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## Origin of the thermal stability of oxygen molecules on the ytterbium nanofilm surface

© M.V. Kuzmin, M.A. Mittsev, A.A. Monyak, S.V. Sorokina

Ioffe Institute,  
St. Petersburg, Russia

E-mail: m.kuzmin@mail.ioffe.ru

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The effect of temperature on the properties of O<sub>2</sub>-Yb-Si(111) film structures has been studied using X-ray photoelectron spectroscopy. It is established that the adsorption of oxygen molecules on the ytterbium nanofilm surface is non-dissociative and leads to the formation of a stable adsorption complex, which is not destroyed when heated at 900–1050 K. The high thermal stability of this complex is due to the fact that the adsorbed molecules have a dipole moment and are oriented to the surface by the negatively charged end and into the vacuum by the positively charged one. It is shown that the molecule polarization depends on the thickness of ytterbium nanofilms (size effect). A model is proposed that allows us to qualitatively explain the results obtained

**Keywords:** surface, nanofilms, oxygen molecule, ytterbium, thermal stability, X-ray photoelectron spectroscopy.

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### 1. Introduction

Nanoscale items, in particular, nanoadsorbents [1] are of high interest owing to unique physical and chemical properties and directional modification capability [2]. In the latter case, it is necessary that various states of the given material are quite similar in energy. rare-earth metals — europium and ytterbium — are among such materials. For them, the energy difference in bivalent (electronic configuration  $4f^n 6s^2$ ) and trivalent ( $4f^{n-1} 5d^1 6s^2$ ) states does not exceed tenths of electronvolt [3]. valence transition to ytterbium may be observed, for example, at high pressure [4].

Another method of Yb<sup>2+</sup> → Yb<sup>3+</sup> transition is based on the action of adsorbed layers on the electronic structure of ytterbium nanofilms [5]. For these investigations, films were made on silicon substrates and O<sub>2</sub> or CO molecules having an unshared electron pair (ligand molecules) were used as adsorbates. Interactions of these molecules with ytterbium produce firm chemisorption bonds that ultimately stimulate the valence transition propagating into the nanofilms to a depth at least 10–16 monoatomic layers (ML) [5–7]. This transition has been shown to be followed by strengthening of interatomic bonds in ytterbium films resulting in passivation of the Yb-Si interface and blocking of silicide processes up to ~ 1000 K [8]. However, previous studies of O<sub>2</sub>-Yb-Si(111) structures performed using the Auger electron spectroscopy (AES) have not provided any findings regarding the adsorption configuration of oxygen molecules. In addition, it is not clear what effect the heating temperature has and what the maximum temperature limit is at which these molecules do not split into atoms yet. All this obviously restricts generalized modeling of molecular layer — Yb nanofilm — silicon substrate structures.

This study attempts to fill the existing gap. The X-ray photoelectron spectroscopy (XPS) method allowed us to get the data on adsorption configuration of oxygen molecules on the ytterbium nanofilm surface at various temperatures and to establish physical reasons behind the high thermal stability of O<sub>2</sub>-Yb-Si(111) systems. In addition, the XPS method ensures higher depth resolution than AES. This helped obtain valuable information on the Yb-Si interface in the given structures.

### 2. Experiment procedure

The experiments were carried out *in situ* in an ultrahigh-vacuum system with a base pressure of  $< 1 \cdot 10^{-10}$  Torr. Ytterbium nanofilms were deposited on phosphor-doped (*n*-type) Si(111) ( $7 \times 7$ ) substrates with resistivity  $\sim 5 \Omega \cdot \text{cm}$ . Silicon surfaces were cleaned by short-term heating at 1530–1550 K. The XPS and low-energy electron diffraction methods were used for cleanliness and structural performance monitoring. For ytterbium sputtering, an evaporator heated using a tungsten coil was used. Sputtering rate was one monolayer (ML) per minute. The sample temperature during filming was maintained at 290–300 K (hereinafter — RT, room temperature). Nanofilms grown in these conditions feature low roughness ( $\leq 4\%$  of thickness) and form a chemically sharp interface with the silicon substrate [9].

Adsorption of O<sub>2</sub> molecules was performed at RT and an oxygen pressure of  $2 \cdot 10^{-7}$  Torr. The dose was 100 Langmuir. According to the findings in [10], saturated adsorbed layers form on the ytterbium nanofilm surfaces in the specified exposure. Heating of O<sub>2</sub>-Yb-Si(111) structures at the pre-defined temperature was carried out during 45 s.

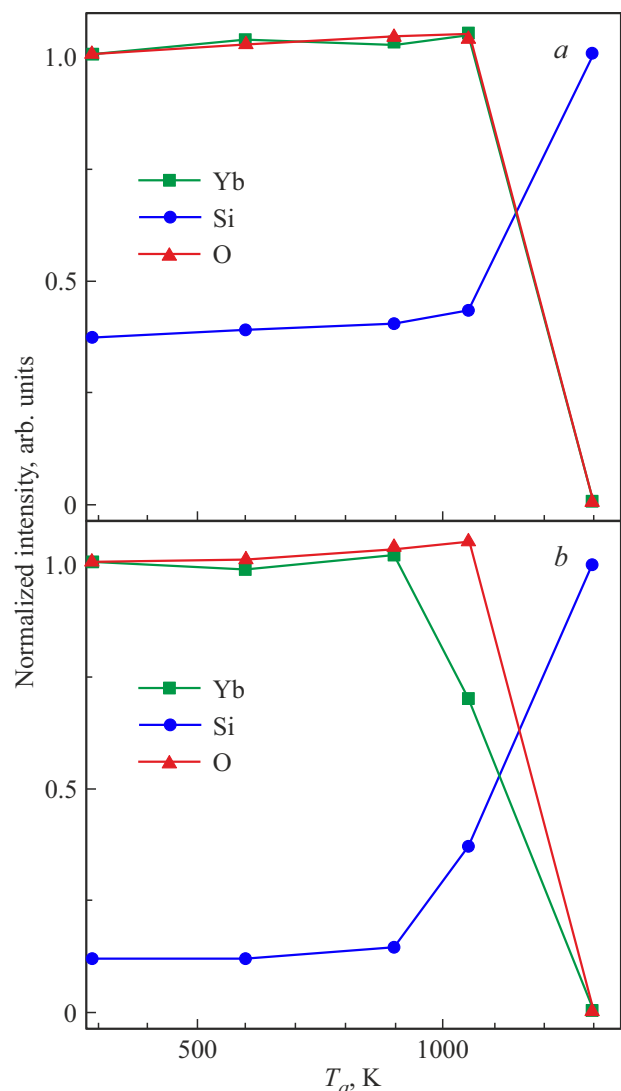
Photoelectronic spectra were recorded using Omicron EA 125 (Germany) hemispherical conical energy analyzer. Full energy resolution was  $\sim 1.0$  eV. For photoelectron excitation,  $K_{\alpha}$ -line of Mg anode with a photon energy of  $h\nu = 1253.6$  eV. was used. The spectra were measured at RT and normal angle of electron yield from the surface. The bond energy scale was calibrated by peak position in  $2p$ -spectrum for clean Si(111) surface ( $E_i = 99.3$  eV). Spectra of  $1s$ -level of oxygen ( $E_i \cong 531$  eV) and  $4f$ -level of ytterbium (multiplet structure at  $E_i \leq 15$  eV). The background was subtracted by the Shirley method [11]. Intensity of photoelectron lines was calculated as an area under curves after background subtraction. For other details of the experiment, see [7,10].

### 3. Findings and discussion

To examine thermal stability of  $O_2$ -Yb-Si(111) film systems, the structures formed at RT were heated at higher temperatures  $T_a$ , photoelectronic lines of oxygen, ytterbium and silicon were recorded and their intensities were analyzed as function of the heating temperature. Figure 1 shows such dependences obtained at ytterbium film thicknesses of 8 and 16 ML. Oxygen and ytterbium signals on these curves are normalized to the corresponding values for unheated structures, while silicon signal is normalized to the peak for clean Si surface. It can be seen immediately that signal intensity from the silicon substrate is quite high even for unheated structures — 0.37 for 8 ML and 0.12 for 16 ML. Its magnitude is associated with the free path length (23.7 Å) of electrons released from  $2p$ -level of Si (kinetic energy  $\sim 1150$  eV) [12]. This means that the XPS method provides data not only on the surface atomic layers in  $O_2$ -Yb-Si(111) structures, but also on deeper layers near the film-silicon substrate interface.

It can be also easily seen in Figure 1, *a* that when  $O_2$ -Yb(8 ML)-Si(111) structures are heated at  $T_a \leq 1050$  K, signal values are almost unchanged. This indicates high thermal stability of these structures and confirms the previous conclusion on silicide process blocking at the silicon interface [8]. It should be noted that in Yb-Si(111) system whose metal surface is free from adsorbed oxygen molecules, mixing between the film and substrate atoms starts at  $T_a \sim 400$  K, and final transition from metallic ytterbium to  $YbSi_{2-x}$  film starts at  $T_a = 600$  K [8]. With further heating temperature increase in  $O_2$ -Yb(8 ML)-Si(111) structures, oxygen and ytterbium signals become equal to zero, while silicon signal becomes equal to 1. This means that oxygen and ytterbium are fully removed from the substrate surface into vacuum.

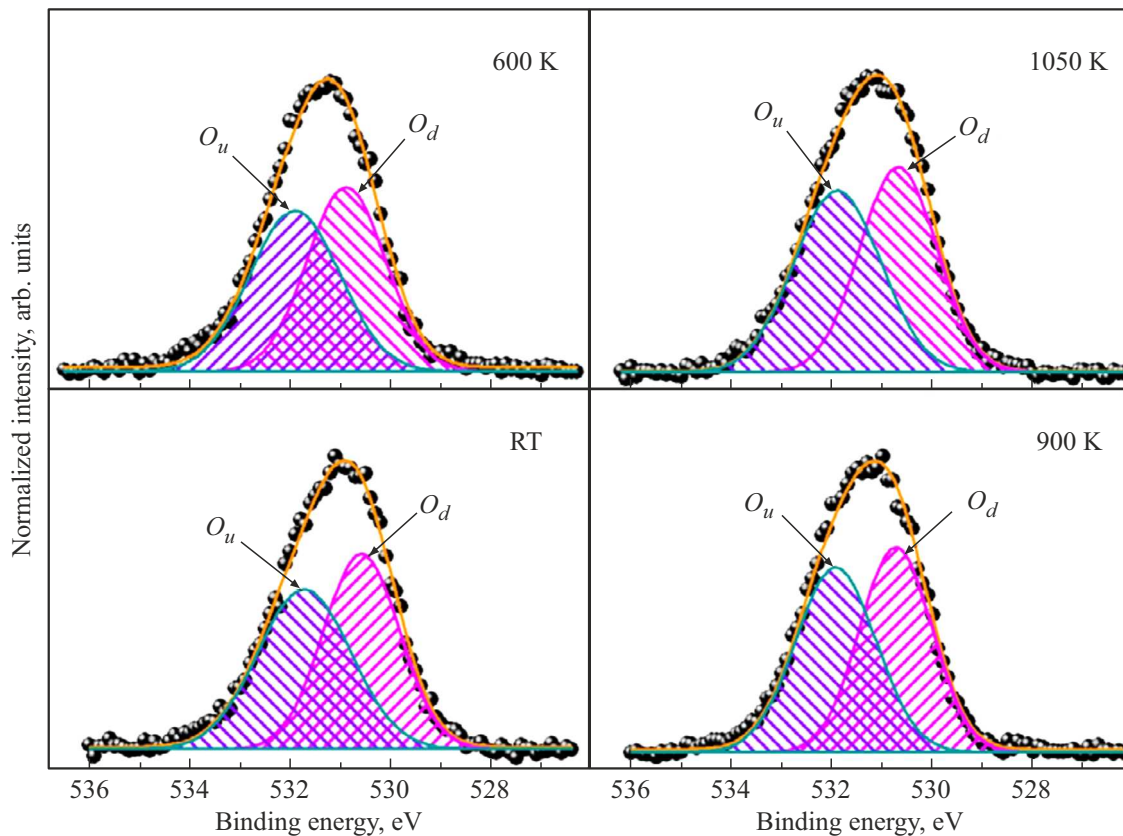
Similar pattern is also observed for  $O_2$ -Yb(16 ML)-Si(111) structures (Figure 1, *b*). For them as well as for  $O_2$ -Yb(8 ML)-Si(111), photoelectron line intensities remain constant in a quite wide temperature range (up to 900 K). At  $T_a = 1050$  K, ytterbium line intensity starts decreasing, while that of silicon



**Figure 1.** Dependences of photoelectron line intensities of ytterbium, silicon and oxygen for  $O_2$ -Yb-Si(111) structures on heating temperature ( $T_a$ ). Ytterbium film thickness: *a* — 8 ML, *b* — 16 ML.

starts increasing. At the same time, oxygen peak is unchanged. Finally, after heating at 1300 K, like for  $O_2$ -Yb(8 ML)-Si(111), the oxygen and ytterbium peaks fully disappear, and the silicon peak has a form specific to a clean surface. Thus, the maximum temperature at which  $O_2$ -Yb-Si(111) structures do not start disintegrating yet and silicide process in them does not start yet depends on the ytterbium film thickness. Reasons behind this dependence will be explained further in the text.

The findings shown in Figure 1 cannot directly answer the question in which form — molecular or atomic — oxygen is on the film surface. To clarify this question, quantitative assay of O  $1s$  spectra was performed. Figure 2 shows such spectra and their resolution into components for  $O_2$ -Yb(8 ML)-Si(111) structures produced at various heating temperatures. Spherical symbols show the experimental



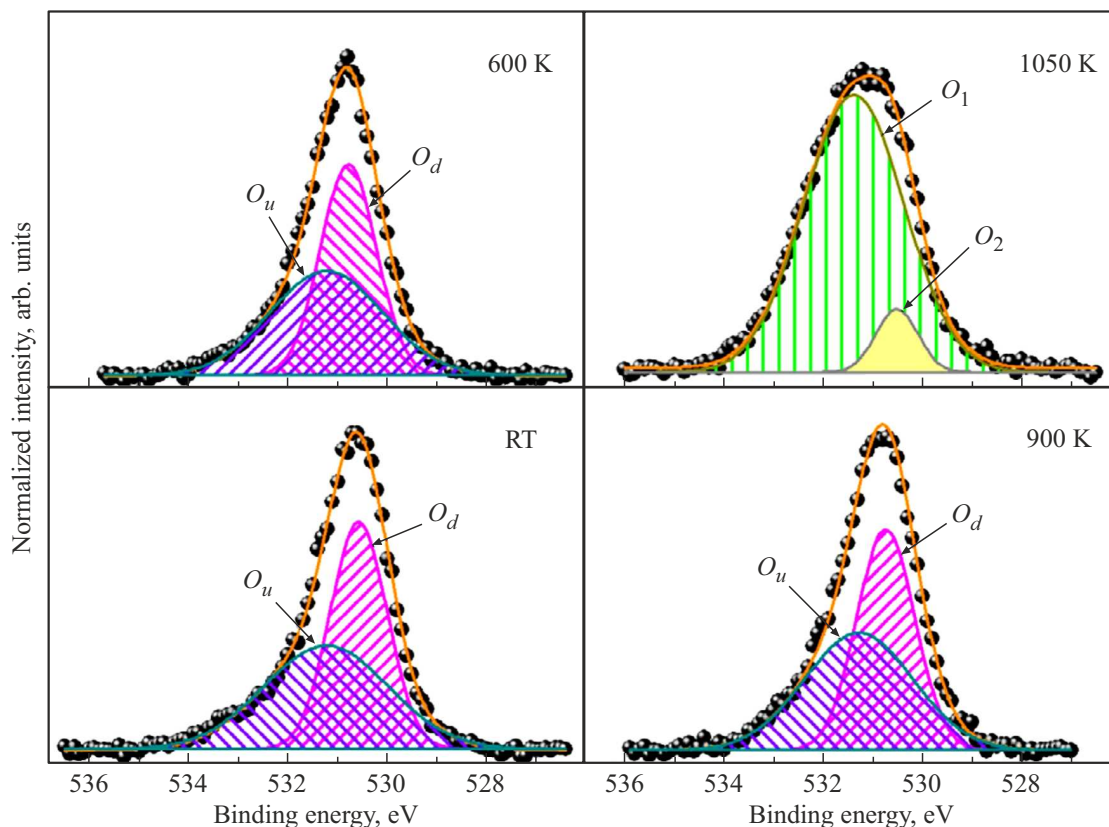
**Figure 2.** Spectra of  $1s$ -level of oxygen and their resolution into components for  $O_2$ -Yb(8 ML)-Si(111) structures produced after heating at various temperatures.

data. Solid lines show fitting results. Decomposition was performed by the least-square method. It used linear combination of the Voigt reference functions being a convolution of the Gaussian and Lorentzian line forms. In literature, for fitting  $1s$ -spectra of oxygen, the Lorentzian proportion in the Voigt function usually varies from 0 to 20% [13,14]. The best results were achieved herein at values of this parameter from 0 to 4%. Figure 2 shows that at RT the spectrum is formed by two peaks. They are denoted as  $O_u$  and  $O_d$ . Energy shift between these peaks is equal to  $\sim 1.1$  eV, and their intensity ratio is 1:1. Form and structure of spectra are not changed during heating. In particular, they remain constant even at  $T_a = 1050$  K.

The results shown above provide an important conclusion: oxygen molecule adsorption on the ytterbium surface is of non-dissociative nature. During transition from gas phase to adsorbed state, bond in them is polarized and the molecules acquire a dipole moment. This is proved by energy splitting of  $O_u$  and  $O_d$  peaks in Figure 2. These peaks are caused by two types of O atoms with different chemical environment and charge state. To have such adsorption configuration,  $O_2$  molecules shall be oriented with one („top“) end into vacuum and with the other („bottom“) end towards the film surface and form a covalent bond with it. Using the data of this study and work function measurements for  $O_2$ -Yb-Si(111) system in [10], it is suggested that O atoms

that are located at the „bottom“ end of the molecules and involved in the exchange interaction with ytterbium atoms are charged more negatively than atoms on the „top“ end that do not form any bonds with the surface. Therefore,  $O_d$  peak may be assigned to the former and  $O_u$  peak may be assigned to the latter in Figure 2. Different width of  $O_d$  and  $O_u$  also calls attention to itself. This also indicates different electronic state of the corresponding atoms in the adsorbed  $O_2$  molecules.

For  $O_2$ -Yb(16 ML)-Si(111) structures  $1s$ -spectra of oxygen (Figure 3) have a similar form in a temperature range from RT to 900 K. they are formed by  $O_d$  and  $O_u$  with equal intensity. This means that conclusions regarding the adsorption configuration of oxygen molecules in  $O_2$ -Yb(8 ML)-Si(111) structures are also valid for the case when the ytterbium film thickness is 16 ML. However, there are some differences. Thus, energy splitting of  $O_d$  and  $O_u$  in Figure 3 is  $\sim 0.6$  eV. This is almost twice as low as the equivalent value in Figure 2. This difference is probably associated with the fact that bond polarization in the adsorbed oxygen molecules decreases (size effect) as the ytterbium film thickness grows. Moreover, widths of  $O_d$  and  $O_u$  also varies.  $O_d$  becomes narrower, while  $O_u$  becomes wider than the corresponding peaks in Figure 2. Correlation between the ytterbium film thickness



**Figure 3.** Similar to Figure 2, but for  $O_2$ -Yb(16 ML)-Si(111).

and features of adsorption oxygen molecules will be addressed in future in a separate paper.

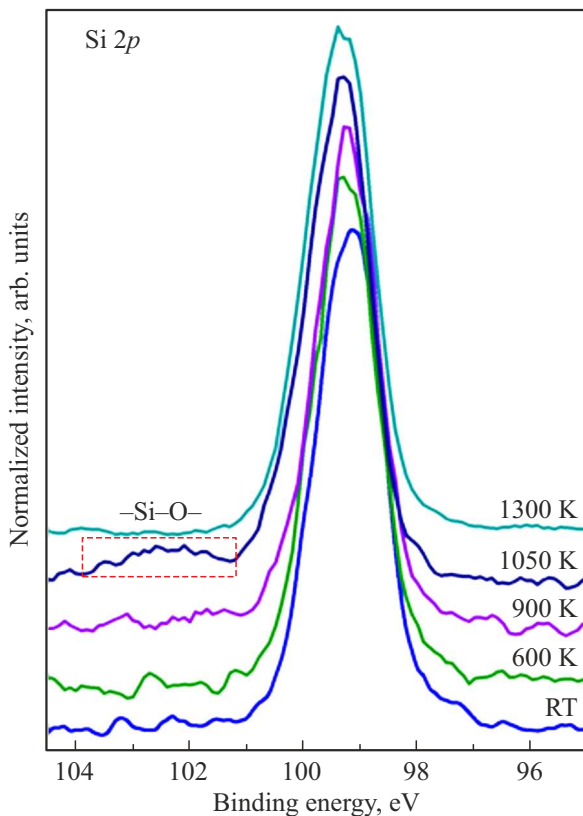
Comparison of results in Figure 2 and Figure 3 also shows another more important difference in  $O_2$ -Yb(8 ML)-Si(111) and  $O_2$ -Yb(16 ML)-Si(111) structures. As shown in Figure 3, a qualitative transformation occurs in 1s-spectrum of oxygen at  $T_a = 1050$  K: instead of  $O_d$  and  $O_u$  components described above, new  $O_1$  and  $O_2$  components appear. The former is shifted by  $\sim 0.15$  eV with respect to  $O_u$  into the higher bond energy region and the latter is shifted by  $\sim 0.25$  eV with respect to  $O_d$  into the lower energy region. Intensity ratio of  $O_1$  and  $O_2$  is  $\sim 10 : 1$ . It is obvious that such transformation indicates dissociation of oxygen molecules in  $O_2$ -Yb(16 ML)-Si(111) structure at 1050 K. It is suggested that one of the consequences of failure of the oxygen molecular layer will be silicon atom diffusion from the substrate into the ytterbium nanofilm. In this case, photoelectron line intensity of silicon shall grow and that of ytterbium shall decrease. This is fully supported by the results shown in Figure 1.

From the foregoing the question arises: what is happening with oxygen molecule decomposition products in  $O_2$ -Yb(16 ML)-Si(111) system at 1050 K? at first glance the released oxygen atoms could be expected to react with ytterbium atoms. Monoxide YbO and sesquioxide  $Yb_2O_3$  are known from the literature [14]. The first of these compounds is unstable and cannot be formed in

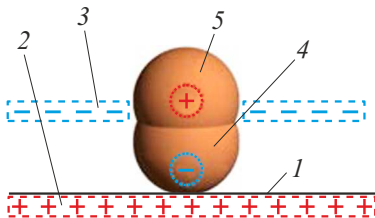
$O_2$ -Yb-Si(111) system at the specified temperature. The ytterbium sesquioxide, on the contrary, is very stable at high temperatures and cannot be removed from the substrate surface at 1300–1500 K. Therefore, formation of stoichiometric ytterbium oxides in decomposition of oxygen molecules in  $O_2$ -Yb-Si(111) structures is unlikely.

Oxygen atoms may also form bonds with silicon atoms. To verify this assumption, this study investigates 2p-level spectra of silicon for  $O_2$ -Yb(16 ML)-Si(111) structures produced at various temperatures  $T_a$ . Some of such spectra are shown in Figure 4. It is shown that a single peak with energy  $E_i \sim 99.2$  eV is present in them in the temperature range from RT to 900 K. Its is caused by the silicon substrate atoms. After heating of structures at 1050 K, an additional feature occurs in the spectrum in the form of a small flattened peak at 101.7–103.7 eV (shown dashed). Its energy position indicates that it is caused by Si atoms that form bonds with O atoms. In other words, after dissociation of  $O_2$ -Yb(16 ML)-Si(111) molecules in  $O_2$ -Yb(16 ML)-Si(111) system at 1050 K, silicon oxide and/or ytterbium silicate phases are likely formed. This conclusion agrees well with the thermal desorption spectroscopy data [15]. According to them, ytterbium evaporates from the silicate phase when  $O_2$ -Yb(16 ML)-Si(111) structures are heated up to  $\sim 1200$  K. Thus,  $O_1$  and  $O_2$  in Figure 3 may be caused by oxygen atoms in ytterbium silicate and/or silicon oxides.





**Figure 4.** Spectra of 2*p*-level of silicon for O<sub>2</sub>-Yb(16 ML)-Si(111) structures produced after heating at various temperatures. The feature caused by Si atoms that form bonds with O atoms is shown dashed.



**Figure 5.** Schematic representation of the double layer and adsorbed oxygen molecule on the ytterbium nanofilm surface. Numbers denote: 1 — surface, 2, 3 — positively and negatively charged sides of the double layer, respectively, 4, 5 — O<sub>2</sub> atoms on which the negative and positive charges are localized, respectively.

Finally, using the achieved results some points may be made that help understand why the oxygen molecules on the ytterbium nanofilm surface have high thermal stability and why the temperature at which they start decomposing into atoms depends on the thickness of these films. As shown in [16], there is a double electric layer on the ytterbium surface. Despite the quantum-chemical nature of such layer [17,18], it is preferable to use a plate capacitor model for simplicity and clarity when examining the layer (Figure 5). In this figure, it is formed by positively charged ion cores on the surface (positively charged plate 2) and a

layer of electrons shifted from the cores towards vacuum (negatively charged plate 3). It is clear that, when there is an adsorbed molecule with dipole moment on the surface, the Coulomb interaction shall occur between it and the double layer. Depending on the double layer geometry and adsorption configuration of the molecule, this interaction may have both stabilizing and destabilizing effect on the adsorbed particle.

As noted above, O<sub>2</sub> molecule adsorbed on the ytterbium films is oriented with its negatively charged end to the surface and with its positively charged end towards vacuum. Bond length in the adsorbed O<sub>2</sub> molecule is unknown. Therefore, we will use the known parameters for the free oxygen molecule with nonpolar bond. Interatomic distance in it is 1.21 Å [19]. Let us compare this value with the distance in the double layer on the ytterbium nanofilm surface. Its mean value is reported to be 1.27 Å [16]. Similarity of the given values suggests that, when O<sub>2</sub> is adsorbed on the ytterbium films, the negatively charged oxygen atom on the bottom molecule end (atom 4 in Figure 5) will interact with positively charged side 2 of the double layer. At the same time, the positively charged oxygen atom on the top end of the molecule (atom 5) will interact with negatively charged side 3 of the double layer. It is obvious that strengthening of the O<sub>2</sub> molecule — nanofilm surface adsorption complex shall take place in such configuration, which makes molecule dissociation energetically unfavorable even at high temperatures.

It is important to note that the dipole moment in the oxygen molecules on the ytterbium nanofilm surfaces increases during transition from O<sub>2</sub>-Yb(16 ML)-Si(111) structures (Figure 3) to O<sub>2</sub>-Yb(8 ML)-Si(111) structures (Figure 2). Owing to reasons described above, such increase shall result in an increase in thermal stability of molecules on the surface. This particular process was observed herein. Figures 1–3 show that the maximum temperature, at which decomposing of the adsorbed O<sub>2</sub> molecules into atoms does not take place yet, rises as the ytterbium film thickness grows from 16 to 8 ML.

## 4. Conclusion

Using the X-ray photoelectron spectroscopy, the effect of temperature on the properties of „O<sub>2</sub> layer — ytterbium nanofilm — silicon substrate“ structures was examined. It is shown that the adsorbed molecule layer and chemically sharp Yb-Si interface remain unchanged when heated to high temperatures. Temperature limit at which O<sub>2</sub>-Yb-Si(111) structures do not disintegrate has been determined and has been found to depend on the ytterbium film thickness (900 K at 16 ML and 1050 K at 8 ML). Quantitative assay of 1*s*-spectra of oxygen for O<sub>2</sub>-Yb(8 ML)-Si(111) and O<sub>2</sub>-Yb(16 ML)-Si(111) structures has been performed. The assay has established that oxygen adsorption has a non-dissociative nature in a wide temperature range and molecules in the adsorbed state have a dipole

moment and are oriented with their negatively charged end to the surface and with the positively charged end to vacuum. Analysis of Si 2*p*-spectra has been also performed. It shows that at high temperatures after dissociation of O<sub>2</sub> the released atoms form bonds with Si atoms diffused from the substrate through the interface to the ytterbium film. A model is proposed to allow qualitative explanation of high thermal stability of the oxygen molecular layers on the ytterbium nanofilm surface and, in particular, explanation of the dependence of their thermal stability on film thickness.

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## Conflict of interest

The authors declare that they have no conflict of interest.

## References

- [1] T.A. Saleh. Surface science of adsorbents and nanoadsorbents. In: *Interface Science and Technology*. Elsevier, Academic Press, London. V. 34. (2022). 324 p.
- [2] Synthesis and modification of nanostructured thin films / Ed. I.N. Mihailescu. MDPI, Basel (2020). 261 p.
- [3] B. Johansson. *Phys. Rev. B* **19**, 6615-9 (1979).
- [4] E.R. Ylvisaker, J. Kuneš, A.K. McMahan, W.E. Pickett. *Phys. Rev. Lett.* **102**, 246401 (2009).
- [5] D.V. Buturovich, M.V. Kuzmin, M.V. Loginov, M.A. Mitsev. *FTT* **57**, 9, 1821 (2015). (in Russian).
- [6] D.V. Buturovich, M.V. Kuzmin, M.A. Mitsev. *Pisma v ZhTF* **38**, 21, 22 (2012). (in Russian).
- [7] M.V. Kuzmin, M.A. Mitsev, *FTT* **64**, 7, 874 (2022). (in Russian).
- [8] M.V. Kuzmin, M.A. Mitsev, N.M. Blashenkov. *FTT* **59**, 8, 1612 (2017). (in Russian).
- [9] M.V. Kuzmin, M.A. Mitsev, *ZhTF* **90**, 8, 1359 (2020). (in Russian).
- [10] M.V. Kuzmin, M.A. Mitsev, *FTT* **64**, 8, 1091 (2022). (in Russian).
- [11] D.A. Shirley. *Phys. Rev. B* **5**, 4709 (1972).
- [12] C.J. Powell, A. Jablonski. NIST Electron Inelastic-Mean-Free-Path Database. Version 1.2. SRD 71. National Institute of Standards and Technology. MD, Gaithersburg (2010).
- [13] G.H. Major, N. Farley, P.M.A. Sherwood, M.R. Linford, J. Terry, V. Fernandez, K. Artyushkova. *J. Vac. Sci. Technol. A* **38**, 061203 (2020).
- [14] G. Adachi, N. Imanaka. *Chem. Rev.* **98**, 1479 (1998).
- [15] M.V. Kuzmin, M.A. Mitsev, *FTT* **54**, 10, 1988 (2012). (in Russian).
- [16] M.V. Kuzmin, M.A. Mitsev, *ZhTF* **93**, 829, 2023 (2013). (in Russian).
- [17] J.R. Smith. *Phys. Rev.* **181**, 522 (1969).
- [18] N.D. Lang, W. Kohn. *Phys. Rev. B* **1**, 12, 4555 (1970).
- [19] G. Grey. *Elektrony i khimicheskaya svyaz'*. Mir, M. (1967), P. 72. (in Russian).

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