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Control of nitrogen flux for growth of cubic GaN on 3C-SiC/Si by RF-MBE

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Abstract

The enhancement of the production rate of nitrogen radical from a radio frequency (RF) discharge plasma is reported through the application of a DC magnetic field under RF-ECR (electron cyclotron resonance of RF) condition. High efficiency of the nitrogen radical production was realized by an optimum magnetic field for the resonance of about 0.5 mT for the electron energy of 2 eV for the 13.56-MHz discharge. The effect of controlling the divergence of the nitrogen radical flux by changing the orifice dimension was studied by measuring the color change of interference due to the film thickness. The aspect ratio of the orifice hole and the distribution of hole position determined the flux diversity. Combinatorial methodology, which realizes various III/V flux ratio without substrate rotation due to non-uniform flux, was used to study the effect of the III/V flux ratio to poly-type formation by photoluminescence. The cubic phase was grown under a stoichiometric condition of slightly Ga-rich side, with an III/V ratio of about one.

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1. Introduction

The cubic group III nitrides and their alloys, which are environmental friendly materials, are suitable materials for hybrid use with the present silicon technology due to its excellent property. Because of the meta-stable nature of the cubic

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phase (c-GaN), the hetero epitaxial growth on a cubic substrate such as 3C-SiC [1,2] is only the way to grow the cubic phase. No cubic bulk nitride crystals for the substrate of homo epitaxial growth are obtained. The growth method using molecular beam epitaxy (MBE) is suitable for growing cubic group III nitrides' devices by low temperature growth and ultra high vacuum (UHV) condition. To grow the group III nitrides with MBE successfully, a large and uniform flux of atomic nitrogen (N) radical is required. Early studies used an electron cyclotron resonance (ECR) type of microwave plasma discharge of 2.45 GHz (μ-ECR) to produce N radicals for c-GaN [3,4]. Ohtani et al. analyzed the μ-ECR plasma and minimized the ion production for the nitride epitaxy [5]. Hughes et al. compared two N plasma sources of μ-ECR-type and a radio frequency (RF)-type without the ECR condition [6]. They concluded that the RF plasma source produced the best quality of GaN because a large fraction of atomic N and first-positive series excited molecular N in contrast to the μ-ECR plasma source that mainly produced second-positive series excited molecular N_2 and molecular ions. Vaudo et al. also studied the two type plasma sources [7,8] and showed details of the atomic N emission lines [8]. Myers et al. compared several RF plasma cells such as an Oxford Applied Research source and an EPI Vacuum Unibulb source [9]. They showed that the smaller size of hole diameter, or aperture, of an orifice reduced the ion flux and increased the contribution from atomic N. The high efficiency of the production of atomic N could be realized at higher pressure with the small holes. A biasable grid was introduced to control the nitrogen species from an μ-ECR plasma source [10]. To increase the plasma excitation, the application of magnetic field in RF discharge is effective. The authors reported surface nitridation of Si to grow c-GaN [11]. They also improve the cubic substrate by carbonization using the alternating exposure method of Si and C_2H_2 through a jet nozzle [2].

In this report, we investigate how to enhance the RF discharge by applying a DC magnetic field under RF-ECR (electron cyclotron resonance of RF) conditions and how to control the atomic N flux by changing aperture dimension. The growth condition for c-GaN of III/V flux ratio was studied by a combinatorial methodology in which the III/V flux ratio was changed in one experiment without substrate rotation due to the flux non-uniformity of both Ga and N. Photoluminescence (PL) and interference color measurement were used to characterize grown c-GaN.

2. Experimental procedure

A VG80H MBE system equipped with a jet nozzle and an IRFS-501 RF N radical source made by Arios, Inc. was used. The external DC magnetic field was applied with an additional electromagnet for a new RF-ECR condition as shown in Fig. 1. Formation of atomic N flux using an induction coupling discharge was controlled usually by a discharge power (max. 500 W), flow of N_2 gas (max. 0.5 sccm), wall material of a discharge chamber (PBN), number of orifice holes of the discharge chamber (185 holes), a diameter of the orifice (0.2 mm), the thickness of the orifice (0.5 and 2 mm), the conductance of the orifice, and the application of a DC magnetic field. A CCD spectrometer (HR-2000, Ocean Optics, Inc.) was used to measure the spectrum of the discharge through a view port of the N-radical cell. The actual N atomic flux was calibrated from the film thickness after the growth. The thickness of c-GaN was obtained using spectroscopic reflectometry

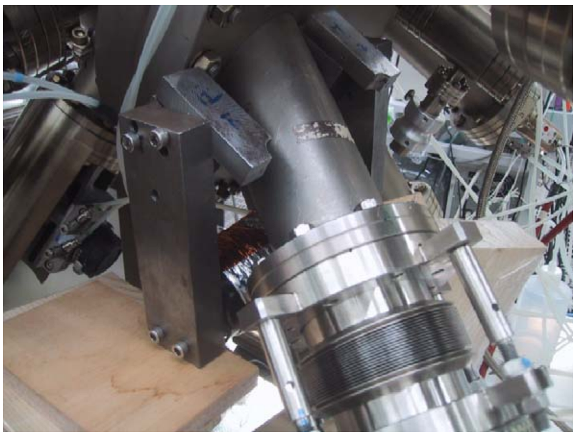

Fig. 1. An electromagnet attached to an RF nitrogen radical port in VG80H MBE chamber.

with a Xe lamp and an Ag reference plate. The growth procedure is the same as reported elsewhere [2,11]. The thickness distribution was measured through interference color.

3. Results and discussion

3.1. Enhancement of nitrogen atomic flux

There were two discharge modes for the N plasma: bright and weak [8]. Fig. 2 shows the enhanced spectrum of the bright discharge mode measured with a CCD HR-2000 spectrometer. The spectra are mainly from N atoms. Three main spectra of N atoms, triplet 747.73 nm for ^4P–$^4S^0$, 7 lines multiplet 822.73 nm for ^4P–$^4P^0$, and 8 lines multiplet 869.26 nm for ^4P–$^4D^0e$, were used for a monitor of the production of N atoms. Figs. 3(a) and (b) show the change of the intensity of 747 nm of N atoms against the magnetic flux density for different flux rates. Figs. 3(a) and (b) were obtained from two orifices of 185 apertures of 0.2-mm diameter with 2 and 0.5 mm thickness, respectively. The figures show the resonant nature against magnetic flux density. The values of the magnetic flux density correspond to the current value of the magnet, of which the maximum value was about 0.5 mT for a PBN discharge chamber. The value of magnetic flux density was not measured directly because the discharge chamber was located inside the MBE growth chamber. The estimated value of the magnetic field was measured separately for the same distance from the pole piece of the magnet. The flow rate dependence of

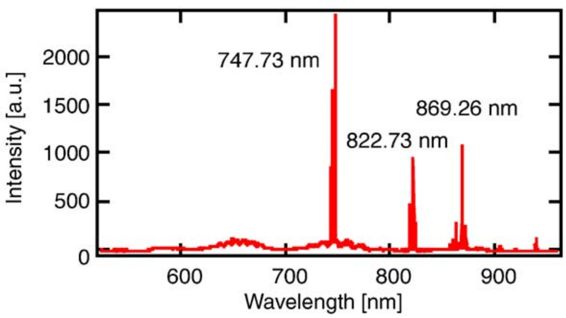

Fig. 2. Spectrum from N discharge with a DC magnetic field.

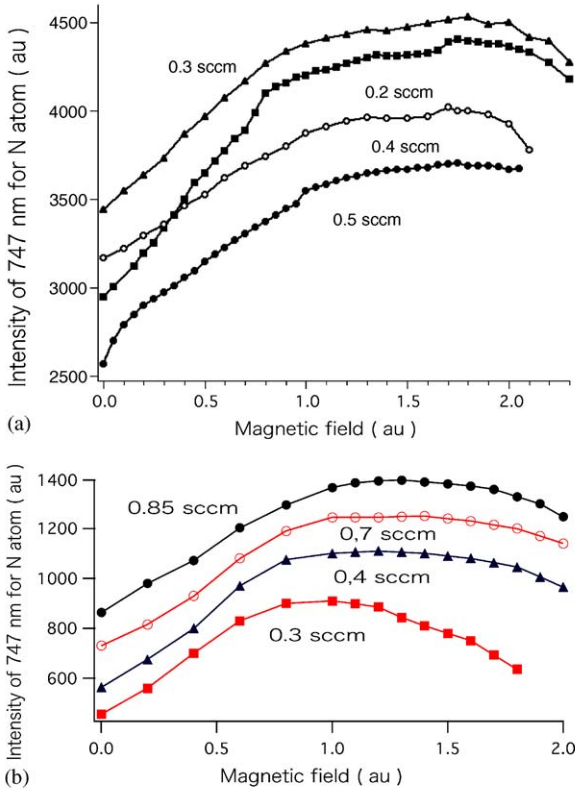

Fig. 3. (a) Change of intensity of the 747-nm N discharge against magnetic flux density for an orifice of 185 apertures of 0.2-mm diameter and 2-mm thickness. (b) Change of the intensity for an orifice of 185 apertures of 0.2-mm diameter and 0.5-mm thickness.

largest 747-nm atomic N intensity as shown in Fig. 3(a) from a thick orifice of 2 mm shows a maximum at 0.3 sccm. The flow rate dependence as shown in Fig. 3(b) shows increasing nature. The total conductance of the orifice with a thickness of 2 mm is smaller than the one of 0.5 mm thickness. The collision of excited N_2 molecules at the larger flow rate reduced the production of atomic N because of the high density of neutral N_2 molecules at the larger flow rate. In case of Fig. 3(a), for 0.3 sccm flow rate, the intensity increased from 3500 to 4500 by the application of a magnetic field.

The ECR frequency is written in the following equation, where q, B and m_e are electron charge, magnetic flux density and electron mass,

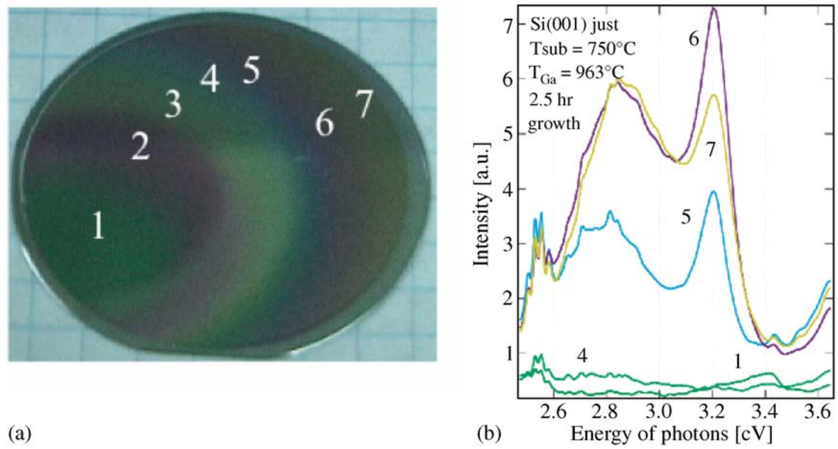

Fig. 4. (a) Interference color for 2.5-h growth at 2.7×10^{-5} Pa BEP of Ga at 750 °C under a near Ga-rich condition without rotation of the wafer Si (0 0 1) under a combinatorial methodology using an orifice of 185 apertures of 0.5-mm thick. (b) The PL at various III/V supply ratios corresponding to the interference colors in Fig. 4(a).

respectively:

$$\omega_{cy} = \frac{qB}{m_e}. \tag{1}$$

For the RF 13.56 MHz the magnetic flux density is then

$$B = \frac{m_e \omega_{cy}}{q} = \frac{9.1091 \times 10^{-31} \times 2 \times 3.14159 \times 13.56 \times 10^6}{1.620210 \times 10^{-19}} = 4.7900 \times 10^{-4}\,\mathrm{T} = 0.48\,\mathrm{mT}. \tag{2}$$

If we assume the thermal energy of electron in the discharge, the electron velocity is calculated as follows:

$$\tfrac{1}{2} m_e v^2 = E = k_B T_e = 2\,\mathrm{eV}$$

$$v = \sqrt{\frac{2E}{m_e}} = \sqrt{\frac{2 \times 2 \times 1.60210 \times 10^{-19}}{9.1091 \times 10^{-31}}} = 8.3876 \times 10^5\,\mathrm{m/s}. \tag{3}$$

The cyclotron radius is about 1 cm, according to the following calculation:

$$r = \frac{v}{\omega_{cy}} = \frac{8.3876 \times 10^5}{2 \times 3.14159 \times 13.56 \times 10^6} = 9.8446 \times 10^{-3}\,\mathrm{m} \approx 1\,\mathrm{cm}. \tag{4}$$

The condition for RF-ECR is confirmed because the diameter of a discharge chamber is 2 cm.

3.2. III/V flux ratio and poly-type

The effective III/V flux ratio affects the morphology of a growing surface and the poly-type of cubic or hexagonal structure. Cubic zincblende GaN (c-GaN) was grown under Ga-rich condition [12–14]. The growth of cubic phase under Ga-rich condition was confirmed by RHEED during growth in situ and by XRD, XRD pole figure [2] and PL measurement at room temperature ex situ. Fig. 4(a) shows the interference color of c-GaN(0 0 1) on Si(0 0 1) for 2.5-h growth at 2.7×10^{-5} Pa BEP of Ga at 750 °C growth temperature under near Ga-rich condition without substrate rotation. This experiment used an orifice of 185 holes of 0.2 diameter with 0.5 mm thickness. This experimental condition is considered as a combinatorial methodology, which was used in the field of drug industry to viriate experimental parameters in one experiment. Because of the non-uniformity of the flux distribution of Ga and N thickness of the film changed due to the III/V flux ratio without rotation of the wafer. Figs. 4(a) and (b) show the interference color and the PL corresponding the same number to at various III/V flux ratio. The growth of c-GaN on Si (0 0 1) was

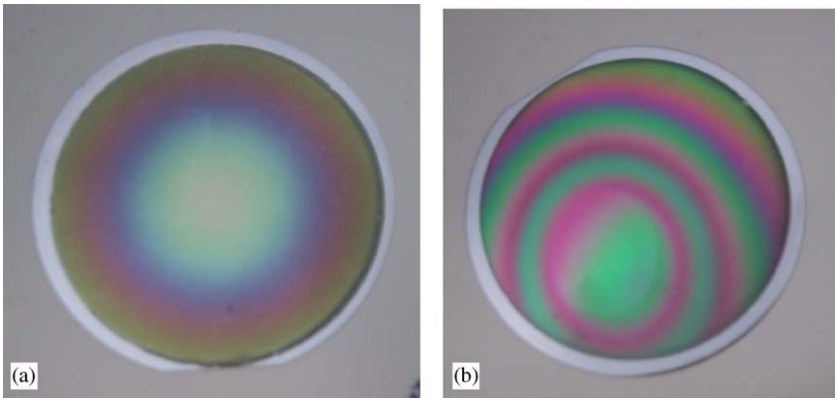

Fig. 5. (a) A surface interference of 2-inch Si wafer after rotating growth for 2 h at 5.6×10^{-5} Pa BEP of Ga at 750 °C under a Ga-rich condition using an orifice of 185 apertures of 2-mm thick. (b) Interference colors for 3.5-h growth without rotation of the wafer by the same growth condition of (a) except for the rotation and growth time.

confirmed at the Ga-rich growth condition area of positions 5–7 in Fig. 4(a) because the measured 3.2 eV PL peak corresponds to the near band edge transition [15]. Other places corresponding to the N-rich place 1–4 shows small luminescence. The grown GaN on Si(0 0 1) under the N-rich condition was hexagonal (0 0 0 1)-oriented columnar GaN having XRD 2θ at 34.5°. The XRD pole figure showed the twisting growth around the $\langle 0001 \rangle$ axis. The previous results for a necessary condition to grow c-GaN [12–14], in which Ga-rich growth condition is required, is confirmed.

3.3. Flux distribution and orifice dimension

Flux distribution of N radical was measured under Ga-rich condition through interference color distribution obtained by two orifice thicknesses of 2 and 0.5 mm thickness. Divergence of N flux corresponds the orifice thickness or the aspect ratio of 10 (= 2/0.2) and 2.5 (= 0.5.0.2), respectively. For N-rich condition the growth rate is controlled by the Ga flux. The Ga flux distribution becomes uniform with the substrate rotation because the surface lifetime of Ga atoms is sufficient to make uniform distribution of Ga atoms by the surface migration of Ga atoms. Rotation of the sample holder was used to form a uniform film thickness or uniform color under N-rich condition. On the other hand, the N atoms do not have a long lifetime and are active on the surface and react instantly when the N atoms reach Ga atoms. The growth, therefore, under Ga-rich condition in order to grow a uniform thickness required the uniform atomic N flux distribution. Current MBE machines however have not enough uniform flux distribution to a 2 inch Si wafer size under Ga-rich condition. Fig. 5(a) shows a surface interference of 2 inch Si wafer after rotating growth for 2 h by 5.6×10^{-5} Pa BEP of Ga at 750 °C under a Ga-rich condition using an orifice of 185 apertures of 2 mm thickness. The interference shows the thickness distribution that corresponds to the N flux distribution. Fig. 5(b) shows the interference color for 3.5 h growth without rotation of the wafer by the same growth condition of (a) except the rotation and growth time. When an orifice of 0.5 mm thickness was used films with more uniform thickness were obtained. It is obvious that a uniform distribution of N atomic flux is necessary to obtain uniform thickness.

4. Conclusions

Control of the nitrogen (N) atomic flux is key for the MBE growth of cubic GaN. Formation of N atom flux using an induction coupling discharge was controlled using the number of the orifice holes in the discharge chamber, the diameter of the orifice, the conductance of the orifice, and application of a DC magnetic field under RF-ECR condition. A high efficiency of N radical production was realized by an optimum magnetic field of about 0.5 mT for the electron energy of 2 eV and 13.56 MHz discharge. The growth of c-GaN on 3C-SiC/Si (0 0 1) for the Ga-rich growth condition was confirmed.

Acknowledgments

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