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More on the Effect of Inhomogeneous Dielectric Coating on Metal Characteristics

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Within the framework of the quantum-statistical functional and the Ritz method, the the problem of finding the surface energy per unit area and work function electrons of a metal flat surface with a inhomogeneous dielectric coating, taken into account in the approximation of a continuous medium. For a uniform coating, the calculated values are insensitive to the selection one-parameter functions for an electronic profile, but sensitive to the gradient series of kinetic energy non-interacting electrons. Calculations are performed for Al, Na and the comparison with the calculations by the Kohn–Shem method is made. Analytically the connection between the theory of the Ritz method for inhomogeneous coatings and calculations by the Kohn–Shem method work function of electrons for metal-dielectric nanosandwiches. As it turned out, the influence inhomogeneous coating on the characteristics of the metal surface can be scaled down to a uniform coverage case. The possibility of using the obtained results in various experimental situations are discussed.

Keywords: Work function, Schottky barrier, dielectric coating.

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1. Introduction

Studies of electronic properties of a metal surface with a complex coating are of interest for modern technologies in the creation, for instance, of materials having a significant sensor response and selectivity. The end task of the coating industry is the engineering of „smart“ coatings that retain their properties in unpredictable conditions.

The complexity of the making of appropriate study objects and measurement methods is evidenced by the comparatively small number of experimental studies, the goal of which is usually quantum-size effects. One of the most important equilibrium characteristics of metal nanostructures is the electron work function.

Films (plates), grown on various substances [1–3], are of technological interest. For instance, the paper [3] experimentally studied the Pb(111) films having thickness L of 1 to 16 monolayers grown on the Ge(111) substrate. The work function to vacuum was measured by the photoemission spectroscopy method.

In a continuous medium approximation, when calculating metal-dielectric interfaces, the insulator is characterized by the dielectric constant ε only. Within the framework of this approach, with the use of local density approximations (LDA), multiple calculations of polarizability and surface plasmonic resonance in metallic nanospheres and threads in different dielectric matrices, nanofilms on dielectric substrates have been performed (see, for instance, [4]), and a change in the sign of positron work function depending on ε of the metal dielectric coating has been predicted [5]. We used the Kohn–Sham method to calculate the surface characteristics of metal-dielectric nanosandwiches [6,7].

Schottky barrier height Φ for the metal-insulator contact is estimated based on the Schottky–Mott rule [8,9] with characteristics of the metal and the insulator isolated from each other

$$\Phi \approx W - \chi, \tag{1}$$

where W and $-\chi$ are the electron work function from metal to vacuum and depth of location of the electron conductivity band in the insulator prior to contact. In case of small gaps of the metal and the insulator, the tail of the electron distribution of a metal is affected by insulator polarization. The rule (1) can be clarified by introducing a dependence $W(\varepsilon)$, where ε is the dielectric constant of the insulator. Then, based on the analysis, it can be assumed that the authors [3] observed Fermi level pinning in a Pb(111) film: all values of $W(\varepsilon, L)$ are below approximately 4 eV (this values corresponds to χ for Ge), while dimension fluctuations are $\Delta W(\varepsilon, L) \in (0.2, 0.5)$ eV. We obtained approximately such values of $\Delta W(L)$ [7] for Vacuum/Al/Al_2O_3 in the absence of pinning (experimental values of the Al and Pb work function are close to each other).

The problem of describing a metal with inhomogeneous coating is directly related to the issue of *anisotropy* of the work function or of *local work function*, which as such corresponds to the local value of effective one-electron potential, dependent on coordinates [10–15]. Such studies are usually conducted either by the Kohn–Sham method [12,14], or by *ab initio* methods [11,13,15],

which often prevent from making a detailed analysis of the obtained results. Such an analysis is possible within the framework of the variational Ritz method using the simplest trial functions that model the electron density profile.

The work goal is determination of the work function and surface energy of a flat metal surfaces, areas whereof are coated with various dielectrics, by the Ritz method.

2. Problem formulation

According to the work goal, it is technically convenient, at first thought, to use the cylindrical coordinate system. For instance, let us imagine that a part of the surface on the butt of a macroscopic cylinder is coated with a dielectric, while the remaining cylinder surface is coated with another dielectric. A limit transition to an infinite cylinder radius is complicated by the arising uncertainties, in particular, the electrostatic part of the problem. This makes us use the spherical coordinate system.

Let us consider a macroscopic metallic solid sphere of radius R, coated with a layer of dielectrics having different constants ε_i (continuous medium approximation).

Guiding by the experience outlined in our previous paper [14], we have adopted infinitely large dielectric thickness to simplify calculations. The rather fast decrease of electron distribution outside the metal (approximately to the distances of 5–10 Angstrom) makes it possible to neglect the effect of the thickness of this coating, the minimum thickness of which must be much greater than the monoatomic (or monomolecular) dielectric layer. Free-path length of electrons in dielectrics is tens of Angstrom [16].

For an analytical solution of the problem, let us assume that only two dielectrics 1 and 2 ($i = 1, 2$) are adjacent on a metallic surface. The dielectric region with ε_1 can be set, for instance, by the polar angle θ_m (Fig. 1). Figure 1 in case of $\varepsilon_2 = 1$ can be applied to a metal drop lying on a dielectric substance with ε_1.

By setting a fraction of the

$$\alpha = S_1/S \tag{2}$$

sphere surface occupied with dielectric 1 ($S_1{=}2\pi Rh$, h is the spherical segment height), we obtain a value of the boundary angle

$$\cos\theta_m = 1 - h/R = 1 - 2\alpha. \tag{3}$$

Distribution of positive (ionic) charge in the metal jelly model is homogeneous and isotropic, and is set by the Heaviside function

$$\rho(r) = \bar{\rho}\Theta(r - R), \quad \bar{\rho} = \bar{n} \tag{4}$$

(it is identical for regions 1 and 2), $\Theta(r - R) = \{1,\ r \le R;\ 0,\ r > R\}$. Here, $\bar{n} = \left(4\pi r_s^3/3\right)^{-1}$ is the electron gas concentration in the metal volume, r_s is the average distance between electrons.

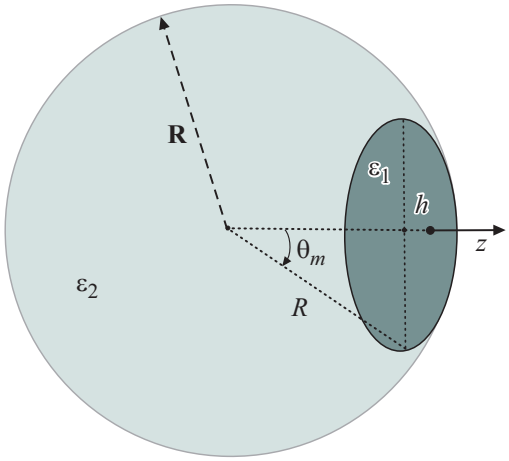

Figure 1. Geometric layout of a metallic surface coated with two different dielectrics.

In the isotropic case, by the example of a jelly-sphere in vacuum ($\varepsilon_i = 1$), with a limitation to electron profiles $n(r)$ in the form of one-parameter trial functions (the Ritz method), it is known that the electron cloud effective radius R' differs from R [17]. This difference is $\propto R^{-1}$ and is found from the electroneutrality condition

$$\int d\mathbf{r}\, \nu(\mathbf{r}) = 0, \quad \nu(\mathbf{r}) \equiv n(\mathbf{r}) - \rho(\mathbf{r}). \tag{5}$$

Acting differently, for a jelly-sphere in vacuum (the same can be also affirmed for a ball with homogeneous dielectric coating), let us equate the electron cloud radius R' to the ion jelly radius R, and let us chose a profile as follows

$$n(r) = \bar{n}\begin{cases} 1 - Ae^{(r-R)/\lambda}, & r \le R, \\ Be^{(R-r)/\lambda}, & r > R, \end{cases} \tag{6}$$

$$A = \frac{1}{2}f, \quad B = 1 - A, \tag{7}$$

where f takes into account the difference of R' from R.

By integration in (5) we obtain

$$f = 1 + \frac{2}{\beta} - \frac{4}{\beta^3}, \tag{8}$$

where $\beta = \lambda/R \ll 1$.

In the flat case ($R \to \infty$, $z = r - R$), the coefficients $A = B = 1/2$ match the profile suggested in [18] in the discussion of electron work function for different crystallographic metal edges and used for the first time in the density functionality method for a flat metallic surface in [19].

In compliance with Fig. 1, each region corresponds to its own profiles. We will use (6) as the first step and for a ball with inhomogeneous coating, by introducing the corresponding indices for $n(r), A, B, f$

$$n_i(\mathbf{r}) = \begin{cases} n_1(r), & \theta \in (0, \theta_m), \\ n_2(r), & \theta \in (\theta_m, \pi), \end{cases} \tag{9}$$

It is known that electron work function $W(\varepsilon)$ for metals with a homogeneous coating decreases as ε increases [14]. Application of different dielectrics ($\varepsilon_1 \neq \varepsilon_2$) on a metal surface will cause electron liquid flow-over near the surface from region 1 into region 2 (or vice versa) due to the arising contact potential difference. The distributions $n_1(\mathbf{r})$ or $n_2(\mathbf{r})$ in this case will shift to opposite sides along the normal line deep either into the metal or the dielectric. This effect can be reflected by introducing the parameter δ into the corresponding coefficients (7):

$$A_i = \frac{1}{2} f_i + \delta_i, \quad B_i = 1 - A_i.$$

The parameters $A_{1,2}$, $B_{1,2}$ and $\lambda_{1,2}$ characterize the dimensions of the local dipole barriers for the regions 1 and 2.

Integration into (5), taking into account (6)–(9) and (3), results in a ratio

$$\delta_1 = -\left(\frac{\alpha}{1-\alpha}\right)\frac{\lambda_2}{\lambda_1}\delta_2 + O\left(\frac{1}{\beta_1^2}, \frac{1}{\beta_2^2}\right). \qquad (10)$$

It is interesting to note that the parameters δ_i in the flat case ($R \to \infty, z = r - R$) should give a nonvanishing contribution to (5), which is related to the fixed value of the coefficient α regardless of transition $R \to \infty$. The opposite sign of δ_1 and δ_2 means a loss of local electroneutrality in regions 1 and 2 due to electron flow-over, but the sphere's full electroneutrality is maintained. In case of $\alpha = 0, 1$, we have $\lambda_1 = \lambda_2$ and $\delta = 0$ (homogeneous coating), and in case of $\alpha = 1/2$, when the sphere area halves are coated with different dielectrics, $\delta_1 = -(\lambda_2/\lambda_1)\delta_2$.

By using (4) in the flat case and calculating the number of electrons flowing over from one region to another, an equation can be made up

$$\bar{\rho}[(1-\alpha)S\,\delta_1] = -\bar{\rho}(\alpha S\,\delta_2),$$

from which it follows that

$$\delta_1 = -\left(\frac{\alpha}{1-\alpha}\right)\delta_2. \qquad (11)$$

Then, by comparing (10) and (11) for the chosen class of trial functions, we obtain an important condition

$$\lambda_1 = \lambda_2. \qquad (12)$$

Let us first consider the case $\alpha = 0, 1$ in Fig. 1 in the limit $R \to \infty$ — a flat metal surface coated with homogeneous dielectric.

3. Homogeneous coating of a flat surface

In a model of conventional jelly (J) and the Ritz method we use a one-parameter electron profile $n(z)$ and a homogeneous distribution of a positively charged background $\rho(z) = \bar{n}\Theta(-z)$. The quantum-statistical functionality with volume density of electron energy g in LDA consists of: quasi-homogeneous kinetic energy of non-interacting electron gas (hereinafter the Hartree atomic units are used)

$$g_{\mathrm{t}}(n) = n\frac{3}{10}(3\pi^2 n)^{2/3};$$

terms of Weizs'cker–Kirzhnits–Hodge gradient decomposition [20] of kinetic energy, which contains the even powers of gradients

$$g_{\mathrm{g}} \equiv g_{\mathrm{g1}} + g_{\mathrm{g2}} + g_{\mathrm{g3}} + g_{\mathrm{g4}} = \frac{|\nabla n|^2}{72n} + \frac{n^{1/3}}{540(3\pi^2)^{2/3}} \times \left[\left(\frac{\nabla^2 n}{n}\right)^2 - \frac{9}{8}\left(\frac{\nabla^2 n}{n}\right)\left|\frac{\nabla n}{n}\right|^2 + \frac{1}{3}\left|\frac{\nabla n}{n}\right|^4\right]; \qquad (13)$$

Dirac exchange energy

$$g_{\mathrm{ex}}(n) = -n\frac{3}{4\pi}(3\pi^2 n)^{1/3}$$

and Pines–Nozieres correlation energy

$$g_{\mathrm{cor}}(n) = n\left[0.0474 + 0.0155\ln(3\pi^2 n)^{1/3}\right].$$

The non-local (electrostatic) component of energy is as follows

$$E_{\mathrm{q}}(n) = \frac{1}{2}\int d\mathbf{r}\,\phi\,\nu \qquad (14)$$

[value of ν was determined in (5)].

Electrostatic potential ϕ is found by solving the Poisson's equation

$$\nabla^2\phi(z) = -\frac{4\pi}{\epsilon(z)}\nu(z) \qquad (15)$$

with a boundary condition $\phi(z) \to 0$ at $z \to +\infty$. The function $\epsilon(z)$ is equal to 1 inside the metal, where the electrons and ions are in vacuum, and is equal to ε outside the metal. A solution of the equation (15) is as follows

$$\phi(z) = \bar{\phi} - 4\pi\int_{-\infty}^{z} dz'\,(z - z')\,\frac{\nu(z')}{\epsilon(z')} \qquad (16)$$

with a potential value in the metal depth

$$\bar{\phi} \equiv \phi(-\infty) = -4\pi\int_{-\infty}^{+\infty} dz\,z\,\frac{\nu(z)}{\epsilon(z)} < 0. \qquad (17)$$

Specific surface energy in the conventional jelly model is by definition equal to

$$\sigma_{\mathrm{J}} = \int_{-\infty}^{\infty} dz\left[g(n(z)) + \frac{1}{2}\phi(z)\,\nu(z) - g(\bar{n})\Theta(-z)\right], \qquad (18)$$

while in the stable jelly model [21,22]

$$\sigma = \sigma_{\mathrm{J}} + \langle\delta v\rangle_{\mathrm{WS}}\int_{-\infty}^{0} dz\,\nu(z). \qquad (19)$$

Table 1. Values of the coefficients in expression (26), calculated using the functions (21) (upper value) and (22) (lower value)

C_q	C_t	C_{ex}	$C_{cor} \cdot 10^3$	$C_{g1} \cdot 10^3$	$C_{g2} \cdot 10^4$	$C_{g3} \cdot 10^4$	$C_{g4} \cdot 10^4$	C_{WS}
0.785	−1.842	0.2502	6.589	9.627	5.115	−4.832	1.611	−1/2
1.886	−2.179	0.3288	3.499	6.944	2.861	−3.359	1.120	−0.693

Stabilization potential is as follows

$$\langle \delta v \rangle_{WS} = 2\left(0.0026 + k_F/8\pi - k_F^2/10\right),$$

$k_F = (3\pi^2\bar{n})^{2/3}$.

Electron work function in the stable jelly model is determined as

$$W = -\bar{\phi} - \frac{dg(\bar{n})}{d\bar{n}} - \langle \delta v \rangle_{WS}. \qquad (20)$$

For comparative analysis, calculations were performed for two functions: „antisymmetric“ function

$$n(z) = \bar{n}\begin{cases} 1 - \frac{1}{2}e^{z/\lambda}, & z \le 0, \\ \frac{1}{2}e^{-z/\lambda}, & z \ge 0, \end{cases} \qquad (21)$$

that coincides with (6) at $R \to \infty$, as well as Fermi functions

$$n(z) = \frac{\bar{n}}{1 + e^{z/\lambda}}. \qquad (22)$$

By substituting (21) and (22) in (16) and (17), and then by integration we obtain

$$\phi(z) = -2\pi\bar{n}\lambda^2\begin{cases} 1 + \frac{1}{\varepsilon} - e^{z/\lambda}, & z \le 0, \\ \frac{1}{\varepsilon}e^{-z/\lambda}, & z \ge 0, \end{cases} \qquad (23)$$

and

$$\phi(z) = \bar{n}\lambda^2\begin{cases} -\frac{1}{3}\pi^3\left(1+\frac{1}{\varepsilon}\right) - 4\pi\sum_{k=1}^{\infty}(-1)^k\frac{1}{k^2}e^{kz/\lambda}, & z \le 0, \\ \frac{4\pi}{\varepsilon}\sum_{m=1}^{\infty}(-1)^m\frac{1}{m^2}e^{-mz/\lambda}, & z \ge 0, \end{cases} \qquad (24)$$

respectively (the potentials join in case of $z = 0$).

The expression (23) coincides with the previous result given in paper [23]. In (23) and (24) with $z = 0$ we can easily trace a relation to the value of electrostatic potential at the boundary of a conducting ball in the dielectric [24]. For this, the contribution of ion jelly and electron cloud must be considered separately in the spherical case.

When developing (24) in internal integration into (16), an expansion of (22) by smallness powers $e^{-|z|/\lambda} \ll 1$ has been used. Such decomposition works well, except the vicinity of $z = 0$. By integration this peculiarity is dropped out during development of $\phi(z)$ and finding of the electrostatic component of surface energy

$$\sigma_q = \frac{1}{8\pi}\int_{-\infty}^{+\infty} dz\,(\nabla\phi)^2. \qquad (25)$$

The result of analytical calculations can be compactly written as

$$\sigma = \bar{n}^2\lambda^3 C_q\left(1 + \frac{1}{\varepsilon}\right) + \lambda\left(\bar{n}^{5/3}C_t + \bar{n}^{4/3}C_{ex} + \bar{n}C_{cor}\right) + \frac{\bar{n}}{\lambda}C_{g1} + \frac{\bar{n}^{1/3}}{\lambda^3}\left(C_{g2} + C_{g3} + C_{g4}\right) + \bar{n}\lambda C_{WS}\langle \delta v \rangle_{WS}. \qquad (26)$$

Values of coefficients C depend on trial function type and are given in Table 1.

Figure 2 gives (for Al) the optimal values of the variational parameter $\lambda(\varepsilon)$, which characterizes the surface profile of the electron distribution, determined from the condition

$$\frac{d}{d\lambda}\sigma(\bar{n}, \varepsilon, \lambda) = 0.$$

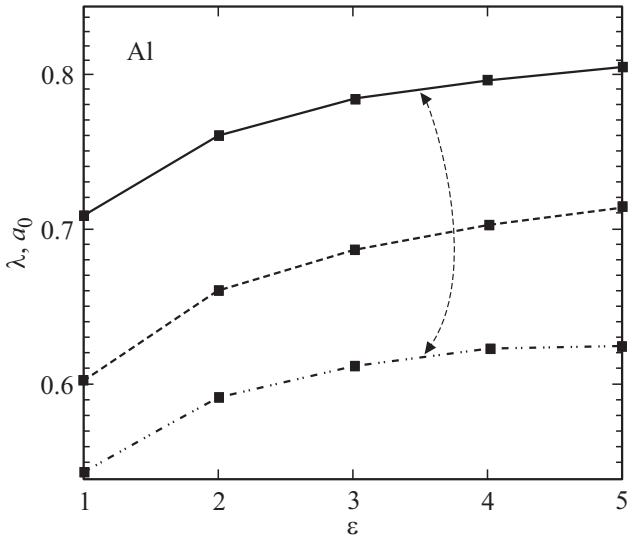

Figure 2. Dependence of the optimized parameter λ („width“ of the transition layer) in the Ritz method for polycrystalline Al ($r_s = 2.07\,a_0$) on the dielectric constant of homogeneous coating: for the function (21) and a full gradient series (the solid line), with Kirzhnits correction (dash-and-dot line); for the function (22) and a full gradient series (dashed line). a_0 is the Bohr radius.

The values of $\lambda(\varepsilon)$ are sensitive both to the used gradient series and to the trial function type. As the coating constant ε increases, the value of the parameter λ increases and levels off. The dependence $\lambda(\varepsilon)$ qualitatively agrees with the behavior of the electron profiles calculated by the Kohn–Sham method, but the values of λ are significantly lesser in case of a conventional comparison with Fig. 3, where Friedel oscillations of electron densities can be seen.

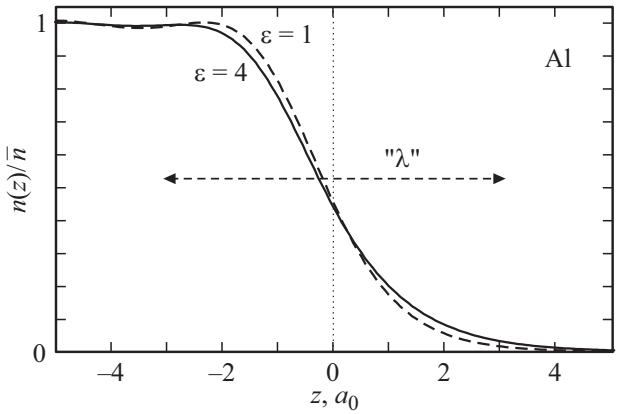

Figure 3. One-dimensional electron profiles calculated by the Kohn–Sham method.

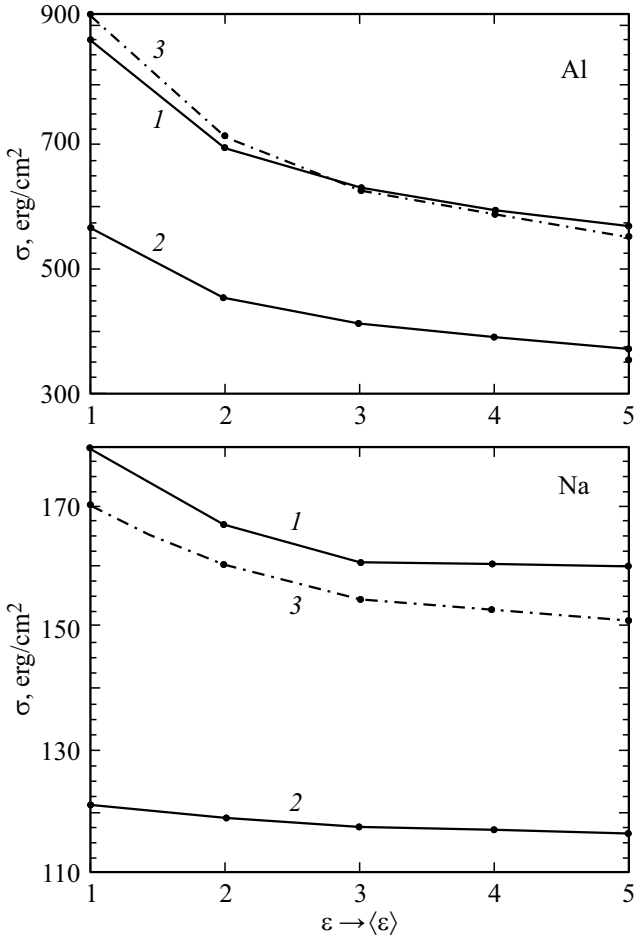

Figure 4. Dependence of specific surface on energy $\sigma(\varepsilon)$ for Al and Na ($r_s = 3.99\,a_0$), calculated with the function (21) for a full gradient series (*1*) and only with a Kirzhnits correction (*2*). The values calculated by the Kohn–Sham method are given for comparison (*3*).

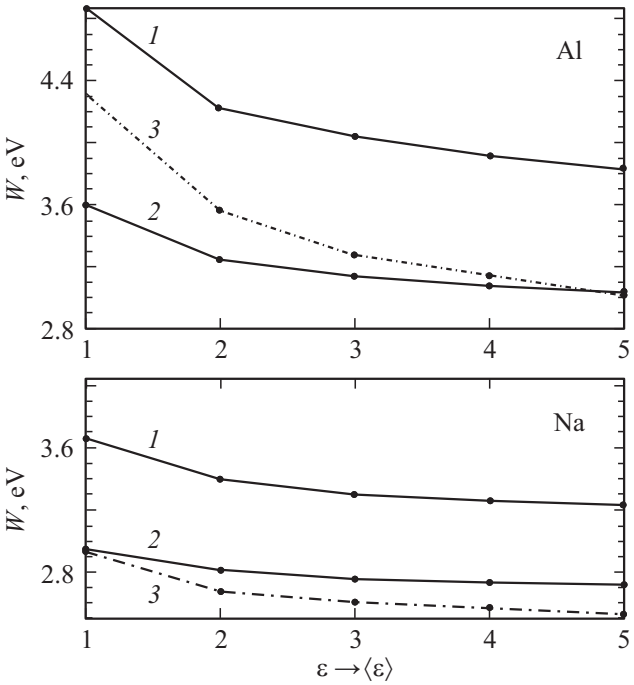

Figure 5. Dependence of electron work function $W(\varepsilon)$ for Al and Na, calculated with function (21). The designations are the same as in Fig. 4.

The fully self-coordinated calculations in the Kohn–Sham method and LDA lead to more significant values of surface layer width, while jointing with the image potential leads to even greater values [7]. Therefore, the used Ritz method of partial procedure self-coordination, though it allows for analytical consideration of such problems, is less efficient in reproducing the profile of the effective one-electron potential $v_{\text{eff}}(z)$ near the surface in case of full self-consistency.

The obtained dependence $\lambda(\varepsilon)$ can be also commented from the viewpoint of „mechanical“ equilibrium of the coated metal in terms of stress or pressure tensor [25].

The stress tensor contains non-electrostatic components, as well as Maxwellian stress tensor. In the general case, it depends on the coating constant ε and makes a contribution $\mp\frac{1}{8\pi}(\nabla\phi)^2$ to the normal and tangential components of pressure, respectively, thereby determining the dependence of electron profile $n(\varepsilon, z)$, i.e. $\lambda(\varepsilon)$, as well as the electrostatic component of surface energy (25). The surface equilibrium conditions require a zero normal component of pressure while external pressure is absent.

This stress tensor in the Kohn–Sham method (see Fig. 3, as well as Fig. 3 in [14]) is responsible for „pulling-out“ of profiles $n(\varepsilon, z)$ and one-electron effective potential $v_{\text{eff}}(z)$ into the dielectric region, and at the same time for „forcing“

of the profile $\phi(z)$ into the metal [$\phi(z)$ is a component of $v_{\text{eff}}(z)$].

Figures 4 and 5 give dependences of surface energy $\sigma(\varepsilon)$ and electron work function $W(\varepsilon)$. As the coating constant ε increases, the values of σ and W decrease and level off. The estimated values of the observed characteristic W, as well as σ, do not much depend on trial function type (the difference is mainly observed in the third significant digit), but are rather sensitive to gradient approximation. The calculations for a full gradient series agree better with the known experimental values in case of $\varepsilon = 1$ and the calculation by the Kohn–Sham method for σ, but at the same time they yield overestimated values for W. Calculations with only a Kirzhnits gradient correction [$C_{g2}, C_{g3}, C_{g4} = 0$ in (26)] ensure, on the opposite, better agreeing in terms of W than in terms of σ. With $\varepsilon = 1$ the experimental values are $\sigma = 926$ erg/cm^2 (Al), 191 erg/cm^2 (Na) and $W = 4.25$ eV (Al), $2.35 \div 2.75$ eV (Na).

4. Inhomogeneous surface coating

Let us consider the case $\alpha = 1/2$ in Fig. 1, when the metallic ball's center is located on the flat boundary of two dielectrics. The Z axis is perpendicular to the boundary ($\theta_m = \pi/2$). By „flattening" the ball into a disk (Fig. 6, *a*), we obtain a *macroscopic* „plate" with thickness L in a dielectric setting — metal-dielectric sandwich with a flat interface (Fig. 6, *b*).

For a sandwich, we choose an electron distribution profile in the form

$$n(z) = \bar{n}\begin{cases} B_1 e^{(z+Z_1)/\lambda_1}, & z < -Z_1, \\ 1 - A_1 e^{-(z+Z_1)/\lambda_1}, & -Z_1 \le z \le 0, \\ 1 - A_2 e^{(z-Z_2)/\lambda_2}, & 0 \le z \le Z_2, \\ B_2 e^{-(z-Z_2)/\lambda_2}, & z > Z_2, \end{cases} \tag{27}$$

where $Z_{1,2} = L/2 + \delta_{1,2}$.

The condition of profile jointing (27) in $z = 0$ for a random L and the electroneutrality condition confirm (12) and are fulfilled at $\delta_1 = -\delta_2 = 0$. The latter can be also easily checked by calculating, for instance,

$$\left[\frac{1}{2}\sigma_t(\lambda_1, \delta_1) + \frac{1}{2}\sigma_t(\lambda_2, \delta_2)\right]_{\lambda_i \equiv \lambda} = \sigma_t(\lambda).$$

A limitation by the condition $\delta_i = 0$ is only a consequence of the use of a one-parameter trial function.

Substituting (27) into the expression of the sandwich electrostatic potential

$$\phi(z) = -4\pi \int_z^\infty dz' \int_{z'}^\infty dz'' \frac{\nu(z'')}{\epsilon(z'')}, \quad \phi(\mp\infty) = 0$$

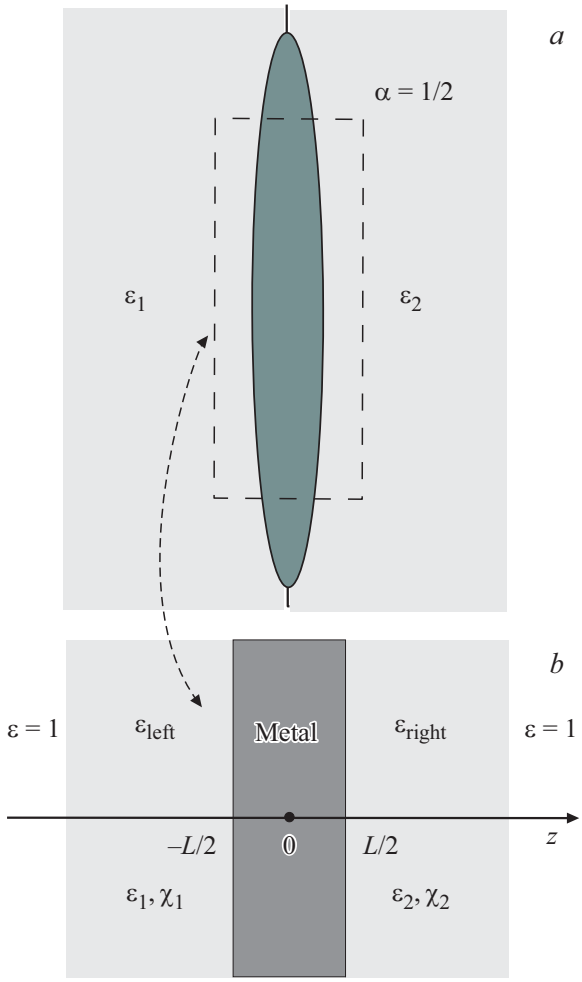

Figure 6. Geometrical construction that explains the relation of the particular case of $\alpha = 1/2$ for a coating with metal-dielectric nanosandwiches from paper [6].

and retaining only the exponential coordinate dependence with $L \to \infty$, we obtain

$$\phi(z) = -2\pi\bar{n}\lambda^2 \begin{cases} \dfrac{1}{\langle\varepsilon\rangle} e^{(z+L/2)/\lambda}, & z < -L/2, \\ 1 + \dfrac{1}{\langle\varepsilon\rangle} - e^{-(z+L/2)/\lambda}, & -L/2 \le z \le 0, \\ 1 + \dfrac{1}{\langle\varepsilon\rangle} - e^{(z-L/2)/\lambda}, & 0 \le z \le L/2, \\ \dfrac{1}{\langle\varepsilon\rangle} e^{-(z-L/2)/\lambda}, & z > L/2, \end{cases} \tag{28}$$

where

$$\langle\varepsilon\rangle = \frac{\varepsilon_1 + \varepsilon_2}{2}. \tag{29}$$

The profile (28) reflects the plate surface equipotentiality directly at the boundary of the positively charged background. Therefore, $\phi(\mathbf{r})$ changes only along the normal line to the surface.

Thus, the same expression (26) can be applied for the plate, using (29), while for the work function $\bar{\phi}$ in (20)

must be replaced by the value of potential in the plate center $\phi(0) = -2\pi\bar{n}\bar{\lambda}^2\left(1 + \langle\varepsilon\rangle^{-1}\right)$.

The formula (29) has analogs. Firstly, there is direct relation to the value of electrostatic potential at the boundary of a conducting ball located symmetrically between two dielectrics having ε_1 and ε_2 [24]. Secondly, the formula (29) is directly related to the numeric results of the Kohn–Sham method [6] of the surface energy and electron work function for metal-dielectric nanosandwiches, e.g., an Al nanoplate, on the left and right of which dielectrics are located: $\{\varepsilon_{\text{left}}|\text{Al}_L|\varepsilon_{\text{right}}\}$ (Fig. 6, *b*).

In the results of the paper [6] some peculiarities have not been explained. The dependences $W(L)$ for sandwiches $\{1|\text{Al}_L|5\}$ and $\{3|\text{Al}_L|3\}$ coincided. The calculation for $\{1|\text{Al}_L|9\}$ and $\{5|\text{Al}_L|5\}$ yielded the same result, i.e. the work function for asymmetric sandwiches $\{\varepsilon_{\text{left}}|\text{Al}_L|\varepsilon_{\text{right}}\}$ matched the work function of symmetric sandwiches $\{\langle\varepsilon\rangle|\text{Al}_L|\langle\varepsilon\rangle\}$ with an arithmetic mean value $\langle\varepsilon\rangle = (\varepsilon_{\text{left}} + \varepsilon_{\text{right}})/2$ (see Fig. 5 in [6]). This was not observed for specific surface energy calculated as an arithmetic mean. The profile of one-electron effective potential was a peculiar „two-faced Janus“ with a potential hump, e.g., for $\{1|\text{Al}_L|5\}$ on the vacuum side ($\varepsilon_{\text{left}} = 1$). Now brief comments can be given based on the Ritz method.

The results of Ritz method calculations for Al and Na with $\alpha = 1/2$ are given in Tables 2 and 3. A comparison of the values of σ and W in case of $\alpha = 1/2$; $\varepsilon_1 = 3$ and $\varepsilon_2 = 1$, as well as $\varepsilon_1 = 5$ and $\varepsilon_2 = 1$, shows a coincidence with the values of σ and W for $\langle\varepsilon\rangle = 2$ and 3 in Figs. 4 and 5.

The potential hump for an asymmetric sandwich $\{1|\text{Al}_L|5\}$ in [6] is related to surface recharging. According to the condition of equilibrium for chemical potential $\mu(z) = \text{const}$, the electrons flowed over from the plate right side to the left one. The Ritz method with monotonous functions cannot reflect this effect.

In case of $\alpha \neq 1/2$ and $R \to \infty$ the potential

$$\phi(\mathbf{r}) = \int d\mathbf{r}' \frac{\nu(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|\epsilon(\mathbf{r}')}$$

is not expressed in analytical functions even approximately, because α is not a small parameter. The following can be done in this case.

In electrostatics, when calculating the capacitance of a plane capacitor partially filled with different dielectrics, the values of ε_i make part of the combinations $\varepsilon_i S_i$, where $S_i = \alpha_i S$ are contact areas. Generalization of the expressions (23) and (26) by the following substitution can be suggested

$$\widetilde{\varepsilon} \to \sum_i \varepsilon_i \alpha_i \tag{30}$$

for a random number of contacts of a *flat* metallic surface with dielectrics. In the case of two dielectrics under consideration

$$\widetilde{\varepsilon} \to \varepsilon_1\alpha + \varepsilon_2(1 - \alpha) \tag{31}$$

and for $\alpha = 1/2$ we have $\widetilde{\varepsilon} = \langle\varepsilon\rangle$.

Table 2. Results of calculations with the function (21) for Al with a full gradient series (upper values) and with a Kirzhnits correction (lower values)

α	ε_1	ε_2	λ, a_0	σ, erg/cm^2	W, eV
1/2	1	1	0.709 0.602	872 567	4.88 3.60
1/2	2	1	0.741 0.638	760 497	4.47 3.39
1/2	3	1	0.760 0.661	698 456	4.25 3.27
1/2	4	1	0.774 0.678	658 430	4.12 3.20
1/2	5	1	0.784 0.687	630 411	4.03 3.16
1/2	4	3	0.791 0.695	609 397	3.96 3.12
1/3	2	1	0.732 0.628	790 516	4.58 3.44
1/3	3	1	0.748 0.647	736 481	4.39 3.34
1/3	4	1	0.760 0.661	698 456	4.25 3.27
1/3	5	1	0.770 0.671	669 438	4.16 3.22
1/3	4	3	0.789 0.692	615 402	3.98 3.13
1/4	2	1	0.727 0.623	807 527	4.64 3.48
1/4	3	1	0.741 0.638	760 497	4.47 3.39
1/4	4	1	0.752 0.651	725 474	4.35 3.32
1/4	4	3	0.787 0.691	619 404	3.99 3.14

Values of the parameter λ, values of σ and W in case of $\varepsilon_1 = \varepsilon_2$ correspond to homogeneous coatings and the points in Figs. 2, 4 and 5. The case $\varepsilon_1 = \varepsilon_2 = 1$ corresponds to a metal-vacuum interface and the „first“ points in the same figures.

Coating inhomogeneity is formally determined by summands

$$\bar{n}^2\lambda^3 C_q\left(1 + \frac{1}{\varepsilon_1\alpha + \varepsilon_2(1 - \alpha)}\right)$$

and

$$\bar{\phi} = -2\pi\bar{n}\bar{\lambda}^2\left(1 + \frac{1}{\varepsilon_1\alpha + \varepsilon_2(1 - \alpha)}\right)$$

for σ and W in (26) and (20), respectively. Therefore, while the combination $\varepsilon_1\alpha + \varepsilon_2(1 - \alpha)$ for different values

Table 3. Results of calculations with the function (21) for Na. The designations are the same as in Table 2

α	ε_1	ε_2	λ, a_0	σ, erg/cm^2	W, eV
1/2	1	1	1.061 0.749	178 121	3.66 2.94
1/2	2	1	1.090 0.775	171 119	3.49 2.86
1/2	3	1	1.107 0.789	167 118	3.40 2.82
1/2	4	1	1.119 0.799	164 117	3.34 2.79
1/2	5	1	1.127 0.805	163 116	3.30 2.77
1/2	4	3	1.132 0.810	162 116	3.28 2.76
1/3	2	1	1.082 0.768	172 120	3.53 2.88
1/3	3	1	1.097 0.780	169 118	3.45 2.84
1/3	4	1	1.107 0.789	167 118	3.40 2.82
1/3	5	1	1.115 0.796	165 117	3.36 2.80
1/3	4	3	1.31 0.809	162 116	3.28 2.76
1/4	2	1	1.078 0.764	174 120	3.56 2.89
1/4	3	1	1.090 0.775	171 119	3.49 2.86
1/4	4	1	1.100 0.783	168 118	3.43 2.84
1/4	4	3	1.130 0.808	162 116	3.29 2.76

of $\alpha, \varepsilon_1, \varepsilon_2$ is integer, then the points in Figs. 4 and 5 for homogeneous coatings correspond to exactly these numbers.

Thus, Figs. 4 and 5 will be the key ones, and values of σ and W for an inhomogeneous coating can be estimated using the ratio (29) as a scale transformation.

While commenting the role of the parameters δ_1 and δ_2, it should be stated that if *monotonous* trial functions of type (21) or (22) are chosen, the electroneutrality condition in the flat case makes it possible to use only one variational parameter (λ). Therefore, the role of δ_1 and δ_2 in this approach is reduced to development of a condition of the equation (12). The sandwich problem is found with precision by solving a system of one-dimensional Kohn–Sham and Poisson equations [6]. These solutions in a three-dimensional case must meet the condition

$$\mu(\varepsilon_i, x, y, z) = \text{const} = -W(\varepsilon_i).$$

A computational procedure in this setting has not still been implemented.

Thus, the paper has made an analytical attempt at demonstrating that the electron work function $W(\widetilde{\varepsilon})$, as electron energy deep in the metal, counted from the vacuum level, is isotropic, regardless of surface shape of the metal sample and dielectric coating. This conclusion results from equipotentiality of the metallic surface [10–12].

A Schottky barrier for inhomogeneous coating

$$\Phi^{(i)} = W(\widetilde{\varepsilon}) - \chi^{(i)}, \tag{32}$$

on the contrary, is an anisotropic value and is determined in transfer processes by the largest value of $\chi^{(i)}$ (the smallest $\Phi^{(i)}$). $\chi = 0.1$, 0.2, 0.45, 0.68, 1.1, 1.35, 4.05 and 4 eV for Ne, Ar, Kr, Xe, Al_2O_3, Si and Ge, respectively.

5. Conclusion

This paper has studied (within the Ritz method framework) the surface energy and electron work function for a flat metallic surface with inhomogeneous dielectric coating. The estimated values for a homogeneous coating are insensitive to selection of one-parameter functions for the electron profile, but are sensitive to the gradient series of kinetic energy of non-interacting electrons. Nevertheless, this did not affect the qualitative conclusions of the paper. The results of calculations by the Ritz method and Kohn–Sham method were also compared.

An analysis by the Ritz method made it possible to interpret some peculiarities of the calculation results of the Kohn–Sham method for asymmetric metal-dielectric nanosandwiches.

It was suggested to reduce the impact of coating inhomogeneity on the metallic surface characteristics to the case of a homogeneous coating by scaling.

It was showed that the electron work function, counted from the vacuum level, is a scalar quantity, regardless of dielectric coating. A Schottky barrier for a composite coating, on the contrary, is an anisotropic quantity.

Two situation regimes should be considered while discussing the possibility of observation of the dependences $W(\varepsilon, \chi)$ for various contacts. If the electron work function to vacuum $W(\varepsilon, \chi)$ is measured as a result of an external photoeffect, this possibility refers only to a metal with dielectric coating having a thickness less than the free-path length (absence of electron's energy exchange with the insulator). Value of W in case of energy exchange can be restored using the formula (32) and measurement of Φ as a result of an internal photoeffect. In the given situations, the electron free-path length in the insulator can be estimated by solving the reverse problem according to the measurements of $W(\varepsilon, \chi)$.

Our study has supposed the absence of chemical changes in the contact, which is rather plausible for insulators having a small χ. The presence of surface states for Si, Ge semiconductors leads to Fermi energy pinning. The problem in this case is solved by the cluster method (see, for instance, [26]).

Specific surface energy in the Ritz method for a metallic surface with dielectric coating plays a secondary part: as a result of optimization, the „true" value of the parameter $\lambda(\varepsilon_1, \varepsilon_2)$ was determined; it is necessary for the measured characteristic–electron work function $W(\lambda)$. The following practical use of the obtained results for $\sigma(\varepsilon_1, \varepsilon_2)$ can be suggested.

Surface tension is determined experimentally by the contact angle of wetting according to the Young law [27]. Thereat, the dependence $\sigma(\alpha, \varepsilon_1, \varepsilon_2)|_{\varepsilon_2=1}$, obtained in this paper, in a sense models a metal drop the area αS of which touches a dielectric substrate with the constant ε_1. The approach suggested in this paper will possibly allow for clarifying the measurements of σ.

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Conflict of interest

The author declares that he has no conflict of interest.

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