Atomic Layer Etching of III-V Compound Materials Using a Low Angle Forward Reflected Ne Neutral Beam

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***Abstract*—Atomic layer etching characteristics of III-V compound materials have been investigated using a Ne neutral beam and Cl_2 gas. At the monolayer etching condition, the roughness of the III-V compound materials surface was remaining similar to that of the un-etched III-V compound materials surface. In addition, the III-V compound materials etched by the atomic layer etching showed the surface composition similar to that before the etching while the III-V compound materials etched by a conventional reactive ion etching such as an inductively coupled plasma etching showed significant change in the surface composition.**

Keywords- atomic layer etching, III-V etching, neutral beam etching

I. INTRODUCTION

III-V compound materials have 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 III-V compound materials 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 process, the surface of the etched III-V compound materials tends to be damaged physically and chemically by structural disruption, intermixing, 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.

Figure 1 shows the concept of ALET used in this experiment. Etching by using ALET is composed of 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, a low energy Ne neutral beam was introduced as the energy source for the desorption and the characteristics of ALET were investigated.

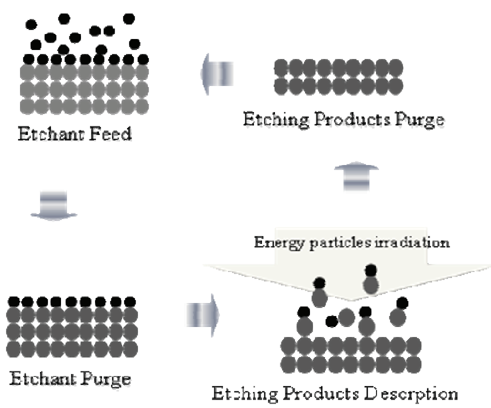

Figure 1. Concept of the ALET Process. This figure was made from the data from the reference 11shown below.

II. 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. 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]

As the samples, GaAs n-type (100) wafers and InP n-type (100) wafers (some wafers were patterned with photoresist) were used and, before the etching, native oxide layer on the sample surface was removed by dipping in a HCl solution followed by cleaning with de-ionized water and N_2 gas blowing. 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 III-V compound materials after the etching was measured by angular resolved x-ray photoelectron spectroscopy (ARXPS, Thermo VG, MultiLab 2000, Mg Kα source). The surface composition of III-V compound materials after the etching by the ALET was compared with that obtained after an ICP etching.

III. Results

Figure 2 shows one monolayer etching region measured as a function of the Cl_2 gas pressure and Ne beam irradiation dose. As shown in the figure, the monolayer etch rate condition can be easily obtained by providing the Cl_2 gas pressure higher than a critical pressure and Ne beam irradiation dose higher than a critical dose. Therefore, even though the process variables, such as Ne beam dose and Cl_2 gas pressure are varied during processing, theoretically, perfect etch uniformity is possible over a large wafer surface for the ALET processing if the energy of the Ne beam is maintained at a constant level.

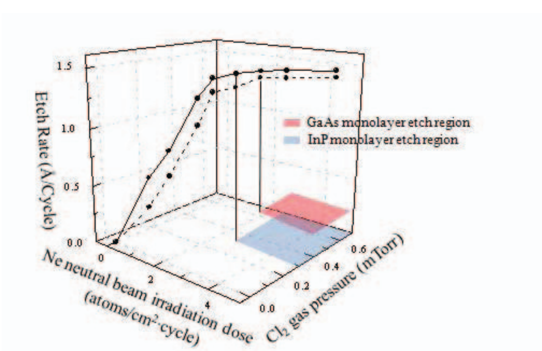

Figure 2. III-V compound materials ALET process window measured as a function of the Cl_2 gas pressure and Ne neutral beam irradiation dose. The Ne beam energy measured before the reflection to the reflector was 32 V. This figure was made from the data from the reference 11, 13 shown below.

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 III-V compound surface. According to the dissociation Langmuir isotherm, the surface coverage (Θ) can be represented by $\Theta = \sqrt{k\,p} / (1 + \sqrt{k\,p})$ [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 only on the Cl_2 pressure. When Cl_2 gas was adsorbed on the III-V compound surface, III material (or V material) chlorides are formed by transferring electrons in the III-V compound to adsorbed Cl_2 and the binding energy between V material (III material) and the III material (V material) chlorides just below the surface is weakened. In addition, because the binding energy of III-V compounds (Ga-As: 2.177 eV, In-P: 2.055 eV) are lower than the binding energy of the III material (or V material) chlorides (Ga-Cl: 4.996 eV, As-Cl: 4.649 eV, In-Cl: 4.434 eV, P-Cl: 2.919 eV), [11-13] during the Ne neutral beam irradiation, the bonds below the III material (or V material) chlorides on the surface are preferentially broken instead of the bonds between III material (or V material) and Cl in the chlorides, and the III material (or V material) 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 III-V compound surface, only the area covered by III material (or V material) 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 obtained, that is, 1.41 Å/cycle for (100) GaAs and 1.47 Å/cycle for (100) InP. This Result and figure were made from the data and sentence taken from the references 11, 12, 13 shown below.

Figure 3 shows surface composition measured by ARXPS at the take-off angle of 55° for the GaAs (or InP) etched by the ALET. As the references, the surface compositions of as-received GaAs (or InP) and the GaAs (or InP) 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 were 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 were used. The etch rate of the ICP etching was 360 Å/min and the etch time was 12 seconds. 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 (or P/In) on the etched GaAs (or InP) surface (As/Ga ratio: 0.819, P/In ratio: 0.84) were similar to those of as-received GaAs surface (As/Ga ratio: 0.823, P/In ratio: 0.84). However, for the ICP etched GaAs (or InP), the atomic percentages and the ratio of As/Ga (or P/In) has changed significantly (As/Ga ratio: 0.607, P/In ratio: 0.604), therefore, the surface became III material-rich surface. For the ICP etching, due to the differences in the vapor pressure of the chlorides between III material chlorides and V material chlorides, the V materials appear to be preferentially removed during the etching. [11, 13] 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. This Result and figure were made from the data and sentence taken from the references 11, 12, 13 shown below.

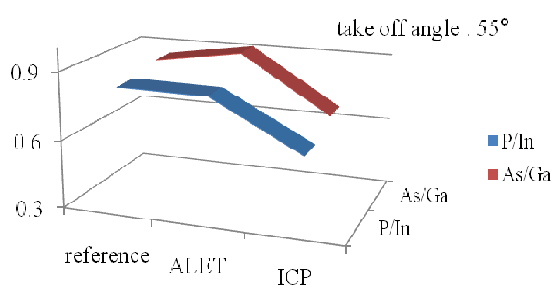

Figure 3. The ratio of V materials/III materials measured using XPS after the Ne neutral beam ALET. The ratio of V materials/III materials measured after the etching by a Cl_2 ICP and that of III-V compound materials reference sample are also shown. (ALET condition: Ne neutral beam irradiation dose of 3.4 X 10^{16} atoms/ cm^2•cycle, Cl_2 gas pressure of 0.4 mTorr. Process condition of ICP etching: inductive power of 700 W, dc bias voltage of - 100 V, and Cl_2 (70 sccm) / Ar (30 sccm) at 10 mTorr). This figure was made from the data from the reference 11, 13 shown below.

IV. CONCLUSIONS

In this study, the III-V compound materials etching by Ne neutral beam ALET was investigated as a function of Cl_2 pressure and Ne neutral beam irradiation dose and its etch mechanism was studied. When the Cl_2 pressure or the Ne neutral beam irradiation dose was lower than the critical values (GaAs; Cl_2 pressure 0.4 mTorr, Ne neutral beam dose 3.03×10^{16} atoms/cm^2 cycle, InP; Cl_2 pressure 0.4 mTorr, Ne neutral beam dose 7.2×10^{15} atoms/cm^2 cycle), the III-V compound materials etch rate increased with the increase of Cl_2 pressure or Ne neutral beam irradiation dose and the rms surface roughness varied with Cl_2 pressure or Ne neutral beam irradiation dose. However, when both the Cl_2 pressure and the Ne neutral beam irradiation dose were higher than the critical values, the III-V compound materials etch rate saturated and remained at one monolayer per cycle of 1.41 Å/ cycle (GaAs), 1.47 Å/ cycle (InP) and the surface roughness remained similar to that of as-received III-V compound materials. Also, during the ALET, the surface composition of III-V compound materials was not changed by the etching.

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