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The electronic structure and reactivity of the oxygen-modified $Mo_2C(0\ 0\ 0\ 1)$ surface

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Abstract

Oxygen adsorption on $Mo_2C(0\ 0\ 0\ 1)$ has been investigated with angle-resolved photoemission spectroscopy (ARPES). When the surface is reacted with O_2, the O 2p-induced states are formed at 4.1 and 5.3 eV at the $\bar{\Gamma}$ point. The emissions around the Fermi level are also intensified by oxygen adsorption, which is due to the formation of a partially filled state. It is found that the reactivity of the surface toward H_2O adsorption is much enhanced by pre-adsorption of oxygen. The reactivity is found to be maximized at $\theta_O \sim 0.2$.

Keywords: Photoemission spectroscopy; Chemisorption; Carbides; Low index single crystal surfaces; Water

1. Introduction

The surface properties of Mo_2C have attracted much attention, because it exhibits catalytic properties similar to those of Pt-group metals, for example, it has been found to have excellent catalytic performance for the hydrogenation of hydrocarbons [1,2]. In addition, it has been reported that the catalytic properties of Mo_2C are often improved by slight oxidation of the surface [3]. The activation of Mo_2C should be closely related to the modification of the surface electronic structure, and thus it has become important to elucidate the change in the surface electronic structure of Mo_2C induced by oxidation and its effect on the surface reactivity.

The surface electronic structure of Mo_2C has been investigated for a C-terminated α-$Mo_2C(0\ 0\ 0\ 1)$ surface using angle-resolved photoemission spectroscopy (ARPES) [4,5]. These studies showed that the valence band is observed at 0–7 eV, and the band is mostly composed of Mo 4d–C 2p hybrid states except for the region near E_F (0–1 eV) where the band is mostly composed of Mo 4d orbitals [4,5]. It has been found that a surface state which is mostly composed of 4d orbitals of the second-layer Mo atoms is formed at 3.3 eV at the $\bar{\Gamma}$ point [5]. Recently the oxygen adsorption on $Mo_2C(0\ 0\ 0\ 1)$ has been investigated by ARPES [6]. The study showed that the adsorbed O atoms sit on the second-layer Mo atoms forming a (1×1) orthorhombic lattice, and that the emission intensity around E_F in normal-emission spectra is enhanced after oxygen adsorption [6]. The reactivity of the surface should be closely related to the surface electronic structure, in particular, in the vicinity of E_F, and thus the reactivity of the oxygen-covered $Mo_2C(0\ 0\ 0\ 1)$ surface is of interest. In this paper, we report the results of the ARPES study on the two-dimensional electronic structure of the oxygen-covered $Mo_2C(0\ 0\ 0\ 1)$ surface. The adsorption of water on the $Mo_2C(0\ 0\ 0\ 1)$ surfaces pre-exposed to various amounts of oxygen are also investigated, and the adsorption states will be discussed.

2. Experimental

The ARPES measurements were performed at BL 1C and 3B of the Photon Factory, High Energy Accelerator Research Organization, using a hemispherical electron energy analyzer (VSW HA54). The measurements of the two-dimensional electronic structure of the oxygen-covered $Mo_2C(0\ 0\ 0\ 1)$ surface were performed at BL 3B, and the ARPES measurements for the surface reacted with water were performed at BL 1C. The total experimental resolutions were estimated to be 0.17 and 0.13 eV at $h\nu = 30$ eV, respectively. The base pressure in the vacuum system was 1×10^{-10} Torr.

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An α-Mo_2C single crystal was grown by the floating zone method at the National Institute for Materials Science [7]. The crystal was cut at a (0 0 0 1) orientation by spark erosion into a disk of ∼1 mm thickness and subsequently polished mechanically. The clean surface was prepared by Ar^+ ion bombardment (1 kV for 60 min) and annealing (<1600 K). The (0 0 0 1) surface of α-Mo_2C is a polar surface, and it has been proved that the surface prepared by the procedure described above is terminated with a C layer, and the ratio of the number of the first-layer C atoms relative to that of the second-layer Mo atoms is estimated to be 0.48 ± 0.04 [5].

3. Results and discussion

The normal-emission spectra of Mo_2C(0 0 0 1) exposed to various amounts of O_2 at room temperature are shown in Fig. 1 (gray lines). For the clean surface, the Mo 4d–C 2p band and C 2s band are observed at 0–7 and 12 eV, respectively. A prominent peak at 3.3 eV is ascribed to a surface state [5]. As the surface is exposed to O_2, the 3.3 eV peak is attenuated, and emissions at 0–1, 4–7, and ∼12 eV are enhanced. For 10 L, peaks are observed at 0.4, 1.1, 4.1, 5.3, 6.6 and 12.3 eV. It has been proved that the initial states of the 1.1, 6.6 and 12.3 eV peaks are substrate's bulk bands, though the emissions are enhanced by oxygen adsorption [6]. On the other hand, it has been found that the peaks at 0.4, 4.1 and 5.3 eV do not show dispersions as a function of $h\nu$, and thus the initial states should be ascribed to the states localized to the oxygen-covered surface [6]. The states at 4.1 and 5.3 eV are ascribed to the O 2p-induced bonding states, which have been theoretically predicted to exist around 5 eV by Ren et al. [8].

The oxygen adsorption model for the (1 × 1) orthorhombic structure proposed in our previous work is shown in Fig. 2(a) [6]. Fig. 2(b) shows the corresponding surface Brillouin zones (SBZs). In this work, we measured ARPES spectra along the $\bar{\Gamma}\bar{X}$ and $\bar{\Gamma}\overline{X'}$ directions. However, since the surface consists of three types of (1 × 1) orthorhombic domains which are rotationally misaligned by 120° from each other, the ARPES measurements along the $\bar{\Gamma}\bar{X}$ (line 1) direction simultaneously

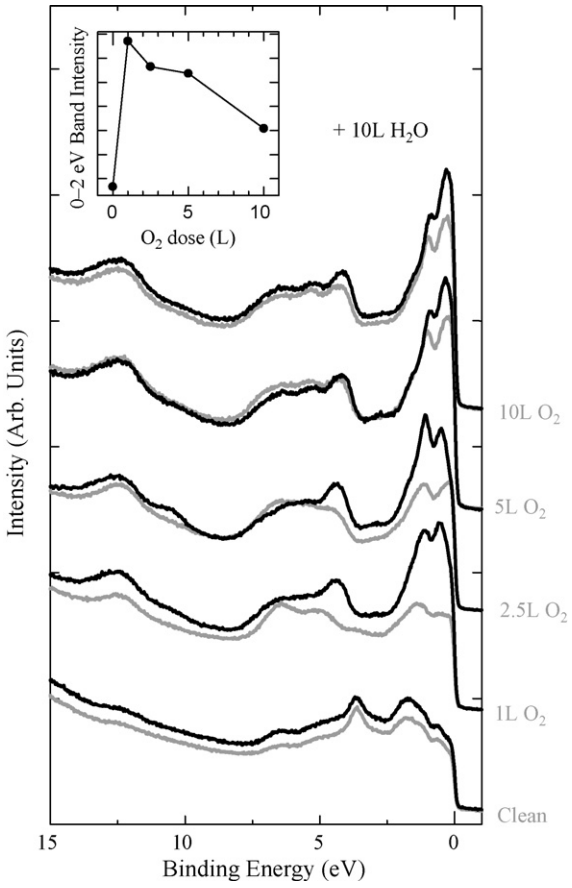

Fig. 1. Normal-emission spectra of Mo_2C(0 0 0 1) exposed to various amounts of O_2 (gray lines) and of the surface subsequently exposed to 10 L of H_2O (solid lines). The incidence angle of the light is 45° and $h\nu$ = 30 eV. The area intensities of the H_2O-induced emissions at 0–2 eV are plotted as a function of O_2 exposure in the inset.

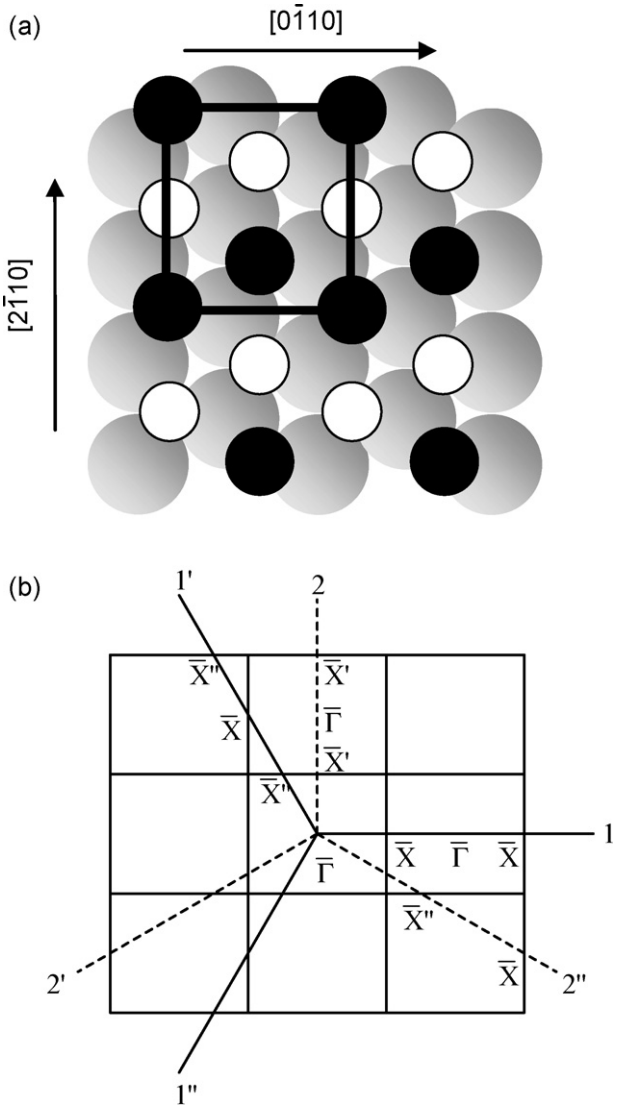

Fig. 2. (a) The adsorption model of the O/Mo_2C(0 0 0 1) system. The gray, open and filled circles represent the second-layer Mo atoms, the first-layer C atoms, and the adsorbed O atoms, respectively. (b) The surface Brillouin zones for the (1 × 1) orthorhombic lattice. The directions probed by ARPES measurements along $\bar{\Gamma}\bar{X}$ (lines 1, 1′, 1″) and $\bar{\Gamma}\overline{X'}$ (lines 2, 2′, 2″) are shown as solid and dashed lines, respectively.