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REVERSIVE SPECTRAL CHARACTERISTICS IN IR-QUENCHING RANGE OF PHOTOCURRENT. THE CASE OF INTERACTING HOLES.

The interaction processes between the basic and excited states of sensitization centres were investigated by reversive procedure. It was stated that all the observed effects can be explained by stimulated level of hole trap occupation and changes in thermal redistribution of captured carriers taking into account that the band scheme was corrected.

Spectral characteristics of semiconductor samples were measured experimentally beginning from the small wavelengths up to the longer ones. Under investigation of intrinsic conductivity the abovementioned procedure gives no influence on experimental result. But this statement is not valid when the processes connected with captures in holes are studied.

Under such procedure the processes for occupation — devastation of holes take place with additional period. Firstly, large concentration of non-equilibrium carriers is created under excitation by wavelengths from intrinsic absorption band. The piece of the mentioned carriers settle in holes. Under rather high intensities of light and velocity of light wavelength change one can create such conditions when the hole by the moment of its excitation is found completely occupied with non-equilibrium charge, independently on the pre-history of processes flowed.

It is convenient. In this case the photoresponse is found large at the expense of considerable carrier release that makes easy to determine the basic parameter — activation energy, i.e. hole depth, that is identical both for equilibrium charge and for non-equilibrium one.

But the processes connected with concentrations of charge carriers on holes that existed there primarily before light exposure can not be examined. At the expense of large number of non-equilibrium charges entering such processes are completely disrupted.

One should wait relaxation times under illumination by each wavelength out of various spectra ranges when the conception about the direction of its change to raise or to decrease lost. Each wavelength of light applied causes the independent effect which is not connected with the foregoing exposure.

In case when equilibrium processes in crystals are studied in participation of holes, one should use the reverse change in radiation wavelength from the greater values (infrared) up to small ones (visible range). In this case the light acts only as the instrument for excitation. Concentration of captured charge existed in holes is only read out with help of light when carriers from holes are excited.

We note that the new conditions take place. Probably this is the reason that such procedure to change spectral content of excitation has been narrow extended.

The carriers shifted from bound to free state are non-equilibrium by definition, but their concentration under usually applied high excitation levels is determined by equilibrium charge located in holes before illumination.

The conditions with interacting holes system, as in our case, between basic and excited states of R-centres are complicated. The long-wave light effect is found to be symmetrical in this time. Under any excitation flow the levels are activated in turn. The direction to change wavelength (from long to short waves or from short to long waves) defines only the order to activate holes — either at first they are activated from narrower excited state and then from the deeper excited one, or vice versa. In the latter case, one should take into account that the part of IR-radiation quanta with energy 1,1 eV (for cadmium sulphide) can excite R-centres in depth 0,9 eV forming hot free holes.

In all variants of current formation in semiconductor crystal, the universality of reversive procedure allows to carry out measurements both traditionally under steady-state conditions and in dynamic regime under different velocity of changes in exciting light wavelength.

The comparison of traditional, steady-state measurements and the procedure under different velocities $\frac{d\lambda}{dt}$ allows to note the following particularities:

1. Firstly, both procedures do not contradict each other . On the contrary, steady-state procedure should be understood as particular case of measurements with null rate $\frac{d\lambda}{dt} = 0$. The possibilities cleared to carry out the analysis under the other magnitudes $\frac{d\lambda}{dt}$ are lacked.

2. The steady-state procedure for measurements of reach photocurrent operates good for significantly occupied holes which concentration is high. The low charge accumulated in holes and/or their low concentration are more typical. The processes connected with this component on photocurrent formation influence only during earlier seconds of exposure. The analysis does not observe them from photocurrent steady-state value because they have been already absent there.

Under dynamic measurements the role of relaxation changes. It stops to be opponent and becomes ally. Under measurements, particularly quick studies, with large values of $\frac{d\lambda}{dt}$ relaxation phenomena effect on photocurrent behavior. When results are compared under different values of $\frac{d\lambda}{dt}$ and then different degrees of relaxation influence, one can show up these mechanisms and, finally, holes parameters and conclude that these mechanisms are forming.

3. Non-equilibrium carriers interchange and balance their energy with lattice during very short time of 10^{-3} — 10^{-1} s [1]. As result, the contributions of equilibrium and non-equilibrium carriers in current can not be divided under steady-state measurements. If dark current is formed exclusively at the expense of charge equilibrium component, it is customary to consider that the value of light current is connected only and exclusively with non-equilibrium charges. This can be come true for high levels of exposure but not correct for low illumination. Later we show that the procedure of studies proposed, particularly within maximum rates $\frac{d\lambda}{dt}$, remove these contradictions.

4. When capturing holes interact, as in our case, between basic and excited state of R-centres, the processes of charge redistribution should occur rather quickly because this is one and the same centre geometrically. The carriers have not waste time to drift from one centre to the other. We should note that the particularities of these processes remain unexplored now. And the procedure of high rate measurements for $\frac{d\lambda}{dt}$ in IR-region can be the effective instrument of such studies.

The investigation of phenomena occurred under different order of excitation clear the opportunity that has not been applied earlier to precise the particularities of processes flowed.

Semiconductor single crystal cadmium sulphide was chosen for investigation as the model material. Its advantages are the following: firstly, high photosensitivity (photoresponse — up to eight orders); secondly, IR-quenching of photocurrent characteristic for rather narrow class of materials; thirdly, it is wideband semiconductor (E_g~2,42 eV), that allows to carry out investigations within wide range of wavelengths from visible area up to 1600 μm.

The range of applied excitation energies is called the area of interacting holes in the sense that interaction to R and R'-levels is excitation of physically single centre in contrast to the common situation with different groups of centres observed in [2,3].

If the model of Bube was realized at activation of R-centres [4], the significant variations between direct and backward spectral dependencies Q(λ) should not appeared. The basic state with activation energy 1,1 eV is primarily excited when illumination wavelength changes from small values to the greater ones. And the occupation of these state by holes decreases respectively. If excitation with energy 0,9 eV is carried out later, the number of activated holes can not be so large and longwave maximum Q(λ) can be observed higher than shortwave one.

The higher rate of wavelength change the stronger decrease in maximum within the range 1400 μm in comparison with maximum 1000 μm. This should take place as result of the following causes. Firstly, the steady-state (but non-equilibrium — intrinsic light effects) occupation of R and R'-centres has no time to restore. Secondly, in order that hole excited by longwave light may transfer to free state, it needs to absorb photon, that needs time. The analogous ratio of Q(λ) maxima heights should be observed under reverse change of wavelength — from large values to small ones.

Thermal excitation (according to Bube theory) influences only on R'-centres, whereas capture cross-section for R and R'-centres is similar. As result, steady-state concentration of holes on R'-centres should be considerably lower than on R-levels. Under quick change of wavelength we read out this picture and longwave maximum should locate lower.

At slow decrease in wavelength of quenching light the situation should have time to equalize slightly at the expense of holes departure from R-centres when light passes energy within the range of ~ 0,9 eV. This process is spread in time that is enough to realize the competitive process — holes created by intrinsic light in valence-band are captured. So, the height of shortwave maximum Q(λ) should prevail. But the other situation is realizes experimentally. At any exposure regimes the maximum of spectral characteristics Q(λ) in 1000 μm area was observed lower than at λ≈1400 μm.

In whole spectral distribution of quenching coefficient at increase of excitation wavelength Q(λ↑) and at its decrease Q(λ↓) for different rates $\frac{d\lambda}{dt}$ is shown in Fig. 1. For steady-state curve we used measurements with relaxation up to 20 minutes in each point to avoid transient processes [5,6]. The sample is exposured for a long time in each cycle at spectrum edges at 1000 and 1600 μm to preserve the inter-influence of curves.

The reverse curves for $\frac{d\lambda}{dt}$ ~1 μm/s that causes the most distinctive modifications is shown in Figure 1. The characteristic changes observed in curve of photocurrent quenching along the whole range of applied rates (from 0,33 up to 2,5 μm/s) are brought together in Table 1.

In order to make the observation more useful we show the corrected shape of band-diagram with both states of R-centres [7] (Fig. 2).

VARIANT A:

Value Q in each of maxima is proportional to the number of holes knocked out by light, correspondingly, for shortwave maximum — from basic state of R-centres and for longwave maximum — from excited state. At increase of wavelength in quenching range beginning from 900 μm the exciting light influences firstly on the deeper basic level (see Fig. 2). The initial occupation of this centre is the same as in steady-state measurements, but the number of activated holes is found smaller because the total time of its exposure is lower depending on rate $\frac{d\lambda}{dt}$. So the value $Q_{max1}(\lambda\uparrow)$ is found lower than the steady-state one. If excitation is carried our from long waves up to short ones, the excited state R' is devastated preliminary. As result of increase in holes number there the flow of thermally excited holes from the basic state raises (in Fig. 2 named as kT). And as result occupation of R-centres is found lower and value $Q_{max1}(\lambda\downarrow)$ becomes smaller when light wavelength decreases up to numbers of order 1000 μm. The optimum rate exists when the discordance $\Delta Q = Q_{max1}(\lambda\uparrow) - Q_{max1}(\lambda\downarrow)$ is the highest accordingly to the model developed in [2,3]. In our case it is approximately 1 μm/s. At further rate increase the discordance decreases because at direct change λ has no time to excite R-state and at reverse change — R'.

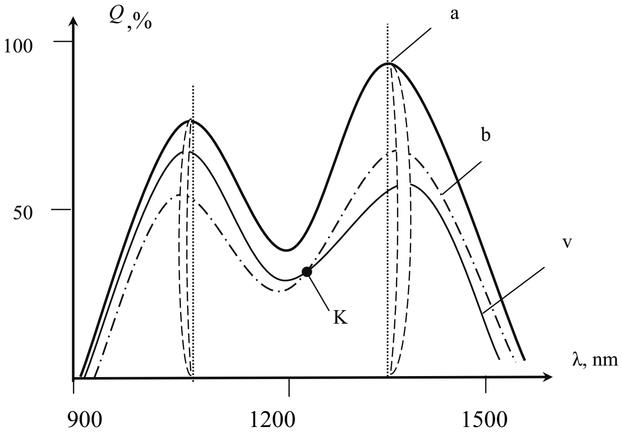

Figure 1. Spectral distribution of quenching at measurements in steady-state conditions (a), at decrease of wavelength (b) and at its increase (v) with rate 1 nm/s.

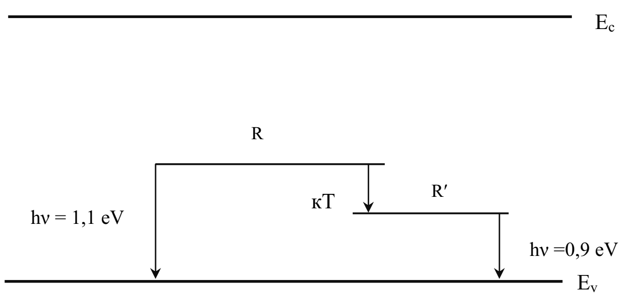

Figure 2. Band diagram of sensitized semiconductor.

VARIANT B:

Now the excitation by long waves meets firstly unexcited occupation of R' states and the value of maximum $Q_{max2}(\lambda\downarrow)$ is defined only by the time of exposure on excited states R' and then rate $\frac{d\lambda}{dt}$. At direct measurements with increase of wavelength the mentioned process has one more cause [2]. Excitation of R-states has occurred before. If raise of hole thermal inflow was characteristic for *Variant A*, now it causes its decrease. Occupation of R'-centres is found lower, namely, $\Delta Q = Q_{max2}(\lambda\downarrow) - Q_{max2}(\lambda\uparrow)$. Let's note the characteristic peculiarity. As $\Delta Q = Q_{max1}(\lambda\uparrow) - Q_{max1}(\lambda\downarrow)$ is correct for the left maximum, according to Bolzano-Cauchy theorem curves $Q(\lambda\uparrow)$ and $Q(\lambda\downarrow)$ should cross without fail. Really, we have observed this effect at any change rates of light wavelength, at all intensities of illumination. This is shown by point "K" in Fig. 1. The similar nuance is the peculiarity of applied procedure and it can not be observed in traditional measurements.

Table 1

The analyses of characteristic changes for curves of Fig. 1 for different rates of changes on wavelength of quenching light.

Coordinate axis / Position of maximum	Y-ordinate (value of quenching Q, %)	X-abscissa (wavelength of irradiation λ)
Shortwave maximum of quenching (1000 — 1100 μm)	**A.** With increase of rate $\frac{d\lambda}{dt}$, the discordance $\Delta Q = Q_{max1}(\lambda\uparrow) - Q_{max1}(\lambda\downarrow)$ increases, reaching the greater values approximately at 1 μm/s, and the decreases anew.	**C.** Both values — $Q_{max1}(\lambda\downarrow)$ and $Q_{max1}(\lambda\uparrow)$ shifted to short wavelengths comparatively with steady-state maximum, but $Q_{max1}(\lambda\downarrow)$ shifted considerably. With increase of rate $\frac{d\lambda}{dt}$ these deviations firstly decrease reaching the greater values approximately at 1 μm/s, and then decrease.
Longwave maximum of quenching (1300 — 1400 μm)	**B.** With increase of rate $\frac{d\lambda}{dt}$, the discordance $\Delta Q = Q_{max2}(\lambda\downarrow) - Q_{max2}(\lambda\uparrow)$ increases, reaching the greater values approximately at 1 μm/s, and the decreases anew.	**D.** Both values $Q_{max2}(\lambda\downarrow)$ и $Q_{max2}(\lambda\uparrow)$ shifted to the greater wavelengths comparatively with the steady-state maximum but $Q_{max2}(\lambda\uparrow)$ shifted considerably. With increase of rate $\frac{d\lambda}{dt}$ these deviations firstly increase reaching the greater values approximately at 1 μm/s, and the decreases anew.

VARIANT C:

Values $Q_{max1}(\lambda\uparrow)$ and $Q_{max1}(\lambda\downarrow)$ changes down differently. Curve $Q(\lambda\uparrow)$ connected with undisturbed occupation of basic states and show simple scaling of steady-state short-wave maximum $Q(\lambda)$. Both its slopes undergo rather the same decrease. The right slope is bigger because some shift of capture-devastation equilibrium is characteristic for measurements with wavelength longer than maximum one. The abovementioned shift is caused by exciting light itself when measurements at wavelengths shorter than 1000 μm were carried out. As result the maximum $Q_{max1}(\lambda\uparrow)$ slightly shifts to the left. The picture changes at measurements when light wavelength decreases. As is was mentioned previously, excited level devastated preliminary. Thermal excitation from R-centres raised and their occupancy decreases. This can be seen clearly at longwave slope of maximum than at shortwave one being studied later. As result the maximum loses its symmetry and depending on rate $\frac{d\lambda}{dt}$ significantly shifted to the left. Obviously this effect will decay with increase in change rate of light wavelength because light has time to knock out the smaller number of holes with decrease in time of influence on the centre.

The total behavior shortwave maxima coordinates $Q_{max1}(\lambda\downarrow)$ and $Q_{max1}(\lambda\uparrow)$ in Fig. 1 depending on applied rate $\frac{d\lambda}{dt}$ is shown by the section of dotted lines. It characterises as half-moon which right side is formed by maxima coordinates $Q_{max1}(\lambda\uparrow)$, and left side — by maxima $Q_{max1}(\lambda\downarrow)$.

VARIANT D:

The similar semi-moon with right convex forms for longwave maximum. Now the curve$Q_{max2}(\lambda\uparrow)$ decreases non-symmetrically because the basic level was devastated preliminary, thermal transmission from R to R' decreased and this is cleared significantly on the left slope of dependence $Q(\lambda\uparrow)$. We note that the whole variety of curve family in Fig. 1 can be explained applying one mechanism [2,3] — raise or decrease in thermal excitation of holes from basic to excited states depending on direction of changes in light wavelength. Namely, the presence of simultaneous effects allows to consider the existence of such channel for intercentre redistribution of charge concentrations to be proved. Its observation became possible owing to reversive method of excitation applied.

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Abstract
The interaction processes between the basic and excited states of sensitization centres were investigated by reversive procedure. It was stated that all the observed effects can be explained by stimulated level of hole trap occupation and changes in thermal redistribution of captured carriers taking into account that the band scheme was corrected.
Key words: spectral characteristics, photocurrent, holes.

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РЕВЕРСИВНЫЕ СПЕКТРАЛЬНЫЕ ХАРАКТЕРИСТИКИ В ОБЛАСТИ ИК-ГАШЕНИЯ ФОТОТОКА. СЛУЧАЙ ВЗАИМОДЕЙСТВУЮЩИХ ЛОВУШЕК

Резюме
Исследованы процессы взаимодействия между основным и возбуждённым состоянием очувствляющих центров с применением реверсивного метода. Установлено, что все наблюдаемые эффекты могут быть объяснены стимулированным уровнем заполнения дырочных ловушек и изменением термического перераспределения захваченных носителей с учётом откорректированной зонной схемы.
Ключевые слова: спектральные характеристики, фототок, ловушка.

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РЕВЕРСИВНІ СПЕКТРАЛЬНІ ХАРАКТЕРИСТИКИ У ОБЛАСТІ ІЧ-ГАСІННЯ ФОТОСТРУМУ. ВИПАДОК ВЗАЄМОДІЮЧИХ ПАСТОК

Резюме

Досліджені процеси взаємодії між основним і збудженим станом чутливих центрів з використанням реверсивного засобу. Доведено, що всі спостережені ефекти можуть бути пояснені стимульованим рівнем заповнення діркових пасток та зміною термічного перерозподілу захоплених носіїв з урахуванням відкорегованої зонної схеми.

Ключові слова: спектральні характеристики, фотострум, пастки.