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# Comparison of trimethylgallium and triethylgallium for the growth of GaN

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GaN films grown by low-pressure metalorganic chemical vapor deposition using trimethylgallium and triethylgallium as gallium precursors are compared. The films were characterized by x-ray diffraction, Hall effect, photoluminescence, secondary ion mass spectroscopy, and etch pit density measurements. GaN layers grown using triethylgallium exhibited superior electrical and optical properties and a lower carbon impurity concentration. © 1997 American Institute of Physics. [S0003-6951(97)03148-3]

The III-nitrides are wide bandgap semiconductors with many important applications including high-power and high-temperature electronics,<sup>1</sup> solar-blind ultraviolet photodetectors,<sup>2,3</sup> and blue and ultraviolet light emitting and laser diodes.<sup>4</sup> However, improved device performance requires better material quality. We have reported III-nitride growth,<sup>5-7</sup> characterization,<sup>8,9</sup> and photodetectors.<sup>2,10</sup> Many authors have reported the metalorganic chemical vapor deposition (MOCVD) growth of GaN using either trimethylgallium (TMGa)<sup>5,11-13</sup> or triethylgallium (TEGa),<sup>14-16</sup> but there have been few comparisons of these gallium precursors recently shown to influence the deep levels<sup>17</sup> and impurities.<sup>18</sup> Here, we compare TMGa and TEGa for the MOCVD growth of GaN.

The GaN was grown in a horizontal low-pressure MOCVD reactor using a high temperature (1100 °C) 35 nm thick AlN nucleation layer. The gallium sources used were special grade TMGa, purified grade TMGa, and oxygen reduced grade TEGa from Morton, and adduct grade TEGa from Epichem. No significant differences were observed in the GaN layers as a function of the grade or supplier of these high purity sources. For purposes of comparison, the films were grown on identical (0001) sapphire substrates, with identical AlN buffer layers, and with identical growth conditions except for the choice of the gallium source. The growth conditions are summarized in the first column of Table I. Compared to other published results for the MOCVD growth of GaN; the V/III ratio is lower, the growth pressure is lower, and the AlN nucleation layer is deposited at a higher temperature. These growth conditions may enhance the differences in the properties of the films grown with the different sources. The values in Table II are averages of the measured properties of all the undoped and *n*-doped GaN films grown on (0001) Al<sub>2</sub>O<sub>3</sub> using thin AlN nucleation layers during the optimization of III-nitride thin films in the low pressure MOCVD reactor. The large spread in the data is due to the

TABLE I. Growth conditions for GaN on (0001) Al<sub>2</sub>O<sub>3</sub> substrates.

Parameter	For direct comparisons	Range for Table II
Growth temperature	1050 °C	600–1200 °C
Growth pressure	10 mbar	10–100 mbar
V/III ratio	1000	100–12 000
Growth rate	0.7 μm/h	0.05–1.8 μm/hour
Thickness	0.7 μm	0.05–3.9 μm

range in the growth conditions as shown in the last column of Table I. Further contributing to the variation were changes in the susceptor shape, buffer thickness, and cleaning procedures. In spite of the wide variety in the environments these films were grown in, the properties exhibit the same trends as the films grown with TEGa and TMGa under otherwise identical conditions.

Figure 1 shows that (0002) GaN open-detector x-ray diffraction rocking curves for GaN grown with TMGa and TEGa were both very narrow compared to those typically found in the literature. The full width at half maximum (FWHM) for the TEGa grown film was 33 arc sec while the TMGa grown film had a slightly broader FWHM of 62 arc sec. Typically, the linewidths are nearly equal for TEGa or TMGa as seen in Table II.

Figure 2 shows that the room temperature near bandgap

TABLE II. Properties of GaN grown by MOCVD on (0001) Al<sub>2</sub>O<sub>3</sub> substrates using high temperature AlN nucleation layers.

Property	TMGa			TEGa		
	Mean	$\sigma$	N	Mean	$\sigma$	N
(0002) GaN x-ray FWHM (arc sec)	690	880	166	550	610	192
$I_{\text{Bandgap}}$ (RT PL)	8	27	100	27	42	186
$I_{\text{Yellow}}$ (RT PL)	5	16	97	5	6	187
$I_{\text{Bandgap}}/I_{\text{Yellow}}$ (RT PL)	7	24	53	10	17	163
$I_{\text{Bandgap}}$ (77 K PL)	64	157	66	161	303	94
$I_{\text{Yellow}}$ (77 K PL)	27	32	63	10	24	94
$I_{\text{Bandgap}}/I_{\text{Yellow}}$ (77 K PL)	14	48	60	45	78	91
RT $\mu_{\text{H}}$ (cm <sup>2</sup> /Vs)	24	25	65	82	70	170

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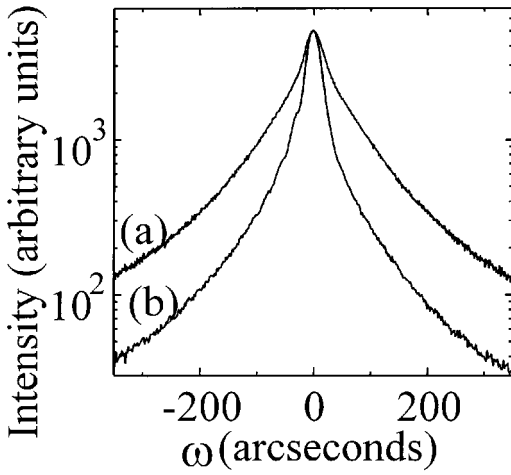


FIG. 1. Open-detector x-ray rocking curves of the (0002) GaN peak of the samples grown with (a) TMGa and (b) TEGa.

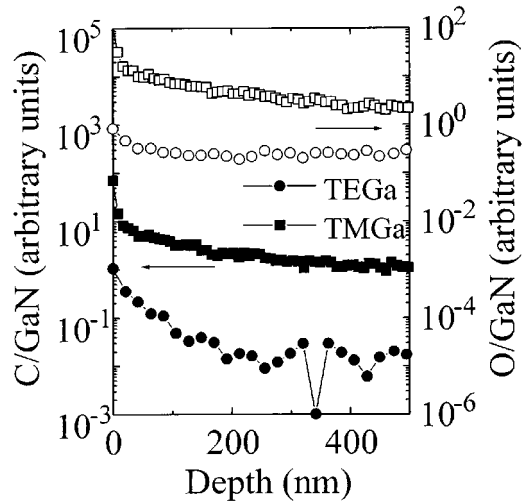


FIG. 4. SIMS depth profiles of oxygen and carbon normalized to the GaN signal in samples grown with TMGa and TEGa.

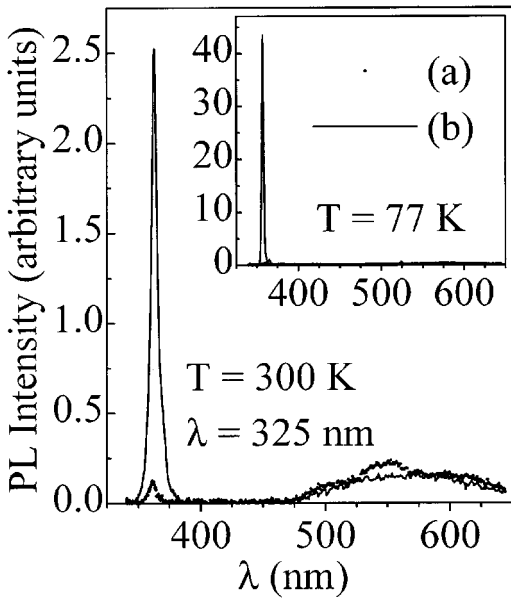


FIG. 2. RT PL spectra of the samples grown with (a) TMGa and (b) TEGa under otherwise identical conditions. (Inset 77 K PL.)

photoluminescence (PL) was much stronger for the samples grown using TEGa, although the yellow PL was approximately the same. The PL spectra taken at 77 K show the same trend. Hence, the films grown using TEGa have better optical quality than films grown using TMGa. Indirect comparisons of Table II also show that the near bandedge PL intensity and its ratio to the yellow intensity were higher for GaN grown with TEGa than with TMGa.

Figure 3 shows the variation of the electron mobility and carrier concentration as a function of the dopant flow rate. The mobility of TEGa grown films was typically much higher than in TMGa grown films for the same carrier concentration. Undoped films were typically insulating for films grown using either TMGa or TEGa. The TMGa grown films required a higher flow rate of dilute SiH<sub>4</sub> in order to achieve conduction, and the resulting mobility was extremely low

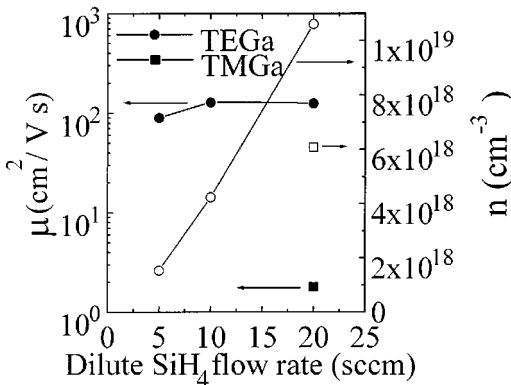
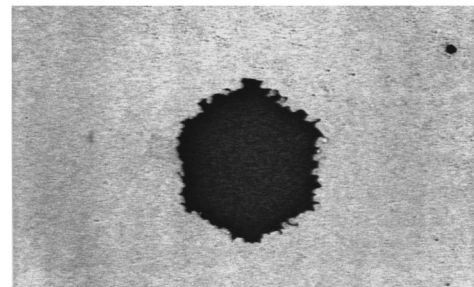
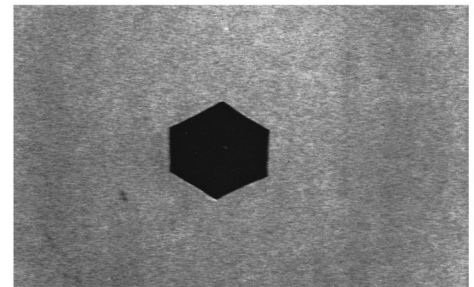


FIG. 3. RT electron mobility and *n*-type carrier concentration for TMGa and TEGa grown samples as a function of the doping level.



(a)



(b)

FIG. 5. Etch pits in GaN grown using (a) TMGa and (b) TEGa.

indicating that the TMGa grown films are heavily compensated. The TEGa grown films were easier to dope and had higher mobilities. For the films grown under various conditions, the averages of the room temperature mobilities for GaN grown with TEGa are higher as shown in Table II.

The secondary ion mass spectroscopy (SIMS) depth profiles (Fig. 4) show that at a depth of 400 nm, the oxygen concentration was 7 times higher, and the carbon concentration was 50 times higher in the TMGa grown film than in the TEGa grown film. The higher impurity concentration in the TMGa grown GaN may be responsible for its poorer electrical and optical properties.

Etch pits revealed by hot  $\text{H}_3\text{PO}_4$  were typically 2–40  $\mu\text{m}$  in size. The bases of the hexagons were determined to be along  $[[11\cdot0]]$  directions, and the walls appear to be nearly vertical, so the etched faces correspond to  $\{10\cdot0\}$  planes. The etch pit density (EPD) was approximately  $10^4 \text{ cm}^{-2}$ , comparing favorably to over  $10^7 \text{ cm}^{-2}$  in early GaN.<sup>19</sup> Although the density of the large etch pits was approximately equal in the films grown using TMGa and TEGa, the borders were very different as seen in the scanning electron microscopy image of Fig. 5. The TMGa grown film had irregular borders while the TEGa grown film had sharp borders. In the TMGa grown film, smaller pits were present with a density of  $10^9 \text{ cm}^{-2}$  and sizes of about 0.05–0.1  $\mu\text{m}$ . It is possible that the border of the large pits extends to envelop the small pits, creating an irregular border. None of these small pits were present in the TEGa grown film grown under identical conditions. The difference may be due to the higher impurity concentration in TMGa grown GaN which enhances the etching rate in the vicinity of defects.

In summary, we conclude that TEGa is the superior gallium source for the MOCVD growth of GaN for the experimental conditions studied. Films grown using TEGa showed stronger near-bandedge PL, higher mobilities, and lower carbon and oxygen concentrations. The EPD was about  $10^4 \text{ cm}^{-2}$  for large pits in films grown with either TMGa or

TEGa, but small pits with a density of  $10^9 \text{ cm}^{-2}$  were also present in the TMGa grown film.

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