Islands, craters, and a moving surface step on a hexagonally reconstructed (100) noble metal surface

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Abstract

Deposition/removal of metal atoms on the hex reconstructed (100) surface of Au, Pt and Ir should present intriguing aspects, since a new island implies hex \rightarrow square deconstruction of the substrate, and a new crater the square \rightarrow hex reconstruction of the uncovered layer. To obtain a microscopic understanding of how islands/craters form in these conditions, we have conducted simulations of island and crater growth on Au(100), whose atomistic behavior, including the hex reconstruction on top of the square substrate, is well described by means of classical many-body forces. By increasing/decreasing the Au coverage on Au(100), we find that island/craters will not grow unless they exceed a critical size of about 8-10 atoms. This value is close to that which explains the nonlinear coverage dependence observed in molecular adsorption on the closely related surface Pt (100). This threshold size is rationalized in terms of a transverse step correlation length, measuring the spatial extent where reconstruction of a given plane is disturbed by the nearby step. \textit{Keywords}: Molecular dynamics; Gold; Surface structure, morphology, roughness, and topography; Low index single crystal surfaces; Vicinal single crystal surfaces; Surface relaxation and reconstruction; Growth.
I. INTRODUCTION

The heavy noble metal (100) surfaces possess the so-called hex-reconstruction, where the top monolayer spontaneously converts from square to (approximately) hexagonal (in fact, triangular), with a lateral density increase of 25 – 30% \cite{1}. The second atomic layer, immediately below the first, remains instead square, with a bulk-like lateral density, and only a minor local perturbation in correspondence of the domain walls, or solitons, which the hex layer forms by (incommensurate) epitaxy onto it.

Let us imagine the flat, hex-reconstructed (100) surface and consider what should happen if we were to ideally deposit one further monolayer on top of it. The new top monolayer should be itself hex-reconstructed, because that is the lowest energy configuration for this surface. However the former top layer, now covered and turned into a second layer, must deconstruct, from the hex state back to a square lattice. Conversely, we may imagine removing the top monolayer. The former, unreconstructed second layer must now acquire some extra atoms, in order to become hex-reconstructed, again because that is the lowest energy state.

The questions now are: how exactly should all this happen? Where do the excess atoms, expelled from the covered layer, go? Conversely, where do the extra atoms needed for top layer reconstruction come from? And what other consequences does this peculiar situation have? A related problem which provided some inspiration for this work is that of the surprising nonlinearity observed, mainly by King \textit{et al.} \cite{2} in surface adsorption of molecules (CO, O\textsubscript{2}, D\textsubscript{2}) versus coverage, on a hex reconstructed Pt (100) substrate.

In this paper we describe work which lays the ground for addressing some of these questions.

We carried out Molecular Dynamics (MD) simulation work addressing specifically the hex-reconstructed Au (100). The temperature dependence of the top layer density allows us to study phenomena associated with density changes by simply changing the sample temperature in a particle-conserving system: upon increasing temperature lateral density of a flat reconstructed Au (100) surface shows a tendency to increase. We find in our
simulations \[3\] an increase from the \( T = 0 \) lateral density of 1.24 with respect to the bulk, to 1.35 for \( T = 1100 \text{K} \). This behavior is in close agreement with experiment for both Au and Pt \[1\]. Thus, heating is equivalent to removing atoms, cooling to adding atoms.

The work done so far includes the following:

- interplay of step and hex reconstruction, showing their important mutual influence;
- sudden formation of a small adsorbed island (spontaneously expelled by heating) with accompanying deconstruction of the covered portion;
- sudden formation of a small crater (spontaneously formed by cooling) with accompanying reconstruction of the uncovered substrate portion;
- sudden step retraction (obtained by heating) with reconstruction of the uncovered substrate portion, via “incorporation” of step edge atoms.

In the following, we shall briefly summarize some of our results, leaving a more proper and detailed account for a separate publication.

**II. METHOD**

The hexagonal reconstruction of Au, Pt and Ir(100) consists of a spontaneously stabilized 2D close-packed monolayer on top of the otherwise (100) crystal. This phenomenon is reasonably well understood, but quite hard to handle at the electronic level \[4\]. We found quite some time ago that it was possible to reproduce it with quantitative accuracy for Au(100) \[5\], using classical potentials of the many-body type, the glue \[4\] potentials, very specially and carefully optimized for Au. Within that approximation, it is possible to carry out extensive simulations of some of the the situations imagined above, and obtain from them a microscopic insight into those otherwise puzzling questions.

With the glue potential for gold, we carried out classical MD simulation. Newton’s equations were integrated numerically, allowing for large length-scales (at least 50 Å lateral
size) and long simulation times, (at least 1 nsec), working at sufficiently high temperature so as to attain sufficient atom mobilities.

The geometry chosen for simulating our surfaces is an N-layer (001) slab, (N=12-16) with periodic boundary conditions (PBC) along the (100) and (010) directions. The top (001) surface was free, whereas the bottom one consisted of 3 frozen bulk-like layers. The typical total atom number ranged from 20000 to 30000 \(^1\).

In order to simulate a surface with a single step, we generated new suitable PBCs which transform an A layer into a B layer (within an ABAB.. (100) stacking sequence) when crossing the slab boundary in the direction orthogonal to the step. This artifact allows the study of an isolated step which interacts only with its repeated image, and the terrace size remains constant during the system evolution.

Temperature was controlled, and the system was carefully and gradually heated through velocity rescaling. Mobility of surface atoms became non-negligible for \( T > 1000K \) (well below melting, \( T_m = 1336K \) for Au).

The simulation of atom addition and removal represents a difficult task in the canonical ensemble. Working fully canonically, i.e., conserving particles, we were able to obtain a similar outcome by exploiting a peculiar feature of the (100) hex reconstructed surface, namely the fact that its lateral density increases with temperature, notably by about 5\% from 700 to 1000 K. \(^4\)

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\(^1\) The free (001) surface of Au is generally reconstructed, with a periodicity which depends on temperature, and is generally incommensurate \(^7\). Our cell can only accommodate a commensurate periodicity (at least in the absence of steps) and we choose that to be \((5 \times 1)\), or \((5 \times 25)\), rather close to the actual one, \((5 \times 34)\). We do not expect these small deviations to be very important. An additional aspect is that of rotations of the reconstructed overlayer. The experimental rotational angle is given as 0.84° \(^8\), jumping to zero at 1000K. Rotations are basically incompatible with periodic boundary conditions, and have been neglected.
When a step is present, as is the case here, it will retract upon heating to accommodate for this top layer density increase. The net movement of the step in fact provides in this way for us a very natural method to gauge the optimal spontaneous change of surface lateral density. Moreover, we can observe how the lateral density varies locally, depending on the planar coordinate relative to the step position.

If we consider now a flat, step-free surface, and we heat it up suddenly, the associated increase of optimal lateral hex layer density will induce a strong tensile surface stress, which cannot be relieved in the absence of a defect. If that stress overcomes a certain critical limit, we can expect the sudden formation of one or more craters, leading to a state quite similar to that which we could have obtained by removing atoms at fixed temperature. Conversely, sudden cooling should lead to compressive stress, and eventually islands of excess atoms will pop up to relieve that stress.

This method is completely ad hoc for our situation, and it can only work in practice if the hex layer is relatively free to slide parallel to itself. Luckily, we found that this is the case for gold in the temperature range 800-1000K used here.

An alternative, and certainly more standard way to add or remove atoms in order to study island or crater formation would be Grand Canonical Monte Carlo (GCMC). Although we did succeed in implementing it for certain Au surfaces, we eventually found the MD technique described above more useful for the present purposes. GCMC is in the first place very difficult to equilibrate, and moreover it does not provide as much desirable information on the dynamics, as MD does.

Conversely, GCMC can be of great help in all cases where a strong density change (like in the square→hex transformation) must be handled. We will demonstrate how that works for Au (100) in a forthcoming paper [8].
III. A STEP ON THE HEX Au (100) SURFACE

We simulated a (100,1,1) vicinal surface of Au (100), with a single step and a wide terrace (maximum terrace size was $50 \times 50$ nearest neighbor distances). Fig. 1 (upper part) shows the side view of the surface with a step.

The atoms of the second layer are marked in white; we note that the part of the second layer covered by the terrace is unreconstructed (A) whereas the (B) part is reconstructed. If we follow the lateral density of the second layer from A to B, we will cross a transition zone in correspondence with the step. The width of this zone marks the surface correlation length as probed by the step, and can be extracted from MD simulations, and the result for the temperature of $T = 900K$ are shown in Fig. 1 (lower part). The correlation length is roughly $5 \, \text{Å}$ at $900K$ and increases to $10 \, \text{Å}$ at $1250K$ (not shown). This result gives a measure of the influence of the step on the lateral coordination in its neighborhood, and reveals an interesting interplay between step and reconstruction.

IV. ISLAND FORMATION

The reconstructed (100) surface of noble metals undergoes an order $\rightarrow$ disorder transition at about $T = 0.8T_m$. Low temperature deconstruction can, however, be induced upon adsorption of molecular species. The Cambridge group [2] has carried out thorough studies of adsorption of light molecules such as CO, D$_2$ and O$_2$ onto a fully reconstructed Pt (100) surface. They found that molecular island form, but that the growth rate of the islands increases extremely slowly at low concentrations, roughly like the fourth power of molecular coverage (we shall call this King’s law). The explanation offered for this phenomenon is that while the hex-reconstructed surface is unreactive, and will bind the molecules, the opposite is true for the deconstructed, square (100) surface. The latter however must nucleate (under the island), and this requires a finite island size, of no less than 4 ad-molecules.

It should be noted that King’s exponent of about 4 implies that about 8 Pt atoms must
switch from hex to square for the adsorption process to grow. Hence King’s law is most likely telling us a property of the clean surface. This is confirmed by the circumstance that the exponent is not very dependent on the adsorbed species. The next observation is that very much the same deconstruction must take place with homoepitaxy. Hence we expect that upon deposition of Pt on Pt(100), or on Au(100), particularly at high temperatures when equilibrium can be established, there should be a minimum critical island size, of order 8 or so atoms, related to deconstruction of the substrate.

We mimicked homogeneous atoms addition/removal through the already mentioned temperature jump technique. An alternative method was to prepare the system with a certain surface excess density, and to wait for the excess atoms to form an island. In both cases, the island/crater growth was mainly determined by the density difference between square and hexagonal phase and not by the initial conditions of the simulation; the dynamics can be therefore trusted as true island/crater growth dynamics, whatever the method used to determine lateral density excess/deficit.

In this section we will focus on island formation case, adding atoms at a temperature of 1200\(K\) in order to have sufficient mobility of surface atoms.

An initial excess density of 0.06 \(\rho_b\) (\(\rho_b\) being the lateral density of a bulk (100) layer) at the surface causes the appearance of small fluctuating islands. However these islands are readsobered quickly by the substrate so long as their size is smaller than about 10 atoms. If the size is greater than 10-15 atoms, however, the island is not readsobered and begins to grow. Figure 2(a) shows the time evolution of the maximum island size on the surface; there is clearly a critical size above which the island size grows.

Our explanation for this critical size is the following: as long as the island is small, there is no deconstruction under it. In other words if the border of the island has the same role of the single step described in the previous section, the island size is too small. No deconstruction occurs until the diameter of the island is greater than the surface correlation length as felt by the step. When the size of the island exceeds this value, only then the substrate can deconstruct and growth can continue, now fueled by the excess atoms ejected by the lower
layer. These atoms correspond to the density difference between hexagonal and square order under the island, and they make the island growth very fast. The deconstruction is almost completed when the island has a size of about 25-30 atoms, as shown in a snapshot of the simulation (t=175 ps), shown in Figure 3.

V. CRATER FORMATION

A symmetric situation with respect to the last section is the formation of craters on a flat surface. We used temperature as the driving force for the density change at the surface, by increasing temperature from 800 to $T = 950K$. At this temperature, surface atom mobility is sufficiently high. The main results concerning craters are the following:

- The formation of craters requires a slightly smaller nucleus with a critical size $N_H$ of about 8–10 atoms. Figure 2(b) shows this behaviour; the size (in atoms) of a crater is plotted versus the simulation time. At a size of about 8, a jump occurs and the crater growth subsequently continues linearly, up to saturation. This jump is associated with reconstruction of the crater bottom.

- The mechanism for further growth of the craters with $N > N_H$ is the following: atoms in the hole, initially arranged in a square lattice, are undercoordinated; atoms at the boundary of the crater are “eaten up” increasing the dimension of the hole. The growth is less dramatic than that of the island.

Summarizing, there appears to be a connection between the critical nucleus for growth of craters and of islands and the reconstruction correlation length as probed by a step on a surface. We can infer from the two situations we have examined (the crater and the island) that reconstruction and deconstruction play a crucial role in determining their onset. The size of the critical nucleus predicted for Au (100) is of 8-10 atoms, in remarkably close agreement with the 8-atom size which can be extracted by King’s exponent of 4 for molecular adsorption on Pt (100)
VI. DISCUSSION

We have found that reconstruction/deconstruction introduces a natural critical size for the nucleation of islands and craters of Au on Au (100). This size does not show the normal dependence upon supersaturation, expected of normal nucleation processes, and appears more as an intrinsic characteristics of that surface. The reason can be as follows. The nucleation free energy barrier as a function of increasing size has a nonstandard shape, with a large, sudden drop around \( \simeq 15 \) atoms, when substrate reconstruction/deconstruction can occur. That drop has the effect of *pinning* the critical size, making it independent of supersaturation and, possibly, also of the adsorbed species. Figure 4 shows a very schematic representation of this point in the crater case. For small craters, the bottom of the crater is not reconstructed. At the radius of about 6 Angstrom, deconstruction can occur and a jump in the free energy is observed; by changing the supersaturation, the jump position (which depends only on the interplay between step and reconstruction), does not change.

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FIGURE CAPTIONS

- Figure 1. Upper part: side view of a surface with a single step. The second layer atoms are drawn in white. (A) denotes the part of the second layer which lies under the terrace and is unreconstructed, (B) denotes the uncovered reconstructed terrace. Lower part: profile of the lateral density in the “second layer” for \( T = 900K \). The layer has a square structure to the left, where it is covered by a terrace, and a dense hexagonal structure to the right. The interface between the two zones is smoothened.
by the presence of a finite correlation length of the step. At $T = 1200K$ (not shown) the profile is smoother, and the correlation length larger.

- Figure 2. (a): the maximum island size for an excess density of about 0.06. There is a jump in the island size and a growth up to a saturation value of about 38 atoms, corresponding to the initial excess density. The arrow indicates the onset of deconstruction of the substrate under the island. This deconstruction is completed at a size of about 20. (b): the crater formation case; time evolution of a crater size. Please note the jump at a critical value for the size.

- Figure 3. (color) Snapshot of the island growth simulation after 175 $ps$. Red atoms are adatoms. The view from the bottom shows the almost complete deconstruction under the red island, bigger than the critical size.

- Figure 4. Schematic profile of Gibbs free energy (at different chemical potential) upon formation of a crater of radius $r$. The jump occurs at the crater reconstruction, and does not depend on sovrasaturation.
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