

## Growth of Hexagonal GaN Films on Si Substrates by MOCVD Using a Novel Single Precursor

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Hexagonal GaN films have been deposited on Si(111) substrates by ultrahigh vacuum metal organic chemical vapor deposition using a novel single precursor,  $\text{Et}_2(\text{N}_3)\text{Ga}\cdot\text{H}_2\text{NNH}_2$ . The precursor is a mononuclear Lewis acid-base adduct in which the coordination sphere of the gallium metal is saturated with a neutral hydrazine ligand. The root mean square surface roughness of a GaN film grown on Si at 750 °C was  $\sim 31$  Å as obtained from the atomic force microscopy image. The donor concentration analyzed by the capacitance-voltage characteristics was low  $10^{16}$   $\text{cm}^{-3}$  in the depth below 50 nm.

### I. INTRODUCTION

Gallium nitride, well known as a compound semiconductor with a direct band gap (3.39 eV), has great potential for optoelectronic devices such as blue light emitting diodes (LEDs) [1] and laser diodes (LDs) [2]. Heteroepitaxy has so far been inevitable for the growth of high quality GaN films, since it is difficult to grow large-sized single crystals of GaN. To date, the GaN films have been grown on a variety of substrates, such as sapphire [3–7], 6H-SiC [8], Si [9], GaAs [10], ZnO [11], etc. Among these, sapphire is most widely employed to obtain epitaxial films because of its thermal stability at high temperatures. However, it has many shortcomings such as high cost and poor lattice and thermal matches [12]. In view of semiconductor devices using the Si technology, silicon is more available as the substrate of GaN than others. Especially, it is a prerequisite to grow the GaN films on large area substrates. In many attempts to deposit GaN films on Si substrates, buffer layers such as AlN [13,14], SiC [15], and GaAs [16] were used to grow high quality GaN films, due to a large lattice mismatch between GaN and Si, as shown in Fig. 1. In this paper, we introduce a new method to deposit high quality GaN films on Si(111) substrates. The GaN films were made by metal organic chemical vapor deposition (MOCVD) using a novel single precursor  $\text{Et}_2(\text{N}_3)\text{Ga}\cdot\text{H}_2\text{NNH}_2$ , which was previously synthesized in this laboratory [17]. The structural and

electrical characteristics of the GaN films grown at 750 °C were investigated by measuring the surface roughness, average grain size, and donor concentration.

### II. EXPERIMENTAL

A Si(111) substrate was cleaned in deionized (DI) water, methyl alcohol, and a hot solution of  $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 3:1$ , in sequence, and subsequently etched in a 5% HF solution. Finally, it was rinsed in DI water. Prior to deposition, the substrate was preheated in the reactor at 800 °C for 10 min. An ultrahigh vacuum metal organic chemical vapor deposition (UHV MOCVD) reactor was used for the growth of GaN films. The system was evacuated to  $\sim 10^{-8}$  Torr by combination of rotary and turbomolecular pumps. The precursor was fed to the reactor by spontaneous sublimation without a carrier gas. Typical growth conditions are summarized in Table 1. The morphology and thickness of the films were observed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The crystallinity and epitaxial orientation of the films were studied by x-ray diffraction (XRD) with  $\text{Cu-K}\alpha_{1,2}$  radiation, double crystal XRD (DCXD), and pole figure analysis. The composition of the films was determined by x-ray photoelectron spectroscopy (XPS). To measure the electric property of a GaN film, Au was deposited as a Schottky-contacted electrode on the film by dc sputtering through a shadow mask, its area being  $8 \times 10^{-3}$   $\text{cm}^2$ . Depth profile of

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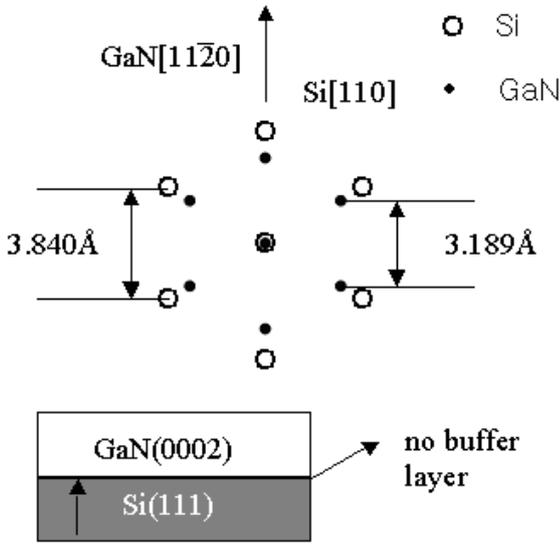


Fig. 1. Crystallographic orientation between the GaN(0002) film and the Si(111) substrate. The lattice mismatch is -17%, and the thermal expansion coefficient mismatch is 55%.

the donor concentration was obtained by a capacitance-voltage (C-V) measurement.

### III. RESULTS AND DISCUSSION

The characteristics of GaN films obtained using the  $\text{Et}_2(\text{N}_3)\text{Ga}\cdot\text{H}_2\text{NNH}_2$  precursor were already introduced in a previous report [17]. In brief, the films were crystallized on Si(111) substrates at temperatures above  $500^\circ\text{C}$  without any buffer layer or carrier gas. The optimum deposition temperature was found to be  $750^\circ\text{C}$ . The crystallinity and morphology were influenced by not only the growth conditions but also the initial states. In this study, we used two different conditions to deposit GaN films at  $750^\circ\text{C}$ : conditions (I) and (II). In condition (I), the temperature of the substrate was increased gradually from  $25^\circ\text{C}$  to  $750^\circ\text{C}$ . In this case, we expected that nuclei would be formed at temperatures lower than  $750^\circ\text{C}$ . In contrast, in condition (II), the substrate was preheated at  $750^\circ\text{C}$  and the precursor was then supplied into the reactor.

Table 1. Typical growth conditions.

Substrate	Si(111)
Precursor	$\text{Et}_2(\text{N}_3)\text{Ga}\cdot\text{H}_2\text{NNH}_2$
Base pressure	$\sim 10^{-8}$ Torr
Working pressure	$2 \times 10^{-6}$ Torr
Substrate temperature	$750^\circ\text{C}$
Precursor temperature	$80^\circ\text{C}$

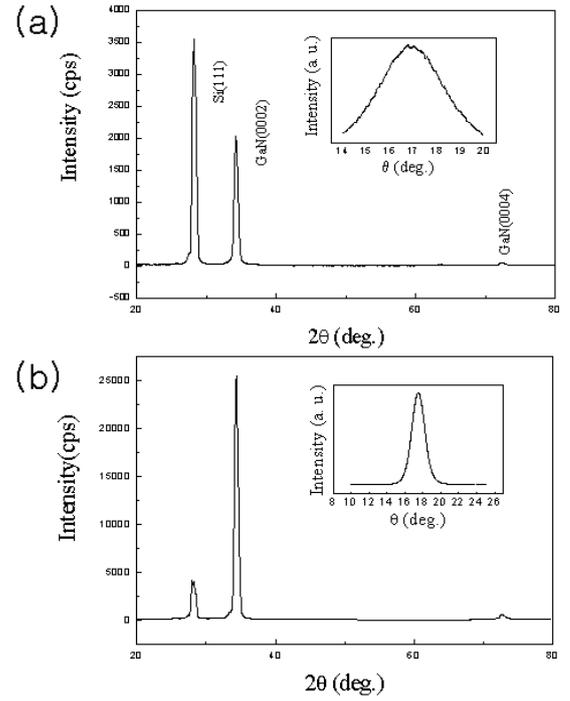


Fig. 2. XRD patterns and DCXD patterns (insets) of the GaN films deposited on Si(111) at  $750^\circ\text{C}$  in (a) condition (I) and (b) condition (II).

Figure 2 shows the XRD and DCXD patterns of GaN films deposited at  $750^\circ\text{C}$ . Both XRD patterns show diffraction peaks associated only with the (0002) and (0004) planes of hexagonal GaN ( $h$ -GaN) at  $2\theta = 34.4^\circ$  and  $72.9^\circ$ , respectively. It indicates that the GaN films on Si(111) substrates have a highly preferred orientation in the  $[0001]$  direction. The intensities of the (0001) peaks

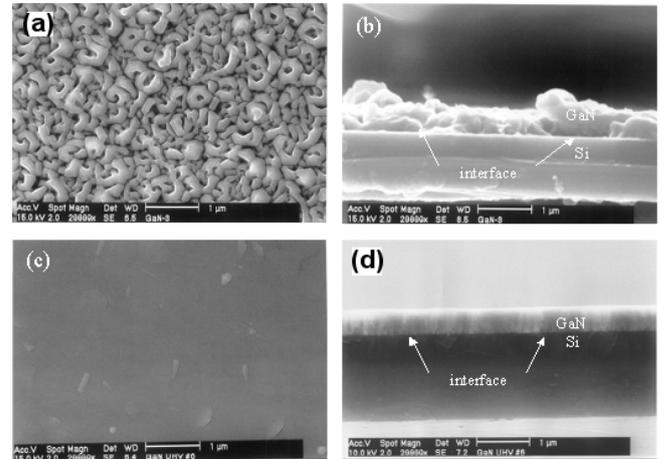


Fig. 3. SEM images of the GaN films deposited on Si(111) at  $750^\circ\text{C}$ : (a) plan view and (b) cross-sectional images in condition (I), and (c) plan view and (d) cross-sectional images in condition (II).

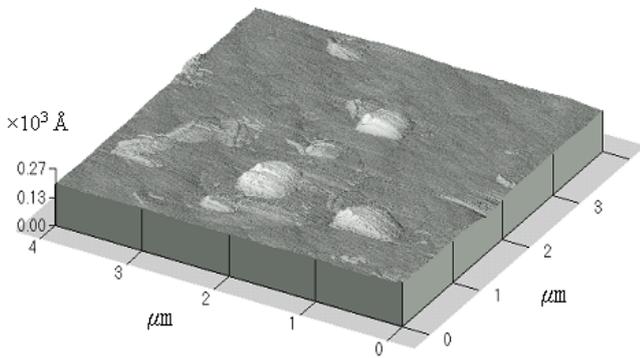


Fig. 4. AFM image of the GaN film deposited on Si(111) at 750 °C.

are very different in conditions (I) and (II). The peak intensity in condition (II) is much higher than that in condition (I). The insets of Fig. 2 show the DCXD rocking curves of the GaN films. The full-width at half maximum (FWHM) values are about 3.2° and 1.5° in Figs. 2(a) and 2(b), respectively, in good agreement with the XRD data.

The plan view and cross-sectional SEM images of the GaN films grown under conditions (I) and (II) are shown in Fig. 3. The GaN film deposited under condition (I) revealed a very poor surface morphology [Fig. 3(a)]. Many small three-dimensional islands are observed to form hexagonally on the surface, whereas, the surface of the film deposited under condition (II) is quite smooth and two-dimensional, as shown in Fig. 3(c). From the cross-sectional images, the thicknesses of the films under conditions (I) and (II) were calculated to be about 0.6 μm and 0.7 μm, respectively. The interfacial layer between the GaN film and the Si substrate in condition (II)

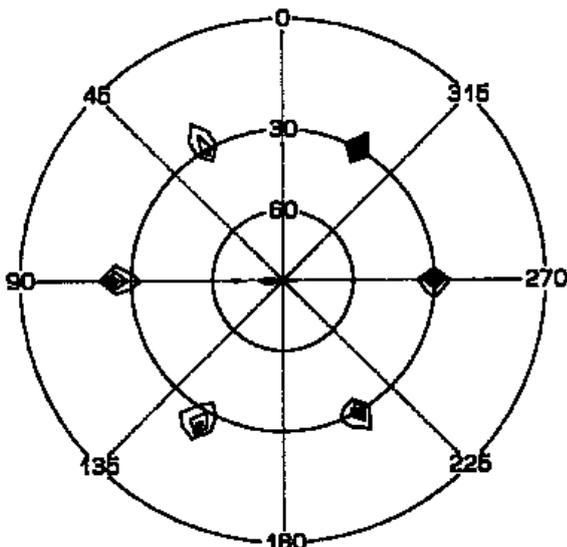


Fig. 5. Pole figure of the GaN film deposited on Si(111) at 750 °C.

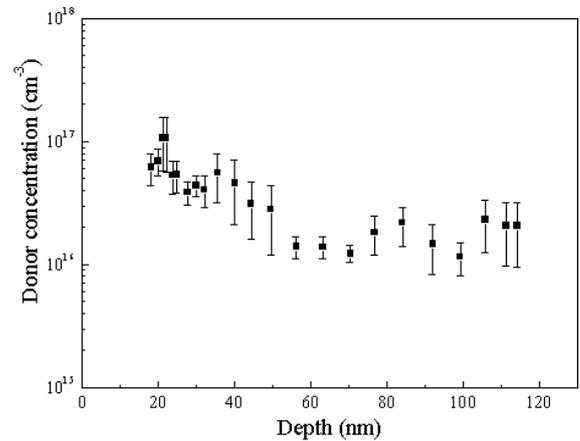


Fig. 6. Depth profile of the donor concentration in a Schottky diode on n-type GaN.

is smoother and more clearly distinguished than that in condition (I). From these results, it was confirmed that high quality *h*-GaN films were obtained on Si(111) substrate under condition (II). From now on, the GaN films grown under condition (II) will be discussed in detail.

Figure 4 depicts an AFM image of the GaN film deposited on Si(111). The image was obtained over the area of 4 μm × 4 μm by a noncontact method and the scan frequency was 0.5 Hz. The surface is very smooth and it is similar to the result of SEM. The root mean square (RMS) surface roughness is ~31 Å and the average grain size is ~200 nm.

To identify the in-plane orientation of the GaN film, a pole figure was obtained. A representative pole figure for the structure of the GaN/Si is illustrated in Fig. 5. The six poles of GaN(10  $\bar{1}$  1) with the polar angle  $\Psi \sim 28^\circ$  give evidence that the *h*-GaN film was epitaxially grown on the Si(111) substrate.

The chemical composition and electron concentration of the GaN films were determined by XPS analyses and C-V measurements, respectively. In XPS spectra (not shown), the GaN films were observed to be nearly stoichiometric, as the atomic ratio of Ga/N was ~1.1. Oxygen and carbon impurities were detected on the surface but decreased to less than 2% after Ar<sup>+</sup> ion sputtering. The C-V measurements were performed for a Schottky contact by applying a small ac amplitude of 10 mV and a frequency signal of 1 MHz. The bias sweep rate was 1.5 V/s. From the C-V characteristics, the donor or electron concentration,  $N_D(x)$ , is generally given as

$$N_d(x) = 2/[q\epsilon_r\epsilon_0 A^2 d(1/C^2)/dV] \quad (1)$$

where  $q$  is the electronic charge,  $\epsilon_r$  is the dielectric constant of GaN,  $\epsilon_0$  is the permittivity in a vacuum,  $A$  is the area,  $C$  is the measured capacitance, and  $V$  is the applied bias voltage [18]. Figure 6 shows the depth profile of donor concentration for the GaN film at room temperature. The donor concentration was high  $10^{16} \text{ cm}^{-3}$  in the depth range from the surface to 50 nm, and low

$10^{16} \text{ cm}^{-3}$  from 50 nm to 120 nm.

#### IV. CONCLUSIONS

Hexagonal GaN films were epitaxially grown on Si(111) by UHV-MOCVD using the novel single precursor  $\text{Et}_2(\text{N}_3)\text{Ga}\cdot\text{H}_2\text{NNH}_2$ . In condition (II), in which the substrate was preheated at 750 °C and the precursor was afterward supplied into the reactor, the GaN films deposited had high crystalline quality, confirmed by the results of SEM, XRD, and DCXD. From the AFM image, the RMS surface roughness was  $\sim 31 \text{ \AA}$  and the average grain size was  $\sim 200 \text{ nm}$ . The donor concentration was low  $10^{16} \text{ cm}^{-3}$  in the depth below 50 nm.

#### ACKNOWLEDGMENTS

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