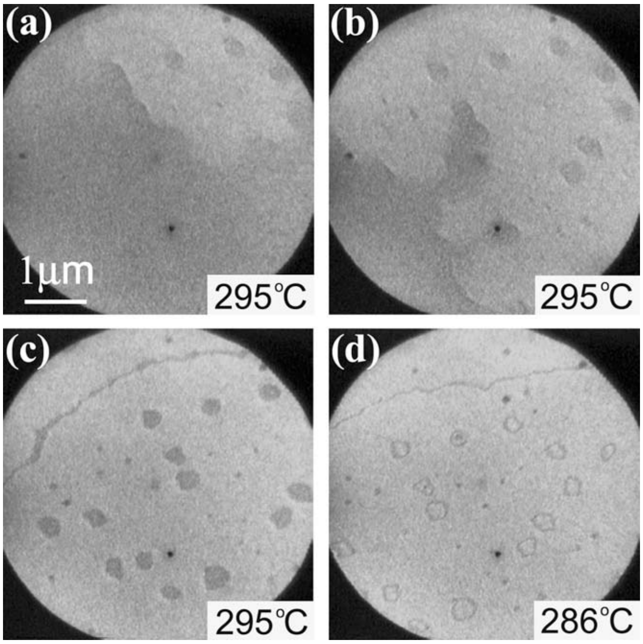

Fig. 2. A sequence of bright-field LEEM images captured during the (1 × 1) (dark) ⇒ β (bright) phase transition of Pb/Ge(1 1 1) for Pb coverage of 1.33 ML. The real-time LEEM movie of the experiment is found in Movie1 online. The sample temperature was decreased slowly at ∼2 K/min. The sample was initially in the (1 × 1) phase, and the phase transformation occurred very rapidly at 295 °C. The electron energy is 6.1 eV. The islands visible on the surface are formed from Ge adatoms released from the c(2x8) reconstruction of the Ge(1 1 1) substrate surface. The black dot in the lower center of the images is a defect on the channel plate. (a) The β phase nucleates at a defect in the upper right corner. (b) and (c) The rest of the surface quickly transforms. (d) The transition temperature of the (1 × 1) phase on the Ge islands is about 10 °C lower than the rest of the surface.

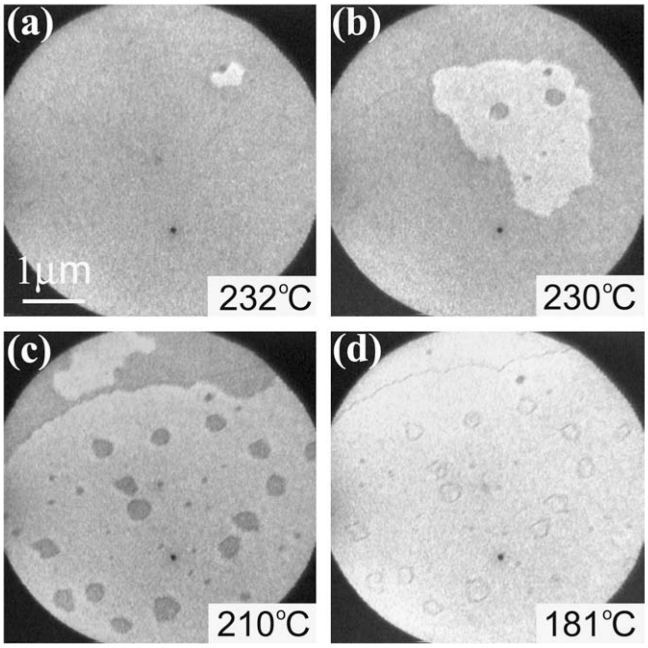

Fig. 3. A sequence of bright-field LEEM images captured during the (1 × 1) (dark) ⇒ β (bright) phase transition of Pb/Ge(1 1 1) after annealing the sample at 350 °C for 1 min. The estimated Pb coverage of the sample is 1.329 ML. Three LEEM movies, Movies 2a, 2b, and 2c, showing the different stages of the experiment and playing at 10× real-time, are found online. The sample temperature was decreased slowly at the rate of ∼1 K/min. Movie2a shows the first stage of the transformation from (a) to (b). Movie2b shows the transition when the temperature is close to 210 °C, corresponding to (c). Movie2c shows the final stage of the transformation when most of the surface has transformed to the β phase, as in (d). The electron energy is 6.1 eV. (a) The β phase nucleates at 232 °C at a defect in the upper right corner. (b) and (c) The β phase grows and covers the rest of the surface as the temperature is lowered to 210 °C. Though it is not clear from these still images, ∼100 nm regions at the phase boundary constantly flip their phases as the phase boundary moves across the surface. (d) At 181 °C, the β phase now finally grows in the Pb film on top of islands of Ge adatoms, completing the phase transformation.

transition, two significant changes have occurred in the transformation process. In contrast to the previous transformation for the coverage of 1.33 ML that occurred at the specific temperature of 295 °C, the nucleation of the β phase now occurs at the lower temperature of 232 °C, and the area fraction of the β phase continues to increase with decreasing temperature until the whole surface finally transforms into the β phase at 200 °C. Moreover, as the area of the β phase continuously grows, ~100 nm surface regions at the phase boundary spontaneously start to switch their phase. Note that the transformation occurs on the neighboring upper terrace at a slightly lower transition temperature. We attribute this difference in the transition temperature between two terraces to non-uniform Pb coverage, i.e., each terrace is at a slightly different point of the phase diagram. In addition, the Pb film grown on the Ge islands has a much lower transformation temperature of 181 °C than the rest of the surface, as shown in Fig. 3(d).

When the sample was annealed again at 350 °C for 5 min, resulting in an estimated coverage of 1.324 ML, the transformation started at the even lower temperature of 198 °C, and the spontaneous phase switching of domains was no longer limited to the phase boundary. Multiple domains started to appear on the terrace and fluctuated between the two phases (see Fig. 4). An interesting observation is that the fluctuations of the phases at the phase boundary are much more frequent than for the domains on the terrace. The whole surface, including the Pb film on top of the Ge islands, finished the transformation to the β phase at 182 °C. Note that the fluctuating domains repeatedly occur at the same places on the surface, presumably due to the presence of defects too small to be resolved in LEEM images [4].

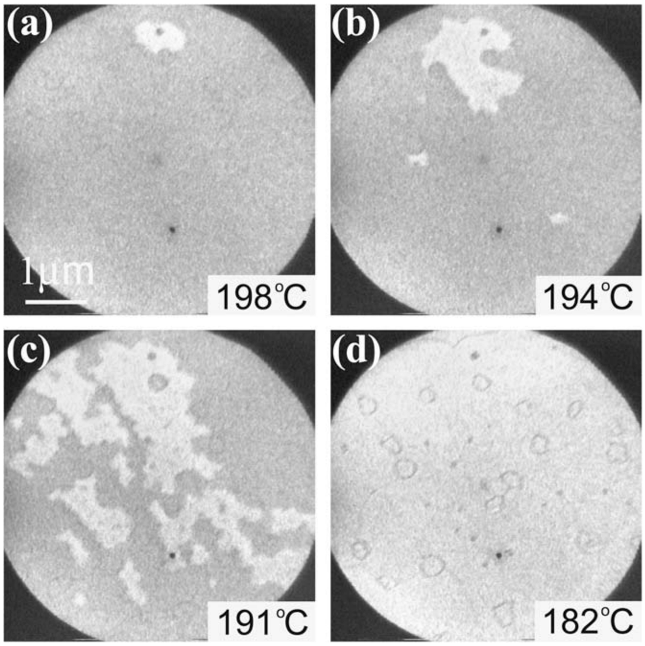

Fig. 4. A sequence of bright-field LEEM images captured during the (1 × 1) (dark) ⇒ β (bright) phase transition of Pb/Ge(1 1 1) after annealing the sample at 350 °C for 5 min. The estimated Pb coverage of the sample is 1.324 ML. The LEEM movie of the experiment, which plays at 10x real-time, is found in Movie3 online. The movie shows the initial stage of the transformation after the β phase nucleated at the defect shown in (a). Note that the occurrence of spontaneous domain switching is no longer limited to the domain boundary between the two phases. The sample temperature was decreased slowly at the rate of ~1 K/min. The electron energy is 6.1 eV. (a) The β phase nucleates at 198 °C at a defect in the top part of the image. (b) and (c) Besides the fluctuating behavior at the phase boundary of larger domains of the β phase, some smaller domains appear and fluctuate on the terrace. (d) At 182 °C, the β phase now grows in the Pb film on top of islands of Ge adatoms, completing the phase transformation.

Further annealing changes the transformation in a similar way. The two temperatures that define the coexistence region shift lower on the phase diagram. In addition, more domains appear and fluctuate on the terraces. The transformation process after the sample was annealed at 350 °C for 15 min is shown in Fig. 5 for a sample with the estimated coverage of 1.303 ML. The phase transformation began at ~180 °C and was completed at 170 °C. Fig. 5(d) shows the time-dependence of the intensity of the fluctuating domain which was circled in Fig. 5(a). Clearly, the domain is fluctuating between two well-defined states.

In a separate experiment, it was confirmed that, after more annealing, the transition is completely characterized by the spontaneous domain switching. The transformation process begins with the appearance of a few to several small domains, which fluctuate between the two phases. Throughout the coexistence region, the appearance and fluctuations of the domains continue until the transformation of the whole surface is complete.

Note that the above data were obtained by annealing higher coverage samples to desorb Pb and obtain samples of particular coverages. Similar observations of the changes in the transformation process can be reproduced by making samples of the same coverages by depositing additional Pb on lower coverage samples. Of the phase transitions discussed above, those which occurred at lower transition temperature, i.e., at lower Pb coverage, were consistently reversible. Those which occurred at higher transition temperature, however, often seemed irreversible with increasing temperature, presumably due to the desorption of Pb and the resultant change in Pb coverage.

3.3. Phase separation mechanism and vacancy concentration

To summarize, when the Pb coverage is reduced slightly by a measurable amount from the saturation coverage of the β phase

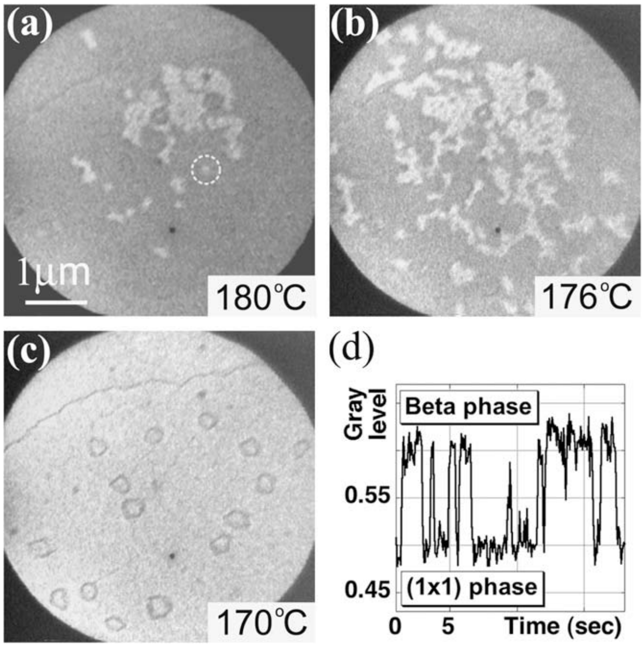

Fig. 5. A sequence of bright-field LEEM images captured during the (1 × 1) (dark) ⇒ β (bright) phase transition of Pb/Ge(1 1 1) after annealing the sample at 350 °C for 15 min. The estimated Pb coverage of the sample is 1.303 ML. The sample temperature was decreased slowly at the rate of ~1 K/min. The electron energy is 6.1 eV. (a) The β phase nucleates at a defect in the upper right corner. Multiple domains appear and fluctuate on the terrace. (b) Additional domains appear and fluctuate until they fluctuate into the β phase, including the Pb film on top of islands of Ge adatoms. (c) The transformation to the β phase completes at 170 °C. (d) The time-dependence of the intensity of a fluctuating domain, circled in (a), during the (1 × 1) ⇒ β phase transition at ~177 °C.

and the coexistence region is entered, the transition temperature is reduced, the temperature range for the transition shifts lower in the phase diagram, and the growth of the β phase proceeds simultaneously with spontaneous domain switching. At higher coverage, the phase fluctuations of the domains initially are limited to the phase boundary between the (1 × 1) and the β phases. At lower coverage, however, spontaneous domain switching occurs everywhere on the surface, although the switching frequencies at the phase boundary are observed to be greater than those in areas where isolated domains are surrounded by regions of the other phase. When the Pb coverage is further reduced, spontaneous domain switching dominates the transformation behavior.

These observations suggest the following picture. The β phase is able to form below its saturation coverage of 1.33 ML, accommodating vacancies in its structure. As the total Pb atom density on the surface decreases, the number of vacancies in the β phase increases. At higher coverage (closer to 1.33 ML), the local variation in the number of Pb atoms due to thermal fluctuations is limited by the small vacancy concentration. On the whole, few domains have density fluctuations comparable to the density difference between the two phases. As the Pb coverage is further decreased, the concentration of vacancies in the β phase increases, making additional possible Pb adsorption sites available. The larger resulting local density fluctuation of Pb, activated thermally, can be comparable to the density difference in many domains, and thus the spontaneous domain switching dominates the transformation. More vacancies also allow disordering of the β phase at a lower transition temperature. Such influence of vacancies on disordering has been observed and modeled using Monte Carlo simulations [21,25]. At the phase boundary near the (1 × 1) phase, it is reasonable to assume that the local density of the β phase would be lower to reduce the boundary energy. This explains why domains at the phase boundary start to fluctuate their phase at higher total Pb coverage than the isolated domains on the rest of the surface do, and why their fluctuations should be more frequent.

Previous models proposed by Hwang *et al.*[8] and Seehofer *et al* [12] to explain the increased transition temperature cannot explain the observed domain switching. Our model of the increasing number of vacancies with decreasing Pb coverage explains the decreasing transition temperatures without assuming the additional β′ phase proposed by Reedijk *et al.*[17]. This phase had also been proposed in order to explain an irreversible change in transition temperature, which is explained in our model by a change in Pb coverage caused by annealing, rather than the redistribution of the excess Pb atoms. In the experiment of Reedijk *et al.*, small and tall islands of excess Pb are likely to be 3D Pb crystallites which form after the first 2D Pb layer is completed [22]. The LEED pattern associated with Pb(1 1 1), however, disappears around the bulk Pb melting temperature of 327 °C [26], which is also approximately the temperature where Reedijk's β′ phase irreversibly disappears. Note that this is at a lower temperature than the 350 °C used to desorb Pb from the first layer in our experiments. Thus, a likely scenario suggested by our data is that annealing first desorbs any excess Pb which is adsorbed on top of the first adsorbed Pb layer. Note that the LEEM images, however, do not provide direct evidence for the presence of excess Pb in the form of islands, due to the limited resolution of ~10 nm.

4. Conclusion

Using LEEM, we have determined that the β ⇔ (1 × 1) transition is a first-order transition, and that the phase separation mechanism within the coexistence region changes critically with Pb coverage, from nucleation and growth at 1.33 ML to spontaneous domain switching. Increased vacancy concentration in the β phase with decreasing Pb coverage makes additional possible Pb adsorption sites available. As a result, the local density fluctuation is no longer limited by the small vacancy concentration and can become comparable to the density difference between the two phases. Our model can explain both the changes in the transformation and in the transition temperature observed in the coexistence region of this system and resolves the existing controversies about this phase transition.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.susc.2009.05.008.

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