THEORETICAL GAS ADSORPTION ISOTHERMS ON SEMICONDUCTOR SURFACES BASED ON CHARGE TRANSFER MECHANISMS

V. J. Lee

ABSTRACT

Theoretical gas adsorption isotherms of neutral and charged particles on semiconductor surfaces have been formulated, based on a generalized model. It is assumed in this model that the temperature is moderately high so that the particles can be ionized with or without dissociation. The combined thermal and electrostatic effects will make the adsorbed particles mobile on the semiconductor surfaces.

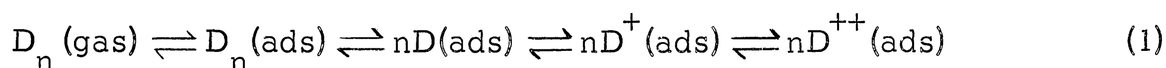
THEORETICAL GAS ADSORPTION ISOTHERMS ON SEMICONDUCTOR SURFACES BASED ON CHARGE TRANSFER MECHANISMS

V. J. Lee

MODEL

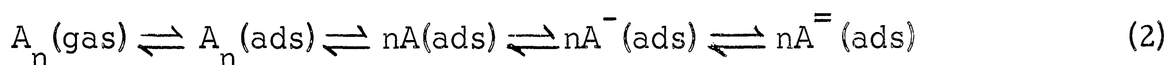
It is postulated in this model that the gas phase is in equilibrium with several adsorbed phases on the surface of a semiconductor. The various adsorbed phases can include the molecular state, the atomic state, the singly charged ionic state, and the doubly charged state. The relative number of particles in each phase is a function of temperature and the properties of the semiconductor.

This model is represented by the following generalized equilibrium equations. For a donor gas,



$$D_n(\text{gas}) \rightleftharpoons D_n(\text{ads}) \rightleftharpoons nD(\text{ads}) \rightleftharpoons nD^{+}(\text{ads}) \rightleftharpoons nD^{++}(\text{ads}) \quad (1)$$

For an acceptor gas,



$$A_n(\text{gas}) \rightleftharpoons A_n(\text{ads}) \rightleftharpoons nA(\text{ads}) \rightleftharpoons nA^{-}(\text{ads}) \rightleftharpoons nA^{=}(\text{ads}) \quad (2)$$

It is further assumed that the system is such that there is at least one phase in the charged ionic state. As a result of the ionic state or states a static space charge region is created beneath the surface of the semiconductor. The static charge in the semiconductor surface distributes itself so that potential peaks or valleys are neutralized, and a substantially equipotential surface is created. Therefore, in the absence of potential wells on the surface which can trap individual ions, it is further postulated that the particles in the adsorbed state are mobile and can be treated approximately as a perfect two-dimensional gas. This also means that these adsorbed species are not covalently bonded to the surface. This assumption is not a gross restriction, however, since covalent bonds would not create an appreciable space charge region beneath the semiconductor surface.

These assumptions mean first that the variations in the surface potential are actually less than kT, so that the kinetic energy of the

species on the surface is large enough to surmount the variation in the surface potential. In addition it means that the ionization energy required to transfer charge between the surface atom and the semiconductor is not excessive with respect to kT.

The periodic potential along the surface is commonly called the van der Waals' potential and is represented by Hill[1] by the relationship

$$V(x,y) = Voo + \frac{Vo}{2}\left(1-\cos\frac{2\pi x}{a}\right) + \frac{Vo}{2}\left(1-\cos\frac{2\pi y}{a}\right) \quad (3)$$

where V_o is the depth of the potential wells on the surface. When there are no static charges V_o is the order of 0.3 to 1.0 K cal per mole (1). No attempt will be made to verify this postulate theoretically. It will be considered true, if the results derived from this postulate agree with the result of experiments.

BASIC THERMODYNAMIC RELATIONS

Let

$\mu_j = \left(\frac{\delta U}{\delta N_j}\right)_{S,V}$ = the partial chemical potential of the jth phase, in energy units/unit particle

Ψ_j = the generalized partial external field potential at the jth phase, such as gravitational potential, van der Waals' potential, or electrostatic potential, in energy units/unit particle

U = internal energy

F = free energy = U-TS

T = absolute temperature, in K^o

S = entropy

W = work

N_j = number of particles in phase j

N = total number of particles

When there is an external potential, Ψ_s, the first law of thermodynamics takes the following form:

$$dU + Nd\Psi = dQ - dW \quad (4)$$

From the second law of thermodynamics,

$$TdS \geqslant dQ \tag{5}$$

therefore,

$$TdS - (dU + Nd\Psi + dW) \geqslant 0 \tag{6}$$

Under isothermal equilibrium conditions, and when there is no work performed either on or by the system, equation (6) becomes,

$$d(TS - U - \Psi) = 0 \tag{7}$$

or,

$$dF + d\Psi = 0 \tag{8}$$

Let us consider that there are two phases, j and k, a species, i, which exists in both phases j and k, and transfers from the j-phase into the k-phase, but the total number of particles of species i remains constant. The following relationships then exist

$$d(N_i)_j + d(N_i)_k = 0 \tag{9}$$

$$dF_i = \mu_{ij} dN_i - \mu_{ik} dN_i \tag{10}$$

$$d\Psi_i = (\Psi_{ij} - \Psi_{ik})\, dN_i \tag{11}$$

Combining equations (8), (10), and (11), one obtains,

$$(\mu_{ij} + \Psi_{ij}) = (\mu_{ik} + \Psi_{ik}) \tag{12}$$

Having established equation (12), the author will outline a procedure to evaluate the number of particles per unit volume or area in each phase under equilibrium conditions.

Since in this model, the phases exchange particles among themselves Gibbs' distribution for a variable number of particles should be used. This distribution will lead to Fermi-Dirac as well as Bose-Einstein statistics as has been shown by Landau-Lifshitz.[2] Under the condition that

$$\exp(\mu - \epsilon_r)/kT \ll 1, \tag{13}$$

both Fermi-Dirac and Bose-Einstein distributions reduce to the Boltzman distribution. Fowler and Guggenheim[3] have discussed this problem in detail and have given it the name, Classical Distribution.

In any phase the mean number of particles at an energy level ϵ_r is given by the relationship

$$n_r = 1/\left\{\left[\exp(\epsilon_{rj} - \mu_{rj})/kT\right] \pm 1\right\} \cong \exp(\mu_{rj} - \epsilon_{rj})/kT \quad (14)$$

Total number of particles in the j phase is given by,

$$N_j = \exp(\mu_j/kT) \sum_r \exp(-\epsilon_{rj}/kT) \quad (15)$$

$$= (\lambda f)_j$$

where

$\lambda_j = \exp(\mu_j/kT) =$ the absolute activity as defined by Fowler and Guggenheim.

$f_j = \sum_r \exp(-\epsilon_{rj}/kT) =$ partition function of the particles in phase j.

FORMULATION OF ADSORPTION ISOTHERMS

For convenience, the phases in equations (1) and (2) are labelled as follows:

$j = 1$, = gas phase

$j = 2$, = D_n (Ads), or A_n (Ads) phases

$j = 3$, = nD (Ads) or nA (Ads) phases

$j = 4$, = nD^+ (Ads) or nA^- (Ads) phases

$j = 5$, = nD^{++} (Ads) or $nA^=$ (Ads) phases

I. Equilibrium Relationship Between Phase 1 and Phase 2.

From equation (12), for component i one obtains

$$\mu_1 + \Psi_1 = \mu_2 + \Psi_2 \quad (12a)$$

That is

$$\exp\frac{\mu_1 + \Psi_1}{kT} = \exp\frac{\mu_2 + \Psi_2}{kT}$$

From equation (15) it follows that

$$\lambda_2 = \lambda_1 \exp\left\{(\Psi_1 - \Psi_2)/kT\right\}$$

Let

$W = \Psi_1 - \Psi_2 =$ the van der Waals' energy difference between the lowest free state and the lowest adsorbed state without

dissociation. (It is noted that if, in the range considered, the van der Waals' force is an attractive force, W will be positive and heat will be evolved upon adsorption.)

Therefore

$$\lambda_2 = \lambda_1 \exp \left\{ W/kT \right\} \tag{16}$$

From equation (15) by definition

$$\lambda_j = \frac{N_j}{f_j}$$

$$N_2 = N_1 \left(\frac{f_2}{f_1} \right) \exp \left\{ W/kT \right\} \tag{17}$$

The partition function of three dimensional and two dimensional gas are given in any standard textbook of statistical physics. For the partition function of particles in a volume

$$f_j = \left(\frac{2 \pi n M_o kT}{h^2} \right)^{3/2} I_j V \tag{18}$$

Correspondingly, the partition function for particles on a surface is

$$f_j = \left(\frac{2 \pi n M_o kT}{h^2} \right) I_j S \tag{19}$$

where

M = atomic weight of D, or A

I_j = partition function of internal degree of freedom in the particle

n = number of atoms per molecule

V = total gas volume in the system, cm^3

S = total adsorbing semiconductor area in the system, cm^2

To simplify the writing let

$$\beta = \left(\frac{2 \pi M kT}{h^2} \right) (\text{in } cm^{-2}) \tag{20}$$

Then

$$f_1 = (n\beta)^{3/2} I_1 V \tag{18a}$$

$$f_2 = (n\beta) I_2 S \tag{19a}$$

Combining equations (17), (18a) and (19a) one obtains

$$\frac{N_2}{S} = \frac{N_1}{V}\left(\frac{I_2}{I_1}\right)\left(\frac{1}{n\beta}\right)^{1/2} \exp\left\{W/kT\right\} \tag{21}$$

For ideal gas approximation

$$PV = N_1 kT$$

$$\left(\frac{N_1}{V}\right) = \left(\frac{P}{kT}\right) \tag{22}$$

For the sake of avoiding confusion in units it is defined that P is in dynes/cm^2, kT in erg, and volume in cm^3. Then (P/kT) is in $[\mathrm{cm}^{-3}]$. Combining equations (21) and (22), and writing $[D_n]$, or $[A_n]$ for $\frac{N_2}{S}$, one has,

$$[D_n] = \left(\frac{P}{kT}\right)\left(\frac{I_2}{I_1}\right)\left(\frac{1}{n\beta}\right)^{1/2} \exp\ (W/kT) \tag{23a}$$

$$[A_n] = \left(\frac{P}{kT}\right)\left(\frac{I_2}{I_1}\right)\left(\frac{1}{n\beta}\right)^{1/2} \exp\ (W/kT) \tag{23b}$$

II. Equilibrium Relationships Between Phase 1 and Phase 3.

In entering phase 3, the molecule D_n or A_n dissociates into n atoms, and the total energy of the particles in phase 1 and phase 2 now is comprised of a chemical energy associated with each particle, μ_3, a generalized external field energy per atom, Ψ_3, and an energy of dissociation per atom, Δ. This can be expressed as

$$\mu_1 + \Psi_1 = \mu_2 + \Psi_2 = n\mu_3 + n\Psi_3 + n\Delta \tag{12b}$$

where

Δ = dissociation energy per atom which is also a form of potential energy.

Following the procedure as in Section I, define

$$nW' \equiv \Psi_1 - n\Psi_3 \tag{24}$$

Now substitution of equation (24) into equations (12b) and (15) gives the relationship

$$\lambda_3 = \lambda_1 \frac{1}{n} \exp\left\{\frac{W' - \Delta}{kT}\right\} \tag{16a}$$

Substitution for the λ's gives

$$\frac{N_3}{f_3} = \left(\frac{N_1}{f_1}\right)^{\frac{1}{n}} \exp\left\{\frac{W' - \Delta}{kT}\right\} \tag{25}$$

Now, defining the partition functions for the atoms on the surface in phase 3

$$f_3 = \left(\frac{2\pi MkT}{h^2}\right) I_3 \ S = \beta I_3 S \tag{19b}$$

Substitution of equations (19b), (22) and (18a) into equation (25) gives

$$\frac{N_3}{S'} = \left[\frac{(\beta I_3)^{\frac{2n}{3}}}{n\beta I_1^{2/3}}\right]^{\frac{3}{2n}} \left(\frac{P}{kT}\right)^{\frac{1}{n}} \exp\left\{\frac{W' - \Delta}{kT}\right\} \tag{26}$$

But since N_3/S is the surface concentration of atoms in phase 3, then for donor atoms, equation (26) can be written as

$$[D] = \frac{\beta I_3}{\sqrt[n]{(n\beta)^{3/2}} \ I_1} \exp\left\{\frac{W' - \Delta}{kT}\right\}\left(\frac{P_{D_n}}{kT}\right)^{1/n} \tag{27a}$$

For acceptor atoms on the surface in phase 3 the result is

$$[A] = \frac{\beta I_3}{\sqrt[n]{(n\beta)^{3/2}} \ I_1} \exp\left\{\frac{W' - \Delta}{kT}\right\}\left(\frac{P_{A_n}}{kT}\right)^{1/n} \tag{27b}$$

Equations (27a) and (27b) relate the concentration of dissociated atoms on the surface coming from an n-atom molecule, to the dissociation energy, the partial pressure of the molecular gas, and other factors as indicated.

III. Equilibrium Relationship of Phases 3, 4 and 5.

With neutral atoms adsorbed on the semiconductor surface, the possibility exists for electronic interactions between the adsorbed atoms and the semiconductor. Furthermore, for the sake of completeness in the development and in order to make comparisons with actual situations, it is assumed that there are singly charged ions as well as doubly charged ions on the surface. The total charge on the surface is given below.

For donors, the surface charge density is related to the ion concentrations by the relationship

$$\sigma_{\square}^{+} = \left\{ [D^{+}] + 2\,[D^{++}] \right\} \tag{28}$$

For acceptors, the relationship is

$$\sigma_{\square}^{-} = \left\{ [A^{-}] + 2\,[A^{=}] \right\} \tag{29}$$

For a donor gas, it is assumed that the neutral adsorbed donor atom such as a hydrogen atom has an uncompensated electron spin. Therefore in going from phase 3 to phase 4 the following reactions can occur:

$$\begin{aligned} D\,(\uparrow) &\rightleftharpoons D^{+} + e^{-} \\ D\,(\downarrow) &\rightleftharpoons D^{+} + e^{-} \end{aligned} \tag{30}$$

Since the electrons initially are in a surface state with energy level E_D, then from the distribution function it follows that

$$[D\,] = 2\,[D^{+}] \exp \left\{ (E_F - E_D)/kT \right\} \tag{31}$$

For the transition from phase 4 to phase 5, with the removal of another electron from the donor atom, the following reaction can occur.

$$D^{+} \rightleftharpoons D^{++}(\uparrow) + e^{-} \tag{32a}$$

$$D^{+} \rightleftharpoons D^{++}(\downarrow) + e^{-} \tag{32b}$$

Obviously, these reactions cannot occur when hydrogen is the donor

atom, but this case is included for completeness of the development of the theory.

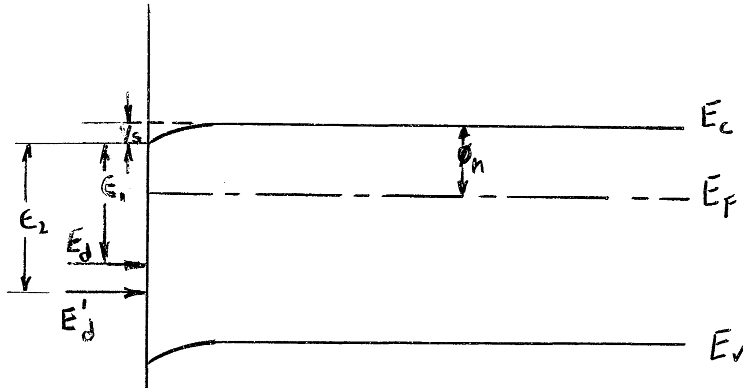
Therefore, from the distribution function, the relationship between the singly ionized donor concentration and the doubly ionized donor concentration can be obtained.

$$[D^{+}] = \frac{1}{2}[D^{++}] \exp\left\{(E_F - Ed') / kT\right\} \quad (33)$$

where

Ed is the donor level of the first electron Ed', that of the second electron.

The factor of 1/2 arises because of the assumption that the electrons leaving the donor atom now combine with the original electrons and form a compensated pair.



Using the bottom of the conduction band as reference,

$$E_F = E_c - \phi_n$$

$$Ed = E_c - Y_s - \epsilon_{d_1}$$

$$Ed^1 = E_c - Y_s - \epsilon_{d_2}$$

Therefore ,

$$E_F - Ed = Y_s + \epsilon_{d_1} - \phi_n \quad (34)$$

$$E_F - Ed^1 = Y_s + \epsilon_{d_2} - \phi_n \quad (35)$$

Substitute (34) into (31),

$$[D] = 2\,[D^{+}]\ \exp\left\{Y_s/kT\right\}\ \exp\left(\frac{E_{d_1} - \phi_n}{kT}\right) \tag{36}$$

Substitute (35) into (33)

$$[D^{+}] = \frac{1}{2}\,[D^{++}]\ \exp\left\{\frac{Ys}{kT}\right\}\ \exp\left\{\frac{E_{d_2} - \phi_n}{kT}\right\} \tag{37}$$

For the acceptor gas, it is assumed that the A atom has all electron spins compensated. When these atoms ionize, then ions with uncomplicated spins can be formed.

$$A \rightleftarrows A^{-}(\uparrow) + e^{+}$$
$$A \rightleftarrows A^{-}(\downarrow) + e^{+} \tag{38}$$

where e^{+} is a hole in the semiconductor surface. Therefore from the distribution function it follows that

$$[A] = \frac{1}{2}\,[A^{-}]\ \exp\left\{(E_F - E_A)/kT\right\} \tag{39}$$

where A^{-} is the total singly charged acceptor ion concentration. For the second ionization of the acceptor atom, the reactions are

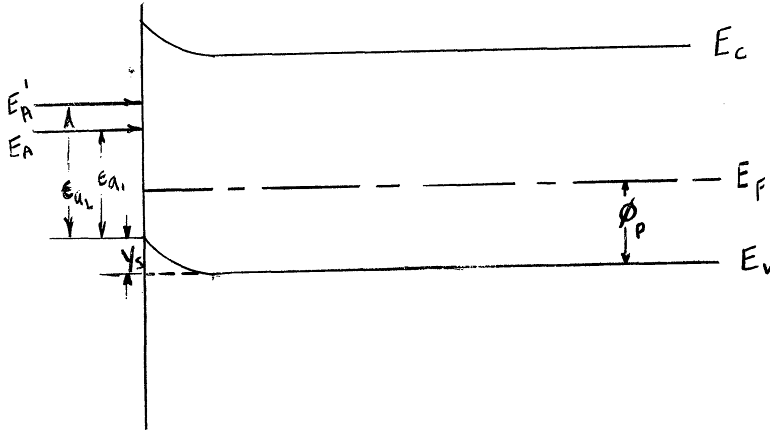
$$A^{-}(\uparrow) \rightleftarrows A^{=} + e^{+} \tag{40a}$$

$$A^{-}(\downarrow) \rightleftarrows A^{=} + e^{+} \tag{40b}$$

The total singly ionized acceptor ion concentration then is related to the doubly ionized acceptor concentration through the distribution function by the relationship

$$[A^{-}] = 2\,[A^{=}]\ \exp\left\{(E_F - E'_A)/kT\right\} \tag{41}$$

where E_A and E'_A are the acceptor levels associated with the ions on the surface.



This case can be looked upon as the transferring of a hole from the acceptor gas atom or ion to the valence band. Choosing the top of the valence band as the energy reference (which is arbitrary since ultimately only energy differences enter into the final equations) the following definition can be made.

$$E_F = E_v - \phi_p$$

$$E_A = E_v - Y_s - \epsilon_{a_1}$$

$$E_A' = E_v - Y_s - \epsilon_{a_2}$$

Therefore

$$E_F - E_A = Y_s + \epsilon_{a_1} - \phi_p \qquad (42)$$

$$E_F - E_A' = Y_s + \epsilon_{a_2} - \phi_p \qquad (43)$$

Substitution of equations (42) and (43) into equations (39) and (41), respectively, gives

$$[A] = \frac{1}{2} [A^-] \exp\left\{\frac{Y_s}{kT}\right\} \exp\left\{(\epsilon_{a_1} - \phi_p)/kT\right\} \qquad (44)$$

$$[A^-] = 2 [A^=] \exp\left\{\frac{Y_s}{kT}\right\} \exp\left\{(\epsilon_{a_2} - \phi_p)/kT\right\} \qquad (45)$$

Having formulated equations (36), (37), (44), (45), one is ready to find the equilibrium relationships between phase 3, phase 4

and phase 5. These relationships will be established by using the relationships between Y_s and σ_0 which were previously derived. These relationships can be regrouped into classes. The first class of cases is associated with accumulation layers on intrinsic or doped semiconductors, and with highly inverted surface layers on nearly intrinsic semiconductors. The second class of cases is associated with depletion region or slightly inversion space charge region.

The Class I cases are discussed first and the adsorption isotherms are derived completely before the Class II cases are considered.

A. Class I Cases: Accumulation Space Charge Regions.

In the next section the relationships between the surface potential and the surface ion concentration which have been previously derived are summarized.

A. Accumulation Layers Produced by Surface Donors.

Case 1. Surface Donors on an Intrinsic Semiconductor.

$$\frac{Y_s}{kT} = \ln \left\{ \frac{L_m}{n_i} \left[\sigma_0^{+} \right]^2 \right\} \tag{46}$$

Case 3. Surface Donors on an n-type Semiconductor.

$$\frac{Y_s}{kT} = \ln \left\{ \frac{L_m}{n_B} \left[\sigma_0^{+} \right]^2 \right\} \tag{47}$$

Highly Inverted Layer Produced by Surface Donors.

Case 9. Surface Donors on a Nearly Intrinsic p-type Semiconductor.

$$\frac{Y_s}{kT} = \ln \left\{ \frac{L_m}{n_B} \left[\sigma_0^{+} \right]^2 \right\} \tag{48}$$

B. Accumulation Layers Produced by Surface Acceptors.

Case 2. Surface Acceptors on an Intrinsic Semiconductor.

$$\frac{Y_s}{kT} = \ln \left\{ \frac{L_m}{p_i} \left[\sigma_0^{-} \right]^2 \right\} \tag{49}$$

Case 4. Surface Acceptors on a p-type Semiconductor.

$$\frac{Y_s}{kT} = \ln \left\{ \frac{L_m}{p_B} \left[\sigma_\square^- \right]^2 \right\} \tag{50}$$

Highly Inverted Layer Produced by Surface Acceptors.

Case 10. Surface Acceptors on a Nearly Intrinsic n-type Semiconductor.

$$\frac{Y_s}{kT} = \ln \left\{ \frac{L_m}{p_B} \left[\sigma_\square^- \right]^2 \right\} \tag{51}$$

The mathematical expressions for these cases are similar. After a more complete development of these cases the remaining four cases will be considered in a later section.

A. Accumulation Layers Produced by Surface Donors.

Case 1. For Donors on an Intrinsic Semiconductor.

Substitution of equation (46) into equation (36) gives,

$$[D] = 2 \frac{L_m}{n_i} \exp \left(\frac{\epsilon d_1^- \phi_n}{kT} \right) \left\{ [D^+] \, [D^+ + 2D^{++}]^2 \right\}$$

where

$$\sigma_\square^+ = [D^+ + 2D^{++}]$$

Furthermore, since

$$n_i = p_i = 2 \left(\frac{2\pi kT}{h^2} \right)^{3/2} (m_n m_p)^{3/4} \exp \left\{ -\frac{\phi_i}{kT} \right\}$$

$$= (N_c N_v)^{1/2} \exp \left\{ -\frac{\phi_i}{kT} \right\}$$

Therefore

$$[D] = 2 \frac{L_m}{(N_c N_v)^{1/2}} \exp \left\{ \frac{\epsilon_{d_1}}{kT} \right\} \left\{ [D^+] \, [D^+ + 2D^{++}]^2 \right\} \tag{52}$$

where

$$\phi_i = \phi_n$$

Substitution of equation (46) into equation (37) gives

$$[D^+] = \frac{1}{2} \frac{L_m}{n_i} \exp\left\{\frac{\epsilon d_2 - \phi_n}{kT}\right\} \left\{[D^{++}] \; [D^+ + 2D^{++}]^2\right\}$$

$$= \frac{1}{2} \frac{L_m}{(N_c N_v)^{1/2}} \exp\left[\frac{\epsilon d_2}{kT}\right] \left\{[D^{++}] \; [D^+ + 2D^{++}]^2\right\} \quad (53)$$

For simplicity, let

$$C_1 = \frac{L_m}{N_c N_v} \exp\left\{\epsilon d_1 / kT\right\} \quad (54)$$

$$C_2 = \frac{L_m}{N_c N_v} \exp\left\{\epsilon d_2 / kT\right\} \quad (55)$$

Then

$$[D] = 2C_1 [D^+] \; [D^+ + 2D^{++}]^2 \quad (52a)$$

$$[D^+] = \frac{1}{2} C_2 [D^{++}] \; [D^+ + 2D^{++}]^2 \quad (53a)$$

Equation (53a) can be rearranged into

$$[D^+] = \frac{\left\{1 - 2c_2 [D^{++}]^2\right\} \pm \left\{1 - 4c_2 [D^{++}]^2\right\}^{1/2}}{c_2 [D^{++}]} \quad (54)$$

One must choose the negative sign before $\pm \left\{1 - 4C_2 [D^{++}]^2\right\}^{1/2}$, so that when $[D^+] \rightarrow 0$, then $[D^{++}] \rightarrow 0$ also.

Since $[D^+]$ must be real and positive number, one also must have

$$1 - 4C_2 [D^{++}]^2 \geq 0$$

In order to obtain a minimum value for the singly ionized donor concentration consider that the radical in equation (54) is zero. That is

$$1 - 4C_2 [D^{++}]^2 = 0$$

Under these circumstances, then

$$[D^{++}]_{max} = \frac{1}{2} C_2^{-1/2} \quad (55)$$

Substitution of this result into equation (54) gives

$$[D^+]_{min} = C_2^{-1/2} \tag{56}$$

A relationship between $[D^{++}]_{max}$ and $[D^+]_{min}$ then follows directly.

$$[D^{++}]_{max} = \frac{1}{2} [D^+]_{min} \tag{57}$$

Now consider the situation wherein the radical in equation (54) is positive and $[D^+]$ is below its maximum value. Therefore

$$1 - 4 C_2 [D^{++}]^2 > 0$$

Under this condition it follows that

$$0 \leq 4 C_2 [D^{++}]^2 < 1$$

One can expand the expression, $\left\{1 - 4 C_2 [D^{++}]^2\right\}^{1/2}$ into an infinite power series for the situation wherein $0 < z < 1$. This series is

$$(1 - z)^{1/2} = 1 - \frac{1}{2} z - \frac{1}{8} z^2 - \frac{1}{16} z^3 - - - -$$

$$= 1 - \frac{1}{2} z - \sum_{m=2}^{\infty} \frac{(2m - 3)!}{m!(m-2)!\,4^{m-1}} z^m$$

Therefore, applied to this situation, the result is

$$\left\{1 - 4 C_2 [D^{++}]^2\right\}^{1/2} = 1 - 2C_2 [D^{++}]^2 - \sum_{m=2}^{\infty} \frac{(2m - 3)!\,4}{m!\,(m-2)!} \left\{C_2 [D^{++}]^2\right\}^m \tag{58}$$

Substitution of equation (58) into equation (54) with the negative sign as indicated gives the result

$$[D^+] = 4 C_2 [D^{++}]^3 \sum_{m=2}^{\infty} \frac{(2m - 3)!}{m!\,(m-2)!} \left\{C_2 [D^{++}]^2\right\}^{m-2} \tag{59}$$

There are two more points that are needed to ponder.

(i) If $[D^{++}] = \gamma [D^+]$,

is it generally true that

$$0 \leqq \gamma \leqq 1/2$$

(ii) If $0 \leqq \gamma < 1/2$ how fast does the series defined in equation (59) converge? Is it converging more rapidly as γ decreases?

To investigate these questions one substitutes the definition

$$[D^{++}] = \gamma\, [D^{+}]$$

into equation (54), and one obtains

$$C_2\, [D^{++}]^2 = \frac{2\gamma}{(1 + 2\gamma)^2} \tag{60}$$

Substitute equation (60) into equation (58)

$$\frac{1 - 2\gamma}{1 + 2\gamma} = 1 - 2\, C_2\, [D^{++}]^2 - \sum_{m=2}^{\infty} \frac{(2m-3)!\, 4}{m!\, (m-2)!} \left[C_2 {D^{++}}^2\right]^m \tag{61}$$

Since, when $4\, C_2\, [D^{++}]^2 < 1$, the right-hand side of equation (61) is greater than zero. Therefore

$$\frac{1 - 2\gamma}{1 + 2\gamma} > 0$$

That is, $\gamma < 1/2$. When this result is combined with equation (57) and the fact that γ cannot be negative is observed, then we have the conclusion that

$$0 \leqq \gamma \leq 1/2 \tag{62}$$

As to question (ii), an examination of equation (60), will show that as γ decreases, the series defined by equation (59) converges more rapidly.

For adsorption isotherms, we can substitute equation (53a) into equation (52a) to give

$$[D^{o}] = C_1 C_2\, [D^{++}] \left\{ [D^{+}] + 2\, [D^{++}] \right\}^4 \tag{53b}$$

Furthermore, using the definition for γ and its restriction imposed by equation (62), equation (52a) becomes

Therefore

$$[D] = 2\,C_1\,(1 + 2\gamma)\;[D^+]^3 \tag{63}$$

Similarly, equation (53b) becomes

$$[D] = C_1 C_2\,(2 + \frac{1}{\gamma})^4\;[D^{++}]^5 \tag{64}$$

These equations can also be written in terms of the charged species as

$$[D^+] = \left(\frac{1}{2C_1}\right)^{1/3}\left(\frac{}{1+2\gamma}\right)^{2/3}\;[D]^{1/3} \tag{63a}$$

and

$$[D^{++}] = \left(\frac{1}{C_1 C_2}\right)\frac{1}{5}\left(\frac{\gamma}{1+2\gamma}\right)^{4/5}\;[D]^{1/5} \tag{64a}$$

Note that when $\gamma = 0$, so that there is only $[D^+]$, one has the relation (63a) only.

Case 3. Surface Donors on an n-type Semiconductor.

Substitution of equation (47) into equation (36) gives

$$[D] = 2\,\frac{L_m}{n_B}\,\exp\left\{\frac{Ed_1 - \phi_n}{kT}\right\}\left\{[D^+]\;[D^+ + 2_{D}^{++}]^2\right\}$$

where

$$\sigma_{\square}^{+} = [D^+ + 2\,D^{++}]$$

Furthermore, since

$$n_B = N_c\,\exp\left\{-\phi_n/kT\right\}$$

then

$$[D] = 2\,\frac{L_m}{N_c}\;\exp\left\{\frac{\epsilon d_1}{kT}\right\}\left\{[D^+]\;[D^+ + 2\,D^{++}]^2\right\} \tag{65}$$

Substitute equation (47) into equation (37)

$$[D^+] = \frac{1}{2}\,\frac{L_m}{N_c}\;\exp\left\{\frac{\epsilon d_2}{kT}\right\}\left\{[D^+]\;[D^+ + 2\,D^{++}]^2\right\} \tag{66}$$

Now define

$$C_1' = \frac{L_m}{N_c}\;\exp\left\{\frac{\epsilon d_1}{kT}\right\} \tag{67}$$

$$C_2' = \frac{L_m}{N_c} \exp\left\{\frac{\epsilon_{d_2}}{kT}\right\} \tag{68}$$

Then

$$[D] = 2\,C_1' \,[D^+]\,[D^+ + 2\,D^{++}]^2 \tag{65a}$$

$$[D^+] = \frac{1}{2} C_2' \,[D^+]\,[D^+ + 2\,D^{++}]^2 \tag{66a}$$

By comparing equations (65a) and (66a) with equations (52a), (53a), one sees that they differ only in constants C_1', C_2' and C_1, C_2. Therefore the remainder of the derivations and results should be the same.

Therefore, equations similar to equations (63a) and (64a) are obtained. These new equations are

$$[D^+] = \left(\frac{1}{2C_1'}\right)^{1/3} \left(\frac{1}{1+2\gamma}\right)^{2/3} [D]^{1/3} \tag{65b}$$

$$[D^{++}] = \left(\frac{1}{C_2'C_1'}\right)^{1/5} \left(\frac{\gamma}{1+2\gamma}\right)^{4/5} [D]^{1/5} \tag{66b}$$

Case 9. Surface Donors on a Nearly Intrinsic p-type Semiconductor.

The results for this case are exactly the same as are obtained for case 3 since equations (47) and (48) are identical and are represented by equations (63a), (64a).

Accumulation Layers Produced by Surface Acceptors.

Case 2. Surface Acceptors on an Intrinsic Semiconductor.

For the neutral atoms in phase 3, substitution of equation (49) into equation (44) gives

$$[A] = \frac{1}{2}\,\frac{L_m}{p_i} \exp\left\{\frac{\epsilon_{a_1} - \phi_p}{kT}\right\} \left\{[A^-]\,[A^- + 2A^2]^2\right\}$$

For the singly charged atoms in phase 4, substitution of equation (49) into equation (45) gives

$$[A^-] = 2\left(\frac{L_m}{p_i}\right)\exp\left\{\frac{\epsilon_{a_2} - \phi_p}{kT}\right\}\left\{[A^=]\ [A^- + 2A^=]^2\right\}$$

But p_i can be expressed as

$$p_i = (N_v N_c)^{1/2} \exp\left\{-\phi_i / kT\right\}$$

and substituted into the above equations to give

$$[A] = 2\frac{L_m}{(N_v N_c)^{1/2}} \exp\left\{\frac{\epsilon_{a_1}}{kT}\right\}\left\{[A^-]\ [A^- + 2A^=]^2\right\} \tag{67}$$

and

$$[A^-] = 2\frac{L_m}{(N_v N_c)^{1/2}} \exp\left\{\frac{\epsilon_{a_2}}{kT}\right\}\left\{[A^=]\ [A^- + 2A^=]^2\right\} \tag{68}$$

For simplicity, let

$$K_1 = \frac{L_m}{(N_c N_v)^{1/2}} \exp\left\{\frac{\epsilon_{a_1}}{kT}\right\} \tag{69}$$

$$K_2 = \frac{L_m}{(N_c N_v)^{1/2}} \exp\left\{\frac{\epsilon_{a_2}}{kT}\right\} \tag{70}$$

Then substitution of equations (69) and (70) into equation (67) and (68) gives

$$[A] = \frac{1}{2} K_1 \left\{[A^-]\ [A^- + 2A^=]^2\right\} \tag{67a}$$

$$[A^-] = 2 K_2 \left\{[A^=]\ [A^- + 2A^=]^2\right\} \tag{68a}$$

The solution to equation (68a) then is

$$[A^-] = \frac{1 - 8K_2 [A^=]^2 \pm \left\{1 - 16 K_2 [A^=]^2\right\}^{1/2}}{4K_2 [A^=]} \tag{71}$$

From the reasoning similar to that given in connection with $[D^+]$ and $[D^{++}]$ following equation (54) it follows directly that

$$16\, K_2\, [A^=] < 1$$

and

$$\left\{1 - 16\, K_2\, [A^=]^2\right\}^{1/2} = 1 - 8\, K_2\, [A^=]^2 - \sum_{m=2}^{\infty} \frac{(2m-3)!\; 4^{(m++)}}{m!\;(m-2)!} \left\{K_2\, [A_2^=]^2\right\}^m \tag{72}$$

By the same reasoning process as before, define γ as the ratio of $[A^=] / [A^-]$. That is

$$[A^=] = \gamma\, [A^-] \tag{73}$$

and the limits on γ again are

$$0 \leqq \gamma \leqq 1/2$$

Therefore from equation (71) it follows that

$$K_2\, [A^=]^2 = \frac{\gamma}{2\,(1 + 2\gamma)^2} \tag{74}$$

From equations (67a) and (68a), one obtains

$$[A] = K_1 K_2\, [A^=]\, [A^- + 2\, A^=]^4 \tag{68b}$$

From equation (67a) and the relation (73)

$$[A] = \frac{1}{2}\, K_1\, (1 + 2\gamma)^2\, [A^-]^3 \tag{67b}$$

From equations (68b) and (73)

$$[A] = K_1 K_2\, (2 + \frac{1}{\gamma})^4\, [A^=]^5 \tag{68c}$$

Therefore, solving equation (67b) for $[A^-]$ gives

$$[A^-] = \left(\frac{2}{K_1}\right)^{1/3} \left(\frac{1}{1 + 2\gamma}\right)^{2/3} [A]^{1/3} \tag{75}$$

and solving equation (68c) for $[A^=]$ gives

$$[A^{=}] = \left(\frac{1}{K_1 K_2}\right)^{1/5} \left(\frac{\gamma}{1+2\gamma}\right)^{4/5} [A]^{1/5} \qquad (76)$$

Case 4. Surface Acceptors on a p-type Semiconductor.

Following the same procedure as in case 3, but defining

$$K_1' = \frac{L_m}{N_v} \exp\left\{\frac{\epsilon_{a_1}}{kT}\right\} \qquad (77)$$

$$K_2' = \frac{L_m}{N_v} \exp\left\{\frac{\epsilon_{a_2}}{kT}\right\} \qquad (78)$$

The results which are obtained then are

$$[A^{-}] = \left(\frac{2}{K_1'}\right)^{1/3} \left(\frac{1}{1+2\gamma}\right)^{2/3} [A]^{1/3} \qquad (79)$$

$$[A^{=}] = \left(\frac{1}{K_1' K_2'}\right)^{1/5} \left(\frac{\gamma}{1+2\gamma}\right)^{4/5} [A]^{1/5} \qquad (80)$$

Case 10. Surface Acceptors on a Nearly Intrinsic n-type Semiconductor.

The formulation is exactly like case 4 above, and the results can be represented by equations (79) and (80).

IV. Equilibrium Relationship Between Phase 1 and Phases 4 and 5.

Having established the relationship between phases 3 and 4, 3 and 5, on various semiconductor surfaces, the authors proceed to formulate the relations between phases 1 and 4, phases 1 and 5, i.e., the dependence of the surface ion concentrations on the partial pressure of the gas in phase 1.

Case 1. Surface Donors on Intrinsic Semiconductor.

The desired relationship can be found by combining equations (63a) and (27a) for singly charged donors. The result is

$$[D^{+}] = \left(\frac{1}{2C_1}\right)^{1/3} \left(\frac{1}{1+2\gamma}\right)^{2/3} \left(\frac{\beta I_3}{\sqrt[n]{kT(n\beta)^{3/2} I_1}}\right)^{1/3} \exp\left\{\frac{W' - \Delta}{3nkT}\right\} p^{\frac{1}{3n}}$$

Since

$$C_1 = \frac{L_m}{(_vN_c)}^{1/2} \exp\left\{\frac{\epsilon_{d_1}}{kT}\right\}$$

Therefore

$$[D^+] = \left\{\frac{\sqrt{N_vN_c}}{2L_m(1+2\gamma)^2}\right\}^{1/3} \left\{\frac{\beta I_3}{\sqrt[n]{kT(n\beta)^{3/2}I_1}}\right\}^{1/3}$$

$$\cdot \exp\left\{\frac{W' - \Delta - n\epsilon_{d_1}}{3nkT}\right\} \quad p^{\frac{1}{3n}} \tag{81}$$

For doubly charged donors the result is obtained by combining equation (27a) and equation (64a). The result is

$$[D^{++}] = \left(\frac{1}{C_1C_2}\right)^{1/5} \left(\frac{\gamma}{1+2\gamma}\right)^{4/5} \left\{\frac{\beta I_3}{\sqrt[n]{kT(n\beta)^{3/2}I_1}}\right\}^{1/5}$$

$$\exp\left\{\frac{W' - \Delta}{5nkT}\right\} \quad p_{D_n}^{\frac{1}{5n}}$$

However, since

$$\left(\frac{1}{C_1C_2}\right)^{1/5} = \left(\frac{N_vN_c}{L_m^2}\right)^{1/5} \exp\left\{-\frac{\epsilon_{d_1} + \epsilon_{d_2}}{5kT}\right\}$$

Then

$$[D^{++}] = \left\{\frac{N_vN_c\gamma^4}{L_m^2(1+2\gamma)^4}\right\}^{1/5} \left\{\frac{\beta I_3}{\sqrt[n]{kT(n\beta)^{3/2}I_1}}\right\}^{1/5}$$

$$\cdot \exp\left\{\frac{W' - \Delta - n(\epsilon_{d_2})}{5nkT}\right\} \quad p_{D_n}^{\frac{1}{5n}} \tag{82}$$

For case 3 and case 9, the results are

$$[D^{+}] = \left\{ \frac{N_c}{2\, L_m (1+2\gamma)^2} \right\}^{1/3} \left\{ \frac{\beta\, I_5}{\sqrt[n]{kT(n\beta)^{3/2} I_1}} \right\}^{1/3} \exp\left\{ \frac{W' - \Delta - n\,\epsilon_{d_1}}{3\, n\, k\, T} \right\} p_{D_n}^{\frac{1}{3m}} \qquad (83)$$

$$[D^{++}] = \left\{ \frac{N_c^2\, \gamma^4}{L_m^2 (1+2\gamma)^4} \right\}^{1/5} \left\{ \frac{\beta\, I_3}{\sqrt[n]{k\,T(n\beta)^{3/2} I_1}} \right\}^{1/5} \exp\left\{ \frac{W' - \Delta - n(\epsilon_{d_2})}{5\, n\, k\, T} \right\} p_{D_n}^{\frac{1}{5n}} \qquad (84)$$

Case 2. Surface Acceptors on Intrinsic Semiconductor.

For surface acceptors on an intrinsic semiconductor equations (75) and (27b) can be combined to relate the concentration of singly ionized acceptors to the partial pressure of the acceptor gas.

$$[A^{-}] = \left(\frac{2}{K_1} \right)^{1/3} \left(\frac{1}{1+2\gamma} \right)^{2/3} \left\{ \frac{\beta\, I_3}{\sqrt[n]{(n\beta)^{3/2} kT\, I_1}} \right\}^{1/3} \exp\left\{ \frac{W' - \Delta}{3n\, k\, T} \right\} p_{A_n}^{\frac{1}{3n}}$$

Since

$$K_1 = \frac{L_m}{(N_v N_c)^{1/2}} \exp\left\{ \frac{\epsilon_{a_1}}{kT} \right\}$$

Therefore

$$[A^{-}] = \left\{ \frac{2\sqrt{N_v N_c}}{L_m (1+2\,\gamma)^2} \right\}^{1/3} \left\{ \frac{\beta\, I_3}{\sqrt[n]{(n\beta)^{3/2} kT\, I_1}} \right\}^{1/3} \exp\left\{ \frac{W' - \Delta - n\,\epsilon_{a_1}}{3\, n\, k\, T} \right\} p_{A_n}^{\frac{1}{3n}} \qquad (85)$$

For doubly charged acceptor the result is obtained by combining equations (76) and (27b).

$$[A^{=}] = \left\{ \frac{N_c N_v\, \gamma^4}{L_m^2 (1+2\gamma)^4} \right\}^{1/5} \left\{ \frac{\beta\, I_3}{\sqrt[n]{(n\beta)^{3/2} kT\, I_1}} \right\}^{1/5} \exp\left\{ \frac{W' - \Delta - n(\,\epsilon_{a_1} + \epsilon_{a_2})}{5\, n\, k\, T} \right\} p_{A_n}^{\frac{1}{5n}} \qquad (86)$$

For case 4 and case 10, the results are

$$[A^-] = \left\{ \frac{2\, N_v}{L_m (1+2\gamma)^2} \quad \frac{\beta\, I_3}{\sqrt[n]{(n\beta)^{3/2} kT I_1}} \right\}^{1/3} \exp\left\{ \frac{W' - \Delta - n\epsilon_{a_1}}{3\, n\, k\, T} \right\} p_{A_n}^{\frac{1}{3n}} \quad (87)$$

$$[A^=] = \left\{ \frac{N_v^2 \gamma^4}{L_m^2 (1+2\gamma)^4} \quad \frac{\beta\, I_3}{\sqrt[n]{(n\beta)^{3/2} kT I_1}} \right\}^{1/5} \exp\left\{ \frac{W' - \Delta - n(\epsilon_{a_1} + \epsilon_{a_2})}{5\, n\, k\, T} \right\} p_{A_n}^{\frac{1}{5n}} \quad (88)$$

V. Adsorption Isotherms Associated with Class II Cases.

The Class II cases are associated with depletion regions or slight inversion space charge regions.

A. Depletion Layers.

Cases 5 and 6 as previously defined represent depletion layers on non-intrinsic semiconductors. For these cases the relationships between surface charge and surface potential are summarized.

$$u_s = \frac{L_m}{N_a^-} [\sigma^+]^2 + 1 \quad \text{for a p-type semiconductor}$$

$$u_s' = \frac{L_m}{N_d^+} [\sigma^-]^2 + 1 \quad \text{for an n-type semiconductor}$$

For a donor gas the surface charge can be defined by equation (28) and for an acceptor gas the surface charge is defined by equation (29).

By combining equations (36) and (37) the result is

$$[D] = [D^{++}] \exp(2\, u_s) \exp\left\{ \frac{\epsilon_{d_1} + \epsilon_{d_2} - 2\,\phi_n}{k\, T} \right\} \quad (89)$$

For a p-type semiconductor equation (89) can be modified by using the relationship

$$\phi_n = E_g - \phi_p \quad (90)$$

where

$\mathcal{E}_g$ = energy gap of the semiconductor.

The energy ϕ_p is related to the bulk hole concentration by the relationship.

$$p_B = N_v \exp(-\phi_p / kT)$$

Therefore

$$e^{+\phi_p / kT} = \left(\frac{N_v}{p_B}\right) \tag{91}$$

Equations (36), (90) and (91) can be combined to give

$$[D] = 2\,[D^+] \exp(u_s) \exp\left\{\frac{\epsilon_{d_1} - (E_g - \phi_p)}{kT}\right\}$$

$$= 2\,[D^+] \exp(u_s) \exp\left\{\frac{\epsilon_{d_1} - E_g}{kT}\right\} \exp \frac{\phi_p}{kT}$$

$$[D] = 2\,[D^+] \exp u_s \left(\frac{N_v}{p_B}\right) \exp\left\{\frac{\epsilon_{d_1} - E_g}{kT}\right\}$$

But since

$$u_s = \frac{L_m}{N_a^-} [\sigma_\square^+]^2 + 1$$

Therefore substitution of the relationship above gives

$$[D] = 2\,[D^+] \exp\left\{\frac{L_m}{N_a^-} [\sigma_\square^+]^2 + 1\right\} \frac{N_v}{p_B} \exp\left\{\frac{\epsilon_{d_1} - E_g}{kT}\right\}$$

$$= (2e)\,[D^+] \exp\left\{\frac{L_m}{N_a^-} [\sigma_\square^+]^2\right\} \frac{N_v}{p_B} \exp\left\{\frac{\epsilon_{d_1} - E_g}{kT}\right\}$$

This relationship can also be written as

$$[D] = (2e) \frac{N_v}{p_B} \left(\frac{N_a^-}{L_m}\right)^{1/2} \left\{\frac{L_m}{N_a^-} [D^+]^2\right\}^{1/2} \exp\left\{\frac{L_m}{N_a^-} [D^+ + 2D^{++}]^2\right\} \exp\left\{\frac{\epsilon_{d_1} - E_g}{kT}\right\}$$

Assume as in previous sections, that $[D^{++}] = \gamma [D^+]$ where $\gamma \not\gg 0$

and also $p_B \cong N_a^-$

The final result is

$$[D] = \frac{2eN_V}{\sqrt{p_B L_m}} \left\{ \frac{L_m}{p_B} [D^+]^2 \right\}^{1/2} \exp\left\{ \frac{L_m}{p_B} (1+2\gamma)^2 [D^+]^2 \right\} \exp\left\{ \frac{\epsilon_{d_1} - E_g}{kT} \right\} \quad (92)$$

However, this expression is still rather intractable. In order to simplify it further, take the logarithm of both sides. This gives:

$$\ln [D] = \frac{1}{2} \ln \left\{ \frac{4e^2 N_V^2}{p_B L_m} \right\} + \frac{\epsilon_{d_1} - E_g}{kT}$$

$$+ \frac{1}{2} \ln \left\{ \frac{L_m}{p_B} [D^+]^2 \right\} + (1 + 2\gamma)^2 \frac{L_m}{p_B} [D^+]^2 \quad (93)$$

Substituting equation (27a) into equation (93) gives,

$$\frac{1}{n} \ln \left\{ p_{D_n} \right\} = \ln \left\{ \frac{(2eN_V)}{\sqrt{p_B L_m}} \frac{\sqrt[3]{(n\beta)^{3/2}} I_1 kT}{\beta I_3} \right\}$$

$$+ \frac{\epsilon_{d_1} + \Delta - W' - E_g}{kT}$$

$$+ \frac{1}{2} \ln \left\{ \frac{L_m}{p_B} [D^+]^2 \right\}$$

$$+ (1 + 2\gamma)^2 \frac{L_m}{p_B} [D^+]^2 \quad (94)$$

Equation (94) is the general isotherm for a donor gas on a p-type semiconductor. Now, if

$\frac{L_m}{p_B} [D^+] \gg 13$ so that the term $\frac{1}{2} \ln \left\{ \frac{L_m}{p_B} [D^+]^2 \right\}$ can

be considered as 10% or less of the total value, then equation (94) can be simplified and written as

$$[D^+]^2 \cong H_{p,1} \left\{ \frac{1}{n} \ln P_{D_n} + H_{p,2} \right\} \quad (94a)$$

where

$$H_{p,1} \equiv p_B / L_m (1 + 2\gamma)^2 \tag{95a}$$

$$H_{p,2} = \ln\left\{\frac{\sqrt{p_B L_m} \quad \beta I_3}{2 N_v e \quad \sqrt[n]{(n\beta)^{3/2} \, I_1 kT}}\right\} + \frac{n E_g + W' - n \epsilon_{d_1} - \Delta}{n k T} \tag{96a}$$

For doubly charged donor gas, equation (89) is used. By similar substitutions, one obtains

$$[D] = \frac{e^2 N_v^2}{p_B \sqrt{L_m p_B}} \exp\left\{\frac{\epsilon_{d_1} + \epsilon_{d_2} - 2 Eg}{k T}\right\}\left\{\frac{L_m}{p_B}\left[D^{++}\right]^2\right\}^{1/2} \exp\left\{2\frac{L_m}{p_B}\left[D^{+} + 2D^{++}\right]^2\right\} \tag{97}$$

By combining the relationship $[D^{++}] = \gamma [D^{+}]$ with equation (27a) and defining the coefficients

$$J_{p,2} \equiv \ln\left\{\frac{\beta I_3 \quad p_B \sqrt{p_B L_m}}{\sqrt[n]{(n\beta)^{3/2} I_1 kT} \, . \, N_v^2 e^2}\right\} + \frac{2 n Eg + W' - n(\epsilon_{d_1} + \epsilon_{d_2}) - \Delta}{n k T} \tag{98a}$$

and

$$J_{p,1} = \frac{\gamma^2 p_B}{2(2\gamma + 1)^2}\left(\frac{p_B}{L_m}\right) \tag{99a}$$

Under the condition, $2\left(\frac{L_m}{p_B}\right)\left[D^{+} + 2 D^{++}\right]^2 >> \ln\left(\frac{L_m}{p_B}\right)\left[D^{++}\right]^2$, equation (97) gives:

$$\left[D^{++}\right]^2 \cong J_{p,1}\left\{\frac{1}{n}\left(P_{D_n}\right) + J_{p,2}\right\} \tag{100a}$$

B. Inversion Layers on Moderately Doped Semiconductors.

For a donor gas associated with a slightly inverted space charge region, the surface potential is defined within the limits

$$u_i < u_s < 2 u_i$$

This corresponds to cases 7 and 8 as previously defined. The surface potential is related to the surface charge through the relationship

$$U_s \cong \frac{L_m}{p_B} \left\{ [D^+] + 2 [D^{++}] \right\}^2$$

By using the procedure which is exactly the same as that outlined in Section V-A immediately above define

$$H_{p,3} = \ln \left\{ \frac{p_B L_m}{2 N_v} \frac{\beta I_3}{\sqrt[n]{(n\beta)^{3/2} I_1 kT}} \right\} + \frac{n \; Eg + W' - n \; \epsilon_{d_1} - \Delta}{n \; k \; T} \qquad (101a)$$

For case 7 the result is

$$[D^+]^2 = H_{p,1} \left\{ \frac{1}{n} \ln p_{D_n} + H_{p,3} \right\} \qquad (102a)$$

For doubly charged donors on the surface of a p-type semiconductor, define

$$J_{p,3} = \ln \left\{ \frac{\beta I_3}{\sqrt[n]{(n\beta)^{3/2} I_1 kT}} \cdot \frac{p_B \sqrt{p_B L_m}}{N_v^{\,2}} \right\} + \frac{2n \;\; Eg + W' - n \; (\epsilon_{d_1} + \epsilon_{d_2}) - \Delta}{n \; k \; T} \qquad (103a)$$

This result then is

$$[D^{++}]^2 = J_{p,1} \left\{ \frac{1}{n} \ln p_{D_n} + J_{p,3} \right\} \qquad (104a)$$

For case 8, an acceptor gas on an n-type semiconductor, the procedure of formulating the isotherms is similar to that used above.

The various constants are defined as follows:

$$H_{n,1} \equiv \frac{n_B}{L_m (1 + 2\gamma)^2} \qquad (95b)$$

$$H_{n,2} \equiv \ln \left\{ \frac{\sqrt{n_B L_m} \;\; \beta I_3}{2 N_c e \sqrt[n]{(n\beta)^{3/2} I_1 kT}} \right\} + \frac{n E_g + W' - n \; \epsilon_{a_1} - \Delta}{n \; k \; T} \qquad (96b)$$

$$H_{n,3} \equiv \ln\left\{\frac{n_B L_m \quad \beta I_3}{2N_c n\sqrt{(n\beta)^{3/2} I_1 kT}}\right\} + \frac{n\,Eg + W' - n\,{}^{\epsilon}a_1 - \Delta}{n\,k\,T} \qquad (101b)$$

$$J_{n,1} \equiv \frac{\gamma^2\, n_B^2}{2(2\gamma+1)^2 L_m} \qquad (99b)$$

$$J_{n,2} \equiv \ln\left\{\frac{\beta\, I_3 - n_B\sqrt{n_B L_m}}{n\sqrt{(n\beta)^{3/2} I_1 k T\; N_c^2\, e^2}}\right\}$$

$$+ \frac{2\,n\,Eg + W' - n\,({}^{\epsilon}a_1 + {}^{\epsilon}a_2) - \Delta}{n\,k\,T} \qquad (98b)$$

$$J_{n,3} \equiv \ln\left\{\frac{\beta\, I_3\, n_B\sqrt{n_B L_m}}{n\sqrt{(n\beta)^{3/2} I_1 k T\, N_c^2}}\right\} + \frac{2\,n\,Eg + W' - n\,({}^{\epsilon}a_1 + {}^{\epsilon}a_2) - \Delta}{n\,k\,T} \qquad (103b)$$

The adsorption isotherms for an acceptor gas on an n-type semiconductor associated with a depletion space charge layer are then summarized in the following equations. For singly charged acceptors on the surface

$$[A^-]^2 \cong H_{n,1}\left\{\frac{1}{n}\ln\left(p_{A_n}\right) + H_{n,2}\right\} \qquad (94b)$$

For doubly charged acceptors on the surface

$$[A^=]^2 = J_{n,1}\left\{\frac{1}{n}\ln\left(p_{A_n}\right) + J_{n,2}\right\} \qquad (100b)$$

The adsorption isotherms for an acceptor gas on an n-type semiconductor associated with a slight inversion layer are also summarized. For singly ionized acceptors

$$[A^-]^2 \cong H_{n,1}\left\{\frac{1}{n}\ln\left(p_{A_n}\right) + H_{n,3}\right\} \qquad (102b)$$

For doubly ionized acceptors

$$[A^=]^2 \cong J_{n,1}\left\{\frac{1}{n}\ln\left(p_{A_n}\right) + J_{n,3}\right\} \qquad (104b)$$

In order to summarize the isotherms for the several cases, it is convenient to define various coefficients. Let

$$A \equiv \left(\frac{I_2}{I_1}\right)\left\{\frac{1}{(n\beta)\ (kT)^2}\right\}^{1/2} \exp\left\{W/kT\right\} \qquad (105)$$

$$B \equiv \frac{\beta I_3}{n\sqrt{(nB)^{3/2}\,kT\,I_1}} \quad \exp\left\{\frac{W' - \Delta}{kT}\right\} \qquad (106)$$

$$C_i \equiv \left\{\frac{\sqrt{N_v N_c}}{2L_m(1+2\gamma)^2}\ \frac{\beta I_3}{n\sqrt{(n\beta)^{3/2} I_1 kT}}\right\}^{1/3} \exp\left\{\frac{W' - \Delta - n\,\epsilon_{d_1}}{3\,n\,k\,T}\right\} \qquad (107a)$$

$$C_e = \left\{\frac{N_e}{2\,L_m(1+2\gamma)^2}\ \frac{\beta I_3}{n\sqrt{(n\beta)^{3/2} I_1 kT}}\right\}^{1/3} \exp\left\{\frac{W' - \Delta - n\,\epsilon_{d_1}}{k\,n\,k\,T}\right\} \qquad (107b)$$

$$F_i = \left\{\frac{N_v N_e \gamma^4}{L_m^2 (1+2\gamma)^4} \cdot \frac{\beta I_3}{n\sqrt{(n\beta)^{3/2} I_1 kT}}\right\}^{1/5} \exp\left\{\frac{W' - \Delta - n(\epsilon_{d_1} + \epsilon_{d_2})}{5\,n\,k\,T}\right\} \qquad (108a)$$

$$F_e = \left\{\frac{N_c^2 \gamma^4 \cdot \beta I_3}{L_m^2 (1+2\gamma)^4\ n\sqrt{(n\beta)^{3/2} kT\,I_1}}\right\}^{1/5} \exp\left\{\frac{W' - \Delta - n(\epsilon_{d_1} + \epsilon_{d_2})}{5\,n\,k\,T}\right\} \qquad (108b)$$

$$K_i = \left\{\frac{2\sqrt{N_v N_c}}{L_m(1+2\gamma)^2}\ \frac{\beta I_s}{n\sqrt{(n\beta)^{3/2} I_1 kT}}\right\}^{1/3} \exp\left\{\frac{W' - n\,\epsilon_{p_1}}{3\,n\,k\,T}\right\} \qquad (109a)$$

$$K_e = \left\{\frac{2N_v}{L_m(1+2\gamma)^2}\ \frac{\beta I_3}{n\sqrt{(n\beta)^{3/2} I_1 kT}}\right\}^{1/3} \exp\left\{\frac{W' - \Delta - n\,\epsilon_{p_1}}{k\,n\,k\,T}\right\} \qquad (109b)$$

$$G_i = \left\{ \frac{N_c N_v \gamma^4}{L_m^2 (1+2\gamma)^4} \; \frac{\beta I_3}{n\sqrt{(n\beta)^2 I_1 kT}} \right\}^{1/5} \exp \left\{ \frac{W' - \Delta - n^{(\epsilon_{p_1} + \epsilon_{p_2})}}{5\, n\, k\, T} \right\} \tag{110a}$$

$$G_e = \left\{ \frac{N_v^2 \gamma^4}{L_m^2 (1+2\gamma)^4} \; \frac{\beta I_3}{n\sqrt{(n\beta)^{3/2} I_1 kT}} \right\}^{1/5} \exp \left\{ \frac{W' - \Delta - n^{(\epsilon_{p_1} + \epsilon_{p_2})}}{5\, n\, k\, T} \right\} \tag{110b}$$

With these defined coefficients one can write:

For a donor gas on any semiconductor substrate

$$[D_n] = A \; {}^{P}D_n$$

$$[D] = B\, ({}^{P}D_n)^{\frac{1}{n}}$$

For ionized donors on an intrinsic semiconductor:

$$[D^+] = C_i \; ({}^{P}D_n)^{1/3n}$$

$$[D^{++}] = F_i \; ({}^{P}D_n)^{1/5n}$$

For ionized donors on an n-type or slightly p-type semiconductor

$$[D^+] = C_e \; ({}^{P}D_n)^{1/3n}$$

$$[D^{++}] = F_e \; ({}^{P}D_n)^{1/5n}$$

For ionized donors on a highly p-type semiconductor, a depletion space charge region is formed, and the adsorption isotherms are

$$[D^+]^2 \cong H_{p,1} \left\{ \frac{1}{n} \ln ({}^{P}D_n) + H_{P_2} \right\}$$

$$[D^{++}]^2 = (J_p)_1 \left\{ \frac{1}{n} \ln (P_{D_n}) + J_{p_2} \right\}$$

For ionized donors on a moderately p-type semiconductor, a slightly inverted space charge region is formed. The adsorption isotherms are

$$[D^+]^2 = H_{p,1} \left\{ \frac{1}{n} \ln ({}^{P}D_n) + H_{p,3} \right\}$$

$$[D^{++}] = J_{p,1}\left\{\frac{1}{n}\ln(^{P}D_{n}) + J_{p,3}\right\}$$

For an acceptor gas on any semiconductor substrate

$$[A_n] = A\,(^{P}A_{n})$$

$$[A] = B\,(^{P}A_{n})^{1/n}$$

For ionized acceptors on an intrinsic semiconductor

$$[A^-] = K_i\,(^{P}A_{n})^{1/3n}$$

$$[A^=] = G_i\,(^{P}A_{n})^{1/5n}$$

For ionized acceptors on a p-type semiconductor or on slightly n-type semiconductor

$$[A^-] = K_e\,(^{P}A_{n})^{1/3n}$$

$$[A^=] = G_e\,(^{P}A_{n})^{1/5n}$$

For ionized acceptors on a highly n-type semiconductor, a depletion space charge region is formed and the adsorption isotherms are

$$[A^-]^2 \cong H_{n,1}\left\{\frac{1}{n}\ln(^{P}A_{n}) + H_{n,2}\right\}$$

$$[A^=]^2 \cong J_{n,1}\left\{\frac{1}{n}\ln(^{P}A_{n}) + J_{n,2}\right\}$$

For ionized donors on a moderately p-type semiconductor a slightly inverted space charge region is formed. The adsorption isotherms are:

$$[A^-]^2 = H_{n,1}\left\{\frac{1}{n}\ln(^{P}A_{n}) + H_{n,3}\right\}$$

$$[A^=]^2 = J_{n,1}\left\{\frac{1}{n}\ln(^{P}A_{n}) + J_{n,3}\right\}$$

Conclusion

Gas adsorption isotherms of ventral and charged particles based on a generalized model have been formulated. Although the formulations

have been based on a molecule which yields n atoms upon dissociation, they can be applied to the cases wherein the molecules, such as D_n or A_n, can be ionized without dissociation. The functional relationship between $[D_n^+]$ or $[A_n^-]$ and the respective pressures in the gas phases can be obtained by treating $[D_n]$ or $[A_n]$ as monatomic molecules. That is, by putting n equal to unity in the respective equations.

Factual confirmations as well as practical applications of the formulations will be presented in subsequent publications.

References

1. Hill, Terrell L., "An Introduction to Statistical Thermodynamics," p. 126, Addison-Wesley Company, Reading, Mass. (1960).
2. Landau, L. D., and E. M. Lifshitz, "Statistical Physics," pp. 105-106; 152-154, Addison-Wesley Company, Reading, Mass. (1960).
3. Fowler, R. H., and E. A. Guggenheim, "Statistical Thermodynamics,' pp. 45-51; pp. 66-67, Macmillan Company, New York (1939).
4. Lee, V. J., and D. R. Mason, "The Relationships Between Surface Charge and Diffusion Potential Beneath Semiconductor Surfaces," Progress Report 04650-3-P, May 1962.