Role of the Metal/Semiconductor Interface in Quantum Size Effects: Pb/Si(111)

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Self-organized islands of uniform heights can form at low temperatures on metal/semiconductor systems as a result of quantum size effects, i.e., the occupation of discrete electron energy levels in the film. We compare the growth mode on two different substrates [Si(111)-(7 × 7) vs Si(111)-Pb($\sqrt{3} \times \sqrt{3}$)] with spot profile analysis low-energy electron diffraction. For the same growth conditions (of coverage and temperature) 7-step islands are the most stable islands on the (7 × 7) phase, while 5-step (but larger islands) are the most stable islands on the ($\sqrt{3} \times \sqrt{3}$). A theoretical calculation suggests that the height selection on the two interfaces can be attributed to the amount of charge transfer at the interface.

PACS numbers: 68.55.Jk, 61.16.Ch, 61.14.Hg

The search for methods to produce highly organized atomic scale structure during epitaxy is an intensively active research area since it holds the promise for novel technological applications. Recently it was found unexpectedly that uniform height islands, with steep edges and flat tops, can be grown on several systems [1–5]. This was surprising since single steps are commonly observed during growth, separating the exposed island levels. In some systems the structures form after deposition at lower temperature followed by annealing to room temperature [1–4]; in Pb/Si(111)-(7 × 7) regular height islands form *in situ* during low temperature deposition $T = 120$–240 K [5]. In this system depending on the growth conditions (i.e., coverage, temperature, kinetic pathway, etc.) islands of uniform heights, 5-, 7-, 9-step, can reproducibly form.

Although the kinetics controlling this unusual growth mode are not fully understood (i.e., how the deposited atoms have such high mobility to build the islands), the driving force of the self-organization is believed to be related to quantum size effects (QSE). The minimization of the energy of the confined electrons favors a preferred thickness [6–10]. This is usually expressed in terms of the boundary conditions that the wave function should satisfy $nd = s\lambda_F/2$, where λ_F is the Fermi wavelength and d is the single step height of the grown crystal with n, s integer numbers. For the Pb(111) $\lambda_F = 0.366$ nm, $d = 0.286$ nm, and since approximately $d = 3/4\lambda_F$ this leads to preferred island heights differing by $2d$.

Originally evidence of the presence of QSE during epitaxial growth was based on the observation of bilayer diffraction intensity oscillations in Pb/Cu(111) [11], oscillations in the film conductivity during the growth of Pb/Si(111) [12], changes in the step height as a function of film thickness in the growth of Pb/Ge(100) [13], imaging a buried interface of a Pb wedge grown epitaxially on stepped Si(111) [14], and the unusual island morphology (i.e., flat shape and uniform heights) described earlier [1–5]. A preliminary theoretical treatment [15] of the dependence of the electron energy on the film thickness takes into account two contributions: the increase of the confined electron energy at small film thickness and the energy gain due to charge transfer at the metal/semiconductor interface as a result of differences in the Fermi level positions across the interface. The film energy vs thickness curve can have, in principle, several energy minima. The depth of the energy minima and the height at the saddle point depend on the relative contribution of the two components to the film energy.

For Pb/Si(111) several energy minima are expected because of the relation between λ_F and d mentioned above. More insight into the role of QSE can be obtained if the growth is studied on different metal/semiconductor interfaces. Different Pb-Si interfaces {[Si(111)-(7 × 7) vs Si(111)-Pb$\sqrt{3} \times \sqrt{3}$]} are well characterized from other experiments [16,17] so both the atomic position and the electronic structure at these two interfaces are known independently.

Our experiments are carried out with spot profile analysis low-energy electron diffraction [18]. The technique uses the distribution of diffracted intensity $I (k_\parallel, k_z)$, the parallel and normal components of the momentum transfer to deduce the vertical and lateral distribution of atoms in the film. A measurement of the spot profile at fixed k_z can be decomposed into two components, a narrow component that measures the long-range arrangement of atoms on lattice sites and a broad component which measures the average island size and separation. The step height is deduced from oscillations of the distribution of the intensity between the two diffraction components as a function of k_z.

Since different types of the $\sqrt{3}$ phase can be realized on the surface depending on the Pb coverage and the annealing process [16], it is important to describe the method of preparation of the $\sqrt{3}$ phase. Initially an amount of 4 monolayer (ML) Pb was deposited at 130 K and the surface was heated to a higher temperature until the weakly bound $\sqrt{3}$-α formed at 470 K followed by partial desorption of Pb until the strongly bound $\sqrt{3}$-β phase formed. Most of the growth experiments were carried out with Pb deposited on the $\sqrt{3}$-β but limited experiments were also carried out on the $\sqrt{3}$-α phase.

Since the main goal of this study is the growth on the two different interfaces, we present results for the same growth parameters of $\theta = 4$ ML and $T = 195$ K. Figure 1 shows σ_0 vs $S = k_z/(2\pi/d)$, where $d = 2.86$ Å is the single step height of Pb(111) and σ_0 is the constant in the denominator of the Lorentzian-$\frac{3}{2}$ fits. The bottom figure is for the (7×7) and the top figure for the $\sqrt{3}$ interface. [σ_0 is smaller by a constant factor, approximately 1.5, than the full width at half maximum (FWHM).]

For growth on the (7×7) interface we see strong 7-step oscillations indicating that predominantly 7-step islands form as found earlier [5] and as confirmed with low temperature scanning tunneling microscopy (STM) [19]; for the growth on the $\sqrt{3}$ phase we see 5-step oscillations which indicates that mainly 5-step islands form. The islands have steep edges as can be seen directly in the STM images or can be deduced with diffraction, by comparing the profiles at the different out-of-phase conditions of the multistep periodicity. This result is intrinsic to the difference in the two interface structures and is not a result of the selected growth conditions. As found earlier for $T = 195$ K on the (7×7) and for any Pb coverage (larger than 2 ML needed to form the wetting layer) we always observe 7-step islands. 5-step islands are observed during growth on the (7×7) at lower temperature $T < 165$ K and for smaller Pb amounts ($\theta < 5$ ML), but after annealing to the higher temperature $T = 195$ K the 5-step islands transform to 7-step islands. This indicates that 7-step islands are the most stable islands on the (7×7). On the other hand for the growth on the $\sqrt{3}$ phase and for coverages $\theta < 5.5$ ML we first see 5-step oscillations, after an amount, of approximately 1 ML, converts the $\sqrt{3}$-β to
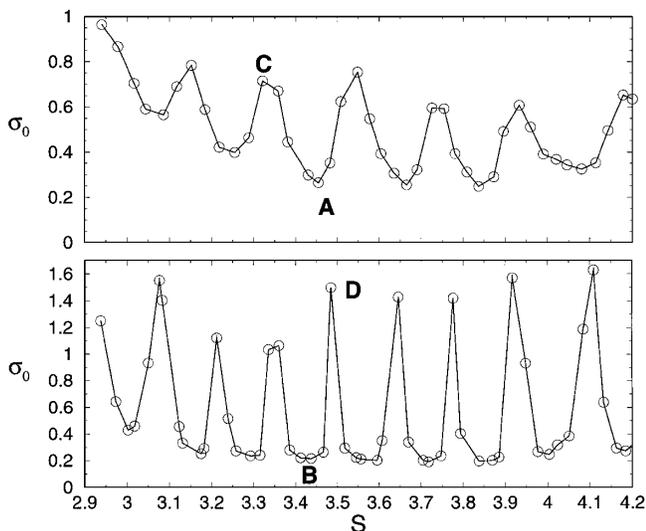
$\sqrt{3}$-α. The 5-step islands are stable and despite prolonged annealing at temperature as high as 240 K they maintain their height although the height distribution broadens and the island edges are less steep as the islands coarsen.

Figure 2 compares typical profiles of the (00) spot at in-phase and out-of-phase conditions for growth on the two different substrates. As can be seen from the comparison of the out-of-phase conditions (i.e., maxima in Fig. 1), the profiles are sharper on the $\sqrt{3}$ than on the (7×7). This directly indicates that larger islands are grown on the $\sqrt{3}$ than on the (7×7). This difference in the island sizes is also supported by the comparison of the FWHMs of the Pb(10) spots on the two phases. The FWHM of the Pb(10) on the $\sqrt{3}$ is narrower by a factor of 2 from the FWHM of the Pb(10) spot on the (7×7). By using the FWHM of the Pb(10) which measures the average island size L, the position of the satellite spots of the (00) which measures the island separation S and the width of the (00) spot which measures the geometric average of L and S, we deduce that $L = 180$ Å, $S = 700$ Å for the growth on the $\sqrt{3}$ and $L = 90$ Å, $S = 310$ Å for the growth on the (7×7) phase. This difference in the size indicates that either the kinetic barriers are lower or the energy minima are deeper for the growth on the $\sqrt{3}$ than the corresponding barriers for the growth on the (7×7).

Figure 3 shows results of the growth on the $\sqrt{3}$ phase if larger Pb amounts $\theta > 5.5$ ML are deposited at $T = 195$ K. We observe islands with heights larger than 5 steps, by bilayer increments, i.e., 7, 9, or 11 steps, depending on the coverage. For example, for $\theta = 7.5$ ML we observe 7-step islands with comparable lateral sizes as observed at lower coverages. If the film is annealed to higher temperature $T = 210$ K, weak 9-step oscillations are observed with a decreased oscillation amplitude and a

FIG. 1. Plots of σ_0 vs S for growth of 4 ML at $T = 195$ K on the $\sqrt{3}$ phase (top) showing 5-fold oscillations and on the (7×7) phase (bottom) showing 7-fold oscillations. The out-of-phase values of σ_0 for the $\sqrt{3} \times \sqrt{3}$ are smaller than the corresponding values on the (7×7) indicating that larger islands are grown on the $\sqrt{3}$ phase.
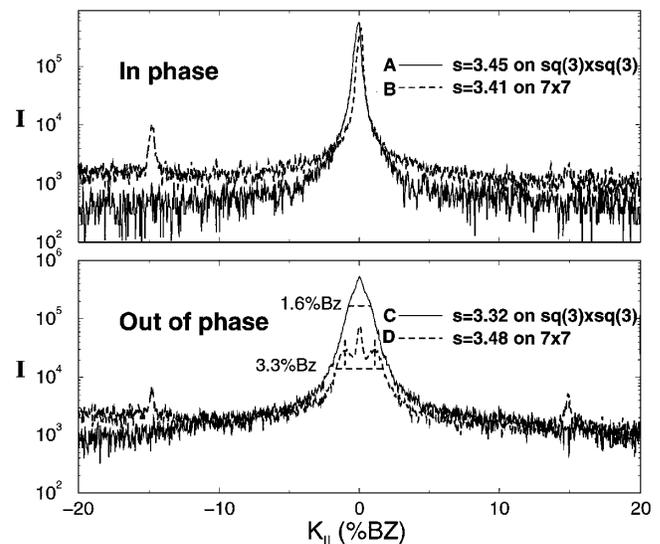

FIG. 2. Typical profiles for the in-phase (top) and out-of-phase (bottom) for the two interfaces showing sharper profiles (and larger islands) are present on the $\sqrt{3}$ phase.
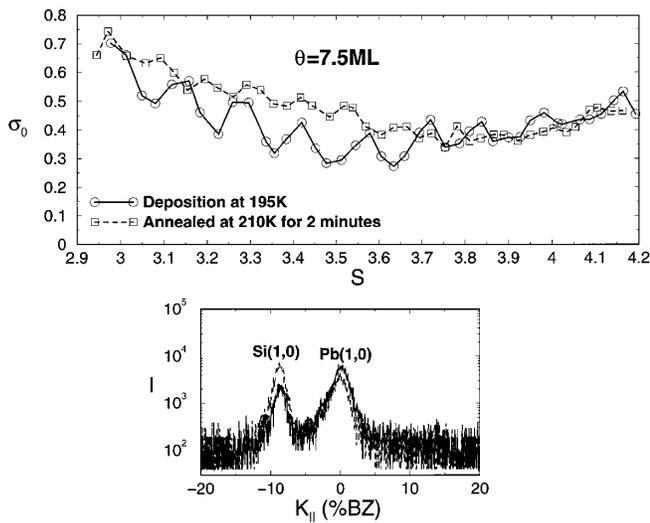
FIG. 3. For $T = 190$ K and larger Pb amounts on the $\sqrt{3}$ ($\theta = 7.5$ ML) 7-step islands are observed. When the islands are annealed to a higher temperature $T = 210$ K 9-step islands are observed. The transfer of atoms to higher levels can be seen also from the decrease of the Pb(10) spot and the corresponding increase of the Si(10) spot intensity.

larger average σ_0 value. The amplitude of the oscillations measures the sharpness of the island height distribution (i.e., what fraction of the islands has the most probable height and/or the island steepness) and the average value of σ_0 measures the average island size. From the results in Fig. 3 we deduce that as the islands grow the height distribution broadens and the islands become less steep. During the annealing process the Si(10) spot increases while the Pb(10) spot decreases in intensity indicating the transfer of Pb atoms already in the islands to higher levels. However, for smaller coverage $\theta < 5.5$ ML we see 5-step islands that maintain their height despite annealing to higher temperatures, which shows that for lower coverage the 5-step islands are the most stable islands on the $\sqrt{3}$.

We observe only 7-step islands [after the formation of the wetting layer on the (7×7)]. The annealing results on the (7×7) are similar to the annealing results on the $\sqrt{3}$: If 7-step islands form at $T = 195$ K, for smaller Pb amounts ($\theta < 5$ ML), they remain 7-step high; otherwise, for larger deposited amounts they grow, after annealing, to islands with the next bilayer increment, i.e., 9-step islands. Since no higher than 7-step islands are observed on the (7×7) directly after deposition, this indicates that a larger kinetic barrier exists, for Pb atoms to move to higher levels, on the (7×7) than on the $\sqrt{3}$ phase, which is consistent with the earlier observation that the island sizes are smaller for growth on the (7×7) than on the $\sqrt{3}$. In addition, since the growth of the islands to heights larger than the stable ones, after annealing, requires a minimum coverage on the surface (approximately 5 ML) and, since as seen in Fig. 3 this is carried out by atoms already in the islands, it suggests that the lateral size for the islands cannot be reduced below a minimum size.

It is worth mentioning a puzzling and unexpected feature for the growth on top of the $\sqrt{3}$ phase to complete the comparison of the growth on the two interfaces. If large amounts of Pb are deposited on top of the $\sqrt{3}$ phase at the same temperature $T = 195$ K we observe larger height islands (we can easily resolve islands up to 11-step height). However, the film does not close and the islands are still separated since the $\sqrt{3}$ phase is still visible. For growth on the (7×7) the film closes after 8 ML [5].

We discuss a possible explanation for the main result of this work, i.e., that the selected height depends on the type of interface present on the surface. Although this is physically expected it has not been observed experimentally before. Both interfaces have been extensively studied with angle-resolved photoemission experiments and with *in situ* conductivity measurements [16,17]. From the photoemission spectra on the different interfaces one can deduce changes in the position of the Fermi level by measuring its energy shift from well-known bulk emission features. It is found that the Fermi level is lower on the $\sqrt{3}$ than on the (7×7) both at low coverage $\theta = 1$ ML (0.08 eV vs 0.18 eV above the valence band, respectively [16]) and at multilayer Pb amounts deposited on the $\sqrt{3}$ vs (7×7) (0.19 eV vs 0.42 eV above the valence band, respectively [17]). Under the assumption [15] that the charge transfer energy depends on the difference in the Fermi level positions between the metal and the substrate, the energy gain on the $\sqrt{3}$ phase will be larger than the energy gain on the (7×7) phase. A more accurate analysis of the energy gain due to charge transfer should take into account the number of carriers transferred between the two films and the substrate. *In situ* conductivity measurements on the $\sqrt{3}$ phase (at 1.3 ML) have shown that the number of charge carriers on the $\sqrt{3}$ is larger than what is expected from simply the space charge layer [16].

The total film energy vs thickness curve on the $\sqrt{3}$ interface should lie lower from the total energy of the film vs thickness curve on the (7×7), moved downward by the larger charge transfer term. This will tend to lower all the kinetic barriers on the $\sqrt{3}$ and can explain why the island sizes on the $\sqrt{3}$ are larger (both the lateral size of the islands and the island height during deposition for high θ). In addition, since the gain due to charge transfer decreases with thickness, a larger contribution is expected at the 5-step than at the 7-step height, so the energy minimum will be affected more at the 5- than the 7-step height.

Based on the analysis of Ref. [15], the energy of the system can be expressed as $E = E_0 - E_c$, where E_0 is the energy of the Pb film (after subtracting the bulk energy) and E_c is an energy gain due to the charge transfer at the interface. E_0 is estimated by a model of free electron gas confined by an infinite hard wall at the Pb/Si(111) interface and a barrier step at the Pb/vacuum interface. The barrier step is equal to the sum of the Fermi energy (9.45 eV) of bulk Pb measured from the bottom of the conduction band and the work function (4.25 eV) of Pb.
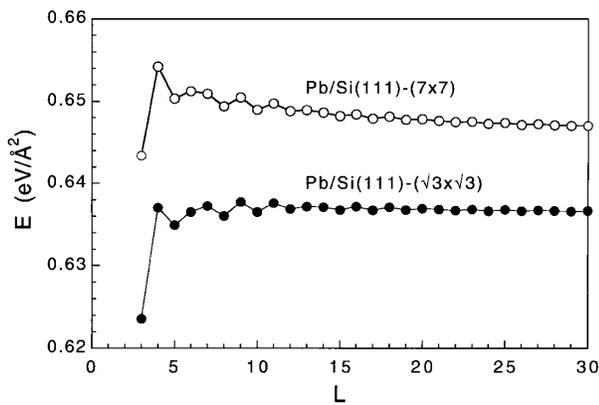
FIG. 4. Calculated film energy vs film thickness L for the two interfaces showing that the energy curve for the $\sqrt{3}$ phase lies lower and has a lower minimum at $L = 5$ than the next minimum $L = 8$; for the (7×7) curve the order of the minima is inverted.

$E_c = C(\Delta E_F)^2$, where ΔE_F is the initial difference between the Fermi energies of the film and the substrate. Using the experimentally determined values of the Fermi level for the two different interfaces [4.75 eV for the (7×7) and 4.98 eV for the $\sqrt{3}$ below the vacuum level] [17] and the calculated Fermi level position for the potential well of thickness L described above, the dependence of $E(L)$ on L is determined for the two interfaces. The results are shown in Fig. 4. C is a phenomenological parameter which is related to carrier changes and the strength of the chemical bonding, across the interface. We have chosen the value $C = 0.033$ eV/Å^2 in the calculation, which is consistent with the measured work function change $\Delta\phi = 0.25$ eV after Pb adsorption on Si(111)-(7×7) [17]. With this choice of C the energy minimum for the $\sqrt{3}$ phase is at $L = 5$ and for the (7×7) is at the next energy minimum (the next calculated minimum is at $L = 8$ instead of $L = 7$). The energy shift downward (~12 meV) of the $\sqrt{3}$ curve below the (7×7) curve can explain the faster kinetics and the larger island sizes observed on the $\sqrt{3}$. Although the model can capture the essential physics of the role of QSE in film growth, it is clearly an oversimplified approach. More realistic calculations based on *ab initio* methods are needed to fully understand the island structures with the lowest energy and the kinetic barriers in the system.

In summary we have studied how the self-organized growth mode of uniform height islands observed on Pb/Si(111) at low temperatures depends on the different substrate structure. 7-step islands are the most stable islands for growth on top of the (7×7), while 5-step islands are the most stable islands for growth on top of the $\sqrt{3}$ phase. This difference apparently is related to the larger charge transfer on the $\sqrt{3}$ than on the (7×7) interface, in good agreement with the results of a theoretical model, based on the difference in the Fermi levels across the interface. The practical significance of these experiments is that they demonstrate that it is possible to select in another way (i.e., by varying the initial phase of the substrate) the preferred island height and to control the type of nanostructures formed in epitaxy.

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