Journal of Crystal Growth 311 (2009) 2987–2991

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Measurement of nitrogen atomic flux for RF-MBE growth of GaN and AlN on Si substrates

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ARTICLE INFO

Available online 20 January 2009

PACS:
81.05.Ea
81.15.Hi
52.50.Dg

Keywords:
A1. Surface
A3. Epitaxy
A3. Molecular beam epitaxy
B2. Semiconduction III–V materials

ABSTRACT

Production and measurement of active nitrogen atoms (N+N*), which consist of ground state nitrogen atoms N and excited state nitrogen atoms N*, in an inductively coupled radio frequency discharge for the growth of group III nitrides and their alloys using a molecular beam epitaxy (MBE) were studied. Two discharge modes of the low brightness (LB) and the high brightness (HB) used in this study to produce excited nitrogen molecules (N_2*) and dissociated active nitrogen atoms (N+N*). The flux of (N+N*) was measured by a Langumuir-like electrode due to the self-ionization of adsorbed (N+N*) on a negatively biased electrode. The self-ionization, which emits electrons from (N+N*), forms an atom current and is confirmed using different electrodes such as Pt and CuBe and different electrode area. The atom current was calibrated by the grown GaN thickness in a VG80H MBE machine. The calibrated flux of (N+N*) per atom current in the VG80H machine is 5.5×10^{-4} ML/s/nA, where ML is monolayer. The atom current is useful to monitor the flux of chemically active nitrogen atoms N+N* for growth of group III nitrides and their alloys. Activity modulation migration enhanced epitaxial growth (AM-MEE) was demonstrated as an application of the measurement of atom current for the growth of the group III nitrides.

1. Introduction

Group III nitrides and their alloy (here after as a short expression, group III nitrides) films were necessary to be grown by hetero-epitaxial way. Silicon is a suitable and desirable substrate because of cost, large area and high thermal conductivity. As use for a template of group III nitrides, nitridation of Si is an attractive theme. An inductively coupled (ICP) radio frequency (RF) discharge is a best nitrogen source for the growth of group III nitrides by a molecular beam epitaxial (MBE) method because the high efficiency of nitrogen atom production under ultra-pure condition [1–4].

An ICP nitrogen plasma source has a mode transition between two discharge modes of the electrostatic one (E-mode) and the electromagnetic one (H-mode) [5,6]. The E-mode, which is a low brightness (LB) mode, is a low-density plasma and generates excited molecules N_2* and ions N_2^+. The H-mode, which is a high brightness (HB) mode, is a high-density plasma and generates additionally dissociated active nitrogen atoms (N+N*), which consist of ground state nitrogen atoms N and excited state nitrogen atoms N*. The HB mode is sustained by the induced azimuth RF electric field, which is produced by the oscillating magnetic field. The transition between these two modes is maintained by changing input RF power and/or inner pressure of nitrogen gas in a discharge tube. Two types of active nitrogen species, such as chemically and physically active species are formed by the mode change between the LB and the HB modes. As chemically active nitrogen species the (N+N*) atoms are generated from the HB mode, and as physically active nitrogen species the N_2* molecules are generated from the LB mode.

As an application of using the mode change the different chemical activity and physical activity periodically, the activity modulation (AM) of nitrogen species is applied for migration enhanced epitaxial (AM-MEE) growth of MBE to grow GaN and AlN films [7,8]. As another application of the discharge mode change, Katayama and Onabe [9] demonstrated the control of N atom irradiation as a shutter-less control of nitrogen flux modulation.

Above mentioned reasons a measurement of chemically active (N+N*) flux is important for the growth of the group III nitrides. Monitoring of (N+N*) flux was reported separately by Wistey et al. [10,11]. In this report a self-ionization, which emits electrons from attached (N+N*) on a negatively biased electrode, is explained and demonstrates to be detected as an atom current for the quantitative measurement. A method of measurement of nitrogen atomic flux in a growth chamber under the HB mode with N shutter close and open operations is presented. The self-ionization is confirming using different electrodes such as Pt and CuBe and different electrode area. The monitoring of (N+N*) flux is useful to control the growth rate under Ga or Al excess condition. AM-MEE is to be demonstrated as an application of the measurement of atom current for the growth of the group III nitrides.

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0022-0248/$ - see front matter
doi:10.1016/j.jcrysgro.2009.01.069

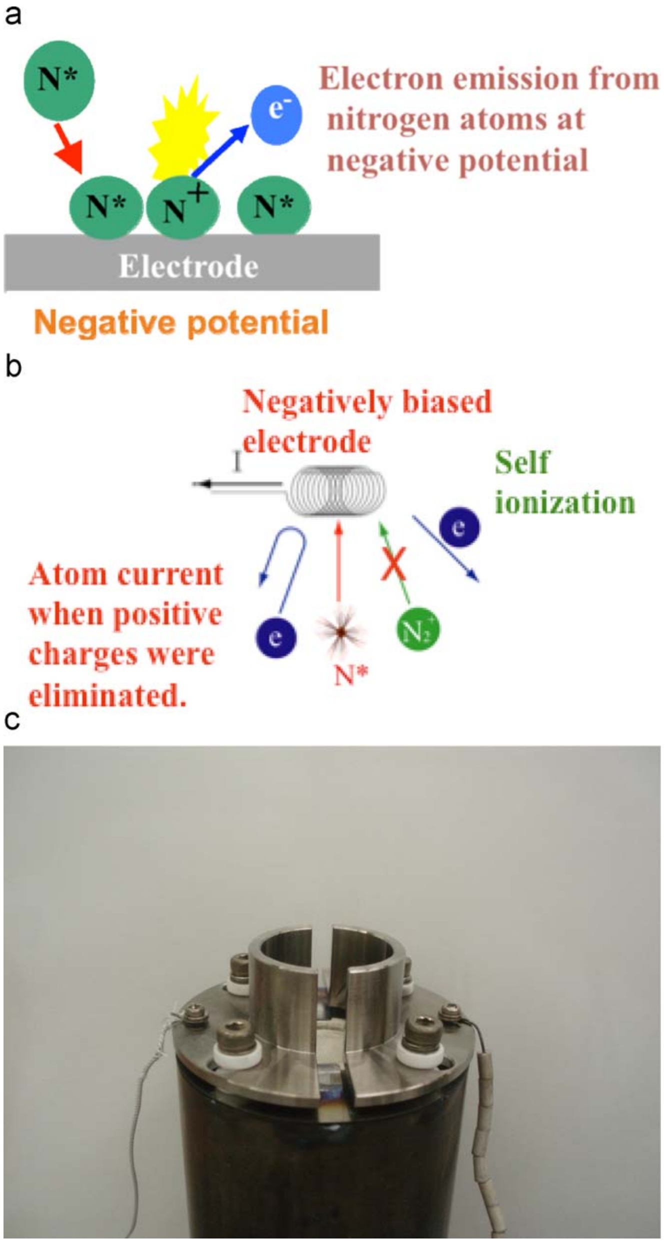

Fig. 1. (a) Schematic model of self-ionization adsorbed on a negatively biased electrode. (b) Electrostatic emission of electron from the nitrogen when charged particles are eliminated. (c) An eliminator to deflect charged particles attached in front of a nitrogen cell.

2. Experimental procedure

2.1. ICP RF discharge nitrogen source

An IRFS-501 RF nitrogen radical source, which is made by Arios, Inc. with an automatic matching and a time sequence controller for a power source, was used. Formation of (N+N*) flux and changing discharge modes was conducted under a time sequence controller of RF power source. Discharge spectra were monitored by a CCD spectrometer (Hamamatsu Photonics PMA-1) from a back port of the nitrogen cell [1]. Optical emission intensity (OES) is a measure of the production of active nitrogen species. The four main spectra of nitrogen atoms, triplet 747.73 nm for ^4P–$^4S^0$, 7 lines multiplet 822.73 nm for ^4P–$^4P^0$, 8 lines multiplet 869.26 nm for ^4P–$^4D^0e$, and 940 nm for ^2P–$^2D^0$ were indicators for the production of active N+N* atoms. Production of N_2* are calculated by spectra of the 1st positive series (580–950 nm) and 2nd positive series (300–450 nm) [1–4]. Intensity data of OES were calculated by numerical integration of each peak and each band [1]. The production rate of (N+N*) flux and N_2* flux is varied discharge condition at HB mode. A strong HB discharge under high RF power and high pressure produce much (N+N*) flux than N_2* flux compared with a weak HB discharge under low RF power and low pressure. Because of long life time of N+N* atoms and N_2* molecules [2] even the nitrogen mechanical shutter was closed under the HB mode, (N+N*) atoms and N_2* molecules could be leaked from the gap between the shutter and the outlet of a cell. The strong HB, which produces mainly (N+N*) atoms, is used as a (N+N*) atom source with the N shutter close condition.

2.2. Self-ionization from nitrogen atoms

For studying the atom flux measurement metal plates as a remote Langumuir-like electrode was used. Fig. 1(a) shows a schematic drawing of self-ionization, which emits electrons electrostatically, when the electrode is negatively biased. Fig. 1(b) shows atomic current through a remote Langumuir-like electrode when no charged particles came into the surface of the electrode. In order to eliminate charged particles from the discharge, a pair of eliminator electrodes, which are shown in Fig. 1(c), is attached in front of an orifice plate of the discharge tube. Increasing the potential difference between the eliminator electrodes charged particles such as electrons and nitrogen molecule-ions N_2^+ are deflected and removed from a nitrogen beam to a growth surface. A special apparatus and setup as shown in Fig. 2 was used to study the discharge characteristics of ICP N cell and self-ionization. Fig. 2 shows a schematic drawing of a chamber for the measurement of (N+N*) flux with the eliminator

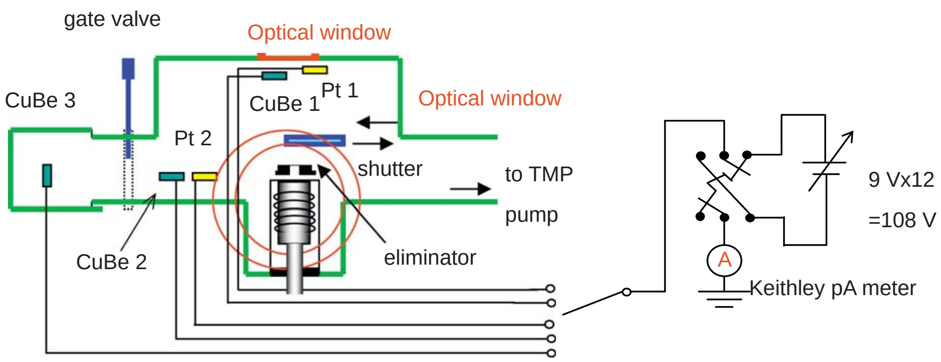

Fig. 2. Schematic drawing of a chamber for the measurement of leaked N+N* atoms with an eliminator electrode attached in front of the orifice plate. A shutter in front of eliminator is placed to control flux impingement directly or indirectly to atom probes. Pt1 and CuBe1 plates ($2 \times 5\,cm^2$) are placed in front of the N cell to measure N+N* atoms directly for shutter open and indirectly for shutter close. Pt2 and CuBe2 plates ($2 \times 5\,cm^2$) are placed at side of the N cell. CuBe3 ($2 \times 5\,cm^2$) electrodes at left side is placed outside of a gate valve.

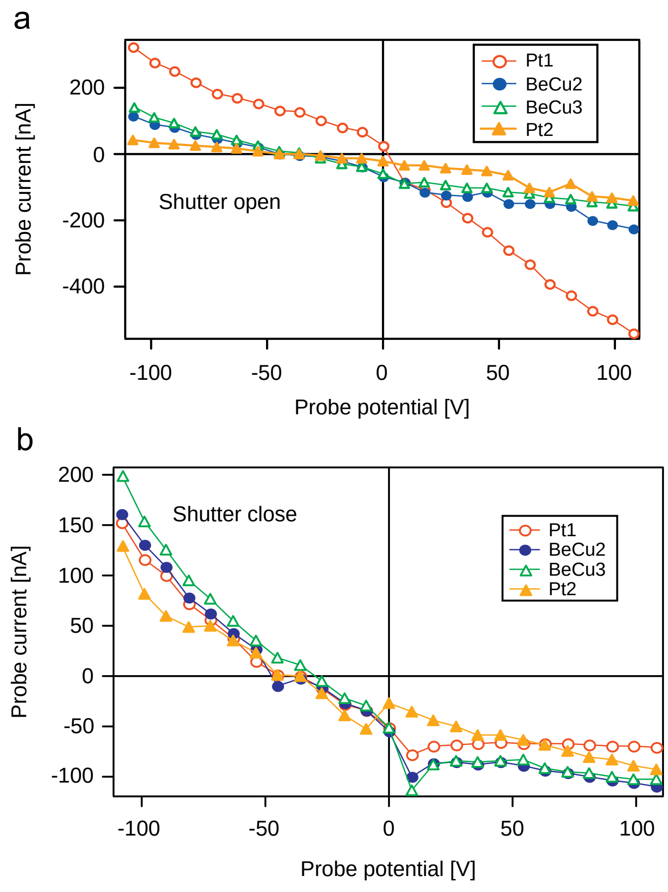

Fig. 3. N+N* atomic current measurement using various electrode in Fig. 2 for open and closed shutter varying the probe potential under 500 V of the eliminator potential.

electrode. A shutter in front of the eliminator is placed to control flux impingement directly or indirectly to atom electrodes of Pt1 and CuBe1 plates (2 × 5 cm^2). Pt1 and CuBe1 plates in a special equipment are placed in front of the N cell to measure (N+N*) atoms directly for the shutter open and indirectly for the shutter close. Pt2 and CuBe2 plates (2 × 5 cm^2) are placed at the side of the N cell. CuBe3 (2 × 5 cm^2) electrode is located outside of a gate valve as shown in Fig. 2.

2.3. *Growth of GaN and AlN on Si*

A remote Langumuir-like probe, which is a grid wire of a BA ionization gauge in MBE chamber for flux measurement, is inserted at wafer position with a negative potential of −108 V, which is produced with series connection of twelve 9 V batteries. This grid wire is used to measure (N+N*) flux as shown in Fig. 1 for real growth operation. Calibration between the atom current and growth rate was made by measuring film thickness. A VG80H MBE system, in which a 800 L/s turbo molecular pump, a 400 L/s ion pump and an IRFS-501 RF N radical source made by Arios, Inc. was used. Quantitative growth control by nitrogen atom N+N* flux provides a precise technique of MBE growth of the group III nitrides.

GaN film was grown on 3 in AlN/Si(111) substrate using AM-MEE under 2 s Ga exposure with 3 s LB (120 W and 70 Pa (1.38 sccm)) discharge and followed by 2 s exposure of the HB (450 W and 70 Pa (1.38 sccm)) discharge without substrate rotation.

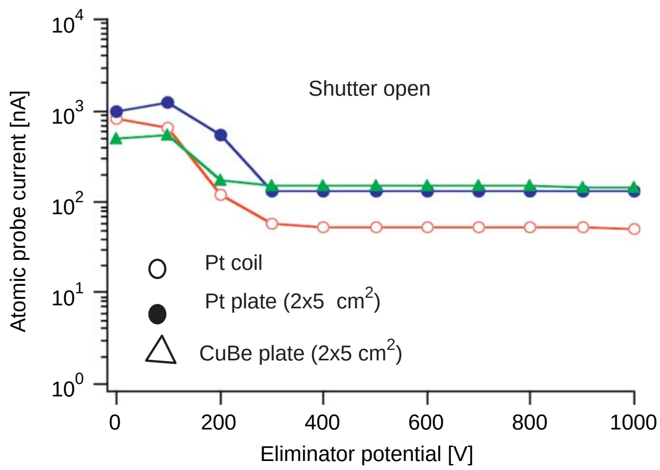

Fig. 4. N+N* atomic current depending on electrode area for closed shutter varying the eliminator potential under −108 V of probe potential. Current depend on area and not materials. Area of the Pt coil is less than 2 × 5 cm^2.

3. Results and discussion

3.1. *Measurement of atom current by the self-ionization*

Fig. 3 shows a Langumuir-like current vs. voltage (*I–V*) characteristics, which demonstrates (N+N*) atom current measurement using various electrodes in Fig. 2 for open and closed shutter position varying the electrode potential under the eliminator potential of 500 V. In Fig. 3(a) for the shutter open operation a data line of Pt1, which received direct incident of (N+N*) flux, corresponds the amount of the self-ionization. The slope at the negative bias region shows the emission dependence on the electrode potential. Data lines for CuBe2, CuBe3 and Pt2, which received indirect flux or leaked flux, are reduced the amount of current. When the shutter is closed in Fig. 3(b), all fluxes indirectly come to the electrodes. A data line of Pt1 coincides other data due to leaked flux between the shutter and outlet of nitrogen source. Other data are the same in the case of shutter close because of indirect incident of (N+N*).

Fig. 4 shows (N+N*) atomic current depending on electrode area for closed shutter varying the eliminator potential under −108 V of atom electrode's potential. The atom current depends on area and not materials. This fact confirms the self-ionization from adsorbed (N+N*) atoms.

3.2. *Production of active species by LB, weak HB, and strong HB*

For growth experiment the atom current was measured by a grid filament of a BA ionization gauge under various discharge condition, and calibrated by the film thickness. Fig. 5 shows an interesting result for production of (N+N*) atoms and N_2* molecules. Fig. 5(a)–(c) show spectra from LB, weak HB and strong HB discharges. Fig. 5(a) shows spectra from a LB discharge under 80 W and 28 Pa (0.5 sccm), in which only molecules' 1st and 2nd positive bands are observed. In case of the LB discharge for Fig. 5(a) the atom current measured by a grid coil of BA ionization gauge was negligibly small or not detectable.

Fig. 5(b) shows spectra from a weak HB discharge under 120 W and 28 Pa (0.5 sccm), in which (N+N*) atoms' spectra at 747.73, 822.73, 869.26, and 940 nm plus molecules' 1st and 2nd positive bands are observed. As input power is small and pressure is low, the production rate of (N+N*) flux and N_2* flux is small. The atom current was 81 nA.

As shown in Fig. 5(c) a strong HB discharge under 500 W and 75 Pa (1.38 sccm) created large amount of (N+N*) atoms' spectra at 747.73, 822.73, 869.26, and 940 nm plus molecules' 1st and 2nd positive bands are observed and small amount of N_2* molecules. A TEFLON film was used as a filter to eliminate saturation of a CCD detector of PMA-11. In this a strong HB discharge the production rate of (N+N*) flux and N_2* flux is large, i.e. only (N+N*) flux was produced effectively. The atom current for the strong HB discharge under 500 W and 75 Pa (1.38 sccm) of Fig. 5(c) was 390 nA for open shutter operation and 35 nA for closed shutter one. By closing a shutter of nitrogen source, the number of (N+N*) atoms was reduced by about 9% compared with one for the open shutter position. It is suitable to supply only (N+N*) flux uniformly to a Si surface.

3.3. Calibration of atom current by GaN film thickness

After the nitridation, a few monolayers of Al were deposited on β-Si_3N_4 firstly and form an Al polarity initial AlN layer. Successive AlN layer and GaN layer were grown by activity modulation migration enhancement epitaxy (AM-MEE) method and/or MBE method. Fig. 6 shows the growth rate measured from grown film thickness of GaN(0 0 0 1) on Si(1 1 1) vs. measured atom current by a grid filament of a BA ionization gauge in V80H MBE chamber. The film thickness was measured from cross-sectional observation by FE-SEM. The growth rate of GaN(0 0 0 1) of 932 nm/h corresponds 1 ML/s. The slope therefore is 0.50 nm/h/nA=5.5 $\times 10^{-4}$ ML/s/nA, where ML is a

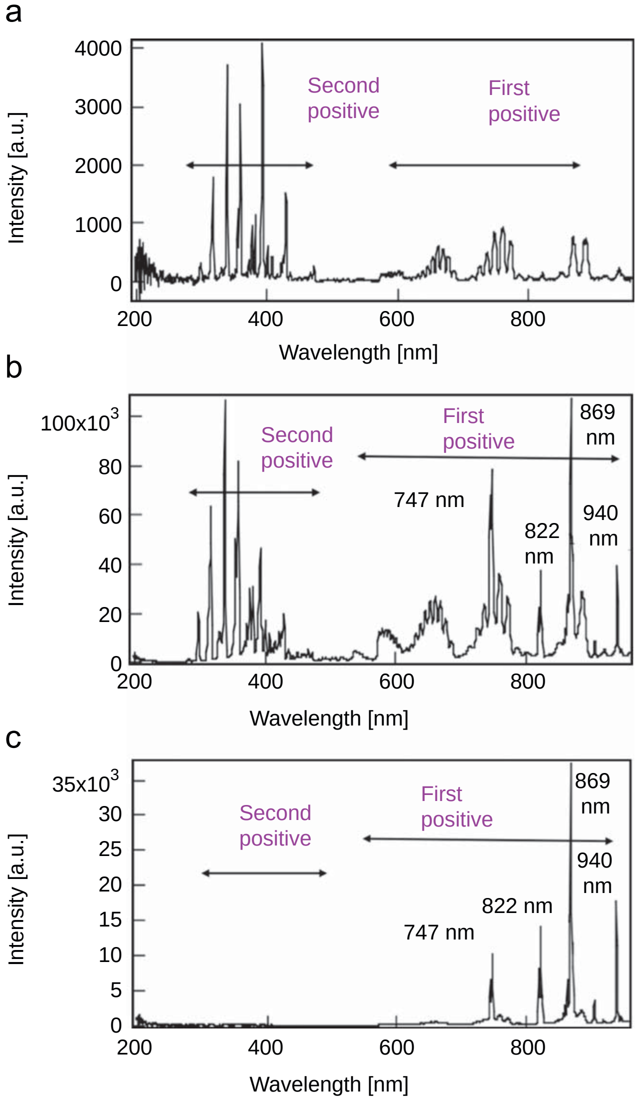

Fig. 5. OES measured by PMA-11 for (a) the LB discharge mode under 80 W, 28 Pa (0.5 sccm), (b) the weak HB discharge mode under 120 W, 28 Pa (0.5 sccm), and (c) the strong HB mode under 500 W, 75 Pa (1.38 sccm) with TEFLON film as a filter to eliminate saturation of a CCD detector of PMA-11.

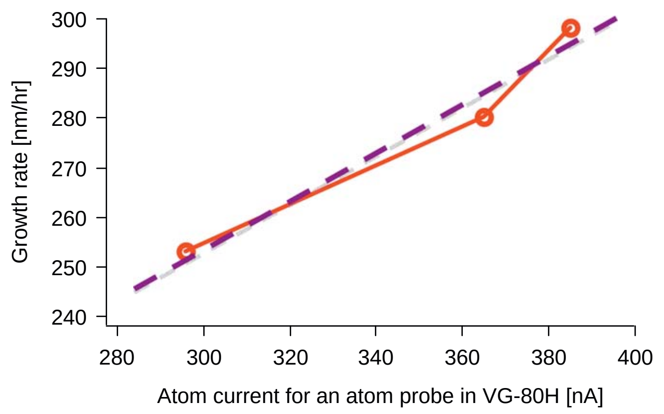

Fig. 6. Growth rate measured from grown thickness of GaN(0 0 0 1) on Si(1 1 1) epitaxial films vs. measured atom current by a grid filament of a BA ionization gauge. The slope is 0.50 nm/h/nA=5.5 $\times 10^{-4}$ ML/s/nA.

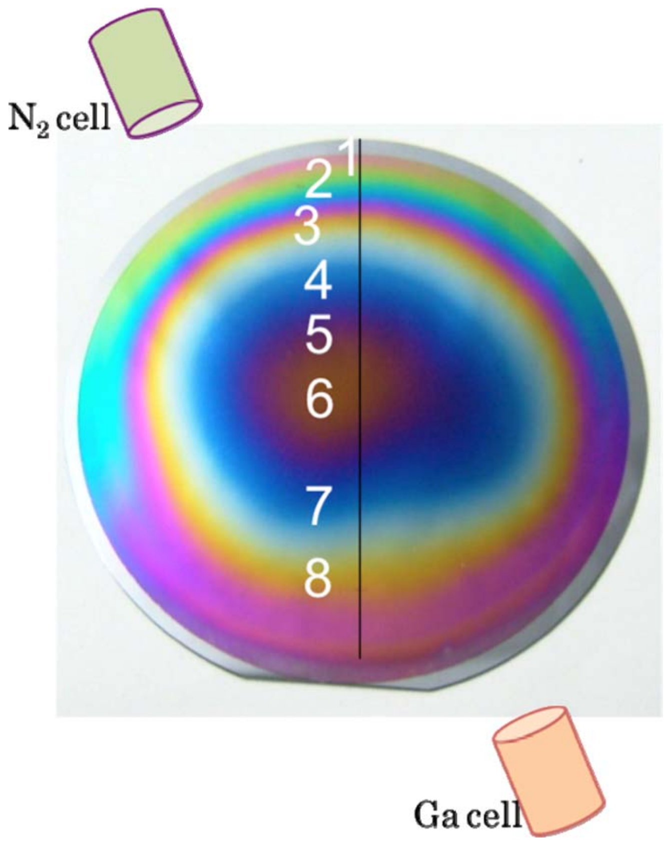

Fig. 7. GaN film grown on 3 inch AlN/Si(1 1 1) using AM-MEE under 2 s Ga exposure with 3 s LB (120 W and 70 Pa (1.38 sccm)) discharge and followed by 2 s exposure of the HB (450 W and 70 Pa (1.38 sccm)) discharge without substrate rotation. N and Ga show cells for N and Ga, respectively. The thickness at 1–8 positions are 130, 150, 120, 70, 50, 40, 80, and 150 nm, respectively.

unit of monolayer. The direct atomic current for the strong HB discharge (500 W and 75 Pa) was 390 nA for open shutter operation, which corresponds to 0.21 ML/s. The atomic current of leakage flux for the strong HB discharge (500 W and 75 Pa) was 35 nA, which corresponds to 0.02 ML/s. For the discharge condition of 120 W, 26 Pa gives direct atom current of 81 nA with open shutter position, which corresponds 0.044 ML/s. In the case of applying AM-MEE to the growth of AlN and GaN the atom current is useful to determine period of LB and HB discharge and input RF power.

3.4. Growth of GaN on AlN/Si

The monitoring of (N+N*) flux was useful to control the growth rate under Ga or Al excess condition. AM-MEE growth of GaN is demonstrated as an application of the measurement of atom current for the growth of the group III nitrides in Fig. 7. The thickness at 1–8 positions are 130, 150, 120, 70, 50, 40, 80, and 150 nm, respectively. The effect of physically active N_2^* was explained by the reduction of film thickness at the position from 3 to 7 and circular thickness distribution without substrate rotation (i.e. combinatorial growth).

4. Conclusion

The flux of chemical active nitrogen atoms N+N* was measured by a Langumuir-like probe due to the self-ionization of adsorbed N+N* on a negatively biased electrode. The self-ionization, which emits electrons from N+N*, forms an atom current and is confirmed using different electrodes such as Pt and CuBe and different electrode area. The atom current was calibrated by the grown GaN thickness in a VG80H MBE machine. The calibrated flux of dissociated nitrogen atoms N+N* per atom current in the VG80H machine is 5.5×10^{-4} ML/s/nA. Atomic current is useful to monitor the flux of active nitrogen species for growth of group III nitrides and their alloys. AM-MEE was demonstrated as an application of the measurement of atom current for the growth of the group III nitrides.

Acknowledgements

This work was funded by Research Center for Interfacial Phenomena, Doshisha University. This research was partially supported by the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Scientific Research (B), 20360011, 2008. One of the authors (T.O) is grateful for Drs. T. Udagawa, M. Odawara, and T. Kikuchi (Showa Denko K.K.) for many helpful comments, discussion and support. We are also grateful for the contributions from students in our laboratories.

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