

High-Speed Nanoprocessing with Cluster Ion Beams

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Cluster ion beam processes can produce higher rate sputtering with lower damage compared with monomer ion beam processes. In particular, it is expected that extreme high-rate sputtering can be obtained using reactive cluster ion beams. Several kinds of hydrofluorocarbon (HFC) (CF_4 , CHF_3 , and CH_2F_2) and Cl_2 gas clusters were generated, and their cluster size distributions were measured using the time-of-flight (TOF) method. Si substrates were irradiated with the reactive cluster ions at acceleration energies in the range of 5–80 keV. The sputtering yield increased with acceleration energy and was about 1000 times higher than that of Ar monomer ions for comparable conditions. Despite the very high sputtering yields, a Si surface irradiated by reactive cluster was smoothed. This high-speed processing with reactive cluster ion beam can be applied to fabricate nanodevices.

Key words: nanoprocess, cluster ion, reactive sputtering, smoothing

1. INTRODUCTION

The gas cluster ion beam process has become a candidate technique for advanced nanofabrication, where both throughput and precise functionality are required. 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 [1–4], shallow implantation [5,6], high rate sputtering [7] and low damage surface processing [8], have been demonstrated using this technique.

A schematic diagram of the cluster ion beam irradiation system is depicted in Fig. 1. The formation of gas cluster beams utilizes the adiabatic expansion of high-pressure gas through a nozzle [9]. The cluster beam enters into high vacuum through a skimmer and the neutral clusters are ionized by electron bombardment. The ionized clusters are accelerated and transported towards targets. High-speed surface processing with gas cluster ion beams

requires a high-current and high-energy cluster ion beam, and in order to achieve this goal, the cluster generator, ionizer and ion extraction have been studied [10,11]. A neutral cluster beam with high intensity was generated by the development of large metal nozzles and efficient ionization and extraction were realized by structural improvements to the ionizer. A beam current of more than 1 mA was achieved in 2004 [11].

Recent progress has enabled very good control of the energy and size of cluster and many kinds of gaseous materials became available as cluster sources. Especially, a gas with chemical reactivity towards the target material has often been applied as a cluster source. It is demonstrated that extreme high-speed and precise nanoprocessing can be realized with reactive cluster ion beams. For example, both the bottom surface and the sidewall of Si pillars could be smoothed by etching a photonic crystal with cluster ion beams [12]. Sidewall smoothing is essential for ultra-low-loss photonic crystals. To date, this technique has been applied to photonic, magnetic [13], electronic [14], and biological materials [15].

SF_6 gas has often been used as a reactive cluster source gas for these applications, but the global warming potential (GWP) of SF_6 is extremely high and other kinds of gaseous materials are required. In addition, both higher speed and higher selectivity are required of this processing. Therefore, the search for suitable cluster source gas materials is important for realizing high-speed and environmentally friendly cluster processing. A fundamental study of mask materials is also needed. In this paper, the etching properties of several kinds of hydrofluorocarbon (HFC) (CF_4 , CHF_3 , and CH_2F_2) and Cl_2 gas clusters were investigated. The GWP of HFC is lower than that of SF_6 . Cl_2 is expected to etch a Si target with high speed as well as fluoride gas. The relation

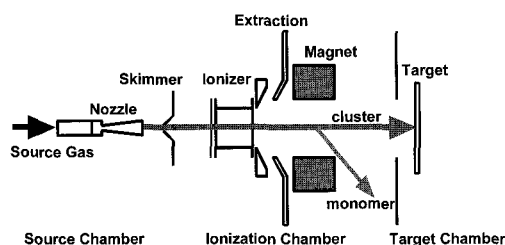
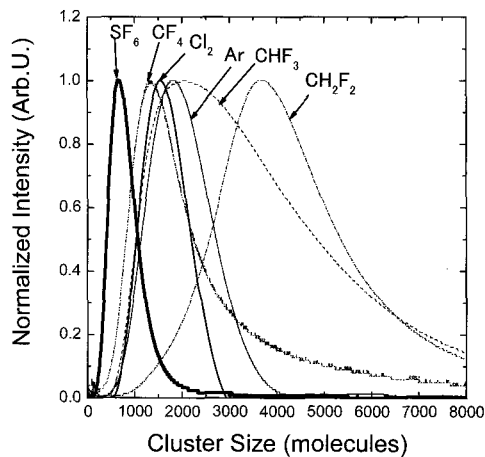


Fig. 1. Schematic diagram of the cluster ion beam irradiation system.

Table I. Source gas pressure and ionization condition.

	Source gas pressure, MPa	Ionization energy, eV	Emission current, mA
Ar	0.53	400	200
SF ₆	0.80	400	200
Cl ₂	0.53	300	100
CF ₄	0.80	500	300
CHF ₃	0.53	500	300
CH ₂ F ₂	0.53	500	300

Fig. 2. Cluster size distributions of Ar, SF₆, Cl₂, CF₄, CHF₃, and CH₂F₂ cluster beams.

between the selectivity and properties of mask materials is also discussed.

2. GAS CLUSTER ION BEAM GENERATION

Etching yields by cluster ion beams are expected to increase with acceleration energy [16]. A high-energy gas cluster ion beam irradiation system was developed, in which high-energy beams of Ar, SF₆, Cl₂, CF₄, CHF₃, and CH₂F₂ clusters were generated. The gas clusters of SF₆, Cl₂, CF₄, CHF₃, and CH₂F₂ are reactive and are expected to etch specific target materials with extremely high speed. SF₆ and CF₄ cluster ion beams can be generated with high intensity by using a high-pressure gas mixed with He. The mean size of Ar, SF₆, Cl₂, CF₄, CHF₃, and CH₂F₂ clusters, measured with a time-of-flight (TOF) system at the source gas pressure and ionization conditions shown in Table I was, respectively, about 1850 atoms, and 650, 1500, 1350, 2000, and 3700 molecules (Fig.2).

3. HIGH-SPEED ETCHING

The sputtering yield of Si calculated using TRIM [17] does not increase with the acceleration energy for Ar monomer, but with Ar cluster the sputtering yield of Si reached about 230 atoms/ion at 80 keV, a value that is about 180 times that obtained with Ar monomer ions (Fig.3). Moreover, with reactive gas clusters the sputtering yields of Si was several times larger than those obtained with Ar cluster ions. In particular, the sputtering yield of Si with SF₆ cluster reached about 3300 atoms/ion

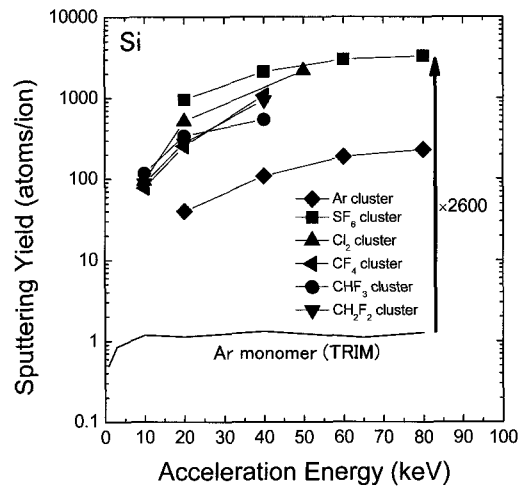
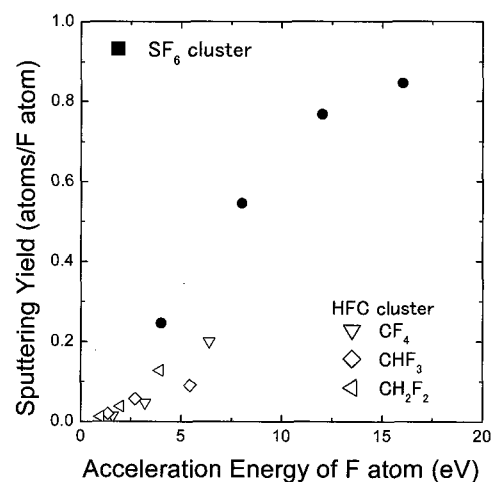


Fig. 3. Sputtering yields of Si with cluster ion beams as a function of acceleration energy.

at 80 keV, i.e. about 2600 times the value obtained with Ar monomer ions (Fig. 3). The sputtering yields of Si with HFC and Cl₂ clusters at 40 keV were more than 400 times higher than with Ar monomer. We found that reactive sputtering occurred with irradiation with cluster ions of SF₆, Cl₂, CF₄, CHF₃, and CH₂F₂. The HFC molecules include carbon atoms. If the carbon atoms accumulated on the surface during irradiation, the carbon layer formed would obstruct the reactive sputtering process. It is expected that H atoms in CHF₃ and CH₂F₂ can remove the carbon layer as some compound of CH_x. However, the CF₄ cluster, which doesn't include H atoms, can etch Si targets with high speed, as well as CHF₃ and CH₂F₂ clusters. This result indicates that the carbon atoms do not accumulate on the surface during HFC cluster irradiation and HFC molecules are usable as cluster ion beam source gas for the Si etching process.

Figure 4 shows the sputtering yields of Si per incident F atom with SF₆ and HFC cluster ion beams as a function of acceleration energy of the F atom. High-rate sputtering

Fig. 4. Sputtering yields of Si per incident F atoms with SF₆ and HFC cluster ion beams

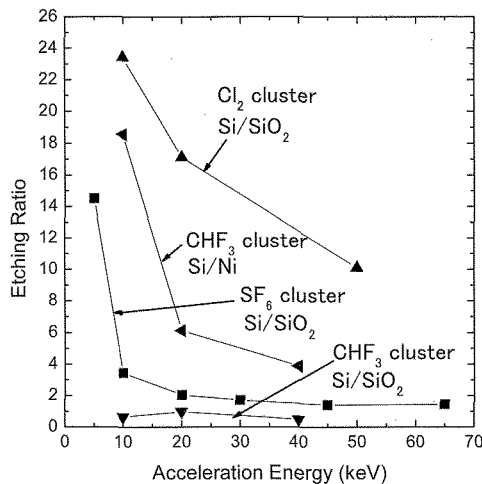


Fig. 5. The etching ratio of Si/SiO₂ or Si/Ni after SF₆, Cl₂, or CHF₃ cluster irradiation as a function of acceleration energy.

occurred with both SF₆ and HFC cluster ion irradiation, despite the low acceleration energy of the F atom of less than 20 eV, an energy range in which sputtering couldn't occur with monomer ion irradiation. This result was attributed to the nonlinear effect of the cluster impact. The sputtering yields per incident F atoms with SF₆ and HFC cluster ion beams increased with the acceleration energy of the F atom, but the values were less than 1. This result indicates that sufficient F atoms were provided by cluster irradiation and the sputtered products could be regarded as SiF_x ($x > 1$) in the irradiation conditions of figure 4.

Figure 5 shows the effect of acceleration energy on the etching ratio of Si/SiO₂ or Si/Ni after SF₆, Cl₂ or CHF₃ cluster irradiation. For SF₆ cluster irradiation, the etching ratio of Si/SiO₂ was high at low acceleration energy, and low (below 2) at high acceleration energy. For CHF₃ cluster irradiation, the etching ratio of Si/SiO₂ was very low (below 1) at acceleration energies in the range 10–40 keV. For Cl₂ cluster irradiation, the etching ratio of Si/SiO₂ was above 10 at acceleration energies in the range 10–50 keV. For a material to be used as a mask for Si etching, its selectivity should be high. Because the sputtering yield of Si is high at high acceleration energy, high-speed fabrication could be realized using cluster ion beams, if the selectivity is also high in this energy range. Thus, SiO₂ is suitable for use as a mask for irradiation with Cl₂ cluster ion beam, which is an advantage for semiconductor processing.

When SF₆, Cl₂ and CHF₃ clusters are accelerated to 40 keV, the acceleration energies per molecule are 62, 27 and 20 eV, respectively. Because these energies are higher than the binding energies of the molecules, the molecules could be broken by cluster impact and each atom in the molecule could react with target atoms individually. The binding energies in the diatomic molecules of Si-O, Si-F, Si-Cl, and C-O and the melting points of their typical compounds are shown in Table II. The melting points of SiF₄, SiCl₄, and CO are much lower than room temperature. Once these kinds of compounds are generated, they are easily removed from the surface.

Table II. Binding energies in diatomic molecules of Si-O, Si-F, Si-Cl, and C-O and melting points of their typical compounds.

	Binding energy, eV	Compound	Melting point, °C
Si-O	8.3	SiO ₂	2950
Si-F	5.7	SiF ₄	-90
Si-Cl	4.2	SiCl ₄	-70
C-O	11.2	CO	-205

Because the binding energy of Si-F is higher than that of Si-Cl, F atoms can replace O atoms in SiO₂ easier than Cl atoms. Therefore, the etching ratio of Si/SiO₂ with SF₆ cluster irradiation was lower than with Cl₂ cluster irradiation. Likewise, because the binding energy of C-O is higher than Si-O, C atoms can replace O atoms in SiO₂ and F atoms can easily combine with Si atoms. Therefore, the etching ratio of Si/SiO₂ with CHF₃ cluster irradiation was lower than that with SF₆ cluster irradiation. On the other hand, with CHF₃ cluster irradiation the etching ratio of Si/Ni was higher than that of Si/SiO₂ at acceleration energies in the range 10–40 keV. Thus, Ni is suitable as a mask for irradiation with HFC cluster ion beams.

4. SURFACE SMOOTHING

The smoothing effect by cluster ion irradiation is derived from the horizontal movement of many surface atoms by cluster impacts [18–20]. On the other hand, on an atomically flat surface, a cluster impact forms a crater [21,22]. A rough surface can be smoothed with Ar cluster irradiation, until it reaches the roughness caused by the crater formation [23]. The surface smoothing effect with reactive gas cluster irradiation has not been sufficiently investigated. Figure 6 shows AFM images of Si surfaces irradiated with CHF₃ and Cl₂ clusters at the acceleration energy of 20 keV and ion dose of 10¹⁵ ions/cm². The average roughness of the initial Si surface was 5.4 nm. Irradiation with a monomer ion beam would normally roughen the surface. However, with both CHF₃ and Cl₂ cluster irradiations the Si surfaces were smoothed, although the sputtering yields with these clusters were very high. This result indicates that high-speed and smooth processing of materials can be realized using

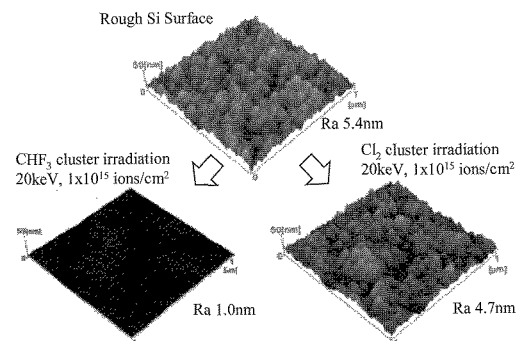


Fig. 6. AFM images of Si surfaces after irradiation with CHF₃ and Cl₂ cluster (acceleration energy: 20 keV; dose: 1 × 10¹⁵ ions/cm²).

CHF₃ and Cl₂ cluster ion beams

5. SUMMARY

The etching properties of several kinds of hydrofluorocarbon (CF₄, CHF₃, and CH₂F₂) and Cl₂ gas cluster were investigated. It was demonstrated that extremely high-speed and smooth surface processing could be realized with these cluster ion beams.

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