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In-Situ XPS Study of Etch Chemistry of Methane-Based RIBE of InP Using N_2

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1. Introduction

Reactive ion beam etching (RIBE) of In-based III-V semiconductors using methane-based mixtures such as CH_4/H_2 has been attracting increasing interest for fabrication of various kinds of devices and nanostructures [1, 2]. Smoothness of the etched surface is an important issue, and addition of N_2 was shown to greatly improve the morphology of the etched surface [3]. However, most work reported to date was concerned with the empirical optimization of etching conditions to get smooth surfaces with low surface damage [4], and no systematic attempt has been made to understand the plasma-surface interaction and underlying etch chemistry.

The purpose of this paper is to investigate etch chemistry of methane-based RIBE of InP using N_2 in relation to important etching parameters and features including surface morphology using *in-situ* X-ray photoelectron spectroscopy (XPS). A smooth etched surface is obtained at higher N_2 gas flow. The chemical mechanism is discussed on the basis of detailed XPS results.

2. Experimental

Figures 1 (a) and **(b)** show the system used in this study. The RIBE chamber is connected to the UHV-based growth/ characterization system including the XPS chamber through the UHV transfer chamber as shown in **Fig. 1 (a)**. A more detailed schematic diagram of the RIBE system used in this study is shown in **Fig. 1 (b)**. The system is composed of a RIBE chamber and a sample preparation chamber. The base pressure of RIBE chamber is in the range of 10^{-10} Torr. An electron cyclotron resonance (ECR) plasma is excited by combination of 2.45 GHz microwave and magnetic field.

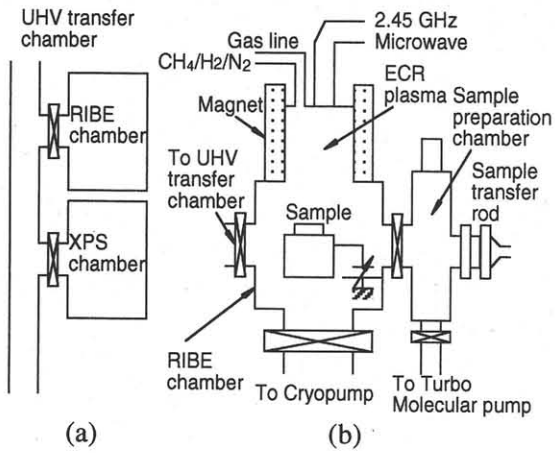

Fig. 1 Schematic diagram of RIBE system.

LEC-grown n^+-InP (001) substrates were used. A flow of 16 sccm of CH_4/H_2 (15% of CH_4 in the mixture) was our standard gas supply. The N_2 gas flow was changed from 0 sccm to 6 sccm. The pressure was kept at 1 mTorr in all the etching process. The microwave power was 200 W and the acceleration voltage was 200 V. As a mask for selective etching, a SiO_2 layer was deposited on the InP surface by plasma enhancement chemical vapour deposition (PECVD), and was patterned by conventional photolithography.

The etched InP surfaces were characterized *in-situ* in the XPS chamber. A Perkin-Elemer PHI 1600C system was used through UHV sample transfer. Etched surfaces were carefully observed by SEM and AFM. The crystalline quality of etched surface was evaluated by Raman measurement using Jobin Yvon TA64000 system.

3. Results and discussion

Figure 2 shows the SEM images of vertical cross-section of InP surfaces etched by mixture gas with N_2=0, 3, 6 sccm, respectively. Although the etching depth remains almost the same with the N_2 gas flow change, morphology is very different. Without the N_2 gas flow, etched bottom surface was very rough, and it was remarkably improved as the N_2 flow was increased. **Figure 3** shows the AFM images of the etched InP surfaces. The same tendency is seen. Without N_2, the surface was granular and gave a root mean square (rms) roughness of 37.1 nm. With 3 sccm N_2 in the

Fig. 2 SEM images of InP surfaces etched by mixture gases with N_2=0 (a), 3 (b), and 6 sccm (c).

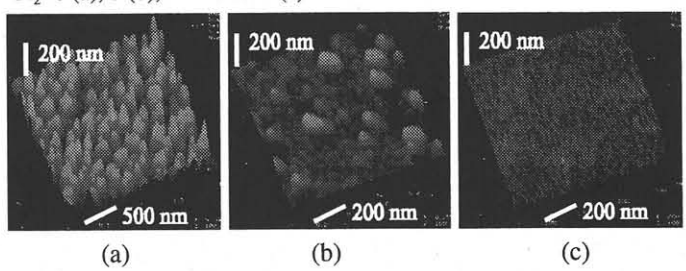

Fig. 3 AFM images of InP surfaces etched by mixture gases with N_2=0 (a), 3 (b), and 6 sccm (c).

gas mixture, the surface was slightly improved being covered with mostly small grains. This gave the rms roughness of 12.8 nm. With 6 sccm N_2, the surface became featureless and the rms roughness was 0.15 nm. This value is comparable with that of the initial InP surface before etching of 0.10 nm. **Figures 4 (a)** and **(b)** summarize the etch rate and the rms roughness as a function of N_2 gas flow. It is seen that the etch rate remains almost constant against the N_2 gas flow, whereas the rms roughness decreases drastically with the N_2 flow.

The $In3d_{5/2}$ and P2p core-level XPS spectra of etched InP surfaces are shown in **Fig. 5**. The $In3d_{5/2}$ peak for the case without N_2 can be deconvoluted into two peaks, one at the lower energy corresponding to the In-In (metallic In) bond, and the other corresponding to the In-P bond. With an increase of N_2 gas flow, the relative intensity of the In-In peak decreases and that of the In-P peak increases. From the P2p core-level XPS spectra, there is just the P-In bond peak when InP is etched by mixture without N_2 gas. On the other hand, as N_2 is added, a peak corresponding to the P-N bond

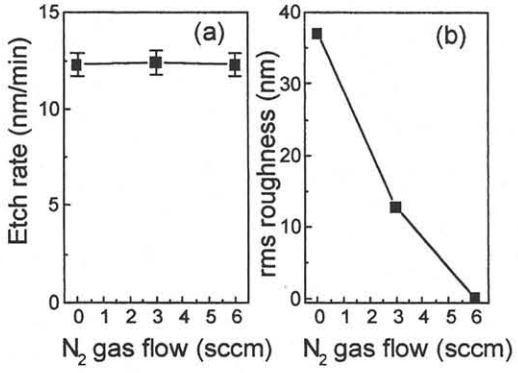

Fig. 4 (a) Etch rate and (b) the rms roughness as a function of N_2 gas flow.

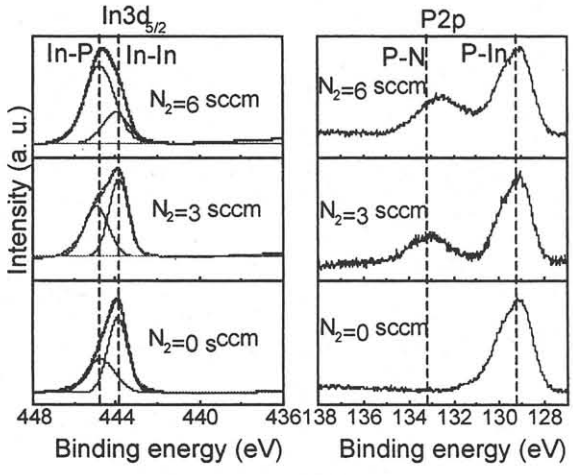

Fig. 5 In3d5/2 and P2p core-level XPS spectra of etched InP.

appears in addition to the P-In peak. The relative intensity of P-N peak increases with increase of the N_2 gas flow.

The above result can be explained in the following way. The basic reaction of methane-based etching is given by $P+3H \rightarrow PH_3$ and $In+3CH_3 \rightarrow In(CH_3)_3$ as discussed recently by Feurprier et al [5]. Here, the rate limiting process for etching is the In-reaction, and the P-reaction tends to cause the preferential etching of P, leading formation of In droplets seen by SEM/AFM and detected by XPS. When the N_2 gas is added to the mixture, preferential escape of P atoms from the InP surface is suppressed due to formation of P-N bonds on the surface. This is because the volatility of P_3N_5 is much lower than that of PH_3. This results in the decrease of In droplets and in a smoother etched surface. The etch rate is kept the same, because it is basically limited by the In-CH_3 reaction due to absence of In-N reaction. Thus, formation of an ultrathin monolayer-level P-N layer controls the overall etching reaction in a favorable direction.

Figure 6 shows the InP LO peaks of Raman scattering for the samples before and after etching. The LO peak shifts to lower frequency after etching, indicating presence of the tensile stress. When the N_2 gas flow was either 0 or increased up to 3 sccm, the full width at half maximum were much wider than that of the initial InP. This indicates that the etched InP surface has amorphous-like structure due to presence of In-droplets. When the N_2 gas flow was increased up to 6 sccm the full width at half maximum decreased remarkably and the peak shift almost disappeared. This indicates that the surface crystalline quality is improved at higher N_2 concentration in gas mixture.

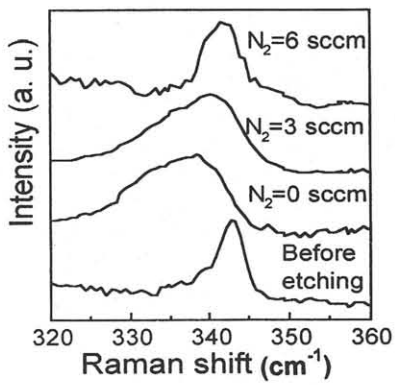

Fig. 6 InP LO peaks of Raman scattering of the samples before and after etching.

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