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Wetting-layer transformation for Pb nanocrystals grown on Si(111)

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We present the results of *in situ* x-ray scattering experiments that investigate the growth of Pb nanocrystalline islands on Si(111). It is conclusively shown that the Pb nanocrystals do not reside on top of a Pb wetting layer. The nucleating Pb nanocrystals transform the highly disordered Pb wetting layer beneath the islands into well-ordered fcc Pb. The surface then consists of fcc Pb islands *directly* on top of the Si surface with the disordered wetting layer occupying the region between the islands. As the Pb nanocrystals coalesce at higher coverage we observe increasing disorder that is consistent with misfit strain relaxation. These results have important implications for predicting stable Pb island heights. © *2004 American Institute of Physics*.
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The confinement of the electron wave function in small objects leads to new energy levels that affect the object's total energy. Conversely, confinement influences an object's size by selecting those sizes that minimize the total energy. As a consequence, such "quantum size effects" (QSE)[1] cause metals grown on semiconductors to have certain film thicknesses or island heights that are more stable than others.[2–5] One example is the growth of Pb nanocrystalline islands on Si(111).[3] In this system the Pb islands grow with a very narrow height distribution that is peaked in increments of two Pb layers. The bilayer stability is partially understood in terms of oscillations in the total island energy as quantum well states pass below the Fermi energy every two Pb layers.[6,7]

While QSE is thought to play a role in Pb island growth on Si(111), predicting QSE energies remains problematic. Two important parameters, the island height and the metal–semiconductor interface structure, must be known before quantitative predictions can be made. The island height determines the quantum well depth while the interface structure determines charge transfer into the islands. The latter effect controls the Fermi level and thus is important in determining the total energy of a Pb island.[6] Despite the significance of the interface structure, there has been no quantitative study of the structure of the Pb–Si interface when islands are present. Our x-ray scattering measurements show that while the wetting layer[8–10] structure between the islands remains the same as the islands grow, the portion of the wetting layer located beneath the islands has been transformed into fcc sites and incorporated into the islands as they nucleate. In other words the Pb islands rest *directly* on the Si(111) surface without a disordered wetting layer beneath the islands. As a consequence, the results reveal a Pb island height that is consistently one monolayer (ML) taller than has been found in studies using surface probes which view only the surface topography.[11–13]

The experiments were performed in the surface x-ray scattering chamber located at the 6ID-C μCAT beam line at Argonne National Laboratory using a 12.4 keV x-ray energy. The films were prepared *in situ* in ultrahigh vacuum ($p=2\times10^{-10}$ Torr). The Si(111) 7×7 surface was prepared using standard techniques.[14] Pb was deposited from a molybdenum crucible using an e-beam evaporator. The deposition flux was calibrated at high coverage by measuring the x-ray intensity oscillations at the anti-Bragg reflection of Pb with the sample held at 55 K.[15] Coverages, θ, are reported in units of a bulk Pb(111) layer (i.e., 1.0 ML$=1.89\times10^{15}$ atoms/cm^2). For all data Pb was dosed onto the substrate at a rate of 0.39 ML/min with the sample held at 230 K. Momentum transfer vectors, $\boldsymbol{q}$, are reported in reciprocal lattice units using the conventional hexagonal Si(111) unit cell. The component normal to the surface is $q_z=la_0^*$ and the component parallel to the surface is $q_{\|}=ha_1^*$, where $a_0^*=0.668$ Å^{-1} and $a_1^*=0.771$ Å^{-1}.

Transverse scans across the Pb(111) Bragg peak were taken as a function of θ and several examples are shown in the inset of Fig. 1. These scans show a lobe structure and a central Bragg component ($h=0$). The Bragg intensity is proportional to the amount of Pb in fcc (111) layers, whereas the diffuse lobes arise from inter-island scattering (Henzler rings).[16] As we will show later, our reflectivity measurements indicate that the Pb layers are 8 ML in height even though only 3 ML were deposited. Thus, these observations signify the formation of three-dimensional Pb islands. Note that at this deposition temperature and coverage LEED measurements indicate that Pb islands grow to seven-layers high.[9] This one-layer discrepancy between LEED measurements and these studies is significant.

To understand this difference, we have plotted the integrated Bragg and diffuse intensities from the Pb(111) transverse scans in Fig. 1. The fact that neither the Bragg nor the diffuse intensity is significant below 1.2 ML clearly shows

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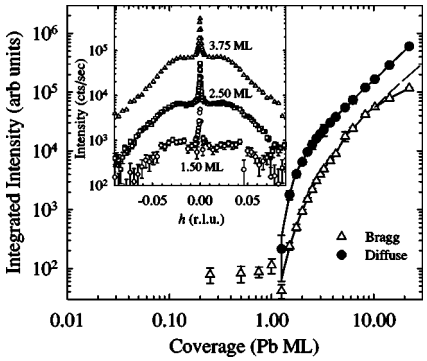

FIG. 1. Integrated Bragg (△) and diffuse (●) intensities vs Pb coverage for the Pb(111) Bragg peak. Solid lines are guides to the eye. The dashed curve is calculated for $\sigma_i=0$ and demonstrates the presence of disorder from misfit strain at high coverage. The inset shows transverse scans across the Pb(111) Bragg peak for selected coverages.

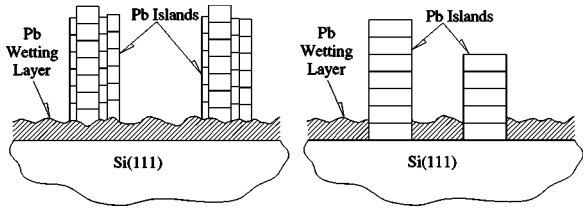

FIG. 2. (a) Schematic of disordered islands on-top the wetting layer. (b) Schematic of the island and wetting layer structure model used to calculate the reflectivity fits.

that the first layer of Pb is highly disordered in the vertical direction and that the disorder has a short correlation length (on the atomic scale). Above 1.2 ML, the rise in both Bragg and diffuse scattering signals the onset of fcc stacked Pb islands. Note that the value of the wetting layer coverage before nucleation begins is in excellent agreement with values from both low and room temperature growth studies of Pb on Si(111).[8,9,15]

It is impossible to reconcile the increase in Bragg scattering at higher coverages with the large vertical disorder in the first layer. If the fcc Pb islands were to grow on top of the wetting layer [see Fig. 2(a)], the vertical displacive disorder at the buried interface would strongly suppress the Bragg intensity.[17] Instead, we suggest that both the Bragg and diffuse intensity versus θ can be explained if the Pb in the wetting layer beneath the islands has been transformed into fcc Pb sites. The picture of the surface is then one of isolated fcc stacked Pb islands on top of the flat Si substrate with a disordered Pb layer in the region between islands [see schematic in Fig. 2(b)].

Additional evidence for fcc Pb islands extending to the substrate interface comes from model calculations used to fit the measured x-ray reflectivities.[18] The model surface structure consists of a distribution $P(N)$ of N-layer Pb islands on top of the Si(111) substrate. Between the islands is a wetting layer with a density 1.2 times that of fcc Pb layer. Thus the total Pb coverage is, $\theta=\theta_W+\Sigma NP(N)$, where θ_W is the wetting layer coverage and the second term is the coverage of fcc Pb. A clean Si(111) reflectivity was fit to set the substrate atomic positions and the substrate roughness, similar to Robinson and Vlieg.[19] The clean surface parameters were then fixed for subsequent fits. The vertical disorder in the wetting layer was modeled[17] by multiplying the scattered amplitude from the wetting layer by a factor $\exp[-(la_o^*\sigma)^2/2]$, where σ^2 is the mean squared displacement corresponding to vertical disorder at the buried interface.

Figure 3 shows the measured reflectivity from 3 ML of Pb deposited at 230 K on Si(111). The intense Pb(111) ($l\sim3.27$) and Pb(222) ($l\sim6.54$) Bragg peaks indicate the presence of well-ordered fcc-stacked Pb layers. Our model calculations[18] give the best fit to the data using a wetting layer that covers 68% of the surface with the remaining area being occupied by the islands. The islands are found to have a height distribution that peaks at $N=8$ with a variance of 1.4 layers. Note that the Pb(222) Bragg peak width is particularly sensitive to the island height, as shown in the inset to Fig. 3. Attempts to fit the data with an identical distribution having a peak at $N=7$ or $N=9$ produce much poorer fits that are significantly broader or narrower, respectively, than the best fit with $N=8$ (the distributions were adjusted to keep the total coverage fixed). Our analysis also confirms that the wetting layer is very rough with $\sigma=0.9$ Å, which is consistent with STM studies where the wetting layer roughness was found to be 1.2 Å.[9] As can be seen, the model reproduces the data very well over a large range of l's. For comparison, a smaller σ, shown by the dash-dotted curve in Fig. 3, produces a much poorer fit to the data.

To further demonstrate the principal conclusion of this work, we included in the model a mean-square displacement, σ_i, corresponding to vertical disorder at the island–substrate interface. We find that $\sigma_i=0$, indicating that the fcc stacking order in the islands is extremely high. For comparison, we calculated the reflectivity for the situation shown in Fig. 2(a) where the islands grow on top of a rough wetting layer with $\sigma_i=0.9$ Å. As shown by the dashed curve in Fig. 3, growth on the rough wetting layer essentially destroys most of the constructive interference at the Pb(111) and Pb(222) Bragg peaks.

We further find that σ_i does not become appreciable until $\theta\sim14$ ML. At and above this coverage the Bragg intensity in Fig. 1 exhibits a marked change as a function of θ from the $\sigma_i=0.0$ Å surface (dashed curve in Fig. 1). Instead $\sigma_i=0.2$ Å at 14 ML and $\sigma_i=0.3$ Å at 22 ML, where the latter was independently determined by transverse scans at the Pb(111) and (222) Bragg peaks. This precipitous increase in σ_i occurs near the coverage where the QSE islands begin to coalesce into a closed film, suggesting its origin is related to misfit strain relaxation between the film and the substrate. Indeed, detailed measurements[18] of the Bragg and diffuse scattering at the Pb(111) and (222) reveal line shapes that have been associated with the formation of misfit dislocations.[17]

In conclusion, we have performed structural studies of the island–substrate interface of QSE Pb islands grown on Si(111) 7×7. It is shown that Pb islands do not grow on top of a Pb wetting layer. Instead the nucleated Pb islands incorporate Pb in the wetting layer beneath them into fcc sites within the islands. The surface therefore consists of Pb islands grown directly on top of the Si substrate with a disordered Pb layer between islands. This layer is gradually consumed as the islands grow in size and coalesces into a two-dimensional closed film. With this model the x-ray data become consistent with the island heights determined by LEED and STM. The actual island heights are one layer higher than determined by these techniques since they measure heights relative to the interisland Pb wetting layer.

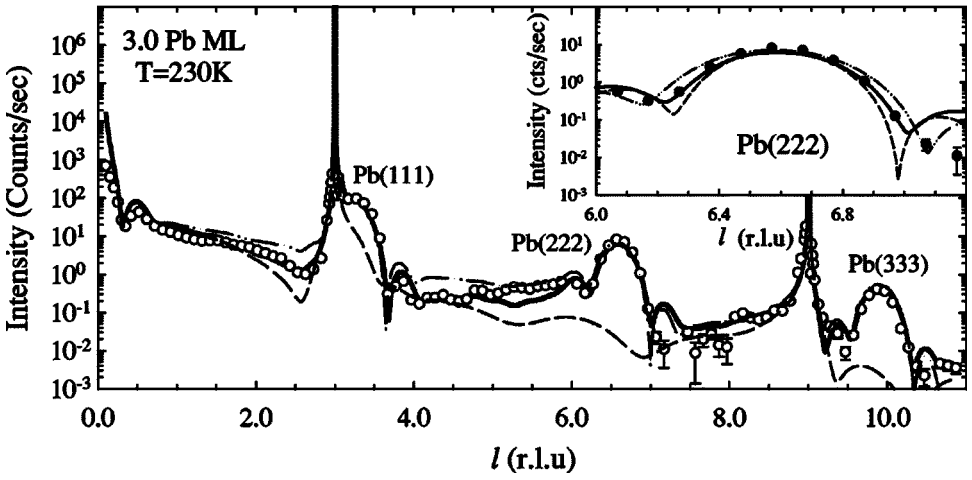

FIG. 3. X-ray reflectivity for 3 ML of Pb deposited on Si(111)7×7 at 230 K. Solid line is the best fit for predominately eight-layer islands grown on top of the Si substrate with a wetting layer roughness of σ=0.9 Å. Dash-dotted line is the same fit with a smoother wetting layer, σ=0.4 Å. Dashed line is a fit with the islands grown on-top of a wetting layer with σ=0.9 Å. Inset shows fits to a portion of the reflectivity near the Pb(222) peak for seven-layer islands (dashed-dot line), eight-layer (solid line), and ning-layer (dashed line) islands.

While these results clearly demonstrate that fcc Pb islands grow directly on top of the Si substrate, they do not address the cause of the initial nucleation. Whether or not the islands nucleate within the wetting layer or on top of the wetting layer is not known. In either case the disordered Pb in the wetting layer near the nucleation site is reconfigured into fcc sites as part of the growing island. These results have important implications for theoretical models used to predict the island height distribution, since they firmly establish the depth of the quantum well used to determine the island total energy contribution from electron confinement. Finally, the smooth island–substrate interface measured in these studies is consistent with the boundary condition for coherent electron scattering necessary to produce quantum well states in the islands.

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