PLASMA SURFACE STATES IN SEMICONDUCTORS

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The existence of an electron work function in semiconductors results in depletion of electrons near the semiconductor surface. The presence of such a surface quantum charge leads to a bending of the conduction band near the surface and to the existence of one or several surface levels. A modification of the classical screening theory is offered.

1. INTRODUCTION

IT is known that application of an electric field to the surface of semiconductors (or the presence of some impurities on the surface) causes a near-surface bending of the energy bands. At the appropriate polarity, this bending forms a near-surface potential well for the conduction electrons. Schrieffer was the first to note[1] that in such a well there can exist one-dimensional bound states for the conduction electrons. In the papers of Duke and Alferieff,[2,3] a detailed analysis was presented for such states in a semi-insulator, and account was taken of the influence of the bound electrons on the form of the near-surface well.

In this paper we pay attention to the fact that the near-surface bending of the bands should exist in an impurity semiconductor (henceforth, for concreteness, we shall have in mind an n-type semiconductor) in the absence of any external influence on the surface. On the boundary of any crystal there exists a jump of the potential energy of the electron, which determines the electron work function. In semiconductors the work function greatly exceeds the characteristic energy of the conduction electrons (the Fermi energy or the thermal energy). Therefore the wave function of the conduction electron should have a node on the wall, as a result of which there is produced a near-surface region from which the electrons are depleted, with a thickness on the order of the characteristic de Broglie wavelength of the electron. The resultant positive near-wall charge can be regarded as equal to the product of the concentration of the impurity ions by the thickness of this region. This surface quantum charge causes bending of the bands near the boundary of the semiconductor. As shown in this paper, there always exists in the produced potential well at least one surface level, which we call the surface plasma level, since the charge producing it is due entirely to the existence of the electron plasma. The energy of this level is on the order of the product of the plasmon energy by the square root of the ratio of the Debye radius to the effective Bohr radius of the conduction electron. The distance between the levels, if there are several of them, will be of the same order of magnitude.

The calculation of the surface plasma levels called for a certain refinement of the classical Debye–Huckel screening theory. Screening of the surface quantum charge (as incidentally of any other positive surface charge) can seemingly always be calculated by classical theory, provided the characteristic de Broglie wavelength is at least several times smaller than the classical Debye radius, i.e., the usual quasiclassical conditions are satisfied. It is shown in the present paper, however, that the use of the classical theory for the one-dimensional distribution of an attraction potential calls for much more stringent conditions, namely, for the existence of a large number of bound states in the well formed by the attraction potential. For this purpose, the characteristic de Broglie wavelength should be at least several dozen times smaller than the dimension of the potential well. Thus, with increasing de Broglie wavelength, violation of the classical conditions occurs from the side of the bound states. Whereas the space of the continuous spectrum can still be quasiclassical so long as the characteristic de Broglie wavelength is smaller than the wall dimension, the bound states will no longer be quasiclassical and this leads to an appreciable change in the screening terms. In most semiconductors, as a rule, the de Broglie wavelength is not small enough, so that the proposed refinement of the screening theory may possibly find applications other than in the problem of surface plasma levels. We therefore present here also results for the modification of the screening terms in the case of a linear charge and a point charge.

For a repulsion potential, no modification is required at all so long as the usual conditions for the quasiclassical character of the potential are satisfied.

2. QUANTUM SURFACE CHARGE AND SURFACE PLASMA LEVELS

Let us find the density of the quantum surface charge for the model of the gas of free electrons in a plate representing a one-dimensional potential well with infinitely high walls at $x = 0$ and $x = 1$. The wave function of the electron in such a plate is given by

$$\Psi(\mathbf{r}) = \frac{\sqrt{2}}{(SL)^{1/2}} \exp\{i(k_y y + k_z z)\} \sin k_x x. \tag{1}$$

Here S is the area of the plate; k_y and k_z are the projections of the wave vector of the electron; $k_x = \pi l/L$, $l = 1, 2, 3, \ldots$.

The electron density n depends only on the coordinate x:

$$n(x) = \frac{4}{(2\pi)^2 L} \sum_{l=1}^{\infty} \int dk_y \, dk_z \sin^2 k_x x f(\varepsilon_k), \tag{2}$$

where

$$f(\varepsilon_k) = (e^{(\varepsilon_k - \mu)/T} + 1)^{-1}, \quad \varepsilon_k = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2), \quad (3)$$

μ is the chemical potential, and T is the temperature in energy units. We assume, for simplicity, that the electron dispersion is isotropic and quadratic.

We change over from integrals with respect to the transverse quasimomentum to an integral with respect to the transverse energy:

$$\varepsilon = \frac{\hbar^2}{2m}(k_y^2 + k_z^2), \quad (4)$$

so that

$$n(x) = \frac{m}{\pi\hbar^2} \frac{1}{L} \sum_{l=1}^{\infty} \int_0^{\infty} d\varepsilon \left(1 - \cos\frac{2\pi l x}{L}\right) f(\varepsilon + E_l), \quad (5)$$

with

$$E_l = \frac{\hbar^2 k_x^2}{2m} = \frac{\hbar^2\pi^2}{2mL^2} l^2. \quad (6)$$

Thus, the electron density is the sum of two terms, one independent of the coordinate x and equal to the average concentration of the donor atoms n_0 (if we regard them as fully ionized), and an alternating-sign term $\nu(x)$ containing the cosine of the right side of (5). The integral of the last term over the thickness of the plate is equal to zero. If this thickness is much larger than the characteristic de Broglie wavelength of the electrons, then an appreciable contribution is made to the sum over l by a large number of terms. Then the $\nu(x)$ dependence can be readily obtained by using the Euler summation formula,[4] which makes it possible to accurately replace the summation over l by integration in similar cases. Thus,

$$\nu(x) \approx -\frac{m}{\pi\hbar^2 L} \left[\int_0^{\infty} dl \int_0^{\infty} d\varepsilon \cos\frac{2\pi l x}{L} f(\varepsilon + E_l) - \frac{1}{2}\int_0^{\infty} d\varepsilon f(\varepsilon) \right]. \quad (7)$$

We have neglected here terms of higher order of smallness in the parameter representing the ratio of the characteristic de Broglie wavelength to the thickness of the plate. The first term in the right side of (7) describes the sharp spike of the electron deficiency near the boundaries of the plate, representing a quantum surface charge. The second term does not depend on the coordinate and describes the homogeneous increase of the concentration in the thickness, such that the total number of electrons remains constant.

So far we have not taken into account the self-consistent electric field that results from the excess or shortage of electrons. This field (which we shall calculate below) causes a shift of the excess compensating electrons to the near-surface regions with characteristic dimensions of the order of the Debye screening length. The action of the self-consistent field on the near-surface electron-density deficit turns out to be, however, much less significant, as will be seen from what follows. Therefore the surface density of the quantum charge can be determined with the aid of (7).

The first term in (7) decreases in the interior of the plate like $\exp(-2mTx^2/\hbar^2)$ in the case of non-degenerate electrons, and like

$$\frac{3}{(2k_F x)^2}\left(\frac{\sin 2k_F x}{2k_F x} - \cos 2k_F x\right)$$

in the case of complete degeneracy ($\hbar k_F$ is the Fermi

momentum). In both cases the integral charge produced by the first term is formed over distances on the order of the characteristic de Broglie wavelength. When the thickness of the plate is much larger than this length, the near-surface deficit and the volume excess of the electrons hardly overlap in space, and the surface density of the quantum charge can be determined as the integral of either the first term of the right side of (7) or the second over half the thickness of the plate. Obviously, the latter is simpler. Thus, the surface density of the quantum charge Q is given by the expression

$$Q = e n_0 \lambda, \quad (8)$$

where λ is the effective thickness of the charged layer next to the wall:

$$\lambda = \left(\frac{\pi\hbar^2}{8mT}\right)^{1/2} \frac{F_0}{F_{1/2}}. \quad (9)$$

Here F_0, $F_{1/2}$, and $F_{-1/2}$ are the standard Fermi integrals,[5] which depend on the argument μ/T, the chemical potential μ being determined from the concentration by means of the equation

$$n_0 = N_c F_{1/2}, \quad N_c = 2(mT/2\pi\hbar^2)^{3/2}. \quad (10)$$

In the case of strong degeneracy of the electrons $F_j = [\Gamma(j+2)]^{-1}(\mu/T)^{j+1}$, so that $\lambda = \frac{3}{8}\pi(\hbar^2/2m\mu)^{1/2}$. In the case of a nondegenerate electron gas $F_j = \exp \mu/T$, so that $\lambda = (\pi\hbar^2/8mT)^{1/2}$.

As already mentioned, owing to the influence of the self-consistent field, the concentration of the excess electrons screening the quantum surface charge differs from zero only in the near-surface region, with the characteristic thickness on the order of the Debye screening length κ^{-1}, where

$$\kappa^2 = \frac{4\pi n_0 e^2}{\varepsilon T} \frac{F_{-1/2}}{F_{1/2}}. \quad (11)$$

If this length is much larger than the effective thickness of the quantum-charge layer, then, just as for the model of nondegenerate electrons, we can speak of weak spatial overlap of the distributions of the quantum surface deficit and of the screening excess of electrons. We can then regard the quantum charge as a surface charge with a density given as before by formula (8). This charge produces near the surface a field

$$E = \frac{4\pi}{\varepsilon} Q = \frac{emT}{\varepsilon\hbar^2} F_0. \quad (12)$$

For a degenerate electron gas the field depends only on the concentration of the electrons and on the dielectric constant of the semiconductor, which for most semiconductors is of the order of 10, so that at concentrations larger than 10^{18} cm^{-3} the field reaches values on the order of hundreds of kilovolts per centimeter and higher. This greatly exceeds the field usually produced by different surface contaminations. Bearing in mind the possibility of such contaminations, we shall not consider concentrations smaller than 10^{16} cm^{-3}, since the field of the surface quantum charge does not exceed several kV/cm in this case.

The field of the surface quantum charge causes bending of the conduction band, producing a near-surface potential well for the electrons. In the usual classical theory of screening, it is easy to find the course of the electrostatic potential φ under the boundary condition
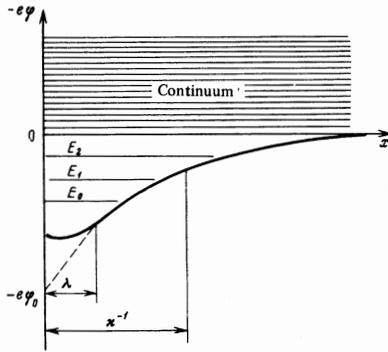
FIG. 1. Plot of the potential energy of the electron near the surface and surface plasma levels.

set by the field of the surface quantum charge (12):

$$\varphi = -\frac{4\pi Q}{\varepsilon \varkappa} e^{-\varkappa x}. \tag{13}$$

This expression is valid at distances larger than the thickness of the surface quantum-charge layer λ. Within the limits of this layer the potential can be regarded as constant and equal to its value at $x = 0$.

The dashed line of Fig. 1 shows the solution (13), and the solid line shows the true variation of the potential. This variation is given for the non-degenerate case. In the case of extreme degeneracy, the course of the potential in the layer λ has a small oscillating increment with an amplitude smaller by a factor of $\lambda \varkappa$ than the depth of the potential well produced as a result of the aforementioned oscillations in the distribution of the quantum-charge density. In the degenerate case there exists also other oscillations connected with the singular character of the screening.[6] When $\lambda \varkappa < 1$ the latter occur at distances that are larger than $\varkappa^{-1}$, with a potential that is already quite small, so that the oscillations likewise have no significant effect in our problem.

In the near-wall potential well there can be produced bound states—surface plasma levels, likewise shown in Fig. 1. Let us find the value of the electric charge due to the electrons localized on these levels. Obviously, the concentration of the bound electrons n_b depends only on the coordinate x and is determined by

$$n_b(x) = \frac{1}{\pi} \frac{m}{\hbar^2} \sum_\beta |\psi_\beta(x)|^2 \int_0^\infty d\varepsilon f(\varepsilon + E_\beta), \tag{14}$$

where $\psi_\beta(x)$ is the wave function of the electron in a state with binding energy E. Since $E_\beta < 0$, it follows that $f(\epsilon) < f(\epsilon + E_\beta)$, so that the integral value of the charge density of the bound electrons per unit area, Q_b, satisfies the inequality

$$Q_b = e \int_0^\infty n_b(x)\, dx > 4NQ, \tag{15}$$

where Q is the surface density of the quantum charge, determined by formula (8), and N is the total number of levels in the near-wall potential well. Thus, if surface plasma levels exist, then the charge of the electrons localized on them is at least four times larger than the surface quantum charge and is obviously of the opposite sign. The foregoing classical theory of screening does not answer the question of what compensates for this

excess of negative charge. We present below a more consistent semiclassical theory of screening, which answers this question and makes it possible to determine the limits of applicability of the classical theory.

3. SEMICLASSICAL THEORY OF SCREENING IN THE PLASMA OF AN ELECTRONIC SEMICONDUCTOR

To explain the features of screening in the case when the Debye screening length is only several times larger than the de Broglie wavelength, let us consider first the simpler problem of screening of a flat charge imbedded in the electron plasma of a semiconductor. We can imagine, for example, that this charge is due to a plane layer of excess concentration of ionized donor impurity, on both sides of which there extends a semiconductor with uniform concentration. In our case it is important here that this flat charge does not give rise by its presence to the sharp potential jump that takes place on the boundary of the semiconductor, and causes only a smooth change of the potential, connected with the screening.

We shall see that screening of a positive flat layer is qualitatively different from screening of a negative layer. We shall therefore consider first a positive flat layer, near which the energy of the electron forms a one-dimensional potential well.

In determining the electron density, we start from the general quantum-mechanical formula for the electron concentration

$$n(\mathbf{r}) = 2 \sum_M |\Psi_M(\mathbf{r})|^2 f(\varepsilon_M). \tag{16}$$

The wave function of the electron $\Psi_M(\mathbf{r})$ and its energy ϵ_M are given by

$$\Psi_M(\mathbf{r}) = L^{-1} e^{i(k_y y + k_z z)} \psi_s(x),$$
$$\varepsilon_M = \varepsilon + E_s, \quad \varepsilon = \frac{\hbar^2}{2m}(k_y^2 + k_z^2), \tag{17}$$

where L is a normalization length. Motion parallel to the plane with concentrated charge (x = 0) is described by plane waves, and motion in the x direction is described by the function $\psi_s(x)$, where s is a quantum number describing both the state of the continuum and the states of the discrete spectrum and the well. The symbol M denotes, obviously, the aggregate of the projections of the wave vector k_y and k_z and of the symbol s. The wave function $\psi_s(x)$ will be determined by different methods, depending on whether it corresponds to the state of the continuum $\psi_c(x)$ or to the state of the discrete spectrum $\psi_\beta(x)$.

For the continuum states we use the quasiclassical approximation

$$\psi_c(x) = \sqrt{\frac{2m}{\tau_c p_c(x)}} \exp\left\{ \frac{i}{\hbar} \int_{-L/2}^x p_c(x')\, dx' \right\} \tag{18}$$

where

$$p_c(x) = \sqrt{2m(E_c + e\varphi(x))}, \tag{19}$$

τ_c is the period of the classical motion from the point x = −L/2 to the point x = L/2 and back:

$$\tau_c = 2m \int_{-L/2}^{L/2} p_c^{-1}(x)\, dx. \tag{20}$$

The wave function (18) is obviously normalized to unity.[1]

Expression (16) with allowance for (17)–(20) leads to

$$n(x) = \frac{2}{(2\pi)^2} \int dk_y\, dk_z \left\{ \sum_c \frac{2mf(\varepsilon + E_c)}{\tau_c p_c(x)} + \sum_\beta |\psi_\beta(x)|^2 f(\varepsilon + E_\beta) \right\}. \tag{21}$$

In the quasiclassical approximation

$$\tau_c^{-1} = \Delta E_c / 2\pi\hbar, \tag{22}$$

where ΔE_c is the distance between the levels of the continuum. Replacing in (21) the summation over c by integration with respect to E_c and changing over from integration with respect to k_y and k_z to integration with respect to ε, we obtain

$$n(x) = n_c(x) + n_b(x),$$

where $n_c(x)$ is the density of the electrons of the continuum:

$$n_c(x) = \frac{2\sqrt{2}}{(2\pi)^2} \left(\frac{m}{\hbar^2}\right)^{3/2} \int_0^\infty d\varepsilon \int_0^\infty \frac{dE_c}{\sqrt{E_c + e\varphi}} f(\varepsilon + E_c), \tag{23}$$

and $n_b(x)$ is the density of the bound electrons, determined by formula (14). In the expression for the density of the electrons of the continuum it is convenient to add and to subtract the integral with respect to E_c from $-e\varphi$ to 0. Then expression (23), together with the added integral, leads to the classical formula for the electron density

$$n_{cl} = N_c F_{1/2}\left(\frac{\mu + e\varphi}{T}\right), \tag{24}$$

And the indicated subtracted integral gives the nonclassical decrease of the electron density

$$\Delta n_c = -\frac{4\sqrt{2}}{(2\pi)^2} \left(\frac{m}{\hbar^2}\right)^{3/2} \int_0^\infty d\varepsilon \int_0^{\sqrt{e\varphi}} dy\, f(\varepsilon + y^2 - e\varphi), \tag{25}$$

so that $n_c(x) = n_{cl}(x) + \Delta n_c(x)$. This decrease of the electron density arises here principally as a result of the increase of the velocity of the electrons of the continuum in the attracting field. The quasiclassical wave function (18) is inversely proportional to the square root of this velocity.

The classical theory of screening contains neither the nonclassical decrease Δn_c nor the term n_b due to the presence of the bound electrons. We shall show that in the classical limit these terms in fact cancel each other. Using the expression for the wave function $\psi_\beta(x)$ of the type (18), with allowance for (22), we get

$$\psi_\beta^2(x) = \frac{\sqrt{2m}}{2\pi\hbar} \frac{\theta(E_\beta + e\varphi)}{\sqrt{E_\beta + e\varphi}} \Delta E_\beta, \tag{26}$$

where $\theta(x)$ is the step function, equal to zero and unity for negative and positive arguments, respectively. Changing over from summation with respect to the energies E_β to integration, and making the change of variable $\sqrt{E_\beta + e\varphi} = y$, we can easily obtain an expression that coincides exactly with (25), but is of opposite sign.

The fact of local compensation of the increase of the electron density as a result of the presence of bound

electrons and the decrease of the density of the electrons of the continuum as a result of their acceleration in an attracting field contains the answer to the question raised at the end of Sec. 2. Thus, in the classical theory (in the region where this theory is applicable) the charge density which enters the Poisson equation should not contain terms due to the electrons of the bound states.

The use of the quasiclassical function of the bound state in the form of (26) and the replacement of summation by integration are valid only at a sufficiently large number of bound states in the well. This proves the statement made above concerning the limits of applicability of the classical theory of screening. On the other hand, if the number of bound states in the well is small, then expressions (14) and (25) no longer cancel each other locally, and the character of the screening changes. In this case the excess of electrons, due to the bound states, and the deficit due to the acceleration, are somewhat separated spatially, so that there is only integral compensation.

Expression (14) for the density of the bound electrons can be reduced to the form

$$n_b(x) = 4n_0\lambda \sum_\beta \frac{F_0((\mu - E_\beta)/T)}{F_0(\mu/T)} |\psi_\beta(x)|^2, \tag{27}$$

where the length λ is given by formula (9).

We shall henceforth assume for simplicity that in the well there exists only one level with energy equal to $-E_0$, which is described by the wave function $\psi_0(x)$. In addition, we shall assume that the potential energy of the electron is much lower than its characteristic kinetic energy. Under these conditions, the expression for the concentration is given by

$$n_{cl} = n_0 + \Delta n_{cl}, \quad n = n_0 + \Delta n_{cl} + \Delta n_c + n_b, \tag{28}$$

where

$$\Delta n_{cl} = n_0 \frac{e\varphi}{T} \frac{F_{-1/2}}{F_{1/2}}, \tag{29}$$

$$\Delta n_c = -\frac{2}{\sqrt{\pi}} n_0 \left(\frac{e\varphi}{T}\right)^{1/2} \frac{F_0}{F_{1/2}}, \tag{30}$$

$$n_b = 4n_0\lambda\psi_0^2(x). \tag{31}$$

Thus, the problem of screening reduces to a simultaneous solution of the Poisson equation

$$\frac{d^2\varphi}{dx^2} = -\frac{4\pi e}{\varepsilon}\left[-n_0\frac{e\varphi}{T}\frac{F_{-1/2}}{F_{1/2}} + \frac{2}{\sqrt{\pi}}n_0\left(\frac{e\varphi}{T}\right)^{1/2}\frac{F_0}{F_{1/2}} - 4n_0\lambda\psi_0^2(x) \right], \tag{32}$$

and the Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_0}{dx^2} - e\varphi\psi_0 = -E_0\psi_0. \tag{33}$$

This system should be solved separately in each concrete case. In the next section we present a solution of this system by a variational method for the problem of screening of a surface quantum charge.

The system (32)–(33) (or the more general system for any number of bound states) corresponds to the Hartree self-consistent field approximation. Generally speaking, this system could be supplemented with exchange terms (the Hartree–Fock approximation). These terms, however, would lead in our case to small corrections of the order of $(\lambda\kappa)^2$.[7,8]

If the charged plane carries a negative charge, then the potential is $e\varphi < 0$, and in this case there are no

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[1] Naturally, such a quantum-mechanical approach is valid only when the electron mean free path exceeds the characteristic dimension of the potential well, which is of the order of κ^{-1}.

bound states. It is now necessary to use for the wave function of the continuum electrons an expression of the type (26), which contains a theta function. Formula (16) then leads directly to the classical expression (24). Thus, screening of the negative charge by electrons always has a classical character, provided, of course, that the potential satisfies the quasiclassical condition.

Analogous calculations can be carried out also to determine the screening terms for charge distributions having a cylindrical or spherical symmetry, starting from the general formula (16) and using semiclassical wave functions $\Psi_M(r)$ for cylindrical and spherical potential wells. The general property of compensation of the non-classical decrease of the electron density Δn_c by the excess due to the electrons of the bound states in an extremely classical potential well, i.e., when many levels are contained in the well, is retained in this case. On the other hand, if the number of levels is small, then it is necessary to take separate account of the two indicated terms in the Poisson equation. We present without derivation the result obtained for the nonclassical decrease of the electron density

$$\Delta n_c = -\frac{2}{(2\pi)^2} \int_{\Omega_\varphi} dk_x\, dk_y\, dk_z\, [e^{(\varepsilon_k - e\varphi - \mu)/T} + 1]^{-1},$$

$$\varepsilon_k = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2). \qquad (34)$$

The integration region Ω_φ is different for different symmetries of the potential $\varphi(r)$. If this is a flat distribution which varies only along the x axis, then the region Ω_φ is a flat layer perpendicular to the x axis and extending from $k_x = -(2me\varphi/\hbar^2)^{1/2}$ to $k_x = (2me\varphi/\hbar^2)^{1/2}$. If the potential has cylindrical symmetry with respect to the z axis, then the region Ω_φ is a cylinder of radius $(2me\varphi/\hbar^2)^{1/2}$, the axis of which coincides with the z axis. If the potential has spherical symmetry, then the region Ω_φ is a sphere of radius equal to $(2me\varphi/\hbar^2)^{1/2}$.

For a plane layer, expression (34) is identical with (25). The classical part of the electron density is always given by (24). When the potential energy of the electron is smaller than its characteristic kinetic energy, the integrals (34) can be easily expressed in terms of the standard Fermi integrals. We can thus obtain the following results.

Cylindrical case:

$$\Delta n_c = -n_0 \frac{e\varphi}{T} \frac{F_{-1/2}}{F_{1/2}}, \qquad (35)$$

$$n_b(\rho) = \left(\frac{mT}{2\pi\hbar^2}\right)^{1/2} F_{-1/2} \frac{1}{\pi} \psi_0^2(\rho), \quad \int_0^\infty \rho\psi_0^2(\rho)\, d\rho = 1. \quad (36)$$

It is interesting to note that in this case the nonclassical decrease Δn_c cancels exactly the classical increment Δn_{cl}, so that the screening is effected only as a result of the density of the bound electrons $n_b(\rho)$.

Spherical case:

$$\Delta n_c = -\frac{4}{3\sqrt{\pi}}\left(\frac{e\varphi}{T}\right)^{3/2} [(e^{-\mu/T} + 1)F_{1/2}]^{-1}, \qquad (37)$$

$$n_b(r) = \frac{1}{2\pi}\psi_0^2(r)\,(e^{-\mu/T} + 1)^{-1}, \quad \int_0^\infty r^2\psi_0^2(r)\, dr = 1. \quad (38)$$

It should be noted that in the spherical case the non-

classical correction Δn_c turns out to be smaller than Δn_{cl} since $\Delta n_c \sim \varphi^{3/2}$ and $\Delta n_{cl} \sim \varphi$. Therefore, the quantum effects have little influence in screening of a point charge.

4. SCREENING OF SURFACE QUANTUM CHARGE

When the classical condition for the bound states is violated, the classical screening theory developed in Sec. 2 is no longer valid. In this case, to find the electron density near the boundary, it is necessary to start from the general formula (16) in which, however, the wave functions of the electrons of the continuum $\psi_c(x)$ cannot be taken in the form (18), and must have the form

$$\psi_c^2(x) = \frac{2m}{\tau_c p_c(x)}\left[1 - \cos\frac{2}{\hbar}\int_0^x p_c(x')\, dx'\right]. \qquad (39)$$

We therefore get in lieu of (21) the following expression for the density:

$$n(x) = \frac{2}{(2\pi)^2}\int dk_y\, dk_z$$

$$\times \left\{\sum_c \frac{2m}{\tau_c p_c(x)}\left[1 - \cos\frac{2}{\hbar}\int_0^x p_c(x')\, dx'\right]f(\varepsilon + E_c) + \psi_0^2(x)f(\varepsilon - E_0)\right\}. \qquad (40)$$

If we assume the de Broglie wavelength for the electrons of the continuum to be smaller than the characteristic dimension of the potential well and the potential energy f the electrons smaller than their characteristic kinetic energy, then the term containing the cosine reduces to the density of the surface quantum charge concentrated in the narrow layer. We arrive in this case at formula (8) for the total value of discharge, and take it into account by means of a suitable boundary condition. The remaining terms of formula (40) lead to the already known expressions (29)–(31). It is therefore necessary to solve (32) and (33) with the boundary conditions

$$-\frac{d\varphi}{dx}\Big|_{x=0} = \frac{4\pi}{\varepsilon}Q, \quad \psi_0(x)\,|_{x=0} = 0. \qquad (41)$$

Solutions of Eqs. (32) and (33) is equivalent to finding the minima of the following functionals:

$$W_f = \frac{\varepsilon}{8\pi}\int_0^\infty \left(\frac{d\varphi}{dx}\right)^2 dx + \frac{n_0 e^2}{2T}\frac{F_{-1/2}}{F_{1/2}}\int_0^\infty \varphi^2\, dx$$

$$-\frac{4}{3\sqrt{\pi}}\frac{n_0 e^{3/2}}{\sqrt{T}}\frac{F_0}{F_\nu}\int_0^\infty \varphi^{3/2}\, dx + 4n_0\lambda\int_\zeta^\infty \varphi\psi_0^2\, dx, \qquad (42)$$

$$W_e = 4n_0\lambda\left[\frac{\hbar^2}{2m}\int_0^\infty \left(\frac{d\psi_0}{dx}\right)^2 dx - e\int_0^\infty \varphi\psi_0^2\, dx\right]. \qquad (43)$$

The functional (42) describes the energy of the electric field per unit surface area; it should be varied with respect to φ, taking ψ_0 to be given. The functional (43) describes the analogous per-unit energy of the electron system; it should be varied with respect to ψ_0 with φ given.

We choose the following trial functions:

$$\varphi = \varphi_0 e^{-\alpha x}, \qquad (44)$$

$$\psi_0 = \sqrt{\beta^3/2}\, x e^{-\beta x/2}. \qquad (45)$$

A function of the form (45) was used for the calculation of the near-surface states in [9]. The question of the
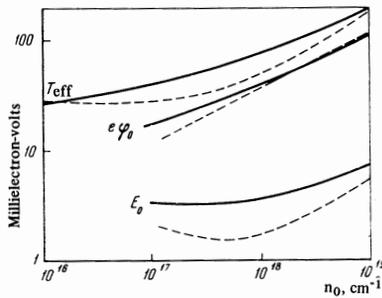
FIG. 2. Binding energy of the surface plasma level and depth of near-surface potential well for GaAs and InSb.

choice of this function for an analogous problem is discussed also in [10].

The conditions for minimizing the functionals (42) and (43) and the first boundary condition (41) enable us to find the variational parameters α, β, and φ_0, expressing them in terms of the parameter $\lambda\kappa$ of the problem. It is possible to find the range of values of this parameter in which a single level exists in the well, as was assumed in the calculations. It turns out that

$$0.33 < \lambda\kappa < 1.4. \qquad (46)$$

If $\lambda\kappa > 1.4$, then there is no bound state at all in the well, but then the proposed theory is not valid, so that this conclusion cannot be regarded as reliable. In other words, within the framework of applicability of the given theory there always exists at least one bound state.

When $\lambda\kappa \leq 0.33$, there appears a second bound state and it must be taken into consideration in the calculation, by introducing one more wave function.

It is interesting to compare the limit $(\lambda\kappa)_2 = 0.33$ with the predictions given by the classical theory. Using the form (13) for the potential well next to the wall, we can obtain on the basis of the Bohr–Sommerfeld quantization procedure the following condition for the appearance of the N-th level in the well:[2]

$$N = \left(\frac{1}{\pi\lambda\kappa}\frac{F_0^2}{F_{-\frac{1}{2}}F_{\frac{1}{2}}}\right)^{\frac{1}{2}} + \frac{1}{4} \quad \text{for} \quad (\lambda\kappa)_N^{cl} = \frac{1}{\pi}\frac{1}{(N-\frac{1}{4})^2}. \quad (47)$$

We have set here the quantity $F_0^2(F_{-1/2}F_{1/2})^{-1}$ equal to unity (it actually ranges from 1 to 1.18 when μ/T is varied from $-\infty$ to ∞). Using (47), we can find that the classical estimate for the limit $(\lambda\kappa)_2^{cl} = 0.1$, which differs greatly from $(\lambda\kappa)_2 = 0.33$.

For such semiconductors as GaAs, InSb, InAs, and GaSb, the value of $\lambda\kappa$ ranges from 0.1 to 0.6 at room temperature and from 0.3 to 0.9 at nitrogen temperature,[3] when the concentration changes from 10^{16} to 10^{19} cm^{-3}, so that the classical theory is not suitable for the description of the surface states in these compounds. The semiconductors Ge, Si, and PbTe have

somewhat smaller values of $\lambda\kappa$, but even for them the number of levels in accordance with the classical estimate is smaller than three when the concentration exceeds 10^{17} cm^{-3}.

It should be noted that calculation of a model that takes into account only one level cannot claim high accuracy, and is more illustrative in character, inasmuch as the necessary inequality $\lambda\kappa < 1$ is satisfied in the region (46) with a very small margin, so that the errors that are not accounted for by the theory, the order of which is $\lambda\kappa$, are large. However, in the region of existence of two or three levels, the proposed theory can be used for the calculation with high accuracy, whereas the classical theory results in this region in an error on the order of magnitude of the calculated quantity itself.

The order of magnitude of the binding energy E_0 of the surface plasma level and of the depth of the potential well $e\varphi_0$, obtained with the aid of the trial functions (44) and (45) for gallium arsenide (dashed curve) and indium antimonide (solid curve) at T = 300°K are shown in Fig. 2. In order to assess the validity of the series expansion in terms of $e\varphi_0$, the figure shows also the effective kinetic energy of the electron T_{eff} = $TF_{1/2}/F_{-1/2}$. The curves for E_0 and $e\varphi_0$ have been drawn only up to the concentration $n_0 = 1.4 \times 10^{17}$ cm^{-3} for GaAs and $n_0 = 10^{17}$ cm^{-3} for InSb. At low concentrations, a second level appears and the calculation must be revised, to take its appearance into account. In the calculations for InSb, we took into account the dependence of the effective mass on the concentration.[11]

The scattering of the electrons leads to a broadening of the surface plasma levels, so that to resolve the latter it is necessary to satisfy the condition

$$E_0\tau/\hbar > 1, \qquad (48)$$

where τ is the relaxation time, which can be estimated from the experimental data on the carrier mobility[12,13]. We have estimated the validity of the inequality (48) in the strong-doping region, where its violation is the most probable. The estimate shows that at $n_0 = 10^{18}$–10^{19} cm^{-3} we get $E_0\tau/\hbar \sim 10$ for InSb and $E_0\tau/\hbar \sim 1$ for GaAs. The aforementioned limitation on the relation between the mean free path and the Debye radius turns out to be less stringent than (48). The condition (48) is satisfied very well in semimetals, owing to the large mean free path at low temperatures. For these materials, however, calculation of the surface states must be carried out with allowance for the presence of two types of carriers and for the anisotropy of the dispersion law, and this complicates the theory.

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[2]The estimate of the distance between levels, referred to in the introduction, can be obtained with the aid of formulas (13) and (47).

[3]Such estimates of $\lambda\kappa$ were carried out in accordance with formula

$$\lambda\kappa = \sqrt{\frac{\pi}{8}}\frac{\hbar\omega_{pl}}{T_{eff}}, \text{ where } \omega_{pl}^2 = \frac{4\pi n_0 e^2}{\varepsilon m}, \quad T_{eff} = T\cdot\frac{F_{\frac{1}{2}}}{F_{-\frac{1}{2}}},$$

which follows from (9) and (11).

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