

Wetting-layer Transformation for Pb Nanocrystals Grown on Si(111)

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Introduction

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, our results reveal a Pb island height that is consistently one monolayer taller than has been found in other studies using surface probes which view only the surface topography [11-13].

Methods and Materials

The experiments were performed in the surface x-ray scattering chamber located at the 6ID-C μ CAT beam line at Argonne National Laboratory using a 12.4 keV x-ray energy. The films were prepared *in situ* in Ultra-High Vacuum ($p = 2 \times 10^{-10}$ torr). The Si(111) 7×7 surface was prepared using standard techniques. Pb was deposited from a molybdenum

crucible using an e-beam evaporator. Coverages, θ , are reported in units of a bulk Pb(111) layer (i.e., 1.0ML = 1.89×10^{15} atoms/cm²). For all data Pb was dosed onto the substrate at a rate of 0.39ML/min with the sample held at 230K. Momentum transfer vectors, q , are reported in reciprocal lattice units (r.l.u.) using the conventional hexagonal Si(111) unit cell. The component normal to the surface is $q_z = la^*_o$ and the component parallel to the surface is $q_{||} = ha^*_l$, where $a^*_o = 0.668 \text{ \AA}^{-1}$ and $a^*_l = 0.771 \text{ \AA}^{-1}$.

Results

The key evidence showing that islands grow on the Si substrate and not on the wetting layer comes from the coverage dependence of the Pb Bragg and diffuse scattering intensity. In the insert of Fig. 1 we show transverse scans across the Pb(111) Bragg peak taken at several values of θ . 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) from the Pb QSE islands [14]. It is important to note that by 3ML reflectivity measurements indicate that the Pb islands are 8 ML in height signify the formation of 3-dimensional Pb islands [15]. At this deposition tem-

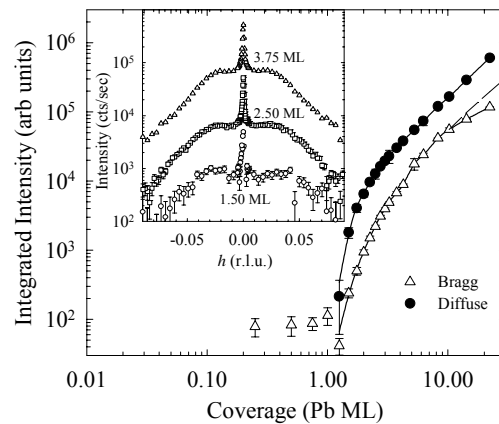


Figure 1 Integrated Bragg (Δ) and diffuse (\bullet) intensities vs. the Pb(111) Bragg peak. Solid lines are guides to the eye. The dashed curve is calculated for $\sigma_i = 0$ and demonstrates the presence of disorder from misfit strain at high coverage. The inset shows transverse scans across the Pb(111)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

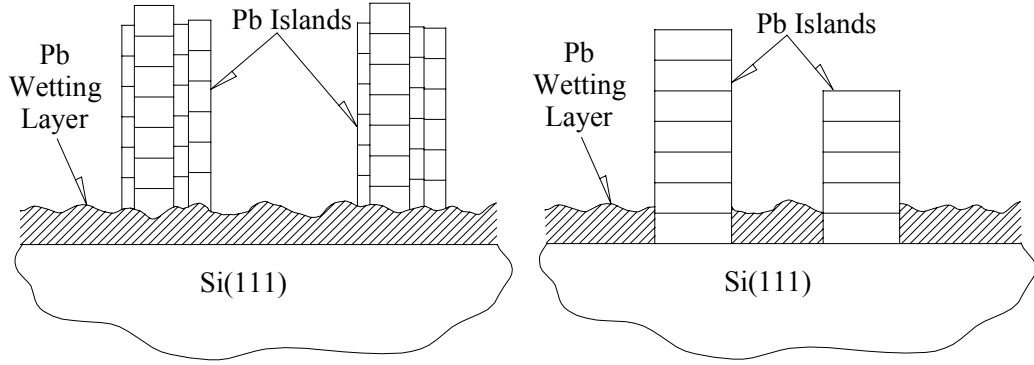


Figure 2 (a) Schematic of disordered islands on-top the wetting layer. (b) Schematic of the island and wetting layer structure model used to calculate the reflectivity fits.

perature and coverage LEED measurements indicate that Pb islands grow to 7-layers high [9]. This 1-layer discrepancy with LEED measurements and these studies is significant.

To understand the 1-layer difference between LEED and X-ray measurements, 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 1.2ML, clearly shows 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 1.2ML, 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) [8,9,16].

Discussion

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 the 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)).

To see this we note that the integrated Bragg, I_B and integrated diffuse, I_D , intensities are given by [18];

$$I_B = B\bar{\Theta}^2 e^{-q_z^2 \sigma^2}, \quad (1a)$$

$$I_D = B e^{-q_z^2 \sigma^2} \left[\overline{\Theta^2} - \bar{\Theta}^2 \right], \quad (1b)$$

where σ^2 is the mean squared displacement corresponding to vertical disorder at the buried interface. The island coverage, Θ , for a distribution $P(N)$ of N -layer Pb islands on top of the Si(111) substrate is given by: $\Theta = \sum N P(N)$. B is a normalization constant.

Fits to the data using Eqs. (1a) and (1b) find that $\sigma_i = 0\text{\AA}$ for all but the highest coverages. In fact σ_i does not become appreciable until $\theta \sim 14\text{ML}$. At and above this coverage the Bragg intensity in Fig. 1 exhibits a marked change as a function of θ from the $\sigma_i = 0.0\text{\AA}$ surface (dashed curve in Fig. 1). Instead $\sigma_i = 0.2\text{\AA}$ at 14ML and $\sigma_i = 0.3\text{\AA}$ at 22ML, 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 [15] 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].

Conclusion

In conclusion, we show that Pb islands do not grow on top of a Pb wetting layer as previously conjectured. 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 2D 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 1-layer higher than determined by these techniques since they measure heights relative to the inter-island Pb wetting layer. 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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