Temperature dependence of surface reconstructions of Au on Pd(110)

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Abstract
Surface reconstructions of Au film on Pd(110) substrate are studied using a local Einstein approximation to quasiharmonic theory with the Sutton-Chen interatomic potential. Temperature dependent surface free energies for different coverages and surface structures are calculated. Experimentally observed transformations from (1×1) to (1×2) and (1×3) structures can be explained in the framework of this model. Also conditions for Stranski-Krastanov growth mode are found to comply with experiments. The domain of validity of the model neglecting mixing entropy is analyzed.

68.35.Rh 68.55.-a 68.35.Md

Reconstructions of (110)-surfaces of d-metals have inspired numerous experimental and theoretical studies. It has been confirmed by Low Energy Electron Diffraction (LEED) [1] and Scanning Tunneling Microscopy (STM) [2] that 4d-metals, (Rh, Pd and Ag) favour unreconstructed (1 × 1) structures whilst 5d-metals (Ir, Pt and Au) exhibit (1×2) reconstructions spontaneously. Reconstructions of pure metals are theoretically fairly well understood either in terms of the relative contribution of the d-electrons to binding [3] or in terms of the range of interatomic potentials [4]. However, conditions for surface reconstructions in heterogenous adsorbate-substrate systems have not been explained in simple terms, yet.

A heterogenous system which has received both experimental and theoretical attention is Au on Ag(110). Rousset et. al. [5] have revealed with STM that at submonolayer coverages Au atoms tend to migrate into the substrate so that a complete Ag layer is formed on the top of the Au adsorbate. They have also shown that at coverages, Θ, beyond a monolayer (1ML) of Au interdiffusion no longer happens but Au atoms tend to form clusters on the top of the Ag layer on the surface. Thus Au grows on Ag(110) in a layer+island or Stranski-Krastanov (SK) growth mode. The first principles calculations by Chan et al. [6] confirm that it is energetically favourable for Au atoms to be covered by one Ag layer at submonolayer regime. This has been reproduced in Surface Embed-
ded Atom Model (SEAM) based Molecular dynamics (MD) simulations, which also show an onset of SK growth mode for coverages beyond $\Theta = 1ML$ [1].

In this Letter the temperature and coverage dependence of Au/Pd(110) system depicted from LEED studies of Schmitz et. al [10] is studied theoretically. The structural phase transformations show four main features: (i) at submonolayer coverages only $(1 \times 1)$ structures are observed, (ii) for $\Theta \approx 1.5ML$ there is a transition from $(1 \times 1)$ structure to a mixture of $(1 \times 2)$ and $(1 \times 3)$ domains at $T \approx 310K$ and back to $(1 \times 1)$ at $T \approx 530K$, (iii) For $\Theta = 2ML$ a sequence of transitions $(1 \times 1) \rightarrow (1 \times n) \rightarrow (1 \times 2) \rightarrow (1 \times 3)$ domains; (iv) increasing coverage beyond $\Theta = 2ML$ leads to ever fainter LEED patterns suggesting clustering of Au atoms on the top of two Au layers, i.e. growth in SK mode. The related LEED studies by Kaukasoina et al. [11] mainly confirm the previous observations apart from two exceptions: they were not able to reproduce the $(1 \times 2)$ pattern for $\Theta = 1.5ML$ and for $\Theta = 2.0ML$ they found a continuous transition from $(1 \times 1)$ pattern via $(1 \times 2)$ to a mixture of $(1 \times 2)$ and $(1 \times 3)$ patterns and then back to $(1 \times 1)$ structure. In addition, for $\Theta = 2.5ML$ they found a $(1 \times 2)$ reconstructed surface with a concentration profile $(1, 0.9, 0.36, 0.67, 0.35)$, i.e., atomic concentration of Au is 100% in the first layer, 90% in the second, etc.

A feasible theoretical method to incorporate vibrational motion into surface free energies is the local Einstein approximation to quasiharmonic theory as formulated by Le Sar et al. [12]:

$$F_E = E_P + 3kT \sum_i \ln \left[ \frac{\hbar |D_i|^{1/6}}{\sqrt{M_i} kT} \right]$$

where $E_P$ is the potential energy and $|D_i|$ is the determinant of the $3 \times 3$ matrix $D_{\alpha\beta} = \frac{\partial^2 E_P}{\partial u_{\alpha} \partial u_{\beta}}$. At surfaces, where the three-dimensional symmetry breaks down, it is more advantageous to use the local Einstein approximation with off-diagonal elements of $D_{\alpha\beta}$ than a Debye-type approximation [13], which utilizes the trace of $D_{\alpha\beta}$ and neglects shear properties. It has been shown in Ref. [14] in a study of grain boundaries in Si, that although Eq. (1) may fail in the absolute values of free energies, the excess free energies between two different structures are remarkably good. An optimal structure is obtained by allowing the system relax to a local minimum of Eq. (1). In this study a modification of Polak-Ribiere optimization method as expressed in Ref. [15], is used with numerical approximants of the gradient of free energy with respect to atomic positions.

It has been shown that the Sutton-Chen (SC) potential predicts the reconstructions of (110)-surfaces of d-metals correctly except for Ir [3]. In addition, SC-potential is easy to apply in Eq. (1), in practice, and there exist simple but physically satisfactory rules to describe bonding between atoms of different species. SC-potential [16] is written as follows

$$E_{SC} = \sum_i \epsilon_i \left\{ \frac{1}{2} \sum_{j \neq i} \frac{a}{r_{ij}}^n - c_i \sqrt{\sum_{j \neq i} \frac{a}{r_{ij}}^m} \right\},$$

(2)

where $(m,n) = (7,12)$ and $(8,10)$, $\epsilon = 4.1790 \times 10^{-3} eV$ and $1.2793 \times 10^{-2} eV$, $a = 3.89 \AA$ and $4.08 \AA$, and $c = 108.27$ and 34.408 for Pd and Au, respectively. In heterogeneous AB-systems the following rules $m^{AB} = \frac{1}{2}(m^A + m^B)$, $n^{AB} = \frac{1}{2}(n^A + n^B)$, $a^{AB} = \sqrt{a^A a^B}$ and $\epsilon^{AB} = \sqrt{\epsilon^A \epsilon^B}$ are found to give satisfactory structural, energetic and elastic properties [17].

The calculations were carried out using a slab of 14 layers in the [110]-direction, each layer consisting of 6 rows and 6 columns $(36 \times 14 = 504$ atoms altogether) with peri-
periodic boundary conditions in the direction of both rows and columns. The size of the calcula-
tional cell is limited by the cut-off radius of the SC potential, \( r_c = 2a \), and the number of rows must be divisible by 2 and 3 for \((1 \times n)\) reconstructions with \( n \) either 2 or 3 and the slab must be thick enough to model substrate bulk properties deeper within the slab. In [110]-direction four layers at the very bottom of the slab are fixed in order to maintain bulk structure. The atoms are labeled according to their species, thus each atom can be defined to be either of \( Au \) or \( Pd \). Rows in top layers are removed to create \((1 \times 2)\) and \((1 \times 3)\) missing row structures.

Before optimizing the surface structure, the slab is allowed to expand uniformly to optimize the bulk free energy of \( Pd \) at each temperature separately. After this the surface free energy is minimized by allowing local relaxations using Polak-Ribiere algorithm. The surface free energy is calculated by summing up the free energies of the atoms in the first eight layers subtracted by the bulk free energy of \( Pd \) per atom and dividing the sum by the area of the surface.

The surface free energies of the following ordered structures were studied: a bare \((1 \times 1)\) surface of \( Pd \), \((1 \times 2)\) reconstructed structure with \( \Theta = 0.5ML \) of \( Au \) and an unreconstructed surface with \( \Theta = 1ML \) of \( Au \). For \( \Theta = 1.5ML \) an ordered \((1 \times 2)\) structure with a concentration profile \((1,1,0)\) is studied as well as an unreconstructed structure with a profile \((1,\frac{1}{2},0)\) with a disordered second layer (and with non-zero configurational entropy). In the case of \( \Theta = 2ML \) there are four simple ordered structures: \((1 \times 1)\) with the profile \((1,1,0)\) [18] (Fig. 1. (a)), \((1 \times 2)\) with the profile \((1,1,\frac{1}{2})\) (Fig. 1. (b)) and two possibilities for \((1 \times 3)\), either with the profile \((1,1,1)\) (Fig. 1. (d)) or \((1,1,\frac{2}{3},\frac{1}{3})\) (Fig. 1. (c)) with \( Au \) distributed along the saw-tooth shaped pattern forming effectively one atom thick layer along the corrugation. The latter \((1 \times 3)\) configuration proved more favourable. An unreconstructed layer with \( \Theta = 3ML \) of \( Au \) is compared with the corresponding structure of \( \Theta = 2ML \) to see whether layering on the top of the second layer should take place. To discuss the concentration profile found in Ref. [18] for a \((1 \times 2)\) reconstructed film of \( \Theta = 2.5ML \) two concentration profiles, \((1,1,1,0)\) and \((1,1,0,1)\), are compared. In addition, some disordered structures for \( \Theta = 2ML \) are analyzed to discuss the effect of configurational mixing entropy.

Five main observations to give a framework for the experimental results can be found (See Fig. 2): (i) At submonolayer range \( Pd \) atoms in the neighbourhood of the vacuum have a very high energy. Thus the free energies of a bare \( Pd \) surface and a \((1 \times 2)\) surface with \( \Theta = 0.5ML \) are quite high in free energy compared to \((1 \times 1)\) structure of a monolayer of \( Au \). Although the bulk free energies of \( Au \) and \( Pd \) are quite close to each other, the relatively long range of \( Pd - Pd \) interactions make it energetically very expensive to expose \( Pd \) atoms to the vacuum. One monolayer with \((1 \times 1)\) structure, whose surface free energy is used as the reference in Fig. 2, is the stablest structure up to room temperature where \((1 \times 2)\) reconstructed surface with \( \Theta = 1.5ML \) becomes virtually equally stable.

(ii) For \( \Theta = 1.5ML \) at low temperatures a reconstructed \((1 \times 2)\) surface has a lower energy than an unreconstructed surface (Fig. 2.) but, the low energy structure \((1 \times 1)\) with \( \Theta = 1ML \) may lead to a possibility of \((1 \times 1)\) domains at low temperatures. Increasing temperature beyond \( T \approx 500K \) the reconstructed and unreconstructed surfaces with \( \Theta = 1.5ML \) have virtually equal surface free energy. However, the unreconstructed structure should gain in configurational entropy at high temperatures, since the randomness of \( Au \) atoms in the second layer has little cost in free energy. Taking into account
this effect, it is to be expected that a LEED pattern of \((1 \times 2)\) structure for \(\Theta = 1.5ML\) is observed at some narrow temperature range (as in Ref. [10]).

(iii) For \(\Theta = 2ML\) there is a sequence of transitions as seen in Fig. 2.: \((1 \times 1) \rightarrow (1 \times n) \rightarrow (1 \times 2) \rightarrow (1 \times 3) \rightarrow (1 \times 1)\) with \(n\) being a mixture of 1, 2 and 3, which is something very similar to what was observed in Refs. [10,11], apart from incorrect temperatures. The phase diagram is complicated due to many factors contributing to the thermal free energy, obviously having very different temperatures of dominance. For example, the higher order the reconstruction is, the more corrugated the surface, and increasing corrugation makes an \(Au\) film effectively thinner, thus bringing \(Pd\) atoms closer to the vacuum, which increases surface free energy. On the other hand, corrugation decreases the proportion of \(Au\) atoms at sites with low coordination, which decreases surface free energy. In addition, missing rows alter the local Einstein frequencies, which also has some complicated effects on free energy. Some care must be taken in interpreting these results, since the coverage is thick enough to facilitate interdiffusion.

(iv) Coverages beyond \(\Theta = 2ML\) are energetically expensive except at high temperatures, where \(\Theta = 2.5ML\) is seen to decrease surface free energy (Fig. 2). Although not shown in Fig. 2, the unreconstructed \(\Theta = 3ML\) surface is very high in free energy throughout the temperature range and the same applies to \((1 \times 3)\) reconstructed film although the latter is clearly less expensive than the unreconstructed surface at high temperatures. This result suggests that layer-like growth beyond \(\Theta = 2ML\) does not take place and the faint LEED patterns at thick coverages \([10]\) are caused by clustering of \(Au\) on the top of the first two layers.

(v) At low temperatures both concentration profiles, \((1,1,1,0)\) and \((1,1,0,1)\) for \((1 \times 2)\) reconstructed film with \(\Theta = 2.5ML\) are virtually equally expensive in free energy (see Fig. 2). Both the configurations approach lower coverages in surface energy as the temperature is increased with a deviation in favour of the profile without an intermediate \(Pd\) layer. However, the difference is so small that inclusion of intermixing could change the figure. Thus the present analysis does not rule out the possibility of intermediate layers with high concentration of \(Pd\) at high coverages as suggested in Ref. [11]. The main condition for such an intermediate layer to exist is a thick \(Au\) coverage that prevents \(Pd\) atoms from being exposed to the vacuum.

The main source of inaccuracy here is the absence of intermixing, which means ignoring configurational mixing entropy. For alloys, it is possible to deal with the mixing entropy using Bragg-Williams type approximation, as is done in Ref. [11]. In that study the ensemble is grand canonical, while here it is canonical due to a fixed coverage. But even in this case the mixing entropy per layer per unit area for randomly mixed layers can be approximated as follows:

\[
S^k = -nk_B[c_k \ln(c_k) + (1 - c_k) \ln(1 - c_k)]
\]

where \(c_k\) is the concentration of \(Au\) atoms in the \(k^{th}\) layer and \(n\) is the number of atoms per unit area. Disorder may increase vibrational free energy, but the increase may be overcome by the contribution of mixing entropy, \(\sum_k TS^k\).

The effect of mixing entropy is roughly estimated for \(\Theta = 2ML\) by calculating the free energy, Eq. (1) and the entropy, Eq. (3), for a couple of energetically favourable concentration profiles with disorder. For an unreconstructed surface the profile \((1,\frac{1}{2},\frac{1}{2})\) has a low cost in free energy despite two randomly mixed layers (The \(Au\) atoms of the \(2^{nd}\) \(Au\) layer are diluted to the \(2^{nd}\) and the \(3^{rd}\) layers). For \((1 \times 2)\) reconstructed sur-
faces a corresponding low cost/high entropy profile would be $(1, 1, \frac{1}{2})$, but with only one randomly distributed layer, leading to a half of the entropy of $(1 \times 1)$ surface. For $(1 \times 3)$ surface only the atoms in the $4^{th}$ layer of the profile $(1, 1, \frac{2}{3}, \frac{1}{3})$ are allowed to be redistributed without a high expense, and the gain in entropy is slightly smaller than for the mixed $(1 \times 2)$ structure. In Fig. 3 are shown the lowest limits of free energies corrected by mixing entropies for mixed layers with for randomly distributed Au atoms as described above. The complicated transition sequence survives the error analysis, because the configurational entropy affects to the same direction for all the structures, although favouring $(1 \times 1)$ surface and disfavouring $(1 \times 3)$ surface. This might change the sequence of transitions more like $(1 \times 1) \rightarrow (1 \times n) \rightarrow (1 \times 2) \rightarrow (1 \times 1)$, which actually is what Ref. [10] suggests. In any case, the effect of configurational entropy is significant above room temperature.

Keeping in mind the restrictions of the model the present study gives results in qualitative agreement with experimental observations. The calculations do not merely reproduce the structural phase transitions observed by LEED but also provide explanations to some of the experiments. The calculations take only a couple of minutes per point on an HP workstation and thus the method can easily be used in planning experiments and interpreting LEED or STM results. Including intermixing and optimization of the concentration profile to the model is a logical and necessary continuation to the present work.

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FIGURES

FIG. 1. Different surface structures for \( \Theta = 2ML \) of Au (black circles) on Pd(110) surface (open circles): (a) \((1 \times 1)\), (b) \((1 \times 2)\), and (c) and (d) \((1 \times 3)\) structures as seen from the side of the slab in the direction of rows. The structure of (c) has lower free energy than the structure of (d).

FIG. 2. Excess free energies for different coverages and surface structures, the surface free energy of \((1 \times 1)\) structure of \( \Theta = 1ML \) being the reference. For \((1 \times 3)\), the structure of Fig. 1 (c) has been used. In the legend, \(2.5ML\) (non.) refers to the nonmonotonous concentration profile of \( \Theta = 2.5ML \).

FIG. 3. The error analysis for excess free energies of different structures for \( \Theta = 2ML \). The symbols without guiding lines show the lower limits of the free energy as corrected with the configurational entropy.