ELECTRON DENSITY ON THE SURFACE OF A DIELECTRIC INTERACTING WITH A PLASMA

A. L. Danilyuk and E. E. Tkharev

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The density functional method is used to calculate the electron density on the surface of a dielectric interacting with a gas-discharge plasma.

Study of the electrophysical properties of a solid surface interacting with a plasma is a scientific field of practical importance. It is also important in solving fundamental problems and practical applications in ever-increasing numbers, including microelectronics, plasma chemistry, contact plasma diagnostics, etc. However, despite significant progress in understanding surface phenomena, at the present there is practically no satisfactory description of such properties available. Since such properties are in the final reckoning determined by electron distribution on the surface, the problem of determining such properties reduces to description of a multielectron system in an external field created by the atoms of the solid and the plasma ions.

The primary problem involved is calculation of the value of the electron density $n(\mathbf{r})$ on the surface of a dielectric interacting with a gas-discharge plasma. To solve such a problem it is necessary to find the distribution of this density and the electrostatic potential $\varphi(\mathbf{r})$ in the negatively charged electron surface layer (ESL) which develops on the plasma–dielectric boundary [1] (Fig. 1).

This distribution is quite inhomogeneous in character, and for its calculation we will employ the density functional method, widely used for study of properties of inhomogeneous electron systems [2]. The method is based on the assumption that there exists a reciprocally unique correspondence between the wave function of the equilibrium electron system and the electron density in the ground state $n(\mathbf{r})$. It follows from this assumption that the thermodynamic quantities (energy, entropy, Ω potential, etc.) of the electronic system are functions of the density $n(\mathbf{r})$ [3-5].

The Ω potential of the system of electrons located in thermodynamic equilibrium at $T \neq 0$ is defined by the minimum value of the functional [4, 5]

$$\Omega = \int V(\mathbf{r})\, n(\mathbf{r})\, d\mathbf{r} + \frac{e^2}{2} \iint \frac{n(\mathbf{r})\, n(\mathbf{r}')\, d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} + G(n,\ T) - \mu \int n(\mathbf{r})\, d\mathbf{r}, \tag{1}$$

where

$$G(n,\ T) = T_s(n,\ T) - TS_s(n,\ T) + F_{xc}(n,\ T), \tag{2}$$

relative to variations of the electron density $n(\mathbf{r})$. From this it follows that the distribution $n(\mathbf{r})$ can be determined if the form of universal functional (2) is known. However, its exact form for inhomogeneous electron systems is unknown, and therefore various approximations are used. One most widely used is the local density functional approximation [2, 5]

$$G(n,\ T) = \int [t_s^h(n,\ T) - TS_s^h(n,\ T) + f_{xc}^h(n,\ T)]\, n(\mathbf{r})\, d\mathbf{r}. \tag{3}$$

Substituting Eq. (3) into Eq. (1) and minimizing the latter, we obtain an equation for determination of the electron density in the form

$$V(\mathbf{r}) + e^2 \int \frac{n(\mathbf{r}')\, d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} + \mu^h(n,\ T) - \mu = 0, \tag{4}$$

where

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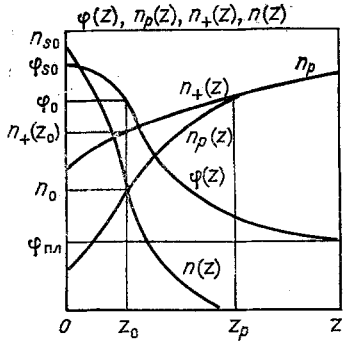

Fig. 1. Distribution of electrostatic potential $\varphi(z)$, plasma electron density $n_p(z)$, and ion density $n_+(z)$, and ESL electron density $n(z)$ on plasma–dielectric boundary.

$$\mu^h(n, T) = \delta G^L(n, T)/\delta n \tag{5}$$

is the chemical potential of a homogeneous electron system with density n at temperature T.

The quantity $\mu^k(n, T)$ is determined by the sum of the ideal component and a contribution produced by interaction of the electrons, dependent on the degree of degeneration and nonideality of the electron system [6].

Considering that the ESL is a nondegenerate electron system, on the basis of the expression for free energy of a slightly nonideal system at $\eta = (4\pi n l^3)^{1/2} \ll 1$ [7] we obtain

$$\mu^h/kT = \ln[(1/2)\Lambda^3 n(1 + 0.1768\Lambda^3 n + \ldots)] - (1/2)\eta - (1/6)\eta^2[\ln(\eta/\xi) + 1] - \eta^2\xi^{-3}[Q(-\xi) - (1/2)E(-\xi)], \tag{6}$$

where $\Lambda = (2\pi\hbar^2/mkT)^{1/2}$; $\xi = (2\pi)^{1/2} l/\Lambda$.

Using the analogous expression for a nonideal electron system presented in [6] for $1 < \Gamma < 155 \pm 10$, where $\Gamma = l/n^{1/3}$, we will have

$$\mu^h/kT = \ln[(1/2)\Lambda^3 n(1 + 0.1768\Lambda^3 n + \ldots)] - 0.143\Gamma + 0.75\ln\Gamma + 0.27. \tag{7}$$

The external field potential V(r) for the electron surface layer is equal to the sum of the potentials of the dielectric surface atoms and the plasma ions located in this layer.

The value of the dielectric surface atom potential is determined with a Heine–Abarenkov type screened pseudopotential approximation [8]

$$U_s(r) = -\frac{R_m}{r}[A_s \operatorname{ch} d + (A_0/d)(\operatorname{sh} d - d \operatorname{ch} d)]\exp(-ar), \tag{8}$$

where $a = 2[(3\pi^2 n_V)^{1/3}/(\pi\hbar^2/me^2)]^{1/2}$; $d = aR_m$; $A_s = Zve^2/R_m$; A_0 and R_m are the surface atom core parameters, the values of which are presented for various elements in [9].

The electrostatic potential $\varphi(r)$ created by plasma ions and electrons in the ESL is determined with the Poisson equation. The ion distribution in the ESL is approximated by a homogeneous positive background with density $n_+(z_0)$ (Fig. 1).

Thus, we find that

$$V(\mathbf{r}) + e^2\int\frac{n(\mathbf{r}')\,d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} = \sum_i U_s(\mathbf{r} - \mathbf{R}_i) + e\varphi(\mathbf{r}) \tag{9}$$

and

$$\nabla^2\varphi(\mathbf{r}) = -(e/\varepsilon_D)[n(\mathbf{r}) - n_+(z_0)]. \tag{10}$$

To calculate the distributions n(r) and $\varphi(r)$ in the ESL with Eqs. (4)-(10) it is necessary to know the boundary conditions and the total number of electrons in the ESL.

The boundary conditions can be found from the following considerations. It is known that the value of the floating potential φ_p, to which the surface of an isolated solid body interacting with a plasma is charged, is determined by commencing from the equality of electron and

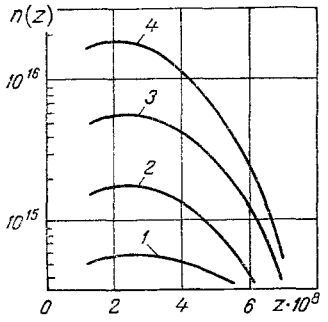

Fig. 2

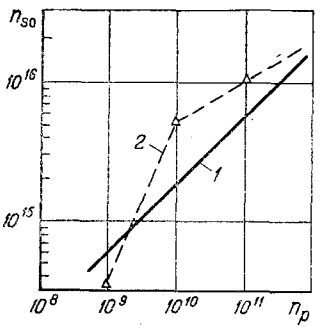

Fig. 3

Fig. 2. Electron density distribution in ESL for interaction of SiO_2 with argon gas discharge at $T_e = 1.85 \cdot 10^4$ °K: 1) $n_p = 10^9$ cm^{-3}; 2) 10^{10}; 3) 10^{11}; 4) 10^{12} cm^{-3}. n(z), cm^{-3}; z·10^8, cm.

Fig. 3. Electron density on SiO_2 surface interacting with argon plasma discharge: 1) calculated values; 2) data obtained from experimental dependence of ESL capacitance on frequency. n_{s_0}, cm^{-3}; n_p, cm^{-3}.

ion flux densities moving from the plasma onto the surface. From this it follows that the value of φ_p lies in the plane in which these densities are equal to each other. It follows from physical considerations that this plane is most probably a plane parallel to the surface and passing through z_0 (Fig. 1). Thus $\varphi_0 = \varphi_p$.

This fact allows us to find the values of the electron density n_0, the potential φ_0, and the field intensity E_0 in the plane passing through z_0 commencing from physical models used for determination of the properties of plasma Langmuir layers [10].

The total number of electrons in the ESL can be calculated from the condition of electrical neutrality of the entire double layer as a whole (Fig. 1):

$$\int_0^{z_p} [n_p(z) + n(z) - n_+(z)]\, dz = 0. \tag{11}$$

Calculations of electron-density and potential distributions in the ESL for the cases of interaction of a gas-discharge plasma with silicon (SiO_2) and aluminum (Al_2O_3) oxides show that the electron density in the ESL is 4-6 orders of magnitude higher than the electron density in the plasma n_p, the voltage drop in the layer is negligibly small in comparison to the potential drop in the Langmuir layer, and the main charge of the ESL is concentrated in a region $(3\text{-}5) \cdot 10^{-8}$ cm in extent. The results obtained for the case of an SiO_2–argon gas discharge are shown in Figs. 2 and 3. It is evident that the ratio $n_{s_0}/n_p = (2\text{-}50) \cdot 10^4$. To confirm the calculated values obtained the electron density on the SiO_2 surface was determined from experimental data (Fig. 3, curve 2) by the method described below.

To determine the value of n_{s_0} from the experimental data the frequency dependence of ESL capacitance $C(\omega)$ obtained from the equation for rate of change of electron density in the ESL (kinetic equation) in the presence of an ac voltage $V_m \sin\omega t$ was compared to the experimental dependence of this capacitance, found in turn by comparing the frequency dependences of capacitance of floating probe–plasma and SiO_2–plasma systems obtained in [11] by the plasma capacitor method for a gas-discharge plasma in argon.

The resulting rate of change of the electron density in the ESL is determined by the difference between the rate of electron arrival from the plasma g_e and the rate of electron recombination with plasma ions on the surface, i.e.,

$$dn_s/dt = g_e - \alpha_e n_s n_+(z_0). \tag{12}$$

Since in the equilibrium state $dn_s/dt = 0$, then

$$\alpha_e = g_e/n_{s0} n_+(z_0). \tag{13}$$

From this it follows that Eq. (12) has the form

$$\frac{d}{dt}(\delta n_s) = -\frac{\delta n_s}{\tau}, \tag{14}$$

where

$$\delta n_s = n_s - n_{s0}, \tag{15}$$

$$\tau^{-1} = g_e/n_{s0}. \tag{16}$$

Solution of kinetic equation (14) in the presence of an ac voltage $V_m \sin\omega t$ leads to an expression for the frequency dependence of ESL capacitance of the form [12]

$$C(\omega) = C_s/(1 + \omega^2\tau)^2, \tag{17}$$

where

$$C_s = dQ_{s0}/d\varphi_{s0} \tag{18}$$

is the maximum ESL capacitance.

It follows from Eq. (17) that knowing the frequency dependence $C(\omega)$, one can determine the parameters C_s, τ, and consequently, find the electron density on the dielectric surface interacting with the plasma.

As is evident from Fig. 3, the values of the electron density on the SiO_2 surface determined by calculation (curve 1) and with the aid of experimental data (curve 2) coincide well.

NOTATION

$V(\mathbf{r})$, external field potential; k, Boltzmann's constant; e, electronic charge; μ, chemical potential of electron system; T, temperature; T_s and S_s, kinetic energy and entropy of noninteracting electron system; F_{xc}, contribution to system free energy from exchange and correlation effects; t_s^h, S_s^h, f_{xc}^h, kinetic energy, entropy, and contribution to free energy by exchange and volume effects per electron for homogeneous system of density n; l, amplitude of electron Coulomb scattering; h, normalized Planck's constant; m, mass of the electron; $Q(-\xi)$, $E(-\xi)$, transcendental functions; n_V, surface atom valence electron density; Z_V, number of surface atom valence electrons; R_i, radius vector of surface atom i; ε_D, absolute dielectric permittivity of dielectric; Z_p, length of plasma Langmuir layer; n_{s0}, n_s, electron density on dielectric surface interacting with plasma in equilibrium state and in presence of ac voltage; V_m, ω, amplitude and frequency of ac voltage; α_e, electron–ion recombination coefficient on dielectric surface; Q_{s0}, ESL charge; φ_{s0}, dielectric surface potential; T_e, plasma electron temperature.

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CHARACTERISTICS OF A LONGITUDINAL GLOW DISCHARGE

R. F. Yunusov

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A system of equations has been solved that describes the positive column in a glow discharge in a cylindrical channel bearing a longitudinal gas flow.

Glow discharges (GD) have been widely used recently in electronics, various technological processes, plasmochemical reactors, and so on. It is therefore important to examine the distributions of the internal GD parameters such as electron concentration, electric field strength, and neutral-particle temperature as affected by external conditions. Some regularities have been established in the electric fields and electron concentrations in longitudinal GD [1-4]. Measurements have been made [5-8] on the temperature patterns in axially symmetrical discharges bearing longitudinal gas flows. In those papers, the neutral-particle temperature in the positive GD column was calculated by solving the energy-conservation equation with a given distribution for the internal heat sources over the positive column. However, in a GD in a gas flow, the output from the internal heat sources varies along the axis and is in fact an unknown function to be determined. It is much more complicated to determine the parameters E, n_e, and T together. In [9], a solution was obtained numerically, and the distributions of the parameters in flowing hydrogen were obtained for certain conditions. However, it is preferable to derive analytic solutions in order to elucidate the general regularities in convective heat transfer in a glow discharge, and these are also useful in checking and improving numerical-calculation programs for more complicated cases.

In the proposed model, the positive column in a cylindrical channel is considered in relation to three forms of particle: neutral particles, electrons, and singly charged positive ions. The following form can be given [10, 11] to the stationary equations of continuity for the electrons and positive ions:

$$\operatorname{div}\vec{\Gamma}_i = \nu n_e - \delta n_e n_i, \tag{1}$$

$$\operatorname{div}\vec{\Gamma}_e = \nu n_e - \delta n_e n_i. \tag{2}$$

The following equations describe the charged-particle flux densities across any area in the discharge zone:

$$\vec{\Gamma}_i = n_i\vec{v} - D_i\nabla n_i + n_i\mu_i\vec{E}, \tag{3}$$

$$\vec{\Gamma}_e = n_e\vec{v} - D_e\nabla n_e - n_e\mu_e\vec{E}, \tag{4}$$

where the first term on the right incorporates the convective charge transport, the second arises from diffusion, and the third from electric-field drift. We add and subtract (1) and (2) term by term and use the condition for plasma quasineutrality ($n_i \approx n_e = n$) with (3) and (4) to get

$$2\operatorname{div}(n\vec{v}) - \operatorname{div}[(D_e + D_i)\nabla n] + (\mu_i - \mu_e)\, n \operatorname{div}\vec{E} + (\mu_i - \mu_e)\cdot\vec{E}\nabla n = 2\nu n - 2\delta n^2, \tag{5}$$

$$\operatorname{div}[(D_e - D_i)\nabla n] + (\mu_i + \mu_e)\vec{E}\nabla n + (\mu_i + \mu_e) n \operatorname{div}\vec{E} = 0. \tag{6}$$

It follows from (6) and (5) that

$$\operatorname{div}(n\vec{v}) = \operatorname{div}(D_a\nabla n) + \nu n - \delta n^2, \tag{7}$$

where $D_a = (D_e\mu_i + D_i\mu_e)/(\mu_e + \mu_i)$.

If the condition $D_a/R^2 \gg n\delta$ is obeyed at any point in the discharge zone, bulk recombination is less important than ambipolar charge diffusion to the wall, and it can be neglected.

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