Electronic Structure of Thermally Oxidized Tungsten

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Abstract—The electronic structure of a pure tungsten surface oxidized at an oxygen pressure of 1 Torr and a temperature of 1000 K has been in situ studied by photoelectron spectroscopy in ultrahigh vacuum. Photoemission spectra from the valence band and O 1s, O 2s, and W 4f core levels at synchrotron excitation in the photon energy range of 80–600 eV have been analyzed. A semiconductor tungsten oxide film is found to form, which contains different oxides of tungsten with the oxidation state from 6+ to 4+. Oxides of tungsten with the oxidation state of 6+ are mainly formed on the surface; their fraction gradually decreases while moving away from the surface, while the amount of oxides of tungsten with the oxidation state of 4+ increases.

Keywords: tungsten oxidation, photoelectron spectroscopy

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1. INTRODUCTION

Tungsten oxide WO3 is widely applied in electronics, gas sensors, electro- and photochromic systems, solar cell, batteries, catalysts of oxidation (reduction) reactions, emitters at thermal ionization of atoms and organic molecules, etc. There exist various methods of formation of tungsten oxide films: magnetron sputtering, thermal evaporation, sol–gel deposition, vapor deposition, liquid-phase methods (including electrochemical synthesis), etc. [1–3]. Thin films of tungsten oxide can also be obtained upon its heating in oxygen.

It is known that molybdenum oxide WO3 has the following main phases: monoclinic II ε phase (T < 230 K), monoclinic I stable γ phase (230 K < T < 603 K), triclinic δ phase (230 K < T < 290 K), stable orthorhombic β phase (603 K < T < 1013 K), and tetragonal α phase (T > 1013 K) [4, 5]. There are also series of substoichiometric tungsten oxides WnO3n−1 and WnO3n−2, which are formed at transformation of the crystal structure due to a smaller amount of oxygen [6]. The WO3 crystal structure is comprised of one tungsten atom and six oxygen atoms, which form an octahedron (slightly distorted for different WO3 phases). For the γ monoclinic WO3 phase, the reconstructed (001) surface is thermodynamically stable [7].

WO3 is a wide gap n-type semiconductor with the band gap of ~2.8 eV. Calculations of the WO3 electronic structure by the density functional theory were presented in some studies (see, e.g., [8–12]), where it was shown that the valence band for the monoclinic WO3 phase is made of the O 2p states with insignificant addition of the W 5d states, while the conduction band is formed by the W 5d states. It was obtained in [8] that the valence band is wide (~8 eV) and has two peaks with the binding energy En = 1 and 4 eV below the valence band maximum EVBM. Similar results were obtained in other studies [9–12].

The electronic structure of tungsten oxides has been well studied for samples obtained in different ways. Investigations were mainly focused on the shape of photoelectron spectra of the W 4f core levels and the valence band spectrum, which depend on both the external conditions and the preparation methods [13–17]. The shape of spectra of the W 4f core levels adequately demonstrates different tungsten oxidation states. Much less attention was paid to studying the O 1s (O 2s) core levels, indicating the influence of adsorbed water on the formation of tungsten oxides [15].

Formation of tungsten oxide films during magnetron sputtering of tungsten in an Ar–O2 atmosphere was investigated in [13]; it was shown that a decrease in the oxygen pressure from 2.4 × 10−2 to 2.4 × 10−3 mbar leads to an increase in the spectral width of the W 4f core states and occurrence of new peaks. For example, at the oxygen pressure of 2.4 × 10−2 mbar, there are only the highest tungsten oxidation states (W6+) in the...
spectrum. When the oxygen pressure decreases to $2.4 \times 10^{-3}$ mbar, three different tungsten oxidation states can be distinguished in the spectrum: $W^{6+}$, $W^{5+}$, and $W^{4+}$. A change in the oxygen pressure does not affect the shape of the O 1s spectrum. The shape of the valence band spectrum remains the same, except for the increase in the fraction of the W 5d states near the Fermi level ($E_F$). In [14], WO$_3$ films obtained at thermal deposition of WO$_3$ powder were investigated. The spectrum of the W 4f core states corresponds to the W$^{6+}$ tungsten state. The valence band spectrum is wide ($\sim 12$ eV) and peaks at 6.3 eV. At the excitation energy corresponding to the minimum photoelectron escape depth ($h\nu = 50$ eV), weak W 5d peaks are observed near the Fermi level. In [15], monoclinic WO$_3$ films were obtained at pyrolyzed sputtering of ammonium tungstate. Two tungsten states ($W^{6+}$ and $W^{5+}$) were observed in the spectrum of the W 4f core states. The spectrum of the O 1s core states contains two peaks: one corresponds to O$^2-$ (530.69 eV), while the other corresponds to oxygen in composition of hydroxyl (532.62 eV). Formation of monoclinic tungsten oxide films during magnetron sputtering of tungsten in an Ar—O$_2$ atmosphere was investigated in [16]. The spectrum of the W 4f core states for as-deposited films corresponded to the W$^{6+}$ tungsten state. Heating of the films shifted the W 4f peaks; in the opinion of the authors of that study, this fact is related to the formation of oxygen-deficient compounds $W_{10}O_{49}$, $W_{24}O_{68}$, and (or) WO$_2$.

As noted above, when studying the electronic structure of WO$_3$ oxide films, tungsten oxidation states of 4+ are sometimes observed in the formed films. However, WO$_2$ has been less thoroughly investigated than WO$_3$, which is determined by its narrower range of application in technologies. In contrast to WO$_3$, oxide WO$_2$ is a metal. Several WO$_2$ phases are known: stable monoclinic phase and metastable orthorhombic for high temperatures [18–20]. In [21], calculation of the electron density of states for both phases showed that the valence band near the Fermi level is formed by the O 2p and W 5d states and the band with the binding energy of higher than 2.5 eV is mainly formed by the O 2p states with small addition of the W 5d states. Notably, the valence band spectrum is wide (10 eV). Calculation of the electronic states of the monoclinic structure of metallic WO$_2$ by the density functional method was performed in [22]; it was shown that the valence band near the Fermi level is formed by the W 5d states with two peaks, while the band with the binding energy above 2.5 eV is mainly formed by the O 2p states. WO$_2$ films, obtained at tungsten oxidation in an Ar—O$_2$ mixture during magnetron sputtering on an Al$_2$O$_3$ substrate, were investigated in [23]. The spectrum of the wide valence band near the Fermi level exhibits two narrow W 5d peaks in the range of 0.8–2.0 eV, which coincides with the calculation [22], and a maximum at $\sim 7$ eV. However, the W$^{6+}$ and W$^{4+}$ states can clearly be seen in the spectrum of the W 4f core states. Similar results were obtained in the earlier studies [24, 25].

The process of tungsten oxidation was investigated in numerous works (see, e.g., [26–28]). However, it is still unclear what tungsten oxides are formed and at what temperatures. The oxide-film thickness depends on temperature, oxygen pressure, and humidity. At temperatures below 600–673 K, oxide WO$_3$ is formed, which makes a protective blue film. When the temperature increases above 780 K, the oxide film is cracked and mixed oxides WO$_2.75$ or WO$_2.92$ are formed due to oxygen diffusion. A WO$_3$ oxide film is formed at temperatures higher than 880 K. At $T > 1000$ K, one observes sublimation of tungsten oxides, and the oxide film is rapidly ruptured at $T > 1200$ K. At $T = 1550$ K, only a monolayer oxygen film can be formed on the tungsten surface [29].

The purpose of this study was to analyze the electronic structure of an oxidized tungsten surface obtained at thermal oxidation of W at the oxygen pressure of 1 Torr and $T = 950$ K. These conditions correspond to the technique of preparing emitters from oxidized tungsten, which is used in thermal ionization atoms and molecules [30].

2. EXPERIMENTAL

In this study, oxidation of tungsten, previously annealed in vacuum, was performed at a temperature of 950 K and the oxygen pressure of 1 Torr for 2 h. Photoemission studies were carried out at the Russian—German Laboratory at the BESSY II synchrotron, Helmholtz-Zentrum Berlin (Berlin, Germany) by photoelectron spectroscopy (PS) upon excitation in the photon energy range of 80–600 eV. Photoelectrons were detected along the normal to the surface; the incident excitation beam made an angle of 45° with the sample surface. The oxidized tungsten thin film was in situ analyzed in vacuum with $P < 5 \times 10^{-10}$ Torr at room temperature. Photoemission spectra near the valence band and spectra of the O 1s, O 2s, and W 4f core levels were recorded. The total energy resolution was 50 meV. For the all spectra given below, the Shirley background subtraction was performed. Before the photoemission studies, the samples were annealed in high vacuum at a temperature of $\sim 900$ K.

3. RESULTS AND DISCUSSION

Figure 1 shows the photoemission spectra of the W 4f$_{5/2}$ and W 4f$_{7/2}$ doublet core level for a pure surface of oxidized tungsten for three excitation energies: $h\nu = 100, 120$, and 600 eV (shown by symbols). One can clearly see up to five peaks in the spectra. The observed peaks can be related by the W 4f$_{5/2}$ and
W4f7/2 doublet levels assigned to different tungsten oxidation states from 4 to 6, which coincides with the results of [13]. The spectrum contained no peaks related to W⁰, which should be located at $E_b = 31.4$ eV and 33.6 eV. It can be seen that the shape of the spectrum changes with an increase in the excitation energy; the reason is that the higher the electron kinetic energy, the larger the photoelectron escape depth. I.e., photoelectrons emerge from the surface region at $h\nu = 100$ eV and from the film bulk at $h\nu = 600$ eV. The levels in the doublet are spaced by 2.2 eV. The experimental spectrum was decomposed by Gaussian function pairs with the spectral splitting equal to 2.2 eV and the intensity ratio of 4 : 3. The decomposition results are also presented in Fig. 1. The obtained parameters of decomposition of the experimental W4f peak (position of the intensity peaks with the binding energy $E_b$ relative to the Fermi level, FWHM of the peak $\Gamma$, and relative area $A$ under the peak in percentage) are listed in Table 1.

It can be seen in Table 1 that only the peak width $\Gamma$ and relative area $A$ for each component change, while the peak positions remain almost the same. The $A_{W^{6+}} : A_{W^{5+}} : A_{W^{4+}}$ component ratio is 67 : 22 : 11 at the excitation energies $h\nu = 100$ and 120 eV and 48 : 27 : 25 at the excitation energy $h\nu = 600$ eV. Since the photoelectron escape depth increases with an increase in the photoemission excitation energy, this change in the component ratio indicates that the concentration of tungsten with a larger oxidation state on the surface is higher. This difference is caused by oxygen diffusion into the sample during tungsten oxidation. It can also be seen that the peak widths increase with an increase in the photoelectron escape depth. This may be indicative of the presence of oxides with some other oxidation states, which is consistent with the known fact of a large number of different stoichiometries of tungsten oxides and oxide phases [4–7, 13–16]. The large width of the W⁶⁺ peak can be related to the presence of not only WO₃ but also other substoichiometric oxides in the oxide.

Table 1. Binding energy of the W4f7/2 levels ($E_b$), peak FWHM ($\Gamma$), and relative area ($A$) under the peak for the oxidized tungsten surface

| Parameter | $W^{4+}$ | $W^{5+}$ | $W^{6+}$ | $W^{4+}$ | $W^{5+}$ | $W^{6+}$ | $W^{4+}$ | $W^{5+}$ | $W^{6+}$ |
|-----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| $h\nu$, eV | 100      | 120      | 600      | 100      | 120      | 600      | 100      | 120      | 600      |
| $E_b$, eV  | 33.05    | 34.31    | 35.74    | 33.05    | 34.30    | 35.78    | 33.04    | 34.36    | 36.08    |
| $\Gamma$, eV | 0.68   | 1.12     | 2.22     | 0.70     | 1.14     | 2.2      | 1.32     | 1.56     | 2.32     |
| $A$, %       | 11       | 22       | 67       | 11       | 22       | 67       | 25       | 27       | 48       |

Fig. 1. Analysis of the normalized photoemission spectrum of the W4f core level for the oxidized tungsten surface at the excitation energy $h\nu = (a) 600$, (b) 120, and (c) 100 eV: (symbols) experimental spectrum and (thick solid lines) contribution from the $W^{6+}$, $W^{5+}$, and $W^{4+}$ states.

Figure 2 shows photoemission spectra from the O 2s ($h\nu = 120$ eV) and O 1s ($h\nu = 600$ eV) core levels for the oxidized tungsten surface. The photoemission spectrum at the excitation energy $h\nu = 120$ eV from the
O 2s core level corresponds to the surface photoemission, because the photoelectron kinetic energy is close to the yield minimum in the universal dependence of photoelectron yield on the kinetic energy \[31\]. The photoemission spectrum at the excitation energy \(h\nu = 600 \text{ eV}\) for the O 1s core level demonstrates yield from the film bulk, i.e., bulk photoemission. When decomposing the spectrum, one can distinguish two peaks at \(E_B = 530.8\) and 532.8 eV with a width of 1.50 eV. These peaks can be assigned to two oxygen states (composition of oxide and hydroxyl, as was obtained in \[15\]).

The ratio of these components is 7 : 1. Similar result was obtained at the excitation energy \(h\nu = 120 \text{ eV}\) in the spectrum of the O 2s core state (photoemission from the oxide surface), which clearly exhibits two peaks with the binding energy at \(E_B = 22.4\) and 26.0 eV with the peak widths increased to 3.6 and 2.4 eV, respectively. The increase in the peak widths can be related to the large contribution on the surface from oxides of tungsten with the oxidation state close to 6+. The ratio of these components is 9 : 1. The presence of hydroxyl on the oxide surface and in the bulk can be fairly explained by the presence of water vapor during tungsten oxidation. These results coincide with the data obtained when studying formation of thermally oxidized molybdenum \[32\].

Normalized photoemission spectra near the valence band for the oxidized tungsten surface at the excitation energy of \(h\nu = (1) 80, (2) 100, (3) 120,\) and \(4) 600 \text{ eV}\).

![Normalized photoemission spectra](image-url)

Fig. 2. Spectra of normal photoemission of the (a) O 2s and (b) O 1s core levels for the oxidized tungsten surface at the excitation energy of \(h\nu = (a) 120\) and (b) 600 eV.

Fig. 3. Normalized photoemission spectra near the valence band for the oxidized tungsten surface at the excitation energy of \(h\nu = (1) 80, (2) 100, (3) 120,\) and \(4) 600 \text{ eV}\).
valence band spectrum of a stainless steel substrate having an ohmic contact with the samples. The oxidized tungsten spectrum near the valence band is ~12 eV wide and has no specific features. Photoelectron spectra of the valence band of thermally oxidized W in air coincide with the well-known spectra of the valence band of oxidized tungsten [13, 14]. The valence band peak has no specific features; its maximum is 4.5–6.5 eV below the Fermi level. This fact coincides with the position of the valence band peak for $h\nu = 600$ eV; the reason is that the fraction of oxide with a smaller oxidation state (4+) increases in the bulk of oxidized tungsten, as can be seen from the spectra of the W 4f levels. One might suggest that the valence band spectrum is determined by the contribution from oxides WO$_2$.

The intensity of the peaks with $E_b = 0.6$ and 2.0 eV, which can be assigned to the W 5d states, increases with an increase in the excitation energy, which demonstrates the increase in the fraction of oxide WO$_2$ with an increase in the probing depth. This fact coincides with the results of [33, 34], where peaks of the W 5d states were shown to decrease near the Fermi level during formation of oxide WO$_3$.

4. CONCLUSIONS
The electronic structure of thermally oxidized tungsten was investigated. It was shown that tungsten oxides with dominant contribution from oxide of tungsten with the oxidation state of 6+ are formed on the tungsten substrate surface. The fraction of the oxide of tungsten with the oxidation state of 4+ increases while moving away from the surface, which can be related to both insufficient oxygen pressure during oxidation and short oxidation time. The presence of a small amount of oxygen in composition of the hydroxyl is related to the presence of water vapor during oxidation. The valence band spectrum corresponds to the semiconductor character of tungsten oxide.

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CONFLICT OF INTEREST
The authors declare that they have no conflicts of interest.

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