Surface Science 604 (2010) 834–852

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Stability of vicinal surfaces and role of the surface stress

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A R T I C L E I N F O

Article history:
Received 13 November 2009
Accepted for publication 9 February 2010
Available online 1 March 2010

Keywords:
Semi-empirical models and model calculations
Stepped single crystals surfaces
Surface energy
Surface stress
Surface tension
Shuttleworth's equation
Copper
Gold

A B S T R A C T

Vicinal surfaces of type $(0,1,M)$ are investigated and compared with surfaces with opposite steps, M being an integer larger than 2. When admitting that the step behaves as a dipole force $\vec{f} = (0, f_y, f_z)$, f_y and f_z being respectively parallel and normal to the surface, the Marchenko–Parshin (*MP*) model gives the surface displacement due to one step equal to $-\Lambda\vec{f}/y$, Λ being an elastic constant and y the position from the step. On vicinals, the *MP* model indicates that the interaction energy between steps varies as $\Lambda\vec{f}^2/L^2$, L being the step–step distance. For Cu$(0,1,M)$ and Au$(0,1,M)$, the components f_y and f_z are deduced from surface displacements obtained by molecular dynamics at $T = 0$ K. Due to the minimization of the terrace stress, we confirm that the terrace is more contracted in the direction parallel to the surface by a factor $(1+X) > 1$ with respect to the *MP* model where X is recursively proportional to the parallel deformation. This leads to an interstep interaction energy increased by a factor $(1+2X)^2$ (instead of $(1+X)^2$ with respect to both the terrace deformation and the *MP* model). This effect due to the terrace stress is larger for Au. We note that $f_y(1+X)$ is close to f_z, opposite in sign to the surface stress of the nominal surface and to the isolated step stress. By comparison with surfaces with opposite steps, the parallel deformation at the step position, $\epsilon_{yy}(0)$, includes a term in L^{-1} in addition to the term in L^{-2} deduced from the *MP* model. The term in L^{-1} corresponds to a weak displacement parallel to the surface towards the descending steps. From the step energy, the first order and second order energies as function of the relaxation deformations can be subtracted. In the *MP* model, the first order one is opposite in sign and twice in magnitude the second order one. For Au, we observe a deviation from this equality due to the minimization of the terrace stress.

In the last part and for vicinals, we confirm that the step–step interaction stress varies as L^{-1} and results from the component f_z multiplied by minus the derivative of the normal displacement due to neighbouring lines of monopole forces, the forces being parallel to the surface and proportional to the homogeneous deformation.

In the literature, it is known that the stability of vicinal surfaces results essentially from the repulsive interstep interaction energy. Concerning the surface stress, the isolated step stress attenuates the surface stress of the nominal surface. Because the interaction stress decreases this attenuation, we note that the steps are repulsive also by the surface stress.

1. Introduction

For last decades, the literature on surface physics shows that the surface stress has attracted an unceasingly increasing interest for understanding the equilibrium of surfaces [1]. Surface stress is an important concept but it is not quite understood for surface scientists. Often, surface stress is wrongly confused with surface energy. To consider only the minimization of surface energy cannot be sufficient in explaining the equilibrium structure of defects on surfaces. For a flat surface, the surface stress is an excess pressure with respect to the bulk pressure for a given temperature. When the bulk pressure is negligible, as is often the case, surface pressure can be important to play a role in the equilibrium of surface nanostructures. Moreover, when the number of surface atoms becomes not negligible with respect to the number of bulk atoms as for nano-objects, the surface stress can modify the equilibrium structure of the small systems with respect to larger systems [2]. Thus, surface stress will be more taken into consideration in nanotechnology. Otherwise, the surface stress is often used in explaining the anisotropy of the surface equilibrium structures. Because surface stress is much sensitive to surface relaxation than surface energy, the surface stress anisotropy is more important than the surface energy anisotropy [3,4].

This paper concerns the equilibrium of stepped surfaces and follows in depth previous Refs. [5,6]. In those references, the surface stress has been mentioned in explaining the equilibrium of surfaces. But up to now, the role of the surface stress is still contested. On vicinal surfaces, the steps behave as lines of force dipoles and

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doi:10.1016/j.susc.2010.02.009

are in interaction together. The stability of vicinal surfaces is due essentially to the repulsive interaction energy between steps. From the Marchenko–Parshin (*MP*) model, it decreases in L^{-2} where L is the periodic distance between steps. This interaction energy results from the second order energy as a function of the deformations, E_{2o}, when supposing that the first order energy E_{1o} is equal to $-2E_{2o}$. However, we shall see that the energy E_{1o} includes an interaction energy in L^{-1} and the energy E_{1o} is quantitatively quasi equal to $-2E_{2o}$ for equilibrium reasons between E_{1o} and E_{2o}. In addition to the interstep repulsion in energy, we shall show that the steps are also repulsive by the surface stress due to the existence of an interaction stress which is positive and varies as L^{-1} [7].

From Ref. [6], we recall that the displacement on the flat surface due to one dipole line varies recursively in the direction of the surface plane y as $f_y[1-\lambda f_y(1-\lambda f_y(\cdots))]/y = f_y[1-\lambda f_y/(1+\lambda f_y)]/y = f_y[1+X]/y$ where y is the position from the dipole line, f_y is the component y of the dipole force and λ is an elastic constant. Moreover, we note that the part due to f_y of the interaction energy between dipole lines varies as $f_y^2(1+2X)^2/L^2$ (instead of $f_y^2(1+X)^2/L^2$). This deviation has been demonstrated as resulting from the minimization of the surface stress (in absolute value) of the terrace between dipole lines even if the total energy of the system increases [6]. The deviation from $\left[f_y^2/L^2\right]$ (*MP* model) to $\left[f_y^2(1+2X)^2/L^2\right]$ will be applied with success to the vicinals Cu(0,1,*M*) and Au(0,1,*M*). The two metals Au and Cu are chosen due to the large difference between their elastic constant λ ($\lambda_{\mathrm{Au}} \simeq 3\lambda_{\mathrm{Cu}}$). We work with vicinal surfaces because they are simple models for which the defects are linear in the direction x. Thus the atoms are displaced in only the two directions y and z. For vicinals of type (0,1,*M*), the distances in the directions y and z between nearest bulk atoms are equal and so the problems due to the anisotropy of the *fcc* metals are avoided at best (x, y and z are the directions of the *fcc* conventional unit cell). This clarifies our understanding of equilibrium of surfaces when calculating the total surface energy and the first order and second order energies as a function of the deformations due to steps. The role of the surface stress on vicinals shall be investigated into details.

We study surfaces with steps due to the emergency of nanotechnology today. Stepped surfaces can be chosen as templates for realizing an ordered ensemble of nanoparticles [8] or long-range-ordered structures at the nanometer scale [9]. Vicinal surfaces require thus to be still studied in depth. Reconstruction and faceting observed on vicinal surfaces remain still a high subject of discussions because they are not entirely elucidated [10,11]. Interesting transition between step bunching and step-meandering has been observed in experiment on Si(111) vicinal surfaces [12]. Intensive studies on Si vicinals and their stability are been recently published [13–16]. Vicinal surfaces are also studied by investigating metal electrodes in contact with an electrolyte [17–20]. On Cu(2,2,3), *Pt*(7,7,9) and *Pt*(15,15,16), Surface X-ray diffraction measurements of Crystal Truncation Rods are compared with Fourier transform of results obtained in the frame of anisotropic linear elasticity [21–23]. For this, the authors B. Croset and G. Prévot suppose that the dipole force which simulates the step is applied upon the flat surface only for the upper corner of the step, the force applied upon the lower corner of the step is located under the flat surface (buried dipole model). So, they showed that the elastic displacements are highly anisotropic and the direction of both the force and lever arm play a major role for the interstep interaction energy. Those authors do not account for the role of the surface stress in the modification on this energy with respect to the *MP* model.

The paper is organized as follows: Section 2 gives the choice of the potential used in our simulations. Section 3 details the definitions of surface energy and surface stress by revisiting the Shuttleworth's equation. In Section 4, we show that we can calculate the step energy on vicinal surfaces by two methods, on the one hand by summing the interatomic potentials and on the other hand by using the deformations with respect to the flat surface and the appropriate elastic constants (first order and second order energies). In this section, we recall the *MP* model often used for giving the surface displacement due to steps. The *MP* model gives a first expression of the step–step interaction energy. The *MP* model supposes that the surface stress is constant with the deformation. In addition, Section 4 gives the modifications of this model due to the (*variation)* of the surface stress. Section 5 is devoted to the study of surfaces with opposite steps (*OSt* surfaces) and of vicinal surfaces (*SSt* surfaces). This permits us to determine the differences between the two types of surfaces in order to study at best *SSt* surfaces. In this section, surface displacements and deformations at the step position are investigated. In Section 6, we discuss the step energies and compare them with the first and second order energies as a function of the deformations. Surface stress of vicinal surfaces is showed at the end of this section before discussion. Section 7 is devoted to vicinal surfaces with homogeneous deformation in order to explain the step–step interaction stress which decreases as L^{-1}. Finally, we summarize and conclude in Section 8.

2. Interatomic potential

Our simulations use the *RGL* potential which is a many-body potential [24]. The potential has been adjusted to the experimental bulk elastic constants and cohesive energy. The lattice constant is equal to the experimental one. For a given system of N atoms, the total energy of the system is the sum of N energies Φ_i, Φ_i being the energy of the atom i. Each atomic energy is calculated by summing the interaction energies between the atom i and its neighbouring atoms $j \neq i$. In order to follow the results obtained in previous papers [5,6], the interactions between atoms i and j are limited to nearest neighbours. For this cut-off radius, the parameters of the *RGL* potential are given in Ref. [24]. This limitation simplifies our calculations by using the derivatives of the atomic potential Φ_i with respect to the deformations between two equilibrium configurations. All the results are obtained at $T = 0$ K by using a quenched molecular dynamics [25,26]. To study the energetics of surfaces, (001) surfaces and vicinal surfaces with (001) terraces, our simulations are computed by using a slab with two free surfaces separated by 200 (001) planes. This is sufficient to ensure the correct reproduction of the bulk properties of the central region between surfaces. We consider thus that the two surfaces do not interact between themselves.

3. Do not confuse surface energy γ_0 and surface stress $\overline{\sigma^0_{\alpha\beta}}$

3.1. Surface energy γ_0

In order to explain at best the difference between surface energy and surface stress, we take simply a (001) flat surface for which the directions x, y and z are the equivalent directions of the *fcc* conventional unit cell (see Fig. 1). The direction z is normal to the surface. This figure displays the length unit = a used in the paper. The lattice constant is equal to $2a$ and the surface area occupied by one atom is $A_a = 2a^2$. The monolayers parallel to the surface are the planes labelled from $p = 1$ for the surface monolayer up to the plane $p = N_p$ for the bulk. N_p is sufficiently large in order to validate that the N_p^{th} plane behaves as in bulk. The surface energy is defined as the excess energy per unit surface area with respect to