Nitride film Growth by Near-Atmospheric Nitrogen Plasma-Assisted Chemical Vapor Deposition

T. Nagata, M. Haemori, J. Anzai*, T. Uehara* and T. Chikyow
National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0044 Japan,
Fax: 81-29-860-4916, e-mail: NAGATA.Takahiro@nims.go.jp
* Sekisui Chemical Co., Ltd., Wadai, Tsukuba, Ibaraki 300-4292, Japan

We have demonstrated the growth of the GaN film by near-atmospheric plasma-assisted chemical vapor deposition (AP-CVD). Pure nitrogen plasma can be generated stably using an alternating pulsed voltage system that applies an alternating pulsed voltage between two parallel plate electrodes. Using this plasma as a nitrogen source, we can obtain crystalline GaN film above 330°C. Blow 330°C, GaN film was amorphous structure due to carbon contamination. To overcome this problem, hydrogen diluted nitrogen gas was used as reagent gas. Optical emission spectrum measurement revealed that the hydrogen diluted nitrogen near-atmospheric plasma decomposed triethylgallium (TEG), which was used as Ga metal precursor, even at room temperature. Using this plasma as a nitrogen source, deposited GaN films showed the epitaxial growth on a sapphire substrate above the growth temperature of 170°C. From the results obtained, we found that AP-CVD has a great potential of being employed in GaN film fabrication under high nitrogen partial pressure and at low temperature.

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

1. INTRODUCTION
Nitride materials are promising materials for high-frequency microwave devices, high-voltage rectifying diodes, and optical devices[1,2]. Potential new applications of nitride materials currently center on solar cells and catalysis[3,4]. To realize these new applications as practical devices, large-scale and low-temperature nitride thin film growth processes are required. If nitride films can be deposited at below 200°C, flexible materials such as polyethylene naphthalate can be used as substrates.

To achieve the large-scale and low-temperature nitride film growth, we have proposed near-atmospheric plasma-assisted chemical vapor deposition (AP-CVD) [5]. At atmospheric pressure region, stable arcless nitrogen plasma generation is difficult. Corona discharging and glow discharging using helium are known to occur in nitrogen plasma at atmospheric pressure. These methods are not suitable for the crystal growth of GaN due to the damage caused by the high-gas-temperature plasma and defects brought about by low nitrogen species density. Some of the authors of this paper have developed a plasma source that maintains stable discharge using various gases such as nitrogen and oxygen without the use of noble gas by applying an alternating pulsed voltage between two parallel-plate electrodes at atmospheric pressure[6]. On the pure nitrogen plasma investigation reported by Hayakawa et al. and us[5,7], this plasma is a high-density and low-temperature plasma. Furthermore, optical emission spectroscopy revealed that the main constituent of the nitrogen plasma is the \(N_2\) second positive system (denoted “2+”), which is suitable as a nitrogen source for the nitride film growth. Herman’s infrared system (denoted “H IR”)[8], which is rarely observed in low-pressure plasma and excited atomic nitrogen, was also observed. Additionally, no spectra due to the \(N_2\) first negative series (denoted “1-”), which is an ionic molecular species that causes film damage[9], were observed.

The conventional nitrogen sources for metalorganic chemical vapor deposition (MOCVD) are ammonia gas or nitrogen plasma[10-13]. 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 ammonia’s high thermal stability[14] and a large waste gas cleaner system. In the case of the nitrogen plasma, GaN films can be fabricated at lower temperatures (~700°C), however it is difficult to achieve a balance between deposition under high nitrogen partial pressure and that under high deposition rates for these plasma sources, which are carried out at pressures ranging from \(10^{-1}\) to \(10^{-4}\) Pa. Compared with these methods, our plasma source generates a large number of nitrogen species without requiring an ammonia process or high vacuum system. Our previous report showed that the GaN grew on a sapphire substrate epitaxially at 400°C, and crystallized at 330°C using trimethylgallium (TMG) as the metal precursor[5]. At temperatures below 330°C, GaN film did not show a crystalline phase, due to carbon contamination. Using triethylgallium (TEG), of which the decomposition temperature is lower than that of TMG by 100°C, the crystalline temperature decreased from 330°C to 230°C. However the problem has been unsolved[15].

In this paper, we report the influence of hydrogen on the low-temperature growth of GaN film by AP-CVD.
Because hydrogen plasma is known as a cleaning source for substrates, and decomposes C-C bonds\cite{16,17}, making it suitable for eliminating the carbon contamination during the GaN film growth.

2. EXPERIMENT

A (0001) sapphire with a thickness of 0.5 mm was used as the substrate. Figure 1 shows a schematic illustration of the AP-CVD system. All experiments were carried out in a vacuum chamber with a background pressure of $2 \times 10^{-4}$ Pa. Two parallel plate electrodes are separated by a 1 mm uniform gap. Nitrogen plasma was generated by alternately applying pulsed voltages, varied from 2 to 8 kV at a frequency of 30 kHz. Nitrogen diluted with hydrogen gas was used as the carrier gas and reactive gas. The gas ratio was controlled by mass flow controllers. TEG was used as the Ga metal source precursor. TEG was carried by the hydrogen diluted nitrogen gas at a flow rate of 0.5 sccm. TEG with the carrier gas was mixed with the reactive gas, after which all gases were led to the chamber. The discharge pressure was 40 kPa, and the substrate temperatures were varied from room temperature to 400 °C. 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 OES to a photonic multichannel spectral analyzer (C7473, Hamamatsu), from which the optical spectra over the range of 200–900 nm were obtained. The crystalline structure was identified by x-ray diffraction (XRD). The XRD measurement system has a 5-kW rotating anode Cu target and a high-resolution 2D detector (Bruker AXS, D8 Discover Super Speed with GADDS). 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. The crystallinity of the film was evaluated at the full width at half maximum value of the $\chi$-rocking curve ($\chi$-FWHM).

2. RESULTS AND DISCUSSION

OES was used to detect electronically excited atomic and molecular species in the N$_2$ and hydrogen diluted N$_2$ ($H_2/N_2$) plasmas at room temperature (RT). Figure 2 (a) compares the OES of an N$_2$ plasma with that of $H_2/N_2$ plasmas (5 %- and 52 %-hydrogen). In the N$_2$ plasma, peaks associated with the N$_2$ 2+ at emission wavelengths of 296, 315, 337, 358, 380, 400 and 427 nm, and HIR at 752, 783, and 806 nm are observed\cite{8,18}. In contrast, in the $H_2/N_2$ plasma, plasma peaks associated with the N$_2$ 2+, N$_2$ first positive (denoted “1+”) at 541, 594, 661, 773 and 889 nm, and the N$_2$ 1- at 391 nm are observed. Additionally, hydrogen atomic peaks via the Balmer line (denoted “H*”) at 656.3 nm were observed. No HIR system was observed in the $H_2/N$ N$_2$ plasma. The hydrogen dilution alters the plasma species. Although intensity ratio of the N$_2$ 1+ system to the N$_2$ 2+ system, and H* to the N$_2$ 2+ system increased with increasing hydrogen concentration, the plasma species showed no hydrogen concentration dependence. The excitation energies of N$_2$ 2+ and HIR are above 11 eV. Relatively, the high excitation threshold of H* is ~ 10 eV\cite{19} and smaller than that of N$_2$ 2+ and HIR. The hydrogen dilution provided a pathway to N$_2$ generation via Penning ionization, as in a He/N plasma\cite{20}. Due to this pathway, generation of N$_2$ 1+ and N 1-, whose excitation...
thresholds are excitation energies (~7 eV) are smaller than that of H*, were enhanced. As a result, the threshold applied electric power drastically decreased after the hydrogen dilution as shown in Fig 2(b).

Figure 3 shows the OES of the N2 and 5 %-H2/N2 plasma including TEG generated at room temperature. Emission peaks of 386, 415 and 419 nm, corresponding to cyanogens (CNs)[8], were observed in the N2 plasma. After the hydrogen dilution, the emission peaks of CN disappeared, and gallium ion emission (denoted “GaI”) peaks at 403 and 417 nm[21] were observed. On increasing the hydrogen concentration, the ratio of Ga to N2 2+ increased and decreased above the 42 % hydrogen concentration as shown in Fig. 3(b). These results suggest that hydrogen dilution reduces carbon species and enhances the excitation of Ga. However, in the H2/N2 plasma, N+2 1- was also observed. On increasing the hydrogen concentration, the ratio of the N+2 1- to N2 2+ increased monotonically. Using an H2/N2 plasma should thus reduce carbon contamination, but ionic species affected the crystal growth of GaN film.

Fig. 3. (a) OES of N2 and 5 %-H2/N2 plasmas including TEG generated at room temperature. (b) hydrogen content dependence intensity ratio of GaI to N2 2+ (solid circle), and N+2 1- to N2 2+ (open circle).

To investigate the effect of hydrogen dilution on the GaN film growth, GaN film was deposited at several hydrogen concentrations. Figure 4 (a) shows the hydrogen concentration dependences of Ga (0002) reflection intensity and its χ-FWHM. The χ-FWHM and peak intensity had peaks around the hydrogen concentration of 42 %, indicating that the 42 %-H2/N2 plasma provided the high crystalline GaN film. This consisted with the GaI peak changing behavior against the hydrogen concentration. These results suggested that excess hydrogen enhanced the excitation of N+2 1- and inhibited the GaN film growth.

Fig. 4. (a) 0-2θ XRD patterns of GaN films deposited using N2, 5 %-, and 57 %-H2/N2 plasmas. (b) hydrogen concentration dependences of Ga (0002) reflection intensity (solid circles) and χ-FWHM (open circles).

Using the 42 % H2/N2 plasma, the crystalline temperature decreased drastically. The deposited GaN films showed crystalline structures at above 55 °C as shown in Fig. 5(a). To identify the epitaxial growth temperature, x-ray pole figure measurements were also performed. The X-ray pole figure was measured with 3° intervals used as scan steps for the φ angle. The range of 2θ and ψ angles are simultaneously detected from 30° to 60° and from 25° to 75°, respectively. The GaN film grown at 170 °C showed six fold symmetric image as shown Fig. 5(b). The value of ψ was 39° for the {4110}− plane of (0001) sapphire. Peaks with six-fold symmetry with 60° in the φ scan can be seen at ψ = 62° for the {1011} plane of GaN. The GaN unit cell grows with its a-axis rotated by 30° from the a-axis of (0001) sapphire, and the epitaxial relationships between GaN and c-sapphire are (0001) GaN || (0001) sapphire and [0121]−− GaN || [1001]− sapphire. This implies that a hexagonal GaN film had grown epitaxially on the c-sapphire substrate with its c-axis normal to the substrate surface. Finally, by using AP-CVD with the hydrogen diluted...
Nitrogen as a reactive gas, GaN thin films grew on sapphire substrate epitaxially at above 170 °C.

Fig. 5. (a) ω-2θ XRD pattern of GaN film deposited at 55 °C using 42 %-H2/N2 plasma. X-ray pole figures for (b) the GaN film on the (0001) sapphire substrate grown at 170 °C and (c) theoretical image.

4. CONCLUSIONS
We investigated the influence of hydrogen on N2 plasma at atmospheric pressure region and low-temperature growth of GaN film by AP-CVD. The hydrogen dilution reduced the carbon species in the N2 plasma, although N+2 was generated. Furthermore, the H2/N2 plasma decomposed the Ga metal source precursor and generated Ga ions even at room temperature. Using the hydrogen diluted nitrogen plasma, we have succeeded in epitaxially growing GaN films on the c-sapphire substrate at 170 °C and crystallizing GaN films at 55 °C. From the results obtained, we found that our process that uses AP-CVD has significant potential for use in GaN film fabrication at lower temperatures.

REFERENCES

(Received December 31, 2009; Accepted March 1 2010)