THE UNIVERSITY OF MICHIGAN

COLLEGE OF ENGINEERING

Department of Chemical and Metallurgical Engineering

Progress Report 04650-12-P

THE DEPENDENCE OF THE THERMIONIC WORK FUNCTION AND THE PHOTOELECTRIC THRESHOLD OF A SEMICONDUCTOR ON SURFACE CHARGES

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ORA Project 04650

under contract with:

TEXAS INSTRUMENTS, INC.

DALLAS 22, TEXAS

administered through:

OFFICE OF RESEARCH ADMINISTRATION ANN ARBOR

March 1963

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ABSTRACT

The variations of thermionic work function, $\Delta\phi_{th}$, and of photoelectric threshold, $\Delta\phi_{ph}$, have been analyzed as a function of surface potential[(1)] and surface dipole. The results of these analyses are compared with experimental observations of the variations of ϕ_{th} and ϕ_{ph} due to adsorption of gases or vapors. The change of electron affinity of semiconductors due to the adsorption of gases or vapors is also discussed.

*Contribution No. 18 from The Semiconductor Materials Research Laboratory, The College of Engineering, The University of Michigan, Ann Arbor, Michigan. This work has been supported by Texas Instruments, Inc.

CHAPTER 4

THE DEPENDENCE OF THE THERMIONIC WORK FUNCTION AND THE PHOTOELECTRIC THRESHOLD OF A SEMICONDUCTOR ON SURFACE CHARGES

INTRODUCTION

The variation of the thermionic work function and/or photoelectric threshold of semiconductors due to adsorption of gases or vapors has been reported by many authors.[2-15] The following empirical results for the dependence of the thermionic work function, ϕ_{th}, on the amount of gas or vapor adsorbed on the semiconductor surface, θ, have been summarized by S. Z. Roginsky:[16] "for reversible and irreversible adsorption, when $|\Delta\phi_{th}| > kT$, the dependence of ϕ_{th} on θ is logarithmic when an accumulation space charge region is generated in the semiconductor and is linear when a depletion space charge region is generated in the semiconductor." These results cannot be explained by either the simple dipole layer model[17, 18] and the most refined dipole layer model[19] or the simple surface states model[20] because none of these models predicts that the functional relationship between ϕ_{th} and θ is associated with the space charge region generated upon adsorption. In this paper, we shall first show that $\Delta\phi_{th}$ is a linear function of the surface potential, Y_s, which was defined and formulated as a function of surface charges in Chapter 2.[1] Then we shall explain the observed empirical trends summarized by Roginsky[16] in the light of the aforementioned formulation.[1] At the same time, the experimental trend serves as a verification of the results presented in Chapter 2. It goes without saying that the author is primarily motivated by the latter aspect.

For the variation of photoelectric threshold, $\Delta\phi_{ph}$, of semiconductors due to the adsorption of gases or vapors, many authors have either tacitly assumed that ϕ_{ph} and ϕ_{th} should vary in a similar manner[14, 17] or have ignored the subject.[20] Recently Redfield,[21] lead by experimental observation has shown that ϕ_{th} and ϕ_{ph} should vary in a different manner. This latter result and analysis is also discussed in this paper.

FUNDAMENTAL DEFINITIONS

The generally accepted[22, 23] definition of work function of a semiconductor is represented by the following equation.

$$\phi_{th} = \chi + (E_c - E_f) \tag{4.1}$$
$$= \chi + \phi_n$$

where χ is defined as the electron affinity of a semiconductor. Physically χ is the energy barrier for the free electrons in the conduction band, which prevents the free electrons from leaving the semiconductor to a point outside the surface field. The potential energy of an electron at this point outside the semiconductor is defined as the vacuum level, E_o. Therefore χ is given by

$$\chi = E_o - E_c \tag{4.2}$$

It follows that

$$\phi_{th} = E_o - E_f \tag{4.3}$$

For the photoelectric threshold, ϕ_{ph}, it has been established[24, 25] that for a non-degenerate semiconductor the majority of the photoemitted electrons are from the valence band. Therefore ϕ_{ph} is written

$$\phi_{ph} = \chi + E_g \tag{4.4}$$

Equations (4.1) to (4.4) are illustrated in Figure 4.1. Before proceeding further in the development of this paper, it should be

pointed out that E_c, E_v, E_f, and E_o are referred to a common reference, which is the only requirement. Consequently any one of these energy levels can be used as that reference. The definitions represented by Equations (4.1) to (4.3) are correct for a semiconductor surface free from space charge region.

Equation (4.1) can also be derived by assuming that the free electrons in the conduction band have a Maxwellian distribution.[22] This assumption can be justified by computing the average energy per electron, in the conduction band of a non-degenerate semiconductor, $\bar{E}_c$. To do this we shall proceed as follows:

Assuming parabolic density of state distribution in the conduction band.

$$\bar{E}_c = \int_{E_c}^{\infty} E\, N(E)\, dE \Big/ \int_{E_c}^{\infty} N(E)\, dE \tag{4.5}$$

where

$$N(E)\, dE = \frac{\left(\frac{4\pi}{h^3}\right) (2m^*)^{3/2} (E - E_c)^{1/2}\, dE}{1 + \exp\left(\frac{E - E_f}{kT}\right)}$$

Since $E = E_c + E - E_c$, Equation (4.5) can be written

$$\bar{E}_c = E_c + \frac{\int_{E_c}^{\infty} (E - E_c)\, N(E)\, dE}{\int_{E_c}^{\infty} N(E)\, dE} \tag{4.5a}$$

To evaluate the integrals appearing in Equation (4.5a), we let

$$E - E_c = \xi kT$$

and

$$\exp (E_f - E_c)/kT = \lambda$$

With these substitutions then

$$\int_{E_c}^{\infty} (E - E_c)\, N(E)\, dE \Big/ \int_{E_c}^{\infty} N(E)\, dE$$

$$= \frac{kT \int_{o}^{\infty} \xi^{3/2} d\xi /(1 + \exp(\xi)/\lambda)}{\int_{o}^{\infty} \xi^{1/2} d\xi /(1 + \exp(\xi)/\lambda}$$

Assume $\lambda = \exp - \left\{ \frac{E_c - E_f}{kT} \right\} \ll 1$ (4.6)

$$\exp(\xi) = \exp(E - E_c)/kT \geq 1,$$

to a good approximation the above integrals can be reduced to the following gamma function

$$kT\, \lambda \int_{o}^{\infty} \xi^{3/2} \exp(-\xi)\, d\xi / \lambda \int_{o}^{\infty} \xi^{1/2} \exp(-\xi)\, d\xi$$

$$= kT \frac{\lambda \Gamma(3/2)}{\lambda \Gamma(1/2)} = 3\, kT/2$$

Substitute the above approximation the average energy per conduction electron $\overline{E}_c$ is obtained,

$$\overline{E}_c = E_c + 3\, kT/2 \tag{4.7}$$

Equation (4.7) has the simple interpretation that the electrons in the conduction band behave as classical free particles in a region of constant potential, E_c. Consequently we can imagine that when temperature is such that some of the electrons can have energy more than E_c, they become as classical free particles moving in a region of constant potential, E_c, free from the periodic field of the individual atoms of the semiconductor. Figure 4.2 illustrates that the conduction

electrons behave as free and independent particles inside the semiconductor, and have a constant negative potential energy, χ , which is the surface barrier energy.

From this model, the assumption of Maxwellian velocity distribution is justified as long as the approximation introduced in Equation (4. 6) is valid.

It should be pointed out further that a constant potential, ψ, defined as $-q\psi = E$ means a region free of space charge, since

$$\frac{\delta\psi}{\delta x} = 0; \quad \frac{\delta\psi}{\delta y} = 0; \quad \frac{\delta\psi}{\delta z} = 0 \tag{4. 8}$$

It follows that

$$\nabla^2\psi = 0 \tag{4. 9}$$

Therefore there can be no space charge in the solid. In the following section, we shall discuss the situation when $\nabla^2\psi = 0$.

EFFECTS OF SURFACE CHARGE

From the previous section, it was seen that the free electrons in the conduction band can be treated as free and independent particles, moving in a region of constant negative potential energy (Figure 4. 2). For a real semiconductor surface, according to the present knowledge,[26 - 29] there are surface charges. The surface charges may produce a surface dipole layer as well as a space charge region at the surface region of a semiconductor.[1] Consequently Equation (4. 9) will not be satisfied in general. It is the subject matter of this section to analyze the possible effect of all types of surface charges on χ, ϕ_{th} and ϕ_{ph}. The constituents of these surface charges and their identification will be discussed in a later section.

Effect of Surface Dipole

We shall consider first the case of a surface dipole layer of atomic dimension but without a space charge region.

First let us imagine that there is a surface dipole layer on the semiconductor surface. This surface dipole layer consists of a layer of negatively charged surface states on the semiconductor surface and a positively charged layer of surface states on top of the negative layer with identical charge density, $q\delta_o^+$, and with a constant spacing, r_o, of atomic dimension between the two layers. Our question at this point is: What would be the effect of this surface dipole layer on χ, ϕ_{th}, and ϕ_{ph}?

From our knowledge of electrostatics, we can immediately say that the energy bands of a semiconductor at the surface region are not affected by the presence of the dipole layer by the argument that the electrostatic flux from the positively charged layer is terminated on the negatively charged layer.

Now imagine that an electron is excited inside the semiconductor surface and moves toward the surface. This electron will not feel any force due to the dipole layers until it moves into the space between the dipole layers. Within this space of thickness, r_o, the electron is pushed by an additional force, $\vec{F}$, with magnitude of $4\pi\delta_o^+ q^2/\epsilon$ and directed away from the surface for the aforementioned charge alignment. After crossing the dipole layer, the electron will gain an additional kinetic energy of the magnitude, $4\pi q^2 \delta_o^+ r_o/\epsilon$. (It will lose the same amount of kinetic energy if the dipole is aligned with its negative end directed outwards.)[18, 19] Therefore the energy barrier layer of the conduction electron is reduced by the amount it gained (or lost) in crossing the dipole layer. That is,

$$\chi = E_o - E_c \mp 4\pi r_o (\delta_o^{\pm}) q^2/\epsilon \qquad (4.2a)$$

where δ_o^+ shows that the dipole layer has its positive end directed outwards, and δ_o^- indicates that the negative end is directed outwards.

For convenience we shall define

$$\Delta\chi = \mp 4\pi r_o (\delta_o^{\pm}) q^2/\epsilon \qquad (4.5)$$

and

$$\chi = \chi^{(o)} + \Delta\chi \tag{4.2b}$$

where $\chi^{(o)} = E_o - E_c$ for a semiconductor without a surface dipole layer. Equations (4.3) and (4.4) can be written as

$$\phi_{th} = \chi + (E_c - E_f) = \chi^{(o)} + \Delta\chi + (E_c - E_f) \tag{4.3a}$$

and

$$\phi_{ph} = \chi + E_g = \chi^{(o)} + \Delta\chi + E_g \tag{4.4a}$$

Effect of Diffusion Potential

Having discussed the influence of the surface dipole layer on χ, we shall now proceed to analyze the effect of diffusion potential,[1] Y, on ϕ_{th} and ϕ_{ph}. For the convenience of representation, let us visualize that a homogeneous rectangular semiconductor bar of macroscopic dimensions is cut into two pieces and separated to a distance r cm. as shown in Figure 4.3. Let us imagine further that the semiconductor consists of conduction electrons, nuclei, and bound electrons. The conduction electrons are free to move in the conduction band, and will be referred to as free electrons. The bound electrons are bound to individual nuclei with definite energies of bonding. Now let the two plates shown in Figure 4.3 be connected with an external agent, such as an emf source. This external agent will charge the plates by moving electrons from plate I to plate II. Since this is exactly the case of charging a parallel plate capacitor, the work performed by the external agent is stored in the electrostatic field. The energy density of the electrostatic field is $\epsilon\mathcal{E}^2/8\pi$, (where $\mathcal{E}$ is the electric field intensity.) It can be considered that the external work done on the system, the capacitor, is stored both in the space charge regions of plate I and plate II, and in the space between the paralled plates. After charging, the external circuit is disconnected

and the electrons in plate II, and positive holes in plate I come to an equilibrium distribution. Here we assume further that the non-degenerate semiconductor is still in a non-degenerate condition. Consequently both the electrons and holes in plate II and plate I will assume a Maxwellian distribution in velocity space, and the usual Boltzman statistics are applicable as used in Chapter 2.

Now let us consider plate II of Figure 4.3, where a negative space charge region is created adjacent to the y-z plane at $x = 0$. According to Chapter 2, the free electron concentration at any point x will be,

$$n(x) = n_B \exp Y(x)/kT \tag{4.10}$$

Where n_B is the free electron concentration in the bulk, $Y(x)$ is the diffusion potential energy at x. From the one dimensional model assumed in Chapter 2, the diffusion potential, Y, is a function of x only. Then

$$\left(\frac{\delta Y}{\delta y}\right)_x = 0; \left(\frac{\delta Y}{\delta z}\right)_x = 0 \tag{4.11}$$

If $q\psi = E \pm Y(x)$ it follows that

$$\left(\frac{\delta^2 \psi}{\delta y^2}\right)_x + \left(\frac{\delta^2 \psi}{\delta z^2}\right)_x = 0 \tag{4.12}$$

Equation (4.12) implies that at any y-z plane at constant x, say $x = x'$, the free electrons experience a constant potential as in Figure 4.2 as long as the electrons are wandering in the two dimensional y-z plane. However, two parallel y-z planes will have different electron concentrations as shown in Equation (4.10).

Now let us consider the thermionic emission flux of an infinitesimal narrow strip at $x = x'$ on the edge of a y-z plane at $z = z_o$. This is <u>not</u> one face of the capacitor but is an edge of capacitor plate which is free of the influence of an electric field in the z-direction. The electron concentration is given by Equation (4.10). That is

$$n(x') = n_B \exp (Y(x')/kT) \tag{4.10a}$$

From the previously assumed Maxwellian velocity distribution, the number of electrons/cm^3 at the plane $x = x'$, with velocity component lying in a specified velocity interval is given by,

$$\bar{n}(x', v_x, v_y, v_z) = n(x') \left(\frac{m^*}{2\pi kT}\right)^{3/2} \exp -\left\{\frac{m^* (v_x^2 + v_y^2 + v_z^2)}{2\,kT}\right\} \tag{4.13}$$

The thermionic flux at the x-y plane at $z = z_o$, $x = x'$ (see Figure 4.3) will be (neglect the reflections)

$$J_z(x') = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{v_{z,o}}^{\infty} v_z \bar{n}(x'; v_x, v_y, v_z)\, dv_x dv_y dv_z \tag{4.14}$$

where $v_{z,o}$ is the minimum velocity component in the z-direction required to overcome the constant negative potential energy barrier, χ, at the surface region. (See Figure 4.2.) That is,

$$\frac{1}{2} m v_{z,o}^2 = \chi \tag{4.15}$$

Integrate Equation (4.14) and substitute Equation (4.15) for χ. The thermionic flux at $x = x'$ on the x-y plane $z = z_o$ is obtained.

$$J_z(x') = \frac{n(x')kT}{(2\pi m^* kT)^{1/2}} \exp (-\chi/kT) \tag{4.16}$$

Since

$$n_B = \frac{2(2\pi m^* kT)^{3/2}}{h^3} \exp \left\{\frac{E_f - E_{c,B}}{kT}\right\} \tag{4.17}$$

Substitute Equations (4.10a) and (4.17) into Equation (4.16)

$$J_z(x') = \frac{4\pi m^* k^2 T^2}{h^3} \exp -\left\{\frac{\chi + E_{c,B} - E_f - Y(x')}{kT}\right\} \tag{4.18}$$

Therefore

$$\phi_{th} = \chi + (E_{c,B} - E_f) - Y(x') \tag{4.19}$$

Since $E_{c,B} - E_f = \phi_{n,B}$, then

$$\phi_{th}(z, x') = \chi + \phi_{n,B} - Y(x') \tag{4.19a}$$

The thermionic emission flux, J, (at x = 0) can be similarly obtained, (for the case there is no field).

$$\phi_{th} = \chi + \phi_{n,B} - Y(o) \tag{4.4b}$$

Now a discussion of χ is in order on the x-y or x-z planes (for example the top face where $z = z_o$). From the analysis in the previous section, we know that χ exists at the solid-vacuum boundary. From Equation (4.19) it is seen also that χ is the surface part of the work function ϕ_{th}. Theoretical analysis on the surface part of work function has been done by Bardeen[30] and Smoluchowski[31] for metals. According to these authors, the surface part of the work function is like the energy barrier produced by a surface dipole layer with anisotropic charge distribution which exists at the neighborhood of the surface within a fraction of the lattice constant. Bardeen has also concluded that "the barrier at the surface is due largely to exchange and polarization forces, rather than to ordinary electrostatic forces." In our case the electron concentration in the y-z plane at x = x', is uniform throughout the plane, but in excess of the neutral condition. It is possible that this excess charge may influence the surface "dipole layer" on the x-y plane at $z = z_o$. However, if the surface dipole layer exists over a region of a fraction of the lattice constant, the influence of the space charge region would not be very large. Consequently to a zero order approximation χ would be independent of x in the x-y plate at $z = z_o$.

The customarily accepted view[21-23, 32-35] is that $\chi = E_o - E_c$ remains unchanged as the diffusion potential varies and also that E_f does not change as the diffusion potential changes. The

view is represented by Figure 4.4. According to this view all the energy bands are bent down by $Y(x)$ in case of a negative space charge region and are bent upwards by $Y'(x')$ in case of positive space charge region. This view is widely accepted, and we have also used it in Chapter 2. Now after a careful analysis, we find the following points need to be considered.

1. Since χ is a constant, then a bending of the vacuum level, E_o, must occur as shown in Figure 4.4 when a diffusion potential is introduced. The difficulty arises from the fact that if the collecting electrode is placed at some macroscopic distance from the semiconductor surface, the vacuum energy level E_o should be independent of the diffusion potential of the semiconductor surface.

2. Granting that the energy bands are bent down as shown in Figure 4.4, and that $\chi = E_o - E_c(x)$, then the average energy per particle at $x = x'$, should be

$$\bar{E}_c(x') = E_c(x') + 3\ kT/2 \qquad (4.20)$$

or since $Y(x') = E_{c,B} - E_c(x')$ then

$$\bar{E}_c(x') = E_{c,B} - Y(x') + 3\ kT/2 \qquad (4.21)$$

Now let us compute $\bar{E}_c(x')$, by assuming that the density of states distribution is parabolic as in the previous section where there is no space charge.

$$N(E)\ dE = \left(\frac{4\pi}{h^3}\right)\ (2m^*)^{3/2}\ \frac{(E-E_{c,B} + Y)^{1/2}\ dE}{1 + \exp\left(\frac{E-E_f-Y}{kT}\right)} \qquad (4.22)$$

where $N(E)\ dE$ is number of electrons in the energy interval $(E, E+dE)$, and the factor $1/\left[1 + \exp\left(\frac{E - E_f - Y}{kT}\right)\right]$ is the Fermi occupation probability function when there is an excess of negative charge. From Equation (4.22), $\bar{E}_c(x')$ can be computed as follows:

$$\bar{E}_c(x') = \frac{\int_{(E_{c,B}-Y)}^{\infty} \frac{(E-Y)\,(E-Y-E_{c,B}+Y)^{1/2}\, d(E)}{1+\exp\,(E-Y-E_f)/kT}}{\int_{(E_{c,B}-Y)}^{\infty} \frac{(E-Y-E_{c,B}+Y)^{1/2}\, dE}{1+\exp\left(\frac{E-Y-E_f}{kT}\right)}} \tag{4.23}$$

Since $E-Y = (E-E_{c,B}) + (E_{c,B} - Y)$, and let

$$\lambda = \exp\; -(E_{c,B} - Y - E_f)/kT \tag{4.24}$$

$$\xi = (E - E_{c,B})/kT$$

When $E - Y = E_{c,B} - Y$, then $E = E_{c,B}$ and $\xi = 0$. Then Equation (4.23) can be written as follows:

$$\bar{E}_c(x') = E_{c,B} - Y + \frac{(kT)\int_0^{\infty} \frac{\xi^{3/2}\, d\xi}{1+\exp(\xi)/\lambda}}{\int_0^{\infty} \frac{\xi^{1/2}\, d\xi}{1+\exp(\xi)/\lambda}} \tag{4.25}$$

If $\lambda \ll 1$ and since $\exp(\xi) \geq 1$, then Equation (4.25) can be approximated and the result is

$$\bar{E}_c(x') = E_{c,B} - Y(x') + 3\,kT/2 \tag{4.21}$$

Indeed Equation (4.21) is obtained as we have expected according to Figure 4.4. There arises a difficulty from Equation (4.21). That is, if there is a thermodynamic equilibrium for the free electrons in the conduction band, the partial free energy, $\frac{\delta G}{\delta n} = \mu$, should be equal everywhere; and $\frac{\delta G}{\delta n}$ should be the energy per particle. Furthermore we come to consider the positive space charge region, the corresponding average energy per electron should be

$$\bar{E}_c(x) = E_{c,B} + Y'(x) + 3\,kT/2 \tag{4.21a}$$

This shows that the energy per particle for the free electrons in the positive space charge region is increased. Consequently the more electrons we removed from a semiconductor, the easier it would be to remove the next one. This is contrary to our experience in charging a capacitor.

3. Suppose one chooses to apply the available field energy density

$$\frac{dE}{dV} = \frac{\epsilon \mathcal{E}^2}{8\pi}$$

to an intrinsic semiconductor, where V is the volume. At any point, x, in the negative space charge region,

$$\mathcal{E}(x) = \pm \frac{kT}{q} \frac{du}{dx} \tag{4.26a}$$

where $u(x) = Y(x)/kT$ as defined in Chapter 2. From Equation (2.17)

$$\left(\frac{du}{dx}\right)^2 = 16\, L_m\, n_i \sinh^2 (u/2) \tag{4.26b}$$

where $L_m = 2\pi q^2/\epsilon kT$. From (4.26a) and (4.26b)

$$\frac{dE}{dV} = 4\, n_i\, kT \sinh^2 (u/2) \tag{4.26c}$$

Consider one cm^2, then $dV = 1. dx\ cm^3$. The total energy stored in the volume with a cross sectional area of 1 cm^3 (of any shape) is then

$$E = 4\, n_i\, kT \int_o^{\infty} \sinh^2 (u/2)\, dx \tag{4.26d}$$

Since $dx = \frac{du}{\left(\frac{du}{dx}\right)}$, from Equation (2.18) Chapter 2

$$\frac{du}{dx} = -4\, (L_m\, n_i)^{1/2} \sinh (u/2)$$

and since

$$x \rightarrow \infty; \qquad u(\infty) \rightarrow 0$$

and

$$x = 0 \qquad u(o) = u_s$$

Therefore

$$E = -2kT \left(\frac{n_i}{L_m}\right)^{1/2} \int_{u_s}^{0} \sinh(u/2)\ d\,(u/2)$$

and

$$E = +2kT\left(\frac{n_i}{L_m}\right)^{1/2}\left[\cosh\left(\frac{u_s}{2}\right) - 1\right] \qquad (4.26d)$$

E is the total energy stored in the volume of 1 cm^2 of cross section throughout the space charge region.

Now we shall choose to compute the total number of electrons transported into the volume concerned. Since:

$$n(x) = n_i e^{u(x)}; \; p(x) = n_i e^{-u(x)};$$

$n(x) - n_i$ = electrons transferred into the conduction band;

$n_i - p(x)$ = electrons transferred into the valence band;

Therefore

$$[n(x) - n_i] + [n_i - p(x)] = n(x) - p(x) = 2\, n_i \sinh[u(x)].$$

The total electrons transferred, N, to the volume of cross section of 1 cm^2 throughout the space charge region is,

$$N = 2\, n_i \int_o^{\infty} \sinh u(x)\; 1\; dx \qquad (4.26e)$$

$$= -2\, n_i \int_o^{u_s} \sinh u(x)\; du/(du/dx)$$

Substitute $\frac{du}{dx} = -4\,(L_m n_i)^{1/2} \sinh(u/2)$ and recall $\sinh u = 2 \sinh u \cosh u$.

Therefore,

$$N = 2\,(n_i/L_m)^{1/2} \int_o^{u_s} + \cosh\frac{u}{2}\; d\left(\frac{u}{2}\right)$$

and

$$N = +2\,(n_i/L_m)^{1/2} \sinh(u_s/2) \qquad (4.26f)$$

Now if $u_s \geqq 8$, $\sinh 4 = \cosh 4 = 27 \gg 1$.

$$E = +2kT\,(n_i/L_m)^{1/2}\ \sinh u_s/2$$

Therefore

$$E = N\,kT \tag{4.26g}$$

To the approximation involved, the total energy stored in a volume with a cross section area 1 cm^2 throughout the negative space charge region is N kT when N electrons are transferred. If the positive space charge region is in the opposite plate of the capacitor, it is also an intrinsic semiconductor, it can be shown that $E = N_p\,kT$. Since $N_p = N$, the the total energy stored in the volume associated with 1 cm^2 cross section, with axis parallel to the field is $E_t = 2N\,kT$. That is, whenever one electron is transferred 2 kT energy is stored in the field of the capacitor.

Equation (4.26g) also implies that the energy stored in the negative space charge region is a product of kinetic energy and the number of excess particles in the volume concerned. Of course, we should not stress this further because the validity of having intrinsic semiconductors as the universal model is problematic. Nevertheless, Equation (4.26g) did not show any form of potential energy due to the bending of the energy band as shown in Figure 4.4.

From the above consideration, we propose an energy band diagram represented by Figure 4.5. That is the Fermi occupation probability function $1/\left[1 + \exp\frac{(E - E_f - Y)}{kT}\right]$ remains the same as before. We regard that instead of all the energy levels being bent down by Y(x), that the <u>effective</u> Fermi parameter is bent up by Y(x). That is, the Fermi occupation probability function is written as

$$F(E) = \frac{1}{1 + \exp\left\{\frac{E - (E_f + Y)}{kT}\right\}} \tag{4.27}$$

instead of

$$F(E) = \frac{1}{1 + \exp\left\{\frac{(E - Y) - E_f}{kT}\right\}} \tag{4.28}$$

And,

$$N(E)\, dE = \left(\frac{4\pi}{h^3}\right) (2m^*)^{3/2} \frac{(E-E_c)^{1/2}\, dE}{1 + \exp (E - E_f^*)/kT} \tag{4.29}$$

where

$$E_f^* = E_f + Y \tag{4.30}$$

$$\overline{E}_c(x') = \frac{\int_{E_c}^{\infty} \frac{E\,(E - E_c)^{3/2}\, dE}{1 + \exp(E - E_f^*)/kT}}{\int_{E_c}^{\infty} \frac{(E - E_c)^{1/2}\, dE}{1 + \exp (E - E_f^*)/kT}} \tag{4.28a}$$

Write $E = (E - E_c) + E_c$ and let $\lambda = \exp\left\{-(E_c - E_f^*)/kT\right\}$

$\xi = (E - E_c)/kT$

Then

$$\overline{E}_c(x') = E_c + \frac{\int_0^{\infty} \frac{\xi^{3/2}\, d\xi}{1 + \exp(\xi)/\lambda}}{\int_0^{\infty} \frac{\xi^{1/2}\, d\xi}{1 + \exp(\xi)/\lambda}} \tag{4.31}$$

if $\lambda \ll 1$, and since $\exp(\xi) \geq 1$, Equation (4.31) can be approximated as before to be

$$\overline{E}_c(x) = E_c + 3\, kT/2 \tag{4.32}$$

Therefore the average energy per particle is unchanged throughout the space charge region. The variation of the effective Fermi level, $E_f^* = E_{f,B} + Y(x)$, [36] adjusts the electron concentration in the space

charge region. By this model as represented by Figure 4.5, the aforementioned consideration can be resolved as follows:

(1) E_o is not changed.

(2) The energy per particle is constant.

(3) If we consider that all the N electrons are transferred into the conduction band, the energy stored in negative space charge region would be 3 NkT/2, but not NkT. The discrepency may be explained by the fact that the electrons are not all in the conduction band. Nevertheless, from the model represented by Figure 4.5, it is natural not to expect any involvement of potential energy in the energy stored in the field [see Equation (4.26g)].

With this proposed energy band diagram (Figure 4.5) for a space charge region, Y(x) can be redefined as

$$Y(x) = E_f^{*} - E_f^{(o)} \tag{4.33}$$

where $E_f^{(o)}$ is the Fermi energy parameter, or Fermi level where no space charge exists. Similarly Equation (4.19) can be written,

$$\Phi_{th} = E_o - E_f^{*} \tag{4.19b}$$

Note that Equation (4.19b) includes Equation (4.3) as a special case.

In concluding the above consideration, it is appropriate to say that the proposed energy band diagram in a space charge region, Figure 4.5, is not firmly established through the aforementioned considerations. It represents merely "thinking otherwise."

For the photoelectric threshold, Φ_{ph}, both Figure 4.4 and Figure 4.5 give the same results, namely, Φ_{ph} is independent to the diffusion potential, and Equation (4.4a) is the correct expression. This has been recently pointed out by Redfield,[21] and further experimental check is underway by him.

IDENTIFICATION OF SURFACE CHARGES

In the previous sections, the dependence of χ on surface dipoles and ϕ_{th} on the diffusion potential have been obtained. In Chapter 2, we have formulated the diffusion potential Y(x) and surface potential, $Y_s = Y(o)$, as functions of net surface charges $\Sigma_{\square}^{\pm}$, for all types of semiconductor. In this section the surface charges will be identified. According to the current knowledge on semiconductor surfaces[26-29, 37] there are two kinds of surface states, namely the fast surface states and slow surface states, both of which can become ionized and produce surface charges. Evidences have been established that the slow surface states with relaxation times from seconds to hours are dependent on the ambient atmosphere[26-28, 37] and are located at the outermost semiconductor surface. The fast surface states with relaxation times of the order of microseconds or milliseconds are independent of the ambient atmosphere.[26-28] It has been reported that most surface states are the slow states, which in turn determine the diffusion potential.[26-27]

In view of the above observations and the observation on the variation of work function on adsorption of gases and vapors,[6-11, 16] we are lead to believe that the slow surface states are the adsorbed species. As for the fast surface states many interpretations have been proposed, and a recent review of these theories is available.[37] According to this review, the exact origin of the fast surface states is not yet definitely established, but it is thought that these fast surface states are connected with structural defects of semiconductor surfaces. In view of the aforementioned observation that the fast surface states are independent of ambient atmosphere, they are not due to adsorption effects.

Let us define $[F^{\pm}]$ as the surface density of charged fast surface states, and $[D^{+}]$, $[A^{-}]$ are slow surface states, due to adsorption. Therefore

$$\Sigma_{\square}^{+} = [D^{+}] \pm [F^{\pm}] \quad (4.34)$$

and

$$\Sigma_{\square}^{-} = [A^{-}] \pm [F^{\mp}] \quad (4.35)$$

From the previous analysis, if $\Sigma_{\square}^{\pm} = 0$, the surface will be either completely free from charges or there are surface dipole layers only. If $\Sigma_{\square}^{\pm} \neq 0$, a space charge region will be generated with or without surface dipole layers. Now let us consider that at the beginning, the surface of a semiconductor is free from adsorbed species, only fast surface states exist, and $\Sigma_{\square}^{\pm} \neq 0$, in general. A space charge region exists in the semiconductor surface region, and the measured ϕ_{th} will not be the value which exists in the absence of a space charge region. Bardeen[38] and recently Gobeli and Allen[15] have used these concepts to explain the observed discrepencies in the observed ϕ_{th} value for n- and p-type semiconductors. They assumed that initially these fast surface states are ionized and a space charge region exists even at high vacuum. Now we shall consider these fast states in connection with slow states due to adions. There are two general cases:

Case i: Adions and fast surface states have same sign of charge.

In this case if initially there is no surface dipole and no adsorbed ions then the initial $\chi^{(o)}$, $\phi_{th}^{(o)}$ and $\phi_{ph}^{(o)}$ can be written down according to Equations (4.3b), (4.4b), and (4.19).

$$\chi = \chi^{(o)}$$

$$\phi_{th}^{(o)} = \chi^{(o)} + \phi_{n} - Y_{s}^{(o)} \quad (4.36)$$

$$\phi_{ph}^{(o)} = \chi^{(o)} + E_{g} \quad (4.37)$$

If the bulk properties $\phi_{n,B}$ and E_g are known, then $Y_s^{(o)}$ can be calculated from measurements of $\phi_{th}^{(o)}$ and $\phi_{ph}^{(o)}$. Through the application of the relations in Chapter 2, the net surface charge density in the fast states $[F^{\pm}]$, can be calculated. For example using Equations (4.36) and (4.37)

$$Y_s^{(o)} = \phi_{ph}^{(o)} - \phi_{th}^{(o)} - (E_g - \phi_n) \tag{4.38}$$

If the addition of adsorbed gases or vapors on the surface will produce adions with the same sign of charge as the initial fast surface states, then the total surface charge, $\Sigma_{\square}^{\pm}$, will be increased, the surface potential $Y_s^{(o)}$ will be increased to Y_s, then

$$\phi_{th} = \chi^{(o)} + \phi_n - Y_s \tag{4.39}$$

and

$$\phi_{ph} = \chi^{(o)} + E_g \tag{4.40}$$

From Equations (4.36)and (4.39)

$$\Delta\phi_{th} = \phi_{th} - \phi_{th}^{(o)} = -Y_s + Y_s^{(o)} \tag{4.41}$$

Therefore the measured incremental thermionic work function is linearly dependent on the surface potential with an additive constant $Y_s^{(o)}$. We shall return to this point in a following section.

Case ii: Adions and fast states have different sign of charge.

When the charges on the adions and ionized fast states are different, a surface dipole layer will be formed. Since, in general, the slow states due to adions are far more numerous, we shall consider this subcase first. The initial condition will be the same as that expressed by Equations (4.36) and (4.37) without adions on the surface. But as adsorption proceeds the fast states become traps, and the space charge region cannot be formed until all the fast state traps are filled. For the condition, that $\Sigma_{\square}^{\pm} = 0$, only a surface dipole layer is formed and the surface potential is zero.

$$\phi_{th} = \chi^{(o)} + \Delta\chi + \phi_n$$

$$\Delta\phi_{th} = \phi_{th} - \phi_{th}^{(o)} = \Delta\chi + Y_s^{(o)} \tag{4.42}$$

and

$$\phi_{ph} = \chi^{(o)} + \Delta\chi + E_g$$

$$\Delta\phi_{ph} = \phi_{ph} - \phi_{ph}^{(o)} = \Delta\chi \tag{4.43}$$

These equations have been presented by Redfield,[21] but he has not identified that the fast states and adions must have opposite signs.

Also, $\Delta\chi$ and $Y_s^{(o)}$ have the same sign, as can be seen from Equation (4.10) and the definition of $Y_s = Y(0)$ in Chapter 2 or Equation (4.33). For example, when the dipole layer produced has its positive charge directed outwards, $\Delta\chi$ is negative, initially the inside negative charge layer will produce a positive space charge region, and Y_s is negative. Therefore

$$|\Delta\phi_{th}| \geqq |\phi_{ph}| \tag{4.44}$$

The equal sign holds when the initial inside layer is unchanged. That is, they are simply empty traps.

For the general case, $\Sigma_{\square}^{\pm} \neq 0$, then

$$\phi_{th} = \chi^{(o)} + \Delta\chi + \phi_n - Y_s$$

and

$$\phi_{th}^{(o)} = \chi^{(o)} + \phi_n - Y_s^{o}$$

Therefore

$$\Delta\phi_{th} = \Delta\chi + Y_s^{(o)} - Y_s \tag{4.45}$$

For $\Delta\phi_{ph}$, Equation (4.43) is not changed according to Redfield.[21] Since $Y_s^{(o)}$ and Y_s have different signs, consequently the general relation is still valid.

COMPARISON WITH EXPERIMENT

In this section, we shall primarily explain the empirical results presented by S. Z. Roginsky[16] mentioned in the Introduction, because it represents a summary and review of many experimental observations. Firstly, we deem it a good attitude that one observation may be wrong, but not the trend of observations. Secondly, the trend of observations on

$\Delta\phi_{th}$ represented by S. Z. Roginsky[16] cannot be explained by the theories mentioned previously and the most recent and most refined dipole layer theory.[19] This is because the dipole layer theories are treating metal surfaces or highly conducting surfaces where there is no space charge region underneath the conducting solid surface.

To explain the observed trend of $\Delta\phi_{th}$ upon adsorption of gases or vapors, we assume that the reader is familiar with Chapter 2.[1]

From Equations (4.41) and (4.45), $\Delta\phi_{th}$ is a linear function of Y_s with an opposite sign. That is, when Y_s is positive, (a negative space charge region is generated), $\Delta\phi_{th}$ is negative, and vice versa. If $Y_s \gg \Delta\chi$ or $Y_s \gg \Delta\chi + Y_s^{o}$, then $\Delta\phi_{th}$ will be mainly due to the variation of Y_s. Let us first assume that it is so, and consider what will be the relation between $\Delta\phi_{th}$ and surface charges produced by adsorption of gases or vapors. Of course, this assumption implies that $[D^+] \gg [F^{\pm}]$ and $[A^-] \gg [F^{\pm}]$, so that the diffusion potential is determined entirely by the adsorbed species. For convenience of discussion, we divide it into two subsections.

I. Adsorption Which Generates An Accumulation Layer

In this subsection we shall discuss $[D^+]$ on intrinsic or n-type semiconductors and $[A^-]$ on intrinsic or p-type semiconductors. The following equations from Chapter 2 are needed for this discussion:

$$\sinh (u_s/2) = (L_m/n_i)^{1/2} (\Sigma_{\square}^{\pm})/2 \qquad (2.19)$$

$$\sinh (u_s/2) = (L_m/n_B)^{1/2} (\Sigma_{\square}^{+})/2 \qquad (2.35)$$

$$\sinh (u'_s/2) = (L_m/p_B)^{1/2} (\Sigma_{\square}^{-})/2 \qquad (2.36a)$$

where $u_s = Y_s/kT$; $u'_s = -Y_s/kT$. From these above equations, it is obvious that when $u_s/2 \gtrless 2$, the hypobolic sine can be approximated by an $\frac{1}{2} \exp (u_s/2)$. That is,

$$Y_s = u_s kT = kT\ln\left[(L_m/n_i)(\Sigma_{\Box}^{\pm})^2\right] \quad (4.46)$$

$$Y_s = u_s kT = kT\ln\left[(L_m/n_B)(\Sigma_{\Box}^{+})^2\right] \quad (4.46a)$$

$$Y_s' = u_s kT = kT\ln\left[(L_m/p_B)(\Sigma_{\Box}^{-})^2\right] \quad (4.46b)$$

Since from the assumption that $[D^+] \gg [F^{\pm}]$, and $[A^-] \gg [F^{\pm}]$, $\Sigma_{\Box}^{+}$ should be replaced by $[D^+]$ or $[A^-]$. From Equations (4.41) and (4.45), since $|Y_s| \gg |\Delta\chi + Y_s^o|$, it follows that for surface donors on an intrinsic semiconductor

$$\Delta\phi_{th} = -kT\ln\left[(L_m/n_i)[D^+]^2\right] + \text{constant} \quad (4.47)$$

for surface acceptors on an intrinsic semiconductor

$$\Delta\phi_{th} = kT\ln\left[(L_m/n_i)[A^-]^2\right] + \text{constant} \quad (4.47a)$$

for surface donors on an n-type semiconductor

$$\Delta\phi_{th} = -kT\ln\left[(L_m/n_B)[D^+]^2\right] + \text{constant} \quad (4.48)$$

for surface acceptors on a p-type semiconductor

$$\Delta\phi_{th} = kT\ln\left[(L_m/p_B)[A^-]^2\right] + \text{constant} \quad (4.48a)$$

From these equations, it is clear that the dependence of ϕ_{th} on $[D^+]$ or $[A^-]$ is logarithmic and further that $\Delta\phi_{th} > kT$, when an accumulation space charge is created in a semiconductor.

Since in experimental practice the data is presented by plotting the total amount of gas adsorbed, θ, a discussion of the relation between charged and uncharged species is in order. For simplicity of representation we shall discuss the case of donors on n-type semiconductor. The other cases follow in analogy and will not be discussed. To start we shall assume that

$$\theta = [D] + [D^+] \quad (4.49)$$

Two extreme cases immediately follow from Equation (4.49). Namely, when $[D^+] \gg [D]$

$$\theta = [D^+] \tag{4.50}$$

or when

$$[D] \gg [D^+] \tag{4.51}$$

and there is an equilibrium between $[D]$ and $[D^+]$, then from Chapter 5[39]

$$[D^+] = \text{constant } [D]^{1/3} \tag{4.51a}$$

That is,

$$[D^+] = \bar{K}\,\theta^{1/3} \tag{4.52}$$

where $\bar{K}$ is a constant independent of θ.

If Equation (4.48) is expanded we have,

$$\Delta\phi_{th} = -2kT \ln [D^+] + kT \ln (n_i/L_m) + \text{constant} \tag{4.53}$$

By substitution of Equation (4.50) into Equation (4.53), we obtain

$$\Delta\phi_{th} = -2kT \ln \theta + \text{constant} \tag{4.53a}$$

Substitution of Equation (4.52) into Equation (4.53),

$$\Delta\phi_{th} = -\frac{2}{3} kT \ln \theta + \text{constant} \tag{4.53b}$$

For the cases between these two above extremes, it is reasonable to expect that

$$\Delta\phi_{th} = -mkT \ln \theta + \text{constant} \tag{4.54}$$

where m should vary between 2 and 2/3, namely

$$2/3 \leq m \leq 2 \tag{4.55}$$

Therefore this model not only predicts that the relation between $\Delta\phi_{th}$ and θ should be logarithmic but also predicts that the slope of $\Delta\phi_{th}$ versus $\ln \theta$ plot should have a limited range of values expressed by Equation (4.55). Roginsky[16] did not report slope. Figure 4.6 for C_3H_7OH (a donor) on ZnO (n-type) and Figure 4.7 for oxygen (acceptor) on NiO (p-type) are from Enikeev.[12] Figure 4.6 gives $m = 1.4$,

Figure 4.7 gives $m = 0.98$, which are within the limits predicted by Equation (4.55). Inspecting Figures 4.6 and 4.7 for the possible cause or causes for the decrease of "m," we see that one apparent reason is that the data represented by Figure 4.7 has a higher range of coverage. This is plausible since the higher the coverage, equilibrium condition expressed by Equation (4.51a) should be approached. Although we have no assurance for the degree of approach to equilibrium at high coverage in Figure 4.7, nevertheless high coverage is a plausible explanation.

II. Adsorption Which Generates A Depletion-Inversion Layer

When donors are adsorbed on p-type semiconductors or acceptors on n-type semiconductors a depletion or an inversion space charge region will be generated. From Chapter 2, the dependence of Y_s on $\Sigma_{\square}^{\pm}$ is given by several simple functions. The mid-range of depletion-inversion region can be represented by a linear equation of the form

$$u_s = Y_s/kT = m' \left[(L_m/p_B)^{1/2} (\Sigma_{\square}^{+}) \right] - \text{constant} \qquad (2.71)$$

The range of u_s which can be approximated by this linear function, is determined by u_B, which is determined by the bulk carrier concentration by the defining equation,

$$u_B = \ln (p_B/n_i)$$

For the oxide semiconductors such as ZnO, CuO, we have no knowledge of the respective values for u_B in each case.

Data presented in Figures 4.8 and 4.9 are from Enikeev[10] for donors, C_3H_6, on a p-type semiconductor, CuO; and acceptors, O_2, on an n-type semiconductor ZnO, respectively. These figures have a low coverage, θ, which agree with Figure 2.4 in Chapter 2. Figure 2.4 of Chapter 2 has also predicted that if the adsorption is followed up to

higher coverage, Y_s and consequently Φ_{th} will deviate from linearity. The range for the linearity of the thermionic work function variations is about 2 $(u'_B + 1)$ kT ev. Here again, the extreme case of complete ionization given by Eq. (4.50) must be valid in order to obtain a linear function between $\Delta\Phi_{th}$ and θ. Other data which show these same trends are reported by Enikeev, Roginsky and Rufov.[13]

In concluding this subsection, we should say that for complete check of the theory, the adsorption must be followed up to a higher coverage to see how $\Delta\Phi_{th}$ deviates from linearity and whether or not it follows the other predictions of Figure 2.4 in Chapter 2. Nevertheless, this model explains why there should be a linear relation between $\Delta\Phi_{th}$ and θ for the adsorption of gases or vapors associated with the depletion-inversion space charge region in semiconductors.

Other work which apparently does not follow the trend summarized by Roginsky has also been reported by Law.[14] Briefly, this work reported that adsorption of oxygen on p-type silicon will change the contact potential difference between silicon and molybdenum oxide by several tenths of a volt and "is a linear function of θ up to values of θ greater than 0.9 . . ." For the adsorption of hydrogen on p-type silicon Law reported that the thermionic work function of silicon first decreased and then increased. All these observations were explained on the basis of simple dipole layers. The most controversial point is that a plot of $\Delta\Phi_{th}$ versus θ for oxygen adsorbed on p-type silicon is linear. Since oxygen is an acceptor, it is expected that an accumulation space charge region would be generated in the surface region of silicon. According to the analysis in subsection I. above, the relationship between $\Delta\Phi_{th}$ and θ should be logarithmic rather than linear as reported. Now then, how could we resolve this controversy?

A careful analysis of Law's observations shows that "a clean silicon surface is more strongly p-type than the bulk" and so strong that oxygen adsorbed as $[O^-]$ or $[O_2^-]$ is negligible. This is manifested from the fact that "the adsorption of a monolayer of oxygen (4 x 10^{-5} mm of Hg x min.) produced a very small <u>increase</u> in surface conductance ($\Delta\sigma_s$), equal to 1 μ mho/$\square$; because small temperature fluctuations produced changes in the bulk sample conductance equivalent to 0.25 μ mho/$\square$, we were unable to obtain sufficient precise data to plot surface conductance vs. surface coverage." In Chapter 3,[40] Figure 3.3, the dependence of $\Delta\sigma_s$ in μ mho/$\square$, has been plotted as a function of surface ion concentration. According to this plot, there should have a great surface conductance increase, if there were a monolayer of $[O^-]$ or $[O_2^-]$ as reported.[14] This consideration lead us to conclude that oxygen was not adsorbed to a significant amount as $[O^-]$ or $[O_2^-]$. Therefore the thermionic work function change was negligible. The reported contact potential difference between silicon and the molybdenum oxide reference electrode is due to the adsorption of oxygen on molybdenum oxide as $[O_2^-]$. Since the stable molybdenum oxide, MoO_3, is an n-type semiconductor,[40] a depletion-inversion space charge could be produced due to the adsorption of oxygen as negative ions. Therefore, the linear dependence of the contact potential difference between silicon and MoO_3 on the amount of oxygen adsorbed measured by the product of oxygen pressure and time interval follows the trend presented by Roginsky. Other observations reported in reference 14 will not be emphasized due to the possible covariance of the reference and the silicon surfaces.

In concluding the comparison of the observed dependence of $\Delta\phi_{th}$ on θ, it is appropriate to say that the trend summarized by Roginsky is fully explained by this model. This implies that the relation,

$|Y_s| \gg |\Delta\chi + Y_s^o|$, is generally valid. In other words, $\Delta\phi_{th}$ is determined by the surface potential, Y_s, which in turn is determined by the adsorbed ions. This confirms the observation that the density of the ambient dependent slow states "is so high that they effectively determine the position of the Fermi level at the surface after equilibrium has been established."[27] This fact has been known since 1953 when Brattain and Bardeen[2] had used different ambient cycle to study the "surface properties of germanium."

There is no definite trend established yet for the variation of $\Delta\phi_{ph}$ as function of adsorption. Reported observations in the literature sometimes showed an opposite trend.[5, 8] Equation (4.43) was due to Redfield,[21] who was lead by some unexpected experimental observations in photoemission measurements on vacuum heat-treated germanium. As "it has been pointed out by Bardeen that . . . . if the threshold corresponds to photoemission of electrons from surface states at the Fermi level rather than from the valence band states,"[39] a deeper consideration and analysis of the origin of the photoemitted electrons may be necessary. Therefore Equation (4.43) was written down with reservation.

CONCLUSIONS

This paper explains the observed dependence of $\Delta\phi_{th}$ on θ through the formulations of Chapter 2. Consequently we have presented a new theory for the dependence of thermionic work function on surface charges on the one hand, and verified the previous formulations and approximations on the other hand.

For the variation of $\Delta\phi_{ph}$ on adsorption of gases or vapors, reported observations indicated the need of deeper consideration. The relation, $\Delta\phi_{ph} = \Delta\chi$, due to Redfield, is considered with reservation.

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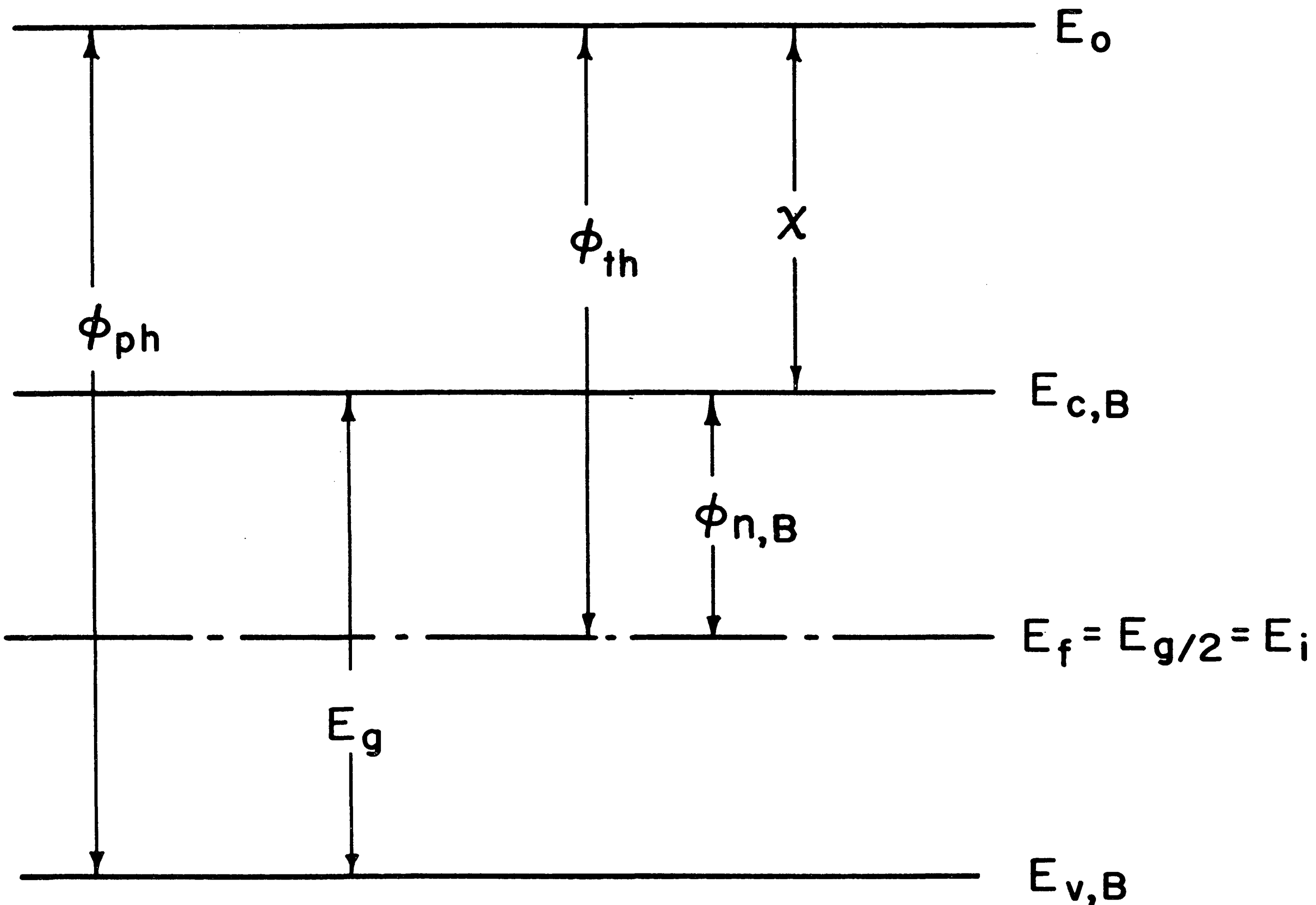

Figure 4. 1 Illustration of definitions at clean straight-band condition of a non-degenerate semiconductor.

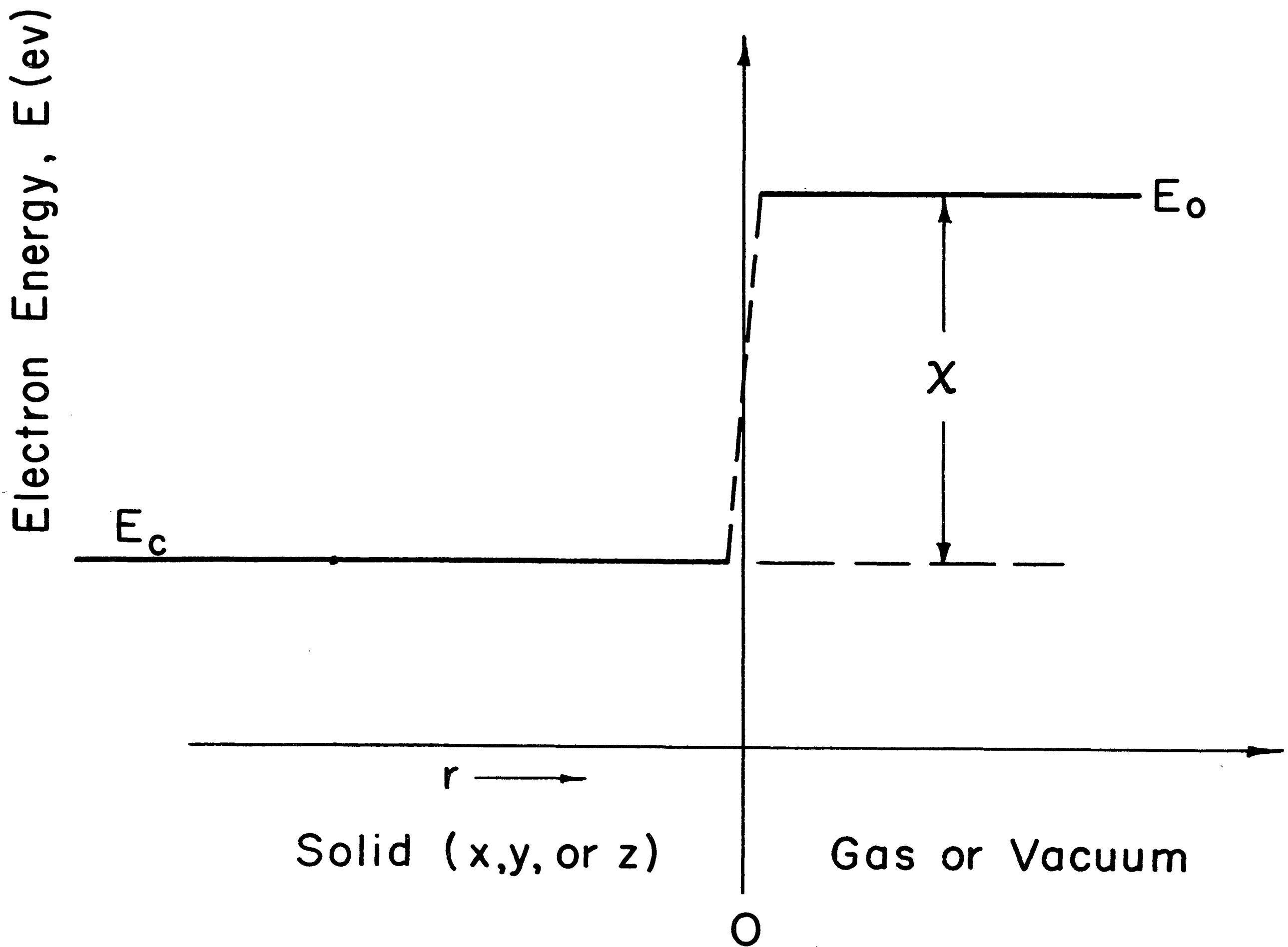

Figure 4.2 Illustration of potential energy barrier for the conduction electrons in a semiconductor at the surface.

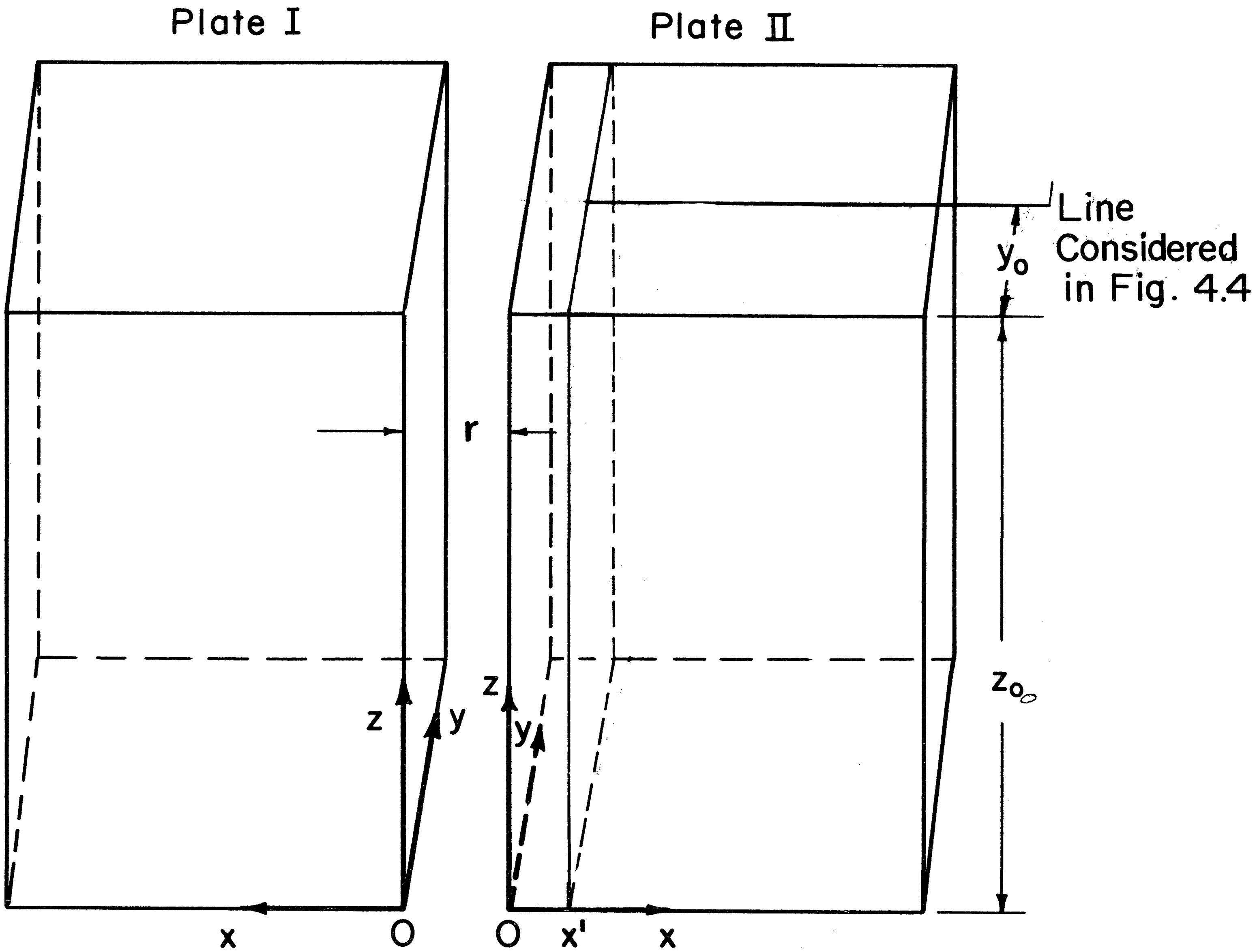

Figure 4.3 Illustration of model to analyze effect of diffusion potential on Φ_{th} and Φ_{ph}.

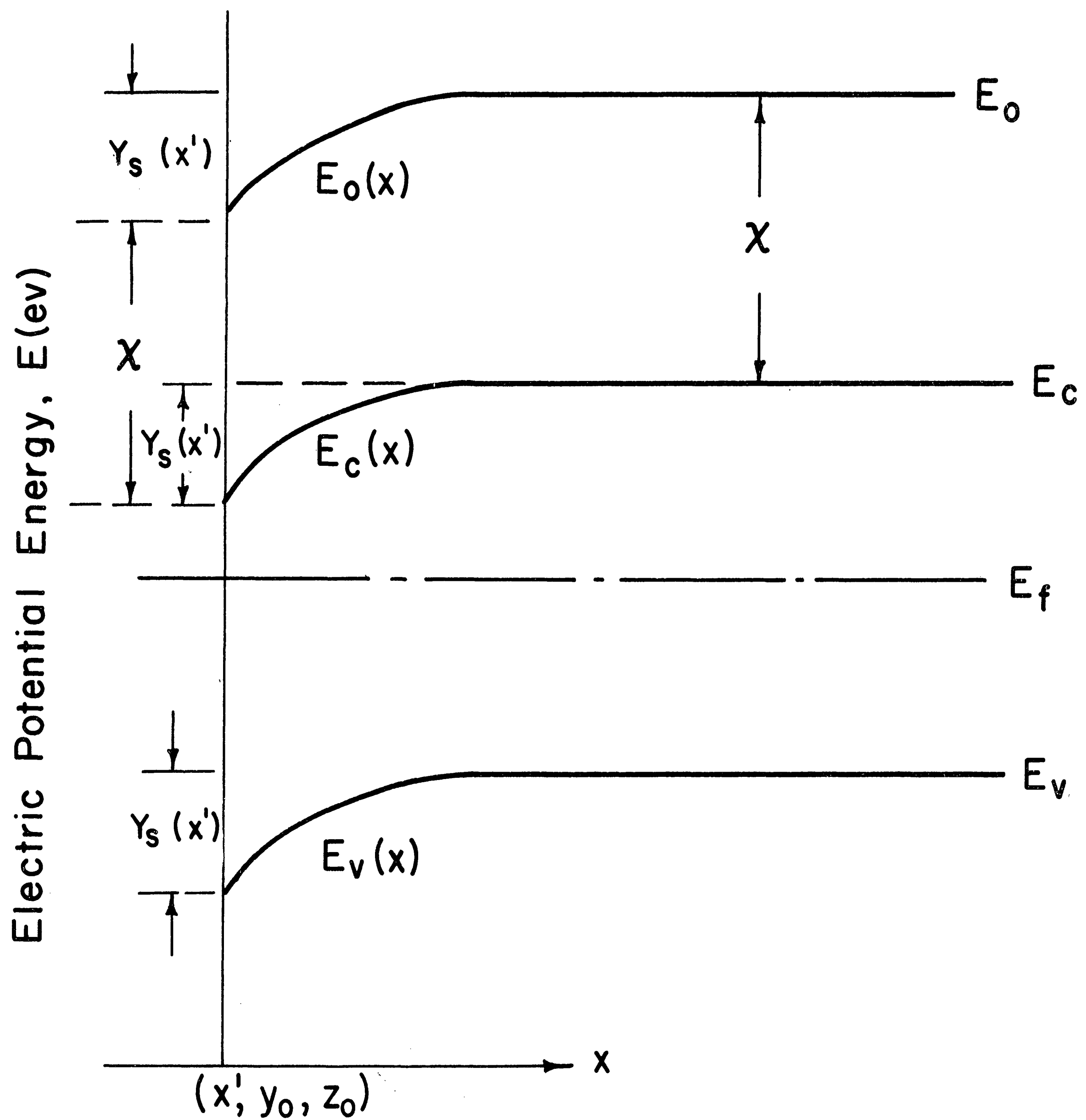

Figure 4.4 Generally accepted view of the variation of energy bands and surface potential, Y_s(x') induced by a varying negative space charge region along the line indicated in Figure 4.3.

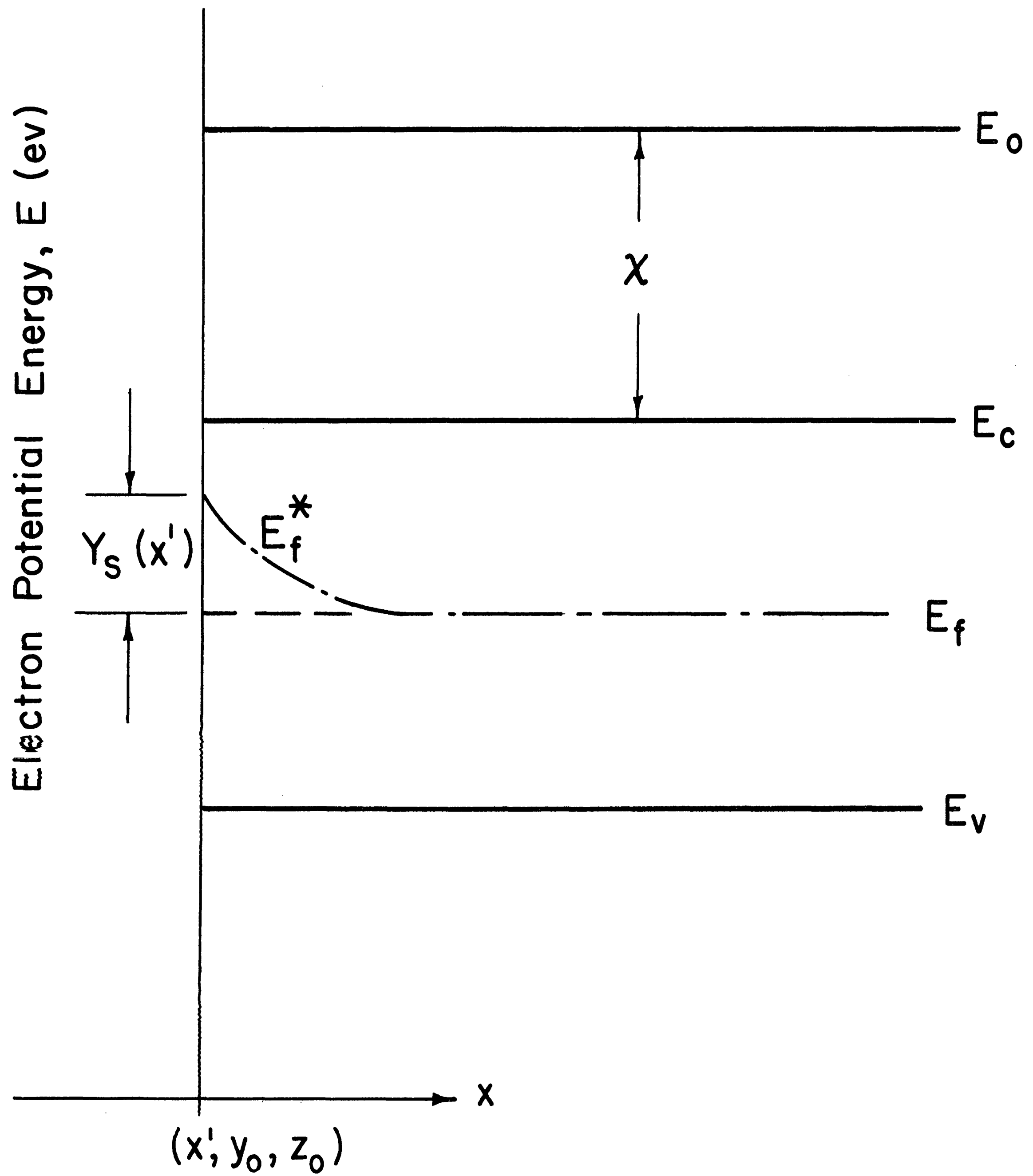

Figure 4.5 Alternate energy band diagram proposed in this chapter induced by a varying negative space charge region along the line indicated in Figure 4.3.

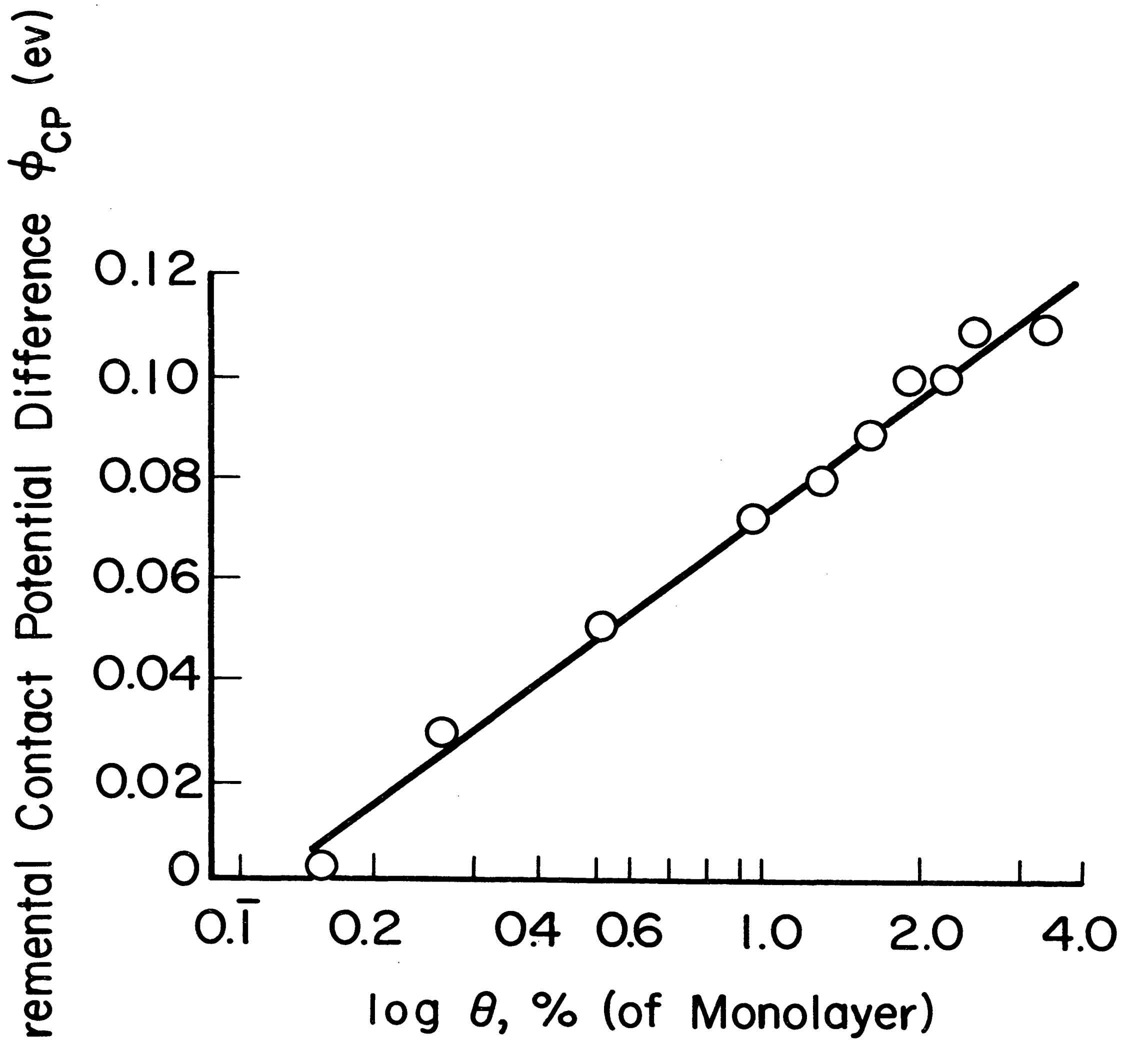

Figure 4.6 Variation of contact potential (work function) of ZnO (n-type) as function of amount of adsorbed iso-propyl alcohol (donor) at 293°K where $\Phi_{CP} = (\Phi_{ref} - \Phi_{ZnO})$.

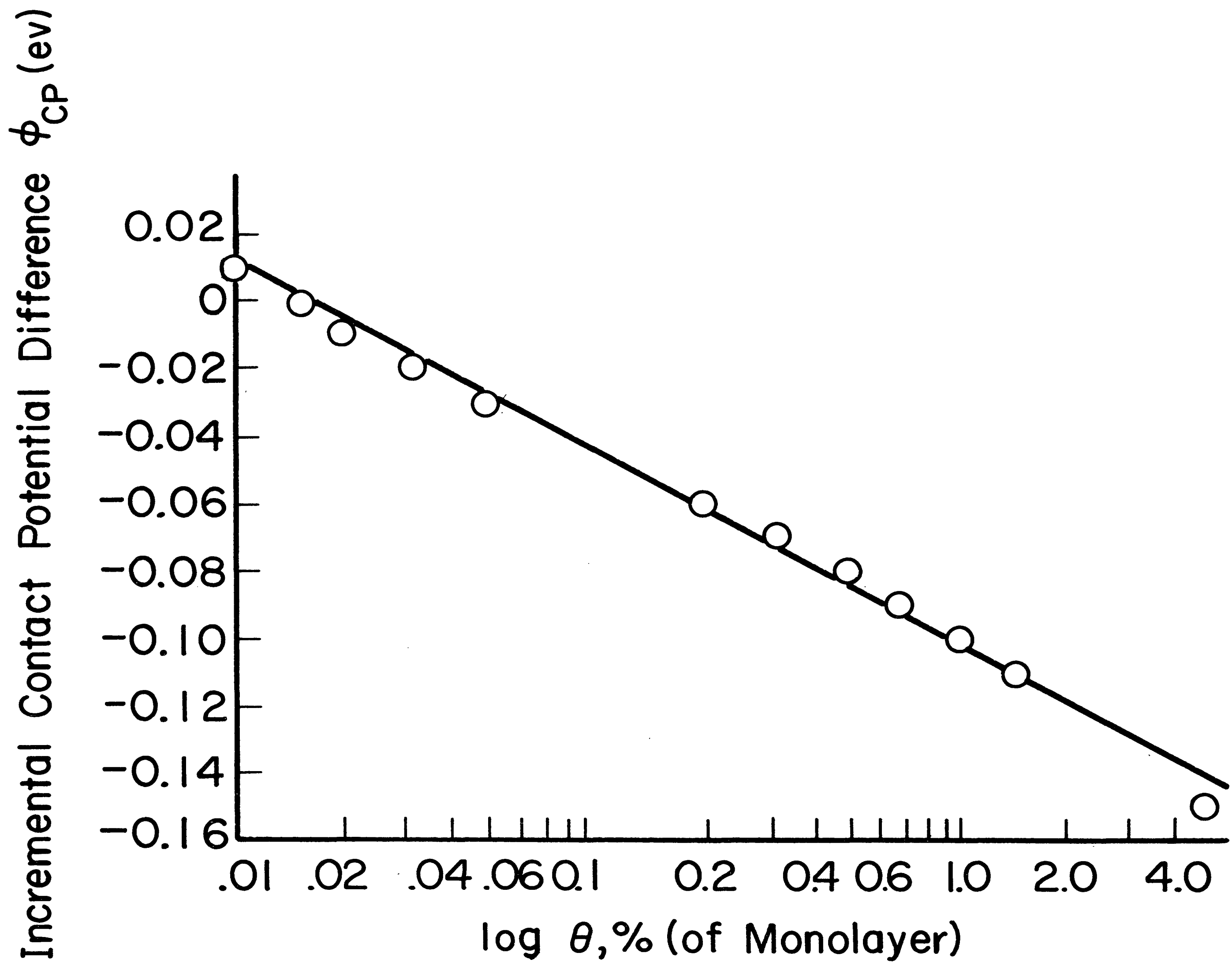

Figure 4.7 Variation of contact potential (work function) of NiO (p-type) as function of amount of adsorbed oxygen (acceptor) at 293°K where $\phi_{CP} = (\phi_{ref} - \phi_{NiO})$.

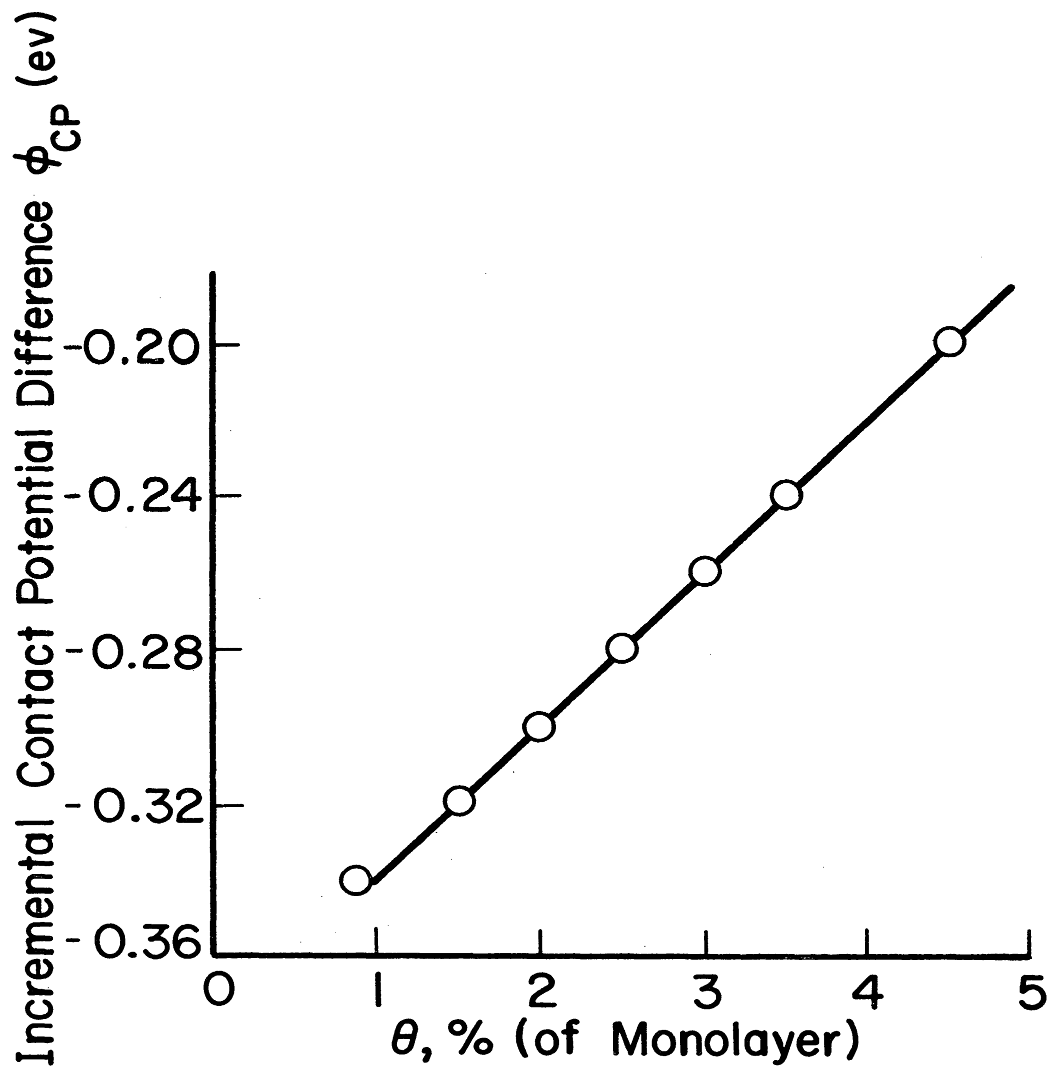

Figure 4.8 Variation of contact potential (work function) of CuO (p-type) as function of amount of adsorbed C_3H_6 (donor) at 80°C where $\phi_{CP} = (\phi_{ref} - \phi_{CuO})$.

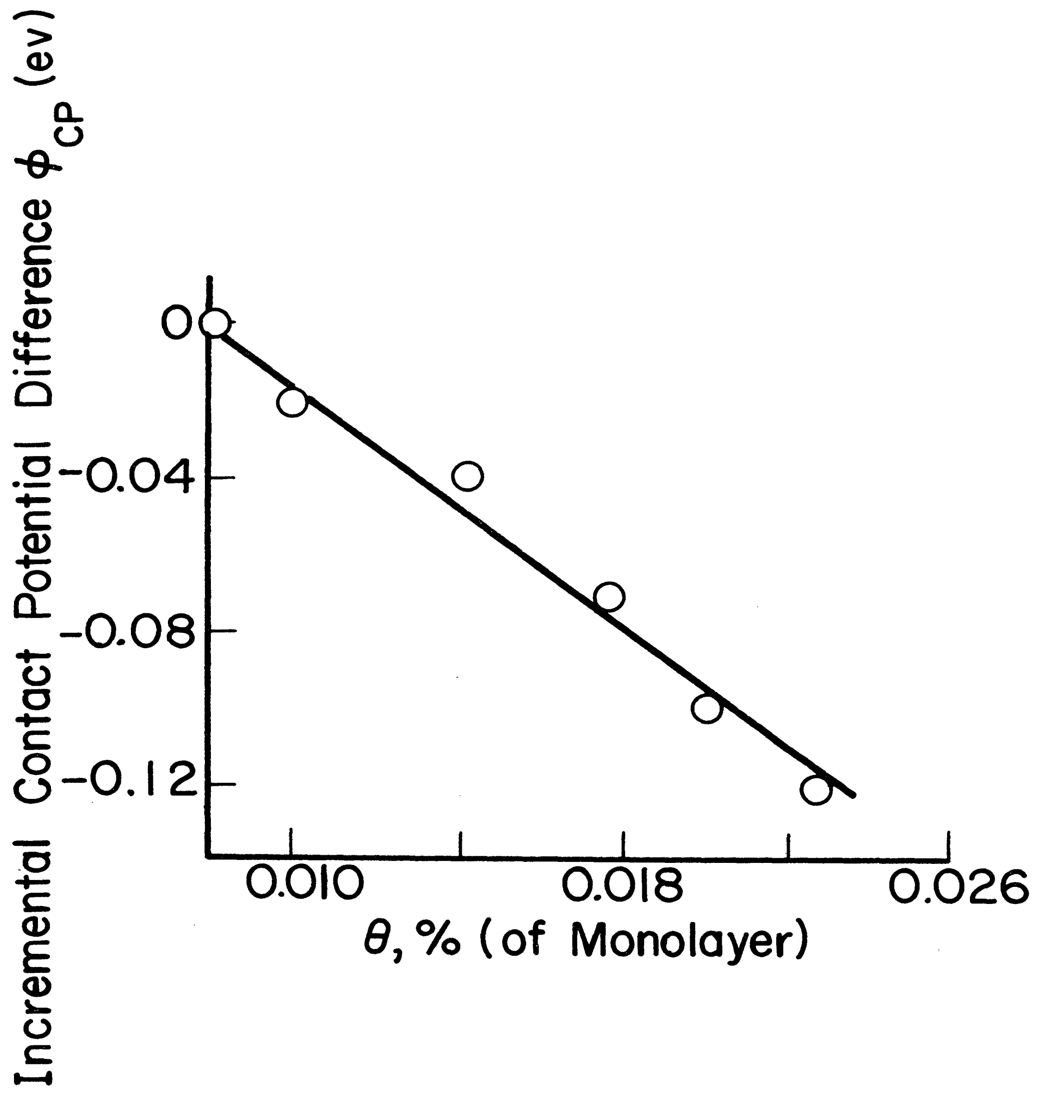

Figure 4.9 Variation of contact potential (work function) of ZnO (n-type) as function of amount of adsorbed O_2 (acceptor) at 293°K where $\Phi_{CP} = (\Phi_{ref} - \Phi_{ZnO})$.