

Irradiation effect of gas-hydrate cluster ions on solid surfaces

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(Abstract)

In our newly developed gas-hydrate cluster ion source, a vapor of water bubbling with carbon dioxide (CO₂) gas was ejected through a nozzle into a vacuum region, and mixed beams of water clusters and carbon dioxide-hydrate clusters were produced by adiabatic expansion. According to time-of-flight measurements, the largest water clusters consisted of approximately 2800 molecules at a vapor pressure of 0.3 MPa. Also, the largest mixed clusters contained approximately 2000 molecules. Copper and silicon substrates were irradiated by the water cluster ions as well as carbon dioxide-hydrate cluster ions. X-ray photoelectron spectroscopy measurements showed that carbon was included in the Cu and Si substrates irradiated by the carbon dioxide-hydrate cluster ions, and a chemical shift owing to the formation of carboxyl radicals occurred on the Cu surface. Furthermore, the Cu surface was sputtered, and the sputtering depth was larger than the distance penetrated by the water cluster ion irradiation. Therefore, the formation of carboxyl radicals played an important role in the sputtering of the Cu surface, which occurred effectively in carbon dioxide-hydrate cluster ion irradiation.

Keywords: Water cluster, Gas-hydrate cluster, Ion beam, Irradiation effect, Sputtering, Surface modification

1.Introduction

In recent years, experimental and theoretical studies have been carried out to investigate the microscopic structure of liquid water in terms of clusters of water molecules [1-3]. Two states, the molecular state and cluster state, have been proposed. The cluster state has a three-dimensional structure of hydrogen bridge networks between the single molecules, which is expected to possibly include gas molecules. Furthermore, the properties of liquid water are influenced by the cluster size as well as the structure [4-6]. On the other hand, gas hydrates, also called clathrate hydrates, are crystalline compounds of water and gas molecules such as methane or carbon dioxide [7,8]. The clathrate is in general a structure in which one of the components (host) forms cages that enclose molecules of another component (guest). The crystalline host lattice (e.g., ice powder) is a thermodynamically metastable phase that is stabilized by the presence of guest molecules in its cavities. The gas hydrates exhibit many features that are advantageous for a number of applications such as flow assurance, safety, energy recovery, gas storage or transportation and climate change [9].

Gas-hydrate formation is usually a relatively slow process, and a large specific surface area is required to reach conceivable growth rates under laboratory conditions. It has been realized that gas hydrates can be grown in fairly quickly from ice powders [7]. Water cluster beams have attracted much interest as another source to quickly form a large amount of gas-hydrates. Water clusters can be produced by adiabatic expansion [10-13], and the clusters produced have a broad size distribution, containing between tens and thousands of molecules. The inclusion of gas molecules into water cluster cages with specific number of cluster sizes could be performed by introducing gas into liquid water for the cluster formation.

Furthermore, in water cluster ion beams, the impact of an energetic water cluster ion on substrate surface represents unique properties [12]. Since thousands of molecules impinge on the substrate at almost the same time, the many-body

interactions between the clusters and substrate atoms are induced by the dense energy deposition. The high-energy-density deposition and the collective motions of the clusters during impact play important roles in the surface process. For example, extremely high temperature and pressure can be obtained in the impact area by accelerating the cluster ion beams [14,15]. Based on these features, distinctive irradiation effects with water cluster ion beams are expected, and these effects are not obtained by conventional ion beam processes, wet processes, or combinations of both.

In order to make water cluster ion beams more functional, we have modified the cluster-ion-beam system. We produced gas-hydrate cluster ions and investigated the interactions of cluster ion beams with solid surfaces. In this paper, we will describe the development of the gas-hydrate cluster-ion-beam system and present the results of the size analysis of the cluster ion beams. The irradiation effects of carbon dioxide-hydrate cluster ions on silicon and copper substrates were also investigated and will be reported here.

2. Experimental

Figure 1 shows the schematic illustration of the gas-hydrate cluster-ion-beam system. Liquid water was introduced into the cluster source and heated to 150 °C by a wire heater attached around the source. When water vapor was ejected through a nozzle into a vacuum, they were cooled down by adiabatic expansion. During the expansion, a large number of water molecules collided with each other, and nucleation and growth occurred spontaneously owing to the perturbation produced by the collisions of vapor molecules, resulting in the formation of water clusters. Also, for gas-hydrate cluster formation, carbon dioxide (CO₂) was introduced into the cluster source, and bubbling of CO₂ gas into the liquid water took place during heating. The amount of CO₂ gas was controlled by a valve containing the T-1000 flow meter made by Fujikin Incorporated (Osaka, Japan). The flow rate was adjusted to a value between 0 sccm and 300 sccm,

and less than 10 % of CO₂ gas was mixed with the water vapor. During the expansion, CO₂ molecules might be captured in the water clusters, resulting in the formation of carbon dioxide-hydrate clusters. The nozzle was made of glass, and it was a converging–diverging supersonic nozzle with a throat diameter of 0.1 mm.

The clusters produced passed through a skimmer and a collimator before entering an ionizer. In the ionizer, the neutral clusters were ionized by electron bombardment. The electron voltage for ionization (V_e) was adjusted to a value between 0 V and 300 V, and the electron current for ionization (I_e) was adjusted to a value between 0 mA and 250 mA. The cluster ions were accelerated by applying an extraction voltage to the extraction electrode. The extraction voltage (V_{ext}) was set between 0 kV and 2 kV. The extracted cluster ions were separated by size via a retardation method; the size-separated cluster ion beams were accelerated toward a substrate, which was set on a substrate holder. The acceleration voltage (V_a) was set to a value between 0 kV and 10 kV. The substrates used were Si(100) and Cu, and the substrate temperature was the same as room temperature. Cu films were grown on the Si(100) substrates, and the film thickness was 500 nm. The background pressure around the substrate was maintained at 2×10^{-7} Torr using a turbo molecular pump.

3. Results and discussion

3.1 Size distribution

The cluster size was measured by the time-of-flight (TOF) method based on the fact that the time of flight is proportional to the square root of mass [16,17]. In the TOF measurements, it was assumed that the cluster ion had a single charge, and multiply charged cluster ions might be dissociated owing to the Coulomb repulsion force [18,19]. Figure 2 shows the size distribution of gas-hydrate cluster ions as a parameter of the CO₂ flow rate Q_{in} . The vapor pressure of water was 0.3 MPa; the acceleration voltage was 6 kV. When the CO₂ flow rate was zero, water clusters without CO₂ molecules

enclosed were produced. Since the atomic mass of a water molecule is 18 u, the cluster contained between a few hundred and several thousand molecules. The largest water clusters contained approximately 2800 molecules. On the other hand, the peak size of water clusters that included CO₂ gas-hydrate clusters varied depending on the CO₂ flow rate, and it shifted to a smaller size that contained approximately 2000 molecules. Since gas-hydrate cluster formation is a relatively slow process, the peak size of the clusters was smaller compared to the water clusters. According to the quadrupole-mass analysis employed, the number of CO₂ gas-hydrate clusters with fewer than 100 molecules was relatively small, although the mass resolution in the analysis was not sufficient. To be compared with the small-size distribution of water clusters, the CO₂ gas-hydrate clusters must contain a minimum of approximately 28 molecules. Furthermore, water clusters without CO₂ molecules were also present, and mixed beams of water clusters and CO₂ gas-hydrate clusters were formed. In the mixed cluster beams, various sizes of gas-hydrate clusters could be included, which resulted in the change in size distribution depending on the CO₂ flow rate.

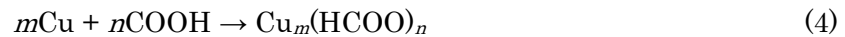
3.2 Irradiation effects

Water is a polyatomic molecule that includes a hydrogen atom and a hydroxyl radical. After impact of the water cluster ions on the solid surface, various species such as hydrogen atoms and hydroxyl radicals were produced. Figure 3 shows the mass spectra for residual gases after impact of (a) water cluster ions and (b) CO₂ gas-hydrate cluster ions on the Si(100) surface. The acceleration voltage was 6 kV. The monomer ions such as water molecular and CO₂ molecular ions were removed by the retardation method. As shown in Fig. 3(a), after water cluster ion irradiation, several peaks appeared at mass numbers 1, 2, 17, 18, and 28, which corresponded to H, H₂, OH, H₂O, and N₂. Some of the H atoms produced reacted with another H atom to form H₂ molecules. Also, as shown in Fig. 3(b), after CO₂ gas-hydrate cluster ion irradiation,

another peak appeared at a mass number of 44 corresponding to CO₂. In addition, a slightly large peak was observed at a mass number of 28, which corresponded to CO. These peaks' intensities increased with increasing CO₂ flow rate and are attributed to the irradiation by CO₂ molecules, which were contained in the water clusters.

The irradiation effects of water cluster ions and CO₂ gas-hydrate cluster ions on the solid surfaces were investigated. The sputtering depths into the Si(100) substrates and Cu films were measured using a step profiler (Veeco Instruments, DEKTAK-3173933, Plainview, NY, USA). Figure 4 shows the dependence of sputtering depth on the Si(100) and Cu surfaces on the CO₂ flow rate. The acceleration voltage was 6 kV, and the fluence was 1.0×10^{15} ions/cm². When water cluster ions without CO₂ molecules hit the surfaces, the sputtering depths on the Si and Cu surfaces were 6.0 nm and 6.8 nm, respectively. Since the binding (cohesive) energy of Si is larger than that of Cu, the sputtering depth on the Si surface was smaller compared to that on the Cu surface. Also, the sputtering depth on the Cu surface increased with increasing CO₂ flow rate, although it remained almost the same on the Si surface. This difference is attributed to the chemical erosion and sputtering of the Cu surface.

The possible chemical reactions on the Cu surface in CO₂ hydrate-cluster ion irradiation are as follows:



Here, m and n are natural numbers. As described in the equations, the water molecule after impact was dissociated into a hydrogen atom and a hydroxyl radical, and they were adsorbed on the Cu surface. The OH radicals and O atoms produced reacted with Cu surface atoms, resulting in the surface oxidation that produced Cu₂O, CuO and

$\text{Cu}(\text{OH})_2$ [20,21]. The copper oxide surface was sputtered because of the momentum transfer by the water cluster ion irradiation. On the other hand, the carbon dioxide molecule was dissociated after impact into a carbon oxide molecule and an oxygen atom, and the carbon oxide molecule reacted with the hydroxyl radical, resulting in the formation of a carboxyl radical. Carboxyl radicals play an important role in the chemical erosion of Cu surfaces [22]. It resulted in the formation of softer structures on the Cu surface, and Cu atoms that were weakly bound to the surface were produced. Thus, the chemical modification of the Cu surface enhanced the sputtering, which occurred as a result of the momentum transfer by the cluster ion irradiation. As a result, the sputtering depth increased with increasing CO_2 flow rate.

The Si(100) and Cu surfaces irradiated were investigated via X-ray photoelectron spectroscopy (XPS) measurements. Figure 5 shows the depth profile of the $\text{C}1s$ peaks for the Si(100) surfaces irradiated by (a) water cluster ions and (b) CO_2 gas hydrate-cluster ions. The acceleration voltage was 6 kV, and the fluence was 1.0×10^{15} ions/cm². As shown in the figure, $\text{C}1s$ peaks were not observed after water cluster ion irradiation. On the other hand, after CO_2 gas hydrate-cluster ion irradiation, a $\text{C}1s$ peak appeared at a binding energy of 283.3 eV at an etching depth of 1.0 nm, indicating that shallow implantation of carbon atoms occurred. Because the incident energy of a CO_2 molecule is the accelerating energy divided by the cluster size, it is in the range of a few electron volts. Therefore, the low-energy irradiation resulted in the shallow implantation.

Figure 6 shows the depth profile of $\text{C}1s$ peaks for Cu surfaces irradiated by (a) water cluster ions and (b) CO_2 gas hydrate-cluster ions. The acceleration voltage was 6 kV, and the fluence was 1.0×10^{15} ions/cm². The results were the same as those for Si(100) surfaces, and $\text{C}1s$ peaks were not observed after the water cluster ion irradiation. On the other hand, chemical shift of the $\text{C}1s$ peaks occurred after CO_2 gas hydrate-cluster ion irradiation, and the peak corresponding to COOH was observed at an etching depth

of 1.0 nm and 2.0 nm. This indicates that the carboxyl radicals were formed, and the CO₂ gas hydrate-cluster ion irradiation led to chemical erosion of the Cu surface.

Because the diameter of a cluster consisting of several thousand molecules was a few nanometers, the cluster interacted with the solid surface over an area of only a few nanometers, which caused multiple collisions between the cluster molecules and surface atoms. Therefore, the incident energy of a cluster ion was deposited at the solid surface, and this dense-energy deposition resulted in an enhancement of the chemical reaction. The rate of chemical reaction (ν) with various kinds of reaction channels, such as dissociation of water or carbon dioxide and formation of carboxyl radicals, is described as follows [23]:

$$\nu \propto N \frac{kT}{h} \sum_{i=1}^n \exp\left(-\frac{Q_i}{kT}\right) \quad (5)$$

where N is the number density of H₂O or CO₂ molecules, h is the Planck's constant, k is the Boltzmann constant, T is the temperature of H₂O or CO₂ molecules after impact, and $Q_i (i = 1, 2, \dots, n)$ is the activation energy for a reaction channel (i). The

equation indicates that the rate of chemical reaction increased with the increase in temperature. For example, when water cluster ions hit the solid surfaces, the cluster ions were broken up, and multiple collisions between the water molecules and surface atoms occurred. As a result, many surface atoms were displaced and vibrated, and the incident energy of the cluster ions was used to heat the collision region of the surface. Therefore, chemical reactions such as chemical erosion and sputtering were enhanced at an elevated temperature owing to the high-density irradiation effect of the cluster ion beams.

4. Conclusion

We developed a gas-hydrate cluster ion source. H₂O vapor mixed with CO₂ gas were

ejected through a nozzle into a vacuum region, and CO₂ gas-hydrate clusters were produced by adiabatic expansion. The TOF measurements showed that the largest H₂O clusters or CO₂ gas-hydrate clusters consisted of a few thousand molecules at a vapor pressure of 0.3 MPa. According to the quadrupole-mass analysis, which should be performed more thoroughly, the CO₂ gas-hydrate clusters contain a minimum of approximately 28 molecules. Also, the mass analysis suggested that H₂O clusters without CO₂ molecules were also present, and mixed beams of H₂O clusters and CO₂ gas-hydrate clusters were formed.

H₂O clusters and CO₂ gas-hydrate clusters were ionized by electron bombardment, and the ionized clusters were accelerated toward a substrate. Cu films and Si(100) substrates were irradiated at an acceleration voltage of 6 kV. The fluence was 1.0×10^{15} ions/cm². The XPS measurements showed that carbon was included in the Cu films and Si substrates irradiated by the CO₂ gas-hydrate cluster ions. Also, a chemical shift resulting from the formation of carboxyl radicals was observed on the Cu surface. Furthermore, the Cu surface was sputtered, and the sputtering depth was larger than that formed by the H₂O cluster ion irradiation. The high-energy density irradiation effect was enhanced by accelerating cluster ions, and the surface temperature of cluster-impact area increased, resulting in enhancement of the chemical reaction between the H₂O and CO₂ molecules. Therefore, the formation of carboxyl radicals had an important role in sputtering of the Cu surface, which occurred effectively in CO₂ gas-hydrate cluster ion irradiation.

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Figure captions

Figure 1: Schematic illustration of gas-hydrate cluster-ion-beam system.

Figure 2: Size distribution of CO₂ gas-hydrate cluster ions as a parameter of CO₂ flow rate. The vapor pressure of waters was 0.3 MPa.

Figure 3: Mass spectra for residual gases after impact of (a) water cluster ions and (b) CO₂ gas-hydrate cluster ions on Si(100) surface. The acceleration voltage was 6 kV.

Figure 4: Dependence of sputtering depth on Si(100) and Cu surfaces on the CO₂ flow rate. The acceleration voltage was 6 kV, and the fluence was 1×10^{15} ions/cm².

Figure 5: Depth profile of C1s peaks for Si(100) surfaces irradiated by (a) water cluster ions and (b) CO₂ gas-hydrate cluster ions. The acceleration voltage was 6 kV, and the fluence was 1×10^{15} ions/cm².

Figure 6: Depth profile of C1s peaks for Cu surfaces irradiated by (a) water cluster ions and (b) CO₂ gas-hydrate cluster ions. The acceleration voltage was 6 kV, and the fluence was 1×10^{15} ions/cm².

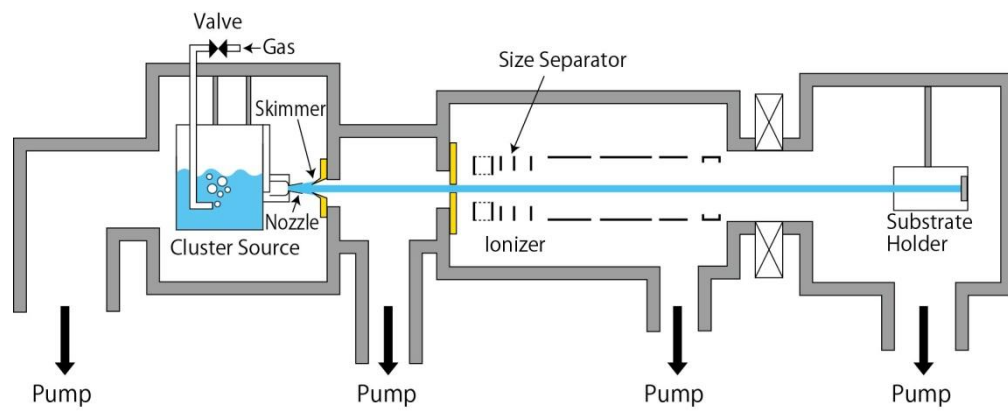


Figure 1: Takaoka et al.

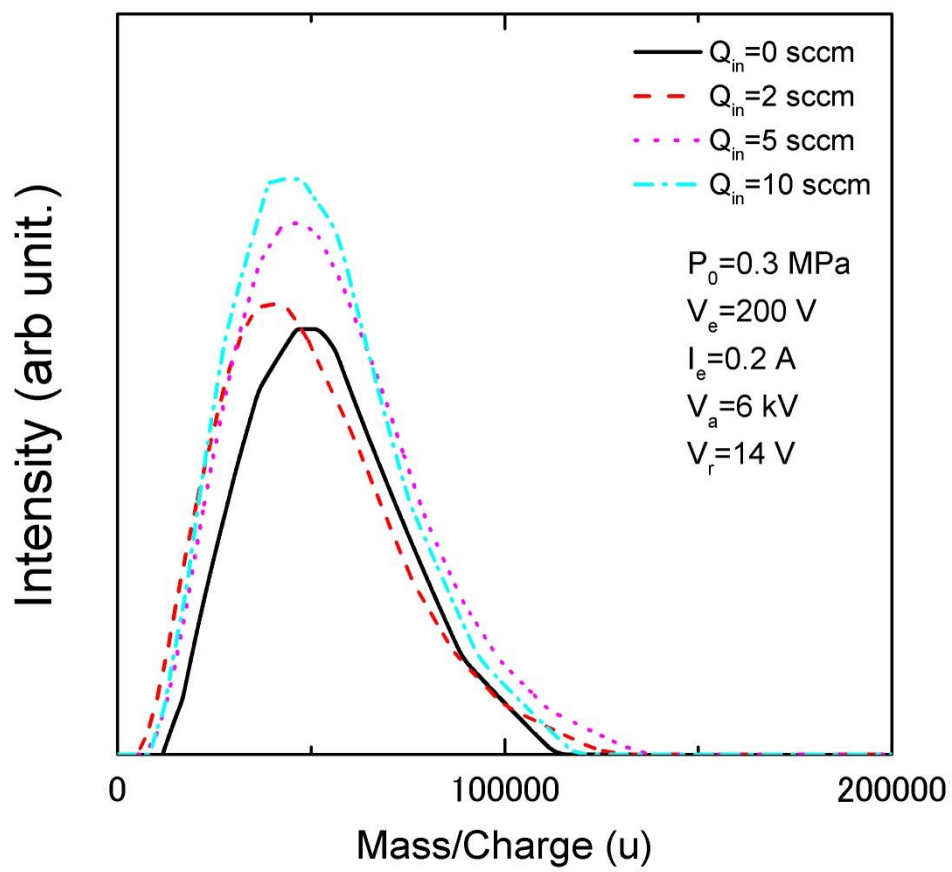


Figure 2: Takaoka et al.

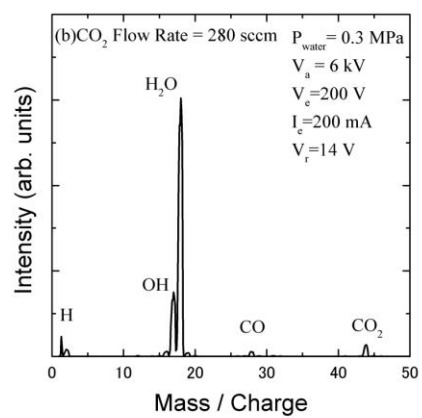
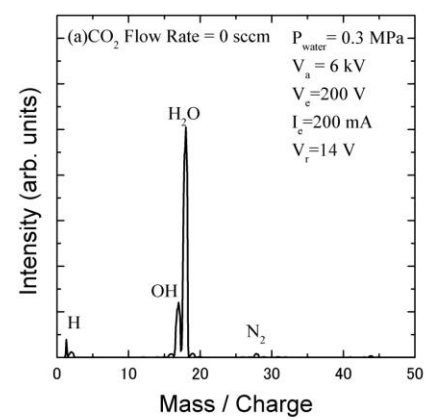


Figure 3: Takaoka et al.

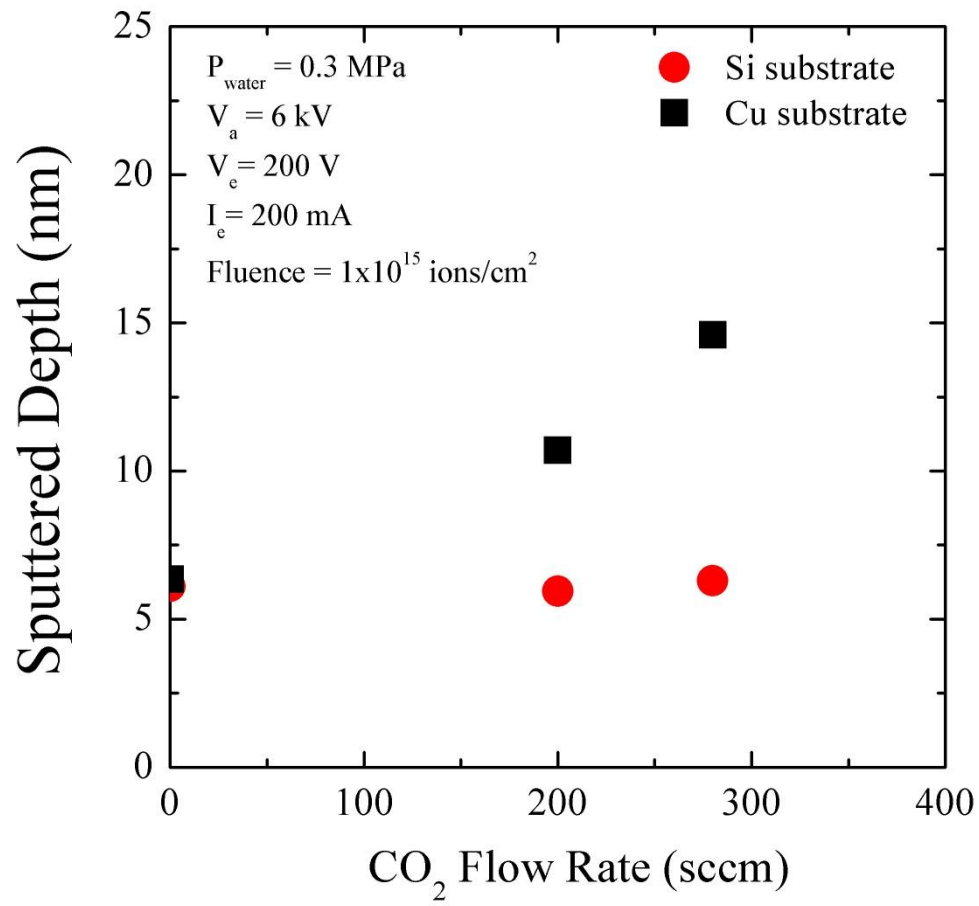


Figure 4: Takaoka et al.

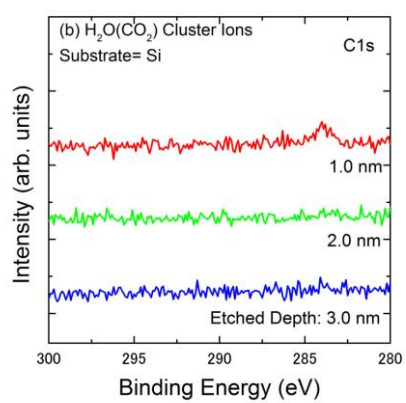
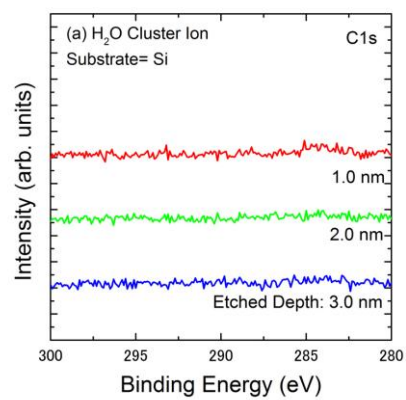


Figure 5: Takaoka et al.

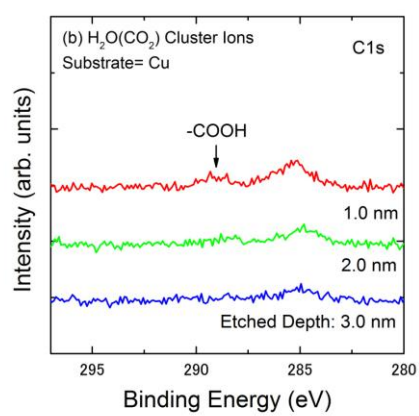
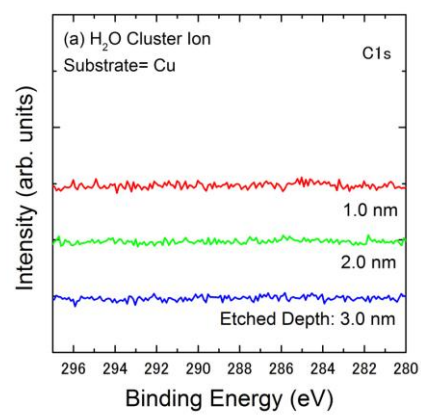


Figure 6: Takaoka et al.