Physical implications of activation energy derived from temperature dependent photoluminescence of InGaN-based materials*

Jing Yang(杨静)[1], De-Gang Zhao(赵德刚)[1,2,†], De-Sheng Jiang(江德生)[1], Ping Chen(陈平)[1], Zong-Shun Liu(刘宗顺)[1], Jian-Jun Zhu(朱建军)[1], Xiang Li(李翔)[1], Wei Liu(刘炜)[1], Feng Liang(梁锋)[1], Li-Qun Zhang(张立群)[3], Hui Yang(杨辉)[1,3], Wen-Jie Wang (王文杰)[4], and Mo Li(李沫)[4]

[1] *State Key Laboratory on Integrated Optoelectronics, Institute of Semiconductors, Chinese Academy of Sciences, Beijing* 100083, *China*
[2] *School of Electronic, Electrical and Communication Engineering, University of Chinese Academy of Sciences, Beijing* 100049, *China*
[3] *Suzhou Institute of Nano-tech and Nano-bionics, Chinese Academy of Sciences, Suzhou* 215123, *China*
[4] *Microsystem & Terahertz Research Center, Chinese Academy of Engineering Physics, Chengdu* 610200, *China*

(Received 5 March 2017; revised manuscript received 7 April 2017; published online 17 May 2017)

Physical implications of the activation energy derived from temperature dependent photoluminescence (PL) of InGaN-based materials are investigated, finding that the activation energy is determined by the thermal decay processes involved. If the carrier escaping from localization states is responsible for the thermal quenching of PL intensity, as often occurs in InGaN materials, the activation energy is related to the energy barrier height of localization states. An alternative possibility for the thermal decay of the PL intensity is the activation of nonradiative recombination processes, in which case thermal activation energy would be determined by the carrier capture process of the nonradiative recombination centers rather than by the ionization energy of the defects themselves.

Keywords: nitride materials, temperature dependent photoluminescence, activation energy

PACS: 71.20.Nr, 71.55.Eq, 73.21.Fg **DOI:** 10.1088/1674-1056/26/7/077101

1. Introduction

InGaN-based materials and the related metal organic chemical vapor deposition (MOCVD) growth technology have attracted a great deal of attention for their successful applications in light emitting devices.[1–4] Being different from GaAs-based materials,[5] the defect density of InGaN-based materials is much higher, but surprisingly, their internal quantum efficiency can still reach as high as 80%–95%. During the last few years, many groups have investigated the emission mechanism of InGaN/GaN multiple quantum well (MQW) materials by using temperature dependent photoluminescence (PL), x-ray diffraction (XRD), and transmission electron microscopy (TEM). These researchers have proposed attributing the high emission efficiency to the existence of localized luminescence centers, with the carriers having only a low probability of interacting with nonradiative recombination defects such as dislocations.[6–8] In this scenario, the defects have little impact on the emission efficiency of the InGaN-based materials, but at high temperature or at high injection current, some kinds of defects may in fact affect the electrical and properties of the devices. So studying and identifying the defects in InGaN-based materials is still very important. In fact, it is known that a lot of defects can introduce intermediate levels in the band gap of III-nitride materials, and through these intermediate levels some carriers can trigger radiative recombination, generating emission peaks such as yellow or blue emission bands in GaN. The intensity of these defect related emission peaks often decreases when the temperature is raised. The activation energy of the corresponding radiative process can often be derived by fitting the temperature dependent integrated PL intensity of a particular emission band, using the Arrhenius plot for GaN materials[9]

$$I_{\rm int}(T) \propto \frac{I_0}{1 + C_0 \exp\left[-E_0/(k_{\rm B}T)\right]}, \tag{1}$$

where $k_{\rm B}$ is Boltzmann's constant and I_0 is the integrated PL intensity at 0 K. Among the fitting parameters, E_0 is the activation energy of the corresponding radiative process, and C_0 is the rate constant related to the density of the radiative defects. Experimentally, E_0 is often derived from the slope of the linear parts of the $\log(I_{\rm int})$–$1/T$ curve. Normally, this fitting serves to obtain the thermal ionization energy of the radiative defects[10–12] and to help identify the defects in the GaN material involved in the related temperature-dependent emission band. In the same way, some researchers have tried to fit the temperature dependent integrated PL intensity of the interband emission with Eq. (1) for the InGaN or GaN materials to obtain the activation energy of the nonradiative recombination centers.[9,13,14] However, because the effective luminescence decay mechanism of the interband emission (nonradiative recombination process activation) differs from the radia-

*Project supported by the National Key R&D Program of China (Grant Nos. 2016YFB0401801 and 2016YFB0400803), the National Natural Science Foundation of China (Grant Nos. 61674138, 61674139, 61604145, 61574135, 61574134, 61474142, 61474110, 61377020, and 61376089), Science Challenge Project, China (Grant No. JCKY2016212A503), and Beijing Municipal Science and Technology Project, China (Grant No. Z161100002116037).

†Corresponding author. E-mail: dgzhao@red.semi.ac.cn

© 2017 Chinese Physical Society and IOP Publishing Ltd

tive defect related PL emission (bounded carriers re-excited back to the valence/conduction band), the physical meaning of the fitted activation energy E_0 of the interband transition emission for the InGaN or GaN material must be different from that of the radiative defect related emission. In addition, in InGaN materials, many localized luminescence centers may exist. It also influences the thermal decay process of the PL peak. Thus, analysis of the activation energy E_0 for the interband emission of the InGaN material is more complex. In the present work, we investigate, in detail, different possible physical meanings of the activation energy obtained from the temperature dependent PL intensity of the InGaN-based material.

2. Experiment

An InGaN/GaN MQW sample was grown by an AIXTRON 3×2 in. Close Coupled Showerhead reactor on a *c*-plane sapphire substrate. The sample consisted of a 2-μm thick Si-doped n-type GaN layer ($n = 3 \times 10^{18}$ cm^{-3}), a 3-period unintentionally doped InGaN/GaN MQW active region, and a p-type GaN layer ($p = 1 \times 10^{17}$ cm^{-3}). The thicknesses of the InGaN well and the GaN barrier are 2.5 nm and 15 nm, respectively. The In content in the InGaN well is nearly 10% (obtained from XRD measurement not shown here). The temperature dependent PL spectra of the InGaN/GaN MQWs were measured from 8 K to 300 K using a 325 nm He–Cd continuous wave laser with an emission power of about 3.5 mW.

3. Results and discussion

PL spectra of an InGaN/GaN MQW sample at various temperatures between 8 K and 300 K are shown in Fig. 1. Two peaks can be observed in each PL spectrum, i.e., a more intense one at about 410 nm and a less intense one centered at about 360 nm. They are the emission peaks of the InGaN/GaN MQW and p-GaN layer, respectively. To analyze the variation of the spectral data of these two peaks with increasing temperature, the integrated PL intensity and peak energy, each as a function of temperature, were extracted respectively, the results are shown in Fig. 2. It is found that the GaN and InGaN/GaN MQW peaks (Figs. 2(b) and 2(d)) show quite different temperature dependencies. For the GaN peak, emission energy decreases monotonously with increasing temperature. However, for the InGaN/GaN MQW peak, emission energy decreases at low temperatures (< 75 K), then increases in the middle temperature range (75–125 K) and decreases again at high temperatures (> 125 K), showing S-shaped behavior. It is well known that the redshift of the peak energy during increasing temperature is typical for the interband emission of bulk GaN, this is attributed to the shrinkage of the band-gap with the increase of temperature.[15] The S-shaped temperature dependence of peak energy is evidence of the presence of localized states in the InGaN wells.[16,17] On the other hand, it can be seen from Figs. 2(a) and 2(c) that strong thermal decay of peak intensity for GaN starts at about 20 K, a temperature considerably lower than that for the InGaN/GaN MQW (75 K). In addition, note that the thermal decay of the integrated PL intensity is accompanied by a blueshift of the peak energy for the InGaN/GaN MQWs, which occurs because the carriers increasingly populate the shallower localization states or escape from the potential minima of the localized luminescence centers. In this case, some carriers may be captured by nonradiative recombination centers, leading to a decrease of the emission peak. When the temperature is increased further, most of the carriers escape from the potential minima of the localized luminescence centers and go into the surrounding two-dimensional (2D) InGaN QW layer, and the integrated PL intensity decreases quickly due to the higher defect density in the surrounding 2D InGaN QW layer. Meanwhile, a redshift of the emission energy appears, due to the temperature dependent shrinkage of the band-gap. The reason for the decrease of the integrated PL intensity is thus attributed to the temperature-induced carrier escaping from the localization centers and an enhanced nonradiative recombination rate. We used Eq. (1) to fit the thermal decay processes of the GaN and InGaN/GaN MQW peaks, as shown in Figs. 2(a) and 2(c). Two activation energies are obtained, i.e., $E_0 = 8.1$ meV for the GaN peak (fitting curve in Fig. 2(a)) and $E_0 = 66$ meV (fitting curve in Fig. 2(c)) for the InGaN/GaN MQW peak. Generally, the nonradiative recombination centers are induced by deep energy defects in GaN or InGaN, because the shallow energy defects are not the effective nonradiative recombination centers. However, unlike the temperature dependent yellow and blue emission of GaN,[10] the activation energy derived from the interband emissions is much smaller than the thermal ionization energy of the involved nonradiative recombination centers, implying that the physical meaning of the activation energy derived from the interband emission is different from the ionization energies of these centers.

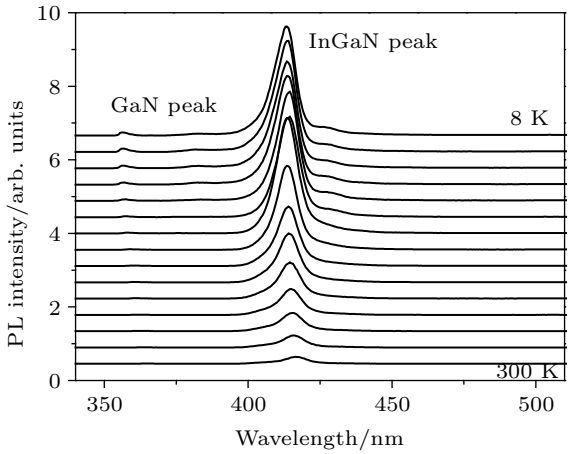


Fig. 1. (color online) PL spectra of InGaN/GaN MQW sample at various temperatures.

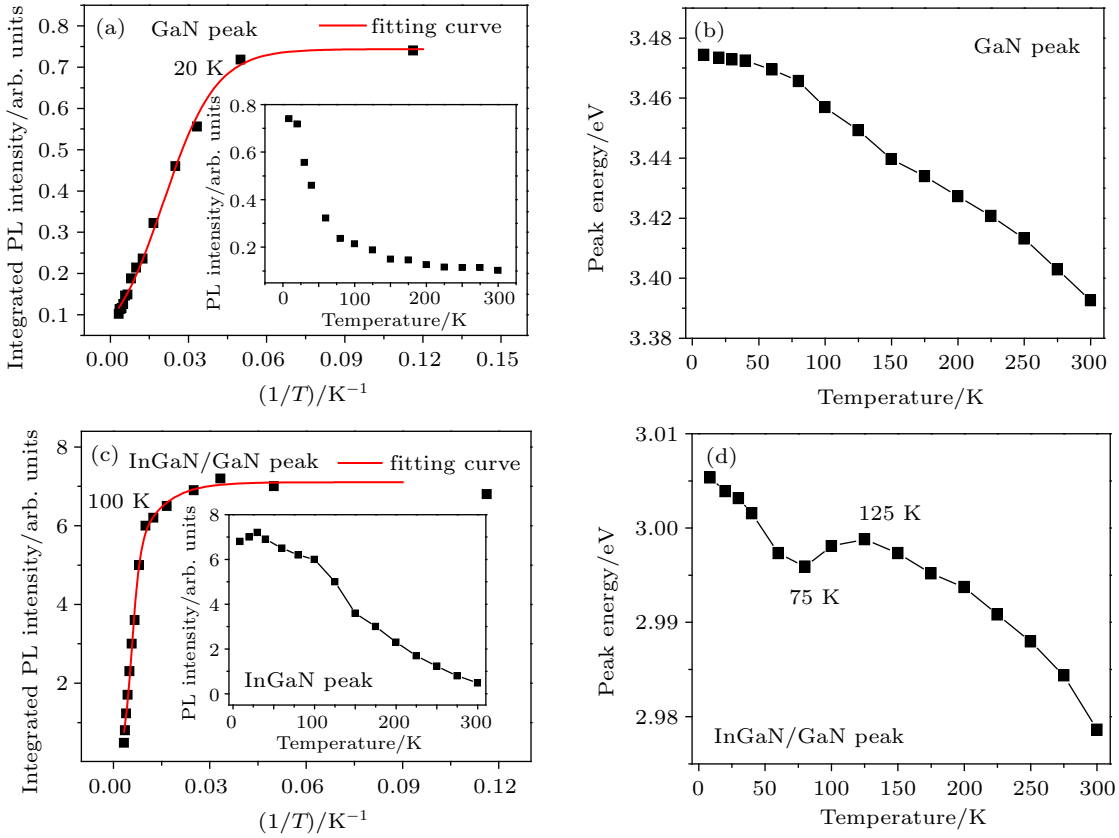


Fig. 2. (color online) Temperature dependencies of integrated PL intensity (a), (c) and peak energy (b), (d) for GaN and InGaN/GaN MQW peaks, respectively. The insets of panels (a) and (c) show the same data of the main panels in another form.

To investigate the physical meaning of E_0 derived from the PL of the GaN or InGaN films, the luminescence decay mechanism of the interband emission for the GaN and InGaN films should be checked. In this section, we will carefully examine the thermal decay processes of luminescence in GaN first. As shown in Fig. 3, the main competing process with the interband emission in the GaN films is the recombinations through the intermediate levels in the band gap (including the defect related emission and the nonradiative recombination). As mentioned before, generally, the intermediate levels, especially the nonradiative recombination centers, are induced by deep energy defects. At low temperature, the nonradiative recombination centers are frozen, so in such cases the internal quantum efficiency of the GaN interband emission can be taken to be approximately 1. However, as the temperature increases, the nonradiative recombination centers are activated and some carriers are captured by these intermediate levels. This statistical redistribution of carriers between the defect energy levels and the energy bands results in decreased emission intensity of the near-band-edge emission for the GaN films. Therefore, by using Eq. (1) to fit the temperature dependent interband emission of GaN, an activation energy E_0 of nonradiative recombination centers can be obtained. However, the main cause of the thermal decay of interband emission is electrons overcoming a potential barrier (E in Fig. 4) to recombine with holes through deep energy defects, as described in a coordinate configuration diagram[18] (Fig. 4). Therefore, the activation energy E_0 is not related to the thermal energy depth of the nonradiative recombination centers, but instead it reflects the potential barrier height ($E_0 = E$ in Fig. 4) that an electron should surmount to undergo nonradiative recombination on the deep energy level. In fact, this potential barrier height is very different from (i.e., much lower than) the thermal energy depth of the deep level. This agrees well with the experimental results that the E_0 derived from Fig. 2(a) is only 8.1 meV, which is far lower than the usual depth of deep defects.

Similar to the case of the GaN material, the activation of the nonradiative recombination centers also results in

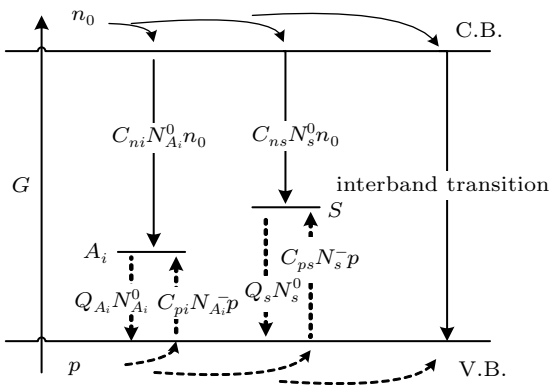


Fig. 3. Schematic of the main transitions in GaN, including radiative recombination through intermediate level (acceptor (A_i)), interband transition, and nonradiative recombination through nonradiative defects (nonradiative recombination center S).

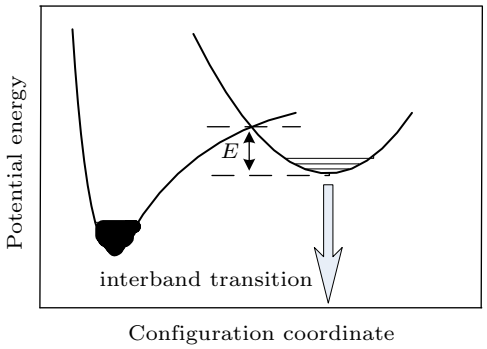


Fig. 4. Coordinate configuration diagram of a deep level defect (shown in the left part of the figure).

a thermal decay of the interband transition PL peak in the InGaN. However, these films differ from binary alloy GaN in that the indium distribution is usually nonuniform in InGaN due to phase segregation, and many In-rich clusters form in the InGaN film where the potential energy is low. Therefore, they act as localization states for the carriers and can prevent the carriers from approaching the areas with dislocation defects. In fact, in many cases the PL peak of InGaN originates from the emission of these In-rich clusters, due to their high luminescence efficiency.[19,20] Therefore, the thermal decay of PL and the physical meaning of E_0 derived in InGaN should be discussed based on the localization state modes, as suggested by Fig. 5.

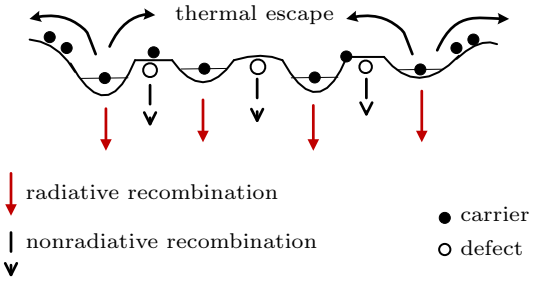


Fig. 5. (color online) Schematic of localization luminescence centers in InGaN. The nonradiative recombination defects (shown by empty circles) are located outside the localized luminescence centers, existing in the surrounding areas between the adjacent localization states.

Generally, defect density in the In-rich clusters is quite low, and most of the nonradiative recombination defects (such as dislocations) exist in the neighboring areas between the adjacent localization states. In this case, the carriers are trapped in the localization states and preferentially radiatively recombine there at low temperature. The emission intensity is thus high. At higher temperatures, however, many carriers escape away from the potential minima of the localized states into the surrounding 2D InGaN QW layer regions with a high density of nonradiative recombination defects. This results in a reduction of PL intensity, due to the increase of the nonradiative recombination rate. This means that the thermal decay of InGaN's luminescence will be dominated by nonradiative recombination only when the carriers have escaped from the localization luminescence centers. Therefore, the activation energy E_0 obtained from the thermal decay of the emission peak of InGaN ($E_0 = 66$ meV in Fig. 2(c)) should be attributed to the energy barrier height of these localized states (e.g., In-rich clusters) rather than the characteristic parameters of the nonradiative recombination defects.

According to the above analysis, we find that the physical meaning of the activation energy E_0 derived from the $\log(I_{\text{int}})$–$1/T$ curve for the interband transition of the GaN and InGaN materials is not the ionization energy of the deep level defects, so we cannot directly obtain the thermal ionization energy of the nonradiative recombination centers by fitting the temperature dependent interband emission. Instead, a much smaller activation energy will be obtained. This differs somewhat from the thermal decay of the shallow acceptor luminescence peak, wherein the obtained temperature-dependent activation energy E_0 of the PL peak may be directly equal to the acceptor ionization energy itself.

4. Summary

Temperature dependence of integrated PL intensity for GaN and InGaN materials is analyzed, and the physical meaning of the fitted activation energy E_0 is discussed in detail based on the theoretical analysis and experimental results. It is found that the physical implication of the derived activation energy is related to the thermal decay process of the PL peak. For the interband transition of InGaN, the thermal decay of the luminescence may be attributable mainly to carriers escaping from localized luminescence centers, in which case the activation energy E_0 would correspond to the energy barrier height of these localized states. Another possibility for the decay of the PL intensity is the activation of a nonradiative recombination process, in which case the activation energy E_0 is related to the thermal activation process described by the coordinate configuration diagram but not to the actual thermal energy depth of the nonradiative deep level defects.

References

[1] Nakamura S and Fasol G 1997 *The Blue Laser Diode* (New York: Springer)
[2] Yang J, Zhao D G, Jiang D S, Liu Z S, Chen P, Li L, Wu L L, Le L C, Li X J, He X G, Wang H, Zhu J J, Zhang S M, Zhang B S and Yang H 2014 *Chin. Phys. B* **23** 068801
[3] Sun Q, Yan W, Feng M X, Li Z C, Feng B, Zhao H M and Yang H 2016 *J. Semicond.* **37** 044006
[4] Jiang L R, Liu J P, Tian A Q, Cheng Y, Li Z C, Zhang L Q, Zhang S M, Li D Y, Ikeda M and Yang H 2016 *J. Semicond.* **37** 111001
[5] Gong X Q, Feng S W, Yue Y, Yang J W and Li J W 2016 *J. Semicond.* **37** 044011
[6] Cho Y H, Gainer G H, Fischer A J, Song J J, Keller S, Mishra U K and DenBaars S P 1998 *Appl. Phys. Lett.* **73** 1370
[7] Moon Y T, Kim D J, Song K M, Choi C J, Han S H, Seong T Y and Park S J 2001 *J. Appl. Phys.* **89** 6514
[8] Li J M, Liu Z, Liu Z Q, Yan J C, Wei T B, Yi X Y and Wang J X 2016 *J. Semicond.* **37** 061001

[9] Hao M, Zhang J, Zhang X H and Chua S 2002 *Appl. Phys. Lett.* **81** 5129

[10] Demechenko D O, Diallo I C and Reshchikov M A 2013 *Phys. Rev. Lett.* **110** 087404

[11] Reshchikov M A and Korotkov R Y 2001 *Phys. Rev. B* **64** 115205

[12] Reshchikov M A and Morkoç H 2005 *J. Appl. Phys.* **97** 061301

[13] Wang Y, Pei X J, Xing Z G, Guo L W, Jia H Q, Chen H and Zhou J M 2007 *J. Appl. Phys.* **101** 033509

[14] Zheng X H, Chen H, Yan Z B, Li D S, Yu H B, Huang Q and Zhou J M 2004 *J. Appl. Phys.* **96** 1899

[15] Sasaki A, Shibakawa S I, Kawakami Y, Nishizuka K, Narukawa Y and Mukai T 2006 *J. Appl. Phys.* **45** 8719

[16] Eliseev P G, Perlin P, Lee J and Osiski M 1997 *Appl. Phys. Lett.* **71** 569

[17] Li X, Zhao D G, Jiang D S, Yang J, Chen P, Liu Z S, Zhu J J, Liu W, He X G, Li X J, Liang F, Liu J P, Zhang L Q, Yang H, Zhang Y T, Du G T, Long H and Li M 2017 *Chin. Phys. B* **26** 017805

[18] Williams F E and Eyring H 1947 *J. Chem. Phys.* **15** 289

[19] Narukawa Y, Kawakami Y, Funato M, Fujita S and Nakamura S 1997 *Appl. Phys. Lett.* **70** 981

[20] Nagahama S, Yanamoto T, Sano M and Mukai T 2001 *Jpn. J. Appl. Phys.* **40** 3075