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<td>Ryuto, H.; Ozaki, R.; Kubo, Y.; Takeuchi, M.; Takaoka, G. H.</td>
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Characteristics of liquid cluster ion beam for surface treatment


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A liquid cluster ion source, which is an ion source for the cluster beams produced with liquid materials, has been developed for the surface treatment of solid materials. The electrodes were designed for increasing the cluster beam intensity by a computer simulation of beam trajectories. The peaks of the cluster size distributions of the water and ethanol cluster ion beams of 3 atm vapor pressure were approximately at $2.4 \times 10^3$ and $1.6 \times 10^3$ molecules, respectively. The cluster size distributions of ethanol clusters were not sensitive to the variations of the acceleration voltages ($V_a$) and currents ($I_e$) of the electrons for ionization when the $V_a$ and $I_e$ were larger than approximately 200 V and 200 mA, respectively. © 2010 American Institute of Physics. [doi:10.1063/1.3264627]

I. INTRODUCTION

The cluster ion beam technique is one of the newly developed ion beam technique that is attracting much interest in various fields such as the semiconductor industry and medical application. A cluster beam is a flow of aggregates of atoms or molecules combined typically with van der Waals force. The condensation phenomenon in an expanding nozzle flow was originally investigated by the Karlsruhe group and unique properties of cluster ion beams were revealed during the decades of investigation by various groups. In addition, the production of clusters from vaporized materials without helium gas was investigated. As well as the properties of the cluster itself, the impact of a cluster ion on a solid surface represents unique properties, which do not appear in the conventional ion beam process. A high sputtering yields, low radiation damage, and surface smoothing effect are the typical features of the interaction between cluster ion beams and solid materials. These features are expected to be the key to applying the cluster ion beam technique in the semiconductor industry, which requires a rapid processing without serious radiation damage. The possibility to use the cluster ion beam technique in medical applications was also investigated. These characteristic properties of the interaction between cluster ion beams and solid surfaces are mainly attributable to the high-density energy deposition and the low-energy irradiation effect.

Moreover, a liquid cluster ion beam, that is a cluster ion beam produced with a liquid material (at room temperature), has unique properties that are induced by the characteristic structure as well as the chemical properties of the molecules that comprise the cluster. Therefore, a liquid cluster ion beam is expected to be a powerful tool to process or modify solid surfaces. Therefore, we have developed a liquid cluster ion source to realize a high intensity cluster ion beam that can be used in the applications in various fields.

II. EXPERIMENTAL APPARATUS

Figure 1 shows a schematic view of the liquid cluster ion source and the focusing elements. The liquid clusters were produced by the adiabatic expansion method. A liquid material such as ethanol and water is filled in the liquid container. In the case of an ethanol cluster ion beam, 150 ml of ethanol is filled in the liquid container for approximately 2 h irradiation. The liquid material is heated to increase vapor pressure using a heater attached on the outer wall of the liquid container. For example, the ethanol temperature is increased to 382 K and the water temperature is increased to 407 K to obtain 0.3 MPa vapor pressure. The typical variation of the temperature is approximately ±1 K, which corresponds to ±10 and ±9 kPa variations of ethanol and water vapor pressures, respectively. The vaporized liquid material is ejected to a vacuum chamber through a Laval nozzle. The temperature of the vapor decreases by the adiabatic expansion, and clusters are formed. The core portion of the flow of neutral clusters is selected using a skimmer to avoid the disintegration of clusters caused by shockwaves. The skimmer opening is 1.3 mm. The remaining vapor is evacuated using a roots pump. The other vacuum chambers downstream are evacuated using diffusion pumps or a turbo molecular pump to avoid the disintegration of clusters by collisions with residual gases.

The neutral clusters are ionized by the electrons emitted from the loop of a tungsten filament. The typical acceleration voltage of the electrons ($V_e$) and their currents ($I_e$) are 200 V and 200 mA, respectively. Singly charged cluster ions are assumed in the following discussion. The ionized clusters are extracted by the voltage applied between the anode and the extraction electrode. Then, the monomers and small-sized clusters are eliminated by the retarding voltage method. The retarding voltage method is based on the phenomenon that the velocity of the nozzle flow is highly uniform, typically within 10%. The kinetic energy of ethanol clusters calculated on the basis of this phenomenon is 0.29 eV/molecule. Therefore, the ethanol cluster whose cluster size (number of molecules that comprise a cluster) is less than 100 is blocked by the retarding voltage ($V_r$) of 29 V applied to the retarding

\[ V_r = \frac{m_e V_e^2}{2} \]

where $m_e$ is the mass of the electron.

\[ m_e = 9.11 \times 10^{-31} \text{kg} \]

\[ V_e = 200 \text{ V} \]

\[ I_e = 200 \text{ mA} \]

\[ V_r = 29 \text{ V} \]

\[ m_e V_e^2 = 1.82 \times 10^{-17} \text{kg m}^2/\text{s}^2 \]

\[ \frac{1.82 \times 10^{-17} \text{kg m}^2/\text{s}^2}{2} = 9.11 \times 10^{-31} \text{kg} \times 200^2 \text{ V}^2 = 3.64 \times 10^{-15} \text{J} = 2.27 \times 10^{-19} \text{eV} \]

\[ 2.27 \times 10^{-19} \text{eV} / 0.29 \text{ eV/molecule} = 7.8 \times 10^{10} \text{ molecules} \]

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electrode. The position and shape of the electrodes were designed for increasing the intensity of the cluster ion beam by trajectory simulations. The openings of the extraction and retarding electrodes are covered by high-transmission nickel fine meshes to make flat equipotential surface. The cluster ion beam is accelerated by an acceleration voltage typically from 3 to 9 kV. The accelerated cluster ion beam is transported to the target using an Einzel lens and electrostatic deflector. The Einzel lens voltage was typically from 0 to 15 kV. The target and a Faraday cup with an electron suppressor approximately at −300 V are set on a linear motion feedthrough.

The cluster size distribution was measured by the time-of-flight (TOF) method. A pulse of an ethanol cluster ion beam was produced by the electrostatic deflector, on which a high voltage pulse was applied. In this work, the beam signal was measured using a Faraday cup instead of a microchannel plate to measure the cluster size distribution of intense cluster ion beams suitable for the application in the semiconductor industry or medical application. The signal extracted from the Faraday cup was observed using a digital oscilloscope. The calculation was made nonrelativistically because the β was approximately in the order of 10⁻⁵. The mass resolution of a linear TOF system is limited, but sufficient to know the shape of the cluster size distribution in general.

### III. RESULTS AND DISCUSSION

Figure 2 shows equipotential lines and trajectories of ethanol cluster ion beams whose cluster size is 1000 with (a) a flat retarding electrode without focusing using the Einzel lens voltage (kV)

![FIGURE 2. Equipotential line and trajectories of ethanol cluster ion beams whose cluster size is 1000 with (a) retarding electrode without rim and V_r=0 V, (b) retarding electrode with 15 mm long rim and V_r=0 V, and (c) retarding electrode with 15 mm long rim and V_r=8 kV.](image)

Figure 3 shows the dependence of beam intensity on Einzel lens voltage measured using Faraday cup with 10 mm diameter collimator.

![FIGURE 3. Dependence of beam intensity on Einzel lens voltage measured using Faraday cup with 10 mm diameter collimator.](image)

![FIGURE 4. Dependences of cluster size distribution on (a) acceleration voltage and (b) current of electrons for ionization.](image)
TABLE I. Statistical values of cluster size distributions.

<table>
<thead>
<tr>
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<th>( V_e ) (V)</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode ( \times 10^3 )</td>
<td>2.0</td>
<td>1.6</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Median ( \times 10^3 )</td>
<td>2.8</td>
<td>2.2</td>
<td>2.1</td>
<td>2.1</td>
<td>2.1</td>
<td>2.1</td>
</tr>
<tr>
<td>FWHM ( \times 10^3 )</td>
<td>2.9</td>
<td>2.3</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
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<table>
<thead>
<tr>
<th></th>
<th>( I_e ) (mA)</th>
<th>50</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>500</th>
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<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Median ( \times 10^3 )</td>
<td>2.8</td>
<td>2.5</td>
<td>2.3</td>
<td>2.1</td>
<td>2.0</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>FWHM ( \times 10^3 )</td>
<td>3.0</td>
<td>3.0</td>
<td>2.3</td>
<td>2.1</td>
<td>1.8</td>
<td>1.8</td>
<td>1.7</td>
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by the larger ionization cross section of larger-sized clusters than smaller-sized clusters. As the case in the \( V_e \), the shift of the peak position caused by the increase in the \( I_e \) was limited when the \( I_e \) was larger than 200 mA. The variations of the mode, median, and FWHM gradually decreased with increasing \( I_e \) and became almost constant when the \( I_e \) was larger than 400 mA. Therefore, the cluster size distribution of an ethanol cluster ion beam can be well controlled by adjusting the acceleration voltage and current of the electrons for ionization with moderate accuracy when the \( V_e \) and \( I_e \) are larger than approximately 200 V and 200 mA, respectively. This phenomenon is useful to realize a reproducible precise processing of high-density semiconductor devises, because the sputtering yield, radiation damage, and surface smoothing effects depend on the cluster size distribution.\(^6\)

IV. SUMMARY

A liquid cluster ion source was developed for surface treatment. To increase the cluster beam intensity, the electrodes are designed by the optics simulation. The maximum beam current density of the ethanol cluster ion beam realized by the apparatus was 290 nA/cm\(^2\). The cluster size distribution of ethanol clusters was not sensitive to the variations of the acceleration voltage and current of the electrons for ionization when the \( V_e \) and \( I_e \) were larger than 200 V and 200 mA, respectively. Therefore, the liquid cluster ion beam can be a powerful tool to realize a reproducible processing of solid surfaces.