AFRL-RY-WP-TR-2019-0075



ELECTRON DRIFT MOBILITY OF DEGENERATE SEMICONDUCTORS DUE TO IONIZED IMPURITY SCATTERING – PHASE I

Daniel Rode

Pendragon Corporation

APRIL 2019 Final Report

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1. Objective

The objectives for Phase I was to derive analytical expressions for the electron mobility of degenerate semiconductors dominated by ionized impurities, including non-parabolic conduction bands, wave function admixture, Rode-Cetnar screening, impurity compensation, and multiply ionized impurities. Also to compare calculated numerical results to results for classical parabolic bands and Thomas-Fermi screening.

2. Motivation

Classical theoretical treatments of the electron mobility of degenerate semiconductors based on parabolic conduction bands and Thomas-Fermi screening are significantly in error, by about fifty to one-hundred percent, in comparison to experiments.¹ In order to explain experimental results with accuracy within a few percent, it is necessary to incorporate non-parabolicity of the conduction band into the theory. However, when the conduction band is non-parabolic, the electron wave functions are necessarily a mixture of s and p wave functions. Since the s and p wave functions are orthogonal, the electron scattering is weakened, as shown below.

The usual method of treating the screening of ionized impurities is by use of the Thomas-Fermi equation. However, this equation applies only to parabolic conduction bands, which is not accurate for degenerate semiconductors. In recent work, non-parabolic bands have been accounted for by the Rode-Cetnar treatment of screening and this work is incorporated herein.²

Since electron mobility at low temperatures is determined predominantly by ionized- impurity scattering when the semiconductor is heavily (i.e. degenerately) doped, it is necessary to treat only ionized-impurity scattering. Thus, other types of electron scattering may be ignored, including lattice vibrations such as piezoelectric and acoustic phonons, and optical and intervalley phonons, as well as surface scattering, grain boundaries, and scattering by other types of defects.

3. Analysis

In general, whether or not degeneracy prevails, electron drift mobility μ_d is given by the perturbation function g of the electron probability distribution under the influence of a weak electric field of strength F. In the following, the electron wave-vector is k and the equilibrium (Fermi-Dirac) probability distribution function is f. In the present work, g is determined entirely by electron scattering due to ionized impurities and, hence, electron mobility is denoted by μ_{ii} to signify the ionized-impurity mechanism. From Rode, including non-parabolic conduction band, the electron drift mobility is given by¹

$$\mu_d = \frac{\hbar}{3m} \cdot \frac{\int k^3 (g/Fd) dk}{\int k^2 f \, dk} \tag{1}$$

The free-electron mass is m, d accounts for changes in effective mass due to non-parabolicity, and the reduced Planck constant is \hbar . When only ionized-impurity scattering is considered, the perturbation g is given by

$$g = -(eF/\hbar v_{ii}) \cdot \partial f / \partial k \tag{2}$$

The magnitude of the electron charge is e and the electron scattering rate due to ionized impurities is v_{ii} . The electron drift mobility due to ionized-impurity scattering is thus given as

$$\mu_{ii} = -\frac{e}{3m} \cdot \frac{\int (k^3 / v_{ii} d) (\partial f / \partial k) dk}{\int k^2 f dk}$$
(3)

The electron scattering rate due to ionized-impurities is¹

.

$$\boldsymbol{\nu}_{ii} = \frac{e^4 Nmd}{8\pi \varepsilon_s^2 \hbar^3 k^3} \cdot \left[D \cdot \ln(1 + 4k^2 / \beta^2) - B \right]$$
⁽⁴⁾

where

$$D = 1 + (2\beta^2 c^2 / k^2) + (3\beta^4 c^4 / 4k^4)$$
(5)

and

$$B = [4k^{2} / \beta^{2} + 8(1 + 2k^{2} / \beta^{2})c^{2} + 6(1 + \beta^{2} / 2k^{2} - 4k^{2} / 3\beta^{2})c^{4}]/$$

$$(1 + 4k^{2} / \beta^{2})$$
(6)

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Wave function admixture and conduction band non-parabolicity are accounted for by the c and d quantities, where c is the fraction of p compared to s wave functions.¹

$$c^{2} = \frac{1}{2} - \frac{1}{2} \sqrt{1 + 2\hbar^{2}k^{2}(m/m^{*} - 1)/mE_{g}}$$
(7)

$$1/d = 1 + (m/m^* - 1)/\sqrt{1 + 2\hbar^2 k^2 (m/m^* - 1)/mE_g}$$
(8)

The concentration of ionized scattering centers (impurities) is N and $1/\beta$ is the exponential screening length of the Coulomb potential surrounding the scattering centers. The effective mass m^* is given by the band curvature at the bottom of the conduction band. The effective mass energy gap is E_g .

Combining the above equations, the electron mobility due to ionized-impurities is

_

$$\mu_{ii} = -\frac{8\pi\varepsilon_s^2\hbar^3}{3e^3Nm^2} \cdot \frac{\int (k^6/d^2) \cdot (\partial f/\partial k) / [D\ln(1+4k^2/\beta^2) - B]dk}{\int k^2 f dk}$$
(9)

In general, the Fermi-Dirac probability distribution function f is a function of electron energy E and Fermi Level E_F .

$$f = \frac{1}{1 + e^{(E - E_F)/\kappa T}} \tag{10}$$

$$\frac{\partial f}{\partial k} = \frac{\partial f}{\partial E} \cdot \frac{\partial E}{\partial k} = -\frac{e^{(E-E_F)\kappa T} / \kappa T}{(1+e^{(E-E_F)\kappa T})^2} \cdot \frac{\hbar^2 k}{md}$$
(11)

or

$$\frac{\partial f}{\partial k} = -\frac{\hbar^2 k}{m d\kappa T} \cdot f(1 - f) \tag{12}$$

Thus, eqs. (9) and (12) give

$$\mu_{ii} = \frac{8\pi\varepsilon_s^2\hbar^5}{3e^3m^3N\kappa T} \cdot \frac{\int (k^7/d^3)f(1-f)/[D\cdot\ln(1+4k^2/\beta^2)-B]dk}{\int k^2f\,dk}$$
(13)

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For the degenerate case where the Fermi Level E_F greatly exceeds the thermal energy κT , the product f(1-f) approaches the behavior of a Dirac Delta Function centered about the momentum at the Fermi Level k_F , and eq. (13) can be written as

$$\mu_{ii} = \frac{8\pi\varepsilon_s^2\hbar^5 k_F^5}{3e^3m^3N\kappa T} \cdot \frac{1/d_F^3}{D_F \cdot \ln(1+4k_F^2/\beta_F^2) - B_F} \cdot \frac{\int k^2 f(1-f)dk}{\int k^2 f\,dk}$$
(14)

r

The quantities d, D, and B, when evaluated at k_F , are termed dF, DF, and BF. Likewise, the reciprocal of the screening length β_F is β evaluated at k_F . From the Appendix, β_F can be expressed in terms of the Fermi Level.

$$\beta_{F}^{2} = \frac{e^{2} (2m)^{3/2}}{2\pi^{2} \varepsilon_{s} \hbar^{3}} \cdot \left[E_{F} + E_{g} m / 2m^{*} - \sqrt{(E_{F} + E_{g} m / 2m^{*})^{2} - E_{F} (E_{F} + E_{g})} \right]^{/2} \times \left[1 - \frac{(m/m^{*} - 1)E_{g} / 2}{\sqrt{(E_{F} + E_{g} m / 2m^{*})^{2} - E_{F} (E_{F} + E_{g})}} \right]$$
(15)

The Fermi Level is given in the Appendix in terms of the free-electron concentration.

$$E_{F} = \frac{(3\pi^{2}n)^{2/3}\hbar^{2}}{2m} - \frac{E_{g}}{2} \left[1 - \sqrt{1 + 2\hbar^{2}(3\pi^{2}n)^{2/3}(m/m^{*}-1)/mE_{g}} \right]$$
(16)

In general, the free-electron concentration is

$$n = \int (k^2 / \pi^2) f \, dk \tag{17}$$

For degenerate conditions, n is denoted by nF.

$$n_F = k_F^3 / 3\pi^2 \tag{18}$$

Therefore, given $n = n_F$, one can calculate E_F and k_F from eqs. (16) and (18); β_F can be calculated from eq. (15); c_F , d_F , D_F and B_F can be calculated from eqs. (5) to (8); and mobility can be calculated as follows. Using the expression in the Appendix for the inverse screening length squared β_F^2 in the degenerate limit,

$$\mu_{ii} = \frac{8\pi\varepsilon_s^2\hbar^5k_F^5}{3e^5m^3d_F^3n_FN\kappa T} \cdot \frac{\varepsilon_s\kappa T\beta_F^2}{D_F \cdot \ln(1+4k_F^2/\beta_F^2) - B_F}$$
(19)

Finally, we have

$$\mu_{ii} = \frac{8\pi\varepsilon_s^3 \hbar^5 k_F^3 \beta_F^2}{3e^5 m^3 d_F^3 n_F N[D_F \cdot \ln(1+4k_F^2/\beta_F^2) - B_F]}$$

$$\mu_{ii} = \frac{8\pi^3 \varepsilon_s^3 \hbar^5 k_F^2 \beta_F^2}{e^5 m^3 d_F^3 N[D_F \cdot \ln(1+4k_F^2/\beta_F^2) - B_F]}$$
(20)

As expected, mobility is independent of temperature under degenerate conditions.

Therefore, given the static dielectric constant, the effective mass, the energy gap, and the freeelectron and impurity concentrations, the mobility due to ionized impurities can be calculated analytically from eq. (20). The concentration of ionized scattering centers N may comprise a) singly ionized donors, b) singly ionized acceptors, and c) doubly ionized acceptors with respective concentrations N_d , N_a , and N_{aa} . The scattering strength of an impurity is proportional to the square of its charge so, according to Look and Leedy,³

$$N = N_d + N_a + 4N_{aa} \tag{21}$$

Results for ZnO are shown in next section.

4. Results

Let K = 8.12, Eg = 3.43 eV, nF = N, and $m^*/m = 0.34$ appropriate to uncompensated ZnO and calculate the electron mobility from eq. (20). See Figure 1.



Figure 1: Electron Mobility versus Carrier Concentration is shown for Conditions of High Degeneracy



The difference between results for parabolic and non-parabolic conduction bands becomes quite large for the higher electron concentrations: 33 percent at 10^{22} /cc and 93 percent at 10^{23} /cc. Part of the difference is due to wave function admixture, given by the quantity c^2 in eq. (7). Figure 2 shows c^2 versus carrier concentration. Above 10^{21} /cc, the proportion of p wave functions becomes significant.



Figure 2: Admixture of p Wave Function versus Carrier Concentration The ratio of p to s functions becomes significant above $10^{21}/cc$ carrier concentration.

The importance of accounting for non-parabolic conduction bands is given by d in eq. (8). For the case of a parabolic band, d is equal to the relative effective mass, but d increases significantly for non-parabolic bands at large carrier concentrations as shown in Figure 3. For small electron concentrations where non-parabolicity is unimportant, d is equal to the relative effective mass 0.34. Increase of effective mass, proportional to d, becomes significant above $10^{21}/cc$ carrier concentration.



Figure 3: Effective Mass indicated by d versus Carrier Concentration begins at $m^*/m = 0.34$

The screening length is likewise significantly affected by non-parabolicity as shown in Figure 4.



Figure 4: Screening Length versus Carrier Concentration For non-parabolic bands, screening becomes much stronger above 10²¹/cc carrier concentration (lower curve).

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Screening Length versus Electron Concentration

As a final example, consider the experimental work on ZnO reported by Look *et al.*⁴ Set the room-temperature value of K = 8.12, $E_g = 3.43 \text{ eV}$, and $m^* = 0.34m$. Look and Leedy have shown the existence of doubly ionized compensating acceptors in this case, with ionized donor concentration $N_d = 1.45E21/cc$, singly ionized acceptor concentration $N_a = \text{zero}$ and doubly ionized acceptor concentration $N_{aa} = 1.71E20/cc$. Space-charge neutrality requires that the free-electron concentration $n = N_d \cdot 2N_{aa} = 1.11E21/cc$ and the scattering concentration $N = N_d + 4N_{aa} = 2.13E21/cc$. Under these conditions, the effective mass at the Fermi Level as given by d is 0.41m, compared to 0.34m for E = 0. Calculation using eq. (20) gives the mobility equal to 33.0, whereas experiment⁴ gives $31.7 \text{ cm}^2/\text{V-s}$, agreeing within 4%. The value K = 8.12 should perhaps be decreased about 3% due to the reduced temperature (T = 20K) used in the experiment. A 3% reduction⁵ in K gives theoretical mobility equal to 31.7, in perfect agreement with experiment. However, the temperature dependence of the effective mass and the energy gap might also be considered; in addition, other possible types of scattering mentioned at the end of Section 2 may be significant, especially interface scattering.⁴

Nevertheless, it appears to be firmly established that the theoretical treatment of Section 3 is capable of giving agreement between theory and experiment within a few percent, which is one of the major goals of this work. Lastly, it should be said that the fine agreement shown here is a tribute to the high quality of the experimental work cited.

5. Acknowledgments

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Appendix: Fermi Level & Ionized-Impurity Screening in Degenerate Semiconductors with Non-Parabolic Energy Bands

The Fermi Level E_F and the inverse screening length β are calculated using non- parabolic Kane bands and Fermi statistics in the degenerate limit, where $E_F/\kappa T >> 1$. Quantities corresponding to degenerate conditions are denoted by subscript F. The unique contribution here is the use of non-parabolic bands.

In general, the free-electron energy, inverse screening length squared, and free-carrier electron concentration are expressed as¹ m is the free-electron mass, ε_s is the static dielectric permittivity, and nF corresponds to the degenerate limit. The static dielectric permittivity can be expressed as $\varepsilon_s = K\varepsilon_0$ where K is the dielectric constant and ε_0 is the free-space permittivity.

$$E_{o} = \frac{\hbar^{2}k^{2}}{2m}$$

$$\beta^{2} = \frac{e^{2}}{\varepsilon_{s}\kappa T} \int \left(\frac{k}{\pi}\right)^{2} f(1-f) dk$$

$$n = \int \left(\frac{k}{\pi}\right)^{2} f dk$$

$$n_{F} = \frac{k_{F}^{3}}{3\pi^{2}}$$
(A1)

The inverse screening length squared is β_{F}^{2} in the degenerate limit. From eq. (A1)

$$\beta^{2} = \frac{e^{2}}{\varepsilon_{s}\kappa T} \int \left(\frac{k}{\pi}\right)^{2} \frac{e^{(E-E_{F})/\kappa T}}{\left(e^{(E-E_{F})/\kappa T}+1\right)^{2}} dk$$

$$\beta^{2} = \frac{e^{2}}{\varepsilon_{s}\kappa T} \int \left(\frac{k}{\pi}\right)^{2} \frac{e^{(\kappa-\varepsilon_{F})}}{\left(e^{(\kappa-\varepsilon_{F})}+1\right)^{2}} dk$$

$$\beta^{2} = \frac{e^{2}}{\varepsilon_{s}\kappa T} \cdot \frac{\partial}{\partial\varepsilon_{F}} \int \left(\frac{k}{\pi}\right)^{2} \frac{dk}{e^{(\kappa-\varepsilon_{F})}+1}$$

$$\beta^{2} = \frac{e^{2}}{\varepsilon_{s}\kappa T} \cdot \frac{\partial n}{\partial\varepsilon_{F}} = \frac{e^{2}}{\varepsilon_{s}} \cdot \frac{\partial n}{\partial E_{F}}$$

$$\beta^{2}_{F} = \frac{e^{2}}{\varepsilon_{s}} \cdot \frac{\partial}{\partial E_{F}} \frac{k_{F}^{3}}{3\pi^{2}}$$

$$\beta^{2}_{F} = \frac{e^{2}k_{F}^{2}}{\pi^{2}\varepsilon_{s}} \cdot \frac{\partial k_{F}}{\partial E_{F}}$$
(A2)

13 Approved for public release; distribution is unlimited. In order to carry out the differentiation in eq. (A2), it is necessary to solve for k_F in terms of the Fermi level EF. For non-parabolic Kane bands,^{1,6} the electron kinetic energy *E* measured upward from the bottom of the conduction band is

$$E = E_o - \frac{E_g}{2} \left[1 - \sqrt{1 + 4E_o(\frac{m}{m^*} - 1)/E_g} \right]$$

$$(E - E_o + E_g/2)^2 = E_g^2/4 + E_o E_g(m/m^* - 1)$$

$$E_o^2 - 2E_o(E + E_g/2) + (E + E_g/2)^2 = E_g^2/4 + E_o E_g(m/m^* - 1)$$

$$E_o^2 + (-2E - 2E_g/2 - E_gm/m^* + E_g) + E^2 + EE_g = 0$$

$$E_o^2 - (2E + E_gm/m^*)E_o + E(E + E_g) = 0$$

$$E_o = E + E_gm/2m^* - \sqrt{(E + E_gm/2m^*)^2 - E(E + E_g)}$$

$$\frac{\hbar^2 k_F^2}{2m} = E_F + E_gm/2m^* - \sqrt{(E_F + E_gm/2m^*)^2 - E_F(E_F + E_g)}$$
(A3)

Therefore, the carrier concentration and Fermi level are related as

$$k_{F}^{2} = (3\pi^{2}n)^{2/3}$$

$$(3\pi^{2}n)^{2/3} = \frac{2m}{\hbar^{2}} \left[E_{F} + E_{g}m/2m^{*} - \sqrt{(E_{F} + E_{g}m/2m^{*})^{2} - E_{F}(E_{F} + E_{g})} \right]$$

$$n = \frac{(2m)^{3/2}}{3\pi^{2}\hbar^{3}} \left[E_{F} + E_{g}m/2m^{*} - \sqrt{(E_{F} + E_{g}m/2m^{*})^{2} - E_{F}(E_{F} + E_{g})} \right]^{3/2}$$
(A4)

and

$$E_{F} = \frac{\hbar^{2} (3\pi^{2}n)^{2/3}}{2m} - \frac{E_{g}}{2} \left[1 - \sqrt{1 + \frac{2\hbar^{2} (3\pi^{2}n)^{2/3}}{m}} (\frac{m}{m^{*}} - 1) / E_{g}} \right]$$
(A5)

$$E_{F} = \frac{(3\pi^{2}n)^{2/3} \hbar^{2}}{2m} - \frac{E_{g}}{2} \left[1 - \sqrt{1 + 2\hbar^{2} (3\pi^{2}n)^{2/3} (1/m^{*} - 1/m) / E_{g}} \right]$$
(A5)

In general, the inverse screening length from eq. (A2) is,

$$\beta^2 = \frac{e^2}{\varepsilon_s} \cdot \frac{\partial n}{\partial E_F}$$
(A6)

Under degenerate conditions the inverse screening length is

$$\begin{split} \beta_{F}^{2} &= \frac{e^{2}}{\varepsilon_{s}} \cdot \frac{\partial n_{F}}{\partial E_{F}}, \text{ where } \\ \frac{\partial n_{F}}{\partial E_{F}} &= \frac{(2m)^{3/2}}{3\pi^{2}\hbar^{3}} \cdot \frac{3}{2} \cdot \left[E_{F} + E_{g}m/2m^{*} - \sqrt{(E_{F} + E_{g}m/2m^{*})^{2} - E_{F}(E_{F} + E_{g})} \right]^{1/2} \times \\ & \left[1 - \frac{1}{2} \cdot \frac{2E_{F} + mE_{g}/m^{*} - 2E_{F} - E_{g}}{\sqrt{(E_{F} + E_{g}m/2m^{*})^{2} - E_{F}(E_{F} + E_{g})}} \right] \\ \frac{\partial n_{F}}{\partial E_{F}} &= \frac{(2m)^{3/2}}{2\pi^{2}\hbar^{3}} \cdot \left[E_{F} + E_{g}m/2m^{*} - \sqrt{(E_{F} + E_{g}m/2m^{*})^{2} - E_{F}(E_{F} + E_{g})}} \right]^{1/2} \times \\ & \left[1 - \frac{(m/m^{*} - 1)E_{g}/2}{\sqrt{(E_{F} + E_{g}m/2m^{*})^{2} - E_{F}(E_{F} + E_{g})}} \right] \\ \beta_{F}^{2} &= \frac{e^{2}(2m)^{3/2}}{2\pi^{2}\varepsilon_{s}\hbar^{3}} \cdot \left[E_{F} + E_{g}m/2m^{*} - \sqrt{(E_{F} + E_{g}m/2m^{*})^{2} - E_{F}(E_{F} + E_{g})}} \right]^{1/2} \times \\ & \left[1 - \frac{(m/m^{*} - 1)E_{g}/2}{\sqrt{(E_{F} + E_{g}m/2m^{*})^{2} - E_{F}(E_{F} + E_{g})}} \right] \\ \end{pmatrix}$$

$$(A7)$$

This completes the derivation of analytical expressions for the Fermi level and the screening length. The particulars of the semiconductor material are specified by three parameters: the effective mass at the bottom of the conduction band, the energy gap, and the dielectric constant. Therefore, given the free-electron concentration, the Fermi level and the screening length are calculated from eqs. (A5) and (A7).