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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 (CO_2) 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.

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.

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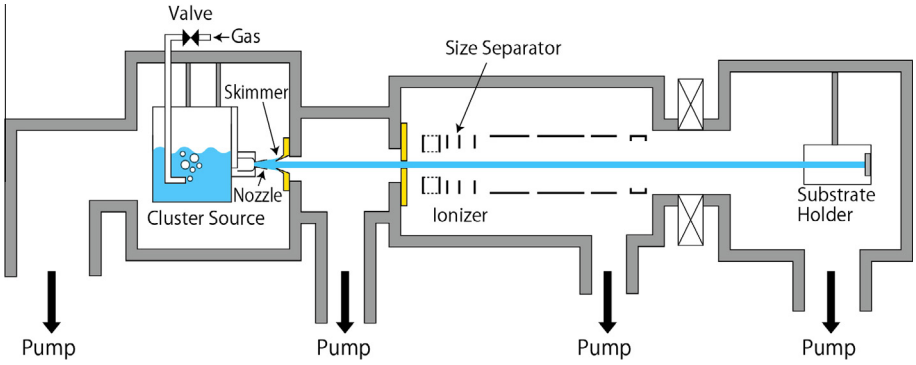

Fig. 1. Schematic illustration of gas-hydrate cluster-ion-beam system.

2. Experimental

Fig. 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 (CO_2) was introduced into the cluster source, and bubbling of CO_2 gas into the liquid water took place during heating. The amount of CO_2 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 and 300 sccm, and less than 10% of CO_2 gas was mixed with the water vapor. During the expansion, CO_2 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 and 300 V, and the electron current for ionization (I_e) was adjusted to a value between 0 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 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 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]. Fig. 2 shows the size distribution of gas-hydrate cluster ions as a parameter of the CO_2 flow rate Q_{in}. The vapor

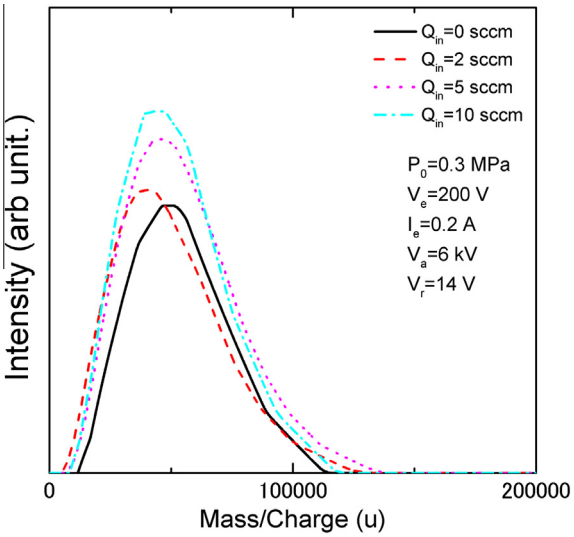

Fig. 2. Size distribution of CO_2 gas-hydrate cluster ions as a parameter of CO_2 flow rate. The vapor pressure of water was 0.3 MPa.

pressure of water was 0.3 MPa; the acceleration voltage was 6 kV. When the CO_2 flow rate was zero, water clusters without CO_2 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 CO_2 gas-hydrate clusters varied depending on the CO_2 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 quadruple-mass analysis employed, the number of CO_2 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 CO_2 gas-hydrate clusters must contain a minimum of approximately 28 molecules. Furthermore, water clusters without CO_2 molecules were also present, and mixed beams of water clusters and CO_2 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 CO_2 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