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Abstract

Full Text

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THE ROLE OF THE SURFACE PROPERTIES OF A SEMICONDUCTOR IN ADHESION PHENOMENA

In works ([1]-[3]) the electrostatic component of the adhesion force at a metal-dielectric contact ([1], [2]) and a semiconductor-metal contact ([3]) was considered. The presence of considerable electric fields at the boundary between solids, under certain conditions, may lead to practically significant values of the adhesion force between solids, of the order of several kilograms per square centimeter. In these calculations, however, the presence of surface states in the semiconductor was not taken into account. Meanwhile, taking them into account appears to be extremely interesting. It is easy to see that, in order for the electrostatic component of the adhesion force to reach values of the order of tens of kilograms per square centimeter, corresponding to the adhesive strength of industrial glues, it is necessary that the values of the electric field at the metal-semiconductor boundary reach several million volts per centimeter—a case unlikely for a metal-semiconductor contact without surface states.

On the other hand, at the contact of two metals precisely such fields arise at the boundary, as is readily verified from simple calculations. When two dissimilar metals are separated, the electrostatic component of the adhesion forces may fail to manifest itself, since, owing to the high conductivity, charges flow from already separated regions to those still in contact (simultaneous separation over the entire contact plane, naturally, never occurs). If, however, the conductivity were negligibly small and no such recombination of charges occurred, there would be a very considerable adhesion of one metal to the other. (We note that recombination of the charges of the double layer due to the tunneling effect, although it does reduce the adhesion force, plays a considerably less essential role than recombination due to the considerable conductivity of the bodies being separated.)

In connection with the foregoing, one should expect that a semiconductor with a large number of surface states is a very favorable object for obtaining considerable adhesion, since, on the one hand, "metallization" of the semiconductor surface occurs (a reservoir for electric charges is created on the surface), while, on the other hand, a large number of experimental facts ([4]) indicate that the surface conductivity of semiconductors is very small. Independently of the con-

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Fig. 1

Figure 1: Fig. 1

siderations set forth, it appears necessary to take surface states into account in order to bring the theoretical scheme closer to real objects.

As is known, surface states may arise both as a result of the interruption of the periodic structure (I. E. Tamm surface bands) and as a result of the presence on the surface of a large number of impurity centers.

In the scheme considered below we shall take into account surface levels of the second type, and we shall assume that there are two types of surface states —donors and acceptors. This scheme essentially coincides with the scheme of Bardeen and Brattain ([4]), proposed to explain the rectifying properties of germanium. The model used has the advantage that it makes it possible to classify qualitative regularities well, while at the same time being of a very general character. As in ([2], [3]), a semiconductor with carriers of one type is considered.

Before turning to the solution of the problem, let us note one more aspect of the problem of surface states in adhesion, which is of general interest. From a microscopic point of view, the electrostatic theory of adhesion should consider the donor–acceptor bond between the surfaces in contact. It is quite evident that the study of the redistribution of the electron-gas density upon contact of solids is completely analogous to the problem of determining the electron density in some heteropolar molecule, with the very substantial difference that, in the case of solids, we can use the methods of statistics and give a phenomenological description of the phenomenon, whereas determining the electron density in a molecule requires difficult quantum-mechanical calculations. Taking surface states into account changes nothing in the method of calculation, and thus we have the possibility of considering phenomenologically the donor–acceptor chemical bond and of taking into account the influence of functional donor or acceptor groups introduced onto the surface.

Fig. 1

It should perhaps be noted that such a bond in the case of bonding solids is of special interest because of the long-range character of the forces (the field of a charged plane is constant), which leads, first, to greater strength of the joint with respect to impact loads, which produce small cavities that close after removal of the load, and, second, to an increase in the work of separation proportional to the square of the number of elementary donor–acceptor bonds.

Statement and solution of the problem. A semiconductor with carriers of one type is considered (for definiteness, in what follows an electron semiconductor is considered). The arrangement of the surface levels is shown in Fig. 1 (i.e., we assume that there are only two types of levels on the surface, with the acceptor levels located above, and the donor levels below, the Fermi level).

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Fig. 2

Figure 2: Fig. 2

The scheme in Fig. 1 corresponds to the case when the surface is negatively charged. Here μ is the Fermi level, N_a and N_d are the acceptor and donor levels at the surface, and $e\varphi^s$ is the magnitude of the band bending at the free surface of the semiconductor. In the case of contact of a semiconductor with a metal through a small gap d, the band scheme has the form shown in Fig. 2. Here the case is shown in which the work function of the metal is greater than the work function of the semiconductor and the field strengths have one and the same sign on both sides of the semiconductor surface. The sign of the surface charge, generally speaking, is not determined. In Fig. 2, E_z and E_{in} denote the electric fields in the gap and inside the semiconductor.

Fig. 2

Another case is also possible. The case shown in Fig. 3 is of interest in that the electric field has different signs on the two sides of the semiconductor surface. It will be convenient for us to divide all cases of contact of a semiconductor with a metal into two groups: 1) the electric field has the same direction on both sides of the semiconductor surface, and 2) the electric field has different directions on both sides of the semiconductor surface.

For the further analysis it is convenient to introduce the quantity V_k^0, equal to the contact potential difference between the given metal and semiconductor,

identical to the given one, but without surface states.

$$eV_k^0 = \varphi_{\text{m}} - \varphi_{\text{p}}^0. \tag{1}$$

Here e is the electron charge, φ_{m} is the work function of the metal, and φ_{p}^0 is the work function of the semiconductor without surface states. It is easy to see that in the case shown in Fig. 2 we have

$$eV_k^0 = edE_3 + e\varphi. \tag{2}$$

In the case corresponding to Fig. 3,

$$|eV_k^0| = |-edE_3 + e\varphi|. \tag{3}$$

We shall assume that the conduction band of the semiconductor is located far from the Fermi level, and then, for the model under consideration, the Poisson equation, as is known, has the form

$$d^2\varphi/dx^2 = \varkappa^2 \operatorname{sh}\widetilde{\varphi}, \qquad \widetilde{\varphi} = e\varphi/kT, \tag{4}$$

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Fig. 3

Figure 3: Fig. 3

where $\varkappa$ is the inverse Debye length.

On the surface of the semiconductor bordering the metal, we have

$$E_3 - \varepsilon E_{\text{vn}} = 4\pi\sigma, \tag{5}$$

where σ is the charge of the semiconductor surface (the direction from the semiconductor into the vacuum is taken as positive). The point in the depth of the semiconductor where $d\varphi/dx = 0$ is chosen as the zero of potential energy, $\varphi = 0$.

Fig. 3

It follows from formula (5) that, in the case of Fig. 2, the surface is charged positively for $E_3 > \varepsilon E_{\text{vn}}$ and negatively for $E_3 < \varepsilon E_{\text{vn}}$. In the case of Fig. 3 the surface is always charged negatively (or always positively if the metal has a negative charge). The surface charge is equal to

$$\sigma = (p_d - n_a), \tag{6}$$

where p_d is the number of free donor centers on the surface, and n_a is the number of occupied acceptor centers on the surface. As is known,

$$p_d = \frac{N_d}{1 + \exp[(\mu - e\varphi - E_d)/kT]}, \qquad n_a = \frac{N_a}{1 + \exp[(E_a + e\varphi - \mu)/kT]}. \tag{7}$$

Here E_a and E_d are the energies of the acceptor and donor levels, respectively. The top of the normal band in the depth of the semiconductor (beyond the space-charge layer) is chosen as the zero of energy. Correspondingly, N_a and N_d are the numbers of acceptor and donor levels on the surface.

Let us now consider the case when the semiconductor surface, in the absence of contact with the metal, was uncharged. In this case $p_d^f = n_a^f$ and $\varphi^f = 0$ (the index f means that a free surface is being considered). From (7) we have, on the free surface,

$$\frac{N_d}{1 + \exp[(\mu - E_d)/kT]} = \frac{N_a}{1 + \exp[(\mu - E_a)/kT]} = C. \tag{8}$$

According to (8), C is the number of ionized centers of one or the other type on the free surface of the semiconductor. After the semiconductor is brought into

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contact with the metal through a small gap d (the gap is introduced for convenience and generality of the treatment), the band diagram has the form shown in Fig. 2. In our case V_k^0 coincides with V_k, the contact potential difference between the metal and the semiconductor with surface states (in the general case V_k^0 and V_k are related by the relation $V_k = V_k^0 - \varphi^f$).

To simplify the analysis, we shall assume that both before and after contact the distances of the donor and acceptor levels from the Fermi level are much greater than kT. Then (8) and (7) take the form

$$N_d \exp\left(-\frac{\mu - E_d}{kT}\right) = N_a \exp\left(-\frac{E_a - \mu}{kT}\right) = C, \tag{9}$$

$$p_d = Ce^{e\varphi/kT}, \qquad n_a = Ce^{e\varphi/kT}. \tag{10}$$

From (5) we have

$$eE_z - e\varepsilon E_{\text{in}} = 4\pi e^2(p_d - n_a) = 2\pi e^2 C \,\text{sh}\,\tilde{\varphi}. \tag{11}$$

The field at the inner side of the semiconductor surface is obtained by integrating equation (4) under the condition $\varphi = 0$ when $d\varphi/dx = 0$. Then

$$\frac{eE}{kT} = \frac{d\tilde{\varphi}}{dx} = 2\varkappa \,\text{sh}\,\tilde{\varphi}. \tag{12}$$

From (11) and (12) we have

$$eE_z = 2\varkappa kT\varepsilon \,\text{sh}\,\frac{1}{2}\tilde{\varphi} + 2\pi e^2 C \,\text{sh}\,\tilde{\varphi}; \tag{13}$$

from (2) and (14)

$$V_k = 2d\left(\frac{\varkappa kT\varepsilon}{e}\,\text{sh}\,\frac{\tilde{\varphi}}{2} + C\pi e \,\text{sh}\,\tilde{\varphi}\right) + \frac{kT}{e}\tilde{\varphi}. \tag{14}$$

Let us find the field in the gap, assuming that

$$d = 5{\cdot}10^{-8}\ \text{cm}, \qquad \varkappa = 10^4\ \text{cm}^{-1}, \qquad kT = 4.16{\cdot}10^{-14}\ \text{erg}\ (300^\circ K), \qquad \varepsilon = 10. \tag{15}$$

The quantities V_k and C are varied. The results of the numerical solution of (13) and (14) are presented in Table 1 (accuracy of the calculations 5%; E in V/cm).

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Table 1 shows that the field in the gap increases rapidly with C, the number of centers ionized before contact. If one assumes that the number of surface levels is 10^{15}–10^{16}, the chosen values correspond to ionization from 10^{-2}–10^{-3} to 10^{-5}–10^{-6} of the total number of impurity centers, i.e., to a quite realistic case.

Table 1

V_k	$C = 10^{10}$	$C = 10^{12}$	$C = 10^{13}$
0.1	$1.7 \cdot 10^5$	$1.35 \cdot 10^6$	$1.87 \cdot 10^6$
0.3	$2.7 \cdot 10^3$	$4.7 \cdot 10^6$	$5.75 \cdot 10^6$
0.5	$6.3 \cdot 10^6$	$8.4 \cdot 10^3$	$1 \cdot 10^7$

The data of Table 1 show that fields arise at the contact which provide an adhesion force of the order of tens of kilograms per square centimeter. Determining the adhesion force by the formula $F = E^2/8\pi$, we obtain for $E = 10^7$ V/cm $F = 40$ kg/cm^2. It can also be seen that the larger the number of ionized centers on the free surface of the semiconductor, the more intense the screening action of the surface and the more significant the part of the contact potential difference that falls in the gap.

In the present work only the main points of the analysis of the problem have been outlined, but the examples already considered show that, in the presence of a large number of surface states at the metal-semiconductor boundary, the occurrence of electric fields providing substantial adhesion is realistic. This result, incidentally, appears quite obvious if one recalls that, when two metals are brought into contact, fields of the order of 10^7 V/cm arise at the boundary, while the surface states "metallize" the semiconductor surface in the sense that there is a reservoir for electric charges on the surface.

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