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X-ray photoelectron spectroscopy of ytterbium nanofilms with oxygen adsorbed on their surface

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X-ray photoelectron spectra of nanoscale-thickness ytterbium films along with adsorbed oxygen layers have been studied for the first time. It is found that the spectra include features from both divalent and trivalent ytterbium. The intensity ratio of these features raises upon increasing the film thickness (the size effect). It is shown that the above behavior is due to the formation of two final states related to divalent and trivalent ytterbium at the photoionization of $4f$-level by photons with the energy of 1253.6 eV, while only the trivalent state is realized by using the photons with the energy of 142 eV.

Keywords: Ytterbium, nanofilms, adsorbed molecules, electronic state, X-ray photoelectron spectroscopy.

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1. Introduction

Previously, in a number of articles, the effect of adsorbed molecules on the state of nanometer-thick films was studied (see, for example, [1–8]). In particular, in some of these articles [7,8] it was found that the non-dissociative adsorption of carbon monoxide and oxygen molecules on nanofilms of the rare earth metal ytterbium is accompanied by its transition from the divalent state to the trivalent state, i.e. transition of the form $[\mathrm{Xe}]4f^{14}6s^2 \rightarrow [\mathrm{Xe}]4f^{13}5d6s^2$, where [Xe] — electronic configuration of the xenon atom. An analysis of the experimental methods used in these articles and the results obtained with their help showed that the studies under consideration actually studied the effect of adsorbates on ~ 10 monolayers (ML) of ytterbium closest to the adsorbed molecules. These limitations are determined by the escape depth of electrons analyzed using the experimental methods used in the article: photoelectron spectroscopy using synchrotron radiation and Auger electron spectroscopy. In the first of these methods, the kinetic energy of the detected electrons was $\sim 125-138$ eV, and in the second — $170-180$ eV. According to the curve of electron free path length λ versus their energy [9], this value is about $6.0-6.5$ Å. This value λ enables to obtain information about ten layers of ytterbium nanofilms closest to the adsorbed molecules.

One of the ways to increase the depth of analysis of nanofilms is to increase the energy of characteristic electrons created during the interaction of photons with the object of study. Such a conclusion follows from the universal curve of dependence of the mean free path length of electrons on their energy. Obviously, an increase in the energy of electrons can be achieved by increasing the energy of photons knocking out electrons from the analyzed solid. One of the ways to achieve this increase is to use X-ray photoelectron spectroscopy (XPS). In one of the variants of this method, as is known, characteristic X-ray radiation is used, the energy of which is equal to 1253.6 eV, if Kα-line of magnesium anode is used, and 1486.6 eV in case of Kα-line of aluminum anode. The aim of this article was to investigate the effect of adsorbed molecules on the electronic state of ytterbium nanofilms using XPES. In this case, the task was to pay special attention to the depth to which the influence of adsorbed molecules propagates in nanofilms.

2. Experimental procedure

Experiments were conducted using an ultrahigh-vacuum (UHV) facility with a baseline pressure below $1 \cdot 10^{-10}$ Torr, comprising three separate UHV chambers that were designed for sample input, treatment, and characterization, had individual evacuation systems, and were connected by a sample holder transport system. Silicon samples of $10 \times 5 \times 0.4$ mm cut from phosphorus-doped wafers (n-type) with a resistivity of $\sim 5\,\Omega \cdot \mathrm{cm}$ were used as substrates. After introduction into the facility, silicon samples were subjected to repeated rapid heating to 1550 K to clean surfaces of foreign impurities. Heating was carried out by passing direct current through the sample. The temperature was determined using a Minolta Land Cyclops 152 optical pyrometer. After cleaning the samples, a diffraction pattern (7×7) was observed with clear reflections from their surface reconstruction. The surface cleanliness was controlled using the XPS method. Ytterbium nanofilms were created on an atomically pure Si(111) substrate (7×7) by sputtering metal from an evaporator heated with a tungsten spiral. Sputtering rate was one ML per minute. Sample temperature was at the same time maintained at 300 K. A value of $7.84 \cdot 10^{14}\,\mathrm{cm}^{-2}$, equal to concentration of silicon atoms on unreconstructed Si(111) surface, was taken as 1 ML. As shown earlier [10], ytterbium nanofilms obtained on Si(111) under the above conditions have a very high thickness uniformity, and mixing in the interface region of the nanofilms with silicon is virtually absent.

Adsorption of O_2 molecules on ytterbium nanofilms was performed in a sample treatment chamber at 300 K by injecting molecular oxygen and holding samples at pressure of $2 \cdot 10^{-7}$ Torr. The dose was 100 Langmuir (L, $1\,\mathrm{L} = 10^{-6}\,\mathrm{Torr} \cdot \mathrm{s}$). According to the results obtained earlier [11], at a given dose, the layer of adsorbed oxygen molecules is saturated on the surface of ytterbium nanofilms. After treatment by the above method, structures of Yb−Si(111) and O_2−Yb−Si(111) type were transferred to an analytical chamber for their subsequent investigation.

The analytical chamber was equipped with an X-ray photoelectron spectrometer with a hemispherical conical energy analyzer EA 125 by Omicron (Germany). To excite photoelectrons from the samples under study, a magnesium anode was used (quantum energy $h\nu$, as already mentioned in Section 1, is 1253.6 eV), since the width of its Kα-line (0.7 eV) less than in the case of an aluminum anode (0.85 eV). The X-ray tube was carefully degassed before the samples were studied. Pressure in the analytical chamber was always lower than $1 \cdot 10^{-9}$ Torr during spectra recording. Energy resolution of the analyzer was 1.0 eV. Photoelectron spectra were recorded at normal angle of electron emission from the sample surface. The Si $2p$ peak for a pure silicon sample surface (bonding energy was 99.3 eV) was used to calibrate the energy scale of the spectra given in the article. The values of the binding energy on this scale are measured relative to the energy of the Fermi level.

3. Results and discussion thereof

Figure 1 shows two types of photoelectron spectra of ytterbium films 16 ML thick. The *1* spectrum was obtained for nanofilms when there are no adsorbed molecules on their surface. It can be seen that this spectrum contains one broad maximum. The position of this maximum on the binding energy scale (~ 2 eV) enables to unambiguously interpret it as a peak corresponding to photoionization of the $4f$-level of divalent ytterbium [12].

The spectrum undergoes significant changes if a layer of adsorbed oxygen molecules is deposited on the surface of ytterbium nanofilms of the same thickness (the dose of molecules is 100 L). Now it already contains several characteristic features (Fig. 1, *2* spectrum). One of them is a peak with energy ~ 2 eV, corresponding to divalent ytterbium Yb^{2+}, and two other features are peaks with energies 8.9 and 12.6 eV, corresponding to trivalent Yb^{3+} [12].

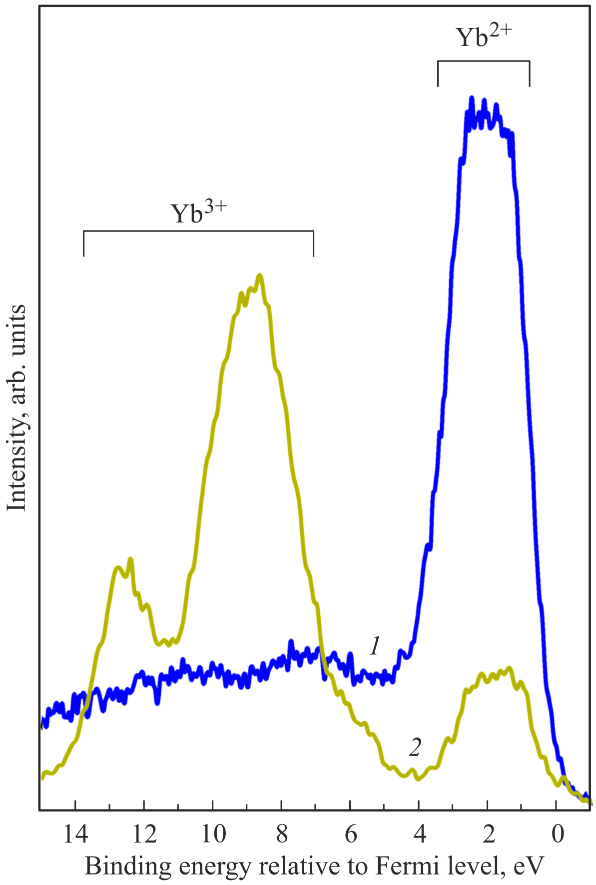

Figure 1. Photoelectron spectra of ytterbium nanofilms with surfaces of two types: *1* — there are no oxygen molecules on the surface (atomically clean surface), *2* — an adsorbed layer of oxygen molecules is formed on the surface (dose 100 L). The horizontal lines above the spectra mark the regions on the energy scale, which correspond to the emission from two- (Yb^{2+}) and trivalent (Yb^{3+}) states of ytterbium atoms. The thickness of the nanofilms is 16 ML.

At first glance, the spectrum *2* in Fig. 1 contradicts the results obtained earlier using Auger electron spectroscopy [7] and photoelectron spectroscopy in its version when synchrotron radiation is used to excite photoelectrons (energy quanta 142 eV) [13]. Using the above methods, it was established that adsorption of O_2 molecules on the surface of ytterbium nanofilms of different thicknesses leads to the $\mathrm{Yb}^{2+} \rightarrow \mathrm{Yb}^{3+}$ valence transition, as a result of which the signal of divalent ytterbium completely disappears and the signal of trivalent ytterbium appears. It is essential that the depth to which this transition propagates inside the films exceeds the depth that can be analyzed by the methods used (~ 10 ML). It was also shown that the valence transition is induced by oxygen molecules located on the surface of nanofilms in the molecular form [7].

To resolve this contradiction, we studied the X-ray photoelectron spectra of ytterbium nanofilms of various thicknesses together with O_2 layer of adsorbed molecules deposited on their surface. The obtained spectra are shown in Fig. 2. A number of important conclusions follow from it. First, features due to ytterbium in both the divalent and trivalent states are present in the spectra of $O_2{-}Yb{-}Si(111)$ structures for all film thicknesses studied in this article (from 2 to 32 ML). Second, the signal intensities of divalent and trivalent ytterbium increase with increasing thickness. And finally, thirdly, photoemission from the trivalent state of ytterbium is dominant at all thicknesses.

To quantitatively analyze the intensity of the signals from divalent and trivalent ytterbium atoms (I_{2+} and I_{3+}, respectively), the background was subtracted from the spectra using the Shirley method [14], and then the areas under the graphs were calculated in the energy interval 0–4 eV for the state Yb^{2+} and 4–15 eV for the state Yb^{3+}. The values of I_{2+} and I_{3+} obtained in this way are presented as dependences on the ytterbium film thickness in Fig. 3. It can immediately be concluded based on it that both dependencies are very similar in nature. Thus, in particular, in the initial region (up to 8 ML), the values of I_{2+} and I_{3+} increase almost linearly with increasing nanofilm thickness. For thicker nanofilms, however, the increase in signal intensity first slows down and, finally, at thicknesses of ≥ 16 ML, the signals are practically independent of the number of monolayers in the film, i.e. the dependences reach saturation.

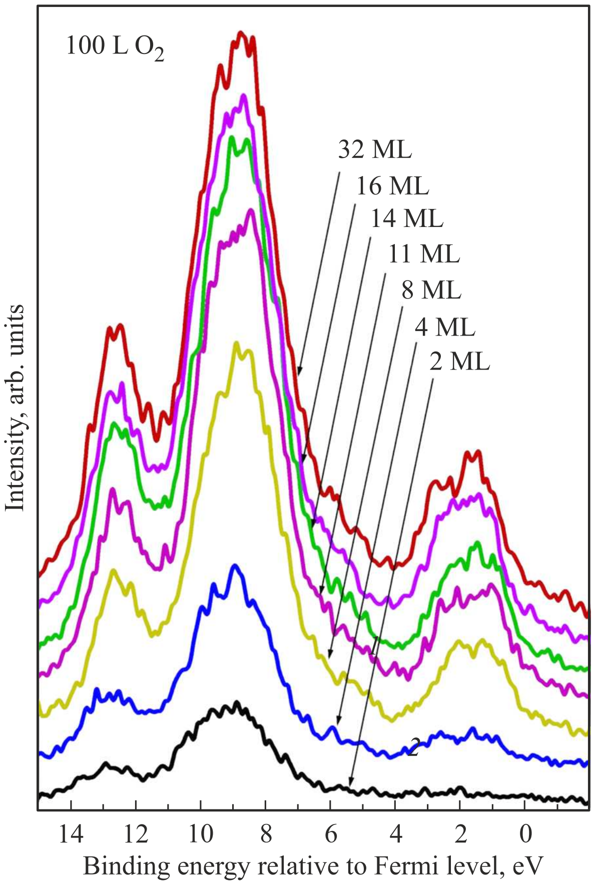

Figure 2. Photoelectronic spectra of $O_2{-}Yb{-}Si(111)$ structures at various thicknesses (from 2 to 32 ML) of ytterbium nanofilms. The oxygen dose is equal to 100 L.

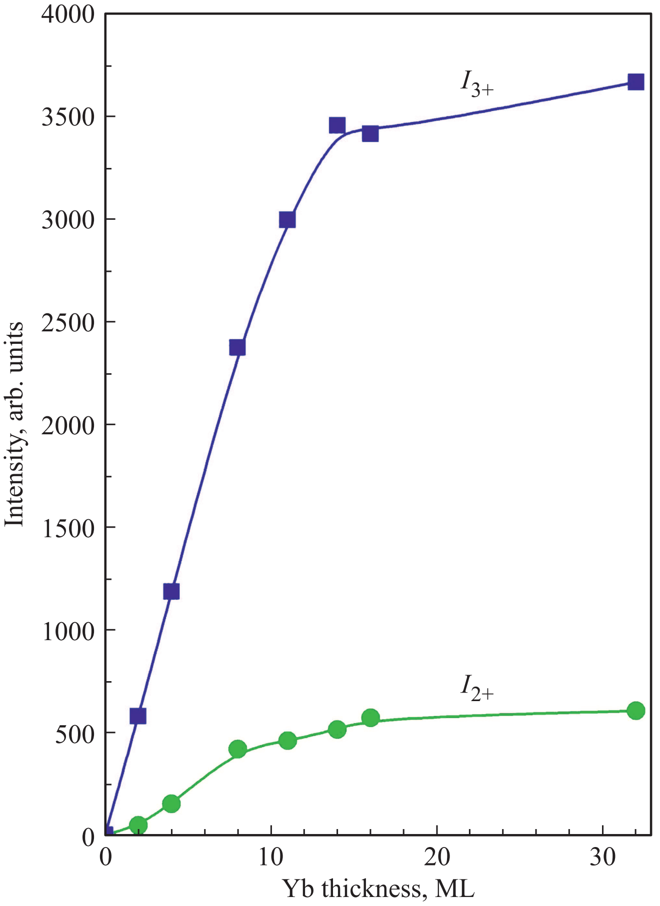

Figure 3. Dependences of signal intensity from ytterbium atoms in divalent (I_{2+}) and trivalent (I_{3+}) states on nanofilm thickness in $O_2{-}Yb{-}Si(111)$ structures.

To understand the nature of the features of the photoelectron spectra of $O_2{-}Yb{-}Si(111)$ structures, the thickness dependence of the intensity ratio I_{2+}/I_{3+} is also important. This dependence is shown in Fig. 4. It can be seen that the signal ratio I_{2+}/I_{3+} increases with increasing thickness. This growth occurs in the thickness range 0–16 ML. A further increase in the thickness does not lead to an increase in the I_{2+}/I_{3+} ratio.

Comparison of all the experimental data obtained in this article with the results of previous studies, and, in particular, the apparent contradiction between them that follows from it, enables to assume that the features in the spectra of Fig. 2 correspond to two final states of ytterbium atoms — $4f^{12}5d6s^2$ and $4f^{13}6s^2$. In one (first) of them, ytterbium is in the trivalent state, and in the other — in the divalent state. This duality is a reflection of the fact that after the removal of the core electron by a photon, the valence electron in the atom can be in the ground state, but it can also be at the excited („shake-up" level of the electron [15]). We also note that intense satellite

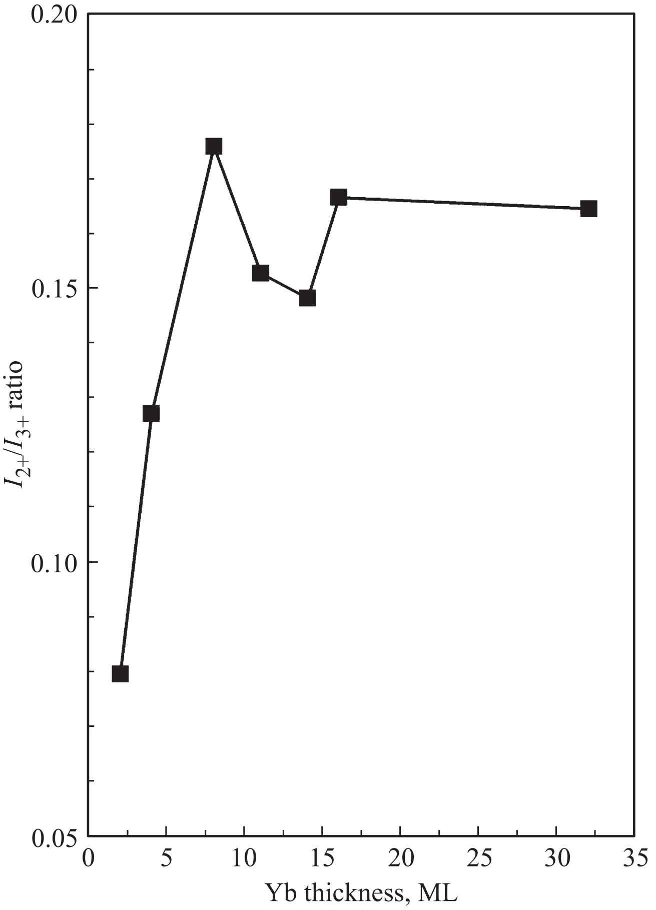

Figure 4. Dependence of the I_{2+}/I_{3+} ratio on the nanofilm thickness for O_2–Yb–Si(111) structures.

peaks due to shaking effects have already been noted in the $4f$-spectra of some rare earth metal compounds having unpaired electrons on $4f$-shells [15]. In structures of the O_2–Yb–Si(111) form studied in this article, upon photoemission of $4f$-electrons the main final state of the Yb atoms is trivalent ($4f^{12}5d6s^2$), and excited state is divalent ($4f^{13}6s^2$). Considering that the initial state of ytterbium atoms in the Yb–Si(111) and O_2–Yb–Si(111) structures is divalent ($4f^{14}6s^2$) and trivalent ($4f^{13}5d6s^2$) configuration, respectively, and that the $\mathrm{Yb}^{2+} \to \mathrm{Yb}^{3+}$ valence transition in nanofilms occurs as a result of the adsorption of O_2 molecules on their surface, it can be assumed that both of these states are close in energy, and therefore, in the XPS spectra obtained in this article for the O_2–Yb–Si(111) structures, not only a trivalent, but also a divalent final state is observed (Fig. 2).

A quantitative estimate of the difference in the energies of the divalent and trivalent states of ytterbium can be made on the basis of an analysis of the photoemission of $4f$-electrons from the Yb–Si(111) and O_2–Yb–Si(111) structures when they are irradiated with monochromatic photons with energy $h\nu$. For the Yb–Si(111) structure, the energy conservation law for such a process can be written in the form [9]:

$$h\nu + E_i(\mathrm{Yb}[4f^{14}6s^2]) = E_{\mathrm{kin}} + E_f(\mathrm{Yb}[4f^{13}6s^2]), \quad (1)$$

where $E_i(\mathrm{Yb}[4f^{14}6s^2])$ and $E_f(\mathrm{Yb}[4f^{13}6s^2])$ are the total energies of the initial and final states of the ytterbium atom, respectively, E_{kin} is the kinetic energy of a photoelectron emitted from the $4f$-shell into vacuum. For the O_2–Yb–Si(111) system, as noted above, there are already two possible photoemission channels from the $4f$-level. For them, the energy conservation laws have the following form

$$h\nu + E_i(\mathrm{Yb}[4f^{13}5d6s^2]) = E'_{\mathrm{kin}} + E_f(\mathrm{Yb}[4f^{12}5d6s^2]), \quad (2)$$

$$h\nu + E_i(\mathrm{Yb}[4f^{13}5d6s^2]) = E''_{\mathrm{kin}} + E_f(\mathrm{Yb}[4f^{13}6s^2]), \quad (3)$$

where $E_i(\mathrm{Yb}[4f^{13}5d6s^2])$ is the total energy of the initial state of the ytterbium atom in the O_2–Yb–Si(111) structure, $E_f(\mathrm{Yb}[4f^{12}5d6s^2])$ and $E_f(\mathrm{Yb}[4f^{13}6s^2])$ are the total energies of the final states, E'_{kin} and E''_{kin} are kinetic energies of electrons emitted from $4f$- level.

Subtracting equation (1) from (3), one can obtain the difference in the energies of the initial states of tri- and divalent ytterbium atoms for a nanofilm 16 ML thick:

$$\begin{aligned}\Delta E_i &= E_i(\mathrm{Yb}[4f^{13}5d6s^2]) - E_i(\mathrm{Yb}[4f^{14}6s^2]) \\ &= E''_{\mathrm{kin}} - E'_{\mathrm{kin}}. \end{aligned} \quad (4)$$

This value can be determined using Fig. 1. It is ~ 0.24 eV. The obtained value agrees with the results of calculations given in the article [16]. According to them, the difference in the energies of the divalent and trivalent states in metallic ytterbium is ~ 10 kcal/mol, which corresponds to ~ 0.43 eV. It is clear that such a small difference in the energies of the two electronic configurations of ytterbium atoms explains why a valence transition occurs in the nanofilms of this rare earth element upon adsorption of various molecules on its surface, affecting a significant number of film layers.

Similarly, based on the analysis of equations (2) and (3), one can obtain data on the energy difference between the divalent and trivalent final states of ytterbium atoms in the O_2–Yb–Si(111) structures. It equals

$$\begin{aligned}\Delta E_f &= E_f(\mathrm{Yb}[4f^{12}5d6s^2]) - E_f(\mathrm{Yb}[4f^{13}6s^2]) \\ &= E''_{\mathrm{kin}} - E'_{\mathrm{kin}} \end{aligned} \quad (5)$$

The value of ΔE_f was determined from the spectra in Fig. 2. It is ~ 7.0–7.1 eV (it was assumed that E'_{kin} is equal to the kinetic energy of electrons, which corresponds to the most intense maximum of the photoelectron line consisting of several multiplets due to the trivalent ytterbium).

A comparison of the results of this article with the data obtained by photoelectron spectroscopy using synchrotron radiation [13] leads to another physically important conclusion. It consists in the fact that if at a photon energy of 1253.6 eV the above „shaking“ of valence electrons occurs, as a result of which two final states are observed, then at $h\nu = 142\,\text{eV}$ (synchrotron radiation) only one, trivalent, final state is implemented.

The proposed interpretation of the results obtained using XPS is in full agreement with the conclusions made in previous studies: ytterbium in nanofilms completely transforms from the divalent to trivalent state when a sufficient dose of oxygen molecules is adsorbed on their surface. The depth to which adsorbed molecules modify ytterbium can be estimated based on the following. The signal of divalent ytterbium can be, as noted above, a partial result of the ionization of Yb atoms in the trivalent state. However, generally, the same signal can also be generated during ionization of Yb atoms located at a large depth in the film, i.e. not transformed into the trivalent state under the action of oxygen molecules located on the nanofilm surface. From this point of view, the fact that the dependences in Figs 3 and 4 saturate simultaneously at the same thickness of 16 ML, indicates that the XPS method enables to analyze ytterbium films to such a depth. In addition, the similar behavior of the dependences of the intensities Yb^{2+} and Yb^{3+} noted above indicates that the depth of modification of ytterbium nanofilms by O_2 adsorbed molecules exceeds 16 ML. This is an abnormally large value. It is due to the fact that, as shown by a quantitative analysis of the experimental results, the divalent and trivalent configurations of ytterbium in the $O_2{-}\text{Yb}{-}\text{Si}(111)$ structures are close in energy.

4. Conclusion

The spectra of nanometer-thick ytterbium films with layers of adsorbed oxygen molecules deposited on their surface were studied by X-ray photoelectron spectroscopy. It is found that the spectra contain peaks of divalent and trivalent ytterbium. The intensity ratio of these peaks increases with increasing film thickness (size effect). It is shown that these features of the photoelectron spectra are the result of the formation of two final states during photoionization of Yb atoms, corresponding to divalent and trivalent ytterbium. The difference in the energies of divalent and trivalent initial states is determined. It is $\sim 0.24\,\text{eV}$. A similar value for the final states is equal to $\sim 7.0{-}7.1\,\text{eV}$. The results obtained also enables to determine the depth of modification of ytterbium nanofilms by adsorbed O_2 molecules. It exceeds 16 ML.

Conflict of interest

The authors declare that they have no conflict of interest.

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