A gas cluster ion beam accelerator

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Abstract

An assembled CO\textsubscript{2} gas cluster ion beam system was assessed using a retarding field analyzer and a time-of-flight mass spectrometer. The CO\textsubscript{2} gas was expanded to form gas clusters at the input pressure of 1–5 bar through a quartz Laval nozzle. At 4 bar, it is confirmed that the clusters consisted of about 500 molecules. Also the dependence of the mean cluster size distribution on source temperature was examined. At the low fluence of ion beam, an isolated gas cluster ion impact on solid surfaces was investigated. CO\textsubscript{2} gas cluster ions were irradiated at the acceleration voltage of 40–60 kV on highly oriented pyrolytic graphite, Si with native oxide layers, and Cu film deposited on Si wafer. After very short exposure of cluster ions, induced hillocks with about 0.8–1 nm in height and 20 nm in width were outgrown from the impacted surfaces. After prolonged irradiation on Si and Cu/Si, humping was more developed and consequently the surface morphology seemed to be saturated because of gradual filling the gap between the hillocks. © 2001 Published by Elsevier Science B.V.

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1. Introduction

A cluster, called nanoparticle, is defined as agglomeration of atoms and molecules with the size of nanometer (nm). This nanostructured particle shows in particular two interesting features which are not found in other atomic and molecular materials: high chemical reactivity due to high surface-to-volume ratio of the constituents and quantum behavior due to its small size. From these intrinsically different natures of clusters from atoms or molecules, clusters have been intensively investigated for mainly catalysts and fabrication of quantum devices in recent nanoscience. In particular, much attention has been paid on gas cluster ion beam characterized by its peculiar and superior properties to conventional monatomic ion beam; for instance a small penetration depth due to large size, large lateral migration effect, low charge-to-mass ratio, multiple scattering phenomenon, and strong chemical reactions at low temperature. Such distinguished features of gas cluster ion beam have been utilized for surface micromachining, high sputtering yield process, shallow-junction formation, ultra surface smoothing, and high quality inorganic thin films such as PbO and GaN [1–3].

A reactive accelerated gas cluster erosion (RACE) system using CO\textsubscript{2} and SF\textsubscript{6} was introduced and developed for surface micromachining of hard materials: natural diamond, CVD-diamond, quartz, glass, and Si etc. The impact of highly intensive beams of nanoparticles accelerated to kinetic energies (KEs) of the order of 100 kV could be used for anisotropic etching of surfaces, providing a process of cluster impact lithography (CIL) [4,5].

Yamada and the co-workers have investigated the damage induced by gas cluster ion bombardment with particular attention to sputtering and implantation in the range of 20–30 kV ion beam energy using Ar, CO\textsubscript{2},
N₂O, SF₆, and O₂ clusters. They also studied the thin films formation and smoothing effect, anisotropic etching, and shallow junction formation [6–8].

In this study, a 150 kV CO₂ gas cluster ion beam accelerator is introduced and its source characteristics were assessed. The existence of clusters and the mean size distribution were measured by both a time-of-flight (TOF) spectrometry and a retarding field analyzer using a reflectron. In the ionization region, a convex electrostatic lens system to reduce the fraction of monomer ions in the stream of cluster ion beam is presented. In order to examine isolated cluster ion impact on solid surfaces, cluster ions were irradiated on highly oriented pyrolytic graphite (HOPG) and Si at quite a low dose of 10⁸–10⁹ ions/cm² and their surfaces were investigated by an atomic force microscope (AFM). A prolonged cluster ion irradiation was carried out on Cu/Si and a smoothing phenomenon at initial stage is examined.

2. Experimental

A 150 kV gas cluster ion beam system was schematically represented in Fig. 1. CO₂ was used for a source gas to generate clusters at room temperature through a quartz Laval nozzle with 26 mm long and neck diameter Ø = 0.11 mm. The inlet pressure was varied from 0.5 to 5 bar. The pressure in the expansion chamber could be pumped down below 7 × 10⁻² Torr by a mechanical booster pump. The base pressure of a main source chamber was 7 × 10⁻⁷ Torr by a turbo molecular pump and the working pressure was not higher than 2 × 10⁻⁵ Torr at the inlet pressure of 5 bar. A thoriated tungsten filament with Ø = 0.3 mm was attached as a cathode electrode and thermal electrons were emitted by DC current heating power unit. The electron emission current was changed from 50 to 200 mA. Neutral clusters were ionized by thermoelectron impact at the bombardment energy of 100–400 eV. For filtering of monomers and small cluster ions, a kind of electrostatic convex potential was formed just ahead of grid and its filtering performance was tested with the variation of the anode potential (Vg).

For the measurement of cluster size, a retarding field analyzer (RFA) was used. It consisted of several circular plates as retarding electrodes. For the build up of uniform electric fields in RFA, the reflectron system, one of TOF measurement systems, was adapted to this RFA system. Since the only species with higher KE than retarding potential can pass the retarding electrodes served as a high-pass filter, it is possible to estimate the size of clusters by retarding potential and the number of cluster by detected ion current at the retarding potential. Cluster size distribution can be obtained from the negative derivative of retarding spectrum [9] and the mean number of clusters can be determined by choosing the retarding voltage at which the ion current was just half of the ion current measured at the retarding potential. The existence and the size of cluster ions were accurately detected by TOF measurement system. The TOF analyzer consisted of a photocoupler, a pulse generator with 10 µs pulse width at every 1 ms, and a channeltron to amplify cluster ion current. The experimental procedure for the TOF analysis was described in detail elsewhere [10]. The extracted beams were accelerated via the acceleration tube at 1–60 kV. In addition, the length of a free drift region shielded with a ground potential was 1.8 m. In this study, cluster size distributions at different source pressures were measured. Moreover, the dependence of cluster size distribution on temperature was investigated with the variation of temperature from 223 to 333 K. For an isolated impact interaction study with solid surfaces, CO₂ cluster ions were irradiated with 10⁸–10⁹ ions/cm² during 2 s at 40 kV on HOPG and Si wafer. Moreover, a prolonged cluster ion irradiation up to ~10¹² ions/cm² was done on Cu/Si surfaces. Induced hillocks generated by the isolated cluster impact and surface smoothing were carefully examined by a Nanoscope III (Digital Instruments) at ambiance. To examine the penetration depth of CO₂ nanoparticle impact, impacted surface of Cu/Si was examined by Auger electron microscopy (AES) using a PHI 670 Auger spectrometer through a slight depth profile.

Fig. 1. Schematic diagram of 150 kV gas cluster ion beam system.
3. Results and discussion

3.1. Cluster size measurement by retarding field analyzer

The gas, which expanded through a Laval nozzle, experiences adiabatic expansion. This means that entropy is converted into KE. Assuming that CO$_2$ gas expands at 0 K, the KE of CO$_2$ monomer is 0.096 eV. Consequently, the KE of a neutral cluster consisting of $N$ molecules is $N$ times larger than that of monomer, e.g., a CO$_2$ cluster with 1000 molecules has 96 eV of KE.

Fig. 2 represents the retarding spectra at different source gas pressures. To take the retarding spectra of residual gas as monomer reference, the working pressure was increased using a variable leak valve (ULV-150, MDC) without injecting CO$_2$ gas into the nozzle. As shown in Fig. 2, the measured current of residual gas was sharply decreased as retarding voltage approached the ionization voltage of represented by 0 V, which means that RFA cut-off quite well the monomer ions. In order to investigate the dependence of cluster formation on the source pressure ($P_s$), $P_s$ was increased up to 5 bar. Up to $P_s = 3$ bar, any tail indicating cluster formation could not found in the RFA spectra. At $P_s = 4$ bar, however, we started to distinctively observe the tail of ion beam current which extended to higher retarding voltage than the ionization energy of 150 V. All data shown in Fig. 2 are normalized due to the intensity difference. In addition, the dependence of cluster size on source temperature was investigated.

Fig. 3 shows the normalized retarding spectra at different source gas temperatures. As the source temperature was lowered from 310 to 254 K, the mean cluster size became larger, which is easily understood by gas condensation to form clusters at lower temperature.

3.2. Characterization of cluster size distribution by time-of-flight mass spectrometer

In view of cluster size measurement, RFA method is not precise because the retarding field is not so uniform and the resolution is too low to exactly estimate the cluster size distribution due to low ion current of large clusters. When the same acceleration voltage is applied to the monomers and clusters, the difference of mass between monomers and clusters makes the velocity difference. Therefore measuring flight times of monomers and clusters at fixed length enables us to estimate the masses of each species.

Fig. 4 shows the TOF mass spectra of CO$_2$ cluster at different source pressures. All TOF mass spectra were obtained at the acceleration voltage of 40 kV to increase the cluster signal by increasing secondary emission in electron multiplier and were normalized. The dependence of the cluster signal on the acceleration voltage could have a relation with the detection probability because there is a threshold voltage for the secondary electron emission [11]. Similar to Fig. 2, the formation of clusters start to the clearly seen at 4 bar as shown in Fig. 5. As $P_s$ was increased up to 5 bar, the position of mean size of cluster was shifted to shorter flight time. This means larger cluster was formed at $P_s = 5$ bar than $P_s = 4$ bar. The cluster size from TOF mass spectra was determined by calibration using calibrated flight time of monomers. Fig. 5 shows the TOF mass spectra of CO$_2$ cluster at different source temperatures. To obtain the...
cluster size from TOF mass spectra, the first peaks shown in all TOF mass spectra were calibrated using the calculated flight time of monomers. By these procedures, the cluster sizes are easily obtained from the ratio of the flight time of clusters to that of monomers. The calculated mean cluster sizes from TOF mass spectra at 223, 298 and 333 K are 480, 685 and 1048 molecules per cluster, respectively.

3.3. Monomer filtering by an electrostatic convex lens

In application of gas cluster ion beam technology, both the removal of monomer ions and the measurements of cluster size are the most crucial factors for refining and obtaining high quality cluster ion beam. In general monomer filtering has been done by a retarding field method, electrostatic lens system using incoherent chromatic aberration, mass selection of cluster can be also done by an E × B filter (Wien filter). The cluster size was also measured by a TOF [11], a RFA [12], and electron diffraction method [6]. According to the literature [7], in a high intensity cluster ion beam source using 38-mm Cu trumpet nozzle, a tungsten diaphragm (0.1 mm aperture) is placed behind the extraction electrode. The extraction voltage is adjusted so that the most probable size of the distribution is focused on this diaphragm. Smaller or larger cluster are out of focus and hit the diaphragm wall.

Yamada et al. [9] reported a low voltage extraction system to reduce the fraction of monomer ions by means of space charge effects. Mass selection of clusters was carried out using electrostatic lens system which was designed to utilize inherent chromatic aberration [8,13]. A simple explanation and a schematic diagram were presented in the earlier reports, but the experimental condition and the results in detail were not found elsewhere. In above both cases, the concept of a chromatic aberration of cluster ion beam was used for selection of desired cluster size. There exists some distribution due to different mass size of molecules, which implies that there is a large KE spreading (chromatic aberration) even though they are accelerated with the same energy after being ionized.

Fig. 6 represents the contour of equipotential lines formed just in the ionization region and cluster ion beam trajectories simulated by using a SIMION program. In this simulation, trajectories of cluster ion beam consisting of \(N = 50\) and \(N = 1000\) were traced and compared at two different \(V_g\) = 100 and 400 V. In this simulation scheme, cylindrical coordinate \((z, r)\) was adopted and \(O (0, 0)\) was designated as an origin. A cluster ion beam having \(\Theta = 7\) mm was used and the points intersected by this ion beam with an anode grid were designated as A \((50, -3.5)\) and B \((50, 3.5)\), respectively. The outer shield was grounded. It is expected that an electrostatic convex lens formed just ahead of grid by \(V_g\) can change the direction of ion beams by a divergent field. Lighter clusters are more sensitively affected by the small change of curvature of electric field, but heavier clusters are less influenced due its large mass.

Among the cluster ion beam of \(N = 50\) with corresponding KE of 48 eV, the farthest one from the center was deviated from B to C \((100, 10.44)\) and thus the trajectory angle was \(\tan \theta = (\Delta r / \Delta z) = (6.94/50)\) at \(V_g = 100\) V (Fig. 6(a)). In case of \(V_g = 400\) V (Fig. 6(b)), the
deviation angle increased up to \( \tan \alpha = (8.19/50) \). For the large cluster ion beam of \( N = 1000 \) (\( KE = 960 \) eV), deviated ion beams of both cases passed the same coordinate of \( C(100,6.65) \) (Figs. 6(c) and (d)) and the deviation angle was \( \tan \alpha = (3.15/50) \). From the above results, small size clusters up to \( N = 50 \) were easily deviated by the convergent electric field and thus well filtered. But the larger size cluster ion beam showed a quite narrow deviation angle and the change of a deviation angle was hardly affected by the change of \( V_g \). Even though large clusters could not be well filtered in this electrostatic convex lens scheme, this aspect will be very perspective because it can make large size cluster preserved without losing them in the stream of cluster ion beam.

Fig. 7 shows a normalized TOF spectra of \( \text{CO}_2 \) cluster ion beam measured at the variation of \( V_g = 100–400 \) V. There is no distinction between a monomer ion signal and cluster one until \( V_g = 150 \) V and the signal related to clusters appears to be buried. At \( V_g = 200 \) V, a peak around \( \tau = 125 \) \( \mu \)s started to be clearly observed. It corresponds to the calculated mean cluster sizes of about 597 \( \text{CO}_2 \) molecules per cluster. At the voltage higher than \( V_g = 200 \) V, the normalized voltage of a molecule ion beam is decreased, but that of cluster is increased. Moreover, the peak position is slightly moved to a longer flight time, corresponding 1000 clusters at \( V_g = 350 \) V. The shift of flight time towards a higher value means the increase of the mean number of cluster size. This result would be closely related to the fact that the increment of an equipotential curvature would rather filter small clusters and reduce their intensity, and this makes the peak position move up to a higher number of cluster size.

It is noteworthy that the ratio between a monomer ion signal and cluster ion one is converted by the increase from \( V_g = 350 \) to 400 V. In the collision of clusters with electrons, it was well known that the ionization efficiency depends on electron bombardment energy. From the literature [14], mean size of \( \text{CO}_2 \) clusters was measured by the variation of electron bombardment energy from 30 to 600 eV, and the minimum took place around 400 eV. Accordingly, \( \text{CO}_2 \) clusters could be probably smashed into small molecules at \( V_g = 400 \) V and this caused directly a monomer signal to increase. Also it is observed that the mean distribution of cluster at \( V_g = 400 \) V was reduced to 703 and the tail of the normalized yield spectrum for \( V_g = 400 \) V was not extended longer than that for \( V_g = 350 \) V. On this point, more systematic investigation will be needed to exactly determine the dependence of the ionization efficiency on an ionization potential.

Although, the secondary emission yield of a channeltron for monomer ions and each cluster ions was not accurately measured, the efficiency of filtering can be phenomenologically estimated by comparing the
maximum value of normalized yield. When the normalized voltage of both signals is compared, the ratio \( c \) of monomer ion signal to cluster one is decreased from \( c = 1.19, 0.58, 0.14, 0.05, \) and 0.025 as \( V_g \) is varied from 200 to 400 V.

3.4. Isolated and prolonged impact phenomenon

Fig. 8 represents the atomic force microscopic images of a HOPG surface irradiated by CO\(_2\) cluster ions at 40 kV and at the fluence of \( 10^8 \) ions/cm\(^2\) s for about 2 s, which were 3D and 2D images scanned in an area of \( 1 \times 1 \) mm\(^2\) (a) and \( 150 \times 150 \) \( \mu \)m\(^2\) (b) respectively. Only cluster ions larger than the size of 500 were bombarded by applying the retarding voltage. As shown in Fig. 8(a), it is clearly shown that hillocks with different sizes were generated from the irradiation of different size cluster ions. After zooming in one of hillocks, more accurate lateral scanning was carried out. From the Fig. 8(b), the induced hillock on HOPG was 0.8 nm in height and about 20 nm in lateral direction. In the literature [14], HOPG surface irradiated by Ar monomer ions was examined by STM and only sub nm scale fluctuation was observed in the lateral scanning. Accordingly the induced large hillocks with the size of 20 nm reveal apparently the existence of the cluster ions. According to Ref. [14], the cluster ions impact with hypervelocity was expected to make craters from the release of shockwaves in the target as well as cluster itself. In this study, the isolated cluster impact on Si with 1000 CO\(_2\) clusters at the acceleration 40 kV induced hillocks instead of craters (Fig. 9). This was described by an elastic rebounce of the compressed materials at impacted liquid. The elastic rebounce probably results from the lack of lattice defects in the impacted nanoscale region that prevents the dissipation of the elastic energy.

Even though our present result is coincident with that of Ref. [14], however, the mechanism about the formation of hillocks due to nanoparticle ion impact will be further studied.

Fig. 9 shows also the AFM images of Si surfaces irradiated at the fluence of \( 10^8 \) ions/cm\(^2\) s for 2 s (a) and 2 h by CO\(_2\) cluster ions at 60 kV. Similar to HOPG, induced hillocks were also observed on irradiated Si surface and the height was about 0.75 nm in Fig. 9(a). After a prolonged irradiation, the swelling of Si surface seems to be evenly evolved by an increment in the number of hillocks and then the saturated surface became

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**Fig. 7.** Normalized TOF spectra of CO\(_2\) cluster ion beam measured at the variation of \( V_g = 100-400 \) V.

**Fig. 8.** AFM images of HOPG surface irradiated by CO\(_2\) cluster ions at 40 kV for about 2 s.
rough. The measured root-mean-square value of surface roughness was increased from 0.13 to 0.25–0.3 nm. From the bottom view of the lateral scanning, long irradiation increased the density of hillocks compatible to single hillock in Fig. 9(a). From the result, further irradiation can be expected to reduce the surface roughness by gradually filling up gaps between spasmodic neighbor hillocks.

Fig. 10 shows the AFM 2D image and lateral scanning profiles of irradiated Cu surface for 2 h at 60 kV. W mesh (200 × 200 µm², Ø = 25 µm wire) was overlaid as a mask. From the height profile plotted from a lateral scanning over 80 × 80 µm² area, it was found that the irradiated area was elevated up to about 3.5–4 nm higher than the masked area. This results from the steady development of hillock formation by such a long irradiation. At last, an isolated nanoparticle ion impact at the very low fluence will predominantly form the hillocks and make a relief on the surface, which can be called ‘nanoscale surface embossment’ instead of engraving like sputtering or erosion of the surfaces.

Fig. 11 represents the AES survey spectra taken from an unirradiated and an irradiated region of Cu films on Si. In case of an as-received specimen, quite a large amount of C and O signal was observed in both regions without any W peaks. This indicates that the W mesh was not effectively sputtered. If small quantity of W was sputtered by the cluster ion beam, AES transition related to W would be probably seen in the AES spectra for the irradiated region. After sputtering of about 2 nm Cu layer, the intensity of C signal from the unirradiated region was much reduced, but that from an irradiated region was still high. The results mean that CO₂ cluster ions made a relief on Cu surfaces and the element of C
and O still can be found in that nanostructured embossment. To the contrary, the carbon adsorbed on the unirradiated part could be easily removed just by slight ion beam sputtering.

4. Conclusions

Gas cluster ions generated through the Laval nozzle is characterized in terms of mean cluster size distribution, monomer ion filtering, and observing peculiar isolated nanoparticle impact on solid surfaces. From both the retarding field analyzer and a TOF spectrometry, it was identified that CO₂ clusters could be created over the inlet pressure of 4 bar and the mean size of the clusters gradually increased as the inlet pressure was increased and gas temperature was decreased. By forming a kind of electrostatic convex lens in the ionization part, monomer ions and small size cluster ions were effectively filtered as the grid potential was increased up to 300 V. From an isolated cluster ion impact on HOPG and Si, induced hillocks with nm size were observed and were believed to manifest an evidence of the existence of nanoparticles. Moreover, the prolonged irradiation of cluster ions at a low dose made a positive relief on the Cu/Si surface, and increased the density of nm hillocks continuously. The observed surface embossment would be closely related to the surface smoothing effect by cluster ion irradiation.

References