



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Vacuum 80 (2005) 204–207

VACUUM

SURFACE ENGINEERING, SURFACE INSTRUMENTATION
& VACUUM TECHNOLOGY

www.elsevier.com/locate/vacuum

Angle-resolved XPS investigations of the interaction between O₂ and Mo₂C/Mo(1 0 0)

László Óvári*, János Kiss

Reaction Kinetics Research Group of the Hungarian Academy of Sciences, University of Szeged, P.O. Box 168, H-6701 Szeged, Hungary

Abstract

The interaction of oxygen with a carbidized Mo(100) surface was investigated at different temperatures (300 K–1000 K) with-angle resolved X-ray photoelectron spectroscopy. A carbide overlayer with a homogeneous Mo₂C stoichiometry (down to the information depth of XPS) was produced by the high-temperature decomposition of C₂H₄ on Mo(1 0 0).

O₂ adsorbs dissociatively on Mo₂C/Mo(1 0 0) at room temperature. Oxidation of the carbide at 800 K results in the partial removal of carbon and leads to sub-surface O migration, accompanied by the appearance of highly oxidized Mo states. Raising the O₂ adsorption temperature to 900 K decreased the carbon content further, without affecting the amount and the distribution of adsorbed O. Performing the oxidation at 1000 K led to an even more effective removal of carbon, but the oxygen content of the surface region was also reduced.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Angle-resolved X-ray photoelectron spectroscopy; Oxidation; Molybdenum carbide

1. Introduction

The favourable mechanical, electronic and chemical properties of transition metal carbides have attracted considerable attention in different fields, such as material science and catalysis [1,2].

The formation and structure of carbide overlayers, generally prepared by the high-temperature decomposition of C₂H₄ on group IVB–VIB transition metal single-crystal surfaces, have been

thoroughly investigated [1]. Similarly, the oxidation of molybdenum surfaces is well documented [3–6]. Oxygen adsorbs dissociatively on α -Mo₂C(0 0 0 1) at 150–300 K [7,8]. At higher temperatures the formation of CO is observed [8], but migration of O into the bulk of the carbide has also been assumed [7,8].

Recently, we investigated the carbidization of the Mo(1 0 0) surface by C₂H₄ decomposition, and also the high-temperature oxidation of the carbide up to 1265 K [9]. The aim of the present work was the characterization of the carbidized Mo(1 0 0) surface as regards the stoichiometry and the C

*Corresponding author. Tel./fax: +36 62 420 678.

E-mail address: ovari@chem.u-szeged.hu (L. Óvári).

concentration profile, and also to obtain a more elaborate picture of its interaction with oxygen at different temperatures.

2. Experimental

Angle-Resolved X-ray Photoelectron Spectroscopy (ARXPS) experiments were performed in a UHV system (base pressure 5×10^{-10} mbar), using an Al K_{α} X-ray anode and a Leybold EA10/100 hemispherical analyser, applying 50 eV pass energy. The sample could be tilted for angle resolved XPS measurements, but the anode and the analyser were at fixed positions. The binding energy scale was referenced to the position of the Mo(3d_{5/2}) peak of the carbide, taken to be 227.95 eV [10,11]. Scofield photoelectric cross-sections [12] and inelastic-mean-free-paths (imfp) obtained by the method of Gries [13] were used for composition and coverage calculations. XP peaks were fitted using Gauss–Lorentz functions, after background subtraction [14].

The Mo(100) single crystal was cleaned by heating in oxygen, followed by argon ion bombardment and annealing at 1500 K. The remaining oxygen impurities could be removed almost completely during carbidization.

3. Results and discussion

A carbide overlayer was prepared on Mo(100), using a similarly to the method of Schöberl [15], by repeating C₂H₄ adsorption (50 L) at 900 K and annealing in vacuum to 1265 K until the C content reached saturation. The C(1s) peak at normal detection ($\theta = 90^\circ$) was found at 282.95 eV (Fig. 1A) that is characteristic of carbides [11]. The C feature, however, had a small tail toward higher binding energies, which appeared as a shoulder (284.3 eV) at low take-off angles, indicating the presence of some graphite contamination. At $\theta = 23^\circ$ emission angle a small, but highly reproducible downward shift (~ 0.1 eV) of the carbon peak maximum was observed, indicating a somewhat different state of the first carbon layer.

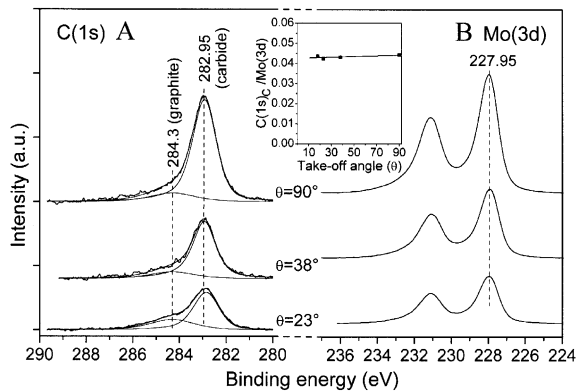


Fig. 1. C(1s) and Mo(3d) regions of the X-ray photoelectron spectra of the carbidized surface collected at different take-off angles (θ). Inset: peak area ratio of the carbidic C(1s) component and the Mo(3d) doublet as a function of θ .

The position of the Mo(3d) doublet, however, did not shift at glancing emission (Fig. 1B).

The peak area ratio of the carbidic C(1s) component and the Mo(3d) doublet was independent of θ (Fig. 1), clearly indicating that C is dispersed homogeneously in the crystal down to the information depth of XPS at normal emission. Based on the homogeneous C distribution, the C/Mo atomic ratio was calculated to be 0.48 indicating Mo₂C stoichiometry. The information depth was estimated to be 5.7 nm (three times the imfp in Mo₂C).

To learn more about the interaction of oxygen with the carbide overlayer, detailed XPS measurements were performed, with $\theta = 23^\circ$ and $\theta = 90^\circ$ emission angles (Figs. 2 and 3). Oxidative treatments caused similar, but more pronounced changes at $\theta = 23^\circ$ take-off angle than at normal emission. For this reason we describe the results obtained at $\theta = 23^\circ$ more thoroughly. Up to saturation (12 L) O₂ exposure at room temperature resulted in a small (0.1 eV) shift of the C(1s) peak toward higher binding energies, but its intensity did not change (Fig. 2). Similarly, a small upward shift and a slight broadening of the Mo(3d) doublet were observed due to O₂ adsorption at 300 K. This feature could be fitted with three components: a carbidic (227.95 eV), a slightly perturbed (228.2 eV) and a weak strongly perturbed (229.3 eV). The latter state is tentatively

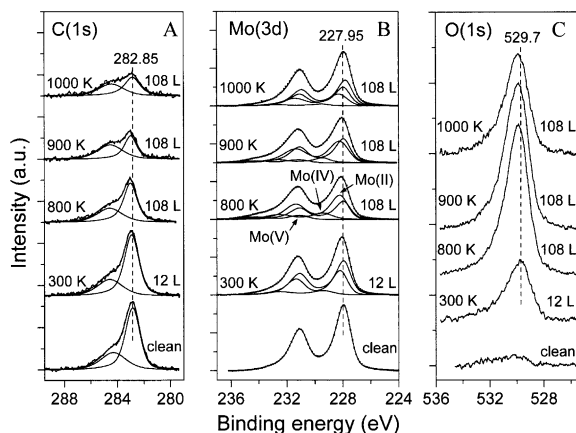


Fig. 2. C(1s), Mo(3d) and O(1s) windows of the XP spectra recorded after different treatments of Mo₂C/Mo(100) in O₂, taken at $\theta = 23^\circ$.

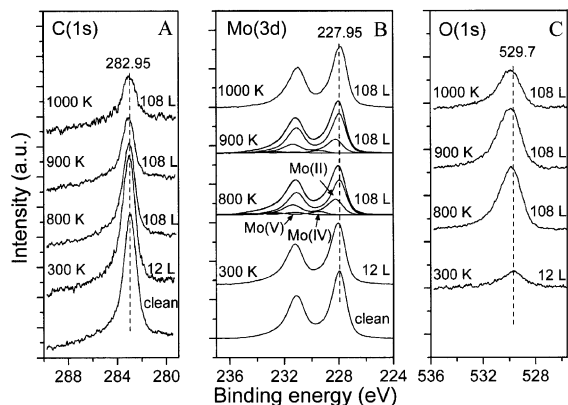


Fig. 3. C(1s), Mo(3d) and O(1s) windows of the XP spectra recorded after different treatments of Mo₂C/Mo(100) in O₂, taken at $\theta = 90^\circ$.

assigned to Mo sites coordinating more O atoms. Room temperature oxygen adsorption induced the appearance of an O(1s) peak at 529.7 eV, characteristic of chemisorbed (atomic) or oxidic oxygen [5,16]. We assume that adsorbed oxygen atoms are located exclusively on the topmost layer at 300 K.

A higher amount of oxygen (108 L) at $T_{\text{ads}} = 800$ K led to a substantial decrease in the carbidic C(1s) component, indicating that C was partially removed by O, possibly in the form of CO. The Mo(3d) area was also diminished due to O₂ adsorption at 800 K, but only to a smaller extent.

It is caused by the dramatic increase in the amount of adsorbed O, acting as a reaction partner for the Mo(3d) and C(1s) photoelectrons. Moreover, oxidized (Mo(II) at 228.25 eV, Mo(IV) at 229.5 eV and possibly Mo(V) at 231.1 eV) molybdenum states appeared [5,16,17]. As regards the assignment of Mo(IV) and Mo(V) peaks, some authors claimed that both the Mo(3d_{5/2}) peak at ~ 229.5 eV and that at ~ 231 eV belong to Mo(IV) in MoO₂ [5,16]. In any case, one part of Mo atoms was oxidized in our case at least to Mo(IV).

The O(1s) peak area obtained at $\theta = 23^\circ$ after 800 K O₂ adsorption was 2.3 times higher than at room temperature. The ratio of the corresponding O(1s) areas collected at $\theta = 90^\circ$ was much higher (3.8), indicating that subsurface migration of oxygen. O is dispersed inhomogeneously at 800 K, because the O(1s)/Mo(3d) area ratio was two times higher at $\theta = 23^\circ$ than at $\theta = 90^\circ$.

Raising the adsorption temperature to 900 K resulted in a further decrease of the carbon content, but the amount of adsorbed oxygen changed only slightly both at $\theta = 23^\circ$ and $\theta = 90^\circ$, implying an oxygen distribution similar to that produced at 800 K. Accordingly, the Mo(3d) lineshape observed at 900 K was very similar to that found at 800 K.

Removal of carbon was even more pronounced at $T_{\text{ads}} = 1000$ K, but the oxygen content was much smaller, probably due to the higher carbon mobility at this temperature, supplying continuously a reaction partner for oxygen. Accordingly, the Mo(IV) component almost disappeared and a new component appeared at 227.8 eV, near the position of metallic Mo [10], assigned in our case to Mo atoms coordinating a few C and a few or no oxygen at all.

4. Conclusions

It was shown by ARXPS measurements that a homogeneous Mo₂C overlayer down to the information depth of XPS was produced on Mo(100) by the high-temperature decomposition of C₂H₄.

O₂ adsorbs dissociatively on Mo₂C/Mo(100) at room temperature. Oxidation of the carbide

overlayer at 800 K resulted in the partial removal of carbon and in subsurface O migration, accompanied by the appearance of highly oxidized Mo states. Raising the O₂ adsorption temperature to 900 K decreased the carbon content further, without affecting the amount and the distribution of adsorbed O.

Acknowledgements

This work was supported by Grant OTKA D38489 and T46351.

References

- [1] Chen JG. *Chem Rev* 1996;96:1477—and references therein.
- [2] Solymosi F, Németh R, Óvári L, Egri L. *J Catal* 2000;195:316.
- [3] Minni E, Werfel F. *Surf Interface Anal* 1988;12:385.
- [4] Kim SH, Stair PC. *Surf Sci* 2000;457:L347—and references therein.
- [5] Schroeder T, Zegenhagen J, Magg N, Immaraporn B, Freund H-J. *Surf Sci* 2004;552:85.
- [6] Smuddle GH, Stair PC. *Surf Sci* 1994;317:65.
- [7] Edamoto K, Sugihara M, Ozawa K, Otani S. *Surf Sci* 2004;561:101.
- [8] St.Clair TP, Oyama ST, Cox DF. *Surf Sci* 2000;468:62.
- [9] Óvári L, Kiss J, Farkas AP, Solymosi F. *Surf Sci* 2004;566–568:1082.
- [10] Brainard WA, Wheeler DR. *J Vac Sci Technol* 1978;15:1800.
- [11] St.Clair TP, Oyama ST, Cox DF, Otani S, Ishizawa Y, Lo RL, et al. *Surf Sci* 1999;426:187.
- [12] Scofield JH. *J Electron Spectroscop Related Phenomenon* 1976;8:129.
- [13] Gries WH. *Surf Interface Anal* 1996;24:38.
- [14] Shirley DA. *Phys Rev B* 1972;5:4709.
- [15] Schöberl Th. *Surf Sci* 1995;327:285.
- [16] Brox B, Olefjord I. *Surf Interface Anal* 1988;13:3.
- [17] Grant JL, Fryberger TB, Stair PC. *Surf Sci* 1985; 159:333.