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Title

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Permalink

<https://escholarship.org/uc/item/0ws132v5>

Journal

Applied Physics Letters, 88(8)

ISSN

0003-6951

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Publication Date

2006-02-01

Peer reviewed

Impact of substrate temperature on the incorporation of carbon-related defects and mechanism for semi-insulating behavior in GaN grown by molecular beam epitaxy

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(Received 12 October 2005; accepted 2 February 2006; published online 24 February 2006)

The electrical conductivity and deep level spectrum of GaN grown by molecular beam epitaxy and codoped with carbon and silicon were investigated for substrate temperatures T_s of 650 and 720 °C as a function relative carbon and silicon doping levels. With sufficiently high carbon doping, semi-insulating behavior was observed for films grown at both temperatures, and growth at $T_s = 720$ °C enhanced the carbon compensation ratio. Similar carbon-related band gap states were observed via deep level optical spectroscopy for films grown at both substrate temperatures. Due to the semi-insulating nature of the films, a lighted capacitance-voltage technique was required to determine individual deep level concentrations. Carbon-related band gap states underwent substantial redistribution between deep level and shallow acceptor configurations with change in T_s . In light of a T_s dependence for the preferential site of carbon incorporation, a model of semi-insulating behavior in terms of carbon impurity state incorporation mediated by substrate temperature is proposed. © 2006 American Institute of Physics. [DOI: 10.1063/1.2179375]

Growth of high quality GaN:C films via rf plasma assisted molecular beam epitaxy (MBE) under Ga-rich conditions using CBr₄ as the carbon source¹ has lead to improved high frequency performance of all-MBE AlGaIn/GaN heterojunction field effect transistor (HFET) devices through incorporation of semi-insulating (SI) GaN:C buffer layers necessary for sharp pinch-off.² Along with the desired SI behavior, however, carbon impurity incorporation may also have inadvertent and potentially deleterious impact on device performance. To emphasize SI behavior via carbon doping while minimizing undesired effects, the overall impact of carbon-related impurity states and, in particular, the precise mechanism for SI behavior in MBE-grown GaN:C must be understood as a function of growth conditions and doping levels. To this end, a recent study of GaN:C:Si films grown under similar conditions used for constituent SI GaN:C buffer layers in HFET devices but at a reduced nominal substrate temperature $T_s = 650$ °C (to better facilitate carbon incorporation) found that SI behavior results from carrier compensation by a carbon-related deep level and near-valence band state.³ Yet AlGaIn/GaN HFET structures are typically grown at higher T_s due to improved structural properties and reduced impurity incorporation, and sensitivity of preferential carbon band gap state incorporation to T_s can be expected. To optimize the use of GaN:C buffer layers in MBE-grown HFET devices, this work extends the investigation of carbon-related deep level activity to T_s that is directly commensurate with device growth.

To focus on the role of carbon impurities in GaN, this study compares the deep level activity of Schottky

GaN:C:Si diodes grown by rf plasma-assisted MBE under Ga-rich conditions using a CBr₄ dopant source as a function of substrate temperature. One series of samples (HT) was grown at $T_s = 720$ °C, which is typical for high performance AlGaIn/GaN HFET devices grown by MBE.² Diode structure consisted of unintentionally doped GaN of 700 Å thickness grown on a Lumilog two-step lateral epitaxial overgrowth template, followed by a 3800 Å n^+ -GaN:Si lateral conduction layer, upon which was grown a 6200 Å GaN:C:Si layer. Mesas were formed by reactive ion etching, and a semitransparent Ni layer and a Ti/Ni/Al/Au stack formed the Schottky and ohmic contacts, respectively. A previously studied series (LT) had a similar device structure but was grown at $T_s = 650$ °C.³ Within both series the [C] of each film was systematically varied with respect to constant [Si]. Table I summarizes the nominal doping levels for all the samples. While the HT series has reduced [C] because the higher T_s limits carbon incorporation, the same nominal [Si]:[C] ratio is maintained for both series. The HT series

TABLE I. Nominal doping for all films.

Sample	[Si] (cm ⁻³)	[C] (cm ⁻³)
LT-LC	1×10^{18}	5×10^{17}
LT-MC	1×10^{18}	1×10^{18}
LT-HC	1×10^{18}	5×10^{18}
HT-LC	1×10^{17}	5×10^{16}
HT-MC	1×10^{17}	1×10^{17}
HT-HC	1×10^{17}	5×10^{17}
HT-AC	...	5×10^{17}

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FIG. 1. Free carrier concentrations determined via C-V analysis for samples HT-MC and LT-MC, both with nominal $[C]=[Si]$.

also included a GaN:C film doped at $5 \times 10^{17} \text{ cm}^{-3}$ with no silicon codoping (HT-ac).

To determine the impact of T_s on carbon compensation efficiency, the free carrier concentration n was determined via capacitance-voltage (C-V) characterization. Films for which $[C]<[Si]$ proved to be n type, and those with $[C]>[Si]$ were fully depleted, regardless of T_s . However, as shown in Fig. 1, n of the LT-MC and HT-MC films, for which the $[Si]:[C]$ ratios are nominally unity, were quite different. The GaN:C:Si layer grown at $T_s=720^\circ\text{C}$ was fully depleted to the underlying n^+ -GaN:Si layer, whereas at $T_s=650^\circ\text{C}$, $n=2 \times 10^{16} \text{ cm}^{-3}$, indicating substantial yet incomplete compensation of the Si donors at the lower growth temperature. This finding suggests that growth at higher T_s enhances the compensation factor of carbon and may favor carbon incorporation at energy levels that more readily facilitate SI behavior.

To gain insight into the deep levels responsible for the observed SI behavior, deep level optical spectroscopy⁴ (DLOS) was employed at 297 K using a quiescent bias of -0.5 and 0 V fill pulse lasting 10 s. The DLOS spectra were corrected for the photon flux profile of the optics system to ascertain the spectral dependence of the optical cross-section $\sigma^0(h\nu)$ from which the optical ionization energy E_o and Franck-Condon energy (d_{FC}) were extracted. Complete details of the DLOS experiment are given elsewhere.⁴ Since the spectral dependence of $\sigma^0(h\nu)$ suffices to determine the salient deep level parameters, the DLOS spectra presented here are offset to present the data clearly. DLOS spectra for fixed T_s were similar for all $[C]:[Si]$ doping ratios, so the data and theoretical fits of the LT-MC and HT-MC samples, which are representative of both series, are shown in Fig. 2(a). Two

band gap states are discerned, one with a sharp onset and another with a broad onset. The sharp $\sigma^0(h\nu)$ spectral features were fit with an expression appropriate for an effective-mass like state.⁵ However, fitting the broader spectra required a more complicated formulation for $\sigma^0(h\nu)$ involving lattice-relaxation effects.⁴

Referring to Fig. 2(a), the comparable spectral dependence of $\sigma^0(h\nu)$ from $E_c-2.6$ to 3.2 eV and 3.28 to 3.40 eV evident for each T_s imply the presence of mutual carbon-related band gap states. Extensive discussion of the LT series has been provided in another publication,³ wherein the positions of these levels were determined to be at $E_c-3.28$ eV (with negligible d_{FC}) and $E_c-3.00$ eV ($d_{FC}=0.40$ eV). The former was attributed to C_N and the latter to a carbon-related deep level, respectively, by, among other means, correlating their concentrations N_t with $[C]$.³ DLOS analysis of the HT series spectra finds the same $E_c-3.28$ eV state, but places the deep level at $E_c-3.19$ eV ($d_{FC}=0.56$ eV). However, consideration of lattice-relaxation effects suggests that the $E_c-3.00$ and $E_c-3.19$ eV levels share a common defect source. The ~ 0.2 eV discrepancies between the fitted E_o and d_{FC} values can be attributed to variation in local atomic relaxation about the same carbon defect center arising from different growth conditions at the two substrate temperatures. Indeed, close agreement between both deep level thermal ionization energies, which is given as E_o-d_{FC} and is not sensitive to lattice-relaxation effects, supports their identification with each other.

Of particular interest is the relative dependence of N_t on T_s for these carbon-related band gap states. The photocapacitance spectra of the LT-HC and HT-HC films (for which $[C]:[Si] = 5:1$) shown in Fig. 2(b) suggest that T_s greatly impacts the site selectivity of carbon between these band gap states when carbon becomes the dominate impurity. The LT-HC film exhibits comparable photocapacitance response $\Delta C/C_0$ for both the deep level (with an onset near $h\nu = 2.6$ eV due to phonon-assisted photoionization) and the $E_c-3.28$ eV state. Conversely, for the HT-HC film, the deep level photocapacitance becomes negligible compared to that of the shallow acceptor level. Thus, a significant redistribution of carbon is apparent between the near-valence band acceptor and deep level when T_s is increased, with higher T_s favoring the former.

While photocapacitance offers compelling qualitative evidence that the $E_c-3.28$ eV deep level becomes dominate for growth at $T_s=720^\circ\text{C}$, this technique does not provide quantitative determination of N_t for the present case where $\Delta C/C_0 \sim 1$ because this term is not proportional to N_t .⁶ Violation of the small signal condition $\Delta C/C_0 \ll 1$ is typical of highly compensated and SI semiconductors and signifies that deep level photoionization induces a significant redistribution of the space charge in the depletion region. This is exhibited for the HT-MC sample in Fig. 3(a), which shows the effective carrier concentration $n_{\text{eff}}(h\nu)$ determined via C-V profiling while the diode is illuminated with monochromatic, subband gap light, i.e., lighted C-V (LCV).⁷ Illuminating the sample HT-MC with photons of energy $h\nu=3.24$ eV photoionizes the deep level while leaving the $E_c-3.28$ eV state fully occupied. Due to the relatively small N_t of the carbon deep level in this film, the depletion region edge remains fixed at the underlying highly doped GaN:Si layer and $n_{\text{eff}}(h\nu=3.24 \text{ eV})$ corresponds to the step in the Si doping.

FIG. 2. (a) DLOS spectra of samples HT-MC and LT-MC along with theoretical fits. (b) Photocapacitance for samples LT-HC and HT-HC.

FIG. 3. Lighted C - V scans for (a) sample HT-MC and (b) sample HT-ac.

Conversely, photoionization of the E_c -3.28 eV deep level with $h\nu=3.42$ eV places the depletion edge well within the otherwise fully depleted GaN:C:Si region, demonstrating that the shallow acceptor concentration is much greater than that of the deep level. Assuming complete photoionization and no recombination in the depletion region, the increase in $n_{\text{eff}}(h\nu)$ is equal to N_t . However, for $h\nu > E_g/2$, where E_g is the band gap energy, simultaneous electron and hole photoemission is possible for a deep level, leading to incomplete photoionization.⁶ Thus, N_t measured here are a lower bound. Taking n to be effectively zero in the GaN:C:Si layer without illumination, $[E_c-3.28 \text{ eV}] \geq n_{\text{eff}}(h\nu=3.42 \text{ eV}) = 3.9 \times 10^{16} \text{ cm}^{-3}$. Due to their inclusion in HFET devices, it is of interest to address the role of carbon in films grown at $T_s = 720^\circ\text{C}$ without Si codoping, i.e., HT-ac. Figure 3(b) shows LCV scans for the HT-ac sample, where again photoionization of the E_c -3.28 eV deep level alone affects the space charge of the GaN:C layer, implying that the carbon deep level concentration is negligible.

The implications of differing carbon incorporation as a function of T_s are now considered in terms of the mechanism for SI behavior in carbon-doped GaN grown by MBE under the present conditions. When carbon becomes the dominant impurity, the data point to a trend where growth at $T_s = 650^\circ\text{C}$ favors carbon incorporation as a deep level with comparable $[E_c-3.28 \text{ eV}]$, whereas the E_c -3.28 eV state becomes the primary carbon band gap state for $T_s = 720^\circ\text{C}$. For the latter case, dominance of the near-valence band acceptor state, combined with the lack of p -type behavior for $[C] > [\text{Si}]$, suggests that the C_{Ga} donor level, which density functional theory calculations place near $E_c-0.2 \text{ eV}$,⁸ may also form with appreciable concentration. Such a donor level lying close to E_c is well above the Fermi level (E_F) of a SI film and might not be observed via capacitance spectroscopy techniques. This scenario implies that for growth at T_s

$= 720^\circ\text{C}$, SI behavior results from E_F pinning via autocompensation by C_N acceptor and C_{Ga} donor states, as suggested for GaN:C:Si films grown by metal organic chemical vapor deposition.⁸ This contrasts with the mechanism for SI behavior in GaN:C:Si films grown under the present conditions at $T_s = 650^\circ\text{C}$, where direct carrier compensation by both the E_c -3.00 and 3.28 eV levels effects SI behavior.³

In summary, the electrical conductivity and deep level spectra of GaN:C:Si films grown via MBE at $T_s = 650$ and 720°C were compared as a function of relative $[C]:[\text{Si}]$ doping levels. Semi-insulating behavior was achieved at both T_s for sufficiently high $[C]:[\text{Si}]$ ratio, but films grown at $T_s = 720^\circ\text{C}$ exhibited SI behavior at lower $[C]:[\text{Si}]$ doping ratios. Similar deep level spectra were evident for films grown at both T_s , though substantial redistribution of carbon-related band gap states was observed. While carbon appears to readily incorporate as both a deep level and shallow acceptor in films grown at $T_s = 650^\circ\text{C}$, there is negligible carbon-related deep level concentration compared to that of the shallow carbon acceptor for films grown at $T_s = 720^\circ\text{C}$. This finding implies that the mechanism for SI behavior in MBE-grown GaN:C:Si films for the present growth condition is sensitive to T_s , wherein films grown at the lower T_s achieve SI behavior via direct carrier compensation, while the mechanism for SI behavior for the higher T_s appears to be E_F pinning via autocompensation of substitutional carbon donor and acceptor states.

The work at OSU was supported by ONR (H. Dietrich) through Contract Nos. N000114-1-0055 and N00014-03-1-0014, and by the ONR MURI—Center for Advanced Nitride Electronics at UCSB. The work at UCSB was supported by ONR (H. Dietrich, program manager) and AFOSR (G. Witt, program manager).

¹D. S. Green, U. K. Mishra, and J. S. Speck, *J. Appl. Phys.* **95**, 8456 (2004).

²C. Poblenz, P. Waltereit, S. Rajan, U. K. Mishra, and J. S. Speck, *J. Vac. Sci. Technol. B* **22**, 1145 (2004).

³A. Armstrong, A. R. Arehart, D. Green, U. K. Mishra, J. S. Speck, and S. A. Ringel, *J. Appl. Phys.* **98**, 053704 (2005).

⁴A. Chantre, G. Vincent, and D. Bios, *Phys. Rev. B* **23**, 5335 (1981).

⁵G. Lucovsky, *Solid State Commun.* **3**, 299 (1965).

⁶P. Blood and J. W. Orton, *The Electrical Characterization of Semiconductors: Majority Carriers and Electron States* (Academic, San Diego, 1992).

⁷A. Armstrong, A. R. Arehart, and S. A. Ringel, *J. Appl. Phys.* **97**, 83529 (2005).

⁸C. H. Seager, A. F. Wright, J. Yu, and W. Goetz, *J. Appl. Phys.* **92**, 6553 (2002).