

## Low-Temperature Growth of GaN film by Near-Atmospheric Plasma-Assisted Chemical Vapor Deposition

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A GaN thin film was fabricated by near-atmospheric plasma-assisted chemical vapor deposition. Pure nitrogen plasma can be generated stably using an alternating pulsed voltage system that applies an alternating pulsed voltage between two parallel plate electrodes. The excited nitrogen species correspond to the N<sub>2</sub> second positive system. Ionic molecular species, which cause film damage, were not observed by optical emission spectrum analysis. Using this plasma as a nitrogen source, metalorganic chemical vapor deposition of GaN thin film was carried out under a nitrogen partial pressure of 40 kPa and substrate temperature of 400 °C. The quality of the GaN thin film was analyzed by means of 2-dimensional X-ray diffraction and X-ray pole figure measurement. The measurements revealed that the film was epitaxial with a 30° rotation of the unit cell with respect to (0001) sapphire in the (0001) basal plane.

Key words: atmospheric plasma, gallium nitride, III-V semiconducting materials, chemical vapor deposition

### 1. INTRODUCTION

Gallium nitride (GaN) is a promising material for high frequency microwave devices and high voltage rectifying diodes, as well as optical devices. This material is already in use in practical applications, such as light-emitting and detecting devices in the blue and ultraviolet region [1-3]. For the fabrication of these devices, large-scale processing of high quality GaN thin film is required. The ratio of gallium and nitrogen is a very important factor in the growth of GaN thin films [4]. Generally, a reactive nitrogen source is introduced into the growth chamber in the form of ammonia gas or nitrogen plasma in conventional growing systems, such as metalorganic chemical vapor deposition (MOCVD) [5-8] and molecular beam epitaxy (MBE) [9-11], that use separate growth sources of gallium and nitrogen.

MOCVD is suitable for the fabrication of nitrogen thin films with good crystalline quality, since it allows growth under high nitrogen partial pressure. Further, chemical vapor deposition (CVD) has the specific advantages of high deposition rates and the potential for large-scale processing. The conventional nitrogen sources for MOCVD are ammonia gas or nitrogen plasma. Although GaN films can be fabricated by MOCVD using ammonia gas under high nitrogen partial pressure, ammonia gas requires the use of high growth temperatures in excess of 1000 °C due to the high thermal stability of ammonia [12]. Additionally, ammonia gas requires a cumbersome waste gas cleaner system. In the case of MOCVD using nitrogen plasma, GaN films can be fabricated at lower temperatures, and a bulky waste gas cleaner system is not required. If nitrogen plasma is used, cyclotron resonance plasma and radio frequency plasma sources are usually utilized. It is difficult to achieve a balance between deposition under high nitrogen partial pressure and high deposition rates using these plasma sources, which require pressures ranging from 10<sup>-1</sup> to 10<sup>-4</sup> Pa. To overcome these drawbacks, we have proposed GaN fabrication using near-atmospheric plasma-assisted chemical vapor deposition. It is difficult to generate arcless nitrogen

plasma reliably at near-atmospheric pressure. Corona discharging and glow discharging using helium are known to generate nitrogen plasma at atmospheric pressure. These methods are not suitable for crystal growth of GaN, however, due to the damage caused by the high gas temperature plasma and defects due to low nitrogen species density. Some of the authors of this paper have recently developed a plasma source that maintains stable discharge using various gases such as nitrogen and oxygen without the use of noble gases by applying an alternating pulsed voltage between two parallel plate electrodes at atmospheric pressure [13, 14]. In this paper we report on the growth of a single crystalline GaN film using near-atmospheric plasma-assisted chemical vapor deposition at low temperature.

### 2. EXPERIMENT

A (0001) sapphire with an atomically smooth surface [15] was used as the substrate. All experiments were carried out in a vacuum chamber at a background pressure of 2 × 10<sup>-4</sup> Pa. Figure 1 is a schematic illustration of the near-atmospheric plasma-assisted CVD system. Two parallel plate electrodes are separated by a uniform gap of 1 mm. Nitrogen plasma was generated by applying alternating pulsed voltages, varied from 3 to 7 kV at a frequency of 30 kHz. Trimethylgallium (TMG) was used as the Ga metal source precursor. TMG was carried by nitrogen gas, with the amount of TMG controlled by the nitrogen flow ranging from 0.5 to 1.5 sccm. TMG with carrier nitrogen gas was mixed with nitrogen gas as the reactive gas, after which all gases were led to the chamber. The discharging pressure was 40 kPa. The optical emission spectrum (OES) from the plasma was monitored through a window in the side wall of the chamber. An optical fiber was used to guide the light to an optical multichannel analyzer (Ocean Optics Inc., HR2000CG-UV-NIR and Hamamatsu C7473) from which the optical spectra over the range of 200-900 nm were obtained. The crystalline phase and structure of the

alloys were identified by X-ray diffraction (XRD). Our XRD measurement system has a 16-kW rotating anode Cu target and a high-resolution 2D detector [Bruker AXS, D8 Discover Super Speed with GADDS (General Area Detector Diffraction Solution)]. By means of the 2D-detector system, a part of the Debye-Scherrer ring is two-dimensionally detected. This system allows simultaneous detection of the  $2\theta$  and  $\psi$  angles can be simultaneously detected.

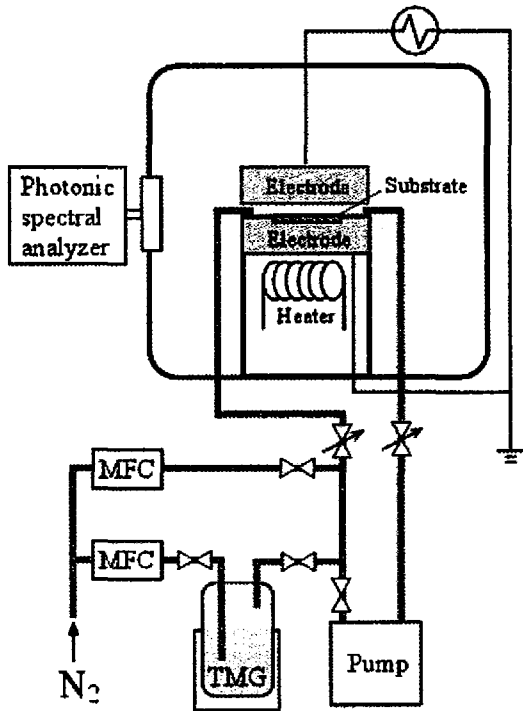


Fig. 1. A schematic illustration of the near-atmospheric plasma-assisted chemical vapor deposition process.

### 3. RESULTS AND DISCUSSION

Figure 2 shows the OES of the nitrogen plasma generated at 40 kPa at room temperature and at 650 °C. At both temperatures, emission peaks that correspond to the  $N_2$  second positive system were observed at wavelengths of 315, 337, 358, 380, and 400 nm [16]. The broad peak observed at wavelengths ranging from 650 to 900 nm at 650 °C is due to infrared light leakage from the substrate heater. The plasma analysis of nitrogen plasma, generated using a similar system at room temperature, has been reported by Hayakawa *et al.* [14]. Our result shows emissions similar to those reported by Hayakawa *et al.*, with the nitrogen species remaining unchanged at high temperatures. In this nitrogen plasma, no spectra due to the  $N_2^+$  second positive system (391 nm), an ionic molecular species that causes film damage [17], were observed, as shown in the inset in Figure 2. Nitrogen plasma including the  $N_2$  second positive system is thus suitable for the crystal growth of GaN thin film. Figure 3 shows the OES of the nitrogen plasma including TMG generated at 650 °C. Emission peaks at 403 and 417 nm, corresponding to gallium, were observed. These results show that nitrogen plasma generates gallium ions. GaN thin films were

prepared using this plasma.

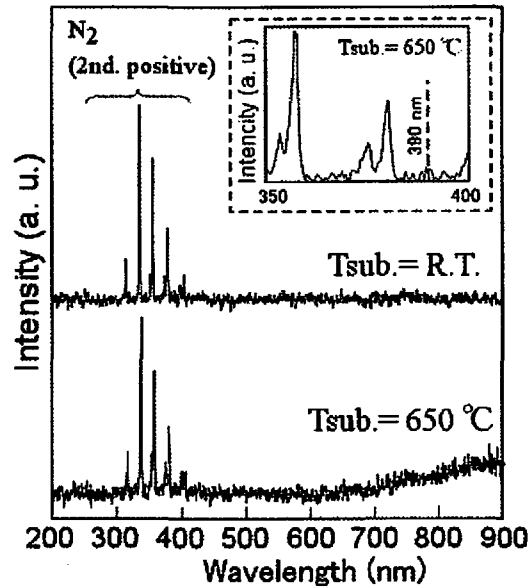


Fig. 2. OES from plasmas generated at room temperature and 650 °C; the inset shows an enlarged view at 650 °C.

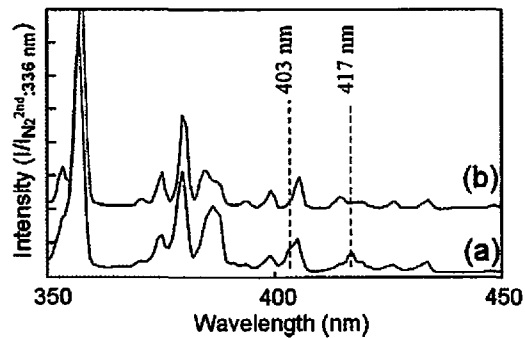


Fig. 3. (a) is OES from nitrogen plasma including TMG generated at 650 °C. (b) is OES from nitrogen plasma, used as a reference OES.

Figure 4 shows the results of the 2-dimensional XRD analysis and  $\omega$ - $2\theta$  XRD pattern of a GaN film with a thickness of 300 nm. The (0002) reflection of the GaN film was observed in the form of spotted shapes, with no other reflection of the GaN film was observed. This implies that the GaN film grew on the (0001) sapphire with (0001) orientation. However, since we could not infer whether the film grew epitaxially on the (0001) sapphire merely on the basis of the results of the 2-dimensional XRD image and  $\omega$ - $2\theta$  XRD pattern, we performed X-ray pole figure analysis, as shown in Fig. 5. The X-ray pole figure was measured with 3° intervals used as scan steps for the  $\phi$  angle. The range of  $2\theta$  and  $\psi$  angles are simultaneously detected from 30° to 60° and from 25° to 75°, respectively. The value of  $\psi$  was 39° for the  $\{10\bar{1}4\}$  plane of (0001) sapphire. In Fig. 5(a), peaks with six-fold symmetry with 60° in the  $\phi$  scan can

be seen at  $\psi = 62^\circ$  for the  $\{10\bar{1}1\}$  plane of GaN. This implies that a hexagonal GaN film had grown epitaxially on the c-sapphire substrate with its c-axis normal to the substrate surface. It can also be inferred from Figs. 5(a) and (c) that the GaN unit cell grows with its a-axis rotated by  $30^\circ$  from the a-axis of the (0001) sapphire, and the epitaxial relationships between GaN and c-sapphire are (0001) GaN  $\parallel$  (0001) sapphire and  $[\bar{1}2\bar{1}0]$  GaN  $\parallel$   $[\bar{1}100]$  sapphire.

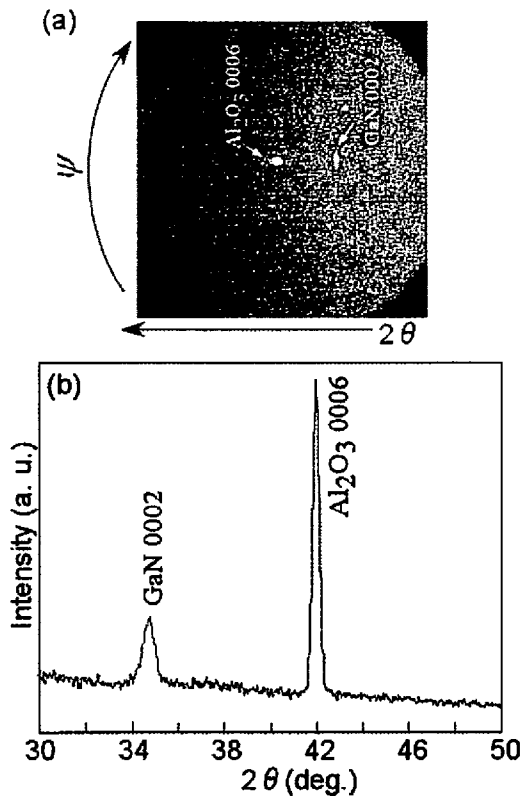


Fig. 4. (a) 2-dimensional XRD analysis and (b)  $\omega$ - $2\theta$  XRD patterns for the GaN film grown at 650 °C.

Using our near-atmospheric plasma-assisted chemical vapor deposition system, we achieved epitaxial growth of GaN thin films at above 400 °C as shown in Fig. 5(b), and the crystallization of GaN thin films at as low as 330 °C (Fig. 6).

#### 4. CONCLUSIONS

We have demonstrated the growth of GaN film by near-atmospheric plasma-assisted chemical vapor deposition. The GaN film grew epitaxially at 400 °C with a  $30^\circ$  rotation of the unit cell with respect to (0001) sapphire in the (0001) basal plane. From the results obtained, we found that the process using near-atmospheric plasma-assisted chemical vapor deposition has major potential for use in GaN film fabrication under high-nitrogen partial pressure and at low temperatures.

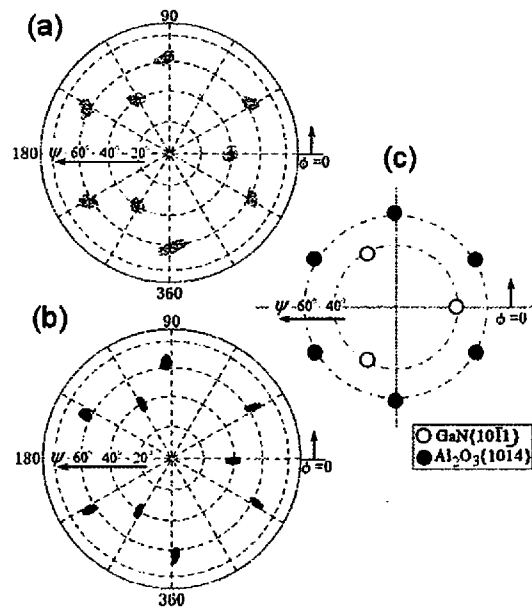


Fig. 5. X-ray pole figures for the GaN film on the (0001) sapphire substrate grown at 650 °C (a), at 400 °C (b), and theoretical image (c).

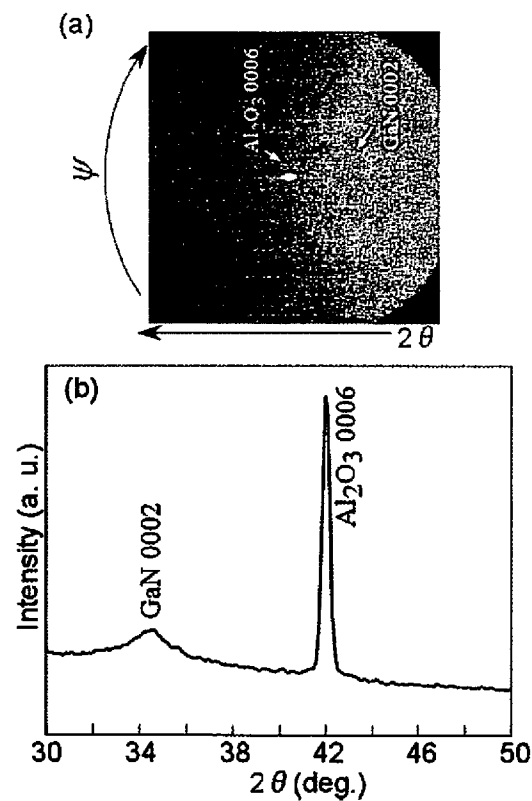


Fig. 6. (a) 2-dimensional XRD analysis and (b)  $\omega$ - $2\theta$  XRD patterns for the GaN film grown at 330 °C.

## ACKNOWLEDGEMENT

The authors would like to thank Y. Takahashi, International Center for Young Scientists (ICYS) NIMS, for technical support with the OES measurements.

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(Received December 25, 2006; Accepted February 1, 2007)