Available online at www.sciencedirect.com
ScienceDirect
Surface Science 601 (2007) 1333–1338
SURFACE SCIENCE
www.elsevier.com/locate/susc

Oxygen induced surface structure of Mo(1 1 0) studied by scanning tunneling microscopy

Arifumi Okada *, Masamichi Yoshimura, Kazuyuki Ueda

Nano High-Tech Research Center, Toyota Technological Institute, Hisakata 2-12-1, Tempaku-ku, Nagoya 468-8511, Japan

Received 12 September 2006; accepted for publication 21 December 2006
Available online 30 December 2006

Abstract

The oxygen induced surface structures formed on Mo(1 1 0) by oxygen exposure at 1300 K in UHV has been studied by scanning tunneling microscopy (STM). Two kinds of oxygen-adsorbed surface structures are observed. One consists of one-dimensional rows running along $[\bar{1}\,1\,1]$ or $[1\,\bar{1}\,1]$ directions at substrate molybdenum lattices, and another shows more complex structure including discrete arrangement of large protrusions and zig–zag alignments of small protrusions. This complex structure is probably a further oxygen-adsorbed structure than the well-known $p(2\times2)$ structure of 0.3 ML coverage. On the basis of STM image, an atomic model is proposed, where adsorbed oxygen atoms occupy both long-bridge and the quasi-threefold sites of molybdenum lattice (0.4 ML coverage). This structure is presumed to be a transient state during site-conversion with increase of oxygen exposure.

Keywords: Scanning tunneling microscopy; Oxygen induced structure; Metal surface

1. Introduction

Molybdenum is industrially important as a heat-resistant and raw-material of alloys. Oxidized molybdenum is also important because of its high catalytic activity for selective oxidation of olefines and alcohols as well as reduction of nitrogen oxides [1–6]. When the oxide films are formed via oxygen adsorption, facetting occurs usually. Thus, it is well-known that MoO_2 and MoO_3 with various shapes including whiskers and nanorods are formed [6,7], leading to the application to nanodevices such as well-controlled arrays of quantum wires and dots. However, in order to design and control the nanostructures, it is important to know the initial oxidation behavior with atomic resolution. Mo(1 1 0) is the closest packed plane having high reactivity [7]. For oxygen adsorption on Mo(1 1 0), low energy electron diffraction (LEED) study has shown that a $p(2\times2)$ structure is formed at first and more complex structure is formed at higher coverage than ~0.3 ML [8,9]. In addition, the initial adsorption sites during oxygen exposure were identified by high-resolution electron energy loss spectroscopy (HREELS) [10,11].

Scanning tunneling microscopy (STM) is a method to observe surface structure in real space with atomic resolution. As for interaction between oxygen and molybdenum surface, STM measurements have been conducted for oxygen adsorption on Mo(1 1 2). Schroeder et al. [12,13] and Santra et al. [14] proposed oxygen induced Mo(1 1 2) surface structures from the analysis of STM images. In their studies, $p(1\times2)$, $p(1\times3)$ and $p(2\times3)$ superstructures have been reported. Furthermore, McAvoy et al. [15] observed many nanostructures including line shaped and checker-flag-like structures on the oxygen adsorbed Mo(1 1 2) with some contaminations. On the other hand, no detailed STM study of the low-indices Mo(1 1 0) surface with oxygen exposure has been conducted so far.

In the present study, oxygen adsorbed structure of Mo(1 1 0) surface at low coverage has been observed by means of STM. The complex superstructures were

* Corresponding author. Present address: Institute of Applied Physics, University of Tsukuba, Tsukuba 305-8573, Japan.
E-mail address: aokada@bk.tsukuba.ac.jp (A. Okada).

0039-6028/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2006.12.071

observed to be formed by our procedure of the oxygen exposure. Furthermore, a structural models were proposed from atom-resolved STM images and were compared with other structure reported using LEED and HREELS.

2. Experiment

The present experiment was carried out at room temperature in an ultra-high vacuum (UHV) chamber with a pressure below 2×10^{-8} Pa. A Mo(1 1 0) specimen (14 mm × 3 mm, 0.25 mm of thickness) was fixed on the ceramic sample holder using Ta plates. STM observations were performed using an electrochemically etched W tip with the constant-current mode. Heating was performed using the ceramic heater underneath the specimen. The temperature of the specimen surface was measured by optical pyrometer.

The specimen was cleaned by Ar^+ sputtering followed by annealing in UHV. Both sputtering and annealing were performed at 1300 K for 1 h. In order to prepare the specimen surface of low oxygen coverage, (1) heating in O_2 (4×10^{-6} Pa for 10 min) and in UHV (for 10 min) were repeated several times, followed by flashing, and then (2) the specimen was annealed at 1300 K in UHV for 5–45 min to prepare atomically well ordered surfaces. Step (2) is similar to the cleaning procedure performed by Kröger et al. [16] except for the heating temperature. They achieved a clean

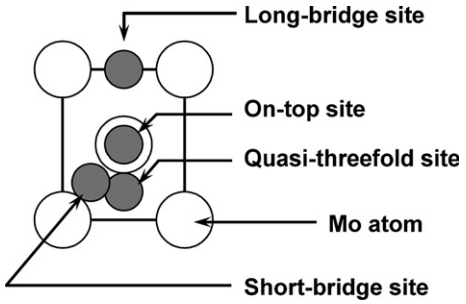

Fig. 1. Adsorption sites on Mo(1 1 0) unit cell. The white and gray balls stand for Mo and O atoms, respectively.

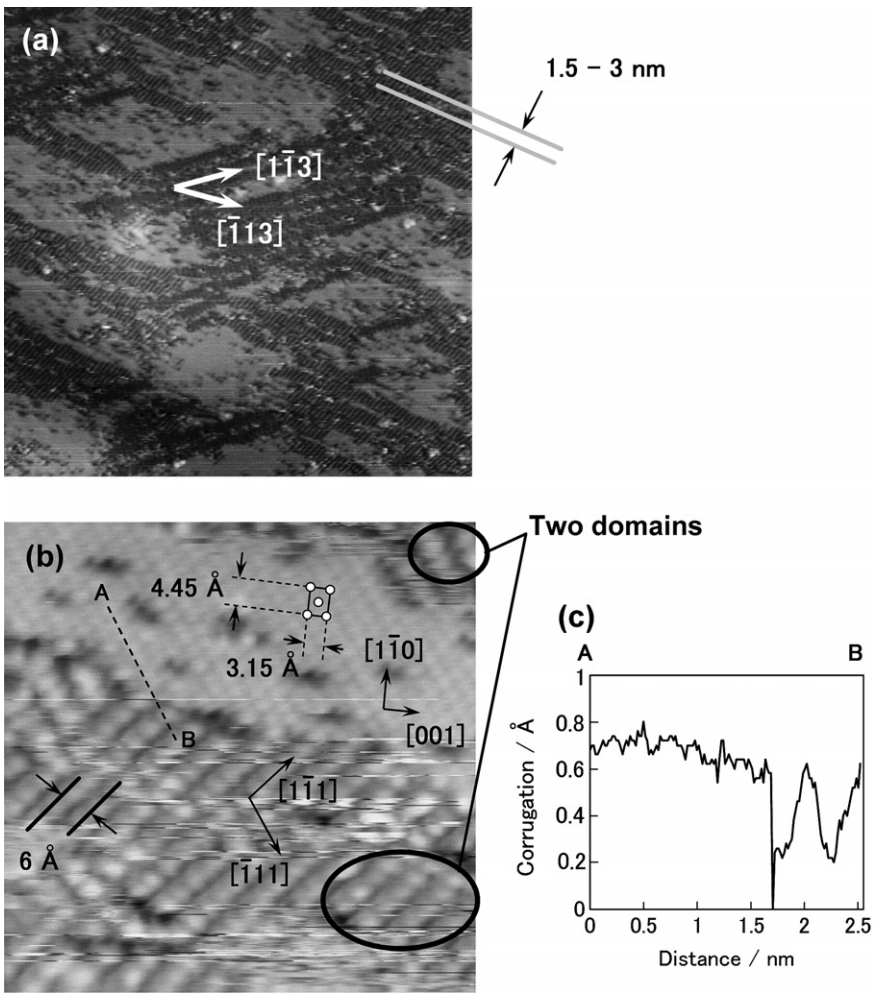

Fig. 2. (a) A STM topographic image of Mo(1 1 0) surface after Ar^+ sputtering and annealing at 1300 K for 1 h (56.9 nm × 56.9 nm, $V_s = -1.0$ V, $I_t = 0.2$ nA). (b) An enlarged image of cleaned Mo(1 1 0) sample (8.1 nm × 8.1 nm, $V_s = -1.0$ V, $I_t = 0.3$ nA). The clean area is observed relatively bright in which the unit cell is indicated. Around the clean area, two-domain structure which shows atomic rows running along [$\bar{1}$ 1 1] and [1 $\bar{1}$ 1] directions due to residual oxygen. (c) A cross-section of the clean area indicated by dashed line AB in (b).