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FEATURES OF THEPMO-OPTICAL TRANSITIONS FROM THE RECOMBINATIONAL CENTERS EXCITED STATES

The model of thermo-optical transitions created is confirmed experimentally. The process of hole release from ground state trough excited one to valence band includes firstly the transition at phonon absorption $E_R \to E_{R'}$ with energy 0,2 eV and then excitation to the free state $E_{R'} \to E_v$ at the expense of photon energy $h\nu = 0{,}9$ eV.

The research in effect of photocurrent infrared quenching to determine the priority of optical-thermal transitions at hole release from R-centers was carried out.

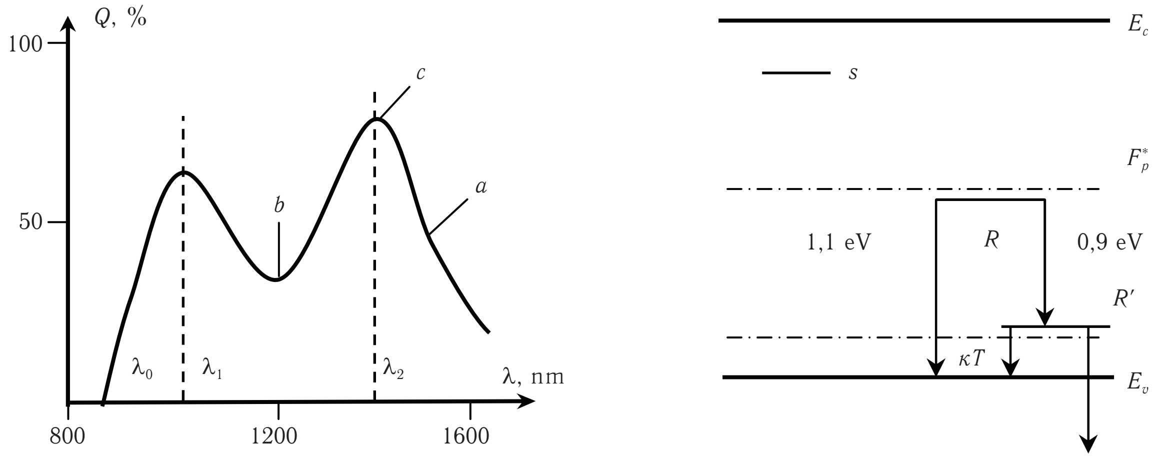
The optical quenching of photocurrent [1] is the direct consequence in recharge of slow recombination centers as the result of additional impurity excitation. The ground of this phenomenon is that photocurrent excited by light from self-absorption area can be decreased (quenched) by light of definite spectral content. This process can be carried out in the crystals that have *S*- and *R*-centers. In the most cases the mentioned effect is accompanied by two maxima in the plot for spectral distribution of quenching ratio $Q(\lambda)$ (Fig. 1, *a*). And so R. Bube [2] offered to observe the excited state of *R*-levels which corresponding zone band presented by Fig. 1, *b*.

Two-leveled model of R. Bube explains the phenomenon of semiconductor sensitization at presence of slow recombination centers. At the same time the model created is semi-phenomenological. The points mentioned below can be considered as its shortcomings:

I. If localized holes from *R′*-levels transit thermally with activation energy 0,2 eV to the free state (Fig. 1, *b*), the light quanta with energy from 0,2 up to 0.9 eV could release them too. In this case the hot vacancies simply appeared in valence band, but longwave sensitivity within the range 1400—1600 μm did not decrease (Fig. 1, *a* — “*a*”).

II. The minimum between two maxima in Fig. 1, *a* — “*b*” could not be observed. The light quanta within the range from $\lambda_1 = 1000$ μm up to $\lambda_2 = 1400$ μm (from 1,1 up to 0,9 eV) can release the carriers from R′-states.

III. In maximum point at 1400 μm (Fig. 1, *a*, — “*c*”) the value Q should be lower than in shortwave range (1000 μm). It should occur because *R*- and *R′*-centers have the equal capture cross-sections for holes, but *R′*-level is influenced by thermal withdrawal of carriers. As the result the steady-state population of *R′* should be lower than for the basic state R. At the moment of illumination by energy 0,9 eV the pattern becomes indistinct because the additional non-equilibrium charge has appeared as the result of vacancies transition from *R*- to *R′*-centers. But resonance light excitation of holes does not occur both to the right and to



a *b*

Figure 1. Spectral distribution of quenching ratio (*a*) and band model of R. Bube (*b*) observed experimentally

the left of point "*c*" in Fig. 1, *a* ($\lambda_{\text{мах}} + d\lambda$ and $\lambda_{\text{мах}} - d\lambda$). If the curve $Q(\lambda)$ is smooth, and only such curves were observed experimentally, $Q(\lambda_2)$ in this case would be lower than $Q(\lambda_1)$.

So the interpretation of Bube model required the additional research. In papers [3,4] the authors showed that intensity of IR-light could not be too much. The number of absorbed IR-photons should correspond approximately to concentration of *R*-centers in order to observe the quenching effect. Since capture cross-sections $S_{\text{pr}} = S_{\text{pr}'}$, IR-photons divide approximately in two between *R*- and *R′*-centers. Two photons are required for transit passage of holes firstly from *R* to *R′*-level and then to valence band. So the longwave maximum would be provided by the smaller number of released holes than the shortwave one. And investigation of such processes requires the greater period of time.

IV. If the model in Fig. 1, *b* was realized, the additional quenching maximum with energy 0.2 eV ($\lambda \sim 7500$ nm) might exist in the remote IR-region when thermal transitions are changed by the optical ones. At the same time, if the maximum is shadowed by phonon activity, its intensity should be raised with increase of crystal illumination by intrinsic light when population of *R′*-levels increases. But such maximum of quenching has not been already observed [5]. We observed that the height of quenching maxima in the nearest IR-region (1000 и 1400 μm) decreases with increase of intrinsic excitation.

V. The symmetry of quenching maxima at λ_1 and λ_2 was observed (Fig. 1, *a*). Two wide bands were determined experimentally, both were slightly smeared to the left of maxima directed to the higher energies. This result explains that hole release from *R* and *R′* levels is carried out directly to the band. At photon energies exceeded activation energy of a trap the vacancies have the possibility to transit to the deeper levels in valence band. Meanwhile, the longwave maximum at 0,9 eV ($\lambda = 1400$ μm) should be weaker than the shortwave one and strongly symmetrical because the transitions $R \to R'$ bears the resonance view.

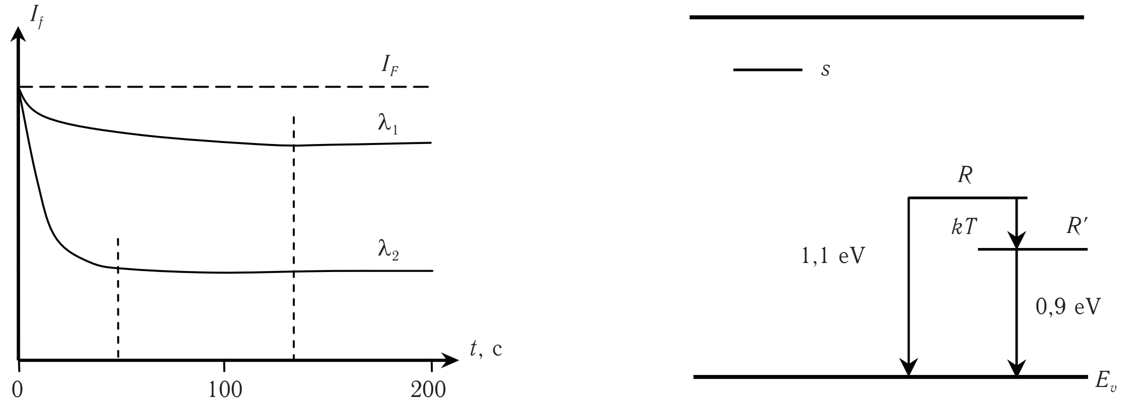
VI. Proceeding from the same suppositions, the straight line should be observed after the second maximum at Fig. 1, *a*. Photons with energy being lower than 0,9 eV can not shift holes from the basic state to the excited one.

VII. If the model from Fig. 1, *b* operates, the distance between the basic and the excited states of sensitization centers $E_R - E_{R'} = h\nu(\lambda_2) = 0{,}9$ eV. That means that at room temperature when spectrum $Q(\lambda)$ was registered (Fig. 1, *a*) this distance is greater by 36 folds than phonon energy $kT = 0{,}025$ eV. If one takes into consideration that namely this temperature causes the splitting of *R′*-centers excited state out of the basic one, such divergence is seemed unlike.

VIII. In accordance with the model, at illumination by light of wavelength λ_2 the intracenter transitions $R \to R'$ take place (Fig. 1, *b*) and occupation of *R′* levels should increase but for the basic levels *R* — decreases. Experimentally we observe the smooth dependencies on intensity of longwave light. This shows that the processes occur in the common way without changes of mechanism along the whole range and large illuminations $p_{R'} \gg p_R$. Owing to large concentration of holes at *R′*, they should be located **under** Fermi quasi-level, i. e. value F_p^* lies within the range between $E_{R'}$ and E_v. But since occupation p_R at large intensities is low these levels are **over** Fermi quasi-level, i. e. the value F_p^* is lower than E_R. These processes can not occur simultaneously because $E_R \gg E_{R'}$.

IX. The excited state of hole interacts with the basic one at any temperature [6]. In the model the states *R′* exchange holes with valence band solely at 300 K. And owing to its depth the basic level can only capture the carriers from there. The interaction between levels is not supposed.

The basis to create the band model in Fig. 1, *b* was taken the shape of spectral characteristics $Q(\lambda)$ in Fig. 1, *a*. But the presence of two quenching maxima with the same activation energies can be explained differently as it was shown in Fig. 2, *b*. The following ex-



a

b

Figure 2. Photocurrent relaxation at additional illumination from quenching maxima (*a*) and the alternative band scheme (*b*)

perimental data support the abovementioned situation.

1. RELAXATION CURVES

The sample was excited by intrinsic light and then additionally by infrared illumination from quenching bands either λ_1 or λ_2 (Fig. 1, *a*) to research photocurrent relaxation (Fig. 2, *a*). The intensities of intrinsic and quenching light were chosen as recommended in [3, 7, 8]. The curves of both plots began from one and the same point corresponded to the value of intrinsic current. The ordinary mechanism of quenching was carried out with the additional influence of IR-light.

A) The steady-state value I_F is defined by level population. The smaller change in photocurrent was observed that fully corresponded to Fig. 1, *a* for lower value Q at illumination light of λ_1 wavelength.

B) The slope of plot at $t = 0$ for the same curve is smaller because it was defined by number of dislodged carriers proportional to concentration of holes in *R*-levels.

C) Fig. 2, *a* shows that a period to adjust steady-state photocurrent differs approximately by three times that is caused by interaction of levels at both quenching procedures. The light of wavelength λ_1 knock out holes from the basic state *R* and the excited state *R′* plays as damper — the part of its holes drops to *R* centers and delays relaxation. When levels *R′* are activated by light of λ_2 wavelength, this role transmitted to *R* centers. And relaxation finishes considerably quicker because the number of holes there is lower. Hence, three particularities of relaxation curves point out the lower occupation in basic state of *R*-centers (point III).

2. MIGRATION-RELAXATION CHANGES. LARGE INTERELECTRODE DISTANCE

Filamentary CdS crystals with interelectrode distance 2—3 mm were chosen to research coordinative redistribution of impurity. The investigation in effect of photocurrent IR-quenching confirmed the existence of *R*- and *S*-centers which concentrations being approximately equal and.

Photosensitivity was not observed completely when samples exposed by intrinsic light and located in darkness for a long time (2—3 months). Then photosensitivity restored during several days besides crystals were exposed by monochromatic light with wavelength 515 nm [9]. The process took place and was independent on number and duration of exposures and remained identical even at one illumination of 10 sec per day. The rate of photosensitivity restoration was observed maximal at the beginning and then its raise decreased. After approximately 100 hours photocurrent became stable and did not respond to 24-hour exposures.

The intensity of photocurrent longtime relaxation was managed to activate at higher temperatures (approximately up to 40—50 °C to avoid photocurrent temperature quenching). The restoration of sensitivity was considerably broken by infrared light with $\lambda = 1400$ nm, 0,9 eV.

The durations of the observed phenomena excluded any electron processes. And ion-migration model were taken to explain the situation.

It was shown the presence of considerable cut-off barriers. After preliminary exposure *R*-centers trapped the positive charge [10] are drawn by near-contact field ($\sim 10^5$ V/cm) into space-charge region and accumulate there. These traps with depth ~ 1 eV can keep holes for a long time and thus migrate even in darkness. As positive charge accumulates in barrier region the height of barrier decreases and the situation becomes more stable. If *R*-centers continue to locate in steady-state-conditions, they slowly recombine and transit to the neutral state but remain in space-charge region as before.

At the following illumination by intrinsic light and under external voltage applied the charged *R*-centers at the expense of diffusion and drift migrate to the central part of crystal and sensitize it. The higher temperatures increase their mobility without changes in charge state because thermal transitions are intra-centre (Fig. 2, *b*). According to this model IR-light (λ_2) knock out holes from the most occupied *R*-levels. Then both diffusion and drift are delayed.

If the other model would exist (Fig. 1, *b*), IR-light caused intra-center transitions and temperature devastated the excited states. The depth of *R′* levels 0,2 eV can not provide the longterm keeping of charge in darkness and accumulation of traps in space-charge region.

3. MIGRATION-RELAXATION CHANGES

Small interelectrode distance. Since near-contact barriers play the significant role in longtime relaxation of photocurrent it was interesting to make this influence enhanced. The contacts on the same samples shifted up 0,1—0,2 mm. In this case the interelectrode distance is comparable to width of space-charge region. Thus, contact barriers and processes occurred control current. In crystals with small intercontact distance after stay in equilibrium conditions we observed the unusual form of photocurrent relaxation.

Photocurrent at low level of intrinsic illumination (1—3 lx) reached the steady-state during several seconds. For higher illuminations

(10—15 lx) photocurrent firstly raised during 3—4 min (1 stage), then during 15 min its value decreased approximately 30 % (2 stage) and then reverted to the same value and stabilized during 45—50 minutes.

These processes can be explained as follows. At the first stage the raise I_F is defined by usual relaxation increase of electron concentration. *R*-levels collected in barrier area captured the charge resulting in lowering of Schottky barrier that could not keep them. Space-charge region widens at the second stage as *R*-centers migrate from here [11]. Its resistance raises and current drops. At the third stage current increases because of two reasons: widening of contact leads to reduction in central part of crystal. Simultaneously it is sensitizing by extracted *R*-centers. This process is longterm because the time to distribute impurity along the crystal is required. As result, current stabilized at the same level as before will formation because the number of centers leaving space-charge region corresponds to the number of centers causes the changes in the central part of the crystal.

Obviously at weak illumination the mentioned processes are not observed — the number of R^+ is considerably small and their doping is seemed to be negligible.

In order to research this model we decreased concentration of charged impurity by IR-radiation with energy 0,9 eV. And all the particularities of relaxation disappeared. Photocurrent curve without minimum point came to saturation during longer periods that in several times prevailed the period when maximum I_F was reached. The absolute value of photocurrent I_F is observed by an order of magnitude lower.

This confirmed the structure of band diagram 2, *b* but do not agree with model in Fig. 1, *b*.

4. ILLUMINATION-CURRENT DEPENDENCIES

A) The dependence of quenching ratio Q on intensity of exciting and quenching light based on model of Fig. 2, *b* was obtained in [3] and the formula has been confirmed experimentally. When the value for absorbed photons of intrinsic light raises *Q* drops, but with raise in intensity of longwave light quenching increases and this is not agree with model 1, *b*. Two-stage transition should minimize the influence of this light on quenching ratio.

B) The analysis in rate for quenching maxima increase was carried out. With raise in number of infrared photons the value of minimum between maxima decreases. This can be explained (see Fig. 2, *b*) as follows: photons with energy between maxima from 0,9 up to 1,1 eV can effectively absorbed by both levels.

C) The conditions when the first maximum of Figure 1a was practically absent were created in the narrow region of relationship between applied field, temperature and intensity of longwave light with $\lambda_1 \sim 1000$ nm [8]. This was explained by the repeated capturing of traps. Directly after activation the hole locates in the vicinity of mother center and has the energy benefits to come back. This is confirmed by the value of quantum yield for IR-light within the range 0,03—0,07 determined in [7] to be anomalously low.

These processes combine very well with the alternative model 2, *b*. And the probability to capture holes to these levels being proportional to the number of free places is considerably lower.

D) In paper [12] it was shown that illumination-current characteristics $I_F(L)$ observed linear when crystal was influenced only by intrinsic light. They became superlinear under additional infrared illumination but at lower absolute values of current. This process was observed both for wavelengths λ_1 and λ_2.

This corresponds completely to band diagram of Fig. 2, *b*. The transitions either from *R*- and *R′*-levels are equivalent here.

5. REVERSAL PLOTS

The performance of $Q(\lambda)$ parameter at reversal mode of excitation was investigated in [13] The plots measured with different rate of wavelength change to increase and then to decrease were compared. The difference consisted in the sequence of center excitation.

Model 1, *b* does not suppose the interaction between levels (see item IX). So the shape of maxima $Q(\lambda)$ should not changes at any procedure of measurements independently on rate of wavelength raise or decrease. Infrared light simply indicates the stage of *R* and *R′* level occupation with holes.

If the levels thermally interacts as shown by the alternative model the pattern changes. In this case the influence on one level changes the dependence on the on the other. If the measurements are carried out beginning from the longer waves to the shorter ones, *R′* centers exited firstly. The holes increase their transitions from the basic states to the released places. So maximum $Q(\lambda_1)$ will be smaller when wavelength decreases up to λ_1 because of smaller occupation of *R*-centers. The time is required for thermal transitions $R \rightarrow R'$. So the value of decrease will be dependent on rate for changes in wavelength $\frac{d\lambda}{dt}$. The higher it will be the smaller changes take place. So, in this case maximum $Q(\lambda_2)$ is observed without changes, but maximum $Q(\lambda_1)$ decreases depending on applied $\frac{d\lambda}{dt}$ value.

If the spectrum is measured to the direction of wavelength increase, the maximum $Q(\lambda_1)$ observed stable. But namely light influence at measurements decreases thermal flow of holes to *R′* centers. When light energy will drop up to $E_{R'}$, the number of hole transitions from spectrum to free state decreases. In this case the maximum $Q(\lambda_2)$ decreases the strongly the longer time was needed for thermal transitions from R-levels, i. e. the slower changes in wavelength the slower rate $\frac{d\lambda}{dt}$.

The decrease of maxima $Q(\lambda)$ by turn in spectral area being remote from the beginning of wavelength change was observed in [13] that was the additional argument in favour of the model 2, *b*.

6. THE PROCESSES ON SHORTWAVE BOUND OF QUENCHING

The authors [14] show that the value I_F does not change at shortwave bound of quenching area because the intensities of photoexcitation and quenching processes are equal. Since each of them depends differently on external effects — the values of light beams, temperature, applied voltage — the changes of these parameters should result in displacement of wavelength to start quenching.

A) We can not observe the changes in λ_0 area (Fig. 1, *a*) connected with variation of voltage applied to sample or intensity of intrinsic light. The raise of intrinsic excitation takes place similarly in both models. This leads to increase of level occupation. On exposure the yield is observed higher, recombination rate increases quickly that rate of photoexcitation at absorption edge. The bound λ_0 shifted to the shorter wavelengths.

One and the same result was reached for the different intensities of IR-light in measurements of spectral dependencies from shorter to longer wavelengths. The greatest effect on λ_0 position gives the followed spectral area $Q(\lambda_1)$ that is connected with transitions from basic states operating similarly in both models.

B) The transitions with energy 0,9 eV and 1,1 eV have the different rates and take place in measurement of $Q(\lambda)$ from longer wavelengths to shorter ones. The higher the intensity of light the more evident particularities observed.

If model 1, *b* operates at preliminary illumination by light with energy 0,9 eV levels R are devastated and at the following excitation with energy 1,1 eV their photoresponse will be lower. The rate of quenching in λ_0 decreases respectively. The value λ_0 should shift to the right and the higher the rate $\frac{d\lambda}{dt}$ the evident the picture. But the opposite situation was observed in experiments. The higher the rate of wavelength change the smaller shift of quenching bound λ_0 to the higher values.

This corresponds to the alternative model 2, *b*. Illumination with energy 0,9 eV devastated R centers. Thermal ejection of holes $R \to R'$ increases because there are larger free places. The shoots of holes from R-centers at the moment of illumination with energy 1,1 eV will be less because of the smaller occupation. The decrease in recombination rate results in shift of λ_0 to the longer wavelengths, but this process is inertial because of the additional stage of thermal transitions limited by probability phenomena.

C) The differentiation connected with temperature change at registered voltage and light intensity is carried out better that is observed at measurement in the increasing wavelength of quenching light.

In model 1b the holes are knocked out from R'-states by thermal energy. The occupation of basic levels does not change there. And the influence of maximum $Q(\lambda_1)$ remains stable. One should expect the registered value λ_0 but it shifted from 920 up to 940 μm along the measurements with temperature raise. This situation takes place because holes shift from R-levels to R' ones. And illumination with wavelength λ_1 knocks out the smaller number of carriers. The processes of quenching are oppressed and the restoration of equality with rate of excitation is possible only at longer wavelengths.

6. CONCLUSION

The experiment which results are unambiguously defined by the active model of Fig. 1, *b* or 2, *b* is described in [3]. The plots $Q(\lambda)$ for room and increased (up to 45—50°) temperatures were compared to avoid the effects connected with temperature quenching.

Spectral position of maximum $Q(\lambda_1)$ did not change under heating. In both models it is bound with hole release from basic state of R-levels.

A) Its height with heating slightly decrease. This testifies to favour of diagram 2, *b*. In this case the number of holes coming to R'-centers should increase. Occupation of R-levels drops. Light of wavelength λ_1 knocks out the smaller number of carriers than in model 1, *b*, where the temperature influences only on R'-levels. When light with wavelength λ_2 is absent the optical transitions $R \to R'$ should not take place. The occupancy, the number of holes released from R-levels and the height of maximum $Q(\lambda_1)$ with temperature increase should be stable.

B) The second maximum $Q(\lambda_2)$ undergoes the greatest changes at heating. The increase of temperature in model 1, *b* results in devastation of R'-centers. In the alternative model occupation of R'-levels should increase because the number of transitions there from the basic state increases. In experiment we observe the increase of longwave maximum $Q(\lambda_2)$.

C) The change in energy position of R'-levels should occur with temperature changes. At $T = 0$ the changes are not observed. With temperature raise the walls of energy well for holes widen in space of quasi-impulse. And the moment when two quantum wavelengths for holes are along between them comes. The excited state R' appears. In model 1, *b* this occurs at 170—190 K for cadmium sulphide [2].

The gap from the basic state (~1 eV) is rather big — see item VII. At the further temperature raise the walls of hole continue to wide. The energy $E_{R'}$ raises. For both models the heating should be accompanied by approach of energy for $E_{R'}$ to E_R.

Our temperature range 20—50 °C was very narrow to observed the mentioned process. But with changes in energy distances the probability to absorb phonons by bound holes changes exponentially. If the model 1b operates, as R'-levels remove from the top of valence band the probability of holes release from them decreases. The probability to absorb photons λ_2 should decrease too. Maximum $Q(\lambda_2)$ becomes shorter. If the gap $E_R — E_{R'}$ decreases in case of model 2, *b*, the greater number of phonons in Maxwell distribution provides the transition of equilibrium holes to R'-levels and their concentration there increases. And light is possible to transit the greater value of charge to free state. Maximum $Q(\lambda_2)$ raises.

Hence, the diagram of Fig. 2, *b* confirms experimentally.

So, the created model of thermal-optical transitions reduces the shortcomings I—IX of model 1, *b* and is confirmed by experimental data 1—7. The process of hole release from the basic state — through the excited one — to the valence band begins from transition with absorption $E_R \to E_{R'}$ of phonon with energy 0,2 eV and only then the excitation to free state $E_{R'} \to E_v$ at the expense photon energy hν = 0,9 eV. Band diagram of Fig. 2, *b* is realized.

Thus, proposed model of thermo-optical transitions proves to be true by the experimental data 1—7. The mechanism of holes release from the ground state through excited in the valence band includes first a transition with a phonon absorption $E_R \to E_{R'}$ at 0,2 eV energy, and only then excitation in the $E_{R'} \to E_v$ free state due to phonon energy $h\nu = 0,9$ eV. The zonal plot Fig. 2, *b* is realized.

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Abstract

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ОСОБЕННОСТИ ТЕРМО-ОПТИЧЕСКИХ ПЕРЕХОДОВ С ВОЗБУЖДЁННЫХ СОСТОЯНИЙ РЕКОМБИНАЦИОННЫХ ЦЕНТРОВ

Резюме

Созданная модель термооптических переходов подтверждается экспериментальными данными. Процесс освобождения дырок с основного состояния — через возбуждённое — в валентную зону включает в себя сначала переход с поглощением фонона $E_R \to E_{R'}$ с энергией 0,2 eV, и лишь затем возбуждение в свободное состояние $E_{R'} \to E_{v'}$ за счёт энергии фотона $h\nu = 0,9$ eV.

Проведены исследования эффекта инфракрасного гашения фототока для определения очерёдности оптико — термических переходов при освобождении дырок с *R*-центров.

Ключевые слова: эффект инфракрасного гашения, оптико-термические переходы, *R*-центр.

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ОСОБЛИВОСТІ ТЕРМО-ОПТИЧНИХ ПЕРЕХОДІВ ЗБУДЖЕНИХ СТАНІВ РЕКОМБІНАЦІНИХ ЦЕНТРІВ

Резюме

Розроблена модель термооптичних переходів підтверджена дослідним шляхом. Процес звільнення дірок з основного стану через збудження —у валентну зону складається спочатку з переходу з поглинанням фонону $E_R \to E_{R'}$ з енергією 0,2 eV, і потім збудження у вільний стан $E_{R'} \to E_{v'}$ за рахунок енергії фотона $h\nu = 0,9$ eV. Проведені дослідження ефекту інфрачервоного гасіння фотоструму для визначення послідовності оптико-термічних переходів при звільненні дірок з *R*-центрів.

Ключові слова: ефект інфра-червонного гасіння, оптико-термічні переходи, *R*-центр.