

# Surface interaction and processing using polyatomic cluster ions

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## Abstract

We developed two types of polyatomic cluster ion sources, one of which was a liquid cluster ion source using organic materials with a high-vapor pressure. Vapors of liquid material such as ethanol and water were ejected through a nozzle into a vacuum region, and liquid clusters were produced by an adiabatic expansion phenomenon. Another type was a cluster ion source using ionic liquids with a relatively low-vapor pressure. Positive and negative cluster ions were produced by a high-electric field emission. In addition, the interaction of polyatomic cluster ions with solid surfaces such as Si(100), SiO<sub>2</sub>, glass, and PMMA surfaces was investigated, and chemical sputtering was predominant for the Si(100) surfaces irradiated by ethanol cluster ion beams. Also, the irradiation damage of the Si(100) surfaces by ethanol and water cluster ion beams was smaller than that by Ar monomer ion irradiation at the same acceleration voltage. With regard to surface modification, PMMA surfaces were chemically modified by water cluster irradiation. Also, glass surfaces changed to electrically conductive surfaces by ionic liquid cluster ion irradiation. Furthermore, to demonstrate engineering applications of high-rate sputtering and low-damage irradiation by ethanol cluster ion beams, micro-patterning was performed on the Si surfaces.

**Key words:** Cluster, Polyatomic ion, Ionic liquid, Sputtering, Micro-patterning, Surface modification

## Experimental

Liquid materials served as a source for the production of polyatomic clusters. They are more appropriate than gaseous materials, as they tend to have more radicals in their polyatomic molecules than gaseous materials. Liquid cluster ion sources for a high-vapor pressure of materials were developed. The details of the source were described elsewhere [1,2]. The liquid materials were heated up to 150°C, and the vapors were ejected through a nozzle into a vacuum region. The time of flight (TOF) measurement showed that the cluster size was distributed between a few hundreds and a few tens of thousands, and the average size (peak size) was approximately 500 to 1000 molecules for ethanol clusters and approximately 2500 molecules for water clusters, respectively. It should be noted that both water clusters and ethanol clusters might have the hydrogen bonding ability. It is different from that of gas clusters, which are loosely-coupled each other by a van der Waals force. Therefore, these liquid clusters might be stronger in the intermolecular force than gas clusters [3].

The polyatomic ion source for ionic liquids was also developed. Ionic liquid used was 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF<sub>6</sub>). A high-electric field method was employed for the ion-emission from a sharp tip made of carbon rod [4]. The diameter of the rod was 0.3 mm. As a tip designed, for example, a needle with a radius of 80 μm was employed. The TOF measurement showed that the peak mass number was approximately 5000 for positive and negative ions. The molecular weight of cation (C<sub>8</sub>H<sub>13</sub>N<sub>2</sub>) and anion (PF<sub>6</sub>) is 139.22 and 144.96, respectively. By assuming that singly charged ions were extracted, ionic liquid cluster ions with a size of approximately 18 molecules were produced. It should be noted that they might have the ionic bonding ability.

## Results and discussion

Polyatomic clusters produced by an adiabatic expansion phenomenon were ionized by an electron bombardment. The electron voltage for ionization (V<sub>e</sub>) was 200 V, and the electron current for ionization (I<sub>e</sub>) was 250 mA. The polyatomic cluster ions such as ethanol and water cluster ions were accelerated toward a substrate. Various kinds of substrates such as Si(100), SiO<sub>2</sub>, glass, and PMMA substrates were irradiated at different acceleration voltages. The irradiation damage by polyatomic cluster ion beams was investigated using the Rutherford backscattering spectrometry (RBS) method.

Figure 1 shows the number of displaced atoms for the Si(100) surfaces irradiated at different acceleration voltages by ethanol and water cluster ions. The ion dose was  $1.0 \times 10^{15}$  ions/cm<sup>2</sup>, and the cluster size used was larger than 100 molecules per cluster. The number of displaced atoms increases with increasing acceleration voltage. The number is less than that for argon (Ar) monomer ion irradiation at the same acceleration voltage. The incident energy of a molecule is the accelerating energy divided by the cluster size, and this is very low for cluster ion irradiation. Therefore, irradiation damage caused by ethanol and water cluster ion beams is less than that of Ar monomer ion beams. In addition, at an acceleration voltage of 1 kV the number of displaced atoms by ethanol cluster ion irradiation is the same as that of the Si(100) surface prior to irradiation. Because the incident energy of an ethanol molecule is less than 10 eV, a damage-free surface can be obtained using the low-energy-irradiation effect of the ethanol cluster ion beams.

In order to investigate the irradiation damage of Si(100) surfaces by ethanol cluster ion beams, the ellipsometry measurement was performed [5]. Figure 2 shows the values of Delta and Psi measured for Si(100) surfaces irradiated by ethanol cluster ions and Ar monomer ions at different acceleration voltages. The ion dose was  $1.0 \times 10^{15}$  ions/cm<sup>2</sup>. For the ethanol cluster ion irradiation, the thickness ( $T_{ox}$ ) of oxide layer increases with increasing acceleration voltage, and it is approximately 9.5 nm at an acceleration voltage of 9 kV. With regard to damage thickness ( $T_d$ ), it is less than 1.0 nm. The total thickness of the oxide and damage thickness corresponds to the damage thickness measured by the RBS channeling. This indicates that the damage layer induced by the ethanol cluster ion irradiation is very thin, and that the oxide layer is thicker than the damage layer. The oxygen as a constituent atom of the ethanol molecule might contribute to the oxide layer formation. At an acceleration voltage of 1 kV, the damage layer thickness by ethanol cluster ion irradiation is extremely thin, although the oxide layer thickness is approximately 1.5 nm. On the other hand, for the Ar monomer ion irradiation, the damage layer thickness increases with increasing acceleration voltage. The oxide layer is thinner than the damage layer, and it is similar to the natural oxide layer formed on the unirradiated surface.

It is well known that the wet process using organic liquid materials has been applied to the surface treatment for solid surfaces. However, etching by organic liquid materials, such as ethanol, is not achieved even at elevated temperatures. Figure 3 shows the dependence of sputtered depth for Si(100) substrates and SiO<sub>2</sub> films on acceleration voltage for ethanol and water cluster ions. The ion dose was  $1.0 \times 10^{16}$  ions/cm<sup>2</sup>. As shown in the figure, the sputtered depth increases with increasing acceleration voltage. For the case of water cluster ions, the sputtered depths of Si and SiO<sub>2</sub> are almost the same. This is ascribed to the physical sputtering by the water cluster ion irradiation. With regard to Si(100) surface, the surface oxidation occurs rapidly after bombardment of the water cluster ions. The OH radicals and oxygen atoms produced after the bombardment have important roles in the oxidation due to the implantation and/or diffusion processes. For the bombardment of water cluster ions after the oxide layer formation, the incident energy is used for physical sputtering of the silicon oxide layers. Hereby, the sputtered depth of Si surfaces is similar to that of SiO<sub>2</sub> surfaces.

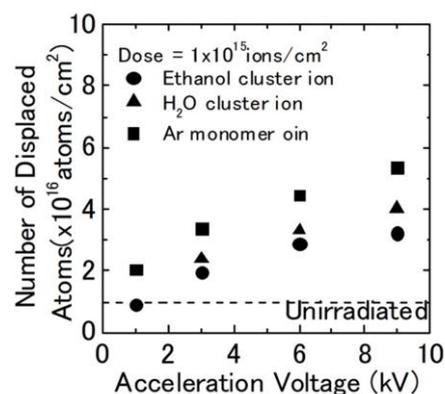


Fig.1 Number of displaced atoms for Si(100) Surfaces at different acceleration voltages.

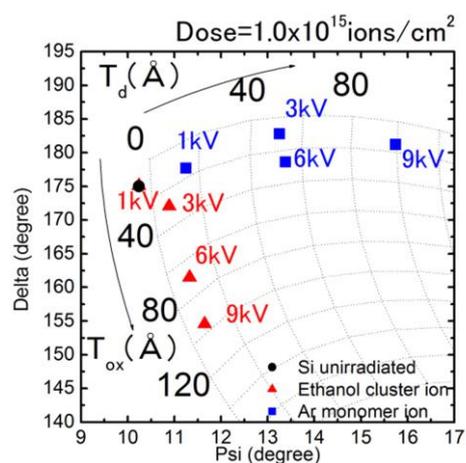


Fig.2 Values of Delta and Psi for Si(100) surfaces irradiated at different acceleration voltages.

In contrast, the sputtered depths of Si(100) and SiO<sub>2</sub> by the ethanol cluster ion irradiation are much different, as shown in the figure. When the acceleration voltage is 9 kV, the sputtered depth is 475 nm for Si(100) and 47 nm for SiO<sub>2</sub>, respectively. The sputtering ratio of Si(100) to SiO<sub>2</sub> is approximately 10. Taking account of the sputtered depth and the ion dose, the sputtering yield can be calculated by estimating the density of Si such as 2.42 g/cm<sup>3</sup>. The sputtering yield of Si at an acceleration voltage of 9 kV for the ethanol cluster ions is 246 atoms-per-ion, which is approximately 100 times larger than that by Ar ion beam sputtering. After bombardment of the ethanol cluster ions, hydrogen atoms are produced, and they react with the Si surface atoms. The selectivity arises from the volatility of the reaction products and the difference in binding energy among the materials [6,7]. This suggests that chemical reactions between Si(100) and ethanol produce silicon hydride which is the dominant etching material for Si(100) surfaces.

Polymethyl methacrylate (PMMA) is a polymer with a molecular structure of CH<sub>3</sub>CCH<sub>2</sub>COOCH<sub>3</sub>. PMMA has attracted interest as an organic glass, and it has been used in various kinds of chemical devices such as microreactors. Figure 4 shows the sputtering yield for PMMA surfaces irradiated at different acceleration voltages by ethanol and water cluster ion beams. Taking account of the sputtered depth and the ion dose, the sputtering yield was calculated by first estimating the density of PMMA to be 1.19 g/cm<sup>3</sup>. As shown in Fig. 4, the sputtering yield increases with increasing acceleration voltage, and the yield was found to be 206 molecules-per-ion for water cluster ion irradiation and 134 molecules-per-ion for ethanol cluster ion irradiation at an acceleration voltage of 9 kV. The high sputtering yield of PMMA substrates occurs because of the ejection of sputtered particles as a monomer unit due to the cluster ion irradiation.

In particular, water cluster ion irradiation exhibits higher sputtering yields than ethanol cluster ion irradiation at different acceleration voltages. For PMMA substrates irradiated by water cluster ions, it is thought that the chemical erosion of the substrate surfaces occurs through the exchange of the CH<sub>3</sub> radical in COOCH<sub>3</sub> with an H atom of the water cluster, or through the exchange of an OCH<sub>3</sub> radical with an OH radical [3]. Therefore, the PMMA surface changes to a polymethacrylic acid surface, which has a melting point lower than room temperature and is dissolvable in water. The impact of water cluster ions on the changed surface enhances the ejection of methacrylic acid molecules in the monomer state from the surface. Thus, the high sputtering yield of PMMA surfaces is achieved by both the chemical erosion of the surface and the momentum transfer of the incident energy of the water cluster ion irradiation.

To demonstrate an engineering application of high-rate sputtering and low-damage irradiation by ethanol cluster ion beams, a patterning process was performed on the Si(100) surface with a photo resist mask. Line, circle, and square mask patterns were commercially available and the line width was in the range of 0.5 μm to 3 μm. The diameter of the circle and the edge length of the square were both 60 μm, and the spacing for the circle and square patterns was 10 μm. The thickness of the photo resist film coated on the Si(100) substrate was approximately 1 μm. Figure 5 shows the scanning electron microscope (SEM) images for the lines, circles, and squares patterned with ethanol cluster ion beams.

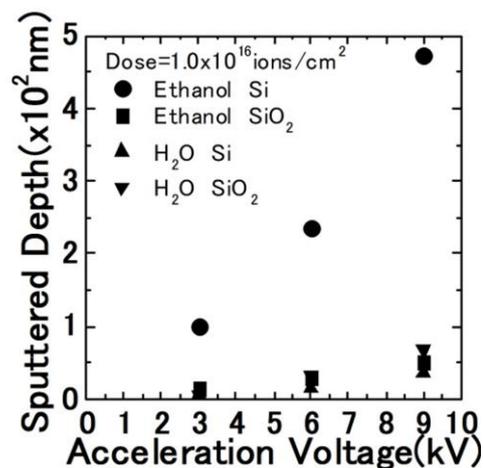


Fig.3 Dependence of sputtered depth for Si(100) and SiO<sub>2</sub> surfaces on acceleration voltage for ethanol and water cluster ions.

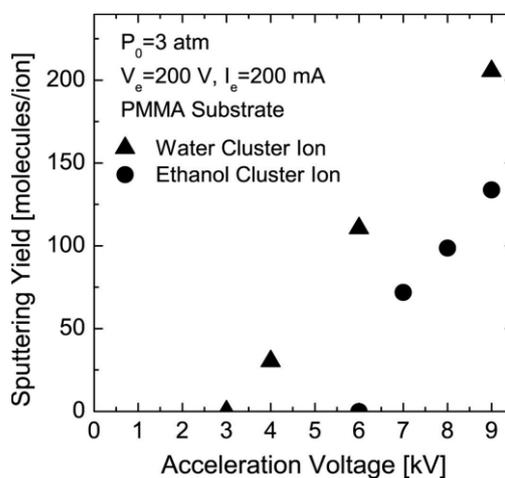


Fig.4 Sputtering yield for PMMA surfaces irradiated at different acceleration voltages by ethanol and water cluster ion beams.

The acceleration voltage was 9 kV, and the ion dose was  $5.0 \times 10^{15}$  ions/cm<sup>2</sup>. After the ethanol cluster ion irradiation, the photo resist film on the Si(100) surface was removed with acetone. As shown in the above figure, the pattern edge is sharp, and the sputtered surface (bright area) is a flat plane. The micropattern has been clearly prepared by the ethanol cluster ion beam. Moreover, the measured sputtered depth was approximately 0.22  $\mu\text{m}$ , which increased with increasing ion dose. A sputtered depth of 0.75  $\mu\text{m}$  was obtained at an ion dose of  $2 \times 10^{16}$  ions/cm<sup>2</sup>, and the maximum depth available was limited by the resist film thickness.

Figure 6 shows (a) SEM and (b) atomic force microscope (AFM) images of glass substrates deposited by positive ions of ionic liquids. The extraction voltage applied to the tip was 6kV. As shown in the figure, the SEM images of glass substrates are observed clearly without charge-up of electron beams. This is due to the deposition of ionic liquids exhibiting electrically conductive property. Furthermore, the glass surface becomes rough after deposition. According to AFM measurement, the surface roughness ( $R_a$ ) is 0.53 nm. It is larger than the surface roughness of the unirradiated glass, such as 0.4 nm. Also, the deposited film was transparent, and the transmittance was larger than 95 %. Furthermore, the X-ray photoelectron spectroscopy (XPS) measurement showed that the composition of the deposited films was the same as ionic liquid (BMIM-PF<sub>6</sub>). This is due to the deposition of ionic liquid clusters, which include both cations and anions.

In summary, polyatomic molecular ions exhibit unique features, one of which is that it can transfer energy and mass as well as fragment radicals toward substrate surfaces. These radicals play an important role in chemical erosion and sputtering, which results in high rate sputtering and low irradiation damage of the substrate surfaces. In addition, a cluster state of polyatomic molecules has several unique features, for example, the clusters enable a link between the atomic state and bulk state. The physical and chemical properties of clusters are different to those of the bulk state. Based on these features of polyatomic cluster ions, we focused on liquid materials such as ethanol, water, and ionic liquid, and produced polyatomic cluster ions by exploiting an adiabatic expansion phenomenon or by using a high-electric field emission of ions. The interactions of liquid cluster ions with solid surfaces were investigated in order to clarify the physics and chemistry of polyatomic cluster ion beams. Applications of the materials processing methods were demonstrated with polyatomic cluster ion beams, including high-rate sputtering of surfaces, micro-patterning, and surface modification.

## References

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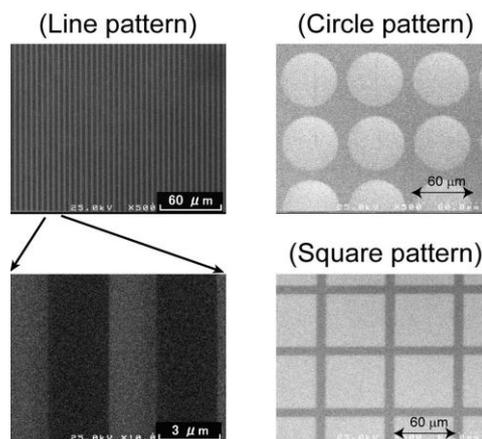


Fig.5 SEM images for the lines, circles and squares patterns on Si surfaces.

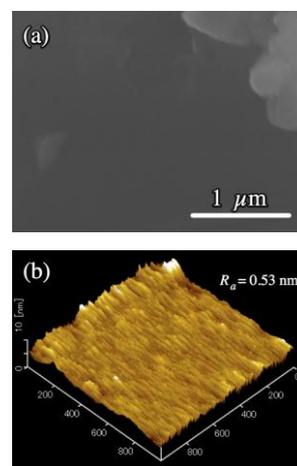


Fig.6 (a)SEM and (b)AFM images for ionic liquid films deposited on glass substrates.