

# Electron and Hole Transport in Degenerate Semiconductors

Concentration-dependent activity coefficients were used in conjunction with dilute-solution transport equations to show the effect of degeneracy on the apparent physical properties of semiconductors and on the performance of photovoltaic cells. The approach presented here allows convenient treatment of degenerate semiconductors in a manner that is both thermodynamically consistent and consistent with the Fermi-Dirac distribution for electrons. These calculations show that neglect of the concentration dependency of the activity coefficients has a large effect on the calculated values for local concentrations in a photovoltaic device, but affects the calculated values of power density and cell potential only slightly. Neglect of the concentration dependency of the activity coefficients does have a significant effect on the calculation of the resistivity of the semiconductor.

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## SCOPE

Dilute-solution transport equations with constant activity coefficients are commonly used to model semiconductors. These equations are consistent with a Boltzmann distribution and are therefore invalid for degenerate semiconductors for which the Boltzmann distribution does not adequately describe electron or hole concentrations. Concentration-dependent activity coefficients were used in conjunction with dilute-solution transport equations to show the effect of degeneracy

on the performance of photovoltaic cells and on the apparent physical properties of semiconductors. The approach presented here allows convenient treatment of degenerate semiconductors in a manner that is both thermodynamically consistent and consistent with the Fermi-Dirac distribution for electrons. This approach is compared to the alternative treatment of degeneracy by modification of the Nernst-Einstein relationship between mobility and diffusivity.

## CONCLUSIONS AND SIGNIFICANCE

A one-dimensional mathematical model of photovoltaic devices is presented that accounts explicitly for the influence of degeneracy. Macroscopic transport equations for electrons and holes in semiconducting materials were made consistent with Fermi-Dirac statistics by inclusion of a concentration-dependent activity coefficient. These equations allow modeling of degenerate semiconductors for which the electron and hole concentrations are less than their respective effective energy band site densities and for which the effective conduction and valence band site densities are greater than the dopant concentration. Calculations are presented for a Schottky-barrier photovoltaic

device and a photoelectrochemical cell modeled under the assumption of constant activity coefficients and with concentration-dependent activity coefficients. Comparisons among the results of these calculations show that neglect of the concentration dependency of the activity coefficients has a large effect on the calculated values for local concentrations. The values of power density and cell potential obtained from these calculations, however, differ only slightly. Incorporation of the activity coefficients into the transport equations does have a significant effect on the calculation of the resistivity of the semiconductor.

## Introduction

In addition to their well-known applications in the electronics industry, semiconductors play a major role in photovoltaic or solar cells, in the corrosion of metals, and as plastic electrodes. Modeling of semiconductors represents an important step toward understanding the behavior of these systems and optimizing their design.

Quantitative calculation of the performance of semiconductor devices requires solution of the macroscopic transport equations for the bulk phases coupled with models of the interfacial regions. Coupled phenomena govern this system, and the equations describing their interaction cannot, in general, be solved analytically. Use of a digital computer in the numerical solution of the governing equations eliminates the need for restrictive assumptions. Such mathematical models of semiconductors (MacDonald, 1962; DeMari, 1968a, b; Choo, 1971, 1972; Laser and Bard, 1976a, b, c; Sutherland and Hauser, 1977; Laser, 1979; Orazem and Newman, 1984a, b) generally lack a satisfactory expression for activity coefficients. This has limited their application to semiconductors with low electron and hole concentrations as compared to the maximum concentration of electrons or holes allowed in the respective energy level. The assumption of a constant activity coefficient (implicit in most semiconductor models) is consistent with assumption of a Boltzmann distribution and is, therefore, invalid for semiconductors for which the Boltzmann distribution does not adequately describe electron or hole concentrations. Such a semiconductor is considered to be degenerate.

Degeneracy is expected in semiconductors for which the electron or hole concentration is large. This condition may occur in response to large dopant concentrations, large electric fields, or kinetic limitations associated with interfaces. These conditions are discussed by Harvey (1962), Lanyon (1981), and Lindholm and Fossum (1981). Highly doped degenerate semiconductors have been suggested as replacements for metal films in Schottky-barrier solar cells (Pavalets, 1982). Large dopant concentrations are also used in semiconductors for high-speed electronic devices. The calculations of Orazem (1983) show that conditions of degeneracy can exist in photoelectrochemical cells under kinetic limitations to charge transfer at the semiconductor-electrolyte interface.

The influence of degeneracy is felt in three ways (Harvey, 1962; Panish and Casey, 1967, 1968; Hwang and Brews, 1971; Lanyon 1981; Dhariwal and Ojha, 1982):

1. Electrons and holes are distributed according to Fermi-Dirac statistics.
2. For large electron concentrations, the energy levels above the lower edge of the conduction band are partially occupied and cannot be assumed to be empty. For large hole concentrations, the energy levels below the upper edge of the valence band are partially occupied by holes.
3. For large dopant concentrations, the energy levels associated with the dopant species merge with the conduction band levels and reduce the band-gap energy. Band gap narrowing may also occur due to interactions among carrier species.

Modeling of degenerate semiconductors requires relaxation of the Boltzmann assumption and consideration of the band-perturbing and band-gap narrowing effects. In this work, the assumption of a Boltzmann distribution is relaxed by incorporating concentration-dependent activity coefficients into the macroscopic transport equations in a manner consistent with the

Fermi-Dirac distribution. Such an approach extends the validity of the mathematical model to regions of mild degeneracy. The influence of electron distribution into higher energy levels and of changes to the band gap is to reduce the value for the activity coefficient. The modeling of very degenerate semiconductors requires consideration of the changes in the energy band structure associated with degeneracy. Such an extension to the model can be accomplished by additional modification of the expression for the activity coefficient.

## Theoretical Development

The concentration of holes and electrons in a semiconductor is given by the Fermi-Dirac distribution (Grove, 1967; Sze, 1969). A Boltzmann distribution is frequently used as an approximation to this distribution in statistical-mechanical analyses of semiconducting systems. Dilute-solution transport equations with constant activity coefficients, consistent with a Boltzmann distribution, are also used in characterizing the behavior of semiconducting systems. These approximate methods are popular because of their relative mathematical simplicity, but are invalid when electron or hole concentrations are close to the maximum concentration allowed in their respective energy level.

Calculation of individual ionic activity coefficients for electrons and holes has been proposed as a means of identifying the regions for which these approximations are justified. Rosenberg (1960), Panish and Casey (1967, 1968), and Hwang and Brews (1971) have presented activity coefficients that are functions of concentration as well as potential. Harvey (1962) discussed the separation of the activity coefficient into parts due to electrical and chemical effects. Landsberg and Guy (1983) have presented an activity coefficient derived from an Einstein relation that includes within it the nonidealities associated with the activity coefficient. Guy (1983) has presented calculations of activity coefficients from partial enthalpies of conduction electrons. Orazem and Newman (1984c) have presented expressions for the activity coefficients of electrons and holes that are explicit functions of concentration as opposed to functions of quasi Fermi energies. These expressions provide local values for activity coefficients that are thermodynamically consistent and that can conveniently be used in the application of macroscopic transport equations to semiconducting systems in a way that is consistent with the Fermi-Dirac distribution.

The activity coefficients of electrons and holes enter the macroscopic transport equations through the electrochemical potential. The electrochemical potential of a given species can arbitrarily be separated into terms representing a reference state, a chemical contribution and an electrical contribution (Newman, 1973; Orazem and Newman, 1985).

$$\mu_i = \mu_i^0 + RT \ln (f_i c_i) + z_i F \Phi, \quad (1)$$

where  $\Phi$  is a potential that characterizes the electrical state of the phase and can be arbitrarily defined. The potential used here is the electrostatic potential obtained through integration of Poisson's equation (Parsons, 1954). Equation 1 can be viewed as the defining equation for the activity coefficient,  $f_i$ .

The flux density of an individual species within the semiconductor is driven by a gradient of electrochemical potential:

$$N_i = -c_i u_i \nabla \mu_i. \quad (2)$$

This can be written for electrons and holes in terms of concentration and potential gradients, as given by Eq. 1 (Gerischer, 1970; Newman, 1973). The flux density of holes,  $N_h$ , is therefore given by

$$N_h = -\frac{u_h RT}{f_h} \nabla(pf_h) - u_h p F \nabla \Phi, \quad (3a)$$

and the flux density of electrons  $N_e$  by

$$N_e = -\frac{u_e RT}{f_e} \nabla(nf_e) - u_e n F \nabla \Phi, \quad (3b)$$

The concentrations of electrons and holes are represented by  $n$  and  $p$ , respectively, and the mobilities  $u_i$  are related to the diffusivities  $D_i$  by the Nernst-Einstein equation

$$D_i = RTu_i. \quad (4)$$

This equation is appropriate for both dilute and concentrated solutions (Newman, 1973). Nonidealities associated with more concentrated solutions are incorporated within the activity coefficient.

Equation 3 can be simplified through the assumption of constant activity coefficients. Under the assumption of constant activity coefficients, Eq. 3 is in harmony with a Boltzmann distribution of electrons and holes. Such an approach is valid for  $p/N_v$  and  $n/N_c$  less than 0.1. The use of concentration-dependent activity coefficients, e.g.,

$$f_h = \frac{1}{1 - p/N_v} \quad (5a)$$

for holes and

$$f_e = \frac{1}{1 - n/N_c} \quad (5b)$$

for electrons (Orazem and Newman, 1984c), extends the validity of the transport equations to regions of mild degeneracy. The expressions given in Eq. 5 are thermodynamically consistent, are valid in regions of charge, and are consistent with a Fermi-Dirac distribution for electrons. These expressions are also consistent with the activity coefficients presented by Landsberg and Guy (1983) and by Hwang and Brews (1971). These expressions do not, however, account for band-perturbing and band-gap narrowing effects associated with heavily doped semiconductors. The neglected terms associated with the distribution of electrons into higher energy states and band-gap narrowing act to reduce the value of the activity coefficient. Equation 5 therefore overestimates the electron and hole activity coefficients. The activity coefficients can be modified to account for these effects, but this modification requires more information on the energy band structure (Harvey, 1962; Panish and Casey, 1967, 1968; Hwang and Brews, 1971; Lanyon, 1981; Dhariwal and Ojha, 1982). Inclusion of activity coefficients is necessary for highly doped semiconductors and for semiconductors subjected to a large electric field.

Another approach to characterization of degenerate semiconductors has been to include the nonidealities associated with

degeneracy within a modified Nernst-Einstein relationship (Landsberg and Hope, 1977; Lundstrom et al., 1981; Marshak and Shrivastava, 1982; and Kumar and Sharma, 1982). The modified Nernst-Einstein relationship (Landsberg, 1978) is given by

$$D_i = RTu_i \frac{F_{1/2}(\eta)}{\frac{\partial}{\partial \eta} F_{1/2}(\eta)}, \quad (6)$$

where  $F_{1/2}(\eta)$  is a tabulated integral and  $\eta$  is proportional to the difference between the electrochemical potential of the species  $i$  and the respective band-edge energy. Approximate formulas for  $F_{1/2}(\eta)$  were given by Shibib (1981) and Aymerich-Humet et al. (1981). Landsberg and Guy (1983) present the relationship between this approach and the activity coefficient used in the above development, i.e.,

$$\frac{F_{1/2}(\eta)}{\frac{\partial}{\partial \eta} F_{1/2}(\eta)} = \left(1 + \frac{d \ln f_i}{d \ln c_i}\right). \quad (7)$$

The validity of the Nernst-Einstein relation rests on the fact that the driving force for both migration and diffusion is the gradient of the electrochemical potential. The decomposition of this driving force into chemical and electrical contributions is arbitrary and without basic physical significance (Guggenheim, 1929). Correction of the Nernst-Einstein relationship, as in Eq. 6, to account for nonideal behavior represents a decomposition of the electrochemical potential gradient such that the diffusional flux density is proportional to the gradient of concentration, not activity as given in Eq. 3. The advantages of the approach represented by Eqs. 1–5 are that the influence of nonideal behavior is separated from transport properties and that only one transport property need be measured for each species. Furthermore, the transport property can be expected to be a weaker function of concentration. The activity coefficients presented in Eq. 5 can also be employed within the framework of the transport theory for concentrated solutions (Bird et al., 1960; Newman, 1973). The quantum mechanical relationships used to obtain a correction to the Nernst-Einstein relationship, as in Eq. 6, can also be used to obtain further modifications of expressions for the activity coefficients.

Homogeneous recombination reactions are also affected by degeneracy. The net rate of generation of holes can be expressed through band-to-band kinetic models (Grove, 1967; 1969) by

$$R_h = G_{\text{photo}} - k_{\text{rec}}(np - n_i^2), \quad (8)$$

where the rate of hole generation by illumination is given by

$$G_{\text{photo}} = \eta m q_0 e^{-m\psi},$$

and the intrinsic concentration  $n_i$  can be obtained from kinetic arguments to be

$$n_i = \left\{ \frac{k_{th}(N_c - n)(N_v - p)}{k_{\text{rec}}} \right\}^{1/2}. \quad (9)$$

A similar expression is obtained from statistical mechanical arguments. The intrinsic concentration can be considered to be constant for a given semiconductor only if the dimensionless concentrations,  $p/N_v$  and  $n/N_c$ , are much less than one. The intrinsic concentration can be written in terms of activity coefficients and its nondegenerate limit  $n_{lim}$  as

$$n_i = n_{lim} \left( \frac{1}{f_e f_h} \right)^{1/2}. \quad (10)$$

Equation 10 also applies for models for which electrons and holes recombine through trap sites.

A material balance for holes can be written in terms of the transport and kinetic equations given above for degenerate semiconductors.

$$\nabla \cdot N_h = R_h, \quad (11)$$

The development presented here, while applicable to p-type semiconductors, is oriented toward analysis of an n-type semiconductor in which holes are the minority carrier. Material balances of holes and electrons are not independent, and conservation of the minority carrier was chosen to improve the numerical computational accuracy. Conservation of majority carriers was replaced by the condition that the divergence of the current be zero; therefore the fluxes of holes and electrons were related by

$$\nabla \cdot N_e - \nabla \cdot N_h = 0. \quad (12)$$

Poisson's equation,

$$\nabla^2 \Phi = - \frac{F}{\epsilon_{sc}} [p - n + (N_d - N_a)], \quad (13)$$

relates the potential to the charge distribution.

## Numerical Method

For a one-dimensional steady state model, Eqs. 11, 12, and 13 result in a system of coupled, nonlinear, ordinary differential equations. These were placed in finite-difference form and properly linearized. The resulting system of tri-diagonal matrices was solved numerically by Newman's (1968) method coupled with Newton-Raphson iteration to characterize the semiconductor behavior. This approach provides a solution to the governing equations without linearization approximations. Potential-dependent concentration variables were introduced to reduce the numerical difficulties associated with concentrations that can vary over 20 orders of magnitude in a short distance. The use of these variables is discussed by Bogatov et al. (1982). Convergence was quadratic. The number of iterations required depended upon the initialization of the variables, but in most cases convergence was achieved in less than 10 iterations.

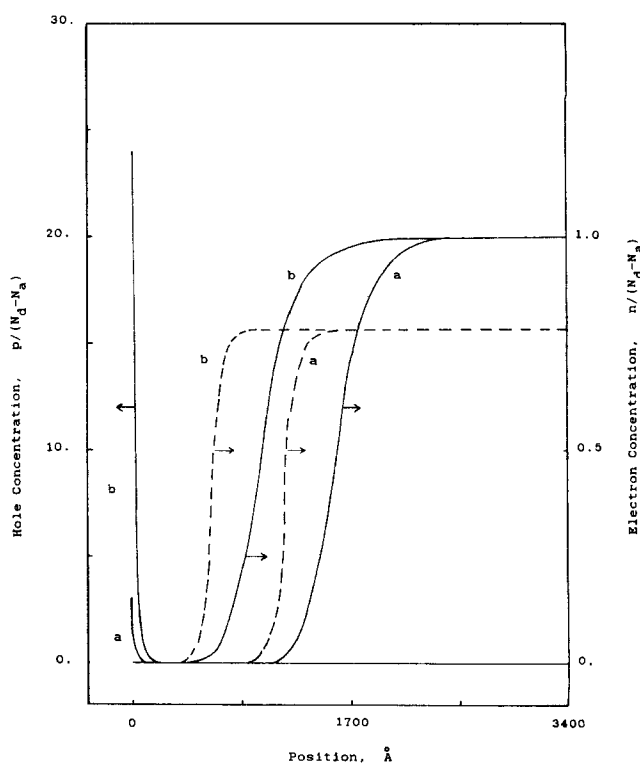
## Results and Discussion

The approach outlined in the previous section was used in this work to model Schottky-barrier photovoltaic cells. Appropriate boundary conditions are given by Fonash (1981) and by Orazem and Newman (1984a, 1985). Facilitated recombination reactions were included at the interfaces. The rate constants for

**Table 1. Model Parameters**

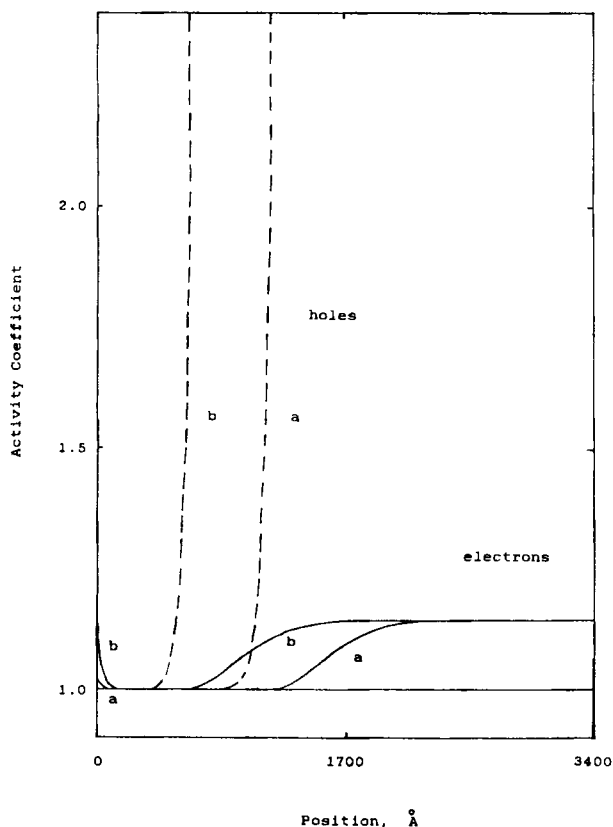
Electron diffusivity, $D_e$	$2.22 \times 10^{-2} \text{ m}^2/\text{s}$
Hole diffusivity, $D_h$	$6.46 \times 10^{-4} \text{ m}^2/\text{s}$
Permittivity, $\epsilon$	$1.06 \times 10^{-10} \text{ C/V-m}$
Dopant concentration, $N_d$	$9.66 \times 10^{-14} \text{ equiv./m}^3$ ( $6.00 \times 10^{16} \text{ cm}^{-3}$ )
Effective valence band site density, $N_v$	$1.16 \times 10^{-11} \text{ equiv/m}^3$ ( $7.00 \times 10^{18} \text{ cm}^{-3}$ )
Effective conduction band site density, $N_c$	$7.80 \times 10^{-13} \text{ equiv/m}^3$ ( $4.70 \times 10^{17} \text{ cm}^{-3}$ )
Mean solar absorption coefficient, $m$	$4.40 \times 10^3 \text{ m}^{-1}$
Homogeneous recombination rate constant, $k_{rec}$	$1.89 \times 10^{13} \text{ m}^3/\text{mol} \cdot \text{s}$
Interfacial recombination rate constant	$1.00 \times 10^{42} \text{ m}^4/\text{mol} \cdot \text{s}$
Charge at ohmic contact	$0.00 \text{ } \mu\text{C/m}^2$
Charge at illuminated interface	$-0.16 \times 10^{-4} \text{ } \mu\text{C/m}^2$

these reactions were large enough that the reactions were essentially equilibrated. Electrons carried current through the rear contact, and holes carried current through the illuminated interface. Transport and kinetic parameters were consistent with an n-type GaAs semiconductor and are presented in Table 1. This model describes a photovoltaic device with a junction created by a metal film or a photoelectrochemical cell for which charge-transfer and ion-adsorption reactions are fast.



**Figure 1. Dimensionless electron and hole concentration distribution.**

a, at equilibrium. b, under  $882 \text{ W/m}^2$  illumination. Parameters given in Table 1, except that for dashed lines  $N_c = 7.8 \times 10^{-8} \text{ equiv./cm}^3$ .



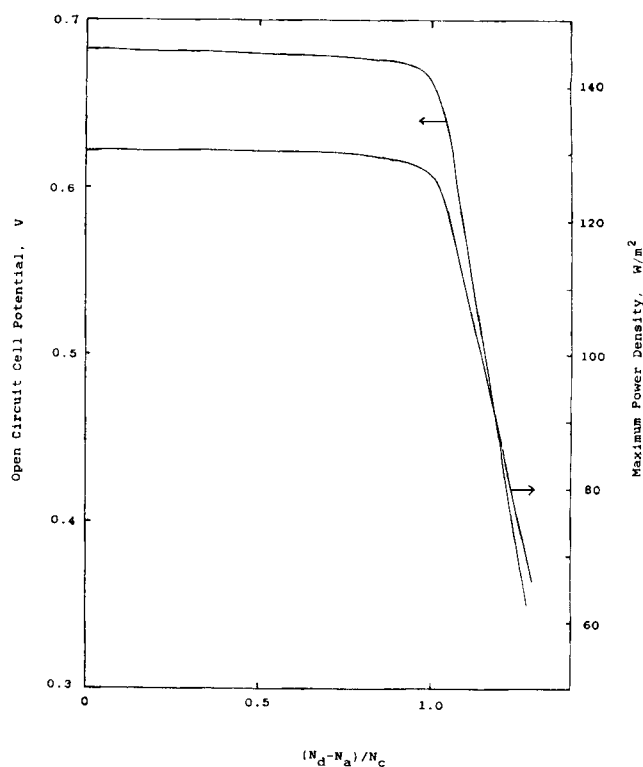
**Figure 2. Electron and hole activity coefficient distribution.**

*a*, at equilibrium. *b*, under 882 W/m<sup>2</sup> illumination. Parameters given in Table 1, except that for dashed lines  $N_c = 7.8 \times 10^{-2}$  equiv/cm<sup>3</sup>.

Concentration distributions are presented as solid lines in Figure 1 for electrons and holes in the semiconductor. Under equilibrium conditions (curve *a*), a negative charge on the junction causes holes to accumulate at the front of the semiconductor (considered here to be the illuminated surface) and electrons at the rear. Generation of electron-hole pairs under illumination at open circuit (curve *b*) increases the electron and hole concentrations, and these electrons and holes are separated by the potential gradient associated with the junction. The electric field associated with the new concentration distribution tends to cancel that which existed at equilibrium and thus creates a driving force for the flow of electrical current.

The corresponding activity coefficient distribution is presented in Figure 2. The activity coefficient for holes is equal to 1.0 in the bulk of the semiconductor and increases slightly near the front to a value of 1.026 in the dark (curve *a*) and 1.266 under illumination. Assumption of constant activity coefficients increases the calculated value of the surface hole concentration under illumination by 8.2%. The activity coefficient for electrons, also presented in Figure 2, is equal to 1.0 in the depletion region and increases to a value of 1.146 in the neutral region. Assumption of constant activity coefficients has little influence on the electron concentration.

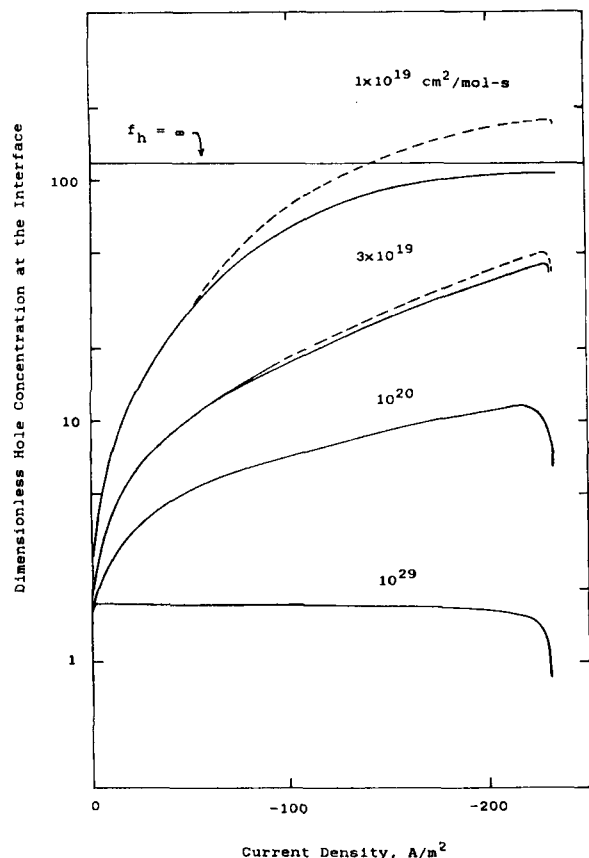
The open-circuit photopotential of this device was calculated to be 0.682 V, and the maximum power density was calculated to be 130.5 W/m<sup>2</sup>. The assumption that the activity coefficients were equal to one results in an overestimation of the open-circuit



**Figure 3. Open-circuit cell potential and maximum power density as a function of the ratio of dopant concentration to effective conduction band site density.**

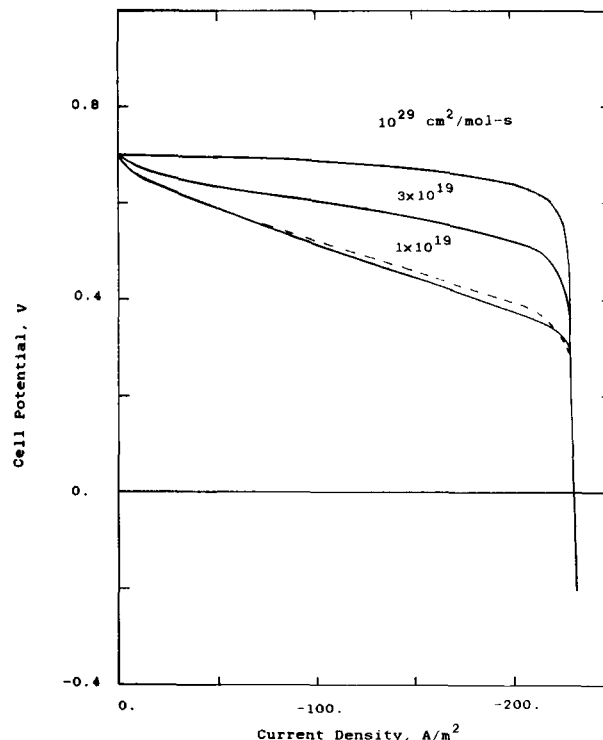
cell potential of 0.09%. The calculated maximum power density was not affected. Inclusion of concentration-dependent activity coefficients had a substantial influence on the calculated hole concentration in a very small region of the semiconductor but had little effect on the calculated values associated with cell performance.

The dimensionless conduction and valence band site densities,  $N_c/(N_d - N_a)$  and  $N_v/(N_d - N_a)$ , respectively, have a major effect on the state of degeneracy. Open-circuit cell potential and maximum power density are presented in Figure 3 as functions of the inverse of the dimensionless conduction band site density. The assumption of constant activity coefficients corresponds to  $(N_d - N_a)/N_c$  equal to zero. A sharp decrease in open-circuit cell potential and maximum power density is seen for values greater than one. Under these conditions, no neutral region can exist in the semiconductor because sufficient sites are not available for electrons to balance the ionized dopant concentration. This situation is illustrated by the dashed lines in Figure 1, and the related electron activity coefficient, presented in Figure 2, reaches a value of  $4.486 \times 10^{12}$ . The mathematical model provides a converged solution for this case that is consistent with the Fermi-Dirac distribution, but this solution describes a nonphysical situation. Accurate modeling of this condition of extreme degeneracy requires relaxation of the assumption of complete ionization of dopant species, accounting for occupancy by electrons of energy levels above the lowest conduction-band energy, and accounting for the band-gap reduction associated with large doping densities. The occupancy by electrons of high energy levels and the band-perturbing effects may be conveniently treated



**Figure 4. Dimensionless hole concentration at the semiconductor-electrolyte interface as a function of current density with charge-transfer reaction rate constant as a parameter.**

Model parameters, Orazem and Newman (1984b).  
 ---- Solutions obtained through assumption of constant activity coefficients.



**Figure 5. Calculated cell potential as a function of current density with charge-transfer reaction rate constant as a parameter.**

Model parameters, Orazem and Newman (1984b).  
 ---- Solutions obtained through assumption of constant activity coefficients.

through modification of the expressions for the electron and hole activity coefficients.

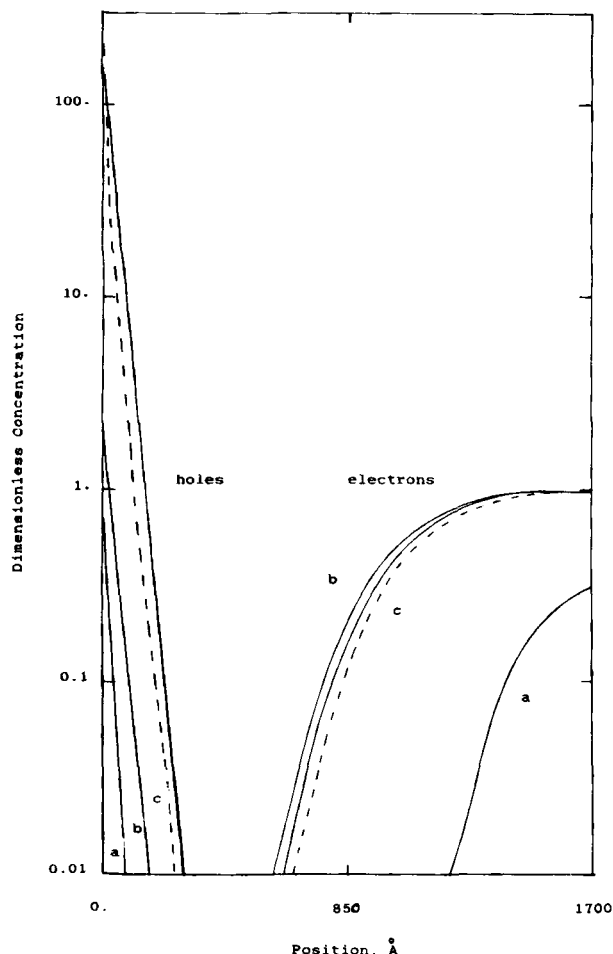
A semiconductor can also become degenerate due to kinetic limitations at an interface, even when the dimensionless conduction and valence-band site densities are substantially greater than one. Kinetic limitations to reactions are compensated by increased potential and concentration driving forces. The influence of kinetic limitations to charge-transfer reactions on interfacial hole concentrations is presented in Figure 4 for a photoelectrochemical cell. Solutions obtained through the assumption of constant activity coefficients are indicated by dashed lines. The two solutions are equivalent for large values of rate constants, but differ considerably with increasing hole concentration. Assumption of constant activity coefficients for very small rate constants leads to up to a 70% overestimation of the hole concentration at the semiconductor-electrolyte interface. The corresponding current-potential curves are presented in Figure 5. Both solutions, including and neglecting the activity coefficient effect, show the reduction of power density associated with kinetic limitations at the semiconductor-electrolyte interface. Neglect of the activity coefficient correction results in a large overestimation of the interfacial hole concentration but only a 5% overestimation of the cell potential and power density. This result is due in part to the fact that only a small region of

the semiconductor is degenerate. The concentration distribution in the semiconductor is presented in Figure 6. Under equilibrium conditions (curve *a*) and under illumination at open circuit (curve *b*), the concentration distribution is not influenced by consideration of degeneracy. Under these conditions, the largest activity coefficient for holes was 1.016. The concentration distribution is affected by degeneracy near the limiting current (curve *c*).

In the range of degeneracy studied, the neglect of the concentration dependency of the electron and hole activity coefficient does not cause a significant error in the calculation of measurable system properties for semiconductors under AM-2 illumination. Neglect of the activity coefficient does cause errors in calculation of measurable properties for semiconductors without illumination. The effective resistivity of the nonilluminated semiconductor was calculated and is presented in Figure 7 as a function of dimensionless doping level. In obtaining this curve, the doping level was varied and  $N_c$  was held constant. The calculations of resistivity including the activity coefficient correction deviate from that assuming unity activity coefficients above a dimensionless doping level equal to 0.2. The resistivity tends toward  $-\infty$  as dimensionless doping level tends toward 1. The expressions for the activity coefficient are invalid in this region.

## Conclusions

A mathematical model of photovoltaic devices is presented that accounts explicitly for the influence of degeneracy. Macroscopic transport equations for electrons and holes in semicon-



**Figure 6. Calculated electron and hole concentration distribution with charge-transfer reaction rate constant =  $1 \times 10^{10}$ .**

Model parameters, Orazem and Newman (1984b).

a, under equilibrium conditions (no illumination).

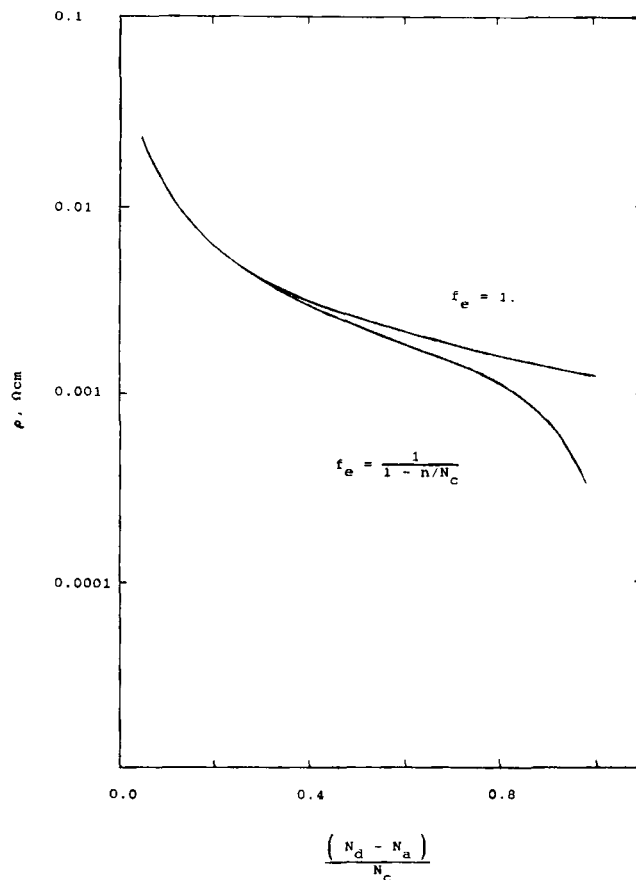
b, under AM-2 illumination at open circuit.

c, under AM-2 illumination at current density of  $-23 \text{ mA/cm}^2$ .

---- Solutions obtained through assumption of constant activity coefficients.

ducting materials were made consistent with Fermi-Dirac statistics by inclusion of a concentration-dependent activity coefficient. These equations allow modeling of degenerate semiconductors for which the electron and hole concentrations are less than their respective effective energy band site density and for which the effective conduction and valence band site densities are greater than the dopant concentration. Extension of this model to allow treatment of higher concentrations requires further modification of the activity coefficient expression to account for the influence of degeneracy on the occupancy and structure of energy bands.

Calculations are presented for a photovoltaic device modeled under the assumption of constant activity coefficients and with concentration-dependent activity coefficients. Comparisons among the results of these calculations show that neglect of the concentration dependency of the activity coefficients has a large effect on the calculated values for local concentrations. However, values of power density and cell potential obtained from these calculations differ only slightly. Incorporation of the activ-



**Figure 7. Calculated resistivity for an unilluminated *n*-GaAs semiconductor as a function of dimensionless dopant concentration.**

ity coefficients into the transport equations does have a significant effect on the calculation of the resistivity of the semiconductor. These results show that for concentrations in the range for which Eq. 5 is valid, mathematical models of photovoltaic devices that neglect the concentration dependency of the activity coefficients provide adequate calculations of measurable device properties. The concentration dependency of the activity coefficients should, however, be taken into account for calculations of unilluminated semiconductor properties at high electron or hole concentrations.

## Notation

- $c_i$  = molar concentration of species  $i$ ,  $\text{mol/m}^3$
- $D_i$  = diffusivity of species  $i$ ,  $\text{cm}^2/\text{s}$
- $f_i$  = molar activity coefficient of species  $i$
- $F$  = Faraday's constant,  $96,487 \text{ C/equiv}$
- $G_{\text{photo}}$  = rate of photoelectron-hole pair generation,  $\text{mol/s} \cdot \text{m}^3$
- $k_{\text{rec}}$  = rate constant for homogeneous electron-hole recombination,  $\text{m}^3/\text{mol} \cdot \text{s}$
- $k_{\text{th}}$  = rate constant for thermal generation of electron-hole pairs,  $\text{m}^3/\text{mol} \cdot \text{s}$
- $m$  = solar absorption coefficient,  $1/\text{m}$
- $n$  = electron concentration,  $\text{mol/m}^3$
- $n_i$  = intrinsic electron concentration,  $\text{mol/m}^3$
- $N_k$  = maximum concentration of energy  $k$ ,  $\text{mol/m}^3$
- $N_a$  = total bulk electron-acceptor concentration,  $\text{mol/m}^3$
- $N_d$  = total bulk electron-donor concentration,  $\text{mol/m}^3$
- $N_i$  = flux density of species  $i$ ,  $\text{mol/m}^2 \cdot \text{s}$
- $p$  = hole concentration,  $\text{mol/m}^3$

$q_0$  = incident solar flux, mol/cm<sup>2</sup> s  
 $R$  = universal gas constant, 8.3143 J/mol · K  
 $R_i$  = net rate of production of species  $i$ , mol/s · m<sup>3</sup>  
 $T$  = absolute temperature, K  
 $u_i$  = mobility of species  $i$ , m<sup>2</sup> · mol/J · s  
 $y$  = distance variable,  
 $z_i$  = charge number of species  $i$

## Greek letters

$\epsilon$  = permittivity, C/V · cm  
 $\eta$  = fraction of incident photons with energy greater than the band gap  
 $\mu_i$  = electrochemical potential of species  $i$ , J/mol  
 $\mu_i^0$  = secondary reference state for species  $i$ , J/mol  
 $\Phi$  = electrical potential, V

## Subscripts

$c$  = associated with conduction band in semiconductor  
 $e$  = relating to electrons  
 $h$  = relating to holes  
 $\lim$  = limiting value at infinite dilution  
 $v$  = associated with valence band in semiconductor

## Literature Cited

- Aymerich-Humet, X., F. Serra-Mestres, and J. Millan, "An Analytical Approximation of the Fermi-Dirac Integral  $F_{1/2}(\eta)$ ," *Solid State Electr.*, **24**, 981 (1981).
- Bird, R. Byron, Warren E. Stewart, and Edwin N. Lightfoot, *Transport Phenomena*, Wiley, New York, 567 (1960).
- Bogotov, N. M., et al., "A Numerical Solution of the One-Dimensional Boundary Value Problem of Charge Transfer in Solar Cells," *Geliotekhnika*, **18**, 7 (1982).
- Choo, Seok Cheow, "Numerical Analysis of a Forward-Biased Step-Junction p-n Diode," *IEEE Trans. Electron Dev.*, **ED-18**, 574 (1971).
- , "Theory of a Forward-Biased Diffused-Junction p-n Rectifier. I: Exact Numerical Solution," *IEE Trans. Electron Dev.*, **ED-19**, 954 (1972).
- Dhariwal, S. R., and V. N. Ojha, "Band-Gap Narrowing in Heavily Doped Silicon," *Solid State Electr.*, **25**, 909 (1982).
- DeMari, A., "An Accurate Numerical Steady-State One-Dimensional Solution of the p-n Junction," *Solid State Electr.*, **11**, 33 (1968a).
- , "An Accurate Numerical Steady-State One-Dimensional Solution of the p-n Junction under Arbitrary Transient Conditions," *Solid State Electr.*, **11**, 1,021 (1968b).
- Fonash, Stephen J., *Solar Cell Device Physics*, Academic Press, New York (1981).
- Gerischer, Heinz, "Semiconductor Electrochemistry," *Physical Chemistry: An Advanced Treatise*, H. Eyring, Ed., Academic Press, New York, **9**, ch. 5 (1970).
- Grove, A. S., *Physics and Technology of Semiconductor Devices*, J. Wiley, New York (1967).
- Guggenheim, E. A., "The Conceptions of Electrical Potential Difference Between Two Phases and the Individual Activities of Ions," *J. Phys. Chem.*, **33**, 842 (1929).
- Guy, A. G., "Calculation of Activity Coefficients of Conduction Electrons in Metals and Semiconductors," *Solid State Electr.*, **26**, 433 (1983).
- Harvey, W. W., "The Relation Between the Chemical Potential of Electrons and Energy Band Parameters of the Band Theory as Applied to Semiconductors," *J. Phys. Chem. of Solids*, **23**, 1545 (1962).
- Hwang, J. C., and J. R. Brews, "Electron Activity Coefficients in Heavily Doped Semiconductors with Small Effective Mass," *J. Phys. Chem. of Solids*, **32**, 837 (1971).
- Kumar, D. Vijay, and S. K. Sharma, "Theory of Open Circuit Photovoltage in Degenerate Abrupt p-n Junctions," *Solid State Electr.*, **25**, 1161 (1982).
- Landsberg, P. T., *Thermodynamics and Statistical Mechanics*, Oxford Univ. Pr., New York, 327 (1978).
- Landsberg, P. T., and S. A. Hope, "Two Formulations of Semiconductor Transport Equations," *Solid State Electr.*, **20**, 421 (1977).
- Landsberg, P. T., and A. G. Guy, "Activity Coefficient and the Einstein Relation," *Phy. Rev. B: Condensed Matter*, **28**, 1187 (1983).
- Lanyon, H. P. D., "The Physics of Heavily Doped n<sup>+</sup>-p Junction Solar Cells," *Solar Cells*, **3**, 289 (1981).
- Laser, Daniel, "Modes of Charge Transfer at an Illuminated Semiconductor Electrode: A Digital Simulation," *J. Electrochem. Soc.*, **126**, 1011 (1979).
- Laser, Daniel, and Allen J. Bard, "Semiconductor Electrodes. VII: Digital Simulation of Charge Injection and the Establishment of the Space Charge Region in the Absence and Presence of Surface States," *J. Electrochem. Soc.*, **123**, 1828 (1976a).
- , "Semiconductor Electrodes. VIII: Digital Simulation of Open-Circuit Photopotentials," *J. Electrochem. Soc.*, **123**, 1833 (1976b).
- , "Semiconductor Electrodes. IX: Digital Simulation of the Relaxation of Photogenerated Free Carriers and Photocurrents," *J. Electrochem. Soc.*, **123**, 1837 (1976c).
- Lindholm, F. A., and J. G. Fossum, "Pictorial Derivation of the Influence of Degeneracy and Disorder on Nondegenerate Minority-Carrier Concentration and Recombination Current in Heavily Doped Silicon," *IEEE Electr. Dev. Letters*, **EDL-2**, 230 (1981).
- Lundstrom, M. S., R. J. Schwartz, and J. L. Gray, "Transport Equations for the Analysis of Heavily Doped Semiconductor Devices," *Solid State Electr.*, **24**, 195 (1981).
- MacDonald, J. Ross, "Accurate Solution of an Idealized One-Carrier Metal-Semiconductor Junction Problem," *Solid State Electr.*, **5**, 11 (1962).
- Marshak, Alan, H., and Ritu Shrivastava, "Calculation of the Electric Field Enhancement for a Degenerate Diffusion Process," *Solid State Electr.*, **25**, 151 (1982).
- Newman, John, "Numerical Solution of Coupled, Ordinary Differential Equations," *Ind. Eng. Chem. Fundam.*, **7**, 514 (1968).
- , *Electrochemical Systems*, Prentice-Hall, Englewood Cliffs, NJ 217-253 (1973).
- Orazem, Mark E., *Mathematical Modeling and Optimization of Liquid-Junction Photovoltaic Cells*, Ph.D. Diss., Dept. Chem. Eng., Univ. California, Berkeley, LBL-16131 (1983).
- Orazem, Mark E., and John Newman, "Mathematical Modeling of Liquid-Junction Photovoltaic Cells. I: Governing Equations," *J. Electrochem. Soc.*, **131**, 2569 (1984a).
- , "Mathematical Modeling of Liquid-Junction Photovoltaic Cells. II: Effect of System Parameters on Current-Potential Curves," *J. Electrochem. Soc.*, **131**, 2574 (1984b).
- , "Activity Coefficients of Electrons and Holes in Semiconductors," *J. Electrochem. Soc.*, **131**, 2715 (1984c).
- , "Photoelectrochemical Devices for Solar Energy Conversion," *Lawrence Berkeley Laboratory Report, LBL-18766*, (Jan. 1985).
- Panish, M. B., and H. C. Casey, Jr., "The Solid Solubility Limits of Zinc in GaAs at 1000°C," *J. Phys. Chem. of Solids*, **28**, 1673 (1967).
- , "The 1040°C Solid Solubility Isotherm of Zinc in GaP: The Fermi Level as a Function of Hole Concentration," *J. Phys. Chem. of Solids*, **28**, 1719 (1968).
- Parsons, Roger, "Equilibrium Properties of Electrified Interphases," *Modern Aspects of Electrochemistry*, John O'M Bockris, Ed., Academic Press, New York, **1**, ch. 3 (1954).
- Pavalets, S. Yu., "Solar Converters Based on Degenerate-Semiconductor/Semiconductor P-N Heterojunctions," *Geliotekhnika*, **18**, 3 (1982).
- Rosenberg, A. J., "Activity Coefficients of Electrons and Holes at High Concentrations," *J. Chem. Phys.*, **33**, 655 (1960).
- Shibib, M. Ayman, "Inclusion of Degeneracy in the Analysis of Heavily Doped Regions in Silicon Solar Cells and other Semiconductor Devices," *Solar Cells*, **3**, 81 (1981).
- Sutherland, J. E., and J. R. Hauser, "A Computer Analysis of Heterojunction and Graded Composition Solar Cells," *IEEE Trans. Electr. Dev.*, **ED-24**, 363 (1977).
- Sze, S. M., *Physics of Semiconductor Devices*, Wiley-Interscience, New York (1969).

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