Photoluminescence Characterization of Nonradiative Recombination Centers in Light Emitting Materials by Utilizing Below-Gap Excitation:
A Mini Review of Two-Wavelength Excited Photoluminescence

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Abstract

We have developed an optical method of detecting and characterizing nonradiative recombination (NRR) centers without electrical contact. The method combines a below-gap excitation (BGE) light with a conventional above-gap excitation light in photoluminescence (PL) measurement, and discriminates the PL intensity change due to switching on and off the BGE. A quantitative analysis of the detected NRR centers became possible by utilizing the saturating tendency of the PL intensity change with increasing the BGE density due to trap filling effect. Some experimental results of AlGaAs, InGaN, and AlGaN quantum wells were shown to allocate the development and present status as well as to exemplify their interpretations.

Keywords: Internal quantum efficiency; photoluminescence; nonradiative recombination; below-gap excitation; defect states.

INTRODUCTION

Light emitting diodes (LEDs) and laser diodes (LDs) in near infrared region realized fiber communication systems in 1970's [1] and provided an infrastructure of the world wide web of huge digital data link. The realization of blue and green LEDs through steady efforts on crystal growth technique of GaN [2-3] opened another revolution in lighting and display applications since three primary colors have been provided by efficient solid state light sources. Light-based science and technology are becoming more and more important for human society as vast information comes from our sense of sight.

An electron in a conduction band (CB) of a semiconductor recombines with a hole in a valence band (VB) either radiatively or nonradiatively [4-5]. The rate of radiative recombination is calculated by the electronic dipole moment, initial and final state wave functions of the material. The rate of nonradiative recombination (NRR) depends both on the nature of the material and deviation from its ideal crystalline lattice. Lattice defects introduced during crystal growth form localized electronic states inside the forbidden energy gap and act as NRR centers whose recombination rates are described by SRH statistics [6]. The internal quantum efficiency is determined by the competition between radiative and NRR rates and the latter depends on the density of NRR centers except extremely high injection condition. Therefore it is crucial for us to detect, clarify and reduce such NRR centers.

Photoluminescence (PL) is widely used as a standard method of evaluation by using an above-gap excitation (AGE) light whose photon energy hv_A is higher than the forbidden energy gap E_g of the material. It gives relative efficiency but no information why such difference arises. Defect states have been studied by photoconduction, photo-capacitance, and deep level transient spectroscopy (DLTS) [7], though they need electrical contact with geometric restrictions. It is desirable to characterize NRR centers directly without electrode.

STUDY BY BELOW-GAP EXCITATION

The use of below-gap excitation (BGE) light with the photon energy hv_B lower than the E_g can be traced back to early qualitative works on absorption and photoconductivity. Spectral dependence of photo-quenching properties in Cu-doped n-type GaP was studied by Grimmeiss and Monemar [8]. Excitation and quenching measurements of a donor-acceptor emission were performed for a deep O donor level in GaP [9]. Tajima used a temporal modulation of the excitation light and made a comparative study of deep levels in undoped GaAs [10].

Consider one NRR center with the density N_t and electron occupation function f_t in the forbidden gap as shown in Fig. 1(a). Under the AGE and the BGE rates G_1 and G_2, respectively, the occupation function f_t, electron and hole densities n and p at both CB and VB are expressed as follows based on SRH statistics [6];

$$\frac{dn}{dt} = G_1 - Bnp - nC_n N_t(1 - f_t)$$

(1)
$$\frac{dp}{dt} = G_1 - Bnp - pC_p N_t f_t + G_2 N_t(1 - f_t)$$

$$\frac{df_t}{dt} = (nC_n + G_2)(1 - f_t) - pC_p f_t$$

$$n + N_t f_t = p + N_0$$

Here B, C_n, C_p, N_0 are radiative recombination coefficient, electron and hole capture rates and donor density, respectively. In this one level model, the BGE raises f_t value, which reduces electronic capture from CB and increases both n and p, resulting in an increase of the PL intensity Bnp.

Next, suppose two mid-gap states 1 and 2 exist and the BGE produces electronic excitation between them as shown in Fig. 1(b). We assume that the NRR to the VB is the dominant process of electrons in the state 2. In the two levels model, the occupation functions of both states f_{t1} and f_{t2}, electron and hole densities n and p at both CB and VB are expressed as;
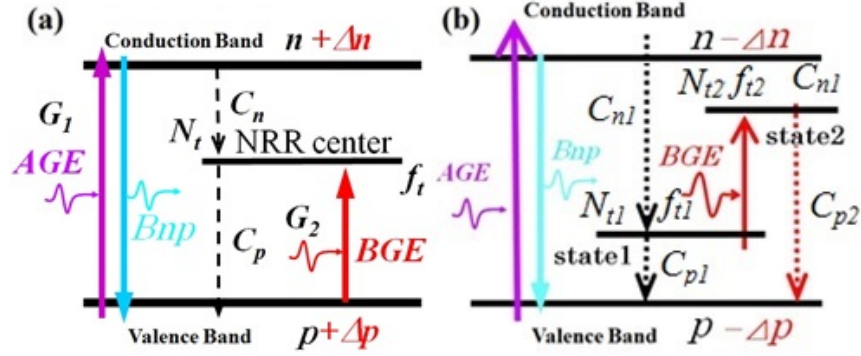
Fig. 1. (a) One level model and (b) two levels model

$$\frac{dn}{dt} = G_1 - Bnp - nC_{n1}N_{t1}(1 - f_{t1})$$

$$\frac{dp}{dt} = G_1 - Bnp - pC_{p1}N_{t1}f_{t1} - pC_{p2}N_{t2}f_{t2}$$

$$\frac{df_{t1}}{dt} = nC_{n1}(1 - f_{t1}) - pC_{p1}f_{t1} - G_2f_{t1}N_{t2}(1 - f_{t2})$$

$$\frac{df_{t2}}{dt} = G_2N_{t1}f_{t1}(1 - f_{t2}) - pC_{p2}f_{t2}$$

$$n + N_{t1}f_{t1} + N_{t2}f_{t2} = p + N_0$$

(2)

Here the BGE raises f_{t2} and reduces f_{t1}, which enhances the electronic capture from the CB to the state 1. As both n and p are reduced due to the BGE, the PL intensity Bnp decreases in contrast to the previous increase in the one level model.

Therefore any increase or decrease of the PL intensity due to the addition of the BGE implies a sign of NRR centers which can be interpreted by either one level model or two levels model at their simplest form. Measurements of GaAs-based quantum wells (QWs) [11-21], GaN/InGaN-QWs [19-23], AlGaN-QWs for deep UV wavelength region [24-25], GaPN [26-27] and $Ba_3Si_6O_{12}N_2$: Eu^{2+} phosphors [28] have been done by such straightforward experimental principle.

IMPROVEMENT OF TWO-WAVELENGTH EXCITED PL
When the f_t value in Fig. 1 (a) approaches unity or zero, the electronic flow from the CB or that of hole from the VB becomes impossible. Resultant saturation of the NRR rate is called as the trap-filling effect [29] and the PL enhancement shows saturation with increasing the BGE density. Suppose the value of f_{t2} in our two levels model of Fig. 1 (b) approaches to unity ($f_{t2} \rightarrow 1$) with increasing the BGE density. It limits further electronic

excitation even though the BGE density increases and the PL quenching shows eventually saturating tendency.

Observation of such saturating tendency is beneficial to improve the precision of our quantitative analysis since one variable, an electronic occupation function, can be set unity or zero in the model. We use the word "Two-Wavelength Excited PL (TWEPL)" in the context of such improved analytical scheme by utilizing the trap-filling effect [12-13, 19].

EXPERIMENTAL PROCEDURE

The TWEPL setup is basically that of PL measurement. Sample is set inside a cryostat whose temperature can be controlled down to 4K. Both the AGE and the BGE light sources are combined according to the material and purpose of the measurement. The PL from the sample is fed to a photo-multiplier or a CCD camera via a monochromator. The scheme of either single photon counting [14] or phase sensitive detection of analog output by a lock-in amplifier can be chosen.

A CW AGE light produces a constant PL, while the BGE light is switched on and off by an optical chopper or a current pulse in case of LDs. The normalized PL intensity is defined as the ratio between the PL intensity with and without the BGE as $I_N = I_{AGE+BGE} / I_{AGE}$. Any change of the I_N from unity indicates the presence of NRR centers.

It is a non-contacting and non-destructive measurement with no geometric restrictions of samples. The excitation beam can be scanned on whole wafer or can be focused down to 200 nm, even below the diffraction limit by using evanescent mode. The tuning of the AGE photon energy, i. e. AGE spectroscopy, selects the layer to be excited. The BGE spectroscopy clarifies the energy distribution of detected NRR centers.

DETECTION OF NRR CENTERS
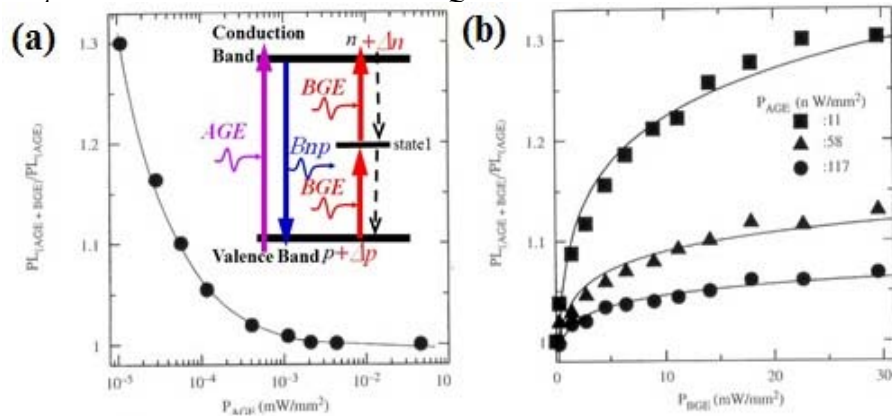
A. Upconversion luminescence in AlGaAs MQW.

Fig. 2. (a) The AGE and (b) the BGE density dependence of I_N in an undoped GaAs/Al$_{0.20}$Ga$_{0.80}$As MQW.

We studied an undoped GaAs/Al$_{0.20}$Ga$_{0.80}$As multiple QW (MQW) grown at 700℃ by MOCVD technique [15]. The MQW region consists of 20 periods of 7nm well and 7nm barrier layers. A He-Ne laser ($hv_A = 1.96$eV) and a Nd:YAG laser ($hv_B = 1.17$eV) were used as the AGE and the BGE light sources. Both the AGE and the BGE density

dependence of the normalized PL intensity I_N were shown in Fig. 2 (a) and (b), respectively. The enhancement of the I_N values with decreasing the AGE and increasing the BGE density agree well with the one level model based on rate equations (1).

In addition to the BGE effect of the PL intensity increase, we noticed that the band-edge PL from well layers, center energy about 1.56eV, appeared only under the BGE irradiation. As the PL peak intensity was proportional to the BGE density, it was not due to a two-photon process but attributed to an up-conversion luminescence via the mid-gap level as shown schematically in the inset of Fig. 2 (a). It directly exemplifies our interpretation by the one level model [15-16].
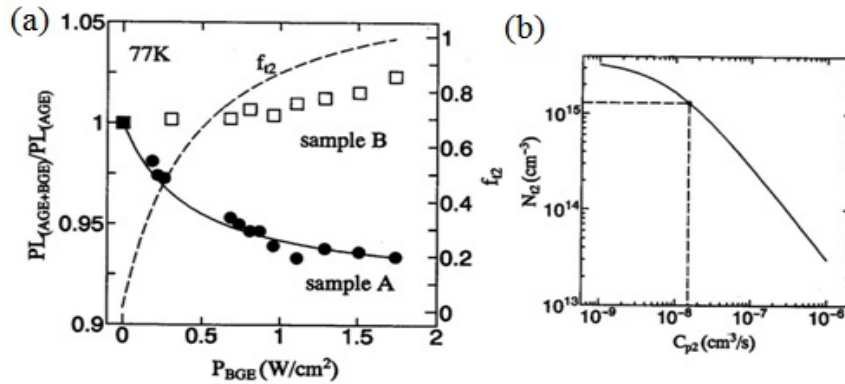
B. First quantitative determination of NRR centers

Fig. 3. (a) The BGE density dependence and (b) the relation between
C_{p2} and N_{t2} in a Se-doped GaAs/Al$_{0.20}$Ga$_{0.80}$As MQW.

A decrease of the PL intensity due to the BGE was observed in the same layered structure but Se-doped GaAs/ Al$_{0.20}$Ga$_{0.80}$As MQW with the doping concentration of 7.5×10^{16}cm^{-3} (sample A) [12]. A visible LD ($h\nu_A$=1.81 eV) and a filtered Xe lamp output ($h\nu_B$=1.20 eV) provided the AGE and the BGE light, respectively. The normalized PL intensity of the sample A decreased from unity with increasing the BGE density and showed a saturating tendency as shown in Fig. 3(a). A set of parameters for the state 1 was determined by systematic PL measurements including the AGE density dependence, quantum efficiency and recombination lifetime as C_{n1}=5.0x10^{-10}cm^3/s, C_{p1}=9.1x10^{-9}cm^3/s and N_{t1}=3.4x10^{16}cm^{-3}. Then by assuming the trap filling condition $f_{t2} \rightarrow 1$ at enough high BGE regime, we obtained the relation between C_{p2} and N_{t2} as shown in Fig. 3 (b). By curve fitting of each pair values, the best fitted result with the parameters C_{p2}=1.5x10^{-8}cm^3/s and N_{t2}=1.3x10^{15}cm^{-3} was shown by the solid curve in Fig. 3 (a). This is the first quantitative determination of NRR centers detected by the TWEPL method [12-13].

In Si-doped GaAs/Al$_{0.2}$Ga$_{0.8}$As MQWs with Si densities of 7x10^{16} and 5x10^{17} cm^{-3}, two levels were detected by the BGE energy of 0.751 and 1.165eV in Al$_{0.4}$Ga$_{0.6}$As outer barrier layers [18], which correspond to the DX center [30]. Time response [21] and temperature dependence [22] of the BGE effect were studied by GaN/InGaN MQWs. Decrease of the BGE effect with increasing temperature is consistent with the prediction of rate equations (2), though more quantitative analysis is necessary to clarify the origin of each NRR centers.

C. Spatial and Energy distribution in InGaN MQW

Spectroscopic study in terms of both the AGE and the BGE energy has been accomplished for a Si-doped $In_{0.3}Ga_{0.7}N/In_{0.04}Ga_{0.96}N$ QW structure with three $In_{0.3}Ga_{0.7}N$ wells (3 nm) separated by $In_{0.04}Ga_{0.96}N$ barriers (5nm) on a GaN buffer layer (20μm) [20]. We denote band-gap energies of the $In_{0.3}Ga_{0.7}N$ well, the $In_{0.04}Ga_{0.96}N$ barrier and the GaN buffer layers as E_{g1} (=2.93 eV), E_{g2} (=3.36 eV), and E_{g3} (=3.46 eV), respectively.

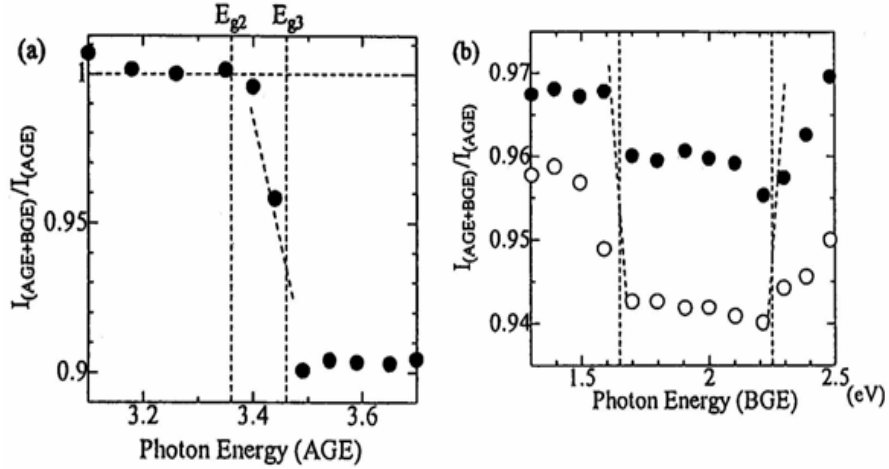Fig. 4. (a) The AGE and (b) the BGE energy dependence of I_N in Si-doped $In_{0.3}Ga_{0.7}N/In_{0.04}Ga_{0.96}N$ MQW.

The AGE energy dependence of the normalized PL intensity at 77K, shown in Fig. 4 (a), revealed a distinct decrease at above E_{g3} as we take into account a relatively wide spectral resolution of the AGE light. It implies that the detected NRR centers are not inside the MQW region but in the GaN buffer layer. The BGE energy dependence was measured at the fixed AGE energy of 3.65 eV as shown in Fig. 4 (b) [20-21], which can be correlated with the result of trap distribution in GaN by electrical measurements [31].

In case of Si-doped $GaAs/Al_{0.2}Ga_{0.8}As$ MQWs with doping density of $1x10^{18}cm^{-3}$, the AGE spectroscopy revealed NRR centers in both 50nm barrier and 6nm well layers of a uniformly doped MQW by the BGE of 1.165eV. In a modulation-doped MQW with the Si-doping only center part of the barrier layers, such NRR centers were not detected inside the well layers [17]. The advantage of the modulation-doping for optical properties was first pointed out in 1986 [32] and exemplified directly by the TWEPL measurement.
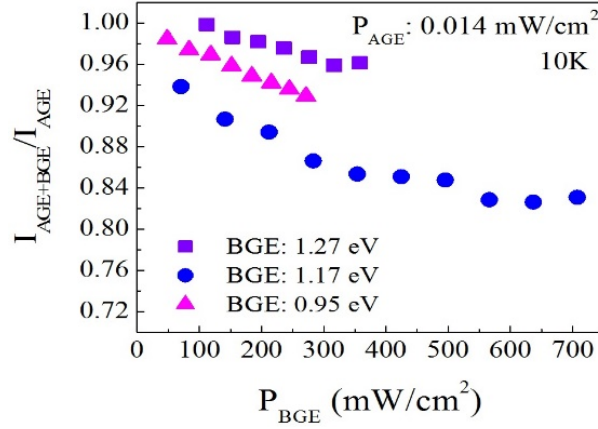
D. AlGaN MQWs for Deep UV Light Emitters.

Fig. 5. The BGE density and energy dependence of I_N in Si-doped AlGaN MQW for deep UV LED.

We studied an MOCVD-grown Si-doped AlGaN MQW with Si density of 1.6×10^{16} cm^{-3}, PL peak wavelength of 285 nm at 10K, thickness of wells and barriers 2 nm and 8 nm, respectively [24]. An SHG Ar-ion laser (hv_A=5.08 eV) was used as the AGE and a Nd:YAG laser (hv_B=1.17 eV) and LDs (hv_B=0.95 eV and 1.27 eV) were used as the BGE sources. The I_N decreased with increasing the BGE density as shown in Fig. 5, indicating the presence of NRR centers described by two levels model. The BGE energy dependence gives us a direct clue for determining the origins and improving the growth condition. An incorporation of small amount In is effective for improving the internal quantum efficiency, but quite sensitive to the growth temperature [25]. These results are to be discussed with previous reports on deep levels in AlGaN as a function of Al composition [33-35].

CONCLUSIONS

By superposing the BGE light on that of AGE and observing the PL intensity change, NRR centers can be detected and discriminated spatially (AGE spectroscopy) and energetically (BGE spectroscopy). The method of TWEPL opened a key research field of detecting and characterizing NRR centers which originate from lattice defects and are essential factors for improving the internal quantum efficiency. We have studied mainly GaAs- and GaN-based MQWs, and are expanding to phosphors and wider optical and electronic materials. Detection of NRR centers depends mainly on the output and tuning properties of BGE light sources. In spite of many results of detecting NRR centers, there are only a few quantitative analyses due to a number of NRR parameters. Non-contacting, non-destructive and spectroscopic nature of the method can be utilized to understand NRR mechanisms and improve device performance by more comprehensive approach.

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