Correlation between height selection and electronic structure of the uniform height Pb/Si(111) islands

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Uniform-height islands, with preferred heights differing by bilayer *height* increments, can be grown on Pb/Si(111) at low temperatures most likely as a result of quantum size effects. With scanning-tunneling-microscope spectroscopy we have determined how the electronic structure of individual islands is related to their stability. Differences between preferred vs nonpreferred island heights are seen at the position of the Fermi level with respect to the highest occupied band and lowest unoccupied band. This difference is supported from oscillations of the measured apparent barrier $\Delta(\ln I)/\Delta z$ with island height.

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Epitaxial growth has been a highly successful technique to grow new materials. Recent experiments have identified the factors controlling the type of growth mode in a film, whether it is three-dimensional (3D) or layer by layer, so it is possible to predict *a priori* whether a uniform film can be prepared in a given system.[1] Uniform films have only one dimension reduced. However a far more challenging problem, with great technological importance, is the growth of regular nanostructures of uniform geometry and shape. If such structures can be fabricated, they will be far more useful in nanotechnology applications because of their smaller size.

Self-organization of the island height and shape has been observed in recent low-temperature experiments on Pb/Si(111).[2,3] The formation of flat-top, steep islands of preferred heights has been observed with spot-profile analysis in low-energy electron diffraction (SPA-LEED) from oscillations of the diffracted intensity with the electron wavelength. The growth has also been verified directly with the scanning-tunneling microscope (STM).[4] Depending on temperature range (120–250 K) and coverage, preferred heights differing by bilayer-height increments [$2d$ where $d=0.286$ nm is the single-step height for Pb(111)] grow. The formation of the islands was attributed to quantum size effects (QSE), i.e., how the energy of the electrons confined within the islands depends on island height.[5–9]

Initial evidence of QSE has been observed in earlier experiments. Bilayer specular intensity oscillations with Pb coverage have been observed in Pb/Cu(111) with He scattering.[10] Changes in the interlayer spacing of Pb/Ge(001) with Pb coverage, observed from variations of the full width at half maximum (FWHM) in elastic He-scattering experiments have been also attributed to QSE.[11] Evidence for QSE was seen in spectroscopic STM measurements on a Pb "wedge" grown over stepped Si(111) with different heights exposed at the top of the "wedge."[12] However the different height columns were part of a single "wedge" (and not the individual uniform height islands of smaller size grown recently[2–4]). More importantly, recent work has shown that specific heights are preferred, implying strong variation in the island energy with its thickness. Also work on QSE has been carried out with photoemission in metallic films.[13]

The purpose of this paper is to determine the electronic structure as a function of island height and to show that islands of preferred heights have different electronic structure than islands of nonpreferred heights. In addition, to demonstrate that the electronic structure of the preferred-height islands confirms that they are the stable ones. This information can be used to attain better control of the grown-island geometry and size. Usually the island-stability condition is expressed in terms of a simplistic "standing-wave" relation $nd=s\lambda_F/2$, with λ_F the Fermi wavelength, nd the preferred height, and s an integer, but clearly the mechanism driving the height selection is more complicated.

The growth of the Pb islands have been studied on two Si interfaces, the (7×7) phase and the Pb-($\sqrt{3}\times\sqrt{3}$) phase. The $\sqrt{3}\times\sqrt{3}$ phase forms either at low coverage (i.e., the strongly bound β-$\sqrt{3}\times\sqrt{3}$ phase with $\theta=\frac{1}{3}$ ML) or at higher coverage (the weakly bound α-$\sqrt{3}\times\sqrt{3}$ phase with $\theta=\frac{4}{3}$ ML).[14] Although the preferred island height is the same on both phases, the lateral size of the grown islands is larger for growth on the α-$\sqrt{3}\times\sqrt{3}$ phase.[14] For spectroscopy measurements, it is essential to have on the surface, islands of wide variation in height (both stable and unstable) so the dependence of the electronic structure on height can be examined with the same tip, to eliminate effects related to the electronic structure of the tip. Since islands grow larger laterally on the α-$\sqrt{3}\times\sqrt{3}$ phase and can expose unstable heights we present growth results on this phase.[14]

Figure 1 shows Pb growth on the α-$\sqrt{3}\times\sqrt{3}$ phase for $\theta=3.3$ ML and $T=195$ K. Most of the islands shown in Fig. 1(a) are of preferred height, which is marked on top of the islands. Some islands of unstable heights are seen: four-step (uncovered region of the five-step island at the bottom right) and six-step (lower right corner) islands. Some of the islands show a modulation on top that originates from the corrugation of the metal/semiconductor interface. This corrugation is projected to the top surface by the confined electrons in the island. The necessary conditions for the projection to be observable and the dependence of the spatial resolution, on island height and electron energy, has been worked out in Ref. 15 for metal systems. Detailed discussion of these effects for Pb/Si(111), which also demonstrates the importance of QSE, will be presented elsewhere.[16] The region between the islands is in the α-$\sqrt{3}\times\sqrt{3}$ phase with the domain walls arranged in stripes [i.e., SIC (striped incommensurate) phase] separated by 3.2 nm.

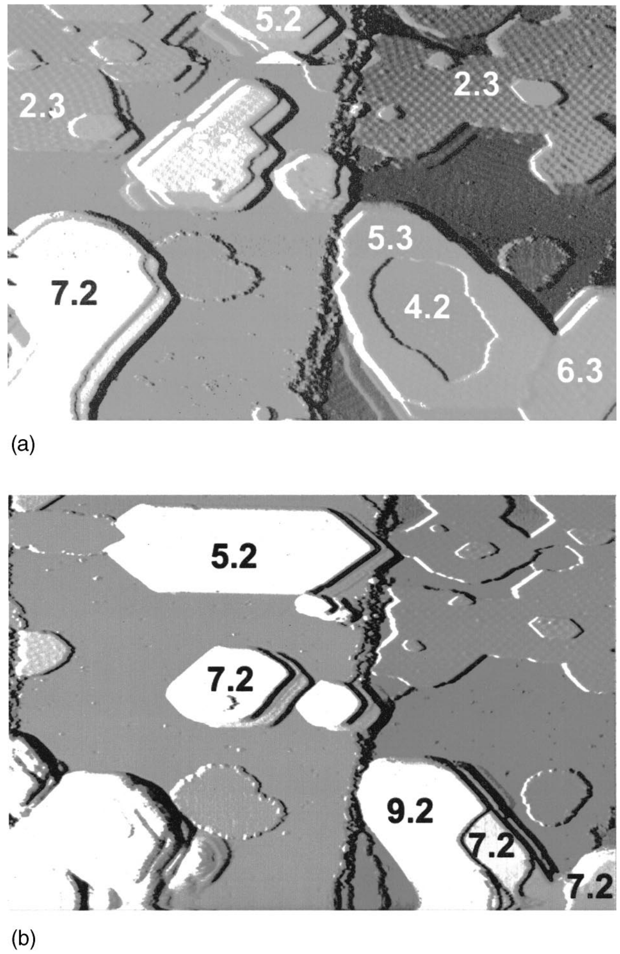

FIG. 1. (a) $100\times200\ \mathrm{nm}^2$ STM images showing different-height islands (stable and unstable). (b) The same area 40 min later showing the evolution to more stable heights.

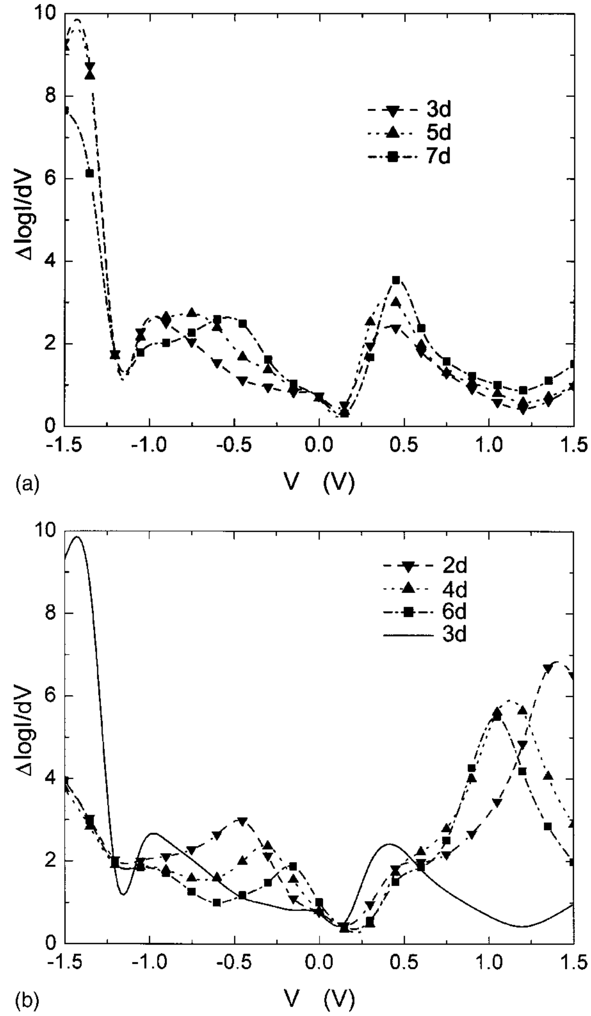

FIG. 2. (a) $\Delta \ln I/\Delta \ln V$ vs V spectra for the odd island heights. The Fermi level is at a larger separation from the HOB. (b) $\Delta \ln I/\Delta \ln V$ vs V spectra for even island heights showing that the Fermi level is closer to the HOB for odd height islands.

However, as Fig. 1(b) shows, obtained 40 min later, the initial island distribution evolves in time towards larger and stable odd heights by bilayer increments. For example, the four-step unfilled area at the bottom island is completed and the height changes to nine steps although the large two-step island to the top right remains unchanged probably because of the small energy difference between two- and three-step islands.

Figure 2 shows the spectroscopic measurements $\Delta \ln I/\Delta \ln V$ vs V for different heights. The normalized derivative $\Delta \ln I/\Delta \ln V$ can be related to the density of states (DOS) if the transparency of the tunneling barrier is taken into account. The measurements are divided into two groups. Figure 2(a) shows spectra for islands of odd height (3,5,7) and Fig. 2(b) shows spectra for the islands of even height (2,4,6).

The discrete energy levels in the islands are clearly seen in the spectra. Electrons occupying a level have a fixed normal component k_z with their parallel component extending from 0 to a maximum value $k\|_{\max}$. They generate a 2D subband and $k\|_{\max}$ is determined by the condition that the total energy of the electrons (i.e., the energy normal and parallel to the surface) is equal to the Fermi energy E_f.

For the simplest model to describe the confinement of the electrons in the island we assume a 1D well of width equal to the island thickness and depth 13.7 eV (i.e., the sum of Pb work function 4.25 eV and the separation of the Fermi level from the bottom of the conduction band 9.45 eV). Such a model ignores the complications related to the Pb band structure but it is adequate for testing some basic experimental parameters. With STM spectroscopy the two levels just below (HOB, highest occupied band) and just above (LUB, lowest unoccupied band) the Fermi level can be measured. The measured separation between the HOB and LUB 1 eV (for the seven-step island) agrees well with 0.92 eV, the result of the simple 1D model. For islands with larger height (i.e., for increasing well width) the level spacing decreases as seen qualitatively in both Figs. 2(a) and 2(b). Only for islands of sufficiently large height the separation should decrease as $1/h$ with h the height of the island, but for islands of smaller height it will depend on the detailed form of the 1D potential well.

The main conclusion from the results of Fig. 2 is the position of the Fermi level with respect to the HOB and

LUB: for the odd heights the Fermi level is at larger separation from the HOB while for even heights the separation to the HOB is smaller. How is the position of the Fermi level related to the stability of the islands?

We can answer this question by invoking an argument used by Schulte to explain how periodic variations in the island work function with thickness are caused by QSE.[5] The number of energy levels increases and the level spacing decreases as the island height increases. As the electronic levels are shifted downwards, a level initially above the Fermi level will be pushed below and electrons will start populating the subband corresponding to this level. The number of electrons occupying a subband increases with the separation of the level from the Fermi level, since $k\|_{\max}$ will be larger. Electrons at the level pushed below the Fermi level are closer to the vacuum than electrons at the lower levels and their wave function extends further outside the well. Charge spills out of the well and because of charge neutrality a dipole layer forms at the surface of the island.[17] As the island height increases, the energy levels are pushed even lower, the wave vector normal to the surface is smaller, but although the number of electrons occupying the level increases, the spilling of the wave function outside the well decreases and correspondingly the strength of the dipole layer formed at the surface is reduced. This variation of the dipole strength results in oscillations of the work function. If we relate the energy of the confined electrons to the amount of charge spilled outside the island, with minimum energy expected when the charge spilled is minimum, then periodic variations in island stability should be expected with island thickness. Heights with larger separation of the HOB from the Fermi level are the stable heights, as observed experimentally. Since the island height cannot increase continuously but only at discrete multiples of the Pb step height md (where $d = 0.286$ nm and m an integer), a height change by $2d$ is approximately equal to $\frac{3}{2}\lambda_f$ [with $\lambda_f = 0.366$ nm the Pb bulk value of the Fermi wavelength in the (111) direction[16]]. It will cause a new level to be pushed below the Fermi level and generate periodic variations of the charge spilled outside the island described above. Other contributions to the electron energy (i.e., charge transfer[3]) can explain further the difference in the Fermi-level position.

The difference between stable and unstable islands can also be seen from the level of the tunneling current in the I-V spectra. In general, the I-V curves for stable islands lie lower than the I-V curves for unstable islands, except in the energy range 0.4–0.5 eV, which includes the LUB for stable islands. One can simply write for the tunneling current

$$I = \sum_i \int_{E_f}^{E_f+eV} dE\,\rho_i(E)\exp[-2m/h^2(\phi - |eV|/2 - E_i)]^{1/2}, \tag{1}$$

where $\rho_i(E)$ is the 2D density of states, V is the applied tunneling voltage, ϕ is the average work function of sample and tip, E_i are the discrete levels normal to the island. It can be easily shown that for tunneling from the occupied states the largest contribution is from the HOB level and Eq. (1) can be approximated (if we take $E_f = 0$) as

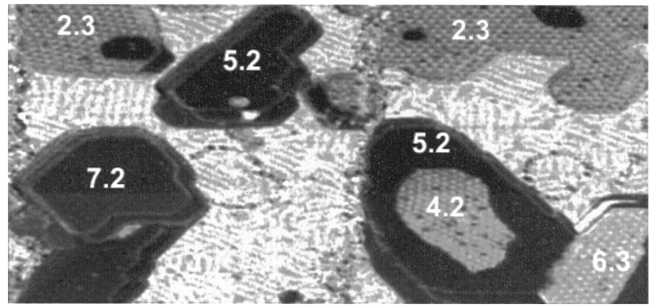

FIG. 3. Current-imaging-tunneling spectroscopy for the same topographic image in Fig. 1(a) obtained at +1.5 V (i.e., the sample is biased) showing that the even-height islands of Fig. 2(b) (two-, four-, six-step heights) have higher intensity.

$$I = |E_{-1}|\rho(E_{-1})\exp[-2z\{(2m/h^2)(\phi - |eV|/2 + |E_{-1}|)\}^{1/2}] \tag{2}$$

with E_{-1} the energy of the HOB. For tunneling into the unoccupied states the main contribution is from the level just below $E_f + eV$ denoted by E^*.

Equation (2) shows that for lower E_{-1}, I will be less. This explains why the tunneling current from odd-height islands is smaller than the tunneling current from even height islands. This is also seen in Fig. 3, which shows a current-imaging-tunneling spectroscopy (CITS) map at $V = -1.5$. The even-height islands (i.e., two-step, four-step, and six-step) have the higher intensity.

The conclusion that the difference in the separation of the Fermi level from the LUB for stable vs unstable islands can be further confirmed by measuring with a modulation technique the apparent barrier height $\Delta(\ln I)/\Delta z$ for different height islands. $\Delta(\ln I)/\Delta z$ was measured for two values of the tunneling voltage $V = 0.75$ and 1.5 V (for $I = 1$ nA). The corresponding energy 0.75 eV is above the LUB level for the stable islands [Fig. 2(a)] and 1.5 eV is above the LUB level for unstable islands [Fig. 2(b)]. Since I is an exponential function of z the apparent height barrier $\Delta(\ln I)/\Delta z$ is simply given by

$$\frac{\Delta \ln I}{\Delta z} = -2\left(\frac{2m}{h^2}(\phi - |eV|/2 - E^*)\right). \tag{3}$$

From Eq. (3) it is first seen that for higher tunneling voltage the lower will be the value of $\Delta(\ln I)/\Delta z$ since the tunneling barrier is lower. This explains why the values of $\Delta(\ln I)/\Delta z$ in Fig. 4 are lower for 1.5 V than for 0.75 V. Equation (3) shows that the value of $\Delta(\ln I)/\Delta z$ is essentially determined by the separation of E^* from $E_f + eV$. What is more interesting in Fig. 4 is the oscillatory variation of $\Delta(\ln I)/\Delta z$ with island height. For tunneling voltage 0.75 V, the odd island heights are at the minima of $\Delta(\ln I)/\Delta z$ while for 1.5 V the even island heights are at the minima. We will show next that this is a direct result of the difference in the position of the Fermi level with respect to the HOB and LUB discussed earlier.

If there was no difference in the position of the Fermi level with respect to HOB and LUB between stable and un-

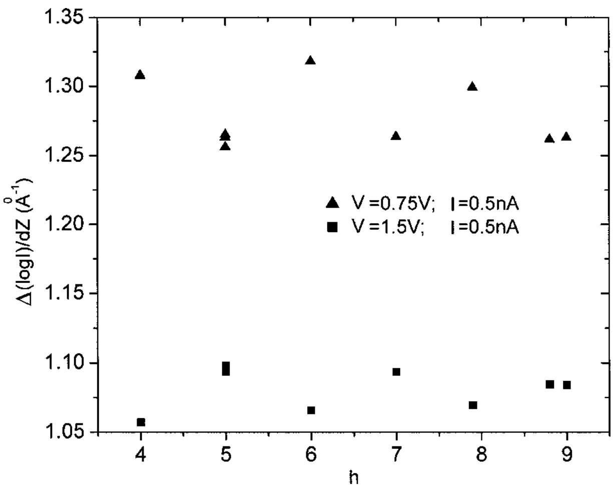

FIG. 4. Apparent barrier height $\Delta(\ln I)/\Delta z$ vs island height measured for two voltages $V=+0.75$ and $+1.5$ V. The oscillations can be explained from the difference in the Fermi-level position (with respect to the LUB and HOB) as shown in Fig. 2.

stable islands, the LUB would move monotonically towards the Fermi level (as the spacing between the levels is decreased). E^* would decrease and as Eq. (3) shows, $\Delta(\ln I)/\Delta z$ would correspondingly increase with island thickness. No oscillations of $\Delta(\ln I)/\Delta z$ with island height are expected in this case. As mentioned before, when discussing Fig. 2, the separation between E_f and LUB is smaller for odd heights than the corresponding separation for even height islands. The measured value of $\Delta(\ln I)/\Delta z$ at 1.5 V for odd-height islands will be at the minima since as seen in Fig. 2(b) their LUB level is close to E_f+eV; but at 0.75 V for the even-height islands, E^* coincides with the HOB, which is at a large separation from E_f+eV and these heights result in maxima of $\Delta(\ln I)/\Delta z$. For odd-height islands the opposite is true: the separation between the LUB is larger at 1.5 V [and odd heights are at the maxima of $\Delta(\ln I)/\Delta z$] while the separation is smaller at 0.75 V [and odd heights are at the minima of $\Delta(\ln I)/\Delta z$].

In summary, we have performed I-V measurements on the uniform-height Pb islands grown on Si(111) at low temperatures as a function of island height. It is possible to distinguish stable from unstable islands by the position of the Fermi level: it is at a larger separation from the HOB for stable islands than unstable islands. This asymmetry explains why stable islands have lower energy and results in oscillations of the apparent height barrier $\Delta(\ln I)/\Delta z$ with island thickness. The spectroscopic studies confirm the importance of QSE and more importantly demonstrate strong correlations between the island's electronic structure and stability.

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