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Impact of carbon on trap states in n-type GaN grown by metalorganic chemical vapor deposition

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The effect of excess C incorporation on the deep level spectrum of n-type GaN grown by metalorganic chemical vapor deposition was investigated. Low-pressure (LP) growth conditions were used to intentionally incorporate excess C compared to atmospheric pressure (AP) growth conditions. GaN samples with high C content are found to be highly resistive, and samples codoped with C and Si are heavily compensated. From a comparison of deep level optical spectroscopy and deep level transient spectroscopy measurements of the LP-grown codoped GaN:C:Si sample with the AP-grown unintentionally doped GaN, two deep levels at $E_c - E_t = 1.35$ and 3.28 eV are observed to have a direct relation to excess C incorporation. Comparing these activation energies to previous theoretical studies strongly suggests that the levels may be associated with a C interstitial and C_N defect, respectively. These results suggest that C forms not only a shallow acceptor level but also a deep acceptor level in GaN, and these levels contribute to the compensation of the free carriers in n-type GaN:C.
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Carbon incorporation in GaN is a topic of substantial interest due to its potential in achieving semi-insulating GaN,[1] in addition to its role in the continued search for efficient p-type doping.[2] However, the nature of carbon-related states in the GaN band gap is complex and not well understood at present, with mounting evidence that suggests C also plays a role in the formation of deep levels,[1,3,4] which may lead to carrier trapping, recombination, and a possible contribution to the formation of semi-insulating material. For example, C doping has recently found application in forming highly resistive (HR) and semi-insulating (SI) nitride buffer layers in high electron mobility transistors (HEMTs),[3] wherein an anticipated C-related shallow acceptor is thought to compensate unintentional donors. However, the current collapse in HEMT structures has been attributed to a deep acceptor due to C in the SI GaN:C layer,[3] but the specific properties of this level are poorly understood. C incorporation as a deep acceptor in GaN is further supported by recent evidence indicating that the yellow luminescence (YL) transition in SI GaN:C may involve a C-related deep acceptor.[4] Clearly, while previous results show C has great potential as a compensating acceptor, the above considerations, coupled with the amphoteric nature of C, suggest that C introduces not just a shallow acceptor state, but is likely to form other defect states within the band gap. Thus, identification and control of C-related states is crucial to the development of C as a practical impurity for achieving SI GaN.

In this letter, we use deep level optical spectroscopy (DLOS) and deep level transient spectroscopy (DLTS) to probe the entire band gap of low-pressure (LP) metalorganic chemical vapor deposition (MOCVD) GaN codoped with Si and C. LP growth conditions were used to incorporate a high level of background C with respect to atmospheric pressure (AP) growth.[5] To gauge the impact of C incorporation, we compare band-gap states in LP GaN:Si:C with those in unintentionally doped (UID) GaN grown under AP conditions. The correlation between the increase in C concentration and band-gap state concentration of levels common to each material, along with the emergence of different trap states, provide insight into the role of C in n-type GaN.

GaN samples were grown by MOCVD on c-plane sapphire substrates having identical 1 μm thick, UID AP-grown GaN-template layers[6] with a similar threading dislocation density ($\sim 6-8 \times 10^8$ cm^{-2}) and character. An n^+-GaN:Si buffer layer with a thickness of 0.8 μm was grown on the template as a contact layer prior to the growth of the n-GaN active layers that were characterized by DLOS/DLTS measurements. The active layers were grown at 1040 °C and at either 76 (LP) or 760 (AP) Torr. The active layer for the AP-MOCVD GaN was unintentionally doped, whereas both UID and Si codoped (nominal Si doping was 2×10^{17} cm^{-3}) active layers were used for the LP-MOCVD structures. Device mesa areas were delineated by Cl_2 reactive ion etching, and an 80 Å thick Ni film was evaporated to form semitransparent Schottky contacts to the active layers of each sample. A Ti/Al/Ni/Au ohmic contact was deposited on the exposed buffer layer to complete the device. All DLOS and DLTS experiments were performed with quies-

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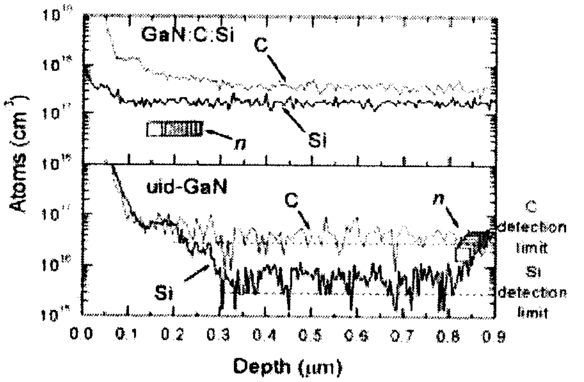

FIG. 1. (Color) SIMS profiles of the C and Si concentrations in the AP (lower) and LP (upper) samples. The dashed lines indicate the detection limits for C and Si (3×10^{16} cm^{-3} and 3×10^{15} cm^{-3}, respectively). Also shown is the free carrier concentration, n, obtained from $C-V$ analysis. The free carrier concentration profile depth is governed by the depletion region width of the diodes.

cent and fill biases of −0.5 and 0 V, respectively. The fill pulse time for DLTS and DLOS experiments was 10 ms, and 10 s, respectively. Complete details of the measurement conditions and standard DLOS/DLTS device structures can be found in earlier publications.[7]

Figure 1 compares the carrier concentration n [found from capacitance–voltage ($C-V$) analysis] with secondary ion mass spectroscopy (SIMS) profiles of C and Si impurities for AP and LP samples. The higher C concentration in LP GaN:C material results in HR behavior, as evidenced by a voltage-independent junction capacitance. In fact, $C-V$ analysis of the GaN:C sample was indeterminate due to the complete depletion of the active layer, implying heavy compensation of the unintentional donors by a high C concentration, as anticipated. To overcome this, a codoped LP GaN:C:Si sample was grown. For the GaN:C:Si active layer, the C concentration is 3.8×10^{17} cm^{-3}, while n is 4.9×10^{16} cm^{-3}, which is much less than the Si donor concentration of 1.8×10^{17} cm^{-3}. For the AP UID-GaN sample, n is found from a $C-V$ analysis to be 2.3×10^{16} cm^{-3}, which matches well with the Si profile at the probed depth and implies that the C concentration is well below its detection limit of 3×10^{16} cm^{-3}. That the LP samples are heavily compensated while the AP sample shows a typical n-type background for UID GaN suggests the formation of acceptor states due to C.

In an attempt to identify the specific band-gap states either introduced or impacted by C that are responsible for the observed compensation and resistive properties of GaN:C, DLOS and DLTS measurements were undertaken. Note that because the SI behavior of the GaN:C results in a voltage-independent junction capacitance, further mention of the LP samples refers only to the GaN:C:Si codoped LP sample. From the steady-state photocapacitance (SSPC) and DLTS spectra shown in Fig. 2, the LP GaN:C:Si sample clearly incorporates a much higher total concentration of band-gap states than does the AP UID-GaN sample with a much lower C content. Consideration of each level individually suggests that several are not directly C related. First, the concentration of the commonly reported $E_c-0.6$ eV level[8,9] is virtually unchanged (1.4×10^{13} cm^{-3} for AP and 1.0×10^{13} cm^{-3} for LP) between samples, which implies that this band-gap state is not related to excess C incorporation and may indeed be an intrinsic defect state of GaN. Second, while the $E_c-2.6$ eV trap concentration increases dramatically for the LP GaN:C:Si sample, this state has been experimentally related to V_{Ga},[9,10] in agreement with theoretical predictions.[11] Further, other reports have shown that C_N-V_{Ga} complexes are unstable for n-GaN.[12] A strong dependence of V_{Ga} incorporation on the growth environment can be expected, and is the subject of a separate paper that comprehensively compares LP- versus AP-MOCVD-grown GaN.[13] Regarding the shallow donor levels shown in the DLTS spectra near $E_c-0.2$ eV, the $E_c-0.25$ eV level is commonly observed in GaN[8,14] and is not evident in the GaN:C:Si sample, implying that it is not related to C. Moreover, it is well established that C-related shallow donor levels are not expected to form in n-type GaN.[12] While a seemingly shallower donorlike state emerges in the GaN:C:Si DLTS spectrum, its concentration is ~5 orders of magnitude below the n-type background concentration, leading to spurious detection of a signal that is too small to analyze with confidence. This leaves only the shallow acceptors at near $E_c-3.2$ eV and the deep state at $E_c-1.35$ as potentially related to C. We now focus on these levels.

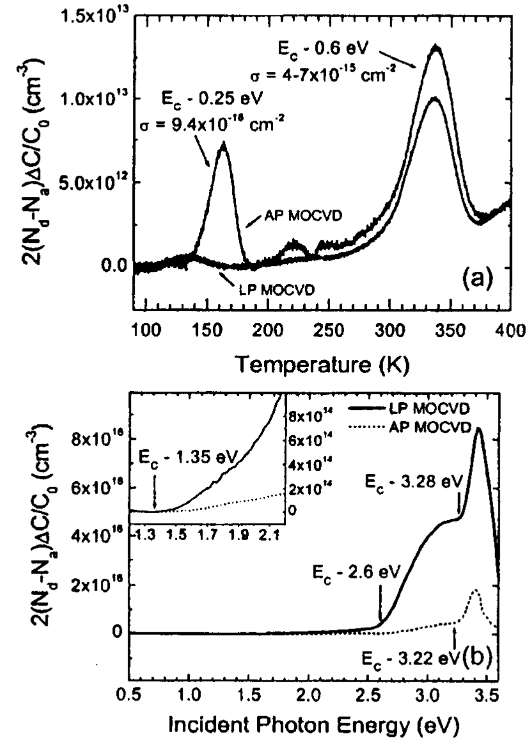

FIG. 2. (a) DLTS spectra ($e=0.005$ s^{-1}) for the AP and LP materials. The apparent peaks near 225 K in the AP spectrum have a concentration ~5 orders of magnitude below the n-type background and do not exhibit typical Arrhenius behavior. Therefore, they are likely spurious and do not correspond to physical levels. (b) SSPC spectra for the AP and LP materials. The inset shows the $E_c-1.35$ eV level.

Figure 2 evinces the presence of a dominant level at $E_c-3.28$ eV with a concentration of 3.6×10^{16} cm^{-3} for the GaN:C:Si sample, compared to a dominant, slightly deeper

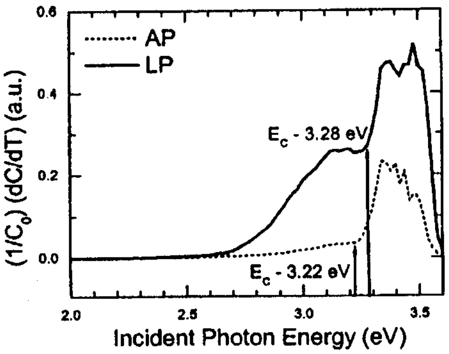

FIG. 3. Time derivatives of the photocapacitance transients from 0–1.0 s for both the AP and LP material. The onset due to emission from the $E_c-3.28$ eV level for the LP sample occurs at distinctly greater illumination energy than emission from the $E_c-3.22$ eV level for the AP sample. An onset due to emission from the level near $E_c-2.6$ eV is also observable in these spectra.

acceptor at $E_c-3.22$ eV with a concentration of 1.3×10^{16} cm^{-3} for the UID-GaN sample. This energy difference is consistently observed, and the derivatives of the photocapacitance transients obtained between 0 and 1.0 s shown in Fig. 3 exhibit these different activation energies more clearly. A modest onset near $E_c-3.22$ eV in the LP photocapacitance transient spectrum suggests this level is also present in the LP sample. However, the slow rise in the SSPC and the similar activation energies of these levels make it difficult to determine if the 3.22 eV level contributes significantly to the defect spectrum in the GaN:C:Si material. Prior work has established that the $E_c-3.22$ eV level results from residual $\mathrm{Mg_{Ga}}$ acceptors.[9,15] A somewhat shallower acceptor state attributed to C_N has been previously observed.[16] Also, theoretical calculations[12,17] assign the C_N state near $E_v+0.15-0.2$ eV, and the $E_c-3.28$ eV level gives an activation energy of 0.16 eV, agreeing very well with previous effective-mass calculations for C_N.[17] Further, the $E_c-3.28$ eV level, but not the $E_c-3.22$ eV, is observed in GaN grown via molecular-beam epitaxy (MBE),[15] which supports the assertion that the $E_c-3.28$ eV level is not Mg-related since residual Mg is negligible in MBE-grown GaN material whereas C is ubiquitous. Considering that the emergence of a shallower dominant acceptor state accompanies a significant increase in the C concentration for the GaN:C:Si sample compared to the UID-GaN sample, we conclude from this preponderance of findings that C_N is likely the origin of the $E_c-3.28$ eV level. Finally, we note that though the C concentration is slightly greater than the Si concentration in the GaN:C:Si sample, we do not observe SI or p-type behavior. The lack of type conversion or HR behavior indicates that for n-type GaN grown by LP-MOCVD under the growth conditions used in this study, C may incorporate in states other than C_N, and these other states are likely closer to midgap and thus are less efficient trapping and compensating centers.

The $E_c-1.35$ eV level is possibly such a C-related deep level. The concentration of this level increases ~six times from 3.9×10^{14} cm^{-3} for the UID-GaN sample to 2.3×10^{15} cm^{-3} for the GaN:C:Si sample, suggesting that the increase could be related to excess C. A prior study of MOCVD-grown GaN also found that the concentration of the $E_c-1.35$ eV state tracks the residual C concentration.[9] It is suggestive that this level is near the theoretically predicted $E_c-1.1$ eV and $E_c-1.2$ eV band-gap states of a C interstitial double acceptor level expected to form in n-type GaN.[12] Further, the $E_c-1.35$ eV level has been detected in every MOCVD- and MBE-grown GaN sample we have studied previously,[9,13,15] which suggests an omnipresent defect such as C or possibly dislocations. However, we consider dislocations to be a less likely primary source since both the AP and LP GaN active layers were grown on identical templates with the same (nominally) dislocation density and character.[6] These compelling considerations notwithstanding, an even more systematic comparison between the $E_c-1.35$ eV state concentration and its relation to C is now underway to verify the physical source for this deep acceptor.

In summary, the concentration of two deep band-gap states detected by DLOS at $E_c-E_t=3.28$ and 1.35 eV demonstrate direct dependence on C concentration in MOCVD-grown n-type, compensated GaN:C:Si. The band-gap positions of these states are in close agreement with theoretical predictions for C_N compensating acceptor and C_I interstitial, respectively, in n-type GaN. The presence of these levels is expected to contribute to the compensating properties of semi-insulating GaN:C.

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[1] C. H. Seager, A. F. Wright, J. Yu, and W. Goetz, J. Appl. Phys. **92**, 6553 (2002).
[2] C. R. Abernathy, J. D. MacKenzie, S. J. Pearton, and W. S. Hobton, Appl. Phys. Lett. **66**, 1969 (1995).
[3] P. B. Klein, S. C. Binari, K. Ikossi, A. E. Wickenden, D. D. Kolske, and R. L. Henry, Appl. Phys. Lett. **79**, 3527 (2001).
[4] R. Armitage, W. Hong, Q. Yang, H. Feick, J. Gebauer, E. R. Weber, S. Hautakangas, and K. Saarinen, Appl. Phys. Lett. **82**, 3457 (2003).
[5] G. Parrish, S. Keller, S. P. DenBaars, and U. K. Mihsra, J. Electron. Mater. **29**, 15 (2000).
[6] X. H. Wu, P. Fini, E. J. Tarsa, B. Heying, S. Keller, U. K. Mishra, S. P. DenBaars, and J. S. Speck, J. Cryst. Growth **189**, 431 (1998).
[7] A. Hierro, D. Kwon, S. A. Ringel, S. Rubini, E. Pelucchi, and A. Franiosi, J. Appl. Phys. **87**, 730 (2003).
[8] P. Hacke, T. Detchprohm, K. Hiramatsu, N. Sawaki, K. Tadatomo, and K. Miyake, J. Appl. Phys. **76**, 304 (1994).
[9] A. Hierro, D. Kwon, S. A. Ringel, M. Hansen, J. S. Speck, U. K. Mishra, and S. P. DenBaars, Appl. Phys. Lett. **76**, 3064 (2000).
[10] E. Calleja, F. J. Sanchez, D. Basak, M. A. Sanchez-Garcia, E. Munoz, I. Izpura, F. Calle, J. M. G. Tijero, and J. L. Sanchez-Rojas, Phys. Rev. B **55**, 4689 (1997).
[11] C. G. Van de Walle, Phys. Rev. B **56**, 10020 (1997).
[12] A. F. Wright, J. Appl. Phys. **92**, 2575 (2002).
[13] A. Armstrong, A. R. Arehart, B. Moran, U. K. Mishra, J. S. Speck, and S. A. Ringel (unpublished).
[14] W. Goetz, N. M. Johnson, H. Amano, and I. Akasaki, Appl. Phys. Lett. **65**, 463 (1994).
[15] A. Hierro, A. R. Arehart, B. Heying, M. Hansen, U. K. Mishra, S. P. DenBaars, J. S. Speck, and S. A. Ringel, Appl. Phys. Lett. **80**, 805 (2002).
[16] S. Fischer, C. Wetzel, E. E. Haller, and B. K. Meyer, Appl. Phys. Lett. **67**, 1298 (1995).
[17] H. Wang and A.-B. Chen, Phys. Rev. B **63**, 125212 (2001).