Improvement of Plasma-Assisted Molecular Beam Epitaxial Growth of Group III Nitrides on Si Controlling Radio Frequency Discharge Modes and Irradiation of Nitrogen Flux

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A radio frequency inductively coupled plasma (rf-ICP) nitrogen discharge was investigated to improve group III nitride growth on Si substrates. Two modes of the rf-ICP discharge, low brightness (LB) and high brightness (HB) discharges, were successfully controlled through mode transition. Direct irradiation and indirect irradiation of nitrogen atoms were applied for the growth of group III nitrides. As an application of indirect irradiation of nitrogen atoms, the growth of β -Si₃N₄ using interface reaction epitaxy (IRE) was studied. As applications of direct irradiation of nitrogen atoms, activity modulation migration-enhanced epitaxy (AM-MEE) and plasma-assisted molecular beam epitaxy (PA-MBE), which are atomic layer epitaxy (ALE) methods, are demonstrated. These growth systems operate to realize a single-growth process from a Si substrate to an AIN or GaN epitaxial layer, i.e., through preparation of a double buffer (DBL) layer of AIN/ β -Si₃N₄/Si after the growth of IRE β -Si₃N₄ and IRE AIN. The electron emission due to the self-ionization of nitrogen atoms on a negatively biased electrode is demonstrated to measure *in situ* direct and indirect nitrogen atom fluxes during the growth. (© 2011 The Japan Society of Applied Physics

1. Introduction

For the production of electrical and optical semiconductor devices using group III nitrides, the hybrid application of group III nitride technology with silicon has great advantages. Group III nitride films are usually grown by heteroepitaxial methods because of a lack of homoepitaxial substrates. Silicon is a suitable and desirable substrate because of its low cost, large surface area, and large thermal conductivity. Molecular beam epitaxy (MBE) is also a suitable method to grow group III nitride devices under lowtemperature and ultra-high vacuum conditions with interface flatness. Silicon substrates and the usage of the plasmaassisted (PA)-MBE method are promising and need to be studied extensively, because of the possibility of growth of metastable cubic zinc-blended GaN (c-GaN) and flat heterointerfaces for electrical and optical semiconductor device applications.

A highly efficient production of nitrogen atoms for MBE growth is achieved by a radio frequency inductively coupled plasma (rf-ICP) nitrogen discharge, which is the main subject of this study. The study of rf-ICP discharge was started in 1927 by Thomson¹⁾ and several reports have been published since then,²⁻⁹⁾ but the mechanism of nitrogen production by rf-ICP is not fully understood yet. A highly efficient nitrogen radical production was realized using an optimum dc magnetic field for the resonance of about 0.5 mT at an electron energy of 2 eV for a 13.56 MHz discharge under the rf-electron cyclotron resonance (ECR) condition.⁹⁾ The effect of controlling the divergence of the nitrogen radical flux by changing the orifice dimension, the aspect ratio of the orifice, and the distribution of hole position was studied previously.⁹⁾ The ICP rf discharge has a transition between two discharge modes, the electrostatic (E) mode and the electromagnetic (H) mode.^{1,3,5} The E mode, which is a low-brightness (LB) mode, is a low-density plasma and produces only excited nitrogen molecules, N2*. The H mode, which is a high-brightness (HB) mode, is a high-density plasma and produces chemically active species such as N+N*, where N and N* are the ground state and the excited state nitrogen atoms, respectively and physically active species such as excited nitrogen molecules, N2*. The HB mode is believed to produce mainly chemical active nitrogen atoms, $N+N^*$. The transition between the two modes is controlled by changing the input rf power.

There are two ways of using the active nitrogen fluxes from the rf-ICP discharge cell as follows. One way is using a direct flux, which reaches the substrate directly from the windows of the cell orifice. The direct flux effuses as a supersonic (SS) jet flow. The SS jet concept was reviewed by Ferguson and Mullins.¹⁰⁾ The pressure difference between the inside of the rf-ICP cell, in which the pressure of a discharge chamber is about 100 Pa, and in a growth chamber, in which the pressure is approximately 10^{-3} Pa, realizes a SS jet flow of active nitrogen species. Depending on the discharge mode, a direct flux produces a SS jet N+N* and N₂* fluxes induced by the HB mode and a SS jet of N₂* flux induced by the LB mode. The other way is using an indirect flux; the lifetime of nitrogen atoms is long enough to reach the substrate after reflection from one of the walls of the growth chamber or shutter. This indirect flux works as adsorbed (ADS) nitrogen atoms, which results in indirect irradiation in the HB discharge mode. Three active nitrogen species are then available for use by PA-MBE, i.e., a chemically active ADS nitrogen flux by indirect irradiation in the HB mode, a SS jet flux of chemically active $N+N^*$ by direct irradiation in the HB mode, and a SS jet flux of physically active N₂* by direct irradiation in the LB mode.

As an application of the change between the HB and LB modes, Katayama and Onabe demonstrated the control of N atom irradiation using the mode changes with a shutterless modulation of nitrogen flux.¹¹⁾ An activity modulation migration-enhanced (AM-MEE) PA-MBE, where the mode of discharge is controlled by the input rf power at a constant vapor pressure (at a constant flow rate of N₂ gas), was also proposed by the present author's group.^{12,13)} MEE was proposed by Horikoshi *et al.*¹⁴⁾ to realize a layer-by-layer growth of GaAs by the MBE method. MEE controls the amount of growth elements to supply to a growing surface using shutter operation individually. *In situ* measurements of SS jet nitrogen atoms were performed using a Langmuir-like electrode based on the self-ionization of adsorbed N+N* on a negatively biased electrode.¹²)

In this report, in order to explain the improvement of MBE growth of group III nitrides on Si substrates by controlling nitrogen rf discharge, a single-growth process

from a Si substrate to an AlN epitaxial layer of a double buffer layer (DBL) of AlN/ β -Si₃N₄/Si using only a nitrogen gas source is presented. First, in situ measurements of the direct and indirect chemically active N+N* flux were carried out using a Langmuir-like probe and parallel plate electrodes, respectively. ADS nitrogen atoms, which allow indirect irradiation in the HB discharge mode, are used for preparing β -Si₃N₄ by interface reaction epitaxy (IRE). AM-MEE, which is another method of improving the control of discharge by periodic irradiation of chemically active N+N* flux and physically active N_2^* flux by the HB and LB discharges, respectively, is shown. A uniform thickness distribution without substrate rotation and thickness reduction by the irradiation of excited N2* molecules in the LB mode is demonstrated. This growth system enables the realization of a single-growth process from a Si substrate to optical and electronic devices with group III nitrides only using nitrogen gas in a PA-MBE chamber.

2. Experimental Procedure

2.1 Production of active nitrogen species from rf-ICP plasma under HB and LB modes

An IRFS-501 rf nitrogen radical source made by Arios Inc. in an MBE system (Oxford Instrument VG80H) was used as a nitrogen plasma source. The specifications of an orifice plate of PBN are 2.0 cm in diameter and 1 mm in thickness with 373 holes of 0.2 mm diameter. Active nitrogen atoms N+N* and excited molecules N2* from a rf-ICP nitrogen source were determined at the three operation sections labeled I, II, and III, as shown in Fig. 1: (I) creation of N, N^* , N_2^* , ions N^+ , N_2^+ and electrons within a discharge tube, (II) effusion of active species through orifice holes as a SS jet, and (III) elimination and deflection of charged particles for the SS jet as a direct irradiation flux or reflection as an indirect irradiation. In (II), charged particles could be eliminated through a wall of an orifice plate of PBN. In (III), a SS jet of $N+N^*$ or a SS jet of N_2^* hits the surface of a crystal, and an ADS N+N* flux following its reflection from the wall of the growth chamber or shutter and reaches the crystal surface with equilibrium vapor pressure. In the inner part of the discharge tube (I), the two LB and HB discharge modes⁴⁾ were controlled. Plasma diagnosis was carried out using optical emission spectroscopy (OES) measurements with a Peltier cooled charge-coupled detector (CCD; Hamamatsu Photonics PMA-11) through an optical window. The PMA-11 was calibrated with the standard wavelength and sensitivity correction from the National Institute of Standards and Technology by Hamamatsu Photonics. Nitrogen gas (99.9999%) was input into the discharge tube after passing a purifier 150 PSIG of a Saes getter and was monitored with a Baratron pressure gauge, installed just before the inlet of gas to the discharge tube.¹²⁾ The inner pressure of the discharge tube was difficult to measure and a calibration curve was measured from the relationship between the outside pressure of rf-ICP cell and flow rate, as shown in Fig. 2. The pressures were higher for larger discharge power because of the larger amount of dissociation of nitrogen molecules at higher rf power.

The phase diagram for the two modes, which would be shown in Fig. 7 was formed by measurement of the mode change by changing rf power at a constant nitrogen pressure



Fig. 1. Schematic drawing of three sections of a rf nitrogen source. Section I: inside; creation of ground state atom N, excited state nitrogen atom N*, excited state nitrogen molecule N_2^* , nitrogen atom ion N⁺, nitrogen molecule ion N_2^+ , and electrons. Section II: orifice with small holes; effusion of active species through orifice holes as a SS jet. Section III: elimination and deflection of charged particles for the SS jet as a direct irradiation flux and equilibrium ADS nitrogen atoms reflected from the wall of the growth chamber as an indirect irradiation flux with equilibrium vapor pressure.



Fig. 2. (Color online) Calibration curve for inner pressure of the discharge tube vs flow rate.



Fig. 3. (Color online) Direct and indirect nitrogen irradiation: (a) Direct irradiation: a SS jet flow of $N+N^*$ or N_2^* , (b) indirect irradiation (1): $N+N^*$ atoms reflected from the wall with the shutter closed, and (c) indirect irradiation (2): $N+N^*$ atoms reflected from the wall with the shutter open in a remote plasma position.

and also by changing nitrogen pressure at a constant rf power.

2.2 Direct and indirect N+N* flux irradiations

A direct flux effused from the cell as a SS jet flow was operated as shown in Fig. 3(a), after eliminating charged particles. An indirect flux as ADS atoms was irradiated with the shutter closed, as shown in Fig. 3(b), or with the shutter open using wall reflection at a remote plasma position, as shown in Fig. 3(c).



Fig. 4. (Color online) (a) Schematic drawing of a Langmuir-like probe using a grid electrode of a flux monitor installed on a V80H. The probe is biased negatively and eliminates charged particles using an eliminator. (b) Atom probe of two parallel stainless electrodes. (c) Electric circuit of atom current for ADS nitrogen atoms in a parallel electrode. The current between the two parallel plates with applied voltage $V_A - V_B = -108$ V corresponds to the electrodes with potential V_A .

2.3 In situ measurement of direct and indirect N+N* fluxes

A direct flux effused from the cell as a SS jet flow was measured using a grid electrode of a flux monitor of an ionization gauge installed on a VG80H, as shown in Fig. 4(a), after eliminating charged particles using an eliminator installed just outside of the rf-ICP cell. Wistey *et al.* used an ionization gauge as a Langmuir-like probe⁷⁾ similarly. By applying a bias potential difference to the eliminator electrodes, as shown in Fig. 4(a), only neutral N+N* atoms and N₂* fluxes reached the surface of a Langmuir-like electrode, of which the potential is negatively biased for atom current by the self-ionization of N+N*.

Figure 4(c) shows an electric circuit to measure an indirect ADS atomic current using the parallel plate atom electrode as shown in Fig. 4(b) when no charged particles come to the surface of the electrodes. There are two ways of indirect irradiation; one way is using a shutter close condition as shown in Fig. 3(b) as an indirect irradiation (1) and the other way is placing the electrodes as a remote plasma position at the side of the nitrogen flux beam as shown in Fig. 3(c) as an indirect irradiation (2). An atom probe of two parallel stainless electrodes [$60 \times 110 \text{ mm}^2$, two plates: 20 mm separation as shown in Fig. 4(b)] is proposed to measure an indirect flux.

The atom potential, V_A is defined as the lowest potential of the negatively biased electrode at the positon A as shown in Fig. 4(c). V_A is equal to $-E_A + V_B$, where $-E_A$ is the potential difference of two parallel electrodes and V_B is called as a Langumuir bias potential. The current between the two parallel plates with an applied voltage $-E_A =$ -108 V corresponds to adsorbed nitrogen atoms on the inside surface of the atom electrodes under the atom voltage $V_{\rm A}$ as shown in Fig. 4(c). The value of 108 V comes from twelve 9 V batteries connected in series. A current, I_A passes through the terminal A is called as the atom current and can be given by $I_A = -\gamma SV_A$, where γ is the self ionization coefficient (A/Vm²), S (m²) is the surface area of the atom electrode. When the Langumuir bias potential $V_{\rm B}$ is biased negatively, i.e., $V_{\rm B} = -E_{\rm B}$, where $-E_{\rm B}$ is the potential difference between position B and the ground. The absolute value of the atom potential V_A increased additionally to the atom parallel plate potential difference $-E_A$ as the following equation $V_A = -E_A + V_B = -E_A - E_B$. Current I_B passes through a picoampere meter connected to terminal B, A_B, measures a current of the self ionization of outside surface of plate B. Currents I_A and I_B were measured using Keithley picoammeters, A_A and A_B.

2.4 Application of indirect irradiation of nitrogen flux: IRE

of β -Si₃N₄ and formation of a DBL of AlN/ β -Si₃N₄/Si As an application of indirect irradiation of ADS atoms, the surface nitridation of Si was performed to form a singlecrystal layer of β -Si₃N₄ by IRE. β -Si₃N₄ showing an 8×8 surface reconstruction was formed epitaxially on a clean 7×7 Si(111) surface at 820 °C by irradiating N+N* flux indirectly in the HB mode for 30 s to 3 min with the N shutter closed.¹²⁾ The ADS atom flux was changed depending on the wall temperature and the amount of ADS nitrogen atoms on the wall. After nitridation of the Si(111) wafer, an AlN template was successively prepared by IRE with about 2 monolayers (MLs) of deposited Al and nitrogen atoms supplied from the β -Si₃N₄ film at about 830 °C.¹³⁾ This thin IRE AlN is a part of DBL, AlN/ β -Si₃N₄/Si.

2.5 Application of direct irradiation of nitrogen flux: AM-MEE growth of AIN and GaN

As an application of direct irradiation of active species of nitrogen discharge, N+N* atoms and excited molecules, N2*, which were produced by the HB and LB modes of rf-ICP discharge, the following activity modulation migrationenhanced (AM-MEE) PA-MBE was proposed.^{12,13} Figure 5 explains the time sequence of AM-MEE operation. Necessary elements for crystal growth of group III nitrides are the group III elements such as Al, Ga or In, and N. A conventional MBE system irradiates both elements continuously during the MBE growth. On the other hand AM-MEE, which is one of the atomic layer epitaxial (ALE) methods, irradiates the elements separately and periodically within one monolayer (ML) growth. One period of growth process, which shows T as shown in Fig. 5, is described $T_1 + T_2$ for the group III elements irradiation, $T_3 + T_4$ for discharge modes transition and $T_5 + T_6$ for nitrogen shutter operation. The AM-MEE operation starts at the time t_0 , which is the time of the trigger of synchronization with the moment of Al or Ga shutter opening. Before the AM-MEE operation the input rf power was kept at a lower value for the LB mode, which will be shown in the phase diagram of Fig. 7. T_1 and T_2 are the duration when the Al or Ga shutter is open and the duration when the shutter is closed,



Fig. 5. (Color online) Time sequence of AM-MEE operation, where T_1 , T_2 , T_3 , T_4 , T_5 , T_6 , α , β , τ , and μ are the duration of the Al or Ga shutter opening, the duration of the Al or Ga shutter closing, the duration of the LB mode, the duration of the HB mode, the duration of the N shutter closing, the delay time of N+N* atoms irradiation after the Al or Ga shutter closes, the duration of removal of excess Al or Ga atoms when the N shutter is open, the delay time of starting the HB mode after the start of Al and/ or Ga irradiation, and the migration time of Al or Ga, respectively. One period $T = T_1 + T_2 = T_3 + T_4 = T_5 + T_6$ is controlled by group III cells and $T_3 + T_4$ is controlled by a rf-ICP discharge system. The migration time of Al or Ga atoms and the duration of removal of excess Al or Ga atoms are μ and β , respectively.

respectively. T_3 and T_4 are the duration of the HB mode and the duration of the LB mode, respectively. T_5 and T_6 are the duration of the N shutter is closed and open, respectively. During T_3 , N+N* are mainly irradiated to the surface and crystal growth reaction between Al and/or Ga and N+N* is completed.

Time t_1, t_2, t_3, t_4 , and t_5 are the opening time of N shutter, the closing time of Al or Ga shutter, the starting time of the HB mode, the starting time of the LB mode, and opening time of Al or Ga shutter, respectively. The duration τ is the delay time of starting the HB mode after the start of Al of Ga irradiation. The duration μ , which is called a migration enhancement time, direct irradiation of physically active N2* flux gives kinetic energy to Al or Ga atoms. The duration α is the delay time of N+N^{*} atom irradiation after the Al or Ga shutter is closed and could be a negative value for overlapping of Al or Ga irradiation and N+N* irradiation. The duration α , which is called as the additional migration enhancement time, gives an additional kinetic energy to Al and/or Ga atoms before the crystal growth reaction. The duration β is the delay time of Al or Ga atom irradiation after starting the LB mode. The duration β , which is called as the cleaning up time, allows N_2^* to remove excess Al or Ga atoms from the surface before the beginning of the next growth sequence at the time $t = t_5$.

2.6 Single-MBE-growth system from a Si wafer for electronic or optical group III nitrides devices

This growth system, which uses indirect irradiation and direct irradiation of nitrogen atoms with group III elements,

operates to realize a single-growth process from a Si substrate to an AlN or GaN epitaxial layer grown by AM-MEE, after preparation of a DBL of AlN/β -Si₃N₄/Si.

A rf-ICP source in VG80H MBE system was an IRFS-501 rf nitrogen radical source made by Arios Inc., with a time sequence controller of rf power source and a matching box. The flux of Al at BEP $(1.0-8.0) \times 10^{-6}$ Pa is produced Al K-cell at $T_{Al} = 1050-1105$ °C. The pressures in the growth chamber during an IRE processes of β -Si₃N₄ and AlN and MBE growth were kept at about 10^{-3} Pa, although the initial pressure was on the order of 10^{-8} Pa. The substrate temperature was monitored using a thermocouple and calibrated to a transition temperature, T_c of a reflection high-energy electron diffraction (RHEED) reconstruction from (7×7) to (1×1) . Hibino and his group¹⁵⁾ showed that the T_c is 856 °C, but they pointed out the hysteresis phenomenon of the transition caused by supercooling and superheating. The published data are changed from 830 to $867 \,^{\circ}C.^{16-19)}$ The thickness of the films was measured by scanning electron microscopy (SEM) for grown GaN and AlN and the thickness of β -Si₃N₄ was measured by X-ray photoelectron spectroscopy (XPS).

Prior to growth, the surface of a 2- or 3-in. Si(111) on-axis wafer was oxidized in HCl : $H_2O : H_2O_2 = 3 : 1 : 1$ to form a thin SiO₂ layer on the Si(111) surface. This oxide layer prevents the formation of SiC islands on the Si(111) surface during heating of the Si substrate to the growth temperature. Afterward, the SiO₂ layer was heated up to 870 °C of the 1×1 surface reconstruction of Si(111) and was kept at this temperature for about 5 min to remove the SiO₂ layer completely in the high-vacuum growth chamber.

IRE nitridation of Si substrates for the growth of a DBL of AlN/ β -Si₃N₄/Si was performed using ADS N+N* flux.¹³⁾ The amount of deposited Al on β -Si₃N₄ for the DBL was controlled by adjusting the period of the mechanical shutter of the Al cell of the temperature of an Al K-cell. After the deposition of Al, the formation of AlN, or the formation of the DBL of AlN/ β -Si₃N₄/Si was confirmed on the basis of the RHEED pattern. Subsequently, 30 nm AlN buffer layer was grown by AM-MEE on the DBL. Finally GaN or AlN were grown by AM-MEE on the buffer AlN. Polarity was determined by KOH etching or the surface from the reconstruction pattern of RHEED in a MBE growth chamber.

3. Results and Discussion

3.1 Two rf-ICP discharge modes: HB and LB modes

A key issue for the rf-ICP discharge is controlling two discharge modes: LB and HB modes. The change in the brightness between the LB and HB modes for rf-ICP nitrogen plasma was viewed from outside of the tube, as shown in Figs. 6(a) and 6(b). The change in brightness is obvious.

Figure 7 shows a phase diagram of N_2 pressure and input power for the LB and the HB modes. The border of the phases was changed by varying the input power or N_2 pressure (flow rate) of the inside of the discharge tube. This phase diagram depends on the rf-ICP cell configuration, such as the orifice hole dimension and number, the diameter and wall material of the rf-ICP cell.



Fig. 6. (Color online) Brightness changes of two discharge LB (a) and HB (b) modes viewed from outside of the tube.



Fig. 7. (Color online) Phase diagram of N_2 pressure vs input power for the LB mode and HB mode. The borders from the LB mode to the HB mode when pressure changes or power changes are different. The borders from the HB mode to the LB mode in the case when both pressure and power coincide. At a constant pressure, the mode can be changed by changing power in the HB mode and the LB modes.

During the AM-MEE operation the time OES evolution of the three main N atom peaks are shown in Fig. 8 for 80 and 130 Pa. The transient intensity between the LB and HB modes, which are controlled by changing the input rf power between 200 and 400 W for 5 s. The three main spectra of N atoms, triplet 747.73 nm for ${}^{4}P{}^{-4}S^{0}$, 7 lines multiplet 822.73 nm for ${}^{4}\text{P}{-}^{4}\text{P}^{0}$, and 8 lines multiplet 869.26 nm for ${}^{4}P{}^{4}D^{0}e$, were indicators of the production of active N atoms. Intensity data were calculated by the numerical integration of each peak.⁸⁾ Inducing the HB mode takes more time at a lower pressure of 80 Pa, in which the number of nitrogen molecules is smaller than that at 130 Pa. The decay from the HB mode to the LB mode was rapid. The time constant at a higher pressure in a discharge tube is smaller than that at a lower pressure. Whether this time delay comes from the matching speed between the two modes of the rf circuit of the ICP cell or the nature of the mode transition itself is still a question at this moment.

3.2 Atomic flux current measurement for direct and indirect irradiation

In order to correlate between optical emission spectroscopy (OES) results and atomic current, the results of OES N, N^{*}, and N₂^{*} are shown first. The intensity of the OES of atoms and molecules is shown in Fig. 9. The spectra were reported in a previous report.¹²) The HB mode contains excited atomic lines (747, 822, 868, 904, and 940 nm) and activated



Fig. 8. (Color online) Time evolution of three atom peaks for N atoms of N 747 nm and exciter N atoms of N* 868 nm and N* 822 nm. The time constant at a higher pressure of a discharge tube is smaller than that at a lower pressure.



Fig. 9. (Color online) OES of atoms and molecules of the HB discharge at 80 Pa and 400 W.

molecule lines and bands (first positive series between 500 and 900 nm and second positive series between 300 and 500 nm). The relative number of excited particles can be calculated from the integrated optical emission intensity.⁸) The rf power dependence on the integrated intensity of OES for the components of N, N^{*}, and N₂^{*} was measured. Figure 10(a) shows the integral intensity of OES for each atom spectrum and molecule spectrum depending on rf power at 80 Pa (1.38 sccm). The total intensities for atoms and molecules are shown in Fig. 10(b).

Figure 11 shows direct atom flux measured using a Langmuir-like probe, as shown in Fig. 4(a), depending on the flow rate or pressure. Results showed that the number of atoms produced increased linearly with input rf power. A pressure increment also increased the production of atom nitrogen flux.

Figure 12 shows the indirect atom flux measured using a parallel-plate probe with voltages between -108 and +108 V. The current at the negative potential corresponds to the atom current caused by the self-ionization of the attached nitrogen atoms N+N*. Usually, a -108 V potential difference was used for successive measurements. Figure 13



Fig. 10. (Color online) (a) The integral intensity of OES for each atom spectrum and molecule spectrum depending on rf power is the same as that in the experiment using 80 Pa (1.38 sccm), as shown in Fig. 8(a). (b) Total OES intensity for atoms and molecules in (a).



Fig. 11. (Color online) Direct atom flux current measured using a Langmuirlike probe, depending on rf power as a parameter of pressure.

shows the effect of changing the bias potential to 1000 V. That is, the atom potential, V_A , changes from -108 to +108 V. The amount of current corresponds to the atom potential V_A . Figure 13 shows a linear increment in the indirect current depending on V_A .

The indirect irradiation flux, which was formed by the reflection from walls of the growth chamber, was found to



Fig. 12. (Color online) Indirect atom flux measured using a parallel plate probe of $60 \times 110 \text{ mm}^2$, as shown in Fig. 4(b). (a) Langmuir-like probe characteristics vs potential difference $V_A - V_B$. (b) Langmuir-like probe characteristics vs potential difference $V_A - V_B$, where V_B changed from 0 to -150 V.



Fig. 13. (Color online) Indirect atom flux current changing bias potential to 1000 V; that is, the negative potential of the electrode for self-ionization, V_A , changes from -108 to -1108 V.

be sensitive to the wall temperature and the amount of ADS nitrogen on the wall. Figure 14 shows the hysteresis behavior of ADS atom flux on the liquid nitrogen temperature of shroud wall in the growth chamber.

3.3 Role of the direct irradiation of excited N₂* molecules during AM-MEE

Preparation of a DBL of AIN/β -Si₃N₄/Si was described elsewhere.¹³⁾ Figure 15 shows the time sequences of AM-MEE growth of GaN for experimental conditions as shown in Table I. All growth were conducted under combinatorial method which grew various III/V flux ratio without substrate rotation. Substrate temperature was 620 °C with



Fig. 14. (Color online) rf power dependence of ADS nitrogen atom flux at liquid nitrogen temperature of shroud wall in the VG80H growth chamber. Hysteresis behavior was observed during power up and down processes due to reflection of N+N+ atoms from the wall.



Fig. 15. (Color online) The time sequences of AM-MEE growth of GaN for experimental conditions as shown in Table I.

Table I. Experimental values of the time sequences for (a) and (b) experiments (units: s).

	T_1	T_2	T_3	α	β
(a)	2	3	2	0	1
(b)	2	3	2	1	0
(c)	2	3	2	0	1
(d)	1	4	3	1	0

500 and 140 W for HB and LB mode of 80 Pa (1.38 sccm), respectively. 1800 AM-MEE cycles were repeated. Time sequences (a) and (b) are $T_5 = 0$ s and are shutterless operation. Migration times μ are 2 and 3s for the time sequence (a) and (b), respectively. During Ga irradiation N_2^* flux was also irradiated to give kinetic energy to Ga atoms. Time sequences (c) and (d) show shutter operation to protect N_2^* flux irradiation. During the irradiation of Ga flux N_2^* flux was not irradiated in these sequences of (c) and (d).

Figure 16 shows the interference photographs of GaN films grown on DBL on Si substrates by the AM-MEE experiment under the experimental conditions as shown in



Table I. The thicknesses measured by SEM photographs for the time sequences from (a) to (d) are shown in Fig. 17. The figures clearly show the effect of the irradiation of excited N_2^* molecules. The thickness became smaller owing to the irradiation of N2*. The largest thickness corresponds to the

Fig. 16. (Color online) Interference photographs of GaN films grown on DBL on Si substrates by the AM-MEE experiment under the experimental conditions

as shown in Table I.

stoichiometric position, where the III/V flux ratio is one. The growth rates at the stoichiometric position were 0.39, 0.26, 0.83, and 0.94 ML/cycle for the time sequence (a), (b), (c), and (d), respectively.

Figure 18 shows the change of RHEED patterns from Si(111) showing the effect of excited N_2^* molecule direct irradiation to the surface of Si(111). Figure 18(a) indicates 7×7 surface reconstruction of a Si(111) clean surface. Figure 18(b) to 18(d) show the change of Si surface RHEED patterns corresponding to the flow rates of 1.3, 3.0, and 5.0 sccm, respectively. They correspond to inside pressures of about 80, 130, and 180 Pa, respectively, as shown in Fig. 2. The Si surface did not change by the direct N_2^* flux irradiation of LB discharge at a lower pressure 80 Pa for 20 min. At higher pressures, the amount of the excited N_2^* molecules increased and the effect of irradiation of the excited N₂^{*} molecules appeared gradually. This finding shows that N₂* can react with Si but the reaction rate is very low compared to that of N+N*. This means that excited N_2^* molecules are not chemically active but are physically active. High chemical activity of N+N* atom is shown by the nitridation of Si(111) using ADS N+N* flux with indirect irradiation from HB mode for 1 min at 710 °C of substrate temperature with 200 W and 80 Pa (1.38 sccm) rf-ICP discharge conditions. Figure 19 shows a RHEED pattern showing the 8×8 surface reconstruction of β -Si₃N₄ obtained by an indirect irradiation of ADS N+N* atoms for 1 min.



Fig. 17. (Color online) Thickness distributions grown by 1800 AM-MEE cycles measured by SEM photographs for the time sequences (a) to (d) shown in Fig. 16. The thickness of time sequences of (a) and (b) became smaller than (c) and (d) owing to the irradiation of N_2^* . The effect of cleaning up time is obvious from the data of the time sequence (a) and (b).



Fig. 18. (a) RHEED pattern of 7×7 surface reconstruction of Si(111) showing a clean surface. (b)–(d) Pressure (flow rate) dependence of the irradiation of N₂^{*} for 20 min on RHEED from $e \parallel [11\overline{2}0]$.

4. Conclusions

With the aim of growing high-quality cubic GaN, the improvement of a nitrogen rf-ICP source and the *in situ* measurement of nitrogen atomic flux during the PA-MBE growth of GaN and AlN on Si substrates were presented. The electron emission due to the self-ionization of nitrogen atoms on a negatively biased electrode was demonstrated to measure *in situ* the nitrogen atom flux during the growth. The rf-ICP rf nitrogen discharge was also investigated to improve the GaN growth on Si substrates. Indirect irradiation and direct irradiation were effectively controlled to realize a single production system from a Si wafer to optical and electronic devices through the heteroepitaxial growth of



Fig. 19. (Color online) RHEED pattern of 8×8 surface reconstruction of β -Si₃N₄/Si(111) from $e \parallel [11\overline{2}0]$.

GaN or AlN on Si. The two discharge modes of the rf-ICP discharge, the HB and LB modes, were studied to apply both IRE of β -Si₃N₄ and AlN, and AM-MEE, which was one of ALE methods. Due to the contribution of direct irradiation of physically active N₂^{*} with kinetic energy during AM-MEE operation the substrate temperature becomes effectively higher. Indirect irradiation of a N+N* ADS atom flux was effectively used to grow a DBL of AlN/ β -Si₃N₄/Si uniformly.

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