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THE STUDY OF CADMIUM SULFIDE HETEROGENEOUSLY SENSITIZED CRYSTALS. PART II. RELAXATION CHARACTERISTICS

The photoelectric properties of CdS crystals with combined doping has been considered. The relaxation of the photocurrent determined by the long-term (months) redistribution of the sensitive impurity has been found. The possibility of creating of a new type of light sensors with super long memory has been shown. The medium-time (minutes) and fast (seconds) relaxation of the photocurrent under excitation by intrinsic and infrared light has been studied.

This article is a continuation of the review [1]. For the sake of maintaining wholeness the numbering of sections were selected transparent. References in each article are given individually.

The term «Heterogenic» is understood in two senses.

Firstly, the process of tactile sensing Bube-Rose you must have at least two classes of centers – R (slow recombination) and S (fast recombination). Moreover, each of these groups may consist of several physically different types. The condition of predominance of concentration of one of the classes $N_R > N_S$ or $N_R < N_S$ creates some features considered in Part I.

Secondly, under the influence of external factors (electric field, light, temperature), spatial redistribution of the sensitive centers is possible. This creates a number of specific effects, discussed below, which are impossible in samples with uniform doping.

3.1. Long-term (hours) migration-dependent relaxation of photocurrent

After pre-lightings of the samples with our own light and long (2-3 months) stay in the dark, we observed almost complete absence of photosensitivity [2,3,4,5]. Then the photosensitivity was restored for several days, while the crystals were exposed to monochromatic light

with a wavelength of 515 nm [6]. The process passed independently of the duration or the number of lightings and remained the same even under lighting for 20 minutes once a day [7,8]. The rate of recovery of photosensitivity turned out to be the maximum at first, then the increase decreased. After about 100 hours, the photocells stabilized and no longer responded to daily lightings.

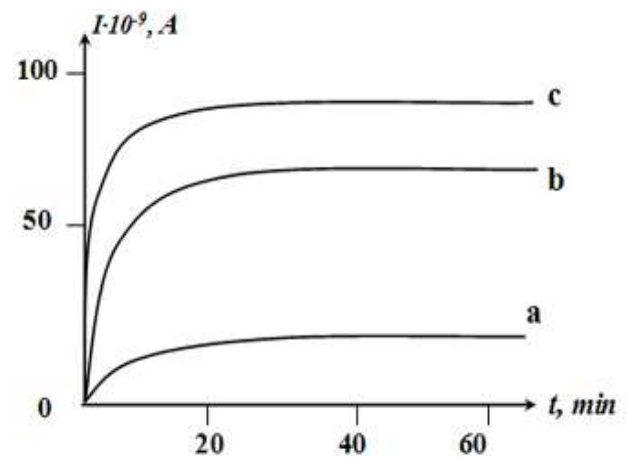


Fig. 3.1 Relaxation of the photocurrent after exposure in the dark for 3 months (curve "a"), then five days ("b") and two days ("c").

At the same time, there was a certain limit level of sensitivity, which could not be exceeded, regardless of the time of illumination, both one-time and total.

The type of relaxation curve depended on the applied field strength. Moreover, if a simple decrease in the applied voltage did not make fundamental changes in the shape of the curve, only reducing the corresponding currents, then an increase in the distance between the contacts to 2 mm at a displacement on the sample was still 50 V led to a modification of the initial stage of changes-at small times of less than 10 min, a section of relatively slow current increase appeared and the relaxation curve as a whole acquired an S – shaped form. Characteristically, in this case, although the strength applied field is decreased approximately four times, the value of flowing current decreases disproportionately, accounting for roughly half of the original value on the plot of saturation after relaxation in 35 – 40 minutes.

The samples had a strong effect of infrared quenching of photocurrent. Even with not very large values of the ratio of the intensity of the quenching light to the intensity of the exciting, the value of the IR quenching coefficient Q easily reached 100 %. The spectral distribution curve $Q(\lambda)$ was typical with two maxima at 1080 and 1400 nm (0.9 and 1.1 eV, respectively).

At temperatures of large 40 – 50 °C for the excitation intensities used, the effect of temperature quenching of the photocurrent with standard characteristics was observed.

The presence of both types of quenching indicates the presence of S – and R – centers of comparable concentrations in the crystal, and the absolute value of the number of centers of each class should be significant.

Since the described situation is close to the existing model with moving S-centers, we have put a special selective experiment. After completion of the relaxation process is already in a sensual state (curve "b,, Fig. 3.1) the polarity of the applied field was reversed.

If the observed phenomena are associated with the migration in the sample of light-charged defects, which play the role of centers of rapid recombination and their gradual accumulation in the anode, then such processes should be expected:

When changing the sign of the pulling field (the light continues to operate and, therefore, the centers retain the charging state), the defects

must migrate in the opposite direction. During the time comparable with the time of the previous relaxation, they first dissipate over the crystal (due to the spread of mobility and fluctuations of the diffusion jumps of V_{Ca}^- vacancies). The sample returns to the pre-relaxation state with low sensitivity. And then, even for the same period of time, there is a spatial repolarization of S-centers with their accumulation at the opposite contact.

Instead, we observed a slight change in the photocurrent within 20-25 minutes no more than 10 – 20 % of the initial value. Given the inefficient process of moving S-centers through the crystal grate as already noted, such time intervals are completely inadequate diffusion of defects of this type.

Thus, the features of the time dependence of the current require to exclude from consideration in our case the movement of S-centers. The difference between this model and the situation under study is the state of contacts to the sample. The study of the light current-voltage characteristics both at different moments of relaxation (instantaneous or almost instantaneous values) and in a stationary, sensitive state, indicates the presence of locking barriers in the entire temperature range and the light intensities used. The curves of the current-voltage characteristic had the form typical for the reverse branches of the diodes. Moreover, we are talking about both contacts, since there were no fundamental differences in the applied voltage at opposite polarities.

The non-ohmic contact with the crystal is also reflected in the volt-farad dependencies. During the measurement times excluding the diffusion of impurities, in the case of anti-lock contacts, the sample capacity should not change at all with the applied voltage. Instead, we observed a volt-farad dependence, although not straightening in standard coordinates $C^{-2}(U)$.

With the increase in temperature, the relaxation process was revived. However, it seems anomaly practically no differences in the graphs in the temperature range from slightly increased to 80 °C.

Contrariwise, temperature rise has proved to be an effective way of returning cadmium sulfide crystals to photosensitivity. Even after long exposure in the dark (situation of “a” Fig. 3.1) as a result of subsequent heating (without photoexcitation and voltage) at a temperature of 40 °C for 4 to 6 hours, the crystal passed to the state characteristic of the dependence “b” Fig. 3.1. At the same time, no accumulation from the photo effect was observed. However, even in this case, we could not achieve an improvement in the transfer of the sample to a state with increased photosensitivity by simply increasing the temperature. The effect of infrared light on our crystals also increased their photo response to their own excitation after a long stay in the dark. The combination of a small heating and IR – effect almost completely removed the relaxation of the photocurrent.

Since the investigated chronological dependence of the current in the samples occurred under the conditions of photoexcitation with the simultaneous presence in the electric field, it was of interest to study the effect of each of these effects individually.

Curve “a” in fig. 3.2 measured under the same conditions as the curve “a” in fig. 3.1 and transferred here as a reference. Curves “b” and “c” in Fig. 3.2 is obtained according to the scenario based on “c” Fig. 3.1 however, an additional stage has been introduced. The sample was kept for one hour either in a light without a field or in the dark but under voltage.

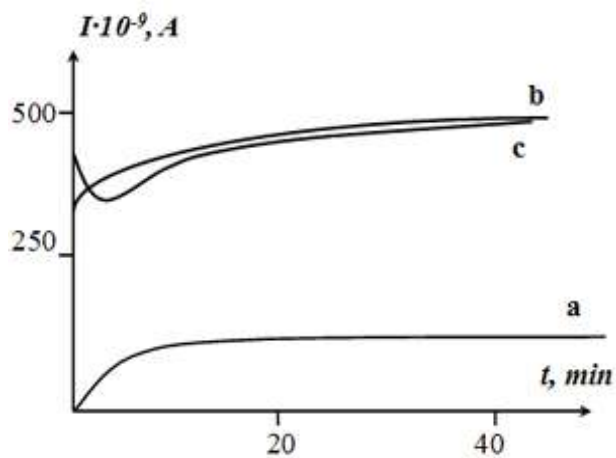


Fig. 3.2 Discrete process impact.

As can be seen from the figure, the introduction of such an additional effect significantly modifies the relaxation graph. In both situations, an initial conduction spike appears, the causes of which are discussed below.

The totality of the data obtained was interpreted as follows.

Direct experiments have proved the presence of S – and R-centers in the studied crystals. The observed duration of current relaxation excludes purely electronic interpretations. At the same time, these intervals are too small, as shown earlier, to participate in the processes of rapid recombination centers. Therefore, in consideration of the concentration changes are introduced for R – centers.

When the external voltage is turned on, the role of the pelotons from the R-centers at the contacts is different. Let the field be directed in such a way that it causes the charged R-centers to move from right to left. Then the left contact centers are compacted and would have to lower the height of this barrier. But at the same time, since its intensity coincides with the external field, it must increase. Because of this competition, the changes taking place here practically do not affect the relaxation of the current of photo excited carriers.

The right peloton has a significant impact. The external field pulls out of it the sensitive centers from a potential hole in the middle part of the crystal, significantly increasing the life time of the main carriers. From the outside, this is manifested in the form of current relaxation. While remaining small due to shut-off contacts, it nevertheless increases from $10^{-10} - 10^{-9}$ A to 10^{-7} A (Fig. 3.1). It is obvious that the barriers are approximately symmetrical, the effect is insensitive to the sign of the applied voltage. When the polarity changes, the left and right barriers change roles.

This also explains the indifference to the sign of the field after the relaxation. A small decline here may be due to the fact that some of the free R-centers of the middle band of the crystal (see Fig. 3.4) goes faster to your contact that they are replaced with the held field R-centers of the opposite potential well. It is clear that the

longer the Central part, the less influence the field injection of the sensitive centers has on it.

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Especially in the initial periods of time, while the concentration of additional agents here is small. Having a depth of about 1 eV, R-centers are capable of holding captured non-equilibrium holes at room temperature for a long time. This, obviously, determines the processes of redistribution of the concentration of the sensitive centers after the light is turned off (Fig. 3.1), if the time spent in the dark was not too long. We see this as a “remembering” the previous crystal effects.

The developed concept easily explains why the increase in stationary current decreases with increasing lighting cycles. At first, when there are many centers in the SCR, their transition to the central part is massive. In descending order of their concentration in the SCR for the subsequent cycles of illumination, the intensity of all the considered processes decreases. The photocurrent is higher due to the sensitive action of R-centers, while the subsequent relaxation is more lively (curves “b” and “c” Fig. 3.1). Limit relaxed sensitivity to external influence in this case is limited to the total concentration of R-centers. No combination of effects on the crystal can increase its conductivity in our model, if all the sensitive centers from the contact area are already involved, which could take part in these processes (curve “c” Fig. 3.1).

Obviously, heating increases the mobility of the centers and accelerates relaxation. However, with increasing temperature there is a competing process – due to the thermal emptying of traps, part of the R-centers, losing charge, ceases to respond to the external field.

The same action produces IR radiation. This explains its ability to return to crystals sensitivity in combination with a small heating. R-centers in those conditions is a Central part of the crystal, sensing it due to the usual mechanisms of diffusion due to concentration gradients from the contacts to the center. Current surges at the

initial moments of time in Fig. 3.2 (curves “b” and “c”) have different nature. With the preliminary influence on the crystal field in the dark, we lower the height of the barrier, the intensity of which is opposite to the external. He is no longer able to hold R-centers in a potential pit and there is a perception of the crystal (curve “b” Fig. 3.2). On the contrary, if the crystal was exposed to illumination without a field, in both contact SCR appear R-centers, captured no equilibrium holes. Because of their charge they lower retaining their intensity of the internal fields, the injection of excess with the appropriate sensitizing. Because both areas at the same time participate in sensitizing, the magnitude of the emission is somewhat larger (Fig. 3.2, curve “c”).

In conclusion, we indicate several ways of recycling the discovered patterns [10]. The relaxation process itself allows the use of CdS samples with locking contacts as timers for tens of minutes. The process of returning to balance, which has lasted for dozens of days, allows for the implementation of long-term devices. In turn, since both processes-increasing relaxation in their own light and their dark aging depend from temperature and IR effects, it is possible to create appropriate sensors with memory. In addition, the relaxation process itself is dependent on the previous exposure to white light, which allows the use of such samples as photoreceptors for illumination.

3.2. Average time (minutes) relaxation of the photocurrent in crystals with inhomogeneous focus

Because the barriers in contacts play an important role in the implementation of long-term relaxation of the photocurrent, it was of interest to strengthen this effect. To do this, the contacts were shifted to 0,1-0,2 mm. In this case, the interelectrode distance is comparable in magnitude to the SCR width. Thus, the contact barriers and the processes taking place there become current controlling. An unusual form of photocurrent relaxation was found on crystals with a small distance between the contacts after staying in equilibrium conditions [5,11].

With a small level of its own lighting (1-3 lx), the photocurrent was installed in a few minutes. For large illuminances (10-15 lx) the photocurrents first also increased during 3-4 min (1 stage); then during the time up to 15 minutes ~ 30 % (2 stage) decreased; and later returned to the same value and stabilized during the period of 45-50 minutes.

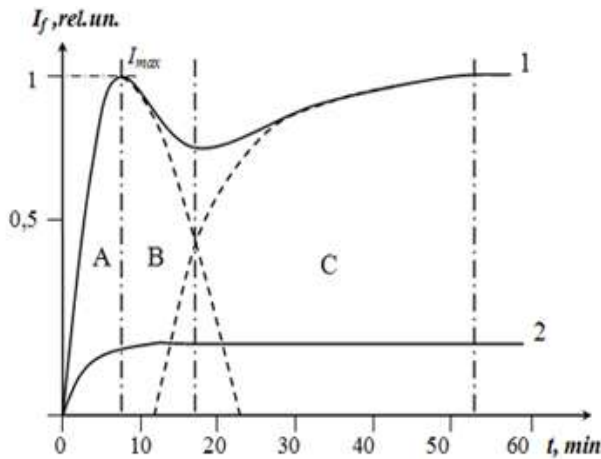


Fig. 3.3. Relaxation of own photocurrent at the level of illumination: (1) – 10-15 lx and (2) – 1-3 lx.

When illuminated with its own light (515 nm) in the sensitive samples CdS have been long time relaxation of the photocurrent in the range of 50-60 min (Fig. 3.3).

Typically, that at low light the photocurrent stabilized within 10 minutes. When the light flux was increasing, a disproportionate increase in the photocurrent occurred. With the increase in the order of the level of illumination, the magnitude of the photocurrent increased only several times. This indicates the flow of several competing processes in the crystal.

In addition, for some crystals, relaxation was accompanied by a decrease of the photocurrent for 10 to 15 minutes. And then the restoration of its value for the period of about 40-50 minutes.

Times like these flowing processes exclude purely electronic interpretation and are typical for migration-ionic phenomena. It was also shown that in the fields $10^4 - 10^5$ V/sm it is possible to move the impurity ions along the crystal grate. When the barrier height is about 1 eV and the width is $\sim 1 \mu\text{m}$, it is possible to reaching such fields in the contact areas of crystals.

At the same time, the fields of the barriers are directed in such a way that they contribute to the outflow of the negatively charged impurity to the Central part and the extraction of the positively charged impurity to the SCR contacts.

In the first approximation for the present consideration it is assumed that in the electric field used the distribution of S-centers remains uniform. They cannot have any noticeable mobility to move around the crystal grate. On the contrary, the R-center is copper in the cadmium sublattice, which is able to move relatively easily through the crystal.

According to the Baby-Rose model, R-centers create levels in the forbidden zone with a depth of 0,9-1,1 eV. It is obvious that in equilibrium conditions, capturing their own holes, these centers are able to hold them for a long time. At the same time, as shown in chapter 2.1 (part I), they charge positively. Under these conditions, under the action of Schottky barrier fields, they are extracted from the crystal areas of the width of the order of diffusion length from the inner boundary of the barriers and the accumulation of this impurity in the SCR contacts.

In General, the distribution of the concentration of R-centers takes the form, as shown in Fig. 3.4. As a result of sluggish recombination processes, some of these centers lose their charge. Therefore, under equilibrium conditions, the concentration of charged N_2^+ centers in the contact areas is much less than their total concentration of N_2 .

When exposed at the same time its own light and external voltage to the crystal (Fig. 3.3) the situation in the crystal changes. Let's first consider the initial state of the contacts.

In the dark, in conditions $N^+ < N$, the charge in the SCR is concentrated on ionized donors. Since the barrier is locking, the influence of free electric charge is neglected. Then

The potential distribution in the SCR is found from the Poisson equation

$$\frac{d^2 \varphi}{dx^2} = \frac{4\pi e^2}{\varepsilon} N_d, \quad (3.1)$$

the standard solution is:

$$\varphi(x) = \frac{2\pi e^2}{\varepsilon} N_d (L-x)^2. \quad (3.2)$$

The value L in (3.2) sets the width of the SCR at the equilibrium height of the barrier φ_0 :

$$L_{dark} = \sqrt{\frac{\varepsilon}{2\pi e^2} \frac{1}{N_d} \varphi_0}. \quad (3.3)$$

When the light intensity is high, the condition $N^+ < N$ is violated. R-centers, already located in the SCR and distributed there evenly, capture appeared in a large number of no equilibrium holes and are completely ionized. We used high-resistance crystals. Consequently, the concentration of donors is low. At the same time, a bright effect of infrared extinction indicates the presence of a large concentration of second-class centers. As a result $N_2^+ = N_2 \gg N_d$.

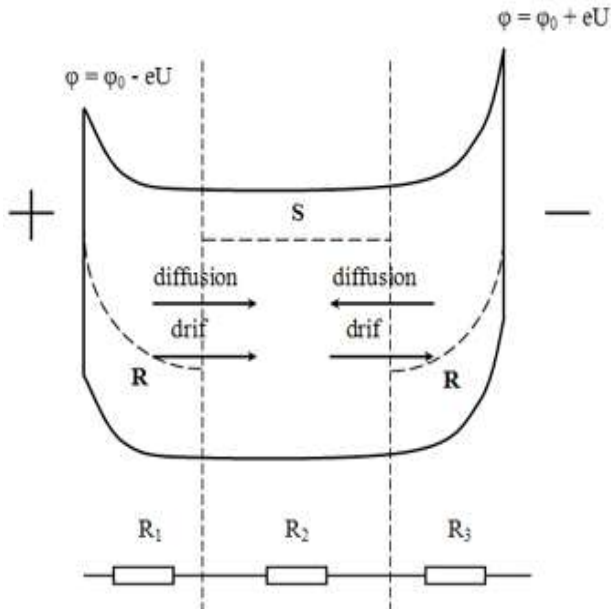


Fig. 3.4. Migration processes in the crystal in the light under the influence of the field.

Positive charge in the SCR is now fixed on R-centers and formulas (3.2) – (3.3) are modified:

$$\varphi_{big}^{illum}(x) = \frac{2\pi e^2}{\varepsilon} N_2 (L-x)^2; \quad (3.4)$$

$$L_{big}^{illum} = \sqrt{\frac{\varepsilon}{2\pi e^2} \frac{1}{N_2} (\varphi_0 - eU)}. \quad (3.5)$$

Here it is taken into account that under the influence of external voltage the height of the barrier has decreased to a value $\varphi(0) = \varphi_0 - eU$. It will be shown below that the changes on the second barrier increasing in the same field are insignificant.

Formulas (3.3),(3.5) allow to explain the increase in the photocurrent in the region “a” Fig. 3.3.

It is seen that the light width of the barrier (3.5) because of the conditions decreased in comparison with the black values (3.3). At the same time it became lower.

Resistance R_1 (Fig. 3.4) this part of the crystal decreases. The current grows. Because processes are limited only by the time the traps are captured, changes occur quickly.

However, the processes that occur with the barrier (in Fig. 3.4-left), more harder. If light quanta are small, then a small concentration of non-equilibrium holes is created. In SCR of the contact they distributed according to the law:

$$\Delta p(x) = \Delta p \exp\left[\frac{\varphi(x)}{kT}\right], \quad (3.6)$$

Where Δp – is the concentration of holes at the bottom of the barrier; $\varphi(x)$ - potential distribution. As a criterion of low light we choose

$$\Delta p \exp\left[\frac{\varphi(x)}{kT}\right] < N_2. \quad (3.7)$$

That is, at any point in the barrier holes are not enough to fill all the R-centers. Under these conditions, a fixed positive charge is the holes, according to (3.7) captured on the R-centers

$$\rho = eN_2^+(x) = e\Delta p \exp\left[\frac{\varphi(x)}{kT}\right]. \quad (3.8)$$

Then the Poisson equation has the form:

$$\frac{d^2\varphi}{dx^2} = \frac{4\pi e^2}{\varepsilon} \Delta p \exp\left[\frac{\varphi(x)}{kT}\right]. \quad (3.9)$$

or:

$$\frac{d^2z}{dx^2} = A \exp(z), \quad (3.10)$$

where

$$z = a\varphi; \quad A = \left(\frac{4\pi e^2}{\varepsilon} \Delta p\right) \frac{1}{kT}; \quad a = \frac{1}{kT}. \quad (3.11)$$

Integration (3.10) gives:

$$\left(\frac{dz}{dx}\right)^2 = 2A[\exp(z) - 1]. \quad (3.12)$$

The equation (3.12) requires numerical integration. However, it can be simplified. The condition (3.7) assumes a small number of holes at the sole of the barrier and, accordingly, a small charge at the centers of the sensitivity. In other words, the far edge of the barrier again depends on ionized donors:

$$\Delta p(L) \exp\left[\frac{\varphi(L)}{kT}\right] < N_d^+. \quad (3.13)$$

Here, small levels of illumination and a small barrier potential are taken into account

$\varphi(L) \rightarrow 0$. Thus, the barrier now consists of two parts, most of which are subject to (3.12), and the edge is defined similarly (3.2). To estimate the width of the SCR of such a barrier is sufficient to use (3.12) in the conditions

\gg

Then

$$\frac{dz}{dx} = \pm \sqrt{2A} \exp\left(\frac{z}{2}\right). \quad (3.14)$$

In all of the SCR with the increasing coordinate value, and hence z , is decreasing (see Fig. 3.4, left barrier). Then, in (3.14), the “+” sign should be discarded as having no physical meaning. We have in view (3.11)

$$\exp\left(-\frac{\varphi}{2kT}\right) = \sqrt{\frac{2\pi e^2 \Delta p}{\varepsilon kT}} (x - L_1) + 1. \quad (3.15)$$

It is not difficult to obtain an explicit form of potential distribution

$$\varphi = 2kT \ln \left[\frac{1}{1 - \sqrt{\frac{2\pi e^2 \Delta p}{\varepsilon kT}} (L_1 - x)} \right], \quad (3.16)$$

moreover, because of the conditions (3.7), equation (3.16) still need to sew with (3.2). However, (3.15) is sufficient to estimate the width of the

SCR. On the left border, at

$$\exp\left(\frac{\varphi_0 - eU}{2kT}\right) = 1 - \sqrt{\frac{2\pi e^2 \Delta p}{\varepsilon kT}} L_1. \quad (3.17)$$

It is taken into account that voltage is applied together with the light (as shown in Fig. 3.4), which lowers the height of the barrier. And

- is only part of the barrier, although large, which is determined by the charge captured on the R-centers:

$$L_1 = \frac{1 - \exp\left(-\frac{\varphi_0 - eU}{2kT}\right)}{\sqrt{\frac{2\pi e^2}{\varepsilon} \Delta p} \frac{1}{kT}}. \quad (3.18)$$

Calculate, taking into account (3.5) for large levels of illumination, the ratio

$$\frac{L_1}{L_{big}^{illum}} = \frac{1 - \exp\left(-\frac{\varphi_0 - eU}{2kT}\right)}{\sqrt{\frac{\varphi_0 - eU}{kT}}} \cdot \sqrt{\frac{N_2}{\Delta p}} \quad (3.19)$$

Or applying (3.13),

$$\frac{L_1}{L_{big}^{illum}} > \frac{\exp\left(\frac{\varphi_0 - eU}{2kT}\right) - 1}{\sqrt{\frac{\varphi_0 - eU}{kT}}}. \quad (3.20)$$

And the equation for $\varphi(x)$ solved, due to the condition $\exp\left[\frac{\varphi(x)}{kT}\right] \gg 1$ for large barriers.

Therefore, the unit in the numerator (3.20) can be discarded. It is obvious that any exponent with an exponent greater than one is greater than its degree. Therefore, finally,

$$\frac{L_1}{L_{big}^{illum}} > \sqrt{\frac{\exp\left(\frac{\varphi_0 - eU}{kT}\right)}{\frac{\varphi_0 - eU}{kT}}} \gg 1.$$

Here L_1 – only part of the barrier in low light conditions. Finally

$$\frac{L_{small}^{illum}}{L_{big}^{illum}} \gg 1. \quad (3.21)$$

That is, at low light conditions the barrier, having the same height, is considerably broadened. And this is the second reason that the current on the curve 2 in the “A” region of Fig. 3.3 much less.

Note also that the $N_2^+ = N_2 \gg N_d$ comparison of (3.3) and (3.5) follows $L^{dark} > L_{big}^{illum}$. At the same time, any appearance of a positive charge in the SCR in the light should reduce its width. Therefore, the logical chain of (3.3), (3.5) and (3.21) is built as $L^{dark} > L_{small}^{illum} > L_{big}^{illum}$. When lighting SCR width is reduced, and the more, the higher the light intensity. This is also consistent with (3.18) (L in the denominator) and (3.5).

Now let’s consider the influence of φ_0 on the formation of ion-coordination mechanisms.

For times of about tens of minutes (area “B” Fig. 3.3) the charged R^+ -impurity can already be moved in the applied electric field. The fate of SCR at both ends of the crystal is different.

Let the polarity of the applied field be as shown in Fig. 3.4. Then it should cause outflow

R^+ -centers from the left barrier and increase

their concentration due to the drift component in the right. At the same time, since R^+ -centers in the light are charged there and there, a diffusion outflow of the R^+ centers from both contacts is formed. The figure shows that for the left barrier both reasons are formed, and for the right – compete with each other. As a result, the applied field and light cause much greater extraction of R-centers from the left contact to the Central part. In this case, its height is reduced by an external field. In the right contact, the outer field would have to raise the height. However, a much greater concentration of the residual

charge R^+ – it lowers. Thus, the parameters of the right SCR are controlled by a set of mutually competing causes. In the first approximation, it can be considered stable and changes in Fig. 3.3 bind to the left contact only. The dominant mechanism for it is the broadening, as shown above. The height of this barrier can also be considered to be slightly changing, since the external field reduces it, and the departure of a positive charge R^+ – increases it.

Thus, area “B” Fig. 3.3 controlled by only one process: the left SCR expands, its resistance increases, the current drops. This process will be the stronger the greater the light intensity. First, then there is more concentration of charged centers. And secondly, as can be seen from (3.21), the twilight lighting barrier and so wide. Its relative changes are much smaller. That is why we have not recorded a long-term decrease in the current on the curve 2 Fig.3.3.

Note that the change of polarity of the applied voltage does not change the picture. Just the barriers are reversed and their roles.

Extracting of contact of the SCR, the centers of tactile sensing include two other mechanisms beyond. Depending on the intensity of the light, as shown above, in the near-surface layer is more or less increased concentration captured on the centers of the positive charge. Accordingly, they leave this area under the influence of diffusion and drift. This should be accompanied by its expansion. This changes the length of the Central part of the crystal.

Since the total length of the crystal-the central part plus two contact areas-remains unchanged, the broadening of one of the contacts should inevitably lead to a narrowing of the central part. At the same time its electrical resistance (at Fig. 3.4) decreases due to simple length reduction. The resistance of the entire tandem increases as part of the inter-electrode space has to be replaced by the high resistance region of the barrier.

This would have to lead to further stimulation to reduce the photocurrent. However, this process is superimposed on another.

Getting into the central part, R-centers are sensitive to it. At the same time, the life time of the main carriers can increase to five orders of magnitude. We were able to show (Chapter 2.1 Part I) that this will be when the concentrations of S - and R - centers are roughly compared: $N_2 \sim N_1$.

In turn, the increase in life time causes an increase in conductivity

$$\sigma = en\mu = e(f\tau)\mu . \quad (3.22)$$

Since the decrease in conductivity with the broadening of the barrier is approximately linear and even sublinear, and (3.22) accompanied by an avalanche increase, the current in the “C” figure. 3.3 increase as shown by dotted line. However, this process is longer. First, unlike area “B “and the more area” A” Fig. 3.3 it is called by several competing mechanisms. And secondly, a simple increase in the concentration of sensory centers in the sole of the SCR does not cause additional changes. It takes time for the resorption of the peloton of the R-centers on the crystal. This is what causes the asymmetry of the pit walls in relaxation in Fig. 3.3.

It is also obvious that in low light conditions these processes are absent (curve 2 Fig. 3.3). - centers are much smaller, and their addition in the Central part of the crystal is insignificant. In addition, the barrier is initially much wider [see (3.21)]. For relatively short samples, the SCR contacts in General can be gathered. Sensitive centers extract nowhere. It is with this that we connect the experimentally observed absence of an increase in the current in the area “C” of the curve 2 Fig. 3.3.

Note in conclusion that at the end of all the redistribution processes for the curve 1 Fig. 3.3 as expected, the current stabilizes again at the same level in the “C” area as in the maximum after the capture processes in the area “A”. This is not difficult to explain, given that just as many of the sensory centers have left the SCR, exactly the same amount eventually caused changes in the Central part of the crystal.

3.3. Experimental confirmation of mobile R-centers model

Thus, we link the peculiarities of relaxation processes of the own photocurrent in samples with two types of recombination centers with the redistribution of charged R-centers from the regions of the space charge in the contact parts of the crystals. To test this model, a special experiment was carried out to artificially change the concentration of such centers. Of course, it is quite difficult to model the physical amount of 1 ligand in the element under study.

However, in our case we are talking about the charged admixture after the capture of non-primary carriers. The number of holes located on the R-levels and providing a change of state [12], is easily regulated by infrared radiation in accordance with the model of the Bube-Rose. Long-wave photons, knocking holes from R-centers, return them to a neutral state, which completely excludes them from drift processes under the influence of an external field.

In addition, since the concentration of the ligand is, of course, much less than the number of basic atoms of the substance, the distance between the neighboring R-centers exceeds several translations of the crystal lattice. This means that the uncharged impurity practically does not interact with each other, which completely excludes the formation of diffusion flows. Thus, the use of IR radiation is a good modulating means for virtual change of the concentration of R-centers, turning them off from the ongoing processes (see also chapter 2.2 Part I).

Figure 3.5 shows the change in the relaxation curve when the crystal is exposed to additional infrared illumination. The curves were normalized to the maximum of the curve 1 photocur-

rent in the region of 10 minutes. It is seen that the additional effect of IR photons, and thus reducing the effective number of R-centers, completely eliminates the feature of the relaxation process with the formation of a cavity (area "B" Fig. 3.3). The photocurrent curve 2 Fig. 3.5 smoothly went to saturation for much longer times several times longer than the time to reach the maximum on curve 1.

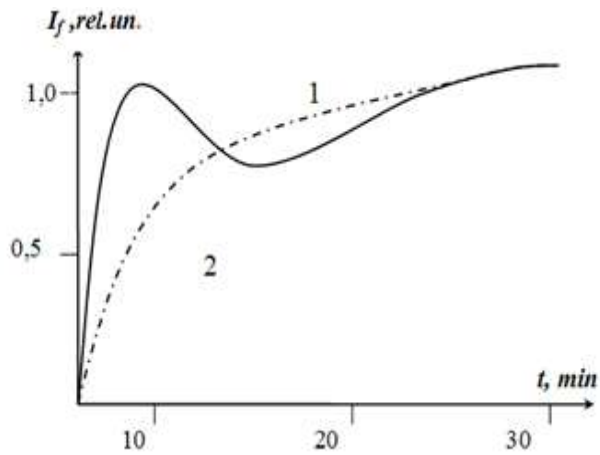


Fig. 3.5. Change of photocurrent with time under the action of only self-illuminating (1) and using IR illumination (2).

The absolute value of the photocurrent was almost an order of magnitude less than in the initial state without IR radiation. This is the expected result, given that under the action of IR radiation from SCR contact areas disappears fixed positive charge. In accordance with the conclusion of chapter 3.2, both barriers become higher and wider, the resistance R_1 and R_3 in the equivalent circuit Fig. 3.4 increases, the current drops.

3.4. Fast (seconds) relaxation of the photocurrent at excitation by own and infrared light

Long-term processes of spatial redistribution of impurities in the sensitive crystals described in sections 2.1 – 2.2 of Part I camouflage fast electronic relaxation. In this regard, it is of interest to study the changes of the photocurrent for the times excluding the influence of ion processes – 10^1 - 10^2 sec, (tens of seconds, up to several minutes). For its observation, the samples were kept for a long time in their own light. The situ-

ations considered in this section occur [8] under already established conditions of dynamic equilibrium and correspond to the ends of the graphs Fig. 3.1 and 3.3.

The sample was illuminated with its own light of different intensity. The luminous flux was regulated stepwise by varying the annular diaphragms in the region of the focusing lens. Usually, the relaxation of the photocurrent is measured from the initial state, i.e. darkness, to a fully steady state, i.e. saturation on the $I_f(t)$ chart. At the same time, they are limited to someone fixed light intensity. Note that the proposed method for the first time to study the comparative changes in the relaxation of the photocurrent with a step change in the intensity of light has a number of advantages over the traditional excitation of "dark \rightarrow full light" or "light \rightarrow dark". This is especially noticeable for complex capture centers, such as R-centers, with the possibility of internal transitions to excited R' states.

In the traditional method, a large number of photons with a wavelength from the self-absorption band appear at once and at the same time a huge number of non-basic carriers are formed, which are able to fill both the main and excited States of the R-centers from the V-zone. Redistribution processes between them are simply not included.

If the photoexcitation and disappears immediately to zero, the effective S-centers of a large concentration of free carriers take to recombine. Against the background of this intensive process, weak amendments related to changes in the population of the R and R' , and even more so, its redistribution between them, are not noticeable.

And of course, apply low light, when the concentration of non-equilibrium charge will be less than the number of free places on the impurity levels. However, since both the concentration of recombination S-centers and the concentration of capture traps for holes are not known in advance, groping for this ratio will lead to the same stepwise method.

The process of changing the flowing current consists of at least two fundamentally differ-

ent phases. At the initial stage, the photo excitation of free media is carried out (area I Fig. 3.6), most of which go to fill existing traps and recombination centers. In the studied sensitive crystals, there are definitely at least effective R-centers for this. The usual mechanisms of perception due to redistribution of carriers between the centers of the first and second classes, and even more so, the center-to-center distribution between R and R' centers have not yet been included. Especially for small light intensities, when the number of photons absorbed is less than the concentration of traps, the non-equilibrium charge capture process dominates. The conditions for the formation of the photocurrent are unfavorable.

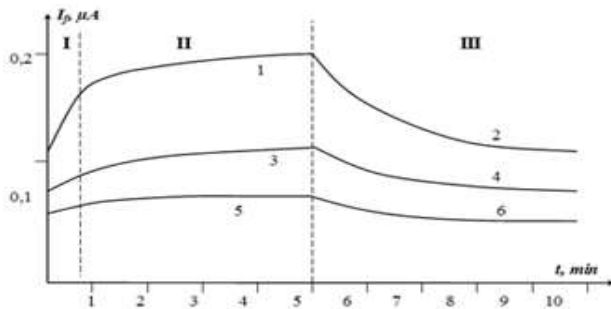


Fig. 3.6. The kinetics of infrared quenching of photocurrent in the high quenches at wavelengths of 1100 nm (1) and 1380 nm (2).

1. – from 4,25 to 9,8 lx;
2. – from 9,8 to 4,25 lx;
3. – from 1,35 to 4,25 lx;
4. – from 4,25 to 1,35 lx;
5. – from 0,6 to 1,35 lx;
6. – from 1,35 to 0,6 lx.

On the contrary, the final stages of relaxation take place in the conditions of quasi-steady equilibrium between the capture-release processes. For our samples, this is done for at least four channels: in addition to the always present adhesion centers, recombination at the S-centers, captures and emissions from the ground and excited States of the R-centers and intra-center transitions between them.

It is this complex ensemble of interactions that mainly represented the subject of research. Therefore, the measurements were carried out under conditions of the existing intensity of the

natural light and the steady-state photocurrent in the transition to higher illumination [13]. For the moment $t=0$ inclusion of additional light was accepted (Fig. 3.6).

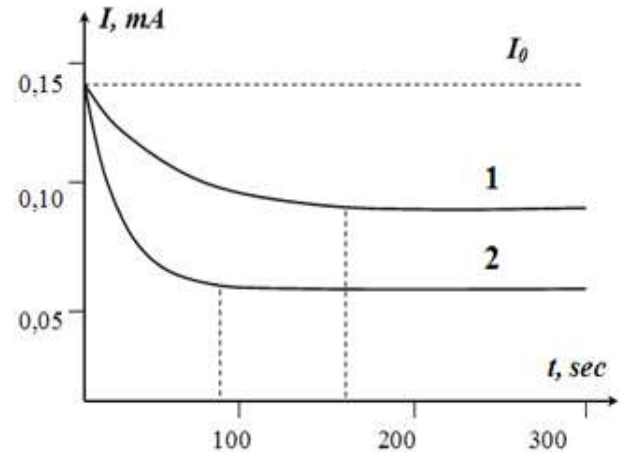


Fig. 3.7. The kinetics of infrared quenching of photocurrent in the high quenches at wavelengths of 1100 nm (1) and 1380 nm (2).

The measurement results were compared with the reverse process, when the illumination returned to its original value. In this case, the determining process becomes a competing-the centers are emptied.

Indeed, the measurements under low illumination, we observed a relatively tight region of the exit to the plateau of the graph $I_f(t)$. At the same time, the decreasing relaxation was faster.

For transitions from smaller to larger illumination at large light fluxes, in addition to the natural increase in the absolute values of the photocurrent, the increasing part increased slightly in time. This is because it is not determined by the parameters of light, and the presence of empty spaces on the traps. The decaying part of the $I_f(t)$ dependence was delayed to a greater extent because it was determined by the large charge accumulated on the traps.

Finally, for relatively high light intensities, as seen in Fig. 3.6, the magnitude of the photocurrent itself depended on the intensity of the light used. The kinetics of its change-both increasing and decreasing, since the time of about two minutes, became more and more identical. With visual superposition of graphs at light intensities

of more than 10 Lux, these parts of the curves coincided.

In addition, it is characteristic that the value of the relaxation interval for the recession (Fig. 3.6 area III) also increased with increasing light intensity.

Short-term plot, less than 2 minutes, was dependent on the temperature at which the measurement was made. The absolute values of the current with increasing temperature decreased both in the saturation region and the current value. In order to exclude the collapse reduction of currents associated with the effect of temperature quenching, not considered in this work, the temperature change region was used below 50-60 °C, characteristic for the beginning of T-quenching. The increase in temperature led to a noticeable recovery of relaxation by 2-3 times. Given the seconds of the duration of the evolutions of the current, we connected the observed variation exclusively with electronic processes. In contact with own light on the sample there is a release of no equilibrium charge carriers. A number of them take part in the formation of the photocurrent. And a significant part, especially in the initial moments of time, goes to fill deep traps. It is obvious that the number of such captured carriers on the traps is large at first, because the traps were empty. But over time it is reduced as the traps are filled. This ensures an increase in the proportion of carriers remaining in the free state with a corresponding relaxation increase in the photocurrent.

At the same time, it is superimposed by a competing process – as the traps are filled under the influence of temperature, the number of thermally ejected carriers increases. In General, the presence of equilibrium is characterized by the approximate equality of the flows of captured and discarded carriers from the traps. As the temperature increases with the same capture intensity, the number of thermal emissions increases. This provides a more rapid achievement of the saturation current.

As noted, when excited by its own light, the formation of the photocurrent is controlled by the recombination processes at the S-centers. The role of R-centers can be made decisive, if you do otherwise-without changing the current

intensity of this light, turn on the infrared. The relaxation curves of the effect of infrared quenching of the photocurrent, not studied earlier, are shown in Fig. 3.7. To observe the relaxation of the photocurrent under the influence of radiation from the long – wave part of the spectrum, the wavelengths corresponding to the damping maxima of 1100 and 1380 nm were used. Optimal values of the Eigen frequency and quenching light intensities were chosen in accordance with [14] – [17] (see chapter 1.1. Part I).

With an ongoing and exciting light, when the photocurrent I_0 achieved relaxation, including infrared light, pre-set to the wavelength of the corresponding maximum damping and started time dependence of the photocurrent.

Both curves start from a single point corresponding to the value of the self-excitation. When the infrared illumination is switched on, the photocurrent is quenched and its value decreases-and the curve 1 corresponding to the wavelength of the short-wave maximum (see Fig. 1.1. Part I) is above the curve 2 for the wavelength maximum and relaxes to the steady-state value longer.

This is explained as follows. Since there is a thermal transition from level R to level R', the probability of transition from this level is greater due to the greater population of the excited States. This determines that the curve 2 corresponding to the transition from levels R' is lower than the curve 1 corresponding to the transition from levels R.

As you can see from figure 3.7, curve 2 relaxes to steady value faster. This is due to only one process, namely-transitions from the levels R'. At the same time, the curve 1 is due to transitions from the levels R and R', plus thermal transitions within the centers of sensitivity from the ground to the excited States. In addition, there is a possibility of reverse capture of the hole from the valence band to the R-centers. In General, the existence of such a complex combination of processes and causes a more protracted front of the observed curve.

Thus, the considered model assumes a large population of R' level holes due to thermal transitions to them from the main state of R-centers.

References

1. Simanovych N.S., Brytavskiy Ye.V., Kotalova M.I., Borshchak V.A., Karakis Y.N.
The study of heterogeneous sensitized crystals of cadmium sulfide. Part I. About charge state of the centers recombination. // *Photoelectronics* – 2017. – n. 26. – s. 121–135.
2. Каракис К.Ю. Релаксационные характеристики полупроводниковых кристаллов с ИК-гашением фототока. // Одесса, Работа – лауреат Областного конкурса (3 место) Малой академии наук, Областное территориальное отделение, Секция “Физика”. Одесса – 2001. с. 1–37.
3. Ю.Н. Каракис, Н.П. Затовская, В. В. Зотов, М. И. Куталова Особенности релаксации фототока в кристаллах сульфида кадмия с запорными контактами // 1-а Українська наукова конференція з фізики напівпровідників. – Одеса, 10-14 вересня 2002. Тези доповідей. Т.2. – с. 138.
4. К.Ю. Каракис, В.А. Борщак, В.В. Зотов, М.И. Куталова Релаксационные характеристики кристаллов сульфида кадмия с ИК- гашением. // *Фотоэлектроника* 2002. – вып. 11. – с. 51 – 55.
5. Melnik A.S., Karakis Y.N., Kotalova M.I., Chemeresjuk G.G. Features of thermo-optical transitions from the recombination centers excited states. // *Photoelectronics* –2011. – n. 20. – s. 23–28.
6. Каракис Ю.Н., Борщак В.А. Затовская Н.П., Зотов В.В., Куталова М.И., Балабан А.П. Исследование релаксации фототока в полупроводниковом устройстве. // *Фотоэлектроника* – 2003. – №12 – с. 132 – 135.
7. Кочергина А.А., Каракис Ю.М. Деградація фоточутливості напівпровідників, зумовлена міграцією домішок. // Всеукраїнська конференція молодих вчених “Фізика і хімія твердого тіла. Стан, досягнення і перспективи”. 20 – 21 жовтня 2010 р. Волинський національний технічний університет. Тези доповідей. Секція 2. “Сучасні фізико-технічні аспекти напівпровідникових пристроїв”. Луцьк. – с. 212 – 217.
8. Софія Зіміна, Юрій Каракіс, Вікторія Федоренко Релаксаційні властивості фотоструму в монокристалах CdS // International Conference of Students and Young Scientists in Theoretical and Experimental Physics HEUREKA -2012. Book of abstracts. April 19-22– Lviv, Ukraine. – 2012 – s. D 19.
9. G.G.Chemeresyuk, Ye. V. Brytavskiy, Yu. N. Karakis (Ukraine) Infrared radiation sensor with selective controlled sensitiviti // The Ninth International Conference “Correlation Optics 2009” – Chernivtsi National University Chernivtsi, Ukraine. September 20 – 24. – 2009. Poster Session. Session 2 – D-2.
10. Кочергина А.А., Каракис Ю.Н., Ницук Ю.А. Датчики инфракрасного света на основе чувствлённых полупроводников // 4 nd International Scientific and Technical Conference “Sensors Electronics and Microsystems Technology” (СЕМСТ-4). Book of abstracts Секция VI “Радіаційні, оптичні, та оптоелектричні сенсори”. – Україна, Одеса, 28 червня – 2 липня 2010 р. ”– s. 100.
11. A.A. Dragoev, A.V. Muntjanu, Yu. N. Karakis, M. I. Kotalova Calculation for migration-dependent changes in near-contact space-charge regions of sensitized crystals. // *Photoelectronics*. – 2010. – n. 19. – s. 74 – 78.
12. Ye.V.Britavsky, Y.N.Karakis, M.I.Kotalova, G.G.Chemeresyuk On the charge state of rapid and slow re-

- combination centers in semiconductors// Photoelectronics. –2008. – n.17. – 2009. – n. 18 – s. 65 – 69.
13. Dragoev A.A., Ilyashenko A.S., Babinchuk V.S., Karakis Yu. N., Kutalova M.I. Features of photocurrent relaxation in sensor-based CdS crystals or features or features of photocurrent relaxation in crystals with fast and slow recombination centres //Photoelectronics. – 2012. – n. 21. – s. 110 – 115.
 14. Новикова М.А. (под научным руководством Ю.Н.Каракис) Особливості інфрачервоного гасіння фотоструму у напівпровідниках CdS. // Работа – лауреат Областного конкурса (1 место) Малой академии наук, Областное территориальное отделение, Секция “Физика”. Одесса, 2005 г., с. 1 – 37.
 15. M. A. Novikova Change of Photoelectric Properties of Semiconductors as a Tool for the Control of Environmental Pollution by Extraneous Admixtures and IR-illumination.// Section of Environmental Science. Finalist of Intel International Science and Engineering Fair. USA, AZ, Phoenix, May 8 – 18. 2005.
 16. Драгоев А.А., Затовская Н.П., Каракис Ю.Н., Куталова М.И. Управляемые электрическим полем датчики инфракрасного излучения.//Материалы 2 nd International Scientific and Technical Conference “Sensors Electronics and Microsystems Technology” Book of abstracts s. 115. Секция IV “Радіаційні, оптичні, та оптоелектричні сенсори”. Україна, Одеса, 26–30 червня 2006 р. “Астропринт”. 2006.
 17. M.A.Novikova, Yu.N.Karakis, M.I. Kutalova Particularities of current transfer in the crystals with two types of Recombination centers. // Photoelectronics- 2005. – n.14. – s. 58–61.

This article has been received in August 2018

UDC 621.315.592

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THE STUDY OF CADMIUM SULFIDE HETEROGENEOUSLY SENSITIZED CRYSTALS. PART II. RELAXATION CHARACTERISTICS

The photoelectric properties of CdS crystals with combined doping are considered.

The relaxation of the photocurrent determined by the long-term (months) redistribution of the sensitive impurity is found. The possibility of creating a new type of light sensors with super long memory.

The medium-time (minutes) and fast (seconds) relaxation of the photocurrent under excitation by natural and infrared light are studied.

УДК 621.315.592

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ИССЛЕДОВАНИЕ НЕОДНОРОДНО ОЧУВСТВЛЁННЫХ КРИСТАЛЛОВ СУЛЬФИДА КАДМИЯ. ЧАСТЬ II. РЕЛАКСАЦИОННЫЕ ХАРАКТЕРИСТИКИ.

Рассмотрены фотоэлектрические свойства кристаллов CdS с комбинированным легированием.

Обнаружена релаксация фототока, определяемая долговременным (месяцы) перераспределением очувствляющей примеси. Указана возможность создания световых датчиков нового типа со сверхдолгой памятью.

Исследованы средневременная (минуты) и быстрая (секунды) релаксация фототока при возбуждении собственным и инфракрасным светом.

УДК 621.315.592

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ДОСЛІДЖЕННЯ НЕОДНОРІДНО ЗЧУВСТВЛЕНИХ КРИСТАЛІВ СУЛЬФІДУ КАДМІЮ. ЧАСТИНА II. РЕЛАКСАЦІЙНІ ХАРАКТЕРИСТИКИ.

Розглянуті фотоелектричні властивості кристалів CdS з комбінованим легуванням.

Виявлена релаксація фотоструму, що пов'язана з довготривалим (місяці) перерасподілом зчувствляючої домішки. Вказана можливість створення світлових датчиків нового типу з сверхдовгою памятью.

Досліджена середньотривала (хвилини) і швидка (секунди) релаксація фотоструму при збудженні власним і інфрачервоним світлом.