Activity Coefficients of Electrons and Holes in Semiconductors

Mark E. Orazem*,[1] and John Newman**

Materials and Molecular Research Division of Lawrence Berkeley Laboratory, and Department of Chemical Engineering, University of California, Berkeley, California 94720

ABSTRACT

Dilute-solution transport equations with constant activity coefficients are commonly used to model semiconductors. These equations are consistent with a Boltzmann distribution and are invalid in regions where the species concentration is close to the respective site concentration. A more rigorous treatment of transport in a semiconductor requires activity coefficients which are functions of concentration. Expressions are presented for activity coefficients of electrons and holes in semiconductors for which conduction- and valence-band energy levels are given by the respective bandedge energy levels. These activity coefficients are functions of concentration and are thermodynamically consistent. The use of activity coefficients in macroscopic transport relationships allows a description of electron transport in a manner consistent with the Fermi-Dirac distribution.

The concentrations of holes and electrons in a semiconductor are given by the Fermi-Dirac distribution (1, 2). 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 respective site concentrations in any region.

Calculation of individual ionic activity coefficients for electrons and holes has been proposed as a means of identifying the regions in which these approximations are justified. Rosenberg (3), Panish and Casey, Jr. (4, 5), and Hwang and Brews (6) have presented activity coefficients for electrons and holes that are functions of potential as well as concentration. Harvey (7) discusses the separation of the activity coefficient into parts due to chemical and electrical effects. Landsberg and Guy (8) present an activity coefficient based upon an Einstein relation that includes within it the nonidealities associated with the activity coefficient (9).

Activity coefficients are derived here that are functions of concentration. This derivation is independent of the Einstein relation. These activity coefficients are thermodynamically consistent and can be used to check the validity of the Boltzmann function as an approximation to the Fermi-Dirac distribution. These coefficients can also be used in the application of macroscopic transport equations to semiconducting systems in a way that is generally valid.

Theoretical Development

The electrochemical potential of a given species can arbitrarily be separated into terms representing a reference state, a chemical contribution, and an electrical contribution (10)

$$\mu_i = \mu_i^\theta + RT \ln (c_i f_i) + z_i \mathbf{F} \Phi \quad [1]$$

where Φ is a potential which characterizes the electrical state of the phase and can be defined in a number of ways. The potential used here is the electrostatic potential which is obtained through integration of Poisson's equation (11). Equation [1] can be viewed as the defining equation for the activity coefficient, f_i.

Under the assumption of a dilute solution, the flux of an individual species within the semiconductor is driven by a gradient of electrochemical potential

$$N_i = -c_i u_i \nabla \mu_i \quad [2a]$$

or

$$f_i N_i = -u_i RT \nabla (c_i f_i) - z_i u_i \mathbf{F} (c_i f_i) \nabla \Phi \quad [2b]$$

where N_i is the flux of species i. Introduction of $A = c_i f_i e^{z_i \mathbf{F} \Phi / RT}$ yields

$$f_i N_i = -u_i RT e^{-z_i \mathbf{F} \Phi / RT} \nabla A \quad [3]$$

Under equilibrium conditions, $\nabla A = 0$, and

$$c_i f_i = A e^{-z_i \mathbf{F} \Phi / RT} \quad [4]$$

where A is a constant. Under the assumption of a constant activity coefficient, Eq. [4] is consistent with a Boltzmann distribution.

The distribution of electrons in a semiconductor is characterized by the Fermi-Dirac function

$$\frac{n_i}{g_i} = [1 + \exp [(E_i - E_f)/RT]]^{-1} \quad [5]$$

where n_i is the number of electrons within an energy level E_i with degeneracy g_i. The Fermi energy E_f is a statistical parameter given the units of J/mol and defined as the energy at which the probability of occupancy of a state is one-half. The Fermi-Dirac distribution enters into the transport development (Eq. [2], [3], and [4]) through introduction of individual ionic activity coefficients: one for electrons and one for holes.

Through Fermi-Dirac statistics the concentration of conduction electrons is given by

$$n = \int_{E_c}^{\infty} \frac{N(E)}{1 + \exp [(E - E_f)/RT]} dE \quad [6]$$

and the concentration of holes by

$$p = \int_{-\infty}^{E_v} \left[1 - \frac{1}{1 + \exp [(E - E_f)/RT]} \right] N(E) dE \quad [7]$$

The concentrations defined above are consistent with the concentrations c_i used in Eq. [1]-[4]. If the distribution of available energy levels is narrow or RT is small, the valence and conduction electrons can be characterized by single-valued energy levels, E_v (the highest energy level of the valence band) and E_c (the lowest energy level of the conduction band), respectively. Thus

$$n = \frac{1}{1 + \exp [(E_c - E_f)/RT]} \int_{E_c}^{\infty} N(E) dE \quad [8]$$

or

$$n = \frac{N_c}{1 + \exp [(E_c - E_f)/RT]} \quad [9]$$

where N_c is the concentration of conduction-energy sites for electrons. A similar term, N_v, is defined as the concentration of valence-band sites.

From the definition of the electrochemical potential, the chemical activity

*Electrochemical Society Student Member.

**Electrochemical Society Active Member.

[1]Present address: Department of Chemical Engineering, University of Virginia, Charlottesville, Virginia 22901.

Downloaded 26 Jun 2008 to 128.227.7.250. Redistribution subject to ECS license or copyright; see http://www.ecsdl.org/terms_use.jsp

$$a_i = c_i f_i \quad [10]$$

can be expressed as

$$a_i = \exp\left[\frac{\mu_i - \mu_i^\theta - z_i \mathbf{F}\Phi}{RT}\right] \quad [11]$$

Note that the activity has units of concentration (see Eq. [1]). In Eq. [9], the concentration of conduction electrons is given as a function of the Fermi energy level. The energy E_c in this equation depends upon potential as

$$E_c = E_c^* + z_i \mathbf{F}\Phi \quad [12]$$

where E_c^* is a constant, independent of potential. The electrochemical potential of conduction electrons and the Fermi energy are related by an arbitrary constant

$$\mu_{e^-} = E_f + \mu^*_{e^-} \quad [13]$$

Equations [11] through [13] can be combined to yield

$$f_{e^-} = \frac{\exp\left[(\mu^*_{e^-} - \mu^\theta_{e^-} + E_c^*)/RT\right]}{N_c}\left[\frac{1}{1 - n/N_c}\right] \quad [14]$$

where f_{e^-} is dimensionless. The secondary reference state quantities, E_c^*, $\mu^*_{e^-}$, and $\mu^\theta_{e^-}$, are chosen to allow the activity coefficient to approach unity as the concentration of conduction electrons approaches zero. Thus, the activity coefficient is obtained as a function of composition

$$f_{e^-} = \frac{1}{1 - n/N_c} \quad [15]$$

The activity coefficient of conduction electrons is equal to 2 for a dimensionless concentration n/N_c equal to 0.5.

A similar activity coefficient can be obtained for the holes as

$$f_{h^+} = \frac{1}{1 - p/N_v} \quad [16]$$

The assumption of unity activity coefficients is in harmony with the assumption of the Boltzmann limits to the Fermi-Dirac distribution. Use of the Fermi-Dirac distribution results in activity coefficients that are functions of concentration.

Discussion

Equations [15] and [16] are consistent with the form of the activity coefficients

$$f_{e^-} = \frac{N_c}{n} e^{(E_f - E_c)/RT} e^{\Delta E/RT}$$

presented by Hwang and Brews (6) and Landsberg and Guy (8). These authors include a term $e^{\Delta E/RT}$ for the shift in electron energy due to the occupation of energy levels above E_c at high electron concentrations (12). Under the assumption that $\Delta E = 0$, Eq. [15] is recovered by introduction of the Fermi-Dirac distribution function for electrons. Calculation of ΔE requires knowledge of the electron site distribution $N(E)$.

The activity coefficients defined above can be checked for consistency with the Fermi-Dirac function. Introduction of the activity coefficient presented for electrons in Eq. [15] into the respective Boltzmann distribution

$$n f_{e^-} = N_c e^{-(E_c - E_f)/RT} \quad [17]$$

recovers the Fermi-Dirac distribution

$$\frac{n}{N_c} = \frac{1}{1 + e^{(E_c - E_f)/RT}} \quad [18]$$

The same is true for the activity coefficient for holes.

A measure of internal thermodynamic consistency is obtained from the second cross-derivative of the Gibbs function, *i.e.*

$$\left(\frac{\partial \mu_i}{\partial c_k}\right)_{T,P,c_j \neq k} = \left(\frac{\partial \mu_k}{\partial c_i}\right)_{T,P,c_j \neq i} \quad [19]$$

where i and k represent components of the system that are not the solvent. This necessary condition for thermodynamic consistency is expressed for the system described here as

$$\frac{RT}{f_{e^-}}\left(\frac{\partial f_{e^-}}{\partial p}\right)_{T,P,n} = \frac{RT}{f_{h^+}}\left(\frac{\partial f_{h^+}}{\partial n}\right)_{T,P,p} \quad [20]$$

This condition is satisfied. (Equation [19] is properly stated in terms of mole numbers rather than concentrations. For the dilute systems involved here, lattice expansion is ignored, and the two are equivalent.)

Use of macroscopic relations for thermodynamics and transport in regions of nonzero electric charge density raises some interesting philosophical questions because transport and thermodynamic properties are not easily measurable as functions of composition including arbitrary departures from electroneutrality. Fortunately, the semiconductors of interest are extremely dilute compared to even dilute aqueous solutions, and theoretical expressions such as the Fermi-Dirac distribution can be used with some confidence. Note that individual ionic activity coefficients are here being introduced in regions of net charge.

The extreme dilution of the semiconductors is also a justification for using the simple transport Eq. [2a] rather than the multicomponent diffusion equation (10), which includes interactions of solute species, and for using the approximate thermodynamic test embodied in Eq. [19].

Conclusions

Activity coefficients are derived here that are functions of concentration. These activity coefficients are thermodynamically consistent and can be used to check the validity of the Boltzmann function as an approximation to the Fermi-Dirac distribution. These coefficients can also be used in the application of macroscopic transport equations to semiconducting systems.

The use of constant activity coefficients in modeling semiconductor systems is valid for dimensionless concentrations n/N_c and p/N_v less than 0.1. Use of the activity coefficients presented in Eq. [15] and [16] allows treatment of systems with dimensionless concentrations ranging from 0 to 1. This approach is restricted, however, by the assumption that valence- and conduction-band electrons are characterized by their respective bandedge energies. Relaxation of this assumption involves integration of Eq. [6] and [7] for a specific distribution of electron energy levels.

Acknowledgment

This work was supported by the United States Department of Energy under Contract no. DE-AC03-76SF00098 through the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, and through the Assistant Secretary of Conservation and Renewable Energy, Office of Advanced Conservation Technology, Electrochemical Systems Research Division.

Manuscript submitted Nov. 21, 1983; revised manuscript received June 6, 1984.

The University of California assisted in meeting the publication costs of this article.

REFERENCES

1. A. S. Grove, "Physics and Technology of Semiconductor Devices," John Wiley and Sons, New York (1967).
2. S. M. Sze, "Physics of Semiconductor Devices," Wiley-Interscience, New York (1969).
3. A. J. Rosenberg, *J. Chem. Phys.*, **33**, 665 (1960).
4. M. B. Panish and H. C. Casey, Jr., *J. Phys. Chem. Solids*, **28**, 1673 (1976).
5. M. B. Panish and H. C. Casey, Jr., *ibid.*, **29**, 1719 (1968).
6. C. J. Hwang and J. R. Brews, *ibid.*, **32**, 837 (1971).
7. W. W. Harvey, *ibid.*, **23**, 1545 (1962).

Downloaded 26 Jun 2008 to 128.227.7.250. Redistribution subject to ECS license or copyright; see http://www.ecsdl.org/terms_use.jsp

8. P. T. Landsberg and A. G. Guy, *Phys. Rev. B*, **28**, 1187 (1983).
9. P. T. Landsberg, "Thermodynamics and Statistical Mechanics," Oxford University Press, Oxford, England (1978).
10. J. Newman, "Electrochemical Systems," Prentice-Hall, Englewood Cliffs, NJ (1973).
11. R. Parsons, in "Modern Aspects of Electrochemistry," Vol. 1, J. O'M. Bockris, Editor, Chap. 3, Academic Press, New York (1954).
12. F. A. Lindholm and J. G. Fossum, *IEEE Trans. Electron. Devices Lett.*, **edl-2**, 230 (1981).

Technical Notes

Polarization Effects in Polyimides

G. Samuelson

Solavolt International, Phoenix, Arizona 85040

S. Lytle*

Motorola, Incorporated, Mesa, Arizona 85202

Polyimide is a class of high temperature, stable organic polymers that has found widespread use in the semiconductor industry. It has been used as an interlevel dielectric in multilevel discrete transistors (1), and as a final passivant (2). More recently, its role in silicon and aluminum MOS integrated circuits has been demonstrated (3).

Some limited-reliability data on polyimide films have been described in the literature. For example, the effect of incomplete cure on device performance was discussed by Gregoritsch (4). The via resistance and leakage current of a multilevel bipolar LSI chip was reported by Mukai *et al.* (5). Finally, the effects of ionic contamination and electrical conduction in polyimide was discussed by Brown (6).

The present work extends the discussion of charge instability within polyimide films by using standard C-V techniques to probe charge effects that are inherent in the polyimide film or are induced by certain processes. Evidence is presented to show that differences in inherent polarizability of several commercially available polyimides exist. Evidence is presented to show that absorbed water causes increases in the polarization time constants. It may be possible to distinguish different kinds of water, based on the fact that different dehydration conditions are required to restore the original time constants of polarization, depending on the relative humidity to which the polyimide film was exposed. Finally, evidence is presented to show that plasmas routinely used in the semiconductor industry may influence the polarization of polyimide films. For example, standard isotropic O_2 plasma etching of polyimide was shown to cause a decrease in the polarization time constant and activation energy.

Experimental

Polarization effects intrinsic to polyimide.—MIS structures were constructed of 8-12 Ωcm phosphorus-doped Si, 1000Å thermally grown MOS-quality SiO_2, 0.8-4.8μ polyimide (du Pont PI2545, PI2555, PI2562, PSH61453, and Hitachi PIQ-13), and 4000Å pure evaporated aluminum, patterned using conventional lithographic techniques. The resulting test wafer was subjected to a 200°C, 20 min dehydration bake immediately prior to measurement. The measurement system consisted of a Temptronic TP350A thermally controlled chuck, an HP4275A LCR meter, and a Fluke 8502A multimeter. A "standard" room temperature trace was performed at 100 kHz from −100V to +100V using a ramp rate of 1 V/s. The stress conditions used to compare measured ΔV_{FB} values against ΔV saturation calculated from classic polarization theory were −5V, 200°C, and 20 min, with cooling to room temperature under bias. At room temperature, the "standard" trace was repeated and the ΔV_{FB} measured. The stress conditions used to determine the time constants of polarization were −5V, 200°C, and times varying from 1 to 40 min, depending on the polyimide under test. Following stress, the MIS structure was cooled to room temperature under bias, the "standard" trace was repeated, and ΔV_{FB} was measured.

Humidity effects on polarization.—C-V analysis was performed on MIS structures which consisted of 4-7 Ωcm p-type Si substrates, 1000Å thermally grown MOS quality SiO_2, 1000Å CVD Si_3N_4, and 1.5μ polyimide, followed by 12 kÅ of sputtered Al-Cu-Si. An MDC computerized semiconductor measurement system consisted of a Boonton 72B capacitance meter, a HP7010B XY recorder, current monitors, and power supplies supported by an 8080S microcomputer system. Standard C-V traces of unstressed samples were made at room temperature over a voltage range of −75 to +25V at 1 MHz. Stressing was done at 225°C under a +5V bias for times ranging from 2 to 20 min. The MIS structure was brought to room temperature under bias, and the ΔV_{FB} was measured as a function of stress time. The time constant of polarization, τ, was calculated from the slope of the ln ΔV_{FB} *vs.* time curves for MIS structures exposed to various humidity ambients. 100% humidity ambient was achieved by placing wafers in an airtight wafer box with water. At no time was the water in contact with the polyimide. All other relative humidities were obtained by exposing wafers to the clean room ambient. Typically, control wafers were stored at 200°C at N_2.

Results and Discussion

Polarization effects vs. polyimide chemistry.—It has been noted by Brown (6) that charge effects in polyimide can cause inversion of underlying silicon and consequent undesired communication between doped areas. An effort was made to distinguish among the various commercially available polyimides with respect to charge instabilities by subjecting them to −5V, 200°C, and 20 min stress, conditions which mimicked realistic operating conditions for certain devices. The ΔV_{FB} of the stressed

*Electrochemical Society Active Member.

Downloaded 26 Jun 2008 to 128.227.7.250. Redistribution subject to ECS license or copyright; see http://www.ecsdl.org/terms_use.jsp