

Effect of an electric double layer on the adsorption and catalytic properties of the ytterbium nanofilm surface

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The influence of an electric double layer on the surface of nanometer-thick ytterbium films grown on a Si(111) substrate on their adsorption and catalytic properties has been studied. It is shown that charge density waves (Friedel oscillations) generated in such nanofilms by the Si interface cause nonmonotonic changes of the distance in the double layer with increasing thickness. In turn, compression and expansion of the double layer lead to size dependences of the adsorption-catalytic properties of the film surface. In particular, as the film thickness increases, the adsorption character and decomposition rate of ammonia molecules on the ytterbium surface change.

Keywords: surface, nanofilms, ytterbium, electric double layer, adsorption, ammonia, catalytic properties, work function.

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Introduction

As it is known, a large amount of studies was devoted to the study the adsorption and catalytic properties of the surface of metals. These studies are still ongoing, this is currently confirmed by two recent publications [1,2] taken as an example. However, until now information about the role of the electric double layer on the surface of metals in the processes of adsorption and catalysis is completely absent in the literature. As shown in Fig. 1, it is formed by the upper positively charged ionic cores of the metal (positively charged „plate“) and a layer of electrons shifted relative to the cores towards vacuum (negatively charged „plate“) [3 ,4]. It can be assumed that this double layer and, in particular, the distance L in it have a significant effect on many properties of the metal surface. The purpose of this paper was to fill, at least partially, the existing gap.

To solve this problem, films of the rare-earth metal ytterbium of nanometer thickness were studied. This choice was due to the fact that charge density waves [5] are formed in these films grown on silicon substrates. Therefore, it was assumed that increase in the thickness d of the films would be accompanied by nonmonotonic changes in the properties of the electric double layer on the surface, including the distance between its „plates“. So, changing the parameter d during experiment for ytterbium films one can obtain information about the double layer effect on the adsorption and catalytic processes on their surface. To test this hypothesis, in the present paper, for ytterbium films, we studied: a) work function vs. their thickness; b) the effect of adsorbed Si atoms on the work function of the surface; c) the effect of the thickness of nanofilms on the ammonia molecules decomposition on their surface. It was assumed

that all of these characteristics shall reveal the effect of the double layer on the films surface on their properties.

1. Experiment procedure

The studies were carried out on ytterbium nanofilms of various thicknesses grown at room temperature on n -type silicon substrates (resistivity $7.5 \Omega \cdot \text{cm}$) with surface orientation (111). The choice of substrates was due to the fact that, as was already mentioned in the Introduction, charge-density waves are formed in ytterbium films grown on Si(111). Besides the ytterbium films formed on the specified substrates at room temperature have high thickness uniformity [6]. And finally, there is no chemical interaction between silicon and ytterbium at room temperature. These features made it possible to create chemically and geometrically sharp interfaces ytterbium–silicon. This is

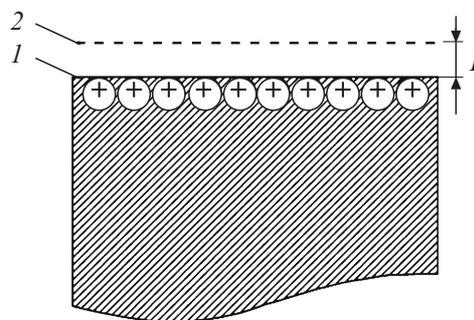


Figure 1. Schematic illustration of electric double layer on metal surface. In the simplest case, it is a flat capacitor. Numbers indicate: 1 — positively charged „plate“, 2 — negatively charged „plate“.

one of the indispensable conditions for the standing electron density waves appearance in nanofilms. Substrate surfaces were cleaned by short-term heating of silicon samples at temperatures 1530–1550 K. The purity and structural perfection of the surface were monitored using Auger electron spectroscopy and low-energy electron diffraction. Ytterbium was deposited onto substrates by evaporation from tantalum ampoules. Also in the paper the deposition of Si atoms on the surface of ytterbium nanofilms was additionally used. It was carried out at room temperature by evaporation from the surface of a heated silicon rod. The pressure in the vacuum chamber during the film structures formation did not exceed $3 \cdot 10^{-9}$ Torr. Sputtering rate was generally ~ 1 monolayer (ML) per minute.

NH_3 molecules were adsorbed onto the surface of ytterbium films at a given constant ammonia pressure in the vacuum chamber. The pressure was chosen in the range from $2 \cdot 10^{-7}$ to $2 \cdot 10^{-6}$ Torr. Gas was supplied to the vacuum chamber using a admission system with differential pumping. Gas purity was monitored by a mass spectrometer placed in the immediate vicinity of the test samples. The dose was determined in Langmuirs ($1 \text{ L} = 10^{-6} \text{ Torr}\cdot\text{s}$).

Work function φ was measured by the method of contact potential difference that, as known [7], allows to find the work function difference $\Delta\varphi$ of the clean surface and the same surface after the adsorbed layer application. $\varphi_0 = 4.63 \text{ eV}$ [8] was used as the work function of the clean surface $\text{Si}(111)(7 \times 7)$. Measurement accuracy $\Delta\varphi$ was $\pm 0.03 \text{ eV}$.

2. Results of the measurements and their discussion

Within the framework of the program outlined briefly in the Introduction, we studied the work function of ytterbium nanofilms vs. their thickness (Fig. 2). In all experiments performed, these dependences had the same oscillating character over a wide range of film thicknesses. Thus, the dependence shown in Fig. 2 exhibits a number of features (marked by arrows): minima at $d \approx 0.6, 2.5,$ and 7.8 ML and maxima at $d \approx 1.1$ and 5.0 ML . At the specified minima and maxima the work function φ according to the order of film thickness increasing is 3.20, 3.32, 2.99, 3.13, and 3.01 eV. Finally, in the range $d \approx 16 \text{ ML}$, the dependence reaches a plateau, where the work function is 3.04 eV. As already mentioned, the nonmonotonic nature of the dependences similar to the curve in Fig. 2 is due to Friedel oscillations (standing waves of electron density) generated by the Yb-Si interface [5]. As the film thickness increases, the phase of the electron density wave changes in the region of its surface. This, in turn, leads to a nonmonotonic change in the distance L in the double layer on the metal surface and, ultimately, is accompanied by oscillations of the work function. Therefore, it is natural to expect that some other physicochemical properties of the surface of such films will change nonmonotonically with increase in the parameter d .

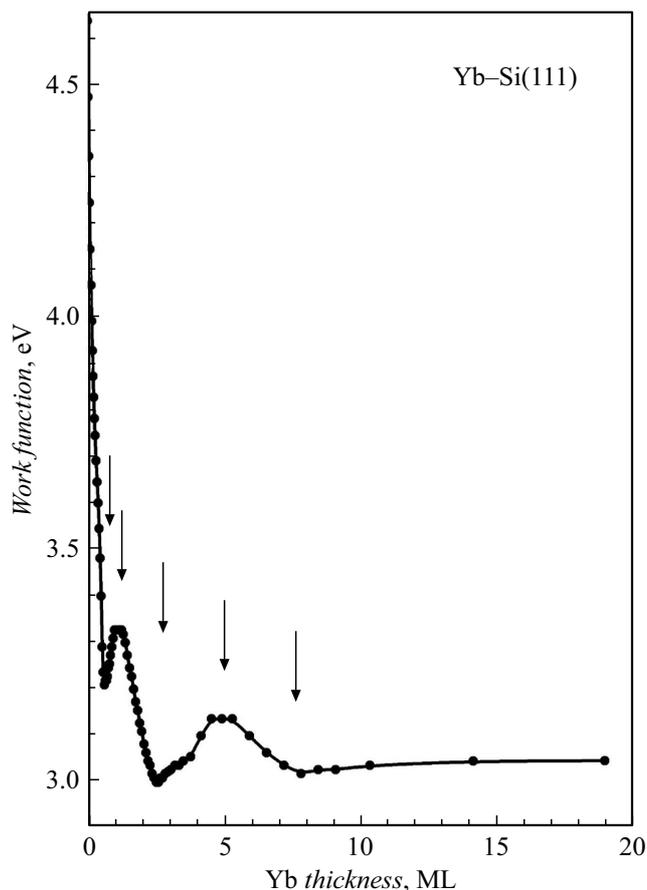


Figure 2. Work function of ytterbium nanofilm deposited on the Si(111) surface vs. thickness. The arrows mark the minima and maxima on the dependence.

To study the characteristics of the double layer and their dependence on the thickness of the ytterbium nanofilms, we used the adsorption phenomenon in this paper. This approach is based on the fact that adsorbed atoms or molecules shall affect the state of the electric double layer and, consequently, the properties of the metal surface, and, in particular, the work function. To implement this approach, we used the adsorption of silicon atoms on the surface of ytterbium films at their different thicknesses $d(\text{Yb})$. In the course of adsorption of these thicknesses the dependences of the work function on the number of silicon atoms on the surface were recorded. Fig. 3 shows such dependences obtained at $d(\text{Yb}) = 2.5 \text{ ML}$ (corresponds to a deep minimum in Fig. 2), 5 ML (maximum), 7.8 ML (less deep minimum) and 16 ML (plateau). At first sight, these results look very unusual. Indeed, at $d(\text{Yb}) = 2.5 \text{ ML}$ the work function noticeably increases with increase in the degree of coverage of the ytterbium surface by Si atoms. At the ytterbium film thickness of 7.8 ML , this growth significantly decelerates, while at 16 ML it is practically absent. Finally, for $d(\text{Yb}) = 5 \text{ ML}$, the change in the work function changes sign to the opposite: the value φ noticeably decreases with increase in the number of Si atoms on the surface.

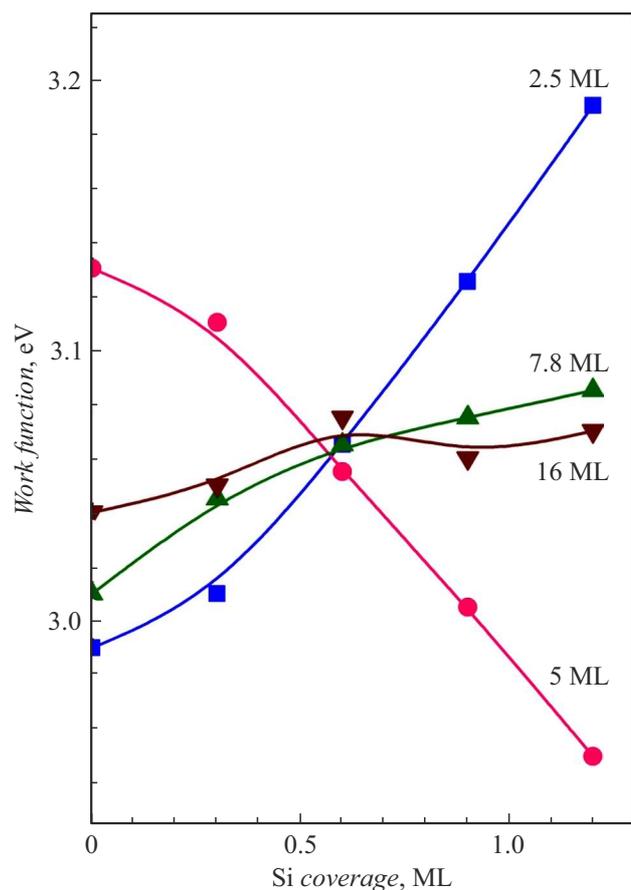


Figure 3. Work function of ytterbium nanofilms of different thickness vs. number of silicon atoms applied to their surface. Thicknesses of nanofilms are given in monolayers (ML).

When explaining the results just considered in Fig. 3, we must take into account that the work function of the metal is determined by the position of the Fermi level in the bulk and by the electric double layer on the surface. To move the electron from metal into vacuum through the electric double layer, it is necessary to do some work. It is component of the value ϕ . The results shown in Fig. 3 can be logically explained if we assume that the adsorbed atoms affect the state of the double layer differently. In some cases, they shift its negatively charged (external) „plate“ towards the crystal lattice, and in other cases — towards vacuum. At other things being equal, in the case of the double layer compression the work function will decrease, and in the case of its expansion it will increase.

Obviously, the sign and magnitude of changes in the work function caused by adsorbed atoms depend on the sign and value of charge localized on these atoms and their size. Indeed, if atoms during adsorption acquire a negative charge then this will occur due to the negatively charged „plate“ of double layer. In this case, the effect of adsorbed atoms on the distance between „plates“ of the double layer, and hence on the work function, can be double. Thus, if the radius r of the adsorbed atoms is

smaller than the distance L in the double layer (Fig. 4, *a*), then the transfer of electrons from it on adsorbed particles will be accompanied by a shift of electrons involved in the double layer formation towards the crystal lattice, and, as a consequence, decrease in the work function ($\Delta\phi < 0$). In the opposite case, when $r > L$ (Fig. 4, *b*), the effect will be reversed ($\Delta\phi > 0$). Finally, at $r = L$ (Fig. 4, *c*) the work function will not change ($\Delta\phi = 0$). From above said an important, was not previously made by anyone conclusion follows that electronegative atoms not only increase the work function, but also decrease it.

The brief analysis just carried out makes it possible to explain the results obtained in this paper in studying the effect of electronegative Si atoms on the work function of ytterbium films of various thicknesses. Indeed, as already noted, the maxima in the size dependences of the work function of these films are due to the fact that the electron cloud of the surface double layer is shifted towards vacuum due to Friedel oscillations. This shift can be so significant that the sizes of adsorbed atoms become smaller than the distance in the double layer (Fig. 4, *a*). In this case, the deposition of silicon atoms on the surface of ytterbium nanofilms shall be accompanied by decrease in the work function. This decrease is due to the fact that the electrons from the negatively charged „plate“ of double layer pass to the electronegative Si atoms. As already noted, this will be accompanied by decrease in the distance between the „plates“ of the double layer, and, consequently, by corresponding decrease in the work function. Such decrease occurs in the system studied in this paper at $d(\text{Yb}) = 5 \text{ ML}$ (Fig. 3).

At the minima of the dimensional dependences of the work function at $d(\text{Yb}) = 2.5$ and 7.8 ML the picture is different. At the indicated thicknesses the negatively charged „plate“ of the double layer is shifted by Friedel oscillations towards the crystal lattice such that the distance in it becomes less than the radius of Si atoms (Fig. 4, *b*), and $L(2.5 \text{ ML}) < L(7.8 \text{ ML}) < r$. It is clear that in this case the transfer of electrons to Si atoms will be accompanied by increase in the work function during the these atoms sputtering on nanofilms, and this increase will be more significant at $d(\text{Yb}) = 2.5 \text{ ML}$ than at $d(\text{Yb}) = 7.8 \text{ ML}$, as it actually happens.

Finally, at $d(\text{Yb}) = 16 \text{ ML}$, the distance L , at which the negatively charged „plate“ of the double layer situated from crystal lattice, is very close to the radius of Si atoms (Fig. 4, *c*). In this case, the transfer of electrons on adsorbate atoms does not lead to either compression or tension of the double layer and, thus, practically does not affect the work function, i.e., $\Delta\phi \cong 0$. And this conclusion is also in full agreement with the obtained data.

The considered results on the adsorption of silicon atoms make it possible to quantify the value L for the electric double layer on the surface of ytterbium nanofilms, and also to trace the dependence of this parameter on the thickness $d(\text{Yb})$. The covalent radius of silicon atoms r is 1.17 \AA [9]. As noted above, the distance in the double layer approximately corresponds to this value at $d(\text{Yb}) = 16 \text{ ML}$, i.e.

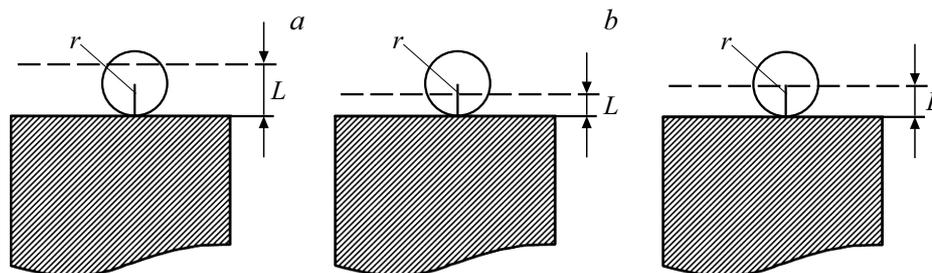


Figure 4. Model of adsorption of electronegative atoms on the metal surface at different ratios r and L : $a-r < L$, $b-r > L$, $c-r = L$. Explanation in the text.

$L(16 \text{ ML}) \cong 1.17$. As follows from Fig. 2, the work function for the given film thickness is 3.04 eV. The question arises: what contribution to this value does the double electric layer make? In papers [10,11] the data of calculations of the work function and parameters of the surface potential of metals based on the self-consistent many-electron theory are published. According to these data, the value $\sim 20\text{--}25\%$ can be taken as an estimate of the double layer contribution to the value of the work function of metals. This means that for ytterbium films 16 ML thick the work function fraction due to the double layer is $\sim 0.61\text{--}0.76$ eV. Based on these estimates, as well as the results presented in Fig. 2, one can easily obtain the dependence of the distance in the double layer on the surface of ytterbium nanofilms on their thickness. Fig. 5 shows two such dependences obtained for the cases when the double layer contribution to the work function is 20 and 25% [10,11]. As can be seen from the analysis of their shape, the smallest distance

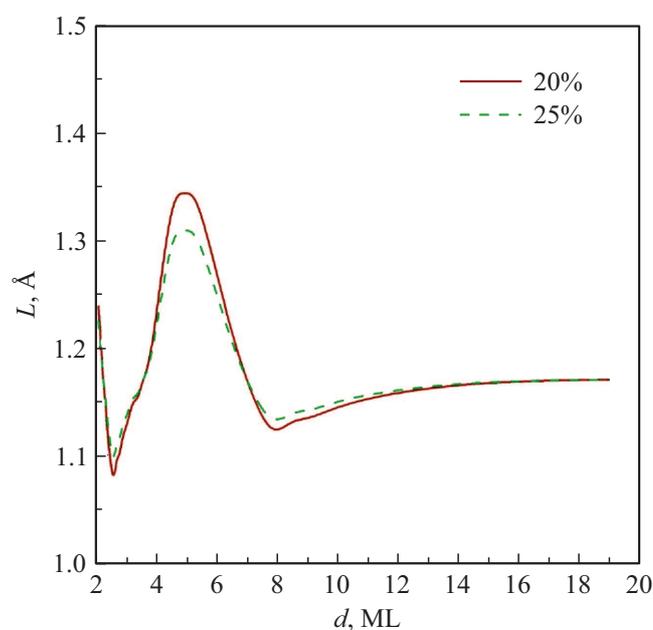


Figure 5. Distance in double layer on surface of ytterbium films vs. their thickness. Obtained for two cases: the double layer contribution to the work function is 20% (solid line) and 25% (dashed line).

in the double layer for ytterbium nanofilms is observed at 2.5 ML, and the largest at 5 ML. These values are 1.08–1.10 and 1.31–1.34 Å respectively. Thus, the position of the negatively charged „plate“ of double electric layer on the surface of ytterbium varies rather strongly with the film thickness increasing. The limits ΔL of these changes are 0.23–0.24 Å, which is $\sim 20\%$ of the total distance between two „plates“ of double layer. It is clear that such noticeable changes in the state (i.e., very strong compression and expansion) of the double layer will most likely affect the catalytic properties of the metal surface.

On the basis of the results presented above, in the present paper we studied the influence of the thickness of ytterbium films on the nature of the adsorption of ammonia molecules on their surface. The choice of this adsorbate is determined by the structural features of molecules NH_3 and their orientation in the adsorbed state. These molecules look like trigonal pyramids with nitrogen atoms at their tops and three hydrogen atoms at their bases. Two unshared electrons are localized at the nitrogen end of the molecules. Therefore, the molecules have a dipole moment equal to 1.47 Debye [12]. The positive end of the dipoles is located on the hydrogen atoms. Based on the foregoing, it is natural to assume that during adsorption the molecules are oriented with their nitrogen end to the surface, forming a donor-acceptor bond with it using unshared electrons, and that the axis of these molecules, which passes through the nitrogen atom and the center of the triangle formed by three hydrogen atoms, is perpendicular to the surface. The height h of the pyramid, taking into account the covalent radii of nitrogen (0.70 Å) and hydrogen (0.28 Å) atoms, is 1.49 Å [12]. If the distance in the double layer L is equal to or close to this value, then the positively charged hydrogen atoms should interact with the electron layer of the double layer, and the negatively charged nitrogen atoms — with the positively charged layer of ionic cores. In other words, if the condition $L \approx h$ is fulfilled, a stable adsorption complex „molecule NH_3 — nanofilm surface“ shall form on the ytterbium surface. The molecule stabilization in such an adsorption configuration shall lead to a significant decrease in the system energy, which, in turn, makes the dissociation of the molecule energetically unfavorable. When the condition $L \approx h$ is not met, the formation of such a stable adsorption complex is impossible, and therefore the

dissociation of ammonia molecules on the surface becomes much more likely.

When molecules NH_3 are adsorbed on ytterbium films, the thickness most suitable for fulfilling the condition $L \approx h$ is $d = 5.0 \text{ ML}$. For a given thickness the distance in the double layer is $L = 1.34 \text{ \AA}$, which is only by 0.15 \AA less than the height of the ammonia molecule. For other nanofilm thicknesses this difference increases. For example, at $d = 16 \text{ ML}$ it is 0.32 \AA . On the basis of the above, it is easy to formulate the purpose of the experiment — to compare the properties of adsorption structures $\text{NH}_3\text{-Yb}$ at $d = 5 \text{ ML}$, on the one hand, and other thicknesses, on the other one. To determine the nature of molecules adsorption (dissociative or non-dissociative), one can use the concepts presented in the paper [13]. According to these representations, the formation of the donor-acceptor bond between ammonia molecules and the ytterbium surface in nanofilms results in a valence transition $\text{Yb}^{2+} \rightarrow \text{Yb}^{3+}$, and its clear indicator is the shape of the Auger line for this metal. It is clear that if ammonia adsorption has a nondissociative nature, the formation of the layer of molecules NH_3 on the surface of ytterbium, which is necessary for the transition of the latter to the trivalent state, will be achieved at relatively low doses of ammonia. Conversely, in the case of dissociative adsorption, ytterbium will not transform into the trivalent state.

Fig. 6 shows Auger spectra of ytterbium nanofilms 5 ML thick during the adsorption of ammonia with increasing of their dose. The spectrum obtained before adsorption (lower curve) has a form typical for divalent ytterbium: it contains two characteristic features *A* and *B* [13]. As the dose of ammonia increases, these features gradually disappear, and new features appear instead of them *C* and *D*, which correspond to ytterbium with a valence of $3+$ [13]. This means that the valence transition $\text{Yb}^{2+} \rightarrow \text{Yb}^{3+}$ occurred in the nanofilm under the action of the adsorbed layer of molecules, and that its full completion occurs in the range of ammonia doses from 6 to 12 L.

A completely different picture is observed for other thicknesses of ytterbium films. Fig. 7 shows the spectra obtained at $d = 10 \text{ ML}$ (*a*) and 16 ML (*b*). As can be seen from this Figure, in both cases the rearrangement of the electronic state of ytterbium does not occur even at the ammonia dose of 40 L. As additional experiments showed such rearrangement requires doses equal to several hundred L. This means that at given thicknesses of ytterbium, the nondissociative adsorption of ammonia on its surface is energetically unfavorable. These results fully confirm the assumptions made earlier, according to which for the formation of the stable adsorption complex „ammonia molecule — ytterbium surface“, it is necessary to ensure the fulfillment of the condition $L \cong h$.

Finally, from the data obtained in this paper, one more question logically arises: whether desorption or dissociation of adsorbed molecules occur in structures $\text{NH}_3\text{-Yb}$ when the condition $L \cong h$ is not satisfied. Indeed, from the energy point of view, in this case, the adsorbed molecule

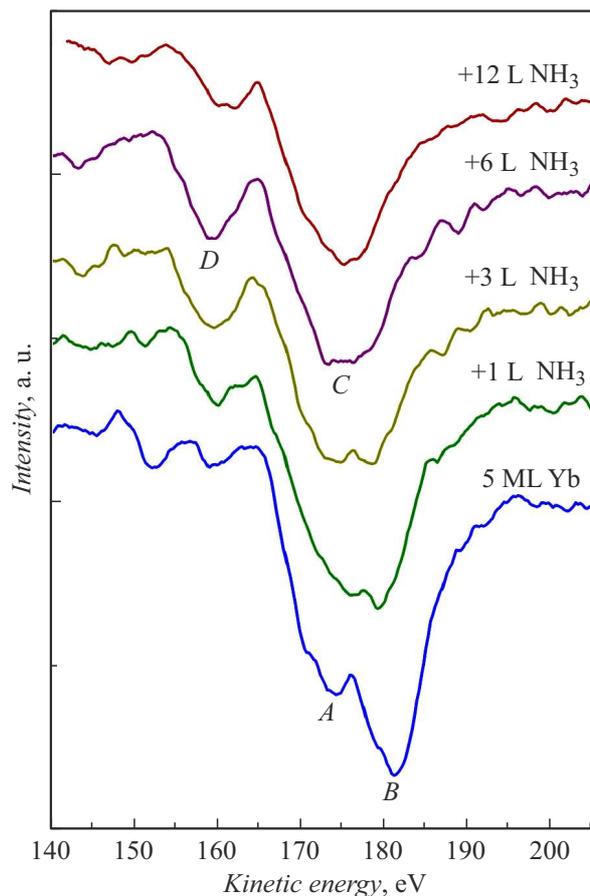


Figure 6. Auger spectra of ytterbium nanofilms 5 ML thick during the adsorption of ammonia molecules with increasing of their dose.

is in an unstable state, and therefore both processes can be energetically favorable. In the present paper the answer to this question was obtained with the help of mass spectrometric methods. Fig. 8 shows the thermal desorption spectra obtained for nanofilms with thickness of 5 ML (lower curve) and 16 ML (upper curve) after ammonia adsorption (in both cases, the dose was 40 L). The mass-spectrometer was set to the line with atomic mass $M=14$ (atomic nitrogen). As can be seen from the Figure, the desorption peak of nitrogen atoms is observed only for the case of ammonia adsorption on ytterbium films 16 ML thick (the maximum of this peak lies in the region $T = 1425 \text{ K}$). At the same time, when ammonia is adsorbed on films 5 ML thick, there is no mass spectrometric signal from nitrogen atoms. This means that in the case of $d = 16 \text{ ML}$, ammonia molecules decompose into nitrogen and hydrogen atoms. Nitrogen atoms diffuse deep into the film in the direction towards the interface with silicon. During sample heating the ytterbium film first evaporates at lower temperatures (it ends completely at $\sim 1300 \text{ K}$), and then at higher temperatures the nitrogen atoms are desorbed from surface of silicon crystal. The dissociative nature of ammonia adsorption at $d = 16 \text{ ML}$ is explained by

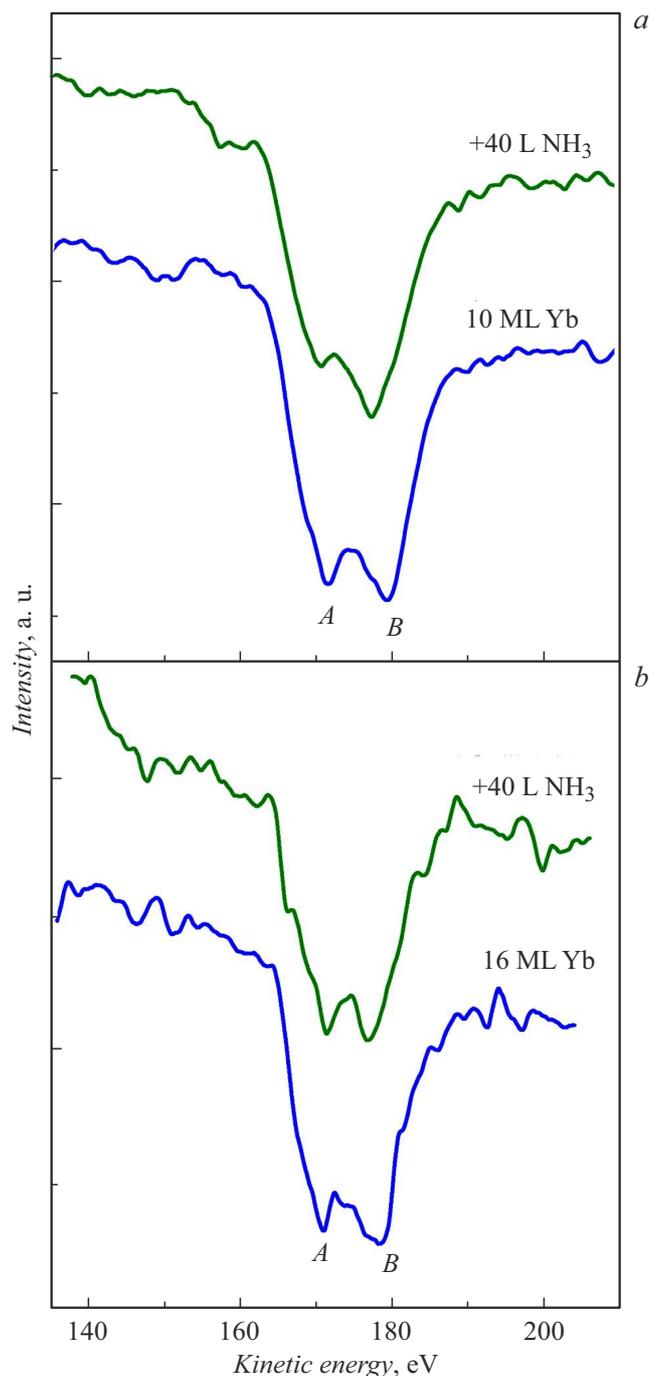


Figure 7. The same as in Fig. 6, but with ytterbium nanofilm thicknesses: *a*–10 and *b*–16 ML.

the instability of the adsorption complex „molecule NH_3 — ytterbium surface“, as discussed earlier.

In the case of films 5 ML thick the ammonia does not decompose into atoms, but, most likely, desorbs from the surface upon heating in the form of molecules. The non-dissociative nature of ammonia adsorption in this case is explained by the stability of the adsorption complex „molecule NH_3 — ytterbium surface“ due to the closeness of the parameters h and L .

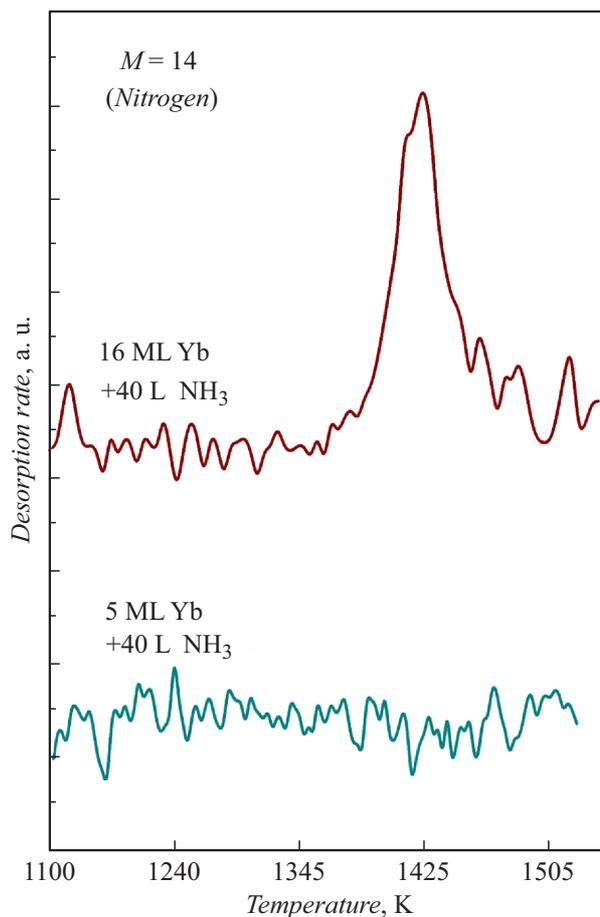


Figure 8. Thermal desorption spectra for structures NH_3 –Yb at nanofilm thicknesses of 5 ML (lower curve) and 16 ML (upper curve). The vertical axis shows the desorption rate of nitrogen atoms in arbitrary units (a.u.). Ammonia dose 40 L.

So, the experimental results obtained in this paper and their analysis show that the surface of ytterbium films with thickness of 10 and 16 ML (in a broader sense — films for which the relation $L < h$ is met), grown on a Si(111) substrate is a catalyst for the decomposition of ammonia molecules. At the same time, the surface of films 5 ML thick may be the catalyst for the these molecules synthesis. Such a strong qualitative dependence of the catalytic properties of ytterbium nanofilms on their thickness (size effect) is ultimately due to Friedel oscillations generated by the Yb–Si(111) interface. Moreover, this interface, through Friedel oscillations, also affects the electronic state of ytterbium films of nanometer thickness, in particular, the ytterbium valence, which, in turn, depends on the stability of molecules that form donor-acceptor type adsorption bonds with its surface.

Conclusion

The effect of electric double layer existing on the surface of metals on their adsorption and catalytic properties were

studied. The studies were carried out on nanometer-thick ytterbium films created on Si(111) substrates. Yb–Si(111) interface generates charge-density waves (Friedel oscillations) in such nanofilms. These waves cause nonmonotonic changes in the distance in the electric double layer on the surface of the films with their thickness increasing. In turn, compression and tension of the double layer lead to nonmonotonic changes in the adsorption and catalytic properties of the ytterbium surface. These changes manifest themselves in the form of nonmonotonic dependences of the work function of ytterbium films on their thickness and in the difference in the rate of decomposition of molecules NH_3 on the surface of films of 5 and 10–16 ML thick. The latter indicates the size dependence of the catalytic properties of ytterbium films.

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Conflict of interest

The authors declare that they have no conflict of interest.

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