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Characteristics of silicon etching by silicon chloride ions

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Plasmas generated from halogen-containing gases, such as Cl_2 or HBr, have been widely used in gate etching processes for semiconductor chip manufacturing. Such plasmas may contain silicon halide ions formed by the ionization of etching products that enter the plasma. In this study, to illustrate Si etching by such silicon halide ions, the sputtering yield of Si by $SiCl_x^+$ (with $x = 1$ or 3) ions has been obtained as a function of the incident ion energy by using a mass-selected ion beam injection system. It has been found that, at sufficiently low energy, the incidence of $SiCl^+$ ions leads to the deposition of Si which may affect profile control in microelectronic device fabrication processes. © *2013 American Vacuum Society*. [http://dx.doi.org/10.1116/1.4793426]

I. INTRODUCTION

Recently, various types of vertical metal–oxide–semiconductor (MOS) devices have been proposed,[1–4] in which some, such as fin-type field effect transistor, have vertical gate structures that are formed by reactive-ion etching (RIE) during the manufacturing process. Since the gate channel surface of a vertical MOS device is subject to direct ion bombardment and surface chemical reactions during the RIE process, damage on the gate channel surface caused by plasma exposure is currently a major concern in gate etching processes. Therefore, fine control of plasma conditions for gate etching processes is of significant importance and a better and detailed understanding of RIE mechanisms is required.

For Si gate etching processes, plasmas generated from halogen-containing gases are widely used to achieve high selectivity, etching anisotropy, and high etching rates, and therefore, reactions of the Si substrate surface with halogen-containing ions have been extensively investigated.[5,6] Among such ions, however, silicon halide ions have been less studied. For example, in chlorine plasmas used for Si etching, silicon chloride ions (such as $SiCl^+$) may also be generated from the ionization of etch products such as SiCl desorbed from the substrate surface. Such ions can be accelerated by the sheath voltage to ultimately reach the substrate surface.[7,8] Reaction of silicon halide ions with various microscopic (or nanoscale) structures on the substrate surface, including sidewalls, may affect the overall Si sputtering rates as well as the etched profiles.

The objective of this study is, therefore, to understand the surface chemical reactions of Si etching by silicon halide ions. To clarify the reactions of silicon halide ions with a Si surface, we have evaluated the Si sputtering yield as a function of the incident ion energy by using a chlorine or silicon chloride ion beam generated in a mass-selected ion beam system. As will be explained, the ion beam system allows one to irradiate the sample surface with a specific ionic species at specific incident energy under ultrahigh vacuum conditions. In this study, we discuss only chlorine as a representative halogen element for Si etching processes and identify major desorbed products generated by the silicon-chloride ion incidence.

II. EXPERIMENT

In this study, we use a multibeam system that can irradiate a sample surface with a mass selected ion beam under ultrahigh vacuum conditions.[9–11] The mass-selected ion beam system consists of three parts—an ion source, a mass selecting magnet, and a reaction chamber. Ions were generated by arc discharge in a Freeman-type ion source and were first accelerated up to 25 keV. The ions with a specific mass were selected by the mass selecting magnet, decelerated to the desired energy by the deceleration electrode, and directed toward the sample surface placed in the ultrahigh-vacuum reaction chamber. The sample was mounted on a manipulator so the angle of incidence for the ion beam can be varied. Desorbed products from the substrate surface can be identified *in situ* by a quadrupole mass spectrometer (QMS) that was installed in the reaction chamber.

In this beam system, the ion energy can be raised up to 2000 eV. The total ion beam current was evaluated by a Faraday cup placed at the sample position, and the ion current density profile was also measured by a movable mask with a pin hole placed in front of the Faraday cup. The sample used for yield measurement was a 1.5 cm^2 Si wafer with (100) orientation covered with a 150 nm thick poly Si formed by chemical vapor deposition.

For the yield measurement in this study, the typical ion dose was set at 1–4 × 10^{17} ions/cm^2. The sputtering yield of a Si sample is defined as the number of Si atoms removed

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from the surface per incident ion. The sputtering yield was determined from the ion dose and the etched depth. The ion dose was evaluated from the ion current density profile on the sample and beam irradiation time and the etched depth was evaluated with a surface profiler (Dektak3ST) and a metal stencil mask placed on the Si sample. The metal stencil mask has many slits with the width of each slit being 0.1 mm. After each beam irradiation experiment, the etched profile was measured by the surface profiler. The maximum etched depth in each experiment was typically set to be deeper than 20 nm, so the profiler can measure with high accuracy the difference in height between the parts of Si sample covered and those not covered by the stencil mask.

Under some conditions of ion irradiation, Si was observed to be deposited on the sample surface (and the stencil mask) and, in these cases, we assigned a negative value to the sputtering yield as a natural extension of the definition above. Namely, a negative sputtering yield in this study means that its absolute value represents the number of Si atoms deposited on the sample surface per incident ion.

III. RESULTS AND DISCUSSION

A. Sputtering yield by SiCl$_x^+$ ion incidence

Figure 1 shows the sputtering yields of poly Si by Cl$^+$, SiCl$^+$, and SiCl$_3^+$ as functions of ion incident energy. A data point for Si$^+$ ion incidence at 300 eV is also shown as a reference. In the experiments, Si$^+$, Cl$^+$, SiCl$^+$, and SiCl$_3^+$ ion beams were produced from SiCl$_4$ gas, and the ion energy was varied from 300 to 1000 eV. Note that the horizontal axis of Fig. 1 is scaled as the square root of incident energy and the ion dose was 1–4 × 10^{17} ions/cm^2. The sputtering yield data by Cl$^+$ ions are the same as those given in Ref. 12 and the solid line represents a fitting curve to the yield data for Cl$^+$ ion etching by other groups given in Refs. 5 and 6 with a fitting curve that follows the formula proposed by Steinbrüchel.[13] It is seen that the Cl$^+$ yield data obtained in this beam system[12] are consistent with the earlier data of Refs. 5 and 6.

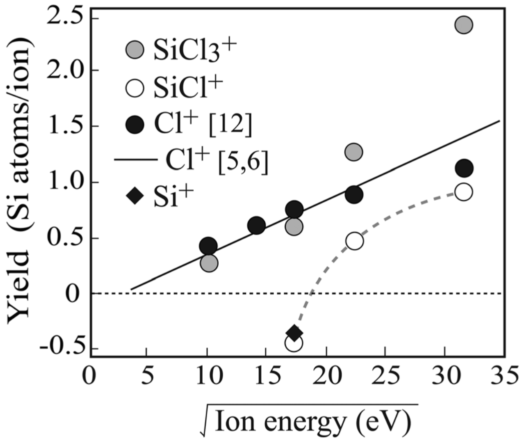

FIG. 1. Sputtering yields of Si by Cl$^+$, SiCl$^+$, and SiCl$_3^+$ ion incidence as functions of ion incident energy. A data point for Si$^+$ ion incidence at 300 eV is also shown as reference. The horizontal axis represents the square root of ion incident energy. The solid line represents a fitting curve to the Si sputtering yield data for Cl$^+$ ions given in Refs. 5 and 6. The dashed curve connecting the data for SiCl$^+$ ion incidence is intended as a guide to the eye. A negative yield means that its absolute value represents the number of Si atoms deposited per incident ion.

It is shown in Fig. 1 that SiCl$_3^+$ sputtering yields are nearly the same as those of Cl$^+$ ions at lower incident energy and higher than those of Cl$^+$ ions at higher incident energy. With three Cl atoms per ion, the SiCl$_3^+$ incident ion beam is likely to be more chemically reactive than the Cl$^+$ ion beam. It is also seen that Si sputtering yields by SiCl$^+$ ions are lower than those by Cl$^+$ ions. At 300 eV, Si deposition takes place with SiCl$^+$ ion incidence, as in the case of Si$^+$ ion incidence at the same energy. When SiCl$^+$ hits the sample surface, it is likely to be neutralized first (by receiving an electron from the surface through an Auger process) and then to break into Si and Cl atoms. Si atoms have a high tendency to stick to the Si surface, whereas Cl atoms tend to form volatile products SiCl$_x$ (with $x = 1$–4, although most likely $x = 1$ or 2) with surface Si atoms and, therefore, etch the surface. Note that the Si and Cl of a 300 eV SiCl$^+$ ion have kinetic energies of 133 and 167 eV, respectively; therefore, a Si atom from a 300 eV SiCl$^+$ ion has a higher probability to stick to the Si surface than a more energetic 300 eV Si$^+$ ion does. However, a Cl atom from an SiCl$^+$ ion also simultaneously etches the Si surface, as mentioned above, which explains why the (negative) sputtering yields of Si$^+$ and SiCl$^+$ ions at 300 eV are similar. The fact that Si atoms that are separated upon impact from the incident SiCl$^+$ ions tend to form covalent bonds with surface Si atoms and, therefore, are deposited on the surface explains why the sputtering yield by SiCl$^+$ ion incidence is generally lower than that by Cl$^+$ ion incidence.

B. Measurements of desorbed products of SiCl$_x^+$ ion incidence

In order to understand surface chemical reactions, time-of-flight (TOF) measurements of desorbed species were performed with the use of pulsed ion beams. Figure 2 shows a schematic diagram of the desorption measurement system. The incident angle of the ion beam was set at 50° against the normal direction of the sample surface. The observation angle of the QMS was set at 30° with respect to the sample

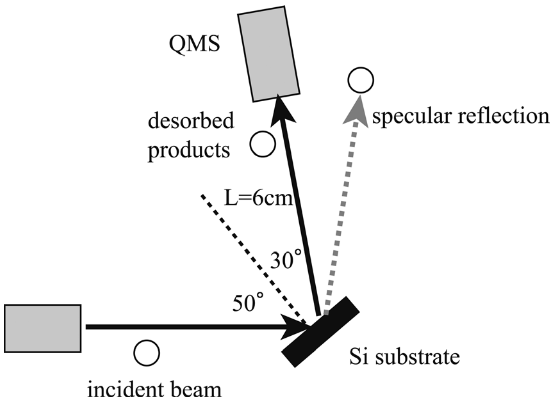

FIG. 2. Schematic diagram of the TOF measurement system for desorbed products from the sample surface.

surface normal, and therefore, ions specularly reflected from the sample surface are not counted in the measurement. The distance between the sample substrate surface and the opening of the QMS is set to be 6 cm. The Si samples used for the TOF measurement were single crystal Si with (100) surface orientation. The electron impact energy used to ionize charge neutral desorbed species for QMS measurement is 70 eV. It should be noted that the QMS signal intensities among different species are not scaled to the magnitudes of the neutral fluxes entering the QMS system since the electron impact ionization rate depends on the species. The ion beam is pulsed so that signals from the desorbed products and the background noise can be distinguished in the QMS measurements. The ion beams employed in this study were Cl^+, $SiCl^+$, $SiCl_3{}^+$ with a pulse width of 200 μs and an ion incident energy of 1000 eV and with an ion flux of 1×10^{14}/cm^2/s.

Figure 3(a) shows the QMS signals for charge-neutral Si (with a mass of 28 amu), Cl (35 amu), and SiCl (63 amu) species desorbed from the surface by Cl^+ ion beam incidence. In this QMS measurement, the Cl and SiCl signal intensities are much lower than the Si signal intensity and, therefore, the Cl and SiCl signals are magnified by 8 and 60 times in Fig. 3(a), respectively. However, as mentioned earlier, the relative intensities of QMS signals among different desorbed species shown here do not represent the relative magnitudes of their fluxes. In this case, Si, Cl, and SiCl were the only desorbed species observed by the QMS and other species, including $SiCl_2$, were below the detection limit.

Similar measurements with $SiCl^+$ and $SiCl_3{}^+$ ion beam incidence were performed and the results are summarized in Figs. 3(b) and 3(c). In these cases, $SiCl_2$ is also observed as a desorbed species in addition to Si, Cl, and SiCl. The Cl, SiCl, and $SiCl_2$ signals are magnified by 10, 40, and 6600 times, respectively, in (b) and 6, 20, and 650, respectively, in (c), as indicated. Although a weak QMS signal may result from a low flux of the desorbed species, the relative intensities of QMS signals among different desorbed species shown here should not be construed to represent the relative magnitudes of their fluxes, as mentioned above.

The desorbed species SiCl and $SiCl_2$ observed in the measurements of Fig. 3 are most likely to be formed as the result of surface chemical reactions rather than the breakdown of incident $SiCl_3{}^+$ ions that are nonspecularly reflected from the surface. This is because the observation angle of the QMS, which is set at 30° against the sample surface normal, is unlikely to allow reflected species to enter the QMS system since the majority of reflection occurs nearly specularly. In addition, the slow rise and decay of the SiCl and $SiCl_2$ signals in Fig. 3 indicate that the kinetic energy of the desorbed SiCl or $SiCl_2$ observed here is in the range of a few eV at most. Reflected species would have much higher kinetic energy since the incident energy used was 1000 eV. Measurement of the energy distribution of desorbed species based on the QMS signals is beyond the scope of the current study, however, and deferred to a separate publication.

Figure 4 shows the ratios of the QMS signal intensities of (a) Cl, (b) SiCl, and (c) $SiCl_2$ to those of Si for the cases of Cl^+, $SiCl^+$, and $SiCl_3{}^+$ ion beam incidence. The ratio represents the ratio of the time integral of the corresponding QMS signal (i.e., the area between the QMS signal curve and the horizontal axis) shown in Fig. 3 to that of the QMS signal for desorbed Si. The experimental conditions are, therefore, the same as those of Fig. 3. It is seen in (a) that the relative fluxes of desorbed chlorine atoms (Cl) are similar in

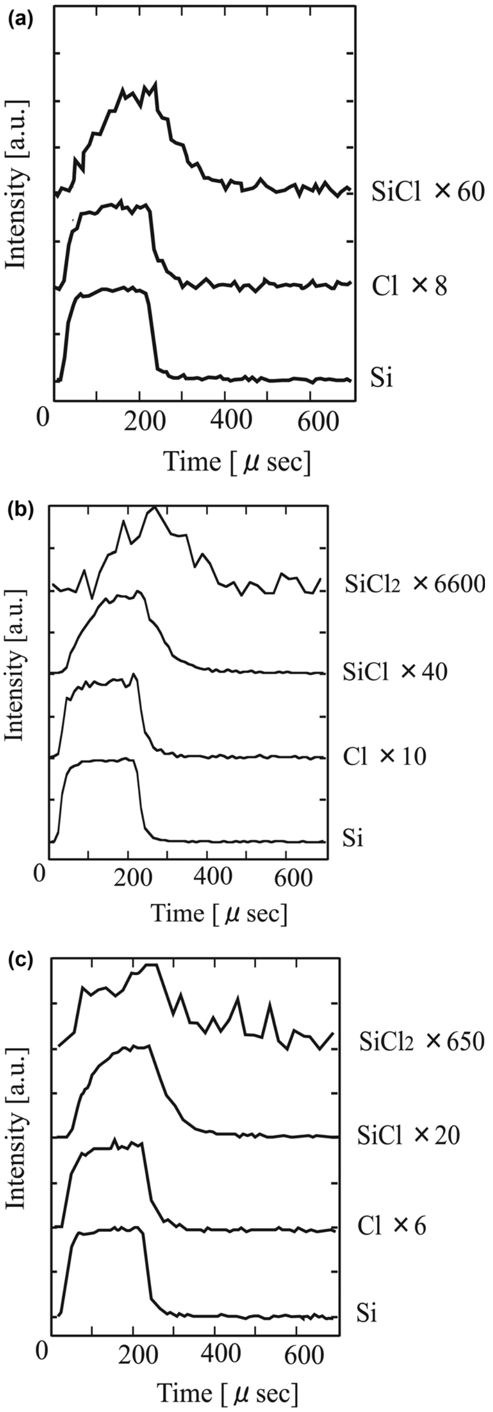

FIG. 3. TOF measurement of various species desorbed from the sample surfaces by pulsed beams of (a) Cl^+, (b) $SiCl^+$, and (c) $SiCl_3{}^+$ ions. The horizontal axis represents time and the vertical axis represents the signal intensity of each desorbed species obtained from the QMS system. The intensity curves are horizontally shifted for clarity. The ion incident energy is 1000 eV and the ion flux is 1×10^{14}/cm^2/s in each case.

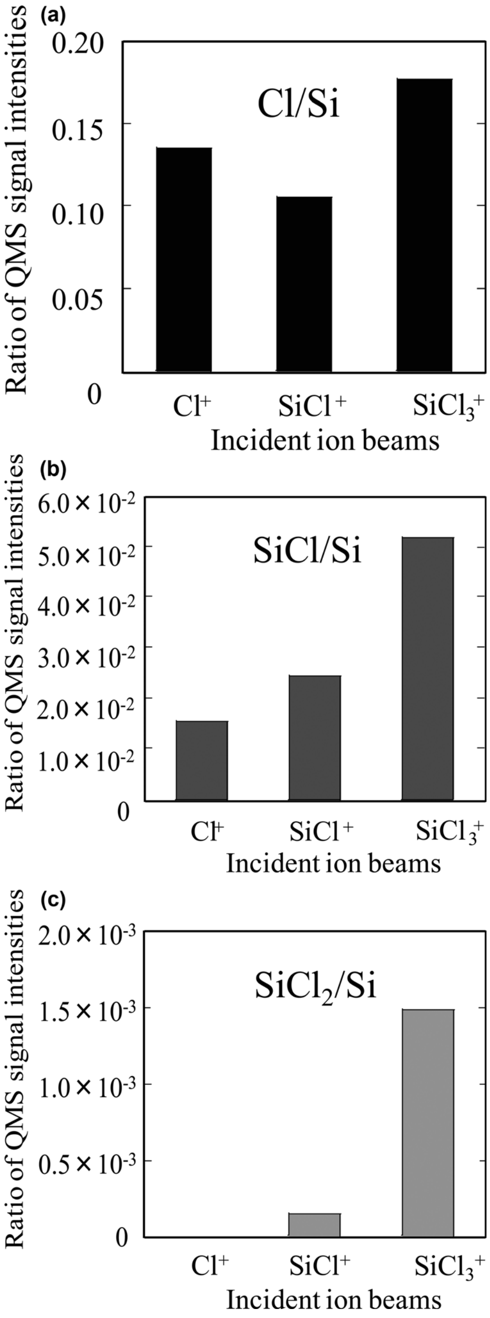

FIG. 4. Ratios of QMS signal intensities of (a) Cl, (b) SiCl, and (c) $SiCl_2$ to those of Si for the cases of Cl^+, $SiCl^+$, and $SiCl_3^+$ ion beam incidence. The experimental conditions are the same as those of Fig. 3.

magnitude among all the cases despite the fact that three times more Cl atoms are incident on the surface in the case of $SiCl_3^+$ ion beam incidence than in the other cases. This similarity in Cl flux is due to the fact that, as shown in Fig. 1, the Si sputtering yield by the $SiCl_3^+$ ion beam is nearly 2.5 times higher than those by the other beams. In other words, in the case of $SiCl_3^+$ ion incidence, more Cl atoms desorb from the surface than in the other cases, but more Si atoms desorb as well.

Figure 4(b) shows, on the other hand, that more Si atoms desorb in the form of SiCl with $SiCl_3^+$ ion incidence than with $SiCl^+$ or Cl^+ ion incidence. This is because more Cl atoms are brought to the surface by the incident beam in the case of $SiCl_3^+$ ion incidence and, therefore, more likely to form covalent bonds with surface Si atoms than in the other cases. For the atomic cluster $SiCl_2$ to be formed in a surface reaction, Cl atoms must be even more numerous on the Si surface and, therefore, desorption of $SiCl_2$ is higher in the case of $SiCl_3^+$ beam incidence than in other cases, as shown in Fig. 4(c).

C. Inference on the gate etching process with HBr plasma

In the recent gate Si etching technology, plasmas based on gases containing HBr are widely used.[12] In HBr plasma, incident ions may contain silicon bromides, i.e., $SiBr_x^+$, since sputtered Si atoms enter the plasma and associate with Br atoms.[7] Both Br and Cl are halogen elements and, therefore, have similar chemical properties although the Si sputtering yield by Br^+ ions is slightly lower than that by Cl^+ ions.[12] Although we did not examine interactions between a Si substrate and $SiBr_x^+$ ions in this study, it is surmised from the present study on $SiCl_x^+$ ions that the incidence of $SiBr_x^+$ on a Si surface can also promote the redeposition of Si atoms. Such a redeposition may in turn affect the etched profiles of microscopic (or nanoscale) structures in gate etching processes.

IV. SUMMARY AND CONCLUSIONS

In this study, using a mass-selected ion beam system, we have obtained the sputtering yields of Si by silicon chloride ions ($SiCl^+$ and $SiCl_3^+$) as functions of the incident ion energy. Major desorbed products created by the ion beam incidence have been also identified by a QMS installed in the beam system.

It is found that Si sputtering yields by $SiCl^+$ ions tend to be lower than those by Cl^+ ions due to the deposition of Si atoms contained in the incident beam, whereas Si sputtering yields by $SiCl_3^+$ ions are determined by the balance among the processes of Si deposition, physical sputtering, and chemical etching by Cl. Observation of the desorbed products in this study also indicates that the formation of $SiCl_2$ by surface reactions is promoted more by $SiCl_3^+$ ion irradiation than by $SiCl^+$ or Cl^+ ion irradiation. This suggests that the high Si sputtering yields by $SiCl_3^+$ ion incidence shown in Fig. 1 are largely accounted for by chemical etching due to a larger supply of Cl atoms.

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