M R S Internet Journal of Nitride Semiconductor Research

*Volume 1, Article 46*

# The Rate of Radiative Recombination in the Nitride Semiconductors and Alloys

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This article was received on June 3, 1996 and accepted on December 30, 1996.

## Abstract

The radiative recombination rates have been calculated for the first time in the wide band gap wurtzite semiconductors GaN, InN and AlN and their solid solutions $Ga_xAl_{1-x}N$ and $In_xAl_{1-x}N$ on the base of existing data on the energy band structure and optical absorption in these materials. We calculated the interband matrix elements for the direct optical transitions between the conductivity band and the valence one using the experimental photon energy dependence of the absorption coefficient near the band edge. In our calculations we assumed that the material parameters of the solid solutions (the interband matrix element, carrier effective masses and so on) could be obtained by a linear interpolation between their values in the alloy components. The temperature dependence of the energy gap was taken in the form proposed by Varshni. The calculations of the radiative recombination rates were performed in the wide range of temperature and alloy compositions.

## 1. Introduction

Nowadays, the nitride semiconductors such as GaN, AlN and InN attract a considerable attention due to their outstanding physical, chemical and mechanical properties and also because of the recent progress in the technology that allowed to produce high quality nitride films with help of MOVPE and MBE (for a recent review, see Ref. [1]). The attractive properties of the nitrides include high heat conductivity, hardness, chemical stability and high luminescence intensity. These wide gap semiconductors are very promising materials for LEDs and semiconductor lasers in wide spectral interval from ultra-violet to green and even orange [2] [3] because their solid solutions may have the energy gap varying from 2eV in InN to 6.2eV in AlN.

Important characteristics of materials used in luminescence devices are the rates of different electron—hole recombination processes. However, there is no information at the moment about the intensities of these processes in the nitrides. In this work, we concentrate on the calculation of the radiative recombination rate in GaN, InN, AlN and their binary alloys $Ga_xAl_{1-x}N$ and $In_xAl_{1-x}N$ on the base of the experimental absorption data that is present in the literature [4] [5] [6] [7] [8], the calculated electron energy band dispersion laws [9] [10] [11] [12] and the temperature dependence of the band gaps in the pure materials [13] [14] [15].

## 2. Energy Spectra of the Nitride Semiconductors

We consider more common and popular hexagonal phase of the nitrides. All of them belong to the crystal class $C_{6v}$. Their conductivity bands are non-degenerate, and their electron states originate from atomic s-functions. In the $\Gamma$ point of Brilluine zone they transform according to $\Gamma_1$, the unite representation of $C_{6v}$. The valence band is complicated and consists of two branches. One of them transforms according to $\Gamma_1$ whereas the other is degenerate and form the two-dimensional representation $\Gamma_6$. If spin—orbit interaction is taken into account, $\Gamma_6$ farther splits into two bands, $\Gamma_7$ and $\Gamma_9$ [15]. However, the latter splitting manifest itself only along $k_x$ and $k_y$, but it equals zero in the very $\Gamma$ point and along $k_z$, z being the direction of the hexagonal axis c which usually coincides with the normal to the film. We will neglect this splitting and consider $\Gamma_6$ as a degenerate band.

https://doi.org/10.1557/S1092578300002180 Published online by Cambridge University Press

According to the results of Ref. [7] [9] [10] [11] [16] [17], the order of levels in the valence band of the nitrides is different: in GaN and InN, $\Gamma_6$ branch lies above $\Gamma_1$, whereas in AlN it lies below $\Gamma_1$. The symmetry of the electron wave functions in different bands and band branches leads to the following selection rules for the radiative transitions:

- For the transition from $\Gamma_1^c$ to $\Gamma_1^v$, only z component of the transition matrix element differs from zero, and correspondingly, the emitted photon is polarized along z axis.
- On the contrary, for the transition from $\Gamma_1^c$ to $\Gamma_6^v$, z component of the transition matrix element equals zero, and the emitted photon polarization is perpendicular to z axis.

## 3. Radiative Recombination Rate: The Method of Calculation

Usually, Shockley-van Roosbroeck formula is used for the calculation of the radiative recombination intensity [17], which allows one to calculate the transition rate if the spectral dependence of the absorption coefficient is known. However, this is not the case in the nitrides where the optical absorption has been measured only in a small vicinity of the band edge, and another method is needed that would allow to express the recombination rate through the material parameters.

A straightforward quantum-mechanical calculation similar to given in Ref. [18] leads to the following expression for the spontaneous radiative recombination rate:

$$R = \frac{ne^2}{m_0^2 c^3 \hbar^2} \mathbf{M}^2 \left[\frac{2k_B T}{\pi\hbar^2}\right]^{3/2} \sqrt{\mu_x \mu_y \mu_z}\ E_g \left[1 + \frac{3k_B T}{2E_g}\right] e^{-E_g/k_B T}$$

where n is the refractive index, $m_0$ is free electron mass, $\mu_x = (m_{e,x}^{-1} + m_{h,x}^{-1})^{-1}$ is the reduced carrier mass in x direction, and similar for y and z, and

$$\mathbf{M}^2 = \frac{1}{4\pi} \sum_{\lambda=1}^{2} \int d\Omega_{\mathbf{k}}\ |\mathbf{e}_{\mathbf{k}\lambda}\ \mathbf{P}_{cv}|^2$$

where $\mathbf{e}_{\mathbf{k}\lambda}$ is the polarization direction of the photon with the momentum {\bf k}, the sum is over two polarizations, the averaging is over all photon momentum directions, and $\mathbf{P}_{cv}$ is the interband transition matrix element at $\Gamma$ point of the Brilluine zone.

Defining the radiative recombination coefficient according to the equality

$$R = B\ \ n\ p$$

where n and p are carrier concentrations, one comes to the following expression:

$$B = \frac{ne^2}{m_0^2 c^3 \hbar^2} \mathbf{M}^2 \left[\frac{2\pi\hbar^2}{k_B T}\right]^{3/2} \frac{1}{(\bar{m}_x \bar{m}_y \bar{m}_z)^{1/2}}\ E_g(T) \left[1 + \frac{3k_B T}{2E_g(T)}\right]$$

where $\bar{m}_\alpha = m_{e,\alpha} + m_{h,\alpha}$ and so on.

## 4. Temperature and Alloy Composition Dependence of the Energy Gap

To derive the accurate temperature dependence of the radiative recombination rate, one needs to know how the gap varies with the temperature in the materials under consideration. In many semiconductors, including the nitrides, the empiric Varshni formula [19] approximates well the observed temperature dependence of the gap:

$$E_g(T) = E_g(0) - \frac{\gamma T^2}{T + \beta}$$

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where $\gamma$ and $\beta$ are parameters. Their values for nitride thin films were found out in Ref. [13] [14] [15]:

AlN: $E_g(300\ K) = 6.026\ eV$, $\gamma = 1.799 \times 10^{-3}\ eV/K$, $\beta = 1462\ K$,

GaN: $E_g(0) = 3.427\ eV$, $\gamma = 0.939 \times 10^{-3}\ eV/K$, $\beta = 772\ K$,

InN: $E_g(300\ K) = 1.970\ eV$, $\gamma = 0.245 \times 10^{-3}\ eV/K$, $\beta = 624\ K$.

There are data (for example, Ref. [15] for GaN) pointing out on a dependence of Varshni's formula parameters on the different methods of fabrication of the nitride films with the same wurtzite structure. In our calculation we have taken values of these parameters found in single-crystal films produced by MBE.

For the gap value in the binary alloys with the components A and B, we used the expression

$$E_g^{(AB)}(x,T) = \left[x\ E_g^{(A)}(T) + (1-x)\ E_g^{(B)}(T) - d\ x(1-x)\right]$$

with d=1.0 for $Ga_xAl_{1-x}N$ and d=2.6 for $In_xAl_{1-x}N$ [4] [20] [21].

## 5. Calculation of the Interband Matrix Element

To calculate the interband transition matrix element, we made use of the formula for the absorption coefficient that also contains $\mathbf{P}_{cv}$ (see, for example, Ref.~ [18]):

$$\alpha(\hbar\omega) = b\sqrt{\hbar\omega - E_g}, \qquad b = \frac{2e^2\sqrt{8\,\mu_x\mu_y\mu_z}}{\hbar^2 m_0^2 n c\, E_g}\ \frac{1}{2\pi}\sum_{\lambda=1}^{2}\int d\phi\ |\mathbf{e}_{k\lambda}\ \mathbf{P}_{cv}|^2$$

where the integration is over all polarization directions in the plane perpendicular to the incident photon momentum.

Extracting the coefficient b from the measured frequency dependence of $\alpha$, one can find $\mathbf{P}_{cv}$ components in the xy plane assuming that the light beam was perpendicular to the film surface. However, this method does not allow us to find $P_{cv,z}$. This is not important for the transitions from $\Gamma_{1,c}$ to $\Gamma_{6,v}$ as in InN and GaN (see selection rules above), but in AlN where $\Gamma_{1,v}$ band lies higher than $\Gamma_{6,v}$, this may cause problems. We still have calculated B for AlN, too, assuming that $\Gamma_{1,v}$ - $\Gamma_{6,v}$ splitting in AlN is rather small [22], and the hole population of $\Gamma_{6,v}$, and hence the transition probability to this band, may be higher than that in $\Gamma_{1,v}$ due to much higher density of states in $\Gamma_{6,v}$. The values of $P_{cv,x}=P_{cv,y}$ found this way together with other material parameters used in calculations are listed below:

AlN: $P_{cv,x}=13.4\times10^{-20}$ g cm/s, n=2.15, $m_e=0.45$, $m_{h,z}=3.68$, $m_{h,xy}=3.78$;

GaN: $P_{cv,x}=6.3\times10^{-20}$ g cm/s, n=2.67, $m_e=0.22$, $m_{h,z}=2.49$, $m_{h,xy}=2.02$;

InN: $P_{cv,x}=11.5\times10^{-20}$ g cm/s, n=2.1, $m_e=0.12$, $m_{h,xyz}=0.5$.

The material parameters for the alloys were found using a simple linear interpolation between the values for the alloy components.

The calculated temperature dependence of the radiative recombination coefficient B is shown in Figures 1 and 2. One can see that B is highest in InN and the compositions close to it, and lowest in GaN and the alloys reached in this material.

## 6. Conclusion

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We calculated radiative recombination coefficients for three nitride semiconductors and their binary alloys. To do it, we extracted values of the interband matrix elements from the absorption data. The matrix elements do not differ considerably in these semiconductors, and the difference between the recombination coefficients is connected also with the difference in the band gap values and carrier masses.

## Acknowledgments

**The work was supported in part by Russian Foundation for Fundamental Research and by the International Science Foundation.**

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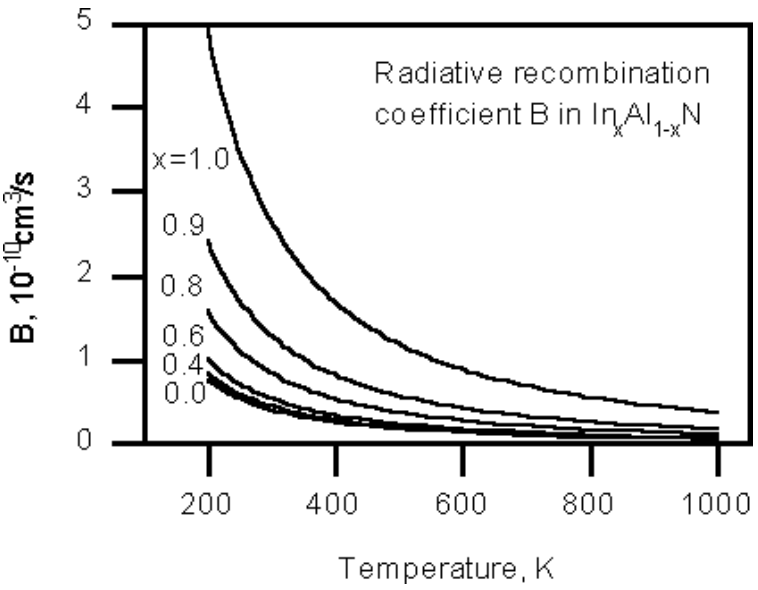


**Figure 1**. The radiative recombination coefficient in the binary alloys (In,Al)N. x is the InN fraction in the alloy.

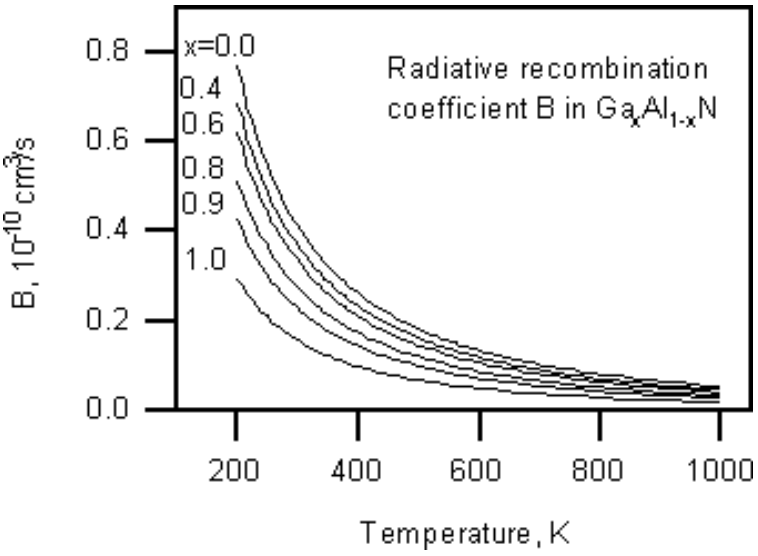


**Figure 2**. The radiative recombination coefficient in the binary alloys (Ga,Al)N. x is the GaN fraction in the alloy.





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