Growth of single crystalline GaN thin films on Si(111) substrates by high vacuum metalorganic chemical vapor deposition using a single molecular precursor

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Hexagonal GaN thin films were grown on Si(111) substrates using single molecular precursor by high vacuum metalorganic chemical vapor deposition at various temperatures from 600 to 800 °C and pressures in the range of 2×10^{-6} to 2×10^{-5} Torr. We first developed and synthesized the single molecular precursor of diethylazidogallium methylhydrazine adduct, $[(Et)_2Ga(N_3)HzMe]$, with the objectives of reducing carbon content in the GaN films and lowering growth temperatures. Results of x-ray diffraction (XRD), x-ray pole figure, and x-ray photoelectron spectroscopy measurements showed that this approach yielded a single crystalline GaN thin film of [0002] orientation with relatively low carbon content. Ga-rich compositions Ga:N of 1:0.92 were obtained at a temperature of 750 °C and a pressure of 2×10^{-6} Torr. However, for growth temperatures below 700 °C, we found the films to be polycrystalline. Scanning electron microscope (SEM) and atomic force microscope (AFM) images showed that the as-grown GaN films have a smooth surface morphology. Based on XRD, AFM, and SEM results, we identified effects of deposition temperature and pressure on the growth rate and crystallinity, and can suggest that our deposition process is governed by diffusion rate control. Optical properties were investigated by photoluminescence, which revealed an emission peak at 3.40 eV with a full width at half-maximum of approximately 100 meV for a GaN film grown at 750 °C and 2×10^{-6} Torr. © *2004 American Vacuum Society.*
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I. INTRODUCTION

GaN is potentially a very important material, because its wide bandgap (3.39 eV at room temperature) allows application for blue, violet, and ultraviolet light-emitting devices.[1–3] For the fabrication of these optical devices, high quality GaN thin film is required.[4] However, a number of drawbacks, including a lack of a lattice-matched substrate and high growth temperature, are still present.

Sapphire(0001) is the most widely used substrate for GaN epitaxial growth.[5,6] However, it is difficult to grow high quality GaN thin films with flat surfaces because of the large lattice mismatch and large difference in thermal expansion between GaN and sapphire.[1,7] Therefore, it is necessary to find a suitable substrate to replace sapphire. In spite of the even larger differences in lattice constant and thermal expansion coefficient between GaN and Si,[8] Si is thought to be one of the most promising candidates because of its high quality, availability in large sizes, and low cost.

The deposition of GaN films by conventional metalorganic chemical vapor deposition (MOCVD) has been carried out using different Ga and N sources, trimethylgallium or triethylgallium and ammonia.[9–11] The high thermal stability of ammonia is a major limitation,[12] since it requires the use of very high growth temperatures, in excess of 1000 °C, and high concentrations of ammonia.[4,13,14] We have developed and synthesized the single molecular precursor of diethylazidogallium methylhydrazine adduct, $(Et)_2Ga(N_3)HzMe$, to solve the problems associated with conventional MOCVD. We used this single molecular precursor with its pre-existing bond between Ga and N to lower the growth temperature as well as to reduce carbon content in the GaN films, obtaining a fairly good composition ratio between Ga and N.[15]

In this article, we report on the growth of single crystalline GaN thin films using this single molecular precursor on Si(111) substrates, and investigate the effect of growth temperature and deposition pressure on surface smoothness and crystallinity. We also report the relationship between growth rate and growth temperature.

II. EXPERIMENT

Single crystalline GaN thin films with hexagonal structure were grown using a single molecular precursor, $Et_2Ga(N_3)HzMe$, by MOCVD. Si(111) was used as a substrate because of the similarity of atomic arrangement to the GaN(0001). In order to form a H-terminated surface, the substrate was prepared by wet chemical processes [i.e., degreased in deionized (D.I.) water and acetone], boiled in a solution of $H_2SO_4:H_2O_2=1:1$, etched in 10% HF and rinsed in D.I. water. The cleaned substrate with H-terminated surface was then loaded into a reaction chamber. The single

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molecular precursor applied in this study was synthesized by following schemes. All solvents used were dried and freed completely, and Et_3Ga was then added to a suspension of $H_2NNHCH_3 \cdot HCl$ in THF. After the mixture was stirred for 6 h, the THF was removed under reduced pressure, resulting in obtaining the $Et_2GaClHzMe$ intermediate.

$$Et_3Ga + H_2NNHCH_3 \cdot HCl \xrightarrow{\text{THF or } Et_2O} Et_2Ga(Cl)HzMe \cdot + EtH\uparrow.$$

$Et_2Ga(N_3)HzMe$ was synthesized by the reaction of $Et_2Ga(Cl)HzMe$ with excess NaN_3. The reaction mixture was refluxed for 12 h, and then filtered out. Finally, $Et_2Ga(N_3)HzME$ was obtained by the removal of solvent from reaction mixture.

$$Et_2Ga(Cl)HzMe + NaN_3 \xrightarrow[\Delta]{\text{THF/Toluene}} Et_2Ga(N_3)HzMe + NaCl\downarrow.$$

GaN thin films were grown in a high vacuum chamber using the synthesized single molecular precursor without carrier gas. Prior to the growth, the substrate was mild annealed at 550 °C for more than 5 h to reduce outgassing from the substrate during deposition. The substrate was then thermally treated to remove the H-layer and to obtain a clean surface at 850 °C for 20 min in the deposition chamber. The temperature of the substrate was measured by an optical pyrometer.

After the pretreatment, deposition of GaN thin film was carried out under the experimental condition as follows. The sample was heated to growth temperatures in the range of 600–800 °C, and precursor was maintained in the range of 60–70 °C during deposition. In addition, film deposition lasted for 5 h under the growth pressure of 2×10^{-6}–2×10^{-5} Torr. Neither buffer layer nor carrier gas was used before film deposition.

The as-grown GaN thin films were characterized by several analysis techniques. The film crystallinity and composition ratio between Ga and N were first determined by x-ray diffraction (XRD), x-ray pole figure, and x-ray photoelectron spectroscopy (XPS) analysis. Film surface morphology was then investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Moreover, photoluminescence (PL) measurement was also performed to study the optical property.

III. RESULTS AND DISCUSSION

We first investigated the effect of the growth temperature on crystallinity of the as-grown films. XRD patterns are shown in Fig. 1 for the GaN films deposited on Si(111) substrates in the range of 600–800 °C and the same deposition pressure of 2×10^{-6} Torr. These results suggest the general consideration that the crystallinity of the grown films is improved as the growth temperature increased. That is, the GaN films deposited at 600–700 °C were polycrystalline, with GaN$(10\bar{1}0)$ and GaN$(10\bar{1}1)$ planes at 2θ=32.4° and 36.5°, as well as a GaN(0002) plane at 2θ=34.4° [see Figs. 1(a) and 1(b)]. Moreover, as the growth temperature decreased,

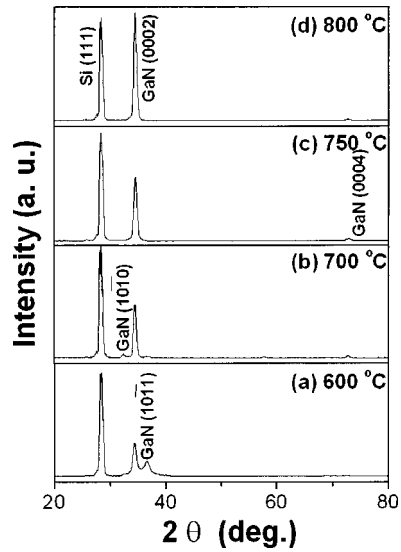

FIG. 1. XRD patterns for the GaN films grown on Si(111) at 2.0×10^{-6} Torr and various growth temperatures.

the intensity of the peak for the GaN(0002) plane weakened and broadened. For example, a weak and broad peak attributed to GaN(0002) plane appeared at 600 °C. At 700 °C, however, the intensity of GaN(0002) peak was increased even though other peaks attributed to GaN$(10\bar{1}0)$ and GaN$(10\bar{1}1)$ planes still remained constant. On the contrary, XRD patterns obtained from the GaN films deposited at 750–800 °C showed highly preferred orientation of GaN(0002) plane without the other plane of GaN$(10\bar{1}0)$ and GaN$(10\bar{1}1)$. In addition, the intensity of the GaN(0002) peak was increased as compared with the intensity of the film grown at 600–700 °C. In more detail, the intensity of the film grown at 800 °C was larger than that of the film grown at 750 °C. As we discuss again later, however, the crystallinity of the film grown at 750 °C was better than that of the film grown at 800 °C according to the x-ray pole figure analysis. That is, the pole figure of the film grown at 750 °C [Fig. 3(a)] showed a clear pattern with hexagonal structure compared with the pole figure of the film grown at 800 °C (not shown). Therefore, these results confirmed that high quality GaN film was obtained under the deposition condition of the growth temperature of 750 °C rather than that grown at 800 °C.

To check the effect of the deposition pressure on the crystallinity of the as-grown GaN films, we performed the GaN thin film growth under the various deposition pressures at fixed growth temperature, and then examined the XRD analysis. Figure 2 shows the XRD patterns for the GaN thin films grown at 750 °C and various deposition pressures in the range of 2×10^{-5}–2×10^{-6} Torr. The XRD patterns of the films that grew at 2×10^{-5} Torr [Fig. 2(a)] and 9×10^{-6} Torr [Fig. 2(b)] showed that two additional weak peaks corresponding to GaN$(10\bar{1}0)$ and GaN$(10\bar{1}1)$ was observed beside a strong GaN(0002) peak. These results indicate that thick polycrystalline GaN thin films could be grown at higher deposition pressure. In the case of a higher deposition pressure of 2×10^{-5} Torr [Fig. 2(a)] and 9×10^{-6} Torr

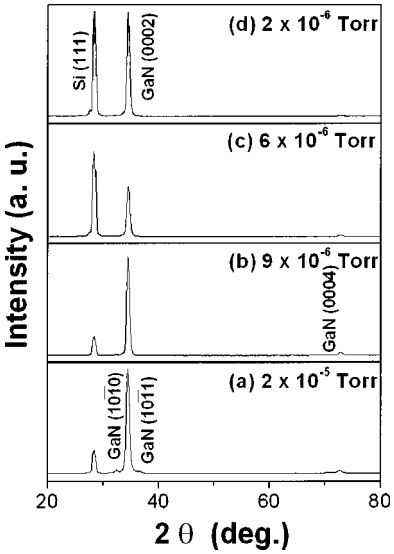

FIG. 2. XRD patterns for the GaN films grown on Si(111) at 750 °C and various deposition pressures.

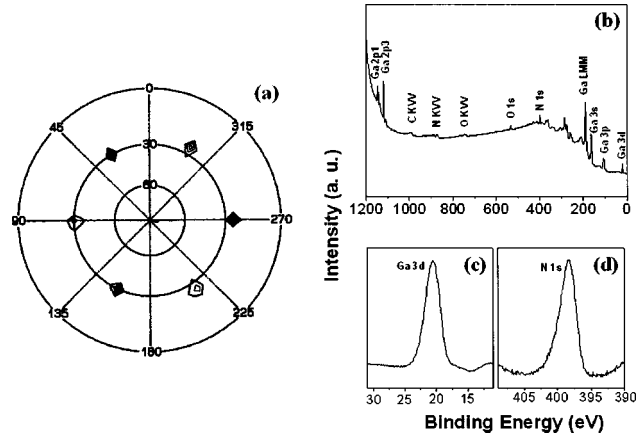

FIG. 3. (a) X-ray pole figure for the GaN film grown at 750 °C and 2×10^{-6} Torr. The XP survey spectrum (b) and high-resolution spectra (c) of Ga 3*d* and N 1*s* obtained from the same GaN film as in (a).

[Fig. 2(b)], we thus obtained GaN thin films with thicknesses of 1000 and 500 nm, respectively, suggesting that the growth rate was proportioned to the deposition pressure. As the deposition pressure was decreased below 6×10^{-6} Torr, however, the crystallinity of the as-grown films was improved. Figures 2(c) and 2(d) show a hint of single crystalline GaN formation. At 6×10^{-6} Torr [Fig. 2(c)], the XRD pattern shows only the GaN(0002) peak and GaN(0004) peak without the other peak, suggesting a high quality film. Moreover, as the deposition pressure was decreased to 2×10^{-6} Torr [Fig. 2(d)], the GaN(0002) peak was more sharpened and the thickness of the film decreased to be about 250 nm. This indicates that the crystallinity can be increased when we take the GaN deposition at very lower pressure. As shown in Figs. 1 and 2, therefore, we obtained GaN films having a high quality and highly [0002] preferred orientation in the lower pressure below 6×10^{-6} Torr and in the higher temperature over 750 °C. Moreover, the temperature as high as 750 °C and the deposition pressure as low as 2×10^{-6} Torr in our experiments were considered as the best conditions of our high vacuum CVD process.

From the results of the XRD θ–2θ scan only, however, we do not explain clearly whether the film is grown epitaxially or not. X-ray pole figure analysis was also performed in order to verify that GaN film was grown epitaxially on Si(111) substrate. X-ray pole figure was measured with 5° intervals of scan step in θ and ϕ angles. The range of θ angle is changed from 0° to 360° and that of ϕ angle is varied from 20° to 90°. Figure 3(a) shows the x-ray pole figure for the GaN thin film deposited at 750 °C and 2×10^{-6} Torr. It reveals that six poles are shown symmetrically with 60° intervals circularly, which indicates that the GaN film with hexagonal structure was epitaxially grown on Si(111) surface.

XPS analysis was also performed to show whether the GaN films have stoichiometric composition or not. In this study, the GaN films with a Ga-rich composition ratio (1:0.92) between Ga and N as well as relatively lower carbon contents than a GaN film grown with other single molecular precursor[16] could be successfully obtained using the single molecular precursor, $Et_2Ga(N_3)HzMe$. Figure 3(b) shows the x-ray photoelectron survey spectrum of a GaN film deposited under the deposition condition at 750 °C and 2×10^{-6} Torr. The survey spectrum displays both the photoelectron and the Auger electron peaks for gallium and nitrogen. If we use the Mg K_α beam with the binding energy of 1253.6 eV as x-ray source, x-ray photoelectron and Auger electron peaks for carbon were not shown because the peaks of C 1*s* overlapped with Ga *LMM* Auger electron peaks. In order to obtain the accurate composition ratio and to avoid the overlapping of between C 1*s* and Ga *LMM* Auger electron peaks, we also used the Al K_α ray with binding energy of 1486.6 eV. Figures 3(c) and 3(d) show the high-resolution x-ray photoelectron spectra of Ga 3*d* and N 1*s*, respectively. According to the areal intensities of Figs. 3(c) and 3(d) with accounting their atomic sensitivity factors, we could estimate the ratio of Ga 3*d*:N 1*s* peaks to be about 1:0.92. We could also examine the carbon contents of the deposited film by XPS analysis more precisely. The surface of the GaN film was etched by Ar^+ ion sputtering for 20 min and then followed by examination of XPS (not shown). The C 1*s* peak intensity was rapidly decreased and the percentage of carbon content was about 2.5%. This indicates that the carbon exist mostly in the surface region of the film. Thus, the carbon incorporation into the film from the precursor itself does not seem to occur during the chemical vapor deposition process. From the above results, therefore, we can conclude that the deposited GaN film has a Ga-rich composition (Ga:N =1:0.92) with relatively low carbon contents (2.5%) compared with other single molecular precursors.[16]

Figure 4 shows the variation of the surface morphologies of the as-grown GaN films that examined by field emission SEM. A morphology for the GaN film grown at 600 °C and 8×10^{-6} Torr for 5 h is shown in Fig. 4(a). The film has a rough and poor morphology, and the image of the film revealed that the film was grown on the Si(111) substrate three-

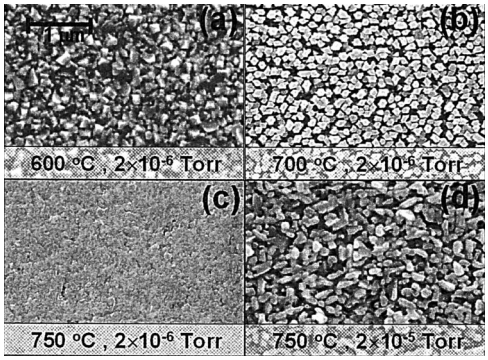

FIG. 4. Surface morphologies of the GaN films grown at (a) 600 °C and 2×10^{-6} Torr, (b) 700 °C and 2×10^{-6} Torr, (c) 750 °C and 2×10^{-6} Torr, and (d) 750 °C and 2×10^{-5} Torr.

dimensionally. Figure 4(b) shows the surface morphology of the GaN film obtained at 700 °C and 2×10^{-6} Torr for 5 h. In contrast to Fig. 4(a), many hexagonal-like small pyramid crystals are observed in this film [Fig. 4(b)]. Figures 4(c) and 4(d) show the surface morphologies of the films grown at 750 °C and in the deposition pressures of 2×10^{-6} Torr and 2×10^{-5} Torr, respectively. As shown in Fig. 4(c), a GaN film with smoother surface than that of Fig. 4(b) was obtained. This suggests that as the growth temperature was increased to 750 °C, it is considered that GaN was in part grown two-dimensionally due to a diffusion controlled process. However, the surface morphology of the film grown at 2×10^{-5} Torr [Fig. 4(d)] shows a rougher surface than that of a film deposited at 2×10^{-6} Torr. These results indicated that the surface morphology was highly affected by both growth temperature and deposition pressure. Therefore, when the growth temperature was increased to be 750 °C and growth pressure was decreased to 2×10^{-6} Torr, the best GaN film with the most smoothest surface morphology can possibly be grown two-dimensionally. For the more exact determination of the surface roughness, AFM characterization (not shown) was also performed on a 5×5 μm^2 area of the film grown at 750 °C. Measured surface roughness of the film was about 200 Å and rms roughness was 67.7 Å.

We examined the relationship between growth rate and deposition pressure. Figure 5(a) showed a variation of growth rate as a function of deposition pressure. In the range between 2×10^{-6} and 2×10^{-5} Torr, the growth rate of the film increased gradually with increasing deposition pressure. This suggests that the amount of flux from the precursor is one of the main factors to influence the growth rate. In this study, an effect of growth temperature on growth rate was also studied. Figure 5(b) showed the changes of growth rate as a function of growth temperature. As the growth temperature was increased from 600 to 800 °C, the growth rate of the film decreased proportionally. Thus, we concluded that the growth rate will increase with decreasing growth temperature, and with increasing deposition pressure. To identify the film growth mechanism, moreover, we investigated the dependency of the film growth rate on the growth temperature. Figure 5(c) showed the Arrhenius plot obtained from Fig.

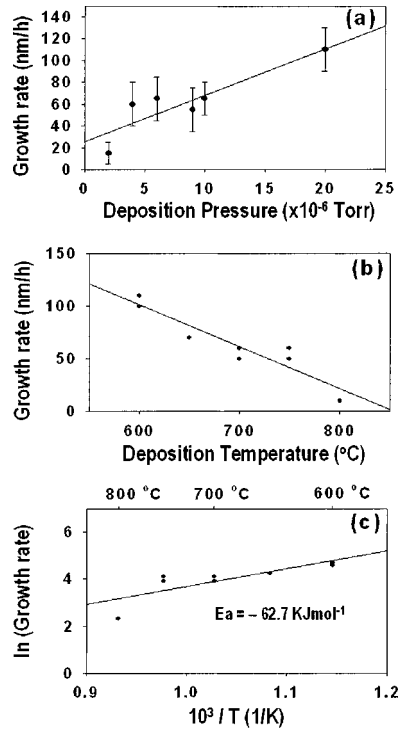

FIG. 5. Growth rates as a function of (a) deposition pressure and (b) growth temperature. (c) An Arrhenius type plot obtained from (b).

5(b). The positive slope in Fig. 5(c) in the region between 600 and 750 °C suggests that the growth rate is controlled by a mass transport of reagents through the boundary layer to the growth surface. This is termed the region of diffusion controlled growth and is a principal feature of the MOCVD process chemistry, in which flux of reactants to the surface is proportional to the concentration of the limiting precursor. At temperatures above 750 °C, however, the growth rate tends to decrease because of an increased desorption rate of film precursors or matrix elements, together with depletion of reactants on the reactor walls, probably due to parasitic side reactions. Using the Arrhenius equation, the activation energy was calculated from the slope of the plot of Fig. 5(c). The obtained activation energy was about -62.7 KJ/mol, indicating that the deposition was mainly processed by a surface diffusion, and that some desorption and/or preadsorption also occurred during the deposition of the GaN thin film.

Finally, in order to investigate the optical property of the film, a PL experiment was carried out at room temperature. Figure 6 shows the PL spectrum of a GaN film grown at 750 °C and 2×10^{-6} Torr. As shown in Fig. 6, a PL spectrum of as-grown GaN film revealed a near-band-edge emission peak at 3.40 eV, which indicated that the film can emit the blue light. The full width at half-maximum (FWHM) of the dominant GaN emission peak was measured to be approximately 100 meV at room temperature.

IV. CONCLUSIONS

Hexagonal GaN thin films with single crystalline nature were grown on Si(111) substrates by high vacuum MOCVD

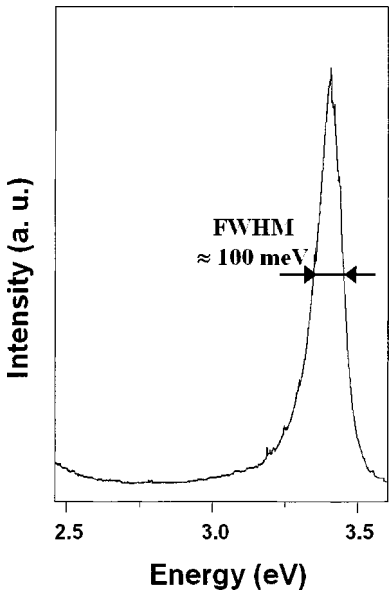

FIG. 6. PL spectrum of the GaN film grown at 750 °C and 2×10^{-6} Torr.

using a single molecular precursor. XRD and x-ray pole figures showed that good quality GaN films were grown epitaxially in the [0002] direction at the growth temperature of 750 °C and deposition pressure of 2×10^{-6} Torr. XPS analysis showed that the GaN films grown at different pressures and at 750 °C have relatively low carbon impurities as well as a Ga-rich composition ratio of 1:0.92 (Ga:N). From the XRD and SEM results, we could identify effects of deposition temperature and pressure on the growth rate and crystallinity.

Moreover, the SEM images showed that we can deposit GaN films with smooth surface morphology. Based on the relationship between the growth rate and growth temperature, we suggested that our deposition process was governed by a diffusion rate control. With PL spectrum measurement at room temperature, furthermore, we investigated that the as-grown GaN film revealed emission peak at 3.40 eV with a FWHM of approximately 100 meV.

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