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Gallium nitride thin film deposition by MOCVD in microwave discharge

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The epitaxial growth of GaN film on the sapphire substrate, the surface of which was prenitrided, in the nitrogen-hydrogen microwave plasma with trimethyl gallium as precursor was investigated. The epitaxial growth of GaN film was identified at the temperture as low as 890K by means of X-ray diffraction, X-ray rocking curve, while the GaN deposition was not identified at the same substrate temperature when the microwave plasma was not applied to the gas mixtures. The activation energy of the growth reaction of the GaN film was around 10^{-1} eV. Since the fragments of trimethyl gallium and NH radicals were identified in the plasma by optical emission spectroscopy, the precursor dissociation and excitation in the gas phase enhance the GaN epitaxial growth.

Key words: **gallium nitride, epitaxiar growth, microwave plasma MOCVD, Arrhenius plot**

1. INTRODUCTION

The gallium nitride (GaN) films as a light emitting diode (LED) have been prepared by means of metal organic chemical vapor deposition (MOCVD) with trimethyl gallium (TMG, $Ga(CH_3)_3$) and ammonia as gallium and nitrogen precursors of thermally heated sapphire substrate at higher tempertures [1]. In the thermal MOCVD, the deposition rate shows dependence on lower temperatures than 700K and little dependence on higher temperatures than 700K [2]. The kinetics of the GaN deposition is controlled by the surface reaction at lower tempertures followed by the mass-transfer reaction at higher temperatures. When the substrate is placed in the plasma and the GaN film is deposited in the plasma, the deposition reaction is expected to proceed at higher deposition rates at lower tempertures, because the active species are prepared in the plasma. For example, the GaN film deposited at relatively lower growth temperature of 600-800K by remote plasma enhanced chemical vapor deposition using plasma exited ammonia and $Ga(CH_3)_3$ as nitrogen and gallium source, respectively [3]. The activation energy for GaN growth was assingned to the dissociation of NH groups as the primary N-atom precursors in the surface reaction with adsorbed $Ga(CH_3)_3$ or its fragments. We have deposited GaN thin films at substrate temperatures as low as 500-700K in the nitrogen/hydrogen microwave discharge with $Ga(CH_3)_3$ as a gallium precursor [4]. The NH radicals and fragments of $Ga(CH_3)_3$ were identified in the plasma by optical emission spectroscopy (OES). The NH radical formation and the decompositon of $Ga(CH_3)_3$ in the plasma may be one of the reason for the lower deposition temperatures of GaN.

The effect of the substrate temperature on the deposition of GaN thin films on the substrate placed outside the microwave cavity was investigated varying the substrate temperature by external heating with the exposure to the plasma to avoid the change of the substrate temperature by the variation of plasma parameters. In the deposition of amorphous and polycrystalline GaN thin films on the fused silica substrate in the microwave plasma MOCVD, we deposited the amorphous films at 350-550 K and the polycrystalline films at 600-900 K, respectively. The activation energy was around 0.1 eV in both cases. Both the temperature and the activation energy were considerably lower than those in the other deposition procedures [5]. Thus the epitaxial growth of GaN films on sapphire substrate at lower substrate temperatures in the same way is expected. In the present paper, we apply the microwave plasma MOCVD method for the epitaxial growth of GaN thin films at lower substrate temperatures. The effect of the plasma on the deposition reaction is investigated with some plasma diagnostics.

2. EXPERIMENTAL

The apparatus used for the epitaxial growth of the GaN thin films is shown in Fig. 1. The electric furnace was placed outside the cavity to externally heat the sapphire substrate to vary the substrate temperature. Before the

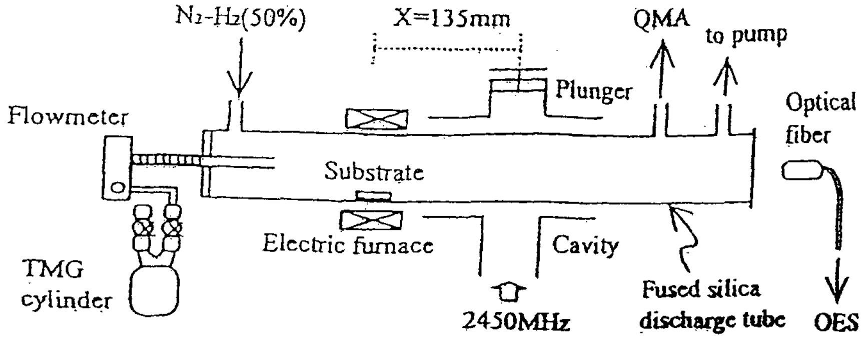

Fig. 1 Schematic diagram of the plasma MOCVD apparatus used for GaN film deposition.

GaN film deposition, the surface of sapphire substrate was nitrided in the N_2/H_2 (1:1) plasma in short time to form the buffer layer of AlN. $Ga(CH_3)_3$ was introduced into the N_2/H_2 (1:1) plasma. The discharges were continued for the period of 0.5-4 h at the substrate temperature of 380-900 K. Other deposition conditions were as follows: the flow rate of $Ga(CH_3)_3$; 0.003 dm^3h^{-1}, the pressure; 650 Pa, the electric power; 150 W of 2.45 GHz. The deposits were identified by means of X-ray diffraction (XRD), X-ray rocking curve (XRC), and X-ray photoerectron spectroscopy (XPS). The optical properties, such as refractive index, UV/Vis spectra, and photoluminescence (PL) spectra were measured. From the thickness of the deposited films, the deposition rates were estimated. An optical emission spectroscopy (OES), quadropole mass analysis (QMA) and electric double probe method were applied to diagnose the plasma.

3. RESULTS

(1) Deposition and identification of the deposits.

The dependence of electron temperature (kTe) on the position in the cavity was measured in the nitrogen-hydrogen plasma generated at the plasma power of 150W. The kTe at the position outside the cavity, where the substrate was placed, was around 4 eV. The substrate was covered with plasma and the activated species in the plasma would contribute to the GaN film deposition.

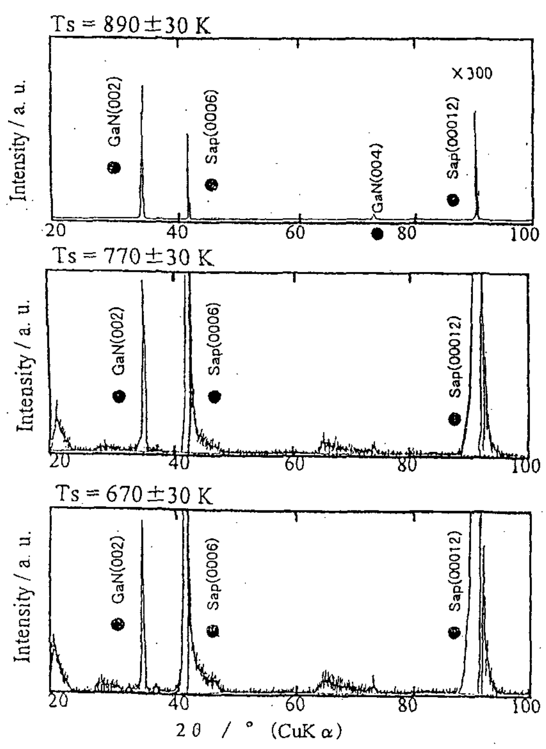

Fig. 2 X-ray diffraction patterns of the deposits in the microwave plasma (θ -2 θ) varying temperature.

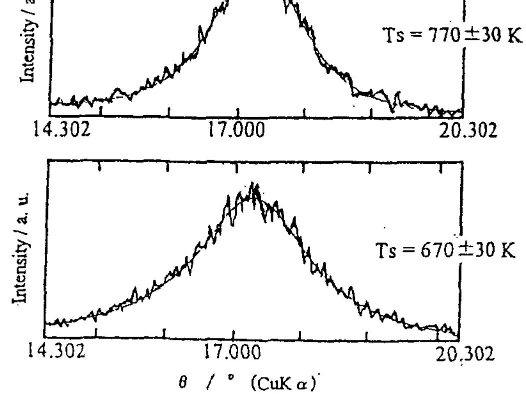

Fig. 3 X-ray rocking curve of the samples in Fig. 2.

XRD patterns (θ -2 θ) of the deposit on the sapphire substrate placed outside the cavity heated at several substrate temperatures are shown in Fig. 2. The c-axis oriented GaN films were obtained at higher temperatures than 670 K. When the deposition temperature was elevated to 890 K, the deposit was approximately the epitaxial single crystal film. X-ray rocking curve of respective deposits are shown in Fig. 3. The symmetrical patterns were obtained at the deposition temperature of 890K, even though the Δ ω was considerably wide. The epitaxial growth GaN film was obtained with microwave plasma CVD method at lower substrate temperature.

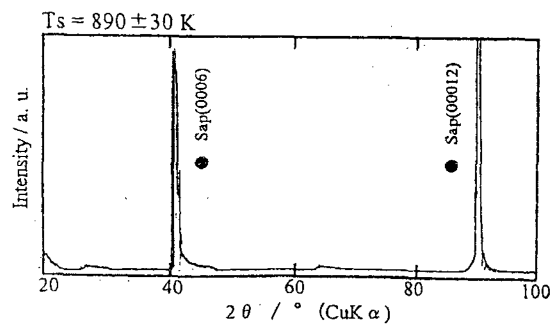

Fig.4 X-ray diffraction patterns of the deposit at 890 K without plasma.

X-ray diffraction patterns of the deposit at 890 K without the application of microwave discharge is shown in Fig. 4.

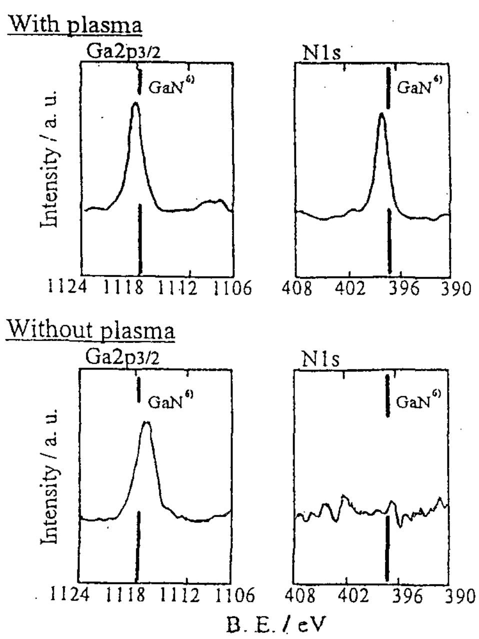

Fig. 5 X-ray photoelectron spectra of the deposits at 890K with or without plasma.

There are no patterns without those due to sapphire substrate. Comparing with the patterns at the same substrate temperature as shown in Fig. 4, the application of the microwave discharge assists the deposition of the epitaxial GaN film at lower deposition temperatures.

X-ray photoelectron spectra of the sample deposited at 890 K in the plasma are shown in Fig. 5 with those of the deposit without plasma at the same temperature. Slightly nitrogen excess GaN film was obtained with plasma, while the peak due to N1s electrons was not identified in the deposit without plasma.

(2) Characterization of the epitaxial growth GaN film

Some characters of the epitaxial growth GaN films were measured. The PL spectrum of the sample is shown in Fig. 6. The peak due to the PL was observed at around 400 nm. The refractive index of the deposited GaN was about 2.2. The formation of AlN layer of thickness of 50 nm was identified in the measurement of the refractive index. The absorption edge of visible light was around 400 nm and the band gap was 3.2 eV. These characters corresponded with those deposited in thermal MOCVD at higher temperatures.

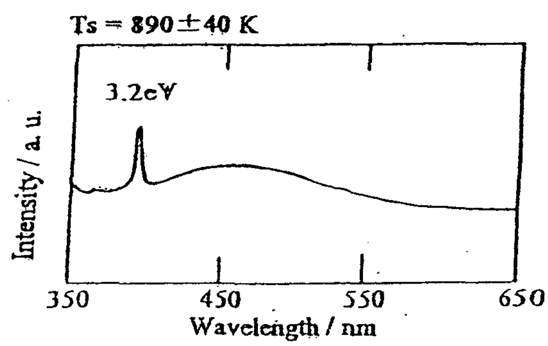

Fig.6 PL spectrum of GaN film deposited in the microwave plasma at 890 K.

4. DISCUSSION OF THE DEPOSITION REACTION AND THE ROLE OF THE PLASMA

The Arrhenius plot for the GaN film deposition reaction with $Ga(CH_3)_3$ as gallium precursor in the nitrogen-hydrogen microwave plasma on the sapphire substrate. The plots is shown in Fig. 7. The plot is linear and the activation energy (Ea) for the deposition of epitaxial GaN film was around 0.1eV. The activation energy was considerably lower than those in the other deposition procedures. The plots for the deposition of the GaN films in the remote controlled deposition in the rf discharge is shown in Fig. 7 as reference [3]. The mass-transport of precursor seems to be the rate limitting step. Moreover, the dissociation of precursors in the plasma would affect the deposition kinetics in the plasma assisted MOCVD of the GaN film.

As the deposition rate showed little dependence on the temperature and the value of Ea in the deposition of GaN films in the microwave plasma MOCVD was considerably smaller than those for the thermal MOCVD method, which was controlled by the surface reaction of the substrate. Thus the following deposition scheme is expected: $Ga(CH_3)_3$ would be dissociated into fragments in the microwave plasma and the deposition reaction of GaN film is proceeded by the recombination of the fragments of $Ga(CH_3)_3$ with N-precursors on the surface of the substrates.

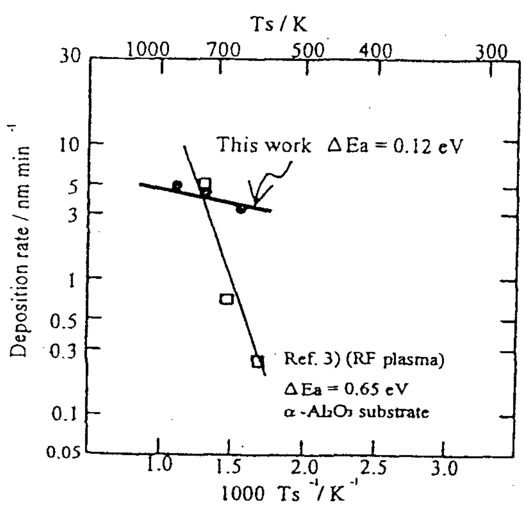

Fig. 7 Deposition rate of GaN films as afunction of substrate temperature (Ts).

The species formed in the plasmas were identified by means of OES. Optical emission spectra of the $Ga(CH_3)_3/N_2/H_2$ microwave plasma are shown in Fig. 8. Strong peaks due to NH radicals ($A^3\Pi_g$-$X^3\Sigma$) and N_2 molecules ($C^3\Pi_u$- $B^3\Pi_g$, $B^3\Pi_g$-$A^3\Sigma_g$) were observed in the spectra. These species easily dissociate and N atoms would be prepared in the plasma. Moreover, CN radicals and Ga atoms which were dissociation products of $Ga(CH_3)_3$ were identified in addition to NH radicals and N_2 molecules.

5. CONCLUSION

The epitaxial growth of GaN film on the sapphire substrate in the nitrogen-hydrogen plasma with trimethyl gallium as precursor was carried out. The epitaxial growth GaN film which was comparable with that deposited by thermal MOCVD at higher temperature was deposited at the temperature as low as 890 K. The activation energy of the growth reaction of the GaN film was around 10^{-1} eV. The activation and dissociation of the precursors in the plasma, which were diagnosed in the plasma, enhance the GaN film epitaxial growth.

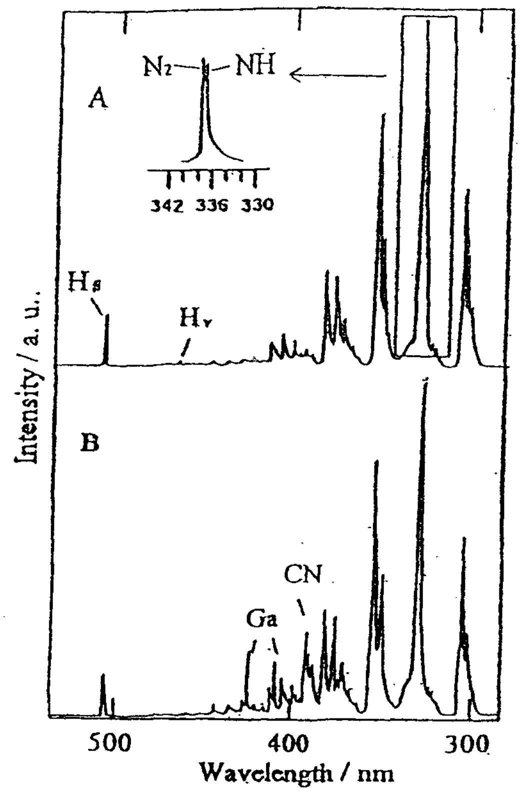

Fig. 8 Optical emission spectra from both pure nitrogen-hydrogen plasma (A) and nitrogen-hydrogen plasma with $Ga(CH_3)_3$ (B).

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