



## Full Length Article

## Honeycomb BeO monolayer on the Mo(112) surface: LEED and DFT study

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## ABSTRACT

From the combined experimental and theoretical investigations, we suggest the formation of a honeycomb structure of BeO monolayer on the Mo(112) surface. This structure is matched to the substrate Mo(112), thus giving the  $(1 \times 1)$  LEED pattern, and its formation is confirmed also by DFT calculations and work function measurements. While a free BeO monolayer is dielectric, the BeO/Mo(112) system is definitely metallic as follows from the bands crossing  $E_F$  and significant density of states at  $E_F$ . The honeycomb BeO monolayer is bound to the Mo(112) surface through O atoms situated atop Mo atoms of the surface rows. A substantial rigidity of the BeO monolayer leads to the appearance of empty space above the Mo(112) surface furrows, which may be filled by some gas or water molecules. Hence, this layered system can be very attractive in various applications where porous materials are explored (e.g. for hydrogen storage purposes).

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## 1. Introduction

Adsorbed layers of metal oxides can dramatically change electronic and catalytic properties of surfaces [1–3]. A detailed understanding of the interaction of the oxides with transition metal surfaces is therefore essential for a further progress in the development of layered and nanostructure materials with desirable properties. The BeO, in particular, is a wide band gap semiconductor, which due to special magnetic and optical properties, high melting point, thermal conductivity, and a high electrical resistance [2–6], has been widely used in various current industrial instruments.

The structural and electronic properties of a bulk BeO and BeO surfaces, as well as of nanotubes, free layers, and ribbons were studied theoretically in a number of papers [7–18]. It was shown that BeO crystallizes in the wurtzite phase, which is more energetically favorable than the zinc-blende phase [8,9]. Then, the possibility to build a monolayer BeO sheet with the graphene-like honeycomb

structure was supported by promising achievements in the fabrication of BeO layers [10] and confirmed by means of DFT calculations [11–14].

The Mo(112) surface is formed by atomic rows separated by furrows, thus providing a unique template for various surface studies due to strongly anisotropic surface relief. The discovery of a great catalytic ability with respect to CO oxidation of the Au films deposited on  $\text{TiO}_x/\text{Mo}(112)$  substrate [19] initiated a number of related studies of equilibrium structures and surface electronic properties of adsorbed layers on the Mo(112) [20–25], and, in particular, of the Au/Mo(112) system [26], for which a high catalytic activity was predicted. A recent advance in studies of the Mo(112) surface includes, apart from detailed band structure calculations and structural relaxations, complex theoretical-experimental studies of many-body phenomena such as the electron-phonon coupling and indirect lateral interaction, mediated by Friedel oscillations of screening electrons [27–31].

Our recent studies of oxygen adsorption on the  $\text{Be}(1 \times 1)$ -covered Mo(112) by LEED, Auger Electronic Spectroscopy (AES), and Contact Potential Difference (CPD) methods [22–25] suggested the formation of BeO species on the surface, which was explained as a non-activated reaction of Be oxidation [32]. In the present paper,

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basing on LEED, AES, CPD, and DFT study, we suggest the formation of a honeycomb structure of the BeO adsorbed layer on Mo(112), pertinent also to monolayers of other II–VI oxides.

## 2. Methods

The low-energy electron diffraction (LEED), Auger electron spectroscopy (AES) and retarding-field contact potential difference (CPD) techniques were used to gain information on the atomic structure and elemental composition of the surface, the work function changes, and the changes in the electronic state of surface Mo, Be and O atoms resulting from the adsorption and surface chemical processes. The Mo(112) sample was prepared as a plate  $4 \times 6 \times 0.5 \text{ mm}^3$  and was equipped with a W-5%Re/W-20%Re thermocouple spot-welded to the plate. Beryllium was evaporated from a small Be plate supported by a tungsten heating loop. Before oxygen adsorption, the beryllium-covered Mo samples were annealed at 400 K for 10 s. Oxygen was let in the chamber from a chemical source using the decomposition of CuO contained in a resistively heated platinum tube. The listed experimental procedures (including cleaning the Mo(112) substrate, depositing the Be film, annealing the sample) were carried out in the ultra-high vacuum chamber equipped with a field emission projector monitoring possible presence of active residual gases at the level of  $10^{-9}$  Pa. Further details of the experimental techniques used in the present study can be found in [23–25].

The semirelativistic DFT calculations using the supercell model and Troullier-Martins [33] norm-conserving pseudopotentials were carried out with the ABINIT [34] set of programs. The exchange-correlation was treated within either LDA [35] or GGA/RPBE (revised Perdew–Burke–Ernzerhof [36]) functional. The adopted 0.002 Ha convergence of total energies was achieved for the energy cutoff 36 Ha and  $6 \times 4 \times 1$  Monkhorst-Pack [37] lattice of k-points.

After a standard Broyden structural optimization of the Mo(112) slabs, BeO layers were deposited on one side of the slab, and positions of all atoms were optimized until the forces on atoms converged to less than 0.02 eV/Å. Hence, the binding energies were determined taking into account the relaxation of clean surfaces as well as the adsorption-induced surface reconstruction. The binding energies calculated for BeO on the 5 and 7-layer Mo(112) slabs were found to be essentially the same, and therefore, in the present study, they were calculated for 7-layer Mo(112) slabs.

The lattice period of bulk bcc Mo, determined by optimization with respect to the total energy was 3.16 Å, consistent with the 3.15 Å experimental value. The lattice periods of the optimized unit cell of the BeO in wurtzite structure, were  $a = 2.716 \text{ Å}$  and  $c = 4.412 \text{ Å}$ , also consistent with experimental values ( $a = 2.6979 \text{ Å}$ ,  $c = 4.3772 \text{ Å}$  [38]). The indirect band gap, however, is found to be of 7.43 eV, which is significantly less than the experimental value.

## 3. Results and discussion

### 3.1. The formation of the $(1 \times 1)$ BeO on Mo(112)

The preparation of the BeO monolayer on Mo(112) typically included (i) deposition of an ample (more than 3 monolayers, as it was found sufficient in our previous studies [22], but usually 10–15 monolayers) amount of Be onto the Mo(112) surface; (ii) subsequent oxidation of the Be layer, and (iii) desorption of the resting non-oxidized Be by annealing at  $T_{an} = 1100\text{--}1400 \text{ K}$ . At room temperature, the synthesis of BeO on the Be-covered Mo(112) surface is spontaneous (as it was suggested from DFT calculations and proven experimentally in our previous studies [25,32] as well as, on the Be(0001) surface, in the earlier paper by Fowler and Blakely

[39]), however, thus obtained Be-BeO layer is essentially disordered, as follows from a total absence of any reflections but a strong background at LEED patterns (Fig. 1). The annealing at  $T_{an} = 1350 \text{ K}$  completely removes the rest of non-oxidized Be (this follows from the analysis of the chemical shifts of Be Auger peaks, see [25] for further details), and an ordered BeO layer is formed thus giving an  $(1 \times 1)$  LEED pattern (Fig. 1d). The BeO coverage  $\theta_{\text{BeO}}$ , estimated for this structure from amplitudes of AES peaks of Be and O, is found to be about 1.6. It should be noted that because of a furrowed relief of the Mo(112) surface, the  $\theta_{\text{BeO}} = 2.0$  coverage, in fact, corresponds to a physical monolayer, that is, to the monolayer entirely covering the surface. Therefore, the formation of the  $(1 \times 1)$  LEED pattern for  $\theta_{\text{BeO}} = 1.6$  may indicate, probably, the formation of  $(1 \times 1)$  segments (islands) having a local coverage 2.0 with some open areas remaining on the Mo(112) surface. The work function, due to the presence of the BeO adsorbed layer, decreases by  $\sim 1.0 \text{ eV}$  with respect to a clean Mo(112) surface.

Hence, the formation of an ordered structure of BeO layer, which is matched to the Mo(112) surface thus giving the  $(1 \times 1)$  LEED pattern, is confirmed also by AES and work function measurement. In the absence of direct STM observations, the structure of the BeO layer, nonetheless, can be suggested from DFT calculations performed for relevant model structures.

### 3.2. A free BeO monolayer

The lattice period of bulk BeO ( $a = 2.72 \text{ Å}$ ), and thus the O–O distance, fits very well the period along the rows of the Mo(112) surface (2.73 Å), which indicates a possibility of the formation of structures of adsorbed layer matched to the substrate. A free BeO monolayer can be formally viewed as built from Be and O hexagonal monolayers cut from the wurtzite structure. However, the buckling is found to be energetically unfavorable, and the free BeO monolayer spontaneously reconstructs to form a flat honeycomb structure (shown in the insert in Fig. 2), in agreement with earlier results by Zheng et al. [13]. The lattice period of the optimized free BeO monolayer is 2.70 Å, and the Be–O bond length of 1.66 Å is the same as in the bulk.

The band structure and DOS for the free BeO monolayer are shown in Fig. 2. The valence band maximum is at K while conduction band minimum is at  $\Gamma$  point. The most interesting result of these calculations is that the indirect band gap for the free monolayer (5.21 eV) is found to be less than for a bulk BeO (7.43 eV), in good agreement with other LDA and also GW calculations [9,13,17]. It should be noted that such a behavior is unusual, because normally band gaps for layers are larger than in the bulk [40]).

### 3.3. The BeO monolayer on Mo(112)

Since the lattice period of free BeO monolayer is close to the period along the rows of the Mo(112), the layer, with only minor distortions (1.2% in this direction), can be naturally adjusted to the surface (Fig. 3a). The flat geometry, pertinent to a free BeO monolayer, is no longer favorable for the adsorbed layer, which acquires substantial buckling (Fig. 3b). The bonding between adsorbed BeO monolayer and Mo(112) surface is accomplished through O atoms situated atop Mo atoms, which is in contrast to favorable positions of O atoms in bridge-on-row sites pertinent to BeO layers on Mo(112) at  $\theta_{\text{BeO}} = 1$  [32]. The binding energy is found to be of  $\sim 0.5 \text{ eV}$  both in LDA and GGA-RPBE calculations. This structure is found to be quite stable. In particular, any attempts to distort it to close the holes formed by hanging segments of the layer above the furrows ends, after optimization, to the restoration of the honeycomb structure. Hence, the structure is found to be quite robust, as is pertinent also to other honeycomb monolayers such as graphene or MoS<sub>2</sub> [40].

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