

## AN ALTERNATIVE MODEL OF THE RECONSTRUCTED (100) SURFACES OF GOLD, PLATINUM AND IRIIDIUM

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Gold, platinum and iridium (100) clean surfaces are reconstructed, the widely accepted model of the reconstruction is that the top layer is a slightly compressed hexagonal (111) plane. The aim of this paper is to show that there is an alternative model to explain the reconstruction that requires very little displacement of the surface atoms. No proof can be given of either model, but both of them should be used in LEED intensity calculations.

### 1. Introduction

Since the discovery of the reconstruction of the (100) surfaces of gold [1–3], platinum [4–6] and iridium [7], several models have been proposed for explaining the  $(5 \times 20)$ ,  $(5 \times 14)$  or  $(5 \times 1)$  observed superstructures. The more universally accepted one consists of an hexagonal arrangement of the surface atoms [3], as shown on fig. 1a. Another model has been proposed by Burton and Jura [8], but has had little echo in the scientific community. They suppose that two out

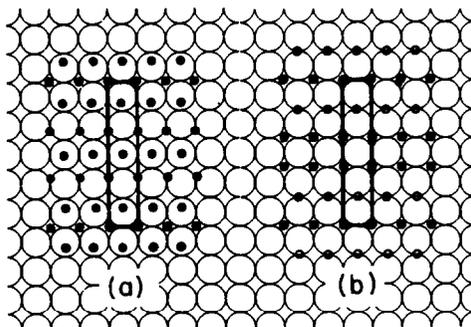


Fig. 1. Large open circles represent the iridium atoms of the second layer, and small circles the surface atoms: (a) hexagonal model; (b) "shifted row model" without relaxation.

of five rows of surface atoms are shifted by half an atomic distance so that these atoms sit in bridge sites instead of the regular four fold symmetry sites as described on fig. 1b. The purpose of this paper is to show that this "shifted row model" with little modifications can be an alternative solution for the reconstruction of the (100) surfaces of gold, platinum and iridium and should be compared to the hexagonal model in future LEED intensity calculations.

## 2. The model

The (100) surfaces of gold and platinum exhibit a so called  $(5 \times 20)$  and  $(5 \times 14)$  structure while the (100) surface of iridium shows an exact  $(5 \times 1)$  superstructure. In this section we limit ourselves to the case of iridium and leave the discussion about gold and platinum for section 4.

In order to understand this model, we analyse the problem of the reconstruction in a way similar to the adsorption of a metal on the surface of another metal: we suppose that the  $(5 \times 1)$  structure is due to the adsorption of a monolayer of iridium on a non-reconstructed (100) surface of iridium.

Several cases of adsorption of metals on (100) surfaces of fcc metals exhibit at the completion of the monolayer a  $c(n \times 2)$  type superstructure:  $c(4 \times 2)$  for bis-

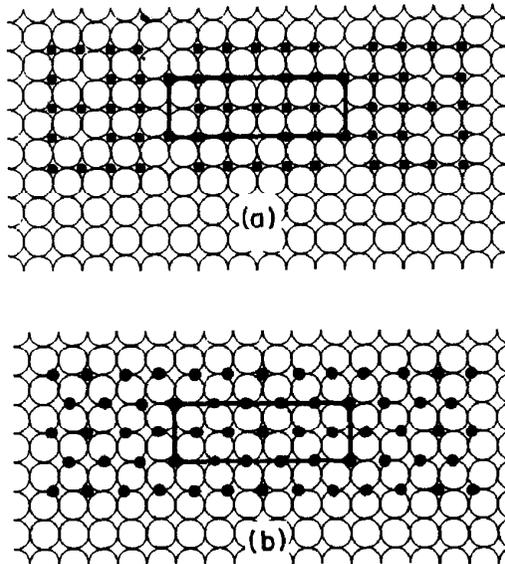


Fig. 2.  $c(6 \times 2)$  structure obtained when lead (small circles) is deposited on a gold (100) surface (large circles): (a) model without relaxation; (b) model with relaxation forming a pseudo-hexagonal layer of lead.

Table 1

Parameters of the pseudo-hexagonal unit cell of the adsorbate for a  $c(n \times 2)$  structure for various values of  $n$

$n$	$a$	$b$	$\gamma$ (deg)
2	2	1.414	45
4	1.333	1.2	56.3
6	1.2	1.666	59.0
8	1.142	1.152	60.3
10	1.111	1.143	60.9
12	1.091	1.139	61.4
14	1.076	1.136	61.7
16	1.067	1.133	61.9
$\infty$	1	1.118	63.4

muth on gold (100) [9],  $c(6 \times 2)$  for lead on gold (100) [10–13],  $c(10 \times 2)$  for silver on copper (100) [14] and  $c(14 \times 2)$  for gold on copper (100) [14]. On fig. 2a is represented a possible high symmetry model for the  $c(6 \times 2)$  structure with the lead atoms in the four fold symmetry sites having the  $c2mm$  symmetry. On fig. 2b, the lead atoms have been relaxed in such a way that the  $c2mm$  symmetry is respected, to take into account the ratio between the diameters of the lead and gold atoms [11,12]. This later model is also pseudo-hexagonal. Similar models can be proposed for all the values of  $n$ .

Table 1 summarizes the values of  $a$ ,  $b$  and  $\gamma$ , the parameters of the pseudo-hexagonal unit cell as a function of  $n$  obtained assuming a uniform distribution of the adatoms, and no buckling of the monolayer. This model of the  $c(n \times 2)$  structures indicates that as the diameter of the adsorbate atoms becomes closer to the diameter of the substrate atoms,  $n$  becomes larger. Fig. 3a shows the model associated with the structure  $c(\infty \times 2)$  which is actually also a  $p(1 \times 2)$  structure.

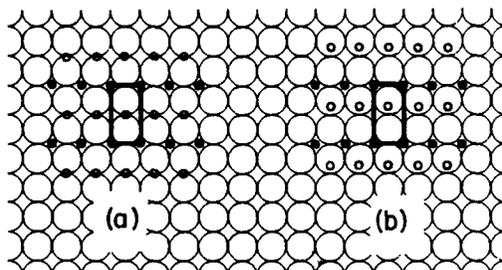


Fig. 3. When  $n$  is infinite, the  $c(n \times 2)$  structure is a  $p(1 \times 2)$  structure: (a) without relaxation, (b) with relaxation. The small full circles represent the adatoms in the four fold symmetry sites, and the small open circles the adatoms out of site.

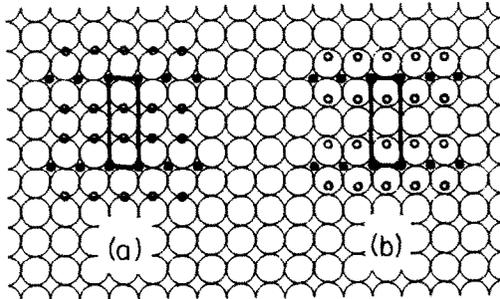


Fig. 4.  $p(1 \times 3)$  structure: (a) without relaxation, (b) with relaxation.

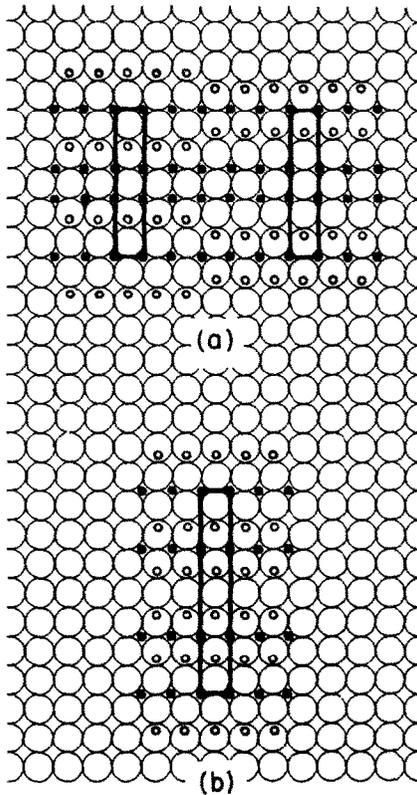


Fig. 5. (a) "Shifted row model" for the  $(5 \times 1)$  structure with two possible relaxations; (b) a similar model for the  $(7 \times 1)$  structure.

Along with the interpretation of the  $(5 \times 1)$  structure, Burton and Jura [8] proposed this model to interpret the  $p(1 \times 2)$  structure. The main problem associated with this model is that the atoms of one row every two are on bridge sites which are unstable. As a matter of fact, Annett et al. [15] have shown that such a structure is unstable based on lattice-dynamics calculations. They show that at long wavelengths the rearranged atoms move back to their unrearranged positions, i.e. in the four fold symmetry sites. The contribution of this paper is to suggest that, in fact, the atoms situated on the bridge sites have a tendency to move towards the unshifted atoms and to sit in the three fold symmetry sites formed by two adjacent atoms of the unshifted row and the atoms situated in the first layer beneath the surface as shown on fig. 3b. The model of fig. 3a has the symmetry  $pmm$ , while the model of fig. 3b has the lower symmetry  $pm$ . Burton and Jura [8] proposed this  $p(1 \times 2)$  reconstruction to explain structures observed during adsorption but so far there is no reconstruction of the (100) surface of this type.

On fig. 4, we show a model for a  $p(1 \times 3)$  structure built on a way similar to the model of the  $p(1 \times 2)$  structure of fig. 3. But the difference is that the “relaxed” model of fig. 4b has the same  $pmm$  symmetry as the “non relaxed” structure of fig. 4a.

The same technique can be used for any  $p(1 \times n)$  structure. On fig. 5, is represented the “relaxed” models for the  $(5 \times 1)$  and  $(7 \times 1)$  structures. For both of them two possible ways of relaxation are shown.

### 3. Discussion

In spite of the fact that only LEED intensity calculations can give a solution of a structure, it is possible to give arguments in favor of the “shifted row model”.  
– The number of surface atoms is the same in the  $(5 \times 1)$  reconstructed structure and in the non-reconstructed surface, while the hexagonal model requires 20% more atoms in the reconstructed surface than in the non reconstructed one.

– Recently gold [16], platinum [17] and iridium [18] have been formed having an unstable non-reconstructed (100) surface. By heating the crystal at 100, 125 and 850°C, respectively, the reconstructed surface is restaured. In the “shifted row model”, very little movement is required to move the atoms from their original positions to the bridge sites. While for the hexagonal model, one row of atoms every five has to be added.

– At room temperature, 10 to 20% of impurities turn the  $(5 \times 1)$  structure into the  $(1 \times 1)$  non-reconstructed surface. The “shifted row model” involves a cooperative phenomenon, i.e. the shift of chains of atoms. The adsorption of impurities breaks the chains and the shift not being possible the superstructure disappears. It is difficult to explain such an effect with the hexagonal model since this layer is attributed to a lower surface energy and as a consequence should remain in the parts of the surface not covered by the impurity atoms.

– The “shifted row model” can be interpreted in terms of chains of atoms in a manner similar to the one used by Biberian and Huber [11] to explain some of the structures of metals adsorbed on (100) surfaces of metals. Also chains have been proposed to explain the  $c(2 \times 2)$  structure observed at low temperature on the (100) surface of molybdenum [19].

– When studying the growth of gold on a palladium (100) surface, Palmberg and Rhodin [14] have first seen a  $(7 \times 1)$  structure after 3 to 4 layers of gold, then the  $(5 \times 1)$  structure. Fig. 5b shows a model for the  $(7 \times 1)$  structure similar to the  $(5 \times 1)$  structure. With an hexagonal overlayer of gold, it is more difficult to understand such a structure. Also recently it has been shown that when gold is deposited on a platinum (100) surface [20], it first appears a  $(1 \times 1)$  structure for submonolayer coverages, then streaks indicative of a distribution of structures of  $(n \times 1)$  type, with a distribution of values for  $n$ . Again such a structure can be easily understood with the “shifted row model”, since any  $(n \times 1)$  structure can be built in a way similar to the  $(5 \times 1)$  structure.

– Recently, Küppers et al. [18] have measured the variation of the work function of the (100) surface of iridium when it transforms from a  $(1 \times 1)$  non-reconstructed surface to the reconstructed  $(5 \times 1)$  surface. They show that such a change is accompanied by a decrease of 150 meV of the work function. This result is easily explained by the shifted row model, since with this model the roughing of the surface increases. On the other hand, with the hexagonal model, an increase of the work function is expected when going from the  $(1 \times 1)$  to  $(5 \times 1)$  structure.

Fig. 5a shows two types of possible relaxations respecting the pmm symmetry of the  $(5 \times 1)$  unit cell, based on the previous arguments. It is not possible to determine which one is more valid, only LEED intensity calculations can give a definite answer to this point.

#### 4. The structure of gold and platinum (100) surfaces

It has been shown in various cases that complex surface structures can be interpreted as antiphase domains of more simple structures [11,21,22]. For gold and platinum (100) surface structures, a similar analysis can be used. The structure observed can be analysed as split  $(5 \times 1)$  structures, the splitting being due to out of phase domains of  $(5 \times 1)$  structures. A complete analysis of this question will be published [23], along with laser diffraction simulation experiments to test the validity of the various proposed models.

There are two kinds of surface relaxation: the perpendicular and the parallel. The perpendicular one can happen keeping the surface unit cell equal to the bulk unit cell, but the parallel surface relaxation will induce a surface reconstruction. In the case of iridium, the perfect  $(5 \times 1)$  structure could be analysed as a surface without parallel relaxation. For gold and platinum, the split  $(5 \times 1)$  structure could be due to a parallel surface relaxation, 2D dislocations catching up the misfit

between the surface and the bulk creating antiphase domains. LEED intensity calculations have determined the amplitude of a large number of perpendicular surface relaxations, but at this point very little is known about the parallel surface relaxation, in other words a surface atom might be non spherical with a perpendicular diameter different of a parallel diameter. Because of the lower symmetry of the surface, there is no reason why these diameters should be equal.

## 5. Conclusion

Gold, platinum and iridium (100) surfaces are reconstructed, the classical model explaining that the reconstruction is the "hexagonal model". In this paper, it has been shown that the "shifted row model" is a possible alternative explanation of the observed superstructures. The main advantage of this model is that it does not require extra atoms at the surface, but only very little movement of the surface atoms.

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