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Influence of growth parameters on the sub-bandgap absorption of MOVPE-grown GaN measured using photothermal deflection spectroscopy

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ABSTRACT

In this work we have compared the sub-bandgap absorptance of nominally undoped GaN samples grown under different conditions. The absorptance is measured using standard transmission measurements and transverse photothermal deflection spectroscopy (PDS). The sub-bandgap absorptance is dominated by an exponential Urbach tail (3.0–3.42 eV) and a defect absorptance (energy range <3.0 eV). By measuring the thickness dependence of the absorptance we show that the defect absorptance has both a surface and a bulk contribution. The defect absorptance decreases by capping the sample with a thin layer of AlGaN. This suggests that the capping layer passivates the contribution of the surface states to the defect absorptance. We show that sub-bandgap absorptance is a sensitive indicator of bulk and surface defects introduced due to changes in carrier gas purity, making it a valuable tool for characterization of nitride semiconductors.

1. Introduction

GaN has proved to be an important material for optoelectronic [1,2] and high power-high frequency applications [3,4]. Although there has been great improvement in the techniques by which epitaxial layers of GaN are grown, the defect density still remains significant (10^8–10^{10} cm^{-2}). In order to improve the quality of the material it is necessary to understand the origin of defects and the effects of various growth parameters on their formation. The commonly used spectroscopic techniques used to study these defects are photoluminescence [5,6], deep-level transient spectroscopy [7] and photoconductivity [8]. Besides these techniques, photothermal deflection spectroscopy (PDS), due to its high sensitivity ($\alpha d = 10^{-4}$–10^{-6}; where α is the absorption coefficient and d is the sample thickness) and non-destructive nature [9,10] can also be used to probe defects in thin GaN films. In comparison with other techniques, there are only few previous reports [11–14] the use of PDS to investigate the defect absorptance in GaN films. In this work, we use PDS to study the origin of sub-bandgap absorptance in MOVPE-grown GaN and its dependence on various growth parameters.

2. Experimental procedure

All GaN samples used in this study were grown using a 3 × 2 inch close-coupled showerhead reactor on *c*-plane sapphire substrates using trimethylgallium (TMGa) and ammonia (NH_3) as precursors via a standard two-step growth process. In all cases the low temperature nucleation layer growth step was identical (530 °C, 6.67×10^4 Pa (500 Torr), 20 nm thick) but the reactor pressure, V/III ratio and growth temperature during the high-temperature GaN growth step were varied. This was used to control the coalescence time, i.e., the thickness over which the GaN layer goes from a rough 3D surface immediately following nucleation and recrystallization, to a smooth 2D growth mode, (when the reflectivity spectrum shows Fabry–Perot oscillations of near-constant amplitude). The reflectivity was monitored in situ at a wavelength of 635 nm using a normal incidence diode-laser reflectometer. A slow recovery of the reflectivity, i.e., a longer coalescence time typically leads to a lower dislocation density in the GaN layer, whereas a quicker return to 2D growth mode is associated with a higher defect density. A faster coalescence can be achieved by growth at relatively higher temperature, lower pressure, and/or higher V/III ratio. Such layers tend to be more resistive and are used as buffer layers for high-electron mobility transistor (HEMT) structures.

The GaN epilayers were deposited on three 2 inch substrates. One of these was removed for characterization, while the others were stored within the N_2 purged glove box for possible use as templates for future growth. For the regrowth of AlGaN, no external cleaning of the substrates was performed, with the GaN

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templates being heated under NH_3 till the growth temperature. A thin GaN layer was grown (to check uniform Fabry–Perot oscillations in the reflectivity), before switching to the growth of AlGaN. The AlGaN layers were grown at 1040 °C and 0.67×10^4 Pa (50 Torr) pressure using trimethylaluminium (TMAl), TMGa, and NH_3. For the HEMT structures the GaN was capped with 20 nm of 26% AlGaN while for the passivation study 0.5 μm of 28% AlGaN was grown. The main carrier gas in the reactor was Pd-diffused hydrogen in all cases, however, the carrier gas through the TMGa bubbler was switched to nitrogen for some samples. Details of the growth parameters of all the samples studied are presented in Table 1.

For the PDS measurements the samples are immersed in CCl_4, which is non-absorbing in the region of interest (300–750 nm) and has a high coefficient of variation of refractive index with temperature ($\partial n/\partial T = 5 \times 10^{-4}\,K^{-1}$). To ensure that the CCl_4 does not influence the sample surface and hence the PDS measurement, the measurements were also performed using perfluorohexane (Fluorinert FC-72) which showed identical PDS signatures. A Xenon arc lamp with a monochromator is used as an exciting source (pump beam). The beam is chopped by a mechanical chopper at a frequency of 11 Hz. When absorption takes place in the sample, a part or all of the absorbed energy is converted into thermal energy. This energy diffuses into the liquid giving rise to a temperature gradient, which in turn creates a refractive index gradient in a thin layer adjacent to the sample surface. A He–Ne laser beam (probe beam) is used to probe this gradient. The deflection of the probe beam is measured using a Si quadrant detector and is related to the absorption in the sample.

For a sample whose thickness is less than its thermal diffusion length, it has been shown that the PDS signal, S, is proportional to the absorptance [9].

$$S = S_0 A = S_0(1 - R - T)$$

where, S_0 is a factor depending only on the thermal properties and geometry of the setup and $R(T)$ is the reflectance (transmittance) of the sample. Above the band gap, the PDS signal saturates and is independent of energy. This provides the normalization (S_0) for the PDS spectrum over the entire range. The transmittance and reflectance of the polished GaN samples were measured using a Cary 5000 UV/VIS/NIR spectrophotometer. The absolute value for the absorptance of each sample was obtained by setting the normalized PDS signal equal to the absorptance obtained from transmittance and reflectance measurements made on the *same* sample in the energy range close to the absorption edge of the sample (366 nm) [15].

The GaN films were structurally characterized by high resolution X-ray diffraction (XRD) on a PANalytical X-pert MRD system with a Hybrid four-bounce monochromator at the incident beam (Cu $K_{\alpha 1}$, $\lambda = 1.54$ Å) having a divergence of ~18 arcsec. Hall measurements in the Van-der-Pauw geometry were used to determine the carrier concentration and the carrier mobility.

3. Results and discussion

Fig. 1 shows the sub-bandgap absorption of four GaN samples (B,D,E and F) grown under different V/III ratios, pressures and temperatures, as measured by PDS. The growth parameters of the samples along with the FWHM values of (0 0 2) and (1 0 1) ω-rocking curves and carrier concentrations are given in Table 1. As seen in the figure the sub-bandgap absorptance is dominated by an exponential Urbach tail just below the band edge (3.0–3.42 eV) and a defect absorptance (energy range <3.0 eV). The defect absorptance is most sensitive to the growth pressure. The growths carried out at a pressure of 0.67×10^4 Pa (50 Torr) have smaller sub-bandgap absorptance than growths carried out at 1.3×10^4 Pa (100 Torr) and above (despite differences in sample thickness and V/III ratio). We find that there is no clear relationship between defect absorptance and the corresponding XRD half width. We see from our data that the defect absorptance is actually lower for GaN films grown at lower pressure having higher XRD widths. This suggests that the defects responsible for sub-bandgap absorptance are not the same as those that degrade the crystal quality. Poor crystallinity certainly degrades the mobility as seen for the samples B and F.

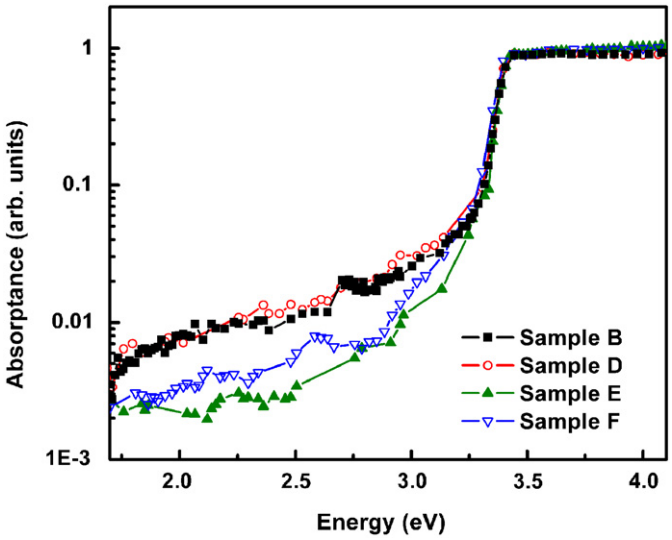

Fig. 1. Comparison of the sub-bandgap absorptance obtained for GaN samples grown under different III/V ratios, pressures and temperatures.

Table 1
Growth parameters of GaN samples along with the FWHM values of (0 0 2) and (1 0 1) ω-rocking curves and carrier concentrations

Sample	Material	Thickness (μm)	Pressure Pascal (Torr)	Temp. (°C)	V/III ratio	Recovery time (s)	μ ($cm^2/V\,s$)	ρ (Ω cm)	n (cm^{-3})	Carrier gas through TMGa source	FWHM 002 (arcsec)	FWHM 101 (arcsec)
A	GaN	2.1	2.7×10^4 (200)	1040	900	1400	545	0.22	5.2×10^{16}	N_2 (through purifier)	333	391
B	GaN	3.2	2.7×10^4 (200)	1040	900	2510	755	0.29	2.9×10^{16}	N_2 (through purifier)	278	350
C	GaN	5.6	2.7×10^4 (200)	1040	900	1010	HR			H_2	253	512
D	GaN	1.9	1.3×10^4 (100)	1040	1350	380	HR			H_2	364	900
E	GaN	1.2	0.67×10^4 (50)	1040	1350	330	HR			H_2	477	1307
F	GaN	2.6	0.67×10^4 (50)	1060	750	440	200	0.24	1.3×10^{17}	H_2	578	1288
G	GaN	1.5	2.7×10^4 (200)	1040	750	2280	355	0.03	6.7×10^{17}	N_2 (bypassing purifier)	437	516
H	GaN	3.5	2.7×10^4 (200)	1040	750	3310	425	0.06	2.6×10^{17}	N_2 (through purifier)	291	456

Recovery time denotes the time from turning on TMGa till reflectivity peak of the Fabry–Perot oscillations reaches 95% of its maximum value. HR denotes that the resistance was too high for reliable Hall measurements.