Original Paper

Extremely Smooth Surface Etching by Giant Cluster Ion Impact

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A new ionization method, electrospray droplet impact (EDI), has been developed for matrix-free secondary ion mass spectrometry (SIMS). The charged water droplets used in EDI are the giant cluster ions with masses of about a few 10^6 u. When the charged water droplets impact on a target, the physical sputtering of the target is suppressed minimal and a molecular-level layer-by-layer etching is realized. The sample surfaces can be etched with the extremely smooth. A comparative study for the etching of InP(111) by Ar^+ and EDI was made. It was found that EDI etching does not suffer from the preference sputtering of InP.

1. Introduction

Recently, the cluster ion projectiles are used to reduce the degradations in cluster/secondary ion mass spectrometory (SIMS). The ion sputtering by Ar_n^+ and C_{60}^+ clusters guarantees the high sputtering rate, the smooth surface sputtering and low sample degradations[1][2]. X-Ray Photoelectron Spectroscopy (XPS) is the most useful technique for the top surface analysis and the depth profiling of the organic and inorganic samples. XPS depth profiling is usually coupled with Ar^+ ion sputtering in many XPS instruments. However, this method induces the degradations of polymer and metal oxide samples. XPS depth profiling with the cluster ion projectiles is expected to reduce the degradations on the samples. The depth profiling using C_{60} was found to reduce the polymer sample damage. However, some carbon absorption and graphitization were still be observed on the polymer samples after C_{60} sputtering [3][4][5]. Recently, a new ionization method, the electrospray droplet impact (EDI) ionization, has been developed for matrix-free SIMS [6][7]. The charged water droplets formed by electrospraying are extremely large cluster ions with masses of about a few 10^6 u. When the charged water droplets impact on a target, the surface is expected to be etched by molecular-level without damaging the sample underneath. In other words, the physical sputtering of the target is suppressed to minimal and a molecular-level etching is established by EDI. In this paper, the EDI as an etching technique is described. The etched surfaces of InP(111) by Ar^+ and EDI were evaluated by scanning electron microscope (SEM), atomic force microscopy (AFM) and XPS.

2. Experimental

The instrumental schematic diagram of EDI ion source coupled with an orthogonal time-of-flight mass spectrometer (TOF-MASS) is shown in Figure 1. The charged water droplets formed by electrospraying 1M acetic acid aqueous solution at atmospheric pressure were sampled through an orifice with 400μm diameter into the first vacuum chamber, and transported into a quadrupole ion guide. The charged ions after exiting the ion guide were accelerated by 10kV, focused by the Einzel lens and impacted on the target. The vacuum system consisted of four vacuum chambers which were evacuated by a rotary pump and three turbomolecular pumps respectively. The vacuum pressure for sample stage was 10^{-3} Pa in operation [7].

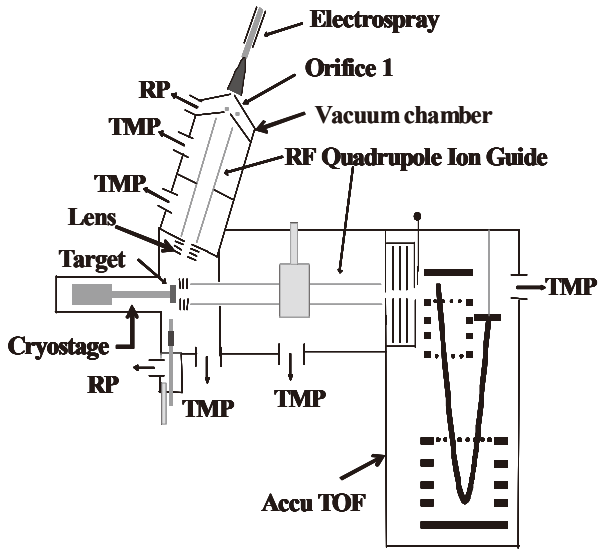

Figure 1. Schematic diagram of the electrospray droplet impact (EDI)/SIMS.

The mass(u) and the number of charges(z) for the droplets are estimated. The quadrupole ion guide was controlled by Mathieu equations which decided the high mass and low mass cut-off boundary condition for m/z in radio-frequency(RF) operation. In this experiment, the m/z of the primary droplet projectiles are estimated from the RF voltage applied to the ion guide to be in the range of $1x10^4$ - $5x10^4$ [8][9]. The charge states of liquid droplets sampled by the ion guide are close to the Rayleigh limit. In general, the charge states of the primary electrosprayed droplets and their off-spring droplet are described by the Rayleigh limit [10]. The number of charge z carried by the droplet with radius R can be represented as

$$z = \left(\gamma \varepsilon_0 R^3\right)^{0.5} \times 8\pi / e \qquad (1).$$

From the surface tension of water $(\gamma : 72 \times 10^{-3} Jm^{-2})$, the dielectric permittivity of vacuum (ε_0: 8.9 x 10^{-12} C^2 J^{-1} m^{-1}) and the density of the droplet was assumed to be the same as that of water (1,000 kgm^{-3}). From the relationship between the Rayleigh limit and the mass sampled by the quadrupole ion guide. the m/z of droplets were in the mass range of $6.2x10^5$ to $1.6x10^7$u and charge number of 62 to 311 for the values of $1x10^4$ and $5x10^4$ sampled by the ion guide [8]. For example, the charged water droplets with z =100 charges may be represented as $[(H_2O)_{90000}+100H]^{100+}$. The kinetic energy of impacting projectile is ~10^6 eV for the acceleration potential of 10kV. An energy per nucleon is about 0.6 eV/u. The diameters of the droplets are estimated to be in the range of 5-14 nm. The impact angle is 60 degrees from the surface normal. The diameter of beam was estimated to be about 3 mm. The secondary ions formed by EDI are transported into a second quadrupole ion guide and mass-analyzed by an orthogonal TOF-MS (JEOL: Accu-TOF). We examined the applicability of EDI to the surface analysis of various materials. After etching the samples by EDI, the surface concentration was analyzed by X-Ray photoelectron spectroscopy (XPS) (JEOL: JPS-9200). The surface roughness was monitored by scanning electron microscope (SEM)(JEOL: JSEM-6700) and scanning probe microscope (SPM) (JEOL:JSPM-5400).

3. Result and discussion

A comparative study for the etching of InP(111) by Ar+ and EDI was made. The SEM images after etching are shown in Figure 2. On the surface of InP etched by Ar+ ion shown Figure 2(A), many etching cones were found to be formed. The reason of the creation of etching cones was the preference sputtering for InP and In ball formation on the surface. By Auger analysis for the etching cones by Ar+, In was remained on the top of the cone with the bright contrast shown at Figure 2(A) after P was sputtered by the preference sputtering.

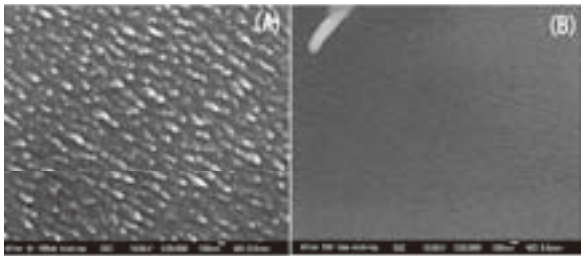

Figure 2.
SEM images after etching by Ar+ ion (A) and EDI (B)

The formation of etching cones of InP by Ar^+ impact can be suppressed by cooling the sample because the formation of etching cone is due to the heat effect [11].

After EDI etching at room temperature, however, SEM image of InP in Figure 2(B) shows no etching cones, almost smooth surface. We observe a little roughness, but it is looking as a small ripple structure. It means EDI etching would be suppressed from the preference sputtering of InP. We supposed that the kinetic energy of im-

pinging water droplet at the moment of EDI impact is efficiently converted to the internal energies of water molecules in the selvedge of the colliding interface. The rest is dissipated as shock waves propagating through the target and the water droplet. Thus, in EDI, the physical ablation as the surface energy of the target is suppressed minimal, i.e., the sample surfaces can be etched layer-by-layer at molecular level without damaging for the layers sample, realizing the extremely smooth surface etching.

The surface roughness of InP before and after etching by Ar^+ ion and EDI was measured by AFM shown in Figure 3 and Table 1. The etching depth was assumed to be the same with the etching depth from the etching rate for the standard SiO_2 thin film.

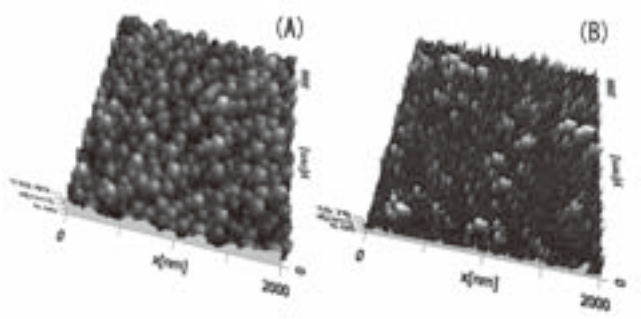

Figure 3.
AFM images after etching by Ar+ ion (A) and EDI (B)

The AFM measurement revealed that the surface average roughness after EDI etching was less than 1.2 nm, which is almost smooth surface for XPS analysis.

The result of In/P relative concentration by XPS are also shown in Table1.

Table1. Surface roughness and In/P relative concentration before and after etching by Ar^+ and EDI.

	As-received InP(111)	EDI etching depth at 48nm (as SiO_2)	Ar^+ Ion (3kV) etching depth at 60nm (as SiO_2)
Surface Roughness Measured by AFM	0.8nm	1.2nm	16.7nm
In/P Relative Concentration of InP by XPS	0.9 (with oxide)	1.0	1.2

By the preference sputtering of InP by Ar^+ sputtering, the relative concentration of In/P was change from 0.9 to 1.2 at 60nm depth. For EDI etching, the relative concentration of In/P was kept 1.0 at 48nm depth. This suggests that EDI etching is does not suffer from the preference sputtering of InP. The FWHM of $In3d_{5/2}$ and P2p were not changed before and after EDI etching. These results verify that EDI is capable of extremely smooth surface etching and no preference sputtering.

4. Conclusion

A comparative study for the etching of InP(111) by Ar^+ and EDI was made. It was found that the surface of InP etched by EDI provided the extremely smooth and no preference sputtering.

The surface etching method by EDI is a unique technique with no degradation for the organic and inorganic films.

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6. References

[1] J.Matuo, C.Okubo, T.Seki, T.Aoki, N.Toyoda and I.Yamada, *Nucl. Instr.and Meth.* **B219** (2004) 463

[2] N.Davies, D.E.Weibel, P.Blenkinsopp, N.Lockyer, R.Hill and J.C.Vickerman, *Appl. Sur. Sci.* **203-204** (2003) 223

[3] N.Sanada, A.Yamamoto,R.Oiwa and N.Ohashi, *Surf. Interf. Anal.* **36**, (2004) 280

[4] F.Kollmer, *Appl. Surf .Sci.* **231-232** (2004) 153

[5] D.E.Weibel, N.Lockyer and J.C.Vickerman, *Appl. Surf. Sci.* **231-232** (2004) 146

[6] K.Hiraoka, D.Asakawa, S.Fujimaki, A.Takamizawa, K.Mori, *Eur.Phys. J.D,* **38** (2006) 225

[7] K.Hiraoka, K.Mori, D.Asakawa, *J.Mass Spectrom.*, **41** (2006) 894

[8] K.Mori, D.Asakawa, J.Sunner and K.Hiraoka, Rapid Commun. Mass Spectrom. **20** (2006) 2596

[9] D.Asakawa, S. Fujimaki, Y. Hashimoto, K.Mori and K.Hiraoka, Rapid Commun. Mass Spectrom. **21** (2007) 1579

[10] Lord Rayleigh, Philos. Mag., **14** (1882) 184

[11] T.Ogiwara, S.Tanuma, Y. Nagasawa, N.Ikeo, Microbeam Anal., **2** (1993) 13