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Dependence of Deep Level Concentrations on Ammonia Flow Rate in n-type GaN Films

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Deep level transient spectroscoppy was used to characterize the deep levels of GaN films grown with various V/III ratios using metalorganic vapor phase epitaxy. Two prominent defects, located at E_C-0.569±0.003 and E_C-1.013±0.091 eV, were detected in this study. When the NH_3 flow rate was increased, we observed a slight increase in trap concentration of the E_C-0.569 eV defect and a significant increase at E_C-1.013 eV. Although a high V/III seems necessary for obtaining good quality GaN film, our results indicate that, if the ammonia is in excessive supply, it may generate a large number of E_C-1.013 eV deep level defects, which deteriorate the film quality – which should be avoided with special care.

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III-V nitrides have been a subject of intense investigations in the applications of optoelectronic and high-temperature power electronic devices. Although substantial advances have been made, high densities of threading dislocations and point defects are still commonly observed in the heteroepitaxially grown GaN films [1]. Such defects may act as nonradiative recombination centers in reducing luminance efficiency [2] and result in a high series resistance [3] and leakage current [4] that degrade the device performance. Therefore, it is very desirable to investigate the origins of deep centers and depress them, in order to improve the film quality. Among all the research techniques, deep-level transient spectroscopy [5] (DLTS) represents one of the effective tools for probing the traps in the mid-gap that are well away from the conduction and valence bands. For n-type GaN, several deep levels located at 0.149-0.270 eV [6-11], 0.490-0.610 eV [6-11], and 0.665-0.670 eV [8, 10-11] have been consistently observed by many nitride investigation groups; however, probably due to the constraints in high-temperature DLTS measurement, relatively little has been reported concerning the defects in n-GaN film deeper than 1.00 eV. In this work, we tentatively measured the transient signals at an emission rate window of 0.125 s^{-1}, much smaller than the typical value of 50-200 s^{-1}, and observed a deep level with an activation energy of E_C-1.013 eV in GaN films prepared by the metalorganic vapor phase epitaxy (MOVPE) method. More interestingly, we found the concentration of this particular trap to be very sensitive to the flow rate of ammonia source precursors.

The GaN films employed in this study were grown on (0001)-sapphire substrates at a temperature of 1100°C using a low-pressure horizontal MOVPE reactor. Trimethylgallium (TMGa) and ammonia (NH_3) were used as Ga and N source precursors during the deposition. In order to investigate the effects of the V/III ratio on the formation of deep levels in GaN, we conducted a series of growths using the NH_3 flow rates of 2.0, 2.5, 3.0, and 4.0 standard liters per minute, while keeping the TMGa flow rate at a constant of 88.4 μmol/min. These combinations led to a change of the V/III ratio from 1010, to 1263, 1516, and 2021, respectively. The as-grown samples were subsequently cleaned in D.I. water, degreased with boiled acetone and isopropyl alcohol, and etched with diluted hydrochloric (HCL: H_2O = 1:1) for 4 min in each step. The Ni/Au (100 nm/20 nm) and Al (1000 nm) metals were later deposited on front of the GaN films through the metal mask to form Schottky and Ohmic contacts using the electron-beam evaporation technique.

Prior to the DLTS measurements, the diodes were first examined by both current-voltage and capacitance-voltage methods. As revealed by I-V measurement, well-behaved thermionic emission current transport characteristics are observed in these diodes. The corresponding ideality factor lies in the range from 1.1 to 1.3, and the Schottky barrier height from 0.9 to 1.1 eV, indicating the good quality of our films.

For the DLTS measurement, the sample was biased at -1 V and periodically pulsed to 0 V for trap filling. The transient capacitance signal, acquired by using a test ac signal of 100 KHz and 100 mV with an emission rate window of 0.125 s^{-1} were recorded at 1 K decrements over the temperature range from 380 to 200 K. The resulting DLTS spectra are illustrated in Fig. 1. As shown in the figure, two distinct deep-Ievel traps were observed in these samples: one at 250 K, the other at 350 K. According to the principle of detailed balance [5], the electron emission time τ_n relates to the trap parameters as given by

$$\tau_n^{-1} = \sigma_n \gamma_n T^2 \exp(-E_T/k_B T), \tag{1}$$

where σ_n is the electron capture cross section, γ_n a constant of temperature with the value of about 7.15×10^{20} cm^{-2} s^{-1} K^{-2}, E_T the trap activation energy, and k_B the Boltzmann constant. The trap energies are derived to be approximately E_C-0.569 $\pm$ 0.003 eV and E_C-1.013 $\pm$ 0.091 eV for the 250 K and 350 K peaks, respectively. The Arrhenius plots of these two traps together with other published results are illustrated in Fig. 2.

It is interesting to note that as the V/III ratio is increased the intensity of the E_C-1.013 eV DLTS spectra in Fig. 1 increases significantly, whereas that of E_C-0.569 eV decreases. As indicated by Lang [5], the respective trap concentration is a function of the DLTS capacitance signal weighted by the I net donor concentration (N_D-N_A) of the sample. Following the formula, we indeed observed a significant increase in trap concentration for the E_C-1.013 eV level from 6.6×10^{13} to 1.26×10^{16} cm^{-3} with an increasing V/III ratio, which follows essentially the variation of its DLTS intensity. As for the E_C-0.569 eV defect, althoush it shows a declining DLTS signal with V/III ratio, we do observe a slight increase in its trap concentration. The calculated trap concentrations are 3.76×10^{14}, 4.47×10^{14} and 5.51×10^{-14} cm^{-3} for the V/III = 1010, 1263 and 2021 samples, respectively. The parameters of the two traps are listed in Table I.

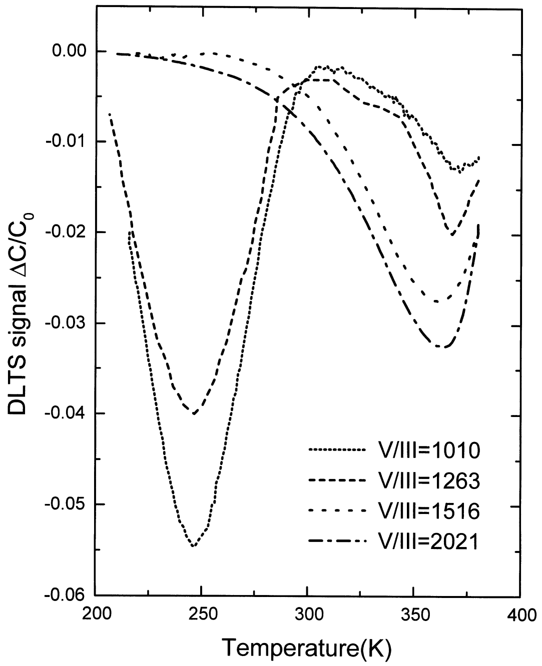

FIG. 1. The DLTS spectra of various V/III ratio samples measured at a rate window of 0.125 s^{-1}.

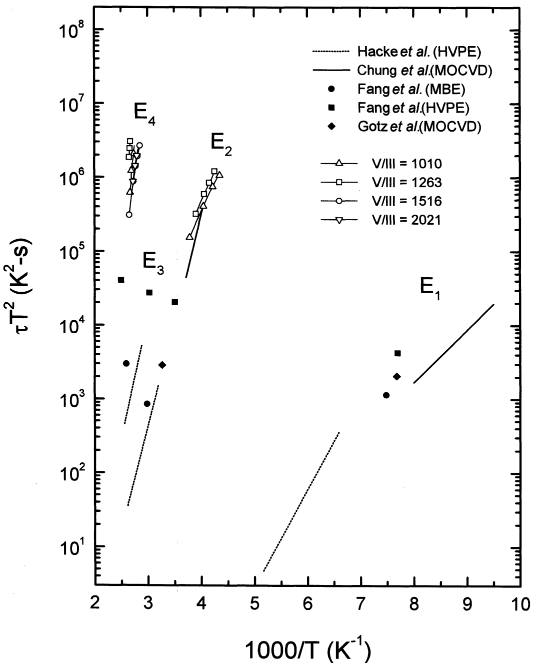

FIG. 2. Arrhenius plots of the inversed emission rate times temperature squared versus reciprocal temperature for our and other groups results. The deep levels in n-type GaN reported in the literature are labeled from E_1 to E_4.

TABLE I. The parameters of trap obtain by C-V and DLTS in different V/III ratio samples

V/III ratio	N_D-N_A	E2			E4		
	(cm^{-3})	E_T (eV)	N_T (cm^{-3})	cross section (cm^2)	E_T (eV)	N_T (cm^{-3})	cross section (cm^2)
1012	2.3e15	0.571	3.76e14	1.48e-15	1.031	6.60e13	4.42e-14
1263	4e15	0.566	4.47e14	1.18e-15	1.035	2.30e14	4.42e-14
1516	7e16	–	–	–	0.922	5.75e15	1.38e-14
2021	1.4e17	–	5.51e14*	–	1.061	1.36e16	2.8e-14

*obtained by fitting transient capacitance response at 250 K

The exact origins of these deep levels remain unclear at the current stage. Since the E_C-0.569 eV one has been observed from a variety of samples prepared by different methods, it is generally believed that this particular trap is one kind of native defect. Hacke assigned it as nitrogen antisite (N_{Ga}), because of the well agreement between the experimental and calculated energies [8]. Our results, discussed in more detail in the next paragraph, seem to be consistent with this hypothesis. Besides, we also believe that the deeper E_C-1.013 eV trap is another type of native defect. This is because any extrinsic point defect, such as an impurity, is very unlikely to be capable of increasing its concentration by nearly three-order of magnitude under a liner change of ammonia flow rate.

According to the thebretical calculation [12], the formation energies of various native defects in GaN grown in nitrogen-rich, quasi-equilibrium conditions are in the order of $V_{Ga} < V_N$ $N_{Ga} < N_1 \ll Ga_N$. Among them, the least probable native defect that lies in the upper half of n-GaN with activation energy deeper than E_C-0.500 eV is doubtlessly gallium antisite, because of its rather high formation energy (about 10 eV). On the other hand, the two most probable deep levels in this region are nitrogen antisite and nitrogen interstitial [12, 13]. Comparing with the experimental results, it is reasonably to allocate the E_C-0.569 eV level as nitrogen antisite from the similarity of the Arrhenius signatures with Hacke's data, as shown in Fig. 2. As for the deeper E_C-1.013 eV energy level, if it is also a type of native defect, we preferentially assign it as nitrogen interstitial, since the nitrogen interstitial bears an energy level deeper than nitrogen antisite, and in fact there is a high possibility for the formation of such a defect in a GaN film under nitrogen-trich growth conditions.

The above assertion seems to agree well with the variation of ammonia flow in our experiment. During the deposition, aside from the nitrogen site, the next favorable position for a nitrogen atom to be incorporates is a Ga site, which will lead to the formation of nitrogen anti site in the epilayer. This may account for the observation of non-negligible trap concentrations of E_C-0.569 eV defects, i.e. nitrogen anti site here, in the films grown at low V/III ratios. Perhaps not too many gallium vacancies are produced with increasing ammonia flow rate, the concentration tends to saturate at a value of $\sim 5 \times 10^{14}$ cm^{-3}. Nevertheless, under high ammonia floW rates, large quantities of excess nitrogen atoms will be generated in the boundary layer; the unescaped nitrogen may simply imbed in the crystal by reason of fast accumulation of reattive species in the growing interface. This may explain the observed sharp increasel of nitrogen interstitial trap concentration from 6.60 $\times$ 10^{13} to 1.36 $\times$ 10^{16} cm^{-3} with the increasing V/III ratio in our samples.

In summary, we have carried out a DLTS study of n-type GaN films grown with various V/III ratios under a constant TMGa flow rate. As the NH_3 flow rate is increased we observe a slight increase of trap concentration for the E_C-0.569 eV deep level, and a sharp 1 increase for the E_C-1.013 eV deep level in our films. We believe both of them are GaN native defects: namely nitrogen antisite for E_C-0.569 eV and nitrogen interstitial for E_C-1.013 eV. Moreover, our results also indicate that, although a high V/III ratio is necessary for obtaining good quality GaN film, a too high ammonia flow rate, however, will end with a formation of large quantities of nitrogen interstitials, causing the degradation of the epilayer and should be carefully avoided during the sample preparation.

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