AIP Applied Physics Letters

Time-resolved photoluminescence study of isoelectronic In-doped GaN films grown by metalorganic vapor-phase epitaxy

H. Y. Huang, C. K. Shu, W. C. Lin, C. H. Chuang, M. C. Lee, W. K. Chen, and Y. Y. Lee

Citation: Applied Physics Letters **76**, 3224 (2000); doi: 10.1063/1.126588
View online: http://dx.doi.org/10.1063/1.126588
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/76/22?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in

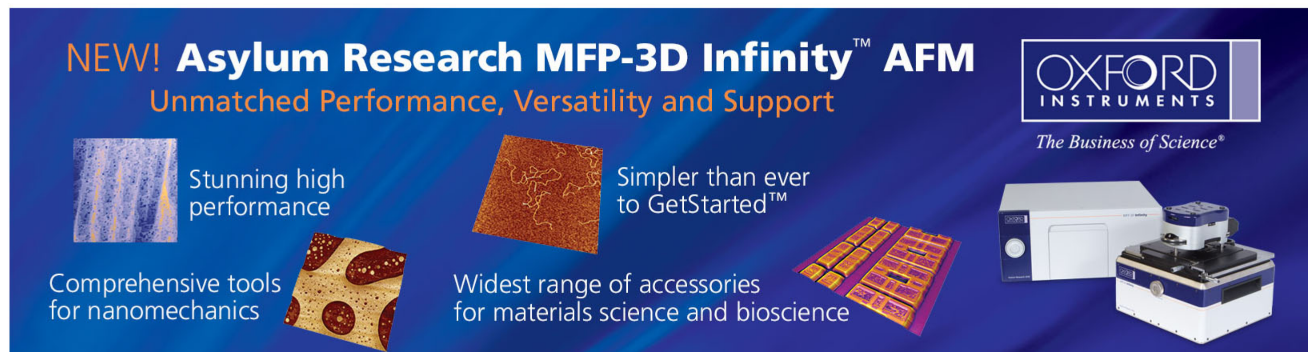
Photoluminescence of Mg-doped GaN grown by metalorganic chemical vapor deposition
J. Vac. Sci. Technol. A **21**, 838 (2003); 10.1116/1.1575214

Time-resolved spectroscopy of strained GaN/AlN/6H–SiC heterostructures grown by metalorganic chemical vapor deposition
Appl. Phys. Lett. **78**, 1062 (2001); 10.1063/1.1350421

Optical spectroscopy of GaN grown by metalorganic vapor phase epitaxy using indium surfactant
Appl. Phys. Lett. **76**, 3388 (2000); 10.1063/1.126655

Time-resolved study of yellow and blue luminescence in Si- and Mg-doped GaN
Appl. Phys. Lett. **76**, 840 (2000); 10.1063/1.125602

Time-resolved photoluminescence studies of free and donor-bound exciton in GaN grown by hydride vapor phase epitaxy
Appl. Phys. Lett. **75**, 838 (1999); 10.1063/1.124530



This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 140.113.38.11 On: Thu, 01 May 2014 07:51:26

Time-resolved photoluminescence study of isoelectronic In-doped GaN films grown by metalorganic vapor-phase epitaxy

H. Y. Huang, C. K. Shu, W. C. Lin, C. H. Chuang, M. C. Lee, and W. K. Chen[a)]
Department of Electrophysics, National Chiao Tung University, Hsinchu, 300, Taiwan, Republic of China

Y. Y. Lee
Synchrotron Radiation Research Center, Hsinchu 300, Taiwan, Republic of China

(Received 18 January 2000; accepted for publication 4 April 2000)

Time-resolved photoluminescence spectra were used to characterize isoelectronically doped GaN:In films. Our results indicate that the recombination lifetime of the donor-bound-exciton transition of undoped GaN exhibits a strong dependence on temperature. When In is doped into the film, the recombination lifetime decreases sharply from 68 to 30 ps, regardless of the measured temperature and In source flow rate. These observations might be related to the isoelectronic In impurity itself in GaN, which creates shallow energy levels that predominate the recombination process. © *2000 American Institute of Physics.* [S0003-6951(00)02622-X]

The recent progress in nitride-based optoelectronic developments of wide-band-gap semiconductors is significant,[1,2] owing to the advent of the number of techniques, such as the two-step growth method, p-impurity activation process, and the epitaxially lateral overgrowth technique.[3,4] In regard to the film quality, it has been reported that with the adding of the isoelectronic impurity, the background carrier concentration and deep trap concentration in GaN can be effectively reduced.[5,6] A resembling tendency is also observed in their optical properties. The linewidth of the luminescence becomes narrower and its intensity is enhanced when the isoelectronic impurity is introduced into the films.[5] It seems that the use of isoelectronic doping can effectively improve the GaN film quality. However, up to now the relevant studies are still few. One paper has dealt with the optical transient study of In-doped GaN grown by gas-source molecular-beam epitaxy (GSMBE).[6] No similar investigation has been performed on metalorganic vapor-phase epitaxially (MOVPE) grown GaN film. We thus employed photoluminescence (PL) and time-resolved photoluminescence (TRPL) measurement to examine the optical transition involved in our MOVPE-grown In-doped GaN.

For the PL measurement, a He–Cd laser operating at 325 nm was used for above-band-gap excitation. A monochromator and a photomultiplier tube were used for detection. Time-resolved photoluminescence experiments were performed with samples thermostated from 12 to 300 K using an UV pulsed laser centered at 323 nm with a repetition rate of 1 kHz and an excitation pulse density of $\sim 40\,\mu$W. The optical transient spectra were detected by a Hamamatsu photomutipilier, and analyzed with an EG&G picosecond timer analyzer.

In order to explore the isoelectronic doping effects, undoped and a series of In-doped GaN samples grown by MOVPE with various trimethylindium (TMIn) source flow rates were employed in this study. Due to the fact of the high volatility of In at high temperatures, only the In/Ga solid concentration not higher than 0.2% can be obtained in these GaN:In films.[5] The PL measurements were conducted at 15 K because of less thermal broadening and better spectral resolution. As can be seen in Fig. 1, we observe no shift of near-band-edge emission (I_2 line), no additional transition peak for In-doped samples, and the intensity of the yellow emission is comparatively lower than that of the near-band-edge emission (<1000), regardless of the different In source supply, which confirms the characteristics of isoelectronic doping rather than alloy formation for all our In-doped GaN films. Additionally, the linewidth of I_2 line is decreased monotonously from 16 to 10 meV (see the inset) and the corresponding carrier concentration is reduced significantly from 1.7×10^{19} to $3\times10^{17}\,\mathrm{cm}^{-3}$, indicating the good crystalline quality of our films, particularly when grown with high-In flow rates.

To further investigate the effects of In doping on the dynamic process of the optical transition, such as the domi-

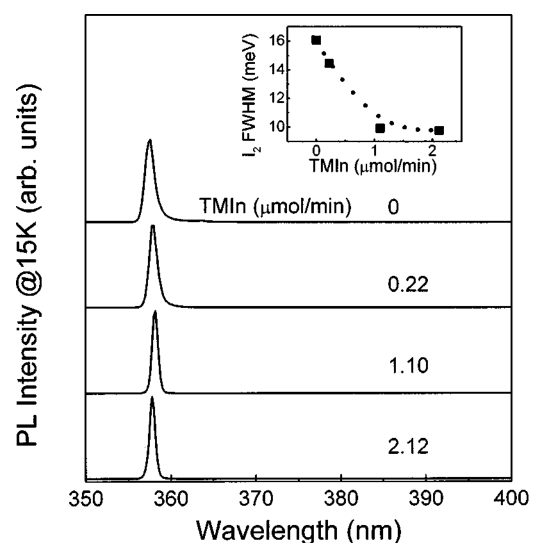


FIG. 1. PL spectrum of GaN samples doped with TMIn flow rates of 0, 0.22, 1.1, and 2.12 μmol/min. The inset shows the decrease of the linewidth with TMIn flow rates.

[a)]Electronic mail: u8721818@cc.nctu.edu.tw

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 140.113.38.11 On: Thu, 01 May 2014 07:51:26

 © 2000 American Institute of Physics

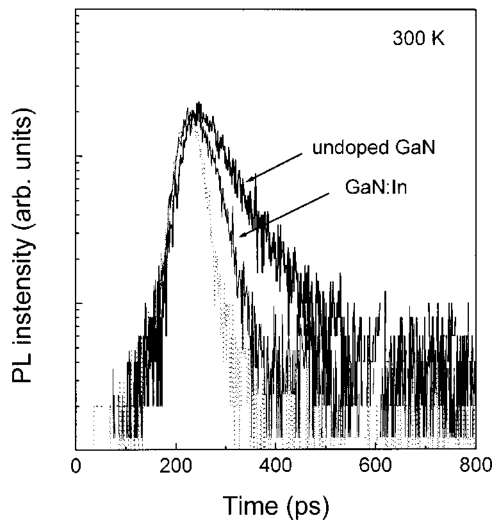


FIG. 2. Temporal variation of I_2 emission for both undoped and isoelectronic-doped GaN (In: 2.12 μmol/min). The dotted line is the system response.

nant I_2 line, a series of TRPL measurements were then carried out in this study. Figure 2 shows the room-temperature recombination lifetimes of undoped and In-doped GaN, for example, grown with a 2.12 μmole/min In source flow rate. Obviously, the decay behaviors between the undoped and doped samples are different. The undoped GaN has a decay time of 68 ps, whereas the In-doped one ~ 30 ps. More interestingly, as we changed the cryostat temperature from 300 to 12 K we can find, in Fig. 3, that the recombination lifetime of the undoped GaN sample decreases from 68 to 42 ps with the decreasing temperature. Nevertheless, an unusual emission process is observed for the In-doped GaN film. Its lifetime remains almost the same, independent of the measurement temperature. To verify whether such a phenomenon is also occurring in other doped samples, more investigations were then performed. The corresponding results are shown in Fig. 4. It is surprising that the recombination lifetime decreases suddenly when the In reactant is added into the reactor and saturates almost at once to its final value, ~ 30 ps,

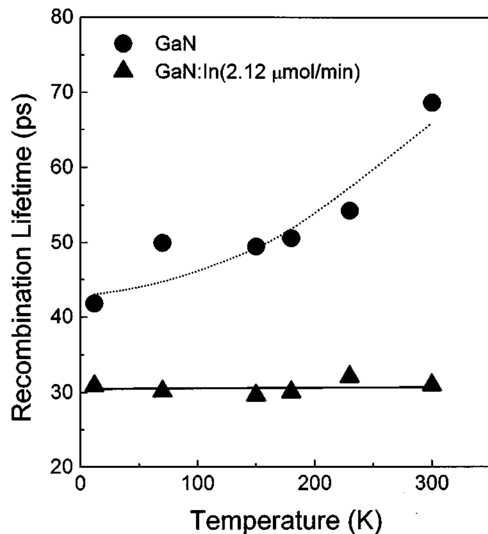


FIG. 3. Recombination lifetimes of undoped and GaN:In (2.12 μmol/min) measured from 12 to 300 K. The dotted line presents the curve fitted by $T^{1.5}$ for the undoped sample.

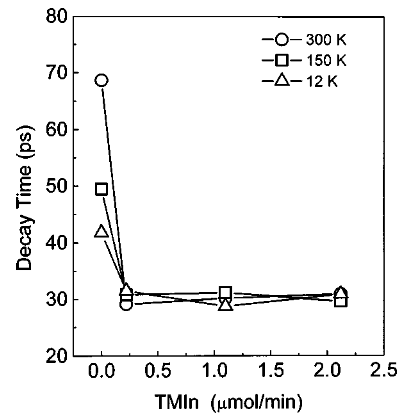


FIG. 4. Recombination lifetimes of doped and undoped GaN films as a function of In source supply measured at 300, 150, and 12 K, respectively.

irrelevant of the TMIn flux. It is worth noting that this decay behavior is essentially independent of the measurement temperature for all of our In-doped samples. This situation is rarely observed in other compound semiconductors.

Tentative explanations of the above recombination behavior are described as follows: In general, the recombination lifetime ($\tau_{\rm PL}$) for salient I_2 line transition is due to the radiative lifetime of the I_2 transition (τ_{I_2}) itself, and the lifetime of other decay processes (τ') associated with the shallow donor energy level.[7–10] It is known that the theoretical value of τ_{I_2} for GaN is about 400 ps.[11] Together with the fact of the much shorter $\tau_{\rm PL}$ (<68 ps) obtained here, we believe the measured lifetime represents virtually the lifetime of a transition other than the I_2 line in all of our GaN samples. For the undoped GaN film considered here, its recombination behavior can be described well by using the Shockley–Read–Hall model (SRH). In this model, the SRH recombination lifetime τ' is closely related to its cross section σ and trap concentration N_t in the epilayer and can be expressed by the following equation:[7,10]

$$\tau' = \frac{1}{\sigma v_{\rm th} N_t}, \tag{1}$$

where $v_{\rm th}$ is the thermal velocity of electrons at the measurement temperature. From the scattering theory, the transition probability is directly proportional to the square of transition matrix, leading to a T^{-2} dependence of the cross section on temperature.[12] Since the thermal velocity $v_{\rm th}$ is a function of $T^{0.5}$, it will result in a dependence of $T^{1.5}$ of $\tau_{\rm PL}$. This can well explain the observation in our undoped GaN film.

As far as the In-doped samples are concerned, it has been reported that deep recombination centers, such as antisites, vancancies, and dislocations in compound semiconductors, can be greatly suppressed by isoelectronic doping to improve the film quality.[5,6] This is also the case for the GaN film, as confirmed by our recent study using deep-level transient spectroscopy.[13] Based on this argument, with the adding of In atoms, we may at first anticipate an increase of the I_2 emission lifetime in the samples. Nonetheless, an adverse effect is observed. As mentioned earlier, the recombination lifetime is not only reduced, but is also independent of temperature and In source supply. The above findings are apparently different from the report by Kumano *et al.*[6] in their

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 140.113.38.11 On: Thu, 01 May 2014 07:51:26

GSMBE-grown In-doped GaN films, in which an increase of emission lifetime from 20 to 70 ps is observed when the film is lightly doped with In. The reason for this discrepancy is not yet clear at present; it might be related to the characteristics of different film properties associated with GSMBE- and MOVPE-grown nitrides, or because too high of an In concentration is doped in our films.

From the aspect of the temperature independence of the recombination lifetime τ_{PL} observed here, we may believe that quantum-dot-like structures existed, which dominate the light emission process in our In-doped films. As we know, the emission properties of quantum dots are essentially insensitive to the temperature due to their zero-dimensional properties.[10,14] With the high density of In doping, quantum dots certainly have the possibility of forming in the epilayer. This explanation seems at first glance to be supported well by the peculiar growth manner of the nitride film, in which the In atom is noted to be easily self-organized into nanostructures in the growing epilayer.[10,14] However, if this is the case, a blueshift feature with respected to the GaN band gap, and a broad linewidth due mainly to the size fluctuation of the quantum dots should be observed. Since no such phenomena occurred, the quantum-dot effects conceivably cannot be the decisive factor responsible for the luminescence process in our samples.

The other likely explanation turns to the isoelectronic nature of the impurity itself.[15,16] For In:GaN, the In atom is used to substitute Ga in the crystal. Since the In atom is heavier and larger than the Ga, it will result in a band-edge degeneracy at the valence band,[15] lifted by spin-orbit interactions, and produce an attractive potential for a hole in the vicinity of the In atom. That is, the In atom acts like a shallow acceptor in the GaN film. Notice that the pseudopotentials are usually closely similar within the same group of the periodic table, which is also true for In and Ga,[16] the energy splitting due to the isoelectronic doping is expected to be relatively small so that its transition cannot be differentiated easily with the ordinary optical detection system. This is probably the reason why no additional transition line can be observed in our In-doped GaN films.

It is known that the GaN film usually contains large densities of structure defects. We believe that during the sample preparation a fraction of In atoms will act as pinning centers to block the stretching of the dislocations, and withhold the generation of point defects,[5,13] so that the film quality can be improved. As more In is introduced into the reactor, the substitution effect of In for Ga is believed to become more pronounced, which create lots of shallow-acceptor-like recombination centers, and could eventually dominate the transition processes. This may be the reason to account for the lifetime shortening in In-doped films. Regarding the temperature independence of the recombination lifetime observed here, it is possibly attributed intrinsically to the characteristics of the isoelectronic doping or connected primarily to the influences of the high-In concentration in the layer. It is interesting to note that the isoeletronic impurity itself, to a certain extent, could resemble as quantum-dot-like region in the structure. From this point of view, the In-doped GaN films may also bear a characteristic of temperature independence in the recombination lifetime. Nevertheless, understanding of the affects of isoelectronic doping in GaN is still in the preliminary stage, more investigations are needed to comprehend its origins in the future.

In summary, we have employed a TRPL spectroscopy to study the dynamic response of undoped and In-doped GaN films grown by the MOVPE method. With the doping of In, the recombination lifetime of the I_2 transition falls immediately when In is introduced into the solid and remains as a constant, nearly independent of the measured temperature and source supply. Such unusual phenomena could be related intrinsically to the characteristics of the isoelectronic doping or due to the factor of the comparatively high-In concentration present in our epilayers.

The authors wish to acknowledge the support by the National Science Council of the Republic of China under Contract Nos. NSC89-2112-M009-016 89N102 and NSC89-2112-M009-012 89N099.

[1] S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, and S. Nagahama, Jpn. J. Appl. Phys., Part 2 **34**, L797 (1995).
[2] M. Harada, Nikkei Electronics Asia, New/Focus, December, 30 (1997).
[3] S. Nakamura, Jpn. J. Appl. Phys., Part 2 **30**, L1705 (1991).
[4] S. Nakamura, K. Kitamura, and N. Sawaki, Jpn. J. Appl. Phys., Part 2 **24**, L1184 (1995).
[5] C. K. Shu, J. Ou, H. C. Lin, W. K. Chen, and M. C. Lee, Appl. Phys. Lett. **73**, 641 (1998).
[6] H. Kumano, K.-I. Koshi, S. Tanaka, I. Suemune, X.-Q. Shen, P. Riblet, P. Ramvall, and Y. Aoyagi, Appl. Phys. Lett. **75**, 2879 (1999).
[7] G. D. Chen, M. Smith, J. Y. Lin, and H. X. Jiang, J. Appl. Phys. **79**, 2675 (1996).
[8] C. I. Harris, B. Monemar, H. Amano, and I. Akasaki, Appl. Phys. Lett. **67**, 840 (1995).
[9] W. Shan, X. C. Xie, and J. J. Song, Appl. Phys. Lett. **67**, 2512 (1995).
[10] Y. Narukawa, S. Saijou, Y. Kawakami, and S. Fujita, Appl. Phys. Lett. **74**, 558 (1999).
[11] R. Klann, O. Brandt, H. T. Grahn, K. Ploog, and A. Trampert, Phys. Rev. B **52**, R11615 (1995).
[12] J. I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1971), Chaps. 6 and 7.
[13] H. M. Chung, W. C. Chuang, Y. C. Pan, C. C. Tsai, M. C. Lee, W. H. Chen, W. K. Chen, C. I. Chiang, C. H. Lin, and H. Chang, Appl. Phys. Lett. **76**, 897 (2000).
[14] Y. Narukawa, Y. Kawakami, S. Fujita, and S. Nakamura, Phys. Rev. B **59**, 10283 (1999).
[15] J. W. Allen, J. Phys. C **4**, 1936 (1971).
[16] L. Bellaiche, T. Mattila, L.-W. Wang, S.-H. Wei, and A. Zunger, Appl. Phys. Lett. **74**, 1842 (1999).

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 140.113.38.11 On: Thu, 01 May 2014 07:51:26