I. A. AKIMOV, A. M. MESHKOV

1965

SovietRxiv

Abstract

Full Text

I. A. AKIMOV, A. M. MESHKOV

DETERMINATION OF THE SIGN OF THE CHARGE OF PHOTOCURRENT CARRIERS BY THE CAPACITOR METHOD

(Presented by Academician A. N. Terenin, 2 XI 1964)

The capacitor method, which has become widely used for studying the photoelectric properties of semiconductors ($^{1-16}$), has most often been applied to determine the spectral distribution of the photoeffect and the signs of photocurrent carriers. The latter was based on the assumption that the photo-emf was explained as the result of diffusion of photocurrent carriers in a semiconductor due to the gradient of their concentration created by absorbed light (Dember emf) (^{2,3}). However, V. E. Lashkarev and co-workers (^{6,8}), on the basis of some of their observations, came to believe that the capacitor photo-emf has the nature of a barrier emf, namely, that it is entirely associated with the presence of boundary band bending and bipolar photoconductivity, and is described by the theory (^{9}). From this it was concluded that the capacitor method cannot be used to determine the sign of photocurrent carriers, since the sign of the photo-emf is determined only by the direction of band bending. However, a detailed consideration of the properties of capacitor photovoltage in the region of weak absorption, in our opinion, makes it possible to explain the photo-emf by a theory based only on the phenomenon of monopolar photoconductivity (^{10}). In this connection, one should consider especially carefully the phenomenon of "polarity reversal," which consists in the fact that, in the photo-emf spectrum, along with the main band located in the depth of the absorption band, whose sign corresponds to the diffusion of the main current carriers in the direction of the incident light, in a number of cases a longer-wavelength band with the opposite sign of photo-emf is observed. This phenomenon has been observed for mercury and lead iodides (^{2,3,7}), silver and thallium halides (^{2,4,5,11}), cadmium, lead, zinc, and indium sulfides and selenides ($^{2,4,6-8,12-15}$), lead oxide and cuprous oxide (^{2,4,6,7}), anthracene, polymers (^{16}), organic dyes of the most varied classes, and also for germanium and silicon (n- and p-types). The appearance of an additional maximum of the photo-emf or a significant change in it can occur under the action of constant illumination from the region of intrinsic absorption of the semiconductor ($^{2,4-7,14,15}$), upon application of an external voltage to the capacitor ($^{2,4-7}$), with special treatment of the semiconductor surface (^{2,4,7,12,17}), and with photochemical changes in the substance (^{11,18}). Sometimes "polarity reversal" is observed in the initial samples under study.

As an example, Fig. 1 shows the spectral curves of the capacitor photo-emf for

Fig. 1

Figure 1: Fig. 1

four layers of germanium and silicon. In the region of strong absorption, in all samples the photo-emf has a positive sign (the sign on the front semitransparent electrode of the capacitor), corresponding to diffusion of electrons into the depth of the layer. In addition, in two layers (curves 2 and 4), at the edge of the absorption band there are additional maxima of the photo-emf of the opposite sign.

All this indicates that "polarity reversal" is not a rare phenomenon for most semiconductors, and that for all of them it has a common nature.

The following explanations exist for the occurrence of "polarity reversal" in the photo-emf spectrum.

1. The photo-emf is of diffusion origin, and the character of the photoconductivity is mixed. As a result of a change in the filling of local electronic levels in the forbidden band (or their appearance), the ratio between the electron and hole components in the long-wavelength region

changes in favor of the one that previously was not dominant, as a result of which, in this region of the spectrum, a new maximum of the photo-emf of the opposite polarity appears ([2,4,5,11]).

2. The character of the photoconductivity is monopolar. The photo-emf is determined both by diffusion (the Dember effect) and by the drift of carriers in the field of the surface charge, which creates an anti-barrier band bending at the illuminated surface of the semiconductor ([18,19,11,14]). For the short-wavelength region, where the absorption coefficient is large, a large concentration gradient of free carriers arises and the diffusion of carriers into the depth of the layer predominates over their drift in the field of the surface charge. In the case of weakly absorbed light, when the distribution of the generated current carriers is almost uniform over the depth of the layer, diffusion of free carriers may be neglected, and the direction of motion of the current carriers will be determined by the field of the surface charge; and if the band bending is anti-barrier, then the carriers will move not into the depth of the layer, but toward the illuminated surface.

It should be noted that the phenomenon of "repolarization" cannot be explained within the framework of the hypothesis according to which the capacitor photo-emf is determined entirely only by the boundary curvature of the bands ([6–8]). In this case the causes producing a change in the band bending should have led to a reversal of the sign of the photo-emf primarily in the region of strong, not weak, absorption, which in fact is never observed.

Fig. 1. Spectral distribution of the capacitor photo-emf for single-crystal

Fig. 2. Spectral curves of photoconductivity ($\Delta\sigma$), capacitor photo-e.m.f. (V_k), and photohall effect (V_{H}) for a monocrystalline AgBr layer

Figure 2: Fig. 2. Spectral curves of photoconductivity ($\Delta\sigma$), capacitor photo-e.m.f. (V_k), and photohall effect (V_{H}) for a monocrystalline AgBr layer

samples of germanium and silicon (n-type) in air: **1** and **2**—Ge, **3** and **4**—Si.

The cause of the appearance of the new maximum also cannot be the photo-emf at the semiconductor-metal contact, as is assumed in ([17]), since the phenomenon of "repolarization"appears identically on the same samples in dynamic and static capacitors, but in the latter case the semiconductor layer is separated from the electrodes by an insulator.

To clarify the nature of the "repolarization," the following experiments were carried out. The question of the validity of the first or the second hypothesis in each particular case can be resolved by comparing the spectra of the photo-Hall effect, photoconductivity, and capacitor photo-emf. If the spectral curve of the photo-Hall effect coincides with the spectrum of the photo-emf, then the first hypothesis is correct; but if the second explanation is correct, then the spectrum of the photo-Hall effect should be similar to the spectral characteristic of the photoconductivity.

A specially constructed setup made it possible to measure the spectrum of the photo-Hall effect on single-crystal AgBr layers with a resistance of 10^{10} ohms. Figure 2 gives the spectra of the capacitor photo-emf V_k, photoconduct-

dependence of $\Delta\sigma$ and of the photohall effect V_{H} for one and the same AgBr layer subjected to a certain preliminary exposure, which led to the appearance, in the region 450-490 mμ, of an additional maximum of the photo-e.m.f. ([11]). As is seen from the figure, the spectrum V_{H} is similar to the spectrum $\Delta\sigma$, which for AgBr argues in favor of the latter hypothesis and proves that the carriers of the photocurrent over the entire investigated spectral region are electrons. This hypothesis not only most naturally explains the appearance of a new photo-e.m.f. band (always at the edge of the absorption band) in the most diverse semiconductors, but also gives the correct signs of the observed photoresponse.

Fig. 2. Spectral curves of photoconductivity ($\Delta\sigma$), capacitor photo-e.m.f. (V_k), and photohall effect (V_{H}) for a monocrystalline AgBr layer

Next, a study was made of the change of the photo-e.m.f. in the region of strong and weak absorption of semiconductors when the magnitude and sign of the surface charge on them were changed by means of adsorption of gas molecules, an external electric field, steady illumination, and photochemical exposure.

Figure 3 gives results on the influence of oxygen on the spectrum of the change in contact potential under illumination for a layer of the dye auramine O, obtained by vacuum evaporation. The dark conductivity of the layer is electronic. In an oxygen atmosphere there is only an "electronic" photo-e.m.f. (curve 1) with

Fig. 3. Spectral curves of the change in contact potential difference under illumination of an auramine O layer at various oxygen pressures: 1 $-p \sim 1$ torr, 2 -10^{-2} torr, 3 -10^{-4} torr

Figure 3: Fig. 3. Spectral curves of the change in contact potential difference under illumination of an auramine O layer at various oxygen pressures: 1 $-p \sim 1$ torr, 2 -10^{-2} torr, 3 -10^{-4} torr

maxima at 390 and 450 mμ and a red boundary at about 500 mμ. This curve is similar to the absorption spectrum of the layer. As the oxygen is pumped out (curves 2 and 3), the electronic photo-e.m.f. increases. Simultaneously with this, at the absorption edge a new photo-e.m.f. band of the opposite sign appears, with a maximum at 510 mμ. The phenomenon is completely reversible upon pumping out and admitting oxygen.

These results contradict the first hypothesis and are readily explained by the second. According to the first hypothesis, the long-wavelength "hole" band in oxygen should increase, not decrease. The suppression of this maximum by oxygen, from the point of view of the second hypothesis, occurs as a result of a decrease in the positive charge on the semiconductor surface and the corresponding decrease in the blocking band bending, as a result of which the drift of photoelectrons toward the surface in the field of this charge decreases.

Fig. 3. Spectral curves of the change in contact potential difference under illumination of an auramine O layer at various oxygen pressures: 1 $-p \sim 1$ torr, 2 -10^{-2} torr, 3 -10^{-4} torr

The changes occurring in the photo-e.m.f. spectra of AgBr and AgCl under photochemical exposure ([11]) are completely explained by the formation of a positive surface···

surface charge at the illuminated surface of a sample with n-type conductivity.

These conclusions were especially convincingly confirmed in experiments on the influence of the field, bias illumination, and adsorbed molecules on the photo-e.m.f. spectra of TlJ, AgBr, and ZnO.

Thus, all the phenomena of the capacitor photoeffect considered can be explained by assuming that the photoconductivity is monopolar and that the photo-e.m.f. is determined by the diffusion of free carriers, on which is superposed the photoconductivity of current carriers in the field of surface charges. In this case, depending on the direction of band bending, the drift current either adds to the diffusion current (blocking bending) or is subtracted from it (antiblocking bending). The theory developed by V. E. Lashkarev [10] is applicable to this case. Since the maximum of the photoconductivity is shifted into the long-wavelength region relative to the maximum of the diffusion photocurrent [5], this is reflected in the photo-e.m.f. spectrum in the following way. In the region of strong absorption, the diffusion photo-e.m.f. under the action of the field of surface charges forming a blocking band bending may be increased up to a certain limit, while with antiblocking bending it may be decreased, in the limiting case, to zero; and the sign of the photo-e.m.f. always coincides with the sign of the diffusion photo-e.m.f., which makes it possible to determine reliably the sign of the charge carriers of the photocurrent in semiconductors by the capacitor method. At the same time, the photoresponse in the region of weak absorption increases in the presence of blocking band bending, while antiblocking bending may not only reduce the photo-e.m.f. to zero but also lead to a change of sign (“reversal of polarity”). Naturally, determining the sign of the current carriers by the capacitor method without an additional investigation of the photo-e.m.f. spectrum, or using nonmonochromatic light, may give erroneous results.

The possibility of applying the capacitor method to the study of surface states of semiconductors is evident, since in a number of cases it is possible to change the magnitude of the surface charge.

On the basis of what has been said, the phenomenon of “reversal of polarity” can be distinguished from the case in which the presence of bands of different signs in the photo-e.m.f. spectrum is in fact connected with the existence of both conductivity components with somewhat different photoeffect spectra. The latter case was clearly demonstrated by the spectra of the capacitor photo-e.m.f. for mechanical mixtures of semiconductors with n- and p-type conductivity [2], and for polymorphic semiconductor layers, when different modifications possess different types of conductivity [20].

In conclusion, we express our sincere gratitude to Academician A. N. Terenin for his constant interest in the work and for valuable advice.

Received
27 X 1964

CITED LITERATURE

[1] L. Bergmann, Phys. Zs., **33**, 209 (1932); **41**, 349 (1940); Zs. Phys., **100**, 50 (1936).
[2] E. K. Pudeiko, DAN, **59**, 471 (1948); **67**, 1009 (1949); **78**, 453 (1951).
[3] V. P. Zhuzhe, S. M. Ryvkin, DAN, **62**, 55 (1948); ZhTF, **18**, 152 (1948).
[4] E. K. Pudeiko, A. N. Terenin, DAN, **70**, 401 (1950).
[5] I. A. Akimov, E. K. Pudeiko, Fiz. tverd. tela, **4**, 1542 (1962).
[6] V. E. Kozhevin, V. E. Lashkarev, Radiotekhn. i elektronika, **2**, 260 (1957).
[7] V. E. Kozhevin, Candidate dissertation abstract, Kiev, 1958.
[8] V. I. Lyashenko, O. V. Snitko, T. N. Sytenko, Fiz. tverd. tela, Collected papers, **1**, 11 (1959).
[9] V. E. Lashkarev, Tr. Inst. fiziki AN USSR, **3**, 3 (1952).
[10] V. E. Lashkarev, DAN, **70**, 813 (1950).
[11] I. A. Akimov, Fiz. tverd. tela, **4**, 1549 (1962).
[12] P. Brauer, Zs. Naturforsch., **14a**, 556 (1959).
[13] P. Ya. Berlage et al., Fiz. tverd. tela, **2**, 3045 (1960); **4**, 2629 (1962); Vest.

Leningrad. univ., No. 4, 41 (1963).
[14] W. Ludwig, Phys. Status Solidi, **2**, 244 (1962); **3**, 1738 (1963).
[15] N. A. Tolstoi et al., Fiz. tverd. tela, **4**, 1966 (1962); **4**, 3177 (1962).
[16] V. S. Mylnikov, A. N. Terenin, DAN, **155**, 1167 (1964).
[17] L. P. Strakhov, Fiz. tverd. tela, **1**, 583 (1959); **3**, 1612 (1961); **4**, 3422 (1962); **6**, 952 (1964).
[18] A. M. Goodman, G. Warfield, Phys. Rev., **120**, 1142 (1960).
[19] A. Kobayashi, S. Kawaji, J. Phys. Soc. Japan, **10**, 270 (1955); **11**, 369 (1956).
[20] V. S. Mylnikov, E. K. Pudeiko, Fiz. tverd. tela, **4**, 772 (1962).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.