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EFFECT OF LASER-ASSISTED RESONANT EXCITATION ON THE GROWTH OF GaN FILMS

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Abstract

Gallium nitride (GaN) films were grown using laser-assisted metal organic chemical vapor deposition (LMOCVD). The vibrational mode (1084.63 cm^{-1}) of ammonia (NH_3) molecules was resonantly excited using a wavelength-tunable CO_2 laser at a laser wavelength of 9.219 μm due to its high absorption cross-section. Through wavelength-matched resonant excitation of the NH_3 molecules, highly c-axis oriented GaN films were successfully deposited on sapphire (α-Al_2O_3) substrates at low temperatures (250 to 600 °C). The strong (0001) GaN peak in X-ray diffraction spectra confirmed the good crystalline quality of GaN films. Additionally, the resonant vibrational excitation of NH_3 in LMOCVD promoted the GaN growth rate considerably compared to that synthesized by MOCVD without resonant vibrational excitation of NH_3 molecules.

Introduction

The growth of high-quality crystalline GaN films requires growth techniques using high temperatures, such as metalorganic chemical vapor deposition (MOCVD, ~950-1100 °C), molecular beam epitaxy (MBE, ~800 °C), and hydride vapor phase epitaxy (HVPE, ~750 °C) [1-3]. However, high substrate temperatures can cause adverse effects, such as biaxial stress within GaN films, nitrogen loss, and GaN decomposition, which degrade the efficiency of GaN-based devices [4-5]. To reduce the thermal stress in GaN films, substrates with a matching lattice, including lithium aluminate ($LiAlO_2$), lithium gallate ($LiGaO_2$), and silicon carbide (4H-SiC), are preferred [6-8]. However, such lattice-matching substrates are too expensive to be commercialized. A high growth temperature will also lead to nitrogen reevaporation and GaN decomposition, which limits the growth rate of GaN films [9]. So far, the growth rates of GaN films synthesized by MOCVD and MBE were reported to be 4 and 1 μm/h, respectively [10-11]. Therefore, a low-temperature synthetic technique is highly desired to efficiently grow crystalline GaN films.

Attempts at promotion of material synthesis have been investigated by exploring infrared (IR)-laser-assisted vibrational excitations of precursor molecules, in which energy is directly coupled into specific molecules towards selective reaction pathways [12-13]. Highly efficient energy coupling through vibrational excitation provides reactant molecules with sufficient energy to surmount reaction barriers and influence reaction pathways [14-15]. In this study, low-temperature growth of highly c-oriented GaN films was achieved using laser-assisted metal organic chemical vapor deposition (LMOCVD). Resonant excitation of the NH-wagging mode (ν_2) in NH_3 molecules was realized using a wavelength-tunable carbon dioxide (CO_2) laser at a matching wavelength of 9.219 μm. GaN films were successfully deposited on sapphire at a substrate temperature as low as 250 °C. A GaN growth rate of up to 12 μm/h was achieved at 600 °C using the LMOCVD method, which is 4.6 times faster than that of conventional MOCVD (2.6 μm/h).

Experimental section

GaN films were grown on c-plane sapphire substrates at different temperatures (250-600 °C). The sapphire substrates, with a dimension of 10 × 10 mm^2, were ultrasonically cleaned with organic solvents, dried, and loaded into the LMOCVD chamber, sequentially. After the chamber was evacuated to a base pressure of 1×10^{-2} torr, Trimethylgallium (TMGa) and ammonia (NH_3) precursors were fed into the chamber for GaN growth. The gas flow rate of NH_3 was 1200 standard cubic centimeters per minute (sccm), and TMGa was carried into the reaction chamber using nitrogen as the carrying gas at a flow rate of 16 sccm. The growth pressure was maintained at 100 torr during the growth process. A wavelength-tunable CO_2 laser (PRC, wavelength range from 9.2 to 10.9 μm) was used to achieve resonant vibrational excitation of the NH_3 molecules. The laser was tuned at a wavelength of 9.219 μm with a power of 80 W to resonantly excite the rotational-vibrational transition of the NH-wagging mode (ν_2, 1084.63 cm^{-1}) of NH_3 molecules and couple the laser energy into the molecules. The laser beam, with a diameter of 9 mm,

was irradiated in parallel to the substrate surface inside the chamber through a zinc selenide (ZnSe) window. The distance between the laser beam and substrate surface was maintained at about 20 mm. The substrate temperature was maintained at a constant temperature of 250, 400, 500, and 600 °C, respectively. The deposition time was kept at 1 hr. To understand the effects of laser-induced energy coupling, GaN films were also synthesized by the conventional MOCVD technique under the same growth conditions (deposition temperature, deposition time, gas flow rate, and growth pressure) without laser irradiation.

After the growth process, the GaN films were characterized as follows. The crystallinity of the GaN films was examined using a powder X-ray diffractometer (Rigaku D/Max B diffractometer, Co $K_{\alpha 1}$ λ= 1.788 Å). Surface morphologies and dimensions of the GaN films were studied using a field emission scanning electron microscope (FESEM, S4700). An energy dispersive X-ray spectrometer (EDX, Oxford X-max 20 mm^2) was applied to analyze the composition of the GaN films.

Results and Discussion

Laser energy absorption

It is difficult to grow GaN films at temperatures lower than 500 °C using a conventional MOCVD method due to the low dissociation efficiency of NH_3 [16]. Therefore, to increase the reactivity of NH_3, is critical in low-temperature growth of GaN. Through resonant vibrational excitation of the NH-wagging mode in NH_3 molecules, the reactivity of NH_3 is enhanced; and the dissociation efficiency of NH_3 at low temperature is promoted.

The absorption spectra of the CO_2 laser power by NH_3 at gas pressure of 10 torr are shown in Figure 1. Three strong absorption peaks were observed at 9.219, 10.35, and 10.719 µm, respectively. The absorptions at these wavelengths were attributed to the resonant vibrational excitation of the NH-wagging mode (ν_2) of the NH_3 molecules [17-18]. NH_3 has a pyramidal shape with three hydrogen atoms forming the base and a nitrogen atom at the top. The NH-wagging mode vibrates in an umbrella inversion way. There is a barrier to umbrella inversion that the nitrogen atom faces on its travels through the hydrogen plane [17]. The existence of the barrier results in a splitting of a fundamental vibrational level of the NH-wagging mode into two components at 932.51 (ν_2+) and 968.32 cm^{-1} (ν_2-), giving rise to the observed absorption peaks at laser wavelengths of 10.719 (932.92 cm^{-1}) and 10.35 µm (966.18 cm^{-1}), respectively [17-18].

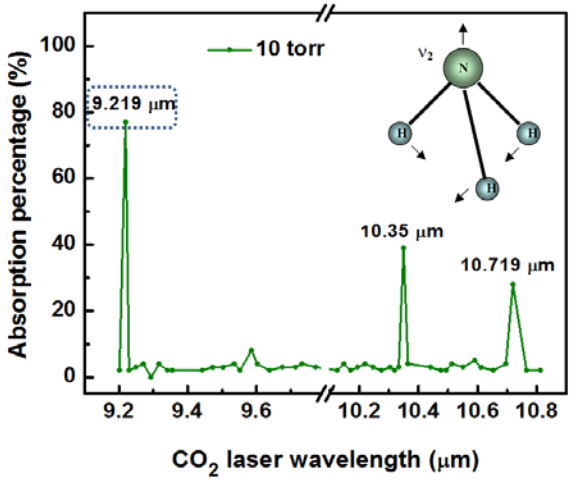

Fig. 1. Absorption of CO_2 laser energy by ammonia from 9.219 to 10.8 µm at pressure of 10 torr.

The strongest absorption peak at 9.219 µm is attributed to a rotational-vibrational transition (J=5 → J'=6, K=0) of the ν_2 mode at 1084.63 cm^{-1}. The perfect match between the CO_2 laser wavelength at 9.219 µm (1084.71 cm^{-1}) and the rotational-vibrational transition line of the NH_3 (1084.63 cm^{-1}) makes a stronger absorption at 9.219 µm than that at 10.35 and 10.719 µm. The rotational-vibrational excitation of NH_3 molecules at 9.219 µm contributes to dissociating of NH_3 molecules at low temperatures.

GaN Growth on sapphire

Figures 2(a) and 2(b) compare the X-ray diffraction (XRD) spectra of the GaN films grown on sapphire by LMOCVD and MOCVD, respectively. A XRD peak attributed to the (0002) plane of GaN is observed for the GaN samples grown by LMOCVD at temperatures 250, 400, 500 and 600 °C. This peak is indexed to wurtzite GaN with a hexagonal structure [19], indicating the high c-plane orientation of the GaN films. Therefore, it can be confirmed that the synthesis of GaN films was achieved at a temperature as low as ~250 °C by the LMOCVD technique with the laser resonant vibrational excitation of NH_3. In contrast, the (0002) diffraction peak was only found for the sample grown by MOCVD at a temperature of 600 °C, suggesting that a much higher substrate temperature is required for the growth of GaN using conventional MOCVD (Figure 2(b)). It was found that the intensity of the (0002) peak increases as the substrate temperature increases from 250 to 600 °C in LMOCVD. The intensity increase is attributed to the improved

crystalline quality of the GaN films due to the substrate temperature increase [20].

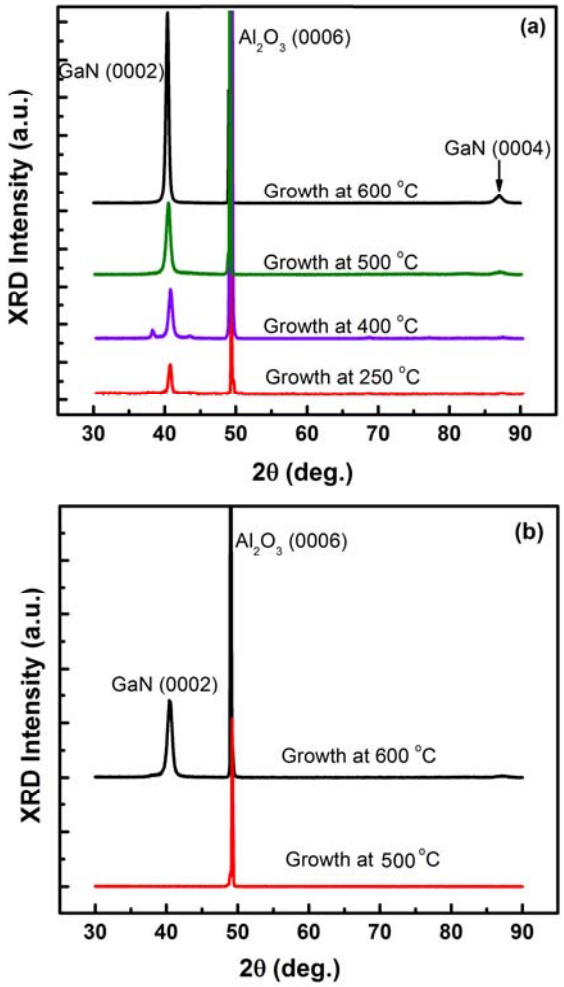

Fig. 2. X-ray diffraction spectra of the GaN films grown on sapphire by (a) LMOCVD (b) MOCVD.

Figure 3 compares the grain size of GaN films grown at different substrate temperatures.

For the GaN film grown with LMOCVD at 250 °C, small domains of about ~30 ± 5 nm with hexagonal facets were obtained. The average domain sizes were ~70 ± 10 and ~110 ± 10 nm for the GaN films grown by LMOCVD at 400 and 500 °C. With a further increase in the substrate temperature to 600 °C, the lateral size of the islands with hexagonal facets increased. With a coalescence of crystallite islands, GaN structures with flat facets were obtained by LMOCVD at 600 °C, as shown in Figure 4(a). In contrast, the surface of the GaN sample grown at 600 °C by MOCVD was rough with obvious hexagonal hillocks (Figure 4(b)). The effectiveness of laser resonant vibrational excitation of NH_3 on the uniformity and surface morphology of GaN films grown on sapphire is clearly shown in Figure 4.

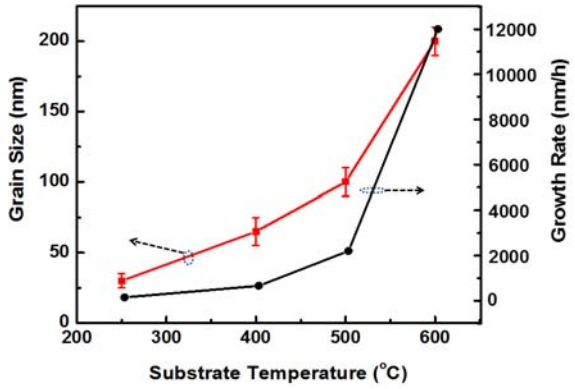

Fig. 3. The growth rate and grain size of GaN films grown on sapphire substrates at different temperatures by LMOCVD.

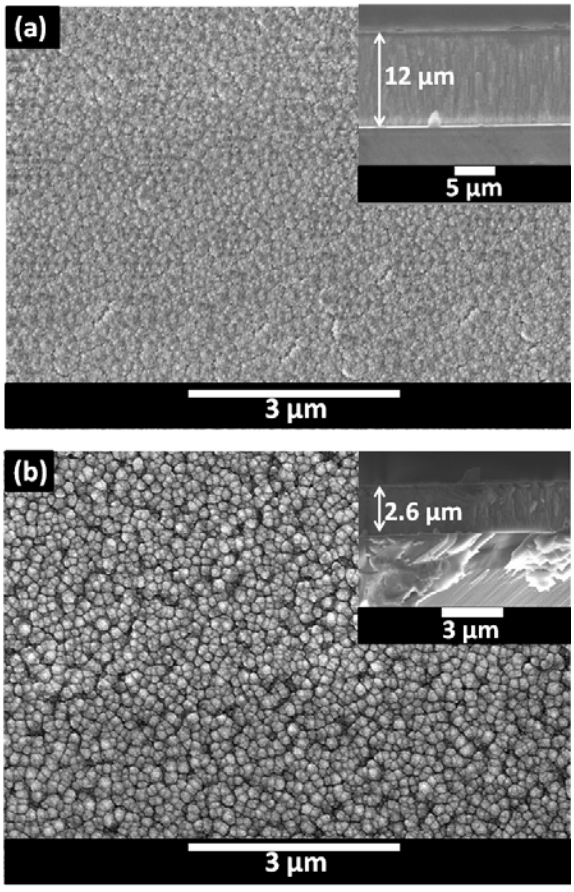

Fig. 4. SEM image of the GaN films grown on sapphire at 600 °C by (a) LMOCVD (b) MOCVD.

The cross-sectional SEM images of the GaN films were obtained to explore the effect of laser resonant vibrational excitation of NH_3 on the growth rate.
As shown in Figure 3, a growth rate of 12 μm/h was achieved by LMOCVD at 600 °C, which is ~4.6 times faster than that of MOCVD (this work, ~2.6 μm/h). Figure 4 also shows the GaN growth rates by LMOCVD at different temperatures from 250 to 600 °C. As the substrate temperature increased, the thickness of the GaN films increased.

The EDX results in Table 1 show the presence of Ga and N elements in the GaN films, as well as carbon (C), oxygen (O), and silicon (Si) as impurities. According to the EDX spectra obtained from GaN films grown at 600 °C by LMOCVD and MOCVD, obvious increases of 5.91% in N concentration and 1.99% in Ga concentration were observed in the sample grown with LMOCVD. The resonant vibrational excitation of the NH bond vibration in NH_3 molecules plays an important role in the dissociation of NH_3 and the increase of N species in the reaction.

Table 1 EDX characterizations of GaN films grown on sapphire at 600 °C by LMOCVD and MOCVD

Atomic %	LMOCVD	MOCVD
Ga	34.98	34.64
N	33.01	27.10
C	24.26	26.25
O	7.21	11.04
Si	0.54	0.97

The increase in N content in the deposited films explains why the GaN growth rate was highly improved using LMOCVD. Furthermore, it is worthy to note that that the impurity content (C, O, and Si) in the GaN film grown with LMOCVD decreased considerably (Table 1). In MOCVD growth, Ga reacts with impurity elements in the absence of sufficient active N atoms or N-related intermediates. However, laser resonant vibrational excitation of NH_3 in LMOCVD increased the production of active N-related intermediates, 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, a full coalescence, and a smooth surface morphology of GaN films.

GaN Growth on Si

To study that the laser-induced resonant excitation of NH_3 can effectively lead in the improvement of crystalline quality of GaN films, the experiment was conducted for growth of GaN on Si (001) substrates. Figure 5 shows SEM image of the GaN films grown on Si substrate at 600 °C by LMOCVD. Figure 6 compares the XRD patterns of GaN films deposited on Si substrates for 1 h by LMOCVD and MOCVD. The prominent peaks are observed at 40.5° and 40.53 for GaN films grown with LMOCVD and MOCVD, respectively, which are due to the (0002) crystal plane of GaN. The intensity of (0002) crystal orientation at GaN film grown with LMOCVD considerably increased compared with that of film grown with MOCVD as shown in Fig. 6. The FWHM of the (0002) reflection rocking curve of GaN film grown by LMOCVD and MOCVD were 0.22° and 0.25°, respectively, which confirmed an improvement in crystallinity of GaN film using LMOCVD. The FWHM of the (0002) plane reflects lattice distortion from screw dislocations and mixed dislocations. The relatively smaller FWHM for the GaN synthesized on Si by LMOCVD indicates that the dislocations present in the GaN layer decreased considerably.

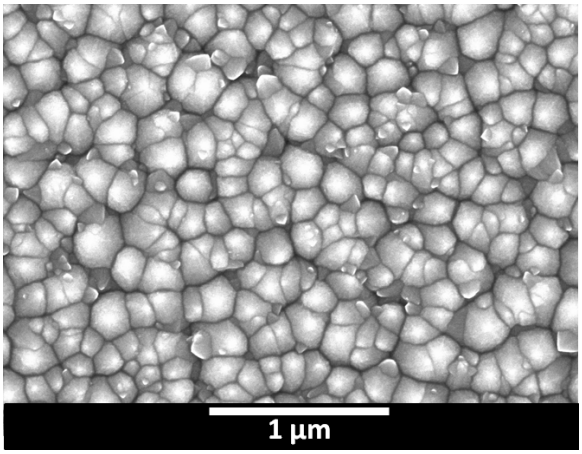

Fig. 5. SEM image of the GaN films grown on Si at 600 °C by LMOCVD.

Conclusion

In this study, an LMOCVD technique was developed for the growth of GaN films through resonant vibrational excitation of NH_3 molecules. The highly c-oriented GaN films were successfully grown on sapphire substrates at temperatures as low as 250 °C, which is ascribed to the enhanced decomposition efficiency of NH_3 via resonant excitation of

rotational-vibrational transition (1084.71 cm^{-1}) of the NH-wagging mode at the laser wavelength of 9.219 μm. SEM images showed that the laser resonant vibrational excitation of NH_3 contributed to the grow of GaN films with smooth and uniform surface morphology. A high GaN growth rate of up to 12 μm/h was achieved on sapphire at 600 °C by LMOCVD, which is ~4.6 times faster than that of conventional MOCVD with 2.6 μm/h.

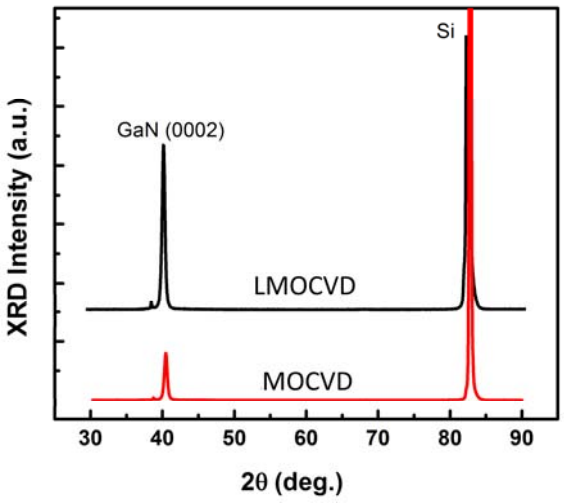

Fig. 6. X-ray diffraction spectra of the GaN films grown on Si at 600 °C by LMOCVD and MOCVD.

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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 in 2012. His current research involves growth of GaN films and nanostructures using laser-assisted metal organic chemical vapor deposition and fabrication of GaN-based electronic devices.