



# 3C-SiC/Si template growth and atomic layer epitaxy of cubic GaN by RF-MBE

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## Abstract

Growth of 2 in cubic gallium nitride (c-GaN) film on a cubic silicon carbide on Si template (3C-SiC/Si) using Si (001) and Si(111) substrates was performed by using a radio frequency molecular beam epitaxy (RF-MBE) system, which was equipped with a jet nozzle. The 3C-SiC/Si template was prepared using alternating exposure of acetylene (C<sub>2</sub>H<sub>2</sub>) gas introduced by the jet nozzle under ultra high vacuum and Si molecular beam from a Si effusion cell. Very smooth 3C-SiC/Si templates with RMS roughness by atomic force microscopy of about 0.2–0.4 nm were grown here. Good crystal quality of low-temperature buffer (LTB) layer was obtained on a good 3C-SiC/Si template and confirmed through the observation of RHEED pattern. A grown c-GaN film's X-ray diffraction full-width at half-maximum of (002) peak was 13.2 arcmin ( $2\theta$ ) for a 544 nm-thick film. c-GaN was also grown using an atomic layer epitaxy (ALE) method. The ALE method proved to be necessary for a uniform and homogeneous atomic nitrogen flux under slightly Ga excess condition to grow the uniform c-GaN using rf-MBE.

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## 1. Introduction

The cubic group III nitrides, e.g., c-AlN, c-GaN, and c-InN, and related alloys have drawn a great deal of attention since they are more environment friendly, and have higher electron mobility, smooth cleaved surface and relative ease of p-type

doping as compared to their hexagonal phase counterparts. Epitaxial growth of the meta-stable c-GaN has been obtained on various substrates, e.g., 3C-SiC [1], 3C-SiC/Si [2–5], GaAs [6,7], Si [8,9] and MgO [10]. Because of its meta-stable nature, it has been difficult to obtain high crystal quality of c-GaN. Presently, the quality of c-GaN film is still inferior to the hexagonal phase one. This is the main reason why few device applications of c-nitrides are reported [11]. On the other

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hand, incorporation of c-nitrides based devices with present silicon technology is very promising for hybrid optical and electronic applications. The molecular beam epitaxy (MBE) method is a suitable growth technique for c-nitrides and hybridization between Si and c-nitrides because MBE allows the growth at low substrate temperature. MBE also has the merits of the precise control of interface smoothness, the composition of alloy crystals, and its economical use as source materials. To grow c-GaN on a Si substrate, surface carbonization of Si substrate must be performed [2–5]. However, if the hydrocarbons, acetylene gas ( $C_2H_2$ ), is introduced into a liquid nitrogen cooled growth chamber, the hydrocarbons freeze at the surface of a shroud in the growth chamber. This could lead to the serious deterioration of the vacuum. Therefore, the carbonization process is not a popular technique in the nitride growth using MBE. We developed a novel jet nozzle, which allows the carbonization of Si under ultra high vacuum (UHV). An alternating exposure technique of  $C_2H_2$  and Si flux was done for the preparation of a good quality 3C-SiC/Si template for c-GaN using the jet nozzle. Subsequent growth of c-GaN at the same MBE system was performed after growing a low-temperature buffer (LTB) layer. The atomic layer epitaxy (ALE) method was used to improve the uniformity of the grown c-GaN.

## 2. Experimental

The carbonization and MBE growth were performed using a VG 80H MBE system. The Si substrates of S(001) and Si(111) were chemically etched with a solution of HF (5%): $H_2O$  (95%) for 1 min and then rinsed with deionized water before loading into the MBE [12]. A jet nozzle, in which 1 mm diameter hole was placed in the middle of a 5 cm long 1/4 in diameter stainless-steel tube to produce jet flow, was used to carbonize the surface of a Si substrate under UHV with the alternating exposure of  $C_2H_2$  and Si flux. During the carbonization, the pressure of the growth chamber was kept below about  $5.0\text{--}10.0 \times 10^{-6}$  Pa. K-cell of Si was maintained at  $1270^\circ\text{C}$  in order to supply

Si. The surface carbonization was started from  $500^\circ\text{C}$  with ramp speed of  $1^\circ\text{C/s}$ . The formation of the 3C-SiC template was monitored using reflection high-energy electron diffraction (RHEED). Subsequent growth of c-GaN of LTB layer was grown at  $400^\circ\text{C}$  for around 6.5 nm thickness template in the same MBE chamber equipped with a radio frequency (RF) nitrogen radical source made by Arios Inc., IRFS-501. Finally, c-GaN was grown on top of the LTB. The Ga flux was maintained at  $5.5 \times 10^{-5}$  Pa (BEP) from Ga temperature at  $985^\circ\text{C}$  and the flow rate of  $N_2$  was kept at 0.5 sccm. The RF input power was held at 500 W. The pressure of growth chamber during growth was less than  $5.0 \times 10^{-3}$  Pa. After the LTB growth, the substrate temperature was elevated to  $650^\circ\text{C}$  for the growth of the c-GaN. The ALE growth consisted of the following four stages: (1) Ga molecular beam exposure for 3.5 s to deposit 1 ML, (2) Ga migration time for 0.5 s, (3) atomic nitrogen exposure for 4.0 s to react 1 ML Ga deposition and (4) purge time of atomic nitrogen for 0.5 s. A 3.5 s exposure of the uniform Ga corresponding to about 1.0 ML of Ga deposition was obtained from thickness measurement. Uniform atomic nitrogen flux was produced by using an orifice with 0.5 mm thicknesses [13].

The layers grown were characterized through RHEED in situ observation. Atomic force microscope (AFM) was utilized to study the surface morphology. Photoluminescence (PL) measurement was performed in a standard system at room temperature. The crystal quality of c-GaN was evaluated by X-ray diffraction (XRD). The thickness of c-GaN was estimated by spectroscopic reflectometry with a Xe lamp and a CCD spectrometer (USB2000, Ocean Optics).

## 3. Results and discussions

For the carbonization, we carried out two trials to check the effect of Si exposure. In the first trial the substrate temperature had been elevated to  $850^\circ\text{C}$  for thermal cleaning and then  $C_2H_2$  was supplied into the substrate only during temperature ramp from  $850$  to  $900^\circ\text{C}$ . In the second trial,  $C_2H_2$  and Si beams were alternately supplied into

the substrate from the substrate temperature of 500 to 900 °C. Fig. 1(a) and (b) show AFM images of the first trial without Si beam exposure and only C<sub>2</sub>H<sub>2</sub> beam was exposed at high substrate temperatures. The 3C-SiC/Si template without Si exposure exhibited distinguishable etch pits. In Fig. 1(b) the biggest etch-pit is 204 nm in width, and 84 nm in depth. Fig. 1(c) and (d) show AFM images of the surface of the grown 3C-SiC with alternating exposure of Si beam and C<sub>2</sub>H<sub>2</sub> from low substrate temperature. The templates produced with Si exposure of the second trial were very smooth and have a roughness of only about

RMS value of 0.2–0.4 nm. No etch pits were observed for the Si exposed sample.

During the carbonization process without Si exposure, the grown surface of the 3C-SiC/Si became rough as indicated by the RHEED patterns in Fig. 2(a)–(d). The RHEED images of un-exposed samples show spotty and ring patterns as seen in Fig. 2(a) and (b). These figures also confirm a twinned formation of 3C-SiC/Si. On the other hand, spotty and streaky patterns can be seen in Fig. 2(c) and (d). This agrees with the result of AFM image as shown in Fig. 1(c) and (d). The mechanism of carbonization on Si(001) in UHV

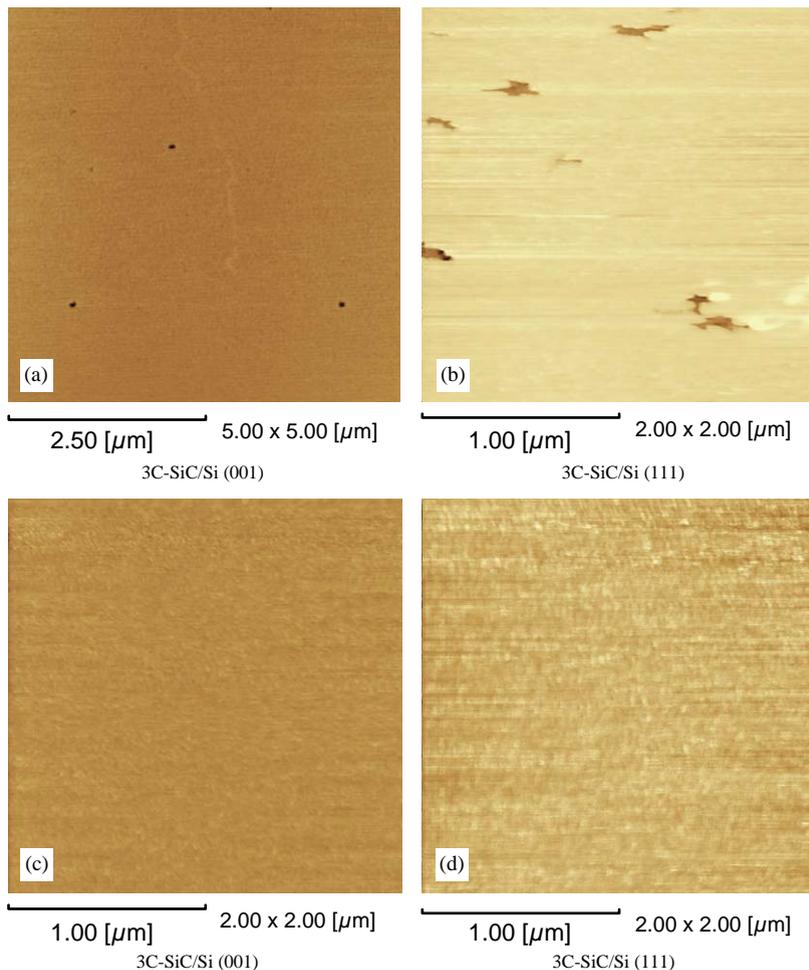


Fig. 1. (a) and (b) AFM images of 3C-SiC obtained by without Si beam exposure on Si(001) and Si(111), respectively. (c) and (d) AFM images of 3C-SiC obtained by with Si beam exposure on Si(001) and Si(111), respectively.

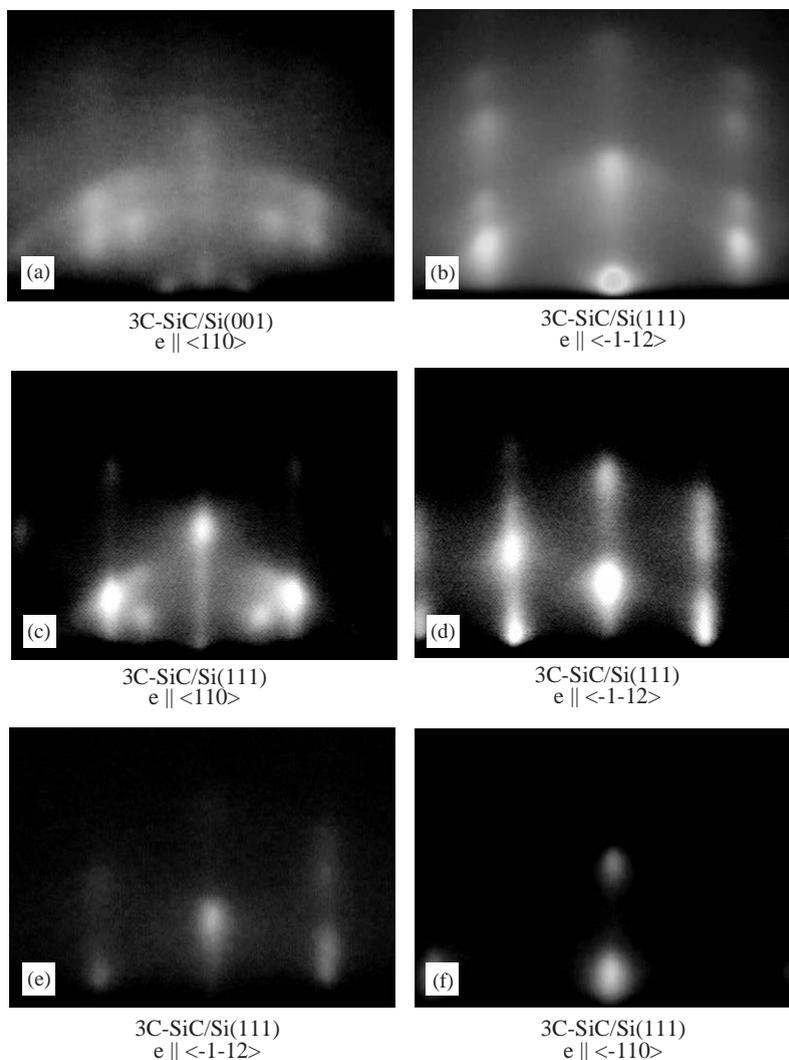


Fig. 2. (a) and (b) RHEED images of 3C-SiC by without Si beam exposure on Si(001) and Si(111), respectively. (c) and (d) RHEED images of 3C-SiC by with Si beam exposure at  $T_{\text{Si}} = 1270^\circ\text{C}$  on Si(001) and Si(111), respectively. (e) and (f) RHEED images of 3C-SiC by with Si beam exposure at  $T_{\text{Si}} = 1100^\circ\text{C}$  on Si(001) and Si(111), respectively.

have been previously reported by Cheng et al. [14], where the absorbed  $\text{C}_2\text{H}_2$  on Si(001) surface starts the carbonization at the substrate temperature of  $500^\circ\text{C}$ , and in the process, a very thin 3C-SiC film was formed. However in our samples, if we followed their procedure, only RHEED patterns associated with the Si substrate were observed during carbonization at 500 to  $800^\circ\text{C}$ ; hence, it can be assumed that the carbonization at low temperatures produces only a very thin amor-

phous SiC/Si. At higher temperatures of the carbonization process, about 800 to  $900^\circ\text{C}$ , Si atoms begin to diffuse from the Si substrate into the 3C-SiC/Si interfaces. The rate of surface migration of Si on 3C-SiC/Si also increased to high value at higher temperature. If the amount of Si atoms supplied by the K cell was sufficient for  $\text{C}_2\text{H}_2$ , the diffusion of Si atoms from substrate was not required. High-quality 3C-SiC layer with minimum or no etch pits can be obtained if there

is enough Si to balance the amount of  $C_2H_2$  supplied from the jet nozzle. The carbonization process with smaller amount of Si atoms, i.e., the Si K cell temperature of  $1100^\circ C$  showed spotty RHEED patterns (Fig. 2(e) and (f)), which indicate that the external Si atom supply was not enough for the  $C_2H_2$  supply. Thus diffusion of Si atoms from the Si substrate has to increase to balance the shortage of Si atoms in the growth surface. This caused to form higher etch pits density as shown in Fig. 1(a) and (b) and spotty RHEED pattern as shown in Fig. 2(a) and (b). To minimize the etch pits and to improve the smoothness of the growth surface, the low temperature amorphous SiC proved to be effective, since it acts as an initial boundary layer between Si substrate and 3C-SiC. The amorphous SiC formed at the low-temperature carbonization is crucial for the fabrication of high-quality and smooth 3C-SiC/Si for c-GaN. Finally carbonization was completed by keeping the substrate temperature at  $800\text{--}900^\circ C$ .

Prior to the growth of c-GaN, the base pressure of the growth chamber was reduced to  $\sim 10^{-7}$  Pa

using a titanium sublimation pump. Subsequently, a LTB layer of c-GaN was grown on the 3C-SiC/Si template. Fig. 3(a) shows a RHEED image of the grown c-GaN, in which the  $(1 \times 1)$  surface reconstruction is readily apparent. This suggests the growth of highly crystalline cubic phase GaN. Fig. 3(b) shows the  $\omega$ - $2\theta$  XRD measurement of the grown c-GaN. Sharp diffraction peak from c-GaN (002) has a full-width at half-maximum (FWHM) of about 13.2 arcmin. The FWHM of the  $\omega$  scan was 32 arcmin. These XRD results are not inferior to the previous works [2–5]. The observed streaky RHEED patterns indicated the surface flatness of the c-GaN. The result of room temperature PL measurement is shown in Fig. 3(c). The PL peak at 3.21 eV corresponds to the energy gap from the near band edge of c-GaN. Spectroscopic reflectometry measurement and reflectivity simulation were carried out to measure the thickness of the grown c-GaN. The single-layer model, which assumes that the c-GaN layer has smooth surface and abrupt interface with the Si substrate using the optical constants of c-GaN obtained from Muñoz et al. [15], was applied in the

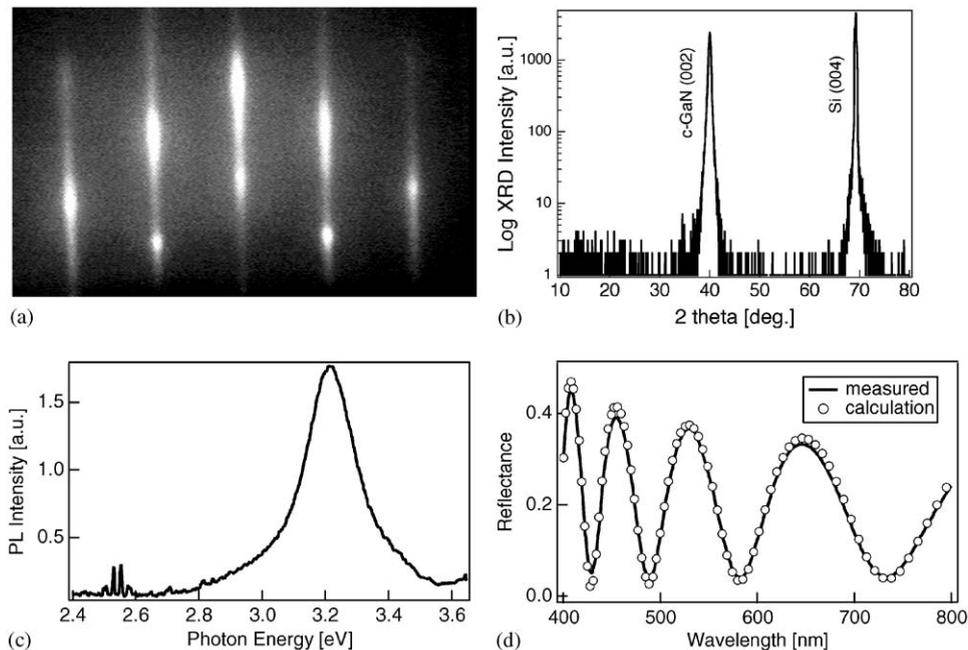


Fig. 3. (a) RHEED image of c-GaN over 3C-SiC/Si ( $e \parallel (110)$ ), (b)  $2\theta$  XRD result of c-GaN, (c) PL spectrum of c-GaN at room temperature, (d) Spectroscopic reflectometry result: dashed line is obtained from single layer simulation.

simulation. The thickness of 3C-SiC template on Si is very thin, and the interface between c-GaN and 3C-SiC is atomically flat. Good agreement between the simulated and the measured reflectivity were obtained. The result of the thickness of c-GaN on 3C-SiC/Si was 544 nm for the film as shown in Fig. 3(d).

Finally, ALE growth technique was applied in c-GaN growth. Fig. 4(b) shows the GaN surfaces grown by ALE method using a highly focused atomic nitrogen beam with substrate rotation under Ga-rich condition. The interference colors correspond with the varying thickness of c-GaN from 252 nm at the center and to 220 nm at the edge. These interference fringes were correlated to the distribution of the atomic nitrogen and not to the Ga flux since the substrate was continuously rotating during the ALE growth with a Ga-rich condition. ALE growth mode usually produces an atomically flat surface. The uniformity of thickness, i.e., the interference color distribution was not remarkably improved here under the Ga-rich condition, because of the non-uniformity of atomic nitrogen flux. When ALE method was applied at reduced atomic nitrogen flux, i.e., Ga-rich

condition, the RHEED pattern showed zincblende spot-streak patterns and also Ga droplets were present in the surface. The RHEED images of the ALE grown sample show spotty wurtzite diffraction patterns if nitrogen excess (N-rich) condition was applied. These results indicate that it is essential to keep the Ga/N (III/V) ratio near one at Ga-rich condition in order to grow cubic phase. When ALE growth was performed under N-rich condition, a uniform of interference color was obtained as showed in Fig. 4(c). The lifetime of atomic nitrogen is quite short, since it is highly reactive with GaN. On the other hand, Ga atomic migration is also limited under N-rich condition, thus stoichiometric condition must be maintained to promote smooth growth surface. If the flux of atomic nitrogen is not uniform, it is possible that in some areas of the wafer the amount of Ga atom would exceed the amount of atomic nitrogen. Therefore, it is necessary to supply uniform atomic nitrogen for a complete reaction between Ga atom and atomic nitrogen on the whole of a 2-in substrate. From the nature of ALE, if the amount of Ga atom and atomic nitrogen are not properly adjusted, a rough surface would be obtained. Therefore, a homogeneous nitrogen flux is required for the successful growth of smooth and flat c-GaN of which necessary growth condition is the Ga rich condition.

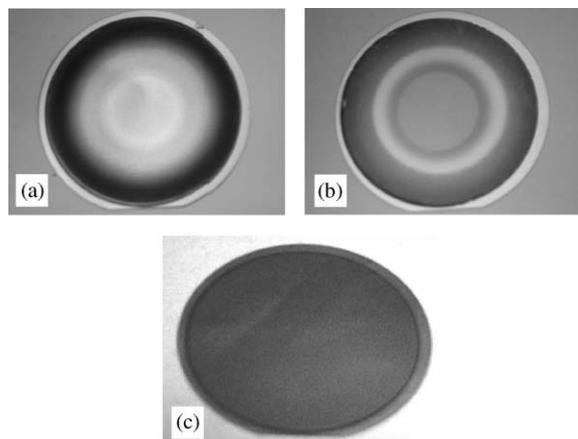


Fig. 4. Photograph images of the interference colors: (a) A film grown under near stoichiometric condition without ALE process. (b) A film grown by ALE under Ga-rich condition with non-uniform and focused atomic nitrogen beam. It shows that the uniform N atom flux is required. (c) A film grown by ALE under N-rich condition using with the diverged atomic nitrogen flux using an orifice of 185 holes of 0.2 mm diameter and 0.5 mm thickness. It shows uniform film thickness.

#### 4. Conclusion

The carbonization of Si substrate was performed for the fabrication of 3C-SiC/Si template using a jet nozzle and alternating exposure of Si flux and  $C_2H_2$  gas. The optimized condition for good quality 3C-SiC/Si templates is that the substrate temperature is elevated from 500 to 900 °C, Si and  $C_2H_2$  molecular beams must be alternately exposed. The templates produced with Si exposure were smooth and have a roughness of about RMS value of 0.2–0.4 nm. No etch pits were observed for the Si exposed sample. A 544 nm c-GaN on 3C-SiC/Si(001) was confirmed by XRD and PL. The FWHM value of  $2\theta$  and  $\omega$  scan were 13.2 and 32 arcmin, respectively. We found that ALE growth under N-rich condition realized the

uniformity of interference colors using substrate rotation even if the Ga flux was not uniform. However, under Ga-rich condition the uniform c-GaN growth was able to realize only uniform N flux exposure. A homogeneous atomic nitrogen flux is crucial for c-GaN growth to maintain under near stoichiometry

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