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Scattering of Carriers in Semiconductors by Screened Surface Charges

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A new theory is given of surface scattering in semiconductors by surface point charges, corresponding to trapping in chemisorption bonds or defects. Interference effects, between waves scattered from different scatterers, are evaluated in terms of the statistical structure factor of the surface-point-charge array. Dielectric image effects are included. The scattering potential is taken from the recent statistical treament of the three-dimensional nonplanar semiconductor-surface space charge given by Greene, Bixler, and Lee. The need for multiple scattering treatment of evanescent states is discussed. Comparison with previous theory is made.

INTRODUCTION

In 1966 Greene and O'Donnell (GO) proposed[1] that the apparent diffuseness of semiconductor surfaces in transport measurements was due to scattering by surface charges, e.g., localized at chemisorbed atoms, defects, etc. They gave a simple calculation of this scattering, finding a rather strong angular dependence. This angular dependence seemed to explain[2] the lack of a surface-mobility cusp[3] in the transport measurements of Davis[4] on InSb surfaces. Further confirmation of the GO theory was provided by the measurements of Kamins and MacDonald[5] on the Si–SiO$_2$ interface. More recent work by Preuss,[6] however, does show evidence of the surface-mobility cusp, suggesting that a closer look at surface scattering is needed. Extensive studies of scattering at Si–SiO$_2$ interfaces have recently been reported (e.g., by Sah *et al.*[7]) also. Motivation for this paper from another quarter may be cited: Recently it has been shown[8] that there exists a general relation between surface-scattering rates and the thermodynamics of chemisorption, where the chemisorption bonds provide the trapped charge which causes the scattering.

The GO theory is oversimplified in several respects: (a) It neglects the interference terms in the scattering from different surface charges; (b) it uses an arbitrary form for the screened potential of the surface charges; and (c) it neglects the dielectric image force. The present paper provides a new theory of surface scattering by discrete surface charges which is free of these limitations. We regard the entire screened array of surface charges as a single scatterer. Interference terms can then be treated exactly, in terms of the statistical structure factor of the surface-charge array. At the same time, we replace the arbitrary GO scattering potential by the potential calculated by Greene, Bixler, and Lee[9] (GBL) of the inhomogeneous-surface space-charge region. We also take into account the GBL dielectric image force which, in its screened form, strongly decouples the scattering potential from electrons with small normal momenta. The qualitative features of the GO theory reappear, but with somewhat different angular dependence.

The calculation of scattering by a partially ordered array of scatterers becomes tractable only with use of the statistical properties of the scattering potential. This is also supplied by the GBL theory which treats the semiconductor-surface space-charge potential as a partially correlated stochastic function of position, determined by the surface distribution of point charges.

The density of surface scatterers is often high enough for scattering interference effects to be very strong. The concept of the differential scattering cross section of individual scatterers then becomes inexact and should be replaced by the dimensionless differential scattering probability of the surface as a whole.

We show that in the Born approximation all interference effects between the scattered and incident waves disappear for a stochastic scattering potential, but the interferences between different scatterers remain. The need for a multiple scattering treatment is pointed out, particularly for the evanescent or surface currents.

I. SURFACE-SCATTERING THEORY IN BORN APPROXIMATION

We represent an ideal crystal surface by an infinite potential step at $z=0$. The unscattered electrons are then described by

$$H^0\psi^0 = E\psi^0\ , \quad z \geq 0\ , \quad H^0 = -\hbar^2\nabla^2/2m \qquad (1.1a)$$

$$\psi^0 = (\sin k_z z)\, e^{i\vec{K}\cdot\vec{R}}, \quad z \geqslant 0 \tag{1.1b}$$

$$= 0, \qquad z \leqslant 0 \tag{1.1c}$$

where $E = \hbar^2 k_0^2/2m$ and $k_0^2 = K^2 + k_z^2$. [We write two-dimensional vectors as capitals, e.g., $\vec{K} = (K_x, K_y, 0)$.] Next we introduce a scattering potential $-e\phi(\vec{R}, z)$ which produces a scattered wave ψ:

$$(H^0 - E - e\phi)\,(\psi^0 + \psi) = 0, \quad z \geqslant 0 \tag{1.2a}$$

$$\psi = 0, \qquad z < 0. \tag{1.2b}$$

In the Born approximation,

$$(H^0 - E)\,\psi = e\phi\psi^0, \quad z \geqslant 0. \tag{1.3}$$

It is convenient to use the two-dimensional transforms of ϕ and ψ

$$\phi(\vec{Q}, z) = \int \frac{d^2R}{2\pi}\, \phi(\vec{R}, z)\, e^{-i\vec{Q}\cdot\vec{R}}, \tag{1.4a}$$

$$\psi(\vec{Q}, z) = \int \frac{d^2R}{2\pi}\, \psi(\vec{R}, z)\, e^{-i\vec{Q}\cdot\vec{R}}, \tag{1.4b}$$

and to transform Eq. (1.3) to $(\vec{Q}, z)$ space,

$$\left(\frac{\partial^2}{\partial z^2} + \Gamma^2\right)\psi(\vec{Q}, z) = \frac{-2me}{\hbar^2}\,(\sin k_z z)\,\phi(\vec{Q} - \vec{K}, z), \quad z \geqslant 0 \tag{1.5a}$$

where

$$\Gamma = (k_0^2 - Q^2)^{1/2}, \quad k_0^2 > Q^2 \quad \Gamma = i(k_0^2 - Q^2)^{1/2}, \quad k_0^2 < Q^2. \tag{1.5b}$$

The solution of Eq. (1.5a), subject to Eq. (1.2b), can be written

$$\psi(\vec{Q}, z) = \frac{-2me}{\hbar^2} \int_0^\infty dz'\, G(z; z')\, \phi(\vec{Q} - \vec{K}, z') \sin k_z z', \quad z \geqslant 0. \tag{1.6a}$$

Here $G(z, z')$ is the one-dimensional Green's function

$$G(z, z') = (1/2i\Gamma)\left(e^{i\Gamma|z-z'|} - e^{I\Gamma|z+z'|}\right), \tag{1.6b}$$

which has the properties

$$G(z, z') = 0 \quad \text{for } z = 0 \tag{1.7a}$$

and

$$\left(\frac{\partial^2}{\partial z^2} + \Gamma^2\right) G(z, z') = \delta(z - z') + \delta(z + z'), \tag{1.7b}$$

which ensure that both Eqs. (1.2b) and (1.5a) are satisfied. The choice of (+) exponents in $G(z, z')$ means that we are requiring that the scattered propagating waves, $Q^2 < k_0^2$, all have the outgoing form $e^{+i\Gamma z}$ for $z \to \infty$, as seems physically reasonable. Moreover, were we to admit incoming scattered waves, these would produce divergent exponential solutions for $Q^2 > k_0^2$.

The GBL potential produced by surface point charges consists of a planar or band-bending term ϕ_p which depends on z only, and an inhomogeneity term $\phi(\vec{R}, z)$ which produces scattering and has the form

$$\phi(\vec{Q}, z) = \phi(\vec{Q}, 0)\, e^{-\kappa z}, \tag{1.8a}$$

where

$$\kappa = (q_s^2 + Q^2)^{1/2}, \tag{1.8b}$$

and where q_s is the effective inverse screening length near the surface:

$$q_s^2 = (4\pi e^2 n_B/\epsilon_+ kT)\, e^{e\phi_{ps}/kT} \equiv q_0^2\, e^{e\phi_{ps}/kT}. \tag{1.8c}$$

Here n_B is the bulk electron concentration and ϕ_{ps} is the value of the band-bending potential at the surface. It might be objected that the use of the Fermi–Thomas approximation in GBL theory is inconsistent with our scattering model, viz., Eqs. (1.1c) and (1.2b), whereby carrier wave functions are terminated at the surface. It has been shown[10] that the screening approximations are negligible for surface fields below about 5×10^4 V/cm in nondegenerate semiconductors. If we use the simple z dependence of Eq. (1.8a), then we can write the scattered solution, Eq. (1.6a), in the explicit form

$$\psi(\vec{Q}, z) = (me/2\hbar^2)\, \phi(\vec{Q} - \vec{K}, 0)\, [F_p e^{i\Gamma z} + F_s(z)], \tag{1.9a}$$

where

$$F_p = F_p^* = \frac{8\kappa k_z}{(\kappa^2 + \Gamma^2 + k_z^2)^2 - 4k_z^2\Gamma^2} \tag{1.9b}$$

and

$$F_s = F_s^* = 2i\left(\frac{e^{i(k_z-\kappa)z}}{\kappa^2 - k_z^2 + \Gamma^2 - 2i\kappa k_z} + \text{c.c.}\right). \tag{1.9c}$$

Here,

$$\kappa = \kappa(\vec{Q} - \vec{K}) = [(\vec{Q} - \vec{K})^2 + q_s^2]^{1/2}, \tag{1.9d}$$

and Γ is given by Eq. (1.5b). The F_p term is a propagating wave for $Q^2 < k_0^2$, but is evanescent for $Q^2 > k_0^2$. The F_s term is evanescent for all values of $\vec{Q}$. Electrons scattered into evanescent states clearly interact strongly with the scattering potential ϕ and will be multiply scattered. A treatment of these states will be given elsewhere.

II. SCATTERED FLUX DENSITY FROM PARTIALLY RANDOM SCATTERER

We now calculate the scattered flux density $\vec{J}$, and then afterwards introduce the statistical or random properties of the scattering potential. The probability flux density for a state $\psi = \psi^0 + \psi$, viz.,

$$\vec{J} = (i\hbar/2m)\,(\Psi\nabla\Psi^* - \text{c.c.}), \tag{2.1}$$

has three distinct terms,

$$\vec{J} = \vec{J}(\psi^0; \psi^0) + \vec{J}(\psi; \psi) + \vec{J}(\psi^0; \psi), \tag{2.2}$$

corresponding to the unscattered wave, the scattered wave, and the interference between the scattered and unscattered waves, respectively. These take on complicated forms when the scattering potential has the complicated form of the inhomogeneous space-charge potential $\phi(\vec{R}, z)$.

Simplifications occur, however, when we make use of the statistical properties of the scattering potential. For our purposes, $\phi(\vec{R}, z)$ may be treated as a random function of $\vec{R}$ with two basic ensemble-average properties:

$$\{\phi(\vec{R}, z)\} = 0 \tag{2.3a}$$

and

$$\{\phi(\vec{R}, z)\,\phi(\vec{R}+\Delta\vec{R}, z)\} = \text{function of } \Delta\vec{R} \text{ and } z\,, \quad \text{but not of } \vec{R}\ . \tag{2.3b}$$

Equation (2.3a) indicates that we have subtracted out the mean value of the space-charge potential, as mentioned above in connection with Eq. (1.8a). Equation (2.3b) means that the various probability density functions for $\phi(\vec{R})$ are uniform in $\vec{R}$. Because of this statistical uniformity, we may equate ensemble averages with spatial averages, e.g.,

$$\{\phi(\vec{R})\} = \bar{\phi} = \lim L^{-2} \int_{L^2} d^2R\, \phi(\vec{R}) \quad \text{as } L \to \infty\ . \tag{2.4}$$

For use in our scattering theory, it is convenient to reexpress conditions (2.3a) and (2.3b) in $\vec{Q}$ space. This is possible because each member of the statistical ensemble of functions $\phi(\vec{R}, z)$ can be represented just as well by its Fourier transform $\phi(\vec{Q}, z)$. Equations (2.3a) and (2.3b) then appear as

$$\{\phi(\vec{Q}, z)\} = 0 \tag{2.5a}$$

and

$$\{\phi(\vec{Q}, z)\,\phi^*(\vec{Q}', z)\} = 4\pi^2\,\delta(\vec{Q} - \vec{Q}')\,g_\phi(\vec{Q}, z)\,, \tag{2.5b}$$

where $g_\phi(\vec{Q})$ is the spectral density of $\phi(\vec{R}, z)$:

$$g_\phi(\vec{Q}, z) = \lim L^{-2} |\phi_L(\vec{Q}, z)|^2 \quad \text{as } L \to \infty$$

$$\phi_L \equiv 0 \quad \text{for } R^2 > L^2\ . \tag{2.5c}$$

Equation (2.5a) follows directly from ensemble-averaging Eq. (1.4a) and using Eq. (2.3a). Equation (2.5b) can be obtained by writing

$$\{\phi(\vec{Q})\,\phi^*(\vec{Q}')\} = \int \frac{d^2R}{2\pi} \int \frac{d^2R'}{2\pi} \times \{\phi(\vec{R})\,\phi(\vec{R}')\}\, e^{i\vec{Q}\cdot\vec{R} - i\vec{Q}'\cdot\vec{R}'}$$

and then imposing the statistical-uniformity condition (2.3b), giving

$$\{\phi(\vec{Q})\,\phi^*(\vec{Q}'\} = \delta(\vec{Q} - \vec{Q}') \int (d^2\Delta R/2\pi)\,\rho_\phi(\Delta\vec{R})\, e^{-i\vec{Q}\cdot\Delta\vec{R}}\,,$$

where

$$\rho_\phi(\Delta\vec{R}) = \lim L^{-2} \int d^2R\, \phi_L(\vec{R}, z)\,\phi_L(\vec{R}+\Delta\vec{R}, z) \quad \text{as } L \to \infty\ .$$

Equation (2.5b) then follows by means of the Wiener–Khinchine relation.[11]

We can now use Eqs. (2.5a) and (2.5b), the statistical properties of the space-charge potential, to simplify the probability flux density $\vec{J}$, when the latter is ensemble averaged. First, we note that in the Born approximation ψ is a linear functional of ϕ, so that

$$\{\vec{J}(\psi^0, \psi)\} = 0\ . \tag{2.6}$$

Particle flux conservation in surface scattering requires that $\{J_z(\psi_0 + \psi,\ \psi_0 + \psi)\}$ vanish exactly, since carriers are assumed neither to go through the surface nor to be created there. Of course, $J_z(\psi_0, \psi_0) = 0$ because ψ_0 is a standing wave. Furthermore, the *exact* ψ contains only outgoing ($k_z > 0$) waves for $z \to \infty$, so that $\{J_z(\psi, \psi)\} > 0$. Therefore the *exact* interference terms $\{J_z(\psi, \psi_0)\}$ + c. c. must be negative. Equation (2.6) then means that our *approximate* ψ fails to conserve particle flux: this will be discussed elsewhere. Next, we point out the great simplification produced by Eq. (2.5b) in the scattered flux density $\vec{J}(\psi, \psi)$ whereby

$$\vec{J}(\psi, \psi) = \frac{i\hbar}{2m}\left(\frac{me}{2h}\right)^2 \int \frac{d^2Q}{2\pi} \int \frac{d^2Q'}{2\pi}\, \phi(\vec{Q} - \vec{K}, 0)\,\phi^*(\vec{Q}' - \vec{K}, 0) \times \{[(F_p e^{i\Gamma z} + F_s)\, e^{i\vec{Q}\cdot\vec{R}}]\, \nabla\, [(F_p' e^{-i\Gamma^* z} + F_s')\, e^{-i\vec{Q}'\cdot\vec{R}}] - \text{c. c.}\} \tag{2.7}$$

is reduced to an expression which, as we shall show below, has a simple semiclassical interpretation and is capable of complete evaluation:

$$\{\vec{J}(\psi, \psi)\} = (me^2/8h^2) \int d^2Q\, g_\phi(\vec{Q} - \vec{K}, 0)\, \{[2\vec{Q} + \vec{1}_z(\Gamma + \Gamma^*)]\, F_p^2\, e^{i\Gamma z - i\Gamma^* z} + 2\vec{Q}\, F_p^2 + 2\vec{Q}\, F_p F_s (e^{i\Gamma z} + \text{c.c.}) - \vec{1}_z F_p \hat{F}_s e^{-\kappa z}\}\,, \tag{2.8a}$$

where

$$-\hat{F}_s = [(\kappa - ik_z)(e^{i\Gamma z} - \text{c. c.}) + i(e^{i\Gamma z} - \text{c.c.})]$$

$$\times M e^{ik_z z} - \text{c. c.} \tag{2.8b}$$

and

$$M = 2i\,[(\kappa - ik_z)^2 + \Gamma^2]^{-1}\ , \quad \vec{1}_z = (0, 0, 1)\ . \qquad (2.8c)$$

The F_p term is propagating for $Q^2 < k_0^2$ and is evanescent for $Q^2 > k_0^2$. The F_s and $\hat{F}_s$ terms are evanescent for all values of $\vec{Q}$. These evanescent fluxes, corresponding to real surface currents, are not correctly given in the Born approximation, because the rescattering of electrons in such states cannot be neglected in any approximation. In this paper we will therefore treat only the propagating flux density

$$\{\vec{J}\}_p = (me^2/4\hbar^3) \int_{Q^2<k_0^2} d^2Q \times F_p^2 g_\phi(\vec{Q} - \vec{K}, 0)\,(Q_x, Q_y, \Gamma). \qquad (2.9)$$

This takes on a clear semiclassical form in terms of the angular coordinates of the scattered waves,

$$Q_x = k_0 \sin\theta \cos\eta\ , \quad Q_y = k_0 \sin\theta \sin\eta\ . \qquad (2.10a)$$

Writing

$$d^2Q = Q\,dQ\,d\eta = -k_0^2\,\mu\,d\mu\,d\eta\ , \quad \mu = \cos\theta \qquad (2.10b)$$

one gets

$$\{\vec{J}\}_p = \int_0^1 d\mu \int_0^{2\pi} d\eta\, f(\vec{K}, -k_z; \mu, \eta)\,\vec{v}\ , \qquad (2.11a)$$

where

$$\vec{v} = (\hbar/m)\,(Q_x, Q_y, \Gamma) \qquad (2.11b)$$

is the scattered velocity vector and

$$f(\vec{K}, -k_z; \mu, \eta) = (me/2\hbar^2)^2\, \mu k_0^2 F_p^2 g_\phi(\vec{Q} - \vec{K}, 0) \qquad (2.11c)$$

is the scattered distribution function, the number of classical electrons per unit solid angle at (μ,η).

Although it has a clear semiclassical interpretation, Eq. (2.11a) is somewhat more complicated than the corresponding expression in the theory of scattering from a finite-range potential.[12] There, only one propagation vector is seen at a distant detector because the scatterer subtends only an infinitesimal solid angle at the detector. The range 2π of scattering angles appear in Eq. (2.11a) because the scattering surface subtends the solid angle 2π at a detector, no matter how far from the surface it may be.

III. DIFFERENTIAL SCATTERING PROBABILITY

The concept of differential scattering cross section, appropriate for finite-range scatterers, is generally not useful for surface scattering except when the surface density of scatterers is low enough to ignore interference effects and screening interactions. The generally appropriate concept is that of the dimensionless differential surface-scattering probability $w(\vec{K}, -k_z; \mu, \eta)$, which we define as

$$w(\vec{K}, -k_z; \mu, \eta) = N(\mu, \eta)/N_0(\vec{K}, -k_z)\ , \qquad (3.1)$$

where $N_0(\vec{K}, -k_z)$ is the number of electrons per second incident on *unit area of the surface* with momentum $(K_x, K_y, -k_z)$, and $N(\mu, \eta)\,d\mu\,d\eta$ is the number of particles per second scattered into solid angle $d\mu\,d\eta$ from *unit area of the surface*.

Equation (2.11a) enables us to find $N(\mu, \eta)$ directly. Evidently,

$$N(\mu, \eta) = \mu\, v f(\mu, \eta)\ . \qquad (3.2)$$

On the other hand, the unperturbed wave function ψ^0 of Eq. (1.1b) describes an incident flux density of magnitude $\frac{1}{4}v$, so that

$$N_0(\vec{K}, -k_z) = \tfrac{1}{4}\,\mu_K\, v\ , \qquad (3.3)$$

where

$$\mu_{\vec{K}} = -k_z/k_0 < 0\ .$$

We thus obtain

$$w(\vec{K}, -k_z; \mu, \eta) = \frac{-\mu}{\mu_{\vec{K}}} f(\mu, \eta) = \frac{-\mu^2}{\mu_{\vec{K}}} \left(\frac{mek_0}{\hbar^2}\right)^2 F_p^2 g_\phi(\vec{Q} - \vec{K}, 0)\ , \qquad (3.4)$$

where F_p is given by Eq. (1.9b), and $g_\phi(\vec{Q} - \vec{K}, 0)$ is the spectral density of the scattering potential for the surface momentum change $(\vec{Q} - \vec{K})$.

This spectral density $g_\phi(\vec{Q}, z)$ is expressed in the GBL theory in terms of the spectral density $g_{\delta\Omega}(\vec{Q})$ of the surface-charge density Ω, or rather of $\delta\Omega = \Omega(\vec{R}) - \overline{\Omega}$ (by means of Poisson's equation, the static electron response function, and the Maxwell boundary conditions):

$$g_\phi(\vec{Q}, z) = \mathcal{R}(\vec{Q})^2 e^{-2\kappa z} g_{\delta\Omega}(\vec{Q})\ , \qquad (3.5a)$$

where

$$\mathcal{R}(\vec{Q}) = (4\pi/\epsilon_+)^2 (\kappa + \gamma Q)^{-2}\ , \quad \gamma = \epsilon_-/\epsilon_+ < 1 \qquad (3.5b)$$

describes the response of the semiconductor-surface space-charge region to an arbitrary surface-charge distribution. Suppose, in particular, that $\Omega(\vec{R})$ consists of an array of point charges, e.g., associated with chemisorption bonds, occupying some of the sites $\vec{A}$ of a regular surface lattice (mesh). In that case $g_{\delta\Omega}$ is essentially the statistical structure factor $S(\vec{Q})$ of that array:

$$g_{\delta\Omega}(\vec{Q}) = (a\overline{\Omega}^2/4\pi^2)\, S(\vec{Q})\ , \qquad (3.6a)$$

$$S(\vec{Q}) = \sum_{\Delta\vec{A}} \left(\frac{p(\Delta\vec{A})}{\overline{n}} - 1\right) e^{i\vec{Q}\cdot\Delta\vec{A}} + \sum_{\vec{Q}_i \neq 0} \delta(\vec{Q} - \vec{Q}_i)\, \frac{4\pi^2}{a}\ . \qquad (3.6b)$$

Here $n(\vec{A}) = 0, 1$ is the occupation number of site $\vec{A}$, $\overline{n}$ is the mean of $n(\vec{A})$:

$$\overline{n} = \{n\} = a\overline{\Omega}\ , \qquad (3.6c)$$

where a is the unit mesh area. Also, $p(\Delta\vec{A})$ is the pair-correlation function

$$p(\Delta\vec{A}) = \{n(\vec{A})\, n(\vec{A}+\Delta\vec{A})\}/\bar{n}\ , \tag{3.6d}$$

$$p(0) \equiv 1\ , \tag{3.6e}$$

and $\vec{Q}_i$ are the reciprocal-mesh vectors

$$\frac{\vec{Q}_i \cdot \vec{A}}{2\pi} = 0, \pm 1, \pm 2, \ldots\ . \tag{3.6f}$$

These reciprocal-mesh vectors determine the features of the evanescent states, but do not directly appear in the propagating flux $\{\vec{J}\}_p$, and so can be omitted in this paper. We thus obtain the explicit form of the differential surface-scattering probability

$$w(\mu, \eta) = w_{\mathrm{GO}}(\mu, \eta) \left(\frac{2\kappa}{\kappa + \gamma|\vec{Q} - \vec{R}|}\right)^2 \bar{n} S(\vec{Q} - \vec{K})\ , \tag{3.7a}$$

where

$$w_{\mathrm{GO}} = \frac{\bar{n}a}{-\mu_{\vec{K}}} \left(\frac{4\Gamma k_z}{(\kappa^2 + k^2 + \Gamma^2)^2 - 4k_z^2\Gamma^2}\right)^2 \left(\frac{2me^2}{\hbar^2 \epsilon_+}\right)^2 \tag{3.7b}$$

is the corresponding result of the GO calculation. The factors multiplying w_{GO} express the effect of properly taking into account the screening potential and the interference of waves scattered from different scatterers.

The simplest interference situation to analyze is, of course, that of no correlation at all in the occupation numbers: If

$$p(\Delta\vec{A}) = \bar{n} \qquad \text{for all} \quad \Delta\vec{A} \neq 0\ , \tag{3.8a}$$

then

$$S^0(\vec{Q}) = S^0(0) = (1 - \bar{n})/\bar{n}\ . \tag{3.8b}$$

If $\bar{n} \ll 1$, then w is linear in $\bar{n}$, and an effective surface-scattering cross section might be introduced. Next, consider the effect of a short-range correlation: If

$$p(\Delta\vec{A}) = \bar{n} \qquad \text{for all} \quad |\Delta\vec{A}|\, k_0 \gtrsim \tfrac{1}{10}\ , \tag{3.9a}$$

then

$$S(\vec{Q}) = S(0) = \sum_{\Delta A} \left(\frac{p(\Delta\vec{A})}{\bar{n}} - 1\right)\ . \tag{3.9b}$$

In both of these cases, the scattering is determined by $S(0)$, which, as has been shown elsewhere,[8] is a thermodynamic property of the chemisorbed charged adatoms if these have reached equilibrium. If the distribution has not reached equilibrium so that $S(0)$ cannot be obtained from statistical thermodynamic arguments, some guidance in the choice of $p(\Delta\vec{A})$ is available from the sum rule

$$\int_{\mathrm{BZ}} d^2Q\, S(\vec{Q}) = (4\pi^2/\bar{n}a)(1 - \bar{n})\ , \tag{3.10}$$

in which the integral goes over one Brillouin zone of the reciprocal mesh, and which arises from Eq. (3.6e).

Finally, we consider the space-charge form factor

$$B = 4\kappa^2 (\kappa + \gamma|Q - K|)^{-2} \tag{3.11}$$

appearing in Eq. (3.7a), which corrects for the arbitrary potential used in the GO treatment, viz., $(e/\epsilon_+ r)e^{-q_0 r}$ for $z \geqslant 0$. For small-angle scattering events, one can see that

$$B = 4 \qquad \text{for} \quad |Q - K| \ll q_s\ . \tag{3.12}$$

Thus, the Fourier coefficients of the Yukawa potential mentioned above are exactly half the correct ones, for $\vec{Q} \to 0$. At the other extreme, one can consider large-angle scattering for $q_s^2/k_0^2 \ll 1$, in which case

$$B = 4(1+\gamma)^{-2} \qquad \text{for} \quad |\vec{Q} - \vec{K}| \gg q_s\ . \tag{3.13}$$

This simply means that large-angle scattering events are determined by the unscreened Coulomb singularity itself, which has the form $(e/\epsilon_+ r)[2/(1+\gamma)]$.

IV. DIELECTRIC IMAGE EFFECTS

The polarization energy of an electron changes as the electron is brought nearer the interface between two dielectrics. This can be expressed[13] in terms of a dielectric image force, and has already entered the scattering potential ϕ directly, as is shown by the factor $\gamma = \epsilon_-/\epsilon_+$ in the spectral density g_ϕ in Eq. (3.5b).

But there is also a direct dielectric image repulsion of each electron from the surface when $\gamma < 1$. In GBL it was shown that for semiconductors the work done on an electron in bringing it and its screening cloud closer to a surface can be expressed in terms of a screened image potential ϕ_I given by

$$-e\phi_I = (be^2/4\epsilon_+ z)\, e^{-q_s z}\ , \tag{4.1}$$

where b is a constant between unity and $(\gamma - 1)/(\gamma + 1)$. Being independent of R, this is not a scattering potential. Nevertheless, the scattering is weakened because ϕ_I decreases the amplitude of the unscattered wave functions ψ^0 near the surface.

This direct dielectric image repulsion can be introduced into the foregoing scattering theory very simply, albeit crudely, by terminating ψ^0 at the classical turning point z_I instead of at the surface $z = 0$, z_I being given by

$$-e\phi_I(z_I) = \hbar^2 k_z^2/2m \qquad (z_I > 0)\ . \tag{4.2}$$

Electrons incident at grazing angles have small k_z, and hence have large values of z_I and are strongly decoupled from the scattering potential. We thus replace Eq. (1.1) by

$$\psi^0 = \sin k_z (z - z_I)\, e^{i\vec{K}\cdot\vec{R}}\ , \qquad z \geqslant z_I \tag{4.3a}$$

$$= 0\ , \qquad z < z_I\ . \tag{4.3b}$$

For the Born-approximation treatment of Sec. I to remain valid, we must correspondingly replace Eq. (1.2b) by

$$\psi = 0\,, \qquad z \leqslant z_I\,. \tag{4.4}$$

The Born-approximation equation (1.5a) is then replaced by

$$\left(\frac{\partial^2}{\partial z^2} + \Gamma^2\right)\psi(\vec{Q}, z) = \frac{-2me}{\hbar^2}\sin k_z(z - z_I)\,\phi(\vec{Q} - \vec{K}, z)\,, \quad z \geqslant z_I\,. \tag{4.5}$$

The scattered-wave equation (1.6a) is now replaced by

$$\psi(\vec{Q}, z) = (-2me/\hbar^2)\int_{z_I}^{\infty} dz'\,G_D(z, z') \times \phi(\vec{Q} - \vec{K}, z')\sin k_z(z' - z_I)\,, \tag{4.6}$$

where now the *displaced* Green's function

$$G_D(z, z') = (1/2i\Gamma)\left(e^{i\Gamma|(z-z_I)-(z'-z_I)|} - e^{i\Gamma|(z-z_I)+(z'-z_I)|}\right) \tag{4.7a}$$

has the properties

$$G_D(z, z') = 0 \qquad \text{for} \qquad z = z_I \tag{4.7b}$$

[which ensures that Eq. (4.4) is satisfied] and

$$\left(\frac{\partial^2}{\partial z^2} + \Gamma^2\right) G_D(z, z') = \delta(z - z') + \delta(z + z' - 2z_I) \tag{4.7c}$$

[which ensures that Eq. (4.5) is satisfied]. Here the fact that

$$\phi(\vec{Q} - \vec{K}, z') = \phi(\vec{Q} - \vec{K}, 0)\,e^{-\kappa z'} = \phi(\vec{Q} - \vec{K}, \Delta z)\,e^{-\kappa z_I}\,, \tag{4.8}$$

where $\Delta z' = z' - z_I$, allows Eq. (4.6) to be written as

$$\psi(\vec{Q}, z) = (e^{-\kappa z_I})(2me/\hbar^2)\int_0^{\infty} d\Delta z'\,G(\Delta z, \Delta z') \times \sin(k_z\Delta z')\,\phi(\vec{Q} - \vec{K}, \Delta z')\,, \tag{4.9}$$

where now $G(\Delta z, \Delta z')$ has exactly the same functional form as the Green's function used in Eq. (1.6a) for the scattered wave *without* this dielectric image effect. Thus, the entire effect of shifting the unscattered wave ψ^0 a distance $z_I(k_z)$ is merely to shift all the scattered waves by the same amount *and* to change their amplitudes by $e^{-\kappa z_I}$.

Because this factor is independent of $\vec{R}$ and z, the scattered current density is unchanged except for the appearance of a multiplicative factor $e^{-2\kappa z_I}$. Thus, for electrons, the differential surface-scattering probability of Eq. (3.7a) becomes

$$w(\mu, \eta) = w_{\mathrm{GO}}(\mu, \eta)\,B\,e^{-2\kappa z_I}\,\bar{n}\,S(\vec{Q} - \vec{K})\,, \tag{4.10}$$

where the space-charge form factor B is given by Eq. (3.11). Here $\cos^{-1}\mu$ and η are the angles of the emerging electron in spherical coordinates.

As noted above, the dielectric image factor $e^{-2\kappa z_I(k_z)}$ strongly decreases the scattering rate for electrons at grazing incidence because z_I increases as k_z decreases. Inasmuch as $\kappa = [q_s^2 + (\vec{Q} - \vec{K})^2]^{1/2}$, it is clear that this suppression of scattering occurs mostly for large-angle scattering. This is indeed plausible, since the spatial shift of the unscattered wave primarily cuts down the overlap of ψ^0 with the more singular part of the scattering potential.

V. FUCHS REFLECTIVITY; CONCLUSIONS

We use the general-boundary-condition formalism[14] to get the Fuchs reflectivity $\mathfrak{p}$ and kinetic specularity W_0 from the differential scattering probability of Eq. (4.10): For an isotropic surface,

$$W_0(\mu_+) = 1 - \int_{-1}^{0} d\mu \int_0^{2\pi} d\Delta\eta(-\mu_-/\mu_+) \times w_s(\mu_-, \eta_- | \mu_+, \eta_+)\,, \tag{5.1a}$$

$$\mathfrak{p}(\mu_+) = 1 - \int_{-1}^{0} d\mu_- \int_0^{2\pi} d\Delta\eta\,\frac{-\mu_-}{\mu_+}\,w_s(\mu_-, \eta_- | \mu_+, \eta_+) \times\left[1 - \cos\Delta\eta\left(\frac{1 - \mu_-^2}{1 - \mu_+^2}\right)^{1/2}\right], \tag{5.1b}$$

where $\cos^{-1}\mu_+$ is the angle between the scattered k vector and the inward normal to the surface, and $\Delta\eta = \eta_- - \eta_+$ is the angle between surface components of scattered and incident k vectors.

These integrations, which could be carried out analytically in the simpler GO theory, unfortunately had to be carried out numerically for w_s given by Eq. (4.10). We carried out the integrations for the completely uncorrelated ("pure random") distribution of surface charges, for which the structure factor (leaving out the Bragg terms outside the Brillouin zone) is

$$S^0(\vec{Q}) \approx S^0(0) = (1 - \bar{n})/\bar{n} \qquad \text{for} \qquad p(\Delta\vec{A}) = \bar{n}\ (\Delta\vec{A} \neq 0)\,, \tag{5.2a}$$

in which case Eq. (4.10) reduces to the simpler form

$$w_s = w_{\mathrm{GO}}\,B\,e^{-2\kappa z_I}(1 - \bar{n})\,, \tag{5.2b}$$

in which case $1 - W_0$ and $1 - \mathfrak{p}$ are linear in $\bar{n}$ for $\bar{n} \ll 1$.

The scatterers are charged so that an uncorrelated distribution is not really to be expected except when $\bar{n}$ is close to zero. Correlation effects can depress $S(\vec{Q})$ and w_s very significantly, as we now show for the case of depressed nearest-neighbor occupation $p(1) < \bar{n}$ of a simple square mesh. From Eq. (3.6b)

$$S(\vec{Q}) = \frac{1 - \bar{n} - 2[\bar{n} - p(1)](\cos Q_x A_0 + \cos Q_y A_0)}{\bar{n}} \geqslant 0\,. \tag{5.3}$$

In the absence of a statistical thermodynamic calculation of $p(1)$, we might *guess* a form [which

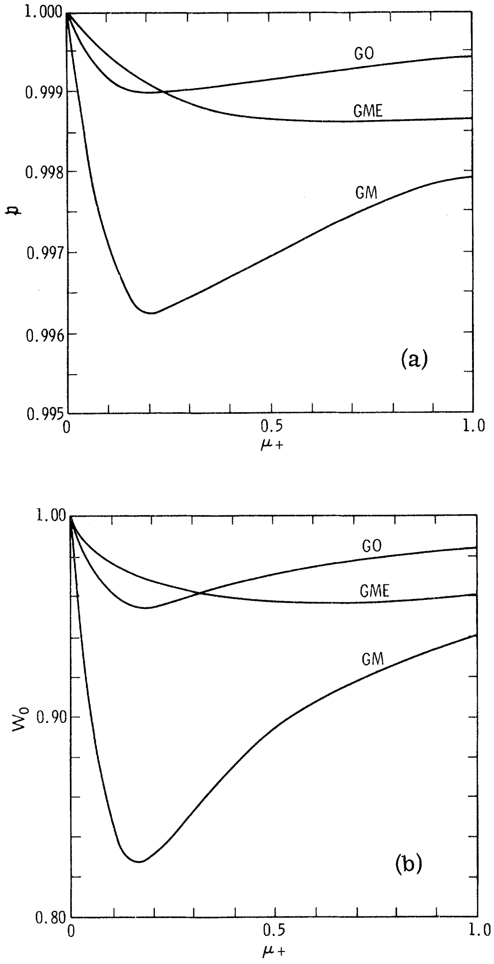

FIG. 1. (a) $\mathfrak{p}$ vs μ_+; $\bar{n}/a = 10^9$ cm^{-2}, $\hbar^2k^2/2m^* = 0.026$ eV, $m^*/m_0 = 0.013$, $\epsilon_+ = 17$, $q_0 = 1.33\times10^5$ cm^{-1}. (b) W_0 vs μ_+; $\bar{n}/a = 10^9$ cm^{-2}, $\hbar^2k^2/2m^* = 0.026$ eV, $m^*/m_0 = 0.013$, $\epsilon_+ = 17$, $q_0 = 1.33\times10^5$ cm^{-1}.

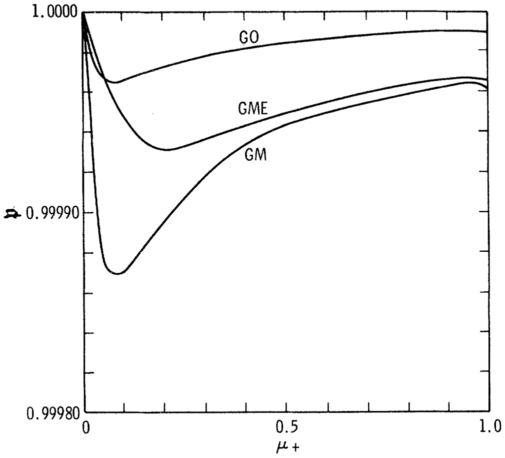

FIG. 3. $\mathfrak{p}$ vs μ_+; $\bar{n}/a = 10^9$ cm^{-2}, $\hbar^2k^2/2m^* = 0.26$ eV, $m^*/m_0 = 0.013$, $\epsilon_+ = 17$, $q_0 = 1.33\times10^5$ cm^{-1}.

keeps $S(\vec{Q})$ positive definite]:

$$\bar{n} = p(1) = \tfrac{1}{4}(1-\bar{n})(1-e^{-\alpha}), \tag{5.4a}$$

where

$$\alpha = \frac{2e^2}{A_0(\epsilon_+ + \epsilon_-)kT} \tag{5.4b}$$

is, roughly, the nearest-neighbor Coulomb energy in units of kT. Since in w_s only small values of Q_x and $Q_y \sim k_0 \ll |A_0|^{-1}$ occur, we can set

$$S(\vec{Q}) = S(0) = \frac{(1-\bar{n})e^{-\alpha}}{\bar{n}} = S^0(0)\,e^{-\alpha}, \tag{5.5}$$

so that our calculated (uncorrelated) values of $1 - W_s$ and $1 - \mathfrak{p}$ have to be multiplied by the very strong factor $e^{-\alpha}$.

The calculations have been carried out for spherical energy surfaces, and so are most directly ap-

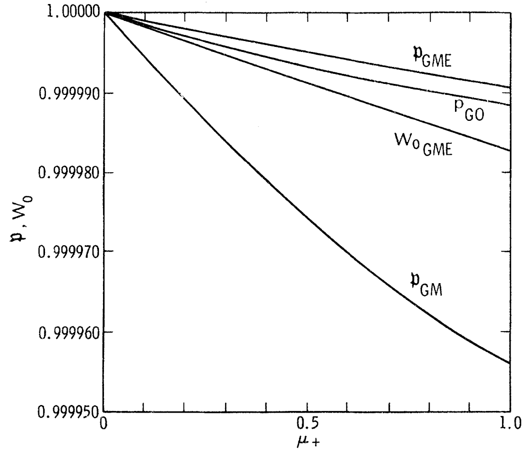

FIG. 2. $\mathfrak{p}$ and W_0 vs μ_+; $\bar{n}/a = 10^9$ cm^{-2}, $\hbar^2k^2/2m^* = 0.026$ eV, $m^*/m_0 = 0.013$, $\epsilon_+ = 17$, $q_0 = 1.33\times10^6$ cm^{-1}.

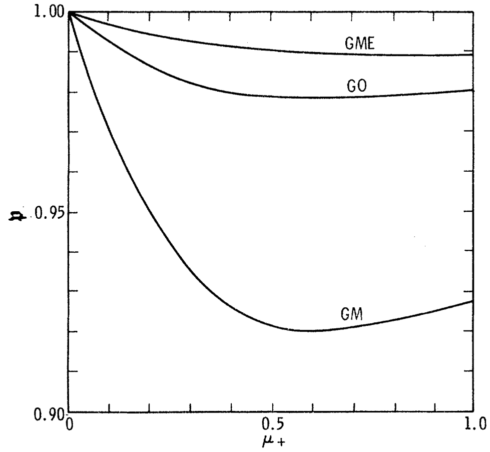

FIG. 4. $\mathfrak{p}$ vs μ_+; $\bar{n}/a = 10^9$ cm^{-2}, $\hbar^2k^2/2m^* = 0.0026$ eV, $m^*/m_0 = 0.013$, $\epsilon_+ = 17$, $q_0 = 1.33\times10^5$ cm^{-1}.

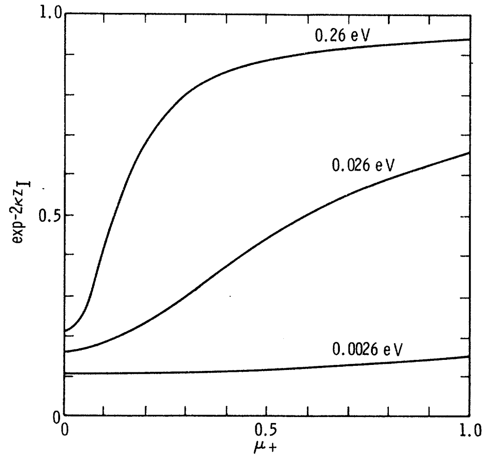

FIG. 5. $e^{-2\kappa z_I}$ vs μ_+ for different values of $\hbar^2k^2/2m^*$, $m^*/m_0 = 0.013$, $\epsilon_+ = 17$, $q_0 = 1.33\times 10^5\ \text{cm}^{-1}$.

plicable to semiconductors like InSb,[15] whose electron effective mass $0.013m_0$ and dielectric constant $\epsilon_+ = 17$ were used. Numerical results for $\mathfrak{p}$ and W_0 versus the emergence angle cosine μ_+ are plotted in Figs. 1–4 for three different forms of differential scattering probability w_s. Curves labeled GME correspond to the use of Eq. (4.10). Curves labeled GM correspond to the use of Eq. (4.10) with the dielectric image factor $e^{-2k z_I}$ omitted, i.e., to Eq. (3.7a). Curves labeled GO correspond to the GO theory,[1] i.e., to the use of w_{GO} of Eq. (3.7b). In Fig. 5 we show the specific effect of the dielectric image factor, expressed as

$$e^{-2\kappa z_I} \equiv (1-\mathfrak{p}_{GME})/(1-\mathfrak{p}_{GM})\ , \qquad (5.6)$$

plotted as a function of the cosine of the emergence angle. The dielectric image factor is more effective for slower particles and nearer grazing emergence because, in both cases, k_z is smaller.

The qualitative features of the simpler GO theory are retained: (a) $\mathfrak{p} \to 1$ for grazing emergence and (b) the Fuchs diffusivity $(1-\mathfrak{p})$ is much smaller than the total scattering probability $1 - W_0$. But the use of a realistic treatment of the screening of the surface-scattering potential has increased its Fourier transform and, hence, $1-\mathfrak{p}$ by about a factor of 4. This is partially compensated by the dielectric image effect, which decreases the Fuchs diffusivity $1-\mathfrak{p}$, particularly at grazing angles. For such angles, k_z is small, z_I is large, and $e^{-2\kappa z_I}$ becomes much less than unity.

Compared with the GO theory, as Figs. 1–4 show, the present theory gives a weakened angular dependence of $\mathfrak{p}$ at grazing angles. This makes cuspid behavior in the surface mobility somewhat more understandable.

One unwelcome feature of the GO theory which is retained in the present theory is the breakdown for larger values of $\bar{n}$, where $\mathfrak{p}$ can become negative. We can now see, however, that this breakdown is not due to the neglect of interference effects, but has to be ascribed to the use of the Born approximation with its neglect of multiple scattering. This is particularly serious for evanescent states, a treatment of which will be given elsewhere.

A Boltzmann transport calculation of surface mobility using the calculated values of the Fuchs $\mathfrak{p}$ now becomes possible and is being carried out. That will then permit the scattering model of the present calculation to be tested against surface-mobility measurements, e.g., those of Preuss[6] on InSb, those of Sah[7] on the Si–SiO$_2$ interface, etc. It should also be possible to test the present surface-scattering theory, or rather the surface-charge structure factor deduced from a fit to transport data, against structure-factor information from chemisorption isotherm data, using the new surface-scattering–chemisorption relation of one of us.[8] Such experiments, involving chemisorption and electrical transport studies in thin single-crystal films of IV-VI semiconductors with exposure to oxygen, hydrogen, etc., are being carried out at the Naval Ordnance Laboratory.[16] Further scattering calculations are also being pursued which replace the Born approximation by a one-particle Green's-function method which conserves particle flux exactly, and which includes ellipsoidal energy surface effects.

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Heat-Pulse Propagation in *p*-Type Si and Ge under Uniaxial Stress*

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Heat-pulse propagation has been studied in *p*-type silicon and *p*-type germanium as a function of uniaxial stress (up to 10^9 dyn cm^{-2}) and of pulse temperature. The coupling between thermal phonons and the stress-split ground state of acceptors has been calculated using the effective-mass approximation for the relevant acceptor-hole wave functions. In addition to the *s*-like parts of the expansion for the envelopes usually considered, *d*-like parts of the expansion have been included here. The important phonon scattering rates due to stress-split acceptor states were derived. The rates were obtained for resonance absorption (for phonons with energies close to the splitting energy), and for several second-order processes. In addition, Rayleigh scattering of phonons by isotopic impurities has been evaluated. A black-body model for phonon emission from the heat-pulse generator was assumed. The total calculated scattering rate agrees with the observed stress dependence of the heat-pulse amplitudes when the effects of internal strains, and, in the case of high acceptor contents, of phonon multiple scattering are taken into account. A fit of the experimental results to the calculated results yields two distinct sets of values for the "static" ($a^*q \ll 1$) and "dynamic" ($a^*q \gtrsim 1$) deformation-potential constants (a^* is the effective Bohr radius of the impurity and q is the wave number of the relevant wave component). This observation resolves the apparent conflict in previously reported values of these constants, obtained from separate studies in the static (e.g., piezoreflectance) and dynamic (thermal-conductivity) regimes. The present theory does not yield such distinctions for the two regimes. It is concluded, therefore, that the effective-mass approximation is not adequate for describing the full range of frequency-dependent stress effects. It should be emphasized that the heat-pulse study is particularly well suited for investigating these differences because the constants for the two regimes are derived within the framework of the same experiment.

I. INTRODUCTION

Neutral shallow impurities in semiconductors are very effective scatterers of thermal phonons at low temperatures. This has been observed as a strong increase in the thermal resistivity of Ge and Si by light doping with *n*-type[1–4] and *p*-type[5–7] impurities. Similar effects have also been seen by propagation of heat pulses in such materials.[8]

The coupling of lattice waves to these impurities can be related to the crystal symmetry at the impurity site. For *p*-type Si and Ge, the ground state of the acceptor holes has the Γ_8 symmetry of the valence-band edge (at the center of the Brillouin zone) and is thus fourfold degenerate.[9] These degenerate levels have been shown to contribute strongly to the thermal resistivity in *p*-type Si and Ge, because of elastic scattering of phonons.[10] Any strain of lower symmetry acting on the impurity site will split the quartet into two Kramers doublets, thus giving additional scattering of phonons. The thermal conductivity is, therefore, predicted to be considerably modified by such splitting.[11]

We previously reported[12] the results of a preliminary study in which this coupling between acceptor holes and phonons was investigated by means of heat-pulse propagation in uniaxially stressed *p* Ge. This approach is especially well suited for systematic studies of phonon scattering by shallow impurities in semiconductors. In particular, the phonon scattering processes can be much better understood and compared more directly with theoretical predictions through heat-pulse investigations than through studies of thermal resistivity.

In this paper we present the results of heat-pulse transmission studies in uniaxially stressed boron-doped Si and gallium-doped Ge. Expressions for the relevant phonon scattering rates have been derived, from which the heat-pulse transmission was computed. The calculated and experimental results are compared and several features of the scattering processes are thereby derived.

In Sec. II a theoretical treatment is presented