Semiconductor physics

Probabilistic patterns in the formation of spectral curves of interband radiative recombination in semiconductors

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Abstract. The basic principles underlying a probabilistic concept for forming interband radiative recombination spectral profiles in semiconductors have been formulated and implemented. Analytical relations for the line shape (form-factor) of the spectral lines have been obtained. A good agreement between the theoretical predictions and experimentally measured radiative recombination spectra of indium phosphide based semiconductor compounds has been demonstrated.

Keywords: semiconductor, radiative recombination, spectral line, line shape (form-factor), Weibull–Gnedenko distribution.

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1. Introduction

Approximating contours of interband radiative recombination spectral lines, namely, deriving analytical relations for the shape function, or form-factor, of spectral curves is a nontrivial task. The form-factor carries information about the distribution of the radiation intensity as a function of wavelength (frequency) and characterizes the position of the maximum, the half-width of the line, and the homogeneity of its broadening.

Lorentzian, Gaussian, Foigian, and other contours are commonly used to analyze experimental results [1–5]. These contours do not always adequately approximate the shape of the spectral curve over the entire frequency range.

It should be noted that even for an abstract isolated quantum system, spectral lines have a certain minimum width. This width is determined by the finite lifetime of the excited state. It is determined by the Heisenberg uncertainty principle and is called natural linewidth. In turn, the spectral lines of real ensembles of quantum particles interacting with their environment undergo broadening caused by defects and spatial inhomogeneities in the crystal lattice as well as thermal vibrations of atoms and ions. One may suppose therefore that broadening of the spectral lines of interband radiative recombination in semiconductor crystals is statistical in nature.

Analysis of photoluminescence (PL) spectral lines remains relevant until now because it allows using non-destructive methods to obtain valuable information about the band structure of a semiconductor and its defect composition [6–8]. In this respect, this article is devoted to the analysis of probabilistic patterns in the formation of a profile of an interband radiative recombination spectral line in order to obtain the corresponding form factors in analytical form.

2. Probabilistic analysis of interband radiative recombination

It is shown in [9] that physical processes in semiconductor materials are based on a probabilistic paradigm. Its basic provisions are as follows [9]. Firstly, the physical processes are caused by random events. Secondly, the course of these processes is defined by a distribution function of respective random variables. The third provision of this paradigm is the following: just as the equation of motion of physical systems is derived based on the least-action principle, the evolution of a nonequilibrium state of microparticles in semiconductor crystals is described by a distribution function of a random variable, which is the minimum of a large number of independently acting variables. The limit distribution of the minimum value of the third type is the Weibull–Gnedenko distribution [9].

From this point of view, interband radiative recombination in semiconductor crystals is caused by a flow of random events such as recombination of nonequilibrium charge carriers (electrons and holes), *i.e.* photon emission. The wavelength of the emitted photons is a random variable. Accordingly, the form-factor of the spectral emission curve is determined by the photon wavelength distribution function.

The shape of the spectral curve of interband radiation is defined by population of energy levels, the energy scale of which is of the order of kT, as well as by effects of spatial inhomogeneity leading to appearance of tails of the density of states, *i.e.* energy levels in the forbidden band. The entire set of the energy levels near the band edges forms a statistical ensemble. Interband radiative recombination results from the entire set of transitions of nonequilibrium charge carriers between pairs of levels in this statistical ensemble, where one of the levels is located near the conduction band edge and the other one near the valence band edge.

The random variable, namely, the wavelength of the emitted photons for each pair of levels, has a distribution, which, as noted above, is called the natural linewidth of the radiation. The distribution function of the wavelength of the emitted photons for the entire set of interband transitions of charge carriers can be determined based on the probabilistic theory of extreme values. Following the B.V. Gnedenko's theorem, we consider a sequence n of identically distributed independent random variables λ_1, λ_2, …, λ_n, which are the wavelengths of the emitted photons during transitions of nonequilibrium carriers between all possible pairs of levels (n is the number of the level pairs). The distribution of each of the random variables λ_1, λ_2, …, λ_n describes the natural linewidth. We form a new random variable ξ_n equal to $\xi_n = \min(\lambda_1, \lambda_2, ...\lambda_n)$. The limited distribution of the third type of the minimum value is the Weibull–Gnedenko distribution.

Then, the Weibull–Gnedenko distribution density for the wavelength of photons emitted during interband recombination, accurate to a constant coefficient, is a function of the shape of the spectral line of the interband radiative recombination.

The three-parameter (lower-bounded) Weibull–Gnedenko distribution function for the wavelength of the emitted photons $F(\lambda)$ has the following form [9]:

$$F(\lambda) = 1 - \exp\left\{-\left[\alpha(\lambda - \lambda_S)\right]^m\right\}, \tag{1}$$

where m is the distribution shape parameter, α is the scale parameter, and λ_S is the position (shift) parameter, respectively. For the values of λ less than or equal to λ_S, the probability of photon emission is zero (the value $\lambda_S = 0$ is meaningless from physical point of view).

For the probability density of photon emission $f(\lambda)$ we write

$$f(\lambda) = \frac{dF(\lambda)}{d\lambda} = m\alpha\left[\alpha(\lambda - \lambda_S)\right]^{m-1} \exp\left\{-\left[\alpha(\lambda - \lambda_S)\right]^m\right\}. \tag{2}$$

3. Form-factors of radiation spectral lines

The form-factor of a radiation spectral line, which represents the distribution of the radiation intensity as a function of wavelength in analytical form, $I(\lambda)$, is

$$I(\lambda) = I_{01} f(\lambda), \tag{3}$$

where I_{01} is the proportionality coefficient.

Substituting (2) into (3), we obtain

$$I(\lambda) = I_{01} m\alpha\left[\alpha(\lambda - \lambda_S)\right]^{m-1} \exp\left\{-\left[\alpha(\lambda - \lambda_S)\right]^m\right\}. \tag{4}$$

We determine the coefficient I_{01} from the condition for the maximum of the function (4):

$$\frac{dI(\lambda_{\max})}{d\lambda} = 0 . \tag{5}$$

For the position of the maximum point $\lambda_{\max}$ we have

$$\lambda_{\max} = \lambda_S + \frac{1}{\alpha}\left(\frac{m-1}{m}\right)^{\frac{1}{m}} . \tag{6}$$

Substituting the value $\lambda_{\max}$ into (4) yields

$$I_{01} = I_{\max} \frac{1}{m\alpha}\left[\exp\left(\frac{m-1}{m}\right) \Big/ \left(\frac{m-1}{m}\right)^{\frac{m-1}{m}}\right], \tag{7}$$

where $I_{\max}$ is the radiation intensity at the maximum point $\lambda_{\max}$.

Then, taking into account Eqs (4) and (7), for the form-factor of the spectral emission line we have

$$I(\lambda) = I_{\max}\left[\exp\left(\frac{m-1}{m}\right) \Big/ \left(\frac{m-1}{m}\right)^{\frac{m-1}{m}}\right] \times \\ \times \left[\alpha(\lambda - \lambda_S)\right]^{m-1} \exp\left\{-\left[\alpha(\lambda - \lambda_S)\right]^m\right\}. \tag{8}$$

The analysis above assumes that the random variable λ is distributed over the interval from λ_S to infinity. When approximating various types of emission spectral lines, this assumption may prove entirely correct. However, a rigorous formulation of the problem requires taking into account the fact that the random variable λ is distributed over the interval $[\lambda_{G1}, \lambda_{G2}]$ with λ_{G1} being the lower threshold value of the random variable and λ_{G2} the upper threshold value.

The corresponding expression for the form factor can be obtained by generalizing the Weibull–Gnedenko distribution to a situation where the random variable is distributed over an interval. In [10–12], an approach to generalizing the known probability distributions (normal, lognormal, Weibull–Gnedenko) for random variables defined within an interval is proposed. With respect to the Weibull–Gnedenko law, the modified distribution function is described by the following expression [10, 12]:

$$F(\lambda) = 1 - \exp\left\{-\left[\beta(\lambda_{G2} - \lambda_{G1}) \ln \frac{1}{1 - \dfrac{\lambda - \lambda_{G1}}{\lambda_{G2} - \lambda_{G1}}}\right]^n\right\}, \tag{9}$$

where β, n, λ_{G1}, and λ_{G2} are the parameters of the distribution, meaning it be a four-parameter distribution.

At $(\lambda-\lambda_{G1}) << (\lambda_{G2}-\lambda_{G1})$, the logarithmic function in (9) may be expanded into series with only the first term of the expansion left. At this, the distribution (9) reduces to a three-parameter Weibull–Gnedenko distribution of the form (1) with the parameters β, n and λ_{G1}.

The wavelength distribution density $g(\lambda)$ of emitted photons has the following form:

$$g(\lambda)=\frac{\beta n\left[\beta(\lambda_{G2}-\lambda_{G1})\right]^{n-1}}{1-\frac{\lambda-\lambda_{G1}}{\lambda_{G2}-\lambda_{G1}}}\left(\ln\frac{1}{1-\frac{\lambda-\lambda_{G1}}{\lambda_{G2}-\lambda_{G1}}}\right)^{n-1}\times$$
$$\times\exp\left\{-\left[\beta(\lambda_{G2}-\lambda_{G1})\ln\frac{1}{1-\frac{\lambda-\lambda_{G1}}{\lambda_{G2}-\lambda_{G1}}}\right]^{n}\right\}. \quad (10)$$

One can write the following relation for the form factor of the radiation spectral line:

$$I(\lambda)=I_{02}g(\lambda), \quad (11)$$

where I_{02} is the proportionality coefficient.

Finally, we obtain:

$$I(\lambda)=I_{02}\frac{\beta n\left[\beta(\lambda_{G2}-\lambda_{G1})\right]^{n-1}}{1-\frac{\lambda-\lambda_{G1}}{\lambda_{G2}-\lambda_{G1}}}\left(\ln\frac{1}{1-\frac{\lambda-\lambda_{G1}}{\lambda_{G2}-\lambda_{G1}}}\right)^{n-1}\times$$
$$\times\exp\left\{-\left[\beta(\lambda_{G2}-\lambda_{G1})\ln\frac{1}{1-\frac{\lambda-\lambda_{G1}}{\lambda_{G2}-\lambda_{G1}}}\right]^{n}\right\}. \quad (12)$$

An analytical expression for I_{02} cannot be obtained by analogy with the previous case. Therefore, I_{02} is the fifth parameter variable in (12) along with β, n, λ_{G1} and λ_{G2}.

Note that, from the application perspective, the Weibull–Gnedenko distribution is highly flexible in the sense that it can be adapted to approximate a wide range of experimental data by varying its parameters.

In conclusion, we make the following clarifications. Wavelength, not frequency, was chosen as a random variable. This is explained by the fact that its dimension is one of the fundamental units of the International System of Units (SI). In our case, it is length. In turn, frequency has a dimension inverse to such basic unit of the International System of Units as time. Therefore, frequency is a derived quantity.

Fig. 1 shows the results of approximating a spectral line of interband radiative recombination of indium phosphide by using a function of the form (8). Fitting the theoretical curve to the experimental one was performed using the least-squares method. The optimal fitting was obtained at the following parameter values for the form factor (8): λ_S = 19.3 nm, $\alpha = 1.115\cdot10^{-3}$ nm^{-1}, and m = 60.

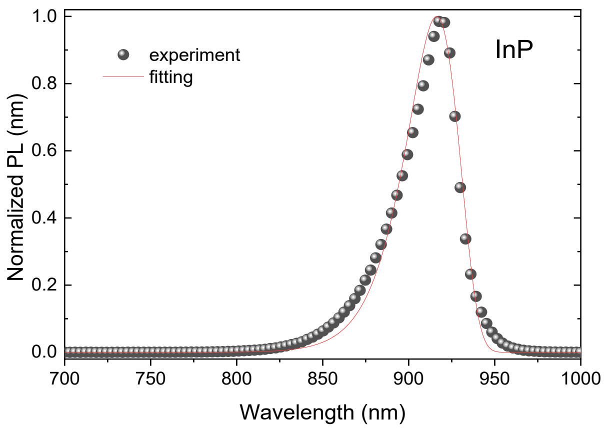

Fig. 1. PL spectrum of InP: circles are the experimental data, line is the fitting.

4. Conclusions

The proposed probabilistic concept of formation of semiconductor emission spectral curves during interband recombination is based on three fundamental principles. The first principle is that interband radiative recombination in semiconductors is caused by a flow of random events such as recombination of nonequilibrium charge carriers, *i.e.* photon emission, and the random variable is the wavelength of the emitted photons. The second principle is formulated as follows: the form-factor of the emission spectral line is determined by the density distribution of a random variable – the wavelength of the emitted photons for the entire set of transitions of nonequilibrium charge carriers within a statistical ensemble of energy levels.

The statistical ensemble includes many energy levels, which appear due to spatial inhomogeneity effects, as well as energy level population effects caused by thermal fluctuations. The third fundamental principle states that the wavelength distribution of the emitted photons is a limited distribution for minima. In turn, the limited distribution of the minimum value of a large number of independently acting quantities is the Weibull–Gnedenko distribution. Approximation of experimentally obtained spectral lines of interband radiative recombination of InP semiconductor crystals by using the form-factors presented in this paper showed good agreement with the theoretical concepts, which testifies appropriateness of the proposed concept to radiative recombination processes.

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Mamykin S.V.: fitting procedure realization, validation.

Ймовірнісні закономірності формування спектральних кривих міжзонної випромінювальної рекомбінації у напівпровідниках

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Анотація. Сформульовано та реалізовано основні принципи ймовірнісної концепції формування профілю спектральних кривих міжзонної випромінювальної рекомбінації в напівпровідниках. Отримано аналітичні співвідношення для форми лінії (форм-фактора) спектральних кривих. Продемонстровано хорошу відповідність між теоретичними передбаченнями та експериментально виміряними спектрами випромінювальної рекомбінації напівпровідникових сполук на основі фосфіду індію.

Ключові слова: напівпровідник, випромінювальна рекомбінація, спектральна лінія, форма лінії (форм-фактор), розподіл Вейбулла–Гнеденко.