

In situ measurement of adsorbed nitrogen atoms for PA-MBE growth of group III nitrides on Si

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Received 2 October 2010, revised 17 November 2010, accepted 22 November 2010

Published online 23 March 2011

Keywords MBE, Si₃N₄, atom flux measurement, nitrogen atom adsorption

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An atom probe of two parallel electrodes is proposed to monitor adsorbed (ADS) nitrogen atoms *in situ* during growth of β -Si₃N₄ using indirect exposure of effusing active nitrogen beam from the radio frequency induction coupled plasma cell. The β -Si₃N₄ film is a component of a double buffer layer (DBL) AlN(0001)/ β -Si₃N₄/Si(111) to grow high quality the group III

nitrides and their alloys on Si. Atom current between the parallel electrodes corresponds to flux of the ADS nitrogen atoms on the inside surface at the atom potential, V_A . The ADS atom current received influence of wall and shutter of the cell, because adsorption of nitrogen atom depended wall condition such as temperature and the concentration of adatoms on the wall.

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1 Introduction To grow high quality group III nitride semiconductors and their alloys on large area Si substrates for energy saving materials, AlN buffer is one of the promising candidates. Wu and his group proposed an coincident-interface AlN/ β -Si₃N₄ double-buffer layer (DBL) structure to grow GaN on Si(111) [1]. Using plasma-assisted molecular beam epitaxy (PA-MBE), the DBL of AlN(0001)/ β -Si₃N₄/Si(111) is also proposed by the group of the present authors [2,3]. Wistey and his group monitored ion flux but not atom flux during MBE growth using a Langmuir-like probe, which was a grid or filament electrode of an ionization gauge of MBE system [4]. The present authors also studied measurement of active nitrogen atoms N+N*, which consist of ground state nitrogen atoms N and excited state nitrogen atoms N*, in a radio frequency induction coupled plasma (rf-ICP) discharge for the growth of group III nitrides and their alloys [5,6]. The rf-ICP discharge has two discharge modes such as low brightness (LB) and high brightness (HB) discharge modes. They measured the direct irradiating flux of active nitrogen atoms N+N* using a Langmuir-like electrode due to the self-ionization of adsorbed (ADS) nitrogen atoms N+N* on a negatively biased electrode, if charged particles impinging to the probe was eliminated [6]. The self-ionization, which emitted electrons from ADS N+N* on an atom electrode, produced the atom current and was confirmed using different electrodes such as Pt and CuBe and different electrode area [6]. The atom current was cali-

brated by the grown GaN thickness in a VG80H MBE system and 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 [6]. As N+N* atoms have long life time and they are also active as ADS atoms during discharge for indirect irradiation at the behind of the shutter or a remote plasma position in a growth chamber. *In situ* measurement of ADS nitrogen atoms is available to use the self ionization of ADS nitrogen atoms on a negatively biased electrode using a parallel plate electrodes [7] and a spiral mesh electrode [8].

One component of the DBL, β -Si₃N₄ is formed by the nitridation of Si(111) substrate using interface epitaxy (IRE) between ADS nitrogen atoms and Si [2,3]. The ADS nitrogen atoms are generated by the indirect irradiation from a rf-ICP cell. The indirect irradiation is able to realize closing a shutter of the rf-ICP cell or placing it at a remote plasma position.

In this report *in situ* measurement of ADS N+N* atoms using a parallel plate atom electrode in a growth chamber of VG80H system or in a special measurement system [6] for an application to the IRE β -Si₃N₄ growth on Si(111).

2 Experimental

2.1 Equipments The production of the chemically active nitrogen atoms N+N* was performed by IRFS-501RF nitrogen radical source made by Arios Inc. under the discharge condition of 1.38 sccm and up to 500 W of

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HB mode [4-8]. *In situ* measurement of ADS $N+N^*$ atoms was performed in a VG80H MBE growth chamber or a chamber for specially designed measurement chamber [6]. The atom probe was placed at the side position in the MBE chamber or at the behind of a shutter for the special chamber. The pressure of the inside of rf-ICP cell, which was important parameter of discharge, was not measure directly. The pressure just before the inlet of the cell was measured and related to the flow meter value. The relation ship between the pressure and the flow rate is different for the MBE chamber and the special chamber such as 0.78, 1.38, 1.68, 1.98, 2.38 sccm correspond to 37, 75, 83, 92, 115 Pa at 500W discharge, respectively for the MBE chamber and 1.38 sccm corresponds 129 Pa at 500W discharge, respectively for the special chamber. The pressure was increased starting of discharge because of dissociation from molecules to atoms.

2.2 Atom current using self-ionization A parallel plate electrode (PEE), the area of which is $60 \times 110 \text{ mm}^2$ and distances of two electrodes are 20 and 6 mm for Fig. 1(a) and (b), respectively, were used to measure ADS atom flux. Figure 2 shows a schematic drawing of a model of the self-ionization of active nitrogen atoms on a negatively biased electrode. The potential at the negatively biased terminal A, where the lowest potential, is called as the atom potential, V_A . The potential at a terminal B, which is used for a Langmuir-like electrode, is called the Langmuir bias potential, V_B .

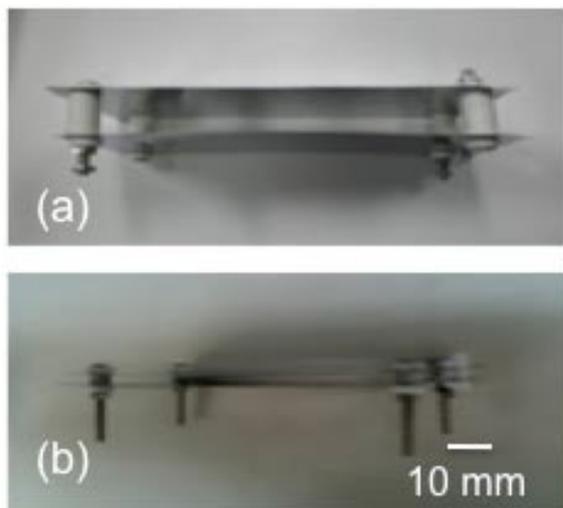


Figure 1 Photographs of PEEs, the area of which is $60 \times 110 \text{ mm}^2$ and distances of two electrodes are 20 mm for Fig. 1(a) and 6 mm for Fig. 1(b).

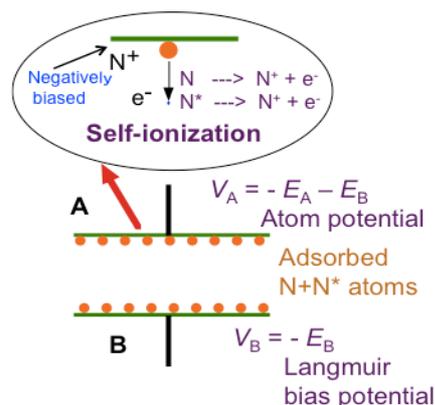


Figure 2 A schematic drawing of a model of the self-ionization of active nitrogen atom flux on a negatively biased electrode.

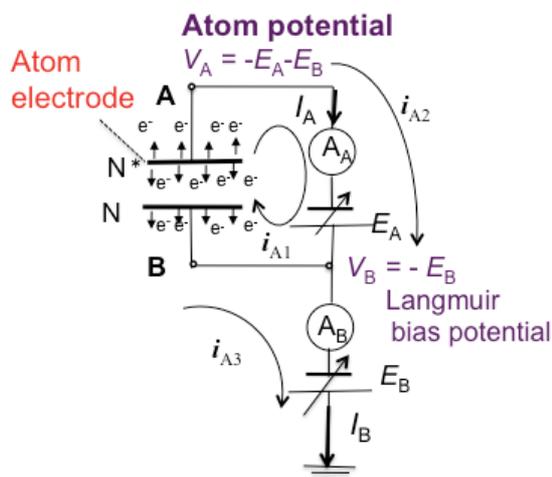
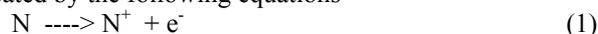


Figure 3 Schematic drawing of an electrical circuit using parallel plate electrodes measuring ADS nitrogen flux.

Electron emission from active ADS nitrogen atoms on an electrode surface such as N and N^* at negative potential created by the following equations



create the atom current I_A [A] as shown in the following equations.

$$I_A = -\gamma S V_A, \quad (3)$$

$$V_A = -E_A + V_B = -E_A - E_B, \quad (4)$$

where γ is the self ionization coefficient [A/Vm^2], S [m^2] is the surface area of the atom electrode, and V_A [V] ($V_A = -E_A < 0$) is the atom potential, which is negatively biased for the self ionization. E_A and E_B are dc variable voltage sources of battery cells array. Figure 3 shows a schematic drawing of an electric circuit for atom flux current measurement using a PPE. The atom potential, V_A is a key potential to determine the I_A i.e. the amount of the self-ionization from the atom electrode. The Langmuir bias potential, V_B affects to the I_A as shown in Eq. (4). The atom current I_A changes linearly by E_A or E_B . The minus sign comes from negative charge of electrons. From the surface

of two plates depending V_A and V_B electron emission by the self-ionization forms currents i_{A1} , i_{A2} , and i_{A3} as shown in Fig. 3. The atom current I_A and the Langmuir-like current I_B are given by the following equations

$$I_A = i_{A1} + i_{A2}, \quad (5)$$

$$I_B = i_{A2} + i_{A3}. \quad (6)$$

Current I_A passes through a picoampere meter, A_A connected to terminals A and B, is the sum of i_{A1} , which is created by the self-ionization of inside surface of plate A and i_{A2} , which is created by the self ionization of outside surface of plate A. Current I_B passes through a picoampere meter, A_B connected to terminal B is the sum of i_{A2} and i_{A3} , which is created by the self ionization of outside surface of plate B. If the Langmuir bias potential V_B is 0 V, i_{A3} is canceled by i_{A2} so that only i_{A1} is measured. The atom current I_A vs the atom potential V_A under $V_B = 0$ V shows E_A dependence only.

As an application of this monitoring system, an interface reaction epitaxial (IPE) growth of β - Si_3N_4 by nitridation of Si with the ADS nitrogen atoms was performed elsewhere [2,3].

3 Results and discussion

3.1 Atom current vs atom potential Figure 4 shows indirect ADS atom current I_A vs the atom potential V_A in the case of indirect irradiation for the 1.38 sccm nitrogen flow rate (129 Pa) at 500 W discharge condition using a special measurement chamber [6]. The distance of two electrodes was 6 mm. Value of E_A was changed from -108 to 108 V between two parallel electrodes. Three Langmuir bias potentials, V_B 0, -75 and -175 V were used. These curves are confirming in the Fig. 4 that I_A follows the Eq. (3) when the atom potential, V_A , is biased negatively. The slope of the line of negative potential range, -9.3×10^{-4} nA/Vcm², corresponds to the value of γ in Eq. (3) for the special chamber. The result, that the three curves do not perfectly coincide with, comes from the fluctuation of ADS nitrogen atoms.

Figure 5 shows indirect ADS atom current I_A vs the atom potential V_A in the case of indirect irradiation for the 1.38 sccm nitrogen flow rate (75 Pa) at 500 W discharge condition using the VG80H MBE chamber. Two kinds of measurements such as changing E_B and E_A were performed. In the case of changing E_B (V_B) using constant $-E_A = -108$ V, V_B was changed from -800 to 0 V. In the case of changing E_A using constant $-E_B = 0$ and -200 V, V_A were changed from -108 to 108 V and -308 to -92 V respectively. Figure 5 shows dark current measurement at $-E_B = 0$ V too. Without making discharge or LB discharge mode no ADS atoms come to an atom electrode. Then no atom current was observed and the self ionization model was confirmed. The slope of the line of negative potential range, -4.5×10^{-3} nA/Vcm², corresponds to the value of γ in Eq. (3) for VG80H chamber. Figure 4 and Fig. 5 show the self-ionization model of Eq. (3) is confirmed. In the $V_A > 0$ region the self-ionization model is not available to use. Near $V_A = 0$ V currents trend vs V_A is different. This comes from

the wall change of measurement system such as the special chamber and the VG80H MBE chamber.

3.2 Influence of distance between two plates

Photographs of PPEs as shown in Fig. 1 shows two electrodes distance of 20 and 6 mm (a) and (b), respectively. Figure 6 shows indirect ADS atom current I_A vs the atom potential V_A in the case of indirect irradiation for the 1.38 sccm nitrogen flow rate (110 Pa) at 500 W discharge condition using the special measurement chamber. Larger distance of 20 mm could correct larger amount of ADS atoms by the indirect irradiation.

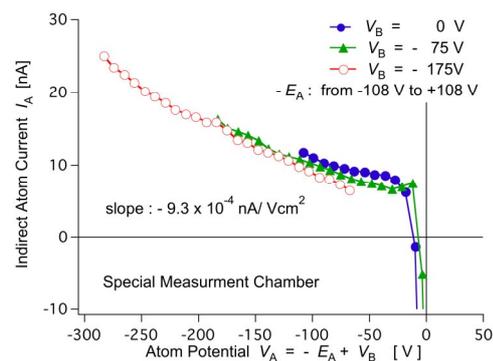


Figure 4 Indirect ADS atom current I_A vs the atom potential V_A in the special measurement chamber.

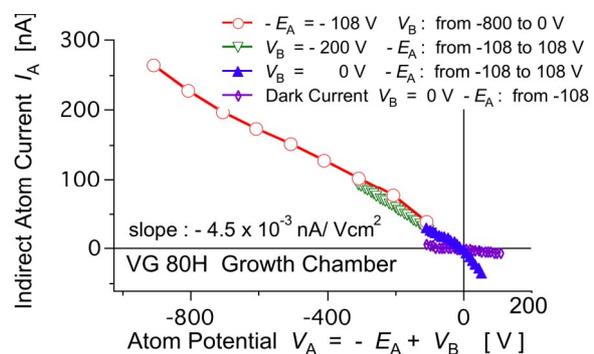


Figure 5 Indirect ADS atom current I_A vs the atom potential V_A in the VG80H MBE chamber.

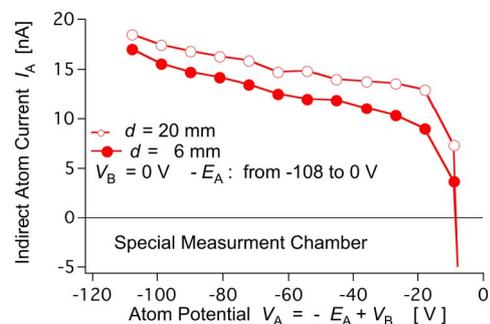


Figure 6 Electrode distance dependence of indirect ADS atom current I_A vs the atom potential V_A in the special measurement chamber.

3.3 Indirect irradiation of nitrogen atoms Influence of a wall of a vacuum chamber for adsorption and amount of $N+N^*$ fluxes is very important to control the amount of nitrogen irradiation to the growth surface. When rf power was increased, the amount of creation of total amount of active nitrogen species increased as linear relationship for $N+N^*$ and increased as monotonically for N_2^* [7]. The atom current I_A , which is correlated with the adsorption of active nitrogen species on a wall and shutter plate in the growth chamber, was measured *in situ* using room temperature and liquid nitrogen temperature conditions as shown in Fig. 7 and 8. Figures 7 and 8 show the rf power and pressure in rf-ICP cell dependences of indirect ADS atom current used a PPE of 6 mm distance in the VG80H MBE growth chamber for $-E_A = -108$ V and $V_B = 0$ V at room temperature and at liquid nitrogen temperature, respectively. The I_A does not increase linearly even effusing nitrogen flux increases by rf power linearly [7]. In Fig. 7 and 8 the flow rate and chamber pressure are shown. The pressures of the inside of rf-ICP cell in the MBE chamber are 37, 75, 83, 92, 115 Pa for 0.78, 1.38, 1.68, 1.98, 2.38 sccm respectively. Hysteresis of upward and downward power change was observed at higher discharge pressures. Amount of ADS were increased at higher pressure. The in-

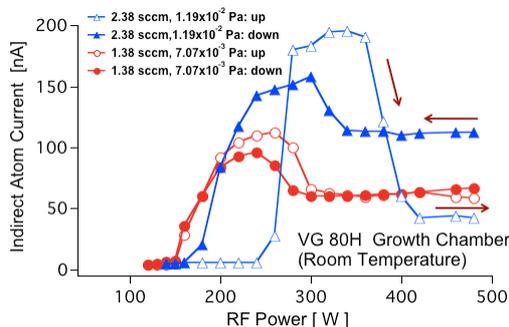


Figure 7 Pressure dependence of discharge of indirect ADS atom current I_A vs rf power for $-E_A = -108$ V and $V_B = 0$ V at room temperature in the VG80H MBE chamber.

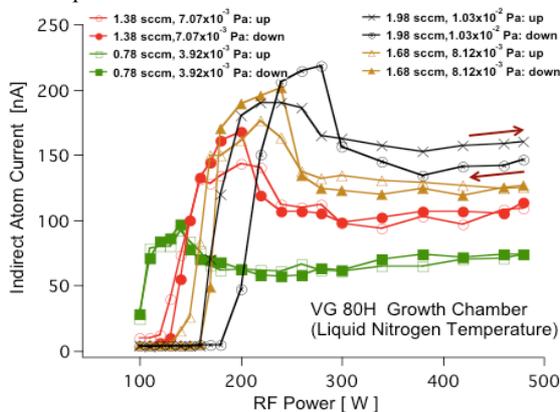


Figure 8 Pressure dependence of discharge of indirect ADS atom current I_A vs rf power for $-E_A = -108$ V and $V_B = 0$ V at liquid nitrogen temperature in the VG80H MBE chamber.

direct ADS current fluctuated and depended on the wall condition and the amount of effusing atom flux, because the reflection from the wall changed at the condition of adsorption on the wall surface. The ADS $N+N^*$ atom flux impinging to the atom electrode changes depending on the position of the atom probe. Indirect atom flux distribution within a vacuum chamber was confirmed changing position of the atom probe.

Although higher wall temperature was expected to reflect larger amount of the ADS atoms, the experimental results of Figs. 7 and 8 showed contradiction. Higher pressure showed hysteresis at larger power on power change. After growth of AlN with Al irradiation I_A was decreased (data were not shown here). The amount of ADS nitrogen atoms depended on various wall conditions. *In situ* measurement is therefore very important to apply ADS nitrogen for nitridation of Si surfaces for producing a DBL of AlN/ β -Si₃N₄/Si [2,3].

4 Conclusion The self-ionization of nitrogen atoms on negatively biased electrodes is demonstrated to measure *in-situ* indirect nitrogen atomic fluxes using a parallel plate electrode as an atom probe. Although effusing direct nitrogen jet of $N+N^*$ atom flux from a rf-ICP increased linearly by rf power, the indirect flux of ADS nitrogen atoms during discharge did not increase, fluctuate depending on wall condition and decreased at higher power discharge. Influence of a wall of a growth chamber was large because of the reflected-flux reduction at the wall. *In situ* measurement of the ADS nitrogen atoms will be used to grow high-quality group III nitride semiconductors and their alloys on large area Si substrates by PA-MBE.

Acknowledgements This work was funded by the Research Center for Interfacial Phenomena, Doshisha University. This research was partially supported by the Ministry of Education, Culture, Sports, Science, and Technology, through a Grant-in-Aid for Scientific Research B (20360011) 2008. We are grateful to the many contributions from the students of our laboratories.

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