A simple model of the trap–assisted recombination with the excitonic Auger mechanism

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Abstract. We present a simple model of the trap–assisted recombination combined with the excitonic Auger mechanism. It has been shown that only six independent transitions of electrons and holes should be taken into account to describe a combination of the Shockley–Read–Hall (SRH) recombination with this excitonic process. This is in opposition to a well known model of the SRH mechanism with the free carriers Auger effect via deep states, where eight separated transitions take place. The derived equation for the effective recombination rate can be useful for modeling the excitonic processes in semiconductors, especially in photovoltaic and optoelectronic devices.

PACS. 71.35.-y Excitons and related phenomena – 72.20.Jv Charge carriers: generation, recombination, lifetime, and trapping

1 Introduction

Currently, a great interest in optoelectronic devices is observed due to their utility in a daily life. Also, the prediction of a crisis in the area of conventional fuels turns attention toward solar cells. The recombination of charge carriers decreases a value of photocurrent in such devices, so it is obvious that a detailed understanding of this process is crucial for further progress of optoelectronics and photovoltaics. Impurities and defects create deep trap states which are located in the middle of a band gap. They can serve as recombination centers for charge carriers. A typical mechanism of the recombination process via deep states is called the trap–assisted recombination or the Shockley–Read–Hall (SRH) recombination [1,2]. This process often takes place in semiconductors. One can formulate a question about additional effects associated with deep defect states which influence on this type of recombination.

Excitonic phenomena can occur both in inorganic and organic materials used in optoelectronic and photovoltaic devices. In general, a role of excitons in inorganic semiconductors is dominant mainly for lower temperatures. However, there has been recently shown that excitons can be observed at room temperatures in a group of 2–dimensional inorganic materials, like MoS_2 and WSe_2 [3].

One of the possible excitonic effects is the Auger excitonic mechanism proposed by Hangleiter [4] to explain experimental results of a nonradiative recombination in silicon. In this process, a free exciton interacts with a deep impurity level causing that an electron, which is a part of the exciton, is captured by the impurity, whereas a hole from this exciton is excited to the valence band. Similarly, we can consider the hole capture by the impurity level from an exciton with a simultaneous transition of an electron between this exciton and the conduction band. In the next paper, Hangleiter has formulated a quantum mechanical description of this mechanism [5]. Recently, a role of the excitonic Auger (EA) effect has been discussed to explain the luminescence quantum yield in the silicon at high concentration of charge carriers [6,7]. It should be noted that the exciton annihilation by deep defects has been also observed in other materials, like $GaAs/Al_{0.3}Ga_{0.7}As$ quantum wells [8] and in monolayer metal dichalcogenides [9] .

The aim of this paper is to combine a trap–assisted recombination with the excitonic Auger mechanism. We will present a derivation of the recombination rate for a coexistence of these two nonradiative processes. Such a model can be useful to simulate excitonic processes in semiconductors.

2 Model

For the SRH recombination mechanism, four transitions for electrons and holes should be taken into account (E_{cap}, E_{em}, H_{cap}, H_{em}) [1,2]; see Fig. 1.

The net for a capture of electrons from the conduction band is given by

$$E_{cap} = C_n n N_t (1 - f_t), \tag{1}$$

where C_n is a capture coefficient for electrons from the conduction band, n represents a concentration of electrons in the conduction band, N_t is a concentration of trap states and f_t denotes the occupancy fraction of electrons.

The emission rate for electrons may be written in the form

$$E_{em} = C_n n_1 N_t f_t. \tag{2}$$

Here, the concentration n_1 can be defined as

$$n_1 = N_c \exp\left(-\frac{E_c - E_t}{kT}\right), \tag{3}$$

where N_c is an effective density of states in the conduction band, E_c represents an energy of the bottom level of the conduction band, E_t denotes an energy level of the trap state located in the midgap, the parameter k is the Boltzmann constant and T represents a temperature.

The net for a capture of holes from the valence band may be written as

$$H_{cap} = C_p p N_t f_t, \tag{4}$$

where C_p is a capture coefficient for holes from the valence band and p represents a concentration of holes in the valence band.

The emission rate for holes is given by

$$H_{em} = C_p p_1 N_t (1 - f_t). \tag{5}$$

The concentration p_1 can be defined as

$$p_1 = N_v \exp\left(-\frac{E_t - E_v}{kT}\right), \tag{6}$$

where N_v is an effective density of states in the valence band and E_v represents an energy of the top level of the valence band.

In the excitonic Auger mechanism [4], we should consider four additional transitions for electrons and holes (E_{cap}^{EA}, E_{em}^{EA}, H_{cap}^{EA}, H_{em}^{EA}); see Fig. 1. Here, E_{cap}^{EA} represents the rate of electrons capture from excitons via deep states, E_{em}^{EA} is the emission rate of electrons from excitons to the conduction band, H_{cap}^{EA} is the rate of holes capture from excitons via deep states and H_{em}^{EA} denotes the emission rate of holes from excitons to the valence band. However, when an electron is captured from an exciton (E_{cap}^{EA}), it causes a simultaneous transfer of a hole from this exciton to the valence band (H_{em}^{EA}). We can see that these two transitions are not independent and should be treated as the same process ($E_{cap}^{EA} = H_{em}^{EA}$). Similarly, the capture of a hole from the exciton occurs together with an electron transfer from this exciton to the conduction band ($H_{cap}^{EA} = E_{em}^{EA}$). It leads to the conclusion that only six independent transitions should be considered to describe a combination of the trap assisted recombination with the excitonic Auger mechanism. Therefore this new model is different than a well known theory of the SRH recombination with the free carriers Auger process via deep states, where eight separated transitions take place [10].

The rate for a capture of electrons from excitons can be defined as

$$E_{cap}^{EA} = A_n X N_t (1 - f_t) = H_{em}^{EA}, \tag{7}$$

where A_n is a capture coefficient for electrons from excitons and X denotes a concentration of excitons.

The rate for a capture of holes from excitons is given by

$$H_{cap}^{EA} = A_p X N_t f_t = E_{em}^{EA}, \tag{8}$$

where A_p represents a capture coefficient for holes from excitons.

Excitons are created under illumination of a material. Therefore, we cannot consider the case of a thermal equilibrium for this model. However, it is possible to derive the effective recombination rate via deep states for steady state conditions. In order to obtain this result, we should start from kinetic equations which describe all electronic and excitonic processes.

For the case, when a light generates electrons and holes via the band–band transition, a set of kinetic equations to describe a time (t) evolution of electrons, holes and excitons can be expressed as

$$\frac{\partial n}{\partial t} = G_{np} - F_X + D_X - E_{cap} + E_{em} + E_{em}^{EA} - R_B - R_A, \tag{9}$$

$$\frac{\partial p}{\partial t} = G_{np} - F_X + D_X - H_{cap} + H_{em} + H_{em}^{EA} - R_B - R_A \tag{10}$$

and

$$\frac{\partial X}{\partial t} = F_X - D_X - R_X - E_{cap}^{EA} - H_{cap}^{EA}, \tag{11}$$

where G_{np} is a generation rate of electrons and holes, D_X represents a dissociation rate of excitons, F_X is a formation rate of excitons from electrons and holes, R_X denotes a monomolecular recombination of excitons and R_B is a bimolecular recombination rate. The parameter R_A represents a trimolecular recombination associated with a typical Auger process, where an electron jumps to the valence band and recombines with a hole while an excess of energy is transfered to other carrier.

For the case of a resonant excitation (a below gap excitation), the light first creates excitons which can dissociate into separated charge carriers. Therefore, a set of kinetic equations looks as follows

$$\frac{\partial n}{\partial t} = D_X - E_{cap} + E_{em} + E_{em}^{EA} - R_B - R_A, \tag{12}$$

$$\frac{\partial p}{\partial t} = D_X - H_{cap} + H_{em} + H_{em}^{EA} - R_B - R_A \tag{13}$$

and

$$\frac{\partial X}{\partial t} = G_X - D_X - R_X - E_{cap}^{EA} - H_{cap}^{EA}, \tag{14}$$

where G_X is a generation rate of excitons.

Considering steady state conditions, we obtain the same formula

$$U = E_{cap} - E_{em} - E_{em}^{EA} = H_{cap} - H_{em} - H_{em}^{EA} \tag{15}$$

independently from both sets of Eqs. (9-11) or (12-14). The quantity U represents the effective recombination rate via deep states for electrons and holes. We can see that only six electronic transitions participate in the considered model, what has been discussed earlier. It should be noted that other recombination rates R_B and R_A are not included in the rate U, because these recombination mechanisms do not need deep states.

Thus, we can calculate the occupancy fraction for electrons

$$f_t = \frac{C_n n + C_p p_1 + A_n X}{C_n(n + n_1) + C_p(p + p_1) + (A_n + A_p)X} \tag{16}$$

and for holes

$$1 - f_t = \frac{C_n n_1 + C_p p + A_p X}{C_n(n + n_1) + C_p(p + p_1) + (A_n + A_p)X}. \tag{17}$$

Knowing that, we obtain the effective rate for the exciton–enhanced recombination via deep states in the form

$$U = \frac{n^* p^* - n_{int}^2}{\tau_p^*(n^* + n_1) + \tau_n^*(p^* + p_1)}, \tag{18}$$

which is a central point of this paper. Here, the effective lifetimes are given by

$$\tau_n^* = \frac{1}{N_t} \frac{1}{C_n + \frac{X}{n_1}A_p}, \tag{19}$$

$$\tau_p^* = \frac{1}{N_t} \frac{1}{C_p + \frac{X}{p_1}A_n} \tag{20}$$

and the effective concentrations are equal to

$$n^* = n\frac{C_n}{C_n + \frac{X}{n_1}A_p}, \tag{21}$$

$$p^* = p\frac{C_p}{C_p + \frac{X}{p_1}A_n}. \tag{22}$$

The parameter n_{int} represents an intrinsic concentration of charge carriers which can be written as

$$n_{int} = (N_c N_v)^{1/2} \exp\left(-\frac{E_g}{2kT}\right), \tag{23}$$

where E_g is an energy of band gap.

It is easy to show that in the absence of excitons ($X = 0$) or for a very low probability of the excitonic Auger mechanism ($A_n \approx 0$ and $A_p \approx 0$), the Eq. (18) converts into the rate for a typical SRH recombination.

$$U_{SRH} = \frac{np - n_{int}^2}{\tau_p(n + n_1) + \tau_n(p + p_1)}, \tag{24}$$

where lifetimes τ_n and τ_p are equal to $\tau_n = (N_t C_n)^{-1}$ and $\tau_p = (N_t C_p)^{-1}$, respectively.

3 Summary

We have derived the effective recombination rate via deep states for the model of a trap–assisted recombination with the excitonic Auger mechanism. The analysis has shown that only six independent electronic transitions are needed to describe the Shockley–Read–Hall mechanism with this excitonic process. This result is different than for a model of the SRH recombination with the free carriers Auger effect via deep states, where eight electrons and holes transitions occur. The determined expression can be applied in the studies of excitonic processes in semiconductors.

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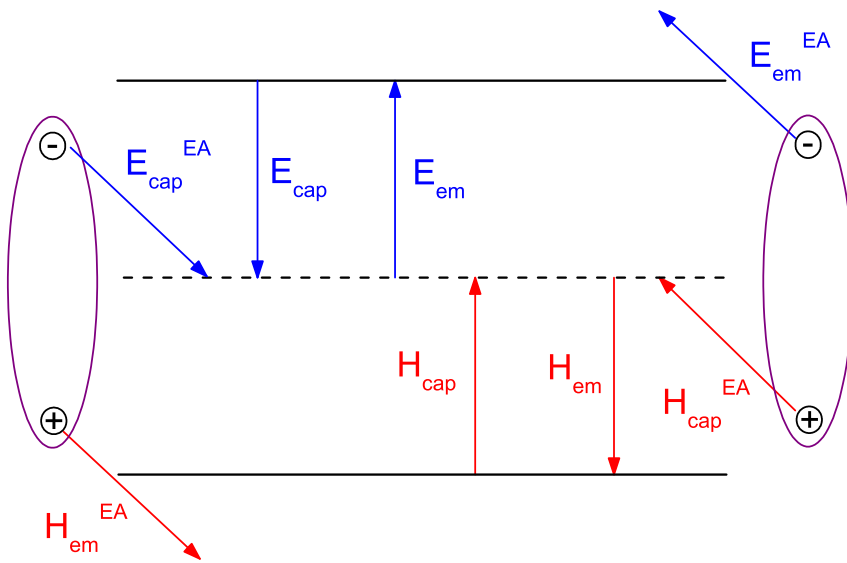10. J.G. Fossum, R.P. Mertens, D.S. Lee, J.F. Nijs, Solid State Electron. **26**, 569 (1983).

Fig. 1. The diagram of electron and hole transitions for the trap–assisted recombination and for the excitonic Auger mechanism.