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Abstract

Full Text

PHYSICAL CHEMISTRY

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INVESTIGATION OF THE PROPERTIES OF THE POLYMER-SEMICONDUCTOR INTERFACE

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The complex of questions relating to the formation of an adhesive bond must be considered within the framework of ideas about surface phenomena at interfaces of solid bodies. The greatest development in recent times has been achieved by theoretical and experimental work in the field of the physics of semiconductor surfaces ($^{1-9}$). Therefore, the investigation of the interface between a semiconductor and the film of a polymer bordering it, by methods developed and applied in the physics of semiconductor surfaces, can provide valuable information on the mechanism of formation of an adhesive bond between a semiconductor and a polymer*.

This question has, in addition to scientific importance, also an important practical significance, since most semiconductor devices are protected from external influences by polymer films in compositions with various ingredients. Adsorption processes underlie adhesive phenomena, since the polymer film is applied to a solid surface from the liquid phase.

Fig. 1. *a* —diagram of the capacitor. 1 —glass plates with a conducting layer of tin dioxide, 2 —germanium specimen, 3 —mica sheets. *b* —circuit for measuring surface conductivity in the field effect.

When a chemisorption bond is formed, the chemisorbed particle can retain near itself a free electron or a free hole of the semiconductor (^{10}). As a result, the surface becomes charged, and in the layer immediately adjacent to it a charge is induced that is equal in magnitude and opposite in sign to the surface charge (owing to the condition of electroneutrality). This leads to bending of the energy

Fig. 2

Figure 2: Fig. 2

bands at the surface of the semiconductor. If charging of the surface took place in the absence of chemisorption, then the chemisorbed particles can change its magnitude, and sometimes its sign, thereby causing a change in band bending. At the same time the work function also changes.

In studies of adsorption processes on semiconductors, the work function is usually measured and the surface charge is calculated from it.

* Since the surface of a metal is always covered with an oxide film—a semiconductor—then in fact, when a polymer film is applied to a metal, a polymer-semiconductor interface arises.

However, at present it is possible to measure this quantity directly by means of the method for determining surface conductivity in the so-called "field effect." In this method, the changes in the surface conductivity of a semiconductor are determined that are caused by a change in the concentration of electrons and holes in the space-charge layer under the action of an external electric field directed perpendicular to the surface of the specimen. To obtain sufficiently large bending of the bands, it is necessary to place the specimen in a strong electric field, of the order of 10^6 V/cm.

Fig. 2. Change in the surface conductivity of germanium with time upon application of an external field.

The object of the investigation was n-type germanium with a resistivity of 40 ohm/cm and a diffusion length of 2.5 mm. The specimen was a plate of dimensions $20 \times 5 \times 0.3$ mm, cut from a single crystal of germanium parallel to the (111) plane. Ohmic contacts were soldered to the ends of the specimen. The specimen was etched in a mixture of hydrogen peroxide with alkali. The quality of the surface after etching was checked each time by measuring the rate of surface recombination by the photoconductivity-decay method ([11]).

To obtain the required field strength, a rectifier of the VSÉ-2500 type was used. The voltage from it was applied to a capacitor (Fig. 1a), one plate of which was the germanium specimen, and the other a conducting layer of tin dioxide on glass. Mica sheets about $20\,\mu$ thick were placed between the capacitor plates. The capacitance of the resulting capacitor was determined by means of a UM-3 bridge. The change in conductivity was recorded with an EPP-09 self-recording potentiometer with a carriage run time of 1 sec, connected into the bridge circuit (Fig. 1b).

One typical example of the change in surface conductivity with time is given in Fig. 2. At the moment the field is switched on, the conductivity increases, then passes through a minimum, after which it again increases, tending toward the initial value. The investigation of the time variations of the surface conductivity

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

is of interest in connection with the fact that on the surface of germanium there exist two types of surface states: the so-called "fast" states, located at the germanium oxide—germanium interface, and the "slow" states, located on the outer side of the oxide or in the oxide itself. Filling of the surface states by charge carriers leads to screening of the external field by the field of these charges. This process determines the time variations of the surface conductivity. In studying both adsorption and adhesion phenomena on real surfaces, primary attention should be devoted to the study of "slow" surface states. This can be done by applying a constant voltage in the "field-effect" method. Before the polymer film was applied, control tests were carried out on the semiconductor—air and semiconductor—vacuum interfaces. Adsorption of atmospheric moisture sharply changes the position of the minimum of the surface-conductivity curve as a function of potential; from this it follows that the surface in air is positively charged, and the space-charge layer is enriched with electrons. The polymers investigated were linear polymers of the vinyl series and copolymers of methyl methacrylate with methacrylic acid.

Fig. 3. Change in surface conductivity in the field effect for a germanium specimen coated with films of copolymers of methyl methacrylate and methacrylic acid. 1 —initial germanium specimen; 2 —specimen with a copolymer film (10% methacrylic acid); 3 —the same with a copolymer film (17.2% methacrylic acid); 4 —specimen with a methacrylic acid film.

The nature and concentration of functional groups noticeably affect the position of the minimum of the surface-conductivity curve (Fig. 3). The experimental data obtained for determining surface conductivity in the "field effect" were compared with the theoretical data calculated for the initial germanium samples.

Calculation shows that a polymer film deposited on the surface of a semiconductor can change the sign of the band bending. At the same time, the magnitude and sign of the charge captured by surface states arising as a result of the adhesion bond between the semiconductor and the polymer also change (Fig. 4a). With an increase in the concentration of carboxyl groups in the polymer chain, the magnitude and sign of the band bending change (Fig. 4b). At a methacrylic-acid concentration in the copolymer equal to 10.8%, the sign of the band bending changes. The carboxyl groups of the copolymer are donors: with an increase in their concentration in the chain, the near-surface layer is enriched with electrons.

Fig. 4. *a* —charge captured by surface states as a function of the band bending ψ caused by an external field. 1 —sample of initial germanium, 2 —germanium sample covered with a polymer film. The arrows indicate points corresponding to the values of ψ in the absence of an external field. *b* —change in the band bending ψ for the germanium—polymer interface as a function of the methacrylic-acid content in the copolymer.

From the obtained curves of the charge captured in surface states, one can calculate the concentration and energy position of the levels arising in the interaction of the polymer with the semiconductor. According to the theory (2–4), the change in surface conductivity is

$$\Delta\sigma = e\left(\mu_n \Delta n + \mu_p \Delta p\right),$$

where e is the electron charge; $\Delta n, \Delta p$ are the excess of electrons and, respectively, holes in the space-charge layer; μ_n, μ_p are the effective mobilities of electrons and holes.

All these quantities depend on the band bending and can be calculated theoretically (3,4). An external electric field affects the value of the band bending ψ and changes $\Delta\sigma$. By comparing the experimental data (Fig. 3) with the theoretical ones, one can calculate the value of the band bending at the polymer—semiconductor interface (Fig. 4). Knowing the dependence of $\Delta\sigma$ on ψ, we can determine the charge captured by surface states

$$Q_{\mathrm{p.s}} = Q_{\mathrm{i}} - Q_{\mathrm{pr}},$$

where Q_i is the charge imparted to the surface and equal to CV, C is the capacitance of the capacitor, V is the applied voltage, and Q_{pr} is the volume charge, which was calculated for each value of the band bending.

Figure 4b presents curves of the charge trapped by surface states as a function of ψ, calculated for the polymer-semiconductor interface. As follows from the figure, as a result of deposition of the polymer film, the sign of the band bending and of the charge trapped by surface states changes. Crosses mark the values of the band bending, and circles the values of the charge trapped by surface states in the absence of an external field.

According to the theory (3,4), in the case where there are m levels on the surface with energy position E_m and concentration N_m, then, for a given value of the surface potential U, the charge trapped by surface states is

$$Q_{\mathrm{p.s}} = \sum_m \frac{eN_m}{1 + \exp(E_m + u)/KT}.$$

Using this equation, one can calculate, on the basis of the data obtained, the density of the electric double layer (12) at the polymer-semiconductor interface.

Investigation of the polymer-semiconductor interface by the “field-effect”method is of great practical importance for the rational selection of varnishes used for coating semiconductor devices. Experiments carried out by us with certain industrial varnishes show that applying them to the surface of a semiconductor leads to a considerable change in the state of the surface, changing its charge and introducing a large number of surface states.

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Note: Figure translations are in progress. See original paper for figures.