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Electronic structure and thermal stability of Be films on the surface of the $(10\bar{1}0)$Re face

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It has been shown that beryllium atoms, when deposited onto the surface of a $(10\bar{1}0)$Re face at room temperature, form a multilayer film growing according to the „simultaneous multilayer" mechanism. When heated, this film rearranges, forming a bulk intermetallic compound at 800−1200 K, and at higher temperatures a surface compound of ReBe. The activation energy for the reactive diffusion of beryllium atoms into rhenium is 2.2 eV. Rearrangement of the film leads to a significant transformation of the shape of the Auger line of beryllium, which is a multiplet with energies of 75, 87, 95 and 104 eV for a multilayer film. The formation of the intermetallic compound gives rise to a peak with an energy of 109 eV, and the transition to a surface compound again leads to the formation of a triplet, but with different peak energies of 81, 104 and 114 eV. These Auger signal transformations can be used as „fingerprints" of the corresponding physicochemical states of beryllium on the surface.

Keywords: beryllium, rhenium, adsorption, bulk intermetallic compound, surface compound.

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1. Introduction

Interaction of atoms of s- and p-elements on surface 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 physics and chemistry of the solid state, the physical materials science, the physics of phase transitions [1,2]. It is the processes on the internal surfaces of metals, at the boundaries of grains and subgrains that determine the most important mechanical properties of alloys, such as strength, toughness and hardness [3].

It was shown earlier [4,5] that interaction of many p-elements with faces of refractory metals, which have a pronounced atomic relief, for example, with (100) BCC and HCP-lattices, leads to formation of specific adsorption states behaving as surface chemical compounds (SC): surface carbides, silicides, sulfides. When they are formed, the surface compounds substantially modify surface properties, in particular, by opening access for subsequent atoms to a substrate bulk, to a dissolved state, by sharply reducing a diffusion barrier for this process [4–6]. 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-chemical properties of common and super-clean materials [7].

Beryllium is a promising element for the aerospace industry and an effective ligand for the production of special-purpose alloys [8,9]. The study of the of beryllium interaction with the surface of rhenium is important, since it characterizes the stability of the alloys, especially under thermal loads, and the manufacturability of their production.

Beryllium combines metallic conductivity, small atomic size, but at the same time it has a very high ionization potential (~ 9 eV), negative electron affinity, which makes it similar to non-metals. Its electron shell is closed, it contains only s-electrons. Chemically, beryllium does not form dimers or clusters, and interacts only with strong oxidizers.

Adsorption of beryllium on the metals, mainly on tungsten, has been studied in a number of the papers [10–15]. In papers [13–15] it is shown that it, like p-elements, forms surface compounds with the faces (100)W, $(10\bar{1}0)$Re and (111)Ir. However, the question of the stability of multilayer films on metals (with the exception of W) and the transformation of their electronic structure during heating practically was not studied. This paper relates to physicochemical and electronic processes during high-temperature interaction of beryllium with thermally stable $(10\bar{1}0)$Re face.

2. Experiment procedures

The experiments were carried out in a ultrahigh-vacuum ($p \approx 10^{-10}$ Torr) electron Auger spectrometer (EAS) of high resolution ($\Delta E/E \approx 0.1\%$) with prism energy analyzer [16]. This made it possible to have a large distance (~ 74 mm) between the samples and the input to the energy analyzer and to obtain without loss of sensitivity the Auger spectra from ribbon samples heated up to 2500 K, which made it possible to analyze the surface composition directly under the conditions of the processes being studied, and not after the sample was cooled.

A primary electron beam with energy of 1800 eV and current $\sim 5\,\mu$A irradiated the working surface of the samples with area of 1 mm^2, from which Auger electrons were collected, which ensured the minimization of thermal loads from the electron gun. The unit had a module to implement the combined method of thermionic emission and surface ionization to determine work function of sample surface [16].

Samples were thin rhenium ribbons sized $50 \times 1 \times 0.02$ mm, heated by direct passage of alternating current. Impurities, mainly carbon, were removed from the ribbons by the standard procedure by successive annealing in an oxygen atmosphere at the pressure of $\sim 1 \cdot 10^{-6}$ Torr and temperature of 1500 K, and in ultra-high vacuum at 2300 K. After such cleaning, only Auger peaks of rhenium are recorded on the surface. During cleaning the rolling texture changes into the recrystallization texture, and the face (1010)Re emerges to the surface, its orientation degree according to X-ray diffraction data was $\sim 99.8\%$ [13]. The work function of the rhenium surface was $e\varphi = 5.15$ eV, which corresponded to the above-mentioned face [17]. The ribbon surface was homogeneous in relation to the work function with an accuracy of ± 0.05 eV.

Beryllium was sputtered by sublimation from a Be-ribbon located parallel to the working one to ensure uniform sputtering. The temperature of the sample and the Be-ribbon was determined with an optical micropyrometer at $T \geq 1100$ K, and in the region of lower temperatures — by linear extrapolation of the temperature dependence on the current of the ribbons to room temperature. The temperature uniformity in the middle part of the ribbon (~ 40 mm) in the pyrometric region was no worse than ± 5 K. Auger peaks of both elements in differential form were used for measurements; for Be this is the KVV or KLL peak, the energy of the main minimum was $E = 104$ eV; for rhenium a NOO triplet with energies $E = 161$, 167 and 176 eV was used. Auger signal intensities were measured „peak-to-peak“.

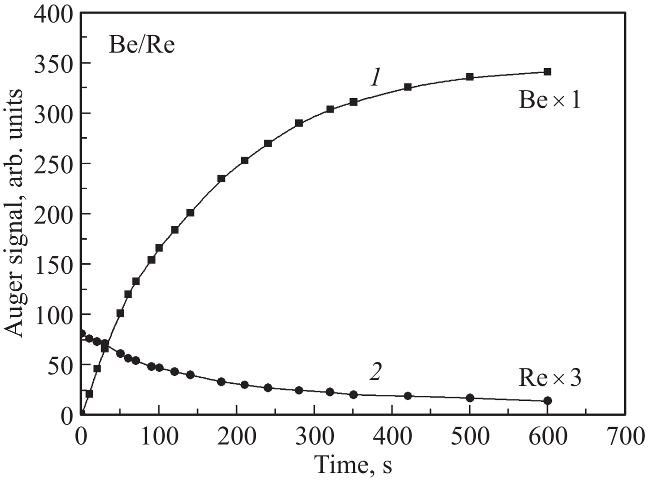

Figure 1. Change in the intensity of the Auger signals Be (*1*) and Re (*2*) vs the time of beryllium deposition on Re(10$\bar{1}$0) at $T = 300$ K with constant Be flux $\sim 1.3 \cdot 10^{13}$ cm^{-2}s^{-1}.

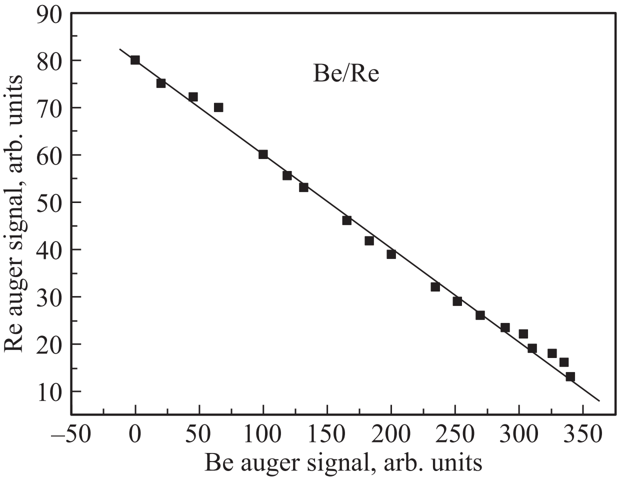

Figure 2. Intensity of Auger-signal of Re vs. Auger-signal of Be during Be deposition on Re(10$\bar{1}$0) at $T = 300$ K with constant Be flux $\sim 1.3 \cdot 10^{13}$ cm^{-2}s^{-1}.

3. Experimental results

3.1. Deposition of Be atoms at $T = 300$ K on (10$\bar{1}$0)Re

Figure 1 shows change in intensity of Auger-signals of beryllium (1) and rhenium (2) vs the time of beryllium deposition on (10$\bar{1}$0)Re at $T = 300$ K by permanent flow. It can be seen that at $t \geq 600$ s the intensity of the Auger signal of beryllium practically ceases to change, and the intensity of the Auger signal of rhenium drops by more than 8 times and is at the noise level of the device. It means that Be film of 5–6 atom layers thick is formed on the surface, 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 [18]. In this case, a very weak Auger signal from the substrate indicates the continuity of the beryllium film. This experiment allows to estimate ν_{Be} — the flux density of beryllium atoms arriving at the surface. In our experiments $\nu_{\mathrm{Be}} = (5{-}6)N_{\mathrm{M}}/t\,\mathrm{cm}^{-2}\mathrm{s}^{-1}$, where $t = 600$ s, and $N_{\mathrm{M}} \approx 10^{15}\,\mathrm{cm}^{-2}$ — concentration of beryllium atoms in a hypothetical close-packed monolayer [19].

Figure 2 shows the same dependence, which is rebuilt in the coordinates $I_{\mathrm{Re}} = f(I_{\mathrm{Be}})$. As one can see, all points of the graph are well approximated by one straight line with no kinks. This nature of the dependence, as well as the absence of kinks in the dependences in Figure 1, make it possible to exclude both layer-by-layer and island (according to the Stranski-Krastanov mechanism) film growth and indicate the formation of the so-called „simultaneous multilayer“, i. e. growth mode implemented at small migration lengths of atoms of the deposited adsorbate, which adhere to the

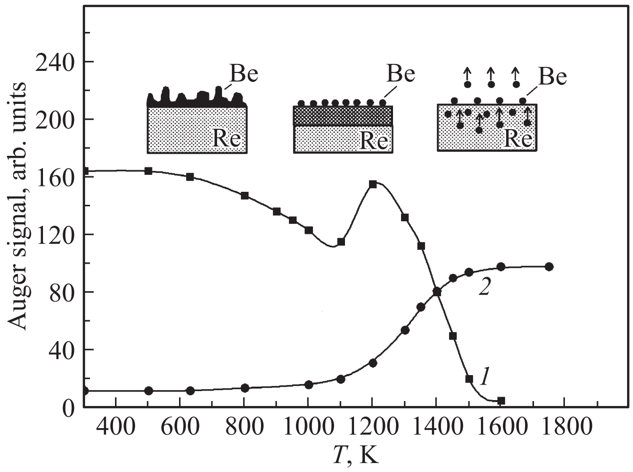

Figure 3. Change in the intensity of the Auger signals of Be (*1*) and Re (*2*) vs. the substrate temperature during annealing of beryllium film ~ 7 layers thick sputtered on Re($10\bar{1}0$) at $T = 300$ K. The annealing time in each point is 30 s. The inserts show the illustration of the processes of interaction between Be atoms and rhenium heated to the appropriate temperatures.

growing film in the place where they statistically fell during deposition [20] (insert in Figure 3).

3.2. Annealing of Be film on ($10\bar{1}0$)Re

Figure 3 shows the change in the intensity of the Auger signals of Be (*1*) and Re (*2*) upon annealing of the beryllium film ~ 7 layers thick (intensity of Auger-signal of rhenium decreased by 10 times), deposited at 300 K, and in Figure 4 — change in the shape of the Auger peak of beryllium during annealing at different temperatures. It can be seen that in the region 300–800 K the intensities of the Auger signals of the adsorbate and the substrate are practically unchanged; the shape of the Auger spectrum of Be also remains constant (spectrum *1* in Figure 4). This indicates the film stability.

At higher annealing temperatures (800–1200 K) the Auger signal of beryllium undergoes significant changes both in intensity (Figure 3) and in the shape of the Auger spectrum (spectra *1–3* in Figure 4). Note that when the shape of the Auger lines of beryllium changes, which corresponds to its different chemical states, a direct comparison of the intensities of the Auger signals „peak-to-peak" is not entirely correct, as we previously observed for different chemical states of carbon on metals [21]. In the same temperature range (800–1200 K) the intensity of the Auger signal of rhenium increases by 3 times which also indicates a strong change in the structure of the adsorbed beryllium film. Direct experiments on the thermal desorption of Be, described in paper [13], indicate that there is no desorption of Be in this temperature range; the only mechanism for the escape of beryllium is its penetration into the bulk of the substrate. Apparently, in this temperature range, the reactive diffusion of the adsorbate into the near-surface region of the substrate bulk prevails with the formation of a bulk intermetallic compound [22], moreover part of the beryllium remains on the surface, and part of the beryllium is built into the lattice of the formed compound (Figure 3, insert).

At $T \geq 1300$ K the Auger signal of beryllium again changes significantly (spectra *3* and *4* in Figure 4). The Auger peak broadens by approximately 6 eV and changes shape — the peak with energy of 95 eV completely disappears, and peaks with energies of 81 and 114 eV appear. At temperatures 1300–1600 K there is a very significant decrease in the Auger signal of beryllium. In this case, the shape of the Auger line of beryllium remains unchanged (spectra *4–6* in Figure 4). In this temperature region the beryllium atoms are actively desorbed from the surface. Note that if complete cleaning of rhenium from beryllium in the surface compound ReBe occurs at $T \approx 1300$ K [13], then for the experiment described above, complete cleaning from Be occurs at $T \approx 1700$ K (Figure 3). The authors attribute this observation to the fact that when the bulk intermetallic compound is destroyed, Be atoms go into a solid solution state and „feed" the beryllium surface compound, through which the desorption of atoms from the surface occurs (Figure 3, insert). This shifts the temperature threshold for complete cleaning of rhenium from beryllium from 1300 to 1700 K. Indeed, the thicker the Be film formed at 300 K is, the higher temperatures are required to completely clean rhenium from beryllium.

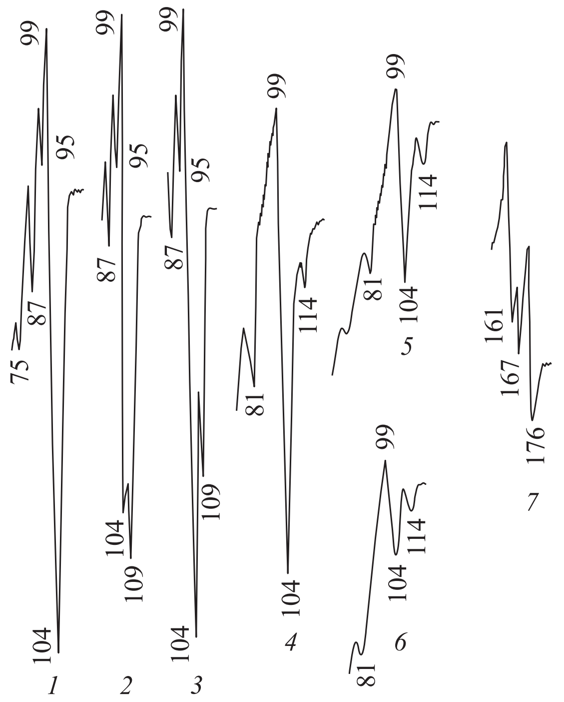

Figure 4. Change in shape of the Auger peak of beryllium during heating of multilayer beryllium film on the Re($10\bar{1}0$) face: *1* — 300, *2* — 800, *3* — 1200, *4* — 1350, *5* — 1450, *6* — 1500 K. *7* — Auger Spectrum of rhenium.

To estimate the activation energy of the reactive dissolution of Be in rhenium, one can use the Frenkel formula for the lifetime of particles on the surface $\tau = \tau_0 \exp[-E/(kT)]$ [23]. Assuming the value of the pre-exponential factor to be equal to $\tau_0 \approx 10^{-13}$ s [23], assuming $T \approx 800$ K, and the characteristic time of the process $\tau \approx 10$ s, we obtain the value $E \approx 2.2$ eV.

3.3. Shape transformation of Auger line of Be on $(10\bar{1}0)$Re

Figure 4 shows the shape change of the Auger signal of beryllium, measured with high resolution, during annealing of the Be film. As you can see, the Auger signal behaves quite unexpectedly. For the multilayer film a wide triplet with three minima is observed at energies of 75, 95 and 104 eV, with the last minimum dominating in intensity.

Heating to 800 K leads to a significant shape transformation of the Auger line — see spectra *1* and *2* in Figure 4. The peak with an energy of 104 eV is splitted into two — an additional peak with energy of 109 eV appears. In this case, the low-energy part of the triplet remains unchanged, and the total peak width does not change when splitting occurs, and remains constant. As mentioned above, in this case the structure of the film is significantly transformed, and a bulk intermetallic compound is formed. The destruction of the intermetallic compound at $T \geq 1350$ K leads to the complete disappearance of the peak with energy of 95 eV, and the appearance of peak with energy of 81 eV. Note that the shape of the Auger spectra *4–6* in Figure 4 corresponds to the surface chemical compound BeRe [13].

Note also that with all the above-described transformation of the shape of the Auger line of beryllium, the shape of the rhenium triplet remains strictly unchanged (spectrum *7* in Figure 4).

4. Discussion

Let's discuss the results. First of all, note that beryllium exhibits a wide variety of Auger spectrum forms, which was previously observed, for example, for carbon [21].

The shape of the Auger line of the multilayer film (spectrum *1* in Figure 4), deposited at room temperature, qualitatively coincides with the shape of the Auger line of metallic beryllium, presented in the classical atlas of Auger spectra [24]. However, in the spectrum presented in the atlas of Auger spectra [24], there is no peak with energy of 75 eV and peak with energy of 87 eV is very weakly expressed. This may be due to both the insufficient resolution of the spectrometer of cylindrical mirror type used in [24] (it was 0.25%), and to differences in the atomic, and therefore in the electronic structure of metallic beryllium, and seven-layer film on the surface of rhenium. In fact, the „simultaneous multilayer“ growth mode creates a highly defective film, the structure of the valence band of which may differ from that of the solid beryllium crystal. Note that the shape of the Auger signal of beryllium, KVV, is determined by the self-convolution of the valence band structure [18].

Let's consider the temperature range 800–1200 K. The shape transformation of the Auger line of beryllium in this range, first of all, the appearance of peak with energy of 109 eV, i. e. shifted by 5 eV compared to the peak from the metal film, shows that in this temperature range a new chemical state of beryllium atoms is formed, that differs from both the state that took place in the multilayer metal film, and the state that was observed at higher temperatures where a surface compound ReBe is formed. The observed line shape suggests that in this range two different phases coexist on the surface: metal film (it gives a peak with energy of 104 eV) and, apparently, a bulk intermetallic compound, which gives the peak with energy of 109 eV. With the temperature increasing within the above-mentioned range, the major part of beryllium atoms is built into the intermetallic compound, which corresponds to increase in the peak with energy of 109 eV compared to the peak of metallic beryllium (spectra *1, 2* in Figure 4).

The nature of the observed energy shift is still not clear. Typically, this magnitude of shift is characteristic of the situation where compounds with strong electronegative atom, such as oxygen, fluorine or carbon, are formed. However, in our case, none of the listed atoms presents on the surface, since their Auger peaks are not observed. Meanwhile, the electronegativities of rhenium and beryllium are close [25].

A more probable situation seems to be that the peak with energy of 109 eV is due to the structure of the filled part of the valence band of the intermetallic compound, which, unfortunately, was not yet calculated and measured on a pure sample. At the same time, the OVV Auger peak of rhenium, which should undergone transformation under such conditions, cannot be measured, since its energy is low (~ 30 eV), and it lies on the slope of a very intense peak of true secondary electrons, and overloads the detection device of any Auger spectrometer.

Finally, consider the line shape corresponding to the surface beryllide ReBe. The rhenium $(10\bar{1}0)$ face is grooved, the substrate atoms are located on it in rows [19]. The beryllium atoms are apparently located between the rows; Most likely, there is a certain reconstruction or relaxation of the face, as it is usually during adsorption.

One might assume that the adsorbed beryllium atoms do not form chemical bonds with each other; then, when forming the Auger line shape, the process occurs only with the participation of electrons belonging to each individual atom, i. e. the peak will have a KLL structure. Qualitatively, this model should correspond to a simple single peak, close in shape to the derivative of the Gaussian, without additional structure. However, in practice, we have a rather complex triple peak with energies 81, 104 and 114 eV, and the intensity ratios of these peaks in the spectrum change with decreasing of concentration of atoms on the surface. Apparently, this means that a two-dimensional valence band is formed for the given surface state, which is responsible for the observed shape of the Auger line. It is interesting to note that similar structure of the KVV Auger line of beryllium is observed not only on rhenium, but also on other substrates, tungsten [14] and iridium [15].

5. Conclusion

It is shown that multilayer beryllium films on the $(10\bar{1}0)$ face of rhenium undergo successive transformations when heated, as a result of which the structure of the KVV Auger line of beryllium significantly changes. This transformation is associated with the restructuring of the filled part of the valence band of the surface, and can be used as an effective indicator of the physicochemical structure of films.

Conflict of interest

The authors declare that they have no conflict of interest.

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