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Effect of Friedel Oscillations on the Work Function of Ytterbium Nanofilms

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The effect of standing waves of charge density (Friedel oscillations) generated by an interface of the metallic ytterbium nanofilm single-crystal silicon substrate type on the work function of ytterbium nanolayers has been studied. It is shown that in the range of nanofilm thicknesses from 0 to 8 monatomic layers, the work function has an oscillating character. This feature of the dependence of the work function on the nanofilm thickness is a consequence of the fact that the standing waves change nonmonotonically the power (momentum) of the electric double layer, which exists on the metal surface and affects the work function of the metal. This ultimately determines the oscillating nature of the dependence of the work function on the thickness of the nanofilms.

Keywords: surface, nanofilm, work function, Friedel oscillations, electric double layer, ytterbium.

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1. Introduction

Much attention is currently focused on the study of nanoscale items [1–3]. But at the same time there is almost no literature data on their catalytic and, specifically, emission properties. Meanwhile, size dependences of these properties may contain the information both of fundamental and practical interest.

The objective of this study is to investigate emission properties of ytterbium nanofilms applied to Si(111) single-crystal surfaces. Selection of substrates was based on the fact that ytterbium films formed on the specified face at room temperature have high thickness uniformity [4]. In addition, there is no chemical interaction between silicon and ytterbium at room temperature. The listed features allow to achieve chemically and geometrically sharp ytterbium–silicon interfaces, which is one of the prerequisites for occurrence of standing electron-density waves (Friedel oscillations) in nanofilms [5–11]. This study was primarily intended to investigate the size dependence of the ytterbium film work function and then to identify the correlation between this parameter and adsorption properties of nanofilms.

2. Experiment procedure

The investigations were carried out *in situ* in an ultrahigh-vacuum system with base pressure lower than $1 \cdot 10^{-10}$ Torr. *n*-type (specific resistance $7.5\,\Omega \cdot \mathrm{cm}$) silicon samples were used as substrates for growing ytterbium films of various thickness. Substrate surfaces were cleaned by short-term heating at 1530–1550 K. Auger electron spectroscopy and low-energy electron diffraction were used to control purity and structural perfection of the surfaces. Ytterbium was applied to atomically clean $\mathrm{Si}(111)7 \times 7$ substrates by evaporation from tantalum vials. Some experiments used Si atom sputtering onto ytterbium nanofilms of various thicknesses. For these experiments, evaporation was carried out from the surface of a heated silicon rod. The substrate was kept at room temperature during formation of all film structures. Deposition chamber pressure was not higher than $3 \cdot 10^{-9}$ Torr. Sputtering rate was generally ~ 1 monolayer (ML) per minute.

CO molecules were adsorbed on the ytterbium film surfaces at a specified permanent pressure of CO in the deposition chamber equal to $2 \cdot 10^{-7}$ Torr, and room temperature. Gas was supplied to the deposition chamber using a gas feed system with differential pumping. Gas purity was monitored by a mass spectrometer placed in the immediate vicinity of the test specimens. Exposure was measured in langmuirs ($1\,\mathrm{L} = 10^{-6}\,\mathrm{Torr} \cdot \mathrm{s}$).

Work function φ was measured by the contact potential difference method that, as known [12], allows to find the work function difference $\Delta\varphi$ of the clean surface and the same surface after application of the adsorbed layer. $\varphi_0 = 4.63\,\mathrm{eV}$ [13] was used as work function of $\mathrm{Si}(111)7 \times 7$ clean surface. Measurement accuracy $\Delta\varphi$ was $\pm 0.03\,\mathrm{eV}$.

3. Experimental findings and their analysis

Figure 1 shows the dependence of the work function (circles) of the ytterbium films applied to the silicon substrate on the film thickness expressed in ML. It can be seen that this dependence has some very typical features. First, and above all, this dependence in the range from 0 to 8 ML ytterbium is substantially non-monotonous (minima and maxima are shown by vertical arrows). Second, the

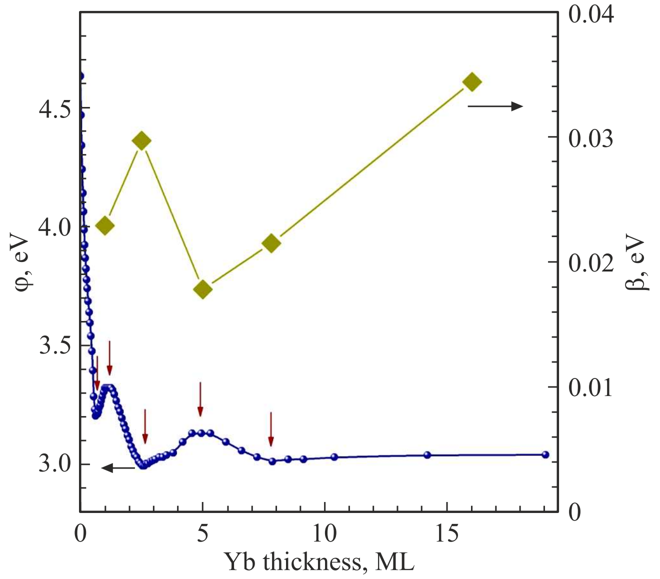

Figure 1. The lower part (circles): dependence of ytterbium nanofilm work function on the number of monoatomic layers (ML) contained in the films. Vertical arrows show typical features of the dependence. The upper part (rhombs): dependence of β on the ytterbium film thickness (for details, see the text below).

nonmonotonicity period increases with the number of film monolayers. Third, the amplitude of these features is reduced with growing ytterbium film thickness. And finally, when the film thickness is about 8 ML, these features disappear completely.

To prove that the obtained results are unbiased, rather than caused by any uncontrolled factors, adsorption of CO molecules on the ytterbium nanofilms of different thickness was studied. Figure 2 shows dependences of the work function for several thicknesses of such films on the number of adsorbed CO molecules. Auger signal of oxygen $KL_{2,3}L_{2,3}$ with the energy of 503 eV was used as a measure of the number of adsorbed molecules. Dependences shown in Fig. 2 exhibit a number of typical features. Originally, CO adsorption is followed by a slow decrease in the work function (except a case when the ytterbium film thickness has the lowest value from those shown in the figure — 1 ML). Then, when the minimum has been achieved, the work function starts growing quickly and almost linearly with the increase in the number of adsorbed molecules. Finally, after this the saturation stage is achieved. At this stage, the work function grows much more slowly with increasing number of adsorbed molecules than at the previous stage. An important feature of the dependences in Figure 2 is that they are shifted towards the larger number of adsorbed molecules with increasing nanofilm thickness (size effect).

Another feature of the results shown in Figure 2 is the non-monotonous dependence of the slope of the linear fast work function growth segments with growing nanofilm thickness. The view of this dependence (experimental data is designated with rhombs) is shown in the upper part og Figure 1. In this figure, the right-hand vertical axis shows $\beta = \partial\varphi/\partial I_{KLL}$ values (where I_{KLL} is Auger signal of oxygen $KL_{2,3}L_{2,3}$) obtained on the fast work function growth segments in Figure 2 for films of various thicknesses. Comparison of this dependence with the dependence of the work function of ytterbium films on their thickness (circles in Figure 1) shows clear correlation between them. This correlation proves obviously that the obtained results are unbiased. Thus, the dependence of the ytterbium film work function on thickness reflects the processes occurring at Yb–Si interface. At this interface, considerable charge flow towards Yb → Si occurs due to the great difference in the ytterbium work function ($\varphi = 2.6$ eV [14]) and silicon work function ($\varphi = 4.63$ eV [13]). As a result, high positive charge is located on the ytterbium and induces Friedel oscillations in the nanofilm that propagate from Yb–Si interface to the ytterbium–vacuum interface. At the metal–vacuum interface, as known [15,16], there is a double electric layer formed by the upper positively charged ion core layer and fast electrons shifted towards vacuum with respect to the cores. Friedel oscillations may change the double layer thickness and, in particular, shift the fast electron cloud above the surface towards the ion cores or, vice versa, towards vacuum depending on the relative positions of the Friedel wave maxima ans minima and the film–vacuum interface. If the oscillation wavelength and nanofilm lattice constant do not coincide, then, when the thickness of the latter changes, the relative positions of

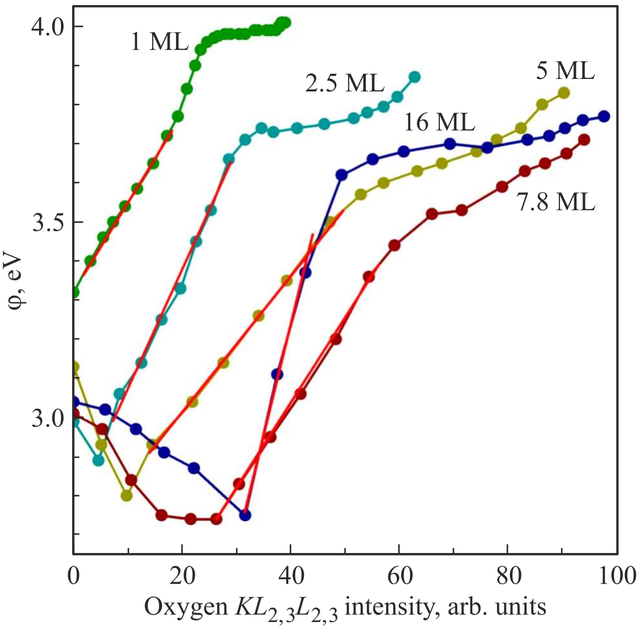

Figure 2. Dependences of the work function of ytterbium nanofilms of different thickness on the number of CO molecules applied to their surface. The horizontal axis shows Auger peak intensities of oxygen $KL_{2,3}L_{2,3}$ (503 eV) which are the measure of the number of molecules on the surface. Line segments show the sections of fast linear growth of the work function.

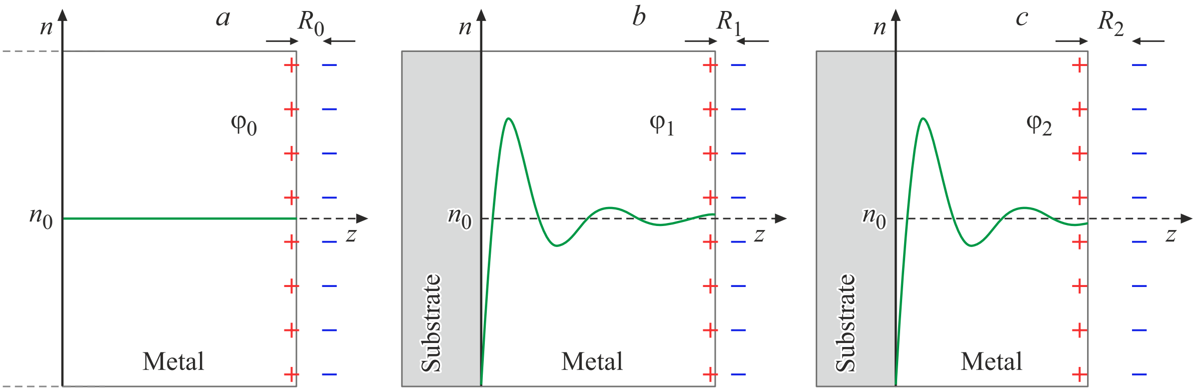

Figure 3. Schematic illustrations of the charge structure on the metal film surface for three cases: *a* — the film has no charge-density waves (Friedel oscillations), i. e. $n(z) = n_0$, *b* and *c* — charge-density waves $n(z)$ propagate from the substrate interface to the film surface with the oscillating dependence maximum and minimum emerging on the surface, respectively. Double layer on the surface is shown by „+“ and „–“. The distance within it is $R_1 < R_0 < R_2$. Work function $\varphi_1 < \varphi_0 < \varphi_2$.

the charge-density wave extremums and film surface will vary non-monotonously. This will result in non-monotonous changes in work function which will be superimposed on the possible size variations of the work function.

The surface double electric layer is reported [17] to contribute to a not quite large portion of the metal work function. Therefore, non-monotonous work function variations caused by the Friedel oscillations cannot have a large amplitude. This conclusion is completely supported by the results shown in Fig. 1.

Besides the non-monotonous dependence of the work function, the presence of electronic density waves are also responsible for the opposite-phase oscillating dependence of β (Figure 1). Such behavior is caused by the fact that electron transition from films into molecules increases with decreasing nanonfilm work function. Such relationship between the electron floe and nanofilm work function is the cause of the dependence of β on the film thickness.

The foregoing means that the addressed charge structure of the metal surface allows to explain non-monotonous work function variations of the ytterbium nanofilms with thickness variation, see Figure 1, as well as the above mentioned features of the dependences of the ytterbium nanofilm work function on the number of CO molecules adsorbed on their surfaces (Figure 2). Figure 3, *a* shows the surface of metal with work function φ_0 without charge-density waves. In this case, the negatively charged „plate“ of the double layer is at some equilibrium distance R_0 with respect to the ion cores. In case shown in Figure 3, *b*, the electronic density wave in the film modifies the electronic cloud state above the metal surface moving the negatively charged „plate“ of the double layer towards the ion cores. The distance in the double layer becomes equal to $R_1 < R_0$. This is accompanied by a decrease in work function $\varphi_1 < \varphi_0$. In the case shown in Figure 3, *c*, on the contrary, the standing electron-density wave increases the distance between the electron layer and ion cores ($R_2 > R_0$) resulting in the increasing work function, i. e. $\varphi_2 > \varphi_0$.

To confirm the foregoing concepts, the influence of the adsorbed silicon atoms on the work function of ytterbium nanofilms of various thicknesses was investigated. Si atoms were chosen on the assumption that their radius r is close to R_0. Three cases are possible. In the first of them, $r > R_0$. Then the work function will increase due to the electron flow from the negatively charged „plate“ of the double layer to the electrically negative Si atoms (Figure 4, *a*). In the second case, when $r < R_0$, the work function will decrease due to the same electron flow (Figure 4, *b*). Finally, in the third case, when $r = R_0$, the work function with Si atom adsorption will not vary.

The experiments have proved the assumptions. Some of the obtained results are shown in Figure 5. All them correspond to the typical points (maxima, minima

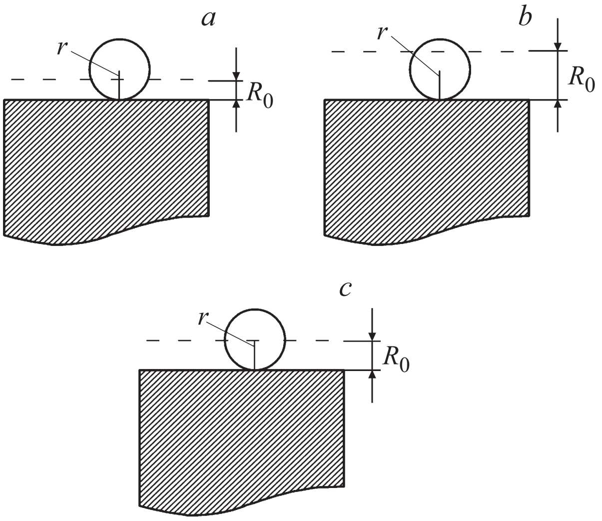

Figure 4. Model of Si atom adsorption on the ytterbium nanofilm surface with double electric layer. Three cases are addressed: *a*) atom radius r is higher that the distance in the double layer R_0, *b*) $r < R_0$, *c*) $r = R_0$.

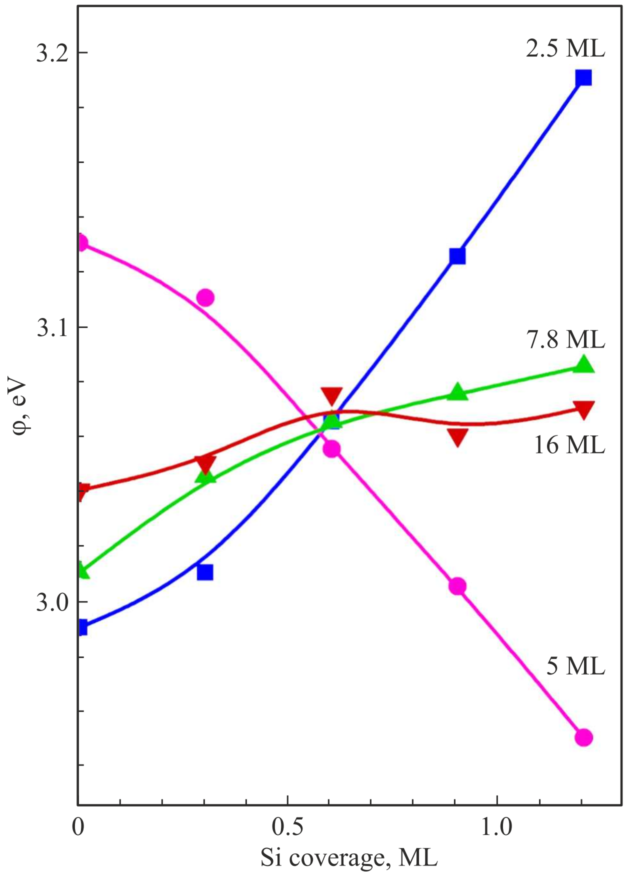

Figure 5. Dependences of the work function of ytterbium nanofilms of different thickness on the number of silicon atoms, expressed in ML, applied to their surface.

and plateau) on the work function dependence shown in Figure 1. It can be seen that, with Si atom adsorption on 2.5 and 7.8 ML ytterbium nanofilms corresponding to the work function minima shown in Figure 1, φ grows with increasing number of silicon atoms in the ytterbium surface. With Si atom adsorption on 5 ML nanofilms corresponding to the work function maximum shown in Figure 1, its thickness is reduced with increasing number of adsorbed particle. Finally, with the ytterbium film thickness equal to 16 ML, when their work function achieves the steady-state level (Figure 1), there almost no work function variations with silicon atom adsorption. Thus, according to the results shown in Figure 5, and the brief analysis provided above, the distance in the double layer of 2.5 and 7.8 ML films is lower than the covalent radius of Si atoms equal to 1.17 Å [18]. For 5 ML films, this distance in the double layer is higher than the silicon atom radius, i. e. exceeds 1.17 Å. And finally, for 16 ML ytterbium films, r and R_0 are approximately equal.

Therefore, the experimental investigations of the emission properties of nanometer-thick ytterbium films and analysis of findings have shown that the surface properties of the test metal depend considerably on the state of the double surface electrostatic layer. This layer is expected to have influence on catalytic and other properties of ytterbium, besides the emission properties.

4. Conclusion

Dependences of the work function of ytterbium nanofilms on their thickness have been investigated. The films were produced by ytterbium deposition on single crystal silicon substrates with surface orientation Si(111). It is shown that the dependences have a set of maxima and minima in the film thickness range from 0 to 8 monolayers. These features are induced by the Friedel oscillations generated by Yb−Si interface. These oscillations influence the double electric layer thickness on the metal surface and, in particular, change the distance between it negatively charged „plate“ and the layer of positively charged ion cores of the lattice. These changes cause the observed work function oscillations of the ytterbium nanofilms.

Conflict of interest

The authors declare that they have no conflict of interest.

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