Physics of the Solid State, 2025, Vol. 67, No. 5

08

Electronic nature of size effects in O_2-Yb-Si(111) film structures

© M.V. Kuzmin

Ioffe Institute,
St. Petersburg, Russia

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

Received May 12, 2025
Revised May 13, 2025
Accepted May 13, 2025

Using X-ray photoelectron spectroscopy, the effect of the nanoadsorbent size (ytterbium film thickness ranging from ~ 0.8 to 12.2 nm) on the properties of the adsorbed molecular oxygen layer, in particular, the saturate coverage, and the adsorption configuration and polarization of molecules on the surface, has been studied. It is shown that the size dependences obtained are due to electronic processes in the bulk and at the surface of ytterbium, occurring during the formation of bonding between the nanofilm and the adsorption layer. The results appear important for the development of physical principles and methods for creating materials with tailored properties.

Keywords: adsorbed layer, nanoadsorbent, oxygen, ytterbium, X-ray photoelectron spectroscopy.

DOI: 10.61011/PSS.2025.05.61499.111-25

1. Introduction

Currently nanoadsorbents have been used more and more frequently to produce materials with specified physical and chemical properties [1–5]. Their primary difference from regular massive three-dimensional substrates consists in the fact that the substantial specific share in these objects is occupied with the surface: the percentage ratio of atom quantity thereon to the full quantity of atoms may amount to 50 % and more. This opens the opportunity for targeted control of nanoadsorbent properties as a whole by using surface phenomena, in particular, adsorption of atoms and molecules.

In recent papers [6–9] it was shown that when the layer of oxygen molecules is adsorbed on the ytterbium films with thickness d from ~ 0.4 to $6-12$ nm, electronic phase transition $4f^{14}6s^2 \rightarrow 4f^{13}5d^16s^2$ (valence transition $\mathrm{Yb}^{2+} \rightarrow \mathrm{Yb}^{3+}$) may occur in its volume. Besides, this transition is accompanied with other important transformations in a nanoadsorbent, for example, change in the nature of bonds between atoms, increased thermal stability and appearance of a band gap in the electronic structure (metal-superconductor transition) [7,8]. Therefore, several questions arise, namely, what is the role of ytterbium film thickness in process of adsorbed oxygen layer formation, will it impact the position and charge state of O_2 molecules on the surface, and which physical processes in the volume and on the surface of the nanoadsorbent provide for the dimension effects in this system? We were able to cast light on some of them in paper [10]. It was found that when the value d decreases from 16 to 8 single-atom layers (ML) (accordingly ~ 6.1 and 3.0 nm), the adsorption complexes of O_2 molecule— ytterbium surface are reinforced, and the maximum temperature, at which the oxygen molecules will not yet decay, increases. However, the nature of the found dimension dependences was not studied in detail in article [10]. It was planned to study it later.

The objective of this paper — to collect information about physical patterns, which define the size effects in the system O_2-Yb. As it is shown further in the article, the key role in these effects belongs to electron processes on the surface and in the space of nanoadsorbent. The paper used the method of X-ray photoelectron spectroscopy (XPS). It is sensitive to many parameters of oxygen molecule adsorbed layer, including their electronic state and adsorption geometry.

2. Experiment procedure

The experiments were carried out in an ultrahigh-vacuum system with a base pressure below $1 \cdot 10^{-10}$ Torr. Ytterbium nanofilms were created on a single-crystal substrate Si(111)(7 × 7) (n-type, $\rho \sim 5\,\Omega \cdot \mathrm{cm}$). To clean the silicon surface, the crystal was heated at 1530–1550 K. The purity of the surface and its atomic structure were controlled using XPS and low-energy electron diffraction. The rate of ytterbium deposition was 1 ML/min. The monolayer coating of its atoms was accepted to be surface concentration $7.84 \cdot 10^{14}\,\mathrm{cm}^{-2}$, which is equal to the atom density on an unreconstructed Si(111) facet. The substrate temperature during metal deposition was equal to ~ 290 K. As it was shown before [11], ytterbium nanolayers obtained by this method have high homogeneity in thickness and form of a chemically sharp interface with silicon. Adsorption of molecules O_2 was carried out at the above temperature and partial oxygen pressure of $2 \cdot 10^{-7}$ Torr. The dose in all the experiments was 100 Langmuir. The monomolecular layer of oxygen, adsorbed by this exposure, reaches the limit (saturing) coating [9]. Transition of ytterbium to non-autonomous trivalent state after oxygen adsorption was controlled using $4f$-spectra of photoemission [9,12].

Photoelectron spectra were recorded using a semi-spherical analyzer EA 125 by Omicron (Germany) at the normal angle of electron release from the target surface. Prior to registration of the spectra, the film structures were not heated. For photoelectron excitation, $K\alpha$-line of Mg anode with a photon energy of $h\nu = 1253.6\,\mathrm{eV}$ was used. The full energy resolution was $\sim 1.0\,\mathrm{eV}$. Calibration of the bond energy scale was done using position of $2p$-line of pure silicon surface ($E_i = 99.3\,\mathrm{eV}$). The background from spectral lines was subtracted by Shirley method [13].

3. Results

Figure 1 shows normalized photoelectron spectra of $1s$-level of oxygen, produced for structures O_2-Yb-Si(111) at various thicknesses of ytterbium films. Round symbols show the experiment data. Solid lines show the results of spectra decomposition into individual components. The decomposition procedure features were previously considered in [10,14,15], therefore, they will not be discussed in the article. As you can see in Figure 1, the oxygen line at all values d from 2 to 32 ML ($\sim 0.8-12.2\,\mathrm{nm}$) includes two peaks O_u and O_d, having approximately equal intensities. Interpretation of this shape of spectra was already give in paper [10]. Let us list briefly the key findings. Oxygen adsorption on the Yb films happens in molecular form. Adsorbed molecules occupy vertical position, where the axis connecting the centers of atoms is directed along the normal line to the surface. Two types of oxygen atoms are specific for this configuration. Atoms O_d, arranged at the other end of the molecules, which is oriented to the surface, start exchange interaction with ytterbium. In Figure 1 these atoms may be associated to peak O_d, displaced towards the lówer values of binding energy. Atoms O_u on the opposite end of the molecules turned into vacuum produce no bonds to the nanofilm. Such atoms have their peak O_u, displaced towards the area of hígh energies in Figure 1. Therefore, O_d and O_u have non-equivalent environment and charge state, which means oxygen molecule polarization in process of a transition from a gas phase to the adsorbed state on nanofilms. It would be reasonable to assume that the dipole moment value for adsorbed molecules will depend on the charge overflow at the interface adsorbed layer — ytterbium surface.

The further analysis of Figure 1 prompts noting that energy splitting ΔE_i of peaks O_u and O_d decreases monotonously with the growth of film thickness d. The progress of dependence $\Delta E_i = f(d)$ is shown in Figure 2, a. From this drawing it follows that polarization of adsorbed molecules is the function of nanoadsorbent size: the higher it is, the lower the value d. Besides, the attention is drawn to the fact that size dependence in Figure 2, a never reaches a plateau, even at $d = 32$ ML. At first sight this fact seems to be somewhat unexpected. Indeed, changes in electron and emission properties of the surface Yb-Si(111) end under much smáller coatings ($d \cong 16$ ML) [16]. But in fact this contradiction is seeming, and its reasons will become clear in section 4. If dependence $\Delta E_i = f(d)$ in Figure 2, a does not reach a plateau, it allows assuming that electronic state of adsorbed molecules in structures O_2-Yb-Si(111) to a large extent depends on the processes in the nanofilm volume.

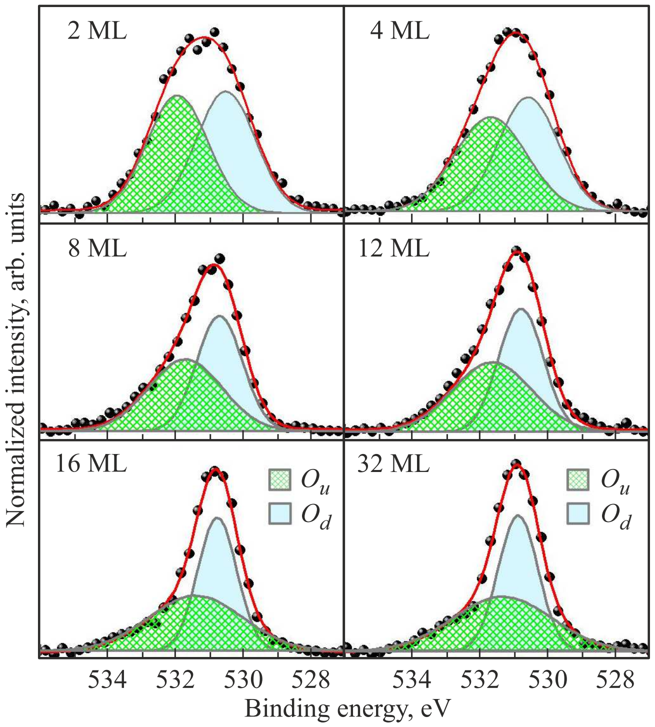

Figure 1. Spectra of $1s$-level oxygen for structures O_2-Yb-Si(111) at different thicknesses of ytterbium nanofilm.

Another manifestation of size effects in the studied structures is the dependences of width (FWHM, *full width at half maximum*) in peaks O_u and O_d (respectively, ω_u and ω_d) of the ytterbium film thickness (Figure 2, b). It is known that the contribution to the widening of peaks or individual spectral components in photo-emission may lead to local disorganization of the crystalline structure, or, in other words, increase in the degree of heterogeneity of the centers that are occupied by the corresponding atoms [17–20]. As it follows from Figure 2, b, at small thicknesses of the width of the peakis O_u and O_d is nearly the same. Thus, for example, at $d = 2$ ML $\omega_u \approx \omega_d \approx 2.1\,\mathrm{eV}$ will be true. Probably, it is due to the fact that the surface molecules have rather close adsorption configurations.

As the ytterbium thickness increases, no widening of peak O_d happens, moreover, the value ω_d even somewhat decreases, reaching $\sim 1.4\,\mathrm{eV}$ at $d = 32$ ML. Most likely, the reason for absence of amplification is the fact that the end of molecules, where atoms O_d are located, is rigidly fixed on the surface, and new types of adsorption centers for oxygen do not appear with the growth of value d.

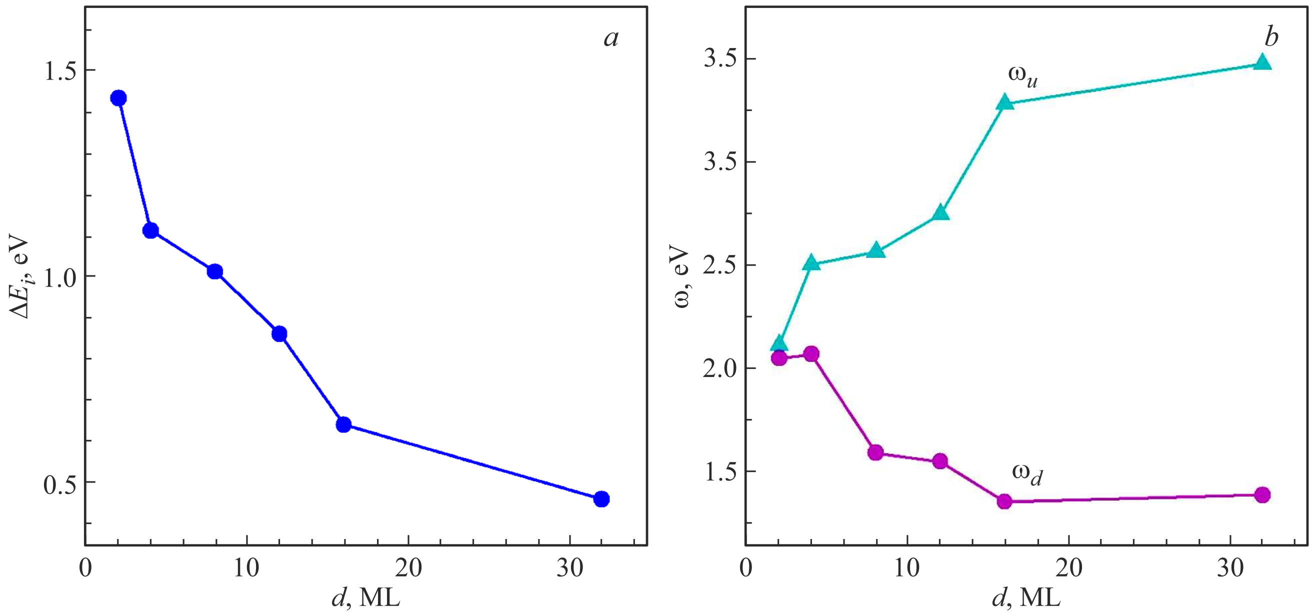

Figure 2. Size dependences of parameters obtained from spectrum decomposition in Figure 1. *a* — ΔE_i, *b* — ω_d and ω_u.

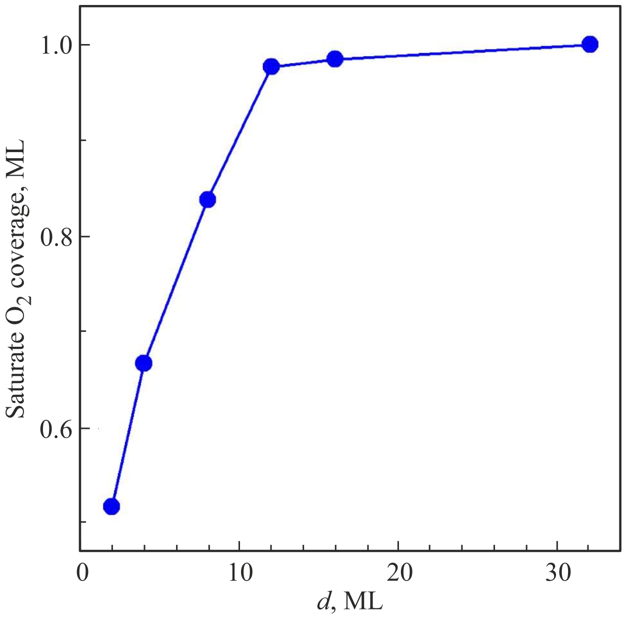

Figure 3. Size dependence of saturating coating of molecular oxygen layer.

A totally different situation is observed for the peak O_u. As the film thickness increases, the width of this maximum increases noticeably and reaches the value of $\omega_u = 3.5\,\mathrm{eV}$ at $d = 32\,\mathrm{ML}$. It means that for thicker films of ytterbium the geometry of oxygen molecules on the surface may vary much stronger than for thinner films. Such variation is due to the fact that the second end of the molecules is not fixed on the surface, and atoms O_u do not form covalent bonds with ytterbium. The reasons for rising disorder in the monomolecular layer of oxygen will be discussed in section 4.3.

As the thickness *d* of ytterbium increases, the maximum number of O_2 molecules that may stay in the adsorbed layer will be changing, too (Figure 3). To obtain such size dependence, the intensity of 1*s*-line of oxygen was used, which after normalization to the value of the signal at $d = 32\,\mathrm{ML}$ served as the measure for limit coating of the molecules expressed in the shares of the monolayer, at the specified thickness of the film (it was assumed that the monolayer coating of adsorbate is achieved at $d = 32\,\mathrm{ML}$). From the given curve you can see that in the area of $d < 12\,\mathrm{ML}$ thicknesses the saturating coating of the adsorbed layer substantially depends on the size of nanoadsorbent and drops sharply as its thickness reduces. At higher values *d* the curve reaches the plateau, and the saturating coating practically does not depend on the yield thickness.

4. Results and discussion

To understand the nature of size dependences in Figures 2 and 3, it is necessary to consider the mechanism of interaction of ligand molecules with the ytterbium nanofilms. Paper [6] suggested a model of carbon monoxide molecules adsorption on such films. The important feature of CO molecules is the presence of an lone electron pair at the highest filled level (5σ-orbitals) [21]. Lone electrons play a special role in the adsorption process: first of all, they do not participate in formation of bonds in the molecules and second, they are used to form chemisorptive bonds with nanoadsorbent. The O_2 molecule, as in CO, also has two unpaired electrons on $\pi^*_{x,y}$ orbitals [21]. Besides, for

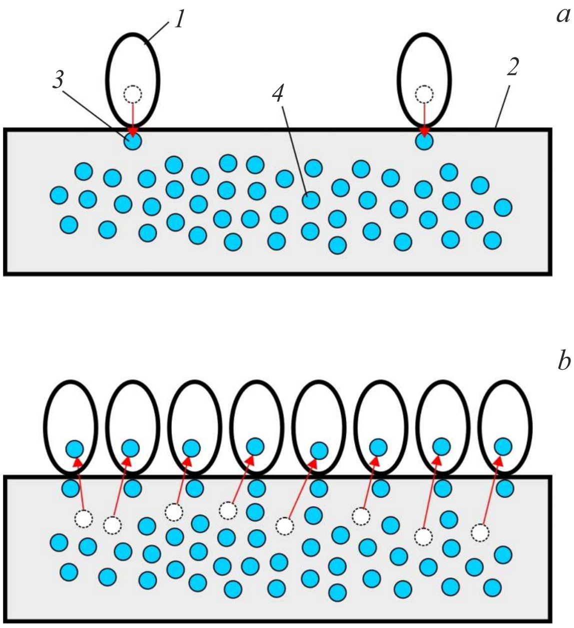

Figure 4. Model explaining the electronic transitions (marked with arrows) at different stages of formation of adsorbed layer of oxygen molecules on ytterbium nanofilms: *a* — stage *I*, *b* — stage *II*. Numbers denote: *1* — molecule, *2* — nanofilm, *3* — electron localized on the surface, *4* — electron gas.

structures O_2-Yb-Si(111) and CO-Yb-Si(111) high similarity of the obtained results is observed [6,7]. Therefore, to explain the size dependences in the O_2-Yb-Si(111) system, it is reasonable to use the representations specified in [6]. Let us assume that at the early stage of O_2 molecule adsorption, when their surface concentration is relatively low (stage *I*), the bond to the ytterbium surface is formed by transfer of some charge from $\pi^*_{x,y}$ states of molecules to the film. For simplicity, in Figure 4, *a* this transfer is shown as a transition (marked with an arrow) of one of two (the second one is not shown) lone electrons of molecules into metal. Such binding electrons are localized on the surface, and their appearance must result in excitation of electron gas in the volume of the adsorbent due to Coulomb repulsion forces, and finally the increase in the system energy. At the later stage of adsorption (stage *II*, Figure 4, *b*), when the number of the molecules bound on the surface becomes rather high, amplified Coulomb interaction in ytterbium creates the conditions of reverse flow of charge, i. e., pushing out some conductivity electrons to the empty orbitals of molecules. Such transitions will be accompanied with the reduction in the system energy: bottom of $5d$-zone of ytterbium must lower below Fermi level, and $4f$-electron will be promoted into it, and electronic structure of the nanofilm will become trivalent ($4f^{13}5d^16s^2$). In particular, the described scenario is fully confirmed by the shape of dependences of the work function on the adsorbate coating for the oxygen-ytterbium system [7]. Thus, at the stage *I*, when adsorbed molecules serve as donors of electrons, the work function reduces with the growth of the particle number on the surface, and at the stage *II*, when molecules are acceptors of electrons, the work function value increases with the increase in the adsorbate quantity.

Within the just considered mechanism of donor-acceptor bonds formation on the surface, nanoadsorbents have certain fundamental differences from 3D substrates. First of all, the total number of charge carriers is limited in nanoadsorbents, whereas for the massive metal substrates such limitation is actually absent: they may be seen as infinite reservoirs of electrons. Second, the average distance between the conductivity electrons and electrons localized on the surface, for the nanoadsorbent is substantially shorter than similar distances for 3D specimens. Finally, third, in contrast to the regular substrates, the change in the characteristic size of nanoadsorbent may substantially disturb the balance between it and the adsorbed layer. Let us now discuss the size dependences in Figures 2 and 3 in more detail.

4.1. Dipole moment

Since polarization of adsorbed molecules (Figure 2, *a*) is related to pushing out electrons from the films, it is evident that amplification or attenuation of electron gas perturbation in the ytterbium volume will directly impact the value of the oxygen dipole moment on the surface. It is useful to assess, at least roughly, how this perturbation depends on thickness d. It is convenient to choose parameter $R = N_s/N_c$ as the quantitative criterion, where N_s — maximum number of electrons, which may transfer from molecules to adsorbent and be localized on its surface at specified thickness d, and N_c — maximum number of conductivity electrons in the film per unit of surface area. The physical sense of parameter R consists in the fact that its value characterizes the value of the charge localized on the surface per one electron in the film. For simplicity let us assume that at $d = 32$ ML the limit concentration of molecules in the adsorbed layer is equal to $1 \cdot 10^{15}\,\mathrm{cm}^{-2}$, and each molecule releases one electron. To count the carriers in the film, let us assume that ytterbium is in regular metal (Yb^{2+}) state, in which each ion transfers two valence electrons to the conduction band. The dependence $R = f(d)$ obtained after simple calculations is shown in Figure 5. The curve shows that as thickness d decreases, the excitation of electron gas in the film should grow more and more. You can also see that changes in the value R do not stop even at $d = 32$ ML.

Using data of Figure 5, it is easy to obtain dependence $\Delta E_i = f(R)$. It is shown in Figure 6. The appearance of this dependence fully confirms the previous assumptions. In particular, it follows from Figure 6 that between the values R and ΔE_i there is a clear correlation: the higher the perturbation of electron gas is in ytterbium, the higher the polarization of adsorbed molecules becomes.

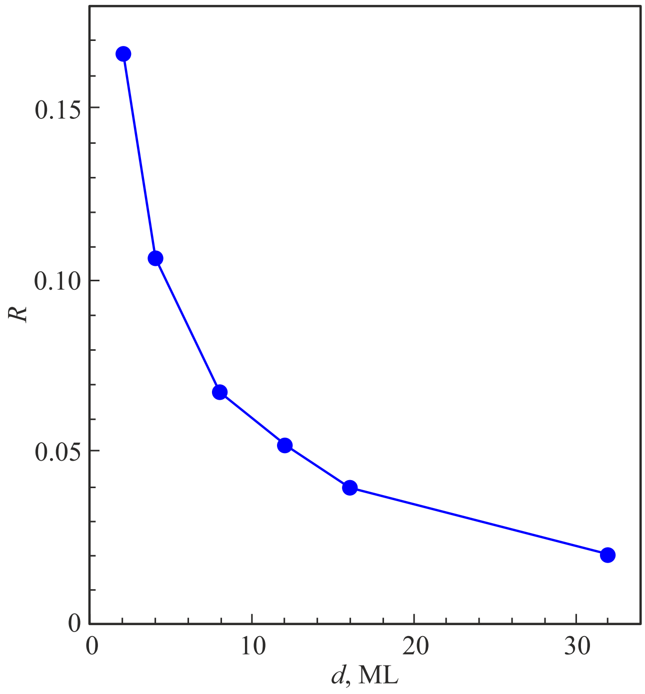

Figure 5. Size dependence of parameter R.

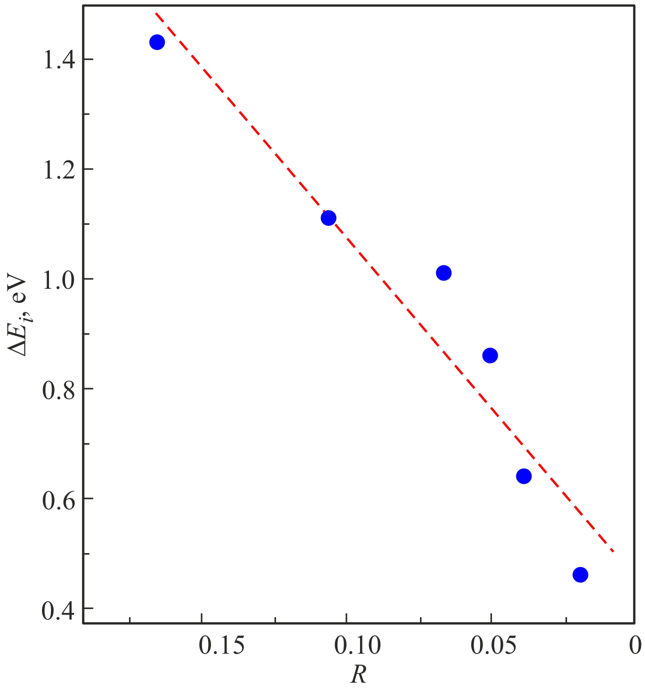

Figure 6. Dependence of energy ΔE_i on R.

4.2. Saturating coating of adsorbed layer

To fill the oxygen layer, it is necessary to meet at least two conditions. First, free adsorption centers must be present on the ytterbium surface. Second, molecules in these centers must be tightly bonded to the adsorbent. Within the above model, the second condition will only be met when some nanofilm conductivity electrons will go to the empty levels in the molecules. It is clear that natural restriction exists for such charge transfer. It is related to the fact that at low values d the share of carries that may in principle participate in the formation of bonds with adsorbate, is a rather significant part of the total number N_c, therefore, the transition of electrons to adsorbate may be limited to the condition of charge equilibrium in the nanofilm volume. For thicker nanofilms such restriction is less significant. Therefore, filling of the molecular layer in the O_2-Yb-Si(111) system will be determined not by the number of available adsorption centers on the surface, but the number of electrons in the adsorbent, which may be displaced into the molecules.

The above makes it possible to explain the course of the curve shown in Figure 3. At $d < 12$ ML the value of the limit coating of oxygen drops sharply as the size of nanoadsorbent decreases. At such thicknesses of the films the filling of the molecular layer is controlled not by the adsorption kinetics, but by restrictions to the charge transfer from ytterbium. It stops even before the reserve of free adsorption spaces for molecules on the surface is exhausted. At $d \geq 12$ ML the number of carriers in the volume of the film becomes adequate for filling all centers on the surface, i. e., the restriction to electronic transitions is removed.

4.3. Adsorption configuration

Paper [10] found that substantial effect on thermal stability of O_2-Yb structures is provided by double electric layer on the ytterbium surface. Despite the crude analogy, it is convenient to use a model of flat capacitor to describe such layer, where positively and negatively charged „plates" are formed accordingly by a layer of ion cores on the ytterbium surface and a layer of electrons exiting the lattice. As shown in [10], electrostatic interaction between „plates" of the double layer, on the one hand, and oppositely charged ends of vertically standing adsorbed O_2 molecules, on the other hand (see Figure 7), causes formation of strong, thermally stable, adsorption complexes on the surface. You may assume that ordering of oxygen molecules in such a system will be higher depending on the strength of their polarization. At low thicknesses d of films the adsorbed molecules have a comparatively high dipole moment (Figure 2, *a*). For this reason their adsorption configuration is quite close (see Figure 2, *b* in section 3). The structure of such molecular layer is schematically illustrated in Figure 7, *a*. When the value d increases, polarization of molecules decreases. This causes increase in the number of adsorption configurations of molecules and higher entropy in the surface layer. Its structure is shown in Figure 7, *b*.

To test the hypothesis just considered, you may use value $\Delta\omega = \omega_u - \omega_d$ as the quantitative measure of disordering in the molecular layer. It is clear that its value should increase with decrease of energy ΔE_i. Figure 8 shows the

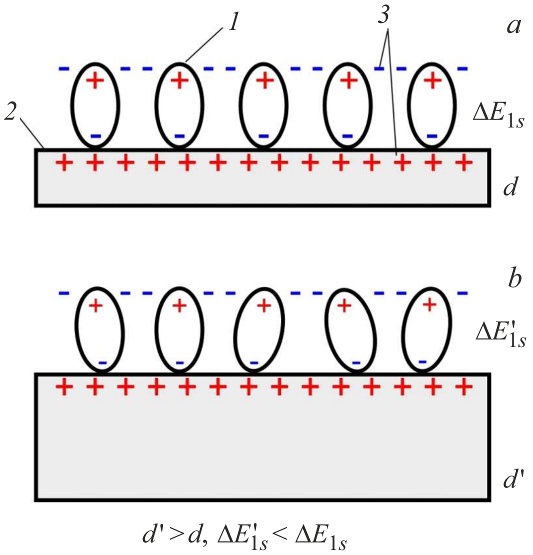

Figure 7. Schematic illustration of adsorption geometry of O_2 molecules on ytterbium nanofilms of various thickness. Details in the text. Legend: *1* — molecule, *2* — nanofilm, *3* — double layer.

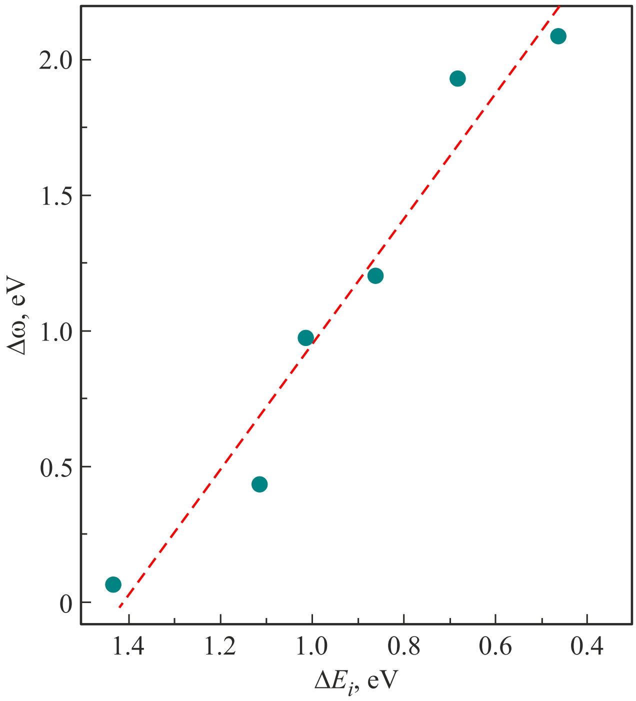

Figure 8. Dependence of value $\Delta\omega$ on energy ΔE_i.

relationship between these values. You can see that the appearance of the obtained dependence fully confirms the conclusions made previously.

5. Conclusion

The paper studied the impact of nanofilm thickness in O_2-Yb-Si(111) structures at electronic state and adsorption configuration of oxygen molecules. Obtained O 1s-spectra show that when the value d changes from 32 to 2 ML, the polarization of molecules on the surface increases. It is explained by the fact that for thinner nanofilms the formation of adsorbate-surface bonds is accompanied with stronger excitation of electron gas in the ytterbium volume and, accordingly, transfer of lárger electron charge from it to the empty orbitals of molecules. It was found that these electronic transitions are limited by the condition of charge equilibrium in the adsorbent, which provides for clear size dependence of the limit coating of the adsorbed layer at $d < 12$ ML. It is shown that the double electric layer on the surface of ytterbium nanofilms also plays an important role. Its presence causes size dependence of adsorption configuration of molecules on the surface and degree of disordering of the molecular layer. The model of oxygen-ytterbium nanofilm film structures is proposed, which may be used to explain the observed size effects.

Conflict of interest

The authors declare no conflict of interest.

References

[1] T.A. Saleh. Surface science of adsorbents and nanoadsorbents. In: Interface Science and Technology. Elsevier, Academic Press (London). Vol. **34**. (2022). 324 p.

[2] Synthesis and modification of nanostructured thin films. Ed. I.N. Mihailescu. MDPI (Basel). (2020). 261 p.

[3] A. Kasprzak, M. Matczuk, H. Sakurai. Chem. Commun. **59**, 9591 (2023).

[4] A.E. Ferenj, D.M. Kabtamu, A.H. Assen, G. Gedda, A.A. Muhabie, M. Berrada, W.M. Girma, ACS Omega **9**, 6803 (2024).

[5] R. Ningthoujam, Y.D. Singh, P.J. Babu, A. Tirkey, S. Pradhan, M. Sarma, Chemical Physics Impact **4**, 100064 (2022).

[6] D.V. Buturovich, M.V. Kuzmin, M.V. Loginov, M.A. Mitsev. FTT **57**, *9*, 1821 (2015). (in Russian).

[7] M.V. Kuzmin, M.A. Mitsev, N.M. Blashenkov. FTT **59**, *8*, 1612 (2017). (in Russian).

[8] M.V. Kuz'min, M.A. Mitsev, ZhTF **91**, *7*, 1189 (2021). (in Russian).

[9] M.V. Kuz'min, M.A. Mitsev, FTT **64**, *7*, 874 (2022). (in Russian).

[10] M.V. Kuzmin, M.A. Mitsev, A.A. Monyak, S.V. Sorokina. FTT **66**, *5*, 775 (2024). (in Russian).

[11] M.V. Kuz'min, M.A. Mitsev, ZhTF **90**, *8*, 1359 (2020). (in Russian).

[12] L.I. Johansson, J.W. Allen, I. Lindau, M.H. Hecht, S.B.M. Hagström. Phys. Rev. B **21**, *4*, 1408 (1980).

[13] D.A. Shirley. Phys. Rev. B 5, 4709 (1972).

[14] 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).

[15] G. Adachi, N. Imanaka. Chem. Rev. **98**, 1479 (1998).

[16] M.V. Kuz'min, M.A. Mitsev, FTT **65**, *6*, 1082 (2023). (in Russian).

[17] A.W. Newton, A. Vaughan, R.J. Cole, P. Weightman, J. Electron Spectrosc. Related Phenom. **107**, *2*, 185 (2000).

[18] A.W. Newton, S Haines, P. Weightman, R.J. Cole, J. Electron Spectrosc. Related Phenom. **136**, *3*, 235 (2004).

[19] T. Marten, W. Olovsson, S.I. Simak, I.A. Abrikosov, Phys. Rev. B **72**, 054210 (2005).

[20] J. Liu, H. Zhang, Y. Li, Z. Liu, J. Phys. Chem. B **122**, *46*, 10600 (2018).

[21] G. Grey. Elektrony i khimicheskaya svyaz'. Mir, M. (1967), s. 72. (in Russian).

Translated by M.Verenikina