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Formation of surface oxide in oxygen adsorption with molecular and atomic fluxes on W(100)

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Adsorption-desorption processes on the W(100) surface involving oxygen and formation of surface oxide are studied. It is shown that oxygen adsorption in the form of O_2 molecules at 1300−1400 K leads to formation of oxygen-deficient surface oxide with stoichiometry $WO_{0.9}$, while oxygen dissolution in the bulk of tungsten is not observed. In the case of mixed adsorption, including both O_2 molecules and O atoms, a surface oxide with stoichiometry WO is formed, after the formation of which oxygen atoms dissolve in the bulk of the metal to form a solid solution. Oxygen dissolved in the bulk increases the thermal stability of the surface oxide due to supply of oxygen coming to the surface. The estimates show that the activation energy of oxygen desorption from W(100) varies from $E_d \approx 4.7$ eV for $\theta_O \approx 1$; up to $E_d = 6.0$ eV for $\theta_O \ll 1$.

Keywords: tungsten, surface oxide, adsorption, desorption.

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1. Introduction

The interaction of O_2 molecules with tungsten has been studied in many experimental and theoretical papers in a wide range of substrate temperature variations [1–9]. The generally accepted concept of the processes is that exposure of face W(100) in an oxygen atmosphere at room temperature to surface layer saturation results in the dissociative oxygen chemisorption up to a concentration close to $1 \cdot 10^{15}\,\mathrm{cm}^{-2}$ [4,5,9], i.e. it leads to the formation of a surface oxide with the stoichiometry WO, and the actual surface oxygen concentration is approximately 10% lower than the nominal [2,5]. Oxygen from the so-created surface compound does not dissolve in the bulk of tungsten, but it is thermally desorbed during heating in the range of $T = 1600-2100$ K [2,4]. The exposure of tungsten in an oxygen atmosphere in the temperature range of 300−1200 K after the formation of a chemisorbed monolayer results in growth of bulk oxides of various compositions [9].

The size of the oxygen atom is small, of the order of 1.3 Å, and it belongs to the typical interstitial impurities [10], therefore, the absence of its diffusion into the bulk in the solid solution state at $T < 1300$ K is surprising. Apparently, this is attributable to the physical inability to accumulate a sufficient concentration of chemisorbed oxygen atoms on the surface in case of the dissociative adsorption of O_2 molecules. The objective of this paper is to study the differences of the formation and thermal stability of surface tungsten oxide during oxygen adsorption by atomic and molecular fluxes; the formation and growth of bulk oxides that are formed and present on a tungsten substrate at $T < 1300$ K [3,9] is not discussed in this paper.

2. Experimental technique

The experiments were conducted using high-resolution multipurpose ultrahigh vacuum electron prism Auger spectrometer ($\Delta E/E \approx 0.1\%$), which makes it possible to obtain Auger spectra from samples heated to 2500 K, which in some cases was of fundamental importance for the correct understanding of physical and chemical processes in films adsorbed on the surface of samples [11].

Thin tungsten ribbons with the size of $50 \times 1 \times 0.02$ mm, heated by direct current, were used. The ribbons were cleaned in an oxygen atmosphere at a pressure of $\sim 10^{-6}$ Torr (mainly from carbon) and at a temperature of 1500 K, and then in an ultrahigh vacuum at $T = 2500$ K. Only tungsten Auger peaks were recorded after such purification, and no annealing resulted in the occurrence of other contaminants on the surface, which indicates the high purity of the sample bulk.

The rolling texture is replaced by the recrystallization one during annealing and a face (100) appears on the surface. The degree of orientation of the face is $\sim 99.5\%$ according to X-ray diffraction data. The work function of the surface is $e\varphi = 4.65$ eV, which corresponds to the face W(100) [12]. The surface was uniform in the work function with an accuracy of ± 0.05 eV.

Oxygen was applied to the surface by two methods. Firstly, by adsorption of O_2 molecules on a heated substrate. Secondly, an oxygen atomizer was used in the form of an auxiliary tungsten ribbon-atomizer installed parallel to the working ribbon at a distance of 10 mm from it at an angle of 45 degrees. It was heated in an oxygen atmosphere at $P \approx 10^{-7}$ Torr to $T = 2400$ K, O_2 molecules falling on its surface dissociated, and the flux of oxygen atoms was desorbed from the surface [5,9]. Two fluxes entered the surface of the working ribbon simultaneously in this case: a flux of O_2 molecules from the vacuum and a flux of O atoms from the surface of the auxiliary ribbon.

The ribbon-atomizer was cleaned using the same procedure as the working ribbon. Its heating in the range of $T = 1000-2500$ K after cleaning in an ultrahigh vacuum did not lead to registration of any elements on the surface of the working ribbon: only tungsten Auger peaks were recorded. This also was indicative of the atomic purity of not only the surface, but also the bulk of the ribbon-atomizer.

A triplet of Auger peaks of tungsten with energies 163, 169, 179 eV and an Auger peak of oxygen with energy 503 eV were used for measurements. The intensity of the Auger signals was measured „peak-to-peak“.

The temperature of the samples at $T > 1100$ K was measured using an optical micropyrometer, and by linear extrapolation of the temperature dependence on the filament current of the ribbon to room temperature in the region of lower temperatures. The temperature uniformity in the middle part of the ribbon (~ 45 mm) was no worse than ± 5 K. The diameter of the „spot“ analyzed by the Auger spectrometer in the middle part of the ribbon was ~ 1 mm.

3. Experimental results

3.1. Formation of surface oxide in molecular and atomic adsorption of oxygen

The formation of surface compounds (SC) of oxygen with tungsten was previously observed in Ref. [4]. The oxygen Auger signal increases in the case of molecular oxygen adsorption at $P \approx 1 \cdot 10^{-7}$ Torr on tungsten heated to $T = 1300-1400$ K (see Figure 1, *a*, curve *1*) and the tungsten Auger signal decreases. Both Auger signals reach a plateau at the adsorption time ~ 150 s, and the intensity of the tungsten Auger signal decreases by ~ 1.3 times which is characteristic for the formation of a surface compound. The accumulation of oxygen on the surface stops after reaching this state and does not depend on further exposure in the atmosphere of O_2. The shape of the oxygen Auger signal intensity curve is well approximated by the Langmuir isotherm.

Oxygen molecules dissociate on the surface in these experiments, and its atoms accumulate in the adsorbed layer to a concentration that was estimated in [5] as $N_O \approx 0.9 \cdot 10^{15}\,\text{cm}^{-2}$. This value is very close to the concentration of surface atoms on W(100) face, which makes us consider the resulting adsorption state to be a surface compound WO with some oxygen deficiency. Experiments on thermal desorption of oxygen performed in Refs. [5,9] show that oxygen does not penetrate into the bulk. It should be noted that the shape of the Auger spectrum of oxygen, as well as other *p*-elements, is very sensitive to its chemical state. In this case, it remains constant throughout the adsorption time (Figure 1, *b*) and is typical for metal oxides [13].

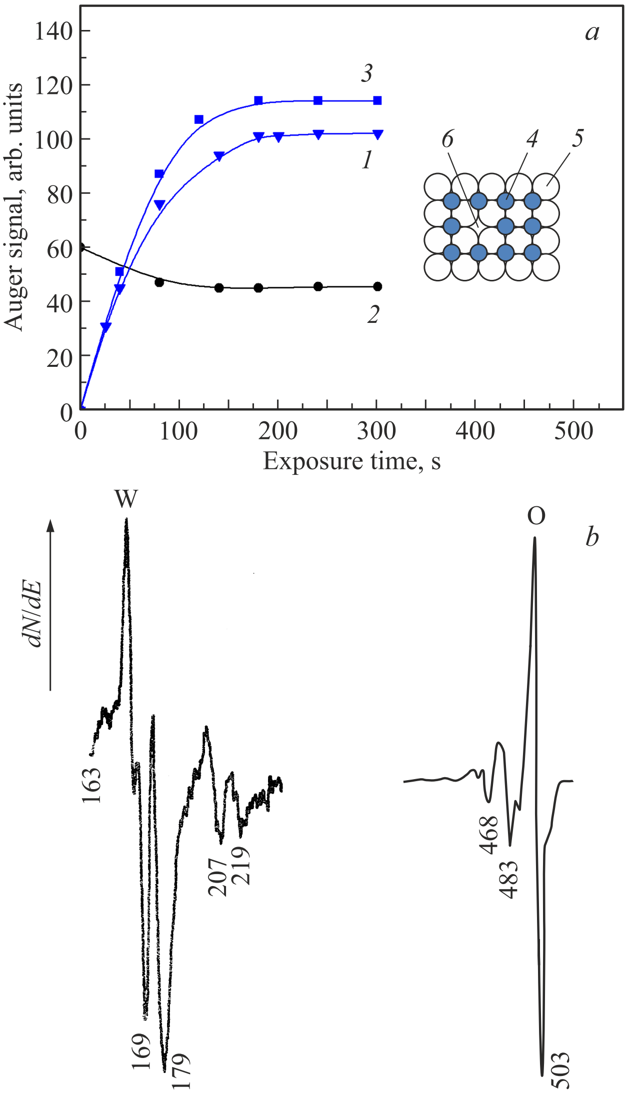

Figure 1. *a* — dependence of oxygen Auger signals (*1, 3*) and tungsten (*2*) on the exposure time of the sample in an oxygen atmosphere at $T = 1300$ K and $P \approx 1 \cdot 10^{-7}$ Torr. *1, 2* — oxygen atomizer is off; *3* — oxygen atomizer is on. The insert shows a simplified illustration of the formation of the surface compound $WO_{0.9}$: oxygen atoms (*4*), tungsten (*5*); *6* — free adsorption center on the face of W(100). *b* — Auger spectra of tungsten and oxygen from a surface compound.

The situation changes if the ribbon-atomizer is turned on simultaneously with the oxygen admission: the experimental results are shown in Figure 1, *a* curve *3*. It can be seen that the rate of oxygen accumulation on the surface slightly increases, the curve becomes more angular, while the intensity of the oxygen Auger signal increases compared to purely molecular adsorption. The intensity of the substrate's Auger signal remains approximately the same as in the

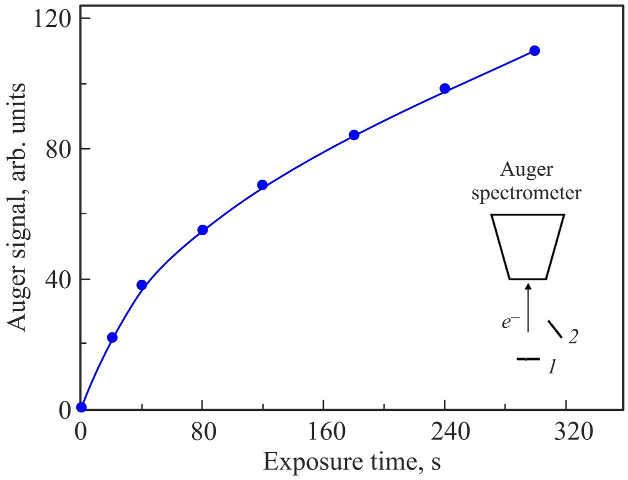

Figure 2. Change of the intensity of the oxygen Auger signal on the surface of the working ribbon (*1* — in the inset) during heating of the auxiliary tungsten ribbon (*2*) — up to 2400 K. Each point on the curve corresponds to a different annealing time of the auxiliary ribbon (*2*) at $T = 1300$ K using combined molecular and atomic oxygen adsorption. The oxygen deposition conditions correspond to those for the curve *3* in Figure 1, *a*.

previous case: the experimental accuracy is not sufficient to measure possible differences.

3.2. Thermal desorption of oxygen

It is important to understand whether oxygen penetrates into the bulk in case of its purely molecular adsorption and when an atomizer is used. An inverse experiment was performed for this purpose: both ribbons were cleaned, and then the auxiliary ribbon was kept in an oxygen atmosphere under conditions similar to those described above for curves *1* and *2* in Figure 1, *a*. The oxygen was pumped out after that, and the main ribbon was cleaned by heating at 2400 K, then the temperature was lowered to 300 K: the surface becomes pure under these conditions and only tungsten Auger peaks are recorded on it. Then the auxiliary ribbon was heated to 2400 K: weak oxygen Auger peaks appeared on the main ribbon at the level of 10−15% monolayer. This corresponded well to the calculated efficiency of atom transfer from the surface of one ribbon to another. The amount of oxygen desorbed from one ribbon to another in such an experiment did not depend on the exposure time of the auxiliary ribbon in oxygen after the formation of a monolayer coating on it (for $t > 150$ s). These data were in good agreement with the experiments on thermal desorption of oxygen with its mass spectrometric registration performed in the study in Ref. [9]. It was also concluded that the accumulation of oxygen in the bulk of tungsten neither in the form of bulk oxides nor in the form of a solid solution takes place at $T > 1300$ K.

A similar experiment was conducted under conditions of combined oxygen adsorption, atomic and molecular adsorption at the same time. This experiment was again inversed: the working ribbon was used as an auxiliary, and the auxiliary was used as a working ribbon. The auxiliary ribbon was annealed at $T = 1300$ K during the oxygen admission, and the working ribbon was heated at $T = 2100$ K, so that a flux of oxygen atoms came from it to the surface of the auxiliary ribbon. The oxygen was pumped out after exposure the system in this mode for 20 s, the working ribbon was cleaned, and the auxiliary ribbon was heated to $T = 2400$ K, and the amount of oxygen desorbed from its surface and deposited on the working ribbon was measured. Then the experiment was repeated: first, both ribbons were cleaned of oxygen, and then the operating time of the atomizer was increased to 40 s, then to 80 s, etc. and the entire procedure described above was repeated. The results of these experiments are shown in Figure 2.

As can be seen, an almost linear growth of the amount of oxygen desorbed from the auxiliary ribbon takes place at the initial stages. Then, this growth slows down at $t > 80$ s, but still continues, and the curve is still almost linear, but with a significantly lower slope.

Thus, an accumulation of oxygen is observed in the bulk of the auxiliary ribbon, which, when heated, acts as a source of atomic oxygen.

3.3. Thermal stability of the surface oxide in case of various methods of its formation

Figure 3, *a* shows the dependence of the oxygen Auger signal on the annealing temperature of the surface oxide WO formed by various methods. As can be seen, when the surface oxide is formed by purely molecular adsorption (curve *1* in Figure 3, *a*) the oxygen Auger signal is practically stable up to $T = 1500$ K, after which it decreases with an increase of T and is completely removed from the surface at $T \geq 2100$ K; the amplitude of the tungsten Auger signal is restored at the same time. The process described by the curve (*1*) in Figure 3, *a* is irreversible — oxygen leaves the surface irrevocably.

The use of thermal desorption spectrometry in Refs. [5,9] allows confidently asserting that the loss of oxygen from the surface is caused mainly by thermal desorption in the form of individual atoms, and oxygen atoms practically are not diffused from the surface oxide WO into the metal bulk.

It should be noted that each of the points represented on the curve *1* Figure 3 is practically stationary, which indicates a strong dependence of the desorption activation energy E_d on the coverage. We studied the kinetics of oxygen desorption from W(100) in Ref. [4] and determined the concentration dependence of the desorption activation energy E_d, which is in good agreement with the results shown in Figure 3, *a*. So, $E_\text{d} \approx 4.7$ eV for $\theta_\text{O} \approx 1$; and $E_\text{d} = 6.0$ eV for $\theta_\text{O} \ll 1$.

The situation significantly changes if the surface oxide is created using an atomizer. The oxygen concentration in the surface oxide phase increases by $\sim 10\%$ in this case, i. e. surface compound with stoichiometry WO is

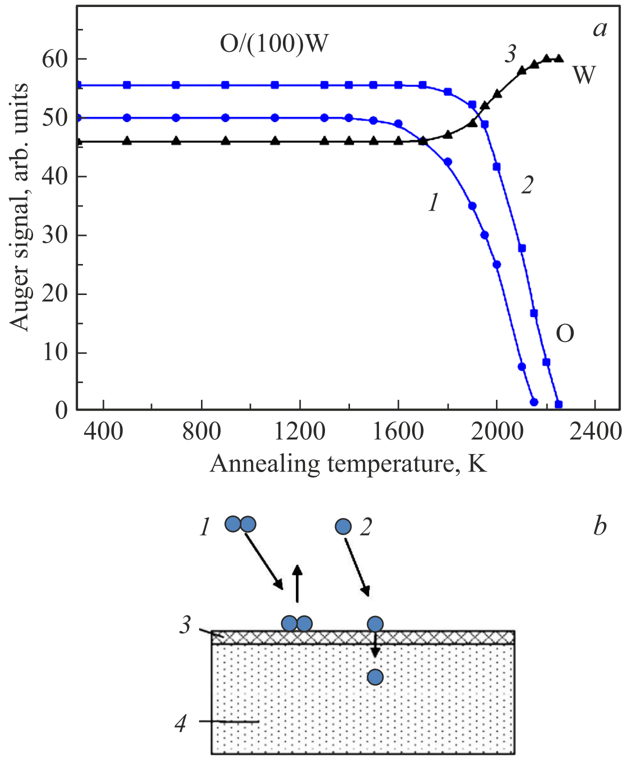

Figure 3. Thermal stability of surface tungsten oxide. *a* — dependence of the intensity of the oxygen Auger signal (*1*) on the annealing temperature of the surface oxide $WO_{0.9}$ obtained by adsorption of O_2 molecules at 1300 K and Auger signals of oxygen (*2*) and tungsten (*3*) on the annealing temperature of the surface oxide WO obtained using an atomizer. The annealing time at each point is 20 s, the measurements were conducted directly at the annealing temperature. *b* — simplified illustration of the processes of oxygen interaction with W(100) with the operating oxygen atomizer: *1* — molecule O_2, *2* — oxygen atom, *3* — surface oxide WO, *4* — tungsten substrate.

obtained. In addition, the experiments described above showed that a channel opens for the diffusion of oxygen atoms into the bulk of tungsten into a solid solution, and there is no formation of bulk oxides (see Figure 3, *b*). The oxygen accumulated in the sample bulk increases the thermal stability of the surface oxide due to supply of oxygen released from the metal bulk. The annealing curve shifts to the region of higher temperatures by almost 200 K in this case — curve *2* in Figure 3, *a*.

4. Discussion of results

Let us discuss the results. Exposure of the face W(100) in an oxygen atmosphere to saturation at $T \approx 1300{-}1400$ K leads to dissociative oxygen adsorption up to a concentration of $\sim 0.9 \cdot 10^{15}\,\mathrm{cm}^{-2}$ [5], i.e. to the formation of a surface layer oxide WO with a slight oxygen deficiency. O_2 adsorption has a dissociative nature if we rely upon the physical picture of oxygen adsorption on W(100) developed in Refs. [2,4]. The authors reasonably assume that the geometric adsorption site of the oxygen atom is the fourfold hollow sites between the four tungsten atoms — the places with the strongest chemical bond — see the insert in Figure 1, *a*. The dissociation of an oxygen molecule on W(100) apparently requires the presence of two adjacent sites free of adsorbate. Obviously, single free sites should occur at the final stage of the adsorption of O_2 — the nearby fourfold hollow sites will be already occupied by oxygen atoms. Modeling of the process of arbitrary collision of O_2 molecules with W(100) shows that $\sim 10\%$ of single sites remain on the surface at the final stage of adsorption. Therefore, a slight oxygen deficiency is possible in the case of the formation of surface tungsten oxide, as noted in Ref. [5].

On the contrary, when an atomizer is used, the oxygen concentration in saturation turns out to be about 10% higher, i.e. it corresponds well to WO stoichiometry. Apparently, oxygen atoms, arriving at the surface together with O_2 molecules, occupy those free adsorption sites that are inaccessible in case of purely molecular adsorption.

It is interesting to note that adsorption of such atoms as C, Si, Be, S, and P on a heated W(100) does not have the above-mentioned features associated with dissociative adsorption, and surface compounds of WC, WBe, WSi, WS, WP stoichiometries are formed on the surface of W(100) [14]. The above compounds are formed by the adsorption of the very first portions of atoms on the surface of metals. Apparently, all the above-mentioned adatoms occupy the same places on the W(100) face — the fourfold hollow sites. The formation of SC dramatically changes the energy of processes on the surface. For example, if C adatom with $\vartheta_C \ll 1$ has a activation energy of dissolution in the bulk of tungsten of $E_s = 5.0$ eV, then newly arriving atoms easily dissolve in the metal at $T = 800$ K after formation of WC surface compound with a dissolution activation energy of $E_s = 2.5$ eV [14]. It should be noted that after the formation, for example, of WSi and WBe surface compounds, a channel opens for the dissolution of newly deposited atoms of these elements into the bulk of tungsten, as is the case with oxygen.

It should be noted once again that oxygen from the composition of the surface oxide WO is strongly bound to the surface tungsten atoms and is completely removed from the surface by desorption at $T \geq 2100$ K (Figure 3, *a*). The use of thermodesorption spectrometry method allows confidently asserting that the loss of oxygen from the surface is due to thermal desorption, oxygen atoms do not diffuse from WO surface compound into the bulk of metal.

It can be assumed that a sharp decrease of the efficiency of further dissociation of O_2 molecules is one of the possible reasons why the oxygen does not dissolve in the metal bulk in case of its molecular adsorption after the formation of WO surface compound.

5. Conclusion

Thus, three factors are necessary for the dissolution of oxygen in the bulk of tungsten with the formation of a solid solution: the formation of a full-value surface oxide, the supply of oxygen to its surface in the form of an atomic flux, and sufficiently high temperatures, $T > 1300\,\mathrm{K}$.

Conflict of interest

The authors declare that they have no conflict of interest.

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