High-speed processing with Cl\textsubscript{2} cluster ion beam

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Abstract

Cluster ion beam processes can produce high rate sputtering with low damage compared with monomer ion beam processes. Cl\textsubscript{2} cluster ion beams with different size distributions were generated with controlling the ionization conditions. Size distributions were measured using the time-of-flight (TOF) method. Si substrates and SiO\textsubscript{2} films were irradiated with the Cl\textsubscript{2} cluster ions at acceleration energies of 10–30 keV and the etching ratio of Si/SiO\textsubscript{2} was investigated. The sputtering yield increased with acceleration energy and was a few thousand times higher than that of Ar monomer ions. The sputtering yield of Cl\textsubscript{2} cluster ions was about 4400 atoms/ion at 30 keV acceleration energy. The etching ratio of Si/SiO\textsubscript{2} was above 8 at acceleration energies in the range 10–30 keV. Thus, SiO\textsubscript{2} can be used as a mask for irradiation with Cl\textsubscript{2} cluster ion beam, which is an advantage for semiconductor processing. In order to keep high sputtering yield and high etching ratio, the cluster size needs to be sufficiently large and size control is important.

Introduction

Gas cluster ion beams have a high potential for material processing in nano-technology devices, such as photonic crystals and MEMS (micro electro mechanical system), because it allows etching of targets with a high-speed and low-damage technique while keeping the surfaces ultra-smooth. A cluster is an aggregate of a few to several thousands atoms. When the many atoms constituting a cluster ion bombard a particular area, high-density energy deposition and multiple-collision processes occur simultaneously. Because of the unique interactions between cluster ions and surface atoms, new surface modification processes could be developed, and surface smoothing \cite{1–4}, shallow implantation \cite{5,6}, high rate sputtering \cite{7} and low damage surface processing \cite{8}, have been demonstrated using this technique.

Extreme high rate sputtering of Si targets can be obtained using reactive cluster ion beams, such as SF\textsubscript{6}, CF\textsubscript{4}, CHF\textsubscript{3}, and CH\textsubscript{2}F\textsubscript{2} \cite{9–11}. SF\textsubscript{6} has often been used as a reactive cluster source gas for these applications, but the global warming potential (GWP) of SF\textsubscript{6} is extremely high and other kinds of gaseous materials are required. In addition, both higher speed and higher selectivity are required in this processing. The GWP of hydrofluorocarbons (HFCs) such as CF\textsubscript{4}, CHF\textsubscript{3}, and CH\textsubscript{2}F\textsubscript{2} is lower than that
of SF$_6$, but etching yields of Si with HFC cluster beams are lower than those of SF$_6$ cluster beam. In this paper, the etching properties of Cl$_2$ gas clusters were investigated. Cl$_2$ was expected to etch a Si target with high speed, similar to fluoride [12]. It was also expected that reactive sputtering of metallic materials occurred and high speed etching of metallic materials can be realized with Cl$_2$ cluster ion irradiation.

**Experimental**

Figure 1 shows a schematic diagram of the Cl$_2$ gas cluster ion beam irradiation system. The methods of formation and ionization of Cl$_2$ gas clusters were similar to those of the conventional cluster ion irradiation [13]. The purity of Cl$_2$ source gas was 5N. The ionized clusters were extracted and accelerated to energies up to 50 keV towards the target. Monomer ions were eliminated by a magnetic field. The mass distributions were measured with a compact time-of-flight (TOF) system. The Cl$_2$ cluster ion beam irradiation system was combined with a TOF measurement system and the cluster size distributions could be monitored just before irradiation. In a previous work it was reported that the size distributions could be controlled by the source gas pressure and ionization conditions [13]. The Cl$_2$ cluster ion beams were generated with different size distributions while controlling the ionization conditions. Figure 2 shows the cluster size distributions at various values of ionization emission current. The source gas pressure and ionization voltage were fixed at 0.39 MPa (3000 Torr) and 300 eV, respectively. It was found that the mean size of Cl$_2$ cluster beams could be varied in the range from 1400 to 3200 molecules.

![Figure 1. Schematic diagram of the Cl$_2$ gas cluster ion beam irradiation system.](image)

![Figure 2. Cl$_2$ cluster size distributions at various values of emission current for ionization.](image)
1400–4300 molecules with controlling the emission current. The mean cluster size \(N_m\) was calculated from the intensity of size distribution \(I(N)\) with the following formula:

\[
N_m = \frac{\int I(N)N_dN}{\int I(N)dN}
\]

If \(I(N)\) was less than 1% of peak intensity, the TOF signal was regarded as noise and \(I(N)\) was taken as 0. The irradiation targets were Si substrates and SiO\(_2\) films and their sputtering yields were measured. The sputtering yields were derived from the etching depth and ion fluence. The etching depth was measured with a contact profiler. The samples were covered with a stainless steel mesh and the height differences measured after irradiation between the masked and unmasked areas were regarded as etching depth. The ion fluence range was \(2\times10^{15}–1\times10^{16}\) ion/cm\(^2\) and the typical etching depth of Si was 1–2 \(\mu\)m. The error in depth measurement was less than 3%. The error in fluence measurement was about 10%, because the stability of the Cl\(_2\) cluster ion beam current was about 10%. Therefore the measurement error of the sputtering yield with Cl\(_2\) cluster was about 10% in this report.

**Results and discussion**

Figure 3 shows the effect of acceleration energy on the sputtering yield of Si with clusters of Cl\(_2\), SF\(_6\), and Ar, and with monomers of Cl and Ar. The mean sizes of Cl\(_2\), SF\(_6\) and Ar clusters were about 3000 molecules, 770 molecules and 1900 atoms, respectively. The sputtering yield of Si with Cl monomers, calculated using TRIM (SRIM 2008) [14], shows the physical sputtering yield without a reactive effect. The sputtering yield of Si with Cl and Ar monomers did not increase with acceleration energy beyond 10 keV. The sputtering yields of Si with clusters, however, increased with acceleration energy. The sputtering yield of Si with Ar clusters was about 2 orders of magnitude higher than with Ar monomers, whereas the sputtering yields of Si with clusters of SF\(_6\) and Cl\(_2\) were about 3 orders of magnitude higher than with Ar monomers. These results indicate that with irradiation of SF\(_6\) and Cl\(_2\) cluster ions reactive sputtering occurred. In particular, the sputtering yield of Si with Cl\(_2\) clusters was higher than with SF\(_6\) clusters and reached about 4400 atoms/ion at 30 keV. These results show that extreme high-speed etching can be realized with
Cl\textsubscript{2} cluster ion irradiation.

Figure 4 shows the variation of the sputtering yield of Si with the number of Cl atoms per incident cluster. Along the solid line, each incident Cl atom would remove one Si atom. The sputtering yield varied only slightly with the number of incident Cl atoms at 20 keV. However, the sputtering yield suddenly decreased with the number of incident Cl atoms decreasing at 30 keV. In order to etch Si reactively, SiCl\textsubscript{x} (x\geq 1) needs to be produced. If the sputtered product by Cl\textsubscript{2} cluster irradiation was SiCl\textsubscript{x} (x\geq 1), the sputtering yield per incident Cl atom should be less than 1. Therefore, the sputtering yields per ion should be less than the number of Cl atoms per incident cluster and the data points should be located below the solid line in figure 4. The sputtering yield at 30 keV decreases with the number of incident Cl atoms decreasing near the solid line. This shows that sufficient Cl atoms for sputtering could not be provided by ion beam irradiation with small size of Cl\textsubscript{2} cluster at 30 keV. Therefore, in order to realize high rate sputtering, a sufficiently large size of Cl\textsubscript{2} clusters must be used for etching. The yield values become constant at large cluster size and depend on the acceleration energy (shown in figure 3). This result indicates that the dependence of the yields on cluster size was low when a sufficient number of Cl atoms were provided for sputtering. At 20 keV, the number of sufficient Cl atoms for sputtering was about 3000 and the sputtering yield was slightly dependent on the number of incident Cl atoms in the range from 2900 to 6000 atoms.

Figure 5 shows the sputtering yields of Si per incident atom with Cl\textsubscript{2} and Ar cluster ion beams as a function of acceleration energy of the incident atom. The yields with Ar cluster ion beams are derived from a previous report [15]. Because the
sputtering yield of Si with Cl monomers is similar to that with Ar monomers (Figure 3), the sputtering yield per incident atom with Ar cluster ion beam can be regarded as the physical sputtering yield without reactive effect during Cl\textsubscript{2} cluster ion beam irradiation. The yields per incident atom with Ar cluster ion beams increased with acceleration energy of the incident atom proportionally, while the yields per incident atom with Cl\textsubscript{2} cluster ion beams were limited to 1. The limitation of yield with Cl\textsubscript{2} cluster ion beam corresponds to the restriction in Cl atom supply. The yields per incident atom with Cl\textsubscript{2} cluster ion beams were 2 orders of magnitude higher than with Ar cluster ion beams. The yield enhancement is due to reactive sputtering.

Figure 6 shows the effect of acceleration energy on the etching ratio of Si/SiO\textsubscript{2} after Cl\textsubscript{2} clusters, SF\textsubscript{6} clusters, and Ar clusters irradiation. The etching ratio of Si/SiO\textsubscript{2} after SF\textsubscript{6} clusters and Ar clusters irradiation was below 3 at acceleration energies in the range 20–60 keV. For Cl\textsubscript{2} cluster irradiation, the etching ratio of Si/SiO\textsubscript{2} was above 8 at acceleration energies in the range 10–30 keV. These results show that SiO\textsubscript{2} is suitable for use as a mask for irradiation with Cl\textsubscript{2} cluster ion beam, which is an advantage for semiconductor processing. Because the etching yield of SiO\textsubscript{2} with Cl\textsubscript{2} clusters increases with acceleration energy, the etching ratio of Si/SiO\textsubscript{2} decreases with acceleration energy, although the sputtering yield of Si with Cl\textsubscript{2} clusters increases (Figure 3).

Figure 7 shows the effect of mean cluster size on the etching ratio of Si/SiO\textsubscript{2} after Cl\textsubscript{2} clusters irradiation at the acceleration energy of 20 keV. The etching ratio rapidly increased with the mean cluster size. This result shows that with large size of Cl\textsubscript{2}
cluster high selectivity can be realized. Because the sputtering yield of Si was slightly dependent on the number of incident Cl atoms at 20 keV, the rapid increase of the etching ratio was caused by the decrease in the etching yield of SiO₂.

Summary

Si substrates and SiO₂ films were irradiated with Cl₂ cluster ions at acceleration energies in the range 10–30 keV. The Si sputtering yield increased with acceleration energy and reached values a few thousand times higher than those of Ar monomer ions. For Cl₂ cluster irradiation, the etching ratio of Si/SiO₂ was much higher than SF₆ and Ar cluster irradiation at acceleration energies in the range 10–30 keV. SiO₂ is suitable for use as a mask for irradiation with Cl₂ cluster ion beam, which is an advantage for semiconductor processing. In order to keep high sputtering yield and high etching ratio, the cluster size has to be sufficiently large and the size control is important.

References