Screened donor impurities in many-valley semiconductors with anisotropic masses

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The binding energy of a conduction electron bound to a donor impurity in a doped semiconductor, using a Lindhard dielectric function, is calculated as a function of the free-carrier concentration, taking into full account the effects of the nonisotropic mass of the bound electron on both the kinetic energy and the screened Coulomb potential. A variational approach is adopted in which the trial wave function is chosen with a form similar to the solution of the problem of an electron bound in the Hulthén potential. The wave function is appropriately warped to account for the asymmetry caused by the nonisotropic masses. This calculation, in the limit of zero carrier concentration, is equivalent to work of earlier authors (Kohn and Luttinger and others) where a hydrogenic trial wave function was used. The method thus obtained is specifically applied to silicon and germanium and the results are compared to calculations done in the isotropic-mass approximation. The electron density where the Mott transition takes place is found to be lowered by introducing the nonisotropy. For germanium where the mass ratio is approximately 20, this effect is quite large. A similar calculation using the simpler Thomas-Fermi dielectric function is included for completeness.

There has been a great deal of interest, both theoretical and experimental, in the properties of shallow impurity states (acceptors and donors) in semiconductor materials in recent years. Much of this work has been reviewed by Kohn[1] and more recently by Bassani et al.[2]

For the case of very low impurity concentration, it is well known that each impurity site can be treated as an isolated center. Then, within the effective-mass approximation, the effective interaction potential between the conduction electron and the central ion of the impurity atom is taken to be Coulombic in nature. Kohn and Luttinger[3] and several other authors[4] have solved the impurity Hamiltonian in this approximation using a hydrogenic trial wave function in a variational calculation. These calculations take into account the effect of the nonisotropic electron masses one finds in multivalley semiconductors.

In the case of semiconductors with moderately high impurity concentrations, one finds significant overlap between the electronic wave functions of neighboring impurity atoms. This overlap enhances the probability of an electron moving from one impurity site to another as the impurity concentration increases, thus allowing an appreciable fraction of these electrons to become relatively mobile. The presence of these free carriers will act to modify the simple Coulombic electron-ion interaction—in effect a form of screening. Earlier calculations, again within the effective-mass approximation, take the basic interaction to be Coulombic but screened by a Thomas-Fermi,[5,6,8] Lindhard,[7,8] or Hubbard-Sham[8,9] dielectric constant. One finds that the binding energy of the electron bound to the impurity ion decreases as

a function of the free-carrier concentration N until at a critical density N_c the electron is no longer bound. This last effect is commonly known as the Mott transition. The effect of the multivalley structure of indirect-gap semiconductors on the screening functions has been taken into account, yet to date all of these screened calculations have been done assuming an isotropic electron mass.

In this paper a calculation of the ground-state energy of an electron bound in a Coulomb potential screened by the Lindhard dielectric function taking into full account the effect of the electron-mass anisotropy on the kinetic energy and screened potential is presented. Similar to the isotropic case, the Lindhard dielectric function is derived within the random-phase approximation for a sea of electrons with anisotropic masses interacting via a Coulomb potential. For simplicity a variational approach is adopted. For the trial wave function a modified form of a wave function originally derived by Hulthén[10] is used, suitably changed to reflect the cylindrical symmetry of the problem. The binding energy is calculated for the particular cases of germanium and silicon where the mass anisotropy is appreciable and accurately measured. The critical Mott transition density is noted and the results are compared with those of other authors who have used an isotropic-mass approximation.

DIELECTRIC FUNCTION

The static density-density response function for a noninteracting gas of electrons with anisotropic mass can be written as

$$\chi(\vec{q}) = \sum_{\vec{k}} \frac{f_{\vec{k}+\vec{q}} - f_{\vec{k}}}{E_{\vec{k}+\vec{q}} - E_{\vec{k}}} \; , \qquad (1)$$

where $f_{\vec{k}+\vec{q}}$ is the Fermi occupation function, which is a functional of the energy,

$$f_{\vec{k}} = \frac{1}{1 + \exp[-\beta(E_{\vec{k}} - \epsilon_F)]} \; . \qquad (2)$$

Here β is the inverse temperature and ϵ_F is the Fermi energy. The energy $E_{\vec{k}}$ is given by

$$E_{\vec{k}} = \frac{k_x^2}{2M_\parallel} + \frac{k_y^2 + k_z^2}{2M_\perp} \; . \qquad (3)$$

If one makes the following substitutions for q and k,

$$k_x = (M_\parallel/M^*)^{1/2} S_x, \quad q_x = (M_\parallel/M^*)^{1/2} t_x \; ,$$

$$k_y = (M_\perp/M^*)^{1/2} S_y, \quad q_y = (M_\perp/M^*)^{1/2} t_y \; , \qquad (4)$$

$$k_z = (M_\perp/M^*)^{1/2} S_z, \quad q_z = (M_\perp/M^*)^{1/2} t_z \; ,$$

one readily finds

$$\chi(\vec{q}) = \chi(q_x, q_y, q_z)$$

$$= \chi^0\left(q_x\left(\frac{M^*}{M_\parallel}\right)^{1/2}, \; q_y\left(\frac{M^*}{M_\perp}\right)^{1/2}, \; q_z\left(\frac{M^*}{M_\perp}\right)^{1/2}\right) \; , \qquad (5)$$

where $\chi^0(\vec{q})$ is the static density-density response function for a noninteracting gas of electrons with isotropic mass M^*,

$$M^* \equiv (M_\parallel M_\perp^2)^{1/3} \; . \qquad (6)$$

At zero temperature this has the familiar form,

$$\chi^0(q) = \frac{3N}{2\epsilon_F}\left(\frac{1}{2} + \frac{4k_F^2 - q^2}{8k_F q} \ln\left|\frac{2k_F + q}{2k_F - q}\right|\right) \; , \qquad (7)$$

where k_F is the Fermi momentum,

$$k_F = (3\pi^2 N/\nu)^{1/3} \; , \qquad (8)$$

N is the total free-electron carrier density, and ν is the number of valleys.

Within the random-phase approximation, the dielectric function can be obtained from the relation

$$\epsilon(q) = 1 - \frac{4\pi e^2}{\kappa q^2} \chi(q) \; , \qquad (9)$$

where κ is the static dielectric constant of the host crystal. In this case we have

$$\epsilon(q) = 1 - \frac{4\pi e^2}{\kappa q^2}$$

$$\times \chi^0\left(q_x\left(\frac{M^*}{M_\parallel}\right)^{1/2}, \; q_y\left(\frac{M^*}{M_\perp}\right)^{1/2}, \; q_z\left(\frac{M^*}{M_\perp}\right)^{1/2}\right) \; . \qquad (10)$$

VARIATIONAL APPROACH

Within the effective-mass approximation, the Hamiltonian for our system can be written

$$H = -\frac{\hbar^2}{2}\left(\frac{1}{M_\parallel}\frac{\partial^2}{\partial x^2} + \frac{1}{M_\perp}\frac{\partial^2}{\partial y^2} + \frac{1}{M_\perp}\frac{\partial^2}{\partial z^2}\right) + V(r) \; , \qquad (11)$$

where the Fourier transform of the potential is given by

$$V(q) = \frac{4\pi e^2}{\kappa q^2 \epsilon(q)} \; . \qquad (12)$$

Since the eigenvalues of the Hamiltonian cannot be obtained in closed form, and indeed, the potential-energy term $V(r)$ has no known analytic form, a variation approach will be adopted.

For the case of isotropic masses, Hulthén found that if the potential $V(r)$ is approximated by a simple analytic form,

$$V(r) = \frac{e^{-\lambda r \lambda}}{e^{-\lambda r} - 1} \; , \qquad (13)$$

the Hamiltonian could be solved in closed form. The wave function for the ground state is given by

$$\psi(r) = e^{-r}\frac{e^{\lambda r/2} - e^{-\lambda r/2}}{r}\left(\frac{4 - \lambda^2}{4\pi\lambda^2}\right)^{1/2} \; . \qquad (14)$$

To solve the problem of an electron bound in a screened Coulomb potential—screened by, say, a Lindhard or Thomas-Fermi dielectric function—this wave function has been used as a trial wave function by earlier authors, where λ is used as a variation parameter to minimize the energy. This approach was first used by Lam and Varsani for the Thomas-Fermi dielectric function. More-recent calculations with the dielectric function using this approach are in excellent agreement with the more-complicated approach of Rogers et al.[6] and Martino et al.[9] who do a direct numerical integration of the corresponding Schrödinger equation. The great success of this method in treating the isotropic-mass case leads one to expect similarly good results in the case of anisotropic masses with a suitably modified wave function.

Since the problem is no longer spherically symmetric, yet one wishes to keep the mathematics somewhat simple, a trial wave function of the following form will be adopted:

$$\psi(r) = \frac{e^{-\rho}(e^{+\mu\rho/2} - e^{-\mu\rho/2})}{\rho}\left(\frac{4 - \mu^2}{4\pi\beta^3\mu^2}\right)^{1/2} \; , \qquad (15)$$

where

$$\rho = (M_\parallel a_\parallel x^2 + M_\perp a_\perp y^2 + M_\perp a_\perp z^2)^{1/2} \; , \qquad (16)$$
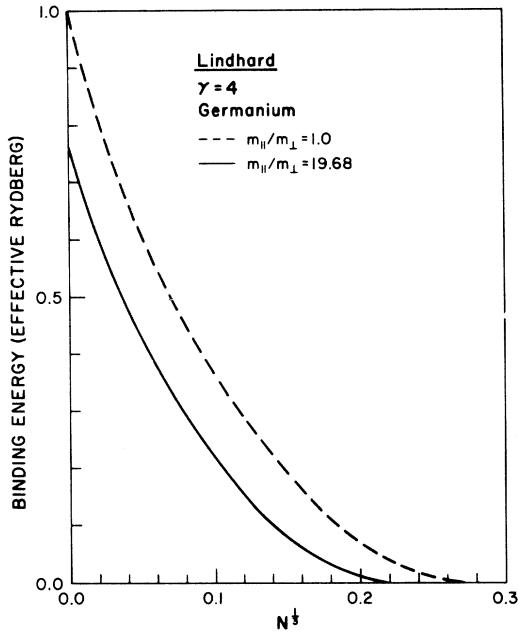
FIG. 1. Binding energy of a conduction electron bound to a donor impurity in germanium, calculated using the Lindhard dielectric function, in both isotropic- and anisotropic-mass approximations.

and

$$a_{\|} = \beta \epsilon^{2/3} , \tag{17}$$

$$a_{\perp} = \beta / \epsilon^{1/3} . \tag{18}$$

The three parameters μ, β, and ϵ are variational parameters chosen to minimize the energy,

$$E \equiv \int \psi^*(\mathbf{r}) H \psi(r) d^3r . \tag{19}$$

Note if $\beta \equiv \epsilon \equiv 1$, this wave function is equivalent to the Hulthén wave-function equation. Similarly if $\beta \equiv 1$ and we take the $\mu = 0$ limit, this trial wave function becomes hydrogenic, similar to those

chosen by earlier authors to solve this problem in the absence of screening.

The units of distance and energy in this calculation are the effective Bohr radius,

$$a \equiv \kappa h^2 / M^* e^2 \tag{20}$$

and the effective rydberg,

$$\mathfrak{R}^* \equiv M^* e^4 / 2\kappa^2 h^2 , \tag{21}$$

In this set of units the expectation value of the kinetic energy is easily calculated giving,

$$\langle T \rangle = \tfrac{1}{3}(a_{\|} + 2a_{\perp}) \tfrac{1}{8}(4 - \mu^2) , \tag{22}$$

The expectation value of the potential energy is much more complicated and cannot be accomplished in closed form, indeed there is no known analytic form for the potential $V(r)$ for a Lindhard screened Coulomb potential. However, this difficulty can be circumvented, following the method used by Krieger and Nightingale,[7] by taking the Fourier transform of the particle density, $\psi^*(r)\psi(r)$, and then obtaining the expectation value through an equivalent calculation in momentum space, one finds

$$\langle V \rangle = -8\pi \int \frac{d^3q\, F(q)}{q^2 \epsilon_q} , \tag{23}$$

where $F(q)$ is the Fourier transform of the particle density, $\psi^*(r)\psi(r)$. This transform is given by

$$F(\mathbf{q}) \equiv F(q_x, q_y, q_z) = F^0(q_x/\sqrt{a_{\|}}, q_y/\sqrt{a_{\perp}}, q_z/\sqrt{a_{\perp}}) , \tag{24}$$

where

$$F^0(\mathbf{q}) = \frac{1}{(2\pi)^3} \left(\frac{4}{\mu^2} - 1 \right) \left[\tan^{-1}\left(\frac{q}{2-\mu} \right) + \tan^{-1}\left(\frac{q}{2+\mu} \right) \right.$$
$$\left. - 2\tan^{-1}\left(\frac{q}{2} \right) \right] \frac{1}{q} . \tag{25}$$

One then has after an appropriate change of variables

$$\langle V \rangle = -8\pi \int \frac{d^3q\, F_0(q_x/(M_{\|}a_{\|})^{1/2}, q_y/(M_{\perp}a_{\perp})^{1/2}, q_z/(M_{\perp}a_{\perp})^{1/2})}{q_x^2 M_{\|} + q_y^2 M_{\perp} + q_z^2 M_{\perp} - 4\pi e^2 \chi^0(q)/k} . \tag{26}$$

This integral can be somewhat simplified for numerical computation, yet cannot be done in closed form, even for the Thomas-Fermi dielectric function.

For each value of the total free-electron carrier density, the total energy

$$E = \langle T \rangle + \langle V \rangle \tag{27}$$

is evaluated numerically and minimized on a three-

dimensional space consisting of β, μ, and ϵ. This is done for silicon and germanium at several densities between zero and the critical density where the system becomes unbound, the Mott transition.

One notes here that to do this for the Thomas-Fermi dielectric function, one defines the response function by taking the following limit:

$$\chi_{TF}(\mathbf{q}) \equiv \lim_{q \to 0} \chi(\mathbf{q}) , \tag{28}$$

TABLE I. Binding energy of a conduction electron bound to a donor impurity in silicon and germanium in both isotropic- and anisotropic-mass approximations using the Lindhard and Thomas–Fermi dielectric functions for different carrier concentrations.

$N^{1/3}$	Germanium				Silicon			
	TF		L		TF		L	
	I	A	I	A	I	A	I	A
0.0	1.0	0.772	1.0	0.772	1.0	0.921	1.0	0.921
0.0001	0.938	0.711	0.996	0.768	0.930	0.851	0.996	0.917
0.0005	0.866	0.641	0.987	0.761	0.848	0.770	0.987	0.909
0.001	0.815	0.591	0.979	0.753	0.790	0.713	0.979	0.901
0.005	0.620	0.413	0.929	0.709	0.575	0.504	0.929	0.805
0.01	0.496	0.306	0.880	0.664	0.441	0.377	0.880	0.543
0.05	0.141	0.0455	0.605	0.421	0.0862	0.0578	0.607	0.315
0.1	0.0211		0.364	0.218	0.0013		0.367	0.243
0.12	0.0053		0.287	0.156			0.290	0.180
0.14			0.219	0.104			0.222	0.125
0.16			0.160	0.0619			0.162	0.0798
0.18			0.110	0.0300			0.111	0.0434
0.20			0.0684	0.0091			0.0677	0.0289
0.22			0.0361	0.0002			0.0341	0.0170
0.24			0.0136				0.0108	0.0023
0.26			0.0018				0.0002	
0.28								

keeping only the lowest order in q—a constant dependent only on angle. Then one has

$$\epsilon_{TF}(\vec{q}) \equiv 1 - (4\pi e^2/q^2)\chi_{TF}(\vec{q}) \ . \qquad (29)$$

The rest of the calculation proceeds as before.

RESULTS

As a prime example of an indirect-gap semiconductor with a large electron-mass anisotropy, a graph of the binding energy of a donor in germanium versus the cube root of the free carrier density is given in Fig. 1. For germanium the mass anisotropy is taken from experimentally accepted values,[1] i.e.,

$$M_\parallel/M_\perp = 19.68 \ .$$

The binding energy is given as a fraction of the impurity Rydberg defined earlier. Note that in this approximation the binding energy is appreciably lowered at all densities and the Mott transition occurs at a lower density. The effect is particularly pronounced in germanium.

In Table I the binding energies for germanium and silicon (with a mass silicon anisotropy of 5.16) are tabulated for various densities. For completeness values for the Thomas-Fermi as well as Lindhard dielectric functions are included. Table II summarizes the values of the Mott-transition densities for the two materials. The isotropic-mass approximation is calculated by setting all masses to the isotropic average, and is completely equivalent to those obtained earlier.[5-8] In the

TABLE II. Critical value for $N^{1/3}$ for germanium and silicon, in the isotropic- and anisotropic-mass approximations for both Lindhard and Thomas-Fermi dielectric functions.

	Germanium	Silicon
Isotropic		
Thomas-Fermi, hydrogenic trial function [a]	0.10	0.08
Lindhard, hydrogenic trial function [a]	0.23	0.23
Thomas-Fermi, Hulthén trial function [b]	0.142	0.108
Lindhard, Hulthén trial function [b]	0.271	0.263
Anisotropic		
Thomas-Fermi, present work	0.10	0.10
Lindhard, present work	0.22	0.25

[a] Krieger and Nightingale (Ref. 7).   [b] Greene et al. (Ref. 8).

limit of zero screening carrier density one finds the expected agreement with earlier calculations[3,4] with hydrogenic trial wave functions for isolated impurities.

While these theoretical binding-energy curves show considerable difference between the isotropic and anisotropic approximations, at present this has little effect on the theoretical agreement with experiment. The random distribution of the donor impurities in the semiconductor crystal cause the Mott transition to be somewhat spread out, leading to some uncertainty in the value of N_c. This randomness is not taken into account in this calculation. A direct comparison of theory and experiment may not be completely reliable; however, the experimentally suggested value of the Mott critical density, in germanium, for example, $N_c \approx 0.22$,[11] is in good agreement with the present calculation.

CONCLUSION

The binding energy of a conduction electron bound to a positive ion of a substitutional impurity atom in an indirect-band-gap semiconductor has been calculated using a Coulomb potential screened by the Lindhard dielectric function. The electron-mass anisotropy caused by the multivalley structure modifies both the kinetic energy and the interaction potential (through the dielectric function). A variational approach has been adopted using a modified form of a wave function originally proposed by Hulthén. Explicit calculations for germanium and silicon show the mass anisotropy has a significant effect on the binding energy over the whole range of free-carrier densities, from zero to the Mott-transition value. The Mott-transition density is found to occur at a significantly lower density.

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