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

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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 CO$_2$ laser. The NH-wagging modes ($\nu_2$) of ammonia (NH$_3$) precursor molecules are strongly infrared active and perfectly match the emission line of the CO$_2$ 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 NH$_3$ 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 NH$_3$ 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 NH$_3$ as the nitrogen precursor [4]. However, the efficiency and reactivity of NH$_3$ 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 CH$_3$D 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 ($\nu_1$) in a CH$_4$ molecule resulted in a reactivity 10 times higher than that of the antisymmetric stretching mode ($\nu_4$) [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 NH₃ 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 NH₃ 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 CO₂ 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 NH₃ molecules was realized using laser irradiation at 9.219 µm matching the NH-wagging modes. It is evidenced that the resonant excitation of NH₃ molecules is more effective in activating/decomposing NH₃ 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 NH₃ were used as the precursors. The Si substrates (10 × 10 mm²) 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 (N₂) as a carrier gas at a flow rate of 20 sccm. The flow rate of NH₃ was fixed at 1200 sccm. The growth pressure was maintained at ~ 10 Torr during the growth process.

A continuous-wave (CW) wavelength-tunable CO₂ laser (PRC Inc., spectrum range: 9.2 - 10.9 µm) was used as the irradiation source achieving resonant excitation and substrate heating. Based on the available emission lines in the CO₂ laser, the NH-wagging mode (ν₂, at 1084.71 cm⁻¹) of NH₃ 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 NH₃. 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.

![Image](318x492 to 546x606)

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

**Measurement of laser energy absorption**

The NH₃ absorption spectrum within the CO₂ 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. NH₃ 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, Co Kα1 λ = 1.788 Å).

The optical emission spectra (OES) of laser irradiated NH₃ 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 cm). A welding torch with a nozzle diameter of 1.5 mm was used to introduce the NH₃ gas with a flowrate of 50 sccm. The CO₂ laser beam was directed perpendicularly to the
NH$_3$ flow. The laser incident power was tuned to keep power density at $1.4 \times 10^4$ W/cm$^2$ 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 NH$_3$ molecules on the GaN growth, the absorption spectra of the CO$_2$ laser (9.2 - 10.8 µm) by NH$_3$ at gas pressure of 10 Torr is investigated. Fig. 2 shows the absorption of CO$_2$ laser energy by NH$_3$ 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 NH$_3$ 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 ($\nu_2$) of the NH$_3$ molecules.

Among the six vibrational modes of the NH$_3$ molecules, the NH-wagging mode has a strong infrared activity within the CO$_2$ laser spectrum range. NH$_3$ 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 (\(\nu_2^+\)) and 968.32 cm$^{-1}$ (\(\nu_2^-\)) which are matched to CO$_2$ 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 CO$_2$ laser power at 9.219 µm. The perfect match of CO$_2$ laser energy at 9.219 µm (1084.71 cm$^{-1}$) to the centers of the NH$_3$ absorption lines at 1084.63 cm$^{-1}$ [5(\(J\) $\rightarrow$ 6(\(J'\)), K=0) in the $\nu_2^-$ 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 $\nu_2^-$ band and the Q- branch at 932.40 cm$^{-1}$ (J=K=2) in the $\nu_2^-$ band, respectively [17]. The mismatch as much as 0.5 cm$^{-1}$ between the laser line and the transition line of NH$_3$ 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 CO$_2$ lasers. The vibrational excitation of NH$_3$ molecules at these three resonant wavelengths contributes to dissociating of NH$_3$ molecules.

**Figure 2.** Absorption of CO$_2$ 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 wavelengths of commercial CO$_2$ lasers.
wavelength of 9.219 µm, respectively, indicating improved GaN crystalline quality under the on-resonant vibrational excitation of NH₃ 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.

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 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 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)Z̅ backscattering geometry, where, Z and Z̅ 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 E₂H and A₁(LO) phonon modes, respectively. These modes are the allowed vibrational states for the wurtzite GaN (0001) epitaxial layer [20].

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

Figure 6. X-ray diffraction spectra of GaN films deposited on Si with CO₂ 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 E₂H mode in Raman spectra of GaN reflects crystalline quality and stress. As observed in Fig. 5(a), the E₂H 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 E2H peak of the GaN samples was measured at on- and off resonant wavelengths. A narrow E2H 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 µm than that with 32 cm⁻¹ in off-resonant wavelength of 9.201 µm, 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 µm and off-resonant wavelength of 9.201 µm, 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 µm than in off-resonant sample of 9.201 µm 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 µm) and off-resonant wavelength (9.201 µm).

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]:

\[
D = \beta^2 / (2 \pi \ln 2) b^2
\]

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 NH₃ 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 NH₃ 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⁺, Hα, N, and Hβ species were observed at 309, 336, 463, 486, 496, and 656 nm, respectively. Strong emissions from NH₂ 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 NH₃ molecules are effectively dissociated under on-resonant vibrational excitation. Very strong emission intensities of OH, NH, NH₂, N, N⁺, and H were observed at the on-resonant wavelength of 9.219 µm. No emission peak was observed at the off-resonant wavelength of 9.201 µm.

N, NH, and NH₂ are active nitrogen species for growing GaN [22]. Growth of high-quality GaN films requires a sufficient supply of active nitrogen species by cracking NH₃ molecules and transporting atomic N to proper lattice sites. However, decomposition of NH₃ molecules requires a high temperature above 1000 °C, which also leads to the decomposition of GaN and N escaping. Therefore, decomposing NH₃ 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 ((CH$_3$)$_3$Ga) and NH$_3$ to form stable adduct ((CH$_3$)$_3$Ga:NH$_3$). The amide formation and decomposition reaction can be expressed by the following equations, respectively:

\[
(CH_3)_3Ga: NH_3 \rightarrow (CH_3)_2Ga: NH_2 + CH_4 \quad (2)
\]

\[
[(CH_3)_2Ga: NH_2]_3 \rightarrow 3GaN + 6CH_4 \quad (3)
\]

The OES results indicated that the resonant vibrational excitation effectively dissociates NH$_3$ molecules and increases the concentrations of the active nitrogen species of N, NH and NH$_2$. 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 NH$_3$, the oxygen impurity might be eliminated by the reaction between hydrogen and oxygen. The detection of OH emission at NH$_3$ 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 NH$_3$ molecules are studied using a tunable CO$_2$ 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 NH$_3$ 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, NH$_2$, N, N+, and H species, leading to eliminate the impurities and improving in crystalline quality and enhancing in deposition rate of GaN films.

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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.