THE RELATION OF VOLUME AND SURFACE EFFECTS WITH A CHARGE BARRIER HEIGHT IN A DYNAMIC *p–i–n*-PHOTODYODE

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The characteristics of the microelectronic dynamic operational *p–i–n*-photodetector have been analyzed. These features are determined by the interaction of volume effects with particles adsorbed on the SiO_2 film surface. The temperature characteristics in the visible light irradiation regime, the anomalous characteristics of the temperature hysteresis, the processes in the adsorbed layer and the charge carriers' transport through the potential barrier in the Si substrate bulk were considered. The photocurrent sensitivity of the device was found to depend nonlinearly on temperature. We proposed a theoretical model that related the processes of thermal- and photo-generation of the charge carriers with the potential barrier parameters. The effects resulted from the formation of the surface charges were revealed. The optimal conditions and regimes for measuring the photocurrent were determined.

Key words: dynamic *p–i–n*-diode; temperature hysteresis; volume effect; charge barrier

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Introduction

Effective photodetectors of electromagnetic radiation in the visible spectral region are in great demand in science and technology, with stringent requirements imposed on their sensitivity, stability, noise level, size and other characteristics. Developing semiconductor devices that meet these requirements is an important task for electronics.

Vacuum photomultipliers are highly sensitive but have no microelectronic equivalent and possess a number of drawbacks, such as high noise level, narrow dynamic range, and no mode for obtaining two-dimensional images; in addition, their photocathodes are prone to degradation. Photomultipliers also have insufficient shock and vibration resistance, and require high-voltage power supplies.

Electron multipliers with microchannel plates are smaller, but their characteristics are unstable under vibrations and are not resistant against ionizing radiation; these devices also require a high-voltage power supply.

Ordinary semiconductor photodetectors and CCD arrays also have their own flaws: they need high-sensitivity broadband preamplifiers and signal integrators, which actually introduce additional high levels of noise and can lose weak signals.

New *p–i–n*-photodiodes [1] are equipped with a metal-oxide semiconductor (CMOS) gate around the built-in *p*-type depletion region in silicon (CMOS is a complementary metal – oxide – semiconductor structure). The spectral sensitivity of the diode is sufficiently high in the visible range of the electromagnetic spectrum (400 – 800 μm). The device operates in dynamic mode with a voltage pulse switching between reverse and forward bias. The measured quantity characterizing the incident light is not the amplitude of the signal applied to the device but the switching time, which depends on the energy dose of the absorbed light. In the initial state and during the delay τ after switching, the electrons and holes are trapped by electrostatic potential barriers corresponding to the Boltzmann equilibrium of drift-diffusion near the boundaries of the depletion regions. After switching from reverse to forward bias, the device keeps operating in a blocking state for a certain delay time τ, for as long as the mobile charge carriers remain trapped by potential barriers. The injected current increases upon irradiation with visible light that generates electron-hole pairs in silicon. The switching time depends on space charge neutralization of the barriers upon injection of charge carriers: electrons into the cathode and holes into the anode region. The carriers produced via thermal generation generate additional injection current. The total current ensures that the depletion region is occupied and the barriers are neutralized over time τ. As current flows and the depletion regions are occupied, potential barriers become lower and narrower. Switching from a state with a low-amplitude current output to a high-current state occurs with a sharp edge, presumably due to tunneling breakdown in a narrowing barrier, and this process is amplified by positive feedback due to reverse transfer of holes to the cathode.

The new *p*–*i*–*n*-photodiodes hold promise for applications in devices for detecting low-level emission in the visible spectral range, including luminometers, spectrum analyzers and other photosensitive devices [1, 2].

However, the characteristics of the device and the physical processes underlying its operation have not been sufficiently studied this far. For instance, the temperature characteristics have to be obtained to correctly describe the processes occurring in the device, as well as to determine its operating conditions and application parameters.

The temperature dependences of the self-triggering time of a diode without external illumination were measured in [2]. A theoretical current flow model was also offered, allowing to interpret the experimental characteristics. It was assumed that only the carriers capable of overcoming the potential barrier due to thermal energy could participate in neutralization processes in self-triggering mode. In the absence of external irradiation, the density J_0 of the current of thermally generated charge carriers, flowing over the potential barrier, was estimated by integrating the Fermi function over the above-barrier energy E_b. A relation describing the dependence of the neutralized part $Q(t)$ of the total barrier charge on time t, temperature T and the current barrier height $E_b(t)$ was obtained as a result:

$$Q(t) \sim \int_0^t dt \cdot T^2 \exp(-E_b(t) / kT). \quad (1)$$

The barrier height $E_b(t)$ depends on the time for two reasons: due to neutralization of the charge by the thermal current and due to a decrease in the barrier height by a thermally generated carrier charge. The diode switches quickly when $Q(t)$ reaches a critical value Q_c with $t = \tau$. This simple model allowed to approximate the experimental temperature dependences rather accurately, but did not yield the temperature characteristics of switching under photodiode illumination by incident light and adsorption of particles from the external environment on the photosensitive layer.

The goal of this study was to further develop the model describing the temperature-dependent processes occurring in the device, and to determine the mechanisms by which external factors affect these processes, including changes in the concentration of the adsorbed layer on the surface of the silicon oxide film in the outer region between the cathode and the gate.

Methods of investigation

The diode was placed in a light-protected thermostat where the temperature was varied and controlled in the range from 275 to 305 K at natural humidity for the duration of the measurements. The temperature was varied under quasi-equilibrium conditions: slowly (by less than 1 deg/min) and in small steps; each step involved a long pause until the new temperature settled, so that the temperature change rate would not affect the results obtained. As photon illumination started, external illumination of the diode surface by visible daylight was controlled by changing the size of the aperture stop in the wall of the thermostat. The effect of humidity on the device was studied as well; the device was not hermetically sealed for this purpose.

Absolute values of the incident light intensity were not measured in the experiments, since relative values were sufficient for our purposes. Non-zero minimum illuminance corresponded to the mode with room temperature and minimal photocurrent, which was undetectable against the thermally generated current. Light intensity was increased in a dynamic range to values exceeding this level by one or two orders of magnitude.

A programmable control circuit with an integrated microelectronic chip was used for supplying power to the diode and for measurements. The diode's self-triggering time and its switching time under illumination were determined from the counts of the circuit and simultaneously controlled with a TDS520 digital oscilloscope.

The processes in the diode were simulated with the COMSOL package, used to determine the potential per unit volume. The geometrical parameters of the diode, the impurity concentrations and the voltages at the diode electrodes were set for the simulations, and the presence of adsorbed water molecules on the outer surface of silicon oxide film in the region between the cathode and the gate was taken into account.

Experimental results and discussion

Typical dependences of normalized inverse triggering time of the diode (plotted on a logarithmic scale) versus temperature are shown in Fig. 1 in three modes: self-triggering by thermally generated charge carriers and switching in two modes under illumination by a constant (time-independent) photon flux (Φ = const). The normalizing value of the maximum time τ_{max} was taken to be constant. It is obvious (see Fig. 1) that the curves obtained for irradiation with visible light differ from those recorded in the thermal generation mode where approximation by formula (1) is possible. The dependences obtained for photogeneration of charge carriers cannot be simulated by linear displacements of curve *1*. The behavior of the quantity τ_{max} / τ as a function of the temperature T under irradiation with an extremely low flux Φ_2 (barely detectable by the device), in curve *2*, indicates two competing types of generation. Curves *2* and *3* remain approximately exponential with different exponents in separate segments: low (about 0.49) with the photocurrent prevailing over the thermal generation cur-

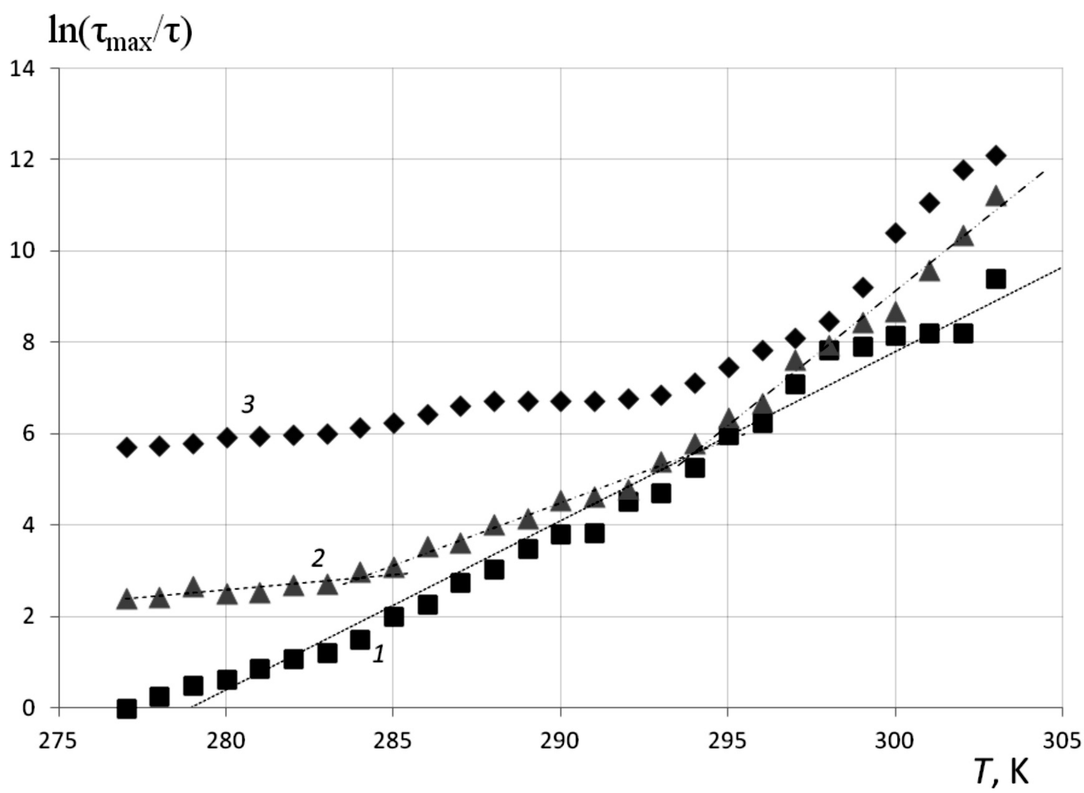

Fig. 1. Temperature dependences of logarithmic inverse switching time of the diode without illumination (*1*) and with illumination (*2*, *3*) by visible light with different photon fluxes Φ: *1*: charge carriers are generated thermally ($\Phi_1 = 0$); *2*: two competing types of generation for an extremely low photon flux ($\Phi_2 > 0$); *3*: the photogeneration process is predominant but thermal generation occurs at higher temperatures ($\Phi_3 > \Phi_2$); τ_{max} = const

rent that is substantial in the temperature range $T > 285$ K; rather small (about 2.11) at 285 K $< T <$295 K and, finally, increased (about 4.61) with the prevailing thermal generation current, when $T > 295$ K.

As the photocurrent increases (curve *3* in Fig. 1), the exponent remains approximately constant and small (about 0.52) with $T < 295$ K, i.e., the switching time in this mode is less dependent on the temperature than in thermal generation mode under zero illumination. The slope of curve *3* becomes considerably steeper with an increase in temperature in the region $T > 295$ K, indicating a greater contribution of the thermally generated current. The incident light Φ_2 was chosen to be extremely low in intensity, but still detectable with respect to the thermally generated current; its signal-to-noise ratio SNR is determined as follows:

$$\mathrm{SNR} = P_{ph} \,/\, P_{th},$$

where P_{ph} and P_{th} are the powers of the total photogeneration signal and the thermal generation signal, respectively.

The SNR value is close to 1 at $T > 290$ K; SNR > 1 at $T < 290$ K, and this segment of the temperature dependence can be regarded as optimal for using the photodiode. However, as we shall discuss below, there are also limitations in the low-temperature region.

The reasons why the temperature dependence of the switching time changes under irradiation with visible light may include nonequilibrium generation of electron-hole pairs that receive an initial excess energy with respect to the lattice temperature in the silicon substrate. The effective height of the confining potential barrier decreases for photogenerated carriers in the region above the equilibrium thermodynamic energy kT. In this case, the flow of the total thermal generation and photogeneration currents can be described by the relation refining formula (1):

$$Q(\tau) \sim \int_0^{\tau} dt \cdot T^2 \exp\left(\frac{-E_b(t) - \Delta E_b(\Phi, T)}{kT}\right), \quad (2)$$

where $\Delta E_b(\Phi,T)$ is the effective decrease in the height of the barrier due to space charge neutralization by photogenerated carriers (Φ is the irradiation dose).

The photocurrent flowing above the barrier is proportional to the irradiation dose, i.e., $I_\Phi(\Phi) \sim \mathrm{const} \cdot \Phi$.

The model corresponding to formula (2) describes the photocurrent entirely from the standpoint of the changes in the barrier height. This model takes into account the contribution of the photocurrent to barrier charge neutralization, modulation of the barrier height by photogenerated carrier charge and the dependence of the barrier height on temperature, allowing to interpret the dependences shown in Fig. 1 more accurately. If divided into segments, the experimental curves can be well approximated by exponential curves with different exponents. This is likely evidence that the change in the effective barrier height $\Delta E_b(\Phi,T)$ depends on temperature. The barrier parameters were determined from the dependences in Fig. 1 for the voltages at the diode electrodes corresponding to the computations using the COMSOL package (see the data in Fig. 3 below). The obtained values of the parameters in formula (2) are in agreement with both the adopted model and with the computational result:

$$W_1 = E_b = 2{,}62\ \mathrm{B};$$

$$W_2 = E_b + \Delta E_b(\Phi,\ T_{<295}) = 0{,}52\ \mathrm{B};$$

$$\Delta E_b(\Phi, T_{<295}) = -2{,}10\ \mathrm{B},$$

where W_1, W_2 are the barrier heights at $\Phi = 0$ irrespective of the temperature and at $\Phi = \Phi_3$ for the temperature region $T < 295$ K, respectively; $\Delta E_b(\Phi,T_{<295})$ is the change in the barrier height under the conditions established for the W_2 quantity.

To further refine the temperature characteristics in the low-temperature region, we performed measurements under cyclic cooling and heating. The first hysteresis loop was observed in the temperature range of about 270 – 280 K, near the computed dew point. It can be seen from Fig. 2 that the diode switching time corresponding to the heating cycle was increased compared with the switching time corresponding to the cooling cycle. The observed hysteresis may be attributed to the dependence of the concentration of adsorbed particles on temperature. Indeed, the particle fluxes incident on the surface and leaving it are equalized under quasi-equilibrium conditions.

However, the concentration of the particles trapped on the surface due to adsorption forces depends on the thermal history even in quasi-equilibrium processes. As the temperature increases, the processes are governed by the increased concentration of the adsorbate, obtained at lower temperatures.

Condensation of water vapor from the surrounding atmospheric volume naturally occurred at a lower temperature on the silicon dioxide layer and a sufficiently adsorbed surface film consisting of water molecules was accumulated. This film gradually thinned under heating, changing the diode switching time, but with a different pattern compared with the temperature dependence of this quantity under cooling.

A possible mechanism by which the hysteretic processes manifest in the measured parameters of the diode is that the surface charges in the film distort the potential distribution and the height of the barriers along charge carrier paths in the near-surface region of the silicon substrate. The charge state of the adsorbed layer is a complicated issue discussed in very few literary sources. The emergence of a charged layer near the surface may be caused by the separation of charges in the film due to their different mobilities [3, 4]. Protons have an abnormally high mobility and are capable of producing H_3O^+ ions and stable complexes [5 – 7]. In addition, such ions can form on the surface during the self-ionization reaction of water [3 – 5]:

$$2H_2O = H_3O^+ + OH^-.$$

The NO^+ cation, capable of forming strong bonds with water molecules, and, accordingly, stable $NO^+ + (H_2O)_n$ clusters, is another active ion [8].

Water molecules bonding with the surface and the corresponding ions forming in the film can also be interpreted in terms of a simple acid-base interaction according to the Lewis theory [9, 10]: the water molecule acts as the electron donor (Lewis base), and the substrate as the electron acceptor (Lewis acid).

While the specifics of this phenomenon have not been explained, the very fact of charging in the presence of water molecules agrees with modern concepts of the adsorbed layer. Surface charges generate an electric field that changes the form of potential barriers in the silicon-based photodiode. Similar phenomena are known in semiconductor biosensors [11].

Computer simulation in the COMSOL

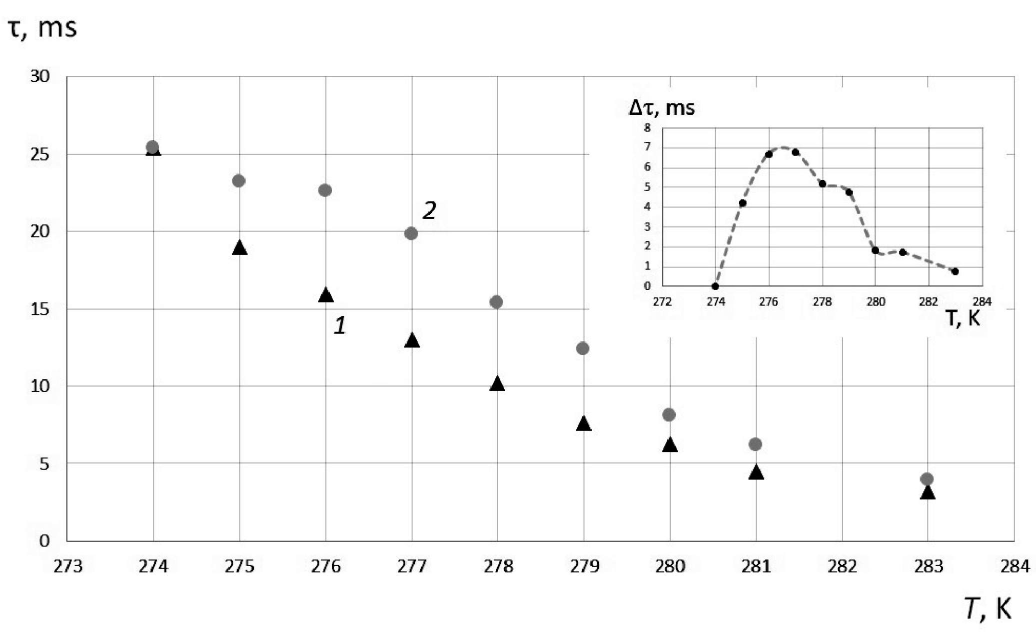

Fig. 2. Temperature dependences of the diode's self-triggering time under initial cooling (*1*) and subsequent heating (*2*). The inset shows the differences in curves *2* and *1* plotted along the vertical axis

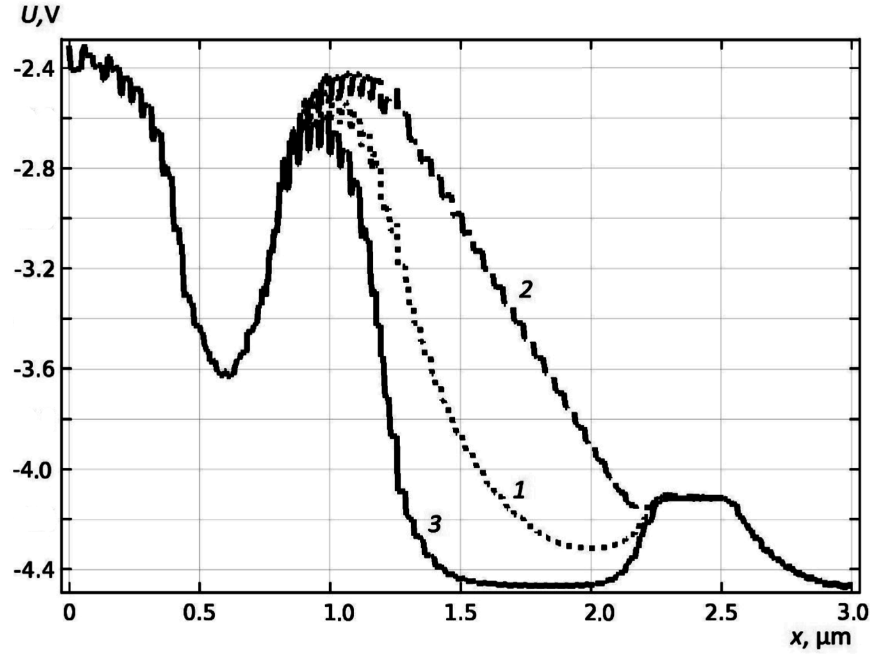

Fig. 3. Computed distributions of static potential along the charge carrier path for different charge states of the adsorbed layer:
1 without adsorbed film; *2*, *3* with the film generating, respectively a positively and a negatively charged layer (the surface charge was taken equal to 0.01 C/m^2)

package was used to further interpret the results. We computed the heights and modulations of potential barriers for the given acceptable values of surface and space charges. We assumed that the molecular film had a small charge with a surface concentration corresponding to an approximately 10% ionic component in the neutral Langmuir monolayer, which can be considered close to the measurement conditions.

We have also determined the profile of the electrostatic potential of the barriers confining the space charge in the switching mode of the *p*–*i*–*n*-diode with an integrated metal-oxide semiconductor gate around the *p*-region. The simulation yielded static spatial distributions of the potential values for different temperatures and different films of adsorbed particles on the outer surface of the SiO_2 film in the region between the cathode and the gate. Fig. 3 shows the potential distribution for forward bias (the anode and the gate have a positive potential with respect to the cathode), computed in a plane located at a distance of tenths of microns from the upper surface of the diode, where the possible particle paths lie. The potential distribution was computed along the charge carrier path.

Evidently (see Fig. 3), there are electrostatic barriers trapping charges in potential wells along carrier paths. The magnitude of the electric field strength rapidly decreases outside the depletion region. The charge carrier mobility is low due to a lack of a sufficiently strong electric field. The molecular film forms a charged layer near the surface; this layer's electric field changes the height and shape of potential barriers, controlling the neutralizing carrier fluxes. Computations of barrier heights based on the data in Fig. 3 are given above for estimating the temperature dependences and parameters according to formula (2) and were also used to determine the ratio of the barrier height E_{bs} with the surface film to the barrier height E_b without the film:

$$\gamma = (E_{bs} / E_b) \cong 1,2.$$

Conclusion

The experimental and theoretical study we have carried out yielded the following results:

the temperature characteristics of a *p*–*i*–*n* -diode with an integrated metal-oxide semiconductor gate have been determined in dynamic mode, under conditions close to real life, i.e., with an external atmospheric environment affecting the sample during photocurrent measurements;

the sensitivity of the device with respect to the photocurrent was found to be nonlinearly dependent on temperature, which is to say that the temperature curves have segments with different slopes;

we have offered a theoretical model linking the processes of thermal generation and photogeneration of charge carriers with the change in the height of potential barriers that depends on temperature and on modulation by mobile carrier charge;

we have found the conditions and modes optimal for measuring the photocurrent;

we have found the effects that may be due to surface charges forming when particles from an external environment are deposited on a silicon dioxide film or on the elements of the optical system, for example, when the device is operating in a humid environment or is depressurized.

The theoretical and experimental results obtained allowed to gain more insight into the dynamic scenarios of the processes occurring in the device, as well as to estimate the device's potential applications and operating parameters in measuring equipment. The effects discovered can be taken into account when developing technical devices with the new photodetector.

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