

## Double stripe reconstruction of the Pt(111) surface

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**Abstract.** We have studied the reconstruction of the Pt(111) surface theoretically, using a 2D generalization of the Frenkel–Kontorova model. The parameters in the model are obtained by performing *ab initio* density functional theory calculations. The Pt(111) surface does not reconstruct under normal conditions but experiments have shown that there are two ways to induce the reconstruction: by increasing the temperature, or by depositing adatoms on the surface. The basic motif of this reconstruction is a ‘double stripe’ with an increased surface density and alternating *hcp* and *fcc* domains, arranged to form a honeycomb pattern with a very large repeat distance of 100–300 Å. In this paper, we have studied the ‘double stripe’ reconstruction of the Pt(111) surface. In agreement with experiment, we find that it is favourable for the surface to reconstruct in the presence of adatoms, but not otherwise.

**Keywords.** Surface reconstruction; platinum; density functional calculations; Frenkel–Kontorova model.

### 1. Introduction

Reconstruction is the rearrangement of atoms at a crystal surface to form a structure with a periodicity and/or symmetry different from that of the underlying crystal planes. The reason for this reconstruction is that the surface atoms have fewer neighbours than atoms in the bulk. The question of the arrangement of atoms at platinum surfaces is of special interest because of the industrial importance of Pt as a catalyst, since it is known that the rate of chemical reactions can be very sensitive to the structure of the catalyst surface.

The unreconstructed (111) surface of the face centred cubic (*fcc*) metals is usually stable. However, *ab initio* calculations (Needs *et al* 1991) on the (111) surfaces of aluminium (Al), iridium (Ir), platinum (Pt) and gold (Au) have shown that these surfaces are under tensile stress, i.e. the surface would like to increase its density. Initially, it was thought that the Au(111) surface was the only *fcc*(111) metal surface which underwent a reconstruction (Harten *et al* 1985, and references therein). In 1992, it was found in X-ray scattering experiments (Sandy *et al* 1992; Grübel *et al* 1993) that the Pt(111) surface also reconstructs, but only at temperatures > 1330 K. Below this temperature the unreconstructed phase of the Pt(111) surface is stable. Shortly thereafter, another group (Bott *et al* 1993) reported that the reconstruction of the Pt(111) surface can also be induced at lower temperatures in the presence of a supersaturated Pt gas phase above the Pt(111) surface. They studied this reconstruction by scanning tunneling microscopy (STM).

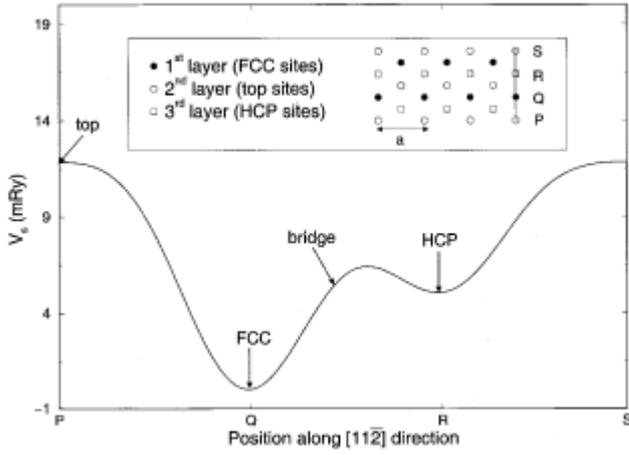
Pt atoms from the supersaturated gas phase get adsorbed on the surface and this collection of adatoms possibly behaves as a particle reservoir, supplying the extra atoms needed in order to increase the surface density.

In our present work, we want to first confirm that the Pt(111) surface will not reconstruct under normal conditions, i.e. when there are no adatoms. Then we want to examine whether the surface will reconstruct if adatoms are available for incorporation in the surface layer.

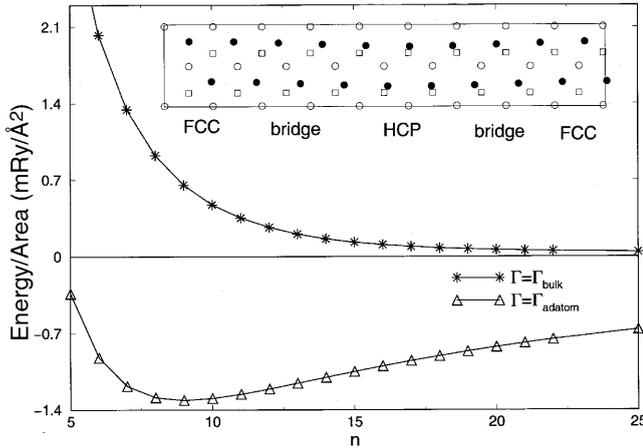
In both sets of experiments mentioned above (Sandy *et al* 1992; Bott *et al* 1993) it has been found that the Pt(111) surface reconstructs into a ‘honeycomb’ structure, with a large unit cell of size 100–300 Å and an increased density of surface atoms. Along the [111] direction of an *fcc* crystal, atoms are arranged in a hexagonal pattern in each layer. Atoms in the topmost layer of the (111) surface can occupy different sites with respect to underlying bulk layers. For example, if the atoms in the topmost layer sit directly above the atoms in the second, third or fourth layers, the surface atoms are said to be occupying the ‘top’, ‘hexagonal close packed’ (*hcp*) and ‘*fcc*’ sites, respectively (as shown in the inset of figure 1). When the surface reconstructs, to make space for the extra atoms (to increase the density), some of the atoms on the surface move from their original *fcc* sites towards the *hcp* sites. In this process, some of the atoms end up sitting at the bridge sites (halfway between *fcc* and *hcp* sites); these atoms will show up as bright spots in STM images as they are raised relative to atoms at *fcc* and *hcp* sites. This structure (shown in the inset of figure 2), composed of *fcc*, *hcp* and bridge domains, is known as the ‘double stripe’.

Similar reconstructions have been found on the Au(111) (Barth *et al* 1990; Huang *et al* 1990), Ag/Pt(111)

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**Figure 1.** The inset shows a top view of the unreconstructed Pt(111) surface. Atoms in the first, second and third layers are shown as filled circles, open circles and open squares, respectively. The top layer is shown occupying *fcc* sites; however in *ab initio* calculations, we slide this layer and put it at *hcp*, bridge (halfway between *fcc* and *hcp* sites) and top sites to calculate the substrate potential,  $V_s$ , as given by (3) along the line PS marked in the inset.



**Figure 2.** Difference in the energy densities of the reconstructed and unreconstructed surfaces as a function of the unit cell length,  $n$ . When we use  $\Gamma = \Gamma_{\text{bulk}}$  (stars), we find that it is unfavourable for the surface to reconstruct; however, when  $\Gamma = \Gamma_{\text{adatom}}$  (triangles), reconstruction is favoured. The inset shows a top view of the unit cell for the reconstructed surface when  $n = 9$ ; atoms in the first, second and third layers are shown as filled circles, open circles and open squares, respectively. *fcc*, *hcp* and bridge domains are marked.

(Bromann *et al* 1997) and Cu/Ru(0001) (Pötschke and Behm 1991; Günther *et al* 1995) surfaces. On Au(111), the double stripes are arranged along two of the three equivalent directions, giving rise to a 'herringbone' structure; however, on Pt(111), all three equivalent orientations of the double stripe are seen, resulting in the

honeycomb shaped superstructure. One reason for the interest in these large scale reconstructions is the possibility of using them as templates for building nanostructures, e.g. in experiments on the growth of Ni, Fe and Co on Au(111) (Chambliss *et al* 1991; Voigtländer *et al* 1991; Tölkes *et al* 1997), Ni, Fe and Co are observed to nucleate at the 'elbows' of the herringbone, resulting in an ordered array of islands.

## 2. Modelling the reconstruction

The very large unit cell of the reconstructed surface makes it impossible to study the reconstruction in a fully *ab initio* calculation; we will, therefore, instead use *ab initio* calculations to parametrize a model that contains all the essential physical features, taking into account all the interactions which favour and oppose the reconstruction. Following previous authors (Takeuchi *et al* 1991; Narasimhan and Vanderbilt 1992; Hamilton *et al* 1999), who performed similar calculations on Au(111) and Ag/Pt(111), we have used a modified two-dimensional (2D) version of the 'Frenkel-Kontorova (F-K) model' (Frenkel and Kontorova 1938). The Hamiltonian is given by

$$H = \sum_i k(l_i - b)^2 + \sum_j V_s(\mathbf{r}_j) + \Gamma N. \quad (1)$$

In this model, nearest neighbour surface atoms (in the topmost layer) interact by a spring potential which is described by the first term in the Hamiltonian, where  $k$  is the spring constant,  $b$  the equilibrium length of the springs and  $l_i$  the length (bond length) of the  $i$ th spring. Because the surface is under tensile stress, the equilibrium length  $b$  of these springs is shorter than the bulk spacing  $a$ , and the springs would like to reduce their length, i.e. the surface layer would like to increase its density. This is the driving force for the reconstruction. However, the surface atoms will create stacking faults if they move from their original *fcc* sites, which will cost energy. Thus the underlying substrate will oppose the reconstruction. So there will be a competition between surface-surface and surface-substrate interactions. The second term in the Hamiltonian is the substrate potential  $V_s(\mathbf{r}_j)$ , where  $\mathbf{r}_j$  is the position of the  $j$ th atom. To increase the density of the surface, we will have to supply extra atoms to the surface, which will also cost energy. This is described by the third term in the Hamiltonian.  $\Gamma$  is analogous to a chemical potential; it is discussed in greater detail in §5 below.

There has been a previous theoretical study of the Pt(111) reconstruction by Mansfield and Needs (1990) who map the 2D surface problem to one dimension along the unfolded zig zag path which connects adjacent *fcc* and *hcp* sites. They assume that the *fcc* and *hcp* sites are

degenerate in energy, and hence they use a sine potential as the substrate potential. They also assume that the force constant,  $k$ , for surface bonds is the same as the force constant for bulk bonds, which they obtain from the value of the bulk modulus. While they correctly predict that Pt(111) will not reconstruct under normal conditions, they also predict that the Au(111) surface does not reconstruct, whereas the reconstruction of the Au(111) surface is well known experimentally and theoretically.

In the calculations presented in this paper, we will retain the full 2D nature of the problem, allow *fcc* and *hcp* sites to have different values of  $V_s$ , and use a value for  $k$  that is appropriate for surface bonds. For these reasons, we believe that our calculations are more realistic than those of Mansfield and Needs.

### 3. *Ab initio* total energy and stress calculations

The *ab initio* calculations are performed using the ‘pwsfc’ package (Baroni *et al* 2001). We solve the Kohn–Sham equations (Kohn and Sham 1965) in a plane wave basis set with a 20 Ry cut off, using an ultrasoft pseudo-potential (Vanderbilt 1990) and the local density approximation (LDA) (Perdew and Zunger 1981) for the exchange–correlation interaction.

To check the possibility of surface reconstruction under different conditions, we have performed a series of calculations on bulk Pt, a Pt slab with (111) surfaces, and a slab with an adatom adsorbed at an *fcc* site. The bulk calculations are performed using 100  $\mathbf{k}$  points in the irreducible Brillouin zone (IBZ) in evaluating Brillouin zone sums. From these bulk calculations, we get the lattice constant,  $a_0$ , as 3.91 Å and the cohesive energy,  $E_c$ , as 543 mRy. The experimental lattice constant and cohesive energy are 3.92 Å and 429 mRy, respectively (Kittel 1976). The discrepancy between the experimental and calculated values of  $E_c$  is presumably due to overbinding of the LDA approximation used in our calculations.

In the surface calculations, we use a slab supercell containing 9 atomic layers and 6 layers of vacuum. 27  $\mathbf{k}$  points are used in the IBZ. We allow the three outermost layers on both sides of the slab to relax. In agreement with experiment (Adams *et al* 1979; van der Veen *et al* 1979; Davies *et al* 1980; Feder *et al* 1981; Hayek *et al* 1985; Ogletree *et al* 1986; Materer *et al* 1995), we find that there is a small expansion of the first interlayer spacing ( $d_{12}$ ) and a small contraction of the second interlayer spacing ( $d_{23}$ ) with respect to the bulk spacing. A summary of the values of  $d_{12}$  and  $d_{23}$  obtained by various techniques is given in table 1.

We obtain the surface stress,  $\mathbf{s}$  as 29.4 mRy/Å<sup>2</sup> and surface energy,  $\gamma$ , as 9.13 mRy/Å<sup>2</sup>. In table 2, we compare our results with those of previous authors; our values of  $\mathbf{s}$  and  $\mathbf{g}$  are in good agreement with those obtained in earlier experiments and *ab initio* calculations. We find

**Table 1.** Percentage change in the first and second interlayer spacing ( $d_{12}$  and  $d_{23}$ , respectively) of the Pt(111) surface, from experiments (\*) and from *ab initio* calculations (†).

	$\Delta d_{12}$ (%)	$\Delta d_{23}$ (%)
Present(†)	0.29	−0.55
Adams <i>et al</i> (1979) (*)	1.1 ± 4.4	
van der Veen <i>et al</i> (1979)(*)	1.4 ± 1.0	
Davies <i>et al</i> (1980) (*)	0.0 ± 0.4	
Feder <i>et al</i> (1981) (*)	0.5 ± 0.1	
Hayek <i>et al</i> (1985) (*)	0.0 ± 2.5	
Ogletree <i>et al</i> (1986) (*)	0.0 ± 1.1	−1.1 ± 1.1
Materer <i>et al</i> (1995) (*)	1.1 ± 0.4	0.0 ± 1.3
Feibelman (1997) (†)	0.44	−0.31
Boisvert <i>et al</i> (1998) (†)	0.4	−0.2

**Table 2.** The results of *ab initio* calculations (a)–(d) and experiments (e) for the lattice constant ( $a$ ), surface energy ( $\mathbf{g}$ ) and surface stress ( $\mathbf{s}$ ).

	$a_0$ (Å)	$\mathbf{g}$ (mRy/Å)	$\mathbf{s}$ (mRy/Å)
(a) Present	3.91	9.13	29.4
(b) Needs and Mansfield (1989)	3.86	10.07	25.7
(c) Feibelman (1997)	3.89	10.07	28.8
(d) Boisvert <i>et al</i> (1998)	3.92	9.12	27.5
(e) Miedema (1978)	3.92	11.69	–

that our value of  $\mathbf{s}$  is closer to that of Feibelman (1997); whereas our value for  $\mathbf{g}$  agrees better with that of Boisvert *et al* (1998). Both these previous calculations have also made use of the LDA, in the form given by Ceperley and Alder (1980).

To calculate the adatom adsorption energy,  $E_a$ , we use a slab containing 5 atomic layers with 9 atoms per layer. An adatom is adsorbed at an *fcc* site on this slab and the coordinates of the adatom and all atoms in the top two layers of the slab are allowed to relax. We take 9  $\mathbf{k}$  points in the IBZ. We obtain  $E_a$  as 426 mRy. This is somewhat larger than the value of 393 mRy obtained by Feibelman *et al* (1994) in an earlier *ab initio* calculation, and still larger than the value of 353 mRy calculated by Jacobsen *et al* (1994), who used potentials derived from effective medium theory (EMT).

The potential from bulk atoms will have the periodicity and symmetry of the unreconstructed surface. Therefore, the substrate potential can be expanded in a Fourier series

$$V_s(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}, \quad (2)$$

where the  $\mathbf{G}$ s are reciprocal lattice vectors and  $V_{\mathbf{G}}$ s are the Fourier coefficients.  $\mathbf{r} = (x, y)$  is the position of an atom in the surface layer. In order to determine the  $V_{\mathbf{G}}$ s,

we calculate the substrate potential at *fcc*, *hcp*, bridge and top sites from *ab initio* calculations, in which we compute the change in the total energy of the slab when the atoms of the outermost layer occupy *hcp*, *fcc*, bridge and top sites instead of *fcc* sites. We find that it suffices to retain the first three shells of **Gs**; the substrate potential is then given by

$$\begin{aligned}
 V_s(x, y) = & \frac{3V_B + V_T}{4} - \left( \frac{V_A - 2V_T + V_C}{9} \right) \\
 & \left\{ \cos \left[ \frac{4\mathbf{p}}{\sqrt{3}a} y \right] + \cos \left[ \frac{2\mathbf{p}}{a} \left( x + \frac{y}{\sqrt{3}} \right) \right] + \cos \left[ \frac{2\mathbf{p}}{a} \left( x - \frac{y}{\sqrt{3}} \right) \right] \right\} \\
 & + \left( \frac{V_A + V_C + V_T - V_B}{9} - \frac{V_B}{4} \right) \left\{ \cos \left[ \frac{4\mathbf{p}}{a} x \right] + \cos \left[ \frac{2\mathbf{p}}{a} (x + \sqrt{3}y) \right] \right. \\
 & \left. + \cos \left[ \frac{2\mathbf{p}}{a} (x - \sqrt{3}y) \right] \right\} + \left( \frac{V_C + V_A}{3\sqrt{3}} \right) \\
 & \left\{ \sin \left[ \frac{2\mathbf{p}}{a} \left( x + \frac{y}{\sqrt{3}} \right) \right] - \sin \left[ \frac{4\mathbf{p}}{\sqrt{3}a} y \right] - \sin \left[ \frac{2\mathbf{p}}{a} \left( x - \frac{y}{\sqrt{3}} \right) \right] \right\},
 \end{aligned} \tag{3}$$

where  $V_A$ ,  $V_B$ ,  $V_C$  and  $V_T$  are the values of the substrate potential at *hcp*, bridge, *fcc* and top sites, respectively and  $a$  the bulk nearest neighbour distance ( $a = \frac{a_0}{\sqrt{2}}$ ). Our results for the substrate potential are plotted in figure 1 for a cut along the [112] direction. Note that the energy difference between *fcc* and *hcp* sites is 5 mRy, suggesting that the assumption of the degeneracy of *fcc* and *hcp* sites made by previous authors (Mansfield and Needs 1990) may lead to errors. In the case of Au(111), the *fcc* and *hcp* energy difference is 1 mRy (Takeuchi *et al* 1991). Hence a stacking fault costs more energy for Pt(111) than Au(111); this is partly why Au(111) reconstructs under normal conditions whereas Pt(111) does not.

#### 4. Values of $k$ and $b$

The force constant,  $k$ , that appears in (1) is the harmonic coefficient when the surface–surface potential is expanded about the equilibrium length,  $b$ . However, we do not know  $b$  *a priori*. In order to simultaneously determine  $k$  and  $b$ , we will make use of two relations coupling them. One is the expression for the surface stress as given by our model,

$$\mathbf{s} = \sqrt{3}k(1 - b/a), \tag{4}$$

the values,  $a$  and  $\mathbf{s}$  are known to us from *ab initio* calculations, as described in §3. The other expression is the empirical Badger's rule (Badger 1934):

$$k = \mathbf{b} \left( \frac{a}{b} \right)^a, \tag{5}$$

where  $\mathbf{b}$  is the surface force constant when the surface atoms are at the bulk spacing,  $a$ . We obtain  $\mathbf{b}$  from density functional perturbation theory calculations (Baroni *et al* 1987) on the unreconstructed surface, where we calculate the dynamical matrix for a 7-layer slab on a  $4 \times 4 \times 1$  grid of wavevectors in the Brillouin zone; we obtain  $\mathbf{b}$  as 183 mRy/Å<sup>2</sup>. We have also verified in these calculations that next-nearest-neighbour interactions are negligible.

Solving (3) and (4) simultaneously, we obtain  $k$  and  $b$  as 294 mRy/Å<sup>2</sup> and 2.608 Å, respectively. For  $\mathbf{a}$  we use the experimentally reported value of (Zeppenfeld 1989) 8.

It should be noted that the way in which we have obtained the surface–surface potential is different from that of earlier authors (Takeuchi *et al* 1991; Hamilton *et al* 1999).

#### 5. Chemical potential, $\Gamma$

The chemical potential,  $\Gamma$ , that appears in (1) can be regarded as the difference between two energies,  $E_1$  and  $E_2$ , where  $E_1$  is the energy required to take an atom from the particle reservoir to infinity, and  $E_2$  the energy to bring an atom from infinity and put it in the surface. Note that  $E_1$  depends upon the nature of the particle reservoir. When the particle reservoir consists of bulk atoms, i.e. when the extra atoms come from the bulk, the chemical potential is  $\Gamma_{\text{bulk}} = E_c - E_2$ , where  $E_c$  is the cohesive energy of bulk Pt. To calculate  $\Gamma_{\text{bulk}}$ , we will equate the surface energy,  $\mathbf{g}$  of the unreconstructed surface from the F–K model Hamiltonian,

$$\mathbf{g} = \frac{3k(a-b)^2 + 2\Gamma_{\text{bulk}}}{\sqrt{3}a^2}, \tag{6}$$

to the  $\mathbf{g}$  obtained from *ab initio* calculations.

When the particle reservoir consists of adatoms, the chemical potential will instead be  $\Gamma_{\text{adatom}} = E_a - E_2$ , where  $E_a$  is the adatom adsorption energy. Upon substituting the values from our *ab initio* calculations for  $E_a$ ,  $E_c$  and  $\mathbf{g}$  we get  $\Gamma_{\text{adatom}}$  and  $\Gamma_{\text{bulk}}$  as –68 mRy and 49 mRy, respectively.

#### 6. Reconstruction

Now that we have obtained all the parameters for the F–K model Hamiltonian, we can check whether or not

the surface will reconstruct into a double stripe (the basic motif of the overall honeycomb reconstruction) under various conditions. To do this, we consider a unit cell of length  $na$  along the  $[1\bar{1}0]$  direction and  $\sqrt{3}a$  along the  $[11\bar{2}]$  direction. If the surface were unreconstructed, this cell would contain  $2n$  surface atoms; however, we instead put in  $2n+2$  surface atoms, i.e. the reconstructed surface has a density that is increased by  $(2n+2)/2n$ . In order to find the optimal surface density, we will minimize the energy per unit area as obtained from (1) with respect to  $n$ . The positions of the surface atoms within the unit cell are optimized by using a steepest descent algorithm and the Hamiltonian of (1). The inset of figure 2 shows a unit cell of the reconstructed surface for  $n=9$ . Note that if the surface does not reconstruct, for all values of  $n$ , the surface energy density will be higher than that of the unreconstructed surface.

Our results for the relative energies of the reconstructed and unreconstructed surfaces are plotted in figure 2. In agreement with the prediction of Mansfield and Needs (1990) and observation in experiments (Sandy *et al* 1992; Bott *et al* 1993), we find that when atoms from the bulk are removed and incorporated into the surface, the surface does not reconstruct, i.e. the surface energy density is higher than that of the unreconstructed surface for all values of  $n$  (stars in figure 2). In contrast, we find that when the particle reservoir instead consists of adatoms, the surface energy density goes below that of the unreconstructed surface, reaching its minimum value for  $n=9$ , for the double stripe reconstruction (triangles in figure 2). This value of  $n$  is less than the experimental value of  $n \approx 40$  (Hohage *et al* 1995) found for the honeycomb structure. In the honeycomb, the compression is divided amongst three equivalent directions; hence the compression along any one direction will be less (and  $n$  will be larger) than for the double stripe, where the compression is uniaxial. Upon partitioning the unit cell into *fcc* and *hcp* domains, we find that 70% of the atoms sit in the *fcc* domain, which is in excellent agreement with the value of 65% found in STM experiments (Hohage *et al* 1995).

Our result that the surface will reconstruct in the presence of adatoms but not otherwise is reasonably robust; for example, replacing the calculated value of  $E_c$  by the experimental value does not change our conclusions. The only empirical parameter we have used is the value of 8 for the power  $a$  in (5); however, our results are not very sensitive to this choice. We have checked that our conclusions remain unaltered for values of  $a$  between 0 and 30.

There is a previous calculation (Jacobsen *et al* 1994) where the Pt(111) reconstruction was studied using potentials obtained from effective medium theory. Though they are primarily interested in the nucleation of the reconstruction in the form of three-legged 'dark stars', they also present data on the double stripe for the single

case,  $n=50$ . They find that incorporation of an adatom into the surface layer is favoured by 7 mRy; in comparison, the corresponding value obtained by us is 63 mRy (for  $n=9$ ). We believe that some (but not all) of this discrepancy may be due to overbinding by the LDA and the relatively small cell sizes used in our adatom calculations.

In future work, we plan to extend this study to the full honeycomb reconstruction.

## 7. Conclusions

We have studied the double stripe reconstruction of the Pt(111) surface, using a 2D generalization of the Frenkel–Kontorova model, with parameters obtained from *ab initio* calculations. We have found that when extra atoms come from the bulk, the surface does not reconstruct i.e. the energy to remove an atom from the bulk is higher than the energy released upon putting the atom in the surface. Therefore the surface does not prefer the reconstruction under 'normal conditions'. However, in agreement with experiment, we find that when a reservoir of adatoms is available for the surface to increase its density, the surface reconstructs.

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