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Surface Compound Formation in Be Adsorption on W(100): absolute concentration and properties

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Be adsorption at $T = 900-1100\,\mathrm{K}$ results in formation of a stable adsorption state; it drops the activation energy of atomic Be dissolution in the substrate bulk, and all newly deposited Be dissolves in the substrate. The absolute concentration of atomic Be in this state has been measured by Auger electron spectroscopy using specially designed ultra high vacuum getter Be source. The concentration is $(1.0 \pm 0.1) \cdot 10^{15}\,\mathrm{sm^{-2}}$ and corresponds to WBe stoichiometry relative to W surface concentration. The layer is destroyed at $T > 1100\,\mathrm{K}$, the atomic Be dissolves in the bulk with the activation energy $\sim 3.5\,\mathrm{eV}$.

Keywords: adsorption, surface, beryllium, tungsten, solid solution.

Elements of the first and second periods with s and p electrons are the most widespread impurities and technologically significant ligands that define the properties of the majority of transition metals and their alloys. The adsorption of these elements on the surface of refractory metals allows one to estimate the key properties of alloys, since it is the inner surfaces (grain boundaries) that play a critical role in materials physics [1–3]. The key factor is the formation of distinctive adsorption states (surface compounds) on the surface that alter the rates of passage of atoms through surface diffusion barriers by many orders of magnitude [4,5].

Beryllium is one of the most promising elements for aerospace applications and ligands in metallurgy; its alloys are used widely in instrumentation engineering and the defense industry [6,7]. It is one of the most interesting elements in terms of its physical and chemical properties: beryllium combines metallic conductivity and a small atom size with a very high ionization potential ($\sim 9\,\mathrm{eV}$) that is typical of non-metal atoms [8]. The adsorption of beryllium on tungsten is especially important, since this combination of elements is used widely as the first-wall material in modern tokamaks (specifically, the International Thermonuclear Experimental Reactor, ITER).

Several papers focused on the Be−W adsorption system have already been published [9–14]. X-ray photoelectron spectroscopy was used in experimental studies [9,12,14] to examine the thermal stability of nanometer beryllium films and the formation of bulk compounds. These studies have a common drawback in that data on the absolute concentrations of deposited beryllium are lacking (primarily due to the technological complexity of its stable deposition in ultrahigh vacuum). The present study is aimed at determining the absolute concentration of beryllium atoms on W(100).

Experiments were performed in an ultrahigh-vacuum high-resolution ($\Delta E/E \sim 0.1\%$) electron Auger spectrometer [15]. The examined samples were thin tungsten ribbons $50 \times 1 \times 0.02$ mm in size with work function $e\varphi = 4.65\,\mathrm{eV}$ that corresponds to the (100) face. The surface was uniform in terms of the work function. According to the X-ray diffraction spectroscopy data, the orientation degree of (100) face was about 99.5%.

Beryllium was deposited from a specially designed source based on the dissolution of Be atoms in iridium and its subsequent thermal desorption. The design of this source will be detailed in a separate paper.

Fig. 1 shows the variation in intensity of Auger signals of Be ($E = 104\,\mathrm{eV}$) and W ($E = 163\,\mathrm{eV}$) in the process of constant-flux deposition of Be onto W(100) at $T = 1100\,\mathrm{K}$. It can be seen that the intensity of the Auger signal of Be increases almost linearly and reaches saturation („plateau") at $t \geqslant 70\,\mathrm{s}$. Similar curves with a „plateau" were observed when the temperature of the tungsten ribbon was varied within the $900-1100\,\mathrm{K}$ range.

It is likely that, just like the other adsorbates (e.g., Si, P, S, C, O) that form surface compounds (SCs) of the WX (X is the adsorbate atom) [4] stoichiometry with tungsten, beryllium forms SC with tungsten. The linear growth of the concentration of Be atoms in the process of deposition, the fact that the curve shape does not depend on T, and the weak screening of the Auger signal (by a factor of 1.8) suggest that, just like Si, P, and S atoms, all deposited Be atoms remain on the surface; in other words, beryllium does indeed form a stable adsorption state similar to an SC.

In order to determine the absolute concentration of deposited Be in SC, we compared the intensity of its Auger signal with the signals of other adsorbate atoms that are also positioned on the surface only with concentrations that were measured earlier. P and Si atoms were used for this purpose.

The dynamics of phosphorus adsorption on the same tungsten ribbon at $T = 1100\,\mathrm{K}$ are presented in
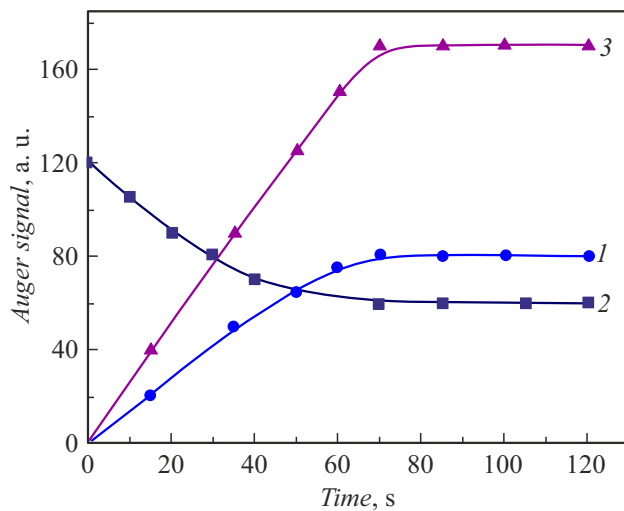
Figure 1. Variation in intensity of Auger signals of beryllium (*1*), tungsten (*2*), and phosphorus (*3*) with time in the process of adsorption of beryllium or phosphorus in the PCl$_3$ compound on W(100) at $T = 1100$ K.

Fig. 1 (curve *3*). PCl$_3$ molecules were used for this purpose: at $T > 1000$ K, these molecules break down, chlorine in the Cl$_2$ form is desorbed, and phosphorus remains on the surface of tungsten and forms SC of the WP stoichiometry, where $N_W = N_P = 1 \cdot 10^{15}$ atom/cm^2 [16]. According to the handbook of intensities of Auger spectra of chemical elements for Auger electron spectroscopy (AES) [17], AES is approximately 2.1 times more „sensitive" to phosphorus than to beryllium. It can be seen from Fig. 1 (curves *1* and *3*) that the Auger signal intensity of phosphorus ($E = 120$ eV) is 2.05 times higher than the signal intensity of beryllium ($E = 104$ eV). The similarity of energies of Auger peaks and the use of the same substrate allows one to compare the intensities of these peaks directly and without regard to the contribution of back-scattered electrons. Therefore, it seems fair to say that the concentrations of P and Be atoms on W(100) in surface compounds are equal and, consequently, beryllium on tungsten forms an SC of the WBe type, where $N_{Be} = (1.0 \pm 0.1) \cdot 10^{15}$ atom/cm^2.

A similar experiment was performed with the SC of silicon on W [5] used as the calibration standard. The value of $I_{Si}/I_{Be} = 3.4 \pm 0.2$ was derived from the direct comparison of Auger signal intensities I_{Si} ($E = 92$ eV) and I_{Be}. This value agrees closely with the one from the handbook of element spectra ($I_{Si}/I_{Be} = 3.5$) [17].

Thus, beryllium on W(100) forms an SC of the WBe stoichiometry in the process of adsorption in the $900-1100$ K temperature range.

Let us consider the thermal stability of the SC of beryllium with tungsten. Fig. 2 shows the variation in intensity of the Auger signal of Be and W in the course of annealing of the WBe SC. It can be seen that the compound breaks down at $T > 1100$ K. At $T = 1400$ K,

the surface is completely free from beryllium, while the intensity of the Auger signal of W is restored to its former value (curve *2* in Fig. 2). The removal of Be from the surface may be associated both with its desorption and with the dissolution of beryllium in the bulk of tungsten. In order to clarify this issue, we used an additional tungsten ribbon positioned at a distance of ~ 20 mm at an angle of 45° to the working ribbon. WBe SC was formed on the additional ribbon at $T = 1000$ K, and the sample was then heated. The expected desorption products were identified by AES on the working ribbon only when the additional ribbon was heated above 2400 K. Therefore, the removal of beryllium atoms from the surface at $T = 1400$ K is induced only by the dissolution of Be in the bulk of the substrate.

Fig. 3 presents the kinetics of intensity variation of Auger signals of Be and W in the process of dissolution of beryllium in tungsten at $T = 1300$ K. Using the well-known expression $\tau = \tau_0 \exp(E/kT)$ [18] for lifetimes τ of adatoms on the surface and setting $\tau_0 = 10^{-13}$ s, we find the following estimate for the energy of activation of the transfer of Be atoms from the surface to the bulk of tungsten: $E = 3.5-3.7$ eV. This energy has a weak concentration dependence $E = f(N_{Be})$. The obtained E value agrees closely with the one calculated theoretically for the (100) W face in [13].

It was demonstrated in our studies [4,5] that the SC formation is related to the fact that the surface of metals (W) features centers with a preferential strength of the chemical bond with the adsorbate, which are occupied first. Incoming atoms start either to dissolve in the bulk of a metal (Si, C) or to desorb (S, P, O) [4,5] only after the filling of these centers. The energy of activation of the corresponding process changes abruptly, altering its rate by a factor of several hundred thousand or several million. Apparently, the case of Be is similar. The experiments demonstrated that when Si atoms are adsorbed at $T = 1000$ K on WBe
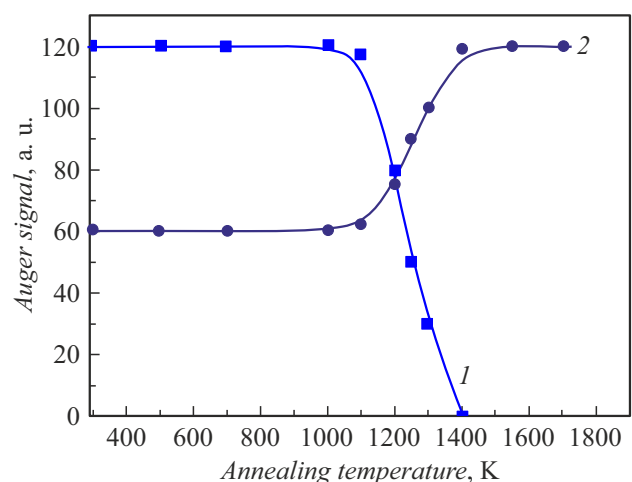

Figure 2. Variation in intensity of Auger signals of beryllium (*1*) and tungsten (*2*) in the process of annealing of the WBe surface compound at different temperatures. The annealing time at each temperature point is 30 s.
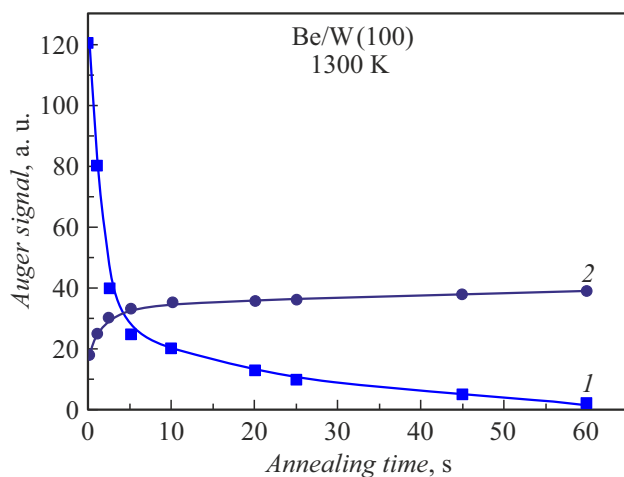
Figure 3. Variation in intensity of Auger signals of beryllium (*1*) and tungsten (*2*) with time in the process of annealing of the WBe surface compound at $T = 1300\,\text{K}$.

SC (all strongly bound centers are occupied by Be atoms), silicon does not accumulate on the surface and starts dissolving immediately. Note that surface compounds react with atoms of other substances [19]. For example, the deposition of $N_{\text{Be}} = 1 \cdot 10^{15}$ atom/cm^2 Be atoms on WSi SC at $T = 1000\,\text{K}$ in our study resulted in complete substitution of Si atoms that dissolved in the bulk of tungsten.

Thus, it was demonstrated that the deposition of Be atoms on a W(100) surface results in the formation of a distinctive adsorption state: a surface compound similar to those that were formed by Si, S, P, C, and O atoms on W(100). Using an ultrahigh-vacuum getter source of a proprietary design and the Auger electron spectroscopy technique, we determined the absolute concentration of Be in this state. This allowed us to reconstruct the physics of the processes involved and use the (100) W face as a „calibration" surface for various atoms (Be included). It is fair to assume that similar SCs with Be should also form on other substrates (especially those that are stable and feature a marked atomic relief).

Conflict of interest

The authors declare that they have no conflict of interest.

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