

University of Nebraska - Lincoln

DigitalCommons@University of Nebraska - Lincoln

Theses, Dissertations, and Student Research from
Electrical & Computer Engineering

Electrical & Computer Engineering, Department of

2015

Influence of resonant and non-resonant vibrational excitation of ammonia molecules in gallium nitride synthesis

Hossein Rabiee Golgir

University of Nebraska-Lincoln, rabiee@huskers.unl.edu

Yunshen Zhou

University of Nebraska-Lincoln, yzhou5@unl.edu

Kamran keramatnejad

kkeramatnejad2@unl.edu

Yongfeng Lu

University of Nebraska-Lincoln, ylu2@unl.edu

Follow this and additional works at: <http://digitalcommons.unl.edu/elecengtheses>



Part of the [Electrical and Computer Engineering Commons](#), and the [Semiconductor and Optical Materials Commons](#)

Rabiee Golgir, Hossein; Zhou, Yunshen; keramatnejad, Kamran; and Lu, Yongfeng, "Influence of resonant and non-resonant vibrational excitation of ammonia molecules in gallium nitride synthesis" (2015). *Theses, Dissertations, and Student Research from Electrical & Computer Engineering*. 82.

<http://digitalcommons.unl.edu/elecengtheses/82>

This Article is brought to you for free and open access by the Electrical & Computer Engineering, Department of at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Theses, Dissertations, and Student Research from Electrical & Computer Engineering by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

INFLUENCE OF RESONANT AND NON-RESONANT VIBRATIONAL EXCITATION OF AMMONIA MOLECULES IN GALLIUM NITRIDE SYNTHESIS

Paper (#N503)

Hossein Rabiee-Golgir, Yun Shen Zhou, Kamran keramatnejad, Yong Feng Lu*

Department of Electrical Engineering, University of Nebraska-Lincoln, Lincoln, Nebraska, 68588-0511, USA

* To whom correspondence should be addressed. Email: yflu2@unl.edu. Tel: +1-402-472-8323.

Abstract

Attempts on the selective promotion of gallium nitride (GaN) growth were investigated by deploying laser-assisted vibrational excitation of reactant molecules, which deposits energy selectively into specific molecules and activate the molecules towards the selected reaction pathways. Laser-assisted metal organic chemical vapor deposition (LMOCVD) of GaN was studied using a wavelength-tunable CO₂ laser. The NH-wagging modes (ν_2) of ammonia (NH₃) precursor molecules are strongly infrared active and perfectly match the emission line of the CO₂ laser at 9.219, 10.350, and 10.719 μm . On- and off-resonance excitations of molecules were performed via tuning the incident laser wavelengths at on-resonant wavelength 9.219 μm and off-resonant wavelength of 9.201 μm . The on-resonant vibrational excitation allowed a largest fraction of the absorbed laser energy coupled directly into NH₃ molecules whereas energy coupling under off-resonant excitations is less efficient in energy coupling and influencing the GaN growth process. The GaN deposition rate was enhanced by a factor of 2.6 accompanied with an improvement of crystalline quality under the on-resonant excitation. Optical emission spectroscopic (OES) studies confirmed that the on-resonant vibrational excitation effectively promotes the dissociation of NH₃ molecules and creates N-containing species favoring the GaN growth. This study indicates that the resonant vibrational excitation is an efficient route coupling energy into the reactant molecules to surmount the chemical reaction barrier and steering the growth process.

Introduction

Gallium nitride (GaN) has attracted enormous attentions as one of the most promising materials for light emitting diodes (LEDs), short wavelength laser diodes, high electron mobility transistors, and numerous other electronic applications [1-3]. GaN films can be obtained via metal organic chemical vapor deposition (MOCVD) and molecular beam epitaxy

(MBE), using NH₃ as the nitrogen precursor [4]. However, the efficiency and reactivity of NH₃ in these growth processes seem to be very low in regard to the usually reported a very high V/III flux ratio typically ranging from 40 (MBE) to 3000 (MOCVD) and high synthesis temperatures [5]. In conventional MOCVD GaN methods, reactant molecules are indiscriminately thermally activated near thermal equilibrium [4-5]. Energy is first deposited to the translational modes of the reactant molecules, and then finds their way to the internal modes (rotation, vibration, and electronic excitation) through collisions. The conventional thermal activation is an inefficient route to cause gases to react. Chemical reactions take place when chemical bonds are broken in reactant molecules and new bonds are formed in the products, which are directed related to the vibrational and electronic excitations [6]. Resonant vibrational excitations of reactant molecules could be more efficient in energy coupling than global thermal heating via direct energy deposition on the molecular bonds to drive the reactions. Besides, the reaction path could be steered through localizing energy to a selected bond of a molecule [6-10]. Laser-assisted MOCVD takes the advantage of matching the laser light wavelength to the energy difference for a specific transition in precursor molecules. By matching laser wavelengths with desired vibrational modes of the reactant molecules, reactions can be promoted with a high energy-coupling efficiency and desired yield. Crim and coworkers have reported the use of infrared laser excitation for controlling gas phase chemical reactions [11-12]. It was reported that selective excitation of different vibrational modes of CH₃D could lead to very different reactivities when reacting with a Cl atom [11]. Yoon *et al* have showed that resonantly exciting the symmetric stretching mode (ν_1) in a CH₄ molecule resulted in a reactivity 10 times higher than that of the antisymmetric stretching mode (ν_4) [13]. In spite of extensive fundamental investigations, practical applications of vibrational excitation in material synthesis are seldom reported.

Xie *et al* revealed that coupling laser energy into chemical reactions through vibrational excitation of

ethylene is very efficient in promoting diamond deposition [14]. In our previous study, we have introduced low temperature growth of GaN films using an IR-laser-assisted MOCVD method, in which NH_3 reactant was selectively dissociated at low growth temperatures via resonant vibrational excitation, and GaN films were successfully deposited at temperatures as low as 250 °C [15]. However, understanding on the role of the vibrational excitation of NH_3 and the energy coupling process in GaN synthesis is absent. Comparison of GaN deposition between on- and off-resonance excitations with the same amount of absorbed laser energy allows further understanding on the energy distribution and its effects on chemical reactions.

In this study, influence of laser excitations on GaN growth was studied using a wavelength-tunable CO_2 laser. The GaN films were grown on silicon substrates at different laser wavelengths (on- and off-resonant wavelengths) using a laser-assisted MOCVD (LMOCVD) technique. Resonant vibrational excitation of NH_3 molecules was realized using laser irradiation at 9.219 μm matching the NH-wagging modes. It is evidenced that the resonant excitation of NH_3 molecules is more effective in activating/decomposing NH_3 molecules and leading to higher growth rates as well as better crystalline quality than off-resonant excitation.

Experimental Section

GaN Growth

The schematic experimental setup of a home-built LMOCVD system is shown in Fig. 1. GaN films were grown on Si (100) substrates. Trimethylgallium (TMGa) and NH_3 were used as the precursors. The Si substrates ($10 \times 10 \text{ mm}^2$) were sonicated in organic solvents (acetone and methanol) and de-ionized water sequentially before loading into the LMOCVD chamber. Then, LMOCVD chamber was evacuated to a base pressure of 1×10^{-3} Torr. TMGa was introduced into the vacuum chamber using nitrogen (N_2) as a carrier gas at a flow rate of 20 sccm. The flow rate of NH_3 was fixed at 1200 sccm. The growth pressure was maintained at ~ 10 Torr during the growth process.

A continuous-wave (CW) wavelength-tunable CO_2 laser (PRC Inc., spectrum range: 9.2 - 10.9 μm) was used as the irradiation source achieving reactant excitation and substrate heating. Based on the available emission lines in the CO_2 laser, the NH-wagging mode (ν_2 , at 1084.71 cm^{-1}) of NH_3 was selected for on-resonant vibrational excitation with corresponding laser wavelength at 9.219 μm . Therefore, laser wavelength centered at 9.219 μm was selected

achieving on-resonant vibrational excitation of the NH-wagging modes of NH_3 . The wavelength at 9.201 μm was selected off-resonant wavelength as reference. The laser incident power was tuned to keep the substrate temperature at 750 °C for all GaN samples grown at different laser wavelengths. The substrate temperature was monitored using a pyrometer (Omega, OS3752). The deposition time for GaN samples was fixed at 5 min.

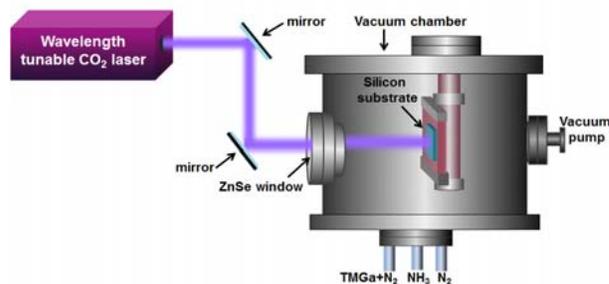


Figure 1. IR-laser-assisted MOCVD setup for GaN film deposition.

Measurement of laser energy absorption

The NH_3 absorption spectrum within the CO_2 laser wavelength range was measured in the vacuum chamber with an absorption path length of 40.64 cm. The chamber was evacuated to a base pressure of 1×10^{-3} torr. NH_3 gas was subsequently introduced into the chamber reaching 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.

Characterization of GaN films

Surface morphologies and dimensions of the GaN films were studied by a field emission scanning electron microscope (FESEM, Hitachi S4700). The qualities of GaN films were evaluated both by a Raman microscope (inVia H 18415, Renishaw) and powder X-ray diffractometer (Rigaku D/Max B diffractometer, $\text{Co K}\alpha 1 \lambda = 1.788 \text{ \AA}$).

The optical emission spectra (OES) of laser irradiated NH_3 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). The IR laser beam was focused to a diameter of approximately 1 mm using a ZnSe convex lens ($f = 25.4 \text{ cm}$). A welding torch with a nozzle diameter of 1.5 mm was used to introduce the NH_3 gas with a flowrate of 50 sccm. The CO_2 laser beam was directed perpendicularly to the

NH₃ flow. The laser incident power was tuned to keep power density at 1.4×10^4 W/cm² for all laser wavelengths. All spectra were taken with a vertical collecting length of 0.5 mm along the emission, centered at the tip of the emission, and with a horizontal slit width of 30 μm, centered at the tip apex of the emission. A background spectrum captured before collecting the emission spectra was subtracted from all spectra.

Results and Discussion

Laser energy absorption

To study the influence of resonant and non-resonant vibrational excitation of NH₃ molecules on the GaN growth, the absorption spectra of the CO₂ laser (9.2 - 10.8 μm) by NH₃ at gas pressure of 10 Torr is investigated. Fig. 2 shows the absorption of CO₂ laser energy by NH₃ at the pressure of 10 Torr. Three strong absorption percentage peaks were observed at the wavelengths of 9.219, 10.35, and 10.719 μm named on-resonant wavelengths at the NH₃ pressure of 10 Torr. However, no absorption percentage peaks were observed in other wavelengths (off-resonant wavelengths). The distinct absorption at these wavelengths arises from the resonant excitation of the NH-wagging vibrational transition modes (ν_2) of the NH₃ molecules.

Among the six vibrational modes of the NH₃ molecules, the NH-wagging mode has a strong infrared activity within the CO₂ laser spectrum range. NH₃ molecule in the NH-wagging mode vibrates in an umbrella inversion way. Due to the barrier that the nitrogen encountered on its travel through the proton plane, the vibrational level is split into two vibrational components at 932.51 (ν_2^+) and 968.32 cm⁻¹ (ν_2^-) which are matched to CO₂ laser wavelengths at 10.719 and 10.35 μm, respectively [16]. This matching gives rise to resonant absorption peaks at these two wavelengths. The NH rotational-vibrational transition at 1084.63 cm⁻¹ has the strongest absorption to CO₂ laser power at 9.219 μm. The perfect match of CO₂ laser energy at 9.219 μm (1084.71 cm⁻¹) to the centers of the NH₃ absorption lines at 1084.63 cm⁻¹ [5(J) → 6(J'), K=0] in the ν_2^- band accompanied a very strong absorption [16-17]. Two other peaks at 10.35 and 10.719 μm belong to the Q- branch at 965.99 cm⁻¹ (J=K=5) in the ν_2^- band and the Q- branch at 932.40 cm⁻¹ (J=K=2) in the ν_2^- band, respectively [17]. The mismatch as much as 0.5 cm⁻¹ between the laser line and the transition line of NH₃ lowers the absorption efficiency at these two points. No obvious absorption was detected at other wavelengths named non-resonant wavelengths especially 10.591 μm which is the

wavelength of commercial CO₂ lasers. The vibrational excitation of NH₃ molecules at these three resonant wavelengths contributes to dissociating of NH₃ molecules.

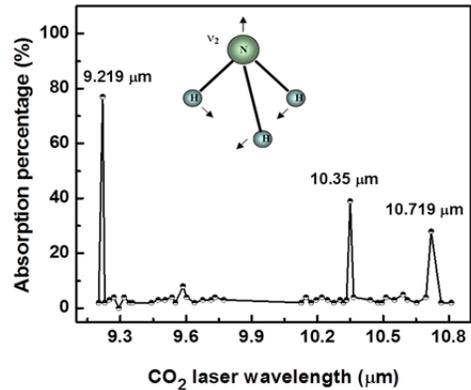


Figure 2. Absorption of CO₂ laser energy by ammonia at the pressure of 10 Torr.

Characterization of GaN films

The morphologies and grain sizes of the GaN films deposited at on- and off laser wavelengths are shown in Fig. 3. Polycrystalline GaN films containing highly oriented grains along the c-axis with hexagonal facets are observed from Fig. 3(a) to Fig. 3(b) which confirm highly textured GaN films with a wurtzite structure.

It is generally accepted that grain boundaries exert significant influence on the electrical and optical properties of corresponding GaN films [18-19]. The grain boundary region contains a large amount of defect states, which become charged after trapping free carriers from the neighboring grains [18]. The inherent space charge in grain boundaries region would result in band bending. In addition to the trap states at the grain boundary regions of the GaN films, a considerable amount of mechanical stress due to lattice dilation modulates the lattice ordering at the grain boundary region, resulting in fluctuating nature of GaN band gap [19]. Therefore, additional indirect optical transitions are resulted below the fundamental band gap of the GaN. The stress due to grain boundaries are, in general, proportional to the total grain boundary area, which in turn would depend inversely on the average grain size. With increases in grain sizes, grain boundaries would decrease, resulting in lesser amount of density of trap states with associated lower stress. Hence, the crystalline quality and optical properties of GaN films are improved [18].

As shown in Figs. 3(a) and 3(b), GaN grains with average grains of 1.0 and 4 μm are obtained at off-resonant wavelength of 9.201 and on-resonant

wavelength of 9.219 μm , respectively, indicating improved GaN crystalline quality under the on-resonant vibrational excitation of NH_3 molecules.

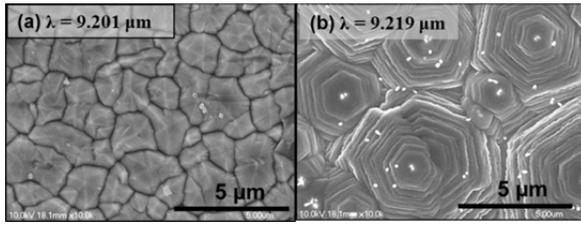


Figure 3. SEM images of GaN films deposited on Si at the off-resonant wavelength of (a) 9.201 μm , and on-resonant wavelength of (b) 9.219 μm .

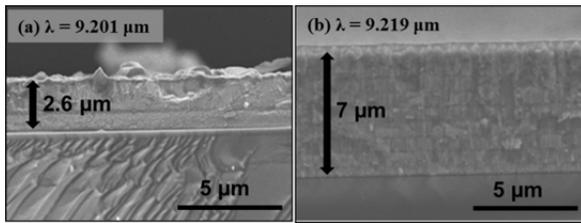


Figure 4. Cross sectional SEM images of GaN films deposited on Si at (a) off-resonant wavelength of 9.201 μm , and (b) on-resonant wavelength of 9.219 μm .

The cross-sectional SEM images of the GaN films deposited at off- (9.201 μm) and on-resonant wavelengths (9.219 μm) for 5 minutes are exhibited in Figs. 4(a) and 4(b), respectively. The on-resonant deposition, Fig. 4(b), results in a thicker film with a thickness of 7 μm than the off-resonant deposition, Fig. 4(a). For the same deposition duration, a thicker film refers to a higher deposition rate obtained from the on-resonant deposition with an enhancement factor of 2.7.

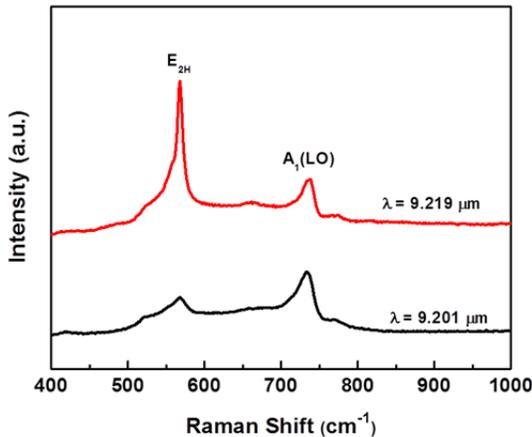


Figure 5. Raman spectra of the GaN films at on-resonant (9.219 μm) and off-resonant (9.201 μm) wavelengths.

The bonding structures in the GaN films were characterized using Raman spectroscopy as shown in Fig. 5. The vibrational modes of the GaN films were studied using a micro-Raman spectroscope under a $Z(X,X)\bar{Z}$ backscattering geometry, where, Z and \bar{Z} represent the projection direction of the incoming and scattered light and X represents the polarization direction of the incoming and scattered light. Raman is a powerful method evaluating the quality, residual stress and carrier concentration of GaN films [20]. Fig. 5(a) shows the Raman spectra of the GaN films grown at different laser wavelengths. Two prominent Raman peaks at 568 and 734 cm^{-1} are observed for all samples, corresponding to the GaN E_{2H} and $A_1(\text{LO})$ phonon modes, respectively. These modes are the allowed vibrational states for the wurtzite GaN (0001) epitaxial layer [20].

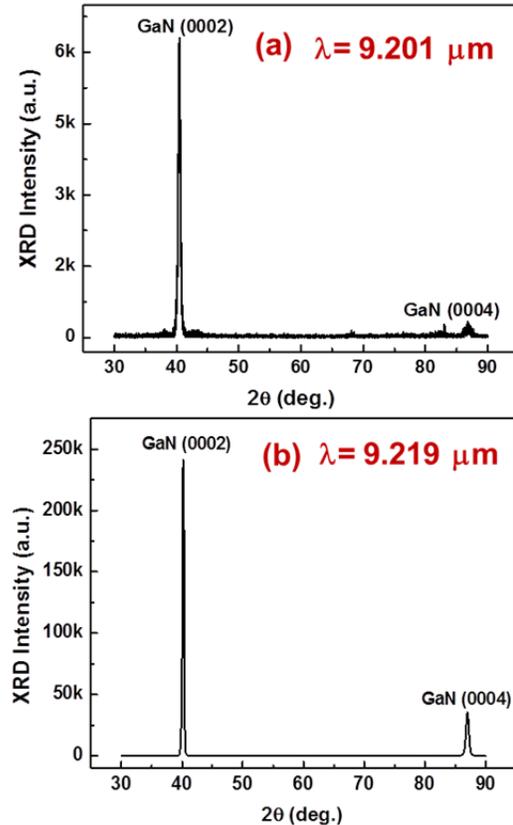


Figure 6. X-ray diffraction spectra of GaN films deposited on Si with CO_2 laser excitations at (a) off-resonant wavelength of 9.201 μm and (b) on-resonant wavelength of 9.219 μm .

It is generally accepted that the E_{2H} mode in Raman spectra of GaN reflects crystalline quality and stress. As observed in Fig. 5(a), the E_{2H} peak is much stronger in on-resonant samples (9.219 μm) than in off-resonant

samples (9.201 μm), indicating lower stress and better crystalline quality of the on-resonant samples. The full-width-at-half-maximum (FWHM) values of the E_{2H} peak of the GaN samples was measured at on- and off resonant wavelengths. A narrow E_{2H} peak, i.e. a low FWHM value, indicates a better crystalline quality. The lower FWHM of 9.3 cm^{-1} is obtained in the on-resonant sample excited at $9.219\text{ }\mu\text{m}$ than that with 32 cm^{-1} in off-resonant wavelength of $9.201\text{ }\mu\text{m}$, indicating the higher GaN crystalline quality.

Fig. 6 compares the XRD spectra of the GaN films grown on Si substrates at the on-resonant wavelength of $9.219\text{ }\mu\text{m}$ and off-resonant wavelength of $9.201\text{ }\mu\text{m}$, respectively. The XRD peaks attributed to the $\{0001\}$ family planes of GaN are observed at 40.2° and 87.02° in spectra of both GaN films. These peaks correspond to the (0002) and (0004) orientations of wurtzite GaN, respectively, indicating the high c-axis orientation of GaN film grown on Si substrates [21]. It can be seen from Fig. 6 that the GaN XRD peaks are much stronger in on-resonant samples of $9.219\text{ }\mu\text{m}$ than in off-resonant sample of $9.201\text{ }\mu\text{m}$ which can be attributed to the improved crystalline quality of the GaN films.

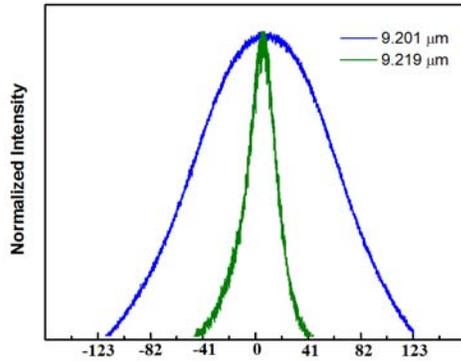


Figure 7. Rocking curve of (0002) diffraction peak for GaN films grown on Si substrates at on-resonant wavelengths ($9.219\text{ }\mu\text{m}$) and off-resonant wavelength ($9.201\text{ }\mu\text{m}$).

The X-ray rocking curves of the GaN films measured for the (0002) plane are shown in Fig. 7. The FWHM on the (0002) reflection peak probes tilt which represents misorientation of sub-grains out-of-plane. The FWHM on the (10-12) reflection peak is sensitive to both tilt and twist. Thus, the FWHM of the (0002) peak is usually used to evaluate the screw or mixed TDs density. Recently some studies have estimated the dislocation density in GaN film using the following equation [21]:

$$D = \beta^2 / (2\pi \ln 2) b^2 \quad (1)$$

Where D shows the dislocation density, β is the FWHM value measured by rocking curve and b is the Burgers vector. As shown in Fig. 7, (0002) FWHM values of 91 and 38 arcmin are obtained for the GaN samples deposited at the off-resonant wavelength of 9.201 and on-resonant wavelength of 9.219 , respectively. The distinctive reduction in the FWHM values of GaN films deposited with on-resonant wavelength than that of with off-resonant wavelength indicates that the laser resonant vibrational excitation of NH_3 leads to a decrease in the screw or mixed TDs density, hence significant improvement in the crystalline quality of the GaN films.

Growth mechanism

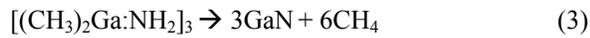
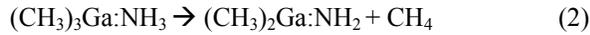
OES investigation was carried out to study the NH_3 excited with IR-laser irradiation at on- and off-resonant wavelengths in open air. OES is frequently applied to estimate relative density of species in ground state. Many optical emissions originate from excited species (e.g. atomic and molecular radicals) where excited species are generated by various processes such as electron collision, dissociation, impact of other excited species, photon absorption, etc. Specific species is identified by the photon energy of the optical emission.

Emissions from OH, NH, N^+ , H_α , N, and H_β species were observed at 309, 336, 463, 486, 496, and 656 nm, respectively. Strong emissions from NH_2 radicals were observed at 525, 543, 569, 603, 629 and 663 nm in all OES spectra of the emission with on-resonant excitation, indicating that NH_3 molecules are effectively dissociated under on-resonant vibrational excitation. Very strong emission intensities of OH, NH, NH_2 , N, N^+ , and H were observed at the on-resonant wavelength of $9.219\text{ }\mu\text{m}$. No emission peak was observed at the off-resonant wavelength of $9.201\text{ }\mu\text{m}$.

N, NH, and NH_2 are active nitrogen species for growing GaN [22]. Growth of high-quality GaN films requires a sufficient supply of active nitrogen species by cracking NH_3 molecules and transporting atomic N to proper lattice sites. However, decomposition of NH_3 molecules requires a high temperature above $1000\text{ }^\circ\text{C}$, which also leads to the decomposition of GaN and N escaping. Therefore, decomposing NH_3 at an appropriate temperature is essential for growing high-quality GaN.

It is generally believed gas-phase reaction formation of the GaN in MOCVD is characterized by three main steps [22]: (i) adduct formation, (ii) amide formation and methane elimination, and (iii) decomposition reaction and creating the N and Ga to form the GaN. The first gas-phase reaction is the spontaneous

interaction between TMGa ((CH₃)₃Ga) and NH₃ to form stable adduct ((CH₃)₃Ga:NH₃). The amide formation and decomposition reaction can be expressed by the following equations, respectively:



The OES results indicated that the resonant vibrational excitation effectively dissociates NH₃ molecules and increases the concentrations of the active nitrogen species of N, NH and NH₂. Therefore, the reaction barriers of (2) and (3) are reduced and the reaction process and GaN formation are accelerated.

It is also worthy to note that the GaN device performance can be limited by parasitic defect-induced emission such as the yellow luminescence observed in GaN [23-24]. Unintentionally doped GaN is generally strongly n-type primarily due to a high concentration of shallow donor Si_{Ga} and O_N [24]. It is suggested that H radicals play a critical role in eliminating oxygen impurities in the synthesis of nitride especially useful for those precursors to be easily oxidized. Considering the high concentration of atomic hydrogen in the resonant vibrational excitation and dissociation of NH₃, the oxygen impurity might be eliminated by the reaction between hydrogen and oxygen. The detection of OH emission at NH₃ excited with laser in open air confirmed the reaction between hydrogen and oxygen. The existence and increments of OH and H radicals can explain why the GaN crystalline quality highly increased in the synthesis of GaN at on-resonant wavelengths than to those at off-resonant wavelengths.

Additionally, the Ga species react with impurities in the absence of sufficient active N atoms and N-containing intermediates because the possibility of impurity incorporation in reaction increases. However, at on-resonant wavelengths, the production of active N and N-related intermediates highly increased, providing the sufficient active N and eliminating the impurity content incorporated into the film during GaN growth. With the reduction in impurities, the GaN crystal islands grow larger in size, leading to higher crystallinity.

Conclusions

In summary, vibrational excitations of NH₃ molecules are studied using a tunable CO₂ laser in growth of highly textured crystalline GaN films on Si (100) substrates. The IR-laser resonant excitations at wavelength of 9.219 μm is highly efficient than that off-resonant excitation wavelength in exciting and dissociating the NH₃ molecules, and enhancing the

GaN deposition rate and quality. The FWHM value of the rocking curves of (0002) diffraction peaks obtained from XRD highly decreases at on-resonant wavelengths, indicating a decrease in the screw or mixed TDs density. The cross sectional SEM image of GaN samples confirms an enhanced deposition rate of ~ 2.6 with laser irradiation at the on-resonant wavelength of 9.219 μm. The FWHM of GaN E_{2H} peaks at Raman spectra are much narrower in GaN grown with on-resonant wavelength in compared to that of off-resonant wavelength, indicating a significant improvement in GaN quality. The resonant excitation of the NH-wagging modes modifies the synthesis process in a way that increases the amount of NH, NH₂, N, N⁺, and H species, leading to eliminate the impurities and improving in crystalline quality and enhancing in deposition rate of GaN films.

Acknowledgement

This work was financially supported by the National Science Foundation (NSF CMMI 1068510 and 1129613). It was also performed in part in Central Facilities of the Nebraska Center for Materials and Nanoscience, which is supported by the Nebraska Research Initiative.

References

- [1] Khan, A., Balakrishnan, K. & Katona, T. (2008) Ultraviolet light-emitting diodes based on group three nitrides, *Nature Photonics* 2, 77-84.
- [2] Avramescu, A., Lermer, T., Müller, J., Eichler, C., Bruederl, G., Sabathil, M., Lutgen, S. & Strauss, U. (2010) True green laser diodes at 524 nm with 50 mW continuous wave output power on c-plane GaN, *Applied Physics Express* 3, 061003.
- [3] Wu, Y., Kapolnek, D., Ibbetson, J.P., Parikh, P., Keller, B.P. & Mishra, U.K. (2001) Very-high power density AlGaIn/GaN HEMTs, *Electron Devices, IEEE Transactions on* 48, no. 3, 586-590.
- [4] Neumayer D.A. & Ekerdt, J.G. (1996) Growth of group III nitrides. A review of precursors and techniques, *Chemistry of Materials* 8, 9-25.
- [5] Mestrine, M., Grandjean, N. & Massies, J. (1998) Efficiency of NH₃ as nitrogen source for GaN molecular beam epitaxy, *Applied Physics Letters* 72, 350-352.
- [6] Zou, Y.S., Yang, Y. Chong, Y.M., Ye, Q., He, B., Yao, Z. Q., Zhang, W.J., Lee, S.T., Cai, Y. & Chu, H.S. (2008) Chemical vapor deposition of diamond films on patterned GaN substrate via a thin silicon

nitride protective layer, *Cryst. Growth Des.* 8, 1770-1773.

[7] Crim, F.F. (2008) Chemical dynamics of vibrationally excited molecules: controlling reactions in gases and on surface, *PNAS* 105, 12654-12661.

[8] Crim, F.F. (2007) Make energy count, *Science* 316, 1707-1708.

[9] Zare, R.N. (1998) Laser control of chemical reactions, *Science* 279, 1875-1879.

[10] Yan, S., Wu, Y.T., Zhang, B., Yue X.F., & Liu, K. (2007) Do vibrational excitations of CHD₃ preferentially promote reactivity toward the chlorine atom, *Science* 316, 1723-1726.

[11] Yoon, S., Holiday, R.J., & Crim, F.F. (2005) Vibrationally controlled chemistry: Mode-and bond-selected reaction of CH₃D with Cl, *The Journal of Physical Chemistry B* 109, 8388-8392.

[12] Metz, R.B., Thoemke, J.D., Pfeiffer, J.M., & Crim, F.F. (1993) Selectively breaking either bond in the bimolecular reaction of HOD with hydrogen atoms, *Journal of Chemical Physics* 99, 1744-1751.

[13] Yoon, S., Henton, S., Zivkovic, A.N., & F. Crim, F.F. (2002) The relative reactivity of the stretch-bend combination vibrations of CH₄ in the Cl (2P_{3/2}) + CH₄ reaction." *The Journal of Chemical Physics* 116, 10744-10752.

[14] Xie, Z.Q., Zhou, Y.S., He, X.N., Gao, Y., Park, J., Ling, H., Jiang, L. & Lu, Y.F. (2010) Fast growth of diamond crystals in open air by combustion synthesis with resonant laser energy coupling, *Cryst. Growth Des.* 10, 1762-1766.

[15] Rabiee Golgir, H., Gao, Y., Zhou, Y.S., Fan, L., Thirugnanam, P., Keramatnejad, K., Jiang, L., Silvain, J.F., & Lu, Y.F. (2014) Low-Temperature Growth of Crystalline Gallium Nitride Films Using Vibrational Excitation of Ammonia Molecules in Laser-Assisted Metalorganic Chemical Vapor Deposition, *Crystal Growth & Des.* 14, 6248-6253.

[16] David, C.W. (1996) IR vibration-rotation spectra of the ammonia molecule," *J. Chem. Educ.* 73, 46-50.

[17] Fan, L. S., Xie, Z.Q., Park, J.B., He, X.N., Zhou, Y.S., Jiang, L., & Lu, Y.F. (2012) Synthesis of nitrogen-doped diamond films using vibrational excitation of ammonia molecules in laser-assisted

combustion flames, *Journal of Laser Applications* 24, 022001.

[18] Ghosh, D., Hussain, S., Ghosh, B., Bhar, R., & Pal, A. K. (2014) Stress and grain boundary properties of GaN films prepared by pulsed laser deposition technique, *ISRN Materials Science* 2014, 521701.

[19] Chowdhury, M.P., Roy, R.K., Chakraborty, B.P, & Pal, A.K. (2005) Beryllium-doped polycrystalline GaN films: optical and grain boundary properties, *Thin Solid Films* 491, 29- 37.

[20] Kuball, M. (2001) Raman spectroscopy of GaN, AlGa_N and AlN for process and growth monitoring/control, *Surface and Interface Analysis* 31, 987-999.

[21] Moram, M. A., & Vickers, M. E. (2009) X-ray diffraction of III-nitrides, *Reports on Progress in Physics* 72, 036502.

[22] Parikh, R. P., & Adomaitis, R. A. (2006) An overview of gallium nitride growth chemistry and its effect on reactor design: Application to a planetary radial-flow CVD system, *Journal of Crystal Growth* 286, 259-278.

[23] Wei-Dong, Y., Pei-Nan, W., Zheng-Ping, L., Lan, M., & Fu-Ming, L. (2002) Characterization of the high-voltage pulsed discharge plasma of ammonia by emission spectroscopy. *Chinese Physics* 11, 260.

[24] Reshchikov, M. A., & Morkoc, H. (2005) Luminescence properties of defects in GaN, *Journal of Applied Physics* 97, 061301.

Biography

Hossein Rabiee-Golgir is currently a Ph.D. student in the Department of Electrical Engineering at the University of Nebraska-Lincoln. He obtained his Master degree from Sharif University of Technology in Tehran, Iran in 2012. His current research involves the growth of GaN films and nanostructures using LMOCVD method and fabrication of GaN-based optoelectronic devices.