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Non-equilibrium behavior of the Pb wetting layer on Si(111)7x7

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The growth and stability of the Pb8x8 wetting layer on Si(111)7x7, which provides a foundation for growing quantum-size-effect nanocrystals, was investigated by in situ x-ray scattering. Our experimental results reveal that the wetting layer structure evolves temporally over a remarkably broad range of temperatures and that there are *two* distinct temperature regimes of non-equilibrium behavior. When grown at lower temperature (below 170°C), it was discovered that the wetting layer structure changes with time, indicating that its disordered structure is not static; annealing in this regime improves the order of the wetting layer. Growth at higher temperature (170°C < T < 250°C), however, leads to a time-dependent degradation of the 8x8 structure due to the deterioration of the underlying Si(111)7x7. Thermal measurements determined an activation energy 0.4 eV in the low temperature regime whereas in the high-temperature regime a two-step process is observed which have activation energies of approximately 1.3 and 1.9 eV. The results provide important new considerations for understanding the anomalous kinetic behavior of quantum-size-effect Pb nanocrystals on Si(111)7x7 that is facilitated by the wetting layer.

I. INTRODUCTION

In the pursuit to understand the growth and formation of nanoscale materials, it has been realized that their reduced physical dimensions can also lead to novel growth behavior. An important example is given by metallic nanocrystals grown on semiconductor substrates where the geometrical confinement of the conduction electrons can affect the overall energy of the nanocrystal¹. Indeed, quantum-size-effects (QSE) have been observed in metallic islands which exhibit certain “magic heights” of atomic-layers^{2,3}.

Because epitaxial crystal growth is usually dominated by kinetic limitations⁴, the equilibrium nature of the growth implied by QSE is unexpected. Experiments on Pb/Si(111)7x7, however, have shown that the growth kinetics are anomalously fast, thereby providing some rationale for achieving the magic heights⁵. The origin of the fast kinetics is still unknown; but the region between the nanocrystals *must* facilitate fast mass transport. For this reason, we are interested in understanding the structure of the wetting layer that exists in the region between the Pb nano-islands.

Depositing Pb on Si(111)7x7 follows a Stranski-Krastanov growth mode whereby the Pb completely wets the substrate with a layer (the “wetting layer”) that is one monolayer in thickness, followed by the formation of islands (the QSE islands) for higher coverage⁶. Previous surface x-ray diffraction investigations into the structure of the wetting layer have found that it forms a highly disordered 8x8 structure that is commensurate with the Si(111)7x7 unit cell⁷. Unfortunately, a complete structural determination was hindered by the disorder within the wetting layer, a limited data set, and by the fact the measurements were performed for a coverage of $\sim 2\text{ML}$, where the surface was significantly covered by islands. STM studies on the Pb/Si(111)7x7 wetting layer have been complicated by an inability to resolve individual Pb atoms in the structure⁸, and several structures have been proposed based on the limited resolution images^{8,9}. Recent x-ray scattering studies have shown that, surprisingly, the portion of the wetting layer directly beneath the islands is transformed to FCC Pb so that the islands consume the wetting layer^{10,11}. The material remaining between the islands, however, continues to exist in the wetting layer structure. Another important complication, as revealed in our present paper, is that the wetting layer structure also changes with time because it is not in equilibrium. Therefore, the detailed structure of the Pb8x8 wetting layer is still left as an open question.

The Pb8x8/Si(111)7x7 wetting layer is known to be metastable because the presence of the metal negates the need for the dimerization that drives the Si(111)7x7 reconstruction. Annealing above 200°C destroys the Pb/Si(111)7x7 and the surface reorders into a Pb/Si(111)1x1^{12,13}. Upon cooling, for coverages around 1 ML, the system orders in the α -phase, which refers to a collection of closely related surface structures based on a $\text{Pb}\sqrt{3} \times \sqrt{3}/\text{Si}(111)$ structure¹⁴. The system exhibits a complex phase diagram that has been shown to derive from large commensurate unit cells that are constructed from combinations of $\sqrt{3} \times \sqrt{3}$ and $\sqrt{7} \times \sqrt{3}$ units¹⁵.

In this paper, we show that the wetting layer is unstable in *two* temperature regimes and our results reveal that the structure of the wetting layer evolves temporally over a remarkably broad range of temperatures due to the fact that there are two physically independent causes of the instability. When grown at lower temperature, the initial wetting layer is found to slowly anneal into a *more-ordered structure*, which suggests that the wetting layer is highly dynamic as it attempts to accommodate the large corrugation of the Si(111)7x7 substrate. At higher temperature, the wetting layer structure is found to slowly *degrade* with time, consistent with the above-mentioned impending destruction of the Si(111)7x7 reconstruction. These effects occur on typical laboratory time scales over a broad temperature range, from below 0°C to over 200°C

II. EXPERIMENTAL DETAILS

X-ray scattering experiments were performed in situ using the surface scattering chamber (base pressure of 1×10^{-10} Torr) on a Psi diffractometer located at the 6IDC beam line at the Advanced Photon Source. The photon energy was 12.4keV and the data were collected using a Bicron detector. We will use hexagonal coordinates $(H, K, L)_H$ to describe the reciprocal lattice of Si, which is defined by the following relationship between hexagonal (H) and cubic

(C) coordinates: $a_H = \frac{a_C}{\sqrt{2}}$ and $c_H = \sqrt{3}a_C$ where $a_C=0.5403nm$ is taken as the room temperature Si cubic lattice constant and $[0, 0, 3]_H = [1, 1, 1]_C$ is along the surface normal direction.

The commercially-available 1mm-thick n-type Si(111) substrates used in these studies had a resistivity in the range of 1-10 Ωcm . Surface miscut angles were determined to be in the range of 0.015-0.05 $^\circ$ by x-ray reflectivity. The Si(111)7x7 surface was prepared by heating the Si(111) substrate to 1200 $^\circ C$ for ~ 1 min and then slowly cooling from 1000 $^\circ C$ over ~ 10 min. to obtain the reconstructed surface. The quality of the surface was determined by transversely scanning the $(\frac{8}{7}, 0, 0.1)_H$ in-plane reflection, which will be referred to as $(\frac{8}{7}, 0)_H$. It exhibited an angular width in the range of 0.02-0.05 $^\circ$, which corresponds to domain sizes in the range of 8000-3300 \AA . This large domain size is on the order of the step length given by the surface miscut angle and was routinely observed for all surfaces that were prepared as described above.

Pb was deposited on the clean Si-7x7 surface from a crucible that was heated by an electron beam with flux feedback (Omicron EFM). Two standard deposition rates, 0.25ML/min and 0.5ML/min, were used where 1ML is measured in Pb(111) $_C$ units (1ML= 9.43x10 14 atoms/cm 2). The deposition rates were calibrated by measuring the rate of intensity oscillations with coverage (for high coverage, >10ML, and T ~ 100 K) at the Pb specular anti-Bragg position (L=1.64), with each oscillation period corresponding to the completion of two Pb(111) layers 16 . The uncertainty and reproducibility of the coverage is estimated to be ± 0.1 ML. The sample was cooled to a minimum temperature of 100K using a He closed-cycle refrigerator. Heating for the purpose of preparing the Si(111)7x7 was performed by electron bombardment whereas maintaining the temperature during the scattering measurements (-50 $^\circ C$ to 450 $^\circ C$) utilized radiative heating from the tungsten filament behind the sample. The temperature was measured by a type K thermocouple connected to the bottom of the sample holder, which was also used for temperature control with a feedback system. The thermal stability during measurements was $\pm 0.5^\circ C$ and the absolute temperature accuracy was better than $\pm 10^\circ C$.

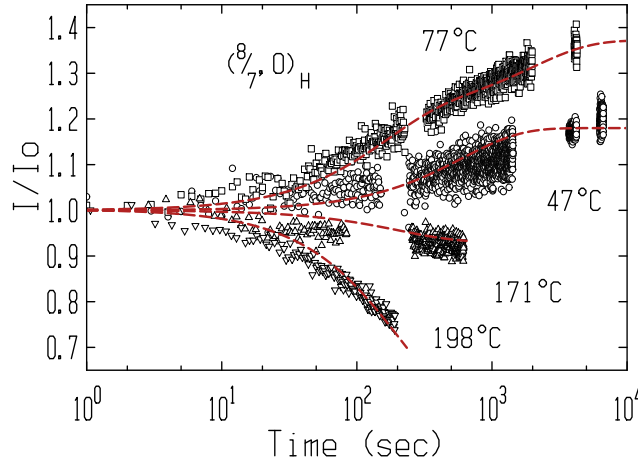


FIG. 1. The $(\frac{8}{7}, 0)_H$ peak intensity measured with elapsed time after depositing 1.2ML of Pb at different fixed substrate temperatures. The intensity has been normalized by the initial peak intensity, I_0 , measured immediately after (~ 1 sec.) deposition. As can be seen, there are two regimes of time-dependence: low-temperature and high-temperature regimes, which exhibit increasing or decreasing intensity with time, respectively. The dashed curves represent fits to the data, as described in the text.

III. RESULTS AND DISCUSSION

The intriguing behavior of the wetting layer is displayed in Fig. 1, which shows the normalized $(\frac{8}{7}, 0)_H$ intensity measured as a function of elapsed time after depositing 1.2ML of Pb on Si(111)7x7 at different temperatures. The $(\frac{8}{7}, 0)_H$ reflection represents the fundamental periodicity of the Pb8x8 wetting layer and, therefore, it is a good indicator of the overall order of the wetting layer. The intensity is normalized by the initial intensity, I_0 , which was measured immediately after (~ 1 sec.) deposition. As can be seen, not only is there a substantial change of intensity with the elapsed time, indicating that the wetting layer is not in equilibrium, but there also exists two *oppositely behaving* annealing regimes: a lower-temperature regime where the intensity is observed to *increase* with time and a higher-temperature regime where the intensity *decreases* with time. Moreover, the rate of annealing increases with increasing temperature in *both* temperature regimes; although, annealing in the lower-temperature regime is expected to eventually give way to a transition to the higher-temperature regime. These two temperature regimes are also apparent in Fig. 2, which shows the temperature-dependence of the initial intensity. The intensity increases more than 10-fold with increasing deposition temperature from -50°C to 170°C , followed by a precipitous decrease for higher growth temperatures, above $\sim 200^\circ\text{C}$.

Similar results are essentially obtained by depositing at a lower temperature and then annealing at a higher temperature. Fig. 3a shows the integrated intensity of the $(\frac{8}{7}, 0)_H$ reflection for a 1.2ML film that was deposited at -20°C and then annealed in successive ~ 10 min steps, at the given temperatures. It can be seen that the general trend of increasing intensity with annealing temperature is observed, although, the intensity increase is somewhat less than in Fig. 2. Therefore, equivalent results can be obtained in three ways: by annealing with time or temperature, or by depositing at a higher temperature.

The increasing intensity of the $(\frac{8}{7}, 0)_H$ reflection indicates that the as-deposited wetting layer is not an equilibrium structure and, moreover, this evolution corresponds to an improving atomic-scale order within the unit cell, as we will now discuss. Fig. 4 shows, for many fractional order $(\frac{m}{7}, \frac{n}{7})_H$ surface reflections, the ratio of the intensity measured on an annealed sample to the initial intensity of the as-grown Pb wetting layer at -45°C . This was measured both during and after annealing. Ratios that are greater than unity correspond to intensities that increased during annealing whereas ratios less than unity correspond to intensities that decreased during annealing. The graph strikingly shows that some peaks grow while others decrease, clearly indicating that the atomic-scale structure within the Pb8x8 unit

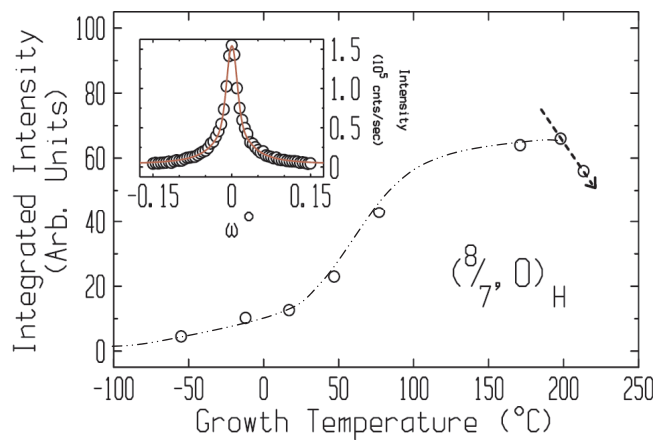


FIG. 2. The $(\frac{8}{7}, 0)_H$ transversely integrated intensity (obtained from scans similar to the one shown in the inset) for 1.2ML of Pb deposited at different fixed substrate temperatures. These intensities were measured shortly after (~ 1 min.) deposition. The dash-dotted curve through the data is a “guide to the eye”. The dashed arrowed line indicates the beginning of the decaying intensity process that was also observed in Fig. 1.

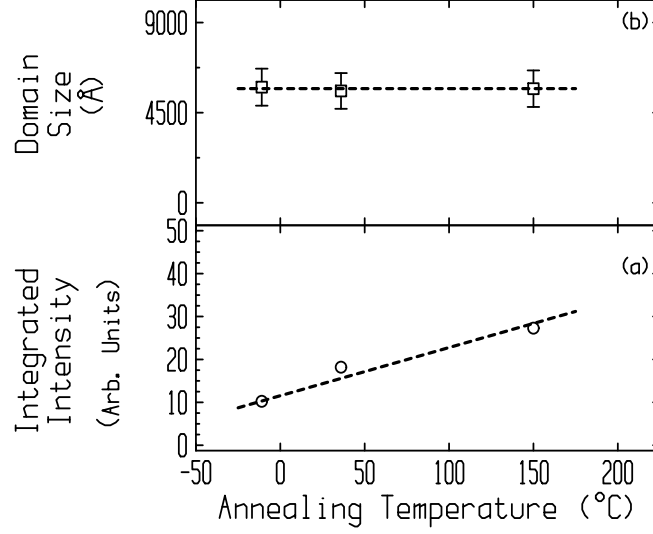


FIG. 3. The evolution of the $(\frac{8}{7}, 0)_H$ reflection as a function of annealing temperature (within the low-temperature regime). 1.2ML of Pb was deposited at -20°C and annealed in 10 min. steps at the given temperatures. (a) The integrated intensity increases with annealing temperature, indicating the improved ordering within the Pb8x8 unit cell as the temperature increases. (b) The domain size, which was determined from the transverse width of the reflection, does not change during annealing.

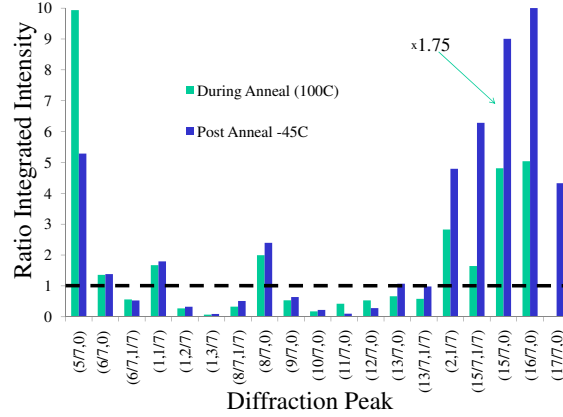


FIG. 4. The intensity ratios of different diffraction peaks $(H, K)_H$ of a 1.2 ML Pb film are shown for two cases of annealing: one measured at the annealing temperature of 100°C (~ 1 hr.) and one measured after cooling to -45°C . The intensity ratio is defined as the intensity of the annealed wetting layer divided by the intensity of the as-deposited wetting layer at -45°C . The horizontal dashed line at a ratio of unity demarks the level of change: an intensity ratio less than unity indicates a reflection that weakens with annealing whereas a ratio greater than unity indicates a strengthening of the reflection. Note that the intensity ratio for the $(\frac{15}{7}, 0)_H$ was reduced by a factor of 1.75 because its large change skews the other peaks.

cell was changed by annealing. Note that the increasing intensity observed in Figs. 1-3, is *not* due to an increasing surface fraction because the domain size does not change (see Fig. 3b). Additionally, there is an approximate pattern to the intensity changes in Fig. 4: reflections that are in the vicinity of integer multiples of $\frac{8}{7}$ tend to increase with annealing whereas the others decrease (an undistorted 8x8 would have peaks only at integer multiples of $\frac{8}{7}$). The peaks that increase are typically the stronger intensities while the ones that decrease are weaker. The only exception is the $(\frac{5}{7}, 0)$, which has very low intensity; however, this does not change the overall trend. Fig. 4 also reveals that

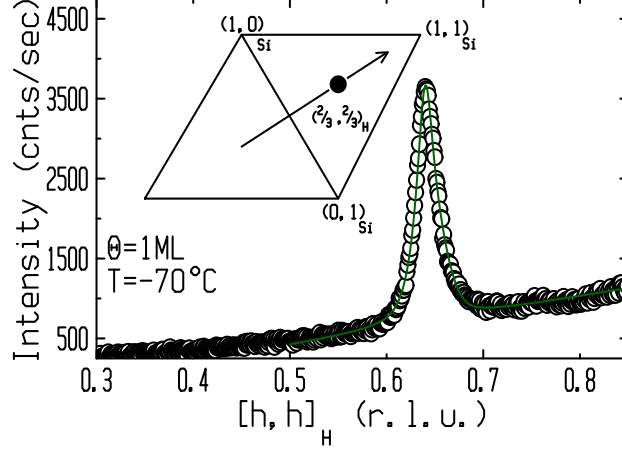


FIG. 5. An $[h,h]_H$ scan shows that annealing 1 ML of Pb above 200°C and cooling to -70°C produces the main Bragg reflection of the α -phase. Therefore the intensity decay observed in Fig. 1 relates to the destruction of the Pb/Si(111)7x7, which leads to the α -phase upon cooling. The solid curve is a Gaussian and background that was fit to the data. The inset schematically shows the hexagonal reciprocal lattice with the direction of the scan.

there is an additional intensity increase at these positions as the sample is cooled after annealing, indicating the effect of a strong thermal Debye-Waller factor. These results, therefore, demonstrate that the ordering within the unit cell *improves* upon annealing.

Turning now to the higher temperature annealing in Fig. 1, we see that the opposite temperature dependence is observed. As discussed in the introduction, it is known that annealing at elevated temperatures leads to the destruction of the underlying Si(111)7x7 surface that gives way to Pb/Si(111)-1x1 structure and, upon cooling, it transforms to the α -phase Pb/Si(111). Figure 5 shows that, indeed, after annealing above 200°C and subsequently cooling, the expected^{7,13,15,20} reflection at approximately $(\frac{2}{3}, \frac{2}{3})_H$ for the α -phase appears. Therefore, the precipitous drop in intensity with temperature above 200°C in Fig. 2 as well as the slow intensity decay above 170°C in Fig. 1 are due to the Pb-induced destruction of the Si(111)7x7. This is further corroborated by the inset to Fig. 6 that demonstrates a decreasing surface fraction of Pb8x8 during annealing: the measured surface reflections exhibit the *same* relative intensity decay, which is in sharp contrast to the lower-temperature annealing results in Fig.4 where some peaks increase while others decrease.

The decaying intensity observed at the higher temperatures in Fig. 1 was investigated in more detail by measuring over a longer period of time and over a larger temperature range, as shown in Fig. 6. The data show a decay rate that is significantly faster during an initial decay period (~ 10 min.) than at later times, suggesting that there are two time regimes. The time-dependent data fit well to a sum of two exponentials,

$$I(t) = I_1 e^{-\frac{t}{\tau_1}} + I_2 e^{-\frac{t}{\tau_2}} \quad (1)$$

where I_j 's are scale constants and the τ_j 's are the time constants. A fit of the data to eq.(1) is shown in Fig. 6. Although we cannot address the physical origin of the two time constants from the present data alone, the form of the decay suggests a two-step process that occurs sequentially in time (an intermediate structure may also be involved).

The time-dependent decay of the intensity, such as that shown in Fig. 6, was measured at different temperatures from which an estimate of the activation energy could be obtained for the destruction of the Si(111)7x7 covered with a monolayer of Pb. The logarithm of the two time constants obtained from a fit of the data to eq. (1) is plotted versus inverse temperature in Fig. 7. I_1 and I_2 were found to be reasonably constant (to within $\pm 12\%$) with temperature so

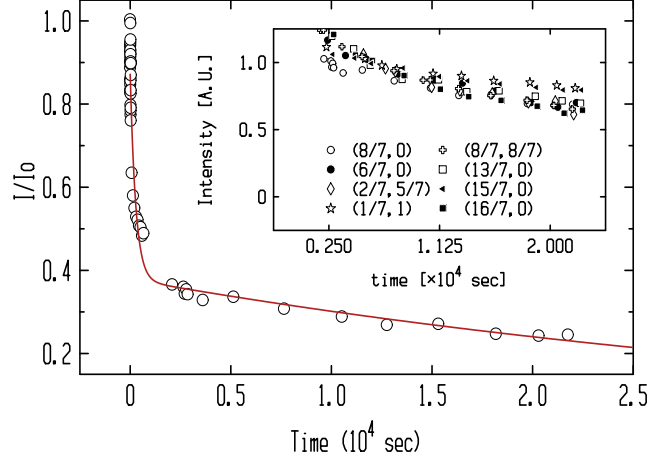


FIG. 6. The $(\frac{8}{7}, 0)_H$ peak intensity, normalized to I_0 , measured as a function of elapsed time after 1.2ML of Pb was deposited at 210°C . The data exhibit a fast initial decay followed by a slower decay at longer time. The solid curve shows that eq. (1), which describes two exponential decay processes, provides a good fit to the data. Inset: Multiple in-plane $(H,K)_H$ reflections show approximately the same rate of intensity decay, indicating the loss of the 7×7 surface fraction with time.

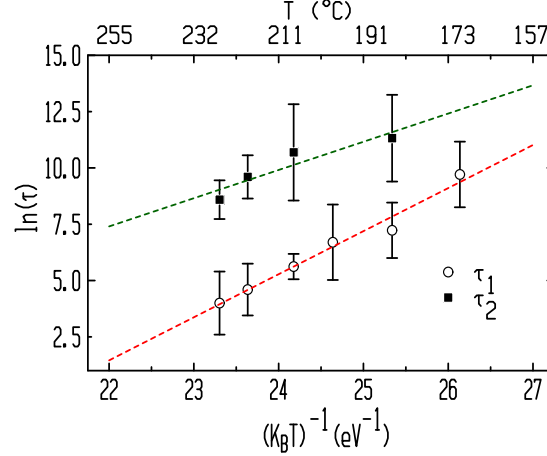


FIG. 7. $\ln(\tau)$ for both time constants, τ_1 and τ_2 , as a function of inverse temperature was obtained from fits of eq.(1) to the time decay of the $(\frac{8}{7}, 0)_H$ intensity at different annealing temperatures. The τ 's are measured in seconds. Two temperatures do not have τ_2 values because there was insufficient time data. The dashed lines represent fits to each set of time constants according to the Arrhenius behavior given in eq. (2).

that only τ_1 and τ_2 are temperature-dependent, giving further support to the notion that eq.(1) represents a two-step decay process. The activation energy, E_b , and attempt frequency, ν , for both time constants were extracted from an Arrhenius law according to,

$$\ln(\tau) = \frac{E_b}{k_B T} - \ln(\nu) \quad (2)$$

The results for both time constants are shown in Table I and by the lines in Fig. 7. It is noted that the slowest process corresponds to the smaller of the two activation energies.

A similar analysis was used to estimate an activation energy barrier for the low-temperature annealing regime using the *increasing intensity* data in Fig. 1. Because these lower-temperature data are more limited compared to our

	τ_1	τ_2
E_b	1.9 (± 0.2) eV	1.3 (± 0.2) eV
ν	$4 \times 10^{17} (\pm 3)$ Hz	$6 \times 10^8 (\pm 3)$ Hz

TABLE I. Activation energy, E_b , and attempt frequency, ν , obtained from fitting eq.(2) to the data in Fig. 7.

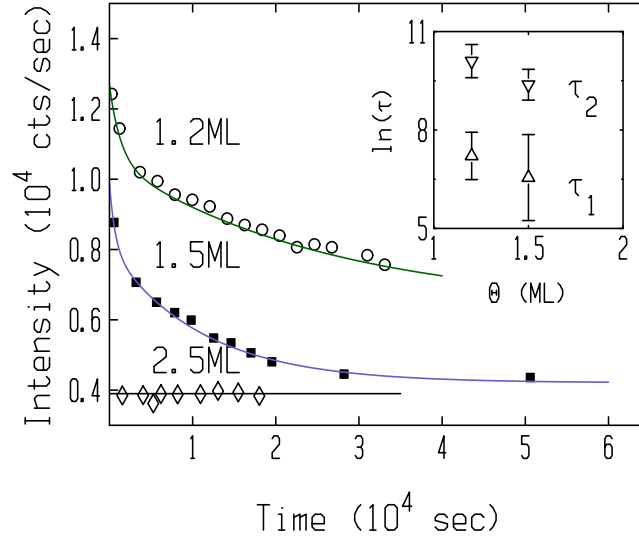


FIG. 8. The decay of the $(\frac{8}{7}, 0)_H$ peak intensity with elapsed time after the deposition of a given coverage of Pb at 185°C. Note that the intensity decays more quickly for 1.5 ML than for 1.2 ML. There is no decay observed for 2.5ML. The solid curves are calculated from eq. (1) which was fit to the data. The inset shows the time constants vs. coverage for the fitted curves.

high-temperature studies, a barrier from only a single time constant was determined: τ_1 is 600(± 60) s at 47°C and 150(± 15) s at 77°C, from which we estimate the activation energy barrier for the low temperature annealing of the Pb8x8 to be $E_b = 0.4(\pm 0.2)$ eV, with attempt frequency $\nu = 2 \times 10^{14} (\pm 1)$ Hz. This barrier is more than three times smaller than for the activation energy determined at higher temperature for the decaying intensities.

The measured energy barriers can be compared to various atomic-scale processes that have been discussed in the literature. For example, Pb adatom diffusion on the wetting layer and on top of a QSE Pb island have barriers of 0.1eV and 0.05eV respectively¹⁷. These values are significantly smaller than the 0.4eV barrier that we measured during the low-temperature annealing. However, rather than simple diffusion across a surface, our diffraction data in the low-temperature regime show that the Pb atoms rearrange within the unit cell, suggesting that atoms move in and out of the wetting layer and/or possibly move within it. Modeling of recent LEEM experiments have suggested a barrier for the mobility of the Pb wetting layer to be 0.2-0.36 eV¹⁸. This is close to our measured value and it gives additional evidence that the low-temperature annealing observed in our experiment arises from an atomic-scale structural rearrangement of the wetting layer. Turning now to the higher-temperature regime, our measurements show a much larger energy barrier that is in the range of 1.3-1.9 eV. Since our measurements show that this annealing regime destroys the underlying Si(111)7x7, having a larger energy barrier is reasonable as it will involve complex motions of both Pb and Si. To our knowledge, an energy barrier for destroying the 7x7 in the presence of a metal layer has not been previously measured. However, the energy barrier for desorption of Pb is known to be in the range 2.31-2.64 eV^{12,19} and this can be taken as an upper-limit. The barrier that we measured at high temperature is considerably less than this, but much larger than the mobility barrier of the wetting layer.

Our studies also reveal that the high-temperature decay of the Pb/Si(111)7x7 depends on the Pb coverage. Figure

8 shows the decaying $(\frac{8}{7}, 0)_H$ intensity with elapsed time for three different coverages that were deposited at 185°C. As can be seen, there is an increase in the decay *rate* in going from 1.2ML to 1.5ML coverage – this is quantitatively shown in the inset where the relaxation time decreases with coverage. In considering the 2.5 ML data in Fig. 8, it should be noted that the *initial* $(\frac{8}{7}, 0)_H$ intensity decreases with increasing coverage above 1.2 ML because the Pb nanocrystalline islands consume the wetting layer directly below the islands and incorporate that Pb into the FCC structure of the islands, as has been reported elsewhere^{11,21}. Thus, the lower intensity for the 2.5 ML data in Fig. 8 is at least partly due to this effect. However, at a coverage of 2.5ML there is no discernable decay of the intensity with time at this temperature. Therefore, we cannot say whether the 2.5 ML data decays faster or slower than the experimental measurement time, although, extending the trend from lower coverage would suggest that it decays faster. The result of Fig. 8 bears similarity to recent LEEM experiments on Pb/Si(111)¹⁸ that have shown anomalous kinetic behavior of the Pb wetting layer in response to a hole generated by a short-pulsed laser. Those experiments showed that the Pb relaxation rate, $\frac{1}{\tau}$, increased with increasing coverage between 1.2-1.3ML with no change in relaxation rate at higher coverages. Some care in making a comparison between the two experiments should be exercised, however, since the activation energies differ by almost an order of magnitude. The higher activation energy in the present experiment is likely to be related to the motion of the Si adatoms that is required to remove the 7x7 reconstruction.

IV. CONCLUSIONS

These experiments demonstrate that there are two unrelated and physically distinct mechanisms by which the Pb/Si(111)7x7 wetting layer is not in equilibrium. One mechanism derives from the fact that the wetting layer is irreversibly metastable because the Si(111)7x7 reconstructed surface is no longer stable once the metal is deposited on it. However, the second mechanism relates to the structure of the Pb wetting layer itself. When Pb is deposited at low temperature, the disordered atomic-scale structure anneals, by time and/or temperature, and the ordering in the wetting layer improves. This suggests that there would be an equilibrium structure of the wetting layer if the Si(111)7x7 were static and not subject to the first instability mechanism. Apparently, the wetting layer does not easily adapt to the highly corrugated surface of the Si(111)7x7 so that there is a slow approach (requiring annealing) to the equilibrium structure. Together, the two mechanisms lead to a broad temperature range (more than 200°C) over which the wetting layer structure is observed to change with time.

Finally, we discuss potential implications of these results for the growth and coarsening of QSE islands which form on the wetting layer. A subtle but important point for kinetic considerations is that the as-grown wetting layer structure is not simply disordered as its native state, which has been the prevailing view. Instead, the wetting layer is disordered as a result of not having attained its equilibrium structure. Therefore, adatoms moving across the wetting layer can encounter a dynamic energy landscape: the *unstable* wetting layer atoms might react to the adatoms, leading to a complex adatom mobility. Secondly, the growth and coarsening of QSE islands could depend on how the wetting layer was prepared, because our results demonstrate that the structure of the wetting layer depends on both the growth and annealing temperatures as well as the annealing time. Therefore, even though the QSE islands are grown at temperatures lower (typically below or near -50°C) than the temperatures used in our present study, the structural foundation for growing the QSE islands is set by the preparation steps used in creating the wetting layer, which we have now shown does not have a unique structure. Although the degree to which these effects influence the growth and coarsening of the QSE islands is not presently known, the wetting layer is, nevertheless, both the conduit for mass transport between the islands and it is the template upon which the islands form. Therefore, the non-equilibrium behavior of the wetting layer revealed in the present work must be an important consideration for understanding the role of the wetting layer in the growth and coarsening of QSE islands.

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