Deep Centers and Persistent Photoconductivity Studies in Variously Grown GaN Films

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ABSTRACT

Deep levels studies on a set of n-GaN films grown by MOCVD and HVPE reveal the presence of electron traps with levels near E_c-0.25 eV, E_c-0.55 eV, E_c-0.8 eV, E_c-1 eV, hole traps with levels near E_v+0.9 eV and a band of relatively shallow states in the lower half of the bandgap. The total density of these latter states was estimated to be some 10^{16} cm^{-3} and they were tentatively associated with dislocations in GaN based on their high concentration and band-like character. None of the electron or hole traps could be unambiguously related with strong changes of diffusion lengths of minority carriers in various samples. It is proposed that such changes occur due to different surface recombination velocities. An important role of E_c-0.55 eV traps in persistent photoconductivity phenomena in n-GaN has been demonstrated.

INTRODUCTION

As the materials system of GaN grows into maturity all the usual problems associated with the influence of deep centers on electrical properties of GaN films become increasingly important. A number of groups have reported the results of studies of deep levels in n-GaN using deep levels transient spectroscopy (DLTS) and related techniques (a recent review and relevant references can be found e.g. in [1]). At the same time there are many indications that nonradiative recombination via deep traps is an important recombination channel in GaN (see e.g. a review in [2]). However, no attempt has been made so far to pinpoint the deep traps that play an important role in generation-recombination of charge carriers in GaN. In this paper we tried to establish such a correlation between the type and density of deep traps and the diffusion lengths in several n-GaN films widely differing by the diffusion length values.

EXPERIMENTAL

The samples studied in this paper were grown either by metalorganic chemical vapor deposition (MOCVD) technique or by hydride vapor pressure epitaxy (HVPE) on basal plane sapphire substrates. The details of growth can be found in [3,4]. MOCVD samples varied from each other by the type of low temperature (LT) buffer (either GaN (sample 598 below) or AlGaN (samples 385, 644, 646 below)). Samples 598 and 646 were lightly Si doped, other samples were undoped. The thickness of all samples was 3-4 µm. Characterization included double crystal high resolution x-ray diffraction (HRXRD) measurements with Mo K_α source, capacitance-voltage (C-V) measurements on Au

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Schottky diodes with the diameter of about 1 mm, deep levels spectroscopy (DLTS) with electrical and optical injection and electron beam induced current (EBIC) profiles measurements at 300K. The latter profiles were used to extract the values of diffusion length of minority carriers. For persistent photocapacitance measurements a series of capacitance versus voltage and capacitance versus temperature (C-T) curves were measured at various frequencies before and after illumination at 85K with deuterium UV lamp and also with various light emitting diodes and with white light source equipped with selective filters. The Au Schottky diodes were prepared as described in [5]. The details of experimental set-ups and measurement procedures can be found in [5,6].

RESULTS AND DISCUSSION

Table I presents the values of the (00.2) x-ray reflection halfwidths, $\Delta_{00.2}$, of room temperature electron concentration established from C-V measurements at 1 kHz (n_{C-V}) and of diffusion lengths (L_d) in various n-GaN samples studied in this paper. It can be seen that the crystalline quality, as assessed by the halfwidth of the (00.2) reflection is the best for the MOCVD sample 598 grown on LT GaN buffer. The quality of the HVPE sample B95 and of the undoped MOCVD sample 385 grown using an LT AlGaN buffer is the worst in the same terms, while the undoped MOCVD LT AlGaN buffer sample 644 and lightly Si doped MOCVD LT AlGaN buffer sample 646 occupy the intermediate position. In search of centers responsible for the observed changes of L_d we first carried out DLTS with electrical injection measurements. DLTS studies on sample 385 have already been published in [6] (this is sample #1 of [6]). They showed the presence of only one dominant electron trap with apparent activation energy of 0.55 eV (the ET4 trap in the system of notation proposed in [1]). The density of these traps was found to be $2.8\cdot 10^{15}$ cm^{-3}. Figure 1 shows DLTS spectra measured for samples 646, B95 and 598 with time windows t_1/t_2=100 ms/1000 ms, with reverse bias of –0.5 V and the forward bias pulse of +1V (the pulse duration was 2s).

For sample 646 the only feature is the peak near 270K corresponding to the same ET4 trap as in sample 385. The concentration of this trap was $6.2\cdot 10^{15}$ cm^{-3}. In sample B95, in addition to the ET4 trap with concentration $2.8\cdot 10^{15}$ cm^{-3}, we observed an electron trap with activation energy 0.25 eV (the ET2 trap [1]) with concentration $2.5\cdot 10^{14}$ cm^{-3}, the electron trap with activation energy of 0.8 eV (the ET6 trap [1]) with concentration of $6.4\cdot 10^{14}$ cm^{-3}, and an electron trap with activation energy of 1 eV that is

Table I. Electrical and structural properties of the studied samples

Sample #	Growth method	doping, cm^{-3}	$\Delta_{00.2}$, arcsec	n_{C-V}, cm^{-3}	L_d, μm
385	MOCVD, LT AlGaN buffer	none	540	$2\cdot 10^{15}$	0.5-0.6
644	MOCVD, LT AlGaN buffer	none	450	$5\cdot 10^{14}$	0.9-1.2
646	MOCVD, LT AlGaN buffer	Si, $<10^{18}$	450	$2.3\cdot 10^{16}$	2
598	MOCVD, LT GaN buffer	Si, $<10^{18}$	180	$2\cdot 10^{16}$	0.9
B95	HVPE	none	540	$1.3\cdot 10^{16}$	2-3

not well resolved for t_1/t_2 windows of 100/1000 ms but was clearly visible with longer windows of 10/50 s (the trap concentration was $9.3\cdot10^{14}$ cm^{-3}). In sample 598 we did not observe the ET4 traps in measurable concentrations. Instead one could observe a broad feature near 300-370K that is obviously a superposition of two or more peaks due to some unidentified electron traps ETX and a trap with activation energy of 1 eV reminding a similar center in sample B95 but having a higher capture cross section. The densities of corresponding traps were $8\cdot10^{14}$ cm^{-3} (ETX) and $2.3\cdot10^{14}$ cm^{-3}(1 eV trap). Comparing the above results with the L_d values in Table I shows that none of the electron traps shallower than 1 eV can account for the observed changes of L_d in various samples. Hole traps can be accessed in Schottky diodes by DLTS with optical injection (ODLTS), although getting the absolute values of the densities of traps depends on one's ability to fully recharge them. Figure 2 presents ODLTS spectra of samples B95, 598 and 646. In all these spectra the dominant feature is the peak near 300K (for the time windows t_1/t_2=100/1000 ms) corresponding to emission of holes from hole traps with the energy level E_v+0.9 eV. This trap was previously observed in various GaN samples (see [1] for discussion and relevant references) and was associated with the deep acceptor participating in the donor-acceptor pairs transition giving rise to the yellow luminescence band (this is the H2 hole trap according to notation proposed in [1]). The concentration of the H2 traps as deduced from the amplitude of the ODLTS peak was about $3.8\cdot10^{14}$ cm^{-3} in sample B95 and close to $2.9\cdot10^{15}$ cm^{-3} in samples 598 and 646. ODLTS measurements for sample 385 have been already published [6] and they showed no detectable signal from the H2 traps. Once again one has to conclude that these traps are not the ones responsible for recombination lifetimes in n-GaN. The origin of the broad band-like signal in ODLTS spectra in Figure 2 at low temperatures is most likely due to a

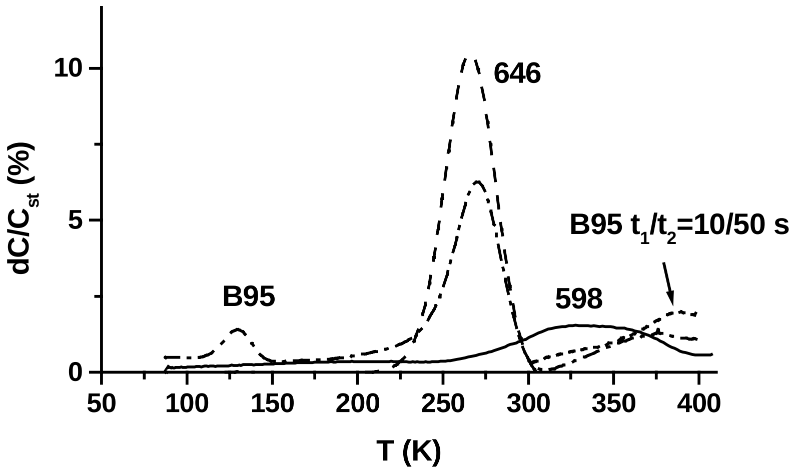

Figure 1. DLTS spectra with electrical injection measured for samples 598, 646 and B95. Measurement conditions: reverse bias of -0.5V, forward bias of 1V (2 s duration), t_1/t_2=100/1000 ms (for sample B95 we also show the high temperature portion of the spectrum measured with t_1/t_2=10/50 s)

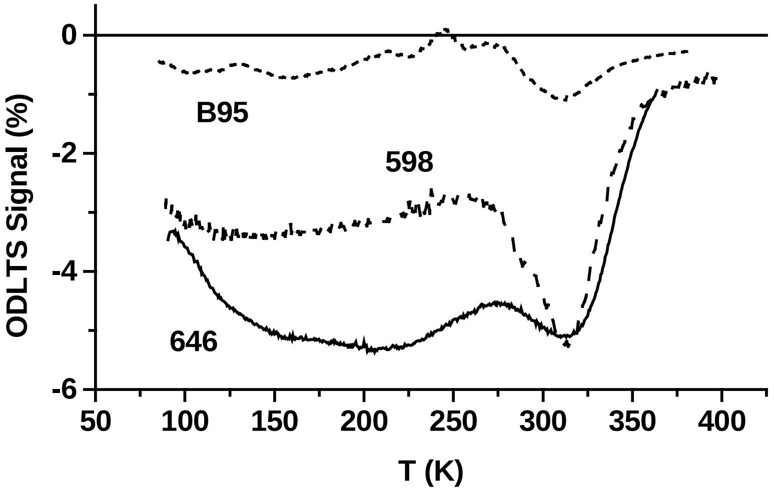

Figure 2. ODLTS spectra in samples B95, 598 and 646; measurements were made at –0.5V reverse bias, with a UV deuterium lamp injection pulse 2 s long; the spectra are shown for time windows t_1/t_2=100/1000 ms.

band of relatively shallow states in the lower half of the bandgap. The nature of this band could be further elucidated by photocapacitance measurements at low temperature and by C-T measurements before and after illumination. These measurements were performed on samples 598, 646, B95. All the samples showed an onset of measurable photocapacitance near 1 eV (about 2 pF in sample 598 and much more pronounced in samples B95, 646), slight increase near 2.5 eV, no further growth for photon energies up to 3.1 eV and a very strong increase of capacitance upon above-bandgap illumination with the deuterium UV lamp. This increase of capacitance persisted after the UV light was switched off and could be either fully (in sample 598) or partially (samples B95, 646) removed by applying forward bias of higher than 0.8 V. That shows that the metastability in question is due to charging of deep traps located below the Fermi level. This trapped positive charge led to a decrease of the built-in voltage of the diodes V_{bi} after illumination (V_{bi}^{PPC}) compared to the built-in voltage in the dark (V_{bi}). The difference, ΔV_{bi} can be used to calculate the density of recharged traps N_t from the expression [7]:

$$\Delta V_{bi}=q\cdot N_t\cdot w_0^2/(2\cdot\varepsilon\varepsilon_0), \qquad (1)$$

where w_0 is the space charge region (SCR) width under illumination, q is the electron charge, ε_0 is the permittivity of vacuum and ε is the relative permittivity. The results of these calculation are shown in Table II. It can be seen the density of traps is very high-on the order of some 10^{16} cm^{-3} in all the samples. Figure 3 shows how these metastable changes of capacitance decrease with temperature. In all three samples this happens in two stages: a broad step at 85K-250K and a step near 270K. The first of these steps is

Table II. Persistent photocapacitance results for various GaN samples

Sample #	N_d, cm^{-3}	V_{bi}, eV	N_d^{PPC}, cm^{-3}	V_{bi}^{PPC}, eV	N_t, cm^{-3}
598	$1.9 \cdot 10^{16}$	0.94	$1.9 \cdot 10^{16}$	0.51	$2.1 \cdot 10^{16}$
646	$3.4 \cdot 10^{15}$	1.06	$5.5 \cdot 10^{15}$	0.42	$1.8 \cdot 10^{16}$
B95	$5.8 \cdot 10^{15}$	1.07	$9 \cdot 10^{15}$	0.51	$2.1 \cdot 10^{16}$

most probably due to a band of relatively shallow hole trap states in the lower part of the bandgap. The second step is definitely due to detrapping of holes from the H2 traps as was demonstrated by 1.3-eV-light optical quenching experiments to be reported elsewhere. We tentatively propose that the extended band of hole trapping states could be due to dislocations which is based on the extended nature of the states we observe and on the fact that the aggregate density of these states - some 10^{16} cm^{-3} - has the right order of magnitude for the dislocation density of ~10^9 cm^{-2}. The major difference between samples 598 and B95, 646 is that the latter ones show persistent increase of electron concentration after illumination while the former does not, as can be seen from shallow donor measurements by C-V in the dark (N_d) and after illumination (N_d^{PPC}) (see Table II). This correlates very well with the absence in DLTS spectra of sample 598 electron traps ET4 which are present in samples 646 and B95 (see Figure 1). These traps have been shown to possess a barrier of about 0.15 eV for capture of electrons [6] and thus should lead to persistent photoconductivity at low temperature. C-T curve 4′ in Figure 3 shows that the step corresponding to capture of electrons by the ET4 trap ends near 200K which is fully compatible with the measured barrier height (the curve was obtained by

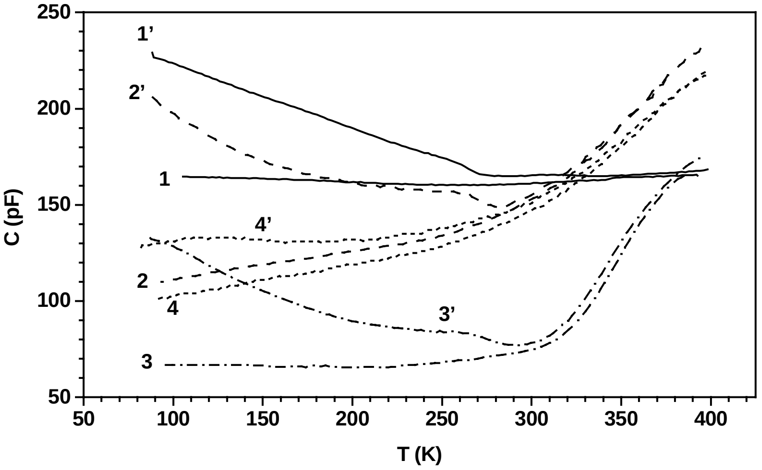

Figure 3. C-T curves for various GaN samples measured at 1 kHz when cooling in the dark (1, 2, 3, 4) and after illumination with the deuterium UV lamp at 85K (1′, 2′, 3′, 4′). Curves 1, 1′ are for sample 598, 2, 2′ for sample B95, 3, 3′ for sample 646. Also shown are the cooling down and heat-up curves for sample B95 illuminated with UV light and quenched with forward bias pulse of 0.8 V (curves 4, 4′; note that only the signal from PPC due to ET4 trap can be seen).

illuminating B95 sample with UV light and filling all the centers but the ET4 traps with a forward bias pulse of 0.8 V; similar results were obtained by illuminating the sample with 1.3 eV light - the results of these experiments will be presented elsewhere).

If the situation with persistent photoconductivity (PPC) is reasonably well understood in our samples the nature of the recombination channel competing with radiative recombination remains elusive. None of the centers described above can aspire to such a role. Perhaps surface recombination could be held responsible here but this question obviously requires further study. It also remains to be seen whether the band-like states near the valence band detected in our ODLTS and photocapacitance measurements could play any significant role in recombination. These states undoubtedly can capture electrons at a certain rate as demonstrated by forward bias pulse filling experiments but the total density of states in the band seems to be almost the same in samples with significantly different L_d values. To us it seems more likely that these band states are rather hole traps and compensation centers. If indeed the states are associated with dislocations they could contribute to forming the barriers for recombination around dislocations and explain lowered radiative recombination efficiency near individual dislocations demonstrated recently by several groups (see an extensive discussion and relevant references in [1]).

CONCLUSIONS

We have shown that in n-GaN there exist band-like states in the lower portion of the bandgap. These states have the total density of some 10^{16} cm^{-3} and can give rise to very large metastable changes of capacitance at low temperatures.

Persistent photoconductivity in n-GaN films is associated in part with the ET4 electron traps having a relatively high barrier for capture of electrons.

In n-GaN there exist unidentified recombination channels that effectively compete with the radiative recombination transitions. But none of the centers detected by capacitance spectroscopy can be associated with such channels.

REFERENCES

1. A.Y. Polyakov, in GaN and Related Materials, ed. S.J. Pearton (Gordon&Breach Science Publishers, Singapore, 1999) pp. 173-233
2. B. Monemar, in the Proceedings of the 2nd Int. Conf. on Nitride Semiconductors (ICNS'97), Tokushima, Japan, 1997, pp. 6-8
3. W.V. Lundin, B.V. Pushnyi, A.S. Usikov, M.E. Gaevski, M.V. Baidakova and A.V. Sakharov, Inst. Phys. Conf. Ser. **155**, 319 (1997)
4. Yu. V. Melnik, I.P. Nikitina, A.S. Zubrilov, A.A. Sitnikova and V.A. Dmitriev, Inst. Phys. Conf. Ser. **142**, 863 (1996)
5. A.Y. Polyakov, N.B. Smirnov, A.V. Govorkov, D.W. Greve, M. Skowronski, M. Shin and J.M. Redwing, MRS Internet J. Nitride Semicond. Res. (MIJ-NSR), **3**, article 37 (1998)
6. A.Y. Polyakov, N.B. Smirnov, A.S. Usikov, A.V. Govorkov and B.V. Pushnyi, Solid-St. Electron., **42**, 1959 (1998)
7. L.S. Berman and A.A. Lebedev, Capacitance Spectroscopy of Deep Centers in Semiconductors (Nauka, Leningrad, 1981) chapter 1, p. 29 (in Russian)