Role of atomic nitrogen during GaN growth by plasma-assisted molecular beam epitaxy revealed by appearance mass spectrometry

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To identify the species which contribute to GaN growth, the authors investigated the discharge parameter (0.3–4.8 SCCM (SCCM denotes cubic centimeter per minute at STP), 150–400 W) dependences of the atomic N flux by appearance mass spectrometry and of the incorporated nitrogen atoms into GaN layers grown by plasma-assisted molecular beam epitaxy (PAMBE) using the rf-plasma source. Ion fluxes were also evaluated by ion current measurements. A good correlation between the supplied atomic N flux and the incorporated nitrogen flux was obtained under a wide range of plasma conditions. It was clarified that the atomic N plays a dominant role in the growth of GaN by PAMBE. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2734390]

Plasma-assisted molecular beam epitaxy (PAMBE) growth of III nitrides including GaN, AlN, InN, and their related alloys has attracted much interests because of its significant potential for forming sharp interfaces, and ultrathin and high purity layers which are needed to achieve enhanced performances of electron devices utilizing their heterostructures.

The rf-plasma sources are most widely used to produce active nitrogen species for growing III-nitride films by PAMBE. Several investigations by using quadrupole mass spectrometry[1–5] and optical emission spectroscopy[2,6,7] reported that their outputs contain atomic N or metastable N_2 or a mixture of them plus N_2 ion which have been proposed as responsible species for growing GaN under metastable growth conditions such as PAMBE.[8] For growing high quality films reproducibly, ions should be eliminated and the ratio between each active species and/or the amount of each active species should be controlled. For the quantitative evaluation of the species in or from a plasma source, appearance mass spectrometry[9] (AMS) or threshold ionization mass spectrometry[1] was generally used. In this method, for example, $m/e=14$ signals produced by reactions $N+e\rightarrow N^+ +2e$ (direct ionization of atomic N), and $N_2+e\rightarrow N^+ + N +2e$ (dissociative ionization of N_2 molecules) in the ionization room of the mass spectrometer are distinguished by analyzing the ionization energy dependence of the signal intensity considering the difference in the threshold energies of these reactions. So far, the active nitrogen species emitted from the N_2 plasma sources were characterized using this method by several authors;[1,3] however, a detailed and systematic study on the relation between the growth and these species was not yet done. In order to identify the species which contribute to the GaN growth, we investigated the discharge parameter dependences of the atomic N flux by AMS and of the incorporated nitrogen atoms into GaN grown by PAMBE using a rf-plasma source. Ions and metastable N_2 fluxes were also evaluated by ion current measurements and AMS, but were negligibly small.

The rf-plasma source used for experiments was a SVT Associates model rf 4.5 with an aperture consisting of 25 holes (0.5 mm in diameter). The analysis chamber equipped with a quadrupole mass spectrometer (QMS), as shown in Fig. 1, was fixed to the conventional MBE chamber. The MBE chamber has the capability of biasing the substrate to repel ions. The rf-plasma source was mounted either to the analysis chamber for mass spectroscopy measurements or to the MBE chamber for growth experiments. The distance between the aperture of the source and the entry aperture (1 mm in diameter) of the QMS was set to be the same as the distance between the source aperture and the substrate during growth. Also, the conductances and the distances between the turbo molecular pump of the MBE system and both the QMS and the growth position were the same. As a result, the pressures behind the source aperture monitored using a Bara-

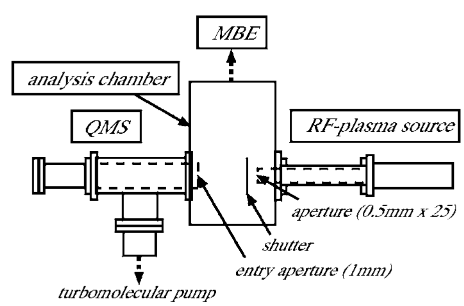

FIG. 1. Schematic illustration of the experimental setup.

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tron gauge during mass spectrometry and growth experiments were the same at fixed nitrogen flows. They were varied from 70 to 450 mTorr by adjusting the nitrogen flow rate from 0.3 to 4.8 SCCM (SCCM denotes cubic centimeter per minute at STP) using a mass flow controller. Therefore, almost identical plasma conditions were ensured for both mass spectrometry and growth experiments. In order to discriminate the directional straight beam component (directly entering the QMS ionizer from the source) from the background component, the incoming beam into the ionizer was modulated by using a shutter. Ion components from the source such as N^+ and N_2^+ were deflected by applying 40 V on a deflector in front of the source aperture.

For measuring the atomic N density at the QMS entry aperture, the mass 14 signal was detected by keeping the ionizing energy at 21 eV which is high enough to ionize atomic N (14.5 eV), but below the dissociation threshold of N_2 molecules (24.3 eV). Similarly, the long-lived (>2.0 s) (Ref. 10) metastable N_2 $(A^3\Sigma_u^+)$ could be detected, as reported in Ref. 1, by detecting the mass 28 signal at the ionizing energy at about 13–14 eV which is below the direct ionization threshold of N_2 (15.6 eV), but high enough to ionize the metastable N_2 (~12 eV). However, no detectable metastable N_2 signal was found though the optical emission from the plasma showed relatively strong peaks associated with the metastable N_2. Also, N^+ and N_2^+ ions were not detected by the QMS (ionizer filament off mode). So, the total ion flux at the growth position was estimated by measuring the substrate current, as reported in Ref. 11. Typically, the ion current was 4 μA when the 6 cm diameter substrate holder was biased at −10 V. Thus, the ion flux was estimated to be less than 10^{12} ions/cm^2 s which is less than 0.1% of the atomic N flux. As a result, it can be said that only atomic N and N_2 were emitted from the source. The absolute atomic N flux at the QMS entry aperture was deduced from the direct ionization of the N_2/atom ionization reaction ratio and the inlet N_2 flux, as follows. N^+ and N_2^+ signals detected in QMS can be described as

$$I_{N^+} = A\frac{\phi_N}{v_{th}^N}\sigma_{N^+}, \quad (1)$$

$$I_{N_2^+} = A\frac{\phi_{N_2}}{v_{th}^{N_2}}\sigma_{N_2^+}, \quad (2)$$

where A is the QMS sensitivity coefficient, ϕ is the flux, ν_{th} is the thermal velocity, and σ is the cross section of the ionization process. According to Eqs. (1) and (2), the atomic N flux ϕ_N is expressed in terms of the N_2 flux ϕ_{N2} as

$$\phi_N = \frac{\sigma_{N^+}}{\sigma_{N_2^+}} \cdot \frac{v_{th}^{N_2}}{v_{th}^N} \cdot \frac{I_{N^+}}{I_{N_2^+}}\phi_{N_2}. \quad (3)$$

The sum of the N_2 flux and a half of the atomic N flux at the measuring position should be proportional to the incident N_2 flow rate Q (SCCM) into the source

$$Q = K\left(\phi_{N_2} + \frac{1}{2}\phi_N\right), \quad (4)$$

where K is a ratio of Q to the sum of the fluxes at the measuring position. Equation (3) and (4) are solved to find the values of ϕ_{N_2} and ϕ_N. The constant K can be deduced from the flux distribution of the source. The flux distribution

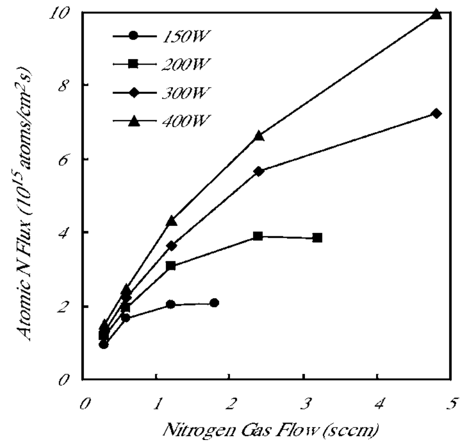

FIG. 2. Atomic nitrogen flux dependence on the nitrogen gas flow rate at four indicated rf powers. The lines through the data points are only there to guide the eye.

was calculated assuming a molecular flow regime considering the real alignment of the substrate and the 25 holes of the source aperture. Figure 2 shows the dependence of the atomic N flux as a function of the incident N_2 flow rate for different source powers. At low discharge powers (150 and 200 W), the atomic N flux tends to saturate at high nitrogen flow rate. For these low-power conditions, no atomic N was observed at high nitrogen flow rate (2.4 and 4.8 SCCM for 150 W, and 4.8 SCCM for 200 W). At high discharge powers (300 and 400 W), the atomic N flux increases as the nitrogen flow rate increases. However, it does not increase in proportion to the increase of the nitrogen flow rate. The dissociation fraction (dissociated nitrogen molecules/supplied nitrogen molecules) was higher at lower flow rate and higher power, and was 33% at 0.3 SCCM and 400 W.

Ga-polarity GaN films were grown on hydride vapor phase epitaxy GaN templates on (0001) sapphire substrates using the MBE system. The substrate temperature was 600 °C where both the Ga desorption and the GaN decomposition could be neglected. The substrate temperature was measured by a thermocouple which was calibrated using the melting temperatures of GaSb, Al, and Ge stuck to GaN templates with In. It is well known that the growth rate is limited by both the Ga flux and the nitrogen flux only when the growth is performed under the critical condition where the reflection high-energy electron diffraction (RHEED) pattern from the growing surface shows the boundary of the streaky pattern (Ga-rich condition) and the three-dimensional-like spotty pattern (N-rich condition). So, the incorporated Ga flux is equivalent to both the supplied Ga flux and the incorporated nitrogen flux when the GaN film was grown under this critical condition. To determine the critical Ga flux for each plasma condition, RHEED patterns were recorded during the GaN growth for more than 10 min under a certain Ga flux, and then the Ga flux was changed by changing the Ga cell temperature. These sequences were repeated until the RHEED pattern changed. Figure 3 shows the dependence of the incorporated nitrogen flux (the critical Ga flux) as a function of the incident N_2 flow rate for different source powers. The incorporated nitrogen flux shows very similar dependence on the plasma parameters to that of the atomic N flux. Figure 4 shows the relation between the supplied atomic N flux and the incorporated nitrogen flux. In the figure, the incorporated nitrogen flux for the plasma condi-

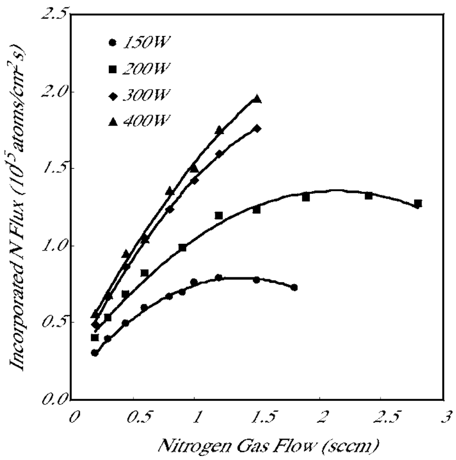

FIG. 3. Dependence of the incorporated nitrogen flux into Ga-polar GaN on the nitrogen gas flow rate at four indicated rf powers. The lines through the data points are only there to guide the eye.

tion in which AMS measurement was performed was deduced from the curves in Fig. 3. As can be seen in Fig. 4, an excellent direct proportional relation was found between the supplied atomic N flux and the incorporated nitrogen flux, although the discharge parameters were widely changed. This direct proportional relation indicates that the atomic N is the active nitrogen species for growing nitrides semiconductor films. From the slope of the straight line in Fig. 4, the sticking efficiency of atomic N to GaN was found to be 36%.

In summary, from the AMS measurements, the atomic N flux under various plasma conditions (0.3–4.8 SCCM, 150–400 W) at the growing surface was obtained and compared with the incorporated nitrogen flux during growth. As a result, a good correlation between the supplied atomic N flux and the incorporated nitrogen flux was obtained under a wide range of plasma conditions. Ions and metastable N_2 fluxes were also evaluated by ion current measurements and AMS, but were negligibly small. It was clarified that the atomic N plays a dominant role in the growth of GaN by plasma-assisted MBE.

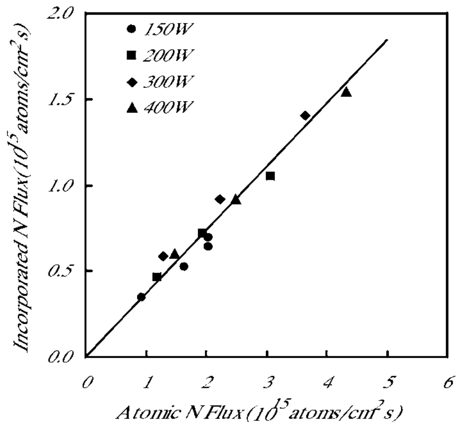

FIG. 4. Incorporated nitrogen flux as a function of atomic nitrogen flux for rf powers of 150, 200, 300, and 400 W.

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