THE ENERGY SPECTRUM OF A DIELECTRIC AT CONTACT WITH A METAL

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PHYSICS

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THE ENERGY SPECTRUM OF A DIELECTRIC AT CONTACT WITH A METAL

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The study of the injection of carriers into dielectrics from metallic electrodes leads to the conclusion that near the electrodes the width of the forbidden band is smaller than far from them.

To determine the width of the forbidden band of a dielectric as a function of the distance x from the metal surface, let us consider the contact of a dielectric with a metal, regarding the surface of contact as plane and directing the x-axis perpendicular to it, while the y- and z-axes are parallel to the metal surface. We shall confine ourselves to the study of the equilibrium case.

If in the dielectric there is an electric field produced by charges located on the surface of the metal and the dielectric, and by volume charges in the dielectric, then, for brevity, we shall call this field macroscopic and set its potential at $x \to \infty$ equal to zero, $\varphi(\infty, y, z) = 0$.

Let us carry out mentally the following process. At a point O, located in the dielectric at an infinite distance from the metal, we create a pair of carriers—an electron and a hole—and separate them by a large distance from one another to points A and A'; in doing so we perform work ΔE, equal to the width of the forbidden band of the dielectric far from the contact (Fig. 1). Then we move the electron from point A to point B, and the hole from point A' to point B'. In moving the electron, energy P_{AB} will be released owing to the work of the image forces, and in moving the hole—energy $P_{A'B'}$. We bring the carriers together at a distance x from the metal at point O' and recombine them; in this process energy $\Delta E(x)$ is released, equal to the width of the forbidden band of the dielectric at the distance x from the metal surface. When the electron is transferred from point O to point O' with coordinates x, y, z, the forces of the macroscopic field perform work $T_\mathrm{e} = e\varphi(x, y, z)$, and when the hole is transferred —work $T_\mathrm{h} = -e\varphi(x, y, z)$, where $\varphi(x, y, z)$ is the potential of the electric field at the point O'.

Fig. 1

Fig. 1

Figure 1: Fig. 1

As a result, after recombination of the electron and the hole we return to the initial state; consequently, the total expenditure of energy is zero:

$$\Delta E - P_{AB} - T_{\mathrm{e}} - P_{A'B'} - T_{\mathrm{h}} - \Delta E(x) = 0. \tag{1}$$

Hence

$$\Delta E(x) = \Delta E - P_{AB} - P_{A'B'}, \tag{2}$$

since $T_{\mathrm{e}} = -T_{\mathrm{h}} = e\varphi(x, y, z)$.

For large x, when the distance from the metal considerably exceeds atomic dimensions, the work of the image forces in moving the electron and the hole can be found by treating the dielectric as a continuous medium with static dielectric permittivity ε, and the width of the forbidd–

tion band. In the case of small x, only approximate estimates can be made.

For large x, the interaction force Φ of an electron with the positive charge reflected in the metal surface, or of a hole with the reflected negative charge, is equal to $\Phi = -e^2/4\varepsilon x^2$, and the work of this force in moving an electron or a hole from infinity to a point at a distance x from the metal surface is determined by the well-known formula

$$P_{AB} = P_{A'B'} = e^2/4\varepsilon x. \tag{3}$$

Substituting the values P_{AB} and $P_{A'B'}$ into equation (2), we obtain

$$\Delta E(x) = \Delta E - e^2/2\varepsilon x. \tag{4}$$

Expressing the forbidden-band width ΔE and $\Delta E(x)$ in electronvolts and the distance x in angstroms, (4) can be rewritten in the form

$$\Delta E(x) = \Delta E - 7.2/\varepsilon x \text{ eV}. \tag{5}$$

The position of the bottom of the conduction band $E_{\mathrm{p}}(x, y, z)$ and the ceiling of the valence band $E_{\mathrm{v}}(x, y, z)$ as functions of the distance x from the metal surface, taking into account the influence of the macroscopic electric field and the work of the image forces at large x, is determined by the formulas

$$E_{\mathrm{p}}(x,y,z) = E_{\mathrm{p}} - e\varphi(x,y,z) - 3.6/\varepsilon x \text{ eV}, \tag{6}$$

$$E_{\mathrm{v}}(x,y,z) = E_{\mathrm{v}} - e\varphi(x,y,z) + 3.6/\varepsilon x \text{ eV}, \tag{7}$$

where E_{p} and E_{v} are the energies of the bottom of the conduction band and the ceiling of the valence band at $x \to \infty$.

It follows from equation (4) that at a distance x_0 from the metal the forbidden-band width of the dielectric becomes zero, with

$$x_0 = 7.2/\varepsilon \Delta E \text{ Å}. \tag{8}$$

For example, at $\varepsilon = 7.2$ and $\Delta E = 5$ eV, the forbidden-band width becomes zero at a distance of 0.2 Å from the metal surface. This result, and the consequences that can be reached by carrying out calculations according to formulas (3)–(8) at small x (of the order of the radius x_1 of the atoms of the dielectric), should be discussed as preliminary and refined on the basis of a more rigorous theoretical analysis and subsequent experimental investigations.

The vanishing of the forbidden-band width in the case $x_0 < x_1$ may be regarded as a reflection, on the energy diagram, of the overlap of the electron shells of the outer layers of the metal and dielectric atoms and of the absence of a sharp boundary between the metal and the dielectric. Just as electrons with energies insufficient for their emission penetrate at the metal surface into vacuum, so electrons with energies lying within the forbidden band of the dielectric far from the metal can leak to a small depth from the metal into the dielectric. The penetration of electrons from the dielectric into the metal is expressed in the appearance in the dielectric of holes with energies lying within the forbidden band of the dielectric far from the contact surface.

In the case $x_0 > x_1$, the surface of the dielectric turns out to be, as it were, metallized, and electrons can readily pass from the metal to the surface layer of atoms of the dielectric and back. If such a dielectric is placed between the closely adjoining plates of a capacitor to which a voltage is applied, then charges from the electrodes will flow onto the surface of the dielectric.

The energy spectrum of a dielectric with intrinsic electrical conductivity at contact with a metal, constructed on the basis of calculations by formulas (6) and (7) in the case $\varphi(x,y,z) = 0$, is shown in Fig. 2; in the calculations it was assumed that the contact potential difference between the metal and the dielectric is equal to zero and that the effective masses of electrons and holes in the dielectric are equal to each other.

For small x, the abstractions that represent the metal surface as a plane, and the reflected positive charge in the metal and the hole in the dielectric as point charges, turn out to be insufficiently rigorous. As yet, concerning the possibility of calculating the energy spectrum of the dielectric at small x, only general preliminary considerations can be expressed and orienting estimates made. Apparently, it will have to be taken into account that the width of the forbidden band depends on the mean energy of the valence electron in some region, just as the ionization energy of an atom is determined by the mean

[Fig. 2 and Fig. 3]

Fig. 2 **Fig. 3**

(potential and kinetic) energy of the electron in the atom. Therefore the width of the forbidden band at the surface of the dielectric may be related to the mean energy of the electron and the hole moving in the layer of surface atoms. Assuming that the dependence of the forbidden-band width on x is determined mainly by the change in the potential energy of interaction of the electron with the positive charge U_n reflected in the metal surface and of the hole with the reflected negative charge U_p, and determining the mean potential energy of the electrons and holes moving in the layer of surface atoms, one can calculate the forbidden-band width $\Delta E(1)$, the position of the bottom of the conduction band $E\,(1)$, and the top of the valence band $E\,(1)$ at the surface of the dielectric adjoining the metal,

$$\Delta E\,(1) = \Delta E + \int \psi_n^* U_n \psi_n \, d\tau + \int \psi_p^* U_p \, d\tau, \tag{9}$$

$$E\,(1) = E\, + \int \psi_n^* [U_n - e\varphi(x, y, z)] \psi_n \, d\tau, \tag{10}$$

$$E\,(1) = E\, - \int \psi_p^* [U_p + e\varphi(x, y, z)] \psi_p \, d\tau, \tag{11}$$

where ψ_n, ψ_n^*, ψ_p, and ψ_p^* are the wave functions of the electron and the hole and their complex conjugates, and $d\tau$ is the volume element.

To estimate the magnitude of the integrals entering expressions (9)–(11), let us assume that the mean value of the potential energy of the electron is equal to the potential energy of an electron located at a distance x_1 from the metal surface (x_1 is the radius of the atoms of the dielectric), i.e., in the integrals we replace U_n, U_p, and $\varphi(x, y, z)$ by constants: $U_n = U_p = -3.6/\varepsilon x_1$ eV and $\varphi(x, y, z) = \varphi(x_1, y, z)$. As a result of this replacement, expressions (9)–(11) reduce to formulas (5)–(7), in which x_1 should be substituted for x, and one should assume that $\Delta E(1) = \Delta E(x_1, y, z)$, $E\,(1) = E\,(x_1, y, z)$, and $E\,(1) = E\,(x_1, y, z)$.

Obviously, two cases may be assumed: in one of them the forbidden-band width at the surface of the dielectric $\Delta E(1)$ differs from zero, while in the other it is equal to zero and the valence band touches or overlaps the conduction band.

Whether or not the forbidden-band width at the surface of the dielectric goes to zero can be established experimentally. If the forbidden-band width of the dielectric differs from zero, then in the absence of ionization we

we must find that electrode 1 is attracted to electrode 3 and presses on dielectric 2 (Fig. 3); moreover, in close contact the pressure is determined by the formula

$$P = 4.52 \cdot 10^{-13} \varepsilon E^2 \text{ kg/cm}^2, \tag{12}$$

where E is the electric-field strength in the dielectric, in volts per centimeter. In this case the charges remain on the electrodes. By raising electrode 1 and thereby reducing the capacitance C formed by the electrodes, we cause positive charge to drain from electrode 1 and a current J to appear in the circuit; its direction is indicated by the arrow and can be determined with the aid of galvanometer G.

If the width of the forbidden band of the dielectric at the contact with the metal goes to zero, then charges drain from the electrodes onto dielectric 2, and the pressure of electrode 1 on dielectric 2 depends only very weakly on the electric-field strength E. In addition, when electrode 1 is removed from dielectric 2, a current flows in the circuit whose direction is opposite to that shown in Fig. 3. This is due to the fact that the potential of electrode 1, in contact with dielectric 2, is determined by the charges located on the dielectric. When electrode 1 is raised, the influence of the positive charges residing on the surface of the dielectric decreases, and in order to maintain a constant value of the potential of electrode 1 it must be charged positively.

If the width of the forbidden band of the dielectric goes to zero between the dielectric and a metal in close contact with it, considerable attractive forces of the dispersion type must arise. These forces are due to the interaction of the electrons and holes that have appeared at the surface of the dielectric with reflected charges. An estimate using the formula $P_0 = Ne^2/4x_1^2$, where $N = 2(n+p)x_1$ is the number of electrons and holes in a monatomic layer of the dielectric per 1 cm^2, and n and p are the concentrations of electrons and holes, shows that the pressure P_0 of the dielectric on the metal can reach several hundred and even a thousand kilograms per square centimeter.

The decrease in the width of the forbidden band of dielectrics near contacts with metals leads to an increase in the conductivity of thin dielectric films situated between metallic electrodes; in particular, the specific conductivity of films 100 Å thick exceeds by several times the specific conductivity of thick layers of the same material.

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