

## Beryllium overlayers on Mo(1 1 2) and Mo(0 1 1) surfaces

A.G. Fedorus\*, A.A. Mitryaev, A.G. Naumovets

*Institute of Physics, Natl. Academy of Sciences of Ukraine, Prospect Nauki 46, UA-03680, Kyiv-28, Ukraine*

### ARTICLE INFO

#### Article history:

Received 14 July 2011

Accepted 12 November 2011

Available online 22 November 2011

#### Keywords:

Low-energy electron diffraction (LEED)

Work function

Phase transitions

Surface structure

Surface alloys

Beryllium

Molybdenum

Materials for thermonuclear reactors

### ABSTRACT

Low-energy electron diffraction, Auger electron spectroscopy and contact potential difference methods have been used to study formation of Be overlayers on the Mo(1 1 2) and (0 1 1) surfaces in the temperature range from  $T = 78$  K up to the beginning of Be desorption. At a coverage  $\theta = 1$ , where  $\theta$  is defined as the ratio between concentrations of adatoms and surface substrate atoms, overlayers were found to be pseudomorphic on both the substrates. Various types of close-packed Be structures were observed at  $\theta > 1$ . Annealing of the Mo samples covered with Be caused not only overlayer ordering, but also a partial solution of Be in the near-surface layer of Mo and creation of a surface alloy. It is inferred that the work function changes, positive on Mo(1 1 2) up to 0.4 eV and negative on Mo(0 1 1) down to  $-0.6$  eV, are caused mainly by changes in surface roughness while the contribution of polarization of the Be–Mo adsorption bond seems to be only minor.

© 2011 Elsevier B.V. All rights reserved.

### 1. Introduction

Investigations of adsorbed monolayers give evidence of essential change in the electronic state of atoms under adsorption, which results in a variation of the work function and heat of adsorption as well as in formation of many peculiar submonolayer superstructures due to specific adatom interactions [1–3]. In particular, adatoms of alkaline-earth metals usually acquire a partial positive charge causing lateral repulsion between adatoms and a strong reduction of the work function. However, beryllium, which also belongs to the group of alkaline-earth elements, does not conform to such a rule. This follows from the studies of Be submonolayers adsorbed on W [4–10]. Indeed, field emission microscopy revealed that the work function changes caused by Be have different signs on different planes of a single-crystal tungsten microtip [4]. In later experiments on tungsten macrocrystals, it was found that the work function changes induced by Be on the (1 1 2) plane are positive rather than expected negative [5], and no long-period Be adsorbate superstructures were observed both on the (0 1 1) and (1 1 2) W surfaces [7,8]. However, those experiments were performed at and above room temperature and it could not be excluded that the superstructures might form at lower temperatures, below the temperature of an order–disorder transition. Actually, for many relevant adsorption systems, order–disorder transitions proceed at rather low temperatures [11–14].

To shed more light on the electron state of Be adatoms and governing factors in formation and properties of Be overlayers, we extended

the investigation of the work function changes and film structures to the adsorption systems Be/Mo(1 1 2) and Be/Mo(0 1 1). In this study we pursued three main goals.

- (i) We intended to establish experimentally whether a substantial dipole–dipole interaction exists between Be adatoms. This information was extracted from analysis of Be adlayer structures observed in a wide temperature range, including temperatures far below room temperature.
- (ii) The next subject of our study was the work function variation caused by beryllium adsorption. Work function is an important characteristic of surface which determines its electron and ion emission properties, affects chemical and electrochemical reactions (including catalysis, corrosion etc.) as well as processes at various interfaces. We recorded changes in the work functions on the Mo(1 1 2) and (0 1 1) surfaces at various coverages and temperatures. These results, being compared with the corresponding data obtained on tungsten, allow assessment of the role of atomic and electronic structure of substrate in the work function changes.
- (iii) Finally, we searched for signs of surface alloying between beryllium and molybdenum and also investigated other phase transitions in Be adlayers in order to get more insight into adsorption interactions in various metal-on-metal systems.

This study has also a practical motivation. Beryllium finds many applications in nuclear and aerospace industries, high-energy particle physics, electronics etc. In particular, it is worth noting that investigation of the formation of Be films on refractory metals is important for solving the problem of the first wall in nuclear fusion reactors [10,15]

\* Corresponding author. Tel.: +380 44 525 7826; fax: +380 44 525 1589.  
E-mail address: [fedorus@iop.kiev.ua](mailto:fedorus@iop.kiev.ua) (A.G. Fedorus).

and also for constructing high-reflectance multilayer mirrors for the ultraviolet range [16].

In this work, we pay the primary attention to adsorption of Be on the Mo(1 1 2) substrate. The physical interest to this system arises due to small atomic radius of Be and existence of atomic channels on the Mo(112) surface where Be adatoms can get “hidden”. The system Be/Mo(0 1 1) is studied in less detail.

## 2. Experimental

Our experimental setup has been described in detail elsewhere [17,18]. In brief, the experiments were performed in an ultra-high vacuum chamber ( $10^{-11}$  Torr) equipped with a 4-grid LEED system, a cylindrical Auger electron analyzer, and a retarding field CPD (contact potential difference) technique. The Auger electrons were excited by a glancing electron beam. The samples ( $6 \times 4 \times 0.5$  mm<sup>3</sup> in size) were cut from a Mo single crystal. The temperature was measured with a W-5%Re/W-20%Re thermocouple spot-welded to the sample. The samples could be cooled either with liquid nitrogen down to 78 K, or with liquid helium down to 5 K, and heated resistively and by electron bombardment up to 2300 K.

An atomic-beam source of Be consisted of a small plate of beryllium metal spot – welded to a tungsten heating loop. AES was used to check the cleanliness of Mo surface and the chemical identity of adsorbate. Within a 1% accuracy, only Be and Mo Auger peaks were recorded in most experiments.

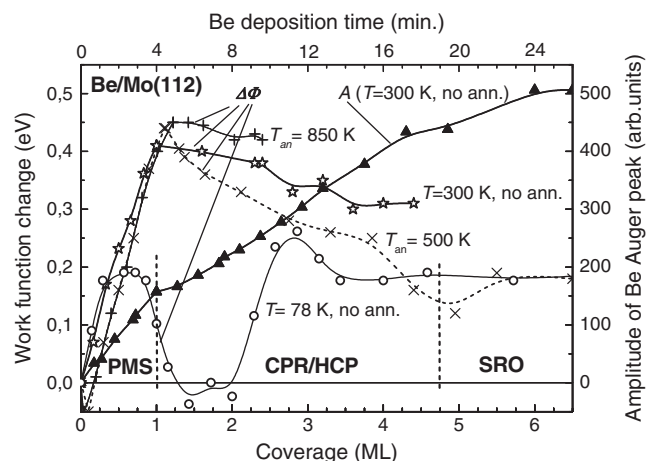
The coverage  $\theta$  is defined in this work as the ratio of the concentration of Be adatoms  $n_{\text{Be}}$  to that of surface atoms on the Mo(1 1 2) and (0 1 1) substrates  $n_s$  ( $8.3 \times 10^{14}$  and  $14.3 \times 10^{14}$  cm<sup>-2</sup> respectively). The adatom concentration was determined, using work function measurements, Be deposition time  $t_{\text{Be}}$  and Auger amplitude data. In turn, the work function change  $\Delta\phi$  and Auger amplitude  $A$  were calibrated with respect to coverage relying on a well-pronounced break in the  $A$  versus  $t_{\text{Be}}$  curve attributed to the geometrical monolayer (see also Refs. [7,8]), which was quantitatively related to the coverage by means of LEED ( $\theta_M = 1$ , see Section 3.1.1).

In most cases Be was deposited on the substrate kept at room temperature, but could be lowered down to 78 K or 5 K. Thereafter the adlayers were annealed. Each annealing step consisted of a sharp temperature rise to a certain  $T_{\text{an}}$ , keeping this temperature for 2–3 s, and a slow (5 min) cooling down to room temperature. The CPD, LEED and AES data were taken first from as-deposited overlayers and then from the same overlayers annealed to successively higher temperatures. The non-overlapping Auger peaks of Be (in the vicinity of 104 eV) and Mo (186 eV) were used for quantitative estimates of the coverage. LEED patterns were mostly observed at the electron beam energy  $E = 65$  eV, providing a sufficiently high intensity of the adlayer diffraction spots. Spot location in the LEED patterns is expressed in units of the surface Brillouin zone (SBZ)  $a_{hkl}^{-1}$ , where  $a_{hkl}$  is the 2D lattice period for corresponding direction  $hkl$ . To determine the location of LEED spots with an appropriate accuracy ( $\pm 0.01$  SBZ un.), the LEED patterns in the case of Mo(1 1 2) substrate were processed by MATLAB image tools including filtering, smoothing and calibration via comparison to well-known patterns. The  $c(4 \times 2)$  O/Mo(1 1 2) pattern was used for calibration [19]. An accuracy of  $\pm 0.05$  SBZ un. was achieved in the case of Mo(0 1 1) substrate.

## 3. Results and their interpretation

### 3.1. Beryllium on Mo(1 1 2)

Fig. 1 presents an overview of changes in the work function, Be Auger amplitude and surface structure in the course of Be deposition at a constant rate. The data taken at different deposition/annealing temperatures in the range of 78–850 K corresponded to various



**Fig. 1.** Coverage dependence of Be Auger amplitude  $A$  (right scale) and work function change  $\Delta\phi$  (left scale) at various deposition or annealing temperatures. Overlayer structures: PMS – pseudomorphic, CPR – close-packed rows along the troughs, HCP – hexagonal close-packed across the troughs, SRO – short-range order.

successions of overlayer structures recorded by LEED, and Fig. 1 summarizes the most typical results. Upon annealing above 850 K, only poorly ordered structures were found. The respective data are not shown in Fig. 1 and will be discussed below. The whole coverage range  $\theta$  can be divided into three parts according to formation of distinct structures marked in Fig. 1. They are considered in detail in further subsections. The relevant LEED patterns are given in Fig. 2 and their suggested structure interpretation in Fig. 3. The whole set of LEED extra spots is determined by linear combinations of the reciprocal lattice vectors of adsorbate and substrate [20].

#### 3.1.1. Structure of Be submonolayers and work function changes on Mo(1 1 2)

During deposition at  $T = 78$  K, no extra LEED features from overlayer appeared within the deposition time  $t_{\text{Be}} \leq 8$  min corresponding to  $\theta \leq 2$ . Most substrate LEED beams decayed slightly with  $\theta$  growth or did not appreciably change (Fig. 4a), indicating diffraction from the substrate partially screened by a non-equilibrated *disordered overlayer*.

Overlayer ordering was attained already under annealing to room temperature. Indeed, comparing the character of the work function change at different deposition or annealing temperatures (Fig. 1), one can see that stabilization of the shape of  $\Delta\phi(\theta)$  dependence in the examined coverage range occurs at  $T_{\text{an}} \approx 300$  K. This observation was considered as a sign of sufficient annealing, which provided adatom mobility necessary for ordering. At the same time, the first stage of deposition (within  $t_{\text{Be}} \leq 4$  min) with subsequent annealing did not produce any extra LEED features (in addition to those from the substrate, cf. Fig. 2a and b). This can be attributed to the formation of a pseudomorphic overlayer (PMS, see Fig. 3a). Beyond  $t_{\text{Be}} = 4$  min, LEED patterns appeared, which contained extra features (Fig. 2c and d), signaling completion of the pseudomorphic monolayer ( $\theta = 1$ ) and transition to a closer overlayer structure shown in Fig. 3b and c. An assignment of PMS completion based on the LEED observation can be reliable if the adlayer structure is sufficiently ordered. To prove this, we studied coverage dependences of LEED intensities. Investigation of LEED intensities versus  $\theta$  at various annealing temperatures (see Fig. 4) showed that annealing does provide formation of a pseudomorphic Be layer. Actually, at  $T_{\text{an}} = 300$ –500 K the intensity of some LEED beams (which can be identified as secondary Bragg peaks at  $E = 65$  eV) was found to rise within the  $\theta = 0$ –1 range, indicating diffraction both from the ordered overlayer and substrate. Just such a behavior of LEED beams from covered surfaces was predicted for pseudomorphic overlayers [21,22]. Thus the surface

Download English Version:

<https://daneshyari.com/en/article/5423093>

Download Persian Version:

<https://daneshyari.com/article/5423093>

[Daneshyari.com](https://daneshyari.com)