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## Sodium Adsorption on the Surface of Thermally Oxidized Tungsten

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Photoelectron spectroscopy was used to study the electronic structure in situ in an ultrahigh vacuum before and after the adsorption of sodium atoms on the surface of tungsten oxidized at an oxygen pressure of 1 Torr and a temperature of 950 K. The photoemission spectra from the valence band and the W 4*f*, O 2*s*, and Na 2*p* core states were studied under synchrotron excitation in the photon energy range 80–600 eV. It is found that a tungsten oxide film is formed containing various tungsten oxides with an oxidation state of 6+ to 4+. The deposition of a 1.1 monolayer of sodium atoms on the surface of oxidized tungsten leads to the reduction of the W<sup>6+</sup> states to W<sup>4+</sup> and the reaction with oxygen in the hydroxyl composition, which is reflected in the change in the spectrum of the W 4*f* and O 2*s* core states. It is shown that the cathodoluminescence spectrum is associated with the luminescence of tungsten oxide.

**Keywords:** adsorption, sodium, tungsten oxides, photoelectron spectroscopy, cathodoluminescence.

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### 1. Introduction

The WO<sub>3</sub> tungsten oxide is widely used in the electronic industry: it is used in creating various gas detectors, in solar energetics, photo- and electro-chromic materials and catalyzers. Thermally oxidized tungsten is also used in the mass-spectroscopy as an emitter for thermal ionization of organic molecules, because it provides the work function value of 6.76 eV [1]. There are various methods of producing the tungsten oxides: magnetron evaporation, thermal evaporation, sol-gel deposition, gas-phase deposition, liquid-phase deposition methods, including electrochemical synthesis, oxidization of tungsten at high temperatures, etc. It is also possible to produce thin films of the tungsten oxide when heating it in oxygen.

There are many tungsten oxides with a various stoichiometry. There are three main ones to be picked up: a WO<sub>3</sub> semiconductor oxide, W<sub>2</sub>O<sub>5</sub> and WO<sub>2</sub> metallic oxides. The WO<sub>3</sub> tungsten oxide has the following phases: a monoclinic stable  $\gamma$ -phase, a triclinic  $\delta$ -phase, a stable orthorhombic  $\beta$ -phase and a tetragonal  $\alpha$ -phase [2,3]. The WO<sub>3</sub> crystal structure is formed by 1 tungsten atom and 6 oxygen atoms, which form an octahedron to be slightly deformable for different WO<sub>3</sub> phases. For the WO<sub>3</sub>  $\gamma$ -monoclinic phase, a restructured surface (001) is thermodynamically stable [4].

The WO<sub>3</sub> is a wide-bandgap semiconductor of the *n*-type with the band gap of  $\sim 2.8$  eV. The WO<sub>3</sub> electron structure was a subject in many papers, for example, [5–9]. For WO<sub>3</sub> monoclinic phase, the valence band is made of the

O 2*p* states with a minor impurity of W 5*d* states, while the conduction band is made of the W 5*d* states. The oxide's valence band is a wide band of  $\sim 8$  eV with two peaks with the binding energies of  $E_b = 1$  and 4 eV below a maximum position of the valence band  $E_{VBM}$  [5]. The W 5*d* states are observed near the Fermi level, e.g. [10,11]. The similar results have been also obtained in other papers [12–16].

Photoelectron spectra of the tungsten oxides are studied to determine a composition of the tungsten oxides both on the surface and in the bulk of the sample. The study of a shape of the photoelectron spectra of the tungsten core level W 4*f* and the valence band spectrum shows that it depends on external conditions and preparation methods [17,18]. The shape of the spectra of the tungsten core level W 4*f* reflects well tungsten states with various oxidization states. Much less attention is paid to study the O 1*s* (O 2*s*) core levels, from which it is possible to distinguish impact of adsorbed water on formation of the tungsten oxides [17].

The paper [10] has studied the formation of tungsten oxide films in magnetron sputtering of tungsten in the Ar-O<sub>2</sub> atmosphere and shown that decrease in the oxygen pressure from 18 to 1.8 Torr leads to increase in the spectrum width of the W 4*f* core levels and occurrence of new peaks. Thus, for the oxygen pressure of 18 Torr the spectrum contains only the tungsten states with the highest oxidation state W<sup>6+</sup>. When reducing the oxygen pressure to 1.8 Torr, the spectrum can be distinguished to have three tungsten states already with different oxidization states: W<sup>6+</sup>, W<sup>5+</sup> and W<sup>4+</sup>.

Tungsten oxidization may form a metal oxide of tungsten with the oxidation state  $4+$  ( $\text{WO}_2$ ), which is much less studied than  $\text{WO}_3$ . The  $\text{WO}_2$  oxide has the following main phases: a stable monoclinic phase and metastable orthorhombic one for high temperatures [12,13,18]. The calculation [14,15] of the electron density of the states shows that the valence band near the Fermi level is made of the O  $2p$  and W  $5d$  states, the band with the binding energy above 2.5 eV is mainly made of the O  $2p$  states with a minor impurity of the W  $5d$  states. At the same time, the valence band spectrum is wide — 10 eV. The studies of the  $\text{WO}_2$  films, produced by oxidization of tungsten in Ar- $\text{O}_2$  mixture in magnetron sputtering onto the  $\text{Al}_2\text{O}_3$  substrate, have shown that the spectrum of the wide valence band near the Fermi level has two evident narrow peaks of W  $5d$  within the range of 0.8–2.0 eV, which coincide with the calculation [16], and that the spectrum has a maximum at  $\sim 7$  eV. However, the spectrum of the W  $4f$  core levels clearly has the  $\text{W}^{6+}$  and  $\text{W}^{4+}$  states [19].

The tungsten oxidization process was studied in many papers, for example, [16,20–22]. However, it is still unclear which tungsten oxides form and at which temperatures. An oxide film thickness depends on the temperature, oxygen pressure and humidity.

Adsorption of alkali metals on tungsten oxides is poorly studied except for studies of adsorption of cesium atoms on the tungsten oxides [23,24]. We have not find any studies devoted to impact of adsorption of sodium atoms on an electron structure of the tungsten oxides.

The purpose of the present paper was to study the electron structure of the surface of the oxidized W, which is produced by thermal oxidization of W, before and after adsorption of the sodium atoms. The vacuum pre-annealed tungsten was oxidized at the temperature of 950 K at the oxygen pressure of 1 Torr during 2 h. At the above conditions, emitters of oxidized tungsten are created, which are used in thermal ionization of atoms and molecules [1]. At the second stage of the study, a layer of sodium atoms was deposited on the surface of oxidized tungsten. Previously, there was no study of the electron structure of such emitter, including after Na deposition.

## 2. Experiment

The photoemission studies were carried out in the Russian-German laboratory on the HZB BESSY II synchrotron (Berlin, Germany) by using the photoelectron spectroscopy method (PES) in excitation within the photon energy range of 80–600 eV. Photoelectrons along the surface normal were recorded, an exciting beam fell on a sample surface at the angle of  $45^\circ$ . The studies of the oxidized thin tungsten film and with deposited sodium were carried out *in situ* in vacuum  $P < 5 \cdot 10^{-10}$  Torr at the room temperature. The photoemission spectra were recorded within the valence band range, and spectra of the O  $1s$ , O  $2s$ , W  $4f$ , Na  $2p$  core levels were also

recorded. The full energy resolution was 50 meV. For all the below spectra the background was subtracted using the Shirley method. The atomically clean Na was deposited onto a clean surface of the sample from a standard source. Note that one Na monolayer (ML) is accepted to be a concentration of  $1.0 \cdot 10^{15}$  at/cm<sup>2</sup>, forming a densely-packed layer of the Na atoms. A coating of sodium atoms was determined by the attenuation of the W  $4f$  and O  $2s$  core peaks at the photoemission excitation energy of  $h\nu = 100$  eV by known values of an output depth of the Na photoelectrons [25]. A probing depth depends on the kinetic energy of the photoelectrons: the more the kinetic energy of the photoelectrons, the more the output depth of the photoelectrons. It should be noted that the photoemission at  $h\nu = 80$ – $120$  eV is mainly contributed by the photoelectrons of a near-surface region, and at  $h\nu = 600$  eV the photoemission is mainly contributed by the photoelectrons out of the depth of the sample.

The cathodoluminescence spectra (CL) were obtained by the CAMEBAX electron probe micro-analyzer (Cameca, France), which is provided with optical spectrometers of original design. The experiment conditions included: an electron energy 15 keV, an electron beam current 50 nA, a beam diameter  $6 \mu\text{m}$ . At such energy of the primary electrons, the cathodoluminescence is excited at the depth up to 400 nm. A cathodoluminescent image was obtained by using the beam of the diameter of  $200 \mu\text{m}$ .

## 3. Experimental results and discussion

For the clean surface of the oxidized tungsten the spectrum of the W  $4f_{5/2}$  and W  $4f_{7/2}$  doublet core level is shown in the Fig. 1, *a* at the photoemission excitation energy of  $h\nu = 100$  eV. The spectrum can be distinguished to have three different states of tungsten with the oxidation state  $6+$ ,  $5+$  and  $4+$ . The similar results were obtained before, see, for example, the paper [10]. The spectrum did not reveal any peaks relating to  $\text{W}^0$ , which should be located at the binding energy of  $E_b = 31.4$  and 33.6 eV. The experimental spectrum was decomposed by pairs of the Gaussian function with spectrum splitting of 2.2 eV and an intensity ratio of 4:3. The decomposition results are also shown in the Fig. 1, *a*. The obtained parameters of component decomposition of the W  $4f$  peak at the photoemission excitation energy of  $h\nu = 100$  eV, as well as for  $h\nu = 120$  eV and  $h\nu = 600$  eV: a position of intensity maximums with the binding energy ( $E_b$ ) in relation to the Fermi level, a full width at the peak half-height ( $\Gamma$ ) and a relative area (A) under the peak in percentage are given in the table.

The photoemission  $h\nu = 100$  eV and  $h\nu = 120$  eV is mainly contributed by  $\text{W}^{6+}$ ; however, the  $\text{W}^{5+}$  and  $\text{W}^{4+}$  states on the surface indicate incomplete surface oxidization. Increase in the excitation energy to  $h\nu = 600$  eV (the photoemission is insignificantly contributed by the surface)

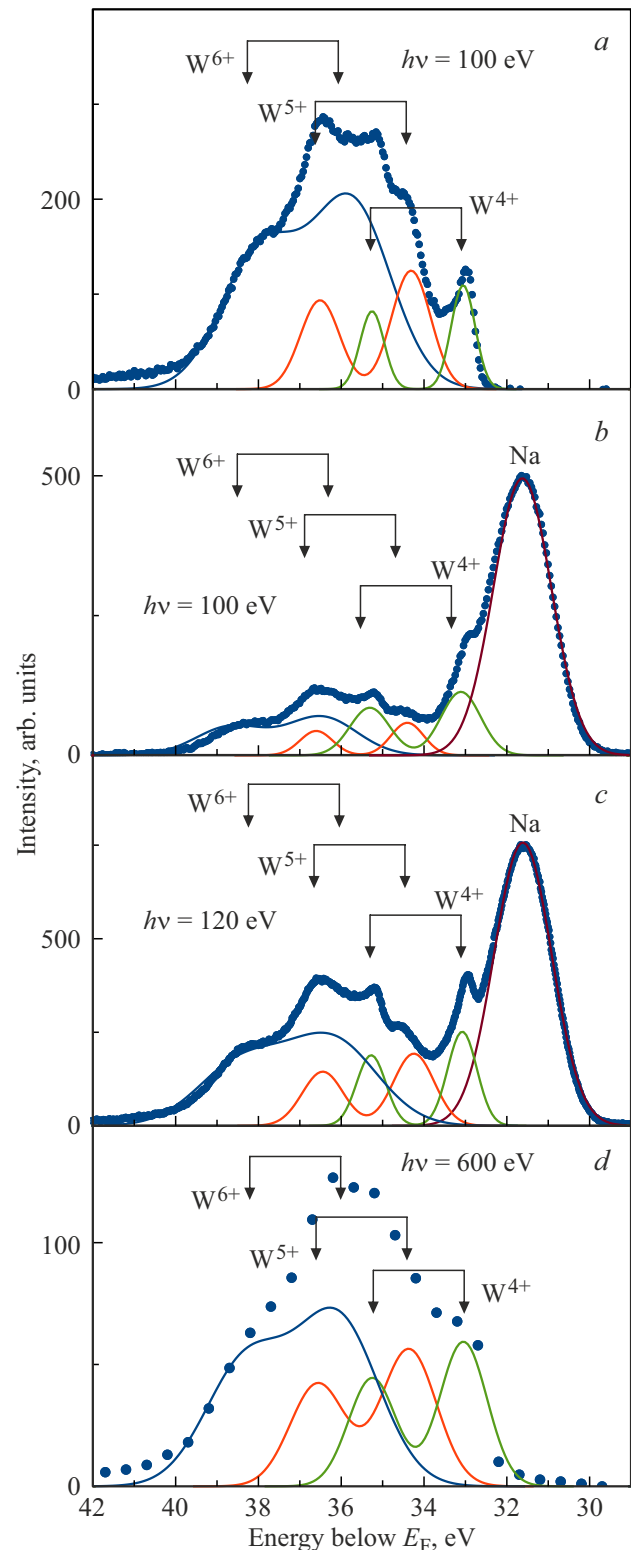
leads to two-fold increase in a fraction of the  $W^{4+}$  states, thereby obviously indicating gradual tungsten oxidization.

Adsorption of Na atoms to the surface of oxidized tungsten leads to changes in photoelectron spectra (Fig. 1), which affect both the valence band range and the core levels. It is clear that with the change of the excitation energy the spectrum shape is changing, which is correlated to different contribution of the surface and the bulk to the photoelectron emission. The experimental spectrum was decomposed by pairs of the Gaussian function with spectrum splitting of 2.2 eV and an intensity ratio of 4:3. The decomposition results are also shown in the Fig. 1, *b, c* and *d*. The obtained parameters of decomposition of the W 4*f* experimental peak into the  $W^{6+}$ ,  $W^{5+}$  and  $W^{4+}$  components: a position of intensity maximums with the binding energy ( $E_b$ ) in relation to the Fermi level, a full width at the peak half-height ( $\Gamma$ ) and a relative area ( $A$ ) under the peak in percentage are given in the table.

It is clear from the table that after deposition of sodium the position of the peaks almost do not change, and noticeable changes take place only for the excitation energy of  $h\nu = 100$  eV. Thus, in four times the peak contribution by the  $W^{4+}$  oxide is increased, and the peak contribution by the  $W^{5+}$  and  $W^{6+}$  oxides is decreased due to reduction of the  $W^{5+}$  and  $W^{6+}$  oxides by the Na atoms. At the same time, the contribution by  $W^{6+}$  is decreased from 67 to 42.8%. With the increase in the excitation energy, the contribution by the  $W^{4+}$  oxide is decreasing due to decrease in a surface fraction of the total contribution of the photoemission signal. It should be noted that for the excitation energy of  $h\nu = 100$  eV there is a drop of intensity for the peaks  $W^{6+}$  in 3 times,  $W^{5+}$  — in 2.5 times, and increase in intensity of the  $W^{4+}$  peak in 1.8 times. For the excitation energy of  $h\nu = 120$  eV these changes are less noticeable (in  $\sim 1.6$  times), which reflects distribution of tungsten oxides along the depth with the prevailing  $W^{6+}$  oxide on the surface. This behavior of the W 4*f* peaks means adsorption of the sodium atoms only on the surface and no diffusion of the Na atoms into the oxidized W substrate.

It is additionally confirmed by the dependence of the intensity of the Na 2*p* core peak on the excitation energy. Thus, it is clear from the Fig. 1 that at the excitation energy of  $h\nu = 100$  eV (which corresponds to the surface photoemission) the peak intensity in relation to the peak intensity of the W 4*f* core level is maximum, while at the excitation energy of  $h\nu = 120$  eV it decreases, and at the excitation energy of  $h\nu = 600$  eV the peak of the core level of the Na 2*p* states is not observed. It is due to the fact that, as mentioned above, the surface contribution to the total photoemission signal at the excitation energy of  $h\nu = 600$  eV is insignificant, as the photoelectrons come out of the big region in the oxide bulk, thereby confirming no diffusion of sodium atoms into oxidized tungsten. Note that the width of the Na 2*p* peak is 1.60 eV.

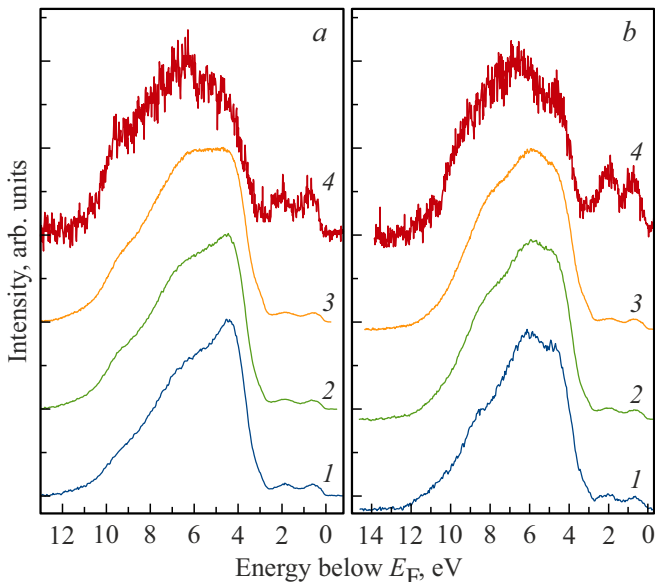
The normalized spectra of the photoemission within the valence band range of the oxidized tungsten before and after



**Figure 1.** Analysis of the photoemission spectrum of the W 4*f* core level for the surface of oxidized tungsten before (*a*) and after (*b, c, d*) deposition of the sodium coating of 1.1 MLs at the excitation energies  $h\nu = 100$  eV (*a, b*),  $h\nu = 120$  eV (*c*) and  $h\nu = 600$  eV (*d*). The experimental spectrum is dotted, while thick solid lines indicate contribution by the  $W^{6+}$ ,  $W^{5+}$  and  $W^{4+}$  and Na 2*p* states.

The binding energy of the W  $4f_{5/2}$  levels ( $E_b$ ), the peak width at the half-height ( $\Gamma$ ) and the relative area (A) occupied by the peak for the surface of oxidized tungsten before and after adsorption the 1.1 monolayer of sodium atoms

	W <sup>4+</sup>	W <sup>5+</sup>	W <sup>6+</sup>	W <sup>4+</sup>	W <sup>5+</sup>	W <sup>6+</sup>	W <sup>4+</sup>	W <sup>5+</sup>	W <sup>6+</sup>
$h\nu$ , eV	100			120			600		
Clean surface									
$E_b$ , eV	33.05	34.31	35.74	33.05	34.30	35.78	33.04	34.36	36.0
$\Gamma$ , eV	0.68	1.12	2.22	0.70	1.14	2.2	1.18	1.52	2.30
A, %	11	22	67	11	22	67	20	27	53
After adsorption of sodium									
$E_b$ , eV	33.08	34.36	35.4	33.03	34.27	36.0	33.04	34.36	36.08
$\Gamma$ , eV	1.12	0.92	2.0	0.70	1.06	2.48	1.32	1.56	2.32
A, %	40.2	17.0	42.8	18.2	19.1	62.7	24.6	26.9	48.5



**Figure 2.** Normalized spectra of the photoemission within the valence band range for the surface of oxidized W before (a) and after deposition (b) of the Na coating of 1.1 MLs at different excitation energies: 1 —  $h\nu = 80$  eV, 2 —  $h\nu = 100$  eV, 3 —  $h\nu = 120$  eV, 4 —  $h\nu = 600$  eV.

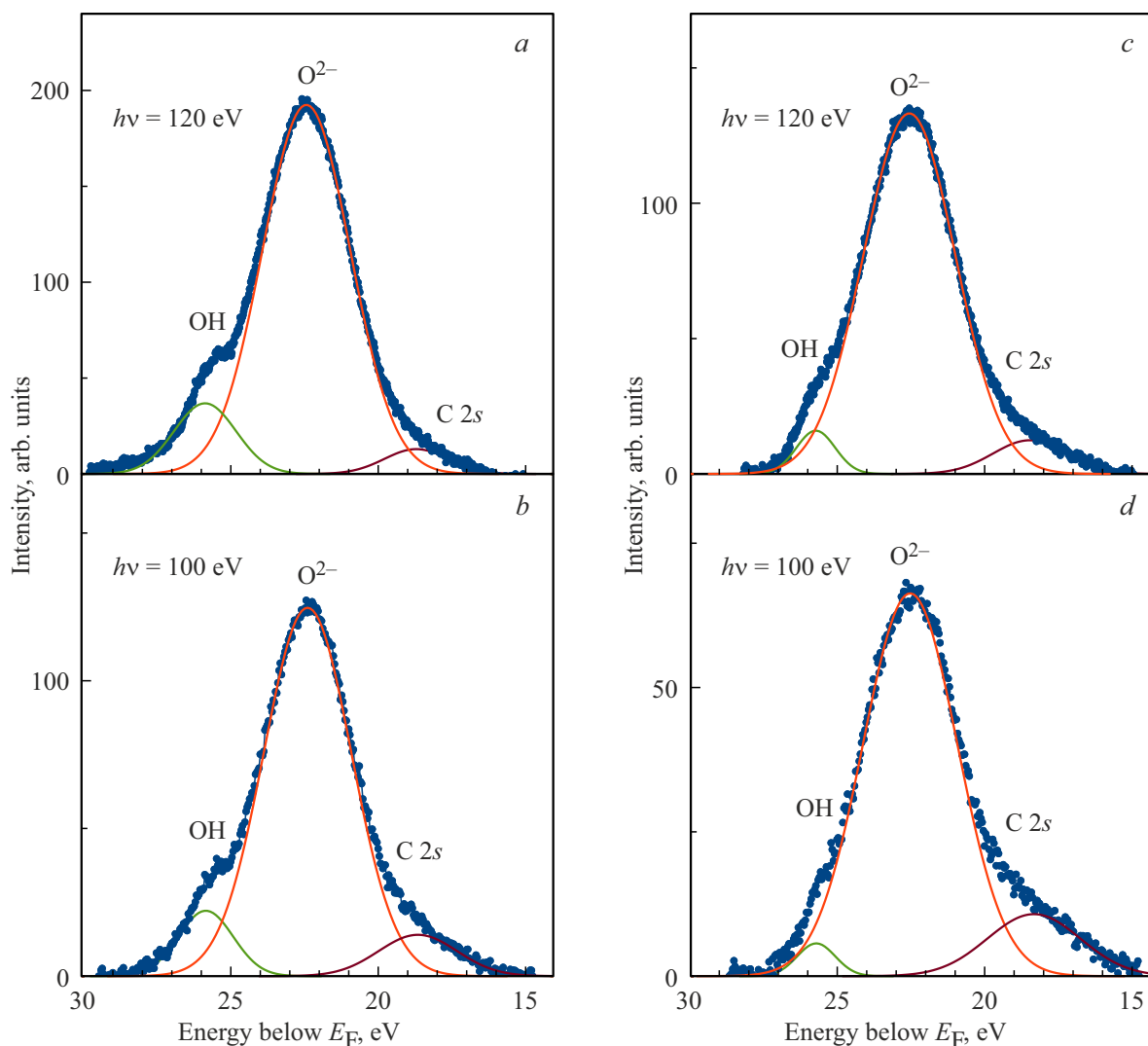
sodium adsorption of 1.1 MLs are given in the Fig. 2 for the excitation energies from 80 to 600 eV. The spectra are reduced to the surface position of the Fermi level ( $E_F$ ), which is determined by linear approximation of the low-energy edge of the valence band spectrum of the stainless steel substrate, with which the samples were in ohmic contact.

Within the valence band range, the spectrum of oxidized tungsten has no noticeable features and has a base width of  $\sim 12$  eV. The photoelectron spectra of the valence band of thermally oxidized W coincide with well known spectra of the valence band of the oxidized tungsten [10,11]. The maximum peak of the valence band is located at  $E_b = 4.5$  eV below  $E_F$  for  $h\nu = 80$  and 100 eV, in the va-

lence band spectrum for  $h\nu = 600$  eV at  $E_b = 6.5$  eV, while for  $h\nu = 120$  eV an intermediate option is observed. There is also a small shoulder in binding energies, bigger than the valence band peak maximum position. A slightly prominent maximum at  $E_b = 6.5$  eV for  $h\nu = 80$  eV coincides with the position of the peak maximum of the valence band for  $h\nu = 600$  eV; it is due to the fact that in the bulk of the oxidized tungsten an oxide fraction with a lesser oxidation degree of 4+ is increased, as it is clear from the spectra of the W  $4f$  levels. It can be assumed that the spectrum of the valence band is determined by the contribution of the  $WO_3$  oxides, as it follows from the analysis of the spectrum of photoemission of the W  $4f$  core level. There are two small peaks with  $E_b = 0.6$  and 2.0 eV near the Fermi level, which can be assigned to the W  $5d$  states and whose intensity increases with increase of the excitation energy, which reflects increase in the fraction of the  $WO_2$  oxide with increase of a probing depth. It coincides with the results of the papers [19,26], which showed decreased peaks of the W  $5d$  states near the Fermi level as the  $WO_3$  oxide is forming.

Adsorption of the sodium atoms causes minor changes in the valence band spectrum. The biggest changes are clear for the excitation energy of 80 eV, at which the surface contribution to the photoemission is maximum in comparison with other excitation energies used. Thus, the maximum at the binding energy of 4.5 eV observed for the clean surface of oxidized tungsten is added by the maximum at 6.2 eV, which can be correlated to the increased contribution by  $WO_2$ . As the energy is increasing, the surface contribution to the total photoemission signal is decreasing, which is manifested in reduced sodium influence on a type of the photoelectron spectrum. For the excitation energy of 600 eV the shape of the valence band spectrum is almost unchanged after the adsorption of sodium atoms.

The Fig. 3 shows photoemission spectra from the oxygen core levels O  $2s$  at the excitation energies of  $h\nu = 120$  eV (a) and  $h\nu = 100$  eV (b) for the surface of oxidized tungsten. These spectra of the photoemission from

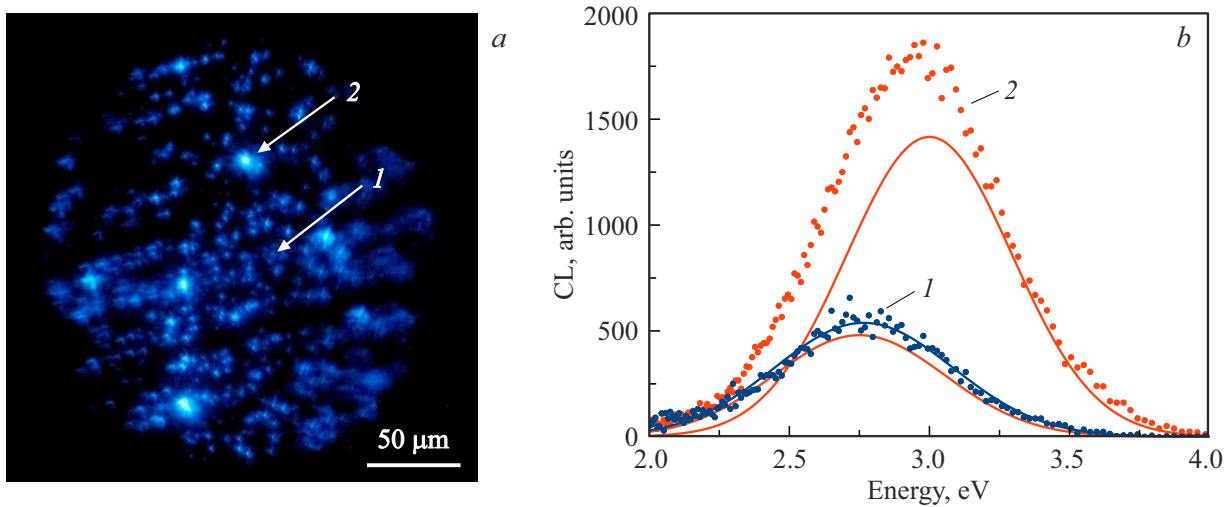


**Figure 3.** Spectra of the normal photoemission of the O 2s core levels for the surface of oxidized tungsten before (*a, b*) and after (*c, d*) deposition of the sodium coating of 1.1 MLs. Excitation energy —  $h\nu = 120$  eV (*a, c*) and  $h\nu = 100$  eV (*b, d*).

the O 2s core level correspond to the surface photoemission, but at  $h\nu = 100$  eV the surface contribution is bigger in comparison with  $h\nu = 120$  eV, as the kinetic energy of the photoelectrons from the O 2s level is less than for  $h\nu = 120$  eV. The spectra have three evident peaks with the binding energy at  $E_b = 18.6, 22.4$  and  $25.8$  eV. The first peak with  $18.6$  eV is correlated with excitation of the C 2s states, which indicates minor surface contamination by carbon. The surface carbon is not a problem, since there is always a minor quantity of carbon on the surface of oxidized tungsten during thermal ionization of organic molecules. The other two peaks  $E_b = 22.4$  and  $25.8$  eV can be correlated to excitation of the O 2s core level included in the oxide and hydroxide, as it has been shown, for example, in the paper [17]. At the excitation energy of  $h\nu = 100$  eV, in the spectrum of the O 2s core level (the photoemission from the oxide surface), there are clearly seen two peaks

with the binding energy at  $E_b = 22.4$  and  $25.8$  eV, with the peak width up to  $3.5$  and  $2.2$  eV, respectively.

Such a peak width can be correlated to big surface contribution of the tungsten oxides with the oxidation degree close to  $6+$ . The ratio of these components is  $9:1$ . The oxygen in the oxide is in two states:  $O^{2-}$  and OH. A hydroxide on the oxide surface and in the bulk thereof can be attributed to water vapor during tungsten oxidation. The hydroxide in place indicates dissociative adsorption of water on the oxide surface. At the excitation energy of  $h\nu = 120$  eV, in the spectrum of the O 2s core level (the photoemission from the oxide surface), there are clearly binding two peaks with the binding energy at  $E_b = 22.4$  and  $25.8$  eV, with the peak width up to  $3.5$  and  $2.5$  eV, respectively. Such a peak width can be correlated to big surface contribution of the tungsten oxides with the oxidation degree close to  $6+$ . The ratio of these components is  $7:1$ .



**Figure 4.** *a* — the cathodoluminescent image of oxidized tungsten after deposition of the sodium coating of 1.1 MLs. *b* — the cathodoluminescence (CL) spectra of oxidized tungsten after deposition of the sodium coating of 1.1 MLs in different regions of the sample. The points — experimental data. Solid lines — approximations of the cathodoluminescence spectra by the Gaussian curves.

The Fig. 3 also shows the spectra of the photoemission from the O  $2s$  core level of oxygen at the excitation energies of  $h\nu = 120$  eV (*c*) and  $h\nu = 100$  eV (*d*) for the surface of oxidized tungsten after deposition of the sodium coating of 1.1 MLs. At the excitation energy of  $h\nu = 120$  eV, in the spectrum of the O  $2s$  core state, in which there are clearly two peaks with the binding energy at  $E_B = 22.5$  and 25.7 eV, with the peak width up to 3.7 and 1.6 eV, respectively. The ratio of these components is 20:1. Decrease in the contribution of the peak at  $E_B = 25.7$  eV and its width in comparison with the clean surface of the oxide can be correlated to a reaction of adsorbed sodium with the hydroxide. A small peak with the binding energy at  $E_B = 18.5$  eV is logically correlated to excitation of the C  $2s$  states, which indicates minor contamination by carbon. At the excitation energy of  $h\nu = 100$  eV, in the spectrum of the O  $2s$  core level, there are clearly seen two peaks with the binding energy at  $E_B = 22.5$  and 25.7 eV, with the peak width up to 3.8 and 1.6 eV, respectively. The ratio of these components is 30:1. Increase in the contribution by  $O^{2-}$  in comparison with the OH contribution at decrease of the excitation energy is logically correlated, as above, to increase in the surface contribution during decrease in the excitation energy. The decrease in the contribution of  $E_B = 25.7$  eV may be correlated to the reaction of adsorbed sodium with the hydroxide.

The Fig. 4,*a* shows the cathodoluminescent image of oxidized tungsten after deposition of the sodium coating of 1.1 MLs, which may make clear a relief corresponding to rolling lines of tungsten foil. The Fig. 4,*b* shows the cathodoluminescent spectra of oxidized tungsten after deposition of the sodium coating of 1.1 MLs. The sample surface exhibits regions with size of several microns with bright blue luminescence. These regions are located along a characteristic relief. The spectra have been obtained

from regions of various intensity of cathodoluminescence. The spectrum shape is typical for  $WO_3$  and  $WO_x$  [27,28]. The spectrum of the middle brightness region 1, shown in the Fig. 4,*b*, the curve 1, has a maximum intensity at 2.75 eV and is typical for the  $WO_3$  stoichiometry oxide [2]. The cathodoluminescence spectrum (Fig. 4,*b*, the curve 2) obtained in the bright region of the region 2, can be represented as a sum of two Gaussian bands: a band with the maximum of 2.75 eV, correlated to luminescence of the  $WO_3$  stoichiometry oxide, and a band with the maximum of 3.0 eV, which can be correlated to luminescence of the oxide with a lesser oxidation degree [28].

#### 4. Conclusion

It is for the first time that a study has been taken for the electron structure of the emitter of the thermally oxidized tungsten, which is used during thermal ionization of molecules in the mass-spectrometry, after adsorption of sodium atoms.

Analysis of the experimental spectra of the valence band and the W  $4f$  and O  $2s$  and Na  $2p$  core levels for the clean surface of the thermally oxidized tungsten and after deposition of sodium atoms thereon makes it possible to conclude as follows. The surface and the layers nearest to the surface have the  $WO_3$  oxide with an impurity of the  $WO_2$  and  $W_2O_5$  oxides formed, which is manifested in the spectrum of the valence band with the minor contribution of the W  $5d$  states near the Fermi level. The valence band spectrum corresponds to a semiconductor type of the tungsten oxide.

In the spectrum of the core levels, the contribution of the  $W^{6+}$  states with the impurity of the  $W^{5+}$  and  $W^{4+}$  states prevails. The surface oxygen is in two states: as

included in the oxide and the hydroxide. With increase in the distance from the surface, the fraction of the  $W^{4+}$  states increases, which follows from the spectra of the W 4f states at different excitation energies. It may be due to both insufficient oxygen pressure during oxidization and to an oxidization time. The oxygen in the oxide bulk is in two states:  $O^{2-}$  and OH. A minor quantity of oxygen included in the hydroxide is correlated to water vapor during oxidization. The hydroxide in place indicates dissociative adsorption of water on the oxide surface.

Deposition of the 1.1 monolayer of sodium atoms leads to a changed spectrum of the W 4f and O 2s core states. The changes are correlated to the reaction of the adsorbed sodium atoms and oxygen included in the oxide, leading to reduction of the  $W^{6+}$  states to the  $W^{4+}$  ones and, to a lesser degree, to the  $W^{5+}$ , as well as with oxygen included in the hydroxide. There are minor changes of the valence band spectrum, which are visible at the excitation energy of  $h\nu = 80\text{--}120$  eV. The adsorption of sodium does not lead to changes of the valence band in the bulk of the sample, which follows from an unchanged shape of the valence band as obtained at the excitation energy of 600 eV.

After deposition of the sodium coating of 1.1 MLs, the cathodoluminescence spectra of oxidized tungsten are recorded, and there is evident luminescence correlated both to  $WO_3$  and to the oxides with a lesser oxidation degree.

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## Conflict of interest

The authors declare that they have no conflict of interest.

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