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Original Paper

Si Wafer Surface Etched by Water Droplet Cluster Ion Analyzed with SEM, SPM and XPS

Yoshitoki Iijima, Masato Kudo*, Yuji Sakai**, and Kenzo Hiraoka***
EO sales promotion group, JEOL Ltd.2-8-3 Akebono, Tachikawa, Tokyo 190-0012, Japan
**MI Division, SEM group, JEOL Ltd.3-1-2 Musashino, Akishima, Tokyo 196-8556, Japan*
***Japan Science and Technology Agency, Clean Energy Research Center, University of Yamanashi, Takeda 4-3-11, Kofu,Yamanashi 400-8511,Japan*
****Clean Energy Research Center, University of Yamanashi, Takeda 4-3-11, Kofu,Yamanashi 400-8511,Japan*

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The surface cleaning and depth profile of Si wafer used by water droplet cluster ion etching method was measured by SPM, SEM and XPS. It was observed that surface roughness of Si wafer after the bombardment of water cluster ion was not caused. Furthermore, the FWHM of Si2p after etching was the same as Si2p before etching. The result shown that water cluster ion etching method is very effective for sample surface cleaning and depth profile analysis of Si wafer by XPS and other surface analysis method.

1. Introduction

In generally, surface cleaning and depth profile analysis by X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) are usually done by the sputter etching method using an inert ion beam (Ar ions etc.), and in the case of Secondary ion mass spectrometry (SIMS), O_2^+ and Cs^+ ion beam are used for depth profile analysis. High energy (>1 keV) ion beam bombardment, however, induces kinds of damages, including surface roughness, decomposition of compounds, change of surface structure and the chemical bonding [1-4]. To avoid these damages, several etching methods, such as the low-energy neutral beam etching, hydrogen plasma etching, have been developed successfully to reduce the surface roughness [5-9]. However, the sample damage is still caused. Recently, as development of the material that the function improved an organic compound in a lamination layer, such as organic electroluminescence materials, has been advanced, the depth direction analysis becomes important more and more in XPS. Recently, C_{60} cluster ion etching method have been developed successfully to reduce surface roughness and decomposition compounds[10]. However, some damages can still be observed when C_{60} cluster ion beam is used. In particular, the surface structure and compositional changes as a function of depth were very proposed in organic polymers and semiconductor materials. Furthermore, sample surface contamination occurs by C_{60} cluster ion bombardment. A useful method for minimizing these etching phenomenons has not yet to be proposed.

To solve the problem of sample damage etched by C_{60} cluster ion, water droplet cluster ion impact is considered to be very effective[11,12]. This etching method (water droplet impact method) which developed by Hiraoka et al is possible in molecular level ion etching[11,12]. Its advantages are, suppression of chemical reaction on the surface, and formation of a uniform etching surface[11-13]. Because of these advantages, the water cluster ion beam etching method seems to be favored for surface analysis, including surface cleaning and depth profile analysis in XPS.

In this study, etched depth of Si (100) wafer due to water cluster ion beam etching has been investigated by XPS, scanning probe microscope (SPM) and scanning electron microscope (SEM).

2. Experimental

Water cluster ion ($[(H_2O)_{90,000} + 100H]^{100+}$) beam used this study is formed from electrosprayed droplet impact ionization source. Reference [11,12] is referred to about detail of this water cluster ion source. The m/z of the primary droplet projectiles range from 10,000 to 50,000. The kinetic energy of this projectiles with extra 100 charges may be ～1000 keV by the acceleration with the potential of 10 kV. This corresponds to the energy per nucleon for the projectile to be ～1 eV/u. This value is just the borderline of the bond breaking, so that this etching method used by the water cluster ion beam can be etched the monolayer-level of the material surface without damaging the sample.

The etching condition in this experiment was acceleration voltage 10 kV [11,12]. The Etching area is 3 x 1 mm, and one water cluster size is 10nm diameter.

The sample used this experimental is a Si (100) wafer (made by Nippon Silicon Ltd.) cleaned by HF solvent. For a Si wafer surface after etching, surface roughness was observed with Field-emission type SEM (JSM-6700, JEOL Ltd.) and SPM (JSPM-5400, JEOL Ltd.). Surface damage was measured with XPS (JPS-9200, JEOL Ltd.).

XPS analysis conditions are as follows. X-rays for excitation are non-monochromatic Mg Kα. Measurement energy resolution for the $Ag3d_{5/2}$ photoelectron peak was 0.9 eV at pass energy of 10 eV. The photoelectron spectrum was calibrated internally with the CH bonding state peak at 284.7 eV of the C1s spectrum. Analysis area of XPS is 1 mm diameter.

3. Results and Discussion

Fig. 1 shows SEM image of a Si wafer surface etched by water cluster ion beam for 60 minutes. An etching trace can be observed on Si wafer clearly from Fig.1. An etching area shows elliptic of 3 x 1 mm, because water cluster ion irradiation angle for a sample surface is 30 degree. Etching rare obtained by this condition is 0.2 nm/min for SiO_2 at 10 kV. This etching rate was very slow in comparison with that of Ar ion that is usually used remarkably.

But, this etching rate has no problem for practical use, because this etching rate satisfies it enough to do etching in layer-by-layer for ultrathin film. In this experimental, we used this etching condition for a Si wafer.

Fig.2 shows SPM image of a Si wafer before (a) , after (b) etched by water cluster ion beam for 60 minutes at 10 kV and after (c) etched by Ar ion beam for 20 s at 300 V.

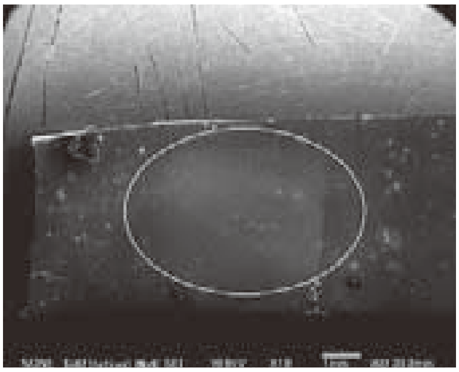

Fig.1 Si wafer SEM image etched by water cluster ion beam for 60 minutes at 10 kV.

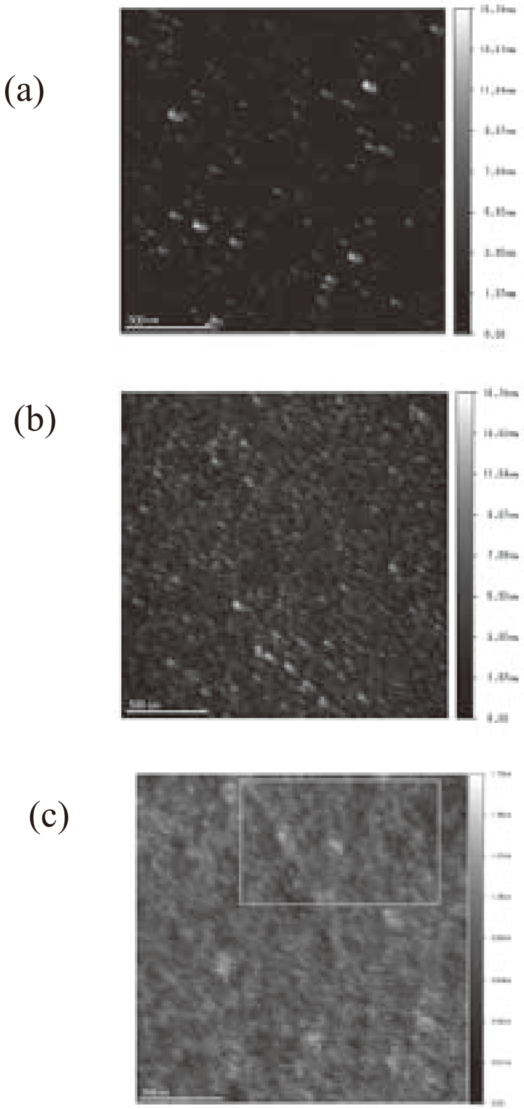

Fig.2 SPM image of Si wafer. (a) Before etching, (b) Etched by water cluster ion beam for 60 minutes at 10 kV, (c) Etched by Ar ion beam for 20 s. at 300 V.

It is observed that surface average roughness of Si wafer was 0.4 nm before etching, on the other hand, surface average roughness was less than 1.0 nm after water cluster ion beam etching. Although surface roughness was increased in the case of Ar ion beam bombardment, the surface roughness not changed by water cluster ion beam etching. As a result, the water cluster ion beam etching method can solve the problem of the surface roughness caused by the etching.

Fig.3 shows the photoelectron spectrum peak of Si2p obtained by XPS from the surface before etching ((a):the surface cleaned by dipping in an HF solution), the surface etched by the water cluster ion beam (b) and from the surface etched by the Ar ion beam (c). The radiation energy was 10 kV and the etching time was 60 minutes for the water cluster ion beam, on other hand, the radiation energy was 300 eV and the etching time was 20 s for the Ar ion beam. The etched depth (1.2nm) is the same as the water cluster ion beam in the Ar ion beam. By comparing the full widths at half-maximum

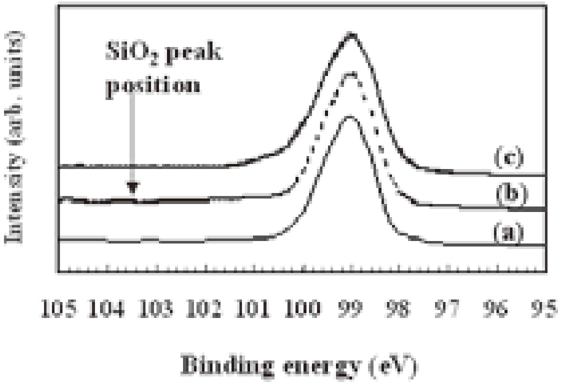

Fig.3 X-ray photoelectron Si2p spectrum of Si wafer. (a) surface before etching, (b) surface etched by water cluster ion beam, (c) surface etched by Ar ion beam (acceleration voltage: 300V, etched depth: 1.2nm .deep).

Table 1 FWHM of Si 2p peak.
Ar ion beam etching: acceleration voltage is 300V, etched depth is 1.2nm. Water cluster beam etching: acceleration voltage is 10kV and etched depth is 1.2nm.

Sample	FWHM of Si2p peak
before etching	1.23 eV
after etching by water cluster beam	1.23 eV
after etching by Ar ion beam	1.37 eV

By comparing the full widths at half-maximum (FWHM) of the Si2p peak for the respective etching methods, it is observed that the FWHMs of the Si2p peak after HF dipping and water cluster ion beam bombardment are, respectively, 1,23 eV and 1.23 eV, and with Ar ion beam bombardment it is 1.37 eV shown in Table 1. The difference between the FWHMs arises from the difference in the surface structure[14]. In general, the broadening of photoelectron peaks arises from the overlap of chemical shift components, which is influenced by the change of Madelung potential caused by confusion of crystal structure due to ion beam bombardment. Accordingly, the photoelectron peak is sharp for crystals and broad for amorphous materials[15]. Fig.4 shows the curve fitting spectra before etching (a), after water cluster ion beam etching (b) and after Ar ion beam etching (c). FWHM of Si2p$_{3/2}$ peak etched by water cluster ion beam is 0.88 eV, this result is the same as that of before etching.

The present experimental result indicates that after water cluster ion beam bombardment the surface structure of Si do not become amorphous, because the FWHM of Si2p$_{3/2}$ peak same as that after HF dipping.

Accordingly, it suggests that the water cluster etching method reduce the surface structure damage.

Adherence of contaminant in etching is not observed shown in Fig.3. In addition, it was observed that SiO_2 and/or Si oxide did not form on Si wafer due to water cluster ion beam bombardment shown in Fig.3, so that, it can be say that water cluster ion beam etching method is a clean etching method.

As the result, the water cluster ion beam etching is carried out more gently so that a Si water surface damage reduced.

4. Conclusion

We studied the effects of water cluster ion beam bombardment on the surface and the radiation damage.

In the present study, it was appearance that surface roughness was less than 1.0 nm and FWHM of Si2p$_{3/2}$ peak was the same as before etching. Therefore, it is shown that sample damage was reduced in comparison with conventional method remarkably.

As the result, the water cluster ion beam can be applied to the monolayer-level top surface sputtering of a Si wafer without damaging the sample.

It can be said that water cluster ion beam is very effective method for sample surface cleaning and depth profile analysis of XPS.

5. Acknowledgement

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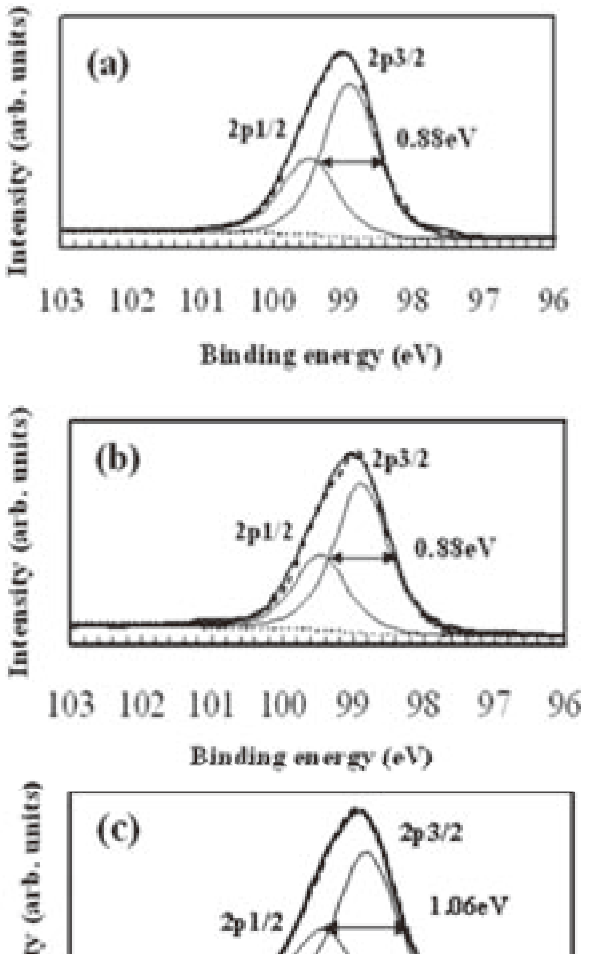

Fig.4 X-ray photoelectron Si 2p curve fitting spectrum of Si water. (a) surface before etching , (b) surface etched by water cluster ion beam (acceleration voltage is 10kV, etched depth is 1.2nm), (c) Ar ion beam etching(acceleration voltage is 10kV, etched depth is 1.2nm)

6. References

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