Atomic layer etching of InP using a low angle forward reflected Ne neutral beam

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In this study, the atomic layer etching characteristics and the etch mechanism of (100) InP as functions of Cl_2 pressure and Ne neutral beam irradiation dose were investigated. When Cl_2 pressure and Ne neutral beam irradiation dose were lower than the critical values of 0.4 mTorr and 7.2×10^{15} at./cm^2 cycle, respectively, the InP etch rate (Å/cycle) and the InP surface roughness varied with Cl_2 pressure and Ne neutral beam irradiation dose. However, when the Cl_2 pressure and Ne neutral beam irradiation dose were higher than the critical values, the InP etch rate remained as 1.47 Å/cycle, corresponding to one monolayer per cycle, and the surface roughness and the surface stoichiometry remained similar to those of InP before etching. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2221504]

Indium phosphide (InP) is a very attractive material for high-speed and high breakdown voltage electronic devices, such as high electron mobility transistors (HEMTs) and heterojunction bipolar transistors (HBTs), due to its high electron mobility and high breakdown voltage.[1] However, InP in these devices is easily damaged during the processing by dry etching, therefore, wet etching has been widely used for damageless etching of InP. Wet etching of InP in these devices has several disadvantages such as the difficulty in controlling the etch rate, severe undercut, etc.; therefore, a few researchers have investigated the dry etching of InP using halogen-based reactive ion etching due to the precise etch-rate controllability, profile control, etc.[2,3] However, these conventional reactive ion processes tend to physically damage the surface of the devices, such as creation of surface defect including structural disruption, intermixing layer or stoichiometry modification, and the increment of surface roughness, due to the use of energetic reactive ions to achieve vertical etch profiles.[3]

Atomic layer etching (ALET) can be the most feasible method for the InP etching of the above devices because it could etch not only without physical damage to InP but also with atomic scale etch-rate controllability. ALET is a cyclic process and conventionally consists of four sequential steps: (i) adsorption of reactant molecules on the surface, (ii) evacuation, (iii) Ar^+ ion beam irradiation to the reactant adsorbed surface for the desorption of surface-reactant chemisorbed species, and (iv) evacuation of the etch products.[4] But, during step (iii), with the Ar^+ beam irradiation, the device could be also damaged electrically due to the charged particles such as positive ions generated in the plasma.

In this letter, the etching of InP was carried out using ALET with Ne neutral beam irradiation instead of Ar^+ ion beam irradiation to reduce possible charge-related damage and to minimize the surface sputtering during the cyclic process. In order to study the InP ALET mechanism by Cl_2 adsorption and Ne neutral beam irradiation, the InP etch rates and the variations of surface roughness as a function of Cl_2 pressure and Ne neutral beam irradiation dose have been investigated.

A low energy Ne neutral beam was generated by a low angle forward reflected neutral (LAFRN) beam technique. The LAFRN beam source was composed of a 13.56 MHz rf ion source and a low angle planar reflector for the neutralization of the ions extracted from the ion source. A three-grid inductively coupled plasma (ICP)-type ion gun was used as the rf ion source. By applying 400 W of rf power to the ion gun while supplying 15 SCCM of Ne (SCCM deontes cubic centimeter per minute at STP) and by applying 5 V to the first grid located close to the ion source (accelerator grid), −250 V to the second grid (extractor grid), and grounding the third grid, the energy and flux of about 27 eV and 1.2×10^{14} ions/cm^2 s could be obtained, respectively, before the neutralization on the planar reflector. The neutralization efficiency after the reflection of the ions on the low angle reflector was above 99%. Details of the LAFRN beam source are described elsewhere.[5]

The ALET process steps performed in this study are as follows. Chlorine gas is supplied for 20 s to the etch chamber during the adsorption period so that chlorine can be adsorbed on the surface of InP. 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 3 s.

The sample used in this experiment was *n*-type (100) InP wafer patterned with a photoresist. Prior to loading into the chamber, the sample was dipped in a HCl solution to remove remaining native oxide on the surface, followed by rinsing with de-ionized (DI) water and blow drying with N_2. The etched step height was measured using a step profilometer (Tencor Instrument, Alpha Step 500). The measured step height was divided by the total number of ALET cycles to

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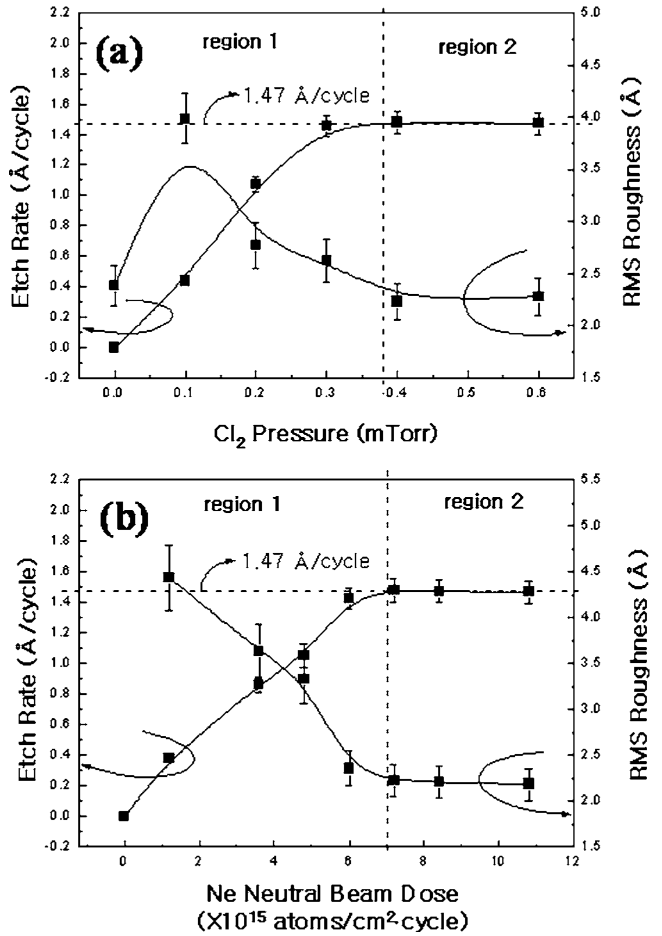

FIG. 1. The etch rate (Å/cycle) and rms surface roughness of InP by neutral beam ALET as a function of (a) Cl_2 pressure at the neutral beam dose of 7.2×10^{15} at./cm^2 cycle and (b) Ne neutral beam irradiation dose at the Cl_2 pressure of 0.4 mTorr.

yield the etch amount per cycle. An atomic force microscope (AFM; Thermomicroscopes, CP Research) was used to measure the surface roughness. An angular resolved x-ray photoelectron spectroscopy (ARXPS; Thermo VG, MultiLab 2000, Mg $K\alpha$ source) was utilized to analyze the modification of InP surface stoichiometry after ALET.

Figure 1 shows the effect of (a) Cl_2 pressure and (b) Ne neutral beam dose (at./cm^2 cycle) on the InP etch rate (Å/cycle) and the root-mean-square (rms) roughness of the etched InP surface. When Cl_2 pressure was varied in Fig. 1(a), the Ne neutral beam dose was maintained at 7.2×10^{15} at./cm^2 cycle, and when Ne neutral beam dose was varied in Fig. 1(b), the Cl_2 pressure was maintained at 0.4 mTorr. As shown in Figs. 1(a) and 1(b), with the increase of Cl_2 pressure and Ne neutral beam irradiation dose, the etch rates of InP initially increased almost linearly as indicated by region I in Figs. 1(a) and 1(b). However, when the Cl_2 pressure and the Ne neutral beam irradiation dose were higher than critical values (that is, Cl_2 pressure: 0.38 mTorr, Ne neutral beam dose: 7.0×10^{15} at./cm^2 cycle), the etch rates of (100) InP saturated independent of the Cl_2 pressure and Ne neutral beam irradiation dose as shown in region II of Figs. 1(a) and 1(b), respectively, and the etch rate remained at 1.47 Å/cycle which corresponds to one InP monolayer per cycle.

In the case of rms surface roughness of InP, in region I, it increased rapidly with the increase of Cl_2 pressure and Ne neutral beam irradiation dose initially and showed the maximum values of 4.4 Å at 0.1 mTorr of Cl_2 pressure and 4.0 Å at 1.2×10^{15} at./cm^2 cycle of Ne neutral beam irradiation dose as shown in Figs. 1(a) and 1(b), respectively. And the further increase of Cl_2 pressure and Ne neutral beam irradiation dose to the critical values decreased the roughness to about 2.3 Å which is close to that of as-received InP. In the case of region II, the rms roughness of InP remained similar at about 2.3 Å regardless of the change of Cl_2 pressure or Ne neutral beam irradiation dose.

The change of InP etch rate and that of rms roughness with Cl_2 pressure and Ne neutral beam irradiation dose shown in Figs. 1(a) and 1(b) are related to the formation of InP chloride by Cl_2 and the removal of the chloride by the Ne neutral beam irradiation. In general, when InP was exposed to Cl_2, by the Langmuir isotherm, the chlorides formed only on the single surface layer of InP and the surface coverage ($\theta_{\mathrm{InP\ chloride}}$) of InP chloride is determined by the pressure of Cl_2 (P_{Cl}).[6] Also, these chlorides are removed by the irradiation of Ne neutral beam and the removed amount of the chlorides on the surface is determined by the Ne neutral beam irradiation dose ($f_{\mathrm{Ne_{neu}}}$). Therefore, during one cycle of the neutral beam ALET, the etch rate of InP (E_{InP}) is characterized by the P_{Cl} and $f_{\mathrm{Ne_{neu}}}$. If P_{Cl} and $f_{\mathrm{Ne_{neu}}}$ are low enough not to cover all of the surface area ($\theta_{\mathrm{InP\ chloride}}<1$) and to remove all chlorides formed on the surface, respectively, due to the insufficient formation of monolayer chloride layer and the insufficient removal of all the chlorides formed on the surface, not only did the etch rate of InP varied at a value less than one monolayer per cycle (1.47 Å/cycle) but also the surface roughness increased due to the accumulation of the partially removed surface layers.

When no Cl_2 was supplied or no neutral beam was irradiated during each cycle, as shown in Figs. 1(a) and 1(b), no etching of InP was observed and the rms surface roughness was similar to that of the reference. Therefore, no spontaneous etching of InP by Cl_2 at room temperature and no pure physical sputter etching of InP by the low energy (<27 eV) Ne neutral beam irradiation occurred during the neutral beam ALET process. By sequentially supplying P_{Cl} and $f_{\mathrm{Ne_{neu}}}$ more than the critical values, all of the surface area is covered by InP chloride and all the chlorides formed on the surface are removed. The etch rate is self-limited to one monolayer per cycle, because the chloride is formed only on the surface layer and only the chlorides are etched during the neutral beam irradiation. No change of the rms surface roughness after the ALET using one monolayer etching conditions indirectly shows the complete removal of one InP monolayer per cycle. Also, during the neutral beam etching, it is believed that InP is mostly removed as indium monochloride (InCl) and phosphorus monochloride (PCl).

Figure 2 shows the atomic percentage of InP surface and the ratio of P/In measured using angle resolved XPS after the neutral beam ALET. For the atomic percentages, carbon, In, and P are shown. (No chlorine was observed.) As references, the ratio of P/In measured after the etching by a conventional Cl_2 ICP and that of as received InP (as is) are also shown. The etching condition for the ALET was a monolayer etching condition using Ne neutral beam irradiation dose of 7.2×10^{15} at./cm^2 cycle and Cl_2 pressure of 0.4 mTorr and the etch cycle was 100 cycles. For the ICP etching, the inductive power was 700 W, the dc bias voltage was −100 V,

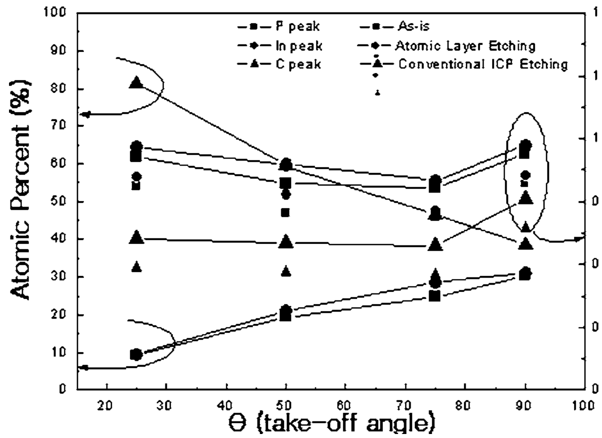

FIG. 2. Atomic percentage of InP surface and the ratio of P/In measured using angle resolved XPS after the neutral beam ALET. The ratio of P/In measured after the etching by a Cl_2 inductively coupled plasma and that of as-received InP (as is) are also shown. ALET condition: Ne neutral beam irradiation dose of 7.2×10^{15} at./cm^2 cycle and Cl_2 pressure of 0.4 mTorr. ICP etching condition: inductive power of 700 W, dc bias voltage of −100 V, and Cl_2 (70 SCCM)/Ar (30 SCCM) at 10 mTorr.

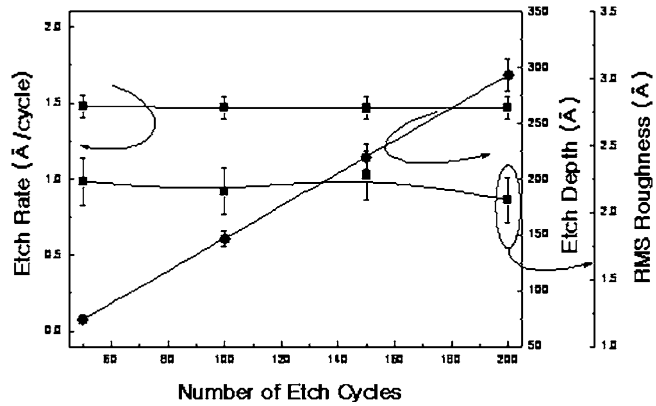

FIG. 3. InP etch rate (Å/cycle), etch depth, and rms roughness measured as a function of etch cycle for a monolayer etching condition. The Cl_2 pressure and Ne neutral beam irradiation dose were kept at 0.4 mTorr and 7.2×10^{15} at./cm^2 cycle.

and the gas mixture was Cl_2 (70 SCCM)/Ar (30 SCCM) at 10 mTorr. The etch rate by the ICP was 12 Å/s; therefore, to maintain the same etch depth as the ALET, the etch time was maintained at 12 s. As shown in the figure, for the sample etched by ALET, with increasing the take-off angle of XPS, the carbon percentage originating from the contamination during the air exposure decreased while the percentages of In and P increased. However, when the ratio of P/In was taken, the ratio remained in the range of 0.87–0.98 and the ratio was similar to that of the as received (0.84–0.95). However, the ratio of P/In for the ICP etched sample was lower than that of the as received and was in the range of 0.6–0.8.

The decrease of the P/In after the ICP etching is related to the differences in the volatility of the by-products such as P chlorides and In chlorides. Due to the higher volatility of P chlorides compared to that of In chlorides formed on the InP surface, P chlorides are preferentially removed on the InP surface, therefore, the P/In of InP surface after the etching by a Cl_2-based conventional plasma etching decreased as shown for the ICP etching.[7] However, in the case of the ALET, the P/In after the etching remained similar to that of the as received, indicating no preferential removal of P or In and the removal of one monolayer of surface atoms regardless of In or P. No significant change of P/In for both as received and InP after the ALET with increasing the take-off angle appears to show that surface of InP is not In terminated or P terminated but mixed due to the surface roughness of as-received InP.

Figure 3 shows the InP etch rate (Å/cycle), etch depth, and rms roughness measured as a function of etch cycle for a monolayer etching condition. The Cl_2 pressure and Ne neutral beam irradiation dose were kept at 0.4 mTorr and 7.2×10^{15} at./cm^2 cycle. As shown in the figure, the InP etch depth increased linearly with the increase of etch cycle while the InP etch rate remained the same at 1.47 Å/cycle. The rms surface roughness also remained similar near 2.3 Å regardless of the number of etch cycles. Therefore, it is believed that, using the ALET, the InP etch depth can be exactly controlled to the atomic level by controlling the etch cycles without increasing the surface roughness and without modifying the surface stoichiometry.

In this study, the InP 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 (Cl_2 pressure: 0.4 mTorr, Ne neutral beam dose: 7.2×10^{15} at./cm^2 cycle), the InP 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 InP etch rate saturated and remained at one monolayer per cycle of 1.47 Å/cycle and the surface roughness remained similar to that of as-received InP. Also, during the ALET, the surface composition of InP was not changed by the etching.

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