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Transient excitation behavior of a donor–acceptor–acceptor Auger molecule in a semiconductor host

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Abstract. Under the particular situation of highly doped and almost compensated semiconductors, a new kind of bound state happens at high external excitation levels, which is formed of a close donor–acceptor molecule and a neighboring second donor or acceptor. The de-excitation behavior of such a bound state resembles characteristics known from Auger transitions and for this reason it is called an Auger molecule. The existence region of Auger molecules is determined in silicon-doped $Ga_{1-x}Al_xAs$ by electron-beam excited luminescence measurements at low temperature. The main peak position and the luminescence intensity of the donor–acceptor recombination channel turn out to be affected in a characteristic manner by the existence of Auger molecules at high excitation levels. An analysis of corresponding rate coefficients for the reproduction of experimental results is also presented.

Key words: $Ga_{1-x}Al_xAs$ semiconductor – Cathodoluminescence – Auger molecule – Nonradiative transitions

1 Introduction

Donor and acceptor ions embedded in a crystalline solid can form bound states and act as stationary molecules. Given the effective Bohr radius of the donor electron and the acceptor hole in a semiconductor with dielectric constant κ, which reaches over several interatomic spacings of the crystal, donor–acceptor pair bonding is established even at rather large separation distances between the constituent ions.

The donor–acceptor radiative transition is frequently found in the luminescence of semiconductors [1–3]. The particular dependence of the luminescence intensity and the photon energy on crystal properties and the external excitation level makes it a still widely studied phenomenon [3–7]. Quenching of the donor–acceptor luminescence, and at the same time an enhancement of the free-to-bound (e.g., donor-to-valence-band) (Fb) luminescence was observed, when an electric field was applied to a sample during luminescence measurements [8–11]. The involvement of Auger transitions is discussed, when emission bands are quenched or even missing, which otherwise should be present [12, 13].

Under the particular situation of highly doped and almost compensated semiconductors, a new kind of bound state which is formed from a close donor–acceptor molecule (DAM) and a neighboring second donor or acceptor may happen at high excitation levels. The de-excitation behavior of such a bound state resembles characteristics known from Auger transitions and for this reason it is called an Auger molecule (AM). A three-body or Auger-type recombination is not unlikely to happen in direct-energy-gap semiconductors, i.e., an electron and a hole recombine and donate the annihilation energy to a third particle, either a hole or an electron. The consequence is quenching of the radiative recombination efficiency of the first transition, often not simple to detect and to relate to this kind of nonradiative process. The donor–acceptor pair recombination, on the other hand, provides a means to discount the existence of AMs by virtue of the common intensity saturation and peak energy behavior of the main emission band.

We present a study of donor–acceptor–acceptor (DAA) AMs in a direct-gap semiconductor host. Their existence and transient bonding state is proven by electron-beam excited luminescence measurements.

2 The DAA AM

An AM in the context discussed here is a bound state between three interacting impurity atoms (d_1, a_1, a_2) within a crystalline semiconductor host, as shown in Fig. 1a. The real-space arrangement of DAMs on substitution sites of the host lattice is demonstrated in the inset of this figure. 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

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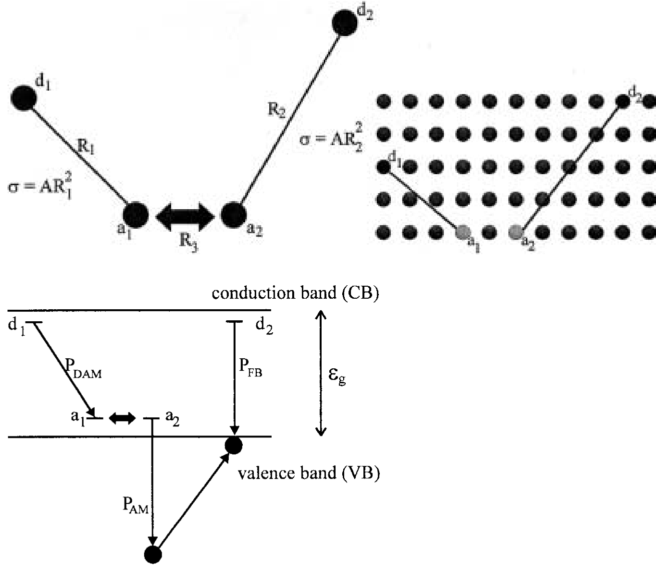

Fig. 1. **a** The donor–acceptor molecules (*DAMs*) d_1a_1 and d_2a_2 are separated by a distance R_3 in the crystal lattice, shown in the *inset* as a real-space arrangement on substitution sites of the crystal. R_1 and R_2 are donor–acceptor pair separation distances. The capture cross sections of the single DAM is proportional to its separation distance, R. **b** Radiative recombination transitions, I_{DAM} and I_{Fb}, and nonradiative Auger transition, P_{AM}

the two acceptors is an important measure for the formation of the AM. It is clear that only highly doped (n-type in the case discussed) and almost compensated semiconductors provide for such a situation. The expected relaxation processes after external excitation are seen in Fig. 1b. Given the relative closeness of a_1 and a_2, the otherwise radiative transition, P_{DAM} between d_1 and a_1 is quenched due to a nonradiative Auger transition $d_1a_1a_2$. As a consequence, an energetic hole is pushed into the valence band, which after thermalization allows a transition, P_{Fb}, between donor d_2 and the free hole.

3 Transient excitation

DAMs with large pair separation, R, are occupied first on external excitation due to their large capture cross section, $\sigma \sim R^2$. At a low external excitation rate, only common DAM spectra are observed.

There exist particular conditions of the pair distribution, and a situation can be built where a distant and a close pair are situated at a separation distance 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 Fig. 1. Such a DAA excitation represents an AM 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 the recombination of the short-lived DAM of close separation is immediately absorbed by the hole of the longer-lived 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 prove on its own, though.

Nevertheless the DAA process leaves an occupied donor of the distant pair molecule behind, as well as an additional hole in the valence band. A donor-to-valence-band transition is likely to happen, with the consequence of a competing intensity between the now three recombination channels, i.e., the common DAM, the AM, the Fb transition. Additionally, a characteristic photon energy distribution of the recombination intensities can be expected.

The recombination intensities are evaluated by the following rate equations:

$$r_{\mathrm{Fb}} = B_{\mathrm{Fb}}\, d_{\mathrm{o}}\, p \ , \qquad d_{\mathrm{o}} \text{ concentration of occupied donors} \tag{1}$$

$$r_{\mathrm{DAM}} = B_{\mathrm{DAM}}\, a_{\mathrm{o}} d_{\mathrm{o}} \ , \qquad a_{\mathrm{o}}\, d_{\mathrm{o}} \text{ concentration of occupied DAMs} \tag{2}$$

$$r_{\mathrm{AM}} = X\, a_{\mathrm{o}}^2\, d_{\mathrm{o}}, \quad X = X(R_3) \ . \tag{3}$$

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 AM and thus, is also a function of the external excitation rate due to occupation probability of the donor–acceptor pairs.

In order to determine a_{o} and d_{o}, the following time-independent balance equations are considered:

$$\frac{\mathrm{d}(a_{\mathrm{o}})}{\mathrm{d}t} = 0 = pT_{\mathrm{A}}(A - a_{\mathrm{o}}) - Xa_{\mathrm{o}}^2 d_{\mathrm{o}} - B_{\mathrm{DAM}}\, a_{\mathrm{o}} d_{\mathrm{o}} - I_{\mathrm{A}} a_{\mathrm{o}} \tag{4}$$

$$\frac{\mathrm{d}(d_{\mathrm{o}})}{\mathrm{d}t} = 0 = nT_{\mathrm{d}}(D - d_{\mathrm{o}}) - B_{\mathrm{DAM}}\, a_{\mathrm{o}} d_{\mathrm{o}} - B_{\mathrm{Fb}} d_{\mathrm{o}} p - I_{\mathrm{D}} d_{\mathrm{o}} \ , \tag{5}$$

with $T_{\mathrm{A}} = v_{\mathrm{h}}\sigma_{\mathrm{A}}$ the acceptor capture coefficient, $T_{\mathrm{D}} = v_{\mathrm{e}}\sigma_{\mathrm{D}}$ the donor capture coefficient, v the thermal carrier velocity, σ the capture cross section, n the excess electron concentration in the conduction band, p the excess hole concentration in the valence band, D the concentration of donors in the host, A the concentration of acceptors in the host, I_{D} the thermal re-emission probability of neutral donors, and I_{A} the thermal re-emission probability of neutral acceptors.

$$a_{\mathrm{o}} = \left(\frac{[B_{\mathrm{DAM}}(nT_{\mathrm{D}}\, D - pT_{\mathrm{A}}\, A) + pT_{\mathrm{A}}\,(pB_{\mathrm{Fb}} + I_{\mathrm{D}} + nT_{\mathrm{D}})]^2}{4(pT_{\mathrm{A}} B_{\mathrm{DAM}} + nT_{\mathrm{D}}\, DX)^2} + \frac{pT_{\mathrm{A}}\, A(nT_{\mathrm{D}} + I_{\mathrm{D}} + pB_{\mathrm{Fb}})}{pT_{\mathrm{A}}\, B_{\mathrm{DAM}} + nT_{\mathrm{D}}\, DX} \right)^{1/2} - \frac{B_{\mathrm{DAM}}(nT_{\mathrm{D}}\, D - pT_{\mathrm{A}}\, A) + pT_{\mathrm{A}}(B_{\mathrm{Fb}} + I_{\mathrm{D}} + nT_{\mathrm{D}})}{2(B_{\mathrm{DAM}} pT_{\mathrm{A}} + nT_{\mathrm{D}}\, DX)} \tag{6}$$

$$d_{\mathrm{o}} = \frac{nT_{\mathrm{D}}\, D}{a_{\mathrm{o}} B_{\mathrm{DAM}} + nT_{\mathrm{D}} + pB_{\mathrm{Fb}} + I_{\mathrm{D}}} \tag{7}$$

The determination of the competing radiative recombination intensities, I_{Fb} and I_{DAM}, follows from Eqs. (1) and (2) with application of Eqs. (6) and (7). It is obvious that a process which depends on carrier-carrier interaction becomes more intense as the excess carrier concentrations (n, p) contained in Eqs. (6) and (7) increase. This relates particularly to the growing number of AMs involved (Eq. 3).

The dependence of the theoretically determined recombination intensities of the DAM and Fb transitions on the excitation density, Δn, following eqs. (1), (2), (6), and (7) and the consideration of the collision process within the AM after Eq. (3) lead to the prediction of Fig. 2. The collision probability, X, is introduced here as a parameter. Without the existence of an AM ($X = 0$) the upper curve (1) of the donor–acceptor pair recombination intensity applies, which runs into a saturation (constant intensity at higher excitation values), known as the usually measured behavior of this kind of transition channel.

This recombination intensity is reduced by several orders of magnitude at an elevated excitation intensity of $\Delta n = 10^{16}\ \mathrm{cm}^{-3}$ and a chosen collision probability of $X \cong 10^{-24}\ \mathrm{cm}^6\ \mathrm{s}^{-1}$, as shown by the lower curve (13). The Fb transition is also given for these parameters. A more familiar appearance of the recombination intensity curves arises when the collision probability is introduced as an analytical function. This, of course, is an involved problem, as X depends in the first place on R_3, but this in turn depends on the occupation function and the recombination probability of DAMs and, thus, finally on the excitation density, Δn. Supposedly, the formation of the AMs does not happen before Δn exceeds a threshold value, Δn_t, where close DAMs in the vicinity of distant DAMs are beginning to be occupied. An empirically determined function reads

$$X = X_o \left[\exp\left(\frac{\Delta n - \Delta n_t}{\Delta n_t} \right) - 1 \right] \quad \text{for } \Delta n \geq 2\Delta n_t \ . \qquad (8)$$

With $X_o = 4 \times 10^{-27}\ \mathrm{cm}^6\ \mathrm{s}^{-1}$ introduced in Eqs. (6) and (7) and applying doping concentrations $A = 10^{18}\ \mathrm{cm}^{-3}$, $D = 2 \times 10^{18}\ \mathrm{cm}^{-3}$, as well as $B_{Fb} = 10^{-9}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$, $T_D = 10^{-8}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$, $T_A = 10^{-6}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$, $B_{DAM} = 10^{-11}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$ already used in Fig. 2, this results in Fig. 3, which strongly deviates from the usually measured donor–acceptor pair transition intensity run.The formation and participation of AMs in the recombination process is clearly visible in the downswing of the net radiative recombination intensity. This defines the existence region of AMs.

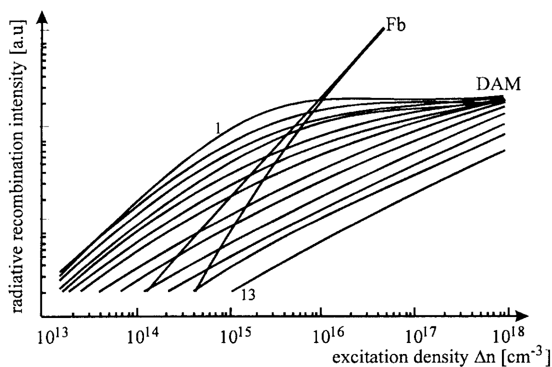

Fig. 2. Radiation recombination intensity as calculated from Eqs. (1) and (2). The collision probability of the Auger molecule (*AM*) is applied here as a parameter for each curve from 2 to 13, corresponding to 10^{27} s cm^{-6}. $X = 2^k \times 10^{-27}\ \mathrm{cm}^{-6}$ s, $k = 1, 2, 3\ldots$; with $X = 0$ in curve 1

4 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 $\varepsilon_d = 54\ \mathrm{meV}$ and deep acceptors with $\varepsilon_A \sim 200\ \mathrm{meV}$. The doping concentrations were determined to be $D = 2 \times 10^{18}\ \mathrm{cm}^{-1}$ and $A = 1 \times 10^{18}\ \mathrm{cm}^{-3}$, respectively. Cathodoluminescence [14] of the samples was induced in a liquid nitrogen cryostat. A common lock-in technique, a cooled photoelectron multiplier, and a Zeiss SPM-2 monochromator were applied for recording the spectra. The concentration of excited electrons and holes in the host was controlled by the current of a 30-keV primary electron beam. Donor-to-acceptor transitions are the dominant radiative recombination process and occur even at low excitation levels. With increasing excitation density, an additional transition, identified as an Fb channel emerges. The radiative DAM transition intensity diminishes, while the Fb transition intensity still increases at the highest excitation levels chosen. The luminescence spectra are shown in Fig. 4.

The DAA AM region is shown in Fig. 5, where for any two donor–acceptor pairs bound into the AM and taken out of the radiative DAM transition channel, one additional excess hole appears in the valence band and one additional neutral donor (Fig. 1b) participates in the Fb recombination channel instead of in the DAM channel. The dependence of peak energy position of the Fb and DAM radiation on the excitation energy is shown in Fig. 6. The blue shift of the Fb line at higher excitation energies suggests a heating of the hole gas by the Auger-induced de-excitation of the second acceptor involved (Fig. 1b). The uncommon large peak shift of the DAM transition toward higher energies is direct proof of the involvement of AMs. The annihilation of distant pairs, which prior to this action were present in the DAM spectra, are now missing on the low-energy

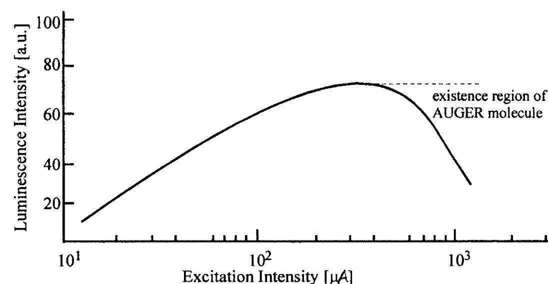

Fig. 3. Existence region of AMs, seen at elevated excitation levels of the host

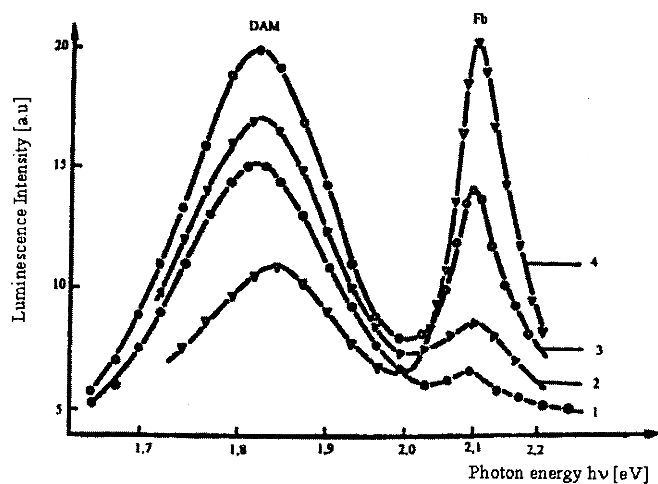

Fig. 4. Cathodoluminescence spectrum of GaAlAs:Si obtained with different excitation intensities: *1* 10^2 μA; *2* 2.5×10^2 μA; *3* 5×10^2 μA; *4* 1×10^3 μA. Sample bulk temperature 83 K

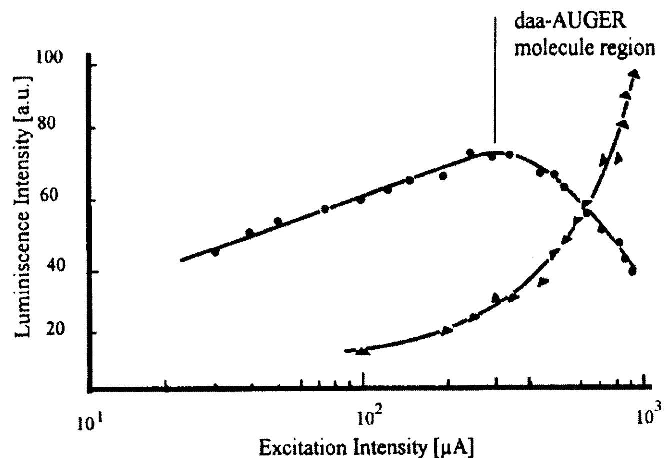

Fig. 5. Experimentally determined photon emission intensity of the donor-to-valence-band (*Fb*) and the DAM transitions. At higher excitation levels donor–acceptor–acceptor (*daa*) AMs are formed. For any two donor–acceptor pairs, bound into the AM and taken off the DAM transition channel, one additional excess hole appears in the valence band

side of the emission spectra. As the main band is a superposition of many single transitions of pairs at different separation distances, the lack of those transitions at larger *R*s pushes the maximum of that band to higher energy values. A bulk temperature effect does not need to be considered here, as sample heating at the highest excitation levels would cause the opposite effect on the peak energy positions.

5 Conclusions

Under particular conditions of doping and excitation of a semiconductor host, DAA AMs are created, which

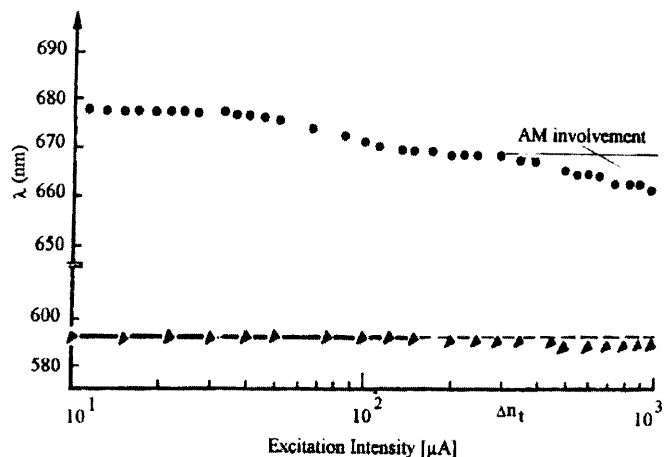

Fig. 6. Peak energy position of the DAM- and Fb radiative transition. While the DAM radiation shows a large peak shift of about 45 meV to higher values with increasing excitation current due to the involvement of the AM, the Fb radiation peak also moves to higher values by about 3 meV at the highest excitation intensities

participate in a characteristic manner as a competing nonradiative recombination channel. The existence region of AMs can be defined in a recombination intensity versus excitation density plot of donor–acceptor transitions. It appears at higher excitation levels between the actual and a theoretically expected luminescence intensity run, or peak energy position run, where AMs in the latter are not included.

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