Energy Characteristics of Metal Nanofilms in the Dielectric Environment

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The influence of a dielectric on the oscillations of the Fermi energy of nanometer metal films has been theoretically investigated. It has been shown within the model of rectangular finite-depth asymmetric potential well that the presence of a dielectric from one side of the film leads to the reduction of the maxima and displacement of the peaks on the left side of the size dependence of the Fermi energy, in contrast to the idealized case of a hypothetical film in vacuum. The calculations have been carried out for Au, Al and Cu films on SiO_2 and Al_2O_3.

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1. INTRODUCTION

Study of thin metal films deposited on substrates of different materials is of interest both from the fundamental point of view and from the point of view of their application in nanoelectronics devices [1-3]. As it turned out, in such systems macroscopic energy characteristics depend on the layer thickness and has an oscillating behavior. In most studies on the oscillation dependences of the characteristics of a metal film on its thickness, oscillations are associated with the size quantization effects [4-12]. However, calculations of the energy characteristics are usually performed for the case of hypothetical films which contact with vacuum on both sides of the surface, while the presence of a dielectric on one side of the film leads to "deformation" of the electronic spectrum [13].

The aim of the present work is to investigate the influence of a dielectric on the dimensional oscillations of the Fermi energy of ultrathin metal films in the model of an asymmetric rectangular potential well. Consideration of the peculiarities of dimensional behavior of the energy characteristics of the films in contact with dielectrics is important, in particular, in the study of their optical characteristics [14, 15].

2. STATEMENT OF THE PROBLEM

Let us consider a thin metal film of thickness L (of the order of the electron Fermi wavelength λ_F^0) and direct the x-axis perpendicular to the film surface.

Profile of the potential energy of electrons of such a system can be simplistically represented in the form of an asymmetric potential box of depth $-U_0$ relative to the vacuum level, $-U_d$ – dielectric-side and width L (see Fig. 1). Further, we will use the following designations: $\hbar^2 k_{01}^2 = 2m_e U_0$, $\hbar^2 k_{02}^2 = 2m_e U_d$, where m_e is the electron mass; $-\chi$ is the conduction band bottom depth of a dielectric with respect to the vacuum level (χ is the electron affinity) that takes into account the presence of a dielectric from one side of the film.

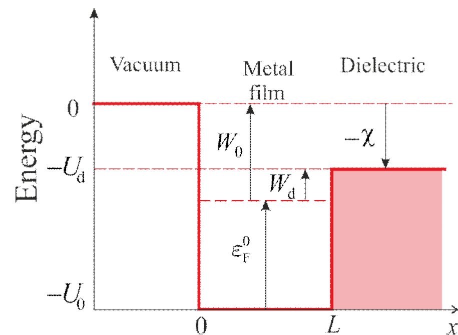

Fig. 1 – Energy diagram of a metal film in the model of an asymmetric potential well

Because of the fact that the longitudinal film sizes a, $b \gg L$, the spectrum can be written as

$$\varepsilon = \frac{\hbar^2}{2m_e}\left(k_{\parallel}^2 + k_{xm}^2\right),$$

where $k_{\parallel}$ is the electron wavenumber in the film plane. The value of the transverse component of momentum $\hbar k_{xm}$ ($m = 1, 2, 3, \ldots$) is determined by the boundary conditions for the electron wave function in this system and by the solution of the following equation:

$$k_{xm} L = \pi m - \arcsin\frac{k_{xm}}{k_{01}} - \arcsin\frac{k_{xm}}{k_{02}}. \qquad (1)$$

The electron state in the **k**-space is designated by the point with coordinates $\{k_x, k_y, k_z\}$. Filling of states with electrons starts from the point $\{k_{x1}, 0, 0\}$ and is performed in the order of increasing energy of states. As a result, it appears that all occupied (with electrons) states are located in the region of the **k**-space limited by the plane $k_x = k_{xm}$ and a hemisphere of radius $k_F = \sqrt{2m_e\varepsilon_F}/\hbar$. To find the total number of occupied states, it is necessary to integrate the density of states of two-dimensional electron gas in the film plane and set equal to the number of conduction electrons. Finally, we will obtain the equation to determine the size-dependent Fermi energy ε_F [13, 15]:

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$$k_F^2 = \frac{1}{m_F}\left(2\pi \bar{n} L + \sum_{m=1}^{m_F} k_{xm}^2\right), \tag{2}$$

where $\hbar^2 k_F^2 = 2m_e \varepsilon_F$; $\bar{n}$ is the concentration of conduction electrons in a $3D$-metal; m_F is the number of the last occupied or partly occupied subzone.

3. RESULTS AND DISCUSSION

Calculations were carried out for Al, Cu and Au nanofilms with concentration of electrons of $\bar{n} = 3/4\pi r_s^3$ with the corresponding values $r_s = 2.07a_0$, $2.11a_0$ and $3.01a_0$ (a_0 is the Bohr radius) deposited on SiO_2 ($\chi = 1.1$ eV, $\epsilon = 4$, here ϵ is the permittivity) and Al_2O_3 ($\chi = 1.35$ eV, $\epsilon = 9$) [16].

Account of the band structure of a dielectric [13] requires a redefinition of the electron work function of the film, and, therefore, the value of the well depth. Thus, in contrast to the case of the film in vacuum, where

$$U_0 = \varepsilon_F^0 + W_0, \tag{3}$$

the presence of a dielectric leads to the decrease in the work function and well depth U_d from the dielectric side

$$U_d = \varepsilon_F^0 + W_d, \tag{4}$$

where W_d is the Schottky barrier (the potential barrier height at the metal/dielectric interface).

There exist two approaches to determination of W_d: I – work function into dielectric is defined as $W_d = W_0 - \chi$, where W_0 is the work function of semi-infinite metal/vacuum, χ is the conduction band bottom depth of a dielectric with respect to the vacuum level (electron affinity); II – the value of W_d is taken from the results of self-consistent calculations (Table 1).

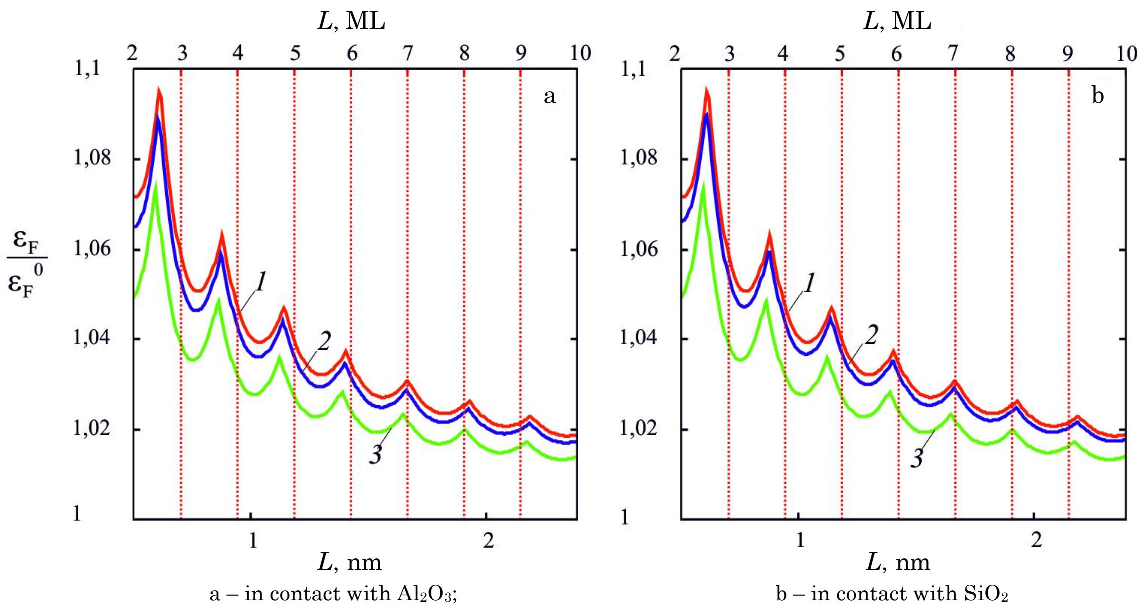
Calculation results of size dependences of the Fermi energy, which illustrate application of the approaches I and II compared with the case of the film in vacuum for Au nanofilms in contact with Al_2O_3 and SiO_2, are presented in Fig. 2a and Fig. 2b, respectively. The vertical dotted lines correspond to the film thickness in monolayers (ML). Curve 1 is the calculation results for a hypothetical Au film in vacuum. Approach I was used in the calculation of the curves 2 to determine the work function into dielectric. A more strict approach II for determination of W_d is represented by the curves 3, where the results of self-consistent calculations for semi-infinite Au/Al_2O_3 and Au/SiO_2 systems are used. The inequality $\varepsilon_F / \varepsilon_F^0 > 1$ holds in the whole range of sizes. Teeth on the size dependence (i.e. jumps of the derivative $d\varepsilon_F / dL$) are located regularly with an approximately constant period $\Delta L \approx \pi / k_F^0$ ($k_F^0 = \sqrt{2m_e \varepsilon_F^0}$). With increasing film thickness $L \to \infty$, amplitude of oscillations tends to zero and their "period" – to infinity.

Table 1 – Results of the self-consistent calculations for semi-infinite Me/Al_2O_3 and Me/SiO_2 systems [17]

Metal	Al		Cu		Au	
Dielectric	Al_2O_3	SiO_2	Al_2O_3	SiO_2	Al_2O_3	SiO_2
W_d, eV	1.29	1.84	1.49	1.89	1.41	1.79

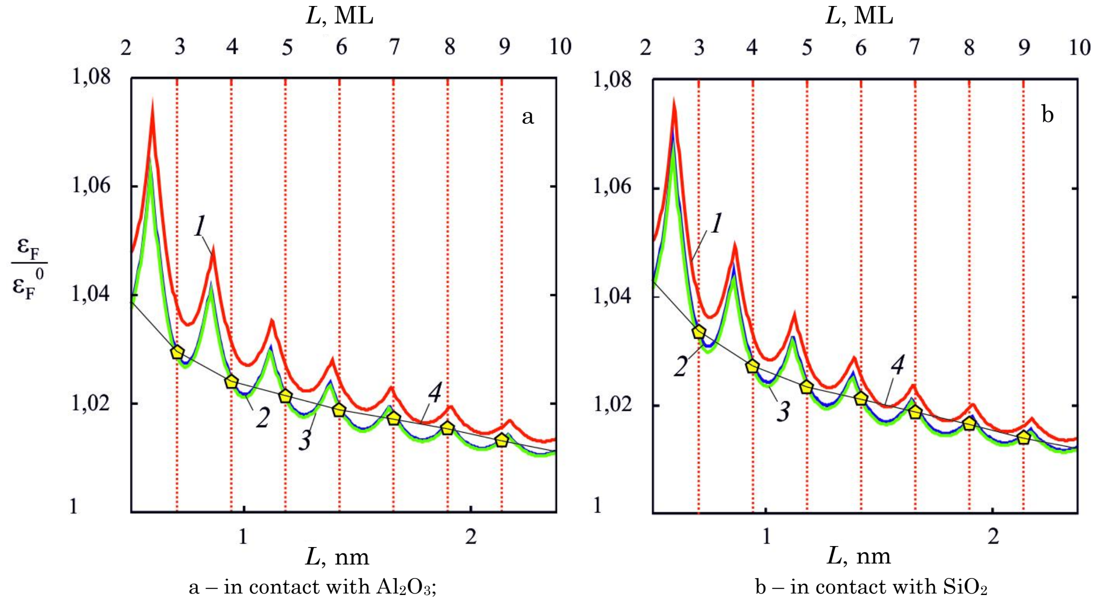
As seen from Fig. 2, account of the dielectric environment leads to the decrease in the Fermi energy in comparison with the case of the film in vacuum (curve 1) with the maintenance of general behavior of the dependence. A more correct account of the dielectric environment in the determination of the work function (previous self-consistent calculations – approach II) conditions a more significant decrease in the minima and shift of the peaks to the left.

It is shown in [18] that presence of a dielectric leads to the change of the metal/vacuum interface – dependence of the work function on the mean value of the environmental permittivities $\langle \epsilon \rangle = (\epsilon_l + \epsilon_r)/2$ (ϵ_l and ϵ_r are the values of the environmental permittivities on the left and on the right of the film, respectively) and decrease



a – in contact with Al_2O_3; b – in contact with SiO_2

Fig. 2 – Size dependence of the Fermi energy of Au nanofilms with different interfaces for $W_0 = 4.105$ eV: 1 – film in vacuum; 2 – approach I; 3 – approach II



a – in contact with Al_2O_3; b – in contact with SiO_2

Fig. 3 – Size dependence of the Fermi energy of Au nanofilms with different interfaces taking into account the well bottom rise: 1 – film in vacuum; 2 – approach I; 3 – approach II

in the potential barrier height from the side of vacuum. Therefore, in Fig. 3 we illustrate the calculation results where the values of $W = 2.87$ eV (Fig. 2a) and 3.07 eV (Fig. 3b) for a dielectric with $\langle \epsilon \rangle$ were taken except the value of the work function into vacuum W_0 [17]. Then, curves 1-3 correspond to the curves 1-3 in Fig. 2a and Fig. 2b, respectively. As seen, curves 2 and 3 for both systems almost coincide. This indicates that the method proposed in this work gives results close to the results of self-consistent calculations. However, in contrast to the results shown in Fig. 2, a more significant decrease in the Fermi energy (curves 2 and 3) compared with the case of the film in vacuum (curve 1) takes place in this case. The reason for such behavior is that the presence of a dielectric, except the decrease in the Fermi level, also leads to the rise of the potential well bottom. At that, the well bottom rise is more essential than the decrease in the Fermi level that leads, as a result, to a more substantial decrease in the Fermi level compared with the case shown in Fig. 2. Moreover, in Fig. 3 we illustrate the curves 4, which join the points of intersection of the curve 3 with the vertical straight lines corresponding to the number of ML in Au film. The specified points are close (and coincide in the case of $L = 7$, 8 and 9 ML) to the maximum and minimum points on the curve 3 that describes the size oscillations of the Fermi energy.

Features of the size dependence of the Fermi energy of different metal films are demonstrated in Fig. 4. In both cases curves $\varepsilon_{\rm F}(L)$ for different metals qualitatively coincide, however, amplitudes and periods are different. Differences in the oscillation periods are explained by the exceptionally different values of $k_{\rm F}^0$. Thus, oscillation scale ΔL is smaller for Al films compared with Au films, since the value of $k_{\rm F}^0$ is larger; oscillation amplitude and smoothed value of $\varepsilon_{\rm F} / \varepsilon_{\rm F}^0$ is smaller. Cu films occupy an intermediate position between Al and Au in this respect.

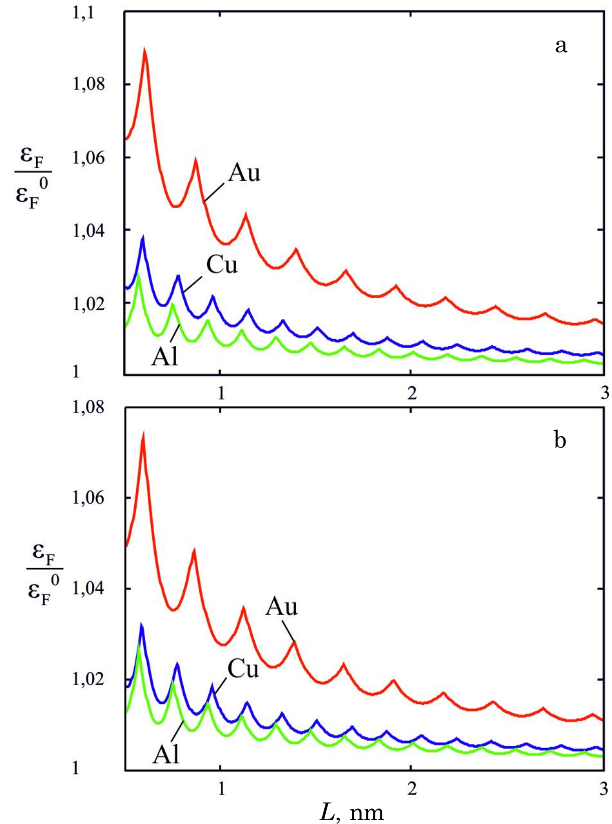


Fig. 4 – Size dependence of the Fermi energy of different metal films in contact with Al_2O_3: a – approach I; b – approach II

In Fig. 5 we present the influence of the permittivity on the Fermi energy of ultrathin metal films (in relative units $\varepsilon_{\rm F} / \varepsilon_{\rm F}^0$, where

$$\varepsilon_{\rm F}^0 = \frac{\hbar^2 \left(3\pi^2 \bar{n}\right)^{\frac{2}{3}}}{2m_e}$$

is the Fermi energy of the uniform electron gas) for Al and Au films of the thickness of $L = 2$ nm.

A slight monotonic decrease in the relative Fermi energy with increasing ϵ takes place in both cases. It is conditioned by the fact that with increasing permittivity, the value of the work function from semi-infinite metal into dielectric W_d decreases [17]. However, since an indirect account of a dielectric by substitution of the values $W_d(\epsilon)$, which are preliminary obtained from the self-consistent calculations, takes place in our model, then "actual" influence of the permittivity on the size oscillations of the Fermi energy will be insignificant.

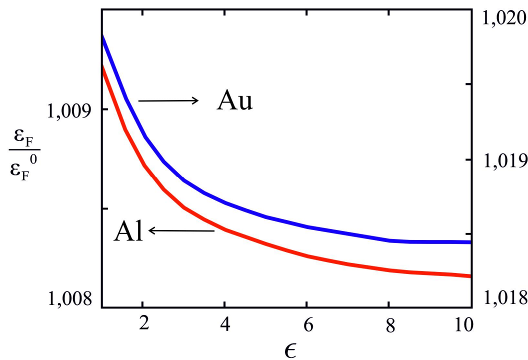


Fig. 5 – Dependence $\varepsilon_F / \varepsilon_F^0 = f(\epsilon)$ for Al and Au films of the thickness of $L = 2$ nm

4. CONCLUSIONS

The electron energy spectrum of ultrathin metal films on a dielectric substrate has been calculated. The expression to determine the size-dependent Fermi energy of a nanofilm with account of a dielectric has been obtained using the model of a rectangular asymmetric potential well by the calculation of the number of occupied electron states in the film.

Influence of the substrate permittivity on the Fermi energy has been studied. It is shown that consideration of the dielectric environment leads to the shift of the Fermi energy with the maintenance of general behavior of the size dependences.

Dependence of the Fermi energy on the film thickness expressed in monolayers (which can be obtained experimentally) implies the necessity of account of the influence of the dielectric substrate on the energy characteristics of ultrathin metal films.

It is established that behavior of size oscillations of the Fermi energy of different metal films is determined by the electron density. Thus, period, oscillation amplitude and smoothed values of the Fermi energy are less for metals with larger concentration.

Analysis of the calculation results indicates the necessity of consideration of the decrease in the well depth from the side of vacuum for the metal/dielectric interface.

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