Atomic layer etching of (100)/(111) GaAs with chlorine and low angle forward reflected Ne neutral beam

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ABSTRACT

Characteristics of atomic layer etching of (100) GaAs and (111) GaAs have been investigated using Ne neutral beam and Cl_2 gas. By using a Ne neutral beam dose and a Cl_2 gas pressure higher than critical values of 3.03×10^{16} atoms/$cm^2 \cdot$cycle and 0.4 mTorr, respectively, steady state etch rates of 1.41 Å/cycle for (100) GaAs and 1.63 Å/cycle for (111) GaAs which correspond to the etch rate of one atomic layer/cycle could be obtained. At the monolayer etching condition, the roughness of the GaAs surface was remaining similar to that of the unetched GaAs surface. In addition, the GaAs etched by the atomic layer etching showed the surface composition similar to that before the etching while the GaAs etched by a conventional reactive ion etching such as an inductively coupled plasma etching showed significant change in the surface composition.

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1. Introduction

Gallium arsenide (GaAs) has been used for the devices such as high electron mobility transistors (HEMTs) [1,2], light emitting diodes (LEDs) [3–5], and quantum dot (QD) devices [6] due to its excellent material properties including high carrier mobility, wide operating temperate range, direct energy band structure, etc. For the fabrication of these GaAs-based devices, reactive ion etching techniques such as capacitively coupled plasma etching, inductively coupled plasma (ICP) etching, etc. are generally applied to obtain anisotropic etching properties. However, due to the energetic reactive ions involved in the reactive ion etch processing, the etched GaAs surface tends to be damaged physically and chemically by structural disruption, inter-mixing, stoichiometric modification, surface roughening, etc. In addition, it is difficult to control the etch depth precisely through the reactive ion etching due to the fluctuation of the etch process. To overcome these problems, various atomic layer etching techniques (ALETs) have been investigated especially as the application to the nano-device processing which requires atomic-scale precision in the etching in addition to the nearly no-damage to the surface during the etching.

Current ALET is composed of the following four steps; i) adsorption of reactant molecules on the surface, ii) evacuation of the excess reactant, iii) energy irradiation to the reactant-adsorbed surface for the desorption of chemisorbed species, iv) evacuation of the etch product. As the method of energy irradiation for the desorption of the chemisorbed species, the irradiation of electron [7], Ar^+ ion [8], XeF excimer laser [9], etc. have been used. Among these methods, the ALET by the irradiation of XeF excimer laser is difficult to be applied for a large area processing and the ALET by the irradiation of electron or Ar^+ ion can damage the material electrically by charging.

Therefore, in this study, instead of the irradiation of the above energetic charged particles, the irradiation of a neutral beam during the ALET of (100)/(111) GaAs materials has been investigated to minimize the electrical damage to the GaAs materials and the effect of the ALET on the properties of the GaAs surface was investigated.

2. Experiment

As the gas, Ne was used and 300 W (13.56 MHz) of rf power was applied to the ICP source to generate a Ne plasma. For the three-grid ion gun system, the 1st grid located near the ICP source controls the energy of the ion beam and the 2nd grid controls the flux of the ion beam. To extract the Ne ion beam, 10 V was applied to the 1st grid while −250 V was applied to the 2nd grid for a high flux and low energy ion beam. The third grid was grounded. When the energy and flux of the extracted ion beam was measured using a Faraday cup before the reflection on the reflector, about 32 eV and 3.7×10^{14} ions/cm^2 could be measured, respectively. (With this neutral beam energy, only Cl-adsorbed GaAs was only removed without etching the bare GaAs due to the differences in binding energies.) After the reflection, the neutralization percentage was measured to be higher than 99%. The more details on the neutral beam source used in the experiment can be found elsewhere [10].

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As the samples, n-type (100) and (111) GaAs wafers (some wafers were patterned with photoresist) were used and, before the etching, native oxide layer on the GaAs surface was removed by dipping in a HCl solution followed by cleaning with de-ionized water and N_2 gas blowing. The ALET process steps performed in this study are as follows. Chlorine gas is supplied for ten seconds at various pressures to the etch chamber during the adsorption period so that chlorine can be adsorbed on the surface of GaAs. Then, the neutral beam source is turned on for tens of seconds to desorb the adsorbed species. Between the above steps, the etch chamber is evacuated for three seconds. Typical experimental parameters and typical sequence/time for the ALET process are shown in Table 1 and Fig. 1, respectively.

The etch depth was measured by an α-step profilometer (Tencor Instrument, Alpha Step 500), and the etch depth per cycle was calculated by dividing the measured etch depth by the etch cycles. The surface roughness was measured using an atomic force microscope (AFM, Thermo-microscopes, CP research) and the surface composition of GaAs after the etching was measured by angular resolved X-ray photoelectron spectroscopy (ARXPS, Thermo VG, MultiLab 2000, Mg Kα source). The surface composition of GaAs after the etching by the ALET was compared with that obtained after an ICP etching.

## 3. Results and discussion

Fig. 2 shows the etch rate (Å/cycle) and root-mean-square (rms) roughness of GaAs measured as a function of Cl_2 gas pressure. The Cl_2 gas pressure was varied from 0 to 0.61 mTorr while the Ne neutral beam irradiation dose was maintained at 3.4×10^{16} atoms/cm²·cycle. Total etch cycles were maintained at 100 cycles. As shown in the figure, when Cl_2 gas pressure was 0 mTorr (no gas flow), no etching of (100) GaAs and (111) GaAs could be observed indicating that there is no sputter etching of GaAs surface with the Ne neutral beam energy of 32 eV used in the experiment. On the other hand, as the Cl_2 gas pressure is increased from 0 to 0.4 mTorr, the etch rate was increased rapidly and, at the pressure higher than 0.4 mTorr, the etch rates of (100) GaAs and (111) GaAs were saturated to 1.41 Å/cycle and 1.63 Å/cycle, respectively, which corresponds to the etching condition of one atomic layer/cycle regardless of the change of the Cl_2 gas pressure. In addition, when the increase of etch rate as a function of Cl_2 gas pressure was the highest, the surface roughness became the highest. Therefore, at about 0.1 mTorr, the rms surface roughness of (100) GaAs and (111) GaAs was the highest as about 4.01 Å and 7.02 Å, respectively, and the further increase of Cl_2 gas pressure decreased the surface roughness. When the Cl_2 gas pressure was higher than 0.4 mTorr, the surface roughness of (100) GaAs and (111) GaAs was remained similar to that of the as-received GaAs samples ((100) GaAs: 1.98 Å, (111) GaAs: 2.84 Å).

The characteristics of the Cl_2 ALET obtained in our experiment as a function of Cl_2 pressure are related to the coverage of Cl_2 adsorbed on the GaAs surface. According to the dissociation Langmuir isotherm, the surface coverage (θ) can be represented by $\theta = \sqrt{kp}/\left(1 + \sqrt{kp}\right)$ [11], where, θ is surface coverage, k is reactive gas adsorption constant, and p is the gas pressure. Even though k is dependent on the substrate temperature, k is remained constant in our experiment because the substrate was kept at room temperature, therefore, θ is dependent

Table 1
Typical experiment parameter of GaAs ALET

Parameter	Value
Base pressure	3.0×10^{-7} Torr
Inductive power	300 W
1st grid voltage	10 V
2nd grid voltage	−250 V
Ne flow rate	70 sccm
Cl_2 supply time	10 s
Substrate temperature	RT
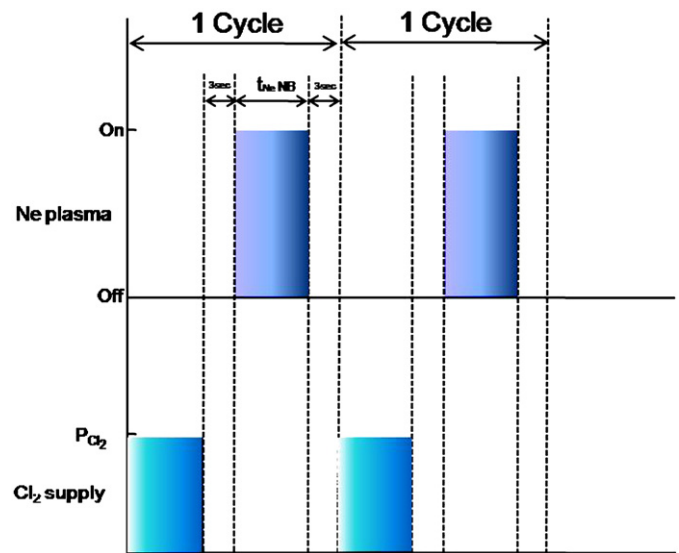
Fig. 1. Sequence of the ALET process used in this experiment.

only on the Cl_2 pressure. When Cl_2 gas was adsorbed on the GaAs surface, Ga (or As) chlorides are formed by transferring electrons in the GaAs to adsorbed Cl_2 and the binding energy between As (Ga) and the Ga (As) chlorides just below the surface is weakened. In addition, because the binding energy of GaAs (Ga–As: 2.177 eV) is lower than the binding energy of the Ga (or As) chlorides (Ga–Cl: 4.996 eV, As–Cl: 4.649 eV), [12,13] during the Ne neutral beam irradiation, the bonds below the Ga (or As) chlorides on the surface are preferentially broken instead of the bonds between Ga (or As) and Cl in the chlorides, and the Ga (or As) chlorides are easily removed. Therefore, when the Cl_2 pressure is lower than 0.4 mTorr, due to the partial coverage of chlorides on the GaAs surface, only the area covered by Ga (or As) chlorides are removed during the irradiation stage by the Ne neutral beam and the etch rate (Å/cycle) is increased with the increase of Cl_2 pressure. However, if the surface coverage becomes 1.0, the further increase of the Cl_2 pressure does not contribute in the increase of surface coverage when the Cl_2 gas follows the Langmuir isotherm, therefore, the etch rate is saturated if the all the chlorides formed on the surface can be removed during the each cycle by the sufficient Ne neutral beam bombardment. When all of the chlorides on the surface are removed, then the etch rate of one monolayer/cycle is reached and, depending on the crystallographic orientation, different etch rate is
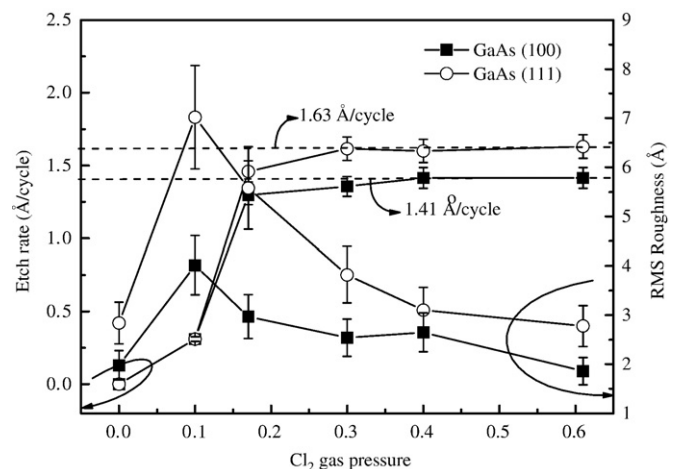
Fig. 2. Etch rate (Å/cycle) and rms roughness of GaAs by Ne neutral beam ALET as a function of Cl_2 gas pressure at the Ne neutral beam irradiation dose of 3.4×10^{16} atoms/cm² · cycle.

obtained, that is, 1.41 Å/cycle for (100) GaAs and 1.63 Å/cycle for (111) GaAs. In the case of the surface roughness, when the Cl_2 pressure is lower than 0.4 mTorr, only the area covered by the chlorides is etched during the desorption cycle and, at the pressure range from 0 to 0.4 mTorr, the roughness was the highest due to the partial etching of surface atoms at each cycle by the Ne neutral beam.

Fig. 3 shows the effect of Ne neutral beam irradiation dose on the GaAs etch rate (Å/cycle) and rms surface roughness during the ALET. The Ne neutral beam irradiation dose was varied from 0 to 4.55×10^{16} atoms/cm^2·cycle while the Cl_2 pressure was maintained at 0.4 mTorr to cover the surface completely with Ga (or As) chlorides. As shown in the figure, when the Ne neutral beam irradiation dose was 0, no etching of (100) GaAs and (111) GaAs could be observed indicating that there is no spontaneous etching by the adsorbed Cl_2. On the other hand, when the Ne neutral beam irradiation dose was increased to 3.03×10^{16} atoms/cm^2·cycle, the etch rate was increased almost linearly with increasing the irradiation dose and the further increase of the irradiation dose saturated the etch rate. The increase of the etch rate with the increase of Ne neutral beam irradiation dose to 3.03×10^{16} atoms/cm^2·cycle was related to the insufficient dose in removing all the chlorides formed on the surface during the each cycle, therefore, when the irradiation dose was higher than the critical dose of 3.03×10^{16} atoms/cm^2·cycle required to remove one monolayer of Ga (As) chlorides formed on the surface, the etch rate was saturated at one monolayer/cycle which corresponds to 1.41 Å/cycle for (100) GaAs and 1.63 Å/cycle for (111) GaAs. The rms surface roughness shown in Fig. 3 decreased with increasing the Ne neutral beam dose and, when the Ne neutral beam dose was higher than the critical dose, the surface roughness was remained at 2 Å and 2.5 Å for (100) GaAs and (111) GaAs, respectively, similar to that of as-received GaAs samples. The decrease of surface roughness with the increase of the Ne neutral beam irradiation was also related to the partial etching of GaAs surface atoms by supplying insufficient beam dose to the Cl-adsorbed GaAs surface for the removal of the Ga–Cl and As–Cl during each cycle. The increase of beam dose during each cycle increases the percentage of the GaAs surface atoms removed during each cycle, therefore, the roughness is decreased with the increase of beam dose. However, when the beam dose was high enough to remove all of the surface Cl-adsorbed GaAs atoms(>3.03×10^{16} atoms/cm^2·cycle), due to the complete removal of Cl-adsorbed surface atoms during each cycle, the further increase of beam dose did not change the surface roughness further and the surface roughness was remained as low as the surface roughness of the as-received GaAs sample.
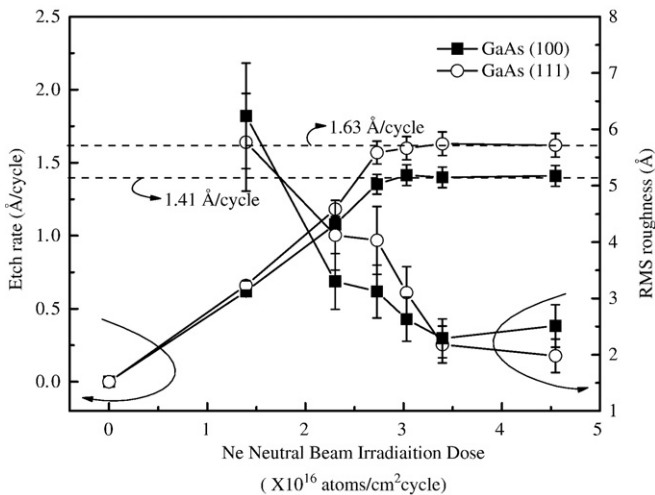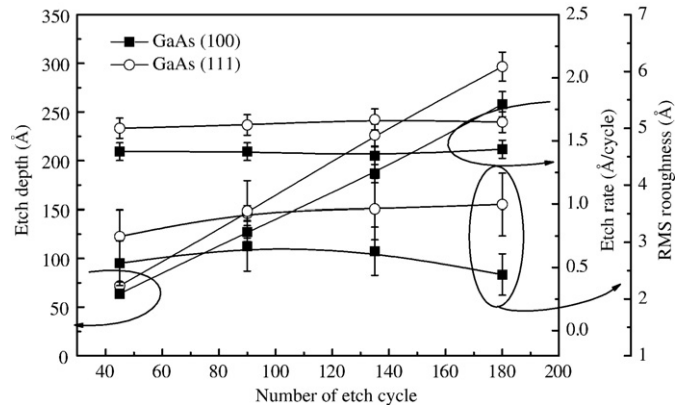

Fig. 4. GaAs etch rate, etch depth, and rms roughness measured as a function of etch cycle for the one monolayer etching condition. The Cl_2 gas pressure and Ne neutral beam irradiation dose were kept at 0.4 mTorr and 3.4×10^{16} atoms/cm^2·cycle, respectively.

Fig. 4 shows the etch rate (Å/cycle), etch depth, and rms surface roughness measured as a function of number of etch cycles at the one monolayer etching condition, that is, 0.4 mTorr of Cl_2 gas pressure and 3.4×10^{16} atoms/cm^2·cycle of Ne neutral beam dose. The etch cycles were varied from 45 to 180 cycles. As shown in the figure, the etch rate and surface roughness were remaining same at one monolayer/cycle and minimum roughness, respectively, regardless of etch cycles and the etch depth was exactly proportional to the etch cycle showing the ability to control the etch depth with atomic-scale precision.

Fig. 5 shows surface composition measured by ARXPS at the take-off angle of 50° for the (100) GaAs etched by the ALET. As the references, the surface compositions of as-received (100) GaAs and the (100) GaAs after an ICP etching were included. For the ICP etching, a conventional planar type ICP etcher was used and, as the etch condition, 700 W of rf power, −100 V of dc bias voltage, Cl_2 (70 sccm)/Ar (30 sccm), and 10 mTorr was used. As the ALET condition, one monolayer etching condition of 3.4×10^{16} atoms/cm^2·cycle of Ne neutral beam irradiation dose and 0.4 mTorr of Cl_2 pressure was used. The etch rate of the ICP etching was 360 Å/min and the etch time was 12 s. Therefore, to compare for the same etch depth, the etch cycle of the ALET was set at 50 cycles. As shown in the figure, after the ALET, the atomic percentages and the ratio of As/Ga on the etched GaAs surface (Ga: 54.96%, As: 45.04%, As/Ga ratio: 0.819) were similar to

Fig. 3. Etch rate (Å/cycle) and rms roughness of GaAs by Ne neutral beam ALET as a function of Ne neutral beam irradiation dose at the Cl_2 gas pressure of 0.4 mTorr.
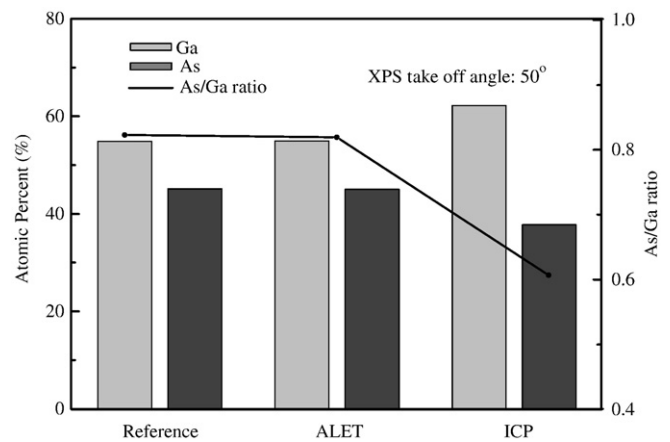

Fig. 5. Atomic percentage of GaAs surface and the ratio of As/Ga measured using ARXPS after the Ne neutral beam ALET. The atomic percentages and the ratio of As/Ga measured after the etching by a Cl_2 inductively coupled plasma and those of GaAs reference sample are also shown. ALET condition: Ne neutral beam irradiation dose of 3.4×10^{16} atoms/cm^2·cycle, Cl_2 gas pressure of 0.4 mTorr. Process condition of an ICP etching: inductive power of 700 W, dc bias voltage of −100 V, and Cl_2 (70 sccm)/Ar (30 sccm) at 10 mTorr.

those of as-received GaAs surface (Ga: 54.88%, As: 45.12%, As/Ga ratio: 0.823). However, for the ICP etched GaAs, the atomic percentages and the ratio of As/Ga has changed significantly (Ga: 62.23%, As: 37.77%, As/Ga: 0.607), therefore, the surface became Ga-rich surface. For the ICP etching, due to the differences in the vapor pressure of the chlorides between Ga–Cl (boiling point: 535 °C) and As–Cl (boiling point: 130.2 °C), the As appears to be preferentially removed during the etching. [14] On the other hand, in the case of the ALET, all of the chlorides formed on the surface are removed every etch cycle by the Ne neutral beam, therefore, no change of atomic composition was observed.

4. Conclusion

In this study, the characteristics of ALET for (100)/(111) GaAs have been investigated as functions of Cl_2 pressure during the adsorption stage and Ne neutral beam irradiation dose during the desorption stage. By using the Ne neutral beam dose and the Cl_2 pressure higher than the critical values of 3.03×10^{16} atoms/cm^2·cycle and 0.4 mTorr, respectively, one monolayer etching condition of 1.41 Å/cycle for (100) GaAs and 1.63 Å/cycle for (111) GaAs could be obtained through the adsorption of one monolayer of Cl_2 during the adsorption stage and desorption of all of the chlorides formed on the surface by the suffi-cient Ne neutral beam irradiation. At the monolayer etching condi-tions, the surface roughness was the lowest and was similar to that of as-received GaAs. Also, the surface composition was remaining similar to that of non-etched GaAs while the GaAs surface etched by a Cl_2 ICP showed Ga-rich surface due to the preferential removal of As due to the higher vapor pressure of As chlorides compared to Ga chlorides. Therefore, the use of ALET condition enabled us to control the etch depth with an atomic-scale precision without damaging the surface physically or chemically.

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