Growth of Silicon−doped GaN Using Ditertiarybutylsilane

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Introduction

Currently III−nitride semiconductors from the GaN family are demonstrating unparalleled performance in short−wavelength optoelectronic devices. Device performance improved rapidly during the 1990s [1,2], owing largely to advances in MOVPE growth of GaN itself, plus the ternary alloys InGaN and AlGaN. Effective doping of AlGaInN materials is critical for electrical−injection devices, and considerable challenges remain with p−doping using magnesium sources. Some of these issues are discussed in our accompanying presentation at this meeting. Meanwhile n−doping of GaN and related alloys has matured sufficiently to justify the exploration of novel dopant sources. Currently the sources of choice in MOVPE are the gaseous silicon hydrides monosilane [2] and disilane. These are used as dilute mixtures (typically 50−200 volume ppm) in hydrogen, posing hazards of flammability and toxicity, and requiring specialised gas−handling equipment. Also, since usage rates are low, there are concerns over long−term decomposition during cylinder storage. It is ultimately desirable to replace silicon hydrides with less hazardous, stable silicon sources, preferably in liquid form. For these reasons, we have explored the use of ditertiarybutylsilane (DTBSi) as a precursor for the growth of Si:GaN.

DBTSi is liquid between –38 and 128°C at atmospheric pressure, and has vapour pressure characteristics suitable for doping in compound semiconductor MOVPE. DBTSi has previously been utilised in the growth of various silicon−containing compounds; early work includes growth of SiC device structures [3], and amorphous hydrogen−doped silicon [4]. To our knowledge, it has not been used before now in GaN growth. However, DBTSi has been demonstrated as an effective dopant source in InP and GaAs growth [5], in work aimed at complete replacement of hazardous hydride gases in growth of these materials.

Experimental procedures

Si:GaN films were grown on sapphire (0001) substrates, under conditions producing wurtzite−phase GaN with (0001) orientation. A horizontal−flow, single−wafer Aixtron 200/4 RF−S MOVPE reactor was employed. Precursors were trimethylgallium (Epichem EpiPure grade), ammonia (Solkatronic 6.4 grade), and either SiH_4 or DBTSi as the silicon source. DBTSi was supplied as a research sample by Epichem Metalorganics, while SiH_4 was used as a commercial 100 volume ppm mixture in hydrogen from Messers Greissheim. Both silicon sources were introduced into the reactor cell through single−stage dilution lines. The carrier and dilution gas used for each of the precursors was hydrogen purified in a palladium diffusion cell.

As mentioned previously, the vapour pressure of DBTSi is ideal to cover the doping regimes of interest. The vapour pressure is given by [6]:−

$$\mathrm{Log}_{10}\,P\ (\mathrm{mm\ Hg}) = 8.2344 - 2148/T\ (\mathrm{K})$$

The molar flow rate of DBTSi was adjusted by varying three parameters in process recipes: the carrier and injection flows, plus the bubbler temperature, within a range of –15 to +17°C. The bubbler pressure of 1000 mbar, and dilution flow of 500 sccm, were not varied. These adjustments allowed DTBSi molar flow rates to be accurately varied by a factor of over 20, although hardware limitations prevent the accurate quantification of the lowest flow rates used in a few growths.

A typical multi−step procedure was implemented for growth of Si:GaN [7]. Firstly, a ~20−nm GaN nucleation layer was grown at 550°C, followed by 1−µm GaN buffer layer grown at 1170°C without intentional doping.

Finally, a ~2−µm layer of Si:GaN was grown on this buffer layer under the specific conditions of interest. The Si:GaN growth temperature was 1130°C except where noted. All high−temperature growth steps were conducted at 200 mbar pressure, in a hydrogen ambient, with trimethylgallium flow rates of 66 µmole/min, and ammonia flow rates of 0.11 mol/min. In situ growth monitoring was provided by a Filmetrics F30 normal−incidence spectroscopic reflectometer, as described previously [7,8]. Film growth rates and cumulative thicknesses were extracted from reflectance versus time data, providing the information on Si:GaN thickness required for the Hall analysis. Typical growth rates for Si:GaN were 1.7−1.8 µm/hr.

Room−temperature Hall measurements were conducted with a locally built system consisting of a Keithley 236 IV source/measure unit, and adjustable permanent magnets producing a magnetic field of ~0.2 T. Square Van der Pauw samples were prepared with indium contacts annealed at 450°C in a nitrogen ambient. Analysis of the Hall results considered a single conductive layer only. This was justified by measured background donor concentrations of ~1 x 10^{16} cm^{-3} in non−intentionally doped (nid) GaN representative of the buffer layers. High−resolution X−ray diffraction (HR−XRD) studies were made on a Philips X'pert Pro MRD system. A 4−crystal Ge (220) monochromator was used to obtain an incident beam divergence of 12 arc seconds. A 1° acceptance slit was placed in front of the detector. Atomic force microscopy (AFM) was performed using a Digital Instruments Nanoscope IIIa instrument, in tapping mode, with silicon probe tips.

Results and discussion

As noted above, SiH_4 is an established dopant source for GaN, and has been proven in commercial device structures. The general methodology for this study was therefore to make comparisons between Si:GaN films grown using DTBSi and SiH4 in parallel experiments. Fig. 1 shows the dependence of measured free carrier concentration on molar flow rate for both dopant sources, presented as a log−log plot for clarity. Five DTBSi−doped films grown in consecutive reactor runs were used to acquire the results shown, and DBTSi molar flow rates were varied from 0.57 to 9.3 nmole/min. The very low activation energy for the silicon donor state in GaN (~20 meV) means that the measured free carrier concentrations can be approximated to the concentrations of silicon atoms on gallium lattice sites. We can conclude that the incorporation efficiency of silicon atoms from DTBSi and SiH_4 is virtually identical, and shows only weak dependence on molar flow rate. The datapoints for the most highly doped samples obtained from each source lie slightly above a linear trend line fitted through the other points. The results summarised in Fig. 1 suggest that critical stages of decomposition of the two silicon sources in the MOVPE reactor may proceed identically at the relatively high temperatures used in GaN growth.

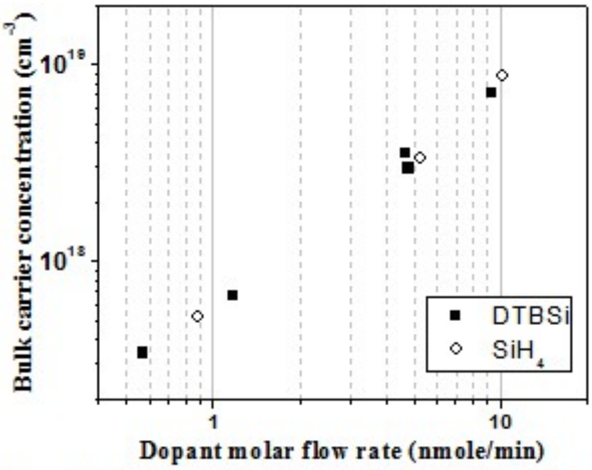


Figure 1 - Dependence of carier concentration on dopant molar flow

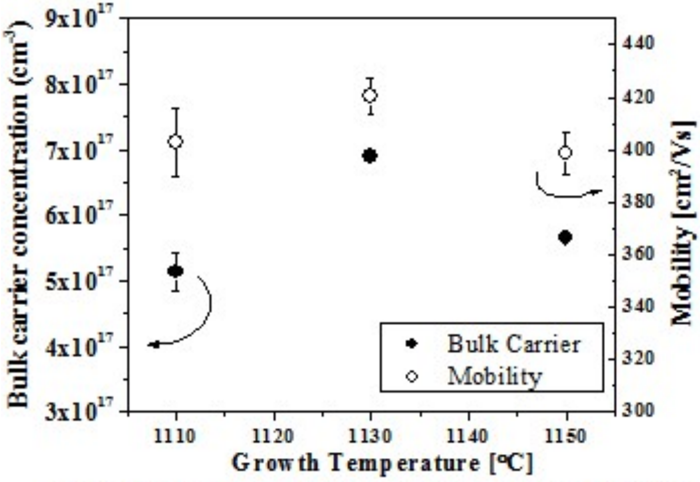


Figure 2 - Dependence of Hall parameters on growth temperature

Fig. 2 shows the dependence of carrier concentration and mobility on growth temperature for three films grown with a DBTSi molar flow rate of ~1.2 nmol/min. Both carrier concentration and mobility are seen to be maximised at the standard growth temperature of 1130°C, although the apparent temperature dependences are fairly modest. Previous Hall studies on our nid−GaN confirmed that carrier mobility can be maximised at a particular growth temperature, and correlated with trends concerning structural quality, and impurity incorporation from the growth ambient [9]. However, it is premature to draw firm conclusions from the in Fig. 2 data without further studies, in view the extent of run−to−run variations suggested by Figs. 1 and 3.

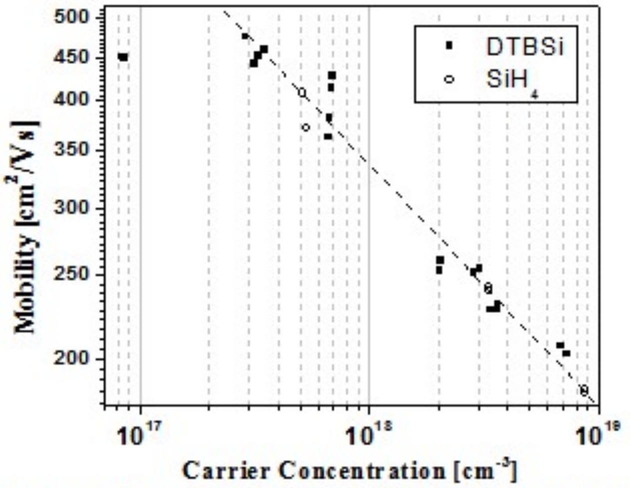
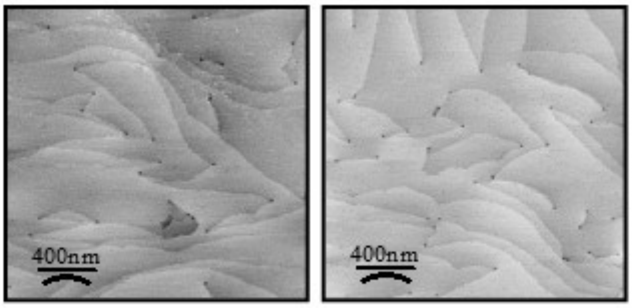


Figure 3 - Variation of mobility with carrier concentration



(a) Si:GaN layer doped using SiH_4 with doping level of 5.1×10^{17}cm^{-3}.

(b) Si:GaN layer doped using DTBSi with doping level of 3×10^{17}cm^{-3}.

Figure 4 – Surface morphology comparison between SiH_4 and DTBSi doped samples

Fig. 3 presents correlations between carrier concentration and mobility, including datapoints for a wider range of Si:GaN samples than discussed so far. The trend line fitted through the datapoints corresponding to samples with carrier concentrations >2 x 10^{17} cm^{-3} suggests the dominance of ionised−impurity scattering in controlling mobilities. This mechanism is discussed in detail elsewhere [10,11]. The fact that SiH_4 − and DTBSi−doped samples fit this same trend line further confirms that the competitive electrical characteristics of material doped using DBTSi. At lower free carrier concentrations, dislocation−related scattering is expected to limit mobilities. This effect may explain why the lowest−doped sample has a mobility well below the prediction from the trend line.

Table 1 – Comparison of XRD rocking curve FWHM between SiH_4 and DTBSi doped samples

Sample and dopant source	Carrier Concentration [cm^{-3}]	Mobility [cm^2/Vs]	0002 FWHM [arcsec]	1-104 FWHM [arcsec]
1 – SiH_4	3.3x10^{18}	240	300	170
2 – DTBSi	2.1 x10^{18}	257	340	210
3 – SiH_4	5.2 x10^{17}	390	180	165
4 – DTBSi	3.04 x10^{17}	460	315	200

Turning to the structural quality of Si:GaN samples, Table 1 summarises HR−XRD results on a highly doped and a more lightly doped sample grown using each dopant source. Although the FWHM of a symmetric 0002 rocking curve is often used a figure−of−merit indicator of GaN structural quality, asymmetric rocking curves such as the 1−104 scans used here actually provide more meaningful informative. Asymmetric reflections are sensitive to the content of pure edge dislocations, which are the dominant type in GaN films [12]. The results in Table 1 show that all samples are of device quality [2]. The 0002 reflection for sample 3 is surprisingly narrow, and this observation may be connected with random variations in substrate misorientation. Trends evident from the other samples suggest a small degradation in the structural quality of the DTBSi−doped samples in comparison with SiH_4 −doped analogues. This may originate from the incorporation of low concentrations of impurity atoms from the DTBSi source, which are electrically inactive, and so do not affect carrier mobilities through the ionised−impurity scattering mechanism.

Fig. 4 compares height−scaled AFM images of Si:GaN films doped to similar levels using SiH_4 and DTBSi respectively. All Si:GaN samples studied showed similar morphologies, which are in turn similar to those of nid−GaN layers grown corresponding temperatures. The surfaces show monolayer−height (c/2) curved steps, corresponding to quasi 2−dimensional growth [13]. The steps are terminated by small pits, which are thought to be associated with threading dislocations (TDs) with a screw component. Areal pit densities vary from 5 x 10^8 to 1 x 10^9 cm^{-3} , consistent with expectations for populations of TDs in GaN grown heteroepitaxially on sapphire. These morphologies are consistent with incorporation of only minor levels of unwanted impurity atoms in Si:GaN layers doped using DTBSi. In connection with the reported use of tetraethylsilane as an antisurfactant in growth of III−nitride quantum dots [14], it is significant that DTBSi induces no obvious change in GaN growth mode at the molar flow rates used.

Finally, we have demonstrated the potential of DTBSi in growth of practical devices by growth of a blue−emitting light−emitting diode (LED) structure. This contains 3 µm of Si:GaN doped to ~2 x 10^{18} cm^{-3} as the lower current−spreading and electron injection layer. Initial tests suggest this structure shows comparable performance to similar structures grown using SiH_4 as the silicon source.

Conclusions

The non−hazardous liquid precursor DTBSi has been shown to be an excellent silicon dopant source in GaN growth by MOVPE. Comparisons between DBTSi and SiH_4 −doped GaN have indicated very similar electrical and morphological characteristics. Silicon incorporation kinetics from DTBSi and SiH_4 are essentially identical, suggesting that critical reaction pathways may be identical for the two sources. DBTSi can readily dope GaN to produce the mobile electron concentrations of 2−3 x 10^{18} cm^{-3} required for standard LEDs. The advantages of reduced storage cost, elimination of expensive gas−handling equipment, and increased safety, make DBTSi a very attractive alternative to gaseous silicon hydride dopant sources.

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