

Photon energy shift in the luminescence of highly excited $\text{Ga}_{1-x}\text{Al}_x\text{As:Si}$ due to Auger effect involvement

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A new bonding state in highly doped and almost compensated semiconductors, the {donor-acceptor/acceptor2}-AUGER molecule, and its existence region is determined in silicon-doped $\text{Ga}_{1-x}\text{Al}_x\text{As}$ by electron-beam excited luminescence measurements at low temperature. The main peak position and luminescence intensity of the donor-acceptor recombination channel turns out to be affected in a characteristic manner by the existence of AUGER molecules at high excitation levels. Carrier transitions via two recombination channels can be generated, which involve the donor-acceptor pair transition at 1.8 eV, and a free-to-bound transition at 2.1 eV. We discuss luminescence data of $\text{Ga}_{0.2}\text{Al}_{0.8}\text{As}$, doped with $3 \cdot 10^{18} \text{ cm}^{-3}$ silicon atoms. Sample excitation is carried out by means of a focused electron beam inside a nitrogen cryostat. Experimental results are analyzed by use of a set of rate equations, incorporating a particular bonding state and an AUGER process. Good agreement between theoretical and experimental results is established.

Keywords: Luminescence measurements; Silicon-doped; Electron beam; AUGER molecule

1. Introduction

The radiative recombination of semiconductors is one of several ways for excess charge carriers to regain their equilibrium state after having experienced an external excitation to higher energetic levels. Between many others is the donor-acceptor (DA) radiative transition frequently found in the luminescence of doped semiconductors [1-3]. Its particular dependence of the luminescence intensity and photon energy on crystal properties and the external excitation level makes it a still widely studied phenomenon [4-7]. A quenching of the DA luminescence, and at the same time an enhancement of the free-to-bound (e.g. donor-to-valence band) luminescence has been observed, when an electric field was applied to the sample during luminescence measurements [8-11]. The involvement of AUGER transitions is discussed, when emission bands are quenched [12, 13]. A particular situation is created, when a highly doped and almost compensated semiconductor is excited to an extent, that close to all existing donor-acceptor (*da*) pairs are involved in the recombination process. Then, a new type of bound state may happen, which is formed of a close *da*-pair and a neighboring second donor or acceptor. The de-excitation behavior of such a bound state resembles characteristics known from AUGER transitions, for this constellation is called an AUGER molecule. The *da*-pair recombination, on the other hand, provides a means to dismantle the existence of AUGER molecules by virtue of the common intensity saturation and peak energy behavior of the main emission band. We have carried out a study of the involvement of an active AUGER molecule, situated in a semiconductor host, in the radiative recombination process of two competing recombination channels. As an interesting result we find a red-to-green color shift of the integral luminescence radiation, when the external excitation density is increased to higher levels.

2. Theoretical consideration

We consider an AUGER molecule in the here discussed context is a bound state between three interacting impurity atoms (d_1, a_1, a_2) within a crystalline semiconductor host, as shown in the following Figure 1(a). In the present case the acceptor of a close pair, formed of donor d_1 and acceptor a_1 , separated by a distance R_1 from each other, is situated near the acceptor of a distant pair (R_2), formed of donor d_2 and acceptor a_2 . The separation distance R_3 between the two acceptors is an important measure for the formation of the AUGER molecule. It is clear, that only highly doped (n-type in the discussed case) and almost compensated semiconductors provide for such a situation. The expected relaxation processes after an external excitation are seen in Figure 1(b). Given a relative closeness of a_1 and a_2 , the otherwise radiative transition P_{DAP} between d_1 and a_1 is quenched due to a non-radiative AUGER transition $d_1a_1a_2$. As a consequence, an energetic hole is pushed into the VB, which after thermalization allows a transition P_{FB} between the AUGER-liberated donor d_2 of the second pair d_2a_2 , and the AUGER-freed hole from a_2 .

In response to external excitation, donor-acceptor pairs (DAP's) with large pair separation are occupied first due to their large capture cross section $\sigma \sim R^2$. At a low external excitation rate, only common DAP spectra are observed. There exist particular conditions of the pair distribution, and a situation can be build, where a distant and a close pair are situated at a separation R_3 such, that once occupied, both pairs interact with each other. Indeed, at high excitation intensities, ever closer pairs are occupied, providing for the formation of a molecule consisting of three components as shown in Figure 1. Such a *daa*-excitation represents an AUGER molecule with a strongly increased probability of a three-body collision, involving one electron and two holes.

No net photon emission occurs, as the energy released by

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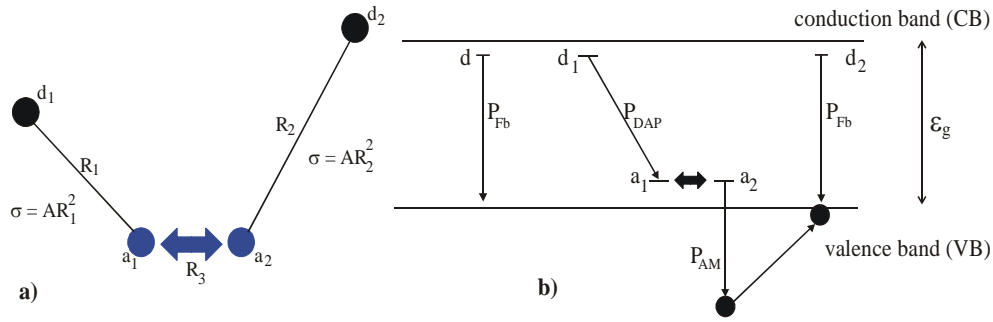


Figure 1. (a): The donor-acceptor pairs (DAP's) d_1a_1 and d_2a_2 are separated by a distance R_3 ; (b): Radiative recombination transitions P_{DAP} and P_{Fb} , and non-radiative AUGER transition P_{AM} .

the recombination of the short living donor-acceptor molecule of close separation is immediately absorbed by the hole of the longer living distant pair, which is excited deep into the valence band and then dissipates this energy by emitting phonons and partly heating up the hole population. This effect would be difficult to be proven by its own, though. Nevertheless the *daa*-process leaves an occupied donor of the distant pair behind, as well as an additional hole in the valence band. An additional donor-to-valence band transition is likely to happen, with the consequence of a competing intensity between the three recombination channels, that is the common donor-acceptor pair (DAP), the AUGER molecule (AM), and the donor-to-valence band (Fb) transition. The recombination intensities are evaluated by the following rate equations:

$$R_{DAP} = B_{DAP} a_0 d_0, \quad a_0 d_0 \text{ concentration of occupied DAP's} \quad (1)$$

$$R_{Fb} = B_{Fb} \cdot d_0 \cdot p, \quad d_0 \text{ concentration of occupied donors} \quad (2)$$

$$R_{AM} = X \cdot a_0^2 \cdot d_0, \quad (3)$$

X is the collision probability between charge carriers on d_1 , a_1 , and a_2 , which is a function of the separation distance R_3 in the AUGER molecule, and thus also a function of the external excitation density due to the occupation probability of the DA pairs. In order to determine a_0 and d_0

the following time independent balance equations are considered:

$$\frac{d(a_0)}{dt} = 0 = pT_A(A - a_0) - Xa_0^2d_0 - B_{DAP}a_0d_0 - I_Aa_0 \quad (4)$$

$$\frac{d(d_0)}{dt} = 0 = nT_d(D - d_0) - B_{DAP}a_0d_0 - B_{Fb}d_0p - I_Dd_0 \quad (5)$$

with $T_A = v_h \cdot \sigma_A$ - acceptor-capture coefficient, $T_D = v_e \cdot \sigma_D$ - donor capture coefficient, v - thermal carrier velocity, σ - capture cross section, n - excess electron concentration in the CB, p - excess hole concentration in the VB, D - concentration of donors in the host, A - concentration of acceptors in the host, I_D - thermal re-emission probability of neutral donors, I_A - thermal re-emission probability of neutral acceptors. The formation and participation of AUGER-molecules in the recombination process is clearly visible in the down-swing of the net radiative recombination intensity in figure 2. This defines the existence region of AUGER molecules.

3. Experimental results and discussion

A single crystalline $Ga_{1-x}Al_xAs$ host ($x = 0.8$) was doped almost to compensation with silicon. Due to its amphoteric behavior, silicon forms both donors with $\epsilon_D = 54$ meV, and deep acceptors with $\epsilon_A \sim 200$ meV. The doping concentrations were determined to $D = 2 \cdot 10^{18} \text{ cm}^{-3}$ and A

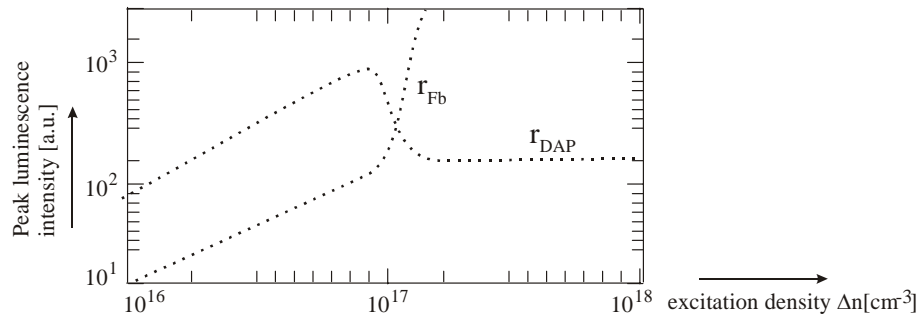


Figure 2. Calculated peak luminescence intensity under consideration of an AUGER annihilation process at high external excitation levels ($A = 10^{18} \text{ cm}^{-3}$, $D = 2 \cdot 10^{18} \text{ cm}^{-3}$, $X_0 = 4 \cdot 10^{-29} \text{ cm}^6 \cdot \text{s}^{-1}$, $\Delta n_i = 10^{16} \text{ cm}^{-3}$, $B_{Fb} = 10^9 \text{ cm}^3 \cdot \text{s}^{-1}$, $T_D = 10^8 \text{ cm}^3 \cdot \text{s}^{-1}$, $T_A = 10^6 \text{ cm}^3 \cdot \text{s}^{-1}$, $B_{DAP} = 10^{11} \text{ cm}^3 \cdot \text{s}^{-1}$).

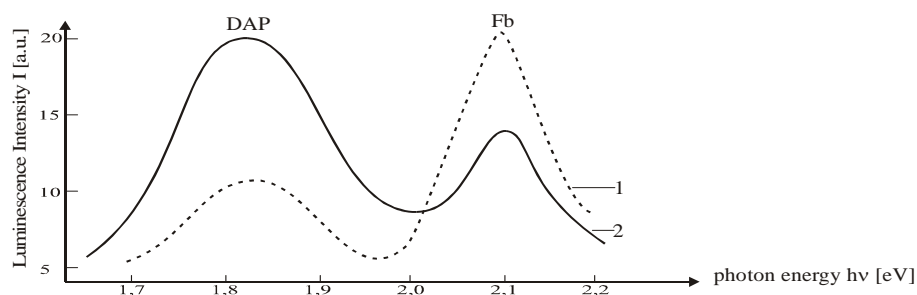


Figure 3: Cathodoluminescence spectrum of $\text{Ga}_{0.2}\text{Al}_{0.8}\text{As} : \text{Si}$ obtained with two different electron beam excitation currents: (1) $1 \cdot 10^3 \mu\text{A}$; (2) $1 \cdot 10^2 \mu\text{A}$.

$= 1 \cdot 10^{18} \text{ cm}^{-3}$, respectively. 30 keV cathodoluminescence of the samples is excited in a liquid nitrogen cryostat [14]. Common lock-in technique, a cooled photoelectron multiplier, and a Zeiss monochromator SPM-2 are applied for spectra recording. The concentration of excited electrons and holes in the host was controlled by the current of the 30 keV primary electron beam. Donor-to-acceptor transitions are the dominant radiative recombination process and occur already at low excitation levels. With increasing excitation density, an additional transition, identified as donor-to-valence band (Fb) channel emerges. The radiative DAM transition intensity diminishes, while the Fb transition intensity increases super-proportional at the highest excitation levels chosen. The luminescence spectra for two different excitation levels are shown in the Figure 3. In the *daa*-AUGER molecule region, for any two donor-acceptor pairs, bound into the AUGER molecule and taken out of the radiative DAM-transition channel, one additional excess hole appears in the valence band, and one additional neutral donor (see Figure 1b) participates in the Fb-recombination channel instead of the DAM-channel. This explains the intensity behavior of the two involved luminescence bands, which at the same time translates into a color change of the luminescence corresponding to the photon energies of the DAM- and Fb-transitions separated by over 200 meV.

4. Conclusions

In the *daa*-AUGER molecule region, for any two donor-acceptor pairs, bound into the AUGER molecule and taken out of the radiative DAP-transition channel, one additional excess hole appears in the valence band, and one additional

neutral donor (see Figure 1b) participates in the Fb-recombination channel instead of the DAM-channel. This explains the intensity shift between the two involved luminescence bands, which at the same time translates into a red-to-green color change of the integral emission corresponding to the peak photon energies of the DAP- and Fb-transitions, separated by more than 200 meV.

5. References

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