Band Discontinuities: A Simple Electrochemical Approach

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***Abstract*—A new, simple but general analytic description of the band discontinuities at a semiconductor heterojunction is derived from the fundamental electrochemical principle. We include the effects of nonuniform band structure and carrier degeneracy (Fermi-Dirac statistics), dielectric image forces, quantum-mechanical exchange-correlation forces, and dipole forces across the interface. These nonideal effects (band model parameters) are expressed in terms of the activity coefficients (thermodynamic parameters) of the carriers. Furthermore, we find a simple but general correlation between the energy band discontinuities and the activity coefficients of the carriers. Such a mathematical link between the two quantities shows that the thermodynamic parameters are important to the physics that determines the band discontinuities.**

I. Introduction

THE interface band discontinuities play a crucial role in carrier transport across a semiconductor heterojunction and in the behavior and response of heterojunction devices [1]. Accurate knowledge of the band discontinuities is thus necessary for the design and modeling of such device applications. Several theoretical approaches based on the physics point of view, as reviewed by Kroemer [2], are used to predict the lineup of the bands at the interface. These include the Harrison atomic orbital theory [3], the Frensley-Kroemer pseudopotential theory [4], the Anderson electron affinity rule [5], and the self-consistent interface potential theories [6]-[10]. It was found that none of these predictive rules meets the needs of the device physicist.

Recently, Unlu and Nussbaum [11] use the fact that the difference in electrostatic potentials for a system in equilibrium is equal to the difference in chemical potentials [12], and they obtained the band discontinuities ΔE_c and ΔE_v for nondegenerate systems as the difference in the effective potentials defined by including the macroscopic and microscopic forces across a heterojunction. The predicted results are in good agreement with experiments cited by Kroemer [1] and Wang and Stern [13] as serving as a test of the predicting theories. It is noted that Unlu and Nussbaum [11] use the formula for a doubly-intrinsic heterojunction to predict the nondegenerate systems. As shown below, however, the exact expressions for the nondegenerate systems are given by (29) and (30), neglecting the carrier degeneracy effect.

In this paper, we present a general analysis that stands on the electrochemical foundation of equilibria. The model includes the effects of the nonuniform band structure, the influence of Fermin-Dirac statistics, and the other potential energy, e.g., due to dipole forces, besides the electrochemical potential. These nonideal effects are expressed in terms of the activity coefficients of the carriers through the electrochemical potential equation and by proper choice of the reference potential. To simplify the analysis, the carrier densities are written in a simple Boltzmann-like form in which the effects associated with nonuniform band structures and carrier degeneracy are described by two quantities: the effective bandgap shrinkage and the effective asymmetry factor (as defined below). We then find a simple relation between the energy-band discontinuities and the activity coefficients of the carriers. Finally, the relation between the built-in potential and the energy-band discontinuities is also discussed.

II. Model Development

Fig. 1 shows the energy-band diagram of an arbitrarily doped semiconductor. The validity of this energy-band model has been discussed by Marshak and van Vliet [14]. From Fig. 1, we have

$$E_L(x) = E_0 + \psi(x) \tag{1}$$

$$E_c(x) = E_L(x) - \chi(x) = E_0 - \chi(x) + \psi(x) \tag{2}$$

and

$$E_v(x) = E_c(x) - E_G(x) \tag{3}$$

where E_0 is the field-free vacuum level, E_L is the local vacuum level, and χ is the electron affinity. ψ is the potential energy and is given by

$$\psi(x) = -qV(x) + \psi_{\text{other}}(x) \tag{4}$$

and

$$\psi_{\text{other}}(x) = \psi_h(x) + \psi_{xc}(x) + \psi_{im}(x) + \psi_b(x) \tag{5}$$

where $V(x)$ is the macroscopic continuous electrostatic potential, $\psi_h(x)$ is the effective potential energy associated with the (graded) heterojunction discontinuity, $\psi_{xc}(x)$ is the local exchange-correlation potential energy, $\psi_{im}(x)$

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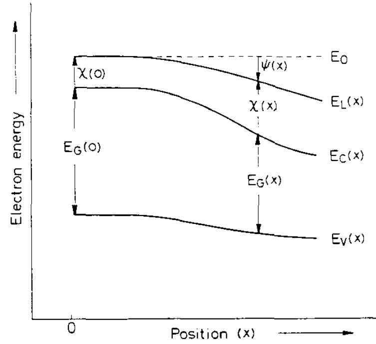

Fig. 1. Energy bands for inhomogeneous material.

is the classical dielectric image force, and $\psi_b(x)$ is the interface dipole bond energy. The first three terms on the right-hand side of (5) is discussed in more detail by Stern and Das Sarma [15], while the last term is included in the calculation of the band discontinuity by Unlu and Nussbaum [11].

If we consider Fermi-Dirac statistics and write a Shockley-like form for the equilibrium carrier densities as

$$n_0(x) = N_c(x) F_{1/2}[\eta_c(x)] = n_i(x) \zeta_c(x) \exp\left[\frac{E_F - E_I(x)}{kT}\right] \quad (6)$$

and

$$p_0(x) = N_v(x) F_{1/2}[\eta_v(x)] = n_i(x) \zeta_v(x) \exp\left[\frac{E_I(x) - E_F}{kT}\right] \quad (7)$$

where

$$n_i(x) = [N_v(x) N_c(x)]^{1/2} \exp\left[\frac{-E_G(x)}{2kT}\right] \quad (8)$$

is the position-dependent intrinsic carrier concentration

$$E_I(x) = E_0 - \chi(x) - \frac{1}{2} E_G(x) + \frac{kT}{2} \ln\left[\frac{N_v(x)}{N_c(x)}\right] + \psi(x) \quad (9)$$

and

$$\zeta_i(x) = F_{1/2}[\eta_i(x)]/\exp[\eta_i(x)], \qquad i = c, v \quad (10)$$

and $F_{1/2}$ is the Fermi-Dirac integral of order one-half with

$$\eta_c(x) = \frac{E_F - E_c(x)}{kT} \quad (11)$$

and

$$\eta_v(x) = \frac{E_v(x) - E_F}{kT}. \quad (12)$$

In thermal equilibrium, the carrier concentrations n_0 and p_0 are related to the electrostatic potential by (6), (7), and (9) as

$$n_0(x) = n_i(0) \exp\left[\frac{-\psi + A\Delta E_g}{kT}\right] \quad (13)$$

and

$$p_0(x) = n_i(0) \exp\left[\frac{\psi + (1 - A)\Delta E_g}{kT}\right] \quad (14)$$

where

$$\Delta E_g = -[E_G(x) - E_G(0)] + kT \ln\left[\frac{N_v(x) N_c(x)}{N_v(0) N_c(0)}\right] + kT \ln[\zeta_c(x) \zeta_v(x)] \quad (15)$$

and

$$A = \frac{[\chi(x) - \chi(0)] + kT \ln\left[\frac{N_c(x)}{N_c(0)}\right] + kT \ln[\zeta_c(x)]}{\Delta E_g}. \quad (16)$$

When deriving (13) and (14), we choose $x = 0$ as the reference position for the potential and $\psi(0) = kT \ln [(-D + \sqrt{D^2 + \zeta_c(0)\zeta_v(0)})/\zeta_v(0)]$ ($D \equiv [N_D^+(0) - N_A^-(0)]/2n_i(0)$, $N_D^+(0) - N_A^-(0) \equiv$ net doping density at $x = 0$), and apply the neutrality condition at $x = 0$. It is clear from Fig. 1 that both ΔE_g and A are positive quantities. ΔE_g is called the effective bandgap shrinkage, and A is called the asymmetry factor [16], which measures the fraction of the reduction in bandgap that occurs in the condition band, $0 \leq A \leq 1$.

To relate the band discontinuities to the activity coefficients of the carriers at the semiconductor heterojunctions, we consider a one-dimensional p-n junction with ohmic contacts at $x = 0$ on the p-side and $x = W$ on the n-side, and with the junction at x_j. The activity coefficient of the carriers is defined in a straightforward manner by the electrochemical potential equation [17]. The electrochemical potential ($\tilde{\mu}_i$), or Gibbs energy per charged particle, of a charged species i in phase α is defined as the sum of its chemical potential and its electric potential energy [17]

$$\tilde{\mu}_i^\alpha = \mu_i^\alpha + z_i q V^\alpha = \mu_i^{*,\alpha} + kT \ln(\gamma_i^\alpha c_i^\alpha) + z_i q V^\alpha \quad (17)$$

where μ_i^α is the chemical potential, $\mu_i^{*,\alpha}$ is the reference state chemical potential (and is a function only of temperature, pressure, and choice of reference state [18]), γ_i^α is the activity coefficient, c_i^α is the concentration ($c_i = n$ for electrons), and z_i ($z_i = 1$ for holes; $z_i = -1$ for electrons) is the elemental charge of species i. The potential V^α is the macroscopic continuous electrostatic poten-

tial, which is obtained through integration of Poisson's equation [15]. It is important to note that the chemical potential in (17) is a function of temperature, of pressure, of the composition and of the other potential energy besides electrostatic potential energy.

The results of a self-consistent analysis between Poisson's equation and the electrochemical potential equation give [19]

$$\mu_n^*(T) = E_I(0) - kT \ln [n_i(0)] - q\psi(0) \quad (18)$$

$$\mu_p^*(T) = -E_I(0) - kT \ln [n_i(0)] + q\psi(0) \quad (19)$$

$$\gamma_{n0} = \exp\left[\frac{-A\Delta E_g + \psi_{\text{other}}}{kT}\right] \quad (20)$$

and

$$\gamma_{p0} = \exp\left[\frac{-(1-A)\Delta E_g - \psi_{\text{other}}}{kT}\right] \quad (21)$$

where ΔE_g, A, and ψ_{other} are defined by (15), (16), and (5), respectively. From (5), (15), (16), and (20), we obtain

$$\Delta E_c(x_j) = kT \ln [\Gamma_{n0}(x_j)] + kT \ln \left[\frac{N_c(x_j^-)}{N_c(x_j^+)}\right] + kT \ln \left[\frac{\zeta_c(x_j^-)}{\zeta_c(x_j^+)}\right] - \Delta\psi_{\text{other}}(x_j) \quad (22)$$

where

$$\Delta E_c(x_j) \equiv \chi(x_j^+) - \chi(x_j^-) \equiv \Delta E_c(x_j^- \to x_j^+) \quad (23)$$

$$\Delta\psi_{\text{other}}(x_j) \equiv \psi_{\text{other}}(x_j^-) - \psi_{\text{other}}(x_j^+) \quad (24)$$

and

$$\Gamma_{n0}(x_j) \equiv \frac{\gamma_{n0}(x_j^-)}{\gamma_{n0}(x_j^+)} \quad (25)$$

represents the relative nonideal behavior of electrons at the junction interface. In a similar way, the valence band discontinuity is obtained from (5), (15), (16), and (21) as

$$\Delta E_v(x_j) = kT \ln [\Gamma_{p0}(x_j)] + kT \ln \left[\frac{N_v(x_j^-)}{N_v(x_j^+)}\right] + kT \ln \left[\frac{\zeta_v(x_j^-)}{\zeta_v(x_j^+)}\right] + \Delta\psi_{\text{other}}(x_j) \quad (26)$$

where

$$\Delta E_v(x_j) \equiv E_v(x_j^-) - E_v(x_j^+) \quad (27)$$

and

$$\Gamma_{p0}(x_j) \equiv \frac{\gamma_{p0}(x_j^-)}{\gamma_{p0}(x_j^+)} \quad (28)$$

represents the relative nonideal behavior of holes at the junction interface. Equations (22) and (26) give the general relation between the band discontinuities and the activity coefficients of the carriers at the junction interface. To obtain agreement with experiment, (22) and (26) will be used with the definition $\Delta E_c + \Delta E_v = \Delta E_G$ for "straddling" lineups [2] and $\Delta E_c - \Delta E_v = \Delta E_G$ for "staggered" or "broken-gap" lineups [2].

It is noted that the band discontinuities $\Delta E_c(x_j)$ and $\Delta E_v(x_j)$ can be related to the carrier densities by (13), (14), (20), (21), (22), and (26) as

$$\Delta E_c(x_j) = kT \ln \left[\frac{n_0(x_j^+)}{n_0(x_j^-)}\right] + kT \ln \left[\frac{N_c(x_j^-)}{N_c(x_j^+)}\right] + kT \ln \left[\frac{\zeta_c(x_j^-)}{\zeta_c(x_j^+)}\right] - \Delta\psi_{\text{other}}(x_j) \quad (29)$$

and

$$\Delta E_v(x_j) = kT \ln \left[\frac{p_0(x_j^+)}{p_0(x_j^-)}\right] + kT \ln \left[\frac{N_v(x_j^-)}{N_v(x_j^+)}\right] + kT \ln \left[\frac{\zeta_v(x_j^-)}{\zeta_v(x_j^+)}\right] + \Delta\psi_{\text{other}}(x_j). \quad (30)$$

Here, we use the fact that $V(x_j^-) = V(x_j^+)$. Clearly, $\Delta E_c(x_j)$ and $\Delta E_v(x_j)$ are doping dependent for the degenerate case.

III. Summary and Discussion

Based on the irreversible thermodynamic point of view, the relationship between the band discontinuities the activity coefficients of the carriers at a semiconductor heterojunction is discussed. A simple but general formulation of the results, which include the effects of energy-bandgap narrowing, carrier degeneracy, the effective density of states, dielectric image forces, quantum-mechanical exchange-correlation forces, and dipole forces across the interface, was presented. The results imply that the thermodynamic parameters are important to the physics that determines band discontinuities. The approach presented here also allows convenient treatment of heterojunction devices in a manner that is both thermodynamically consistent and consistent with the energy-band parameters.

We note that, for a doubly-intrinsic heterojunction, (29) and (30) are reduced to

$$\Delta E_c(x_j) = kT \ln \left[\frac{n_i(x_j^+)}{n_i(x_j^-)}\right] + kT \ln \left[\frac{N_c(x_j^-)}{N_c(x_j^+)}\right] - \Delta\psi_{\text{other}}(x_j) \quad (31)$$

and

$$\Delta E_v(x_j) = kT \ln\left[\frac{n_i(x_j^+)}{n_i(x_j^-)}\right] + kT \ln\left[\frac{N_v(x_j^-)}{N_v(x_j^+)}\right] + \Delta\psi_{\text{other}}(x_j). \quad (32)$$

Furthermore, using (8) for the intrinsic concentration, (31) and (32) become

$$\Delta E_c(x_j) = \frac{1}{2}\left[E_G(x_j^-) - E_G(x_j^+)\right] + \frac{kT}{2}\ln\left[\frac{N_c(x_j^-)\,N_v(x_j^+)}{N_c(x_j^+)\,N_v(x_j^-)}\right] - \Delta\psi_{\text{other}}(x_j) \quad (33)$$

and

$$\Delta E_v(x_j) = \frac{1}{2}\left[E_G(x_j^-) - E_G(x_j^+)\right] + \frac{kT}{2}\ln\left[\frac{N_c(x_j^+)\,N_v(x_j^-)}{N_c(x_j^-)\,N_v(x_j^+)}\right] + \Delta\psi_{\text{other}}(x_j). \quad (34)$$

Equations (31), (33), and (34) give the same results as those given by Unlu and Nussbaum [11], but with a different treatment, as discussed here. The model has been used to predict the heterojunction band discontinuities found in good agreement with the experiment for many systems [11].

It is of interest to note that the built-in potential is readily derived from (13). After some algebraic manipulation, the result is given by

$$qV_{bi} = \psi(0) - \psi(W) = \Delta E_c'(x_j^+ \to x_j^-) + kT\ln\left[\frac{n_0(W)}{n_0(0)}\right] + kT\ln\left[\frac{N_c(0)}{N_c(W)}\right] + kT\ln\left[\frac{\zeta_c(0)}{\zeta_c(W)}\right] \quad (35)$$

where

$$\Delta E_c'(x_j^+ \to x_j^-) = -\Delta E_c(x_j^- \to x_j^+).$$

For the nondegenerate case, (35) reduces to

$$qV_{bi} = \Delta E_c'(x_j^+ \to x_j^-) + kT\ln\left[\frac{n_0(W)/N_c(W)}{n_0(0)/N_c(0)}\right]. \quad (36)$$

Equation (36) has been used to calculate the conduction band discontinuity from the built-in potential for a GaAs/AlGaAs HJ [20], [21] and gives a reasonably good agreement with the value predicted from Dingle's rule [22]. Note that (35) should be used for degenerate carrier statistics. For the nondegenerate case, comparing (29) with (36) gives

$$qV_{bi} = kT\ln\left[\frac{n_0(W)}{n_0(0)}\right] + kT\ln\left[\frac{n_0(x_j^-)}{n_0(x_j^+)}\right] + \Delta\psi_{\text{other}}(x_j). \quad (37)$$

The last two terms in (37) are the corrected quantities that deviate from homojunctions.

Finally, it should be pointed out that all results presented here are quite general and can be used for n-N and p-P heterojunctions. The results can also be readily extended to a self-consistent solution with Schrodinger's equation.

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