Evaluation of Si etching yields by Cl+, Br+, and HBr+ ion irradiation

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Abstract.
Cl₂ and HBr plasmas are widely used for poly-Si gate electrode etching processes in the semiconductor industry. In this study, sputtering yields of poly Si by Br+ ion injections, simultaneous injections of thermal H atoms and energetic Br+ ions, and successive injections of an energetic H⁺ and Br⁺ ion beams, have been evaluated with the use of a multi-beam system equipped with a mass-selected ion beam injector and a H radical source. It has been shown that there is little difference in sputtering yields among all these processes, which indicates that such hydrogen has little effect on the Si sputtering yield by Br+ ion injections. The result contrasts with an earlier speculation that hydrogen in HBr plasmas significantly enhances the Si sputtering yield by Br+ ion injections. In addition sputtering yields of poly Si by Cl+ ion bombardment obtained from similar beam experiments have been presented for comparison.

1. Introduction
Reactive ion etching (RIE) by HBr plasmas are widely used for poly-Si etching in semiconductor manufacturing processes. In a RIE process, various chemically reactive charge neutral species (such as atomic Br) generated in the plasma as well as ions (such as Br⁺) accelerated by the sheath voltage near the substrate surface enable anisotropic etching of silicon. For the development of highly controllable etching technologies for nano-scale structures used in the modern semiconductor industry, a better understanding of interactions between Si surfaces and reactive species in plasmas is highly desirable.

Atomic hydrogen (H) is highly reactive and spontaneously reacts with Si. It has been widely believed that, in RIE processes of Si by HBr plasmas, the presence of hydrogen enhances the Si sputtering yield. Indeed the experiments by Vitale et al. [1] showed with the use of a plasma-beam system that the sputtering yields of poly Si by HBr plasmas is approximately twice larger than those by Br₂ plasmas under the same beam energy, which the authors of Ref. [1] attributed to the presence of hydrogen in the system.

In the plasma beam system used in Ref. [1], the beam was extracted from a plasma source and injected into the sample surfaces without mass selection. Therefore the beam contains various ionic and neutral species. Although such plasma beams may be considered to resemble the fluxes to which substrates are subject in actual plasma processing tools, it could be difficult in such systems to separate the roles that individual ionic or atomic species play for surface chemical reactions.
The goal of this study is therefore to re-examine elementary chemical reactions of HBr\(^+\) and Br\(^+\) ions as well as other related reactions on Si surfaces with the use of a different type of beam system. Especially of interest is to determine the role that hydrogen plays in such surface reactions. To this end, we have used a multi-beam system that can simultaneously inject a low-energy neutral beam and a mass-selected ion beam.

In this work, to examine Si etching reactions by bromine, we performed three sets of experiments. In the first set of experiments, Br\(^+\) and HBr\(^+\) ions were injected into Si substrates and their sputtering yields were measured as functions of the injection energy. In the second set, Si substrates were exposed to simultaneous injections of energetic Br\(^+\) ions and charge-neutral thermal H atoms near room temperature. The flux ratio of H to Br\(^+\) used in the experiments was about 1\(\times\)10. In the third set of experiments, Si substrates were exposed to Br\(^+\) ion injections after energetic H\(^+\) ion injections with a sufficient fluence (dose). Injections of energetic H\(^+\) ions are expected to damage the Si substrate, which may affect the penetration of Br\(^+\) ions that are subsequently injected into the substrate.

![Radical beam source]

**Figure 1.** A schematic diagram of the reaction chamber of the multi-beam system used in this study [2].

## 2. Experiments

In this study, we used a multi-beam system that can irradiate a sample surface by independently controlled atoms, molecules and ions fluxes. The multi-beam system consists of a mass selected ion beam injector and a reaction chamber that is equipped with two independently controllable neutral radical/molecular beam injectors.

For the mass selected ion beam injector, a Freeman type ion source is used as the ion source, where ions are produced by arc discharges. Ions generated in the source are extracted by a high voltage and accelerated to 25keV, which sufficiently suppresses the beam emanation due to space charge. Ionic species of interest are then selected by the mass selecting magnet. The selected ions are then decelerated to a desired energy by the deceleration electrode before reaching the sample substrate in the reaction chamber. In this system, the beam energy at the substrate surface can be varied from 0 to 2keV.

Charge neutral species such as radicals that leak out of the ion source may have strong influence on etching reactions on the sample surface. In the multi-beam system, three differential pumps between the ion source and the reaction chamber reduce the density of neutral species in the beam line. The reaction chamber is always maintained in ultrahigh vacuum conditions with the pressure of about 10\(^{-10}\) Torr, which minimizes the effect of back ground gases on the sample surface. The sample substrate is set on a manipulator and can be tilted against the ion beam line, which allows a selection of the beam incident angle on the substrate. The reaction chamber is equipped with two charge-neutral radical
sources; one based on a radio-frequency (RF) plasma and another for a supersonic molecular beam. These beams may be independently controlled and therefore simultaneously injected into the sample surface, as may be seen in Fig. 1. In this study, we have used the ion beam injector and the H radical source based on hydrogen RF plasmas (HD25 Oxford Applied Research). The ion injection angle was normal to the sample surface whereas the average angle of incidence for the H radical flux was 60° (measured from the normal direction of the sample). Typically the ion beam flux was $10^{13}/\text{cm}^2/\text{sec}$ whereas the H radical beam flux was about $10^{13}-10^{14}/\text{cm}^2/\text{sec}$ at the substrate surface. The kinetic energies of H radicals are typically close to that of room temperature.

The etching yield (i.e., sputtering yield) of a Si substrate is defined as the number of desorbed Si atoms per ion injection. In this study, the ion dose was calculated from the exposure time and ion current that was measured by a Faraday cup. The number of desorbed Si atoms was evaluated from the etched depth that was measured by a surface profiler (Dektak3ST). The sample used in this study was a 1.5 cm square wafer on which a 150 nm thick poly Si was formed by CVD. Before use, its native oxide was removed by hydrofluoric acid treatment. For a typical yield measurement, the ion dose on the sample surface was approximately $1\times10^{17}/\text{cm}^2$.

3. Experimental Results

3.1 Etching by Cl+ ion beams

Before discussing etching processes associated with bromine, we first present our measurement results of Si sputtering yields by energetic Cl+ ions. Sputtering yields by chlorine ions and plasmas have been widely studied and the sputtering yield data that we have obtained may be compared with those obtained in the past.

Figure 2 shows sputtering yields of poly Si by Cl+ ion injections as functions of the injection energy. The data obtained in this study (denoted by filled circles), by Chang and Sawin [3] (denoted by filled squares), and by Tachi and Okudaira [4] (denoted by filled diamonds).

![Figure 2. Sputtering yields of Si resulting from Cl+ bombardment. The solid, broken, and dotted lines are fitting lines to the data obtained in this study (denoted by filled circles), by Chang and Sawin [3] (denoted by filled squares), and by Tachi and Okudaira [4] (denoted by filled diamonds).](image)

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Figure 2 shows sputtering yields of poly Si by Cl+ ion injections as functions of the injection energy. The data obtained in this study are denoted by filled circles whereas data obtained by the earlier studies [3,4] are also shown for comparison. It is clearly seen that the yield obtained in this study (as
well as those from the previous studies) is a linearly increasing function of the square root of the injection energy, following the well-known formula by Steinbrüchel [5].

It is also shown that, for the energy range over 300eV, the yield obtained in this study and by Tachi and Okudaira [4] are overall in good agreement. The yield data of Ref. [4] were obtained from a mass-selected ion beam system with the pressure of approximately $10^{-8} \text{Torr}$ during the beam injection. The pressure is higher by two orders of magnitude compared with that of this study.

The yield data by Chang and Sawin [3] shown in Fig. 2 are based on their plasma-beam experiments, where the beam was not mass selected. Their data are higher than those of [4] as well as this study. The difference may arise from the effects of neutral Cl atoms, which are known to enhance the yield significantly when they passivate the surface [3]. The reaction chamber pressure in the experiments by Chang and Sawin was about $10^{-6} \text{Torr}$ [3] and therefore the flux ratio of Cl atoms to Cl$^+$ ions is considered to have been about 0.1-0.01 on the sample surface. Since the flux ratio of Cl$^+$ ions to Cl atoms is $10^{-3}$ or less in our experiments due to the high vacuum condition of $10^{-10} \text{Torr}$, the difference in neutral flux may account for the difference in yield data given in Fig. 3.

3.2 Etching by HBr$^+$ or Br$^+$ ion irradiation

Sputtering yields of various bromine-based etching processes of poly Si are shown in Fig. 3. The yield data for Br$^+$ ion injections are denoted by filled squares and the linear fit to the data with respect to the square root of the ion injection energy is given by the solid line. The data for HBr$^+$ ions injections are also shown in Fig. 3, given by the filled triangles. As shown in Fig. 3, the data are somewhat scattered and no clear difference in etching yield between Br$^+$ and HBr$^+$ injections has been observed in our study. We also note that the yields shown in Fig. 3 are far smaller than the yield data given in Ref. [1], in which, for example, the poly Si sputtering yield by a Br$_2$ plasma beam at an injection energy of 100 eV is shown to be approximately 1.

3.3 Simultaneous irradiation of low-energy H radicals and energetic Br$^+$ ions

The sputtering yield data for simultaneous injections of low-energy charge-neutral H atoms and energetic Br$^+$ ions (denoted as “H$_{\text{radical}}$ + Br$^+$”) are given by filled circles in Fig. 3. As mentioned earlier, the atomic hydrogen flux is about 1 - 10 times larger than the Br$^+$ ion flux and therefore Br$^+$ ions enter the Si surface that is considered to be mostly covered with H radicals in these processes. Yields of
spontaneous etching of poly Si by H atoms are known to be negligibly small compared with the sputtering yields obtained here. The data of Fig. 3 suggest that simultaneous injection of low-energy H radicals has little effect on sputtering yields of Br⁺ ion injections into poly Si.

3.4 500eV H⁺ ion irradiation prior to Br⁺ ion irradiation
In actual Si RIE processes by HBr plasmas, energetic H⁺ ions that enter the substrate can damage the surface and subsurface region of the substrate. Such damages may affect the rates of reactions between incoming Br⁺ ions and substrate poly Si. To check this possibility, we irradiated a poly Si substrate surface initially by 10¹⁷ /cm² of 500eV H⁺ ions and then subsequently by a similar dose of Br⁺ ions. The sputtering yields obtained from such processes are given by filled diamonds (denoted by “H⁺+Br⁺”) in Fig. 3. Given the uncertainty associated with the data shown in Fig. 3, there seems no clear effect of 500eV H⁺ ion injections prior to Br⁺ ion injections on the Si sputtering yields.

4. Conclusions
In this study we have evaluated sputtering yields of poly Si by Cl⁺, Br⁺, and HBr⁺ ion injections, using a multi-beam system with a mass-selected ion beam injector. Due to the high vacuum (with the typical gas pressure in the reaction chamber being at 10⁻¹⁰ Torr during the beam injections) of the beam system, we can eliminate the effects of background gas adsorption on the sample surface. To add effects of neutral gas adsorption on the sample surface, on the other hand, we have used a low-energy neutral beam injection system that can be controlled separately from the ion beam injection system.

Since one of the goals of this study is to clarify effects of hydrogen in HBr RIE processes, we have also evaluated Si yields by Br⁺ ions simultaneously injected with H atoms. Also obtained have been sputtering yields by Br⁺ ion injections of Si substrates that were previously bombarded by 500eV H⁺ ions.

These cases were examined because of a possibility that such atomic or ionic hydrogen can modify the sample surface and therefore affect the sputtering yields by Br⁺ ion injections. The yield data obtained in this study, summarized in Fig. 3, have shown, however, that sputtering yields by Br⁺ beams, HBr⁺ beams, simultaneous injections of H radicals and Br⁺ beams, and successive injections of H⁺ and Br⁺ beams, take more or less the same values as functions of ion beam injection energy. In other words, hydrogen introduced in these processes has little effect on Si sputtering yields by Br⁺ ion injections.

It has been long speculated that hydrogen of HBr plasmas enhances Si etching by Br⁺ ion bombardment. However our experimental observations above have shown otherwise. The Si yield data given in Ref. [1], which show that the Si yields by HBr plasmas are typically twice larger than those by Br₂ plasmas and the yield values are much larger than those given in Fig. 3, were obtained from plasma beams that contain neutral fluxes much larger than the ionic fluxes. Therefore the difference in yield between HBr plasmas and Br₂ plasmas given in Ref. [1] may reflect the effects of charge-neutral Br atoms that passivate the Si surface, rather than hydrogen radicals or ions. Passivation effects of neutral Br on Br⁺ ion etching are beyond the scope of the present work and deferred to future study.

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