Semiconductor Physics, Quantum Electronics & Optoelectronics. 1999. V. 2, N 1. P. 42-46.

PACS 61.72.Ji, 61.72.Yx, 72.40.+w, 72.80.Ey, 78.55.Et

Electron-enhanced reactions responsible for photoluminescence spectrum change in II-VI compounds

N. E. Korsunskaya, I. V. Markevich, B. R. Dzhumaev, L. V. Borkovskaya, M. K. Sheinkman***

Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, Kyiv, 252028, Ukraine,
tel: (044) 265-72-34, fax: (044) 265-83-44, e-mail: kors@lumin.semicond.kiev.ua;
**tel: (044) 265-63-40, *Fax: (044) 265-63-40, *e-mail: moishe@photel.semicond.kiev.ua.*
***Turkmen Polytechnic Institute, Ashgabat, 744025, Turkmenistan*

Abstract. Electron-enhanced reactions in II-VI compounds are shown to be caused by the presence of some mobile defects which diffusion is not enhanced under excitation. At the same time, electron-enhanced diffusion can be imitated in these reactions due to carrier trapping by deep centers that do or even do not take part in the reaction. To elucidate the real defect reaction mechanism a detailed study is required in every case. For this purpose, a method of mobile defect detection and their diffusion characteristic direct investigation has been elaborated.

Keywords: electron-enhanced reactions; II-VI compounds; mobile defects.

Paper received 25.12.98; revised manuscript received 08.04.99; accepted for publication 19.04.99.

1. Introduction

Processes of two types, namely, dislocation multiplication and electronically enhanced point defect reactions are known to be responsible for II-VI compound light emitting device degradation. The processes connected with dislocation motion and multiplication are well investigated. At the same time, there is a little information about defect reactions in light emitting devices based on II-VI compound crystals and layers. This state of affairs may be due to the difficulty of required information extraction under finished device investigation. Such information can be obtained more easily under investigation of materials used for device preparation.

This report deals with mechanisms of point defect reactions in CdS, CdSe, CdSSe crystals which are used as working elements of pulsed electron-beam-pumped lasers [1]. A number of defect reactions resulting in some electric, photoelectric and optical characteristic changes were found by us in these crystals earlier [2]. These reactions were proved to be processes of rearrangement of pre-existed defects and were shown to be reversible [2]. The activation energies of reaction process, E_R, and initial state restoration one, E_I^{therm}, were found to be 0.15÷0.35 and 0.4÷1.2 eV ranges, respectively, the relation $E_R < E_I^{therm}$ being observed for each reaction [2].

As a rule, point defect rearrangements both in the presence and absence of excitation are supposed to be controlled by defect diffusion. So, the relation $E_R < E_I^{therm}$ is usually explained by reduction of defect diffusion activation energy under excitation (electron-enhanced diffusion) [3-5], partially, by phonon-kick mechanism [5]. In the latter case the equality $E_{eq} = E_{ex} + E_t$ takes place, where E_{ex} and E_{eq} are the defect rearrangement activation energies under excitation and equilibrium conditions, respectively, E_t is the energy depth of the defect that takes part in the reaction [5]. However, our investigations showed that the same equality can take place when excitation does not affect defect diffusion.

 © 1999, Institute of Semiconductor Physics, National Academy of Sciences of Ukraine

2. Results and discussion

Photoluminescence (PL), photocurrent (PC), thermally stimulated current (TSC) and EPR spectra were measured in CdS, CdSe and CdS_xSe_{1-x} crystals. PL was excited with 0.365 μm mercury lamp line. The results of reaction mechanism investigations for two different defect reactions are adduced below.

2.1. Reaction resulting in degradation of PL intensity and photosensitivity.

This reaction occurs in "pure" and Cu-doped CdS, CdSe crystals in 300÷400 K temperature range under illumination with visible light from the regions of photocurrent maxima. It results in dramatic decrease of crystal photosensitivity and extrinsic PL intensity [6]. After heating up to 450 K and subsequent cooling in the dark the initial state restores. At T < 300 K, when the reaction is "frozen", the sample characteristics can be investigated both in the initial state and after reaction carrying out. PL spectra at 80 K in these two states for CdS:Cu crystal are shown in Fig. 1.

It was found from TSC investigations that the density of shallow electron traps T1 ($E_1 = E_C$ - 0.03 eV) decreased and the density of deep electron traps T2 ($E_2 = E_C$- 0.9 eV) increased as a result of reaction (Fig. 2, curves 1,2). It was proved that T2 center appearance resulted from rearrangement of T1 centers, probably, due to their association [6]. As EPR investigations showed, T1 centers were hydrogenlike donors [7]. It was found that T2 destruction and T1 reappearance under heating in the dark occurred in fact simultaneously with T2 thermal ionization. The activation energies of both the reaction and initial state restoration were obtained from process rate temperature dependencies by the method described in [8]. These values were found to be equal to in 0.35 and 1.25 eV, respectively. Therefore, the equation $E_I^{therm} = E_R + E_2$ takes place.

Since the initial state restoration occurs simultaneously with T2 thermal ionization one may suppose that it is the latter which controls restoration process. To verify this supposition we tried to ionize T2 optically. For this purpose the sample after reaction carrying out had been irradiated with IR-light at 80 K and than TSC spectrum was measured. An effective ionization of T2 by λ = = 0.8÷1.1 μm IR light was observed. It was also found that such irradiation enhanced initial state restoration process and decreased its activation energy down to 0.35 eV. Therefore, initial state restoration process can be also the photo-enhanced one, moreover, its activation energy in this case E_I^{opt}, is equal to E_R.

One can see also that $E_I^{therm} = E_I^{opt} + E_2$, i.e. the equality $E_{eq} = E_{ex} + E_t$ is valid here. Nominally, such equality allows to assume that the phonon-kick mechanism [5] or the mechanism of diffusion enhancement caused by center transition into excited state [9] takes place in the process under consideration. However, proceeding from received results one can conclude that the investigated reaction as well as initial state restoration after T2 optical ionization is controlled by the T1-center thermal diffusion, while E_I^{therm} includes E_2 value. Let us show that in this case above mentioned equality really can be valid.

The kinetics of T2-center destruction is described by the system of equations:

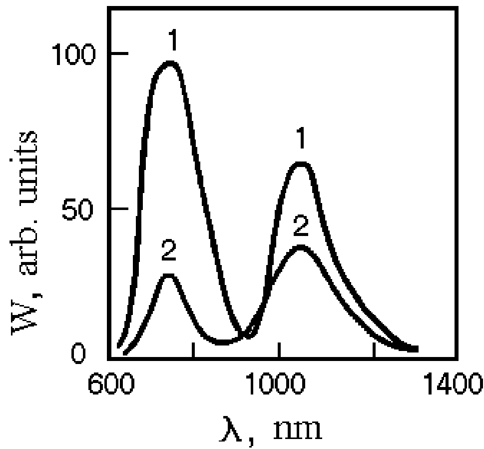

Fig. 1. Luminescence spectra of CdS:Cu crystal in initial state (1) and after reaction (2), T = 80 K.

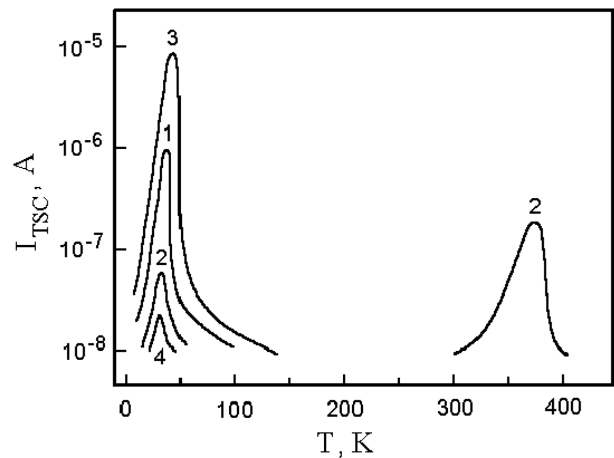

Fig. 2. TSC spectra of CdS:Cu crystal: (1) in the initial state; (2) after degradation reaction; (3,4) after electric field application at 350 K during 10 min, when the investigated region is the cathode (3) and the anode (4).

$$\frac{dN_2}{dt} = -Bp_2,$$

$$\frac{dp_2}{dt} = -A(N_2 - p_2) - Cp_2 - Bp_2,$$

where N_2 is the T2-center density, p_2 is the hole density on T2-centers, $B = B_0 e^{-E_{dif}/kT}$ is the probability of T2-center diffusional dissociation, E_{dif} is the T1 center diffusion activation energy, $A = vS\, N_C e^{-E_{T2}/kT}$ is the probability of thermal excitation of electrons from T2-centers to the *c*-band (v – thermal velocity of electron, S – cross-section of electron capture by T2-center, N_C – state density in the *c*-band), and $C = nvS$ is the probability of electron retrapping (n – free electron density).

Since reaching the generation-recombination equilibrium in the system is a much faster process than T2-center destruction, it may be supposed that n = const. The solution of this system of equations may be represented as

$$N_2 = C_1 e^{-t/\tau_1} + C_2 e^{-t/\tau_2},$$

where C_1, C_2 are integration constants, and

$$\frac{1}{t_{1,2}} = \frac{(A+B+C) \pm \sqrt{(A+B+C) - 4AB}}{2}.$$

The activation energy of T2-center destruction is determined by the slope of the straight line $\tau_{1,2}(1/T)$. Depending on the correlation of A, B and C, E_I may take different values from E_{dif} up to $E_2 + E_{dif}$.

If retrapping is available and the probability of empty T2-center destruction is much less than the probability of T2-center thermal ionization ($B << A$) in the temperature range where $p_2 << N_2$ and, therefore, $p_2 \sim A$, the concentration of dissociated centers ΔN_2 is proportional to $B \cdot p_2 \sim e^{-E_2/kT} \cdot e^{-E_{dif}/kT}$ and $E_I = E_2 + E_{dif}$.

Hence, phonon-kick mechanism [5] or excited state mechanism [9] can be imitated when a reaction under excitation is controlled by defect thermal diffusion. To elucidate the real defect reaction mechanism a method using the mobile defect drift in external electric field was elaborated [10]. It was shown that investigation of PC and PL characteristic changes in sample areas near electrodes after electric field ($E = 10^2 \div 10^3$ V/cm) application allows to detect mobile defects and to identify their nature [10,11]. Defect drift activation energy which is equal to defect diffusion activation energy was obtained from the temperature dependence of drift rate [10].

Application of electric field to investigated crystals at T = 350÷400 K was found to result in accumulation of T1 centers near the cathode (Fig. 2, curve 3), which was in accordance with their donor nature [7]. This effect was accompanied by the λ = 4869.5 Å bound exciton line intensity increase. This line is known to be caused by radiative annihilation of exciton bound to shallow donor Cd_i [11]. Thus, shallow donors that participate in reaction are Cd_i atoms. This donor diffusion activation energy, E_{dif}, was found to be independent on nonequilibrium carrier density (intensity of the light) and equal to 0.4 eV. Hence, $E_{dif} \approx E_R$, i.e., the reaction is really controlled by T1 thermal diffusion.

Defect rearrangement activation energy can also be influenced by carrier trapping at centers that do not take part in defect reaction at all. This effect takes place, for instance, in donor-acceptor pair (DAP) dissociation reaction which is considered below.

2.2. Photosensitizing reaction in CdS_xSe_{1-x} *crystals.*

As it was shown earlier [2], in CdS and CdS_xSe_{1-x} crystals dissociation of DAPs consisting of shallow donors (E_d = = E_C - 0.03 eV) and deep acceptors ($E_a = E_C$ - 1.2 eV) occurred under intrinsic band illumination in the 150÷300 K temperature range. The reaction results in the increase of PC and intensity of λ = 1.03 µm PL band which is due to radiative recombination of free electrons at the deep acceptor. Since this acceptor is the center of photosensitivity (*r*-center [12]), the dissociation reaction leads to the increase of PC both in the intrinsic maximum I_{ph}^{int} and in the extrinsic one I_{ph}^{ex} (Fig. 3, curves 1,2). The latter is due to excitation of electrons from *r*-centers to the *c*-band [12]. Heating the sample to 400 K

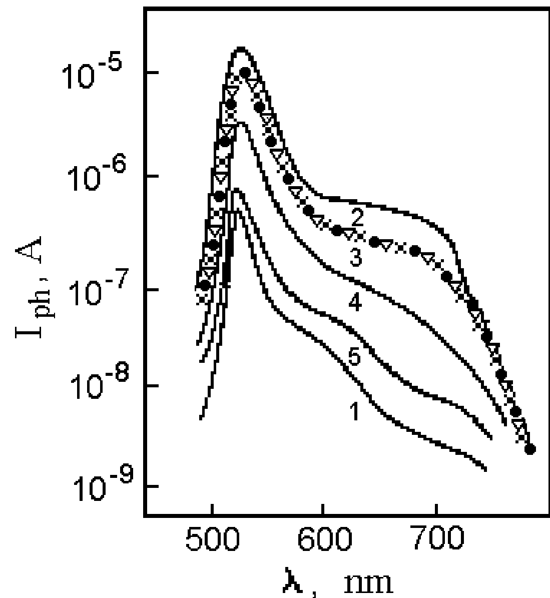

Fig. 3. Photocurrent spectra of type 2 crystal at 80 K after: cooling in the dark from 400 K (1); cooling under intrinsic band illumination from 300 K (2) and followed by heating in the dark (3) to 220 (x), 230 (•), 235 (∇) and 280 K(5); cooling under intrinsic band illumination from 300 K and irradiation with IR-light at 80 K followed by heating in the dark to 230 K (4).

and subsequent cooling in the dark results in restoration of the initial state. In order to obtain the activation energies of the dissociation and association processes both the kinetics of r-center density (N_r) increase under illumination and N_r decrease in the dark were investigated at different T. N_r was estimated from I_{ph}^{ex} value.

Two types of CdS_xSe_{1-x} crystals were found. For both types DAP dissociation activation energy was shown to be equal to 0.17 eV. In crystals with $0 < x \le 0.5$ (type 1) DAP association in the dark was found to occur in the same temperature range (200 ÷ 230 K) as their dissociation under illumination.

At the same time, in crystals with $0.5 < x \le 1$ (type 2), heating to 200 ÷ 235 K resulted in a very small N_r decrease and only near 280 K did an abrupt photocurrent drop take place (Fig. 3). The curves $\Delta I_{ph}^{ex}/I_{ph}^{ex}(\max) = f(\Delta t)$ (Δt is time interval that the sample was hold for in dark) proved to be exponential for crystals of both types and therefore, the investigated process was a reaction of the first order. From the slope of $\ln 1/\tau_a = f(1/T)$ plot (τ_a was time constant) the activation energies of the association process $E_{eq} = 0.17 \pm 0.05$ eV for type 1 crystals and $E_{eq} \sim 0.8$ eV for type 2 crystals were obtained (Fig. 4). So, in type 1 crystals the association activation energy coincides with the activation energy of dissociation, i.e. $E_{eq} = E_{ex}$ in this case. This means, to all appearances, that both processes are controlled by diffusion of the same defect, with a diffusion activation energy that is not affected by excitation.

In type 2 crystals the relation $E_{eq} > E_{ex}$ holds. The TSC investigation showed that in type 2 crystals (unlike in type 1 ones) deep electron traps were present, which caused a TSC peak at 300 K. The trap ionization energy $E_t = 0.8$ eV obtained from the TSC curve coincides rather well with the DAP association energy (Fig. 4). It may be supposed, therefore, that the DAP association kinetics in type 2 crystals is controlled by a trap emptying process. To verify this supposition, the following experiment was carried out. A sample of type 2 crystal was first cooled from 300 to 80 K under intrinsic illumination. The intrinsic light was then switched off and the sample was illuminated with IR light to ionize deep traps and consequently to recharge the r-centers. Emptying traps was controlled by TSC measurements. It was found that after IR illumination heating to 220 ÷ 230 K resulted in a considerable decrease of N_r (Fig. 3). At the same time IR light did not affect the association process in type 1 crystals.

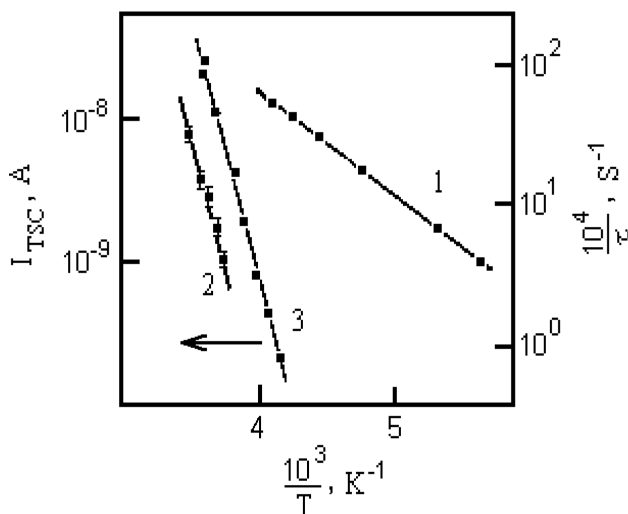

Fig. 4. The association reaction kinetics for type 1 crystal (1) and type 2 crystal (2). TSC for type 2 crystal in the 240÷280 K range (3).

So, illumination-enhanced diffusion does not take place in the investigated process. The relation $E_{eq} > E_{ex}$ in this case occurs because the acceptor can recharge only after deep electron trap ionization. In principle, donor itself can play the role of trapping center. Let us show that in this case equality $E_{eq} = E_{ex} + E_{dif}$ can take place.

A set of equations which describes the association reaction, i.e., the process of the decrease of isolated donor density, is:

$$\frac{dN_d}{dt} = -BN_d^+N_a^- ,$$

$$\frac{dN_d^+}{dt} = -BN_d^+N_a^- + A(N_d - N_d^+) - CN_d^+ ,$$

$$\frac{dN_d}{dt} = -\frac{dN_{DAP}}{dt} ,$$

where $A = C_d N_C e^{-E_d/kT}$, $B = 4\pi D r_0 N_a^-$, $C = nC_d$, N_d, N_a and N_{DAP} is the donor, acceptor and DAP density, respectively, D is the diffusion coefficient of the mobile component, $(N_d - N_d^+)$ the density of donors filled with electrons, C_d the coefficient of electron capture by the donor, N_C is the density of states in the c-band, n – the free electron density and r_0 is the largest distance between donor and acceptor centers at which association is still possible.

Consideration similar to that carried out for degradation reaction shows that when strong retrapping is present and $C >> A$ the equation $E_{eq} = E_d + E_{dif}$ will take place.

3. Conclusions

Carrier trapping is shown to be able to influence essentially on defect reaction in semiconductors. When deep traps are present, the kinetics of defect reaction can be controlled by thermal ionization of these traps. In this case illumination (injection) enhanced diffusion, in particular, by the phonon-kick mechanism may be imitated. This is the case which is proved to take place in CdS and CdSSe crystals. Defect drift in an external electric field is proposed as an effective method for defect reaction mechanism study.

References

1. O. V. Bogdankevich, N.N. Kostin, E.M. Krasavina, I.V. Krukova, E.V. Markov, E.V. Matveenko, V.A. Teplitsky, *Izv. Akad. Nauk SSSR, Neorg. Mater*. **23(10**), pp. 1618-1622 (1987).
2. M. K. Sheinkman, N.E. Korsunskaya, I.V. Markevich, T.V. Torchinskaya, The recharge-enhanced transformations of donor-aceptor pairs and clusters in CdS // *J. Phys. Chem. Sol.* **43**(5), pp. 475-479 (1982).
3. D. V. Lang, Recombination-enhanced Reactions in Semiconductors // *Annu.Rev.Matt.Sci*., Palo Alto, California **12**, pp. 377-400 (1972).
4. M.K. Sheinkman and L.C.Kimerling, The mechanism of electronically enhanced defect reactions in semiconductors, in *Defect Control in Semiconductors*, eds. K.Sumino, Elsevier Science Publishers B.V., North-Holland (1990).
5. J. D. Weeks, J. C. Tully, L. C. Kimerling, Theory of Recombination-enhanced Defect Reactions in Semiconductors // *Phys.Rev.* **B12**(8), pp. 3286-3292 (1975).
6. N. E. Korsunskaya, I. V. Markevich, T. V. Torchinskaya, M. K. Sheinkman, Photosensitivity Degradation Mechanism in CdS:Cu Single Crystals // *Phys. stat. sol. (a)* **60**(1), pp. 565-572 (1980).
7. N. P. Baran, B. R. Dzhymayev, N. E. Korsunskaya, I. V. Markevich, L.Yu. Khomenkova, E.P.Shulga, Investigation of EPR spectra of shallow donors responsible for electronically enhanced defect reactions in CdS // *Fiz. Tverd. Tela* **38**(6), pp. 1735-1741 (1996).
8. N. S. Koparanova, A. Drangazhova, Thermal and Optical Restoraiton of Photoelectric Sensitivity of CdS Single Crystals after Optical Degradation // *Compt. Rendus de l'Academie Bulg. Sci*., **30**(7), pp. 989-992 (1977).
9. M. K. Sheinkman, New explanation of recombination-enhanced phenomena in semiconductors // *Pisma v Jurn. Expe. i Tech. Fiz.* **38**(6), pp. 278-279 (1983).
10. N. E. Korsunskaya, I. V. Markevich, T. V. Torchinskaya, M. K. Sheinkman, Investigation of defect drift in electric field in CdS:Li crystals // *Fiz. Tekn. Poluprov.* **13**(3), pp. 435-440 (1979).
11. N. E. Korsunskaya, I. V.Markevich, T. V.Torchinskaya, M. K. Sheinkman, Electrodiffusion of shallow donors in CdS crystals // *J. Phys. p.* **13**(4), pp. 1275-1278 (1980).
12. V. E. Lashkarev, A. V. Lyubchenko and M. K. Sheinkman, *Neravnovesnye Procesy v Fotoprovodnikakh*, Naukova dumka, Kiev (1981).