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Evolution of deep centers in GaN grown by hydride vapor phase epitaxy

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Deep centers and dislocation densities in undoped *n* GaN, grown by hydride vapor phase epitaxy (HVPE), were characterized as a function of the layer thickness by deep level transient spectroscopy and transmission electron microscopy, respectively. As the layer thickness decreases, the variety and concentration of deep centers increase, in conjunction with the increase of dislocation density. Based on comparison with electron-irradiation induced centers, some dominant centers in HVPE GaN are identified as possible point defects. © 2001 American Institute of Physics.
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Hydride vapor phase epitaxy (HVPE) is a promising technique for growing thick GaN layers to be used as substrates for the subsequent growth of device structures. The material quality of HVPE GaN has been found to improve greatly with thickness, mainly because of the presence of a highly defected layer at the GaN sapphire interface.^{1–4} In an earlier study,³ deep centers in a 13- μm -thick GaN film grown by HVPE on GaCl-pretreated sapphire were characterized by deep level transient spectroscopy (DLTS). It was found that both the species and the concentrations of the detected deep centers were nearly constant as the film was thinned by mechanical polishing from the original thickness to a thickness of $\sim 1.2\ \mu\text{m}$. Recently, we have conducted a comprehensive study of impurities and defects in undoped *n*-GaN grown by HVPE. The material quality was characterized by many techniques, including electrical, optical, chemical, and structural methods. The nominal thickness of the layers varied from 1 to 68 μm , depending on growth time. Five samples, with layer thicknesses ranging from 5 to 68 μm , were chosen for DLTS characterization. Two samples, with nominal thicknesses of 5 μm and 68 μm , were selected for transmission electron microscopy (TEM) characterization. In this letter, we present the evolution of deep centers (both in species and concentrations) as layer thickness is reduced. The possible identities of the dominant centers will be discussed based on a comparison with electron-irradiation (EI) induced centers, and the correlation of DLTS centers with the threading dislocation density measured by TEM.

The GaN layers used in this study were grown on ZnO-pretreated sapphire in a chloride-transport HVPE vertical reactor. Details of the GaN growth and the sapphire pretreatment techniques are described elsewhere.⁴ Scanning electron microscopy was used to measure the layer thicknesses, which usually varied somewhat within a wafer. For capacitance–voltage (*C–V*) and DLTS studies, five samples

with nominal thicknesses of 5, 11, 15, 39, and 68 μm were used. Schottky barrier diodes (SBDs), with planar structures on the top surface, were fabricated by using electron-beam and thermal evaporations and lithographic processing. In the planar structure, small Ni/Au Schottky contacts with diameters of 250 μm were surrounded by large-area Ti/Al/Ti/Au ohmic contacts. A Bio-Rad DL4600 system with a 100-mV test signal at 1 MHz was used to take *C–V* and DLTS data. To determine the activation energy E_T of the deep centers, the DLTS spectra were taken at different rate windows, from 0.8 to 200 s^{-1} , and were analyzed by the standard Arrhenius technique. For TEM studies, two samples with nominal thicknesses of 5 μm and 68 μm were selected, and cross sectional specimens were prepared. In order to obtain electron transparent areas from all parts of the 68 μm layer, the sample was ion milled down successively in several steps.

Carrier concentrations in the top regions of the five samples, determined by *C–V* measurements, were found to be in the $10^{17}\ \text{cm}^{-3}$ range; these results are similar to those found by Hall effect measurements, corrected for the degenerate interface layer.² Without this correction, the “apparent” (average) Hall carrier concentration for the 5 μm sample was quite high, about $1.1 \times 10^{18}\ \text{cm}^{-3}$. As the sample thickness decreased from 68 to 5 μm , the apparent (average) mobility dropped from 740 to 190 $\text{cm}^2/\text{V s}$, which are similar numbers to those reported in Ref. 3. For the three thickest samples (68–13 μm), the apparent carrier concentrations were found to increase from 1.3×10^{17} to $2.6 \times 10^{17}\ \text{cm}^{-3}$. Typical current–voltage (*I–V*) characteristics, measured at 300 K for those three samples, are shown in Fig. 1. It can be seen that the reverse leakage currents, which show typical electric-field enhanced soft-breakdown characteristics (believed to be related to carrier tunneling or hopping through defect states associated with threading dislocations), are significantly reduced by almost three orders of magnitude due to the increase of layer thickness. Forward *I–V* characteristics, described by an ideality factor *n*, are also affected; i.e., the thicker the layer, the closer the *n* value to unity. These results imply that dislocation densities in the top regions of

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FIG. 1. Typical I - V characteristics of SBDs on HVPE-GaN with different thicknesses.

the samples are reduced with increasing thickness, which is verified in the TEM images presented as follows. Typical DLTS spectra for all five samples are presented in Fig. 2. Note that the spectra in Fig. 2 have different base lines, separated by $0.5 \times 10^{14} \text{ cm}^{-3}$. From Fig. 2, we see that: (i) for the two thickest samples (see curves a and b), the dominant centers are A_x ($E_T \sim 0.72 \text{ eV}$), A ($E_T = 0.67 \text{ eV}$), and B ($E_T = 0.61 \text{ eV}$), with concentrations in the 10^{13} – 10^{14} cm^{-3} range, (ii) for the $15\text{-}\mu\text{m}$ sample (see curve c), a center with $E_T = 0.20 \text{ eV}$ (labeled as D) appears at low temperatures, (iii) for the $11\text{-}\mu\text{m}$ sample (see curve d), in addition to a center with $E_T = 0.17 \text{ eV}$ (also labeled as D) at low temperatures, the center A_1 ($E_T = 0.89 \text{ eV}$), with a higher concentration in the 10^{14} – 10^{15} cm^{-3} range, arises, and (iv) for the $5\text{-}\mu\text{m}$ sample (see curve e), B becomes a prominent center and A_1 drops significantly, as compared to its value in the $11\text{-}\mu\text{m}$ sample, and the other observed centers are A , C ($E_T = 0.41 \text{ eV}$), and D ($E_T = 0.23 \text{ eV}$). Thus, we can state that as the HVPE-GaN samples become thinner, both the species and concentrations of the deep centers increase. Interestingly, most of deep centers found in HVPE GaN have been also observed by us in n GaN grown by other techniques, such as metalorganic chemical vapor deposition (MOCVD) and reactive molecular beam epitaxy (RMBE).

FIG. 2. Typical DLTS spectra for HVPE-GaN samples with different thicknesses. The carrier concentration of each sample is shown in the legend.

FIG. 3. Cross sectional TEM images of a thick HVPE-GaN sample: (a) in the top region, (b) in the middle region, and (c) in the region close to GaN sapphire interface.

Depending on the material quality (like the layer thickness, electron mobility, and dislocation density), the concentrations of these deep centers can be as low as 10^{13} – 10^{14} cm^{-3} for a $4.5\text{-}\mu\text{m}$ -thick MOCVD GaN, with an electron mobility of $765 \text{ cm}^2/\text{V s}$ and an estimated dislocation density of low- 10^8 cm^{-2} , and as high as 10^{15} – 10^{16} cm^{-3} for $0.5\text{-}\mu\text{m}$ -thick RMBE-GaN layers, with electron mobilities below $250 \text{ cm}^2/\text{V s}$ and dislocation densities in the 10^9 – 10^{10} cm^{-2} range.⁵

Cross sectional TEM images, corresponding to three different regions of the nominally $68 \text{ }\mu\text{m}$ thick sample (the real thickness, t , of the TEM sample is $55 \text{ }\mu\text{m}$) are shown in Fig. 3. As indicated in Fig. 3, the dislocation densities clearly increase from 1×10^8 in the top region (at $t = 55 \text{ }\mu\text{m}$), up to $3 \times 10^8 \text{ cm}^{-2}$ in the middle region (at $t = 20 \text{ }\mu\text{m}$), then up to 1.6×10^9 and $1 \times 10^{10} \text{ cm}^{-2}$ in the region close to the interface (at $t = 3 \text{ }\mu\text{m}$ and $1 \text{ }\mu\text{m}$, respectively). From a cross sectional TEM image for the nominally $5 \text{ }\mu\text{m}$ thick sample (not shown here), the dislocation densities at $t = 4.5 \text{ }\mu\text{m}$, $3 \text{ }\mu\text{m}$, and $1 \text{ }\mu\text{m}$, are $9 \times 10^8 \text{ cm}^{-2}$, $1.7 \times 10^9 \text{ cm}^{-2}$, and $4 \times 10^9 \text{ cm}^{-2}$, respectively. The fact that the results obtained on the $5 \text{ }\mu\text{m}$ thick sample are very similar to those obtained in the interface region of the $55 \text{ }\mu\text{m}$ thick sample implies a fairly good reproducibility of HVPE growth. Therefore, the dislocation densities in the top regions of all five samples can be considered to be roughly the same as those measured at corresponding thicknesses in the thickest sample. By comparing these three experimental results (i.e., the increase of the reverse leakage current of the SBDs, the evolution of the deep centers, and the increase of dislocation density, with decreasing thickness), it appears that the formation of deep

centers in HVPE-GaN layers is closely associated with the presence of threading dislocations.

Experimentally, threading dislocations in GaN are electrically active, providing defect states and acting as traps and nonradiative recombination centers, which have been demonstrated by studies of scanning capacitance microscopy⁶ and plan-view TEM along with cathodoluminescence imaging.⁷ Recently, a theory of charged-dislocation line scattering was developed within the framework of the Boltzmann transport equation.⁸ A fit of the theory to temperature-dependent Hall effect data in GaN gave dislocation densities in excellent agreement with those measured by TEM. Theoretically, threading dislocations in GaN have been predicted to have V_{Ga} or V_{N} defects in their core structures, depending on doping (or type) and growth stoichiometry; i.e., formation of the V_{Ga} structure is favored under N-rich conditions and is most stable in n -type material, whereas formation of the V_{N} structure is favored under Ga-rich conditions and is most stable in p -type material.⁹ Because of the uncertainty in the formation energy calculations, a mixture of core structures is also possible. Thus, edge dislocations are predicted to behave as electron traps in n -type GaN and may act as hole traps in p -type GaN, depending on growth conditions. To discuss the possible point defect natures of the main centers found in n GaN, we emphasize two important experimental facts: (i) high concentrations of deep centers in n GaN are closely associated with high dislocation densities, no matter what growth technique is used, and (ii) there exists an anticorrelation relationship between centers A_1 and B for the two thinnest samples (see curves d and e in Fig. 1). The anticorrelation relationship was also observed in other n -GaN materials (e.g., for thin MOCVD GaN, see Fig. 4 in an earlier study,¹⁰ and for thin RMBE GaN, see Figs. 3 and 4 in Ref. 5), which means that a strong increase in trap B is usually accompanied by a significant reduction of trap A_1 . The center B (also named $E2$ in the literature) has been extensively studied. Earlier studies suggested that the center could be due to chemical impurities, like C (Ref. 11) or Mg (Ref. 12). In a later investigation, the photoionization of $E2$ in n GaN was characterized by using capacitance transient spectroscopy, yielding an optical activation energy of $E^o = 0.85$ eV at 90 K and resulting in a Franck-Condon shift of 0.3 eV, indicating a possible defect nature.¹³ A recent study showed that $E2$ could be effectively suppressed by isoelectronic In doping and it was suspected of being N_{Ga} defect.¹⁴ To understand the nature of A_1 , we need to recall the EI induced centers in n GaN. In a DLTS study of MOCVD-GaN after 1-MeV electron irradiation, we found two EI induced centers: trap E (at ~ 120 K), which consisted of two components, with each having a thermal activation energy of 0.06 eV; and trap A_2 (at ~ 420 K), with $E_T = 0.85$ eV. There is good evidence that E is related to the nitrogen vacancy (V_{N}), and because A_2 shows a production rate close to that of E , it is possible that A_2 might be a N_{I} related defect, created by the reaction $N_{\text{N}} \rightarrow V_{\text{N}} + N_{\text{I}}$.⁵ In the study of EI, we also found that some pre-existing centers in MOCVD-GaN, including B , are not affected by 1-MeV EI at all, thus ruling out the possibility of B being related to a V_{N} defect. Since center A_1 is very similar to the EI induced center A_2 and since B shows an anticorrelation with A_1 , we tentatively

assign A_1 to a N_{I} related defect and B to N_{Ga} . N_{Ga} can be easily formed by the reaction $V_{\text{Ga}} + N_{\text{I}} \rightarrow N_{\text{Ga}}$. According to the theoretical prediction mentioned above, V_{Ga} should be available in n GaN with a high dislocation density. Indeed, the presence of V_{Ga} in undoped MOCVD-GaN has been verified by positron annihilation spectroscopy.¹⁵ The center D , with $E_T = 0.17 - 0.23$ eV, also shows a correlation with the thickness reduction or the dislocation increase, which means that D , as an electron trap, could possibly be a defect complex involving V_{Ga} (such as $V_{\text{N}} - V_{\text{Ga}}$).

In summary, HVPE-grown n -GaN layers with different thicknesses have been characterized by DLTS and TEM. As the layer thickness decreases, an increase of deep centers, both in species and concentrations, was clearly observed, which is believed to be closely associated to the significant increase of threading dislocations in the regions near the GaN/sapphire interface. Based on a comparison with EI induced centers and an observation of anticorrelation, A_1 is tentatively assigned to N_{I} , and B to N_{Ga} .

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