Supersonic jet epitaxy of gallium nitride using triethylgallium and ammonia

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Gallium nitride (GaN) films were grown on GaN(0001)/AlN/6H-SiC composite substrates at 700–780 °C by supersonic jet epitaxy using triethylgallium (TEG) and NH₃. TEG was seeded in He and N₂ supersonic free jets to obtain kinetic energies of ~2.1 and ~0.5 eV, respectively, and NH₃ was supplied from a variable leak valve. Higher TEG beam intensities (by about a factor of 5) were obtained by seeding in He. *In situ* reflection high-energy electron diffraction indicated a transition from three-dimensional to two-dimensional (2D) growth between 730 and 750 °C for films grown using TEG seeded in He and a constant NH₃/TEG flux ratio. *Ex situ* atomic force microscopy of films grown at 730 and 750 °C revealed smooth surfaces comprised of quasi-2D islands with irregular perimeters. Cross-sectional transmission electron microscopy evidenced that the film grown at 750 °C was homoepitaxial α -GaN with a high density of planar lattice defects. Secondary ion mass spectrometry detected high residual carbon concentrations in the films. The GaN growth rate at 750 °C was found to depend on TEG flux and NH₃ pressure in a manner consistent with Langmuir–Hinshelwood kinetics. Films grown under NH₃-rich conditions were faceted and microscopically rough, whereas nonfaceted, basal-plane growth was observed under Ga-rich conditions. The first-order dependence of growth rate on TEG flux under NH₃-rich conditions was used to estimate Ga incorporation efficiencies for high- and low-energy TEG beams. The Ga incorporation efficiency is lower for high-energy TEG beams, consistent with a decrease in the sticking coefficient for dissociative chemisorption. © 2003 American Vacuum Society.

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I. INTRODUCTION

Metal–organic chemical vapor deposition (MOCVD) is the primary technique used to grow GaN thin films for optoelectronics applications.^{1–7} Molecular beam epitaxy (MBE) has potential advantages for GaN growth that include lower growth temperatures, precise control of layer thickness, and *in situ* doping. In chemical beam epitaxy (CBE), a group III metal–organic compound and a group V hydride are used to grow III–V semiconductor films in a high-vacuum environment.⁸ Typically, the growth precursors are transported to the surface via effusive molecular beams in which the kinetic energy of the molecules is fixed by the source temperature. Only a few studies have explored CBE growth of group III nitride materials.^{9–12} Triethylgallium (TEG) and NH₃ have been used for GaN growth. The substrate temperature was found to exert a profound influence on GaN film quality as measured by x-ray diffraction. Previous investigators have reported that the optimum temperature for GaN CBE is approximately 800 °C.^{11,12} Shen *et al.* also observed that the quality of GaN films deposited on sapphire was improved by increasing the NH₃ flux.¹² Moreover, better crystalline quality was obtained for GaN films deposited on 6H-SiC(0001) than on sapphire(0001).

Supersonic jet epitaxy (SJE) is a novel growth technique that employs seeded supersonic free jets to impart hyperthermal kinetic energy (1–10 eV) to precursor molecules.¹³ Hyperthermal kinetic energies are achieved by seeding a heavy molecule (e.g., Si₂H₆) in a lighter gas (e.g., He) and expanding the gas mixture through a pinhole orifice into high vacuum. Increasing the kinetic energy of impinging molecules will increase the sticking coefficient for dissociative chemisorption if the process is direct and activated (i.e., it does not involve an adsorbed precursor). Direct dissociative chemisorption has been demonstrated for group IV compounds on metal and semiconductor surfaces [e.g., CH₄ on Ni(111)¹⁴ and Si₂H₆ and SiH₄ on Si(100) and Si(111)¹⁵]. Imparting hyperthermal kinetic energy to Si₂H₆ enhances its dissociative chemisorption probability on Si(100),¹⁵ and this enhancement translates directly into higher Si epitaxial growth rates under low hydrogen coverage conditions.^{16,17} Recently, SJE has been employed to grow SiC¹⁸ and III-nitride semiconductor^{19,20} films with the objective of lowering the substrate temperature for epitaxial growth. Low-temperature epitaxial growth of SiC films on Si was achieved using a seeded supersonic jet of methylsilane in H₂.¹⁸ Methylsilane has also been shown to undergo direct dissociative chemisorption on β -SiC(100).¹⁵ Brown *et al.* used triethylaluminum (TEA) and NH₃ for SJE of AlN and reported that imparting hyperthermal kinetic energy to TEA by seeding in

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H₂ or He increased the growth rate markedly.²⁰ Consequently, Brown *et al.* inferred an activation barrier for direct dissociative chemisorption of TEA on AlN that was surmounted via the hyperthermal kinetic energy of the impinging molecules. In contrast, molecular beam scattering measurements have shown that dissociative chemisorption of group III metal–organic compounds, such as TEA, on semiconductor surfaces is unactivated and typically occurs via a precursor-mediated reaction channel.²¹ Moreover, if a precursor-mediated dissociative chemisorption channel is operative, the sticking probability should decrease with increasing kinetic energy of the impinging gas molecule.

In this work, homoepitaxial GaN films were grown by SJE on GaN(0001)/AlN/6H–SiC composite substrates at 700–780 °C using TEG-seeded supersonic molecular beams and NH₃ from a variable leak valve. High (~2.1 eV) and low (~0.5 eV) kinetic energy TEG beams were formed by seeding TEG in He and N₂, respectively. The resultant films were characterized by scanning electron microscopy (SEM), secondary ion mass spectrometry (SIMS), atomic force microscopy (AFM), and cross-sectional transmission electron microscopy (TEM). Flux measurements using a quadrupole mass spectrometer (QMS) were used to establish the relative TEG beam intensities obtained by seeding in He and N₂ supersonic free jets. GaN growth rates were measured as a function of TEG flux at 750 °C under NH₃-rich conditions and used to determine Ga incorporation efficiencies for low- and high-energy beams.

II. EXPERIMENT

A. Apparatus

The custom-fabricated SJE chamber (low 10^{−9} Torr base pressure) is equipped with a QMS (UTI 100C), a 10 keV reflection high-energy electron diffraction (RHEED) gun, and dual doubly differentially pumped supersonic molecular beam sources.²² The SJE chamber is connected via a cryopumped transfer line (low 10^{−9} Torr base pressure) to a load lock. TEG [(C₂H₅)₃Ga] was supplied from a commercial bubbler (Epichem, electronic grade) that was immersed in a temperature-controlled water/ethylene glycol bath. The diluent (carrier) gas (He or N₂) is split into two streams: the first stream is regulated by a 50 sccm mass flow controller (MKS) and passes through the TEG bubbler, and the second is regulated by a 500 sccm mass flow controller and bypasses the bubbler. The two streams are recombined and mixed before entering the TEG nozzle. The TEG delivery lines are kept isolated from air and are wrapped with heating tape and baked periodically. A capacitance manometer (MKS Baratron) is used to measure the pressure in TEG bubbler, and a second is used to measure the nozzle pressure. The TEG flow rate can be adjusted by varying the TEG bubbler temperature and the carrier gas flow rate into the TEG bubbler. The TEG mole fraction can be fine-tuned by varying the flow rate through the bypass line. The TEG nozzle was fabricated from stainless steel and has a 50 μm laser-drilled Pt orifice. A conical skimmer with a 1 mm aperture and a 20 mm base

(Beam Dynamics) is used to form the supersonic molecular beam. A 5 × 5 mm² beam-defining aperture separates the SJE chamber from the second differential pumping stage. The molecular beam is incident on the substrate at an angle of 6° with respect to the surface normal, and the deposition area on the substrate is 15 × 15 mm². The QMS was used to measure relative TEG beam intensities, as described previously for NH₃.²² The TEG molecules are thermalized by scattering in the deposition chamber before detection.

B. Film growth and characterization

The substrates were 1.5-μm-thick GaN(0001) films grown by MOCVD on on-axis 6H–SiC using a 0.1 μm AlN buffer layer. The MOCVD-grown GaN surface was atomically smooth with a roughness of 0.17 nm rms (1 × 1 μm² image size).²³ Substrates (1 × 1 cm²) were metallized with tungsten on the backside (SiC face) to absorb radiation from the pyrolytic boron nitride-coated graphite heater. The GaN substrate temperature was measured using a calibrated infrared optical pyrometer.

Ex situ substrate cleaning was effected by ultrasonic degreasing in trichloroethylene for 20 min. *In situ* cleaning of the GaN substrates was accomplished by annealing in NH₃ (1.5 × 10^{−5} Torr) at 800 °C for 30 min. After *in situ* cleaning, the substrate temperature was adjusted to the desired growth conditions. The NH₃ background pressure during growth was established by adjusting a variable leak valve (Varian). RHEED patterns were recorded before and after growth using a charge-coupled-device (CCD) camera and software from kSpace Associates.

SEM images of the films were obtained using a JEOL 6400FE SEM with a 5 kV cold field emission electron gun. TEM images were obtained using a Topcon EM-002B with a point-to-point resolution of 0.2 nm. AFM measurements were made using a Digital Instruments Dimension™ 3000 scanning probe microscope (SPM) having AFM and scanning tunneling microscopy (STM) capabilities; tapping mode was chosen for AFM measurements. SIMS depth profiles were measured on a Cameca IMS instrument at a mass resolution of 20 000 using a Cs⁺ sputtering source. Cross-sectional SEM images of the GaN films were used to determine the film thickness and, hence, the growth rate. It was possible to differentiate GaN films grown by SJE using TEG and the GaN substrate by compositional contrast (Z contrast) produced by backscattered electrons in the secondary electron image.

C. Estimating the TEG kinetic energy

The average kinetic energy achieved by species *i* in an ideal free jet expansion of a binary gas mixture (assuming zero velocity slip) is given by the following expression:

$$E_{\text{ideal}} = \frac{W_i}{\bar{W}} \bar{C}_p T_0, \quad (1)$$

where $\bar{C}_p$ is the average heat capacity at constant pressure, $\bar{W}$ the average molecular weight of the mixture, W_i the mo-

Fig. 1. Growth rate vs reciprocal temperature for homoepitaxial GaN films grown by SJE using 0.55 sccm TEG seeded in He. NH_3 pressures during growth are indicated in the legend.

molecular weight of species i , and T_0 the nozzle temperature.²⁴ Assuming that $\bar{C}_p$ is approximately the heat capacity of the diluent gas, the average kinetic energies of TEG molecules seeded at 1% in supersonic beams of He and N_2 are 1.8 and 0.48 eV, respectively. Differences between the mean velocities of the individual species (velocity slip) can be substantial when a large molecule, such as TEG, is seeded in He; nonetheless, the average kinetic energy of TEG molecules seeded in a He supersonic beam will be significantly higher than that of TEG molecules seeded in N_2 .

III. RESULTS AND DISCUSSION

The GaN substrate initially gave a streaky 1×1 RHEED pattern indicative of a smooth surface without a thick native oxide layer. Subsequent *in situ* annealing at 800 °C under an NH_3 pressure of 1.5×10^{-5} Torr reduced surface oxygen and carbon contamination to background levels (as evidenced by x-ray photoelectron spectroscopy) and produced a starting growth surface exhibiting a streaky 1×3 RHEED pattern.²³ The surface roughness increased after annealing from 0.17 to 0.28 nm rms, as indicated by analysis of $1 \times 1 \mu\text{m}^2$ AFM images. GaN films were grown at substrate temperatures of 700–780 °C using NH_3 from a variable leak valve and a high-energy beam of TEG seeded in He. NH_3 pressures of 1.5×10^{-5} and 7.7×10^{-6} Torr and a TEG flow rate of 0.55 sccm were used. An Arrhenius plot of the GaN growth rates is shown in Fig. 1. There appear to be two growth regimes that are characterized by different NH_3 reaction orders and slightly different apparent activation energies. The transition between the two regimes occurs between 730 and 750 °C at an NH_3 pressure of 1.5×10^{-5} Torr; a $\sim 30\%$ decrease in growth rate is observed on increasing the substrate temperature from 730 to 750 °C. The growth rate is nearly independent of NH_3 pressure for substrate temperatures greater than or equal to 750 °C; however, the growth rate is increased markedly by increasing the NH_3 pressure from 7.7×10^{-6} to

Fig. 2. RHEED patterns along the $(2\bar{1}\bar{1}0)$ azimuth and SEM images of GaN films grown at (a) 700, (b) 730, (c) 750, and (d) 780 °C using 0.55 sccm TEG seeded in He. The NH_3 pressures during growth were 1.5×10^{-5} Torr, except for (d) 7.7×10^{-6} Torr.

1.5×10^{-5} Torr at 730 °C. The apparent activation energies are 0.52 and 0.34 eV for the high- and low-temperature growth regimes, respectively.

RHEED patterns along the $[2\bar{1}\bar{1}0]$ azimuth recorded after growth and corresponding 50k $\times$ top-view SEM images of selected GaN films are displayed in Fig. 2. The films were grown using 0.55 sccm TEG seeded in He and 1.5×10^{-5} Torr NH_3 , unless otherwise noted. The spotty 1×1 (transmission) RHEED pattern of the film grown at 700 °C [Fig. 2(a)] indicates a microscopically rough surface, and this asperity is visible in the corresponding SEM image. The surface roughness decreases with increasing substrate temperature up to 750 °C. The streaky 1×1 RHEED pattern of the film grown at 750 °C [Fig. 2(c)] corresponds to a smooth featureless surface, as evidenced by SEM. The RHEED pattern of the film grown at 730 °C [Fig. 2(b)] is transitional with a higher background intensity. The SEM image (not shown) of a film grown at 765 °C revealed a flat surface with pits approximately 20 nm in diameter. When the growth temperature was increased to 780 °C, the GaN surface became faceted and microscopically rough (consistent with a higher effective N flux). The film morphology at 780 °C was im-

(a)

(b)

FIG. 3. AFM images of homoepitaxial GaN films grown at (a) 730 and (b) 750 °C using 0.55 sccm TEG seeded in He and an NH_3 pressure of 1.5×10^{-5} Torr. The image gray scales are (a) 15 and (b) 10 nm.

proved somewhat by reducing the NH_3 pressure from 1.5×10^{-5} to 7.7×10^{-6} Torr. The RHEED pattern and SEM image of this film are shown in Fig. 2(d). SEM reveals that the surface is flat, consistent with the streaky RHEED pattern, but there are large irregularly shaped pits in the film. The RHEED data indicate that a transition from three-dimensional (3D) to two-dimensional (2D) GaN growth occurs between 730 and 750 °C.

Ex situ AFM images of GaN films grown at 730 and 750 °C using 0.55 sccm TEG seeded in He and 1.5×10^{-5} Torr NH_3 are shown in Fig. 3. The surface of the film grown at 730 °C [Fig. 3(a)] is comprised of quasi-2D islands with highly irregular perimeters. Deep crevices are also visible between the islands. The rms roughness calculated for this $1 \times 1 \mu\text{m}^2$ image is 1.7 nm, and the image gray scale is 15

(a)

(b)

FIG. 4. (a) Cross-sectional TEM image of a GaN film grown at 750 °C (using 0.55 sccm TEG seeded in He and an NH_3 pressure of 1.5×10^{-5} Torr) on a MOCVD GaN(0001) substrate. LEED pattern (inset) of the surface recorded at 136 eV. (b) Higher magnification TEM image comprising the GaN film and the substrate, showing the selected area diffraction pattern in the $[2\bar{1}\bar{1}0]$ beam direction.

nm. When the growth temperature is increased to 750 °C, the islands become larger, and they appear to be elongated in the direction along the diagonal from the lower left to upper right in Fig. 3(b). AFM line profile analysis indicates that the step height between adjacent islands varies between 2 and 4 nm. The rms roughness calculated for this $1 \times 1 \mu\text{m}^2$ image is 1.3 nm, and the image gray scale is 10 nm. We infer that the higher substrate temperature promotes lateral growth and island coalescence.

A cross-sectional TEM image comprising the 250 nm

TABLE I. SIMS analysis of GaN films grown using TEG-seeded beams.

Substrate temperature (°C)	TEG flow rate (sccm)	NH ₃ pressure (10 ⁻⁵ Torr)	Carrier gas	TEG K.E. (eV)	At. % C	At. % O	Growth rate (nm/h)
730	0.55	1.53	He	2.1	2.28	0.23	90
765	0.55	1.53	He	2.1	0.40	0.06	71
750	0.41	1.53	He	2.2	0.57	0.08	59
750	0.55	0.77	He	2.1	1.14	0.14	63
750	0.63	0.77	N ₂	0.5	1.14	0.07	64
750	0.43	0.77	N ₂	0.5	1.08	0.03	45

TABLE II. SIMS analysis of GaN films grown at 750 °C by GSMBE and by SJE using NH₃-seeded supersonic beams.

NH ₃ seeding condition	NH ₃ flux (10 ¹⁵ cm ⁻² s ⁻¹)	Ga flux (10 ¹⁴ cm ⁻² s ⁻¹)	NH ₃ K.E. (eV)	At. % C	At. % O	Growth rate (nm/h)
1% in H ₂	1.26	2.95	1.48	0.006	0.007	112
1% in H ₂	1.26	2.95	0.74	0.007	0.006	95
50% in N ₂	0.63	2.95	0.13	0.003	0.004	113
GSMBE	1.33	4.50	0.03	0.002	0.006	280

TABLE III. Kinetics data for GaN growth by SJE at 750 °C.

Carrier gas	Carrier flow rate (sccm)	TEG mole fraction (%)	TEG flow rate (sccm)	TEG K.E. (eV)	NH ₃ pressure (10 ⁻⁵ Torr)	Growth rate (nm/h)
He	100	0.55	0.55	2.1	1.53	64
He	100	0.41	0.41	2.2	1.53	59
He	100	0.31	0.31	2.3	1.53	43
He	100	0.55	0.55	2.1	0.77	63
He	100	0.41	0.41	2.2	0.77	51
He	100	0.31	0.31	2.3	0.77	35
He	100	0.41	0.41	2.2	0.15	41
He	100	0.31	0.31	2.3	0.15	14
N ₂	50	1.26	0.63	0.5	1.53	46
N ₂	50	0.86	0.43	0.5	1.53	41
N ₂	50	0.70	0.35	0.5	1.53	27
N ₂	50	1.26	0.63	0.5	0.77	63
N ₂	50	0.86	0.43	0.5	0.77	45
N ₂	50	0.70	0.35	0.5	0.77	26
N ₂	50	0.70	0.35	0.5	0.15	20

FIG. 5. SEM images of GaN films grown using TEG seeded in He. The TEG flow rates (sccm) and NH_3 pressures (Torr) are indicated in the right margin and at the bottom of the figure, respectively.

GaN film grown at 750 °C and the GaN(0001) substrate is shown in Fig. 4(a). By comparison, the film contains a high density of planar lattice defects. The inset in Fig. 4(a) shows a 1×1 low-energy electron diffraction (LEED) pattern of the GaN(0001) surface. Figure 4(b) shows a higher magnifica-

tion TEM image of the film and substrate; the inset is the corresponding selected area diffraction (SAD) pattern. The SAD pattern contains only one set of diffraction spots in the $[2\bar{1}10]$ beam direction, indicating that the film is homoepitaxial α -GaN.

Substrate temperature and NH_3 pressure are the primary factors determining the carbon concentrations in GaN films grown using TEG-seeded beams. SIMS results for GaN films grown using TEG-seeded supersonic beams are given in Table I. The residual carbon concentrations are high (0.5–2 at. %), and the carbon and oxygen concentrations in the films exhibit some correlation. Increasing the substrate temperature reduces the residual carbon concentration, especially in the 730–750 °C range. The film grown at 750 °C exhibits a four-fold reduction in carbon concentration as compared to the film grown at 730 °C using the same NH_3 pressure. A more modest decrease in carbon contamination is observed on increasing the substrate temperature from 750 to 765 °C. Increasing the NH_3 pressure from 7.7×10^{-6} to 1.5×10^{-5} Torr results in a 50% reduction in carbon contamination in films grown at 750 °C. The small decrease in the TEG flow rate from 0.55 to 0.41 sccm is not believed to have a significant impact on carbon concentrations, based on the data for films grown using low-energy beams of TEG seeded in N_2 . These data indicate that TEG incident kinetic energy has little effect on the concentrations of contaminants in the films.

SIMS analysis was also performed on films grown at 750 °C by gas-source MBE (GSMBE) using elemental Ga and NH_3 from a variable leak valve and SJE using elemental Ga and NH_3 -seeded supersonic beams.²² As shown in Table II, the carbon concentrations in these films are two orders of magnitude lower than in the films grown using TEG-seeded beams, and the oxygen concentrations are one order of magnitude lower. The contamination levels in the films grown using NH_3 -seeded supersonic beams are comparable to those found in the GSMBE film, indicating that effusion of background gases from the differential pumping stages was not a significant source of contamination. We conclude from these results that TEG was the primary source of carbon contamination in GaN films grown using TEG-seeded supersonic molecular beams. The carbon incorporation mechanism may be similar to that reported for GaAs growth using TEG.²⁵

The kinetics of GaN growth were investigated at 750 °C using high- and low-energy supersonic beams of TEG obtained by seeding in He and N_2 , respectively. The experimental GaN growth rates are given in Table III. The growth rates exhibit saturation behavior with respect to NH_3 pressure and TEG flow rate consistent with Langmuir–Hinshelwood kinetics. Comparable growth rates were obtained using high- and low-energy beams at an NH_3 pressure of 7.7×10^{-6} Torr; higher growth rates were obtained using high-energy TEG beams at a NH_3 pressure of 1.5×10^{-5} Torr.

Top-view SEM images of GaN films grown using high-energy TEG beams are shown in Fig. 5. The surface of the film grown using the highest V/III ratio [Fig. 5(f)] is faceted

FIG. 6. SEM images of GaN films grown using TEG seeded in N_2 . The TEG flow rates (sccm) and NH_3 pressures (Torr) are indicated in the right margin and at the bottom of the figure, respectively.

FIG. 7. Relative TEG flux (beam intensity) as a function of TEG flow rate for TEG seeded in He and N₂ supersonic molecular beams.

and microscopically rough. In contrast, films grown using lower V/III ratios are nonfaceted and smooth. The film grown using the lowest V/III ratio [Fig. 5(a)] may be Ga rich, as suggested by the surface contrast in the secondary electron image. A transition from nonfaceted (2D) to faceted (3D) growth with an increase in the NH₃ flow rate has been reported for GaN films grown on AlN-buffered 6H-SiC(0001) using TEG and NH₃ at 850 °C.¹² A similar influence of the V/III flux ratio during growth on the surface morphology of homoepitaxial GaN films grown by plasma-assisted MBE has been reported.²⁶ Tarsa *et al.* and others have suggested that a high nitrogen coverage under N-stable growth conditions limits the Ga adatom surface diffusion length to less than the mean distance between adjacent bonding sites resulting in “quenched” growth and stochastic roughening of the surface.^{26,27} Top-view SEM images of GaN films grown using low-energy TEG beams are shown in Fig. 6. Most of the films exhibit surface roughness consistent with growth under N-stable conditions. The films tend to become smoother as the V/III ratio is decreased (by either reducing the NH₃ pressure or increasing the TEG flow rate), mirroring the trends observed in Fig. 5.

The growth rate enhancement (at 1.5×10^{-5} Torr NH₃) and the improvement in surface morphology of films grown using high-energy TEG beams led us to suspect that a higher TEG flux (beam intensity) was obtained by seeding TEG in He (as compared to N₂), for equivalent TEG flow rates. To test this hypothesis, TEG beam intensities were measured using a QMS located in the growth chamber. The relative beam intensities are plotted versus TEG flow rate for the high- and low-energy seeded beams in Fig. 7. The data evidence that the TEG beam intensity is higher by about a factor of 5 for the high-energy beams. A likely explanation lies in the different mass separation (“focusing”) effects for TEG–He and TEG–N₂ mixtures. Significant differences between the beam flux composition and the source gas composition are typically observed for seeded supersonic molecular beams; the heavier species is focused along the centerline of

FIG. 8. GaN growth rate versus relative TEG beam intensity for TEG seeded in He and N₂ supersonic molecular beams. Data are included for NH₃ pressures of 7.7×10^{-6} and 1.5×10^{-5} Torr.

the beam while the lighter species is segregated to periphery.²⁴ The contributions of pressure diffusion,²⁸ Mach-number focusing,²⁹ and skimmer interference³⁰ to mass separation have been discussed in the literature. The magnitude of the effect is typically a strong function of apparatus parameters, and we have observed significant mass focusing for NH₃ seeded in He and H₂ using the current experimental apparatus.²²

A plot of GaN growth rate versus TEG beam intensity is shown in Fig. 8. The TEG beam intensities were estimated using the linear regression fits shown in Fig. 7. The GaN growth rate exhibits a linear dependence on TEG flux for both low- and high-energy beams under NH₃-rich growth conditions. The slopes of the dashed lines through the origin in Fig. 8 are proportional to the Ga incorporation efficiencies for low- and high-energy TEG molecules. Thus, the experimentally determined Ga incorporation efficiency is higher for TEG molecules impinging on the surface at ~ 0.5 eV than at ~ 2.1 eV kinetic energy. We infer that the lower Ga incorporation efficiency for high-energy TEG molecules reflects a decrease in the sticking coefficient for dissociative chemisorption. As noted in the introduction, organometallic compounds such as TEG typically undergo precursor-mediated dissociative chemisorption on semiconductor surfaces.²¹ The chemisorption of TEG on GaAs(100) has been studied by several groups using thermal desorption (TPD),^{31–34} molecular beam scattering,^{26,35–37} and high-resolution electron energy-loss spectroscopy.^{31,38} TEG dissociatively chemisorbs on the GaAs(100) at room temperature. The initial sticking coefficient is nearly unity and drops very sharply to zero at a critical surface coverage consistent with precursor-mediated adsorption.²⁶ Lam and Vohs have demonstrated that trimethylgallium (TMG) dissociatively chemisorbs on GaN(0001) at room temperature.³⁹ If the dissociative chemisorption pathway for TEG on GaN(0001) is also precursor

mediated, increasing the kinetic energy of TEG molecules should decrease the sticking coefficient.

V. CONCLUSIONS

Homoepitaxial GaN films were grown on GaN(0001)/AlN/6H-SiC composite substrates using TEG-seeded supersonic molecular beams and NH₃ from a variable leak valve. A transition from 3D to 2D growth was observed between 730 and 750 °C for films grown using high-energy TEG beams and a fixed V/III flux ratio. Films grown at 750 °C under NH₃-rich conditions were faceted and microscopically rough; decreasing the V/III flux ratio resulted in 2D growth. SIMS and cross-sectional TEM analysis of selected samples revealed high concentrations (~1 at. %) of carbon (originating from TEG) and high densities of planar lattice defects in the epitaxial layers. A lower Ga incorporation efficiency was found for high-energy supersonic molecular beams of TEG seeded in He. This result is consistent with a decrease in the sticking coefficient for TEG dissociative chemisorption with increasing kinetic energy.

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