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X-ray photoelectron spectra of oxygen molecules adsorbed on ytterbium nanofilms

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The adsorption of oxygen molecules on ytterbium nanofilms of various thicknesses has been studied by X-ray photoelectron spectroscopy and contact potential difference measurements. It has been established that the maximum number of O_2 molecules that can be adsorbed on the films increases with the film thickness. Such behavior is observed at thicknesses less than 10 monolayers. This size effect is ultimately due to the fact that an indispensable condition for the adsorption process at high doses of oxygen is the electron transfer from the film to molecules, and that the maximum number of electrons that can participate in this process depends on the nanolayer thickness. Localization of a negative charge on O_2 molecules occurring in at high doses of adsorbate, causes a weakening of the bonding of $1s$-electrons in these molecules. In addition, it should lead to a weakening of the bond between oxygen atoms in O_2 molecules.

Keywords: oxygen, ytterbium, adsorbed molecules, nanofilms, X-ray photoelectron spectroscopy, work function.

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1. Introduction

One of relevant problems of modern nanoelectronics is creation of materials with predetermined properties [1–5]. In particular, adsorption of foreign particles on the surface of nanoobjects carried out under controlled conditions (ultrahigh vacuum, optimal adsorbate dose and sample temperature, etc.) can be used to solve this problem. For example, it was shown that formation of an adsorbed layer of carbon monoxide molecules (carbon monoxide, CO) and oxygen (O_2) on nanofilms of rare-earth metal ytterbium (Yb) is accompanied by significant changes in its properties [6]. Ytterbium in adsorption of molecules of the above gases passes from divalent to trivalent state, and transition of metal–semiconductor [7] happens therein. It is essential that gas molecules do not dissociate into atoms when adsorbed on ytterbium nanofilms, but remain on the surface in molecular form. These ytterbium transformations propagate into a film to an abnormally large depth of at least 16 monolayers (~ 6.1 nm) [8]. From the above, it is clear that to understand the mechanisms of adsorbed particle effects on the properties of nanoobjects, it is necessary to have detailed information on the complex mechanism of adsorption of molecules and their properties in the adsorbed state. Based on the above, the objective of this paper was to study the adsorption of oxygen molecules on ytterbium nanofilms of different thickness.

2. Experimental procedure

Two experimental methods were mainly used in the study. One of them — was the method of X-ray photoelectron spectroscopy (XPS). The second — is the contact potential difference method (CPD), which is known to give an opportunity to measure changes in the work function of the surface under study [9].

X-ray photoelectron spectra were recorded in 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 specific resistance of $\sim 5\,\Omega \cdot$ 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. 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 monolayer (ML) per minute. Sample temperature was at the same time maintained at 300 K. A value of $7.84 \cdot 10^{14}\,\text{cm}^{-2}$, 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, $1\,\text{L} = 10^{-6}\,\text{Torr} \cdot \text{s}$). According to the results obtained earlier [11], at such a dose, a saturated layer of adsorbed oxygen molecules is formed 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). A magnesium anode with energy of quanta equal to 1253.6 eV was used to excite photoelectrons from the studied samples. 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. Electron bonding energies were counted relative to the Fermi level.

The CPD method was implemented on another facility assembled on the basis of ultrahigh-vacuum chamber USU-4 with a base pressure of $4 \cdot 10^{-11}$ Torr, equipped with an electron gun, an electron Auger spectrometer, and a diffractometer for slow electrons. Changes in work function were recorded by shear in electron gun's volt-ampere characteristics. The measurement error was ± 0.03 eV.

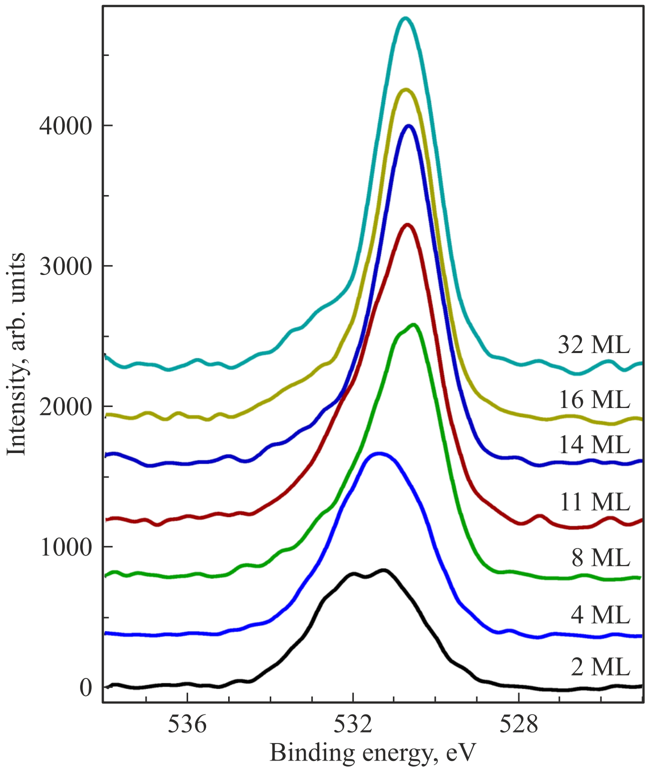

Figure 1. X-ray photoelectron spectra of $1s$-oxygen level for $O_2$$-Yb-$Si(111) structures at different thicknesses of ytterbium nanofilms expressed in ML. The dose of oxygen molecules is 100 L.

3. Results and discussion

Fig. 1 shows photoelectron spectra of oxygen molecules adsorbed on ytterbium nanofilms of various thicknesses. These spectra are due to photoionization of $1s$-oxygen level [12]. For all film thicknesses, dose of gas injected was the same, equal to 100 L. As noted above, this dose is sufficient to form saturated layers of adsorbed molecules [11] on the surface of the nanofilms.

Spectra shown in Fig. 1 exhibit a number of characteristic features. First, for all thicknesses of d films, except for $d = 2$ ML, spectra have a simple form of single maxima. Second, magnitude of these maxima at the same oxygen dose increases with increasing nanofilm thickness. Finally, thirdly, spectra shift toward lower bonding energies as thickness of the films increases.

A quantitative analysis of the results shown in Fig. 1 was carried out. Thus, Fig. 2 shows dependence of the area under the spectra of Fig. 1, which is a characteristic of the number of oxygen molecules adsorbed on the film surface, on the thickness of nanolayers. It can be seen that the number of adsorbed molecules increases with the film thickness (dimensional effect). This growth ends at about $d = 11$ ML. This suggests that when thicknesses of ytterbium films exceed 11 ML, a filled layer of oxygen molecules is formed on their surface, i.e., the degree of surface coverage $\theta = 1$. Within this suggestion, dependence of θ value on thickness of the films will have the form shown in Fig. 2, where the ordinate axis of θ is on the right.

Fig. 3 shows dependence of spectral maxima position (Fig. 1) on the number of oxygen molecules on the surface, the measure of which is either the intensity of these peaks (the area under them, plotted on the lower horizontal axis) or the θ value (plotted on the upper horizontal axis). It can be seen that decrease of the $1s$-oxygen level bonding energy occurs in the interval of $0.52 \leq \theta \leq 0.84$ oxygen layer coatings on ytterbium surface. This decrease is equal to 0.95 eV.

To understand the physical nature of the results shown in Figs. 1$-$3, it is necessary to take into account the fact that according to the previously obtained results, oxygen molecules do not dissociate into atoms when adsorbed on ytterbium films at room temperature, but remain on the surface in the molecular form [8]. In addition, in order to interpret the results obtained, more information is needed on the electronic transitions accompanying the adsorption process of oxygen molecules. Such information can be obtained by recording the dependences of the work function of ytterbium films on the oxygen dose. These dependences for three film thicknesses are shown in Fig. 4. It can be seen that all dependences are similar in shape. In addition, they have minima, the position of which on the dose scale depends on the film thickness. But, as evaluations have shown, at all thicknesses of ytterbium nanofilms, oxygen molecules occupy no more than 50% of the spaces available for adsorption in the minima of the work function. When the dose exceeds 40 L, the yield work for all film thicknesses is practically independent of

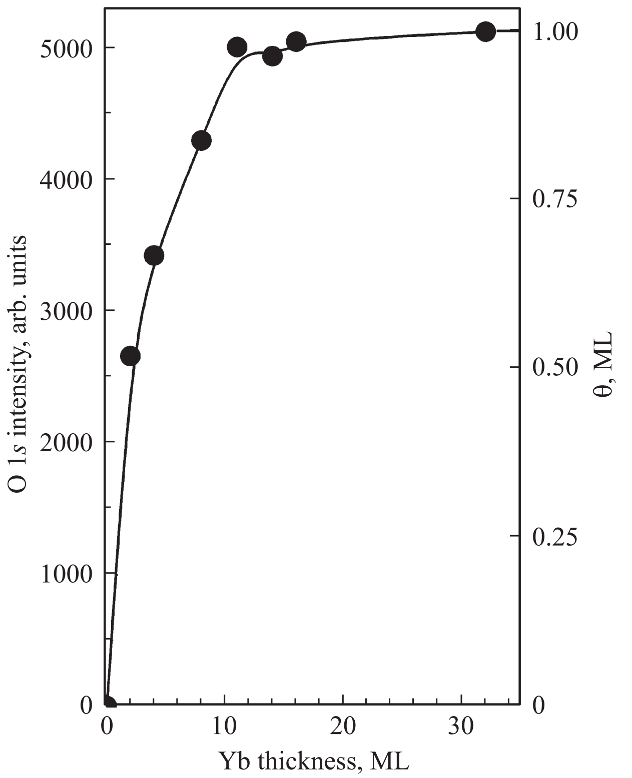

Figure 2. Dependence of *O*1*s* peak intensity (area under spectrum) on ytterbium nanofilm thickness. The oxygen dose is equal to 100 L. The value of filling degree for the adsorbed layer of oxygen molecules on film surface is plotted on the vertical axis to the right.

the dose. The results obtained are easy to understand when one considers that O_2 molecules, as well as CO molecules having a similar electronic structure, form a donor-acceptor bond [6] with ytterbium films when adsorbed on them. It is formed by two electrons that do not participate in the bond formation in the molecules, i.e. their transition from the molecules to the ytterbium surface. This transition is accompanied by a decrease in the work function. The electrons that form a bond between the molecules and the surface interact with ytterbium conduction electrons by electrostatic forces. Therefore, when the number of adsorbed molecules increases, this electrostatic interaction will begin to displace the electrons from the film into the molecules. This process will be accompanied by an increase in the work function. It follows that at high doses of oxygen, a negative charge is localized on the adsorbed O_2 molecules. As a consequence, there will be an electrostatic (Coulomb) repulsive interaction between these molecules, which will lead to a decrease in the bonding energy of the electrons in the molecules. Obviously, this interaction will depend on the population of the adsorbed layer. As the population increases, it will increase. And since, according to Fig. 2, the number of O_2 molecules on the surface at the same dose increases with nanofilm thickness, bonding energy of the electrons populating the 1*s*-oxygen level will also decrease with the transition from thin films to thicker ones. This qualitative conclusion is in complete agreement with the results shown in Fig. 3.

Another consequence of the localization of the uncompensated negative charge on the molecules should be a weakening of the bond between the oxygen atoms in the O_2 molecules. And the bond will weaken as the number of molecules on the surface increases. The latter follows from the fact that as the population of the adsorbed layer increases, and thus the average distance between the O_2 molecules decreases, Coulomb interaction between them will increase on the surface.

The experimental results obtained in this paper and their analysis make it possible to at least qualitatively explain the above dimensional effect, i.e., the dependence of the number of adsorbed oxygen molecules on film thickness. Indeed, for metallic ytterbium nanofilms, the number of atoms in a single monolayer does not exceed the value $8 \cdot 10^{14}\,\mathrm{cm}^{-2}$. In this case, each atom has two valence electrons. Then in a film 10 ML thick, there will be $1.6 \cdot 10^{16}$ of valence electrons per unit surface area. The maximum number of O_2 molecules in the adsorbed layer is $1 \cdot 10^{15}\,\mathrm{cm}^{-2}$. This analysis shows that the number of valence electrons in the films and the number of adsorbed molecules are comparable quantities. And if the essential condition for the adsorption of molecules is electron flow from the volume of the films

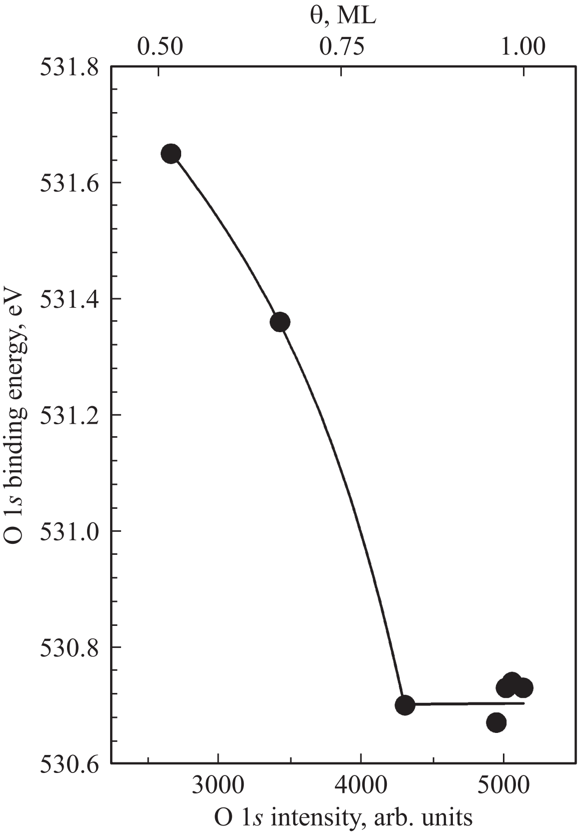

Figure 3. Dependence of bonding energy 1*s*-oxygen level on signal intensity (area under the spectrum). The filling degree of the adsorbed layer of oxygen molecules is plotted on top.

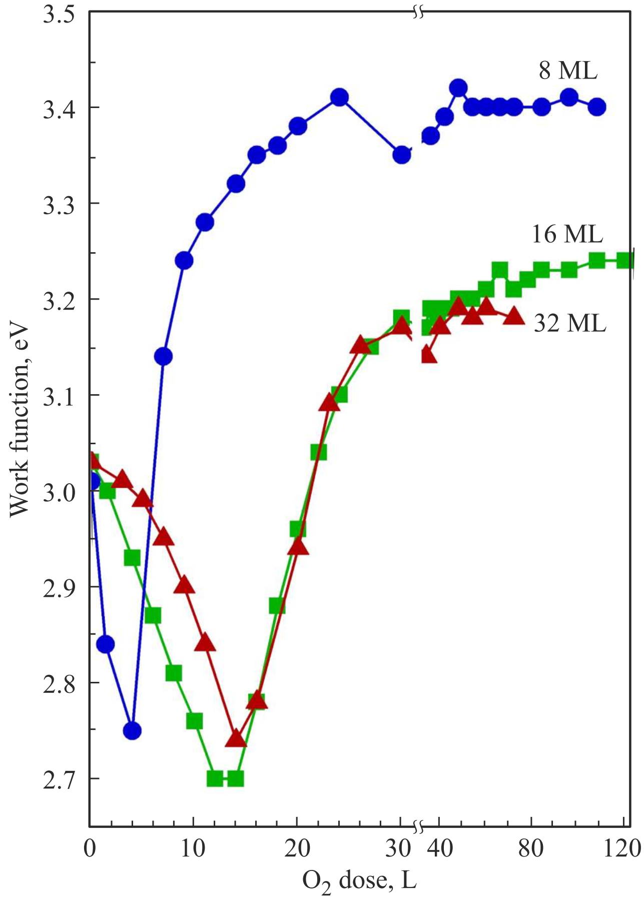

Figure 4. Dependences of surface work function on oxygen dose for O_2–Yb–Si(111) structures at different thicknesses of ytterbium nanofilms.

to the surface, then the above process will be determined not by the number of centers available for it, but by the number of carriers that can make the transition. Obviously, the specified number is limited by the disturbance of charge equilibrium in the volume of the films, which will be created by the departure of some of the electrons. And the thinner the films, the smaller this amount will be.

Thus, the results obtained in this paper make it possible to draw a number of conclusions concerning the nature of adsorbed molecules interaction with the surface of ytterbium nanofilms and among themselves.

1. Adsorption of O_2 molecules on the surface of ytterbium films at high oxygen doses is accompanied by electron transfer from the nanolayers to the molecules.

2. The number of electrons transferring from films to molecules is limited. It increases as the thickness of the films increases. This dependence on thickness causes a dimensional effect: the maximum number of molecules that can be adsorbed on the surface increases with increasing film thickness.

3. Electrostatic repulsive interaction between adsorbed oxygen molecules leads to a modification of their electronic structure, in particular, a weakening of the 1s-electron bond.

4. Negative charges localized on the adsorbed O_2 molecules should weaken the bond between the atoms in those molecules.

4. Conclusion

Adsorption of oxygen molecules on ytterbium nanofilms of various thicknesses has been studied by X-ray photoelectron spectroscopy and contact potential difference measurements. It was found that the maximum number of O_2 molecules which can be adsorbed on the films increases as their thickness increases. This increase is observed at thicknesses less than eleven monolayers. The above dimensional effect is ultimately due to the fact that the essential condition for the adsorption process is the transfer of electrons from films to molecules and that the maximum number of electrons that can participate in the above process depends on the thickness of the nanolayers.

Localization of the negative charge on the adsorbed molecules causes weakening of the 1s-electron bond. It should also lead to a weakening of the bond between the oxygen atoms in the adsorbed molecules.

Conflict of interest

The authors declare that they have no conflict of interest.

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