The Reconstruction of Pt(111) and Domain Patterns on Close-packed Metal Surfaces

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We have studied the reconstruction of Pt(111) theoretically using a two-dimensional Frenkel-Kontorova model for which all parameters have been obtained from ab initio calculations. We find that the unreconstructed surface lies right at the stability boundary, and thus it is relatively easy to induce the surface to reconstruct into a pattern of FCC and HCP domains, as has been shown experimentally. The top layer is very slightly rotated relative to the substrate, resulting in the formation of “rotors” at intersections of domain walls. The size and shape of domains is very sensitive to the density in the top layer, the chemical potential, and the angle of rotation, with a smooth and continuous transition from the honeycomb pattern to a Moiré pattern, via interlocking triangles and bright stars. Our results show clearly that the domain patterns found on several close-packed metal surfaces are related and topologically equivalent.

PACS numbers: 68.35.Bs, 61.72.bb, 68.35Md, 68.55.-a

Due to its enormous importance as a catalyst, Pt(111) is one of the most widely studied surfaces. Under “normal” conditions, it has the flat topography expected of a bulk-truncated face-centered-cubic (FCC) (111) surface. However, experiments have shown that one can induce the surface to reconstruct into either a honeycomb structure or a pattern of interlocking triangles – for example, by heating the surface above 1330 K [1], or by placing it in a supersaturated Pt vapor [2]. The reconstructed structure is comprised of domains where the bulk FCC stacking sequence is retained, alternating with domains where the surface atoms instead occupy hexagonal-close-packed (HCP) sites, sitting directly above atoms two layers below.

This is one of a family of similar reconstructions, formed by a tessellation of FCC and HCP domains, seen on Au(111) as well as various heteroepitaxial systems on the (111) faces of FCC metals, and the structurally similar (0001) faces of HCP metals [3, 4, 5, 6]. These structures have attracted a great deal of interest, especially because they can be used as templates for growing ordered arrays of nanoparticles [7, 8, 9]. Possible applications for such nanostructures include nanoelectronics, information storage, and nanoscale chemical reactors. To design such nanostructures, it is desirable to understand the factors controlling the geometry and spacing of the reconstruction patterns.

In this paper, we study the structure of the Pt(111) surface theoretically. We show that the unreconstructed Pt(111) surface is in fact teetering right at the brink of a domain of stability. Thus, slight changes in the environment can trigger a reconstruction, whose periodicity and geometry are very sensitive to various extrinsic and intrinsic parameters. In addition to obtaining excellent agreement with the structures reported experimentally for Pt(111), we also observe most of the structures reported experimentally for other systems.

The presence or absence of such reconstructions involves a very delicate balance between various contributions to the total energy, and it is therefore desirable to have as accurate a description of interatomic interactions as possible. Unfortunately, the very large unit cells of the reconstructed surfaces make it unfeasible to perform a fully ab initio calculation. However, one can use ab initio calculations to parametrize a model; this is the approach we will follow.

The driving force for the reconstruction of these close-packed surfaces is tensile surface stress, i.e., surface atoms would like to be closer together than the bulk nearest-neighbor (NN) spacing \( a \). This tendency is however opposed by the fact that (in general) it costs energy when: (i) surface atoms lose registry with the substrate (ii) extra atoms must be provided to increase the surface density. These factors are incorporated in the Frenkel-Kontorova (FK) model, which has been widely used to study commensurate-incommensurate transitions [10]. In its original form, the model consists of a one-dimensional chain of atoms connected by harmonic springs of equilibrium length \( b \neq a \), sitting in a sinusoidal substrate potential. This has the advantage of being exactly solvable, and can serve as a useful guideline for studying structural stability.

However, a proper description requires a generalized version of the FK model, with a two-dimensional (2D) layer of atoms interacting via a more realistic anharmonic potential \( V_{ss} \), and sitting in a 2D potential due to bulk atoms, \( V_{sb} \), with competing minima at FCC and HCP sites. The Hamiltonian is given by [11]:

\[
H = \sum_i V_{ss}(l_i) + \sum_j V_{sb}(r_j) + \Gamma N, \tag{1}
\]
where \( i \) runs over all NN bonds of length \( l_i \) between surface atoms, and \( j \) runs over all atoms at positions \( \mathbf{r}_j \) in the surface layer. \( N \) is the total number of atoms, and \( \Gamma \) is a chemical potential that contains information about the energy required to incorporate an atom into the surface layer; this depends on where the atom comes from (bulk, step edge, adatom, etc.).

To obtain \( V_{ss} \), \( V_{sb} \), and \( \Gamma \), we have performed \textit{ab initio} density functional theory calculations to study the energetics of compressing the surface layer, making surface stacking faults, and extracting atoms from various sites. We use the PWSCF package \cite{12}, with a plane wave basis with a cut-off of 20 Ry, ultrasoft pseudopotentials \cite{13}, and the local density approximation to the exchange-correlation potential. Surface calculations have been carried out using supercells with 9 layers of atoms, separated by a vacuum of 6-layer thickness. A Monkhorst-Pack grid corresponding to 27 \( \mathbf{k} \)-points in the irreducible part of the surface Brillouin zone is used to sample reciprocal space for calculations using a \((1 \times 1)\) surface cell; the grid is varied commensurately when using larger surface cells. We obtain the bulk lattice constant as \( a_0 = 3.92\AA \), and find that the first interlayer spacing \( d_{12} \) is slightly expanded by 0.3% relative to the bulk interlayer spacing, and the next two interlayer spacings \( d_{23} \) and \( d_{34} \) are slightly contracted by 0.55% and 0.18% respectively. We obtain the (unreconstructed) surface energy \( \gamma \) and surface stress \( \sigma \) as 9.13 and 29.45 mRy/\( \AA^2 \) respectively. These results are in good agreement with experiments and previous calculations \cite{14,15,16}.

The trickiest part of the parametrization concerns \( V_{ss} \), the interaction between surface atoms. Earlier authors (who studied other systems), either used “physically reasonable” parameters \cite{17}, or did calculations to study the energetics of a monolayer of atoms on a jellium \cite{18}; the ambiguity in the latter approach arises from the uncertainty in the choice of jellium density. We have chosen instead to calculate the variation in the surface stress when compressing a slab of atoms \cite{20}. The distance \( d_{12} \) is allowed to relax, and it is therefore a good approximation to assume that the variation in surface stress comes entirely from the surface-surface bonds that we are interested in. We use these results to parametrize a Morse potential \( V_{ss} = A_0 \{1 - \exp[-A_1(a - b)]\}^2 \); we obtain \( A_0 = 60.2 \) mRy, \( A_1 = 2.062 \) \( \AA^{-1} \), and \( b = 2.638 \) \( \AA \), i.e., surface bonds would like to shorten their length by 4.7% from the bulk NN distance \( a = a_0/\sqrt{2} = 2.77\AA \).

To obtain \( V_{sb} \), we study surface stacking faults. We find that the energy cost (per surface atom) of having the surface layer occupy HCP, top and bridge sites instead of the most favored FCC site is 5.05, 11.85 and 5.89 mRy respectively. These values are then used to expand \( V_{sb} \) in a 2D Fourier series, using the first two shells of reciprocal lattice vectors for the 2D surface lattice \cite{18,19}. Fig. 1 shows \( V_{sb} \) for a line cutting through the surface along the \([112]\) direction. Note that though the HCP site is a local minimum, it lies considerably above the FCC site in energy.

Finally, to obtain \( \Gamma \), we use our \textit{ab initio} results for the bulk cohesive energy, the surface energy, the adatom adsorption energy and the energy needed to detach an atom from a kink site at a step edge \cite{20} to obtain \( \Gamma_N = 4.56 \) mRy for bulk atoms, \( \Gamma_a = -67.12 \) mRy for adatoms, and \( \Gamma_k = 50.4 \) mRy for kink atoms.

To see how stable the unreconstructed surface is, one can map the 2D problem onto a 1D FK model \cite{11}, and evaluate the dimensionless parameter \( R = (3\pi a)(4\gamma - \gamma)/8\sqrt{2}kW \), where \( k \) is the spring constant for NN surface bonds and \( W \) is the amplitude of \( V_{sb} \) along the zigzag line connecting adjacent FCC and HCP sites. If \( R > 1 \), the surface will not reconstruct. Mansfield and Needs \cite{11} have obtained \( R = 0.73 \) for Pt(111) and \( R = 0.44 \) for Au(111), i.e., they predict that unreconstructed Au(111) should be more stable than Pt(111), whereas it is well known that Au(111) reconstructs even at low temperatures. We believe that the deficiency lies not with their model but with the values they used to obtain \( R \). Upon approximating \( V_{ss} \) by a harmonic potential in the region of interest, we obtain \( k = 370 \) mRy/\( \AA^2 \). Using \( W = 5.89 \) mRy, we get \( R = 0.998 \), i.e., we find that the unreconstructed surface is only just stable. This explains why it is relatively easy to induce the surface to reconstruct by increasing the temperature (reducing \( W \)) or by placing the surface in a supersaturated vapor (effectively increasing the numerator of \( R \)).

For a more precise determination of structural stability, we work with the full 2D Hamiltonian of Eq. 1. We study the variation in the surface energy \( \gamma \) as a function of \( \Delta \rho \), the excess density in the surface layer (relative to the unreconstructed case), and \( \theta \), the angle between the unit vectors of the top layer and the substrate. (Though optimizing \( \theta \) makes only a very small difference to \( \gamma \), we will show below that allowing for \( \theta \neq 0 \) is crucial to explain the “rotors” at intersections of domain walls.) In all cases, we start with a uniformly compressed layer of surface atoms, and obtain the atomic positions that min-
imize \( \gamma \), using a conjugate gradient algorithm.

For Pt(111), we find that isotropically compressed structures, with threefold symmetry and sixfold atomic coordination everywhere, are always lower in energy than the uniaxial “stripe” patterns or structures with point dislocations. Fig. 2(a) shows how \( \Delta \gamma \), the change in the surface energy (relative to the unreconstructed surface) and \( \theta \), the angle of rotation of the top layer, depend on the excess density \( \Delta \rho \); (c) and (d) show how the optimal excess density \( \Delta \rho_{\text{min}} \) and the periodicity \( l \) vary with the chemical potential \( \Gamma \).

Our most striking results are obtained upon examining the domain patterns using a simple technique to obtain the surface corrugation and thus simulate STM images. The height of each atom in the unit cell is obtained using a 2D Fourier expansion similar to that used for \( V_{ab} \), expanding about the heights at FCC, HCP, bridge and top sites. From our \textit{ab initio} calculations on surface stacking faults, we obtain these heights as 0, 0.03, 0.29 and 0.06 Å respectively. These are smaller than the corrugations measured experimentally [20]. However, we find that \textit{ab initio} simulations of the reconstructed structure (for small cell sizes accessible to computation) support our smaller values [20]. As has been reported recently for Au(111), it appears that the STM exaggerates the value of the corrugation [21]. In any event, we are primarily interested in the domain patterns, rather than in the absolute heights.

A sequence of simulated STM images is shown in Fig. 3. In all six images, black, dark grey, and white areas correspond to regions where atoms sit at FCC, HCP, bridge and top sites respectively. A non-linear grey scale has been used to show the domain walls (bridge sites) clearly. Fig. 3(a) shows the pattern obtained when \( \Delta \rho=2.9\% \), and \( \theta = 0 \). Large hexagonal FCC domains are separated from narrow HCP domains by domain walls that form a honeycomb network. Alternate vertices of the hexagons are extremely bright; atoms here sit at top sites. Between these bright vertices, there is a “three-pointed star” similar to that obtained in an earlier simulation of the nucleation of the reconstruction [22]. Fig. 3(b) shows the structure obtained for the same \( \Delta \rho \), but with \( \theta \) at its optimal value of 0.14°. It is evident...
from a comparison of the two images that breaking the symmetry by even this tiny amount has a big impact on the structure. The bright vertices are now transformed into “bright rotors”, which are indeed observed experimentally. The similarity between Fig 3(b) and the experimental STM images is striking. Our finding that the rotors arise from a rotation of the top layer relative to the substrate explains why, in a given region, experiments tend to find either all clockwise or all anticlockwise rotors. The honeycomb pattern occurs in a region where \( \Gamma \) is very sensitive to \( \Delta \); we believe this explains why STM images usually show irregular hexagons.

As \( \Gamma \) is lowered, the surface layer densifies further. Figs. 3(c) and (d) show the structures obtained when \( \Delta \rho \) is increased to 4.0% and 6.8% respectively. The honeycomb transforms into a pattern of interlocking wavy triangles. Such structures have been observed on dense terraces of Pt(111). This structure has also been seen for Na/Au(111) and for 3 ML of Cu/Ru(0001). As \( \Gamma \) is lowered and \( \Delta \rho \) increased still further, the wavy domain walls straighten out, resulting in the “bright star” pattern shown in Fig. 3(e), for a value of \( \Delta \rho \approx 10.2\% \). This pattern has not been seen on Pt(111) as it requires a very low \( \Gamma \) (high adatom coverage); however it is seen on other surfaces, e.g., Ni/Ru(0001). \( \Delta \rho_{\text{min}} \) for Pt(111) has a maximum value of 12% (when \( \Gamma = \Gamma_c \)); it is nevertheless instructive to see what happens for larger \( \Delta \rho \). The triangular domains of the bright star transform into hexagons, resulting in the Moiré pattern shown in Fig 3(f). The density distribution on the surface is now almost uniform. This pattern is also observed experimentally, e.g., for 4 ML of Cu/Ru(0001).

The sequence of images shown in Fig. 3 makes it clear that all these structures “morphe” smoothly into one another and are topologically equivalent. Progressively larger values of \( \Delta \rho \) can be favored either by lowering \( \Gamma \) [as for Pt(111)], or by increasing the surface stress – e.g., by depositing more overlayers in a heteroepitaxial system. Indeed, a similar progression of structures with overlayer thickness has been observed for the Cu/Ru(0001) system. Our results show that the same physics is operating in all the systems mentioned above, and it is only slight changes in parameters that are responsible for the various domain patterns observed on different surfaces.

To summarize: we have shown that the unreconstructed Pt(111) surface is only just stable, and can thus be easily induced to reconstruct. We have confirmed that Pt(111) will reconstruct if the chemical potential is lowered by the presence of a large number of adatoms. In addition to the methods tried to date, we suggest that it should also be possible to induce the surface to reconstruct in an electrochemical environment or by depositing alkali metals on it. The domain patterns we obtain for Pt(111) are in excellent agreement with experiment. We have also shown that slight variations in conditions can lead to many of the other domain patterns seen on similar surfaces. We have shown that the periodicity of the reconstruction can be controlled by varying the chemical potential; this is important if one would like to use such surfaces as templates for growing ordered nanostructures.

We thank S. de Gironcoli for providing the Pt ultrasoft pseudopotential, and X. Gonze, I.K. Robinson, H. Brune and U.V. Waghmare for helpful discussions.

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In principle, only the top layer should be compressed; however for commensurate compressions of $2/3$, $3/4$ and $4/5$ we have verified that the two procedures give essentially the same result.