High-Rate Sputtering of Si and SiO₂ with Atomically Flat Surfaces by Using Ethanol Cluster Ion Beams

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In order to investigate the interactions of ethanol cluster ion beams with solid surfaces, various kinds of substrates such as Si(111), SiO₂ and Au substrates were irradiated at different acceleration voltages and retarding voltages for ethanol cluster ions. RBS channeling measurement showed that the irradiation damage of the Si surfaces by the ethanol cluster ions was smaller than that by the Ar monomer ion irradiation at the same acceleration voltage. It was also found that the formation of damage-free surface was achieved by adjusting the acceleration voltage and the retarding voltage for the ethanol cluster ions. Furthermore, the sputtering process was investigated by changing the retarding voltage and the incident angle, and chemical sputtering was found to be predominant for the Si surfaces. The surface roughness decreased with increase of the retarding voltage, and it was less than 1.2 nm. On the other hand, for SiO₂ and Au surfaces, physical and lateral sputtering was achieved, and the sputtered depth decreased with increase of either the retarding voltage or the incident angle.

Key words: Ethanol cluster, Ion beam, Sputtering, Irradiation damage, Silicon

1. INTRODUCTION
The cluster ion beam process, which is one of the basic technologies in nanostructure fabrications, has attracted much interest. We have succeeded in producing vaporized liquid-clusters such as ethanol and water clusters by an adiabatic expansion phenomenon [1,2]. The property of the liquid cluster itself might be different from that of the bulk state. In addition, their impact on solid surfaces induces various kinds of irradiation effects such as high density irradiation effect, low energy irradiation effect and surface modification effect [3,4]. Since the diameter of the liquid cluster with a size of several thousands molecules is a few nanometers, the cluster impacts on the solid surface in an area of only a few nanometers, which causes multiple collisions between cluster molecules and surface atoms. As a unique characteristic of the liquid cluster ion irradiation, for example, ethanol cluster ion irradiation exhibits high rate sputtering, in which two kinds of sputtering such as physical and chemical sputtering is available according to different material surfaces. All of the impinging energy of the cluster ion is deposited at the surface region, and this dense energy deposition as well as the chemical reaction on the surface is the origin of enhanced sputtering yields. On the other hand, with regards to the low energy irradiation effect, the incident energy of a single molecule in a cluster corresponds to the accelerating energy divided by the cluster size. For example, when the acceleration voltage is 1 kV for the cluster ion with a cluster size of 1000 molecules, one molecule in a cluster has an incident energy of 1 eV. Therefore, there is no damage by the cluster ion irradiation, if the displacement energy of surface atoms is larger than 1 eV.

In order to clarify high-rate sputtering process as well as low-damage formation by the ethanol cluster ion beams, the size control is of much importance. In particular, the minimum size of the cluster ions is a key factor for the formation of irradiation damage. Furthermore, the relationship between sputtering and damage is trade-off in the conventional ion beam process, and it is not possible to achieve high-rate sputtering without irradiation damage. In this article, the size distribution of ethanol cluster ions is studied using a time of flight method and a retarding potential method. In addition, irradiation damage and sputtering process is investigated by changing parameters such as the acceleration voltage, the retarding voltage and the incident angle. Based on these properties, the interaction of ethanol cluster ions with solid surfaces such as Si(111), SiO₂ and Au surfaces is discussed.

2. EXPERIMENTAL PROCEDURE
The details of the experimental apparatus used have been described elsewhere [5]. A liquid material, such as ethanol, is placed into a cluster source, and heated to 150 °C by a wire heater attached around the source. The vapors of ethanol are ejected through a nozzle into a vacuum region, and ethanol clusters are produced by an adiabatic expansion phenomenon. The clusters produced pass through a collimator and enter an ionizer. In the ionizer, the neutral clusters are ionized by electron bombardment. The electron voltage for ionization (Ve) varied between 0 V and 300 V, and the electron current for ionization (Ie) varied between 0 mA and 300 mA. The ethanol cluster ions are extracted by applying an extraction voltage, and the extracted cluster ions are size-separated by a retarding potential method. Cluster ions with cluster sizes larger than 100 molecules were accelerated toward a substrate, which was set on a substrate holder. The acceleration voltage (Va) varied between 0 kV and 10 kV. The substrates used were Si(111), SiO₂ and Au substrates. For the SiO₂ substrates, SiO₂ films with a thickness of 100 nm were grown on Si(100) substrates by a thermal oxidation method. The incident angle of the cluster ion beams was adjusted by
changing the substrate plane from horizontal to oblique. The ion dose to the substrate was determined based on the ion current. When the desired ion dose was attained, the shutter was closed to terminate the ion irradiation. The background pressure around the substrate was 1.33 x 10^{-5} Pa, which was attained using a turbo-molecular pump.

The cluster size distribution was measured by the time of flight (TOF) method. The minimum size of the cluster size distribution was controlled by adjusting the retarding voltage. The sputtered depth for the substrates irradiated with ethanol cluster ions was measured by a step profiler (XP-2, Ambios Technology Inc.). The surface morphology of the substrates was observed using an atomic force microscope (SPI 3700, SII Nano Technology Inc.), and the surface roughness defined as the average roughness was measured. With regards to the irradiation damage, this was measured using Rutherford backscattering spectroscopy (RBS) method.

3. RESULTS AND DISCUSSION

Figure 1 shows the cluster size distribution measured by changing the retarding voltage for ethanol cluster ions. The distribution is normalized by the total current of cluster ions at different retarding voltages. The retarding voltage (V_r) was changed from 28 V to 112 V, which corresponded to the minimum size of cluster ions from 100 molecules to 400 molecules. The source temperature was 109 °C, and the vapor pressure of ethanol was 3 atm. The acceleration voltage (V_a) was 9 kV. As shown in the figure, the peak size of ethanol cluster ions is approximately 2000 molecules, and the minimum size as well as the peak size of the cluster ions increases with increase of the retarding voltage. This is ascribed to the removal of cluster ions with smaller sizes from the ion beams by applying the retarding voltage.

In order to investigate the irradiation damage by the ethanol cluster ion beams, the number of displacement atoms was estimated based on the RBS channeling spectra measured. Figure 2 shows the number of displacement atoms for the Si(111) surfaces irradiated at different acceleration voltages as a parameter of the retarding voltage (V_r). The ion dose was 1.0x10^{15} ions/cm^2. The number of displacement atoms for the ethanol cluster ion irradiation is less than that for the Ar monomer ion irradiation at the same acceleration voltage. For the case of the ethanol cluster ion irradiation, the incident energy of an ethanol molecule is the accelerating energy divided by the cluster size, and it is very low. Therefore, the irradiation damage induced by ethanol cluster ion beams is less than that by Ar monomer ions. With regard to the acceleration voltage dependence, the number of displacement atoms increases with increase of the acceleration voltage. This is due to the acceleration voltage dependence of implanted depth, in which all Si atoms are displaced for the ethanol cluster ion irradiation at higher doses than 1.0x10^{17} molecules/cm^2. Furthermore, it approaches to a saturated value at higher acceleration voltages, which is due to another reason such as the removal of damaged layers by the ethanol cluster ion irradiation. In addition, at an acceleration voltage of 1 kV for V_r = 28 V and 3 kV for V_r = 84 V, respectively, the number of displacement atoms by the ethanol cluster ion irradiation is the same as that of the unirradiated Si(111) surface. The formation of the damage-free surfaces depends on the minimum size of ethanol cluster ions. Because the incident energy of an ethanol molecule is less than 10 eV per molecule, the damage-free surface is obtained by extremely low energy irradiation of the ethanol cluster ion beams.

Figure 3 shows the dependence of the sputtered depth on the retarding voltage of the ethanol cluster ions for (a) Si(111) and (b) SiO_2 surfaces as a parameter of the acceleration voltage (V_a). Taking account of the sputtered depth and the ion dose, the sputtering yield can be calculated by estimating the density of Si and SiO_2 such as 2.42 g/cm^3 and 2.63 g/cm^3, respectively. For the Si(111) surfaces, the sputtered depth at an acceleration voltage of 9 kV and a retarding voltage of

![Fig. 1: Cluster size distribution measured at different retarding voltages for ethanol cluster ions.](image1)

![Fig. 2: Number of displacement atoms for the Si(111) surfaces irradiated at different acceleration voltages for ethanol cluster ions and Ar monomer ions as a parameter of the retarding voltage (V_r).](image2)

![Fig. 3: Dependence of the sputtered depth on the retarding voltage of the ethanol cluster ions for (a) Si(111) and (b) SiO_2 surfaces as a parameter of the acceleration voltage (V_a).](image3)
28 V is 37 nm, and the sputtering yield is 192 atoms per ion. It is approximately 100 times larger than that by Ar ion beam sputtering. The high-rate sputtering is due to the chemical sputtering. The incident energy of the cluster ions is used for heating an impact region of the surfaces [6]. Therefore, the thermal vibration frequency of the ethanol molecules becomes extremely high, and the barrier height for the chemical reaction becomes relatively low [7,8]. As a result, several chemical reactions such as silicon hydride and organic reactions are performed almost at the same time even for a very short time by the ethanol cluster ion irradiation. The confirmation was resulted from X-ray photoelectron spectroscopy measurement for sputtered particles.

In addition, as shown in the figure, the sputtered depth has a maximum value at a retarding voltage between 40 V and 80 V. When the retarding voltage increases, both the minimum size and the peak size of the ethanol cluster ions increase. This indicates that the implanted depth of the ethanol cluster ions decreases with increase of the retarding voltage, and it becomes smaller than the region of the chemical reaction near the Si(111) surface at higher retarding voltages. Furthermore, the total current of cluster ions decreases with increase of the retarding voltage. When ethanol cluster ion irradiation is performed keeping the ion dose constant, the chemical reaction frequency increases with an increase of the retarding voltage starting from 28 V to an optimum voltage. As a result, the sputtered depth due to the chemical reaction has a maximum value at a retarding voltage. On the other hand, for the SiO2 surfaces, the sputtered depth decreases with increase of the retarding voltage. In this case, the physical sputtering occurs by the ethanol cluster ion irradiation. For the physical sputtering, the incident energy per molecule in a cluster has an important role. When it decreases, the sputtering effect is suppressed. Furthermore, when the incident energy of the cluster ions becomes much lower, many molecules in the cluster are ejected or reflected from the substrate surface at larger retarding voltages. As a result, the sputtered depth becomes relatively small.

Figure 4 shows the dependence of the surface roughness for Si(111) and SiO2 surfaces on the retarding voltage of the cluster ions. The acceleration voltage (Va) was 9 kV, and the ion dose was 1.0x10^{15} ions/cm^2 for Si(111) surface and 5.0x10^{15} ions/cm^2 for SiO2 surface, respectively. The surface roughness of the unirradiated Si(111) and SiO2 surfaces was 0.18 nm and 0.20 nm, respectively. As shown in the figure, the surface roughness decreases with increase of the retarding voltage, although it is larger than that of the unirradiated surface. The minimum size of the cluster ions increases with increase of the retarding voltage, and the migration effect of the cluster ions after impact increases with increase of the cluster size. As a result, the lateral sputtering effect by ethanol cluster ion irradiation increases with increase of the retarding voltage. Therefore, the surface flatness is improved by the ethanol cluster ion irradiation at larger retarding voltages.

Figure 5 shows the dependence of the sputtering yield on the incident angle (θ) of the ethanol cluster ions for Si(111) and Au surfaces. The acceleration voltage for Si and Au surfaces was Va = 6 kV and 9 kV, respectively. The incident angle was defined with respect to the normal direction, which corresponds to θ°.
for normal incidence. As shown in the figure, the sputtering yield for the Si(111) surface has a maximum value at an incident angle between 10° and 30°. When the incident angle changes from normal to oblique, the chemical reaction frequency in the near surface region becomes high, and the number of particles ejected by chemical sputtering increases, resulting in a high sputtering yield.

In contrast, for the case of physical sputtering of the Au surface by ethanol cluster ion irradiation, the sputtering yield decreases with increase of the incident angle, and it changes according to $\cos \theta$. For normal incidence, the penetration depth is the greatest, and most of the incident energy is deposited onto the surface atoms. For the physical sputtering, the sputtered atoms are ejected horizontal to the substrate surface due to the lateral sputtering effect. However, for oblique incidence, sputtered atoms are ejected in the forward direction of the cluster ion beams, and the atoms in the backward direction are re-deposited on the substrate surface. Therefore, the sputtering yield decreases with increase of the incident angle.

Fig. 5: Dependence of the sputtering yield on the incident angle ($\theta$) of the ethanol cluster ions for Si(111) and Au surfaces.

4. CONCLUSION

Ethanol clusters were produced by an adiabatic expansion phenomenon. The cluster size was distributed between a few tens and a few thousands, and the peak size was approximately 2000 molecules per cluster. Furthermore, the cluster size distribution was measured by changing the retarding voltage, and it was found that the minimum size as well as the peak size increased with increase of the retarding voltage.

In order to investigate the interactions of ethanol cluster ion beams with solid surfaces, various kinds of substrates such as Si(111), SiO$_2$ and Au substrates were irradiated by changing the acceleration voltage and the retarding voltage for ethanol cluster ions. RBS channeling measurement showed that the irradiation damage of the Si surfaces by the ethanol cluster ions was smaller than that by the Ar monomer ion irradiation at the same acceleration voltage. It was also found that the damage-free surface formation was achieved by adjusting the acceleration voltage and the retarding voltage. This was ascribed to the low energy irradiation effect by the cluster ion beams. Furthermore, the sputtering process was investigated by changing the retarding voltage and the incident angle. It was found that chemical sputtering was predominant for the ethanol cluster ion irradiation on the Si surfaces. As a result, the sputtering yield was a few hundreds times larger than that for the Ar monomer ion irradiation. The surface roughness decreased with increase of the retarding voltage, and it was less than 1.2 nm. This was explained by the enhancement of the lateral sputtering effect, because the cluster size increased with increase of the retarding voltage. On the other hand, for SiO$_2$ and Au surfaces, physical and lateral sputtering was achieved by the ethanol cluster ion beams. For these surfaces, the sputtered depth decreased with increase of either the retarding voltage or the incident angle. The surface roughness also decreased with increase of the retarding voltage.

Thus, the ethanol cluster ion irradiation has represented unique characteristics such as high rate sputtering with extremely low-irradiation damage and smooth surface formation at an atomic level.

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REFERENCES


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