Roles of Atomic Nitrogen/Hydrogen in GaN Film Growth by Chemically Assisted Sputtering with Dual Plasma Sources

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ABSTRACT: The growth of sputtered GaN at low temperature is strongly desired to realize the dissemination of low-cost GaN high electron mobility transistor devices for next-generation communication technology. In this work, the roles of atomic nitrogen (N)/hydrogen (H) in GaN film growth on AlN/sapphire substrates by chemically assisted dual source sputtering are studied at a low growth temperature of 600 °C under a pressure of 2 Pa using vacuum ultraviolet absorption spectroscopy. The lateral growth was strongly enhanced with an appropriate H/N flux ratio of 1.9 at a GaN growth rate of ∼1 μm h⁻¹. X-ray photoelectron spectroscopy measurements indicated that N removal from the grown GaN surface by atomic hydrogen promoted the migration of Ga. A smooth GaN surface was achieved at a suitable N/Ga supply ratio of 53 and a H/N ratio of 1.9 with the addition of 0.5% chlorine to the Ar sputtering gas.

1. INTRODUCTION

High electron mobility transistors (HEMTs) using GaN materials hold promise for the development of next-generation communication technology due to their high-output characteristics, low energy loss, and high thermal conductivity. To fabricate these devices, heteroepitaxial growth of GaN has been performed by metal–organic chemical vapor deposition (MOCVD) and hydride vapor phase epitaxy (HVPE).1–3 Although these high-temperature processes at over 1000 °C ensure the high-quality growth of GaN, these processes have potential cost issues with the reactant gas due to the low decomposition efficiency.

Sputtering is not a major method for the growth of GaN, although it has an advantage of growth on large substrates at low temperature and low cost.4–7 Crystalline GaN growth below 600 °C8–9 has been achieved by reactive sputtering using a mixture of Ar and N₂ gases, despite contamination of polycrystalline phases. Additionally, a pulse sputtering deposition (PSD) method using Ga targets under ultrahigh vacuum (<10⁻⁷ Pa) has been proposed to realize epilayer growth by sputtering.10,11 Precise time control of sputtering plasma has enabled the enhancement of Ga surface migration at temperatures below 760 °C. On the other hand, the PSD method has issues of film quality control for large size wafers, a requirement of high-temperature annealing, and unavoidable nitridation of the Ga target during continuous growth when a single plasma source system is applied.11,12

Here, we propose another method, namely, a dual-source deposition system that uses argon/chlorine plasma for Ga sputtering and nitrogen/hydrogen plasma for the supply of nitrogen/hydrogen precursors to achieve growth on large size wafers by individual control of the nitrogen precursor supply and to prevent nitridation of the Ga target.13 Presently, there remains an issue of the highly roughened surface that results from this method. The roughness originates from pit formation due to chlorine plasma etching at the growth temperature of 670 °C, even though H₂ and Cl₂ are added during the process to enhance lateral growth.

A low-temperature process is necessary to reduce the etching effect; however, the surface migration of sputtered Ga is then limited, which results in columnar growth. Chemical reactions between additive gases and the grown surface should thus be controlled precisely to achieve a flat grown surface with high crystallinity. With regards to the reaction between H₂ and the GaN surface, conventional sputtering growth of GaN with H₂ degrades the grown GaN film due to the formation of hydrogen-related bonds with the host lattice atoms.9,14 On the other hand, the promotion of molecular beam epitaxy (MBE)
GaN growth with the addition of atomic hydrogen showed the possibility of crystalline control, even though the chemistry was not apparent. There is also a potential for chlorine plasma chemistry on the GaN surface to improve the film quality by controlling the etching effects of GaN.

In this study, we have first evaluated the influence of the supply conditions of atomic nitrogen and hydrogen onto GaN films grown with a dual source sputtering system at a low temperature of 600 °C using vacuum ultraviolet absorption spectroscopy (VUVAS). The effects of atomic hydrogen were examined with respect to the diffusion length of Ga on the GaN surface. Finally, the contribution of sputtering using a mixture of chlorine and argon gases on GaN growth was investigated.

2. EXPERIMENTAL SETUP AND METHODS

2.1. Dual Plasma System. The concept of a dual plasma system was constructed based on individual control of the supply of both pure Ga and a high density of nitrogen atoms. Figure 1 shows a schematic diagram of the dual plasma system with two plasma sources for GaN film growth. The details are described in ref 13. This system consists of three chambers: a heating unit for substrates, a magnetron capacitively coupled plasma (CCP) source, and a high-density nitrogen plasma source with low impedance antenna (LIA) inductively coupled plasma (ICP).

The CCP chamber was used to supply the Ga precursor. Argon was introduced at a flow rate of 40 sccm. For chemical sputtering, 0.5% chlorine was mixed with Ar while the total flow rate was maintained. The Ga target was prepared by melting 6 g of metallic gallium pellets (Nilaco, USA, 99.9999%) on a 25 mm diameter nickel dish at 100 °C and then by cooling down to room temperature. The dish was placed at the bottom of an electrode and the CCP was discharged by the application of a 13.56 MHz radio frequency at an output power of 1 kW. The atomic nitrogen and hydrogen were transferred from the LIA-ICP chamber to the growth chamber through a pipe [length (L), 120 mm; diameter (Φ), 60 mm]. The main chamber was evacuated to a pressure less than 6.0 × 10⁻⁴ Pa by a turbo molecular drag pump combined with a dry drag pump. The CCP chamber was separated from the main chamber by an earthed 30 mm diameter mesh plate of nickel filled with 2 mm diameter holes at an opening ratio of 40%. This plate inhibited the supply of high-energy ions in the CCP to the wafers and prevented nitridation of the Ga target by suppressing the intrusion of nitrogen gas into the CCP chamber. The mesh was positioned at distances of 15–35 mm away from the wafer surface by replacing the cover with mesh. A standard distance of 15 mm was selected to enhance the reaction between chlorine plasma and the grown GaN surface at a low temperature as related in a later section.

2.2. GaN Growth Processes. A susceptor holding the substrate was heated by infrared radiation from a tungsten coil heater during deposition. The substrate temperature was controlled at 600 °C by a current feedback unit. Commercially available AlN-on-sapphire wafers (Kyma Technologies, Inc.) were used for GaN growth. A 20 nm-thick AlN(0001) was grown on top of a sapphire substrate by plasma vapor deposition. The full width at half maximum (FWHM) of the AlN(0002) diffraction from an X-ray rocking curve (XRC) was less than 0.1°.

Prior to growth, the substrate was cleaned ultrasonically in acetone for 3 min and in pure water for 3 min. The substrate was then placed on the susceptor and heated at 500 °C for 2 h in a vacuum. A shutter was inserted in front of the sample surface and CCP discharge was performed for 20 min for stabilization before the sputtering process. Deposition was performed with LIA-ICP discharge for 1 h at 2 Pa.

2.3. Film Characterization. The crystallinity of the grown GaN films was evaluated using X-ray diffraction (XRD; Rigaku, ATX-G) with Cu Kα radiation, a Ge(220) monochromator, a 2.0 × 0.5 mm² collimator, and a 5.0 × 1.0 mm² receiving slit. XRCs for the symmetric (0002) plane of the GaN layers were measured in the step-scan mode with a step of 0.005°. The film thickness and the surface morphology were measured using scanning electron microscopy (SEM; Hitachi High-Technologies, SU-8230) with an acceleration voltage of 10 kV, and
ordering of the atoms was observed using high-resolution transmission electron microscopy (HRTEM; JEOL, JEM-ARM200F) with an acceleration voltage of 200 kV. The N/Ga ratio of the grown GaN surface was determined from X-ray photoelectron spectroscopy (XPS) measurements (Ulvac-Phi, XPS 1600) with a Mg Kα (1253.6 eV) X-ray source. The take-off angle of photoelectrons was 90° with respect to the surface. Elemental compositions were calculated from the integration ratio of each component for Ga 3d and N 1s.

2.4. Measurements of Atomic Nitrogen and Hydrogen Densities. The atomic nitrogen and hydrogen densities generated from the LIA-ICP source were measured using VUVAS.17−19 Figure 2 shows a schematic diagram of the VUVAS system employed. Focused light with wavelengths of 120.1 and 121.6 nm were emitted from the micro-discharge hollow-cathode lamp and passed 15 mm above the substrate. The light absorption in the nitrogen and argon mixture plasma was measured by the VUVAS spectrometer and a photomultiplier tube (PMT). The absorption length was adjusted to 35 mm using optical guides with lenses. The atomic nitrogen or hydrogen flux \( \Gamma \) to the substrate surface can be calculated using the evaluated atomic nitrogen or hydrogen density \( n \), and the relation given by

\[
\Gamma = \frac{n \overline{V}}{4} = n \sqrt{\frac{kT}{2\pi m}} \tag{1}
\]

where \( \overline{V} \) is the thermal velocity, \( m \) is the mass of atomic nitrogen or hydrogen, \( k \) is the Boltzmann constant, and \( T \) is the translational temperature of atomic nitrogen. \( T \) was previously evaluated as 513 °C from the average temperatures between the substrate and the mesh plate.

3. RESULTS AND DISCUSSION

3.1. Influence of Added Hydrogen on the Growth Mode. Figure 3 shows surface and cross-sectional SEM images of GaN films grown with various \( H_2/N_2 \) flow rates. Columnar growth was observed without \( H_2 \), as shown in surface SEM images of Figure 3a−c and in Figure 3i, which is the cross-sectional SEM image of Figure 3b. In every case, the growth rates were almost constant at 1.10−1.28 μm h⁻¹. The grain size grown at a \( N_2 \) flow rate of 5 sccm was around 500 nm, which is larger than the grains (≈300 nm) grown at \( N_2 \) flow rates over 10 sccm. On the other hand, laterally enhanced growth was observed in the GaN film grown at a \( H_2 \) flow ratio of 10%, as shown in Figure 3d−f. In each case, pits with facets at six crystalline faces with angles of around 62° to the horizontal were observed on the grown surfaces as shown in Figure 3j, which is the cross-sectional SEM image of Figure 3e. Grain interfaces partially remained at a \( N_2 \) flow rate of 5 sccm. A relatively flat surface with a pit density of \( 1.0 \times 10^{10} \text{ cm}^{-2} \) was observed at a \( N_2 \) flow rate of 9 sccm. At a \( N_2 \) flow rate of 20 sccm, the growth mode was changed to pit-dominant, and the density of pits was around \( 1.4 \times 10^{11} \text{ cm}^{-2} \). At a \( H_2 \) flow ratio...
of 20%, the columnar growth reappeared on the surface with a large number of droplets, as shown in Figure 3g. An entirely droplet-covered surface without crystallization was formed on the substrate at a H$_2$ flow ratio of 40%, as shown in Figure 3h.

Columnar growth without H$_2$ has often been reported for low-temperature sputtering growth at less than 600 °C with a single plasma source using Ar/N$_2$ mixture gases. From the present growth results without H$_2$, Ga migration was not promoted sufficiently, even with the dual source system at 600 °C, regardless of the N$_2$ flow rate. The separate supply of Ga and N can decrease the formation of intermediate products of Ga–N$_2$ on the target, although this effect did not directly contribute to enhance the migration of Ga on the growth surface. The larger grain size at a low N$_2$ flow rate of 5 sccm indicates Ga migration was slightly enhanced, even though the growth directions of each grain were not oriented.

On the other hand, the laterally enhanced growth by the addition of H$_2$ shown in Figure 3d–f has not been reported for sputtering growth of GaN by a single source system. The differences with the previous report are the suppression of highly energetic hydrogen from the sputtering source and the higher growth temperature. The formation of H-bonds in the host lattice atoms might be decreased by the remote supply of hydrogen atoms and the thermal relaxation of the grown film, which resulted in the suppression of grain formation. The droplet-rich surface at a H$_2$ flow ratio of 20% indicates the N atoms on the grown GaN surface were removed by atomic hydrogen. One possibility for the columnar growth at a H$_2$ flow ratio of 20% is that nuclei with different surface orientations are grown during the initial growth stage due to the excessively Ga-rich surface. Such irregularly grown grains do not easily bridge each other, which results in a roughened surface. The same mechanism could be applied to the formation of grain interfaces at a low N$_2$ flow rate of 5 sccm, as shown in Figure 3d.

Figure 4 summarizes the growth rates observed for Figure 3b,d–h as a function of the N$_2$ flow rate and added H$_2$ flow ratio. The H$_2$ flow ratio was fixed at 10% in Figure 4a, and the total gas flow rate to the ICP source was fixed at 10 sccm in Figure 4b. The growth rates were measured from the highest positions of the grown GaN films by cross-sectional SEM observations. The change in the growth rates with the N$_2$ flow rate (5–20 sccm) was 0.95–1.05 μm h$^{-1}$, as shown in Figure 4a. The growth rates without the addition of H$_2$ were approximately 0.23–0.33 μm h$^{-1}$ faster than the growth rates with 10 or 20% H$_2$, as shown in Figure 4b.

The growth rates are generally determined by the amount of Ga atoms supplied on the grown GaN surface because the Ga supplied is not evaporated from the surface at 600 °C due to the lower evaporation pressure of Ga. The decrease of the growth rates with H$_2$ is due to etching of the grown surface by atomic hydrogen. Yeh et al. reported that the inversion domains with surfaces of GaN(0001) and GaN(1011) were preferentially etched by hydrogen plasma, while the GaN(0001) surface was not readily etched. The effect of etching on the grown GaN surface enhances flat surface growth without three-dimensional growth.

3.2. Atomic Nitrogen and Hydrogen Fluxes Evaluated by VUVAS. To identify the roles of atomic nitrogen and hydrogen from the ICP source on the GaN growth, atomic nitrogen and hydrogen fluxes during GaN growth were evaluated using VUVAS at a fixed mesh-substrate distance of 15 mm. During this evaluation, Ar gas without Cl$_2$ was supplied at a flow rate of 40 sccm from the sputtering source. Figure 5a shows the atomic nitrogen/hydrogen fluxes as a function of the N$_2$ flow rate to the substrate at a fixed H$_2$ flow ratio of 10%. The densities of atomic nitrogen and hydrogen at a N$_2$ flow rate of 9 sccm were 2.4 × 10$^{17}$ cm$^{-2}$ and 1.2 × 10$^{17}$ cm$^{-2}$, respectively. From eq 1, the atomic nitrogen/hydrogen fluxes

![Figure 4](https://dx.doi.org/10.1021/acsomega.0c03865)

**Figure 4.** Dependences of the growth rates (a) on the N$_2$ flow rate when the added H$_2$ ratio is 0.1, and (b) on the added H$_2$ ratio when the N$_2$ flow rate is 10 sccm.

![Figure 5](https://dx.doi.org/10.1021/acsomega.0c03865)

**Figure 5.** Atomic nitrogen and hydrogen fluxes as a function of (a) N$_2$ flow rate and (b) added H$_2$ ratio. Note that the vertical scales for the fluxes are in units of 10$^{16}$ cm$^{-2}$ s$^{-1}$, except for panel (b) in 10$^{17}$ cm$^{-2}$ s$^{-1}$.
supplied were then estimated to be $6.6 \times 10^{16}$ and $1.3 \times 10^{17}$ cm$^{-2}$ s$^{-1}$. The atomic nitrogen flux was gradually increased with the N$_2$ flow rate. The atomic hydrogen flux was also increased at almost the same rate as the atomic nitrogen flux. The atomic hydrogen/atomic nitrogen flux ratio (H/N) was slightly decreased from 2.1 to 1.8 with an increase in the N$_2$ flow rate from 5 to 20 sccm.

The collision frequencies of atomic nitrogen and hydrogen onto the grown surface were increased at higher N$_2$ flow rates, while the total balance of Ga nitridation and nitrogen removal from the grown GaN surface was dominated by the H/N flux ratio. A pit-dominant surface was formed at a N$_2$ flow rate of 20 sccm because Ga migration was suppressed by the slightly lower H/N flux ratio of 1.8. Relatively flat growth was observed with an increase in the H/N flux ratio because Ga migration was assisted by the removal of N from the grown surface by atomic hydrogen. From these results, the suitable H/N flux ratio was determined to be around 1.9. Precise control of the atomic nitrogen/hydrogen supply is thus important for appropriate growth to produce a flat surface.

Figure 5b shows the supplied atomic nitrogen/hydrogen fluxes to the substrate as a function of the H$_2$ flow ratio to the total flow rate. The total gas flow rate supplied to the ICP source was fixed at 10 sccm, and the H$_2$ flow rate was increased from 0 to 40% to the total flow rate. The atomic nitrogen flux was slightly decreased with an increase in the H$_2$ flow ratio while the atomic hydrogen flux was abruptly increased. The H/N flux ratios at H$_2$ flow ratios of 20 and 40% were 2.9 and 10.6, respectively. The significant change of the atomic hydrogen flux at a H$_2$ flow ratio of 40% was attributed to not only the increase of the collisions between electrons and hydrogen molecules with the increase of the hydrogen partial pressure but also the formation and dissociation of N$_2$H$_4$ with larger dissociation cross sections. These tendencies between the H/N fluxes and the H$_2$ flow ratio are consistent with those of the previous report. Consequently, a flat growth surface was obtained with a H/N flux ratio around 1.9, whereas columnar growth was enhanced at higher H/N flux ratios.

### 3.3. Mechanism of GaN Growth with Atomic Hydrogen

When considering the diffusion behavior of a supplied Ga atom on a grown GaN surface, the averaged diffusion length of the Ga atom is expressed as:

$$L_{Ga} = \sqrt{D_{Ga} \exp \left(\frac{E}{kT}\right) \tau}$$  \hspace{1cm} (2)

where $D_{Ga}$ is the diffusion coefficient of a Ga atom on GaN, $E$ is the diffusion energy barrier, $k$ is the Boltzmann constant, $T$ is the growth temperature, and $\tau$ is the diffusion lifetime. Using 0.007 cm$^2$ s$^{-1}$ for $D_{Ga}$ and 2.48 eV for $E$ approximated from measured results using reflection high-energy electron diffraction (RHEED) in ref 24, the diffusion length was calculated to be 0.56 Å when the diffusion time was dominated by the thickness of the GaN monolayer (0.253 nm)/growth rate. On the other hand, the diffusion length is longer in the physically enhanced sputtering process. The diffusion length of a Ga atom on the grown GaN surface was elongated by the increase of surface temperature around the landing point of sputtered Ga by the exchange of kinetic energy. When defining a heating radius that agrees with the diffusion length $L_{Ga'}$, and assuming all collisional energy between the sputtered atoms and growth surface is converted to thermal energy without consumption by surface reconstruction (see Figure 6), the balanced equation for the sputtered-atom energy $E_{sp}$, the diffusion length $L_{Ga'}$, and the increase of temperature $\Delta T$ around the landing point of sputtered Ga is expressed as:

$$\frac{E_{sp}}{\rho C \Delta T} = \frac{2\pi}{3} (L_{Ga'})^3$$  \hspace{1cm} (3)

Here,

$$L_{Ga'} = \sqrt{D_{Ga} \exp \left(\frac{E}{k(T + \Delta T)}\right) \tau}$$

When using the typical sputtered atom energy of 2 eV for $E_{sp}$, the area within the 2.0 nm radius ($L_{Ga'}$) is heated to an average temperature of 841 °C, which results in a higher mobility of Ga atoms on the GaN surface. In the present system, the averaged sputtered-atom energy at the grown GaN surface is decreased to around 0.1 eV by the high collision rate (~10) between the sputtered atoms and gas molecules in the atmosphere; therefore, the heating radius is smaller than 1.0 nm.

On the other hand, the collision frequency between Ga and atomic nitrogen influences the Ga migration time. A much higher atomic nitrogen flux than the Ga flux is generally required for GaN growth because the atomic nitrogen is easily reflected or dissociates from the grown GaN surface. When the atomic nitrogen flux is in excess of the growth rate, the collision probability between migrated Ga and atomic nitrogen is increased, which results in the formation of three-dimensional nuclei with different facets. The diffusion time in eq 2 is then inversely proportional to the rate of atomic nitrogen supply, i.e., $\tau \propto \nu N^2$, as introduced in ref 26. The small grains grown at N$_2$ flow rates over 9 sccm without H$_2$ is presumably attributed to such nuclei.

The laterally enhanced growth with the addition of H$_2$ is attributed to the reaction between atomic hydrogen and the grown surface. XPS measurements of the grown GaN surfaces were performed to elucidate the change of the surface stoichiometry by H$_2$ addition. Figure 7a shows the N/Ga compositional ratio of GaN grown without and with H$_2$ addition. The H$_2$ flow ratio was 10% because the droplet formation at higher H$_2$ flow rates disturbed the accuracy of the XPS measurement. A GaN substrate grown by HVPE was used as a reference. The N/Ga compositional ratio of the GaN surface grown without H$_2$ was almost equal to 1, the same as that of the reference. On the other hand, the ratio of N on the GaN surface grown with H$_2$ was decreased to around 0.79.

From the XPS results, 21% of N atoms on the grown GaN surface were volatileized with atomic hydrogen. The binding energy of Ga–H was reported to be 2.69–2.81 eV at room temperature; however, the energy should be limited at a high
temperature of 600 °C due to the instability of the GaH₄ structure. The diffusion barrier of Ga atoms (0.3 eV) on a Ga-terminated GaN surface was reported from simulations based on the density functional theory. When linearity of the diffusion barrier between the Ga-terminated GaN surface (0.3 eV) and the grown GaN surface (2.48 eV) is assumed, the diffusion barrier on the grown GaN surface with 10% H₂ is 1.98 eV. The diffusion length of Ga atom on the grown surface is then around 1.6 nm, which is much longer than the diffusion length enhanced by bombardment of the sputtered atoms.

These results indicate that atomic hydrogen inhibits the formation of Ga–N₃ bonding on the grown GaN film, which disturbs Ga migration by the adsorption of atomic nitrogen, as illustrated in Figure 7b,c. Consequently, the lateral growth is enhanced with atomic hydrogen, even at a higher N₂ flow rate. Considering the flat grown surface at a lower N₂ flow rate, the frequent formation of Ga-rich nuclei also seems to be inhibited by the enhanced diffusion length of Ga due to the volatilization of nitrogen from the nuclei surfaces.

3.4. Effect of Chlorine Addition on Initial Growth.

Even though lateral growth was promoted by the addition of H₂, pits remained on the grown surface. Similarly, chlorine plasma etching of GaN at higher temperatures promotes pit formation due to the preferential etching of inversion domains (IDs) beneath the pits. However, Cl₃ addition to the Ar sputtering gas has the potential to suppress the formation of nuclei for IDs at the initial growth stage. Here, the effect of added Cl₃ gas to Ar sputtering gas on the AlN interface was elucidated.

Figure 8 shows the GaN surface morphology observed using SEM after 1 min of growth with and without Cl₂. The flow rates of N₂ and H₂ gases were 9 and 1 sccm, respectively. Nuclei with diameters of tens of nanometers were initially grown on the AlN surface without chlorine. In contrast, a surface flattened by the bridging of nuclei was observed by the addition of chlorine.

To understand the initial growth with Cl₂, the interface region of AlN/GaN was observed using HRTEM. The hexagonal ordering of Ga and N was confirmed in the grown film from the bright field TEM image shown in Figure 9a.

Chlorine atoms seem to be absent in the GaN surface grown in the c axis direction. Ga polarity was observed in the initial growth stage, as reported for the MBE growth of GaN on sapphire substrates using an AlN buffer layer. The c and a axis lattice constants determined from the TEM image were 5.43 and 3.36 Å, respectively, which are 5 to 6% larger than the literature values of 5.17 and 3.18 Å, which is considered to be due to the instability of the acceleration voltage and the magnetic field with TEM imaging. Threading dislocations were observed in the grown GaN film at intervals of tens of nanometers, as shown in Figure 9b. Nuclei with sizes of tens of nanometers grown at 62° to the surface were also observed on the surface of the AlN substrate. The heights of the nuclei were in the range of 30–50 nm.

Nanoscale nuclei are formed initially, even in the presence of chlorine, as considered from the dislocations in the film with the same intervals as the nuclei diameters. The bridging of each nucleus was also presumably enhanced by the preferential etching of terminated nitrogen atoms on the nucleus surface when a nucleus encounters another nucleus after the growth, the chlorinated Ga-rich surface with a high surface energy promotes the agglomeration of these nuclei. The obliquely grown nucleus at 62° indicates a surface with the GaN(1011) direction, which was considered to be originated from the defects on the AlN surface.

Figure 10 shows SEM images of the GaN surfaces grown with Cl₂ for 1 h at various N₂ flow rates from 5 to 20 sccm and with H₂ flow rates of 0.6 to 2.2 sccm to the ICP source. GaN growth without pit formation was achieved in every case. Hillocks were frequently observed in the macroscopically flat areas of the surface grown at a N₂ flow rate of 15 sccm. The hillock shape was a triangular prism with sizes around 350 × 1100 nm and a height of around 200 nm. Smaller hillocks of around 300 × 800 nm and a height of around 100 nm were observed in the surface grown at a N₂ flow rate of 20 sccm. On the other hand, flat surfaces without hillocks were obtained at lower N₂ flow rates. A slightly roughened surface with droplets was observed when the films were grown at a N₂ flow rate of 5 sccm.
The appearance of hillocks at higher N\textsubscript{2} flow rates is due to the nuclei that survived during growth with etching. The formation of hillocks is typically influenced by the supply ratio of N/Ga. In previous studies on the MBE growth of GaN on sapphire substrates at low growth temperatures below the sublimation temperature of 750 °C, pyramid-shaped hillocks were formed on a flat GaN surface under N-rich conditions.\textsuperscript{15} The formation of hillocks resulted from the higher growth rate of IDs with the opposite polarity. The hillock shapes in the present work were slightly different due to the different substrates. The samples grown with excess Ga in ref\textsuperscript{15} were free of hillocks, as was the case with lower N\textsubscript{2} flow rates in the present work. The droplet formation at a N\textsubscript{2} flow rate of 5 sccm indicates that the effect of nitrogen removal by chlorine plasma overcame Ga-nitridation with a lesser supply of atomic nitrogen.

Figure 11 shows XRD 2θ/ω scan profiles for GaN films grown at various N\textsubscript{2} flow rates. GaN(10\bar{1}1) diffraction peaks were intensified at N\textsubscript{2} flow rates of 15 and 20 sccm, but were decreased to less than 1/20th by a decrease in the N\textsubscript{2} flow rate from 15 to 9 sccm. In contrast, epitaxial GaN(0002) peak intensities were increased with a decrease in the N\textsubscript{2} flow rate. At a N\textsubscript{2} flow rate of 20 sccm, a shoulder appeared on the lower angle side of the GaN(0002) and GaN(0004) peaks (Figure 11). Small XRD peaks at 44° due to a gallium oxynitride spinel phase appeared because the system was contaminated by a trace amount of oxygen.

From the intensified GaN(10\bar{1}1) diffraction peaks at higher N\textsubscript{2} flow rates, the hillocks were grown in the GaN(10\bar{1}1) direction, as observed in the TEM images. The shoulders of the GaN(0002) and GaN(0004) peaks for a N\textsubscript{2} flow rate of 20 sccm indicated the coexistence of two phases along the direction normal to the surface, i.e., the shoulders were due to the initially grown GaN(0001) grains distorted by hillock formation. The slightly roughened surface with droplets formed at a N\textsubscript{2} flow rate of 5 sccm could be caused by the promotion of chlorine etching and the suppression of nitridation. In the case of PSD, similar droplets were formed on the grown GaN surface at lower N\textsubscript{2} flow rates.\textsuperscript{13}

Figure 12 shows XRD 2θ/ω scans of GaN films grown with or without H\textsubscript{2}/Cl\textsubscript{2}. The flow rate to the ICP source was maintained at 10 sccm. Then, 10% of H\textsubscript{2} was added in the conditions with H\textsubscript{2}. GaN(0002) and GaN(0004) peaks were intensified with H\textsubscript{2}. The FWHMs for GaN(0002) and GaN(0004) peaks were narrowed from 0.28 to 0.22° and from 0.56 to 0.26°, respectively with the addition of Cl\textsubscript{2}. A GaN(10\bar{1}0) peak was found without H\textsubscript{2}/Cl\textsubscript{2}. A GaN(10\bar{1}1) peak was found in every cases. The peak was decreased with addition of H\textsubscript{2} and further decreased with the addition of Cl\textsubscript{2}.

The intensified GaN(0002) and GaN(0004) peaks with H\textsubscript{2} indicate the growth to the GaN(0001) direction was promoted due to the enhanced Ga migration. The narrower FWHMs for the GaN(0002) and GaN(0004) peaks with Cl\textsubscript{2} are attributed to the flatly grown surface at the initial growth stage. The etching by hydrogen atoms suppressed the growth of IDs with the GaN(10\bar{1}0) and GaN(10\bar{1}1) surfaces. Considered from the smallest peak of GaN(10\bar{1}1) with Cl\textsubscript{2}, the further etching of the GaN(10\bar{1}1) surface was also promoted at the initial growth stage, even though the effect was limited at the N\textsubscript{2} flow rate as low as 9 sccm. Figure 13 summarizes the growth rates for GaN(0001), hillocks, and the N/Ga supply ratio as a function of the N\textsubscript{2} flow rate. The growth rate of hillocks at a N\textsubscript{2} flow rate of 9 sccm was estimated from TEM observations, and the rates at N\textsubscript{2} flow rates over 15 sccm were evaluated from cross-sectional SEM images. A maximum GaN(0001) growth rate of 0.88 μm h\textsuperscript{-1} was obtained at a N\textsubscript{2} flow rate of 9 sccm. The growth rate was
decreased to 0.54 μm h⁻¹ by an increase in the N₂ flow rate to 20 sccm and was decreased to 0.73 μm h⁻¹ by a decrease in the N₂ flow rate to 5 sccm. The growth of hillocks was suddenly enhanced at a N₂ flow rate of 15 sccm.

In our previous report, GaN growth was enhanced by an increase in the N₂ flow rate under high temperature (670 °C) conditions because the rapid nitridation of supplied Ga inhibited chlorine etching.³⁷ For growth at 600 °C with a slight etching effect, the formation of hillocks with IDs was enhanced at higher N₂ flow rates. The slower growth rates of GaN(0001) at higher N₂ flow rates indicate that the supplied Ga was used for the formation of IDs and the regions were preferentially etched by chlorine precursors. Chlorine precursors also enhanced the etching of Ga supplied onto the growth surface at a low N₂ flow rate of 5 sccm, which resulted in slightly slower growth of GaN(0001). Consequently, an abundant or lesser supply of atomic nitrogen decreased the growth rates of GaN(0001).

If all Ga supplied onto the substrate surface could be converted to GaN, then the flux of Ga was estimated to be 1.2 × 10¹⁵ cm⁻² s⁻¹ at a N₂ flow rate of 9 sccm. From these results, the suitable supply ratio of N to Ga for flat growth was estimated to be around 53 with 0.5% chlorine added to Ar at a H₂ flow ratio of 10% as gases for nitridation and at a growth temperature of 600 °C. The order is almost the same as that for MBE growth evaluated from the lifetimes of radicals determined by optical diagnostics.³⁵

To achieve a detailed understanding of the etching effect, GaN films were grown by changing the mesh-substrate distance to 25 or 35 mm with the addition of chlorine and hydrogen. Under all conditions, the plasma was slightly diffused from the mesh plates. The morphologies for each mesh-substrate distance are shown in Figure 14. Columnar growth was observed in both samples. The growth rates for mesh-substrate distances of 25 and 35 mm were 1.28 and 1.10 μm h⁻¹, respectively.

The density of neutral species such as atomic chlorine or GaCl⁺ in the vicinity of the substrate surface is considered to be unaffected by the change in the mesh-substrate distance because the chlorine partial pressure was sufficiently low at 10⁻³ Pa for the recombination of atomic chlorine to Cl₂ by three-body collisions.⁴⁶ On the other hand, the flux of diffused chlorine ions from the mesh plate to the substrates could be increased with a decrease in the mesh-substrate distance. The dominant ions in the chlorine plasma are assumed to be Cl₂⁺, as considered from the growth pressure and the output power of the plasma.³⁷ The intrusion length of chlorine ion into GaN crystals was over 0.7 nm, even at a typical self-bias voltage of 20 eV, as calculated by Monte Carlo simulation using the stopping and range of ions in matter (SRIM) package.³⁸ The chlorinated surface on nuclei with high affinity enhanced the bridging of initial nuclei.

Figure 15 shows a summary of the low-temperature growth of GaN with the addition of Cl₂ to the Ar sputtering gas. The growth of nuclei for IDs on AlN is suppressed relatively selectively by chlorine ion etching, which leads to the flat growth. The nuclei grown with GaN(0001) easily bridge each other; therefore, flat growth is enhanced, even at the initial growth stage.

As a result, a GaN(0001)-dominant surface is obtained at a N/Ga supply ratio of 53. The growth of hillocks is enhanced at a N/Ga supply ratio of over 80 because the etching effect of nuclei of hillocks is limited.

Therefore, precise control of Cl/H/N/Ga in a dual-source sputtering system causes the GaN surface to grow flat with high crystallinity, even at lower temperatures.

4. CONCLUSIONS

The roles of atomic nitrogen/hydrogen in GaN film growth were examined for a chemically assisted sputtering system with separate plasma sources for sputtering of Ga and nitridation at a growth temperature of 600 °C under a pressure of 2 Pa. With the appropriate addition of H₂ to the nitrogen plasma source, the lateral growth was enhanced due to the elongated Ga diffusion length on the GaN growth surface. From the atomic nitrogen/hydrogen fluxes measured by the VUVAS method, the suitable H/N flux ratio to enhance lateral growth was determined to be around 1.9. Droplet formation was observed at higher H/N flux ratios over 2.9 because N atoms on the GaN growth surface were forcibly removed by atomic hydrogen. A flat growth surface without pits was achieved by the addition of Cl₂ to the Ar sputtering gas because the chlorine ions etch the nuclei of IDs and bridged the nuclei grown on the AlN substrate, despite the further increase of etching by chlorine ions. It was estimated that the supply ratio of N/Ga to suppress droplet or hillock formation was 53. These results indicate that flatter and higher crystalline GaN films can be grown using two plasma sources of chlorine-added argon plasma and hydrogen-added nitrogen plasma at low temperatures.

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REFERENCES

(1) Maruska, H. P.; Tietjen, J. J. The preparation and properties of vapor-deposited single-crystalline GaN. Appl. Phys. Lett. 1969, 15, 327–329.

(2) Amano, H.; Sawaki, N.; Akasaka, I.; Toyoda, Y. Metalorganic vapor phase epitaxial growth of a high quality GaN film using an AlN buffer layer. Appl. Phys. Lett. 1986, 48, 353.

(3) Nakamura, S. GaN growth using GaN buffer layer. Jpn. J. Appl. Phys. 1991, 30, L1705.

(4) Hovel, H. J.; Cuomo, J. J. Electrical and optical properties of rf-sputtered GaN and InN. Appl. Phys. Lett. 1972, 20, 71.

(5) Lakshmi, E.; Mathur, B.; Bhattacharya, A. B.; Bhargava, V. P. The growth of highly resistive gallium nitride films. Thin Solid Films 1980, 74, 77.

(6) Zhang, C. G.; Bian, L. F.; Chen, W. D.; Hsu, C. C. Effect of growth conditions on the GaN thin film by sputtering deposition. J. Cryst. Growth 2007, 299, 268.

(7) Knox-Davies, E. C.; Shannon, J. M.; Silva, S. R. P. The properties and deposition process of GaN films grown by reactive sputtering at low temperatures. J. Appl. Phys. 2006, 99, 073503.

(8) Schieber, Z. S.; Leite, D. M. G.; Bortoleto, J. R. R.; Lisboa-Filho, P. N.; da Silva, J. H. D. Effects of substrate temperature, substrate orientation, and energetic atomic collisions on the structure of GaN films grown by reactive sputtering. J. Appl. Phys. 2013, 114, 183515.

(9) Leite, D. M. G.; Pereira, A. L. J.; da Silva, L. F.; Dias da Silva, J. H. Nanocrystalline GaN and GaN:H films grown by RF-magnetron sputtering. Braz. J. Phys. 2006, 36, 978.

(10) Shon, J. W.; Oh, J.; Ueno, K.; Kobayashi, A.; Fujioka, H. Fabrication of full-color InGaN-based light-emitting diodes on amorphous substrates by pulsed sputtering. Sci. Rep. 2014, 4, 5325.

(11) Kobayashi, A.; Ohta, J.; Fujioka, H. Pulsed sputtering epitaxial growth of m-plane InGaN lattice-matched to ZnO. Sci. Rep. 2017, 7, 12820.

(12) Flauta, R.; Kasuya, T.; Ohachi, T.; Wada, M. Thin film formation of gallium nitride using plasma-sputter deposition technique. Sci. Diliman 2003, 15, 57.

(13) Tanide, A.; Nakamura, S.; Horikoshi, A.; Takatsuji, S.; Kohno, M.; Kinose, K.; Nadahara, S.; Nishikawa, M.; Ebe, A.; Ishikawa, K.; Hori, M. Hetero-epitaxial growth of GaN film by the combination of magnetron sputtering with Ar/Cl2 gas mixtures and a separate supply of nitrogen precursors from a high density radical source. Jpn. J. Appl. Phys. 2019, 58, SAAF04.

(14) Miyazaki, T.; Takada, K.; Adachi, S.; Ohtsuka, K. Properties of radio-frequency-sputter-deposited GaN films in a nitrogen/hydrogen mixed gas. J. Appl. Phys. 2005, 97, No. 093516.

(15) Myers, T. H.; Hirsch, L. S.; Romano, L. T.; Richards-Babb, M. R. Influence of growth conditions, inversion domains, and atomic hydrogen on growth of (0001) GaN by molecular beam epitaxy. J. Vac. Sci. Technol., B 1998, 16, 2261.

(16) Setsuhera, Y.; Takenaka, K.; Ebe, A.; Nishisaka, K. Production and control of large-area plasma for meters-scale flat-panel-display processing with multiple low-inductance antenna modules. Plasma Processes Polym. 2007, 4, S628.

(17) Takashima, S.; Hori, M.; Goto, T.; Kono, A.; Ito, M.; Yoneda, K. Vacuum ultraviolet absorption spectroscopy employing a micro-discharge hollow-cathode lamp for absolute density measurements of hydrogen atoms in reactive plasmas. Appl. Phys. Lett. 1999, 75, 3929.

(18) Tada, S.; Takashima, S.; Ito, M.; Hori, M.; Goto, T.; Sakamoto, Y. Measurement and control of absolute nitrogen atom density in an electron-beam-excited plasma using vacuum ultraviolet absorption spectroscopy. J. Appl. Phys. 2000, 88, 1756.

(19) Nagai, H.; Takashima, S.; Hiramatsu, M.; Hori, M.; Goto, T. Behavior of atomic radicals and their effects on organic low dielectric constant film etching in high density NF3, H2 and NH3 plasmas. J. Appl. Phys. 2002, 91, 2615.

(20) Lieberman, M. A.; Lichtenberg, A. J. Principles of Plasma Discharges and Materials Processing, 2nd ed.; Willey-Interscience Publication: New York, 2005; p 37.

(21) Lekhal, K.; André, Y.; Trassoudaine, A.; Gil, E.; Avit, G.; Celliers, J.; Castelluci, D. Exceptional crystal-defined bunched and hyperbunched GaN nanorods grown by catalyst-free HVPE. Cryst. Growth Des. 2012, 12, 2251.

(22) Yeh, Y.-H.; Chen, K.-M.; Wu, Y.-H.; Hsu, Y.-C.; Lee, W.-J. Hydrogen etching of GaN and its application to produce free-standing GaN thick films. J. Cryst. Growth 2011, 333, 16.

(23) Hamilton, J. R.; Tennyson, J.; Huang, S.; Kushner, M. J. Calculated cross sections for electron collisions with NF3, NF2 and NF with applications to remote plasma sources. Plasma Sources Sci. Technol. 2017, 26, No. 065010.

(24) Brandt, O.; Yang, H.; Ploog, K. H. Surface kinetics of zinc-blende (001) GaN. GaN. Phys. Rev. B 1996, 54, 4432.

(25) Stepanova, M.; Dew, S. K. Estimates of differential sputtering yields for deposition applications. J. Vac. Sci. Technol., A 2001, 19, 2805.

(26) Wu, C.; Yu, J.; E, Y.; Luo, Y.; Hao, Z.; Wang, J.; Wang, L.; Sun, C.; Xiong, B.; Han, Y.; Li, H. Model for low-temperature growth of gallium nitride. Cryst. Growth Des. 2016, 16, 5023.

(27) Chen, S.; Lu, Y.; Kometani, R.; Ishikawa, K.; Kondo, H.; Tokuda, Y.; Sekine, M.; Hori, M. Photoluminescence recovery by in-situ exposure of plasma-damaged n-GaN to atomic hydrogen at room temperature. AIP Adv. 2012, 2, No. 022149.

(28) Grandusky, J. R.; Jindal, V.; Raynolds, J. E.; Guha, S.; Shahrabipour-Sardkh, F. Density functional calculations of the strain effects on binding energies and adatom diffusion on (0001) GaN surfaces. Mater. Sci. Eng., B 2009, 158, 13.

(29) Liu, Z.; Pan, J.; Kako, T.; Ishikawa, K.; Takeda, K.; Kondo, H.; Oda, O.; Sekine, M.; Hori, M. Suppression of plasma-induced damage on GaN etched by a Cl2 plasma at high temperatures. Jpn. J. Appl. Phys. 2015, 54, 06GB04.
(30) Shen, X. Q.; Ide, T.; Cho, S. H.; Shimizu, M.; Hara, S.; Okumura, H.; Sonoda, S.; Shimizu, S. Essential change in crystal qualities of GaN films by controlling lattice polarity in molecular beam epitaxy. Jpn. J. Appl. Phys. 2000, 39, 2.

(31) Xu, K.; Yano, N.; Jia, A. W.; Yoshikawa, A.; Takahashi, K. Polarity control of GaN grown on sapphire substrate by RF-MBE. J. Cryst. Growth 2002, 237-239, 1003−1007.

(32) Sumiya, M.; Fuke, S. Review of polarity determination and control in GaN. MRS Internet J. Nitride Semicond. Res. 2004, 9, 1.

(33) Fujikane, M.; Inoue, A.; Yokogawa, T.; Nagao, S.; Nowak, R. Mechanical properties characterization of c-plane (0001) and m-plane (1010) GaN by nanoindentation examination. Phys. Stat. Solid. C 2010, 7, 1798.

(34) Steib, F.; Remmele, T.; G{"u}link, J.; Fundling, S.; Behres, A.; Wehmann, H.-H.; Albrecht, M.; Str{"a}ßburg, M.; Lugauer, H. J.; Waag, A. Defect generation by nitrogen during pulsed sputter deposition of GaN. J. Appl. Phys. 2018, 124, 175701.

(35) Sato, M. Nitrogen radical densities during GaN growth by molecular beam epitaxy, plasma-assisted metalorganic chemical vapor deposition, and conventional metalorganic chemical vapor deposition. Solid-State Electron. 1997, 41, 223.

(36) van Roosmalen, A. J.; Baggerman, J. A. G.; Brader, S. J. H. Dry Etching for VLSI; Plenum Press: New York, 1991; p 56.

(37) Donnelly, V. M.; Kornblit, A. Plasma etching: Yesterday, today, and tomorrow. J. Vac. Sci. Technol., A 2013, 31, No. 050825.

(38) Ziegler, J. F.; Ziegler, M. D.; Biersack, J. P. SRIM - The stopping and range of ions in matter. Nucl. Instrum. Methods Phys. Res. B 2010, 268, 1818.