Polaron-related states in the photoluminescence of gallium nitride crystal

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Abstract. Polaronic model of luminescence processes in nominally pure gallium nitride has been proposed and developed. The model is based on two mechanisms which co-exist and are of a common origin. One of them is recombination luminescence of charge transfer vibronic excitons (bi-polaronic excitons) trapped by charged defects with different effective charge, like Ga- or N-related vacancies with different number of trapped electrons or holes, or interstitial O$^{2-}$ and O$^-$ ions, in the visible range (yellow-green luminescence). The other is recombination luminescence (blue band) of non-correlated self-localized electronic and hole polarons in the violet region. The model allows us to explain experimental results including the fine structure of yellow – green luminescence.

1. Introduction

Interest in gallium nitride and related nitride wide-band-gap semiconductors is associated with swelling use in optoelectronic devices operating in the green to ultraviolet spectral range. Consequently, a thorough understanding of the electronic and radiation properties of such materials is of fundamental importance. In spite of excellent success in the light-emitting devices technology based on III-nitrides, the mechanism of effective radiation in both the green - yellow and blue luminescence bands is not yet fully clarified. Different models, including transitions from a shallow donor or the conduction band to a deep acceptor, from a shallow donor to a deep donor have been proposed to explain that luminescence, but it is still an open question (see [1] and references therein). In present paper a different approach to analyze green - yellow luminescence has been suggested.

Green or Yellow-Green Luminescence (GL) in undoped ionic-covalent crystals with strong enough electron-lattice interaction is a very well known phenomenon especially for ferroelectric oxide crystals [2-10]. This phenomenon was explained during the last years as a result of recombination of self-localized Charge Transfer Vibronic Exciton CTVE (see [10] and references therein). CTVE state (bi-polaronic charge transfer exciton) was verified on the basis of both GL investigations and comparison of these experimental results with quantum-chemical computations for extended system of ionic-covalent crystals [4, 6-8].

In the present work a new GaN matrix from the same extended group with respect to ionic-covalent behaviour has been investigated. In order to elucidate the origin of luminescence-active states we could consider the essential electron-lattice interaction in GaN. Namely, such an approach is key-like and makes it possible to ground bi-polaronic excitons effect. The approach leads to experimental data explanation in the framework of phenomenological treatment based on the Landau type "charge

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transfer – lattice displacements” expansion [10]. Moreover, direct contribution of the charged defect fields that are typical of GaN case has been taken into account.

2. Experimental results and interpretation

GaN epilayers of thickness d ~ 3 ÷ 4 µm are grown on a (0001) sapphire substrate by metal-organic chemical-vapor deposition (MOCVD) epitaxy. They are Si-doped with electron concentration \(2\times10^{17} \text{cm}^{-3}\). Hall measurements indicated mobility 400-600 cm\(^2\text{V}^{-1}\text{s}^{-1}\) at room temperature. TEM has revealed perfect bulk structural properties and AFM probing has shown the atomically smooth surface. Photoluminescence spectra have been studied using He-Cd laser excitation (325nm) with power 25 W/cm\(^2\).

Photoluminescence studies of GaN epilayers exhibit two characteristic bands. First, a broad band (2.0 eV - 2.35 eV), so called the Yellow-Green Luminescence band, has been observed. The band exhibits a sample dependent line shape modulation that is presented feature (figure1). Here, the period of a modulation is equal to approximately 0.09 eV and 0.07 eV for the samples “1” and “2”, respectively. Second, more narrow “blue” luminescence (BL) band centered at 3.1 eV and at 3.2 eV in violet range (figure2) co-exists with GL band presented above. BL band corresponds to emission impending GaN energy gap. In the close vicinity of energy gap the Wannier-Mott excitonic photoluminescence band (~360nm) is observed.

![Figure 1. Room temperature photoluminescence spectra of n-type GaN epilayers: 1 – thickness d=3.3 µm, 2 – thickness d=4.0 µm. Light excitation of He-Cd laser with power 25 mW/cm\(^2\).](image_url)

Three aspects are important in connection with such behaviour: the elucidation of GL nature as well as BL nature and of the mechanism of GL line shape modulation in GaN.

The analysis of quantum energy values as well as of line shape features for GL and blue-luminescence detected allows us to suggest the polaronic nature for both of them. Indeed, in the framework of the approach suggested we treat GL as a result of GaN related CTVE recombination. Then, GL co-exists with BL which corresponds to emission impending GaN energy gap. These facts allow us to treat this type of luminescence again as a result of a electron polaron – hole polaron
recombination but for non-correlated localized polarons case. Indeed, the CTVE-formation provided by UV-pumping creates electrons and holes in conduction and valence bands respectively with their following transformation in to electronic and hole polarons and, finally, to correlated electronic polaron – hole polaron pairs (CTVEs) originating GL phenomenon. In fact, electronic and hole polarons can directly recombine resulting in BL in parallel way. The latter leads to BL, which co-exists with GL naturally as the second channel of common origin recombination process.

Last not the least, the CTVEs obey strong by enough electric dipole moment interacting with internal electric fields and with corresponding polarizations. Special role in such an interaction belongs to the CTVEs trapped by charged defects with different own effective charges. Among this type defects Ga- and N-related vacancies [1] with different number of trapped holes and electrons (and hence, with different effective charges) as well as O$^-$ and O$_2^-$ interstitial ions [1] could be an efficient source of internal local polarization responding to the trapped CTVEs.

![Figure 2](image.png)

**Figure 2.** Room temperature photoluminescence spectrum in the violet range, near band gap emission (Wannier-Mott excitonic) band, and blue band centered at 380 nm are presented. Light excitation is He-Cd laser.

As a result, these differently charged defects lead in this context to the superposition of a system of GL lines with the same spacing but with different intensities. They could be treated as simultaneous effect of the recombination of the free CTVEs in the bulk (corresponding to the central, strongest GL line, figure1) on the one hand, and the CTVEs trapped by strong Coulomb defects creating some definite internal electric field, which induces side GL lines (figure1), on the other hand. Indeed, this field leads to definite shifts of different CTVE-minima that cause diversity of emission bands (see figure3). Moreover, we have to deal with a set of such a GL lines with divisible shifts of new lines, and with their characteristic period defined on the energy scale. That is, the GL spectral superstructure is appearing.

Then, the model of periodic modulation for the GL band explains both experimental effects: periodic GL line structure and definite sample dependence of modulation period (see figure1).

Note, that BL doublet structure (see figure2) can be related to co-existence of two type geometries for electronic polaron - hole polaron non-correlated pairs which active in recombination luminescence. Namely, these are two geometries with two types of the dipole pair directions: along the $C_6$ axis and
visa versa. Here, polar crystalline field near the surface leads to pseudo-Stark splitting of corresponding levels for polaronic pairs with dipole moments in the opposite directions. Note also, that these pairs are corresponded to highly excited states and are not related to trapping on the charged defects as the low lying states of the CTVEs discussed above.

3. Theoretical analysis of the Yellow-Green Luminescence phenomenon

We propose to use phenomenological approach for GL spectral dependence treatment which is based on the ‘charge transfer – lattice displacements’ expansion of the system free energy [10].

\[
\begin{align*}
\hbar \omega_{GL} &= \Delta E - \frac{2K(\Delta E)^2}{(4K\alpha - C^2)} \left\{ 3 + \frac{C^2}{(4K\alpha - C^2)} \right\} \pm n \frac{4\pi}{3} \gamma_{eff} d_{CTVE} E_{loc} \quad (1)
\end{align*}
\]

where parameter \( \Delta E \) is the electronic part of the CTVE-excitation energy \( \Delta Eq \), where \( q \) is the charge transfer magnitude. Parameters \( C, K, \alpha \) [10] \( (K > 0, \alpha > 0) \) correspond to parameters of the bilinear charge transfer - lattice interaction, to elasticity parameter for quasi-local harmonic vibrations, and to elasticity parameter for charge transfer harmonic fluctuations of CTVE-active ionic pair respectively. Other parameters \( \gamma_{eff}, d_{CTVE}, E_{loc} \) are average local field factor for the CTVE, its effective electric dipole moment, and local electric field acting on the CTVE trapped by charged defect, respectively. At last, factor \( n \) is related to effective charge of such a trapping center and equals to \( n = 0, 1, 2 \ldots \) .

Figure 3. Internal defect field induced pseudo-Stark splitting of CTVE-states accompanied by Yellow-Green Luminescence band GL splitting on two, GL +, and GL −, bands.
We assume here that the criterion of the charge transfer – lattice instability, $C^2 > 4K\alpha$, is not fulfilled, although the situation of the proximity to such an instability is not disregarded. The last situation leads to GL strengthening.

It is seen that the last item in (1) could be responsible for periodic spectral GL super-structure appearance detected here. This term is really sample dependent due to rather different values of local electric fields induced by different type Coulomb-type trapping centers for CTVEs.

We can conclude that such a phenomenon can be treated as the superposition of a set of GL lines with the same spacing but with different intensities. This is the simultaneous effect of the recombination of both the free CTVEs in the bulk and the CTVEs trapped by strong defects creating some definite internal electric field. These fields lead to definite shifts of different CTVE-minima that cause diversity of emission bands as well as their periodic spectral super-structure.

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