"Devil's Staircase" in Pb/Si(111) Ordered Phases

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(Received 5 November 2002; published 29 May 2003)

With scanning tunneling microscopy we have found that ordered phases in Pb/Si(111) are one of the best examples of the "devil's staircase" phase diagram. Phases within a narrow coverage range ($1.2 < \theta < 1.3$ monolayers) are constructed with the rules similar to the ones found in theoretical models.

DOI: 10.1103/PhysRevLett.90.216106 PACS numbers: 68.35.Rh, 68.35.Bs, 68.37.Ef

Self-organization on surfaces is of great recent interest because it results in atomic scale regular structures, which are of fundamental and technological importance. Self-organized structures are manifested whenever the system can spontaneously select the preferred structure size and geometry. A common condition to attain such selectivity is the presence of competing interactions. For the special case of interactions which have competing periodicities an exceedingly rich set of closely related phases (in coverage and spatial modulation) can form [1–4]. Theoretical models where competing interactions produce such structures are the 1D Ising model with long range repulsive interactions [5], a 1D chain of electrons experiencing Coulomb interaction [6], and the ANNI model of dimensionality $d > 2$ with short range interactions of competing sign [7]. Although the experimentally realized phases have seemingly complex forms, they are built with simple formation rules. On the practical side, these phases can provide in principle, an infinite number of well-ordered substrates to be used as initial templates for growth or as testing grounds of the physics of low dimensional electron systems.

The problem of systems with competing periodicities is commonly described in terms of a periodic potential U and a nonperiodic interaction $J(x)$. For the special case of a convex interaction $J(x)$ [i.e., $d^2J(x)/dx^2 < 0$] a highly complex phase diagram, i.e., a "devil's staircase," is generated consisting of numerous spatially modulated phases which vary infinitesimally in coverage and modulation wave vector. The experimental realization of the predicted phases, especially in two dimensions, is a major experimental challenge, despite outstanding theoretical predictions [1–4].

In general, in systems with competing periods two periodic functions are necessary to specify the atom location, one related to the substrate lattice constant a_0 and the other period a_i incommensurate to a_0 [4]. Such mixed periodicities produce ordering wave vectors $k = 2\pi(s/a_0 + t/a_i)$ where s, t are integers. X-ray and neutron scattering have been used to identify devil's staircase phases in 3D systems [8,9]. Diffraction is also ideally suited for temperature dependent measurements to deduce the nature of the commensurate-incommensurate transition [10,11].

It is also possible to use real space techniques to identify phases which differ infinitesimally in coverage. As we show below this is done with scanning tunneling microscopy (STM) in the coverage range $1.2 < \theta < 1.3$ ML (monolayer) close to the dense Pb/Si(111)-$\sqrt{3} \times \sqrt{3}$ phase. The STM can directly detect small increments in the unit cell size while the adatom location with respect to the substrate atoms is deduced easier by diffraction [12].

Although the dense Pb/Si(111)-$\sqrt{3} \times \sqrt{3}$ phase has been extensively studied, conflicting results exist in the literature. Recently we have identified experimentally and confirmed with first principles calculations the atom position, domain wall arrangement, and stoichiometry of the phase [13]. The interior of the domains is built out of $\sqrt{3} \times \sqrt{3}$ unit cells while the domain walls consist essentially of $\sqrt{7} \times \sqrt{3}$ unit cells with the coverages of 4/3 and 6/5 ML, respectively.

Figure 1 shows an image over a large 100 nm × 100 nm area of a few terraces covered with a 1D phase of three equivalent orientations. This particular phase has a $9 \times \sqrt{3}$ unit cell built out of one $\sqrt{3} \times \sqrt{3}$ and three $\sqrt{7} \times \sqrt{3}$ cells with coverage $\beta = (4 + 18)/(3 + 15) = 1.222$ ML. For tunneling voltage 1.5 V, the $\sqrt{3} \times \sqrt{3}$ is seen as two adjacent bright rows, while the $\sqrt{7} \times \sqrt{3}$ phase is imaged as long dark rows, because only Pb atoms at $H3$ positions are seen.

The experimental evidence that a system displays a devil's staircase is to observe the presence of as many phases as possible, constructed hierarchically, within a narrow $\Delta\beta$. We show in Figs. 2 and 3 only small rectangular segments of the different phases observed. Each phase consists of dark rows ($\sqrt{7} \times \sqrt{3}$ phase) and bright double rows ($\sqrt{3} \times \sqrt{3}$ phase). Although only small areas are shown, the phases extend over the whole terrace as seen in Fig. 1. In Fig. 2 we show eight phases in the range $1.2 \leq \beta \leq 1.25$ ML and in Fig. 3 we show four phases in the range $1.2 \leq \beta \leq 1.3$ ML.

Stronger evidence that these phases are a realization of the devil's staircase is the simple formation rules, similar to the formation rules in the theoretical models: they are built from a combination of $n(\sqrt{7} \times \sqrt{3})$ and $m(\sqrt{3} \times \sqrt{3})$ unit cells with n, m integer numbers. For example, the ideal $(\sqrt{7} \times \sqrt{3})$ phase has $n = \infty$, $m = 0$ while the ideal

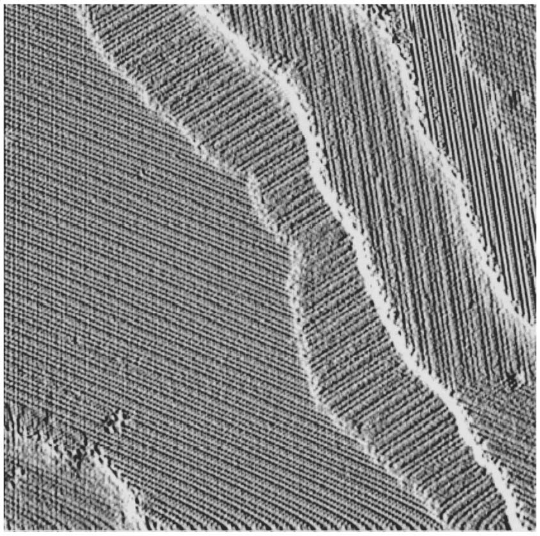

FIG. 1. 100 nm × 100 nm differential STM image showing the nucleation of three equivalent domains of the linear $\sqrt{3} \times 9$ phase ($n = 3, m = 1$) on adjacent terraces. For tunneling voltage $V = 1.5$ V bright rows correspond to $\sqrt{3} \times \sqrt{3}$ and dark rows to $\sqrt{7} \times \sqrt{3}$ arrays of unit cells.

($\sqrt{3} \times \sqrt{3}$) phase has $n = 0, m = \infty$. A phase is denoted by the string of successive values of n "3233233233," i.e., the number of $\sqrt{7} \times \sqrt{3}$ separating the $\sqrt{3} \times \sqrt{3}$ unit cells.

Figure 4 shows schematically a ball model of the Si(111) surface illustrating the different types of unit cells. At the top the $\sqrt{3} \times \sqrt{3}$ (right) and the $\sqrt{7} \times \sqrt{3}$ (left) unit cells are shown. The unit cell shown in the middle is for the $n = 3, m = 1$ phase and the one below is for the $n = 2, m = 1$ phase.

We summarize theoretical predictions [5–7,14] about the θ vs μ dependence of the regular devil's staircase, with θ the coverage of the pattern forming atoms (to be distinguished from the experimental coverage $\beta = 1 + \theta$). It was shown that a "complete" staircase includes all phases with coverage $\theta = p/q$ corresponding to any irreducible rational number p/q between the coverages θ_1, θ_2 of the two generating phases. The lengths of the unit cells of the two generating phases differ by 1, i.e., q_1 and $q_1 + 1$ (with $[\theta_1 = 1/q_1, \theta_2 = 1/(q_1 + 1)]$).

Because of the convexity condition on $J(x)$, the energy of the system is a minimum, when the separation between neighboring atoms can take only two values: either integ$\{q/p\}$ or integ$\{(q/p)\} + 1$ with the function integ denoting the integer part of the fraction q/p. In addition if the p atoms are indexed by j in the sequence $\{1, 2, \ldots, j, \ldots, p\}$, it can be shown that the separation between any two jth neighbors must take only two values integ$\{jq/p\}$ or integ$\{(jq/p)\} + 1$.

We have earlier identified as the two generating phases the $\sqrt{3} \times \sqrt{3}$ and $\sqrt{7} \times \sqrt{3}$ phases. Because of the large lattice mismatch between the Si and Pb lattice constants, a stress mediated interaction $J(x) = 1/|x|^\eta$ holds effectively between the high symmetry atoms. This implies that $\theta_1 = 1/5$ ML (for the $\sqrt{7} \times \sqrt{3}$ with $\beta = 1.2$ ML) and $\theta_2 = 1/3$ ML (for the $\sqrt{3} \times \sqrt{3}$ phase with $\beta = 1.33$ ML) since $\beta = 1 + \theta$. As shown in Fig. 4 the high symmetry Pb atoms occupy $H3$ sites [12]. The geometric constraint imposed by the Si(111) substrate adds a novel feature to the system and generates a different devil's staircase. Adjacent corner atoms in the unit cells are shifted by $\sqrt{3}a_0/2$ in the $[\bar{1}\,\bar{1}\,2]$ and by an odd number of $a_0/2$ in the $[\bar{1}10]$ direction. For example the length of the $\sqrt{7} \times \sqrt{3}$ unit cell in the $[\bar{1}10]$ direction is $q_1 = 5$ and the length of the $\sqrt{3} \times \sqrt{3}$ unit cell is $q_2 = 3$ in units of $a_0/2$. This novelty has important implications about the stability and structure of the devil's staircase since the unit cells of the generating phases differ by two lattice

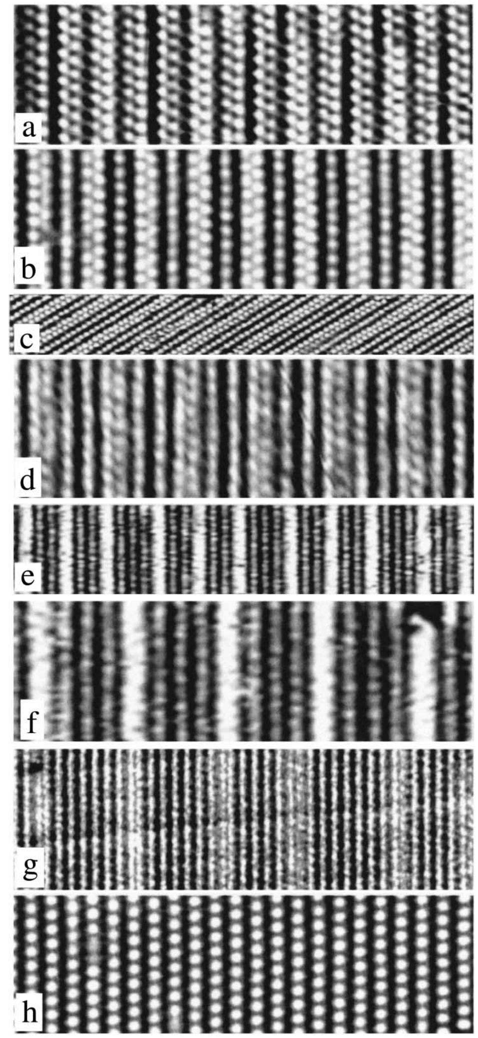

FIG. 2. Linear phases observed in the range $1.2 < \beta \leq 1.25$ ML: (a) $n = 1, m = 1$ $\beta = 1.25$ ML; (b) $n = 2, m = 1$ $\beta = 1.2307$ ML; (c) $n = 3$ and 2, $m = 1$ $\beta = 1.2226$ ML; (d) $n = 3, m = 1$ $\beta = 1.222$ ML; (e) $n = 4$ and 3 $m = 1$ $\beta = 1.2203$ ML; (f) $n = 4, m = 1$ $\beta = 1.217$ ML; (g) $n = 7$ and 5 $m = 1$ $\beta = 1.21$ ML; (h) $n = \infty, m = 0$ $\theta = 1.2$ ML.

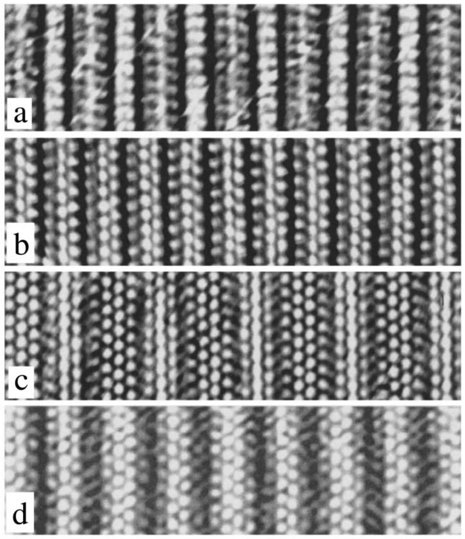

FIG. 3. Linear phases in the range $1.25 < \beta < 1.3$ ML: (a) $n = 1, m = 1$ and 2 $\beta = 1.263$ ML; (b)$n = 1, m = 2$ $\theta = 1.27$ ML; (c) $n = 1, m = 3$ and 2 $\theta = 1.28$ ML; (d) $n = 1, m = 3$ $\theta = 1.285$ ML.

constants (i.e., $q_1 = 3$ and $q_1 + 2 = 5$ in units of $a_0/2$) instead of one as in the regular staircase.

For comparing the two staircases we have determined the stability range of a phase of coverage $\theta = p/q$ by calculating the chemical potential interval $\Delta\mu$ over which the phase has the lowest energy [15]. This interval is determined from the difference of the two energies $\Delta\mu(p/q) = E_+(p/q) - E_-(p/q)$ where E_+ is the energy change after one atom is added and E_- is the energy change after one atom is removed from the system. We found that this energy difference can be written as

$$\Delta\mu(p/q) = \frac{1}{2}\sum_{l=1}^{l=\infty} l\overline{q}\{J(l\overline{q}+2) + J(l\overline{q}-2) - 2J(l\overline{q})\}, \tag{2}$$

with $\overline{q}$ the length of the phase unit cell and $l = 1, 2, \ldots$. The energy terms in Eq. (2) are evaluated at $lq \pm 2$ (instead of $lq \pm 1$ for the regular staircase) which increases $\Delta\mu$, because the convexity of $J(x)$ implies $J(l\overline{q}+2) + J(l\overline{q}-2) > J(l\overline{q}+1) + J(l\overline{q}-1)$.

A second difference of the new versus the regular staircase is that the unit cell length of phase (m, n) must be of the form $3m + 5n$ and therefore the coverage $\theta = m + n/(3m + 5n)$, because it is built with m unit cells of length 3 and n unit cells of length 5. It can be easily shown that any rational number $1/5 < p/q < 1/3$ can be written in this form with $m/n = (5p - q)/(q - 3p)$, so phases with all rational numbers p/q are realized. However if the numbers $(5p - q)$ and $(q - 3p)$ do not have a common denominator then $m = 5p - q$, $n = q - 3p$ and the length of the unit cell is $\overline{q} = 3(5p - q) + 5(q - 3p) = 2q$. This occurs when p and q are of opposite parity, otherwise when they both are odd, $\overline{q} = q$. For the regular staircase always $\overline{q} = q$.

The two differences between the new and the regular staircase, i.e., the change of $l\overline{q} \pm 1$ into $l\overline{q} \pm 2$ in Eq. (2) and the doubling of the unit length when p and q have different parity, have opposite contributions to $\Delta\mu$. Phases of period $2q$ (when p and q have opposite parity) have smaller $\Delta\mu$, while phases with p and q odd have larger $\Delta\mu$ in the new versus the regular staircase for which a period is always q. One obvious consequence of this, shown in Fig. 5 for the case $\eta = 2$, is that the new staircase is steeper than the regular one.

How close are the experimental results shown in Figs. 2 and 3 to the theoretical predictions? First, as already mentioned, we see 12 closely related phases within $\Delta\theta \sim 0.1$ ML which is one of the largest number of phases observed so far [16,17]. As stated above the frequency of observing a phase increases as its unit cell size decreases. Our data qualitatively confirm this prediction, since no phases with unit cells larger than $n > 8$ (for $m = 1$) and $m > 3$ (for $n = 1$) are seen.

The predicted changes in $\Delta\mu$ for the new staircase are in excellent agreement with observations. For example, phases with $n = 2, m = 1$ ($\theta = 3/13$ ML) and $n = 1, m = 2$ ($\theta = 3/11$ ML) are more stable than the phases with $\theta = 2/9$ ML and $\theta = 2/7$ ML despite their larger q. This is a property of the new staircase because of the

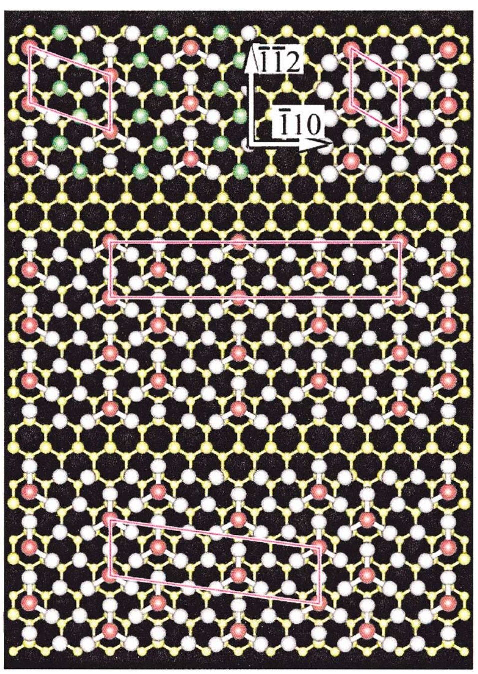

FIG. 4 (color). Schematic model of the Si(111) with several unit cells of the linear phases: $\sqrt{7} \times \sqrt{3}$ (top left), $\sqrt{3} \times \sqrt{3}$ (top right), $\sqrt{3} \times \sqrt{9}$ (middle $n = 3, m = 1$), $\sqrt{43} \times \sqrt{3}$ (bottom $n = 2, m = 1$). The Pb atoms at high symmetry positions ($H3$) are shown in red. There are 6 Pb, 5 Si atoms in the $\sqrt{7} \times \sqrt{3}$ and 4 Pb, 3 Si atoms in the $\sqrt{3} \times \sqrt{3}$ unit cell.

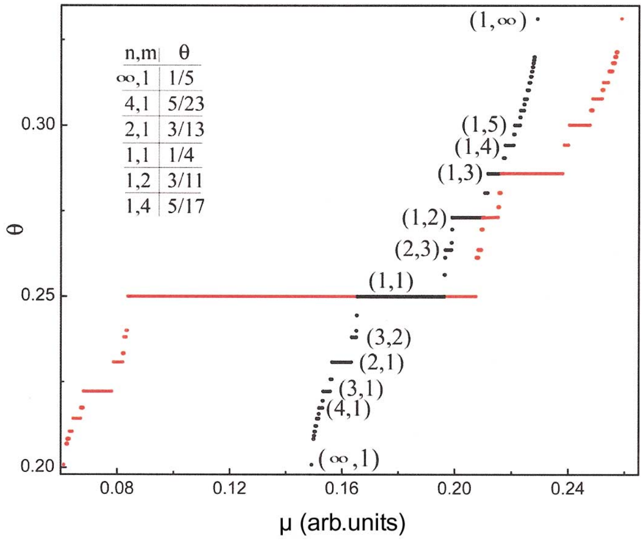

FIG. 5 (color). Comparison of the regular (red) versus the new (unit cells of lengths 3 and 5) staircase for the range $1/5 < \theta < 1/3$ and interaction energy $J(x) = 1/|x|^{\eta}$ with $\eta = 2$. The stability intervals $\Delta\mu$ of the new staircase for phase with coverage p/q (with p, q odd) are longer, while for all other coverages are shorter, than the corresponding intervals of the regular staircase.

effect of parity as discussed before. It should be stressed that these phases are the ones more commonly seen in experiments, i.e., the $\sqrt{43} \times \sqrt{3}$ and $\sqrt{31} \times \sqrt{3}$ phases, respectively [13]. In addition, because of the higher steepness of the novel staircase (because the $1/5$ and $1/3$ phases have larger $\Delta\mu$), phases of larger unit lengths have smaller stability differences which can account for the presence of mixed phases.

Since the experimental chemical potential $\mu(F, T(x))$ varies slightly with surface location x (either because of a small temperature gradient $dT/dx \neq 0$ or because of defects), phases with both n, m larger than 1 do not show always the theoretically expected sequence error free. For example, we observe the string for $m = 1$ and variable $n = 2$ or 3,“33223222333232333333,” with coverage $\beta = 398/325$ ML; a slightly rearranged pattern with the same β, “33233233233233233232“ i.e., the phase with $n = 8$ and $m = 3$) has lower energy. The presence of “wrong” strings is a result of the finite temperature, which makes the probability of string configurations of slightly higher energy small but nonzero. In addition, the real system is two dimensional (although the phases which form are linear) while the theoretical models are one dimensional. Because of the two dimensionality, kink excitations along the $\sqrt{3} \times \sqrt{3}$ rows are sometimes seen.

These linear highly equilibrated commensurate structures can also explain the formation of phases studied in the literature [13,18,19]: the “hexagonal incommensurate phase” and “striped incommensurate phase” built from the $\sqrt{3} \times \sqrt{3}$ phase in the interior and the $\sqrt{7} \times \sqrt{3}$ phase in the domain walls, fluctuating at higher temperature.

We have presented evidence that the linear Pb/Si(111) structures in the range $1.2 < \beta < 1.3$ ML observed at low temperatures with STM are one of the best realization of the devil's staircase in two-dimensional overlayers. This is supported from the multitude of phases (~ 12) clearly resolved with the STM within a narrow coverage range $\Delta\beta \sim 0.1$ ML and the similar rules obeyed in how the phases are constructed by combining unit cells of the two generating phases. However because the Si(111) geometry requires the use of generating phases which differ by two lattice constants, a novel staircase of different stability and mathematical structure results.

Ames Laboratory is operated by the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This work was supported by the Director for Energy Research Office of Basic Energy Sciences.

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