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Abstract

Full Text

Physical Chemistry

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ELECTRONIC THEORY OF THE ADHESION OF METALS JOINED BY A SEMICONDUCTING INTERLAYER

In works (^{1}) it was shown that electrostatic forces, in a wide class of phenomena, play a decisive role in adhesion. In work (^{2}) a consideration was given of the electrostatic component of the adhesion force at a semiconductor-metal boundary, arising owing to the presence of a double layer, on the basis of the modern theory of the semiconductor-metal contact. However, the study of the double layer and, correspondingly, of the adhesion force for a thin semiconducting interlayer enclosed between two, in the general case different, metals—a study of considerable practical interest—was carried out mainly qualitatively.

Using the mathematical identity of the problem with that of the electrostatic interaction of two unequally charged surfaces separated by an electrolyte layer, developed in the theory of heterocoagulation and of colloids, we shall obtain a rigorous solution.

As in work (^{2}), we shall restrict ourselves to consideration of the case in which carriers of only one kind are present in the semiconductor, and only a small fraction of the impurity centers is ionized. As is known, in this case the equilibrium distribution of charges is determined by the Poisson-Boltzmann equation

$$\frac{d^2\widetilde{V}}{dx^2} = \varkappa^2 \operatorname{sh} \widetilde{V}, \tag{1}$$

where $\widetilde{V}$ is the dimensionless potential energy of an electron in the conduction band, $\widetilde{V} = eV/kT$, $\varkappa = \sqrt{8\pi n_\infty e^2/\varepsilon kT}$ is the reciprocal screening length, ε is the dielectric constant, and n_∞ is the concentration of conduction electrons in a free semiconductor. The adhesion force of the film to each metal is equal to $F = \varepsilon^2 E_{\mathrm{gr}}^2/8\pi$, where E_{gr} is the field strength inside the semiconductor at the boundary with the corresponding metal. Thus the problem consists in determining E at the right and left boundaries of the film.

Fig. 1

Fig. 2

Figure 1: Fig. 2

It is clear in advance that, when the thickness of the semiconductor film is of the order of $1/\varkappa$, so that the double electric layers arising at the boundaries with the metals overlap, $E(0)$ and $E(l)$ are functions of the film thickness l.

Let us denote by φ_{mA}, φ_{pp}, and φ_{mB} the work functions of metal A, the semiconductor, and metal B (Fig. 1, where φ is the potential energy, μ is the Fermi level). Then the boundary conditions for equation (1) have the form

$$\widetilde{V}(0) = e(\varphi_{\mathrm{mA}} - \varphi_{\mathrm{pp}})/kT, \qquad \widetilde{V}(l) = e(\varphi_{\mathrm{mB}} - \varphi_{\mathrm{pp}})/kT. \tag{2}$$

Although Fig. 1 presents the case in which the work functions of both metals are greater than the work function of the semiconductor, the mathematical solution of the problem is carried out without this specialization. It should be noted, however, that the case presented in Fig. 1 is the most interesting for analysis, since

as if $\varphi_{mA} < \varphi \ < \varphi_{mB}$ (Fig. 2), then it is clear that the field strength at the right and left ends of the film increases as its thickness decreases, since the potential difference between the left and right boundaries is a constant quantity. Equation (1), with conditions (2), is absolutely identical to the formulation of the problem in the theory of heterocoagulation of colloids for the case of interaction through a binary symmetric electrolyte. The physical reasons for this analogy are quite clear, and we shall not dwell on them.

Fig. 2

A certain difference consists in the following. The force of interaction through an electrolyte of two flat plates charged to potentials φ_1 and φ_2 and separated by a distance l is determined by the expression

$$F(l) = \frac{\varepsilon}{8\pi}\left[E_2^2(0) - E_1^2(0)\right] = \frac{\varepsilon}{8\pi}\left[E_2^2(l) - E_1^2(l)\right], \tag{3}$$

where E_2 and E_1 are the field strengths at the outer and inner surfaces of the plates.

In our case the role of the charged plates is played by the metal surfaces; however, the force of adhesion, equal to $F\ (l) = \varepsilon E^2/8\pi$, is to be determined. Translating into the language of the theory of heterocoagulation, F is the force acting on the inner surface of the plate. In this case, naturally, $F\ (0) \neq F\ (l)$. Let us clarify what physical meaning E_2 has in our problem (in the theory of heterocoagulation, it is the force acting on the outer side of the charged plate). E_2 is easily determined as the first integral of equation (1), with the potential at

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Fig. 3

Figure 2: Fig. 3

infinity equal to zero and on the plate surface equal to the prescribed value (Fig. 3).

Fig. 3

In our problem $E_2(0)$ and $E_2(l)$, consequently, determine the force of adhesion of an infinite semiconductor to metal A and B, respectively, since the solution of equation (1) with the conditions $\widetilde{V}(0) = e[\varphi_M - \varphi\ ]/kT$, $\widetilde{V}(\infty) = 0$ corresponds precisely to this case. In connection with this, the analogue of the force of interaction of two plates in our problem will be the change in the force of adhesion of the film to metal A or B in comparison with the adhesion of an infinite semiconductor layer to the same metal.

From what has been said one may immediately conclude that, when the film thickness is varied, the change in the force of adhesion is the same for both metals. Indeed, the fact that

$$F(0) = \varepsilon/8\pi \left[E_2^2(0) - E_1^2(0)\right] = F(l) = \frac{\varepsilon}{8\pi}\left[E_2^2(l) - E_1^2(l)\right], \tag{4}$$

in the theory of heterocoagulation was simply a statement of Newton' s third law and followed naturally from the solution of equation (1) with conditions (2) (see ([3,4])). Since our problem, as already indicated, is mathematically absolutely identical to it, equality (4) also holds, although its physical content is now somewhat different. In what follows we shall investigate precisely the quantity

$$\Delta F \ = \frac{\varepsilon^2}{8\pi}\left[E_{mA\infty}^2 - E^2(0)\right] = \frac{\varepsilon^2}{8\pi}\left[E_{mB\infty}^2 - E^2(l)\right], \tag{5}$$

where $E_{\mathrm{mA}\infty}, E_{\mathrm{mB}\infty}$ are the field strengths at the boundary of an infinite semiconductor layer with metals A and B, respectively. First, because, as shown in the theory of heterocoagulation, in solving equation (1) with conditions (2) it is very convenient to determine precisely (5), and, second, in order to preserve the analogy and to be able, relying on it, to use the results found earlier.

From what has been said it is clear that the subsequent mathematical analysis is a repetition of work on the theory of heterocoagulation ([3]). It is convenient to reduce equation (1) to dimensionless form by introducing the variable $\nu = \varkappa x$. Then we obtain

$$d^2\tilde{V}/d\nu^2 = \operatorname{sh}\tilde{V}, \tag{6}$$

whence

$$(d\tilde{V}/d\nu)^2 = \operatorname{ch}\tilde{V} - C. \tag{7}$$

The integration constant C is determined so that the value ν_2, corresponding to the potential $\tilde{V}_2 = e[\varphi_{\mathrm{mB}} - \varphi_{\mathrm{p.p}}]/kT$, under the condition that at $\nu = 0$, $\tilde{V}_1 = e[\varphi_{\mathrm{mA}} - \varphi_{\mathrm{p.p}}]/kT$, is equal to $\varkappa l = H$.

As shown in the theory of heterocoagulation, the repulsion between plates per unit area, and in our case the change in the adhesion force, is equal to

$$\Delta F_{\mathrm{ad}} = \varepsilon k T n(\infty)\omega = C - 2. \tag{8}$$

The relation between H and ω for particular values of the parameters $\tilde{V}_1$ and $\tilde{V}_2$ has been established in the theory of heterocoagulation (see (^{3})). We shall give here the principal results, referring for their derivation to (^{3}). Let us first note that a positive value of the dimensionless force ω, corresponding in the theory of heterocoagulation to repulsion of the plates, in our case means a decrease in adhesion, while a negative value of ω (corresponding to attraction) means an increase in the adhesion of the semiconductor film.

1. In the case where $\tilde{V}_1$ and $\tilde{V}_2$ have different signs (the work function of one of the metals is greater, and that of the other is less, than the work function of the semiconductor), ω is negative for all values of H and increases monotonically in absolute value as H decreases.

As $H \to 0$, ω tends to negative infinity in accordance with the asymptotic law

$$\omega \approx -(\tilde{V}_2 - \tilde{V}_1)^2/H^2. \tag{9}$$

The relation between H and ω is given by the elliptic integral

$$H = \int_{\tilde{V}_1}^{\tilde{V}_2} \frac{d\tilde{V}}{\sqrt{4\operatorname{sh}^2\tilde{V} - \omega}}, \qquad \omega < 0. \tag{10}$$

Consequently, the adhesion of the film increases monotonically as H decreases.

2. In the case where $\tilde{V}_1$ and $\tilde{V}_2$ have the same sign, the dependence of ω on H is represented schematically by the following graph (Fig. 4). Here the adhesion force at first decreases as H decreases. At a certain value H_m, the decrease in the adhesion force reaches a maximum in absolute magnitude, after which the adhesion begins to increase; at $H = H_0$ it reaches the adhesion value of an infinite semiconductor layer, and with further decrease of H continues to increase monotonically. The region $\omega < 0$ is described by formulas (9) and (10) given above. The maximum decrease in the adhesion force ω_m is determined by the expression

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Fig. 4

Figure 3: Fig. 4

$$\omega_m = 4\,\mathrm{sh}^2(\widetilde{V}_{\min}/2), \tag{11}$$

where $\widetilde{V}_{\min}$ denotes the smaller, in absolute value, of the numbers $\widetilde{V}_1$ and $\widetilde{V}_2$. Thus, the maximum decrease in the adhesion force is determined only by that one of the metals whose work function differs less from the work function of the semiconductor, and is completely independent of the other.

The value H_0 at which ω changes sign is equal to

$$H_0 = \int_{\widetilde{V}_1}^{\widetilde{V}_2} \frac{d\widetilde{V}}{2\,\mathrm{sh}(\widetilde{V}/2)} = \frac{1}{2}\ln\left\{\frac{\left(e^{\widetilde{V}_2/2}-1\right)\left(e^{\widetilde{V}_1/2}+1\right)}{\left(e^{\widetilde{V}_2/2}+1\right)\left(e^{\widetilde{V}_1/2}-1\right)}\right\}, \qquad \widetilde{V}_1 < \widetilde{V}_2 \tag{12}$$

Fig. 4

The thickness H_m corresponding to the minimum of the adhesion force is equal to

$$H_m = \frac{1}{\sqrt{2}}\int_{\widetilde{V}_1}^{\widetilde{V}_2} \frac{d\widetilde{V}}{\sqrt{\mathrm{ch}\,\widetilde{V} - \mathrm{ch}\,\widetilde{V}_1}}, \qquad \widetilde{V}_1 < \widetilde{V}_2. \tag{13}$$

The elliptic integral (13) is reduced to the form

$$H_m = k\int_{u_0}^{1} \frac{du}{\sqrt{(1-u^2)(1-k^2u^2)}}, \tag{14}$$

where

$$k = \frac{1}{\mathrm{ch}(\widetilde{V}_1/2)}, \qquad u_0 = \frac{\mathrm{ch}(\widetilde{V}_1/2)}{\mathrm{ch}(\widetilde{V}_2/2)}, \qquad \widetilde{V}_1 < \widetilde{V}_2. \tag{15}$$

As is seen from Fig. 4, each value of ω (except, of course, ω_m) greater than 0 can be realized at two different values of H. The analytic expression determining the relation between H and ω is given in [3]. The relation between H and ω is determined by elliptic integrals, and therefore the numerical determination of ω as a function of H and of the parameters $\widetilde{V}_1$ and $\widetilde{V}_2$ requires tabulation. A number of graphs expressing the dependence of ω on H are given in [3].

One of the most interesting conclusions appears to us to be the fact that, with a sufficient decrease in the thickness of the film enclosed between two dissimilar metallic surfaces, it is always possible to obtain an increase in the density of the double layer and, correspondingly, in the adhesion force. It is possible that one of the reasons for the increase in adhesion of thin adhesive interlayers as their thickness decreases is connected precisely with this circumstance. It should be noted, however, that in our calculations we have throughout assumed a small depletion of impurity centers, although with a considerable decrease in the film thickness the depletion will become very significant. This will lead to the adhesion force increasing not without bound, but only up to a certain finite value. Another important factor determining the adhesion forces may be the presence of surface states. Consideration of these circumstances is planned for the future.

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REFERENCES

1. B. V. Deryagin, N. A. Krotova, *Adhesion*, Publishing House of the Academy of Sciences of the USSR, 1949; B. V. Deryagin, N. A. Krotova, DAN, 61, No. 5 (1948).

2. V. B. Sandomirskii, V. P. Smilga, ZhTF (in press).

3. B. V. Deryagin, *Kolloid. zhurn.*, 16, issue 6 (1954); B. V. Deryagin, V. G. Levich, DAN, 98, No. 6 (1954).

4. B. V. Deryagin, Izv. AN SSSR, OMEN, ser. khim., 5, 1153 (1937); *Acta Physicochim. URSS*, 10, 333 (1939); *Trans. Farad. Soc.*, 36, 1, 203 (1940); 36, 2, 730 (1940); *Kolloid. zhurn.*, 6, 291 (1940); 7, 285 (1941); B. V. Deryagin, L. D. Landau, ZhETF, 2, 802 (1941); ZhETF, 15, 662 (1945).

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