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PHOTOLUMINESCENCE STUDY OF GaN

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Photoluminescence study of undoped, doped GaN grown on (00.1), (11.0), (01.2)Al₂O₃ (100), (111)Si, and (00.1)6H-SiC substrates have been conducted. Strong bandedge emissions from all undoped samples and dopant-related emissions from doped samples were observed. Deep-level yellow emission centered around 2.2 eV was not observed from undoped GaN grown on 6H-SiC substrate, undoped GaN with optimum Ga source flow and doped GaN. The experiment data strongly suggest that Ga vacancies are the origin this deep-level emission.

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GaN has a direct bandgap of 3.4 eV and is therefore a promising material for blue-near ultraviolet optoelectronic devices, including light emitting diodes (LEDs) and laser diodes (LDs). Blue LEDs have been fabricated and become commercially available. However, because of the lack of suitable substrates, it has been very difficult to grow high quality defect-free GaN films. Even in the most efficient GaN-based LEDs to date, there is a high density of defects, especially near the interfaces [1]. These defects create deep-level states in the forbidden gap, and reduce the efficiency of the radiative recombinations desired from the active layers. The nature and elimination of these defects need to be resolved in order to realize laser diodes.

One of the well-known deep-level luminescence emission from GaN is the so-called "yellow luminescence" (YL), which is centered around 2.2 eV and has a linewidth of about 400 meV. This emission band is even observed in high quality GaN [2]. Various authors have proposed interpretations for the origin of this deep-level state [3, 4]. But this issue is still controversial because of the lack of experimental data. We have already reported the comparative study of GaN grown on (00.1) and (01.2) sapphire (Al₂O₃) [5, 6]. In this paper, we report the photoluminescence study of GaN grown on (00.1), (11.0), (01.2)Al₂O₃, (100), (111)Si, and (00.1)6H-SiC, Ge-doped GaN and Mg-doped GaN. The effect of substrate orientations, Ga source flow and dopant on the YL was conducted, which strongly

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suggested that YL was related to the Ga vacancies. Activation energies of Ge and Mg in GaN were estimated to be 34–50 meV and 140–164 meV, respectively.

All the films described in this report were grown by low-pressure metalorganic chemical vapor deposition (LP-MOCVD). The starting materials were trimethylgallium (TMGa), trimethylaluminum, ammonia, biscyclopentadienylmagnesium (Cp_2Mg) and H_2 -diluted germane (GeH_4) for the Ga, Al, N, Mg and Ge elements, respectively. The growth conditions have been reported earlier [2]. Several types and orientations of substrates were used, including (00.1), (11.0), (01.2) Al_2O_3 , (100), (111)Si, and (00.1)6H-SiC.

Photoluminescence measurements were carried out with a He-Cd laser as the excitation source (325 nm, power ≈ 10 mW). Figure 1 shows the room temperature PL of GaN grown on different substrates. From top to bottom, the substrates used were: (a) Al_2O_3 (01.2); (b) Al_2O_3 (11.0); (c) Al_2O_3 (00.1); (d) 6H-SiC(00.1); (e) Si(100); (f) Si(111). All the spectra were in the same scale but shifted vertically for clarity. Bandedge emissions were detected from all samples. It is important to notice that no deep-level YL was detected from the samples grown on (00.1)6H-SiC. Among all the substrates that were used, basal plane 6H-SiC is expected to provide the best quality of GaN with the lowest density of defects because it has the closest lattice and thermal match with GaN crystals. Wetzel et al. have also shown that no YL was observed from high quality GaN grown on 6H-SiC [7].

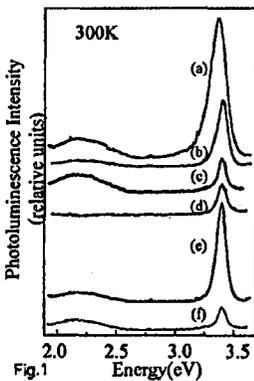


Fig.1

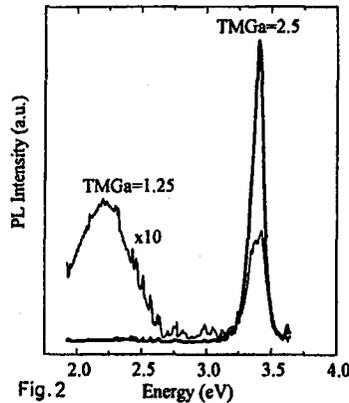


Fig.2

Fig. 1. Room temperature photoluminescence of GaN grown on different substrates. The substrates are: (a) Al_2O_3 (01.2), (b) Al_2O_3 (11.0), (c) Al_2O_3 (00.1), (d) 6H-SiC(00.1), (e) Si(100), (f) Si(111).

Fig. 2. Room temperature photoluminescence of undoped GaN with different TMGa flow rates: (a) TMGa = 1.25 sccm, (b) TMGa = 2.5 sccm.

Figures 2a and b show the room temperature photoluminescence of undoped GaN on (00.1) Al_2O_3 which was grown with TMGa flow rates of 1.25 and 2.5 sccm, respectively. All other parameters were kept the same for these two growths. Deep-level YL can be observed from GaN with a lower TMGa flow rate while

it was absent from the samples with a higher TMGa flow rate. Since fewer Ga vacancies are expected in the case of a higher TMGa flow rate, these experiments strongly suggest that YL results from Ga vacancies. It is unlikely that YL is also related to C impurity [3] since higher TMGa ($(\text{CH}_3)_3\text{Ga}$) flow would increase the C incorporation in the epilayer and enhance the YL emission, which is not the case here.

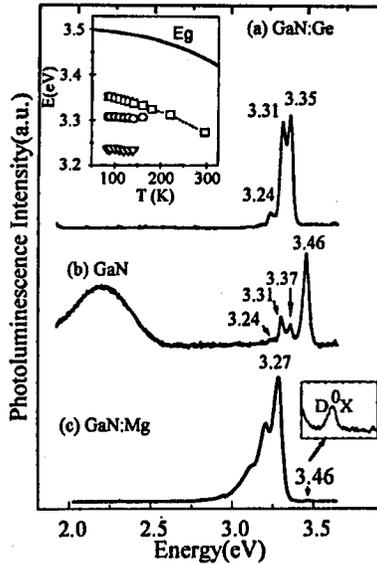


Fig. 3. 77 K temperature photoluminescence of (a) Ge-doped GaN, (b) undoped GaN, (c) Mg-doped GaN. The inset in (a) is the temperature characteristics of the peaks observed in GaN:Ge. The inset in (c) is the weak I_2 line.

GaN:Ge and GaN:Mg were grown by using the same growth condition of undoped GaN which showed YL emission except that doping sources were introduced into the reactor. The 77 K photoluminescence of Ge-doped GaN, undoped GaN and Mg-doped GaN are shown in Figs. 3a, b and c, respectively and detailed structures of the photoluminescence are revealed. Clearly shown is the absence of YL emission from both GaN:Ge and GaN:Mg on $(00.1)\text{Al}_2\text{O}_3$. Such emission was not observed from doped layers on other substrates either. Ge (group IV) acts as a donor and Mg (group II) as an acceptor in GaN by substituting to Ga (group III) sites. In this instance, the removal of the deep-level YL in Ge-doped or Mg-doped GaN is consistent with the Ga-vacancy hypothesis because Ge or Mg atoms would fill the Ga vacancies. Complementary evidence can be found in the results reported by Nakamura et al. [8]. They showed that the YL was eliminated when GaN was doped with Mg and activated by low energy electron beam irradiation or thermal annealing treatments.

Another interesting feature shown in Fig. 3 is the emission lines at 3.24 eV,

3.27 eV, 3.31 eV, 3.35 eV, 3.37 eV and 3.46 eV appeared in doped and undoped samples. Among these emission lines, the 3.46 eV peak in undoped GaN, known as the I_2 line, has been assigned to an exciton bound at neutral donor sites [9]. In GaN:Mg, the emission at 3.27 eV and its lower energy satellite peaks have been verified by time-resolved spectroscopy (TRS) to be donor-to-(Mg) acceptor recombination and its phonon replicas [10]. However, the identification of the other peaks at 3.24 eV, 3.31 eV, 3.35 eV and 3.37 eV have proved slightly problematic. Dingle et al. [9] reported two lines at 3.37 eV and 3.29 eV and assigned them to the LO and 2-LO phonon replicas of the I_2 line at 3.46 eV. More recently, Brandt et al. [11] observed a photoluminescence line at 3.35 eV after hydrogenation of as-grown n -type ($n = 10^{18} \text{ cm}^{-3}$) GaN layers and suggested it was due to "hydrogen induced donor states". Wetzel et al. [7] have also reported the line at 3.31 eV resulted from the band to shallow acceptor transition and speculated that carbon related acceptor states may be responsible.

From Figs. 3a and b, after Ge-doping, the 3.24 eV, 3.31 eV, 3.35 eV peaks are greatly enhanced. Thus we believe that these peaks are Ge-donor related and exclude the possibility that the 3.31 eV peak in GaN:Ge is a conduction band to shallow acceptor emission [7]. An interesting point of these peaks is that the 3.35 eV peak follows the bandgap of GaN while the 3.31 eV and 3.24 eV peaks are essentially temperature independent from 77 K to 180 K (see inset of Fig. 3a). This might partly be explained by the electron kinetic energy correction, which accounts for [12] about half of the shift expected. Low energy phonon interaction could also influence the peak position. The temperature dependence of the integrated peak intensity of 3.35 eV is shown in Fig. 4. By fitting the data to the function [13]

$$I(T) = \frac{I(0)}{1 + C \exp(-E_a/kT)},$$

where C is a constant, E_a is the activation energy of the impurity, we obtained an activation energy of $34 \div 50$ meV for Ge-donor, which is very close to the estimation of Lagerstedt [12] and Dingle et al. [9] and thus confirm that Ge as a donor has been successfully incorporated into the GaN layer. On the other hand, the difference between 3.35 eV, 3.31 eV, 3.24 eV and the bandgap of GaN (3.47 eV at 77 K) are approximately 120 meV, 160 meV and 230 meV, respectively. These are quite different from the activation energy of the Ge-donor. Thus the only possibility is that these peaks are all related to Ge-donor to acceptor emission. Since the 3.31 eV peak intensity is almost as high as that of the 3.35 eV peak and these two peaks are so close (40 meV difference), it is unlikely that the 3.31 eV peak is the phonon replica of the 3.35 eV peak. A plausible assumption is that these two peaks are transitions from the same Ge-donor but to different acceptors. As for the 3.24 eV peak, its energy is around 70 meV smaller than that of the 3.31 eV peak and its intensity is much weaker, which suggests that it is a phonon replica of the 3.31 D - A recombination. The phonon mode is at 570 cm^{-1} , which is the $E_1(\text{TO})$ mode of GaN [14].

The 3.35 eV peak was only observed in the doped samples. Dopant-hydrogen complexes [8, 11] may well account for this peak because hydrogen was used as the carrier gas in the LP-MOCVD growth. The 3.37 eV peak was only observed in undoped GaN with the I_2 line. The energy difference between this peak and the I_2

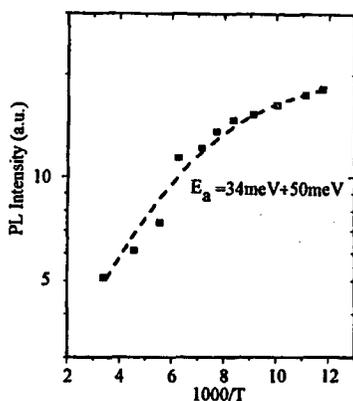


Fig. 4. Integrated PL intensity of Ge donor related emission in GaN:Ge. Activation energy of 34–50 meV is obtained.

line is approximately 90 meV or 735 cm^{-1} , which is one of the LO phonon mode energy of GaN. Therefore this peak is the phonon replica of the I_2 line, which is consistent with the observation by Dingle et al. [9].

Various authors have reported the activation energy of Mg in GaN:Mg with values of 125 meV [15], 155–165 meV [15, 16] and 190 meV [17]. In Fig. 3a the difference between the weak I_2 line and the $D-A$ emission is 190 meV, from which the activation energy of Mg in GaN can be estimated to be $140 \div 164$ meV taking into consideration of the donor activation energy we obtained above. This is consistent with the above reported values.

In conclusion, room temperature photoluminescence study was conducted on undoped and Ge-doped GaN grown on (00.1), (11.0), (01.2)Al₂O₃, (100), (111)Si, and (00.1)6H-SiC substrates. Deep-level yellow luminescence emission could not be detected from undoped GaN grown on (00.1)6H-SiC. This emission was also not observed when undoped GaN was grown on (00.1)Al₂O₃ with a higher TMGa flow rate. Finally, Ge-doped and Mg-doped GaN did not yield any deep-level yellow luminescence either. All this strongly suggests that Ga vacancies are responsible for the yellow luminescence centered around 2.2 eV. The activation energies of Ge and Mg in GaN were estimated as 34–50 meV and 140–164 meV, respectively.

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