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Interaction of Be atoms with (111) Ir surface.

© E.V. Rut'kov, E.Y. Afanas'eva, N.R. Gall

Ioffe Institute,
St. Petersburg, Russia

E-mail: rutkov@ms.ioffe.ru

It is shown that, when sputtered onto the surface of the (111) Ir face in the temperature range $1100-1250\,\mathrm{K}$, beryllium atoms form a surface chemical compound of stoichiometry Ir_3Be with a concentration of adsorbed beryllium $N_{Be} = 5 \cdot 10^{14}\,\mathrm{cm}^{-2}$, after which the newly deposited beryllium atoms dissolve metal bulk. The Ir_3Be surface compound itself is destroyed due to the dissolution of beryllium in the temperature range of $1250-1400\,\mathrm{K}$ with an activation energy increasing from $3.2\,\mathrm{eV}$ to $3.7\,\mathrm{eV}$ with decreasing Be concentration. At $T > 1400\,\mathrm{K}$, the thermal desorption channel is switched on. The formation of the Ir_3Be surface compound significantly lowers the energy barrier E for the dissolution of Be atoms in the bulk of iridium by $\Delta E > 1.7\,\mathrm{eV}$.

Keywords: iridium, beryllium, surface chemical compounds, dissolution, bulk intermetallic compounds.

1. Introduction

Adsorption of atoms of *s*- and *p*-elements on surfaces of transition metals and initial stages of their interaction with the substrate are interesting in terms of science and important in terms of practice. This subject is significant for many branches of science: the solid state physics, the physics and chemistry of the surface, the solid state chemistry, the physical materials science, the physics of phase transitions [1,2].

It has been shown earlier [3,4] that interaction of many *p*-elements with faces of refractory metals, which have a pronounced atomic relief, for example, with the faces (100) of BCC- and HCP-lattices, leads to formation of specific adsorption states behaving as surface chemical compounds (SC): surface carbides, silicides, sulfides. When SC are formed, they substantially modify surface properties, in particular, by opening access for subsequent deposited atoms into a substrate bulk, to a dissolved state, by sharply reducing a diffusion barrier for this process [4]. Apparently, it is the formation of the surface compounds on internal surfaces of the solid body, such as grain boundaries, that defines differences in physical and chemical properties of common and super-clean materials [5].

Beryllium is one of the most promising elements for the aerospace industry, its alloys are widely used in metallurgy, instrumentation, defense industry [6,7]. Interaction of beryllium with refractory metals is important, since it characterizes alloys' stability, particularly under thermal loads, and their manufacturability.

From the physical and chemical viewpoint, beryllium is one of the most interesting elements that combine metallic conductivity, small atom size, a very high ionization potential ($\sim 9\,\mathrm{eV}$), typical for non-metal atoms and negative electron affinity. It has a closed *s*-shell, does not form dimers and clusters and chemically interacts only with strong oxidizers.

Adsorption of beryllium on the metals, mainly on tungsten, has been studied in a number of the papers [8–12]. The papers [11,12] have shown that similar to *p*-elements, it forms surface compounds with the faces (100) W and ($10\bar{1}0$) Re. However, the question of formation of such compounds with smooth faces is still unsolved. The present study is devoted to high-temperature interaction of beryllium with an atomically-smooth and thermally stable surface Ir(111).

2. Experiment methods

The experiments were carried out in an ultrahigh-vacuum high-resolution ($\Delta E/E \sim 0.1\%$) electron Auger spectrometer. Use of the prism energy analyzer [13] allowed a big distance ($\sim 74\,\mathrm{mm}$) between the samples and the energy analyzer, thereby, in turn, allowing obtaining Auger-spectra of ribbon samples heated up to $2500\,\mathrm{K}$ with no loss in sensitivity. It was important since it allowed analyzing a surface composition directly in conditions of the processes under study, but not after the sample is cooled down.

A primary electron beam with the energy of $1800\,\mathrm{eV}$ and current $\sim 5\,\mu\mathrm{A}$ irradiated the samples' working surface with the area of $1\,\mathrm{mm}^2$, from which Auger electrons were collected. The unit had a module to implement a combined method of thermionic emission and surface ionization [13].

Samples were thin iridium ribbons sized $50 \times 1 \times 0.02\,\mathrm{mm}$, heated by direct passage of current. Impurities, mainly carbon, were removed from the ribbons by the standard procedure consisting of successive annealing of the ribbons in an oxygen atmosphere at the pressure

of $\sim 10^{-5}$ Torr and temperature of 1500 K and in ultra-high vacuum at 2100 K. After such purification, only iridium Auger peaks are registered on the surface by the electron Auger spectroscopy (EAS) method. Due to purification, the rolling texture changes into the recrystallization texture and the face (111) emerges to the surface, its orientation degree was $\sim 99.5\%$ as per X-ray diffraction data [13]. The work function of the iridium surface was $e\varphi = 5.75$ eV, which corresponded to the face (111) [14]. The iridium surface was homogeneous in the work function with an accuracy of ± 0.05 eV.

Beryllium was deposited by sublimation of beryllium ribbons fixed on tungsten and rhenium ribbons being heated by direct passage of current and spaced from the Ir one at the distance of ~ 20 mm.

In order to correctly understand a physical picture on the iridium surface with adsorbed beryllium with the change of the temperature, the same iridium ribbon with small beryllium pieces of thin foil was placed at the angle of $\sim 45°$ at the distance of ~ 20 mm near the operating one. The tests with this tape made it possible to separate surface adsorbate removal processes either by thermal desorption or by dissolution in a metal pieces (see below).

The sample temperature was determined using an optical micropyrometer at $T \geq 1100$ K, while in the lower temperatures — by linear extrapolation of the temperature dependence on the ribbon heating current to the room temperature. Uniformity of the temperature in the ribbon middle part (~ 40 mm) was not worse than ± 5 K.

3. Adsorption of Be atoms at $T = 300$ K on Ir(111)

The Fig. 1, *a* shows Changes in intensities of Auger-signals of Be ($E = 104$ eV, the curve *1*) and Ir ($E = 154-171$ eV, the curve *2*) depending on the beryllium sputtering time on Ir(111) at $T = 300$ K by means of the constant flux. It is clear that at $t \geq 260$ s the intensity of the beryllium Auger-signal stops changing, while the iridium Auger-signal drops to a level of instrument noise. It means that the surface has the Be film of the five−six atom layers' thickness, i.e. it is equal to two−three lengths of a free path for the Auger electrons being used — the thickness, which „is sensed" by the EAS method [15], while no Auger-signal of the substrate means discontinuity of the beryllium film. This test allows estimating the density ν of the beryllium atoms' flux which falls on the surface. In our tests $\nu = (5-6)N_{\mathrm{m}}t^{-1}$ cm^{-2} s^{-1}, where $t = 260$ s, and $N_{\mathrm{m}} \approx 10^{15}$ cm^{-2} — the concentration of beryllium atoms in a hypothetical densely-packed mono-layer [16].

The Fig. 1, *b* shows the same dependence, which is rebuilt in the coordinates $I_{\mathrm{Ir}} = f(I_{\mathrm{Be}})$ yet. As it is clear, all the points are laid on one straight line, indicating no layer-by-layer growth and formation of the so-called „simultaneous
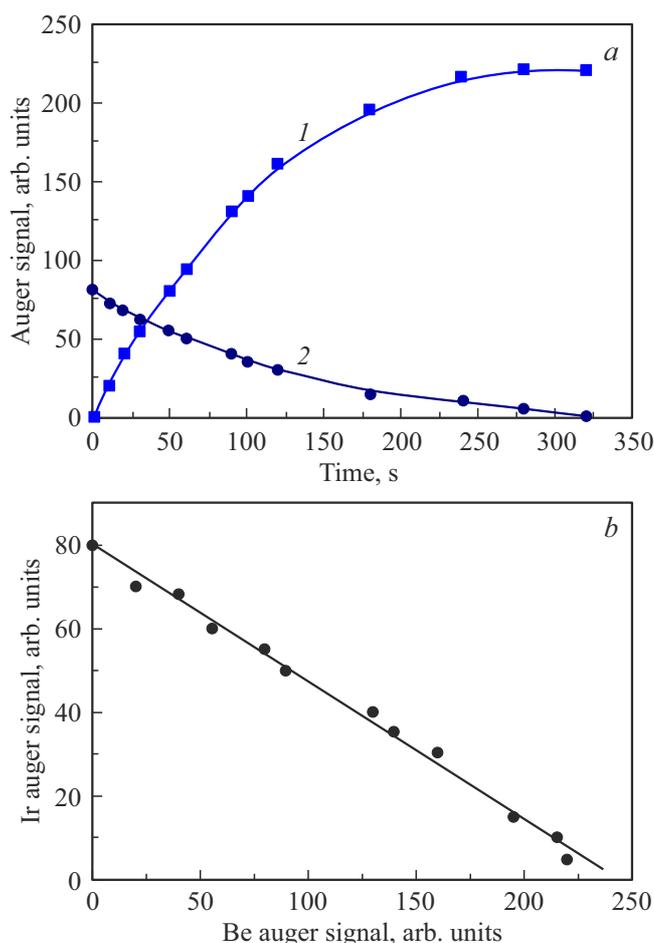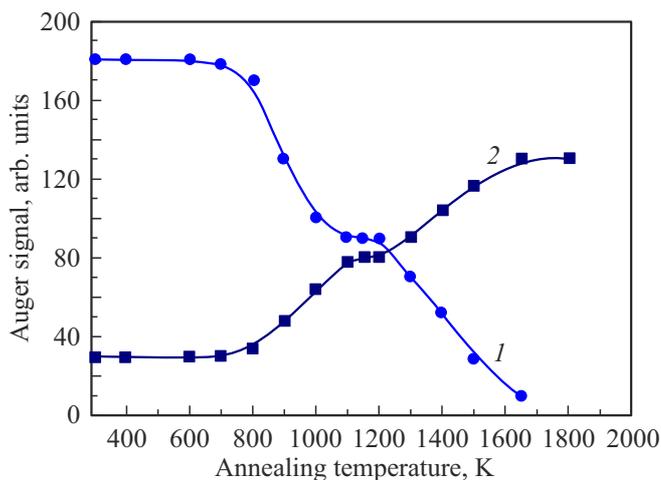

Figure 1. Changes in intensities of the Auger-signal of Be (*1*) and Ir (*2*) vs. Be adsorption time (*a*) and the dependence of the intensity of the Ir Auger-signal on the Be Auger-signal (*b*) in Be deposition on the (111) Ir face at $T = 300$ K.

multilayer", i.e. a growth mode being implemented at very small adsorbate migration lengths [17].

4. Annealing of the Be film on Ir(111)

The Fig. 2 shows a changing intensity of the Auger-signal of Be (*1*) and Ir (*2*) when annealing the beryllium film of a thickness of about three layers, formed at 300 K. It is clear that within the range of $300-700$ K the film is stable (Fig. 2). At $T \approx 1100-1200$ K, there is „an evident plateau", which is most likely correlated to formation of a bulk compound of Be with Ir (see the next sections of the article). Note that additional sputtering of Be atoms within the temperatures corresponding to „the plateau" in the Fig. 2 at $T = 1150$ K does not change the intensity of the Auger-signal of neither beryllium, nor iridium, which seems to be correlated to growing of the bulk compounds of Be with Ir into the substrate, which is weakly sensed by the EAS method. The special tests of direct observation of the pieces of Be foil on the iridium ribbon show that they „disappear"

Figure 2. Changes in intensities of the Auger-signal of Be (*1*) and Ir (*2*) vs. substrate temperature in annealing the beryllium film of a thickness of about three layers, formed on Ir(111), at $T = 300$ K. The annealing time in each point is 30 s.
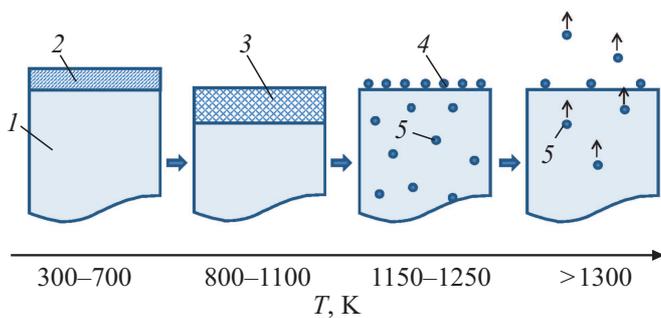
Figure 3. Simplified illustration of the processes of interaction of Be atoms with heated iridium: *1* — the Ir substrate, *2* — the Be film, *3* — the bulk compounds of Be with Ir, *4* — the surface chemical compound Ir$_3$Be, *5* — the dissolved Be atoms.

when heating the substrate to $T \approx 900-1000$ K, to be replaced by areas with a lower emissivity factor. At the same time, „disappearance" of the Be pieces is not correlated to beryllium desorption, as the surface of the operating iridium ribbon, which could be hit by the Be atoms, is still free (clean) of beryllium. Only when the auxiliary ribbon is heated above 1500 K, the iridium starts to function as a source of beryllium atoms. That is why a reduced intensity of the beryllium Auger-signal at $T > 800$ K and a growing intensity of the iridium Auger-signal may be correlated to dissolution of the beryllium in a metal bulk (Fig. 2).

If we use a known expression for lifetimes of particles on the surface $\tau = \tau_0 \exp[E_1/kT]$ [18] and assume that a value of the pre-exponential factor is $\tau_0 \approx 10^{-13}$ s, then for $T \approx 800$ K and a characteristic time of the process $\tau \approx 1$ s we obtain an activation energy of dissolution of Be in iridium, when there are several layers of the adsorbate on the surface, $E_1 \approx 2$ eV.

Thus, it is reasonable to assume that during annealing of several layers of adsorbate or beryllium pieces of foil within the middle temperatures $T = 800-1100$ K the bulk compounds of beryllium with iridium are forming (Fig. 3). Analysis of these compounds is not a task of the present study.

5. Deposition of Be on Ir(111) at $T = 1200$ K

The Fig. 4 shows a changing intensity of the Auger-signal of Be (*1*) and Ir (*2*) in Be deposition on Ir(111) at $T = 1200$ K. Due to weak change of high-energy Auger-peaks of iridium ($E = 154-171$ eV) in these tests a more intense Auger-signal of the low-energy peak of iridium ($E = 54$ eV) has been recorded. It is clear that for $t \geq 50$ s the Auger-signals are stabilizing. The similar results were obtained when sputtering beryllium on iridium within the substrate temperatures of $1100-1250$ K. Weak influence of this beryllium coverage even on the low-energy Auger-signal of iridium means a small surface concentration of Be in these tests.

No thermal desorption of beryllium atoms means that deposition of beryllium at $t > 50$ s leads to dissolution of Be atoms and their accumulation in a substrate bulk. Using an evaluation density of the Be atoms' flux ν (see above), it is also possible to estimate the beryllium concentration corresponding to the „plateau" of the Fig. 4: $N_{Be} = \nu t \approx (5 \pm 2) \cdot 10^{14}$ at · cm^{-2}. Note again that additional deposition of Be atoms at concentration values corresponding to the „plateau" in the Fig. 4 at $T = 1200$ K leads to dissolution of newly arriving atoms in the metal bulk — iridium „functions" in this case as an accumulator of the Be atoms.
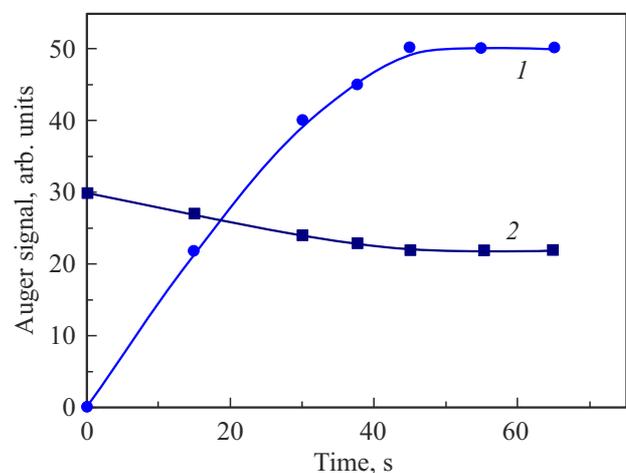
Figure 4. Changes in intensities of the Auger-signal of Be (*1*) and Ir (*2*) vs. time of Be deposition onto Ir (111) at $T = 1200$ K.

6. Surface chemical compound of Be with Ir(111)

Previously, our papers [19–23] have shown that at the middle temperatures the adatoms Si, P, S, O, C form surface chemical compounds (SC) of the stoichiometry WSi, ReSi, WP, MoC, etc. on such metals as W(100), Re(10$\bar{1}$0) Mo(100). Let us call a compound of Be with iridium the surface chemical compound, too and define its stoichiometry. For this, we compare in one test the intensities I of the beryllium Auger-signals from the surface compound WBe, where $N_{Be} = 1 \cdot 10^{15}$ at/cm^2 [12] and from the surface compound of Be with iridium.

It turned out that $I_{Be/Ir} \approx 0.5 I_{Be/W}$, and, consequently, $N_{Be/Ir} = 0.5 N_{Be/W} = 5 \cdot 10^{14}$ at/cm^2. Taking into account that the surface concentration of the iridium atoms for the face (111) is $N_{Ir} = 1.5 \cdot 10^{15}$ at/cm^2, we are dealing with the surface compound of the stoichiometry Ir$_3$Be. Knowing a crystal geometry of the face (111), it is reasonable to assume that the Be atom in the Ir$_3$Be surface compound occupies „a pit" between the three iridium atoms.

The Fig. 5 shows the KVV Auger-spectrum of beryllium from the Ir$_3$Be surface compound, as well as the Auger-peaks of iridium ($E = 54$ eV and $E = 154-171$ eV). In its form, the beryllium spectrum is close to that which is observed in the paper [11] in formation of the surface compound of beryllium on rhenium: there is also a shoulder at the energy of $E = 87$ eV, which is absent in a multi-layer film of beryllium [24].

Note that if dissolution of beryllium atoms from the thick film on iridium or after formation of Ir$_3$Be is observed at $T \geq 800$ K with the dissolution activation energy of $E_1 \approx 2$ eV, (see above), then the Be film corresponding to the Ir$_3$Be surface compound is stable up to $E = 1250$ K (Fig. 4). Let us estimate the dissolution activation energy corresponding to this temperature as it has been done above: $\tau = \tau_0 \exp[E_2/kT]$. For $T = 1250$ K, $\tau_0 = 10^{-13}$ s, $\tau \approx 1$ s we obtain $E_2 \approx 3.2$ eV. In fact, this energy can be higher, but when the temperature increases above 1400 K, then processes of desorption of beryllium from iridium begin (Fig. 3). In other words, even at $T \approx 1400$ K at small coverages the beryllium atoms are still on the surface, which corresponds to the dissolution activation energy of $E_2 \geq 3.7$ eV.

7. Thermal stability of the Ir$_3$Be surface compound

The Fig. 6 shows a changing intensity of the Auger-signal of Be from the Ir$_3$Be surface compound during its annealing. It is clear that at $T > 1250$ K the intensity of the Auger-signal is decreasing due to dissolution of beryllium in the substrate bulk. At $T \geq 1450$ K beryllium is fully removed from the iridium surface, wherein in this temperature range the thermal desorption is already noticeable — direct tests of desorption of Be from Ir are described above.
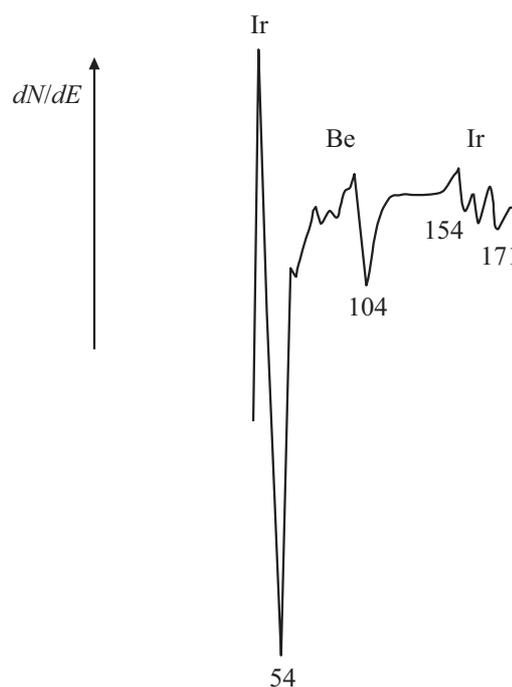
Figure 5. Auger-spectra of iridium ($E = 54$ eV), beryllium ($E = 104$ eV) and iridium ($E = 154-171$ eV) for the Ir$_3$Be surface compound.
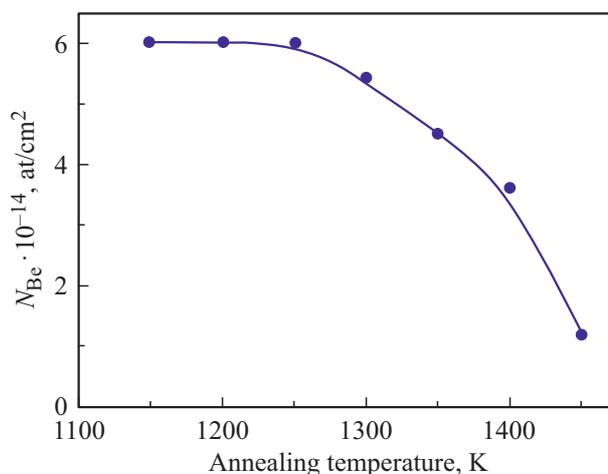
Figure 6. Changes in intensity of the Auger-signal of beryllium vs. iridium annealing temperature. The initial state corresponds to the Ir$_3$Be surface compound. The annealing time in each point is 30 s.

Let us use the known expression for the lifetimes again $\tau = \tau_0 \exp(E/kT)$ [9] and, if assuming that $\tau_0 = 10^{-13}$ s, then it is possible to estimate the bond energy E of the adatoms Be with Ir(111): $E = 3.2-3.7$ eV depending on the concentration of Be on the surface.

Returning to the Fig. 2, it should be noted that the observed „plateau", with which we correlate formation of the bulk compound of Be with Ir, corresponds to noticeable reduction of the Auger-signal of the substrate (approximately in 1.6 times), wherein the Ir$_3$Be surface

compound has almost no impact on the high-energy Auger-signal of iridium. Thus, the Be thick films are annealed on iridium via its dissolution stage with formation of the bulk compound with iridium.

8. Discussion of results

Specific compounds on a condensed phase surface, i.e. surface compounds (SC), were first represented in the works of Defoe and Prigogine [25]. They included chemical compounds, which can exist on a surface of solid bodies and not necessarily have any analogs among bulk compounds consisting in the same components. The work of Guttmann and McLean [26] had given a more specific sense to this important thermodynamic notion: The surface compound was already interpreted as a compound of surface metal atoms with adsorbate atoms. It is important to distinctly oppose the surface compounds and initial stages of growth of the bulk compounds, but it is not always easy to separate them experimentally.

It makes sense to speak of the surface states when their formation sharply changes the physical and chemical properties of the surface, for example, by opening a way for penetration of newly arriving adsorbate atoms into the bulk. The formation of the surface compounds on faces with a pronounced atomic relief is traditionally interpreted as occupation of places with the strongest bond, for example, pits on the faces (100) of BCC-metals, by the adsorbate atoms.

But this approach is admittedly improper on the FCC (111) face, in particular, such a face of iridium. It seems, in this case, that formation of the surface compound means a substantial relaxation of atoms of the substrate first layer, which sharply reduces the activation barrier for dissolution of the newly arriving beryllium atoms, opening the way for them into the bulk, into a state of the solid solution.

Note that annealing the multi-layer Be film at $T = 1100-1200$ K leads to formation of the initial stages of the bulk intermetallic compound, as the Be atoms sputtered over the surface compound at the same temperatures are removed into the bulk without being accumulated in the near-surface region. We think that it is correlated to a magnitude of the flux of dissolving atoms: at relatively small fluxes each atom moves independently in the substrate lattice, forming a solid solution. At high fluxes (dissolution of the multi-layer film), the near-surface regions of the substrate are involved into a formation reaction of the intermetallic compound. We observed the similar picture before when adsorbing beryllium onto (100)W and $(10\bar{1}0)$Re [11,12].

9. Conclusion

Thus, it is shown that deposition of beryllium onto the atomically-smooth face (111) of iridium results in formation of the surface compounds (SC) with the Ir_3Be composition. In its formation this surface compound

substantially modifies the physical and chemical properties of the surface, substantially reducing the activation barrier E for penetration of the newly arriving Be atoms into the substrate, to the dissolved state, by more than 1.7 eV. It has been shown a difference between the surface compound and the initial stages of formation of the bulk intermetallic compound and outlined the physical causes of the differences observed. It seems that developed notion can be true in relation to adsorption of the other s- and p-elements on smooth faces of the metals.

Conflict of interest

The authors declare that they have no conflict of interest.

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