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Solid-Phase Diffusion of Carbon into GaN Using SiN_x/CN_x/GaN Structure

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We performed a feasibility study on the solid-phase diffusion of carbon into GaN using a SiN_x/CN_x/GaN structure prepared by electron-cyclotron-resonance-assisted chemical vapor deposition. An X-ray photoelectron spectroscopy study on the CN_x layer deposited on GaN showed that its energy positions and spectrum features are very close to those of a C-N bond, and the N composition was estimated to be 24 %, indicating a highly C-rich layer. No degradation in the chemical properties of the GaN surface was found after the diffusion process at 1000 °C. A secondary ion mass spectrometry result clearly showed a diffusion of carbon into GaN. We also observed an increase in resistivity for the C-diffused GaN layer.

KEYWORDS: doping, carbon, diffusion, GaN, CN, SiN, XPS, ECR-CVD

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GaN and related materials are very promising for use in high-power and high-frequency devices owing to their excellent properties such as a high breakdown field and high saturation electron velocity. Unlike Si- and GaAs-based technologies, however, many issues remain to be solved for the development of the fabrication process for high-performance GaN-based devices. In particular, it is a serious problem that the controllability of n- and p-type postgrowth doping is lacking in the GaN device processing technology. Although an aim of ion implantation of Si into GaN has been at the realization of n-type conduction, an annealing process at temperatures higher than 1200 °C is required for the activation of Si donors and the recovery of implantation-induced crystalline defects.¹⁾ This high-temperature annealing can cause serious damage to the GaN surface, even when the GaN surface is covered with an insulating film such as SiO₂ or SiN_x. Several results have been reported on the implantation of Mg into GaN to achieve a p-type material.^{2,3)} However, the thermal problem remains, and consistent data are still too sparse to allow the realization of

practical device processing technology.⁴⁾

In comparison with ion-implantation process, less damage at the GaN surface is expected for conventional diffusion process. However, there has been little work on the conventional postgrowth diffusion of Si and Mg into GaN.⁵⁻⁷⁾ Although carbon is one of the candidates for p-type dopant in III-V semiconductors, efforts to produce p-type GaN:C have had only limited success. The C doping during epitaxial growth of GaN typically produces a highly resistive layer,⁸⁾ except for the p-type conductivity in cubic-phase GaN grown on GaAs by rf-assisted molecular beam epitaxy using electron-beam evaporation of graphite.⁹⁾ Such highly resistive GaN is sometimes used as a semi-insulating buffer layer in high electron mobility transistors. However, the compensation mechanism as well as energy states for C acceptors and/or the C-related complex is not understood at all. In addition, a very limited study was reported for the implantation and diffusion of carbon into GaN.¹⁰⁾

Here, we report a feasibility study on the solid-phase diffusion of carbon into the GaN layer using a SiN_x/CN_x/GaN structure prepared by electron-cyclotron-resonance-assisted chemical vapor deposition (ECR-CVD). A carbon-rich CN_x layer was utilized as a diffusion source of carbon, while SiN_x acted as a capping layer. The nitride-based structure is expected to prevent an excess desorption of nitrogen from GaN during a thermal diffusion process at high temperatures.¹¹⁾

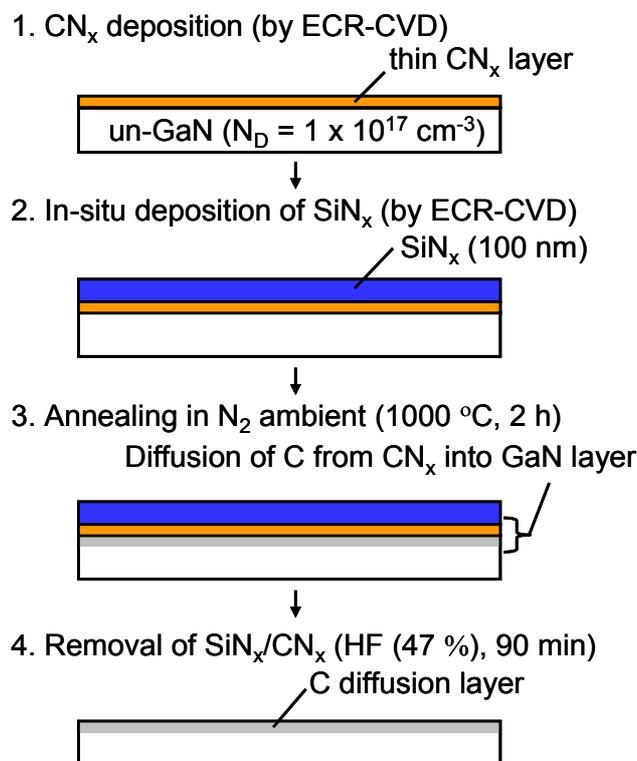


Fig. 1 Process flow for solid-phase diffusion of carbon into GaN.

Figure 1 shows a process flow for the solid-phase diffusion of carbon. We used

undoped n-type GaN with an electron concentration of $1 \times 10^{17} \text{ cm}^{-3}$ grown on a sapphire substrate by metal-organic chemical vapor deposition. The GaN surface was cleaned in an organic solvent, and treated by ECR-excited N_2 plasma. Then, a thin CN_x layer (thickness: 2 - 10 nm) was deposited on GaN by ECR-CVD at room temperature, using the gas mixture of CH_4/N_2 (6/6 sccm) as a source. The microwave power was 200 W. In the in situ stage, the CN_x/GaN structure was capped with a SiN_x layer with a thickness of 100 nm by ECR-CVD, using SiH_4 and N_2 . For the diffusion of carbon from the CN_x layer, the sample was then annealed at $1000 \text{ }^\circ\text{C}$ for 2 h in N_2 ambient. Finally, the SiN_x/CN_x bilayer was removed from the GaN surface in a 47 % HF solution. The chemical properties of the CN_x layers and the GaN surface were characterized using an X-ray photoelectron spectroscopy (XPS) system (Parkin-Elmer PHI 1600C) with a spherical capacitor and a monochromatic Al $K\alpha$ radiation source ($h\nu = 1486.6 \text{ eV}$). The energy scale was calibrated with the Au4f spectrum ($h\nu = 84.0 \text{ eV}$). The carbon density of the GaN layer after the diffusion process was characterized using a secondary ion mass spectrometry (SIMS) system with quadruple PHI-6650 and ADEPT1010 instruments (ULVAC-PHI Inc.). For a resistivity measurement, we deposited a Ti/Al/Ti/Au multilayer, followed by annealing in N_2 ambient at $800 \text{ }^\circ\text{C}$ for 1 min.

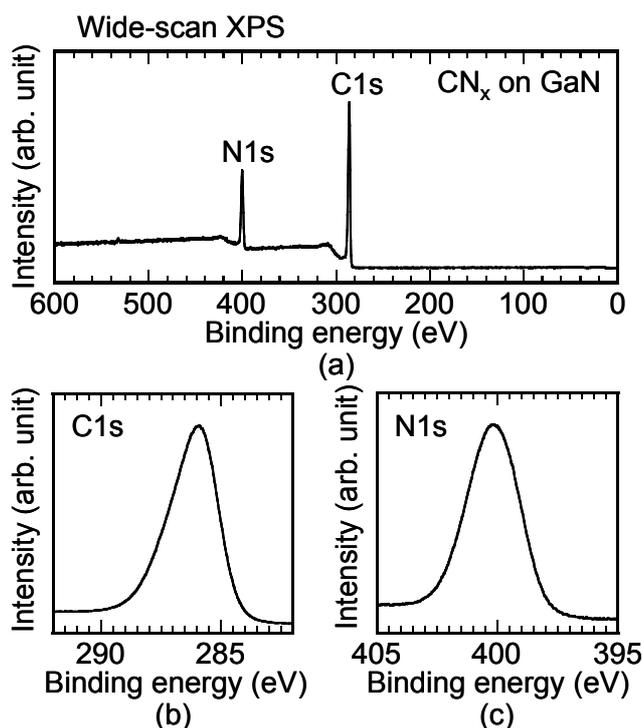


Fig. 2 In situ XPS spectra of CN_x layer deposited on GaN surface:(a) wide-scan spectrum, (b) C1s core-level spectrum, and (c) N1s core-level spectrum.

Figure 2 shows in situ XPS spectra of the CN_x layer deposited on the GaN surface. As seen in the wide-scan spectra [Fig. 2(a)], the C1s and N1s core-level spectra are clearly observed. No impurity-related peak was detected. The narrow-scan spectra of the C1s and N1s levels are shown in Figs. 2(b) and 2(c), respectively. Their peak-energy positions and

spectrum features are very close to those of the chemical bonding states reported for CN_x layers prepared by CVD.¹²⁻¹⁵⁾ We estimated the composition of the CN_x layer deposited from the integrated intensities of the C1s and N1s levels by taking into account their XPS sensitivity factors. The N composition was estimated to be 24 %, indicating a C-rich layer. Such a C-rich composition is commonly reported for amorphous CN_x layers formed by CVD and pulsed laser deposition.¹²⁻¹⁵⁾ Namely, the N composition is limited to below 40 % for the amorphous structure.¹²⁻¹⁵⁾ Although the reason for this is still unclear, such a C-rich nature is desirable in terms of the C diffusion from the CN_x layer into GaN.

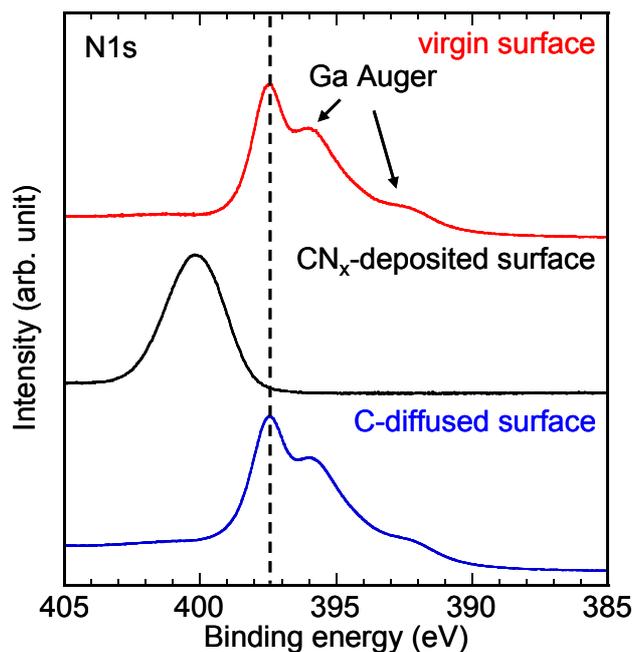


Fig. 3 Comparison of N1s XPS spectra for virgin, CN_x -deposited, and C-diffused GaN surfaces.

We investigated the chemical properties of the GaN surface after the C-diffusion process. For the C-diffused sample, the XPS measurement was carried out after removing the SiN_x/CN_x layer from the GaN surface using a 47 % HF solution. We confirmed the removal of the SiN_x/CN_x layer from the GaN surface by monitoring the N1s spectra in detail. As shown in the middle of Fig. 3, the N1s spectrum showed the chemical bond corresponding to CN_x . After removal in the HF solution, the spectrum feature completely recovered to the Ga-N bonding state, as shown in the bottom of Fig. 3, allowing us to conclude that no residue of CN_x remained on the GaN surface after the removal process.

Figure 4 shows a comparison of the wide-scan XPS spectra of the GaN surface before and after C diffusion. Before the process, the GaN surface showed a slight intensity of the C1s and O1s peaks originating from surface contamination and natural oxide, because the surface was exposed to air. Thus, the C-H bond (285.0 eV) and C-O bond (~289.0 eV) are included in the C1s spectrum, as shown in the inset of Fig. 4. The C-diffused process clearly brought change in the C1s spectrum, i.e., a higher intensity and a chemical shift, as shown in

the bottom inset of Fig. 4. Its spectrum shape and energy position are not those of the C-H bond but very close to those of amorphous carbon or graphite.¹⁶⁾ The thickness of such a carbon layer was estimated to be 1 nm or less from the ratio of the C1s intensity to the Ga3d (N1s) intensity originating from the GaN underneath. It is likely that the accumulation of carbon takes place at the CN_x/GaN interface in the initial stage of the diffusion process, and that carbon can diffuse into GaN under a high-temperature condition. A graphite- or amorphous-carbon-like feature in the C1s spectrum seen in Fig. 4 indicates a trace of such C diffusion. Even after the diffusion process, the host core-level spectra (Ga and N) as well as Ga Auger spectra remained unchanged, which was also confirmed in the narrow-scan spectra. This indicates that the SiN_x/CN_x structure can protect the surface from chemical degradation during the high-temperature annealing process for C diffusion.

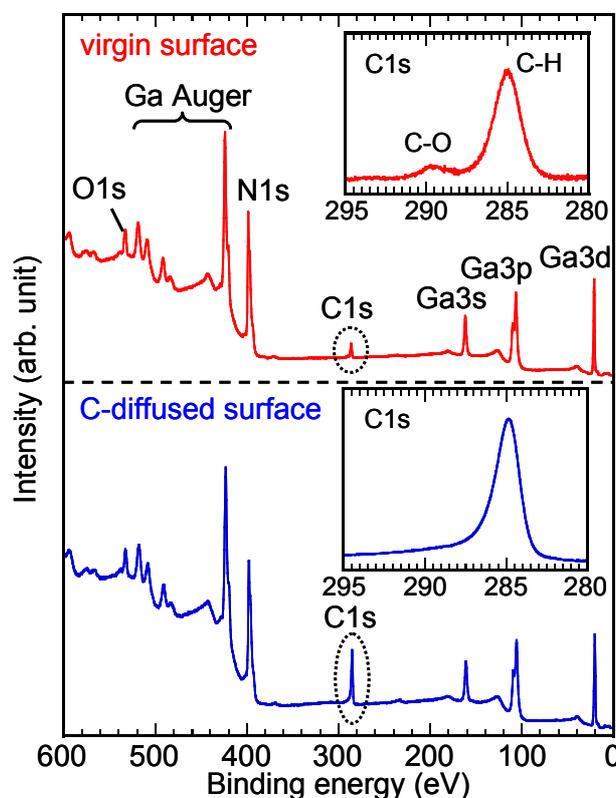


Fig. 4 Comparison of wide-scan XPS spectra of virgin GaN surface and C-diffused surface. The narrow-scan C1s spectra are shown in the insets.

A density profile of carbon diffused into GaN was investigated using SIMS. Figure 5 shows SIMS profiles of C₁₂⁺ intensity for the virgin and the C-diffused samples. The detection limit was determined by measuring C₁₂⁺ intensity in an intentionally C₁₂⁺-implanted GaN sample. Note that the steep intensity increase near the surface (<50 nm) for both profiles is due to the so-called surface effect. The result shown in Fig. 5 clearly shows the diffusion of carbon with a depth of 200 - 300 nm for the processed GaN sample. Pan and Chi⁶⁾ reported a similar diffusion depth for Mg at 1000 - 1100 °C for 1 h. The graphite- or amorphous-carbon like C1s spectrum observed by XPS (Fig. 4) may indicate a trace of such C diffusion into

GaN.

Finally, we measured the change in the resistivity of the GaN surface before and after the diffusion process. The resistivity of the virgin n-GaN was $0.3 \text{ } \Omega\text{cm}$. After the C diffusion, it increased to $0.9 - 2.2 \text{ } \Omega\text{cm}$, indicating that the carrier transport process of the GaN surface was affected by the diffused carbon. One of the possibilities for this is that the diffused carbon acts as a deep acceptor in the form of an interstitial atom (C_I) or in the complex form with some defects,^{17,18)} resulting in a partial compensation of donors in n-GaN. There is also another possibility that the diffused carbon occupies the N site to act as a shallow acceptor (C_N). In this case, the C acceptor may also compensate residual shallow donors in n-GaN. In addition, a formation of a thin p-type layer may cause mixed conduction at the GaN surface, increasing the resistivity owing to significantly lower mobility for holes than that for electrons in GaN. To obtain insights into the diffusion mechanism and electrical properties of the diffused layer, however, further investigation is needed.

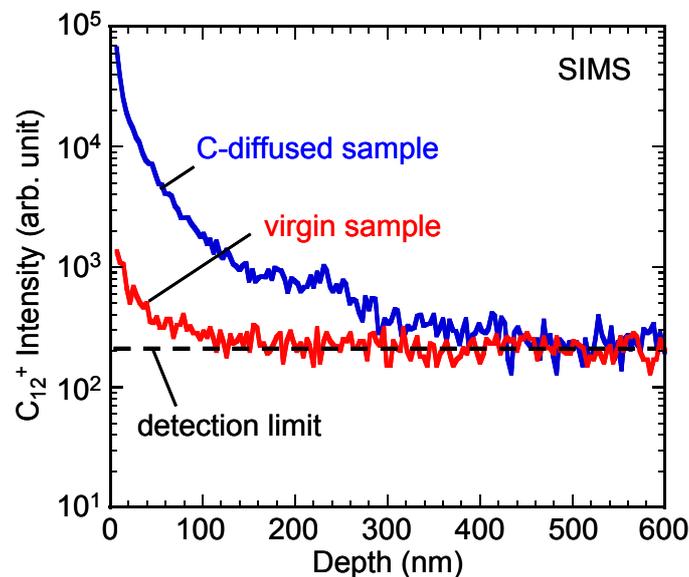


Fig. 5 SIMS profiles of C_{12}^+ intensity for virgin and C-diffused samples.

In summary, a feasibility study on the solid-phase diffusion of carbon into GaN was performed using a $\text{SiN}_x/\text{CN}_x/\text{GaN}$ structure prepared by ECR-CVD. An XPS study on the ECR-CVD-deposited CN_x showed that energy positions and spectrum features are very close to those of the chemical bonding states reported for CN_x layers prepared by CVD. The N composition was estimated to be 24 %, indicating a highly C-rich layer. Even after the diffusion process at $1000 \text{ } ^\circ\text{C}$, it was found that the chemical properties of the GaN surface remained unchanged. The SIMS result clearly showed the diffusion of carbon into GaN with a depth of 200 - 300 nm. The increase in resistivity for the C-diffused GaN was also observed. The results obtained indicate that the $\text{SiN}_x/\text{CN}_x/\text{GaN}$ structure is promising for the realization of the solid-phase diffusion of carbon into GaN.

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