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STM study of the Mo(1 1 2) and Mo(1 1 1) surfaces

I.N. Yakovkin [a,*], M. Kuchowicz [b], R. Szukiewicz [b], J. Kołaczkiewicz [b]

[a] *Institute of Physics of National Academy of Sciences of Ukraine Prospect Nauki 46, Kiev 03028, Ukraine*
[b] *Institute of Experimental Physics, University of Wroclaw pl. M. Borna 9, 50-204 Wroclaw, Poland*

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Abstract

The Mo(1 1 2) and Mo(1 1 1) surfaces have been studied by STM and DFT/GGA modeling. Due to high quality and cleanness of the surfaces, for the first time good STM images of large fragments of the Mo(1 1 2) and Mo(1 1 1) have been obtained. Lack of atomic resolution in the rows of the Mo(1 1 2) surface is attributed to flatness of distribution of density of the electronic states along the rows. This suggestion is illustrated by comparison of STM images for Mo(1 1 1) and Mo(1 1 2) and model calculations of STM pictures for these surfaces.

Keywords: Scanning tunneling microscopy; High-index transition metal surfaces; DFT; Density of states

1. Introduction

Recent achievements in epitaxial growth of silica layers on the Mo(1 1 2) [1,2] and compound Au/TiO_2 films [3] invoke a special interest to properties of this surface. In particular, the $Au/TiO_2/Mo(1\,1\,2)$ adsorption system has been found to be a quite promising catalyst for reaction of CO oxidation [3]. The Mo(1 1 1) surface, in turn, can be explored as a template for preparation of novel "pyramid" catalysts [4], based on faceting of the (1 1 1) surface of bcc transition metals, induced by adsorption of Pt, Pd, Ag, or Au [4–7]. Hence, the issue of stability of structures of the Mo(1 1 2) and Mo(1 1 1), both clean and under adsorbed layers, is of a primary importance for development of new catalysts based on these surfaces.

There are several indications for reconstruction of the Mo(1 1 2) surface induced by adsorption. For example, carbon and oxygen contaminations effect a complex reconstruction of the surface on annealing at elevated temperatures [8–10]. High-temperature annealing of adsorbed Dy films also leads to irreversible surface reconstruction with forming "glass" compound [11]. However, a clean Mo(1 1 2) surface does not show reconstructions, but, as follows from IV-LEED study [12] and recent DFT calculations [13–15] demonstrate a significant relaxation (contraction of the spacing between surface layers).

Nonetheless, no good quality STM images of a clean Mo(1 1 2) have been reported to date. At best, only some small fragments of the image with resolved atomic rows were obtained [10,16]. In large part, complications with obtaining STM images result from a high adsorption activity of the Mo(1 1 2) surface (pertinent to transition metals), which makes preparation of a clean surface and preservation of its purity from contaminations during experiments (which usually require a great number of surface scans) a quite difficult task. Hence, we believe that the lack of good STM images of the Mo(1 1 2) surface is caused not by possible reconstruction, but appears due to surface contaminations.

The geometry of the Mo(1 1 2) surface, built from close-packed atomic rows (with interatomic spacing $a_1 = 2.73$ Å) with rather large spacing between them ($a_2 = 4.45$ Å), allows for relatively easy separation of the atomic rows in STM images, but obtaining of the resolution of individual atoms within a row is complicated by the close spacing

* Corresponding author.
E-mail address: yakov@iop.kiev.ua (I.N. Yakovkin).

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between the atoms, which results, as we show in the present paper, in essentially flat space distribution of electronic density of states along the rows. In contrast, the spacing between surface atoms for Mo(1 1 1) is large, so that the electron density has rather corrugated relief and therefore obtained STM images do show atomic resolution. These suggestions are further illustrated by direct comparison of STM images, obtained for Mo(1 1 2) and Mo(1 1 1), with model STM images of these surfaces.

2. Experimental and calculational methods

The measurements were carried out in an UHV chamber with a base pressure better than 8×10^{-11} Torr. The system was equipped with electron energy retarding field analyzer (RFA), used for low-energy electron diffraction (LEED) observations as well as for Auger electron spectroscopy (AES), and with OMICRON scanning tunneling microscope (STM). The STM images were processed using the WSxM program from Nanotec Electronica [17]. All of the measurements were performed at room temperature. STM measurements were performed at constant-current mode.

The samples with Mo(1 1 1) and Mo(1 1 2) surfaces were cut from single crystals (of 5 N purity) perpendicular to the $\langle 1\,1\,1\rangle$ and to $\langle 1\,1\,2\rangle$ directions, respectively, with accuracy better than $\pm 0.1°$. The samples were carefully decarbonized (by heating for several hours at 1200–1300 K in oxygen atmosphere of about 10^{-7} Torr), and then cleaned by several flashes up to 2100 K. This procedure was repeatedly performed until the Auger peaks of O and C became 300 times less than the peak of Mo (186 eV) and, as thus, were practically not distinguishable from the instrument noise.

It should be noted that formation of a clear (1×1) LEED pattern does not guarantee that the surface is clean enough to obtain good STM images. In fact, such a "clean" surface can contain a large number of defects and contaminations [9,16]. Thus, the surfaces were believed to be clean indeed when STM topographic images showed no or few defects caused by adsorption of residual gases.

The DFT/GGA semirelativistic calculations, using norm-conserving Troullier–Martins pseudopotential [18] with exchange-correlation part in Perdew–Burke–Ernzerhof form [19], were carried out with ABINIT code [20]. To restore periodicity in the direction normal to the surface, the repeat-slab model was adopted. Thickness of the Mo(1 1 2) and Mo(1 1 1) slabs was of 7 atomic layers, which was found to be sufficient to describe correctly the most important structure and electronic properties of the surfaces. The energy cut-off 40 Ry and $4 \times 4 \times 1$ Monkhorst–Pack set of k points [21] provided the mRy accuracy in total energy and correct positions of atoms after optimization. For accurate calculations of local density of states (LDOS) the k-points set was increased to $8 \times 8 \times 1$, and the Mo atomic radius was 1.87 Å. Simulations of STM images were performed by Tersoff–Hamann method [22].

3. Results and discussion

For the bulk Mo crystal, the equilibrated bcc structure was obtained with the lattice constant of 3.16 Å, in a good agreement with other calculations [13–15] and the experimental value (3.15 Å). Calculated parameters of the Mo(1 1 1) surface relaxation (relative variations of the interlayer spacing with regard to the (1 1 1) interplane spacing in the bulk Mo) were of −16.5%, −13.2%, +5.8%, where minus sign denotes contraction and plus – expansion of the spacing for the layers sequentially numbered from the surface. Worth noting that the hexagonal symmetry of the surface unit cell remains unchanged and seemingly prevents reconstruction of the Mo(1 1 1) surface.

The Mo(1 1 2) surface relaxation results in significant contraction (−13.4%) of the spacing between the surface and next to the surface layers, accompanied by a small (1.9%) shift of the surface atomic rows along the $\langle 1\,1\,\underline{1}\rangle$ direction (obtained parameters of the Mo(1 1 2) relaxation are consistent with previous calculations and IV-LEED results [12,14,15]). High stability of a clean Mo(1 1 2) surface has been suggested also from LEED studies [8–12] and DFT calculations [13–15]. This means that the surface itself must be stable with regard to step formation and therefore there are no hindrance to obtaining large flat areas with a perfect Mo(1 1 2) surface structure. Hence, the Mo(1 1 2) surface should give good STM images, while previous attempts to obtain STM pictures of relatively large surface fragments failed, probably, because of insufficient cleanness of the surface. It is due to well developed procedure of the surface treatment (described above) and good vacuum conditions that the STM image of the Mo(1 1 2), presented in Fig. 1a, does present a large area of a high quality surface.

In the STM image of the Mo(1 1 2), atomic rows of surface atoms are well resolved due to relatively large distances between them. It is very difficult to obtain atomic resolution for Mo atoms in the rows, and therefore model STM image appears "better" than the real one (that is, obtained in experiment) (Fig. 1b and c). To better illustrate the origin of difficulties in obtaining atomic resolution along the rows of surface atoms, space distribution of states in the energy range from E_F to $E_F - 0.05$ eV (just these states are responsible for forming the STM images for tip bias of +0.05 eV) has been calculated. The distribution of the states in the $(1\,\underline{1}\,0)$ plane (that is, in the plane drown through the rows normally to the surface) is shown in Fig. 2.

There are two important features evident from the figure: (i) The local density of states in the topmost surface layer is increased dramatically for the cost of the layers next to the surface. In this energy range, DOS of a bulk Mo has a pronounced minimum and therefore surface resonances provide the main input to electron density at the surface (Fig. 3). This is consistent with significantly higher charge density at the surface Mo(1 1 2) atoms, as is seen in Fig. 2. (ii) Due to the close spacing (2.74 Å in present