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# Resonant and nonresonant vibrational excitation of ammonia molecules in the growth of gallium nitride using laser-assisted metal organic chemical vapour deposition

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The influence of exciting ammonia (NH<sub>3</sub>) molecular vibration in the growth of gallium nitride (GaN) was investigated by using an infrared laser-assisted metal organic chemical vapor deposition method. A wavelength tunable CO<sub>2</sub> laser was used to selectively excite the individual vibrational modes. Resonantly exciting the NH-wagging mode ( $\nu_2$ ) of NH<sub>3</sub> molecules at 9.219  $\mu\text{m}$  led to a GaN growth rate of 84  $\mu\text{m/h}$ , which is much higher than the reported results. The difference between the resonantly excited and conventional thermally populated vibrational states was studied via resonant and nonresonant vibrational excitations of NH<sub>3</sub> molecules. Resonant excitation of various vibrational modes was achieved at 9.219, 10.35, and 10.719  $\mu\text{m}$ , respectively. Nonresonant excitation was conducted at 9.201 and 10.591  $\mu\text{m}$ , similar to conventional thermal heating. Compared to nonresonant excitation, resonant excitation noticeably promotes the GaN growth rate and crystalline quality. The full width at half maximum value of the XRD rocking curves of the GaN (0002) and GaN (10–12) diffraction peaks decreased at resonant depositions and reached its minimum value of 45 and 53 arcmin, respectively, at the laser wavelength of 9.219  $\mu\text{m}$ . According to the optical emission spectroscopic studies, resonantly exciting the NH<sub>3</sub>  $\nu_2$  mode leads to NH<sub>3</sub> decomposition at room temperature, reduces the formation of the TMGa:NH<sub>3</sub> adduct, promotes the supply of active species in GaN formation, and, therefore, results in the increased GaN growth rate. Published by AIP Publishing. [<http://dx.doi.org/10.1063/1.4962426>]

## I. INTRODUCTION

Gallium nitride (GaN) has attracted an enormous attention as a versatile functional material for the high-power and high frequency electronics, the short-wavelength optical devices (such as light emitting diodes, lasers, and photodetectors), and other optoelectronics.<sup>1–3</sup> Synthetic techniques of high growth rates are in demand for the scalable production of quality GaN films to satisfy the steadily increasing quest.<sup>4–8</sup> In addition, a high growth rate helps reducing the cycle time in device fabrication. Various approaches such as the hydride vapor phase epitaxy (HVPE), ammonothermal growth, and Na-flux method have been developed to achieve high GaN growth rates.<sup>9–11</sup> However, achieving a prolonged growth with a high growth rate is still a challenge.

The high-quality commercial GaN films are usually grown by the metalorganic chemical vapor deposition (MOCVD) technique on expensive substrates such as sapphire and SiC substrates at a growth rate around 2  $\mu\text{m/h}$ .<sup>12–14</sup> Recently, interests in the epitaxial growth of thick GaN films on Si substrates arose for a scalable production of

power-switching devices at an affordable cost.<sup>6,8</sup> However, the MOCVD technique is accompanied with a parasitic reaction between the precursors at high temperatures, which restricts the growth rates and impairs the epitaxial growth of thick GaN films.<sup>13–16</sup> In addition, the high growth temperatures ( $\sim 900$ – $1200^\circ\text{C}$ ) lead to GaN decomposition and nitrogen reevaporation, therefore resulting in the reduced GaN growth rates and a degraded crystalline quality.<sup>17,18</sup> Moreover, there is a series of Ga-Si reactions at elevated temperatures that could directly deter the growth of GaN on Si.<sup>19</sup> However, a high reaction temperature is required for effective ammonia (NH<sub>3</sub>) decomposition and overcoming the energy barriers on precursor adsorption and surface adatom migration.<sup>13–16</sup> An ultraviolet laser-induced MOCVD growth of group-III nitrides was developed<sup>20,21</sup> with the potential to overcome these disadvantages and was principally intended to provide the reactive radicals Ga and N by photolyzing corresponding precursors at low substrate temperatures. However, the density of the reactive N-containing fragments from NH<sub>3</sub> was not high enough even at high volume ratios, and the GaN growth rate was low. To address the challenges without introducing the heterocatalysts, we have recently developed an infrared laser-assisted MOCVD (LMOCVD) method to achieve the GaN growth at a substrate temperature

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as low as 250 °C.<sup>22</sup> A selective NH<sub>3</sub> decomposition at room temperatures was realized by resonantly exciting the rotational-vibrational transition of the NH-wagging mode at 1084.63 cm<sup>-1</sup> using a CO<sub>2</sub> laser beam, which was allowed to travel along the path parallel to the substrate surface. A high GaN growth rate of up to 12 μm/h was achieved by the LMOCVD, which was ~4.6 times faster than that of the conventional MOCVD without using laser. However, there are unanswered questions in understanding the roles of the vibrational excitation in the NH<sub>3</sub> decomposition and GaN formation. There are six vibrational modes and numerous vibrational bands in the NH<sub>3</sub> molecules. Will vibrational excitation of each mode contribute equally to the NH<sub>3</sub> decomposition and GaN growth? How will each mode impact the NH<sub>3</sub> decomposition and GaN growth?

In this study, we investigated the influence of exciting NH<sub>3</sub> molecular vibration in the growth of GaN on Si(100) substrates using a LMOCVD method. Based on the available irradiation lines, the NH<sub>3</sub> NH-wagging modes at 932.51 (ν<sub>2+</sub>) and 968.32 cm<sup>-1</sup> (ν<sub>2-</sub>) and the NH rotational-vibrational transition at 1084.63 cm<sup>-1</sup> were resonantly excited, leading to significantly improved GaN growth rates. Compared to the laser-induced thermal heating at the nonresonant wavelengths, the resonant excitations lead to a more effective NH<sub>3</sub> decomposition, higher concentrations of active species, higher GaN deposition rates, and a better GaN crystalline quality.

## II. EXPERIMENT

### A. Sample preparation

The schematic experimental setup of a home-built LMOCVD system is shown in Figure 1. The GaN films were grown on p-type Si(100) substrates. From the point of view of integrating GaN devices with the silicon technology, the Si(100) substrate is preferred because Si(100) is most widely used in the silicon mainstream technology. The Si substrates (10 × 10 mm<sup>2</sup>) were etched with 10% hydrofluoric to remove oxide layers, cleaned, and dried before loading into the LMOCVD chamber. Trimethylgallium (TMGa) and NH<sub>3</sub> were used as the Ga and N precursors, respectively. The LMOCVD chamber was evacuated to a base pressure of 1 × 10<sup>-3</sup> Torr. Then, the laser thermal cleaning of Si substrates was carried out at 900 °C under H<sub>2</sub> flow for 5 min to remove the native oxide on the substrate surface, followed by nitridation at 750 °C. The nitridation lasted for 5 min

under 54 mmol/min NH<sub>3</sub> flow at a reactor pressure of 100 Torr. It has been widely reported that a silicon nitride layer is formed due to the nitridation surface treatment process on the silicon substrate.<sup>23,24</sup> Nitridation of Si surface helps to release the strain in the GaN-on-Si growth and favours the growth of the wurtzite GaN.<sup>25–27</sup>

The molar flow rate of NH<sub>3</sub> was maintained at 54 mmol/min. The TMGa was carried into the growth chamber using a nitrogen carrier gas (N<sub>2</sub>) at a molar flow rate of 88 μmol/min. The chamber pressure during the growth process was maintained at ~10 Torr. A continuous-wave wavelength-tunable CO<sub>2</sub> laser (PRC, Inc., 9.2–10.9 μm) was used as the irradiation source, achieving a reactant excitation and a substrate heating. Based on the available emission lines of the CO<sub>2</sub> laser, the NH-wagging modes (ν<sub>2</sub>, at 932.51, 968.32, and 1084.71 cm<sup>-1</sup>) of NH<sub>3</sub> molecules were selected to be resonantly excited at the corresponding laser wavelengths of 10.719, 10.350, and 9.219 μm. Two other wavelengths at 9.201 and 10.591 μm were selected as the nonresonant wavelength references realizing only the conventional laser heating. The GaN nucleation layers (40–60 nm in thickness) were deposited at 500 °C for 30 s followed by an epilayer growth at 750 °C for 5 min. The laser incident power was tuned to keep the substrate temperature same for all the GaN samples grown at different laser wavelengths. The substrate temperature was monitored using a pyrometer (Omega, OS3752).

### B. NH<sub>3</sub> absorption spectrum within the CO<sub>2</sub> laser wavelength range

In order to find the appropriate wavelengths achieving a resonant vibrational excitation of NH<sub>3</sub> molecules, it is essential to find out the available emission lines matching the NH<sub>3</sub> molecular vibrational modes within the CO<sub>2</sub> laser wavelength range (9.2–10.8 μm). The NH<sub>3</sub> absorption spectrum within the CO<sub>2</sub> laser wavelength range was measured in a vacuum chamber with an absorption path length of 40.64 cm. The chamber was evacuated to a base pressure of 1 × 10<sup>-3</sup> Torr. Gaseous NH<sub>3</sub> was subsequently introduced into the chamber and reached a pressure of 10 Torr. The incident laser power was kept at 220 W. A power meter was used to measure the laser power before and after passing through the chamber. The drop in laser power was calculated as the absorption percentage.

Three strong absorption peaks were observed at 9.219, 10.35, and 10.719 μm (resonant wavelengths), corresponding to the NH-wagging modes (ν<sub>2</sub>) at 1084.63, 968.32, and 932.51 cm<sup>-1</sup>, respectively.<sup>22,28</sup> Among all the six vibrational modes of NH<sub>3</sub> molecules, the NH-wagging mode is strongly infrared active. A NH<sub>3</sub> molecule in the NH-wagging mode vibrates in an umbrella inversion way.<sup>29,30</sup> Due to the barrier that the nitrogen atom encounters on its travel through the proton plane, the vibrational level is split into two components at 932.51 (ν<sub>2+</sub>) and 968.32 cm<sup>-1</sup> (ν<sub>2-</sub>), which correspond to the observed absorption peaks at 10.719 and 10.35 μm, respectively.<sup>28–32</sup> The strongest absorption peak at 9.219 μm is ascribed to the NH rotational-vibrational transition at 1084.63 cm<sup>-1</sup> [5(J) → 6(J'), K = 0].

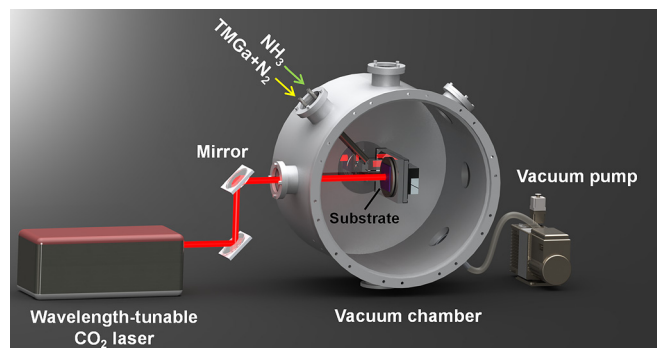


FIG. 1. The schematic of the LMOCVD system.

### C. Characterization

The surface morphologies of the GaN films were studied using a field-emission scanning electron microscope (FESEM, Hitachi S4700). The qualities of the GaN films were examined using a Raman microscope (Renishaw inVia H 18415, Argon ion laser,  $\lambda = 514$  nm) and an X-ray diffractometer (Rigaku D/Max B diffractometer, Co K $\alpha$   $\lambda = 1.788$  Å). The doping type, carrier concentration, and mobility of the GaN films were obtained via the van der Pauw method at room temperature. The optical emission spectra (OES) of the laser irradiated NH<sub>3</sub> were taken in open air using a spectrometer (Shamrock SR-303i-A, Andor Technology) coupled with an intensified charged coupled device (ICCD) (iStar DH-712, Andor Technology), as shown in Figure 2. The IR laser beam was focused to a diameter around 1 mm using a ZnSe convex lens ( $f = 25.4$  cm). A welding torch with a nozzle diameter of 1.5 mm was used to introduce the NH<sub>3</sub> gas at a flowrate of 50 sccm. The CO<sub>2</sub> laser beam was directed perpendicularly to the NH<sub>3</sub> flow. The laser incident power density was fixed at  $1.4 \times 10^4$  W/cm<sup>2</sup> for all laser wavelengths. All spectra were taken with a vertical collecting length of 0.5 mm along the emission, centred at the tip of the emission, and with a horizontal slit width of 30  $\mu$ m centred at the tip apex of the emission. A background spectrum captured before collecting the emission spectra was subtracted from all spectra.

## III. RESULT AND DISCUSSION

### A. FESEM images of the GaN films

The morphologies and grain sizes of the GaN films deposited at different laser wavelengths are shown in Figures 3(a)–3(e), respectively. The crystalline GaN films containing highly oriented grains along the c-axis with the hexagonal facets are observed, indicating the formation of wurtzite GaN films on the Si(100) substrates. Generally, a mixture of cubic and hexagonal GaN tends to grow on Si(100) substrates because the (001) plane of Si possesses a fourfold symmetry.<sup>23–27</sup> However, the nitridation process promotes the silicon nitride formation and prohibits a cubic GaN nucleation. Therefore, the hexagonal GaN dominates the GaN growth.<sup>23–27</sup>

It is generally accepted that the grain boundaries impact negatively on the electrical and optical properties of the GaN films.<sup>33,34</sup> Increasing the grain sizes leads to the reduced grain boundaries and results in a reduced amount of defects

and stress. Therefore, the crystalline quality and optical properties of the GaN films are improved accordingly.<sup>33,34</sup> Figure 3(f) compares the average grain sizes of the GaN films grown at different laser wavelengths. As shown in Figures 3(a) and 3(d), GaN grains with average grain sizes of 1.0 and 2.1  $\mu$ m are obtained at the nonresonant wavelengths of 9.201 and 10.591  $\mu$ m, respectively. The average grain sizes increase to 4.0, 3.8, and 3.1  $\mu$ m at resonant wavelengths 9.219, 10.350, and 10.719  $\mu$ m, as shown in Figures 3(b), 3(c), and 3(e), respectively.

The cross-sectional SEM images of the GaN films deposited at the non- (9.201  $\mu$ m) and resonant wavelengths (9.219  $\mu$ m) for 5 min are exhibited in Figures 4(a) and 4(b), respectively. The resonant deposition, Figure 4(b), results in a thicker GaN film (7  $\mu$ m) than the nonresonant deposition, Figure 4(a), indicating a higher growth rate (around 2.7 times higher) at the resonant deposition. Figure 4(c) compares the deposition rates obtained at all the five wavelengths. It is obvious that the resonant depositions result in higher GaN growth rates than the nonresonant depositions. The highest growth rate (84  $\mu$ m/h) is achieved at 9.219  $\mu$ m, which is  $\sim 42$  times higher than that of the conventional MOCVD (2  $\mu$ m/h).<sup>6,12,13</sup> Although not as significant as those obtained under the resonant wavelengths, the promoted GaN growth rates are also observed at the nonresonant wavelengths, 9.201 and 10.591  $\mu$ m, and are ascribed to the coupled energy via laser irradiation. However, the same amount of energy coupled at different wavelengths yields obviously divergent results, as observed in Figures 3(f) and 4(c).

### B. Raman spectra of the GaN films

The Raman spectroscopy is a powerful method evaluating the quality and residual stress of the GaN films.<sup>35</sup> The Raman spectroscopic studies were conducted under a Z(X,X) $\bar{Z}$  backscattering geometry, where Z and  $\bar{Z}$  represent the projection direction of the incoming and scattered lights, respectively, and X represents the polarization direction of the incoming and scattered lights. Figure 5 shows the Raman spectra of the GaN films grown at different laser wavelengths. Two prominent Raman shifts at around 567 and 733 cm<sup>−1</sup> are observed from all the samples, corresponding to the GaN E<sub>2H</sub> and A<sub>1</sub>(LO) phonon modes. These modes originate from the allowed vibrational states in the wurtzite GaN epitaxial layer.<sup>35</sup> The exact positions of the GaN E<sub>2H</sub> phonon peak of the samples are summarized in Table I.

It is well known that the E<sub>2H</sub> mode in the GaN Raman spectra reflects the crystalline quality and stress of the crystals.<sup>35</sup> The E<sub>2H</sub> peaks shift to lower wave-numbers (red-shift) compared with that of the strain-free GaN at 567.8 cm<sup>−1</sup>. The shifts of the E<sub>2H</sub> peak are observed to be around 1.7, 1, 1.3, 1.3, and 1.2 cm<sup>−1</sup> for the samples grown at laser wavelengths of 9.201, 9.219, 10.35, 10.591, and 10.719  $\mu$ m, respectively. The red-shift indicates the tensile stress in the GaN films. The stress of the GaN epilayers can be calculated using the following equation:<sup>36</sup>  $\sigma = \Delta\omega/4.3$ , where  $\sigma$  is the biaxial stress, and  $\Delta\omega$  is the E<sub>2H</sub> phonon peak shift. The corresponding tensile stresses are calculated and summarized in Table I. The Raman spectra indicate that the GaN films grown at the laser wavelength of 9.219  $\mu$ m exhibit the lowest stress.

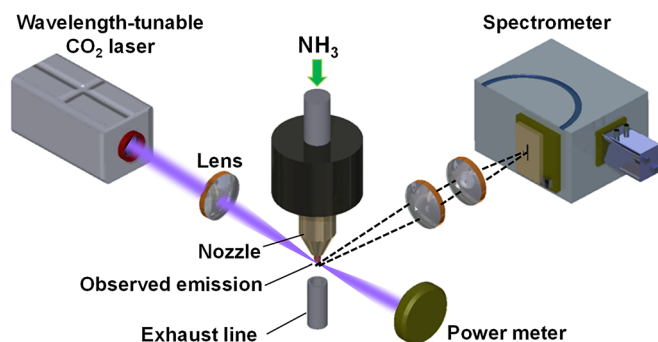


FIG. 2. A schematic experimental setup for the OES measurements in open air.



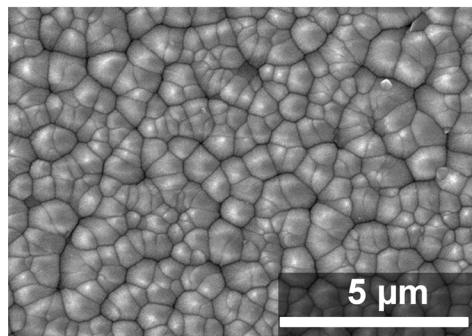
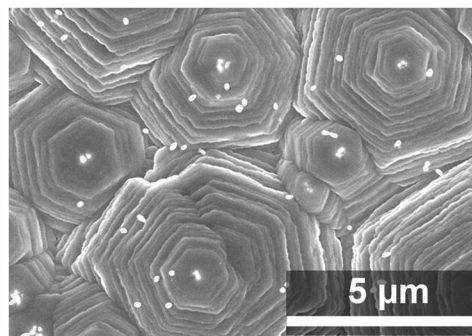
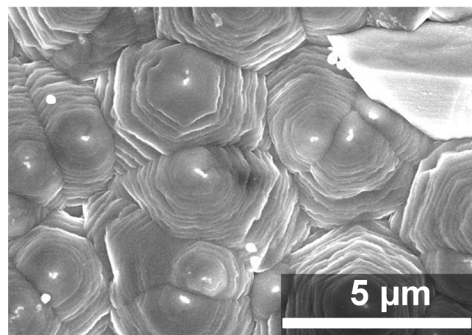
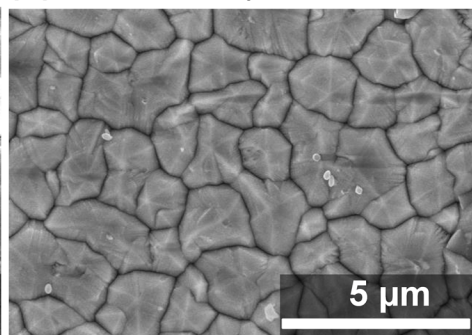
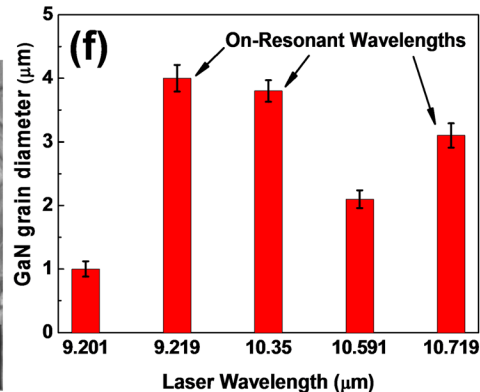
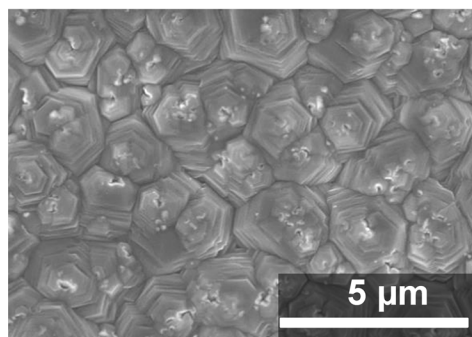
**(a)  $\lambda = 9.201 \mu\text{m}$** **(b)  $\lambda = 9.219 \mu\text{m}$** **(c)  $\lambda = 10.350 \mu\text{m}$** **(d)  $\lambda = 10.591 \mu\text{m}$** **(e)  $\lambda = 10.719 \mu\text{m}$** 

FIG. 3. The SEM images of the GaN films deposited on Si (100) at excitation laser wavelengths of (a)  $9.201 \mu\text{m}$ , (b)  $9.219 \mu\text{m}$ , (c)  $10.350 \mu\text{m}$ , (d)  $10.591 \mu\text{m}$ , and (e)  $10.719 \mu\text{m}$ . (f) A chart showing average GaN grain sizes obtained at different laser wavelengths.

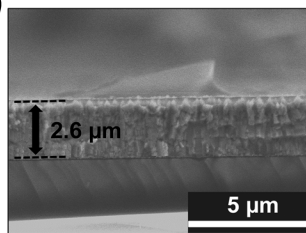
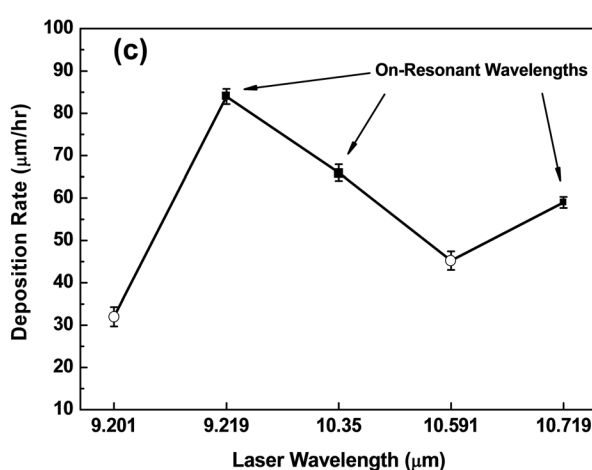
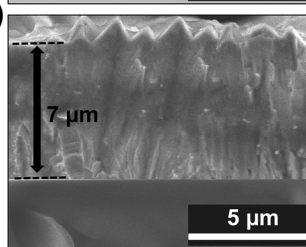
**(a)****(b)**

FIG. 4. Cross-sectional SEM images of SEM GaN films deposited on Si (100) for 5 min with  $\text{CO}_2$  laser excitation at (a) the nonresonant wavelength of  $9.201 \mu\text{m}$  and (b) the resonant wavelength of  $9.219 \mu\text{m}$ . (c) GaN deposition rate plotted as a function of laser wavelength.

Moreover, as observed in Figure 5, the  $E_{2H}$  peak is much stronger in the resonant samples ( $9.219$ ,  $10.35$ , and  $10.719 \mu\text{m}$ ) than in the nonresonant samples ( $9.201$  and  $10.591 \mu\text{m}$ ), indicating a better crystalline quality of the

resonant samples. The strongest  $E_{2H}$  peak is observed when resonantly excited at  $9.219 \mu\text{m}$ , denoting the highest GaN crystalline quality. The full-width-at-half-maximum (FWHM) values of the  $E_{2H}$  peaks of the GaN samples are summarized

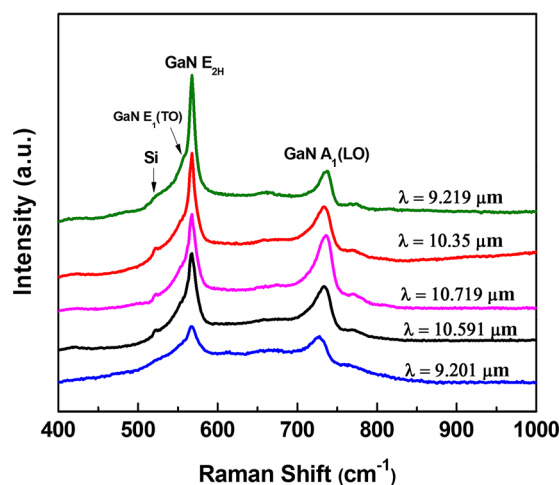


FIG. 5. The Raman spectra of the GaN films grown at the resonant (9.219, 10.35, and 10.719  $\mu\text{m}$ ) and nonresonant (9.201 and 10.591  $\mu\text{m}$ ) wavelengths.

in Table I. A narrow  $E_{2H}$  peak, i.e., a low FWHM value, indicates a better crystalline quality. According to Table I, it is obvious that FWHMs of the resonant samples are lower than those of the nonresonant samples. The lowest FWHM,  $9.3\text{ cm}^{-1}$ , was observed in the resonant sample excited at  $9.219\text{ }\mu\text{m}$ , indicating the highest GaN crystalline quality.

### C. XRD characterization of the GaN films

Figures 6(a) and 6(b) exhibit the XRD diffraction curves of the GaN films obtained at  $9.219\text{ }\mu\text{m}$  (resonant wavelength) and  $9.201\text{ }\mu\text{m}$  (nonresonant wavelength), respectively. The XRD peaks at around  $40.2^\circ$  and  $87.02^\circ$  are observed in both the curves and are attributed to the GaN {0001} family planes. These peaks correspond to the (0002) and (0004) orientations of wurtzite GaN, respectively, indicating a high c-axis orientation of the GaN films deposited on the Si(100) substrates.<sup>37</sup> It is observed from Figures 6(a) and 6(b) that the GaN XRD peaks are much stronger in the resonant sample than those in the nonresonant sample, which is attributed to the improved crystalline quality.

The GaN (0002) rocking curves of the GaN films deposited at the resonant ( $9.219\text{ }\mu\text{m}$ ) and nonresonant ( $9.201\text{ }\mu\text{m}$ ) wavelengths are exhibited in Figures 6(c) and 6(d), respectively. FWHM values of the rocking curves of the (0002) symmetric and (10–12) asymmetric diffraction peaks are summarized in Table I. It is well known that the FWHM of XRD in the (0002) reflection reveals information about the out-of-plane misorientation of domains (tilt), while the FWHM of the GaN (10–12) peak is sensitive to both a tilt

and a twist. Thus, the FWHM of the (0002) peak is usually used to evaluate the screw or mixed threading dislocations (TDs) density, and the FWHM of XRD in the (10–12) reflection corresponds to the lattice distortion from all the components of the TDs, including edge, screw, and mixed screw-edge dislocations.<sup>37,38</sup> Low FWHM values indicate low TDs density and better crystalline quality.

As shown in Table I, (0002) FWHM values of 92 and 60 arcmin and (10–12) FWHM values of 99 and 67 arcmin are observed for the GaN samples deposited at the nonresonant wavelengths of  $9.201$  and  $10.591\text{ }\mu\text{m}$ , respectively. For the GaN film deposited with resonant excitation, the FWHMs of (0002) are 39, 45, and 55 arcmin and the FWHMs of (10–12) are 43, 53, and 61 arcmin at the resonant wavelengths of  $9.219$ ,  $10.350$ , and  $10.719\text{ }\mu\text{m}$ , respectively. The distinctive FWHMs decrease in the resonant samples compared to those with the nonresonant samples indicates an improved GaN crystalline quality and a reduced TDs density by using resonant excitation. However, the crystalline quality of the GaN films are inferior to that reported for the conventional MOCVD,<sup>6</sup> which is attributed to the high growth rates of GaN, a large crystal lattice mismatch (16.9%), and a thermal coefficient of expansion mismatch (113%) between the GaN epilayer and the Si substrate.<sup>6,8</sup> Further investigations are underway to improve the GaN crystalline quality while maintaining the high growth rates.

### D. Hall measurement of the GaN films

Hall measurements using the van der Pauw method were conducted to characterize the carrier concentrations and mobilities of the GaN films deposited at the resonant ( $9.219\text{ }\mu\text{m}$ ) and nonresonant ( $9.201\text{ }\mu\text{m}$ ) wavelengths. Both the GaN films were demonstrated to be n-type semiconductors. The corresponding carrier concentrations and mobilities are  $8.27 \times 10^{17}\text{ cm}^{-3}$  and  $299.5\text{ cm}^2/\text{V s}$  for the resonant sample and  $4.9 \times 10^{18}\text{ cm}^{-3}$  and  $119.1\text{ cm}^2/\text{V s}$  for the nonresonant sample. The relatively high carrier concentration indicates a high concentration of unintentionally doped impurities. However, the resonant sample possesses a lower carrier concentration but higher mobility, compared to the nonresonant sample.

## IV. MECHANISM OF THE RESONANT VIBRATIONAL EXCITATION

### A. Optical emission spectra of $\text{NH}_3$ under laser irradiation

According to aforementioned experimental results, two points are clearly demonstrated. The first is that resonant

TABLE I. Summary of GaN films characterization grown on the Si (100) substrates at different laser wavelengths.

| Sample | Laser wavelength ( $\mu\text{m}$ ) | Average grain sizes ( $\mu\text{m}$ ) | Growth rate ( $\mu\text{m}/\text{h}$ ) | GaN $E_{2H}$ peak position ( $\text{cm}^{-1}$ ) | $\sigma$ (GPa) | GaN $E_{2H}$ peak FWHM ( $\text{cm}^{-1}$ ) | GaN (0002) peak $\omega$ -FWHM (arcmin) | GaN (10–12) peak $\omega$ -FWHM (arcmin) |
|--------|------------------------------------|---------------------------------------|----------------------------------------|-------------------------------------------------|----------------|---------------------------------------------|-----------------------------------------|------------------------------------------|
| I      | 9.201                              | 1                                     | 32                                     | 566.1                                           | 0.395          | 19                                          | 92                                      | 99                                       |
| II     | 9.219                              | 4                                     | 84                                     | 566.8                                           | 0.233          | 9.3                                         | 39                                      | 43                                       |
| III    | 10.350                             | 3.8                                   | 66                                     | 566.5                                           | 0.302          | 10.1                                        | 45                                      | 53                                       |
| IV     | 10.590                             | 2.1                                   | 45                                     | 566.5                                           | 0.302          | 11.9                                        | 60                                      | 67                                       |
| V      | 10.719                             | 3.1                                   | 59                                     | 566.6                                           | 0.280          | 11.2                                        | 55                                      | 61                                       |

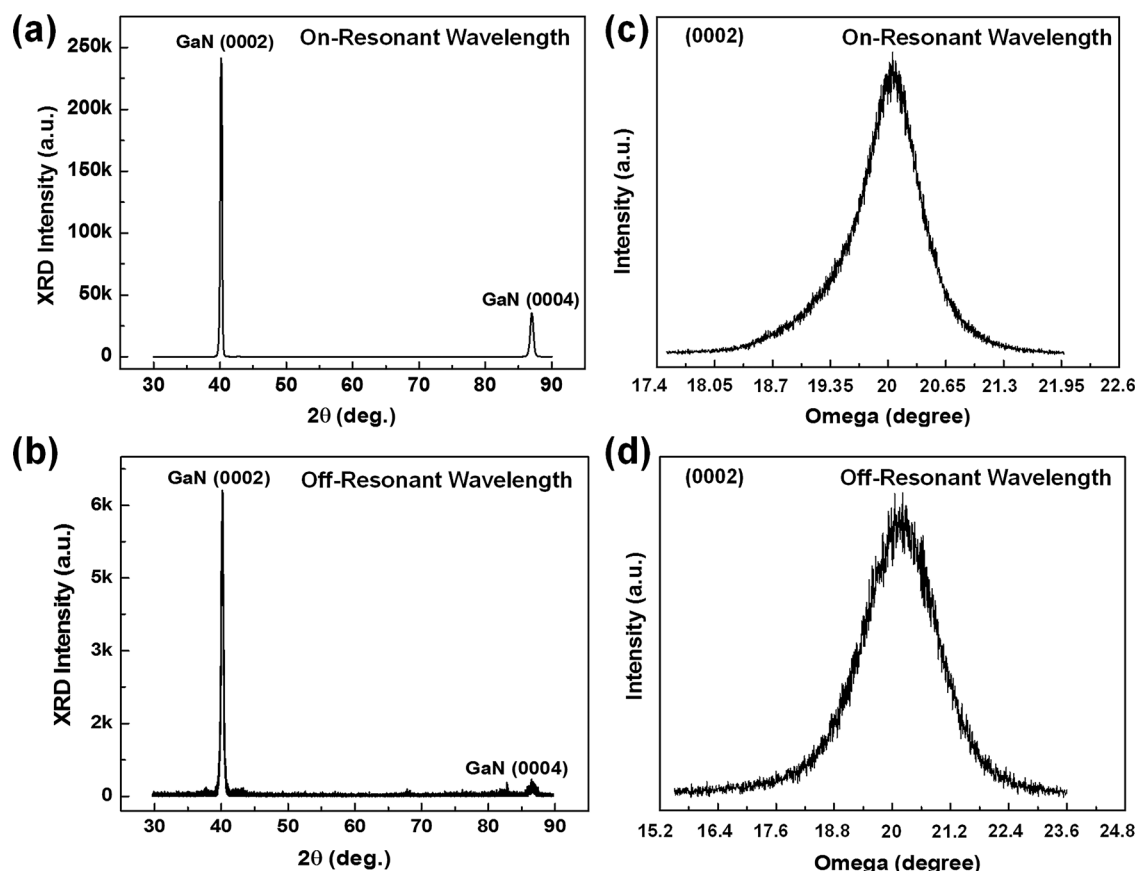


FIG. 6. The X-ray diffraction curves of the GaN films deposited at (a) the resonant wavelength of  $9.219\ \mu\text{m}$  and (b) the nonresonant wavelength of  $9.201\ \mu\text{m}$  (x-ray diffractometer: Rigaku D/Max B diffractometer, Co K $\alpha$   $\lambda = 1.788\ \text{\AA}$ ). The rocking curves of (0002) diffraction peaks of the GaN films deposited at (c) the resonant wavelength of  $9.219\ \mu\text{m}$  and (d) the nonresonant wavelength of  $9.201\ \mu\text{m}$ .

vibrational excitation can significantly promote the GaN growth rates and improve the GaN crystalline quality when compared to the conventional thermal heating and nonresonant laser irradiation. The second is that the same amount of energy coupled into different vibrational states leads to diverse results. In this study, the resonant excitation of the NH rotational-vibrational transition at  $1084.63\ \text{cm}^{-1}$  [ $5(J) \rightarrow 6(J'), K=0$ ] leads to the highest GaN growth rate, best crystalline quality, and highest carrier mobility. To understand the reasons behind the difference, the optical emission spectroscopic (OES) investigations were carried out to study the evolution of  $\text{NH}_3$  molecules under laser irradiation at the resonant and nonresonant wavelengths in open air. Figure 7

shows the optical images of the  $\text{NH}_3$  flows under laser irradiation at different wavelengths. Stronger emissions are observed from  $\text{NH}_3$  flows when irradiated at the resonant wavelengths (i.e.,  $9.219$ ,  $10.350$ , and  $10.719\ \mu\text{m}$ ) than those at the nonresonant wavelengths (i.e.,  $10.591$  and  $9.201\ \mu\text{m}$ ). The shape and brightness of the laser-induced plasma reflect dissociation of the  $\text{NH}_3$  molecules under the laser irradiation. According to Figure 7, resonant excitations lead to  $\text{NH}_3$  flows of brighter colors and expanded diameters due to an accelerated  $\text{NH}_3$  dissociation, promoted chemical reactions, and increased reactive species concentrations.<sup>39</sup> The brightest and strongest  $\text{NH}_3$  flow is observed under the resonant excitation at  $9.219\ \mu\text{m}$ .

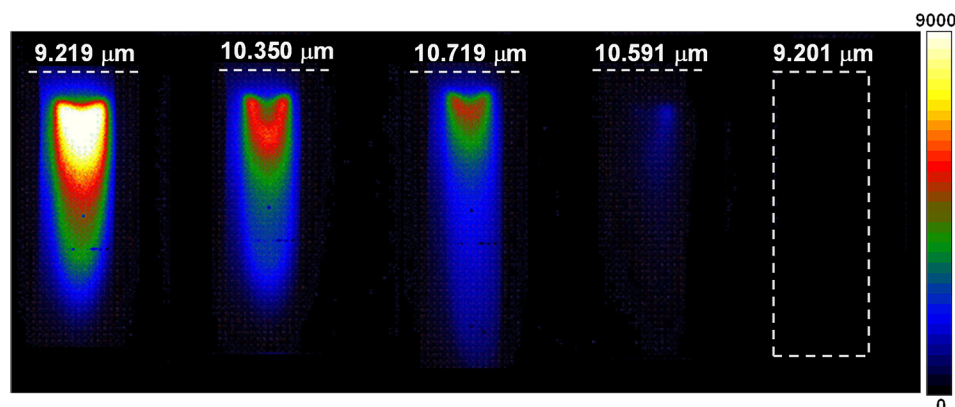


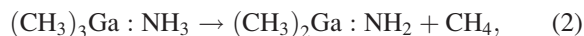
FIG. 7. The optical images of  $\text{NH}_3$  flows when irradiated at different laser wavelengths in open air.



The OES spectra of the laser-irradiated  $\text{NH}_3$  are shown in Figure 8. Emissions from OH, NH,  $\text{N}^+$ ,  $\text{H}_\alpha$ , N, and  $\text{H}_\beta$  are observed at 309, 336, 463, 486, 496, and 656 nm, respectively. Strong emissions from  $\text{NH}_2$  radicals are observed at 525, 543, 569, 603, 629, and 663 nm in all the OES spectra from the resonantly excited  $\text{NH}_3$  flows, indicating an effective dissociation of  $\text{NH}_3$  molecules. Obviously increased emission intensities of OH, NH,  $\text{NH}_2$ , N,  $\text{N}^+$ , and H are observed at the resonant wavelength of  $9.219 \mu\text{m}$ . However, only very weak emission intensities of the NH and  $\text{NH}_2$  radicals are identified when irradiated at the nonresonant wavelength of  $10.591 \mu\text{m}$ . No emission peak is observed at the nonresonant wavelength of  $9.201 \mu\text{m}$ .

N, NH, and  $\text{NH}_2$  are active nitrogen species for the growth of GaN.<sup>20,21,40</sup> The growth of high-quality GaN films requires a sufficient supply of active nitrogen and gallium species by cracking  $\text{NH}_3$  and TMGa molecules, respectively, and transporting atomic N and Ga to proper lattice sites. The dissociation energies for dissociating TMGa into active gallium species have been reported to be much lower than those of  $\text{NH}_3$ .<sup>20,21</sup> It is found that, with the laser photons, the TMG molecules undergo fragmentation with a relative ease in an analogy with their thermolytic instability.<sup>20,21,41</sup> However, effective decomposition of  $\text{NH}_3$  molecules requires a high temperature around  $1000^\circ\text{C}$ , which also leads to increased parasitic reactions, GaN decomposition, and N escaping.<sup>13</sup> Therefore, decomposing  $\text{NH}_3$  at an appropriate temperature is essential for growing a high-quality GaN.

It is generally believed that the formation of GaN in MOCVD includes four key steps:<sup>13,40</sup> (i) TMGa: $\text{NH}_3$  adduct formation, (ii) amide formation and methane elimination, (iii) trimer formation, and (iv) decomposition reaction and creating N and Ga to form GaN. The first gas-phase reaction is a spontaneous reaction between TMGa and  $\text{NH}_3$  to form a stable adduct  $[(\text{CH}_3)_3\text{Ga}:\text{NH}_3]$ . It is reported that the formation of the adduct as a parasite reaction significantly degrades the GaN film quality and growth rate at high temperatures.<sup>13,21,40</sup> The amide formation, trimer formation, and decomposition reaction can be expressed by Equations (2), (3) and (4), respectively<sup>13,40</sup>



The OES results indicate that the resonant vibrational excitation effectively dissociates the  $\text{NH}_3$  molecules and increases the concentrations of the active nitrogen species, i.e., N, NH, and  $\text{NH}_2$ . Based on the reported 4-step mechanism, an effective decomposition of  $\text{NH}_3$  is suggested to reduce the formation of the TMGa: $\text{NH}_3$  adduct<sup>21</sup> in the first step and decrease the energy barriers for the rest of the steps and, therefore, results in the increased GaN growth rate.

It is noteworthy that the performance of a GaN-based device is limited by a parasitic defect-induced emission, such as the yellow luminescence observed in GaN.<sup>42,43</sup> Unintentionally doped GaN is generally a n-type semiconductor due to a high concentration of shallow donor  $\text{Si}_{\text{Ga}}$  and  $\text{O}_{\text{N}}$ .<sup>43</sup> It is reported that H radicals can form neutral complexes with shallow donors and acceptor dopants. These reactions help eliminating oxygen impurities, reducing impurity density, and increasing in carrier mobility and resistivity of gallium nitride films.<sup>42</sup> Considering the concentration of atomic hydrogen resulted from  $\text{NH}_3$  decomposition, the oxygen impurities in GaN are expected to be reduced. It is suggested that, with the increments of H radicals, Figure 8, the GaN crystalline quality and carrier mobility increase under resonant excitations, compared to those at the nonresonant wavelengths.

Therefore, GaN films of better crystalline quality, lower impurity densities, and high deposition rates are obtained under the resonant vibrational excitation. The results are in good accordance with the SEM, Raman, and XRD results.

## V. CONCLUSION

In summary, vibrational excitations of  $\text{NH}_3$  molecules were studied using a tunable  $\text{CO}_2$  laser in growing the crystalline GaN films on Si(100) substrates. The resonant vibrational excitation at  $9.219$ ,  $10.350$ , and  $10.719 \mu\text{m}$  were more efficient than the nonresonant excitation in dissociating  $\text{NH}_3$  molecules and enhancing the GaN deposition rate and quality. The OES results showed the resonant excitation of the NH-wagging modes modifies the synthesis process in a way that increases the supplies of NH,  $\text{NH}_2$ , N,  $\text{N}^+$ , and H. This leads to the enhancement in the GaN deposition rates and improvement in the crystalline quality. The extremely high GaN growth rate of  $\sim 84 \mu\text{m/h}$  with an improved crystalline quality was achieved under the resonant excitation at  $9.219 \mu\text{m}$ . The red-shifts of the  $\text{E}_{2\text{H}}$  in Raman spectra indicate that the GaN films grown on Si suffer from the tensile stress. The GaN films grown at the laser wavelengths of  $9.219 \mu\text{m}$  exhibit the lowest stress. The FWHM value of the XRD rocking curves of GaN (0002) and GaN (10–12) diffraction peaks decreased at resonant depositions and reached its minimum values at  $9.219 \mu\text{m}$ , indicating a reduced TDs density. The XRD  $\omega$ -FWHM of  $45 \text{ arcmin}$  for the GaN(0002) and of  $53 \text{ arcmin}$  for the GaN(10–12) reflection were

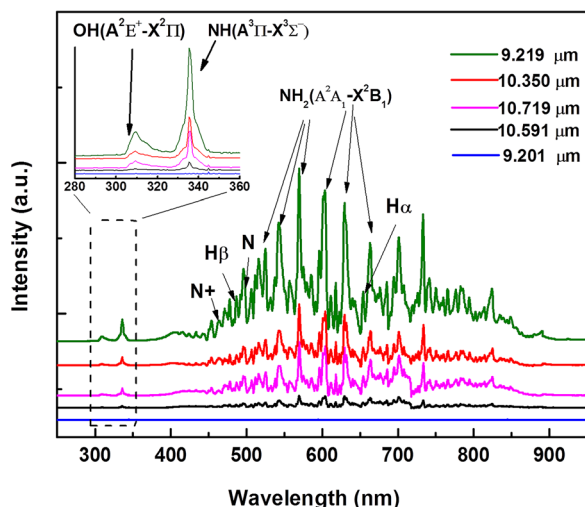


FIG. 8. The optical emission spectra of the  $\text{NH}_3$  under laser irradiation at different wavelengths in open air.



measured for samples grown at a laser wavelength of 9.219  $\mu\text{m}$ ; the FWHMs of the GaN(0002) and GaN(10–12) planes are about 3–5 times broader than those of the best GaN epilayer samples reported in literatures.<sup>6</sup> Further investigation are underway to improve the quality of the GaN films deposited via the LMOCVD techniques while maintaining the high growth rates.

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