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Uniform, self-organized, seven-step height Pb/Si(111)-(7×7) islands at low temperatures

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An unusual growth mode has been observed during low temperature growth at T=185 K in the system Pb/Si(111)-(7×7) with the formation of uniform seven-step, steep-edged, flat-top islands up to coverages $\theta = 7.5$ ML. The evidence is based on the spot profile analysis–low-energy electron diffraction diffracted intensity distribution as a function of $k_{\|}$, k_z the parallel and normal components of the momentum transfer which show sevenfold oscillations over the range in k_z where single step oscillations are expected. The formation of these highly uniform, self-organized structures implies that unconventional kinetic mechanisms operate at these low temperatures.

Epitaxial growth has been widely used for the fabrication of custom-made materials by searching for the optimal combination of deposited material/substrate to produce well-ordered, self-organized nanostructures with preferred length scales. Electron confinement in these nanostructures results in low dimensional electronic systems with sharply quantized energy levels of adjustable spacing, which can have important technological applications. For a given combination of materials, the final outcome of the growth is not unique but depends on the growth conditions used since epitaxial growth is a nonequilibrium process with the final outcome determined from kinetic limitations.

Unusual growth modes have been discovered on several epitaxial systems with remarkable degree of self-organization: uniform multistep height islands with flat tops and steep edges have been observed during annealing experiments on Ag/GaAs(110),[1,2] and Ag/Si(111).[3,4] A possible explanation of these unexpected phenomena is based on quantum size effects, i.e., the dependence of the energy of the confined electrons on the film thickness, as the electrons progressively occupy the discrete energy levels in the film. Quantum size effects were initially observed during the growth of Pb on Cu(111) with He scattering.[5]

However, it is still not clear what are the key kinetic processes responsible for this unusual degree of perfection of the film morphology; normally disorder and imperfections are expected in the film, with pyramid-shaped islands and atoms occupying different levels of monatomic step separation. The unusual film morphology and the selection of a preferred height can result from the balanced interplay of several kinetic processes: fast terrace diffusion of the deposited atoms to reach the nucleated islands, hopping from lower to higher levels to build up the multilayer islands, and atom retainment at the preferred level. In earlier studies,[2–4] the uniform height islands were formed by deposition at a lower temperature followed by annealing to room temperature, so most likely, thermal diffusion is responsible (at least partially) for the observed structural perfection. More information about the nature of the kinetic mechanisms operating can be obtained if this type of growth is observed directly at low temperatures, without the need for annealing.

Searching for self-organized structures on a different system Pb/Si(111) can reveal additional insights on the nature of the kinetics since this system has a similar growth mode as Ag/Si(111). Previous work with diffraction to monitor the specular beam intensity oscillations vs coverage (with all three surface sensitive diffraction probes reflection high-energy electron diffraction (RHEED), He scattering, and x rays) has already revealed some puzzling features.[6,7] Regular oscillations of bilayer period have been observed at temperatures as low as 90 K for coverages exceeding 6 ML, after an initial transient period of low and irregular diffracted intensity. These structural regularities in the film at such low temperatures (and especially the double oscillation period) were attributed to quantum size effects. The boundary conditions imposed on the free electron wave function at the two edges of the film are satisfied when the film thickness has a specific relation to the Fermi wavelength. For the kinetic mechanism to build the well-ordered islands, a large nonthermal contribution to diffusion was assumed; otherwise, unphysically low diffusion barriers (less than 0.1 eV) are needed.[6] *In situ* four-probe measurements of the resistivity in the film has also revealed oscillations with coverage which also were attributed to quantum size effects.[7]

Despite the previous evidence for the importance of quantum size effects, additional work is necessary to clarify further the island morphology (i.e., island height, size, shape, etc.) and the kinetic mechanisms operating. Diffraction experiments carried out at low temperatures and with the ability to deduce the structural characteristics of the islands from diffraction spot profile analysis can add valuable information about the origin of the self-organization. This is particularly important since diffraction intensity oscillations used in the earlier experiments[6,7] reveal limited information about the structures formed (i.e., they simply measure the amount of deposited material to reach on the average the same surface condition but not the details of the island morphology). Furthermore, the interpretation of the intensity oscillations (especially with RHEED) has been an open question in the literature.

We have studied the growth of Pb/Si(111) as a function of coverage at $T=185$ K, a temperature within the regime where regular oscillations have been observed. Similar results obtained at different temperatures within this regime will be published in the future. The growth is monitored with high resolution electron diffraction [spot profile analysis

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–low-energy electron diffraction (SPA-LEED)] where the distribution of the diffracted intensity in reciprocal space $I(k_\parallel,k_z)$, as a function of the parallel $k_\parallel$ and normal k_z momentum transfer components, can be used to deduce the distribution of lateral and normal length scales in the film.[8] Strong seven-fold oscillations of the narrow component of the $I(k_\parallel,k_z)$ profiles vs k_z (instead of a single oscillation expected over the range in k_z corresponding to Pb single steps $d=2.86$ A). Pb islands with heights seven times the single step height d are formed. As will be discussed shortly, based on the profile line shapes and the analysis of the additional spots [Pb(10) of the Pb(111) crystalline islands, (1/7,0) superstructure spots of the (7×7) phase], we conclude the island shapes are similar to the ones observed in the Ag/Si(111) system with flat tops and steep edges. The formation of seven-step islands during growth, without the need to anneal to room temperature, is a far more complex and demanding process than the formation of two-step islands. The origin of this unusual growth mode most likely is related to quantum size effects; since the grown Pb islands have (111) structure with the same in plane lattice constant 3.5 A as for bulk Pb(111) stress is ruled out as the driving force.

The experiment was carried out in a UHV chamber of base pressure 2×10^{-11} equipped with SPA-LEED and an Auger spectrometer. Pb was deposited from a fully outgassed Knudsen cell at a rate of 1 ML/min. Coverage calibration was based on the break in the Si-Auger line vs Pb coverage indicating the completion of a monolayer as observed in earlier studies.[9]

In a diffraction experiment, the measured intensity $I(k_\parallel,k_z)$, can be written[8] as the sum of a narrow instrumentally limited component $\delta(k_\parallel)$ and a broad component $L(k_\parallel$:

$$I(k_\parallel,k_z)=A(k_z,\theta)\,\delta(k_\parallel)+B(k_z,\theta)L(k_\parallel). \tag{1}$$

Information about the vertical arrangement of atoms in the film is contained in the dependence of the two complementary functions $A(k_z,\theta)$, $B(k_z,\theta)$ on k_z while information about the lateral arrangement of atoms in the film is contained in the dependence of the broad component $L(k_\parallel)$ on $k_\parallel$ when a value of k_z corresponding to an out-of-phase condition is chosen. A possible variation of the atomic scattering factor on k_z can be factored out if the two terms $A(k_z,\theta)$, $B(k_z,\theta)$ in Eq. (1) are integrated over the Brillouin zone to construct the normalized profile components (this can be carried out also when A, B depend weakly on $k_\parallel$).

$$p_1=\frac{A(k_z,\theta)\int\delta(k_\parallel)d^2k_\parallel}{A(k_z,\theta)\int\delta(k_\parallel)d^2k_\parallel+B(k_z,\theta)\int L(k_\parallel)d^2k_\parallel}, \tag{2}$$

$$p_2=1-p_1.$$

The step height d is obtained from the oscillatory dependence of $A(k_z,\theta)$ on k_z since constructive interference between the different levels (and therefore maxima of p_1) are expected when k_z changes by $2\pi/d$. In particular, for measurements of the specular intensity (00) it can be easily shown[10,11] that the fraction of intensity distributed within the narrow component becomes simply a one-dimensional summation over the exposed level occupation θ_n (i.e., the fraction of atoms at level n exposed at the vacuum interface):

$$p_1(k_z)=\left|\sum_{n=1}^{n=N}\theta_n\exp(ik_znd)\right|^2. \tag{3}$$

So, by expressing $p_1(k_z)$ in terms of its different Fourier components, the unknown exposed level coverages θ_n can be obtained. In particular, for the special case in which growth involves the formation of islands of step height a multiple of the single step height $d_l=ld$, with flat tops and steep edges one expects to see a single periodicity $2\pi/ld$ in the p_1 vs k_z curve (i.e., one Fourier component) to indicate that only two levels are exposed. The presence of a single Fourier component is easily seen in the p_1 vs k_z curve, since the maxima reach the same level.

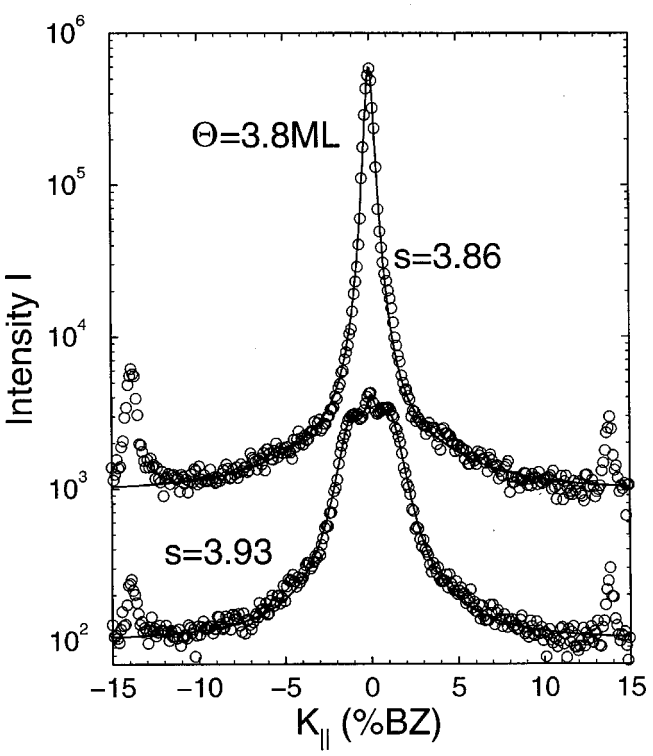

FIG. 1. Typical in-phase ($s=3.86$) and out-of-phase ($s=3.93$) profiles for 3.8 ML Pb deposited on Si(111)-7×7 at $T=185$ K. Such a large variation of profile line shapes over a small change of s indicates the presence of seven-step high islands.

Figure 1 shows typical (00) profiles for $\theta=3.8$ ML at the in-phase and out-of-phase conditions (with respect to the seven-step height) with the peak intensity at the in-phase condition larger by more than one and a half order of magnitude from the peak intensity at the out-of-phase condition. The phase, defined by the $s=k_z/(2\pi/d)$, is 3.86 and 3.93, respectively, for the profiles shown. Spot profiles are obtained over a large phase range $s=3$–4.4. They are fitted to the sum of a narrow (Lorenztian 3/2 form) and a broad ringlike component. Figure 2 shows the results for the renormalized narrow component p_1 vs k_z for different coverages. Strong seven-fold oscillations are present indicating the presence of predominantly seven-fold steps in the coverage range $\theta=2$–7.5 ML. For $\theta<2$ ML, Pb forms a wetting layer,

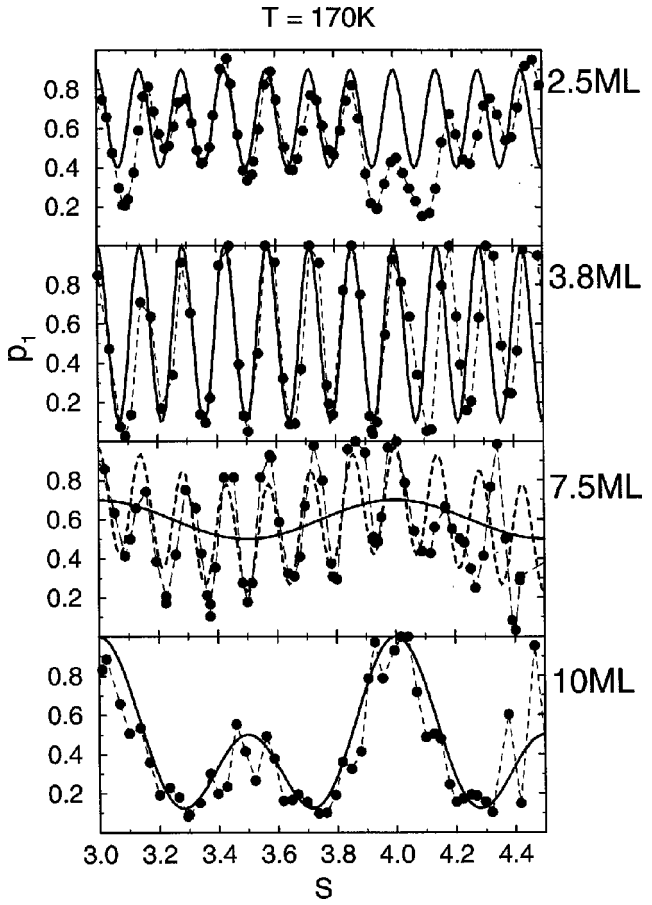

FIG. 2. Variation of the narrow component of the profiles p_1 vs s for different coverages of Pb deposited on Si(111)-(7×7) at $T=185$ K. For coverages $\theta \leqslant 7.5$ ML, seven-fold oscillations are present indicating the presence of seven-step high islands.

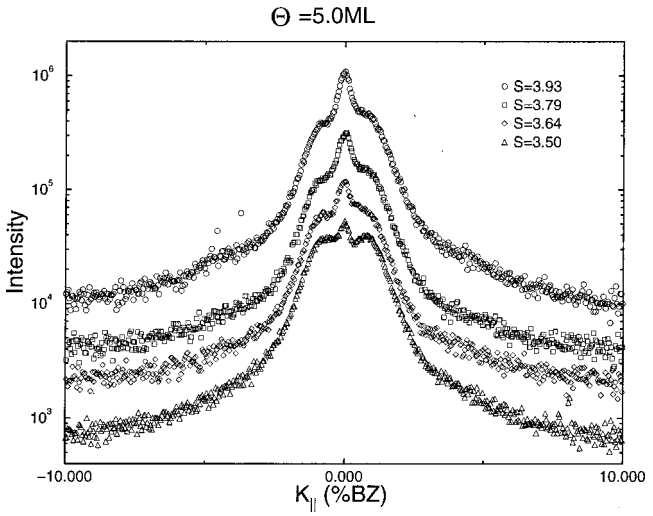

FIG. 3. Profiles of the (00) spot at $\theta=5$ ML Pb deposited on Si(111)-(7×7) at $T=185$ K for different phases s corresponding to the different out-of-phase conditions of the seven-step high islands. The similarity of the line shapes confirms that the islands have steep edges.

before (111)-oriented Pb islands are formed, and this minimum coverage is necessary before the (10) Pb spot can be clearly discerned, in agreement with other studies.[9] At $\theta=7.5$ ML, we see a weak single step modulation indicating that a small fraction of single steps is present, most probably because single step islands form on top of the seven-step height islands before the seventh layer perfectly closes. For higher coverage $\theta=10$ ML, we see no evidence for seven-fold steps, but a combination of double and single steps.

It is remarkable that the narrow component p_1 recovers to the same intensity level for all maxima, indicating that the islands have no single steps and therefore they have steep edges. One-dimensional simulations of the p_1 vs k_z curves for different coverage distributions θ_n confirm this conclusion and reproduce the experimental results of Fig. 2 very well. Details of the simulations will be given in a forthcoming publication.[12]

Additional support that the islands are steep is found by comparing the shapes of the out-of-phase condition profiles (for $s=3.5,3.64,3.78,3.93$) shown in Fig. 3. The coverage is $\theta=5$ ML but similar results are obtained at other coverages. If the number of single steps present is negligible, because the edges of the islands are steep, then all the different out-of-phase conditions for seven-step heights are equivalent, and the profiles $I(k_{\|})$ should be similar; but if the island edges are faceted with single steps present, then the profile at $s=3.5$ (which is also an out-of-phase condition for single steps) will be broader than the profile at $s=3.93$ (which is close to an in-phase condition of single steps), since for the latter value of s the scattering is insensitive to single steps. As can be seen from Fig. 3, the profiles have similar shapes with the full width at half maximum (FWHM=2.6% BZ) practically the same at all values of s shown, consistent with the islands having steep edges.

Since the film has the morphology of a two-level system with a new height $de=2$ nm, a plot of the (00) intensity vs θ should follow the expected oscillatory dependence for layer-by-layer growth where the intensity maximum should be observed close to the completion of the film and a minimum of the intensity close to half this coverage. This is shown in Fig. 4 where the 2-d integrated (00) intensity vs θ is plotted at two out-of-phase conditions (for steps of height 7d). For both diffraction conditions, the intensity has a minimum at $\theta=4$ ML, approximately as expected for a two-level system with 7d step height. The intensity reaches a maximum approximately at 8 ML for $s=3.53$ (which is closer to the out-of-phase condition of single steps) while for $s=3.93$ has higher intensity since this condition is close to an in-phase condition for single steps. Although the exact position of the minimum and minima depend on possible differences in the scattering factors[11] [between the Pb(111) islands and the Pb wetting layer covering the Si(111) substrate] and the exact Pb amount needed for the completion of the wetting layer, the overall picture is consistent with a two-level system of seven-fold height islands.

The dependence of the superstructure (1/7,0) spot intensity vs Pb coverage, further supports the previously outlined growth scenario. The (7×7) superstructure spots are still visible, during the formation of the wetting layer, because the arrangement of the Pb atoms within the wetting layer follows the symmetry of the (7×7) unit cell. At the onset of the growth of the Pb(111) islands, the (1/7,0) intensity decreases with Pb coverage until it decays to zero close to $\theta=7.5$ ML, the same coverage where the (00) reaches a

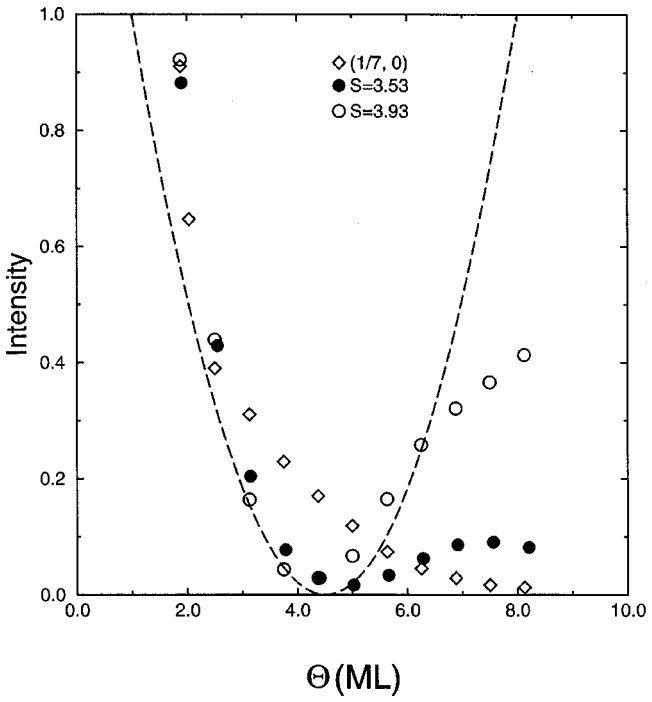

FIG. 4. Dependence of 2-d integrated intensity vs deposited Pb coverage on Si(111)-(7×7) at $T=185$ K of the (00) spot at two out-of-phase conditions for seven-steps $s=3.93$ (open circles), 3.53 (closed circles), and the superstructure spot (1/7,0) spot (open diamonds). The dependence of the (00) shows a minimum at approximately $\theta=4$ ML and the superstructure spot (1/7,0) decays to zero at $\theta=7.5$ ML as expected for a two-level system with seven-step height islands.

maximum in Fig. 4 confirming the completion of the layer. The size of the Pb(111) islands is obtained from the FWHM of the Pb(10), and the island separation is obtained from the position of the satellite spots of the broad component of the (00) line shape at the out-of-phase conditions for the seven steps. From this analysis of the (10) and (00) spots we conclude that the island size increases from 80 to 300 A, while the island separation increases from 300 to 500 A as the Pb coverage increases to 7.5 ML.

As discussed earlier, previous diffraction studies[7,13] at lower temperatures than in our study ($T=80$–100 K) have shown the presence of regular oscillations which have been attributed to quantum size effects. A simple calculation to determine which multiple of the Pb single layer thickness are multiples of half the Fermi wavelength (i.e., $2nd=w\lambda_F$ n,w integers with $d=2.86$ A, $\lambda_F=3.66$ A) shows that $n=7$ is a preferred value (when $w=11$) as found in our study. Additionally, the high degree of self-organization attained at these low temperatures (without the need to anneal at high temperatures) suggests that unusual kinetic mechanisms operate and confirms the need of some type of nonthermal diffusion, as suggested earlier.[6] However, future theoretical work is necessary to clarify further all the kinetic steps.

Recent studies in other systems have also suggested that quantum size effects can influence the film morphology. He scattering has been used to study Pb/Ge(001) growth at low temperature $T=130$ K from spot profile analysis similar to our studies.[13] Changes in the oscillation period of the FWHM of the (00) spot vs k_z were used to deduce variations in the interlayer spacing of the film in order for the film thickness to be an integer multiple of $\lambda_F/2$. He-scattering studies[14] of Ni on hydrogen terminated C(111) surfaces at higher temperatures $T=800$ K have shown the formation of multiple height islands with flat tops, as deduced in our study (from similar analysis of the distribution of the diffracted intensity with $k_\parallel, k_z$).

In summary, we have shown, with the use of SPA-LEED, that seven-step, flat-top islands with steep edges form during the deposition of Pb/Si(111) at low temperatures. This is based on the analysis of the diffracted intensity profiles as function of k_z, $k_\parallel$ to determine the island height and shape. It is further confirmed from the similarity of the profile line shapes as a function of $k_\parallel$ at the different out-of-phase conditions of the seven-step height. Most likely, the origin of this unusual growth mode is related to quantum size effects and supports the presence of unusual kinetic mechanisms at these low temperatures.

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