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Model for electrostatic screening by a semiconductor with free surface carriers

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For free carriers on a semiconductor surface, we model screening with a local but unspecified relationship between the chemical potential and the density. The carriers can reside either in surface states or in a thin conducting overlayer. The semiconductor is taken to have a dielectric constant due to polarizable bound charge, and cases both with and without bulk free carriers are considered. At small and intermediate distances from a source charge on the surface, the surface potential is similar to a screened Coulomb potential, with a characteristic surface screening length; however, the asymptotic vacuum potential is dipolar and vanishes on the surface, and the asymptotic surface potential is quadrupolar. This model may be relevant to the short screening length inferred from surface-vacancy interactions in recent scanning tunneling microscopy experiments on *p*-type InP with a (110) surface at a relatively high surface vacancy concentration. Assuming that such vacancies cause occupancy of surface free carrier states, a reasonable value for the surface free carrier density yields good agreement with the experimentally inferred surface screening length.

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I. INTRODUCTION

Reference 1 applied Debye-Hückel theory to screening of charge by a semiconductor with a dielectric constant due to polarizable bound charge and bulk free carriers, but without surface free carriers. For an isolated charge on the surface, it established that, at small and intermediate distances, the linearized surface potential is a screened Coulomb potential, with surface screening length R_s equal to the bulk screening length R_b. That result precisely corresponds to the ansatz $R_s^{exp} \approx R_b$ commonly employed to analyze scanning tunneling microscopy (STM) images of space-charge regions surrounding isolated charges on III-V(110) cleavage surfaces.[2] Such a correspondence is not surprising, since: (i) for ideal III-V(110) cleavage surfaces, the intrinsic surface states are either completely filled or completely empty, and thus cannot contribute to surface screening,[3] (ii) in the dilute defect limit the bulk charge distribution is almost unperturbed, so that flat band conditions prevail up to the surface.

More recently, Ref. 4 used room-temperature STM to determine the spatial correlations between positively charged phosphorus (P) vacancies at the (110) surface of *p*-type InP. Here the fractional concentration *c* of vacancies was significant — *c* of order 1% — but, as argued in Ref. 4, it was sufficiently low that the pair interaction $\phi_s(\rho)$ could be accurately determined from the logarithm of the pair correlation function. Their $\phi_s(\rho)$ was then fitted to the empirical form

$$\phi_s(\rho)_{fit} = \frac{Ze}{4\pi\varepsilon_0\varepsilon_{eff}} \frac{\exp(-\rho/R_s^{exp})}{\rho}, \quad \varepsilon_{eff} = \frac{\varepsilon+1}{2}. \quad (1)$$

With $Z=1$ and $R_s^{exp}=R_b$, for moderate distances this fitting equation is practically indistinguishable from the central result derived in Ref. 1 [Eq. (35)]. However, to fit their data to Eq. (1), the authors of Ref. 4 found that they had to employ the much shorter screening length $R_s^{exp} \approx \frac{1}{3}R_b$. This indicates that screening is more effective than predicted using the bulk carrier density. Note that the variation in measured potential is relatively small, so that a linearized theory should apply.

A possible mechanism for more effective screening by near-surface free carriers would be for the near-surface hole density to exceed the bulk value — hole *accumulation.* However, to obtain the surface screening length given in Ref. 4, the near-surface hole density would have to exceed the highest achievable hole density in *p*-type InP.[5] This argues against the additional screening being due to near-surface holes. Moreover, as noted in Ref. 1, photoemission[6,7] indicates that substantial hole *depletion* (rather than accumulation) occurs in freshly cleaved *p*-type InP(110) following thermal anneals similar to those of Ref. 4. If the samples of Ref. 4 were depleted, then the decreased near-surface hole density argues against additional screening due to near-surface holes. Band-bending consistent with hole depletion for *p*-type InP can be found in Ref. 8.

Another mechanism for more effective screening by near-surface free carriers would be for the fractional concentration *c* of positively charged P vacancies to attract a high density of electrons to the vicinity, thus causing *inversion* near the surface. However, the magnitude of the photoemission shift in *p*-type InP indicates depletion rather than inversion,[6,7] thus arguing against this mechanism.

It thus appears unlikely that bulk free carriers are responsible for the short screening length observed in Ref. 4. In the present work we assume that, in addition to bulk free carriers and polarizable bound charge, surface free carriers (i.e., associated with a surface band) contribute to the screening. This was suggested in Refs. 4 and 9, but the formalism was not developed. The surface free carrier assumption is consistent with photoemission data[6,7] that demonstrates mid-gap pinning of the surface Fermi level; indeed, such pinning is often attributed to a partially filled surface band.[10] Such an assumption has a long history, including Bardeen's work on the work function of semiconductors.[11]

Screening by a bulk semiconductor, thought of as a plasma of free carriers superimposed on a background of polarizable bound charge that produces a uniform dielectric constant, has already been treated by Ref. 1, assuming an unspecified but local relationship between the chemical potential and the *bulk* carrier density. At high densities this leads to Thomas-Fermi theory (where Fermi-Dirac statistics applies and the energy is essentially quantum kinetic energy), and at low densities this leads to Debye-Hückel theory (where Maxwell-Boltzmann statistics applies), but the relationship can be more complex.[12] A generalization of this model, more appropriate at microscopic length scales, is discussed in Ref. 13. These works consider screening for fields small enough that the linearized version of the theory applies.

In the same spirit as Ref. 12, we will treat the screening due to surface carriers by assuming an unspecified but local relationship between the chemical potential and the *surface* carrier density. As usual, we consider the linearized theory. We have recently studied the polarizability of conducting nanotubes using this assumption,[14] finding very good agreement with results obtained from a more microscopic theory.[15] In addition, this work considers the totality of screening of charged surface defects by a semiconductor, including bulk-free carriers, bulk bound charge (through the dielectric constant), and surface free carriers. Only the long-range properties of the defect (i.e., its charge state) and the macroscopic properties of the system (e.g., the density of free carriers) are needed to study, at distances that exceed the atomic scale, the electrostatic screening of the defect by the system. Hence the present theory should be appropriate to describe the experiments of Ref. 4.

Section II presents a model of a two-dimensional conducting film, which is used to analyze the effect of surface free carriers alone. Although directed toward free carriers due to surface states, the free carriers could also be due to a thin conducting overlayer, such as a metallic monolayer or submonolayer, or a layer of doped semiconductor. In all cases we assume the degree of freedom normal to the plane is frozen out. For any external field to penetrate the film, the film thickness must be negligible compared to the length scale associated with the screening. Section III discusses screening by such a film above a dielectric. Section IV discusses screening by a semiconductor with both bulk free and surface free carriers. Section V compares the theory with experiment of Ref. 4. Section VI provides a Summary. The Appendix gives certain calculational details.

For later reference, note the following screening lengths (two bulk, three surface) that appear in our discussion:

(i) $R_{b_0}=k_{b_0}^{-1}$ is the bulk screening length associated with bulk free carriers alone.[16,17]

(ii) $R_b=k_b^{-1}$ is the bulk screening length associated with both bulk free carriers and bulk dielectric.[14]

(iii) $R_{s_0}=k_{s_0}^{-1}$ is the surface screening length associated with surface free carriers alone.

(iv) $R_s=k_s^{-1}$ is the surface screening length associated with both surface free carriers and bulk dielectric.

(v) R_s^{exp} is the inferred experimental surface screening length of Ref. 4.

II. ELECTROSTATIC SCREENING BY A CONDUCTING FILM

Consider a conducting film with negligible thickness relative to the resultant screening length and for which the energy to excite electronic states normal to the film is so high as to be irrelevant. Moreover, consider that no matter the origin of the surface free carriers, the extension of their wave function normal to the surface is small relative to any dimension along the surface.

Just as bulk free carriers are treated assuming a local, but unspecified, relationship between the chemical potential and the bulk carrier density in three dimensions,[12,16,17] so we treat surface free carriers assuming a local, but unspecified, relationship between the chemical potential and the surface carrier density in two dimensions. For specificity we consider the surface free carriers to be electrons; however, the screening length is independent of the sign of the carriers. Therefore, the density of states is $g(\vec{k})=g_s S d^2\vec{k}/(2\pi)^2$, where $g_s=2$ is the spin degeneracy, and S is the surface area. A general reference on two-dimensional electron systems is Ref. 18.

Let $\phi_s(\rho)$ be the potential $\phi(\vec{r})$ along the semiconductor surface. Then the electrochemical potential is given by $\tilde{\mu}_s=\mu_s-e\phi$, where μ_s is the chemical potential. We take $\phi_s\rightarrow 0$ as $\rho\rightarrow\infty$, so that $\tilde{\mu}_s=\mu_s$ at infinity.

In equilibrium, $\tilde{\mu}_s$ is a constant, and the equilibrium number density of surface free carriers is given by

$$n_s(\vec{\rho})=\int \frac{d^2\vec{k}}{2\pi^2}\,\frac{1}{\exp\{\beta[E(\vec{k})-e\phi_s(\vec{\rho})-\tilde{\mu}_s]\}+1},$$

$$E(\vec{k})=\frac{\hbar^2k^2}{2m_e}. \tag{2}$$

Here m_e is electron mass (if the electrons are treated as dressed particles due to their surrounding, then m_e should be replaced by the effective electron mass m^*). For $\phi_s=0$, Eq. (2) yields the position-independent equilibrium number density $n_s^{(0)}(\mu_s)=n_s(\rho)|_{\phi_s=0}$. Corresponding to this is a surface charge density $-en_s^{(0)}(\mu_s)$ that is compensated by a positive ionic background charge density $\sigma_{ionic}=en_s^{(0)}(\mu_s)$.

For $\phi_s\neq 0$ and spatially varying, Eq. (2) yields the position-dependent number density $n_s(\rho)\equiv n_s^{(0)}(\tilde{\mu}_s+e\phi_s)$. Corresponding to this is a surface charge density $-en_s^{(0)}(\tilde{\mu}_s+\phi_s)$. Thus, the net surface charge-density induced by ϕ_s is

$$\sigma_s=-en_s^{(0)}(\tilde{\mu}_s+e\phi_s)+en_s^{(0)}(\tilde{\mu}_s). \tag{3}$$

We now expand Eq. (3) for small ϕ_s, thus linearizing the theory. The relationship $\tilde{\mu}_s=\mu_s$ at infinity permits us to replace $\tilde{\mu}_s$ by μ_s, understood to be evaluated at infinity. This yields[16]

$$\sigma_s=-e^2\frac{\partial n_s}{\partial\mu_s}\phi_s=-k_{s_0}\varepsilon_0\phi_s, \quad k_{s_0}\equiv\frac{e^2}{\varepsilon_0}\frac{\partial n_s}{\partial\mu_s}. \tag{4}$$

The partial derivative $\partial n_s/\partial\mu_s$ in Eq. (4) is evaluated at the equilibrium carrier density $n_s^{(0)}$, which corresponds to n_s for $\rho\rightarrow\infty$. Consider now the low- and high-temperature limits:

(i) If $T \ll T_F$, then Fermi-Dirac statistics hold (Thomas-Fermi theory), so neglecting the effects of interactions (i.e., only kinetic energy is included), $\partial n_s/\partial\mu_s = m_e/\pi\hbar^2$;

(ii) If $T \gg T_F$, then Maxwell-Boltzmann statistics hold (Debye-Hückel theory), and $\partial n_s/\partial\mu_s = n_s/k_BT$.

This film response Eq. (4) is equivalent to a $2d$ wave-vector-dependent dielectric function $\varepsilon_{2d}(k_2)=1+k_{s0}/2k_2$ that relates the Fourier transform in the plane of the total potential $\phi(\vec{\rho},z=0)$ to the Fourier transform in the plane of the external (source) potential $\phi^{ext}(\vec{\rho},z=0)$. Specifically, with $\vec{k}_2$ a $2d$ wave vector, $\phi(\vec{k}_2,z=0)=\phi^{ext}(\vec{k}_2,z=0)/\varepsilon_{2d}(k_2)$. Moreover, details of the surface (e.g., confining potential) determine the nature of the surface states, and details of both surface and bulk determine the density of the occupied surface states, which is subsumed into k_s.

For completeness, the remainder of this section would work out the screening for a charge on the surface of a $2d$ conducting film. Instead, however, the following section works out the screening for a charge located on the surface of a $2d$ conducting film that itself resides on a semiconductor with dielectric constant ε. Taking $\varepsilon=1$ gives screening by the $2d$ conducting film alone.

III. SCREENING BY A CONDUCTING FILM AND DIELECTRIC

The response of a dielectric, with dielectric constant ε, to a source charge located near its surface is well known.[19] The physical picture is:

(i) If the source charge $q>0$ is in *vacuum,* above the dielectric surface, then q polarizes the dielectric. A net charge $-q(\varepsilon-1)/(\varepsilon+1)$ is induced on the surface. The bulk polarization charge density (due to bound charge) is everywhere zero. Spread over distant surfaces is a charge equal to that on the near surface, but of opposite sign.

(ii) If the source charge is within the *dielectric,* a charge $-q(1-1/\varepsilon)$ is induced in its vicinity, due to polarization. The bulk polarization charge density is everywhere zero, whereas a charge $q(1-1/\varepsilon)>0$ is spread over all surfaces; hence if the source charge is near the surface, the surface charge on the near surface is positive.

We now discuss electrostatic screening of a source charge in vacuum above a dielectric covered with a conducting film or, equivalently, surface free carriers. Both polarization charge and free carriers on the film contribute to the screening. We consider the following geometry, shown in Fig. 1.

The dielectric, of dielectric constant ε, occupies the region $z<0$, whereas the conducting film occupies the surface ($z=0$ plane). Vacuum occupies the region $z>0$. The source charge q is placed on the z axis, at position $\mathbf{r}_0=(0,0,z_0)$, where $z_0\geq 0$.

A. Electrostatic potentials

When the source charge q is at $\mathbf{r}_0$, the electrostatic potential ϕ_v in vacuum satisfies

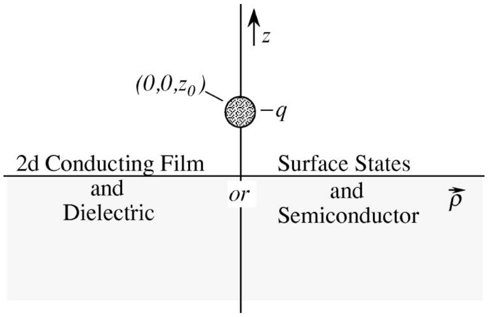

FIG. 1. Source charge geometry for the models used in Sec. III (conducting film and dielectric) and Sec. IV (surface states and semiconductor).

$$\nabla^2\phi_v=-\frac{q}{\varepsilon_0}\delta(\mathbf{r}-\mathbf{r}_0)=-\frac{q}{2\pi\varepsilon_0}\frac{\delta(\rho)}{\rho}\delta(z-z_0)\quad(z>0). \tag{5}$$

The electrostatic potential ϕ_d in the dielectric satisfies Laplace's equation

$$\nabla^2\phi_d=0\quad(z<0). \tag{6}$$

By axial symmetry, Eqs. (5) and (6) can be solved analytically in terms of zeroth-order Bessel functions $J_0(k\rho)$.[19] The vacuum and dielectric solutions have the form [see Eq. (A3)]

$$\phi_v=\frac{q}{4\pi\varepsilon_0}\int_0^\infty dkJ_0(k\rho)[\exp(-k|z-z_0|)+C_v(k)\exp(-kz)]\quad(z>0), \tag{7}$$

$$\phi_d=\frac{q}{4\pi\varepsilon_0}\int_0^\infty dkJ_0(k\rho)D_d(k)\exp(kz)\quad(z<0), \tag{8}$$

where $C_v(k)$ and $D_d(k)$ are determined by two boundary conditions on the $z=0$ plane. First, continuity of the tangential component of the electric field yields continuity of the electrostatic potential across the interface, or

$$\phi_v(\rho,z_0)=\phi_d(\rho,z_0)\quad(z=0), \tag{9}$$

We denote the surface potential by ϕ_s, so $\phi_s(\rho)=\phi_v(\rho,z=0)=\phi_d(\rho,z=0)$. Second, the discontinuity of the normal component of the **D** vector is proportional to the surface free charge density σ_s of Eq. (4), via

$$-\frac{\partial\phi_v}{\partial z}+\varepsilon\frac{\partial\phi_d}{\partial z}=\frac{1}{\varepsilon_0}\sigma_s=-k_{s_0}\phi_s\quad(z=0). \tag{10}$$

From Eqs. (9) and (10), $C_v(k)$ and $D_d(k)$ are given by

$$C_v(k)=-\frac{k_{s_0}+(\varepsilon-1)k}{(\varepsilon+1)k+k_{s_0}}\exp(-kz_0), \tag{11}$$

$$D_d(k)=\frac{2k}{(\varepsilon+1)k+k_{s_0}}\exp(-kz_0). \tag{12}$$

From Eqs. (11) and (12), if k_{s_0}/ε is small (either large dielectric constant, or low density of surface free carriers), then the conducting film can be neglected. If k_{s_0}/ε is large, then the metallic properties dominate, and the metal film screens q completely, as in the vacuum-ideal conducting case $[D_d(k)\rightarrow 0,\phi_d\rightarrow 0]$.

Now let the source charge be in the plane of the film $(z_0\rightarrow 0^+)$. The solutions for ϕ_v and ϕ_d then follow from Eqs. (7) and (8) in the limit $z_0\rightarrow 0^+$. At large distances above the source $[zk_{s_0}\gg 1$ and $\rho=0$, where $J(k\rho)=J(0)=1]$, ϕ_v can be obtained analytically. In the integral Eq. (7), at large z the term $\exp(-kz)$ causes only small k values to have non-negligible contributions. Then from Eqs. (7) and (11), the asymptotic vacuum potential is

$$\phi_v\rightarrow \frac{q}{4\pi\varepsilon_0}\int_0^\infty dk \ \ \exp(-kz)\frac{2k}{k_{s_0}}=\frac{1}{4\pi\varepsilon_0}\frac{2q}{k_{s_0}}\frac{1}{z^2} \qquad (zk_{s_0}\gg 1,\ z_0=0,\ \rho=0). \tag{13}$$

This is a dipole potential (a dipole along the z axis, centered at the origin), with dipole moment

$$p=\frac{2q}{k_{s_0}}. \tag{14}$$

On the surface, Eq. (8) yields

$$\phi_s(\rho)=\frac{q}{4\pi\varepsilon_0}\int_0^\infty dk J_0(k\rho)D_d(k) \quad (z=0). \tag{15}$$

Equation (15) has an analytical solution[20]

$$\phi_s(\rho)=\frac{q}{4\pi\varepsilon_0}\frac{2}{\varepsilon+1}\frac{1}{\rho}\left[1-\frac{\pi}{2}(k_s\rho)[\mathbf{H}_0(k_s\rho)-N_0(k_s\rho)]\right] \quad (z=z_0=0), \tag{16}$$

where

$$k_s=\frac{k_{s_0}}{\varepsilon+1}. \tag{17}$$

In Eq. (16), $\mathbf{H}_0$ is the zeroth-order Struve function, and N_0 is the zeroth order Neumann's function.[20] From Eqs. (16) and (17), the characteristic length $R_s=k_s^{-1}$ for radial variations of ϕ_s depends on both bulk dielectric and surface carrier properties. For small and intermediate ρ, $\phi_s(\rho)$ can be approximated by a screened Coulomb potential, with screening length k_s^{-1}. The potential due to a free $2d$ conducting surface is obtained by taking $\varepsilon=1$ in Eqs. (16) and (17).

B. Asymptotic behavior of the surface potential

For large ρ $\phi_s(\rho)$ of (16) is not a screened Coulomb potential, but rather has the form [see Eq. (A4)]

$$\phi_s(\rho)=\frac{q}{4\pi\varepsilon_0}\frac{2}{\varepsilon+1}\frac{1}{k_s^2\rho^3} \quad (z=z_0=0; \quad \rho k_s\gg 1). \tag{18}$$

This inverse cube variation in ρ is characteristic of a quadrupole. We now compare $\phi_s(\rho)$ of Eq. (18) with the quadrupolar potential due to a charge distribution $\rho_0(\mathbf{r})$

$$\phi_Q=\frac{1}{4\pi\varepsilon_0}\frac{1}{2}\sum_{i,j}\frac{Q_{i,j}x_ix_j}{r^5},$$

$$\text{where } Q_{i,j}=\int d\mathbf{r}(3x_ix_j-\delta_{i,j}r^2)\rho_0(\mathbf{r}). \tag{19}$$

Employing the tracelessness of the $Q_{i,j}$ tensor, and axial symmetry, we find that

$$Q_{xx}=Q_{yy}=-\frac{1}{2}Q_{zz}=\frac{4q}{(\varepsilon+1)k_s^2}. \tag{20}$$

Thus, although the asymptotic vacuum potential ϕ_v of (13) is dipolar, the asymptotic surface potential ϕ_s of Eq. (18) is quadrupolar.[1] An asymptotic quadrupolar response along the surface has also been obtained in the extreme quantum limit of the two-dimensional electron gas with no dielectric above or below.[21] Related work was done in Ref. 22. Setting $\varepsilon=1$ gives the response of a free $2d$ conducting surface.

Reference 23 considers a $2d$ electron gas in the quantum limit, confined to the $z=0$ plane and separating two semi-infinite regions of dielectric constants ε_1 and ε_2. The authors employ a hydrodynamic-like theory, using a continuity equation and an equation of motion with a force density due to the quantum self-pressure and the external electric field (the sum of these two terms is proportional to the gradient of the electrochemical potential). The response to an external charge density $\rho_{ext}(k,\omega,z)$ is expressed in terms of the number density, linearized about the equilibrium value n_0. An expression is obtained for ϕ due to a charge q fixed at $z=z_0$, which in general cannot be evaluated analytically. For $z=z_0=0$, $\varepsilon_1=1$, and $\varepsilon_2=\varepsilon$, Ref. 23 gives a ϕ_s that agrees with our Eq. (16). However, they do not evaluate ϕ_s asymptotically, so that the dipole moment and quadrupole moment are not obtained. This approach yields k_s in the quantum limit only $(T\ll T_F)$, whereas the present approach applies for any T. Note that Ref. 23 considers a charged sheet, whereas the present work assumes an overall neutral surface.

IV. SCREENING BY A SEMICONDUCTOR WITH BULK AND SURFACE FREE CARRIERS

We now consider the additional contribution of bulk free carriers to surface screening. The source of these bulk free carriers is a uniform bulk charge density right up to the surface.[1] However, the results derived here apply more generally (that is, to weak depletion or accumulation) under two conditions: (i) the near-surface free carrier density, taken to be a fitting parameter, is employed, rather than the bulk free carrier density deep within the bulk; (ii) the screening length of the near-surface region is much shorter than the spatial scale over which the bulk carrier concentration varies.

For an isolated surface charge (e.g., a semiconductor surface defect), we first obtain the electrostatic potentials in vacuum and in bulk (ϕ_v and ϕ_b, for $z_0\geqslant 0$, in the geometry of Fig. 1). We then study the surface charge distribution and the total charge induced on the surface.

A. Screening of a charge above the surface

The surface free carriers have no effect on the electrostatic equations for vacuum or bulk semiconductor. Thus, for vacuum, Eq. (5) still applies, whereas for a bulk semiconductor

$$\nabla^2 \phi_b = -\frac{1}{\varepsilon_0 \varepsilon}\rho_{free} \quad (z<0). \tag{21}$$

Assuming a local relationship between the chemical potential and the bulk carrier density, the effective bulk free charge density is

$$\rho_{free} = -e^2 \frac{\partial n_b}{\partial \mu_b}\phi_b, \tag{22}$$

where n_b is the bulk electron number density and μ_b is the corresponding chemical potential. From Eqs. (21) and (22), the bulk screening length k_b^{-1} is given by

$$k_b^2 \equiv \frac{e^2}{\varepsilon_0 \varepsilon}\frac{\partial n_b}{\partial \mu_b} \equiv \frac{k_{b0}^2}{\varepsilon}. \tag{23}$$

(This serves to define both k_b and k_{b0}.) Then, employing Eq. (23) in Eq. (22), ϕ_b must satisfy

$$\nabla^2 \phi_b - k_b^2 \phi_b = 0 \quad (z<0). \tag{24}$$

The solution for the potential in vacuum is given by Eq. (7), with a new $C_v(k)$. The solution for the potential in the bulk semiconductor, rather than Eq. (8), has the form

$$\phi_b = \frac{q}{4\pi\varepsilon_0}\int_0^\infty dk D_b(k) J_0(k\rho)\exp(z\sqrt{k^2+k_b^2}) \quad (z<0) \tag{25}$$

with $D_b(k)$ in place of $D_d(k)$. The boundary conditions at $z=0$ are given by Eqs. (9) and (10), with ϕ_b of Eq. (25) instead of ϕ_d of Eq. (8). Instead of Eq. (11) and (12), we now have

$$C_v(k) = \frac{k-\varepsilon\sqrt{k^2+k_b^2}-k_{s_0}}{k+\varepsilon\sqrt{k^2+k_b^2}+k_{s_0}}\exp(-kz_0), \tag{26}$$

$$D_b(k) = \frac{2k}{k+\varepsilon\sqrt{k^2+k_b^2}+k_{s_0}}\exp(-kz_0). \tag{27}$$

Equations (26) and (27) show that, for arbitrary values of ε, k_b, and k_{s_0}, all three types of semiconductor response—dielectric (bulk bound charge), bulk free carrier, and surface free carrier—contribute. If both k_b and k_{s_0} are small (i.e., low densities of both bulk free carriers and surface free carriers), the dielectric properties dominate.[19] If $k_b \gg k_{s_0}$, screening by the bulk free carriers dominates. If $k_{s_0} \gg \varepsilon k_b$, screening by the surface free carriers dominates, and Eqs. (26) and (27) reduce to Eqs. (11) and (12).

The total surface charge density σ_s^{tot} is the sum of σ_s^{bound} from polarized bulk dielectric molecules and of σ_s from surface free carriers. It is given by

$$\sigma_s^{tot} = \varepsilon_0\left[-\frac{\partial \phi_v}{\partial z} + \frac{\partial \phi_b}{\partial z}\right] \quad (z=0). \tag{28}$$

Using Eqs. (7), (25), (26), and (27), this yields

$$\sigma_s^{tot} = -\frac{q}{2\pi}\int_0^\infty dk J_0(k\rho) k \frac{(\varepsilon-1)\sqrt{k^2+k_b^2}+k_{s_0}}{k+\varepsilon\sqrt{k^2+k_b^2}+k_{s_0}}\exp(-kz_0). \tag{29}$$

From Eq. (29), the total surface charge (exclusive of the source charge, if $z_0 \to 0$) $q_s = 2\pi\int_0^\infty d\rho\ \rho\sigma_s^{tot}(\rho)$ is

$$q_s = -q\int_0^\infty d\rho\rho\int_0^\infty dk J_0(k\rho)\ \ k\frac{(\varepsilon-1)\sqrt{k^2+k_b^2}+k_{s_0}}{k+\varepsilon\sqrt{k^2+k_b^2}+k_{s_0}} \times \exp(-kz_0). \tag{30}$$

We have not evaluated Eq. (30) analytically, except for a few limiting cases:

(i) If $k_b z_0 \ll 1$ and k_{s_0} is comparable to k_b, then $q_s = -q(\varepsilon-1)/(\varepsilon+1)$, as in the vacuum-dielectric case.[19] [See Eq. (A11).]

(ii) If $k_b z_0 \ll 1$ and $k_{s_0} z_0 \gg 1$, then $q_s = -q$, i.e., the source q is completely screened by the surface free carriers.

(iii) If $k_b z_0 \gg 1$, then Eq. (30) can be evaluated analytically for k_{s_0} comparable with k_b, giving [see Eq. (A15)]

$$q_s = -q\frac{(\varepsilon-1)+\alpha}{\varepsilon+\alpha}, \quad \alpha = \frac{k_{s_0}}{k_b}. \tag{31}$$

If $\alpha \gg \varepsilon$, then $q_s = -q$, and the surface free carriers dominate the screening. If $\alpha \ll \varepsilon$, then $q_s = -q(1-1/\varepsilon)$, and the bulk free carriers dominate the screening.[1]

In all cases, on moving into the bulk, the residual charge $Q = q + q_s$ is screened by the bulk; the total charge induced in the bulk is $-Q$. Of that, the bulk free charge is $-\varepsilon Q$, whereas the bulk polarization charge is $(\varepsilon-1)Q$.

B. Screening of a source charge on the surface

If q is on the semiconductor surface, the solutions for ϕ_v and ϕ_b follow from Eqs. (7), (25), (26), and (27), in the limit $z_0 \to 0^+$. The solution for ϕ_v, at large distances from the surface ($zk_b, zk_{s_0} \ll 1$), and for $\rho=0$, can be obtained analytically, as in Sec. III. From Eqs. (7) and (24), the asymptotic vacuum potential is

$$\begin{aligned}\phi_v &= \frac{q}{4\pi\varepsilon_0}\int_0^\infty dk\exp(-kz)\frac{2k}{\varepsilon k_b + k_{s_0}} \\ &= \frac{1}{4\pi\varepsilon_0}\frac{2q}{\varepsilon k_b + k_{s_0}}\frac{1}{z^2} \quad (zk_{s_0} \ll 1, \rho=0).\end{aligned} \tag{32}$$

From Eq. (32), ϕ_v is a dipole potential, with dipole moment

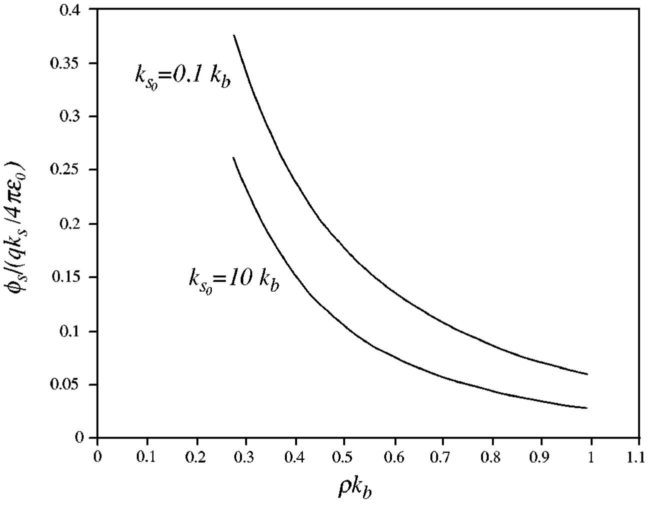

FIG. 2. Numerically integrated surface potential of Eq. (34) in two limits: $k_{s0} \ll k_b$ and $k_{s0} \gg k_b$.

$$p = \frac{2q}{\varepsilon k_b + k_{s_0}}. \tag{33}$$

As $k_b \to 0$, Eq. (33) goes to Eq. (14), as expected. As $k_{s0} \to 0$, Eq. (33) goes to $2q/\varepsilon k_b = 2qR_b/\varepsilon$, as expected.[1]

The surface potential ϕ_s is obtained from Eqs. (25) and (27) on setting $z = z_0 = 0$. Then

$$\phi_s = \frac{q}{4\pi\varepsilon_0}\int_0^\infty dk J_0(k\rho)\frac{2k}{k + \varepsilon\sqrt{k^2 + k_b^2} + k_{s_0}}. \tag{34}$$

Note that $k_{s_0} \to 0$ gives the correct limit when there are no surface free carriers.[1] However, in general Eq. (34) must be numerically integrated[24] to determine the effect of k_{s_0}. Figure 2 shows ϕ_s for two values of k_{s_0}: $k_{s_0} = 0.1k_b$ and $k_{s_0} = 10k_b$. The two curves are clearly separated over the entire interval $\frac{1}{3}k_b^{-1} < \rho < k_b^{-1}$, with a nearly constant shift for all ρ.

For large ρ, ϕ_s of Eq. (34) has the asymptotic form [see Eq. (A9)]

$$\phi_s(\rho) = \frac{q}{4\pi\varepsilon_0}\frac{2}{k_b^2\rho^3}\frac{q}{\left(\varepsilon + \dfrac{k_{s_0}}{k_b}\right)^2}. \tag{35}$$

Like Eq. (18), this is quadrupolar. However, Eq. (35) does not yield Eq. (18) in the $k_b \to 0$ limit because the expansion of Eq. (34) that yields Eq. (35) holds only for $k_b\rho \gg 1$. Comparing ϕ_s of Eq. (35) with ϕ_Q of Eq. (19), the components of the $Q_{i,j}$ tensor are

$$Q_{xx} = Q_{yy} = -\frac{1}{2}Q_{zz} = \frac{4q}{(\varepsilon k_b + k_{s0})^2}. \tag{36}$$

For small and intermediate ρ, numerical evaluation[24] of Eq. (34) yields an exponential-like behavior for ϕ_s.

V. APPLICATION TO EXPERIMENT

The model discussed in Sec. III should be appropriate to screening by surface free carriers: the conducting film corresponds to mobile surface states and the dielectric corresponds to a depleted near-surface region of p type. For the theory to be self-consistent, $R_s = 1.1$ nm must exceed the characteristic atomic length $a = 0.587$ nm, as it does. Each unit cell contains one anion and one cation and occupies an area $A_0 = (0.587\times 10^{-9})^2/\sqrt{2} = 2.4\times 10^{-19}$ m^2, with corresponding density of 4.1×10^{18} m^{-2}. Hence, at $c = 1\%$ the density of the surface vacancies is $0.01/A_0 = 4.1\times 10^{16}$ m^{-2}. The mean vacancy separation of about 10 lattice constants (5 nm) should give small vacancy wave function overlap, a narrow energy band, and an effective mass m^* satisfying $m^* > m_e$. This is relevant to the statistics of the surface free carriers:

If Fermi-Dirac statistics apply (Thomas-Fermi theory), the screening length $R_s = k_s^{-1}$ is given by Eqs. (17) and (4) with $\partial n_s/\partial\mu_s = m^*/\pi\hbar^2$. Setting $R_s = R_s^{exp} = 1.1$ nm yields $m^* = 0.13m_e$, in conflict with the narrow energy-band requirement $m^* > m_e$. Therefore, if there are surface free carriers they likely are not described by Fermi-Dirac statistics.

If Maxwell-Boltzmann statistics apply (Debye-Hückel theory), the screening length $R_s = k_s^{-1}$ is given by (17) and (4) with $\partial n_s/\partial\mu_s = n_s/k_bT$. A surface charge density of $n_s = 1.7\times 10^{16}$ m^{-2} then reproduces the experimental value of $R_s^{exp} \approx 1.1$ nm. This corresponds to 0.4% per surface cell, or roughly 0.4 per phosphorus vacancy (based on the $c = 1\%$ quoted in Ref. 4).

Let us assume that the effective free carrier density $n_s = 0.4N_v$ even at the lower surface defect densities of Ref. 2 Since $k_s \sim n_s \sim N_v$, and N_v is down by a factor of 100 for the low-density experiments, k_s at low densities is down by a factor of 100, making it about 1/10 of the observed low-density value[2] and about 1/30 of the value observed in Ref. 4. Hence the low-density experiments had no need for surface free carriers to provide screening because in that case bulk screening dominates.

We now apply the screening theory of Sec. III (which includes surface free carriers and dielectric, but no bulk free carriers) to the inferred interaction of Ref. 4. Figure 3 compares the interaction $U = e\phi_s$ using ϕ_s of Eq. (16), with both the original inferred results and the empirical fit (1), where in Eq. (1) we take $\varepsilon = 12.6$, $Z = 1$, and $R_s = R_s^{exp} = 1.1$ nm. There is good agreement over much of the range of interest. It is unnecessary to apply the more complex theory of Sec. IV to the data, because the surface carriers dominate. On the other hand, for intermediate concentrations, such as $c = 0.1\%$, bulk and surface carriers would contribute nearly equally, and the theory of Sec. IV would have to be applied.

It is possible that the distance scale over which the dielectric theory becomes valid (i.e., in the absence of free carriers, no screening at short distances, and screening by ε at large distances) is larger than we have assumed. However, that would give significantly *less* screening at short distances than is observed in Ref. 4. For microscopic calculations of the spatial dependence of dielectric screening in bulk, without free charge carriers, see Refs. 25–27. For a treatment that

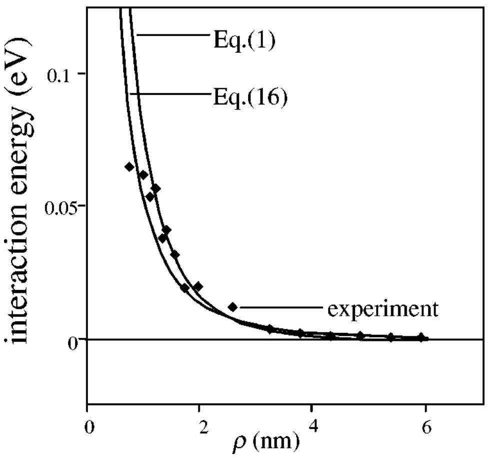

FIG. 3. Surface vacancy interaction energy $U=e\phi_s$: experimental results, U due to the empirical fit Eq. (1) and U due to the theoretical result Eq. (16).

is more phenomenological but much simpler analytically, see Ref. 28.

VI. SUMMARY

Assuming a local relationship between the chemical potential and the carrier density, we have studied electrostatic screening of a point charge by a semi-infinite semiconductor with both bulk and surface free carriers, when the applied field is small enough that the theory can be linearized. The surface free carriers can be due to surface states or to a thin conducting overlayer. The model is applicable only on spatial scales longer than an atomic distance, and only for static screening. We also have presented results applicable to screening of a point charge above (in vacuum) and on the semiconductor surface.

The screening depends on all the semiconductor properties, i.e., on the values of ε, k_b, and k_{s_0}: (i) if both k_{s_0} and k_b are small, the dielectric properties dominate, and polarization provides the screening; (ii) if k_{s_0} is large, the screening occurs in the immediate vicinity of the surface; (iii) if $k_{s_0} \ll \varepsilon k_b$, the bulk free carriers dominate screening within a few R_b of the surface.

For a source charge on the surface, the asymptotic vacuum potential is dipolar, vanishing at the surface. The asymptotic surface potential is quadrupolar. Exponential-like behavior of the surface potential, from Sec. IV, can only be obtained in the small and intermediate ρ regions. We have compared our surface potential ϕ_s with the inferred form ϕ_{fit} of Ref. 4. To reproduce the experimental results, screening by the surface free carriers must dominate.

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APPENDIX

1. Potentials for source above surface

The potential $\phi_v^{(1)}$ due to q localized at $\mathbf{r}_0$ can be expanded in terms of the zeroth-order Bessel function as[19]

$$\phi_v^{(1)}=\frac{q}{4\pi\varepsilon_0}\frac{1}{\sqrt{\rho^2+(z-z_0)^2}}$$

$$=\frac{q}{4\pi\varepsilon_0}\int_0^\infty dk J_0(k\rho)\exp(-k|z-z_0|). \qquad \text{(A1)}$$

The total potential ϕ_v of Eq. (4) is the sum of $\phi_v^{(1)}$ and a term $\phi_v^{(2)}$ that satisfies Laplace's equation, due to charge in the region $z<0$. To expand $\phi_v^{(2)}$ in terms of $J_0(k\rho)$, we separate in the variables ρ and z, writing $\phi_v^{(2)}=\int_0^\infty dk C_v(k)R(k,\rho)Z(k,z)$. By standard methods,[19] we obtain differential equations for $R(k,\rho)$ and $Z(k,\rho)$, whose solutions are $R(k,\rho)=J_0(k\rho)$ and $Z(k,\rho)\sim\exp(-k|z|)$. Thus

$$\phi_v^{(2)}=\frac{q}{4\pi\varepsilon_0}\int_0^\infty dk C_v(k)J_0(k\rho)\exp(-k|z|). \qquad \text{(A2)}$$

The above form is also general solution for ϕ_d (with $C_v\rightarrow C_d$), since ϕ_d also satisfies Laplace's equation.

Summing over $\phi_v^{(1)}$ and $\phi_v^{(2)}$ yields

$$\phi_v=\frac{q}{4\pi\varepsilon_0}\int_0^\infty dk J_0(k\rho)[\exp(-k|z-z_0|)$$

$$+C_v(k)\exp(-kz)] \quad (z>0). \qquad \text{(A3)}$$

2. Surface potentials at large radial distances

(i) The large ρ behavior of the surface potential in the dielectric-conducting film case (where $k_b=0$) for large ρ is obtained from the large ρ behavior, in Eq. (15), of the term $\mathbf{H}_0(k_s\rho)-N_0(k_s\rho)$. We have[20]

$$\mathbf{H}_0(k_s\rho)-N_0(k_s\rho)\approx\frac{1}{\pi}\left(\frac{2}{k_s\rho}+\frac{\Gamma(3/2)}{\Gamma(-1/2)}\frac{8}{(k_s\rho)^3}\right)$$

$$=\frac{2}{\pi}\left(\frac{1}{k_s\rho}-\frac{1}{(k_s\rho)^3}\right) \quad (k_s\rho\gg 1). \qquad \text{(A4)}$$

Employing Eq. (A4) in Eq. (15) yields Eq. (17).

(ii) The asymptotic behavior of ϕ_s is obtained as follows. Substitution of $k\rho=x$ in Eq.(33) yields

$$\phi_s=\frac{1}{4\pi\varepsilon_0}\frac{2q}{\rho}\int_0^\infty dx J_0(x)\frac{x}{x+\varepsilon\sqrt{x^2+(k_b\rho)^2}+k_{s_0}\rho}. \qquad \text{(A5)}$$

Addition and subtraction of the $x\rightarrow\infty$ limit of the integrand in Eq. (A5), $1/(\varepsilon+1)$, gives

$$\phi_s=\frac{1}{4\pi\varepsilon_0}\,\frac{2}{\varepsilon+1}\,\frac{1}{\rho}\Bigg[\int_0^\infty dx J_0(x)+\int_0^\infty dx J_0(x)\,\frac{\varepsilon x-\varepsilon\sqrt{x^2+(k_b\rho)^2}-(k_{s_0}\rho)}{x+\varepsilon\sqrt{x^2+(k_b\rho)^2}+(k_{s_0}\rho)}\Bigg]. \tag{A6}$$

Using $\int_0^\infty dx\ J_0(x)=1$, and dividing the numerator and the denominator of the integrand of the second term in Eq. (A6) by $\varepsilon k_b\rho$ (k_b is nonzero), we obtain

$$\phi_s=\frac{1}{4\pi\varepsilon_0}\,\frac{2}{\varepsilon+1}\,\frac{1}{\rho}\times\left[1+\int_0^\infty dx J_0(x)\,\frac{\dfrac{x}{k_b\rho}-\left[1+\left(\dfrac{x}{k_b\rho}\right)^2\right]^{1/2}-\dfrac{k_{s_0}}{\varepsilon k_b}}{\dfrac{x}{k_b\rho}+\left[1+\left(\dfrac{x}{k_b\rho}\right)^2\right]^{1/2}+\dfrac{k_{s_0}}{\varepsilon k_b}}\right]. \tag{A7}$$

On multiplying the integrand of Eq. (A7) by $\exp(-\delta x)$, taking the limit $\delta\to 0$, and expanding the integrand to second order in $x/(k_b\rho)$ we obtain

$$\phi_s\approx\frac{1}{4\pi\varepsilon_0}\,\frac{2}{\varepsilon+1}\,\frac{1}{\rho}\left[1-\lim_{\delta\to 0}\int_0^\infty dx J_0(x)\times\exp(-\delta x)\,\frac{a-\dfrac{x}{k_b\rho}+\dfrac{1}{2}\left(\dfrac{x}{k_b\rho}\right)^2}{a+\dfrac{1}{\varepsilon}\,\dfrac{x}{k_b\rho}+\dfrac{1}{2}\left(\dfrac{x}{k_b\rho}\right)^2}\right],$$

$$a=1+k_{s_0}/(\varepsilon k_b). \tag{A8}$$

By further expanssion in x we obtain

$$\phi_s\approx\frac{1}{4\pi\varepsilon_0}\,\frac{2}{\varepsilon+1}\,\frac{1}{\rho}\left[1-\lim_{\delta\to 0}\int_0^\infty dx J_0(x)\exp(-\delta x)\times\left(1+\frac{1}{a^2}\,\frac{\varepsilon+1}{\varepsilon^2}\,\frac{1}{(k_b\rho)^2}x^2\right)\right]. \tag{A9}$$

Terms proportional $J_0(x)\exp(-\delta x)x$ have been omitted, because they disappear upon integration.[20] Integration of Eq. (A9) gives Eq. (34).[20] This result holds only for $k_b\rho\gg 1$.

3. Total surface charge q_s

The total surface charge of Eq. (29) can be evaluated analytically only for a few limiting cases. To reverse the order of integration in Eq. (29), we multiply the integrand by $\exp(-\rho\delta)$ and take the limit $\delta\to 0$. Then, changing variables to $x=kz_0$ and $z_0\delta=\delta'$, we obtain

$$q_s=-q\lim_{\delta'\to 0}\delta'\int_0^\infty dx\frac{(\varepsilon-1)x\sqrt{x^2+(k_bz_0)^2}+x(k_bz_0)\alpha}{\varepsilon\sqrt{x^2+(k_bz_0)^2}+x+(k_bz_0)\alpha}\times\frac{\exp(-x)}{\sqrt{x^2+\delta'^2}^3}. \tag{A10}$$

(i) If $k_bz_0\ll 1$ and if $\alpha\equiv k_{s0}/k_b$ of Eq. (30) is of order unity, we may neglect the terms $(k_bz_0)^2$ and $x(k_bz_0)\alpha$ in the integrand of Eq. (A10). Then, substituting $x=\delta' y$ yields q_s

$$q_s=-\frac{q(\varepsilon-1)}{\varepsilon+1}\lim_{\delta'\to 0}\int_0^\infty dy\,\frac{y}{\sqrt{y^2+1}^3}\exp(-y\delta')$$

$$=-\frac{q(\varepsilon-1)}{\varepsilon+1},\quad k_bz_0\gg 1,\quad \alpha=O(1). \tag{A11}$$

If $\alpha\ll 1$, so that $(k_bz_0)\alpha$ cannot be neglected, an analytical evaluation of Eq. (A10) can be performed only for $(k_bz_0)\alpha=k_{s_0}z_0\gg 1$. Then Eq. (A10) becomes

$$q_s=-q\lim_{\delta'\to 0}\delta'\int_0^\infty dx\frac{(\varepsilon-1)x^2+x(k_bz_0)\alpha}{(\varepsilon+1)x+(k_bz_0)\alpha}\,\frac{\exp(-x)}{\sqrt{x^2+\delta'^2}^3}. \tag{A12}$$

Due to the term $\exp(-x)$, for $k_{s_0}z_0\gg 1$ the $\alpha(k_bz_0)=k_{s_0}z_0$ term dominates the contributions to the integral (A12). Thus, q_s becomes

$$q_s=-q\lim_{\delta'\to 0}\delta'\int_0^\infty dx\frac{x\exp(-x)}{\sqrt{x^2+\delta'^2}^3}=-q,$$

$$k_bz_0\ll 1,\ \ \alpha k_bz_0\gg 1. \tag{A13}$$

(ii) If $k_bz_0\gg 1$, an analytical evaluation of Eq. (A10) can be performed for $k_{s_0}z_0\gg 1$ and α of order unity. We then neglect x in the $\sqrt{x^2+(k_bz_0)^2}$ terms, and we neglect x in the denominator of the integrand of Eq. (A10). Thus we rewrite Eq. (A10), so

$$q_s=-q\lim_{\delta'\to 0}\delta'\int_0^\infty dx\frac{(\varepsilon-1)x+\alpha x}{\varepsilon+\alpha}\,\frac{\exp(-x)}{\sqrt{x^2+\delta'^2}^3}. \tag{A14}$$

Integration of Eq. (A14) gives

$$q_s=-q\,\frac{(\varepsilon-1)+\alpha}{\varepsilon+\alpha}. \tag{A15}$$

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