Computer Modeling the Excitonic Reflection and Photoluminescence Spectra of GaN Epitaxial Layers

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Abstract

Photoluminescence (PL) and reflection excitonic spectra of GaN single layer grown on sapphire substrate by MOVPE were modeled with aim to estimate a basic parameters of free A- and B- excitons. The calculations were performed in the frame of two-oscillator model for dielectric function ε(E). Three layered model of crystal was used for fitting of reflection spectrum which was measured at T=80K. In this way the dead layer thickness d = 6 nm, resonance energies E_A= 3.4916 eV and E_B = 3.5008 eV as well as the broadening parameters Γ_A = 5.27 meV and Γ_B = 7.14 meV of the free excitons were obtained. These parameters were used then for fitting of PL spectra in assumption of the thermal equilibrium for excitons taking into account the self-absorption of resonance emission. The values of diffusion coefficients D_A = 0.3 cm^2/s, D_B = 0.1 cm^2/s and exciton lifetimes τ_A = 37 ps, τ_B = 17 ps were estimated.

1. Introduction

GaN and related nitrides have attracted strong interest for application such as blue-UV light emitting diodes, blue-UV laser diodes, video displays, full color TV systems, high - density optical memory systems for computer networks. The technological development of GaN based optoelectronic devices makes the investigation of the properties of an excitonic states of great practical importance. Fundamentally the analysis of the line shape of free exciton reflection and PL spectra can provide a way for determination of energetic structure of semiconductors and estimation of basic parameters of radiative recombination processes. However it meets with a serious difficulties practically because of both observed PL and reflection spectra are usually transformed to a variable degree. It is well known that resonance reflectance in region of exciton transitions is very sensitive to state of the surface of the crystal. Various treatments of crystals (illumination, etching, electron and ion

bombardment, field effect, temperature variation, ets.) may alter radically the exciton line shape. The phenomena has been interpreted initially in terms of free exciton layer (FEL) model which was introduced to account for the exciton repulsion from surface arising from the image potential [1]. The interference between light waves reflected at the outer and inner boundaries of the layer proved to have a important role on the reflectivity spectra. We used FEL model in present work to obtain theoretical reflectance curve for comparison with experiment.

It is not such widely known , that the FEL approach can be applied also to solution of the opposite problem: description of excitonic emission from crystal under photogeneration [2]. The experimentally observed PL lineshape in resonance region of free excitons is determined greatly by transmission coefficient of light originating from crystal volume [3, 4]. Solving of this problem can be very useful for interpretation not only excitonic PL spectra but also absorption spectra as well as spectra of Raman and Brillouin scattering [5]. In present work we calculated the transmission coefficient in terms of the PL light interference at the FEL boundaries. Self-absorption of resonance radiation was also taken into account. The results of calculations was used then for fitting of PL spectra of the free A- and B- excitons in the GaN epitaxial layer.

2. Growth and experimental procedure

The 2 μm thick undoped single GaN layer was grown on c-plane sapphire substrate by MOVPE in an AIXTRON reactor. The layer shows n-type conductivity with a free electron concentration $5 \cdot 10^{17}$ cm^{-3}.

Photoluminescence was excited using He-Cd laser with λ_{exc} = 325 nm. The excitation intensity I_{exc} was 0.5 W/cm^2. The PL and reflection spectra were registered using a diffraction monochromator and a photomultiplier and then re-calculated to include the spectral sensitivity distribution of the monochromator - photomultiplier system. The spectral resolution was less than 0.3 meV (20-80K) and <1 meV above 80K.

3. Theoretical calculations

3.1. Reflection spectra

Optical properties of a medium with complex refractive index $\tilde{n} = n - i\kappa$ are determined in investigated spectral region by an excitonic oscillators with following parameters: resonance frequency ω_0 (or energy E_0), the broadening (or decay) parameter Γ, the exciton polarizability $4\pi\alpha$, the background dielectric constant ε_b [5].

We assume a model of two coupled oscillators for the dielectric function near A and B free exciton transition energies:

$$\tilde{\varepsilon}(\omega) = \varepsilon_b + \frac{4\pi\alpha_A\omega_{0A}^2}{\omega_{0A}^2 - \omega^2 - i\omega\Gamma_A} + \frac{4\pi\alpha_B\omega_{0B}^2}{\omega_{0B}^2 - \omega^2 - i\omega\Gamma_B}, \quad (1)$$

where indexes A and B correspond to the A and B exciton states respectively.

To calculate the reflection spectra R(ω) taking into account the interference in FEL we used the methods described in [1] and corresponding formulas:

$$R(\omega) = \tilde{r}(\omega)\cdot\tilde{r}^*(\omega),$$

$$\tilde{r}(\omega) = \frac{r_{12} + \tilde{r}_{23}(\omega)e^{2i\Theta}}{1 + r_{12}\tilde{r}_{23}(\omega)e^{2i\Theta}}, \quad (2)$$

with

$$\Theta = 2\pi d / \lambda_m,$$

where λ_m is the light wavelength within the medium, d is the FEL thickness, and

$$r_{12} = \left(1 - \sqrt{\varepsilon_b}\right)\Big/\left(1 + \sqrt{\varepsilon_b}\right);$$

$$\tilde{r}_{23}(\omega) = \left(\sqrt{\varepsilon_b} - \tilde{n}(\omega)\right)\Big/\left(\sqrt{\varepsilon_b} + \tilde{n}(\omega)\right);$$

$$\tilde{n} = \sqrt{\varepsilon(\omega)}.$$

The complicating factors such as the possible inhomogeneous broadening, the frequency dependence of Γ, the temperature dependence of polarizability and background dielectric constant, as well as the anisotropy of ε_b, were neglected, because the inaccuracy caused by these factors is small [6].

3.2. Luminescence spectra

The evaluation of excitation levels, used in our experiments, shows that at created concentration of carries about 10^{12} cm^{-3} at I_{exc}=0.5 W/cm^2 estimated by generation rate, any degeneracy does not take place. Thus, the radiation line shape is described in steady-state case in one-coordinate approximation by the following equation [7]:

$$I_{PL}(\omega) = \rho(\omega)\left(1 - R'(\omega)\right) \times \int_0^{\hbar} n_{ex}(x)\exp\left(-k(\omega)x\right)dx, \quad (3)$$

where h is the epilayer thickness, $\rho(\omega)$ is the probability per unit time of emitting a photon with the frequency ω by exciton annihilation, $R'(\omega)$ is the reflectivity of light with the frequency ω incident on the surface from the epi-layer, $k(\omega)$ is the absorption coefficient of GaN, $n_{ex}(x)$ is the excitonic concentration. The probability of exciton-photon transition $\rho(\omega)$ was calculated as the probability of the process reciprocal to the absorption of photons [8].

Under the conditions of quasi-equilibrium between the free carrier gas and excitons, the value of $n_{ex}(x)$ can be obtained [7]:

$$n_{ex}(x) = \frac{I_{exc}\,k\,\tau}{L^2 - k^2 - 1} \times \left[\frac{k - \frac{S}{D_{ex}}}{\frac{1}{L} - \frac{S}{D_{ex}}} \exp\left(-\frac{x}{L}\right) - \exp(-kx) \right], \quad (4)$$

where S is the surface recombination rate, k is the absorption coefficient on the pump wavelength, τ is the total life time of exciton, D_{ex} and L are diffusion coefficient and the diffusion length of the exciton respectively.

3.3. Fitting procedure

The optimizing of parameters was carried out by the coordinate-wise descent method [9] with parabolic interpolation. The function

$$F = \sum_{j=1}^{N} \left(Y_{calc_j}(\omega) - Y_{exp_j}(\omega) \right)^2 + \beta \sum_{j=1}^{N} \left[\frac{Y_{calc_j}(\omega) - Y_{exp_j}(\omega)}{\Delta\omega} \right]^2, \quad (5)$$

where N is the number of the experimental points, $Y_{exp\ j}$ and $Y_{calc\ j}$ are experimental and calculated values of the reflectance or the PL intensity, respectively, β is the weight parameter of the curve shape, was used as an "aim function". The first term in (5) characterizes the fitting of absolute values of the reflectivity or the PL intensity, the second one represents the rate of their changes, i.e. the curve shape.

At initial stage of optimization the curve shape had the greater weight (the greater β parameter), then, after each 25 iterations, the parameter α decreased in 0.68 times (the golden mean), which allowed to adjust the absolute values of Y in given spectral region after fitting the shape of the curve.

4. Results and discussion

The major difficulty from standpoint of quantitative analysis of free excitons line-shape of GaN epilayers is the overlapping of PL lines which is observed generally over all temperature region. The PL spectra at low temperature (Fig1.a) exhibit a low intensity PL band $A_{n=1}$ (3.4946 eV) attributed to the free exciton annihilation and a line I_2 bound to the neutral donors , which in reality includes the set of at least three overlapped lines [10].

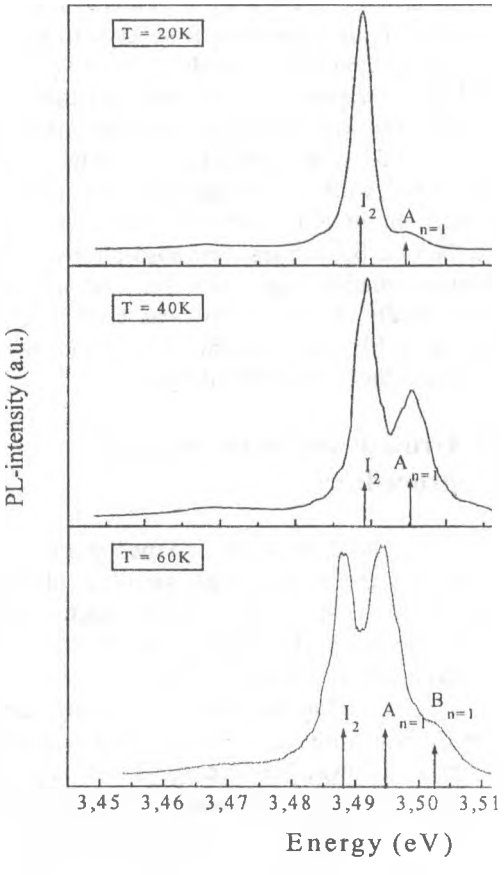

Fig.1. PL spectra of GaN epitaxial layer in the exciton region.

The dominance of bound exciton band in observed PL spectra together with low intensity of $A_{n=1}$ lines gives no way to reliable analysis of free exciton lineshape. Fortunately an increase of temperature leads to an efficient quenching of the bound exciton line due to of small activation energy (Fig.1). The I_2 band disappear gradually from the spectrum above

60-80K. Therefore to avoid problems with overlapping of luminescence lines we used for analysis the PL spectra measured at T=80K. At this temperature, lines related to the annihilation of the free exciton states become dominating in the PL spectra (Fig.2,a).

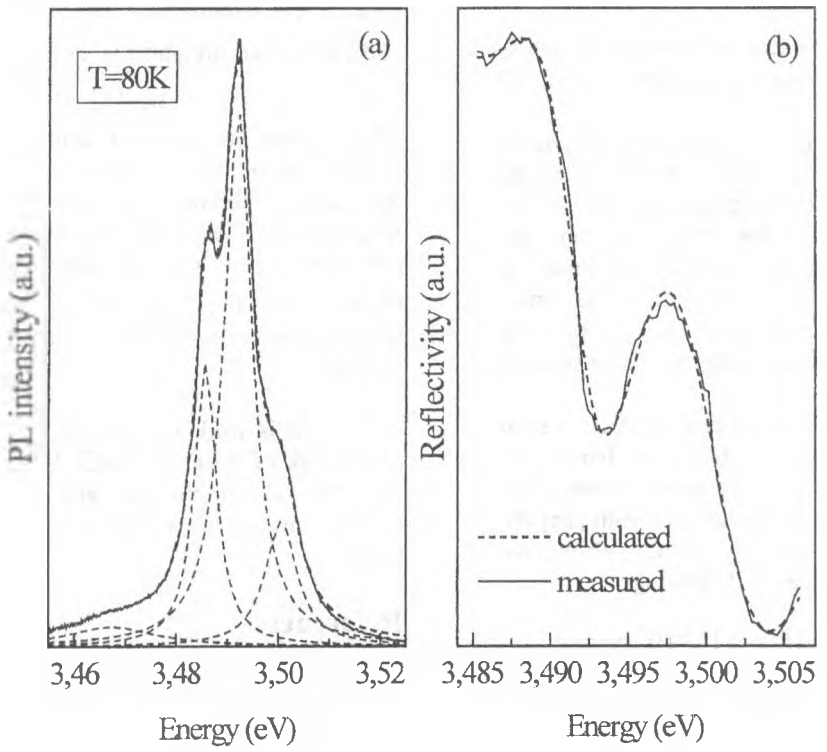

Fig.2. Experimental (solid curves) and calculated (dashed curves) PL (a) and reflection (b) spectra of a GaN sample for T=80K.

An additional reason for our choice was an assumption that the spatial dispersion (SD) effect can be eliminated from consideration at this temperature. Including of the SD effect (it means a dependence of dielectric function $\varepsilon(\omega)$ on wave vector $\bar{k}$) leads to substitution of the additional term $\hbar\bar{k} / M^*$ (where M* is the effective mass of exciton) in to denominator of equation (1). Though the energy position of the exciton resonance E_0 does not depend on whether we include or neglect the SD effect in the calculations [2], the last substitution results in a serious complication of computation procedure.

The temperature region where the SD effect should be taken into account, can be estimated by calculation of the critical broadening parameter Γ_{cr}. The transition to classical dispersion model is marked by the beginning of the strong temperature broadening of the exciton absorption band (or, what is the same, of the Γ parameter) [11]. It means that Γ parameter must be greater than the Γ_{cr} at fixed temperature.

Calculation of Γ_{cr} was performed using formula [11]:

$$\Gamma_{cr} = \sqrt{\frac{\hbar\omega_T^2 \varepsilon_b \Delta_{LT}}{2M^* c^2}},$$

where $\Delta_{LT} = \omega_0\left(\sqrt{1+\frac{4\pi\alpha}{\varepsilon_b}} - 1\right)$ is the longitudinal-transversal splitting, and $\omega_0 = \omega_T$ was assumed. The calculation gives Γ_{crA}=4.8 meV and Γ_{crB}=6.8 meV for A- and B- exciton respectively, if we admit $M^* = 0.97m_0 = 0.49567\times10^6$ eV [13], $4\pi\alpha_A=2.7\times10^{-3}$ [14], $4\pi\alpha_B=3.1\times10^{-3}$ [14] and ε_b=5.2 [14].

The fitting of experimental reflection spectrum was performed using the procedures described above to check the admissibility of neglecting of SD effect. The experimental and calculated reflection spectra are given in Fig.2 demonstrating an excellent agreement among them. The next parameters of exciton transitions of epitaxial layer GaN were evaluated:

$E_{0A}= \hbar\omega_{0A}$ =3.4912 eV,

Γ_A = 5.27 meV,

$f_A = 0.0043$,
Δ_{LTA} =9.1 meV (for $A_{n=1}$ exciton);

$E_{0B} = 3.5008$ eV,
$\Gamma_B = 7.14$ meV,
$f_B = 0.0049$,
Δ_{LTB} =1.0 meV (for $B_{n=1}$ exciton);
d = 6.1 nm.
The values of the oscillator strength f_A and f_B were calculated using the equation $f = \alpha / 0.2$ [15].

The values of broadening parameter obtained from the "best fitting" of the experimental reflection spectra exceed the corresponding critical ones. Thus, we can conclude that SD effect does not play an important role at indicated temperature. The most probable cause of that is a possible inhomogeneous broadening of the excitonic lines.

Integrated absorption coefficient K of A- and B- free exciton absorption bands was also estimated using the obtained values of the oscillator strength. In accordance with [16] the total integration intensity of the absorption peak can be expressed as following :

$$K = \int k(E)dE = 110 \cdot 10^6 \frac{f}{n\Omega_0}$$

where Ω_0 -is the volume of GaN lattice cell (in A^3), n is the refractive index.

Using of our data we evaluated integrated absorption coefficient to be $K_A = 4.459 \times 10^3$ eV/cm and $K_B = 4.149 \times 10^3$ eV/cm for A - and B- exciton bands respectively.

To calculate $I_{PL}(E)$, the parameters E_0, Γ and d obtained from results of the fitting of the experimental reflection spectra were used. The reflection coefficient of excitonic radiation falling on the surface from volume of the epilayer $R'(\omega)$ was calculated at fixing of these parameters. Formulas analogous to (2) was used, where r_{12} is replaced by the complex reflectivity at inner plane of FEL $\tilde{r}_{12}$ and instead of $\tilde{r}_{23}$ the real reflectivity at external surface of sample r_{23} is used. The absorption coefficient k(ω) was calculated as $\frac{2\omega \operatorname{Im} \tilde{\varepsilon}(\omega)}{c}$, where c is velocity of light.

Parameters $I_{exc} = 1.6 \times 10^{18}$ photon$\times$cm^{-2}s^{-1}, k = 10^6 cm^{-3} and S=100 cm/s were used. The PL intensity calculations were performed separately for each exciton band and then results were summed. The simple Lorentz model was used for modeling of emission bands placing in low energy side from A-exciton peak position. Only two free exciton parameters, namely the exciton diffusion coefficient and the exciton lifetime were varied during of fitting procedure described above. The the experimental and calculated PL spectra are given in fig.2,a.

By fitting the experimental PL spectra, the exciton diffusion coefficient D_{ex} and the exciton lifetime τ were estimated: D_{ex}^A = 0.3 cm^2/s, τ_A = 36 ps, D_{ex}^A = 0.1 cm^2/s, τ_B = 17 ps, giving the values of diffusion length L_A = 0.033 μm and L_B = 0.013 μm. As one can see the exciton lifetimes and values of diffusion length in our sample is very short, such that diffusion processes can be neglected. It should be noted that the value of τ is confirmed by time-resolve experiments in the picosecond regime.

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