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Adsorption of boron on a Mo(110) surface

Tamerlan T Magkoev[1,3], Anatolij M Turiev[1], Natal'ja I Tsidaeva[1], Dmitrij G Panteleev[1], Georgij G Vladimirov[2] and Gennadij A Rump[2]

[1] Department of Physics, University of North Ossetia, Kesaev 121-83, Vladikavkaz 362020, Russian Federation
[2] Department of Physics, University of Saint Petersburg, Uljanovskaya 1-1, Saint Petersburg 198904, Russian Federation

E-mail: t_magkoev@mail.ru

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Abstract
Adsorption of boron atoms in submonolayer to multilayer coverage on atomically clean Mo(110) surfaces has been studied by Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), electron energy loss spectroscopy (EELS) and work function measurements. According to Auger results there is a layer-by-layer growth mode of the film on the substrate held at room temperature. In the submonolayer region the work function gradually increases with boron coverage until a saturation value of 5.8 eV is achieved after completion of the first monoatomic layer. The B–Mo(110) adsorbate system formed on the substrate at room temperature is not stable, dominated by a strong tendency of the boron atoms to diffuse into the bulk of the crystal. The latter is manifested by dramatic Mo(110) surface plasmon mode transformation upon boron adsorption, presumably as a result of penetration of boron atoms into the topmost substrate layer even at $T = 300$ K. Slight annealing up to 450 K facilitates this trend, leading to total dissolution of deposited boron atoms in the bulk of the crystal under further annealing, restoring the initial state of the Mo(110) surface after achieving a temperature of approximately 2000 K.

1. Introduction

For the last several decades the adsorption of the vast majority of elements on metal surfaces has been quite extensively studied by a variety of surface science techniques [1–5]. As an elemental adsorbate the main focus was on alkali, alkali-earth, simple, transition and rare-earth metals, as well as on oxygen, nitrogen, sulfur, phosphorus, chlorine, noble gases and some other elements. Such an enhanced attention is motivated by the high technological relevance of the corresponding interfaces and thin films as well as by the necessity of the further development of the fundamental science of surface and interface area and thin film growth. In this regard one of the elements suffering an extreme lack of attention is boron, even though it is an immediate neighbor in the Periodic Table to elements already listed and is widely used in material science and technology [6]. In fact, the surface science studies of the adsorption of boron on atomically clean metal single-crystal faces are the early works of Tucker [7] and Miyasaki [8]. No other works studying adsorption phenomena of boron atoms on atomically clean metal surfaces have been reported so far. In relation to this the aim of the present study is to investigate submonolayer to multilayer adsorption of boron atoms on a metal surface, for which Mo(110) is used. The latter is chosen for the following reasons. On the one hand, Mo(110) is proven to be an appropriate substrate for adsorption and thin film growth studies of numerous elements due to surface flatness and stability [1–5]. On the other hand, boron is an additive which dramatically changes the properties of refractory metals [6, 9], making molybdenum a potentially interesting candidate as a substrate. Another point in favor of the study of the interaction of boron with a refractory metal surface is that boron is a component of rare-earth metal hexaborides—materials of high thermionic efficiency [10, 11]. Since most hexaboride electron emitters are fabricated in the form of a film on a refractory metal support [12], it is interesting to study the interaction of its individual components with the metal surface. In this sense almost all efforts were directed to the study of the adsorption of rare-earth metal atoms [13–17], whereas the adsorption of boron remains almost completely unexplored.

[3] Author to whom any correspondence should be addressed.

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2. Experimental details

Measurements have been carried out in an ultra-high vacuum (UHV) system (base pressure: 2×10^{-10} Torr) consisting of a stainless steel chamber equipped with a retarding four-grid hemispherical electron analyzer with a coaxial electron gun for Auger electron spectroscopy and electron energy loss spectroscopy, twin-anode x-ray source and hemispherical deflector for x-ray photoelectron spectroscopy, low-energy electron gun, operating at energies lower than 10 eV for work function measurements (the Anderson method), a sample holder allowing heating to temperatures as high as 2800 K, a quartz microbalance and adsorbate sources. The chamber was also equipped with a leak valve for controlled oxygen dosing and a residual gas mass spectrometer. Energy resolution of the four-greed electron spectrometer derived from the elastic peak width was lower than 1%. The sensitivity of AES measured via the controlled dose of oxygen was 0.03 monolayers. The Auger spectra were measured in $\mathrm{d}N/\mathrm{d}E$ whereas EELS was measured in $N(E)$ form with constant $\Delta E/E$ and 7 V modulation. The EELS in the configuration used was mainly sensitive to collective and interband transitions. XPS measurements were performed using Al Kα radiation (photon energy: 1486.6 eV) and a hemispherical energy analyzer adjusted to a constant pass energy (15 eV). The Mo(110) sample of a rectangular shape ($10 \times 5 \times 0.3$ mm^3) was mounted on the sample holder with WRe 0.3 mm diameter wires spot welded at the four corners on the back of the sample. Direct current through these wires allowed heating of the sample to about 1400 K. Higher temperatures were achieved by electron bombardment of the sample by the tungsten filament placed in a tantalum screen behind the sample. The temperature was measured by a W–WRe thermocouple spot-welded to the upper back side of the sample. Boron evaporation to produce the flux of boron atoms on the substrate surface was done by electron bombardment from the 0.2 mm diameter grounded tungsten spiral wrapped around the piece of bulk boron (approx. 1 mm^3) fixed in a positively biased (+2 kV) tantalum rod and placed in a tantalum screen. Tantalum foils and tungsten filaments used for construction of the source were preliminary outgassed in a separate chamber at a pressure of approx. 10^{-8} Torr. After being placed in the UHV chamber the source was carefully outgassed for a prolonged time until no contamination was detected by AES. The deposition flux of the adsorbate was measured by the quartz microbalance and verified by AES via monitoring of the Mo signal attenuation and the growth mode. For correct determination of the flux, and hence the adsorbate coverage, the similarity of deposition geometries for the sample and the quartz crystal was achieved by their strictly coaxial and coplanar placement on a manipulator. A combination of quartz microbalancing (assuming unity sticking probabilities on the sample and the quartz crystal) and AES allowed measurement of the surface concentration (n) with an accuracy of approx. 0.15 of one monolayer coverage (θ). It was assumed that the value of $n = 2.7 \times 10^{15}$ cm^{-2} corresponds to unit boron coverage ($\theta = 1$). The Mo(110) crystal was cleaned by the usual procedure of heating at 1300 K in oxygen ambient at a partial pressure of 10^{-6} Torr to remove carbon and sulfur contamination and subsequent high temperature (2700 K) flashing cycles in UHV. The surface was considered clean if no contamination can be monitored by AES at the most sensitive scale. After each set of adsorbate deposition and measurement cycles the surface was cleaned by cycles of high temperature flashing and checking by AES. Sometimes, after a certain set of measurements, even after high temperature flashing the carbon C (KLL) signal could still be detected by AES. In this case annealing of the sample in oxygen ambient to remove carbon contamination was applied.

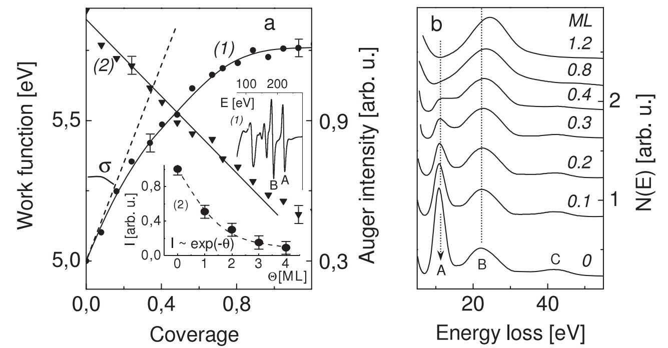

Figure 1. (a) Work function (1) and Mo MVV Auger intensity (2) versus coverage upon boron adsorption on Mo(110) held at room temperature. Inlay 1: Mo MNN Auger spectrum with MVV (221 eV) and MNV (188 eV) transitions labeled as A and B, respectively. Inlay 2: dependence of Mo MVV Auger intensity on B film thickness. (b) Electron energy loss spectra transformation with boron coverage increase. Lines labeled as A (10.5 eV), B (21 eV) and C (47 eV) on curve (1) for bare Mo(110) correspond to surface and bulk plasmon modes and 4s4p interband transitions, respectively. The dotted lines are drawn for convenience to follow the peak shift.

3. Results and discussion

The Anderson method used in this study is sensitive to the work function change which was determined by measuring the linear part of the shift of the monitored retarding curve [18]. In order to get the absolute values of ϕ, the work function of clean Mo(110) was assumed to be 5.0 eV [19]. Special care to ensure adsorbate cleanliness was taken to measure the work function plots, because it was found that oxygen and carbon contamination which were hardly detectable by AES noticeably affect the plot, especially changing the initial slope of the curve and change in the total work function. Upon adsorption of boron on Mo(110) held at room temperature in the submonolayer region the work function versus coverage continuously increases until saturation at 5.8 eV occurred at an adsorbate surface concentration of approx. 2.7×10^{15} cm^{-2} (figure 1(a), curve 1). In the framework of the dipole model of the work function change [3, 5] the observed increase of the work function upon boron adsorption on Mo(110) can be attributed to formation of an effective dipole layer with the negative end shifted towards the vacuum as a result of chemisorption bond polarization. Using the Helmholtz equation $\Delta\phi = 4\pi\mu\theta e$, the work function versus coverage plot allows us to estimate the dipole moment (μ)

of the interface bond from the initial slope of the curve (σ) (figure 1(a)), which is 0.2 D (at $\theta \rightarrow 0$) (1 D = 3.33×10^{-30} C $\times$ m). The value of the dipole moment derived in this way relates to a single adatom which is not influenced by the depolarization effect of other adatoms. Comparison of Mo and B atomic diameters (4.02 and 2.06 Å, respectively) shows that the above surface concentration of boron corresponds to coverage of about one monolayer. No noticeable work function change was observed above this coverage, which is indirect evidence of the formation of a complete layer totally covering the Mo(110) surface. The latter is confirmed by the way the Mo MVV (221 eV) Auger signal (denoted as A in figure 1(a), inlay 1) attenuates with boron coverage increase (figure 1(a), curve 2): to a good approximation a linear decrease indicates the formation of a two-dimensional boron film [20], at least, in the submonolayer region. The Auger uptake curve of the KLL boron line (179 eV) cannot be unambiguously drawn due to its strong intersection with the Mo MNV signal at 188 eV, denoted as B in figure 1(a), inlay 1. For boron coverage corresponding to the second and third monolayers the conclusion about the growth mode based on the form of the Mo Auger signal intensity decrease is not straightforward due to enhanced data point scattering of the substrate Auger signal at higher adsorbate coverage. However, taking into account the observed fact that, at the boron coverage corresponding to approx. 5 monoatomic layers, the Auger spectrum of the B–Mo(110) system in the energy range 50–300 eV consists of only one B KLL line, favoring the assumption of layer-by-layer growth mode up to this coverage. This is also confirmed by the decay rate of the Mo MVV Auger signal with increasing boron film thickness. The experimental points at boron film thicknesses of 1, 2, 3, and 4 monolayers can be fitted by an exponential function (figure 1(a), inlay 2), which is evidence of a layer-by-layer growth mode [20].

Apart from the Mo Auger intensity decrease the adsorption of boron on the substrate held at room temperature does not result in a change of the Auger peak shape and energy. However, the EEL spectra undergo a dramatic transformation upon boron adsorption. The spectrum of bare Mo(110) consists of three losses at 10.5, 21 and 47 eV denoted as A, B and C in figure 1(b) (curve 1) which are attributed to surface and bulk plasmons, and interband 4s4p transitions, respectively [21, 22]. Already at the very early stage of boron film growth the Mo(110) surface plasmon mode drastically attenuates and subsequently loses intensity, disappearing at boron coverage of approx. 0.8 ML. At the same time the Mo(110) bulk plasmon mode is altered less, at least at low boron coverage. At a coverage exceeding one monolayer, the EEL spectrum consists of one broadened band centered at approx. 24 eV which is attributed to the bulk plasmon of boron [23]. Unlike the surface plasmon region the transformation of the spectra in the bulk plasmon region, to a good approximation, can be viewed as superposition of Mo and B plasmon lines with opposite changes in intensity. Assuming the threefold dip of the Mo(110) plane as an adsorption site of B, in line with the case of the parent O–Mo(110), N–Mo(110), C–Mo(110) and S–Mo(110) systems [24, 25], and taking into account the boron atom being about half the size compared to Mo, the boron film

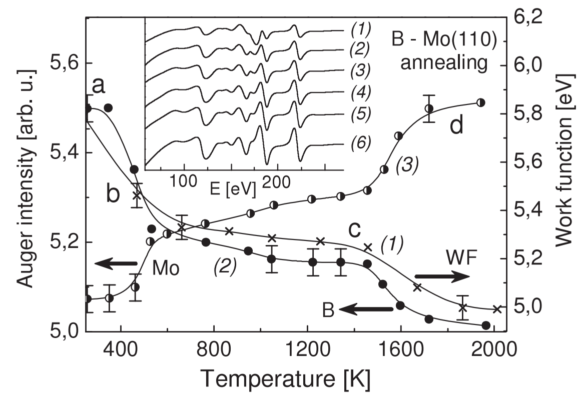

Figure 2. Dependence of the work function (1) and Auger intensity of B (2) and Mo MVV (3) on the annealing temperature of the B–Mo(110) system at an initial boron coverage of two monolayers. Inset: transformation of the Auger spectra upon annealing, showing no shift of B and Mo Auger lines. Annealing temperature (K): 1–300; 2–500; 3–600; 4–1150; 5–1500; 6–1750. Annealing time is 15 s. Spectra and the work function were measured at room temperature.

may be viewed as being almost coplanar with the Mo(110) topmost layer. This may affect the lateral integrity of the outermost Mo(110) layer, violating the longitudinal collective motion of electron density responsible for the surface plasmon mode [26–28]. A rather small initial dipole moment of *B* (0.2 D) is additional evidence of the negligible shift of boron outwards from the Mo(110) plane.

Thus a significant change of the electronic state of Mo(110) upon boron adsorption at room temperature is manifested in the dramatic change of the surface plasmon mode related mainly to the topmost substrate layer. This can be viewed as a precursor of the stronger interaction and possible chemical bond formation which occurs upon annealing of the B–Mo(110) system. Even a slight thermal treatment causes a dramatic change of the properties of the system. Transformation of the Auger spectra as well as the dependence of the work function, and Mo and B Auger intensities, on the annealing temperature is shown in figure 2. It is seen that at a temperature of about 450 K all the measured characteristics of the system notably change: the work function decrease is accompanied with the abrupt drop in boron Auger intensity and the corresponding Mo Auger signal increase. The subsequent increase of annealing temperature enhances this tendency (part ab) until at a temperature of approx. 700 K up to 1500 K there is only a moderate change of the properties (part bc), again followed by a dramatic change (part cd). In the whole annealing temperature interval the change of both boron and Mo Auger line positions was not detected (figure 2, inset). This means that the observed temperature-dependent variation of the work function and the Auger intensities are mainly due to the diffusion of B into Mo(110) without compound formation.

The latter, however, cannot be totally ruled out, taking into account the stabilization part (bc) which may be evidence of the formation of molybdenum borides limiting the B–Mo(110) interdiffusion process. Actually this is reflected in the x-ray photoelectron spectra shown in figure 3 in which the spectra monitored for a 2 ML B–Mo(110) system before (300 K) and

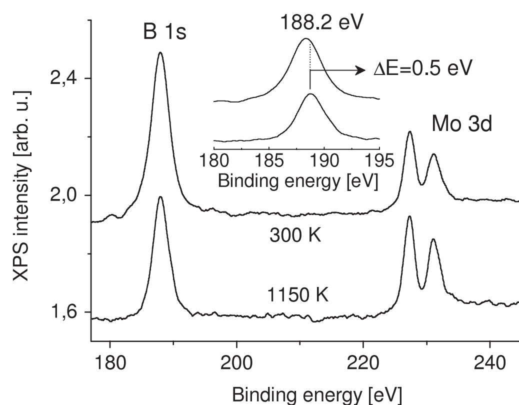

Figure 3. XPS spectra of 2 ML B–Mo(110) system before (300 K) and after annealing at 1150 K. Inset: B 1s photoelectron line region on an extended scale showing a blue energy shift by 0.5 eV upon annealing.

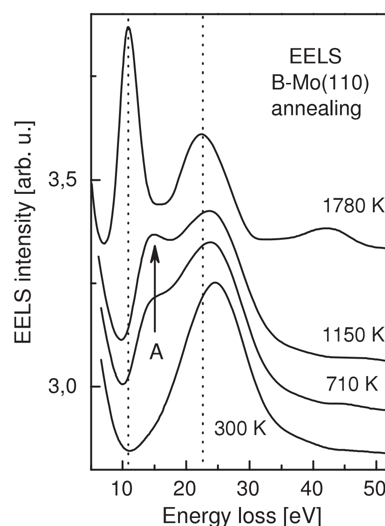

Figure 4. Electron energy loss spectra upon annealing of a 2ML B–Mo(110) system at indicated temperatures. A new band at 13.5 eV denoted as 'A' emerges upon annealing.

after annealing at 1150 K are shown. An apparent feature is the B 1s line intensity drop accompanied by the Mo 3d intensity increase, reflecting the diffusion of boron from the surface into the bulk of the Mo crystal upon annealing. Closer inspection of the B 1s photoelectron line position reveals an energy shift of 0.5 eV (inset) which is likely to be attributed to bond formation between B and Mo. The fact that in this case the shift of the B Auger line was not observed is due at least to two reasons: (1) upon B–Mo chemical bond formation the B 1s and 2sp levels may shift simultaneously by about the same values, so the B KLL Auger transition energy does not change and (2) the B KLL Auger line strongly intersects with the Mo MNV line (figure 2, inset), thus masking any possible changes of individual Auger lines. The possibility of chemical interaction between B and Mo is also reflected by the change in EEL spectra shown in figure 4. The observed spectral features upon annealing are different from those occurring when boron concentration on Mo(110) held at room temperature changes (figure 1(b)). Specifically, the appearance of a new band 'A' centered at 13.5 eV, observed neither for Mo(110) nor for bulk boron, indicates the formation of interatomic B–Mo bonds.

The observed tendency of boron to diffuse into the Mo(110) bulk at elevated temperatures supports the above assumption of boron layer inward shift upon adsorption at room temperature as a precursor of boron diffusion into the bulk. Behavior of B–Mo(110) at higher annealing temperatures (1500–2000 K), as can be seen in figure 2, is dominated by the boron concentration decrease and its total disappearance from the surface region at approx. 2000 K, as judged by AES and the work function approaching that of bare Mo(110). The EEL spectrum at the above temperature is also close to that of a clean substrate after high temperature flashing. Therefore, assuming molybdenum boride formation in the surface and subsurface region upon annealing at moderate temperatures (part bc), one should expect their high temperature dissociation and subsequent boron diffusion into the bulk, not accessible with the techniques used, almost totally restoring the initial state of the Mo(110) surface (part cd).

Additional support of this interpretation of the behavior of the B–Mo(110) system upon annealing is provided by

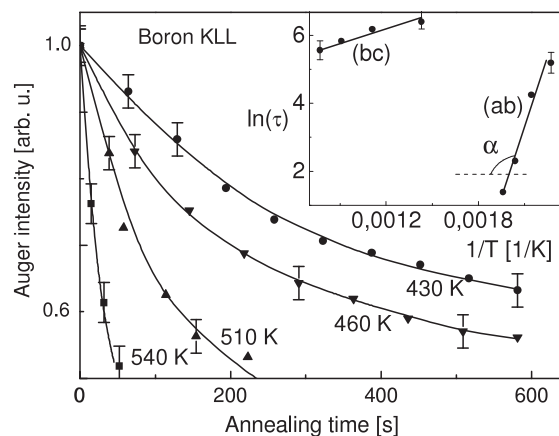

Figure 5. Dependence of the boron KLL Auger intensity on the annealing time for four different similarly prepared B–Mo(110) systems annealed at different temperatures. Initial boron coverage for all systems is 2 ML. Inset: dependence of $\ln(\tau)$ on reciprocal temperature $(1/T)$ for two different annealing temperature intervals corresponding to parts (ab) and (bc) of figure 2. τ is the time required to decrease the initial boron Auger intensity to a certain value (65% of the initial Auger intensity).

measurement of the boron Auger intensity decay rate at fixed temperature. The corresponding plots for four different annealing temperatures of four similarly prepared B–Mo(110) systems are shown in figure 5. Assuming a temperature-activated process the activation energy for the corresponding process can be determined from these dependences redrawn in a semilogarithmic plot of the relaxation time (τ) after which the B KLL intensity had dropped to a certain level (65% of the initial intensity) versus the reciprocal temperature (inset). The corresponding activation energy of the process occurring in the temperature range of 450–600 K derived by slope angle (α) (plot ab) is 0.4 eV, whereas the same value for the process in the 800–1400 K annealing interval (plot bc) is about an order of magnitude higher: 3.8 eV. Such a dramatic difference is a result

of different processes determining the boron concentration variation in the corresponding temperature range. The initial part of curves (ab) (figure 2) may be attributed mainly to the diffusion of boron atoms into the bulk with no chemical reaction, whereas in the higher temperature regime (part bc) the boron concentration decay is limited by the bond breaking of the Mo–B surface compound formed, totally disappearing from the surface region upon further temperature increase (part cd). Thus, the boron film formed on Mo(110) held at room temperature is in a nonequilibrium state, tending to totally diffuse into the bulk of the crystal, the case occurring upon slight annealing of the system. This effect is to be taken into account when considering the stability of complex boron-containing films on Mo support, such as for example lanthanum and rare-earth metal hexaboride-coated refractory metal supports.

4. Conclusions

Adsorption of boron atoms on Mo(110) surfaces has been studied by Auger electron spectroscopy, electron energy loss spectroscopy and work function measurements. There is a gradual increase of the work function upon boron concentration increase in the submonolayer coverage region from the value of 5.0 eV for bare Mo(110) up to the stationary value of 5.8 eV achieved at unitary boron coverage. According to AES results there is a layer-by-layer growth mode of boron film on Mo(110) held at room temperature at a film growth rate of about 0.1 ML min^{-1}. The film formed in this way is not stable: even at room temperature the deposited boron atoms penetrate into the topmost layer of the substrate, thus changing its electronic structure as shown by the dramatic transformation of the surface plasmon mode. Subsequent slight annealing to about 450 K results in an abrupt drop of concentration of boron atoms in the surface region due to their diffusion into the bulk of the crystal with possible Mo–B chemical bond formation. Further annealing results in the total disappearance of boron from the surface and subsurface area detectable by the techniques used, restoring the initial state of the Mo(110) surface as judged by AES, EELS and work function measurements.

Acknowledgments

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