Available online at www.sciencedirect.com
ScienceDirect
Surface Science 601 (2007) 3383–3394
SURFACE SCIENCE
www.elsevier.com/locate/susc

Surface structure and composition of the missing-row reconstruction of $VC_{0.8}$(1 1 0): A LEED, GIXRD and photoemission study

Y. Gauthier [a,*], I. Zasada [b], M. De Santis [a], V. Langlais [a,c], C. Virojanadara [d,e], L.I. Johansson [e]

[a] *Institut Néel, UPR 2940 – CNRS, 25 av. des Martyrs, BP 166, 38042 Grenoble, France*
[b] *Solid State Physics Department, University of Lodz, ul. Pomorska 149/153, 90-236 Lodz, Poland*
[c] *Universitat Autonoma de Barcelona, Departamento de Fisica, 08193 Bellaterra, Barcelona, Spain*
[d] *Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany*
[e] *Department of Physics, Linköping University, S-58183 Linköping, Sweden*

Received 26 March 2007; accepted for publication 8 June 2007
Available online 13 June 2007

Abstract

Low energy electron diffraction, grazing incidence X-ray diffraction and photoemission were used to decipher the detailed structural arrangement and chemical composition of the surface region of a transition metal carbide, $VC_{0.8}$(1 1 0). In agreement with previous scanning tunneling microscopy (STM) studies, we find that the surface reconstructs with a ridge-and-valley grating structure along the $[1\bar{1}0]$ direction resulting from {0 0 1} faceting for the (3×1) and the (4×1) phases.

Both superstructures terminate on the vacuum side with a nearly stoïchiometric VC region due to C segregation, in contrast with the conclusions drawn from this previous STM study. However, the present experiments clearly show that these phases are metastable, and slow cooling results in a (1×1) surface, which is highly C depleted, similarly to the (1 0 0) face.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Carbide; Low energy electron diffraction; Vanadium; Surface relaxation and reconstruction; Surface segregation; Surface X-ray diffraction; Vacancy; Photoemission

1. Introduction

Transition metal carbides (TMC) are mostly known for their outstanding wear resistance and for their chemical stability in a hostile environment that makes them perfectly fit for catalytic reactors. Structural data and surface composition have been derived for a number of surfaces with (1 0 0) or (1 1 1) orientation: NbC [1,2], TiC [3–5], ZrC [5,6], HfC [7], TaC [8] and VC [9,10]. These surfaces exhibit flat and unreconstructed structures, with the exception of $VC_{0.8}$(1 1 1) [9,11]. On the contrary, the (1 1 0) face of TMCs tends to reconstruct with a ridge-and-valley morphology. This is observed for TiC [12], TaC [13] and probably NbC [2]. Nevertheless, in spite of the considerable data drawn from these previous studies, the knowledge is only partial regarding this type of compounds and particularly for $VC_{0.8}$(1 1 0) (see review of Ref. [14]).

The fcc (1 1 0) surfaces of noble metals (Ir, Pt, Au) that reconstruct with a missing row structure (MR in the following) offer a ridge-and-valley morphology providing good opportunities to grow metallic nanowires along the grooves for magnetic and/or catalytic applications. They may also be considered as templates for self-organised molecular films.

The (1 1 0) face of carbides and nitrides with NaCl structure stabilizes in a similar manner, yielding larger and deeper valleys and much larger metal-metal distances. These distances are 2–9% bigger than for Au and, for instance,

---

[*] Corresponding author.
E-mail address: yves.gauthier@grenoble.cnrs.fr (Y. Gauthier).

0039-6028/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2007.06.012

up to ∼15% than for Ir. While Ir, Au and Pt(110) reconstruct with (1 × 2) MR structures, $VC_{0.8}$, NbC and TaC(110) exhibit (3 × 1) and (4 × 1) mixtures, (4 × 1) and (5 × 1) mixtures and average (6 × 1) periodicities, respectively.

These larger troughs can be exploited to grow molecular layers with unusual stacking, orientation and ordering. Such tuneable environments and molecular stacking may thus be adapted for metallic clusters to be hosted by the molecules. In addition, these wider valleys offer the opportunity to build up metallic wires with tuneable sections and large separation. An extra parameter is the amount of bulk C vacancies that is accompanied by a variable surface layer content and a variable interatomic distance: the final vacancies amount on "C-sites" may favour or inhibit adsorption and, in turn, drastically modify the resulting arrangement of adsorbed species. A further advantage of TMCs over metallic substrates is their much higher mechanical wear resistance and their temperature stability that make easier to form and order surface films and wires without surface alloying and bulk diffusion.

As a preliminary step towards industrial applications, a better knowledge of these surfaces is required. The present study is devoted to the first full determination of the surface structure of the (110) face of vanadium carbide, and more particularly of the atomic arrangement and composition of the facets that form the ridge-and-valley structure. Low energy electron diffraction (LEED) and grazing incidence X-ray diffraction (GIXRD), were used in parallel to obtain the details of the surface layers. Special attention was paid to the density of C and/or vacancy that do not show up in the scanning tunneling microscopy (STM) images [11]. Photoemission experiments were also made to reveal differences in the composition from core level and valence band spectra collected for the differently reconstructed surfaces.

The paper is organised as follows: we first describe the details of the experiments along with the known behaviour of VC with temperature, in connection with the vacancy amount and with surface reconstruction. The next section reports on the LEED calculations and on the analysis of the (3 × 1) phase. In the fourth section we describe the GIXRD calculations for the (3 × 1) and (4 × 1) structures. Section 5 describes the Photoemission experiments. The results are discussed in Section 6. Section 7 draws the main conclusions.

2. Experiment

2.1. Experimental details

The GIXRD, LEED and Photoemission measurements were performed in separate chambers with base pressures in the low 10^{-10} mbar range or below. All are equipped with the usual means for surface preparation and cleanliness control by Auger spectroscopy (AES).

The GIXRD set-up (BM32 line, ESRF, Grenoble) consists of an UHV chamber mounted on a z-axis diffractometer described elsewhere [15]. The GIXRD measurements were performed at 18 keV photon energy, which allows a large portion of the reciprocal space to be explored. Diffraction rods were measured at an incidence angle of 0.4° from the surface of the crystal.

The photoemission experiments were performed at the MAX synchrotron radiation laboratory I311 beamline (Lund), which is equipped with a modified SX-700 monochromator and an end station built up around a large hemispherical Scienta electron analyzer. Normal emission and an incidence angle of 40° were chosen as the experimental geometry. A total energy resolution (monochromator + analyser) of 100–300 meV for photon energies from 330 to 600 eV was selected for the C 1s and V 2p core levels, and valence bands were collected at an energy resolution of about 150 meV. The same surface preparation procedures as described below were used and the surface cleanliness and order were checked by photoemission and LEED.

The LEED (performed in Linköping) and GIXRD experiments were performed on freshly polished samples, cut from the rod that was used for previous studies of this carbide [9–11]. The photoemission study was conducted on the same sample as for the X-ray diffraction analysis. After introduction in the UHV chambers, the samples were flash annealed at ∼1100 °C in order to re-crystallize the surface perturbed by polishing. A clean surface was then routinely obtained by cycles of argon ion bombardment (typically 20 min, 6–17 μA, 5×10^{-6}–2×10^{-4} mbar, 1–1.5 kV) followed by 5 min annealing at temperatures in the range 850–1150 °C. Impurities (mainly S, in the initial stages, and O) were kept below the AES detection level for the final measurements on the clean surfaces. Additionally, after 4 h of measurements, photoemission spectra did not show any noticeable pollution. Furthermore, superlattice reflections were measured periodically during the GIXRD data collection (more than 12 h compared to 10 min for LEED). These reflections did not show any change in shape and decreased only a few percent in intensity, indicating a clean stable structure.

In the following, superstructures and reciprocal lattice positions are defined by the usual Miller indices (HKL) in a unit cell with $\mathbf{A}_1$ and $\mathbf{A}_2$ in the surface plane and $\mathbf{A}_3$ perpendicular to it: $\mathbf{A}_1 = (a/2) \times [1\bar{1}0]$, $\mathbf{A}_2 = a \times [001]$ and $\mathbf{A}_3 = (a/2) \times [110]$ ($a = 4.148$ Å being the bulk lattice constant of $VC_{0.8}$). The atomic layers are numbered from surface (layer 1 or top layer) to bulk.

The periodicity of the surface was controlled at room temperature by LEED, except in the X-ray chamber where reflection high-energy electron diffraction is available. In the latter chamber, we used GIXRD to follow the variations with temperature and to ensure that the ($n \times 1$) (n = integer) structures were well established, looking for the maximum intensity of the corresponding superstructure peaks: the heating power supply was then switched off abruptly to quench the structure.

Download English Version:

https://daneshyari.com/en/article/5425865

Download Persian Version:

https://daneshyari.com/article/5425865

Daneshyari.com