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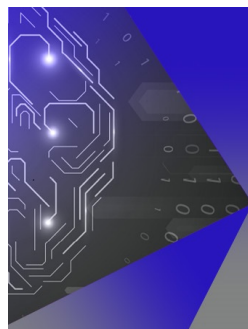
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Optimization of parameters for generating nitrogen plasma in plasma-assisted MOCVD growth of InGaN thin films

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ABSTRACT

The deposition of InGaN thin films by plasma-assisted metalorganic chemical vapor deposition is achieved using nitrogen plasma as a nitrogen source. The generation of nitrogen plasma is optimized using optical emission spectroscopy, and the plasma is dominated by excited molecular nitrogen, which emits in the range 300–420 nm. The emission intensity of the plasma significantly depends on the flow rate of nitrogen gas and heater temperature and are optimally 70 SCCM and 650 °C, respectively. A further increase in these parameters results in a decrease in the intensity of the nitrogen plasma emission. An optimal flow rate and heater temperature are used to grow InGaN thin films on c-sapphire substrates. InGaN thin films grown with a TMIn vapor concentration (x_v) of 0%, 50%, and 100% at a growth temperature of 650 °C are highly oriented to the (0002) plane in a hexagonal structure. The film grown with a vapor concentration of 50% has an indium concentration of 55% and no indication of phase separation. Increasing the growth temperature above 650 °C results in a decrease in the growth rate.

I. INTRODUCTION

The growth of GaN and its alloys by metalorganic chemical vapor deposition (MOCVD) is challenging because the molecular nitrogen used as a nitrogen source is inert at normal growth temperatures. Active nitrogen species are required to react with gallium, and to create them, two approaches are commonly employed: using ammonia as the nitrogen source because it dissociates freely at high temperatures and using nitrogen plasma, which, by definition, contains reactive nitrogen species.

Growth of InGaN thin films by MOCVD is also challenging if a high concentration of indium is required in ternary alloys. The high concentration of indium is difficult to achieve due to its high volatility at high growth temperatures.[1–4] Furthermore, the crystalline quality of the InGaN film is poorer compared with that of the GaN film. A large compositional in-homogeneity and phase separation are frequently present in the InGaN film due to a large

difference in either the lattice constants or the equilibrium vapor pressure of nitrogen between the binaries GaN and InN.[5,6] In addition, the large difference in the interatomic spacing between GaN and InN (~11%) can give rise to a solid-phase miscibility gap.[7]

The growth of high-quality InGaN films at high temperatures is problematic because the InN component becomes unstable. The In–N bond is weak compared with the Ga–N bond and is easily broken at high temperatures, leading to poor indium incorporation into the film.[8,9] To enhance indium incorporation, a high partial pressure of nitrogen is needed to suppress the dissociation of InGaN during epitaxial growth.[10] Alternatively, the growth temperature may be reduced, requiring the nitrogen source to be more active. To reduce the growth temperature and to activate the nitrogen source, plasma-assisted growth may be employed. To generate nitrogen plasma, a plasma generator using radio waves or microwaves may be employed. Both types of plasma generators produce reactive

nitrogen species, such as excited molecular, ionic, and atomic nitrogen species, together with free electrons.[11]

To determine the types of reactive species produced by nitrogen plasma, methods such as optical emission spectroscopy (OES), time-of-flight mass spectroscopy, laser-induced fluorescence spectroscopy, and the Langmuir probe method are employed.[12–15] Among species-detection methods, the OES method has several advantages: it is simple, has high resolution, and is highly capable of characterizing the reaction process inside the reactor without affecting the plasma.[12–16]

Understanding the mechanism involved in nitrogen plasma generation to optimize it for the growth of InGaN thin films is essential. To date, several investigations of nitrogen plasma using OES have focused on the identification of the active species produced by several plasma generator sources and on the growth of group III-nitrides using RF-plasma-assisted MBE growth. Since MBE growth requires high vacuum, the use of nitrogen to generate reactive nitrogen species most often involves low flow rates of nitrogen gas, typically around 1 SCCM–5 SCCM.[11,17]

It has been established that the species types of reactive nitrogen produced by nitrogen plasma depend significantly on pressure. In the case of MOCVD growth of group III-nitrides, to produce good quality films, growth most often uses a very high V/III ratio. Consequently, the flow rate of nitrogen here is much higher than that commonly used in RF-plasma-assisted MBE. The higher nitrogen flow rates lead to much higher pressure inside the MOCVD reactor. The characteristics of nitrogen plasma produced at high nitrogen flow rates are important for a better understanding of plasma-assisted MOCVD growth of group III-nitrides. In this paper, we report the optimization of parameters for generating nitrogen plasma by investigation of its optical emission. The nitrogen plasma is then used to grow InGaN thin films by plasma-assisted MOCVD. We investigate the growth characteristics of InGaN for various flow rates of nitrogen gas, growth temperatures, and indium compositions.

II. EXPERIMENTAL DETAILS

A. Optical emission spectroscopy (OES)

Nitrogen plasma was generated inside a plasma-assisted MOCVD reactor. The reactor is equipped with a downstream cavity type 2.45 GHz ECR plasma source with a maximum power of 250 W (ASTeX) and is connected to a vacuum system consisting of a rotary vane pump (Balzers, DUO 030A) and a root blower pump (Balzers, WKP 250A). The reactor is also equipped with a 2-in. resistive heater that is electronically controlled using a PID temperature controller and is used to heat the substrates and gases inside the reactor. A high purity (99.999%) of nitrogen gas was used to produce the nitrogen plasma. Emission spectra of the nitrogen plasma were analyzed using OES. Light from the plasma inside the reactor is focused on a UV fiber optic and transmitted directly to a monochromator with a low-resolution grating. The monochromator is equipped with a photomultiplier detector to improve the signal-to-noise ratio; lock-in detection was used as the data acquisition method. The spectral response of the monochromator/detector was calibrated using a halogen lamp. To optimize plasma generation parameters, the experiment was performed varying the nitrogen gas

flow rate and heater temperature. The flow rate was varied between 60 SCCM and 130 SCCM, while the heater temperature was varied between 500 °C and 700 °C.

B. Plasma-assisted MOCVD growth of InGaN

InGaN thin films were grown on (0001) sapphire substrates using optimized parameters for nitrogen-plasma generation as growth parameters. Trimethylgallium (TMGa) and trimethylindium (TMIn) were used as sources of gallium and indium, respectively, and synthesized reactive nitrogen species were used as a nitrogen source. Hydrogen gas was used as a carrier gas, purified by passing it through a heated palladium cell. Before the growth of the InGaN films, the (0001) sapphire substrates were cleaned chemically by rinsing with acetone and methanol in an ultrasonic bath. Substrates were subsequently washed with deionized water (DI-water) and then etched in a solution of DI-water:H_3PO_4:H_2SO_4 = 1:1:3 at 70 °C for 10 min. Finally, the substrates were placed under running deionized water and then dried using a nitrogen jet. The substrates were immediately loaded into the reactor and heated to 650 °C for thermal cleaning in ambient H_2. *In situ* hydrogen plasma cleaning of the substrates was carried out for 10 min using 200 W plasma power with a H_2 flow rate of 50 SCCM, followed by the deposition of a GaN buffer layer. This layer was grown with a TMGa flow rate of 0.12 SCCM and an N_2 flow rate of 90 SCCM at 500 °C, which produced a GaN buffer layer of about 25-nm thickness. After deposition of the buffer layer, the substrate temperature was raised to the required growth temperatures. The total flow rate of the group-III precursor was kept at 0.12 SCCM for all depositions, while the TMIn vapor composition was thus varied: 0%, 50%, and 100%.

The grown InGaN, GaN, and InN films were characterized by x-ray diffractometry (XRD) with monochromatic Cu Kα radiation (λ = 1.5406 Å) to identify the crystal phase and its orientation. A scanning electron microscope (SEM) was used to examine the films' cross sections to estimate the film thickness. An energy dispersive x-ray spectrometer (EDS) was used to identify the atomic composition of the thin films.

III. RESULTS AND DISCUSSION

A. OES measurement

The reactive nitrogen species that may exist in nitrogen plasma are excited neutral molecular nitrogen, atomic nitrogen, and ionized nitrogen, and the species type is determined using optical emission spectra. Emission from nitrogen plasma appears whitish-violet to the eye. Figure 1 shows typical emission spectra of nitrogen plasma generated by using the ECR plasma source of 200 W at 650 °C with a nitrogen flow rate of 70 SCCM. The spectra are characterized by four emission peaks in the range of 300 nm–420 nm that correspond to the excited states of neutral N_2^* molecules in the second positive system with the $C^3\Pi_u \rightarrow B^3\Pi_g$ energy level transition.[18] Figure 1 also shows a lack of peaks in the band of ionic nitrogen and atomic nitrogen, which usually emit at 390–430 nm and 540–820 nm, respectively.

The observed spectra are different from the spectra typically found by other researchers. The spectra of nitrogen plasma generated by an ECR microwave plasma source usually include a mix
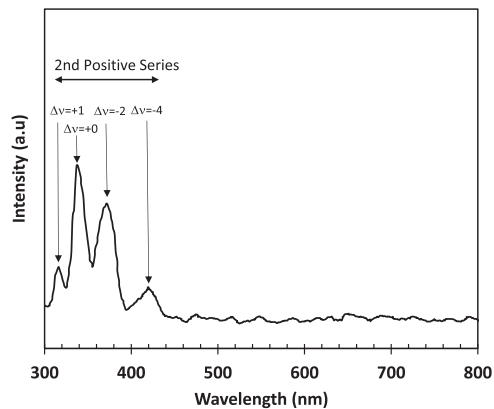
FIG. 1. Typical spectra of optical emission of nitrogen plasma generated by the ECR plasma source with a power of 200 W and a heater temperature of 650 °C. The spectra are dominated by excited states of neutral N_2^* molecules in the second positive system with the $C^3\Pi_u \rightarrow B^3\Pi_g$ energy level transition. Note that Δv is the vibrational quantum number difference between two excited levels, $C^3\Pi_u$ and $B^3\Pi_g$.

FIG. 2. Dependence of the emission intensity of nitrogen plasma for the 337-nm peak on the flow rate of nitrogen gas at a substrate temperature of 650 °C. Lines between points are only included as guides to the eye. Intensity reaches its maximum at a nitrogen flow rate of 70 SCCM.

of excited states of nitrogen molecules, ionic nitrogen, and atomic nitrogen. We believe that the absence of ionic nitrogen and atomic nitrogen bands in the observed spectra is related to the relatively high pressure inside the MOCVD reactor. Pressure affects the type of species of generated nitrogen plasma, as reported by Boivin *et al.*[19] They showed that the line intensity of atomic and ionic nitrogen emission is greatly reduced for pressures higher than 10 mTorr. This pressure is far below the working pressures of the MOCVD reactor used in this study, which are in the range 400–700 mTorr for nitrogen flow rates of 60–120 SCCM.

During the growth process, a reaction between gallium and/or indium precursors with reactive nitrogen species occurs if the reactive nitrogen species have the requisite energy for the growth of InGaN. The excited neutral molecular nitrogen ($A^3\Sigma_u^+$, $B^3\Pi_g$, $a^1\Pi_g$, and $C^3\Pi_u$), ionized molecular nitrogen ($^2\Sigma_g^+$), and atomic nitrogen (^4S, ^2P, and ^2D) have energies that are sufficient to form group III-nitrides.[20] To grow high quality group III-nitrides and their alloys using plasma-assisted MOCVD, the creation of N_2^+ ions is avoided because they are highly energetic and are likely to damage the surface of films. Therefore, in terms of the energy of reactive nitrogen species, the growth of thin group III-nitride films using plasma nitrogen that is dominated by excited neutral molecular nitrogen (N_2^*) is favorable.

The emission characteristics are further studied by plotting the intensity of the dominant emission peak at 337 nm, which is the fundamental transition band of the second positive series between the excited levels $C^3\Pi_u$ and $B^3\Pi_g$ of the neutral nitrogen molecule, as a function of the nitrogen flow rate at a heater temperature of 650 °C. As shown in Fig. 2, the peak intensity increases as the nitrogen gas flow rate is increased from 60 SCCM to 70 SCCM. This indicates that the increase in the nitrogen gas flow rate creates the additional nitrogen source for the generation of nitrogen plasma, resulting in the population increase of generated reactive nitrogen species. If the flow rate is further increased to 120 SCCM, the emission intensity of the nitrogen plasma decreases. The increase in the flow rate
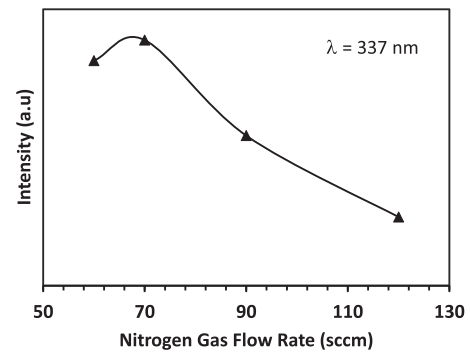
increases the pressure inside the reactor, which leads to a decrease in the energy per N_2 molecule required to excite nitrogen molecules. As a result, the excitation efficiency of N_2 molecules in the plasma decreases, resulting in a decrease in the emission intensity. A similar characteristic of pressure dependence of the emission intensity—where the emission intensity maximizes at a specific pressure—was also observed.[21] The optimum flow rate that produces the maximum emission intensity is 70 SCCM. Under these conditions, the more reactive the species are in the plasma, the more likely it is that bonding occurs between gallium/indium and nitrogen during nitride-based material deposition.

The dependence of emission intensity on the heating temperature was studied by varying the heater temperature, while the flow rate of nitrogen gas was kept at 70 SCCM. The emission spectra are similar to those in Fig. 1 (not shown), characterized by four peaks in the range 300–420 nm, with a dominant peak at 337 nm. The effects of temperature on the intensity of the nitrogen plasma emission peak at 337 nm at various flow rates are shown in Fig. 3. At a constant flow rate of nitrogen gas, as the temperature increases from 500 °C to 650 °C, the intensity of nitrogen plasma emission increases. The increase in temperature gives additional energy to the plasma so that more excitation takes place. The additional thermal energy from the heater increases the energy of the neutral molecules in the ground state so that the energy is high enough for excitation. This means that the population of excited neutral molecules increases, leading to the increase in the optical emission intensity.

If the temperature is further increased to 700 °C, the additional thermal energy from the heater causes an increase in electron energy, resulting in more electron collisions. To estimate the relative population of reactive nitrogen species, the electron impact cross section can be used as an approximation.[19] In nitrogen plasma, the electron impact cross section increases with electron energy until it reaches a maximum at an electron energy of around 12 eV, after which it decreases. We believe that the decrease in the emission intensity at heater temperatures higher than 650 °C is associated with a decrease in the electron impact cross section. From this result, the optimum heater temperature, i.e., that which produces the highest emission intensity is 650 °C.
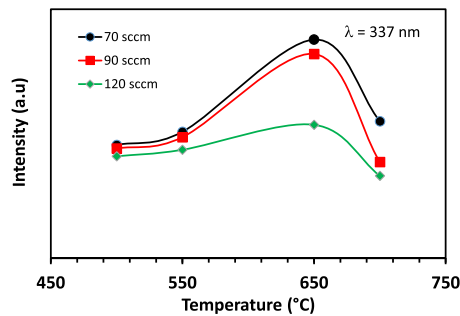
FIG. 3. Dependence of emission intensity of nitrogen plasma for the 337-nm peak on the heater temperature at various nitrogen gas flow rates. Lines between points are solely guides to the eye. The intensities for all nitrogen gas flow rates reach their maximum at a temperature of 650 °C.
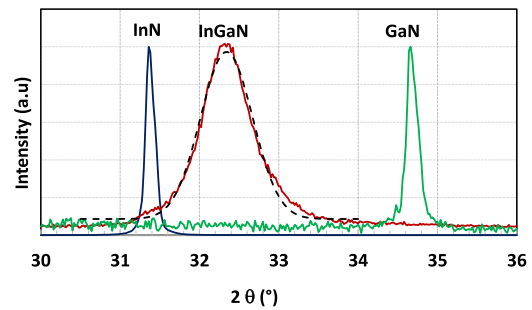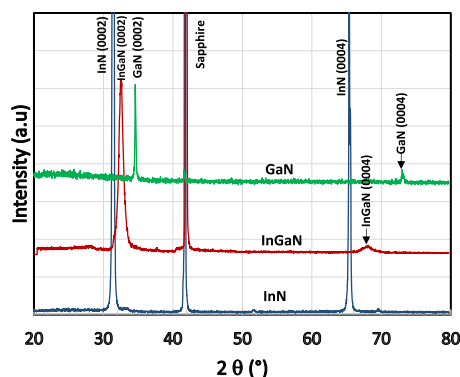

FIG. 5. XRD spectra of InN, InGaN, and GaN thin films on the sapphire substrate with normalized intensity. The diffraction peak of InGaN is shifted to the lower angle, indicating indium incorporation into the GaN–InN system. The dashed line is the Gaussian curve fitting to the InGaN diffraction peak that is matched to the original curve, indicating no phase separation in the InGaN films.

B. Growth of InGaN

Figure 4 shows the XRD spectra of the InGaN thin films grown using the optimized growth temperature of 650 °C. The deposition was carried out for a TMIn vapor composition (x_v) of 0% (GaN), 50% (InGaN), and 100% (InN). The spectra show that all films are highly oriented in the (0002) plane with a hexagonal structure. The diffraction angles, 2θ, of the (0002) peak intensities are 34.7°, 32.4°, and 31.4° corresponding to GaN, InGaN, and InN, respectively. The other diffraction peaks are attributed to the (0004) planes of GaN, InGaN, and InN.
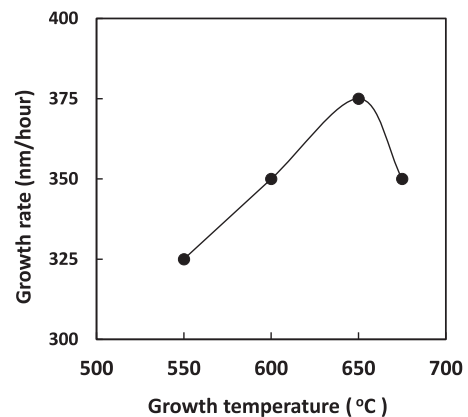
In the case of InGaN with an indium vapor composition of 50%, no additional diffraction peaks, except those originating from the (0002) plane, are observed. This implies that the grown film has no crystallographic phase separation. The diffraction-intensity distribution of the (0002) plane is matched with a Gaussian distribution fitted to the curve, as shown in Fig. 5; however, the FWHM of the diffraction-intensity distribution of InGaN is slightly wider compared with that of GaN or InN. The broadening of the InGaN diffraction peak is attributed to the finite crystalline domain size effect.[17]

The normalized diffraction intensities of the (0002) peaks for GaN, InGaN, and InN are shown in Fig. 5. The diffraction peak of InGaN is shifted toward the lower diffraction angle relative to that of GaN by incorporating indium into the GaN matrix. The concentration of indium in the InGaN films is determined by calculating the relative shift of the InGaN (0002) diffraction peak with respect to the GaN (0002) peak and applying Vegard's law, revealing an indium concentration of about 55%. This result is close to the result obtained from the EDS measurement, which is 54%.

Figure 6 shows the temperature dependence of the growth rate of InGaN in the range 500–700 °C for an indium vapor composition of 50%. At temperatures of up to 650 °C, alkyl decomposition and excited N_2^* neutral molecules species control the growth rate. As the growth temperature increases, the growth rate also monotonically increases. However, a further increase in temperature results in a decrease in the growth rate due to a decrease in the availability of excited N_2^* neutral molecules, as reflected in the decrease in the emission intensity. Moreover, in this temperature region, the desorption of gallium and indium from the growth surface starts to dominate the process, leading to a decrease in the growth rate.[22,23]

FIG. 4. XRD spectra of InN, InGaN, and GaN thin films on the sapphire substrate grown at a temperature of 650 °C and a nitrogen flow rate of 70 SCCM. InN was grown using the same growth parameters as those of InGaN, but with a TMIn vapor concentration of 100%, while GaN was grown using a TMIn vapor concentration of 0%.

FIG. 6. Growth rate of InGaN as a function of the substrate temperature at a nitrogen gas flow rate of 70 SCCM.

IV. CONCLUSION

An ECR plasma source has been successfully employed to produce reactive nitrogen species that react with TMGa and/or TMIn at substantially low substrate temperatures during the growth of InGaN by plasma-assisted MOCVD. OES revealed that reactive nitrogen inside the plasma is dominated by excited N_2^* neutral molecules. The excited N_2^* neutral molecules are vaporable for the growth of group III-nitrides and their alloys since they are not high energetic species that are possible to grow films at reduced damage. The emission intensity of the plasma relates to the population of generated reactive nitrogen species and depends significantly on the substrate temperature and flow rate of the nitrogen gas. The optimum temperature and flow rate that produce the maximum population of reactive nitrogen species are $650\,^\circ$C and 70 SCCM, respectively. The GaN, InGaN, and InN thin films grown on sapphire substrates at $650\,^\circ$C and 70 SCCM show a highly oriented, hexagonal crystal structure in the (0002) plane. The InGaN film grown using a TMIn vapor concentration of 50% has an indium atomic composition of 54%, and this value is in good agreement with the estimated indium concentration calculated using Vegard's law. The temperature dependence of the growth rate of InGaN films is indicated by the temperature dependence of emission intensity such that the optimum growth rate occurs at $650\,^\circ$C.

ACKNOWLEDGMENTS

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