

ON SOME PROBLEMS OF LUMINESCENCE IN SEMICONDUCTORS

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ABSTRACT

Some problems of luminescence in semiconductors under electron-beam or optical excitation are discussed. Theoretical remarks, based on a quasi-equilibrium approximation of luminescence in III-V compounds and a non-equilibrium approach for free-carrier heating are included. The origin of a given luminescence channel is determined by line-shape analysis.

RESUMEN

Se discuten algunos problemas de luminiscencia en semiconductores cuando son sometidos a un haz de electrones o excitación óptica. Se incluyen notas teóricas basadas en una aproximación de cuasiequilibrio de luminiscencia en compuestos III-V y una aproximación de no-equilibrio para el calentamiento de los portadores libres. El análisis de la forma de la línea sirve para decidir el origen de una determinada línea de luminiscencia.

I. INTRODUCTION

Irradiation of semiconductors with electromagnetic radiation may excite the electronic subsystem to a nonequilibrium state. The recombination process of electron hole pairs thus results in luminescence radiation which involves characteristic properties of the substance under examination.

In general the investigation of optical and optoelectronic phenomena in semiconductors aims at a selection of both optimum material and optoelectronic devices that are primarily designed for practical applications⁽¹⁾.

The generation of effective semiconductor light sources is based on the fundamental knowledge of recombination mechanism, the elucidation of which comes foremost from studies of optical fluorescence⁽²⁾. Radiative

recombination processes of high efficiency require relevant materials as well as appropriate devices⁽³⁾. The properties of the material may be recognized in most cases by the energy spectrum of the crystal electrons, i.e. by the band structure. It turns out that efficient luminiscence is possible only up to photon energies comparable with the basic energy band gap of the semiconductor. Moreover, ideal requirements with regard to doping and transition probabilities should be taken into account, which means that the material must be dopable in an amphoteric manner. The transition probability of excess charge carriers must be high, which is a main characteristic of semiconductors with direct band structure where recombination between electrons and holes occurs without momentum change. Therefore, these semiconductors offer a high quantum yield. In contrast, the indirect structure allows recombination of an electron with a hole only by momentum change. Here additional collision partners, lattice defects or impurities are needed, which receive the momentum difference.

In some cases, alloys may be produced from different semiconductors. If two semiconductors, one with a direct band-structure and the other with an indirect band-structure, are mixed in a determined proportion then direct and indirect transitions may coexist. In general, the band gap E_g increases with the concentration of the indirect component⁽⁴⁾. The expected quantum yield depends on the ratio of the components⁽⁵⁾.

In order to induce a semiconductor to emit recombination radiation, it is provided with energy. This may be done by the impact of ionizing radiation (electrons, α -particles, γ -rays, x-rays, or protons are most commonly used⁽⁶⁾), or by illumination with light whose frequency ν is usually greater than E_g/h (where h is Planck's constant). A different method is injection of a current into the crystal through a metal contact or through a junction between differently doped regions of a single piece of crystal (p-n junction). There is no doubt that among the excitation methods the injection of charge carriers into the active region of a p-n junction is the most important from the technical viewpoint. The generation of recombination radiation of a given color is one of the goals of semiconductor research. Another aspect is the application range of LEDs, the utility of which can be considerably increased when the outgoing light is modulated via the carrier injection. The theoretical upper frequency limit is determined by the time constant of the elementary processes. Its value amounts to about $5 \cdot 10^{10}$ Hz for the

radiative recombination of minority carriers in semiconductors, however it is not reached in all cases. Therefore, on the one hand, attempts are made to enlarge the practically useful frequency range (validity of quasi-stationary approximation). On the other hand optoelectronic phenomena in the cut-off frequency range have been observed, which are of considerable interest^(7,8). Thus, the study of dynamic processes in semiconductors is of equal significance compared to the large efforts to synthesize semiconductors with optimum luminescence properties. In particular, injection luminescence by p-n transition, photo excitation, and electron beam excitation are supplementary investigation methods. The electron beam excitation of semiconductors is distinguished by the fact that it owns a high excitation density of excess carriers which is almost independent of the width of the band gap. However, due to the very high energy of primary electrons (e.g. 30 keV) compared with the Fermi energy of the electron gas in semiconductors (a few meV), a strong non-equilibrium occurs in the system of free charge carriers. From another standpoint, kinetic phenomena related to energy relaxation of hot electrons are of interest^(9,10). The effects of highly excited charge carriers promise, among others a rise in the cut-off frequency compared to conventional components⁽¹¹⁾. Their role with radiative recombination needs further investigation.

Chapter 2 provides a short review on radiative recombination processes observed most frequently as well as a mathematical description of the line shapes in the spectrum formed by these transitions. Since line shape analyses represent a powerful method for spectrum identification, we also mention here effects modifying the luminescence spectrum.

Some luminescence investigations of (Ga, Al)P and GaN are dealt with.

2. THEORETICAL CONSIDERATIONS

The luminescence of III-V compounds is sensitive to many factors. It depends mostly on the individual structure of the semiconductor, i.e. on its band structure, as well as on crystal perfection, doping, composition⁽⁵⁾, ambient temperature⁽¹³⁾ applied pressure or stress⁽¹⁴⁾, presence of electric or magnetic fields⁽¹⁵⁾, mode of excitation, and so on.

Emphasis is laid on a general characterization of materials by lu-

minescence investigations, in particular, to get an optimum of the luminescence effects by crystal growth.

2.1 Frequently observed radiative transitions and their line shape features.

This section provides some examples for radiative transitions frequently observed with luminescence investigations and the effects of high doping and strong excitation. We restrict ourselves to those luminescence transitions detected unambiguously in the semiconductors under consideration. Non-radiative recombination processes which control the luminescence efficiency, are outside the scope of this synopsis (cf.e.g.⁽¹⁶⁾).

Recombination radiation is emitted by a semiconductor, when excess carriers are recombining. It can occur (see Fig. 1) via any one of several paths, i.e. band to band, band to defect level, defect level to band, defect level to defect level or by decay of special elementary excitations. No matter what path may be followed by the recombining carriers, the intensity of emitted light is proportional to the excess carrier population. This, in turn, for fixed excitation intensity, is proportional to the carrier lifetime. The area under the various lines or bands is a measure of the relative probabilities of recombination via the various paths⁽¹⁸⁾. In addition, the half widths of the lines or bands give an indication of how well defined the recombination level is, i.e. whether it is a discrete level or a band of levels.

The identity of a given radiative transition is determined by its line shape and peak energy as well as their dependence on temperature and excitation density. However, there are still numerous features to which the radiative transition may react in a specific manner, such as splitting of the exciton lines both in a magnetic field and under uniaxial stress, decay in time under different excitation conditions, etc. In this connection, GaP has been extensively studied and turns out to be a model for radiative and nonradiative transitions.

In what follows, we treat only the line shape, since commonly it is the first experimental information obtained from the spectrum.

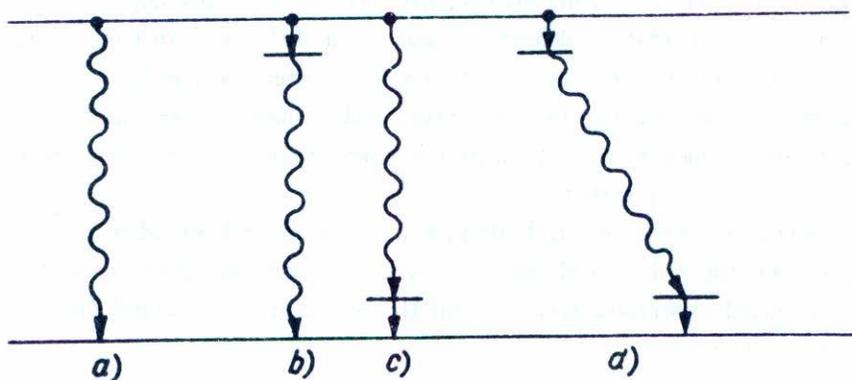


Fig. 1. Scheme of energy levels of radiative transitions frequently observed.

2.1.1. Interband Transitions

Experimental interband transitions are observed either in semiconductors with low impurity concentration, or with strong perturbation of the electron equilibrium distribution, which means that the concentration of the excited electron-hole pairs is essentially higher than that of the impurities present.

The shape of the intrinsic luminescence band has been calculated for the case of direct recombination from a degenerate electron distribution to a nondegenerate hole distribution with no contribution from the exciton transitions. The luminescence intensity is⁽¹⁷⁾

$$I(h\nu) \sim \omega^2 (h\nu - E_g)^{1/2} \exp \left[- \frac{(h\nu - E_g)}{k_B T} \cdot \frac{m_e}{m_e + m_h} \right] \\ \cdot \left\{ \exp \left[\frac{m_h}{m_e + m_h} (h\nu - E_g - E_F) / k_B \cdot T \right] + 1 \right\}^{-1}$$

where E_g is the energy gap, m_e and m_h stand for the effective electron and hole masses, E_F is the quasi-Fermi level of the electrons, and k_B is the Boltzmann constant. A modification is likely to occur in such direct III-V semiconductors, where $m_e < m_h$. This causes a considerable decrease in the donor binding energy, and already with low doping concentrations and excitation densities (more than 10^{17} cm^{-3} in GaAs, more than 10^{15} cm^{-3} in InSb) a degenerate free electron distribution occurs. The transition probability for radiative band-to-band recombination in indirect semiconductors is 2 to 3 orders lower than that for semiconductors with direct band structure.

A degenerate electron distribution at 4.2K in InSb yielded a good match between the calculated intensity behavior and the spectral distribution obtained experimentally even on the basis of thermalized free carriers⁽¹⁷⁾ (Fig. 2).

Most semiconductors show optical transitions from impurities, in particular for not too strong excitation densities, due to residual impurity concentrations ($10^{14} \dots 10^{16} \text{ cm}^{-3}$).

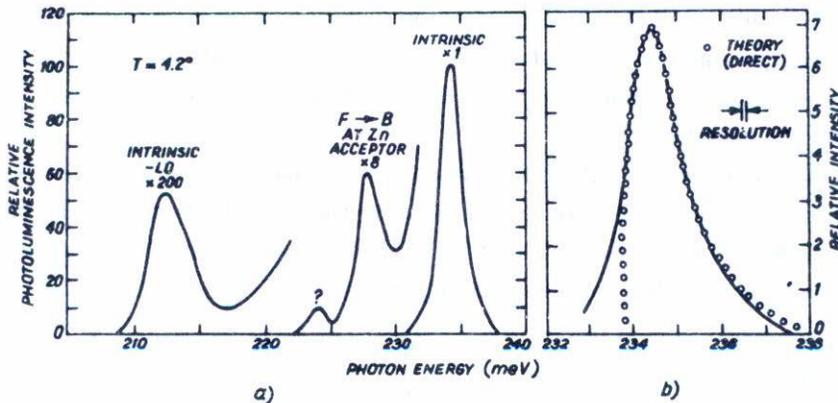


Fig. 2. Photoluminescence spectrum of pure InSb with $n=5.10^{13} \text{ cm}^{-3}$ at 4.2K; a) intrinsic recombination b) calculated line shape and experimental line shape; after Mooradian and Fan⁽¹⁷⁾

2.1.2. Free-to-bound and bound-to-bound transitions

We are concerned with a free-to-bound transition (FBT) when an excited electron (hole) is captured by a donor (acceptor) and enters the other energy band by radiative recombination. When both recombination partners are captured by corresponding impurities before recombination, it is donor-acceptor pair radiation (DAP) (see Fig. 1, b, c, d).

A free-to-bound process includes carriers on neutral donors or acceptors or on charged isoelectronic centers. An important distinguishing feature of the FBT is that the peak of the free-to-bound recombination line shifts with respect to the band with temperature. This shift arises from the energy dependence of the capture cross section $\delta(E)$, and what is presumably of more significance, from the thermal distribution of free carriers. The zero-phonon line shape $I(h\nu)$ of the emitted radiation is discussed by Eagles⁽²²⁾.

Provided that the electrons in the conduction band are in equilibrium with the lattice, with a quasi-Fermi level well below the conduction band, $I(h\nu)$ may be expressed as

$$I(h\nu) \sim (h\nu - E_g + E_I)^{1/2} \cdot \exp \left[-(h\nu - E_g + E_I) / k_B \cdot T \right] .$$

Here E_I is the impurity ionization energy and $\delta(E)$ is considered independent on the kinetic energy. The latter requires a careful consideration in case of a strong energetic nonequilibrium in the system of free charge carriers. The binding energy of the impurity involved in this transition is determined^(23,25) from the position of the peak energy, $h\nu_{\max}$ as follows:

$$E_I = E_g - h\nu_{\max} + k_B \cdot T/2 ,$$

This holds as long as the impurity concentration is not too high (Fig. 3).

The bound-to-bound process as an effective recombination procedure has been subject of extensive studies⁽²⁶⁻²⁸⁾, in a great number of semiconductor compounds, especially of the III-V type. Semiconductors are usually compensated to a level of at least 10 percent. Excess electrons

and holes are captured by compensated donor-acceptor pairs, where the pair recombination band dominates in the spectrum at sufficiently low temperatures.

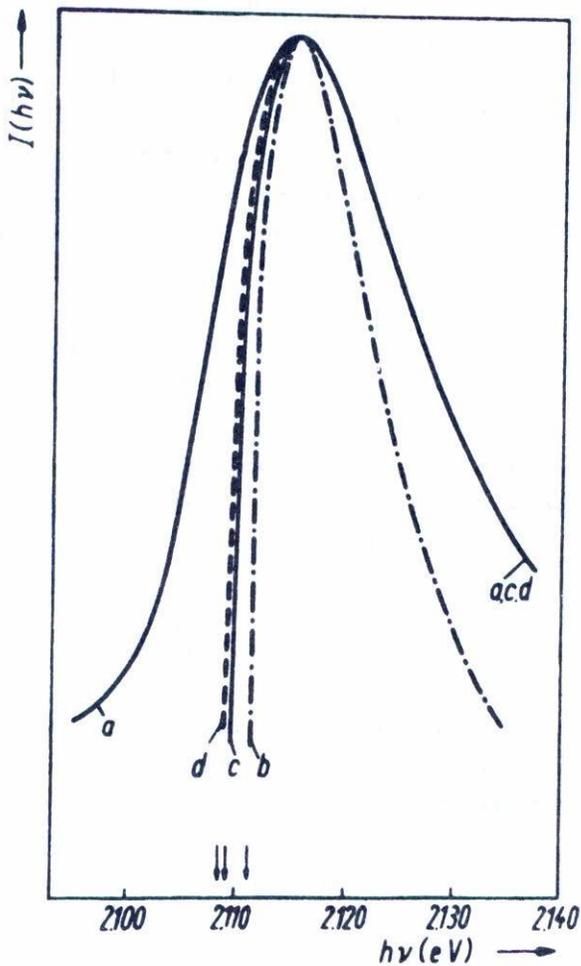


Fig. 3. Intensity I of the free-to-bound emission line of cathodo-excited (Gas,Al)As versus the energy $h\nu$; a) experimental curve, b) equilibrium model (after Eagles²²), c) nonequilibrium model, stationary regime, d) nonequilibrium model, pulsed regime. The arrows indicate the difference between the energy gap, E_g , and the binding energy of the impurity level, E_I , obtained from the peak maximum by use of the different models (after⁽⁵³⁾).

Taking into account a polarization term, the photon energy may be written as

$$h\nu = E_g - (E_D + E_A) + \frac{e^2}{\epsilon r} - \frac{e^2 b^5}{\epsilon r^6}$$

where r is the pair distance, ϵ is the dielectric constant, E_D and E_A the donor and acceptor binding energy, e is the elementary charge and b a constant of the dipole-polarization interaction between the neutral centers. The Coulomb term $E_C(r) = e^2/\epsilon \cdot r$ describes the interaction between oppositely charged ions and is responsible for a great number of discrete lines of energy $h\nu(r)$. These lines are related to the lattice geometry and, for large r , merge into a continuous spectrum⁽²⁹⁾. In general, the polarization term is neglected in comparison with the Coulomb term.

On the basis of a statistical distribution of both donors and acceptors, the emission intensity per unit energy at energy E is given by⁽²⁷⁾

$$I(E) \sim r^4 \cdot \exp \left[-r/R_d \right] \cdot \exp \left[-\frac{4}{3} \pi N r^3 \right] \cdot \left[1 - \exp(-g \cdot \sigma(r)) \right]$$

This expression is a combination of the pair distribution function

$$P(r) dr \sim 4\pi r^2 N dr \cdot \exp \left[-\frac{4}{3} \pi N r^3 \right],$$

of the radiative transition probability F

$$F \sim \exp \left[-r/R_d \right],$$

and the population function f_e , given by

$$\frac{df_e}{dt} = (1-f_e) \cdot g \cdot \sigma(r) - f_e \cdot F$$

Here $\sigma(r)$ is the capture coefficient and R_d is half of the Bohr radius a_0 .

The energy of the main emission peak is gotten by maximizing $I(E)$ with respect to r .

We may distinguish between several cases according to experimental findings. For example, with rising excitation density the main emission peak shifts towards a higher photon energy (typically $\sim 10\text{meV}$ for 1000-fold increase in excitation intensity). This is due to a smaller value of r , a consequence of a denser pair population (Fig. 4). A shift to higher transition energies can be also produced by increasing the temperature, since the widely separated pairs (low transition probability) become thermally ionized before recombination can occur^(30,31). Together with free-to-bound recombination, the binding energies of donors and acceptors may be evaluated⁽³²⁾.

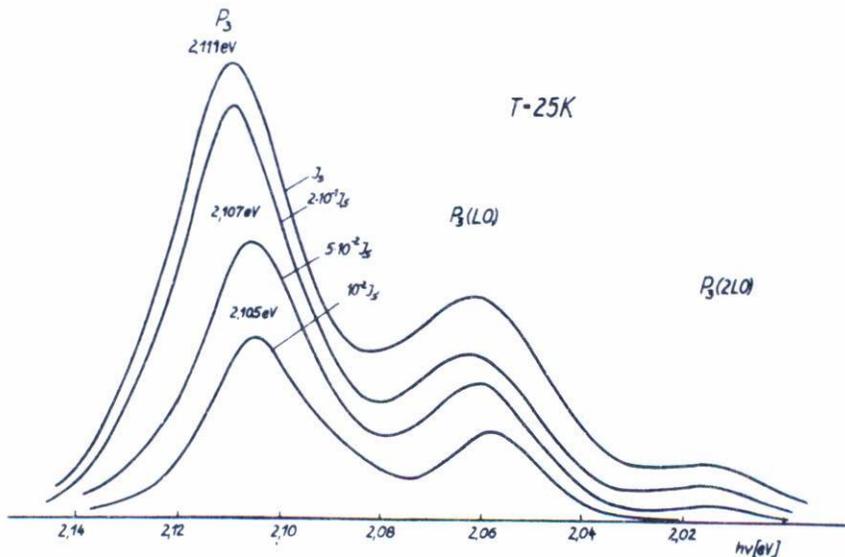


Fig. 4. Donor-acceptor pair radiation of $\text{Ga}_{1-x}\text{Al}_x\text{As}$ at 25 K ($x=0.16$) and relevant phonon replicas. An excitation-dependent peak shift is detectable (I_8 corresponds to the strongest excitation).

2.1.3. Excitons

In semiconductors excitons provide energy-rich radiative transitions. Free excitons are elementary excitations which might be imagined either as electron-hole pairs with hydrogen-like binding character (at a large distance between electron and hole compared to the lattice constant) or as excited states of an atom (at small distances). They can freely move in the crystal as neutral elementary excitations.

Bound excitons are elementary excitations of the crystal when the electron and the hole are localized at an impurity. Up to the present time, the exciton state in semiconductors has been studied quite extensively^(33-36,40).

The energy of the free exciton, for example, is composed of the internal energy of the electronic excitation and the energy of its overall motion. When free excitons are recombining without any phonons, the photon energy is $h\nu = E_g - E_x$ (E_g is the band gap energy, and E_x is the exciton binding energy). Commonly, such a line shows weak intensity. In the process of phonon-assisted annihilation, excitons with any value of the kinetic energy can take part so that these lines are broadened and also become more intense due to diminished reabsorption. For this case, the photon energy yields $h\nu = E_g - E_x - E_{\text{phonon}}$.

At low temperatures transitions are observed due to excitons bound to impurities. The respective binding energy E_d of the excitons is relatively low. The photon energy for the direct process is $h\nu = E_g - E_x - E_d$ and the analogue for the indirect process $h\nu = E_g - E_x - E_d - E_{\text{phonon}}$. With luminescence of (Ga, Al)P such transitions are very meaningful. Their spectrum is plotted in section 2.3.

When the crystal is strongly excited, in the sense of a high density of excess carriers, new emission phenomena related to exciton molecules are observed⁽³⁷⁾. Evidence of a collective interaction forming a Bose-Einstein condensed phase of excitons or of exciton molecules has been obtained in various materials⁽³⁸⁾. Effort has been devoted to the investigation of the emission line shape⁽³⁸⁾, which is in qualitative agreement with those from the experiment. However, such phenomena do not play any role in the matter discussed.

2.2 Modification of emission line shape features

Luminescence is influenced, on the one hand, by density-of-states tails, and on the other, by the eventually existing non-equilibrium distribution of free charge carriers. Apart from a change in luminescence efficiency, the phenomena mentioned before cause other line shapes and peak energy positions. For the demonstration of the conditions of free-to-bound transitions we shall restrict ourselves mainly to conduction-band to acceptor transitions without forgetting that there may be implied also other transitions.

2.2.1. Density-of-states tails

Heavily doped semiconductors have energy states which form so called band tails extending into the forbidden gap. The density of states ρ at an energy E in these tails, is given in rough approximation by $\rho_E = \rho_0 \exp(E/E_0)$, where the "band tail parameter" E_0 increases with rising impurity concentration⁽⁴¹⁻⁴³⁾. For GaAs, a relation between impurity concentration N_D , N_A and band tail parameter E_0 is given as follows⁽⁴⁴⁾:

$$E_0 = \frac{e^2}{4\pi\epsilon\epsilon_0} \cdot \left(4\pi \frac{N_D + N_A}{2} L \right)^{-1/2}$$

where L is the screening length. The broadened state density is given by

$$\rho_E \sim E_0^{1/2} F_{-1/2}(E/E_0)$$

where $F_{-1/2}$ is the Fermi integral $F_n(\xi)$

$$F_n(\xi) = \frac{1}{n!} \int_0^\infty \frac{y^n dy}{1 + \exp(y - \xi)}$$

corresponding to $n = -1/2$.

The intensity distribution of FBT yields for the broadened state density, in the case of non-degeneration,

$$I_{\text{FBT}}(E) \sim E_0^{1/2} F_{-1/2}(E/E_0) \exp(-E/k_B \cdot T) \quad .$$

In the case of a degenerate system of free carriers, taking into account the quasi-Fermi energy E_F involved in the band, the intensity distribution is

$$I_{\text{FBI}}(E) \sim E_0^{1/2} F_{-1/2}(E/E_0) \cdot \{ 1 + \exp (E-E_F)/k_B \cdot T \}^{-1} .$$

Provided that a broadened state density exists, the peak energy $h\nu_{\text{max}}$ is given by

$$h\nu_{\text{max}} = E_g - E_I + E_m ,$$

where E_m may be evaluated by maximizing the above expression for the intensity. Nondegeneration furnishes a maximum value of $E_m = 0.6 k_B T$. Note now the uncertainty of the definitions of E_g and E_I . There are some investigations, where changes in temperature and excitation density are used for scanning the shape of the band tail^(45,46).

2.2.2. Nonequilibrium distribution of excited carriers

The starting point of the considerations up to now has been the fact that excess carriers are thermalizing before recombination. There are sufficient experimental hints as to the influence of recombination due to nonequilibrium states of the excess carriers on the recombination behaviour in general, and, in particular, on the line shape. The generation of highly excited electron states depends on the excitation mode of the semiconductor. The excitation of semiconductors with highly energetic particles modifies the carrier distribution. Due to the generation of a high density of free carriers, the electron temperature exceeds that of the lattice^(9,47-49). On the one hand, the capture behavior of the impurities is influenced by hot carriers^(50,51), and on the other, radiative recombinations of band-to-band processes are detected which surmount the gap energy by a multiple of $k_B \cdot T_1$ (T_1 being the lattice temperature⁽⁵²⁾). A characteristic of the participation of hot carriers in band-to-band or free-to-bound recombination is a band tail extending widely into the high energetic area (Fig. 5) as well as an increase in peak energy⁽⁵³⁾. An extension of the argument concerning recombination rates suggests that the free-to-bound emission should re-

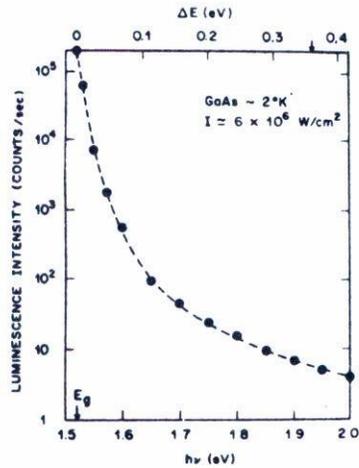


Fig. 5. Luminance radiation of hot excess charge carriers in GaAs at intense optical excitation. The high energy luminescence tail is extended up to 2eV (after Shah and Leite(52)).

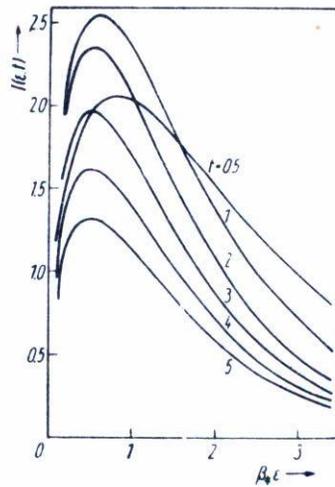


Fig. 6. Intensity distribution $J(\bar{\epsilon}, \tau)$ versus photon energy $\bar{\epsilon}$ and time t after a δ -pulse excitation; $(\tau_n/\tau_{e1}=10$; t in units of τ_{e1} ; β_4 is the inverse lattice temperature). Radiative recombination from non-equilibrium states causes a band tail in the high-energy region. A peak shift to the equilibrium value is seen with growing time t (after(54)).

veal a shift of the time-dependent emission peak towards longer wavelength with increase in time. Such an effect would be due to the cooling of the hot electrons in the conduction band. If this is true, an ambiguity arises in that, the observation of a time dependent shift of the emission peak under electron beam excitation does not necessarily imply that the emission is of the bound-to-bound type.

Fig. 6 represents the spectral behavior of a FBT in a semiconductor after pulse-shape electron beam excitation versus the cooling time of the excess carriers. (c.f. ⁽⁵⁴⁾). The ratio of relaxation time τ_{e1} and recombination time τ_n of the excess carriers plays an essential role. The line shape of FBT as a function of time t at the end of the excitation yields

$$I(\bar{\epsilon}, t) \sim \bar{\epsilon}^{-1/2} \cdot \exp \left\{ - \frac{\bar{\epsilon}}{k_B \cdot T_1} \left[1 - \exp(-t/\tau_{e1}) \right] \right\} \cdot \exp(-\frac{t}{\tau_n}) \quad .$$

The relation for the quasi-equilibrium distribution indicated by Eagles ⁽²²⁾ is meant here to be a borderline case ($t \gg \tau_{e1}$). Both the relaxation time τ_{e1} and recombination time τ_n are considered here to be known values. - The calculation of such properties is an actual problem of the physics of nonequilibrium. It can be treated according to the formalism developed by Zubarev ^(55,56) and McLennan ⁽⁵⁷⁾. Further, there are methods ⁽⁵⁸⁾ to measure rather weak signals in the range of some 10^{-10} s with direct time resolution, and to determine the thermalization time of electrons and excitons by interaction with acoustic phonons.

2.2.3. Spatial inhomogeneities

When luminescence properties are dependent on the excitation density, the question of the homogeneity of excitation arises. In particular, with electron beam excitation, and sometimes also with photoexcitation, the excitation density is always a local function in the semiconductor crystal. The measured luminescence spectrum is a superposition of spectra from semiconductor regions with different excitation density.

This situation is still aggravated in p-n layer structures. Light generation takes place here in a region with strongly changing doping concentration. Moreover, the excess carrier density shows an exponential distribution by p-n junctions in the case of carrier injection.

Another item is the influence of self-absorption of the passive bulk material on the emission spectrum.

The internally generated spectrum $I_i(\bar{\epsilon})$ is related to the externally measured spectrum $I_e(\bar{\epsilon})$ by the simple relation

$$I_e(\bar{\epsilon}) = I_i(\bar{\epsilon}) \exp(-\alpha(\bar{\epsilon}, r) d)$$

where $\alpha(\bar{\epsilon}, r)$ is the locally dependent optical absorption coefficient, and d is the appropriate optical path length. It is usually difficult to use this equation for spectral correction in p-n diodes because neither d , nor $I_i(\bar{\epsilon})$ are known exactly. This is due to the possibility of multiple internal reflection of the luminescence in a region of locally varying optical absorption and to heterostructure effects.

However, even under such conditions it is possible to identify recombination mechanisms^(61,63,68).

2.3 Quasi-equilibrium approach: luminescence of $Ga_{1-x}Al_xP$

The quasi-equilibrium approximation is based on the assumption of a complete thermalization of the excess carriers before recombination, which leads to the depopulation of the corresponding bands. This assumption proved to be useful for the characterization of the materials. At constant excitation density this approximation does not lead to contradictions between cathodoluminescence and photoluminescence. In what follows, we present findings from our own luminescence investigations of $(Ga,Al)P$, which is of interest for optoelectronic applications.

There is a great interest in semiconducting compounds and alloys of aluminum because of their wide bandgaps. Although their high melting point and instability in a humid atmosphere create some problems, over the years research has yielded positive practical results. In particular, this concerns efficient electroluminescence of $(Ga,Al)As$ heterostructures. The mixed crystal of GaP and AlP provides good results, too.

On the one hand, the efficient 1,79eV Zn-O band of GaP peaks in the red portion of the spectrum where the sensitivity of the human eye is less than 1% of its maximum. A bandgap shift of 100 meV by admixture of AlP would move this Zn-O band to a region where the sensitivity of the eye is increased by nearly one order of magnitude. On the other hand,

this material is suitable for acoustic modulation of light because of its large refractive index and consequent large strain-induced birefringence, which is better than that of GaP. At room temperature the latter shows high absorption ($\alpha \sim 100 \text{ cm}^{-1}$) for the 5145 Å argon ion laser line as well as for the 5300 Å YAG: Nd laser line (second harmonic), which is reduced to about 4 cm^{-1} by admixture of AlP. Indeed, the application requires crystals of high optical quality, which are rather difficult to find in the case of complicated alloys.

Finally, this mixed compound is of interest from the point of view of material research: the band structures of GaP and AlP are almost identical. Larger deviations may be detected only in the energy difference $\Gamma_{1C} - X_{1C}$ of the conduction band being 0.54 eV for GaP and 1.15 eV for AlP. This difference allows to study the effect of the band structure on the radiative recombination process in a large scale of the mole fraction x .

The following items refer to $\text{Ga}_{1-x}\text{Al}_x\text{P}$ layers, which were grown under flowing H_2 in a vertical sliding graphite boat from a solution, containing Al and Ga, by liquid-phase epitaxy on (111) oriented GaP substrate. Starting at 900°C , the temperature was reduced by 1 to 2 deg/min. Fig. 7 shows specific luminescence spectra of undoped $\text{Ga}_{1-x}\text{Al}_x\text{P}$ layers of different composition x . Luminescence has been excited either by a mercury vapour lamp or by a 30 keV electron beam.

The sample belonging to spectrum 1 contains only a small quantity of Al ($x \sim 0.01$). The discrete lines originate from C-S pair recombination. The energy of the pair lines and the 1LO-phonon maximum at $h\nu = 2.216 \text{ eV}$ corresponds to C-S pairs in GaP. In addition, there appears a less distinct band (E_x) at 2.302 eV. It lies in an undoped, solution-grown GaP crystal at 2.300 eV and is shifted to lower values with rising acceptor concentration. The single pair lines vanish with the increasing amount of Al.

Further, the no-phonon maximum shifts to higher energies. A very intense high energy peak E_x occurs in spectrum 6. The energetic distance $E_x - E_p$ is 66 meV and comes out to be 15 to 17 meV smaller than those of spectra 1 to 3. The pair band is very similar in spectra 1 to 5, whereas spectrum 6 is broadened and the phonon structure is less well resolved. These properties imply participation of another donor (probably Si) in the DAP recombination in spectrum 6. The increasing residual

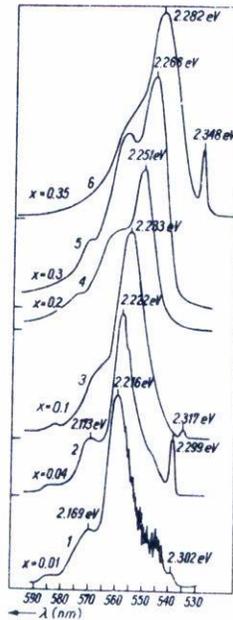


Fig. 7. Luminescence emission spectra of undoped $\text{Ga}_{1-x}\text{Al}_x\text{P}$ at 4.2K with variable x , showing essentially donor-acceptor pair and bound exciton radiation.

Si concentration with growing Al content in $\text{Al}_x\text{Ga}_{1-x}\text{P}$ makes this interpretation plausible. The intensity ratio of the no-phonon and 1 LO-phonon band growing in favour of the latter (cf. spectra 1 to 5) is thought to correspond to an increase in the conduction band difference $\Gamma_{1c} - X_{1c}$.

From symmetry arguments, and because of the small difference $\Gamma_{1c} - X_{1c}$ in GaP, the no-phonon intensity dominates, when the donor substitutes a P site. Increasing $\Gamma_{1c} - X_{1c}$ reduces the influence of the conduction band states near Γ_{1c} on the donor wave function, and as a consequence, the intensity of the no-phonon line. Due to the unchanged symmetry the same phonons are coupled (LO-phonons) causing the increase of the 1-LO-phonon band, in particular.

2.4 Nonequilibrium approach: Free carrier heating

Cathodoluminescence or high energetic photo-excitation commonly produces effects of hot charge carriers. Such, for example, are the results obtained from GaN.

GaN often has a density of free carriers of $n=10^{18} \dots 10^{20} \text{cm}^{-3}$ at room temperature. Bombardment of the GaN layer with fast electrons .

results in a very high carrier density. The energy relaxation of a non-equilibrium distribution of free carriers takes place essentially via interaction of the electrons with lattice vibrations. Interelectronic collisions redistribute energy and momentum among the carriers, but do not change the total energy of the distribution. When the carrier density is high enough, e-e collisions dominate, and we find a thermal distribution of electrons at a temperature T_e , which is substantially higher than the lattice temperature T_l . The free exciton with a peak energy of $h\nu = 3.476$ eV has been measured as that transition in GaN having the highest photon energy, although luminescence spreads in a long tail up to 3.5 eV. This tail is excitation-dependent, that means, at high excitation density it attains the high-energetic regions. Investigation at liquid neon temperature yielded the following results⁽⁷⁴⁾:

i) The electron ensemble may be described by a Maxwell distribution with an electron temperature $T_e > T_l$ which increases with the rising excitation density. ii) The exponential behaviour according to the Boltzmann factor is well reproduced only above $E = 3.5$ eV. iii) Between this energy and that of $E = 3.476$ eV (free exciton) a further radiative transition occurs at 3.495 eV, the nature of which is still obscure although a band-to-band transition could be responsible. iv) The dominant energy-relaxation process is the dispersion of polar-optical phonons. The energy of these phonons is measured to be $E_p = 89.2$ meV obtained from excitation-dependent measurements, which is in good agreement with $E_p = 90$ meV observed with pair radiation investigations. For the verification of the dependence of the lattice temperature on the excitation density, the GaN epitaxy on ruby as described in ref.⁽⁷⁵⁾ may be recommended. As known, luminescence excitation of ruby (via GaN recombination radiation or directly by an electron beam) leads to radiative transitions at 692.8 nm and 694.3 nm, their relative intensity being determined by the (temperature-dependent) population of two adjacent energy levels.

3. CONCLUSIONS

Radiative transitions in semiconductors show a typical energetic distribution in the luminescence spectrum. Thus, line shape analyses are the first approach to decide the origin of a determined luminescence

line. Care has to be taken with "side effects" which may influence the spectrum considerably. Particularly, hot carrier effects have to be included if the excitation mode results in the formation of a nonequilibrium distribution of excess carriers.

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