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# PHOTODIELECTRIC EFFECT

Dielectric properties of semiconductors and dielectrics are controlled by different parameters, such as temperature, pressure, frequency, electric field strength, and so on. The changes in the dielectric properties of a semiconductor, namely in the real ( $\varepsilon'$ ) and imaginary ( $\varepsilon''$ ) parts of the complex dielectric permittivity  $\varepsilon * = \varepsilon' - i \varepsilon''$ , caused by absorption of radiation of a given visible wavelength, are called the *photodielectric effect (PDE)*. If a change of the capacitance of a capacitor is caused by an increment in the  $\varepsilon'$  of the photoconductor that is used as a dielectric, then this phenomenon is called the *first-type effect* (PDE I). If a change of the photoconductivity and consequently of the effective thickness of the photodielectric, then it is called the *second-type effect* (PDE II).

In 1909 Lenard and others for the first time observed a change of capacitance due to illumination of a dielectric capacitor. Subsequently, in the 1920s, Gudden and Pohl (1) studied this phenomenon at greater length in powdered zinc sulfide (ZnS). Further research has revealed PDEs in a multitude of photosensitive semiconductor compounds used in solid-state electronics (CdS, CdTe, ZnO, SbSI, etc.). The effect has been thoroughly studied in many inorganic and organic photoconductors on powder samples with or without a binder, in the form of vacuum-evaporated layers or monocrystals.

Research on the PDE as well as measurement of dielectric properties makes it possible to obtain information on the behavior of the charge carriers (CCs) with restricted motion in a photoconductive material. Besides, as was noted by Bube (2), research on this effect serves as an informative additional noncontact method of measuring the photoconductivity in an alternating electric field. PDE can also be helpful when studying the band structure of complex semiconductors that present problems in producing monocrystals with sufficient size and the desired orientation for usual methods.

The phenomenon considered has considerable promise for simultaneous study of photoconductivity in, and the photoelectret states of, complex compounds with high resistance and high density of deep traps, and for studying photosensitive ferroelectric materials. In addition, the PDE makes it possible to design some new optoelectronic elements.

## **Theoretical Basis of PDE**

In the earliest stage of PDE research, the explanation of the capacitance increment under the influence of exciting light was given on the basis of Lenard's theory. This theory stated that phosphorescence processes take place inside a special *center* consisting of an activator atom and a set of molecules of base material, and the PDE was related to the photodipole effect. Later, in 1923, two explanations of this effect were outlined: (1) displacement of conduction electrons in the centers, or (2) loose binding of the knocked-out electron to the atom that captured it. Thus, the PDE was related either to conduction electrons or to trap-level electrons.

Based on the investigations carried out, the following hypotheses can be offered to explain the PDE:

- (1) It is caused by polarization of traps (3, 4).
- (2) It arises from the increasing concentration of free CCs in a nonuniform illuminated sample (5,6,7).

- (3) It is caused by space charge on the grain boundaries (8,9,10,11).
- (4) A change in the permittivity during illumination is caused by the change of nonequilibrium hopping conductivity in an alternating electric field (12).

The acceptability of the hypotheses stated above is limited by the type and structure of the material studied, the geometry of the sample, the temperature range, the frequency and electric field intensity ranges, and other experimental conditions. The main models of the effect are considered below in detail.

**Polarization on the traps.** Some of the optically generated electrons are localized in traps near the conduction band and appear to be not so tightly bound as the valence-band electrons. In an electric field, a trap–loosely-bound-electron system can yield abnormally high polarizability values, which result in an increase of the permittivity.

Garlick and Gibson (1947), in their early research on the PDE in crystalline powdered ZnS phosphors (3), provided an explanation for the increase in capacitance and thus in the dielectric constant of samples. They attributed this phenomenon to resilient polarization due to displacement of the electrons localized on shallow impurities. The reasons why the photocapacitance (PC) effect was related to the local conditions were as follows. First, both the temperature dependence of the capacitance and the distribution of electron density in traps were exponential. Second, the transient phosphorescence process was considerably faster than the emptying of the traps or the change in capacitance, whereas the relaxation time found from the frequency measurements of the photodielectric response corresponded to loosely bound electrons on the trap. However, a number of factors could not be explained from the standpoint of the model presented, in particular, the experimentally determined temperature dependence of the relaxation time.

The influence of temperature on the PDE has found an explanation in the polarization of local-state electrons, which is similar to ionic polarization. Analyzing the PDE's frequency dependence, Roux (1956) reached the conclusion (4) that when the frequency of the measuring electric field is f > 1 KHz, the PDE is also caused by polarization of systems connected with localized electrons. A model of a polarizing complex has been offered (4), in which the trap level represents a double potential well with an internal barrier separating two possible equilibrium positions of the local-state electron. When the external electric field is imposed, the majority of electrons displace against the field due to thermal energy, and thus an additional dipole moment is created. Such polarization is similar in nature to thermal ionic polarization of displacement in the ion crystals; electrons on the trap levels in this case perform the role of the localy bound ions.

In Roux's model the dielectric permittivity  $\epsilon$  and the dielectric loss tangent tan  $\delta$  are determined by the following expressions:

$$\varepsilon = \varepsilon_{\infty} + \frac{4\pi A}{T(1+\omega^2\tau^2)} \tag{1}$$

$$\tan \delta = \frac{\frac{A}{\overline{T}}\omega\tau}{\frac{\varepsilon_0}{4\pi} + \frac{\varepsilon}{4\pi}\omega^2\tau^2 + \frac{A}{\overline{T}}}$$
(2)

where  $\tau = B \exp(U/kT)$  is the relaxation time of the electrons captured on the traps, which is one of the most important features of the PDE, reflecting the dispersion domain position; *B* is the pre-exponential multiplier; *U* is the depth of the internal potential barrier between the local-state levels; *k* is Boltzmann's constant; *T* is the absolute temperature,  $\omega$  is the angular frequency of the applied electric field;  $\varepsilon$  and  $\varepsilon_{\infty}$  are the permittivities

at the frequencies  $\omega$  and  $\infty$ , respectively;  $\varepsilon_0'$  is the dielectric constant; and the parameter A is proportional to the trap-level electron concentration.

Furthermore, the investigations carried out revealed a relaxation time corresponding to certain trapping centers, in particular for ZnS; this also pointed to PC due to traps. In this case, the permittivity increment under light excitation can be evaluated from the following formula:

$$\Delta \varepsilon = \frac{4\pi N x_0^2 e^2}{3kT} \tag{3}$$

where N is the concentration of CCs, e is the electron charge, and  $x_0$  is the electron displacement.

The PC response  $\Delta C$ , that is, the increment in capacitance under illumination, is comparable with the dark value. The response calculation indicated that displacement of local-state electrons is of the order of 1 nm to 10 nm, that is, tens or hundreds of interatomic distances, which implies considerable dimensions of the traps. For shallow traps the dependence  $\Delta C(T)$  agreed with the conclusions of the analysis. However, electron displacements of the same order in the presence of deep traps called for further investigations.

Specifically, it was found that if the trap carried an excess positive charge, large electronic displacements were possible in the presence of deep traps of order 0.3 eV. Besides, it was found that, taking into account dislocation theory and the known relation between atomic and ionic radii, a dislocation itself or a part of it can perform the role of a trap.

**Effect of photoconductivity.** If a material absorbs radiation strongly, the light intensity should decrease exponentially as the distance from the illuminated surface increases. This means that the material near the surface will be more conductive than any other part. That is, an effective reduction of the insulating layer thickness takes place, which, in particular, causes a capacitance increase under light excitation.

Kallmann et al. (5), in order to give a theoretical interpretation of the PDE mechanisms in heterogeneous photoconductive crystalline powdered phosphors with a binder under ultraviolet excitation, offered a structural model that consisted of two layers. The first layer is insulating due to the binder, and the other one is photosensitive. The corresponding equivalent circuit, presented in Fig. 1(a), shows the first layer as a fixed capacitance  $C_b$  connected in series with a combination of a resistor R and a capacitor C connected in parallel. This combination represents the photosensitive layer. The resistor R is the component that varies with light intensity; therefore, the PDE is caused by nonuniformity in photoconductivity instead by a real change in the material's permittivity.

The total impedance of the material was determined as a sum of the impedances of the two layers. Thereby, it was taken into account that the changes in excitation conditions can involve both changes in the conductivity  $\sigma_{\rm p}$  and relative changes in photoconductor grain capacitance,  $\Delta C/C_0$ , that is,

$$\frac{\Delta C}{C_0} = \frac{d_2}{(d_1 + d_2)(\varepsilon \omega / \sigma_p)^2 + d_2}$$
(4)

where  $C_0$  is the dark capacitance, and  $d_1$  and  $d_2$  are the thicknesses of the radiation-sensitive and -insensitive layers, respectively.

Low-frequency dielectric dispersion of the PDE II frequencies is observed in heterogeneous semiconductors. As a first approximation, a heterogeneous semiconductor is simulated by the equivalent scheme presented in Fig. 1(b). One of the branches  $(R_1C_1)$  corresponds, for example, to the surface layer, the other  $(R_2C_2)$  to the bulk of the crystal. The relaxation time  $\tau$  of such a binary system is given by the formula

$$\tau = (C_1 + C_2) (R_1 + R_2)^{-1} R_1 R_2 \tag{5}$$



**Fig. 1.** Equivalent circuit of metal-photodielectric-metal structure. (a) This circuit represents the photosensitive layer. The resistor R is the component that varies with light intensity. (b) As a first approximation, a heterogeneous semiconductor is simulated by this equivalent scheme. One of the branches  $(R_1C_1)$  corresponds to the surface layer, the other  $(R_2C_2)$  to the bulk of the crystal. (c) A circuit representing the physical processes that take place in a metal-photodielectric-metal structure, where the branch  $C_m || R_m$  characterizes a metal-dielectric contact,  $C_p$  is the interelectrode gap capacitance,  $R_p$  is the photodielectric layer resistance, and  $R_e$  is the series resistance of the film electrodes.

The change in relaxation time and effective system capacitance is determined by the change in the relations between the values of  $R_1R_2$ ,  $1/\omega C_1$ , and  $1/\omega C_2$  under illumination. The circuit for Maxwell and Wagner's two-layer model is similar; in this model a change in permittivity is interpreted as due to the polarization of a space charge represented by two time constants  $\tau_1 = C_1R_1$  and  $\tau_2 = C_2R_2$ . In order to describe the physical processes that take place in a metal-photodielectric-metal structure, the circuit presented in Fig. 1(c) is often applied, where the branch  $C_m || R_m$  characterizes a metal-dielectric contact,  $C_p$  is the interelectrode-gap capacitance,  $R_p$  is the photodielectric-layer resistance, and  $R_e$  is the series resistance of the film electrodes.

Later, Kallman et al. (5) measured capacitance increases by factors from 2 up to the order of  $10^9$  for monocrystalline CdS with transparent gold contacts. It was concluded that such large increases in PC cannot result from electron polarization on the traps, but must be a photoconductivity effect, which causes a reduction of the effective material thickness. Kronenberg and Accardo (6) concluded that in some other substances, for example, ZnS and ZnO, PDE can be also related to photoconductivity in the heterogeneous photodielectric of a capacitor; thus the decay of the photodielectric response does not depend on temperature.

An analysis of possible PDE I manifestation, as well as a more coherent theory of the PDE in terms of conductivity due to unbalanced CCs in granular samples (PDE II) of a number of crystalline phosphors, has been presented by Vergunas and Malkin (13). These researches set the criteria for PDE I, at least for semiconductor phosphors: tan  $\delta$  is prone to saturation when the illumination flux *L* increases, and the curves of tan  $\delta$  versus frequency at different illumination values do not intersect. The following conditions are characteristic of PDE II: tan  $\delta$  (*L*) is the maximum value and the curves of tan  $\delta$ (*f*) at different *L* values intersect. Furthermore, as

*L* increases, a maximum that shifts to higher frequencies should be observed, and the PC should tend to a constant value. For the most part the conclusions presented were supported by experiments.

When studying ZnS monocrystals, Broser and Reuber (14) discovered that the photodielectric response was due to thermoactivation and established various temperature intervals for the occurrence of PDE I and PDE II. A photodipole effect takes place at a low temperature of about 78 K, whereas at room temperature  $(T \approx 298 \text{ K})$  the PDE can be viewed as a conductivity effect; in the case of large binder-photodielectric ratio, PDE II prevails. For the same semiconductor, Krispin and Ludwig (11) showed that the Debye's relaxation model could be used to describe the photodielectric response. Later, Oksman (12) conjectured the existence of a relation between the PDE and changes in the nonequilibrium hopping conductivity.

Kneppo and C ervenák (7) described a PDE model for one-dimensional stationary conditions based on a photodielectric that is electrically homogeneous with one carrier type—holes—in which the gradient of free-CC concentration in the illuminated dielectric assumes a nonzero value. Most of the results of this theory agreed satisfactorily with experimental results on thin-film metal–CdTe–metal structures.

Using the results of Ref. 7 as a basis, Pilai et al. (8) presented an improved theoretical model of the PDE in semiconductors, which includes the influence of traps. The model agrees with experimental data on real photocapacitors, in particular with the dielectrics ZnO, ZnO:Li, and PbI<sub>2</sub>.

The authors of Ref. 8 modified the equations obtained in Ref. 7 for the case of a conduction gradient induced by the PDE and with allowence for capture on traps under the conditions of nonequilibrium light excitation. The following expressions for the relative change in capacitance and conductivity, respectively, were established:

$$\frac{\Delta C}{C_0} = \frac{\lambda_0}{d(1+n_{\rm t}/n_0)^{1/2}} \left[ \ln\left(1 + \frac{2SI_0}{\nu\sigma_0(1+n_{\rm t}/n_0)^{1/2}}\right) \right] \tag{6}$$

$$\frac{\Delta G}{G_0} = \frac{nl_0}{2d(1+n_{\rm t}/n_0)^{1/2}} \left[ \ln\left(1 + \frac{2SI_0}{\nu\sigma_0(1+n_{\rm t}/n_0)^{1/2}}\right) \right] \tag{7}$$

Here  $\Delta G$  is an increment of conductivity under illumination,  $G_0$  is the dark conductivity for alternating current,  $n_0$  is the equilibrium concentration of local states,  $n_t$  is the density of filled electronic traps,  $\sigma_0$  is the dark conductivity for direct current,  $\lambda_0 = (\varepsilon k T/2e^2 n_0)^{1/2}$  is the Debye shielding length with no account taken of traps,  $\nu = 1 + (\varepsilon \omega / \sigma_0)^2$  (with  $\omega$  the angular frequency), and  $S = \varepsilon \mu_n \eta \alpha / 2n_0$  (with  $\mu_n$  the electron mobility,  $\eta$  the quantum efficiency,  $\alpha$  the optical absorption coefficient, and  $\gamma$  the recombination coefficient). The relation  $\lambda' = \lambda_0/(1 + n_t/n_0)^{1/2}$  determines the Debye effective length reflecting the fact that local states are present.

Thus, two main explanations of the PDE had been established: (1) trap-level electron polarization, which is characterized by such behavior as dipole absorption (PDE I), and (2) photoconductivity of semiconductor material grains, which displays the Maxwell–Wagner effect for a heterogeneous system (PDE II). In both cases the expressions derived for the real and imaginary parts of  $\varepsilon *$  as functions of frequency and temperature are approximately the same, and the two cases are rather difficult to distinguish. The relative contribution of a particular mechanism is determined either by special features of the semiconductor samples (such as geometry or technological history), or by experimental conditions (measuring equipment, temperature, frequency of electric field, and mode of light excitation, as well as light intensity and spectral composition).

Many photoconductors can manifest PDE I and II simultaneously. That PDE I is not observed in some photoconductive substances can be explained in terms of the masking influence of conductivity electrons in a heterogeneous sample. It is necessary to note that the concentration of impurities and the presence of defects in the structure determine the effect in monocrystals. It should be also noted that materials with small

concentration of free CCs, low CC mobility, and weak photoconductivity are unable to display much response, though it would correspond to PDE II.

**Space charge on grain boundaries.** The model based on the occurrence of space charge on the grain boundaries is applicable for polycrystalline materials only. Particularly, the PDE is probably caused, according to Garlick, by dipole layers on boundaries between grains. With the Maxwell–Wagner theory and the Cole–Cole diagram method for analysis of measurements of impedance made on photoconductive crystal ZnCdS powders with alternating current, Mark and Kallmann (9) came to the conclusion that the PDE in powders is probably caused by dipole layers in the boundary domain between the grains. At low frequencies the charges move to the surfaces of photoconductive regions and contribute to the material's polarization. At high frequencies, the free charges move too slowly to follow the alternating electric field, and therefore relaxation takes place. Polarization at low frequencies is proportional to the free-carrier number, with the result that a PDE takes place.

A model supposing that the PDE is caused by space charge on grain boundaries has also been offered by Dropkin (10), and an interpretation of the effect, as Krispin and Ludwig (11) believed, is possible using the linear theory of space-charge polarization. According to Ref. 8, it is anticipated that polarization caused by a space charge can be observed in the low frequency range of PDE measurements, in which dispersion caused by electronic, ionic, and orientation contributions appears to be insignificant.

Possible mechanisms of space-charge formation are the following: equilibrium CC polarization under the influence of an electric field, photogenerated CC polarization, and CC injection into electrode material. The last factor, apparently, need not be taken into account if the electrostatic intensity is sufficiently low.

Space-charge formation can take place at the grain boundaries of a polycrystalline structure close to the electrodes, at the surface, and in the bulk. An attempt has been made to determine the PDE mechanism by parallel measurements of photocurrent and dark current along with measurement of alternating-current electrophysical parameters as functions of temperature. Analysis of the results obtained from measurement of alternating- and direct-current impedance have indicated that observable regularities of the PDE could be explained, in this case too, by formation of a space charge on grain boundaries of polycrystalline samples of semiconductor material.

Along with inorganic photoconductors, prospective materials for studying the PDE include organic materials, pigment dyes in particular. The molecular structure of organic materials allows us to produce structures with considerable change of dipole moment under irradiation, with formation of polarized states of CCs in internal and external parts of molecules. Moreover, the formation of polar structural varieties is possible near local states, which also gives a considerable contribution to the PDE. Notable effects can accompany electronic processes, such as nonlinear optical phenomena (e.g., generation of second harmonics), separation of CCs, formation of electron-hole pairs inside molecules, photoconductivity, etc.

The PDE for organic materials appears to be mainly a result of changes in dipole moment and polarizability in excited states. This conclusion is based, first of all, on the small concentration of free CCs and their low mobility in those materials, which because of the weak photoconductivity inherent in organic materials preclude appreciable PDE II. The linear theory of space-charge polarization, in which a considerable role is played by CC charges caught on traps, is also incapable of describing adequately the obtained experimental results.

## PDE Technique

**Samples for PDE Measurements.** It is fairly easy to produce photocells with large areas out of highresistance photoconductive layers containing binders. This makes them useful for research and many practical applications. The technology of preparing such layers consists in mixing the initial photoconductor powder with binder dissolved in organic solvent, for example, methylbenzene in various proportions. Polystyrene, Teflon, or



**Fig. 2.** Schematic representation of the structure of the experimental sample for PDE measurements. The layer under study has the simultaneous functions of a photoconductive and a dielectric medium.

organosilicon binders can be used. A binder made of such materials consists of a high-resistance layer tolerant of light excitation, which sits between photoconductive grains and does not affect PDE measurements.

When a homogeneous suspension is achieved, a mixture of photosensitive powder and binder is put on a substrate covered by a conducting transparent layer, for example, tin dioxide  $(SnO_2)$ . After a lapse of time, the solvent evaporates and a smooth photoconductor layer with binding is formed. In most cases a value of the binder/photoconductor ratio is chosen to reduce the capacitance between grains while preserving contact between the powder particles. The second electrode can be formed on the outside surface of the photoconductive layer by thermal vacuum deposition of metal or in some other way.

Measurements of the PDE are usually performed with sandwich structures, because they are best suited for calculation of the permittivity and the resistivity. Figure 2 shows a schematic structure of the system Me-photodielectric– $SnO_2$ , in which the layer under study has the simultaneous functions of a photoconductive and a dielectric medium.

**PDE measurements.** Figure 3 shows a block diagram of a setup for PDE analysis with a low-frequency alternating electric field. In order to measure photodielectric responses, the intensity of illumination can be adjusted by a change of slit width in the monochromator, as well as by using a set of neutral-density filters. Light excitation of samples under study can be carried out by means of a ribbon or spiral filament lamp, a xenon or mercury lamp, or a laser. When calculating spectral characteristics, the dispersion of the monochromator and the spectral characteristics of the irradiation source should be taken into account.

Measurement of photodielectric increments in  $\varepsilon *$  over wide temperature and frequency ranges is carried out mainly with the aid of standard bridge-circuit schemes. To avoid appreciable polarization, low amplitudes of measuring voltage (from an oscillator) are used. The indicator diagonal includes an indicator or selective amplifier. The dielectric loss tangent and complex permittivity are determined from measurements of the capacitance and conductivity by balancing the ac bridge circuit. The instrumentation delay should be less than the relaxation time of the the PDE, and the effect itself can be studied if in addition a constant voltage bias is applied to the analyzed sandwich structure.

## **Experimental Analysis of Photodielectric Phenomena**

The first PDE studies contained measurements of capacitance increments made only under illumination of semiconductor samples; consequently the PDE was referred to as a photodipole effect. By the end of the 1940s, however, PDE research had begun that was based on measurement of dielectric losses with simultaneous study of the permittivity increment under exposure to various wavelengths.



**Fig. 3.** A block diagram of the apparatus for complex PDE measurements up to 20 kHz (15). The cell with the sample under study is placed in a darkened vacuum chamber or cryostat. Illumination is introduced through quartz windows of the cryostat, using a system of lenses, which ensure focusing of the light beam on the sample, and either a monochromator tunable over a wide spectrum, or a combination of colored glass filters.

A considerable amount of research has been devoted to the experimental study of the PDE in various inorganic and organic materials. During PDE analysis, dielectric parameters of sample are determined when there is a change of various parameters, such as field frequency, irradiation intensity, and length of irradiation wave. Proceeding from the fact that electrons transit, due to photoexcitation, into conductive band, many authors believed those dielectric phenomena to originate only in the photoconductivity of samples. This bias made it difficult to consider any other mechanisms that could be observed under special experimental conditions only, for example, at low temperatures or high frequencies of the applied alternating field. According to the literature, most PDE measurements were carried out on powder samples with binding, in which the effect



**Fig. 4.** Plot of the overlap coefficient  $K_{\rm L} = C_{\rm L}/C_{\rm D}$  against frequency and luminous flux for a Pb<sub>3</sub>O<sub>4</sub> photocapacitor (15). According to the results obtained for various intensities and audio frequencies of the measuring field, a negative dispersion of  $K_{\rm L}(f)$  takes place. When the illumination intensity increases, an appreciable displacement of the experimental curves at the higher frequencies occurs. This leads one to believe that the photodielectric response in the analyzed structure is determined by the change of conductivity, or more precisely, by its growth in a heterogeneous photoconductor, which can be referred in turn to the occurrence of PDE II.

was identified, as a rule, with conduction electrons of granular structures (PDE II). The fraction of PDE II in monocrystals can be large and can be determined, first, from the conductivity due to the presence of donor impurities.

Since the binder is not a photoconductor and there is a need to exclude possible influence of frequency and temperature changes of its dielectric characteristics, one usually studies the behavior of corresponding increments  $\Delta C$  and  $\Delta \tan \delta$ , which are caused by nonequilibrium light excitation. The experimental results presented below have been obtained on metal–Pb<sub>3</sub>O<sub>4</sub>–SnO<sub>2</sub> sandwich structures. Selection of the polycrystalline photoconductor minium (Pb<sub>3</sub>O<sub>4</sub>) as a model object of experimental analysis is made because of its photosensitivity to visible light over a wide range of wavelengths, the stability of its physical properties, and the possibility of practical application in optoelectronics (15). Trilead tetraoxide samples have high enough resistance ( $\rho \sim 10 \text{ T}\Omega \cdot \text{m}$ ) and are photosensitive, so that they meet the requirements on semiconductors for studying their photodielectric properties.

Dispersion characteristics. Measurements of the frequency dependence of dielectric parameters are very important for understanding of the PDE. In Fig. 4, the frequency dependence of the overlap coefficient  $K_{\rm L} = C_{\rm L}/C_{\rm D}$  is given, where  $C_{\rm D}$  and  $C_{\rm L}$  are the capacitance values for the dark and light modes of measurement in Pb<sub>3</sub>O<sub>4</sub>, respectively. The initial part of the analyzed frequency range displays good separation of the PC and dark capacitance curves. As the frequency increasers, this separation decreases, and it practically vanishes at high frequency, independently of the illumination level. The observed dependences generally agree in character with the basic laws of permittivity dispersion for conductivity and polarization of the relaxation type.

One should treat polarization of space charge and interlayer polarization as another probable mechanism underlying the PDE for the analyzed polycrystalline photoconductor. Electric nonuniformity in the form of space charge can become a source of dielectric losses and polarization in the electric field. The influence of a given charge is more appreciable at low frequencies of measurement, since the change of the PDE response takes place in phase with the change of applied electric field.



**Fig. 5.** Variation of capacitance increment with temperature for  $Pb_3O_4$  photocapacitor at various frequencies of the applied ac electric field (15). This parameter increases with *T*, but the nature of the relaxation remains the same, testifying to the large contribution of space charge to the PDE.

Additional CCs are generated in an illuminated sample, resulting in larger increment values  $\Delta C = C_{\rm L} - C_{\rm D}$  for frequencies at which space-charge polarization dominates. The reduction of the latter at high frequencies results in a corresponding decrease of dielectric losses and PC values. The increase of dielectric losses at high frequencies observed for some semiconductors under illumination is apparently explained by oscillatory processes in dipole formation, which respond to the point defects in the sample.

In Fig. 5 and Fig. 6 are shown the temperature dependences of capacitance increments and tan  $\delta$ , respectively, under light excitation of the analyzed structure at different frequencies of the electric measuring field. The values of those parameters increase with T, but the nature of the relaxation remains the same, testifying to the large contribution of space charge to the PDE. This charge is generated by additional thermogeneration of CCs due to displacement of the Fermi level into the region of exponential distribution of trap states.

The saturation of the density of PCs for most photoconductors might be explained by saturation of trap occupation. From the standpoint of PDE II, the same curve can explain the rise of shunting conductivity due to PC. It might be assumed as well that with increase of illumination intensity, increasing numbers of CCs are generated, causing an increase of the total space charge.

At high frequencies, the permittivity photodielectric response can be determined indirectly from measured data on the cavity resonator frequency. In addition, dielectric losses can be determined from the Q factor characterizing the resonance peak from the following relation:

$$Q = \frac{f_{\rm m}}{\delta f} \tag{8}$$

where  $f_{\rm m}$  is the resonance frequency, and  $\delta f$  is the frequency deviation at half peak height.

**Spectral Dependences.** PDE spectral study helps to collect information on the energy structure of semiconductors. In contrast to photothermal ionization, thermal ionization of excited states thus can be avoided. The energy-band structure of certain compounds has remained unstudied because of a lack of monocrystals



Fig. 6. Peaks of dielectric-loss-tangent relaxation at various frequencies (15).

of sufficient size for the usual methods: spectral reflection, absorption, photo- and electroluminescence, or modern techniques of modulation spectroscopy such as electro- and thermoreflection. In such cases, it is evidently useful to study photodielectric spectra, that is, the dependence of the photoresponses  $\Delta C$  and  $\Delta$  tan  $\delta$  on the wavelength  $\lambda$  of radiation falling on powder samples, which can be used both for express evaluation of the bandgap of semiconductor compounds such as GaAs and CdTe, and for analysis of their energy-band fine structure. In Fig. 7 are shown dependences  $\Delta C(\lambda)$  for Pb<sub>3</sub>O<sub>4</sub> obtained at two temperatures. Polarization of photogenerated CCs causes the formation of additional space charge, which in turn increases the capacitance, conductivity, and dielectric losses.

**PDE Kinetics.** The kinetics of high-speed constituents of the PDE can be studied with the aid of an unbalanced ac bridge circuit connected ultimately to a data plotter. The experiments indicate, that the capacitance rise and dielectric losses increase when samples are illuminated. The decay of these parameters after the illumination is switched off is not instantaneous, and is characterized, as shown in Fig. 8, by definite time dependences.

It was found for a number of materials, particularly organic semiconductors, that both the increase of  $\epsilon$  under illumination and its decrease in darkness are activated by temperature (16):

$$\left(\frac{d\varepsilon}{dt}\right)_1 \propto \exp\left(-\frac{E_{\rm A}}{kT}\right)$$
 (9)

$$\left(\frac{d\varepsilon}{dt}\right)_{\rm d} \propto \exp\left(-\frac{E_{\rm D}}{kT}\right) \tag{10}$$

where  $E_{\rm A}$  and  $E_{\rm D}$  are the thermal energies of activation and deactivation for the PDE, respectively.

The exponential dependence of the dielectric-parameter changes on time confirms that the decay process of molecular excited states has an activation nature, with formation of charge carriers. In particular, the decrease



**Fig. 7.** PDE spectra for a  $Pb_3O_4$ -based photodielectric structure at various temperatures (15). Peaks of photocapacitance can be associated with photoexcitation of CCs corresponding to the optical absorption edge in the material.

of PDE delay with decreasing temperature (Fig. 8) can be explained by probable capture on traps, which in fact show complete absence of thermal discharge. When the temperature is high (close to room temperature), a long delay in the PC decrease might be caused by the difficulty of irreversible capture of charge carriers on the same traps, in that the thermal discharge grows exponentially and impedes shielding of CCs captured on traps.

Experimental PDE research on semiconductors also establishes the dependence of the kinetic curves on the intensity of the flare. Large relaxation times, on the order of thousands or more, usually point to "photomemory" in the PC mode. When light excitation is removed, the residual PC substantially depends, as investigations indicate, on the wavelength, and in smaller degree on the illumination intensity, as is characteristic for long-term processes related to changes in the concentration of CCs, and not their mobility. Moreover, some authors believe that a PC effect in photoconductors can result from drift barriers formed by interlayers included sequentially in crystal growth. Besides the influence of barriers on grain boundaries in polycrystalline samples, the specified processes, according to data, can be influenced by collective repulsive barriers that surround a group of traps with small capture cross section. Hence, one can conclude that PDE kinetic processes in polycrystalline structures probably have bulk nature.

**Photoferroelectric Phenomena.** The work of Fridkin (17) and others gives detailed information on photodielectric phenomena in semiconductors with polar symmetry of crystalline lattice structure (so-called ferroelectric semiconductors), and shows that PDE study in ferroelectric semiconductors complements the



**Fig. 8.** Experimental transient data for  $Pb_3O_4$  (dielectric parameters and a step change in light intensity): time-domain representation of a photodielectric response for a  $Pb_3O_4$ -based photocapacitor (15). Analysis of the photodielectric response kinetics reveals appreciable influence of temperature on the changes in dielectric parameters in response to light excitation: thus, the thermoactivative nature of the PDE is confirmed.

techniques based on ferroelectric and pyroelectric phenomena. It was found out that light excitation changed the conditions for the establishment of ferroelectric domain structures; namely, the change in  $\varepsilon$  under illumination can be related to a change of conditions for motion of domain boundaries, which is caused in turn by a change in conductivity. In the case of photoferroelectrics, photohysteretic and photodomain effects, as well as shielding of spontaneous polarization by nonequilibrium carriers, should be considered as the most probable reasons for PDE.

Detection of considerable photosensitivity in barium titanate  $BaTiO_3$  revealed that this ferroelectric displays the influence of unbalanced CCs on the high-temperature transition from the tetragonal phase to the cubic one. Under the influence of unbalanced CCs, a decrease in the Curie temperature, according to the theory of thermodynamic transitions in ferroelectrics, took place, and the dependence of shift value on light intensity appeared to saturate. The temperature dependence  $\varepsilon(T)$  under illumination in the domain of photosensitivity revealed temperature hysteresis of the phase transition to SbSI. Measurements conducted at equal energies indicate that the photohysteretic effect is connected with an increase of the crystal's photoconductivity. Illumination of these crystals in the state of maximum photoconductivity at low temperature results in metastable recharging of levels, which is preserved in darkness for a long time, dependent on the temperature and the activation energies of levels.

### Photocapacitance Spectroscopy of Deep Local States

Deep centers (DCs), that is, centers possessing deep energy levels (for instance,  $\approx 0.2$  eV to 0.5 eV for Si) in the bandgap of a semiconductor, are tightly connected with defects due to heat treatment, irradiation defects, and

impurities (Au, Ag, Zn, S, etc.) and influence its electrical and optical properties. They are usually multiplecharge, that is, several deep levels that belong to each atom of such a defect are formed at once in the bandgap of the semiconductor.

In some cases, the existence of DCs leads to useful or, on the contrary, undesired properties of semiconductor materials and instruments. In optoelectronic instruments particularly, such as light-emitting and laser diodes and photoconductive detectors, DCs reduce the efficiency of transforming electric energy into optical energy and influence parameters of semiconductor materials and ready-made instruments much more strongly than shallow centers.

Along with conventional methods of DC research (Hall effect, photoconductivity, lifetime of minor carriers), PC spectroscopy of trapping centers has been developing over many years in such widely used semiconductors as Si, GaAs, and GaP. It is based on change of barrier capacitance, that is, registration of charge-density changes in p-n transitions, the depleted layer of a Schottky diode playing the part of the capacitor or metal-insulator-semiconductor (MIS) structure when the sample in excited by monochromatic ionizing irradiation.

Advantages of capacitor methods are high sensitivity, the opportunity to determine DC parameters when there is a change in their occupation by both majority and minority carriers, and the opportunity to study DCs both in semiconductor instruments produced with industrial technology and in unfabricated semiconductor materials. PC spectroscopy of deep levels in semiconductor crystals began with experiments on the fixed PC of diode structures, from which, in the initial research stages, one could obtain information on optical energy required to ionize specified levels. PC was studied directly for the first time in GaAs, in which the PC spectrum was later observed by monochromatic methods.

According to the nature of the PC change, it can be determined whether the level being measured is near the bottom of conduction band, or near the top of the valence band. Recharging of deep levels can be carried out also by irradiation of impurities with photons of energy smaller than the bandgap. In this case, the energy of deep-level activation can be determined from the PC spectrum, and the excitation line is broader than for thermal excitation, since photoexcitation takes place. The method considered can be varied: it is possible to register the capacitance change under illumination while imposing a direct-current voltage on the diode; it is possible as well to register capacitance change on the diode in the steady state caused by illumination of the source with the necessary range of photon energies.

The PC spectroscopy methods have been applied to wide-spectrum investigations. The most important ones are studies of spectral dependences of optical cross sections for transitions between deep levels and bands of a crystal. Substantial DC influence on properties of semiconductor materials and structures has led to increasing work on the determination of recombination parameters of deep levels by PC techniques.

Special features of PC spectroscopy of DCs were examined in detail by Berman and Lebedev (18). The change in the diode barrier capacitance on recharging DCs with their own light takes place, as a rule, according to an exponential law and is described by the formula

$$\frac{C^2 - C_{\rm s}^2}{C_{\rm s}^2} = \frac{N_{\rm d}}{N_{\rm s}} \exp\left(-\frac{t}{\tau_{\rm n}}\right) \tag{11}$$

where  $C_s$  is the fixed capacitance value,  $N_d$  is the concentration of deep donors,  $N_s$  is the concentration of small-sized donors, and  $\tau_n$  is the time constant for a level filled with electrons.

After measuring the time constant of this process, it is possible to determine the capture cross section  $\sigma_n$  for CCs on DCs using the formula

$$\sigma_{\rm n} = \frac{e v_{\rm d}}{j \tau_{\rm n} v_t} \tag{12}$$

where  $v_d$  is the drift velocity of electrons,  $v_t$  is the thermal velocity of electrons, and j is the current density in a reverse-biased p-n junction.

Measurement of PC allows determining the distribution of DCs according to the depth of the p-n transition. The concentration of ionized centers in the charge-depleted layer, the capacitance of the diode, and the voltage are connected by the well-known relation

$$N_{\rm i} = \frac{2}{e\varepsilon\varepsilon_0 S^2} \frac{dU}{d(1/C^2)} \tag{13}$$

where S is the p-n transition probabiality, and U is the constant return displacement. Let us define  $w = \varepsilon \varepsilon_0 S/C$ , as the width of the space-charge domain (SCD) at the preset voltage U. By changing the latter, it is possible to obtain the dependence N = f(w) in dark mode and under illumination by impurity light. For determination of the DC distribution, the concentration of DCs will be defined in this case by the expression

$$N_{\rm d}(w) = N_{\rm i}^{\rm l}(w) - N_{\rm l}^{\rm d}(w) \tag{14}$$

where  $N_{i}^{1}(w)$  and  $N_{i}^{d}(w)$  are the concentrations of charged centers in SCD before and after recharging of DCs for the same value of w, respectively.

The instrumentation for measuring PC includes an optical part for optical excitation, an electric measuring part for measurement of capacitance, a thermostatic controller circuit, and a computer control system. Figure 9 is a block diagram of the setup for PC spectroscopy. Measurement of the structure's capacitance is performed with the aid of a small alternating voltage coming from oscillator and imposed on the large dc bias voltage.

Utilization of the phase detector increases the sensitivity of the installation and reduces the influence of interference. When the deviation of the bridge from balance is slight, the imbalance voltage is proportional to the change in the diode's capacitance, if its conductivity remains constant. The bridge balance can be checked also with the oscillograph. Sample illumination is provided by means of the optical system, which include a light source and monochromator.

The procedure of measurement includes several phases. First, the structure under study is placed in the chamber of the optical cryostat, entirely shielded from scattered light, and is fixed in a holder supplied with system of cooling and heating for adjustment of temperature within preset limits, and then it is cooled without illumination at null voltage in order to allow electrons to occupy all deep levels initially. The temperature selected is low (for example, 77 K) to reduce the heating rate. Then a reverse voltage is applied to the structure, and it is illuminated with monochromatic light in the region of impurity absorption.

Since the heating rate is low, any change in the structure's capacitance is caused solely by change of the space-charge density due to photoionization of deep traps. This condition, at temperature 77 K, usually is achieved for levels with  $\Delta E > 0.18$  eV in germanium, silicon, and gallium arsenide.

Differential capacitance measurement on diodes is conducted in the conventional way with the aid of a small alternating signal, which is imposed on a large bias. Capacitor methods of DC research have as their special feature a need to measure small changes of capacitance against the background of large values of cable parasitic capacitance and initial diode capacitance in darkness. Bridge-circuit methods of capacitance measurement meet these requirements best. In many cases, digital instruments for capacitance measurement can be applied.

Electrical measurements are carried out with aid of direct-current voltage controller on the diode and a capacitance meter. At measurement, the values of  $C_0$  frequency, and signal amplitude are specified. These parameters are first varied, and after determination of their optimal values, they are fixed. In principle it is required to enter a correction for the relation between the reciprocal frequency 1/f and lifetime  $\tau$  of captured CCs. The operating frequency range in the measuring setup is 10 kHz to 10 MHz, and the voltage is varied



**Fig. 9.** A block diagram of the experimental system for PC spectroscopy, where S is the sample (diode structure), T is a thermocouple, and CS is a computer system. The diode structure S under study is placed in the vacuum chamber and is connected in series with a blocking capacitor to the input of an ac bridge circuit. The bridge unbalance voltage is amplified by the selective voltmeter with high sensitivity, then fed to the input of the phase detector and registered by the data plotter or computer system display.

from 1 mV to 250 mV. When PC spectra are measured, evaluation of the time dependence C(t) is necessary to determine more sharply the termination of the DC recharging process at given photon energy.

The following main requirements are applied to the optical part of the instrumentation for PC measurement: the spectral range of the monochromator is determined by the energy of ionization of the deep levels under study, and by the experiment temperature, on which the time constant of DC recharging depends. When PC is measured, careful shielding of the sample is necessary to exclude scattered light, since the latter can cause considerable DC recharging when the monochromatic irradiation source is switched off.

When the capacitance is being determined, it is required to shield the sample carefully from scattered light, especially at short wavelengths, that might fall on the sample from the monochromator. Therefore, light filters are placed just before the sample, excluding short-wave radiation. Exciting light is fed to the sample by means of mirrors and fiber optics. For the optical system a shutter is provided, which is opened only after the lamp has stabilized and the light intensity has become constant. The shutter also determines the beginning of illumination when measuring photogeneration of carriers, that is, optical cross sections.

PC is measured on samples in the form of diodes with diffusion, and of alloyed or epitaxial p-n junctions, as well as Schottky barriers. The last-mentioned, however, are of special interest, in that they allow determining the DC concentration in unfabricated crystals.

Experimental realization of PC spectroscopy has as its special feature measurement of small changes of capacitance under illumination in the presence of large capacitances of the structure and large input capacitances of the measuring instrument. Both the sensitivity of the instrument and the stability of the resistance characteristic of the structure under study determine the actual sensitivity of the method. The technique is limited moreover by the photoionization cross section of deep levels and the intensity of impurity light. The sensitivity of the measuring setup, the total capacitance of the diode structure, the photoionization cross section for the monochromatic luminous flux in use as a function of intensity, and other factors determine the minimum DC concentration that can be measured with the aid of PC.

With the use of bridge-circuit methods of capacitance measurement, the minimum value of the ratio  $\Delta C/C$  is on the order of 0.001 to 0.01, and minimum concentration of deep centers that can be measured by PC is  $N_{\rm c} \approx 2N_{\rm d} \Delta C/C = 2 \times 10^{-3} N_{\rm d}$ . Hence, in samples with inpurity concentrations of the order of  $10^{13}$  cm<sup>-3</sup> it is possible to detect DCs if their concentration is on the order of  $10^{10}$  cm<sup>-3</sup> to  $10^{11}$  cm<sup>-3</sup>.

In many applications, with the use of thermal irradiation sources with continuous spectrum, the density of monochromatic luminous flux does not exceed  $10^{15}$  to  $10^{16}$  quanta  $\cdot (\text{cm}^2 \cdot \text{s})^{-1}$ , which creates, for levels with ionization cross section  $10^{-20}$  cm<sup>2</sup>, a time constant for optical recharging equal to  $10^4$  s. Measurement of such slow processes requires a setup of high stability and reliable samples.

One modification of the PC method is based on the application of an additional source of light with fixed wavelength for steady-state filling of deep levels, which eliminates the slow drift of the capacitance structure due to thermal emission of electrons and holes. The initial steady-state filling can alter under the influence of the second source of light with alternating wavelength. The signal is differentiated so that it can be processed electronically.

### Practical USE off the PDE

**Photocapacitors.** A number of instruments that use the PDE have been designed. In recent years, interest in light-sensitive capacitors has seen considerable growth. Depending on the application, photocapacitors are required with various ranges of operating frequencies, temperatures, and dark and light characteristics.

Wide variation of photocapacitors' properties is possible in the event that they consist of photosensitive (active) and nonphotosensitive (inert) layers (structural photocapacitors). Such structure allows production of a photocapacitor with capacitance varying over several orders of magnitude. These elements have as an active layer consisting of monocrystals, pressed powders, or thin layers of inorganic semiconductor materials. Sihvonen and Boyd (19) tested a two-layer photocapacitor with an active layer of CdS and an inactive layer of either  $BaTiO_3$  or silicon-organic plastic. At low light intensities, the active material behaved as an insulator, and the equivalent permeability of the instrument corresponded to

$$\varepsilon = \frac{\varepsilon_1 \varepsilon_2 (d_1 + d_2)}{\varepsilon_1 d_2 + e_2 d_2} \tag{15}$$

where the *d*'s are thicknesses, the subscript 1 stands for the inert material, and 2 stands for the active one. When the light intensity is high, the active domain behaves as a short circuit, and the permittivity equals the value of  $\varepsilon$  for the passive domain. A capacitance increase of 2500 times was obtained with the use of barium titanate as a passive layer at frequencies up to 0.22 MHz, and increases up to 20 times were obtained for CdS on silicon-organic plastic at frequencies up to 10 MHz. The usefulness of such instruments was limited by a delay in response to a change in light excitation. The dissipation factor was also important under certain conditions.

Gordon et al. (20) made a photocapacitor consisting of powdered CdS dissolved in plastic and intended for use in resonant circuits for increased sensitivity in cases where slow response was acceptable. Saturation was reported when the PC reached approximatly 1 to 6 times its reference value.

It is worthy of note that the number of materials suitable for this purpose is not large, and manufactured components have shortcomings that limit their technical application. Thus, photocapacitors based on ZnS, CdS, and ZnO are characterized by low values of the quality factor Q and by large times of photoresponse and relaxation to dark values on the order of several minutes, which have prevented them from having wide technological application. Structural photocapacitors based on Si and SiO<sub>2</sub>, though having fast operating response (~1 ms), have low operating voltage and unsatisfactory dielectric characteristics. Photocapacitors on CdS and CdSe with dielectric made of SiO<sub>2</sub>, BaTiO<sub>3</sub>, or silicon plastic had considerable time delay (~0.1 s) and poor dark characteristics, as well as a piezoelectric effect for CdS. These shortcomings due to properties of materials also hinder wide application of structural photocapacitors. A number of such problems might be solved by the use of organic photodielectrics with essentially different characteristics.

**Photocapacitors on MIS structures.** Transformation of light energy into an electric signal and its parametric amplification combined in one instrument are realized in the photovaricap (PV), which has as its principle of operation the dependence of a p-n junctions capacitance on the illumination. Also promising for application as photocapacitors are MIS structures. MIS PVs (21, 22) use capacitance modulation of the isolated SCD due to an increase in the number of CCs under illumination. A schematic representation of a typical MIS photocapacitor in a metal–SiO<sub>2</sub>–(n-Si) system and appropriate band diagrams in the dark and under illumination are shown in Fig. 10. The resistance of the dielectric interlayer determines the large input resistance of such a photocapacitor. This ensures a high Q factor and low enough noise when the PV is used in infrared engineering. For application in optoelectronics, the main requirements are high efficiency and short switching time.

Classical materials for the photoconductor layer are Si and GaAs. As a dielectric,  $SiO_2$  is most often used, produced by vacuum deposition and pyrolysis decomposition methods. Ferroelectric  $BaTiO_3$  and  $Bi_4Ti_3O_{12}$  find application as well: dielectric hysteresis arises in them, which is used in memory elements. Dielectric films are required to display good light transmission in the operating spectral range.

The capacitance of an MIS capacitor is given by

$$C = \frac{C_{\rm s}C_{\rm d}}{C_{\rm s} + C_{\rm d}} \tag{16}$$

where  $C_s$  and  $C_d$  are the capacitances of the SCD layers of the semiconductor and dielectric, respectively. The capacitance C, in this instance, varies between the maximum

$$C_{\rm d} = \frac{\varepsilon_0 \varepsilon_{\rm d}}{L_{\rm d}} \tag{17}$$



Fig. 10. Schematic section of MIS capacitor for (a) dark and (b) illuminated states; (c) and (d) show the corresponding band diagrams.

determined by the thickness  $L_d$  of the dielectric layer, and the minimum

$$C_{\rm s} = \frac{\varepsilon_0 \varepsilon_{\rm s}}{L_{\rm s}} \tag{18}$$

determined by the thickness  $L_s$  of the SCD layer. In these equations  $\varepsilon_d$  and  $\varepsilon_s$  are the dielectric permittivities of the dielectric and the semiconductor, respectively, and  $\varepsilon_0$  is the dielectric constant.

MIS elements are more easily manufactured and can be based on planar technology, which reduces the optical and recombination losses in such devices. If the technology of producing MIS structures is developed enough, losses on leakage currents can be decreased to 30%. This will increase the efficiency of MIS photosensors by 1.5 to 2 times over usual devices. MIS PVs can be produced easily as part of optoelectronic integrated microcircuits.

The photosensitivity of a varicap rises with increase of the overlap coefficient  $K = C_d/C_s$ . Thus the efficiency of an MIS capacitor as a varicap can be increased by reducing the dielectric thickness. For operation with minimal luminous flux one needs a steep capacitance-voltage characteristic, that is, a large relative

change of PV capacitance per unit of luminous flux F, which characterizes its coefficient of photosensitivity:

$$K_{\rm p} = \frac{1}{C} \frac{\partial C}{\partial F} \tag{19}$$

The overlap coefficient and photosensitivity coefficient depend substantially on the operation mode of the PV. The photosensitivity coefficient is defined by the formula

$$K_{\rm p} = K_{\rm n} \frac{\partial U}{\partial F},\tag{20}$$

where  $K_n$  is a nonlinearity coefficient, defined by the expression

$$K_n = \frac{1}{C} \frac{\partial C}{\partial U} \tag{21}$$

The characteristics of a PV in general are functions of the voltage applied to the shutter, the illumination, the rates of generation and surface recombination, and the rate of surface CC adhesion. When operating with large luminous fluxes, the nonlinearity in the capacitance of a PV is characterized by the change of its capacitance from the minimum dark value  $C_0$  to the value  $C_m$  that correspond to the preset luminous flux.

Theoretical dependences of total capacitance on shutter voltage lie between the low-frequency and highfrequency values. This is caused by the reduction of the generation time of surface CCs under illumination. When the modulation frequency of the illumination is preset, the dependence of PC on applied voltage approaches its low-frequency limit with increase of illumination rate. On the contrary, when the illumination intensity and high light modulation frequency are preset, the PC approaches its high-frequency limit.

High photosensitivity is provided by the minimal level of noise in a PV. Indeed, in contrast to the photoresistor and the p-i-n detector, which contain sources of noise even in the ideal case, an ideal MIS PV is substantially a noiseless device. A real device makes noise mainly because of the resistance, caused by electron states on the dielectric-semiconductor boundary and in the inversion layer. One may consider the possibility of creating a PV that makes use of the dependence of surface capacitance on illumination.

An MIS capacitor, when operating in the mode of measuring the capacitor photoelectromotive force, is charged up to voltage of such a level and sign that the semiconductor surface turns out to be in conditions of weak inversion. Excitation of the transparent electrode by irradiation in the range of its own semiconductor absorption results in a change of voltage on the electrodes of the MIS structure. From theoretical evaluation, the capacitor photoelectromotive force for the duration of the illumination impulse ( $t \ll \tau$ , where  $\tau$  is the lifetime of minority CC) is equal to

$$\Delta U_{\rm g} = \frac{q \,\Delta Q_{\rm p} L_{\rm sch}}{\varepsilon_0 \varepsilon_{\rm s}} = \frac{q \, I \, t}{C_{\rm s}} \tag{22}$$

where  $\Delta Q_{\rm p}$  is the change of minority CC charge, and  $\varepsilon_{\rm s}$  is the dielectric permittivity of the semiconductor.

The presented expression indicates that in order to increase the sensitivity of the MIS capacitor in the specified mode, the value of  $C_s$  should be lowered. This can be achieved by a decrease of alloying level and an increase of bias voltage. However, because of the requirement to maximize the load resistance and the corresponding increase of the time constant RC, structures used in capacitor photoelectromotive-force mode have a low operation rate.

MIS capacitors can be used also in the mode of milking-current registration, where the capacitance change in the MIS capacitor under illumination causes leakage of recharging current through the load resistance. The operational speed of the structure is greater in this case, since the photocapacitor is in series with the load; but this, in turn, limits the operating frequency range.

Some research has considered the possibility of transforming light energy into electrical energy with the aid of the PDE (23). When the photodielectric in a capacitor system, under constant bias, is illuminated with chopped light, alternating current arises in the external circuit, whose energy, as released at the load, includes part of the light energy. The advantage of such a converter is that the whole volume of photosensitive material is utilized. However, for to obtain 1% to 10% conversion, a number conditions are required, namely: (1) there must be a considerable increase in dipole moment on photoexcitation of the dielectric; (2) the modulation frequency should exceed the reciprocal of the lifetime of the excited state; (3) the direct-current field should be maximum, and take on values on the order of typical breakdown fields.

PVs with sufficiently high overlap coefficient ( $\sim 100$ ) can find application as active components of oscillating resonant systems. Use of semiconductor capacitors as dynamic capacitors is rather promising, in that in this case there will be an easy solution to the problem of isolating the circuits for the modulating voltage and for the transformed signal. A PV based on a symmetric dielectric–semiconductor structure should allow the production of various discrete photosensitive elements such as are widely used in automation and photometry.

Besides their application in discrete photoconductive detectors, MIS PVs can be used as components of optoelectronic voltage modulators (22). In this case, along with a high quality factor, a large coefficient of optoelectronic transformation is required, equal to ratio of the produced alternating signal to the constant signal at the input. The coefficient of optoelectronic transformation in a system with a GaAs(GaP) light-emitting diode and a PV based on a  $SnO_2-SiO_2-Si$  structure reaches 0.01.

The MIS PV can be also used for optoelectronic isolation in the signal amplification circuits, for high-frequency frequency modulation in RC and LC circuits, and in parametric amplifiers. Since such structures have a large range of capacitance change, they can find application in various resonant electronic circuits—oscillators, amplifiers, modulators, etc.

The possibilities of scientific PDE research, new techniques of PC spectroscopy, and engineering applications of the phenomena under consideration are far from exhausted (24). The authors of Refs. 25,26,27 conducted investigations at low frequencies in semiconductor and ferroelectric systems and found PDEs caused by photocapacitance phenomena, photoconductivity, and space charge due to the generation of additional CCs. Grabchak and Cocivera have developed an advanced method for measuring transient microwave photoconductivity. Measurements of changes in the real and imaginary parts of dielectric constant may exploit their relation to a change of cavity resonance frequency and quality factor after sample illumination. Since additional conduction electrons cause a change in a materials conductivity, which leads to a change of quality factor, this method permits the investigation of both free- and trapped-electron kinetics.

Further development in solving problems related to studying photodielectric properties of semiconductors will promote the progress of optoelectronics within the frame of photon technologies.

## **BIBLIOGRAPHY**

- 1. B. Gudden R. Pohl Lichtelektrische Beobachtungen an isolierenden Metallsulfiden Z. Phys., 1 (1): 361–372, 1920.
- 2. R. H. Bube Photoconductivity of Solids, New York: Wiley, 1960.
- 3. G. F. J. Garlick A. F. Gibson Electron traps and dielectric changes in phosphorescent solids, *Proc. R. Soc.*, **188A** (1015): 485–509, 1947.
- 4. J. Roux L'effet photodiélectrique dans sulphure et dans l'oxyde de zinc, Dissertation, Paris, 1956.
- 5. H. P. Kallman B. Kramer P. Mark Impedance measurements on CdS crystals, Phys. Rev, 99 (4): 1328-1370, 1953.
- 6. S. Kronenberg C. A. Accardo Dielectric changes in inorganic phosphors, Phys. Rev., 101 (3): 989-992, 1956.

- 7. I. Kneppo J. Červenák Photodielectric effect in thin-film metal-CdTe-metal structures, *Solid State Electron.*, **15** (5): 587–593, 1972.
- P. K. C. Pilai C. K. Pilai R. G. Mendiratta Space-charge polarization in ZnO photoconductors, J. Phys. D Appl. Phys., 12 (6): 961–968, 1979.
- 9. P. Mark H. P. Kallmann Ac impedance measurements of photoconductors containing blocking layers analyzed by the Maxwell–Wagner theory, J. Phys. Chem. Solids, 23 (8): 1067–1078, 1962.
- 10. J. J. Dropkin Report 6-ONR-26312, NR- 015-310, Polytechn. Inst. of Brooklyn, 1952.
- 11. P. Krispin W. Ludwig Photodielectric investigation on ZnS phosphors, Phys. Stat. Sol., 5: 573-582, 1964.
- 12. Ya. A. Oksman Photodielectric effect in semiconductors, Dissertation, Leningrad, 1971.
- 13. F. I. Vergunas G. M. Malkin The main signs of photodielectric effect attributed to conduction in a granular sample. (in Russian), *Dokl. Akad. Nauk SSSR*, **137** (3): 560–563, 1961.
- 14. I. Broser C. Reuber Photokapazitive Messungen an Zinksulfid, J. Phys. Chem. Solids, 27 (3): 527–534, 1966.
- 15. V. T. Avanesyan Dielectric properties of photoconductive lead oxides (in Russian), Dissertation, Leningrad, 1979.
- 16. L. D. Rozenstein Research on the electronic phenomena in organic semiconductors (in Russian), Dissertation, Leningrad, 1970.
- 17. V. M. Fridkin Photoferroelectrics (in Russian), Moscow: Nauka, 1979.
- L. S. Berman A. A. Lebedev Capacitance Spectroscopy of the Deep Centers in Semiconductors (in Russian), Leningrad: Nauka, 1981.
- 19. Y. T. Sihvonen D. R. Boyd Analysis and performance of a light-sensitive capacitor, Proc. IEEE 53 (4): 378-385, 1965.
- F. Gordon, Jr., et al. Cadmium sulfide photocapacitor, Institute of Radio Engineers National Convention Record, Part 3, pp. 40–48, 1957.
- 21. V. I. Stafeev (ed.) Semiconductor Photodetectors (in Russian), Moscow: Radio & Communication, 1984.
- 22. N. F. Kovtoniuk E. N. Salnikov *Photosensitive MDS Devices for Transformation of the Images* (in Russian), Moscow: Radio & Communication, 1990.
- R. W. Glazebrook A. Thomas Solar energy conversion via a photodielectric effect, J. Chem. Soc. Faraday Trans. Pt. 2, 78 (12): 2053–2065, 1982.
- 24. J. Robinson Application of photodielectric techniques to study the photoactivity of titanium dioxide pigments, Dissertation, Manchester Metropolitan Univ., 1996.
- 25. S. Devi S. G. Prakash Photodielectric effect in CdS–ZnO solid solution. Indian J. Pure Appl. Phys., 30 (2): 75–78, 1992.
- 26. S. Devi S. G. Prakash Photodielectric measurements in (ZnO–CdO) lattice, *Indian J. Pure Appl. Phys.*, **28** (9): 504–507, 1990.
- D. R. Akopov, et al. Photodielectric effects in cadmium pyroniobate (in Russian), Izv. Akad. Nauk SSSR Ser. Fiz., 54 (4): 764–767, 1990.
- 28. S. Y. Grabchak M. Cocivera Transient photoconductivity analysis using multiple trapping for rectangular and linear distributions of localized states, *Phys. Rev. B*, **79** (1): 49–61, 1999.

VACHAGAN T. AVANESYAN GENNADII A. BORDOVSKII SERGEI A. POTACHOV Hertzen State Pedagogical University of Russia, Faculty of Physical Electronics, Department of Physics