Collision-induced dissociative ionization of Ar diluted CH_2F_2 plasma

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Ion densities of CH_2F^+ and CHF_2^+ were determined by dissociative ionization pathways in channels of charge exchange collisions, i.e., $CH_2F_2 + M^+ \rightarrow CH_2F^+ + F\cdot + M^*$ and $CHF_2+ + H\cdot + M^*$ (M=Ar, Kr) in CH_2F_2 plasmas diluted by a rare gas (M). These channels simultaneously generated counter fragments of charge-neutral H and F atoms of interest for plasma etching processes. In Ar-diluted plasmas, CH_2F^+ ions predominated due to dissociative ionization between Ar^+ (ca. 15.8 eV) and C-F appearance (dissociative ionization) energy (ca. 16 eV) to form CH_2F^+. In contrast, for Kr-diluted plasmas, C-H appearance energy (ca. 13.8 eV) predominated to produce a larger amount of CHF_2^+ ions due to a similar channel for charge exchange collisions between Kr^+ (ca. 14 eV) and CH_2F_2. Thus, adding ratio of Ar and Kr gas to CH_2F_2 plasmas provided control over the fraction of CH_2F^+ and CHF_2^+ ion densities. In evaluation of etching rates of silicon nitrides (SiN), SiO_2, and poly-Si films for CH_2F_2 plasmas diluted with rare gases, the SiO_2 etching rate was insensitive to ion fluxes of the incident CHF_2^+ and CH_2F^+. The SiN etching rate was considerably affected by the dilution gas used. The SiN surface reaction was promoted by F-rich chemistry in the Ar-diluted CH_2F_2 plasma.

1. Introduction

In ultra-large-scale integrated circuit (ULSI) fabrication, hydrofluorocarbon molecules, CH_xF_{4-x} (x=1,2,3), are frequently used for etching of dielectric SiO_2 and Si_3N_4.[1] The ability to control the dimensions of the etched features is necessary for SiO_2 etching for contact holes and for Si_3N_4 etching for gate spacers. To achieve this, a high level of selectivity to protect the underlying film is a key performance feature during etching. In general, reducing spontaneous etching of the Si is accomplished by reducing the quantity of F atoms in the gas phase, because F atoms react with Si to form SiFx. To reduce the F density, a fluorocarbon gas containing hydrogen can be used.

The present study examined the ions and radicals produced in CH_2F_2 plasmas diluted with Ar or Kr gas. For these plasmas, the dominant pathways for dissociative ionization of CH_2F_2 in plasma are determined by the charge exchange collision reactions due to resonantly occurring dissociation at energies similar to the ionization of rare gases. Furthermore, selective dissociation of C-F or C-H bonds and the density of CH_2F^+ and CHF_2^+ ions obtained by adding Ar or Kr gas to the plasma was shown to control the dissociation process.

2. Experimental

A quadrupole mass spectrometer was installed in the plasma etching reactor at the chamber wall. A 100-μm diameter aperture was installed in the QMS entrance. The QMS head was electrically grounded, and collected ions from the bulk plasma through the ion sheath. For measurements for radicals, electron energy of 12 eV was used.

3. Dissociative ionization [3]

In positive-ion mass spectra for the CH_2F_2 plasma diluted with pure Ar or pure Kr, CH_2F^+ and CHF_2^+ ions were dominantly observed. In the ionization pathway generated for these ions, two channels are involved. The reaction schemes for the dissociative reactions in electron collisions are given by:

$$CH_2F_2 + e^- \rightarrow CH_2F^+ + F + 2e^- \quad (1)$$

$$CH_2F_2 + e^- \rightarrow CHF_2^+ + H + 2e^- \quad (2)$$

The counter fragments of charge-neutral H and F atoms were generated simultaneously through these dissociation-mechanisms. Figure 1 shows cross sections of CHF_2^+ and CH_2F^+ produced by electron collision with CH_2F_2, ionization thresholds. These threshold energies were observed at 13.8±0.5 eV for CHF_2^+ and at 15.8 ±0.5 eV for CH_2F^+. These values agreed with the literature values of 13.10 eV for CHF_2^+ and 14.43 eV for CH_2F^+.[2] The threshold for dissociative ionization for CH_2F^+, which is the same as the C-F appearance energy for CH_2F_2 (15.8 eV), is close to that for Ar (16 eV). In the Kr-diluted plasma, the dissociative ionization of CHF_2^+ (C-H bond cleavage) occurred via charge exchange collisions of Kr^+ ions. The dissociative ionization of CH_2F^+ (C-F bond cleavage) selectively occurred via charge exchange collisions of Ar^+ ion in the Ar-diluted plasma.

Figure 2 shows the relative fraction of these ions. The density-fraction of CHF_2^+ ion decreased with similar to the increase in the CH_2F^+ ion density as the

Ar fraction increased. The relative CHF_2^+ ion density correlated with that for Kr^+, which indicates that the effect of charge exchange collisions greatly influenced the density of CHF_2^+ and CH_2F^+ ions.

4. Radical generation [3]

Moreover radical density fraction of charge-neutral CH_2F and CHF_2 against all other CHxFy neutrals depended on the rare gas mixture ratio, Ar/Ar+Kr. In the results, CH_2F radical is a dominant species. This can be interpreted that dissociation channels by excitation are more dissociative in $CH_2F_2 \rightarrow CH^2F + F$ compared with $CH_2F_2 \rightarrow CHF_2 + H$. As the Ar/(Ar+Kr) fraction ratio changed, the densities of CH_2F and CHF_2 decreased and increased *vise verse*. This phenomenon also failed to explain only electron collision induced with electron temperature changes in the Ar and Kr mixture ratios. For possible explanations, we suggest that Ar and Kr metastables contributes on dissociation via excitation. In the situation of large dilution by rare gas, the positive ions of rare gas were dominated in plasma. Thus the dissociative ionization rate with collisions of rare gas ions would be comparable to electron collision processes. Three processes of radical production, (1) dissociative ionization, (2) radical ionization, and (3) Penning (metastables) ionization are roughly considerable. By using cross-section data, with assumption of the electron temperature for 3 eV of Ar and for 2.6 eV of Kr, an estimated radical density fraction, CH_2F/CHF_2, can be explained 0.3:0.1:0.6 in the best fit of the experimental results. Almost half density is possibly considered to be generated by the Penning ionization.

5. Etching performance [4]

Etching rates of (a) SiO_2 and (b) SiN films were depended on a gas mixture of CH_2F_2 with a flow rate of 30 sccm and Ar or Kr with a total flow rate of 300 sccm. An RF bias of 1000 W was applied and the peak-to-peak voltage (Vpp) was approximately 1 kV. The VHF power ranged between 600 and 1200 W was applied. The etching rate of SiN in the Ar dilution case was always higher than that in the Kr dilution case. In SiN etching, both H and F atoms may work as etchants for the enhanced formation of volatiles such as HCN. Thus, the dominant species of H and F atoms, as well as CH_2F^+ and CHF_2^+, might contribute to the surface reactions on SiN in the Ar case.[3] The Ar dilution resulted in a F-rich condition that might assist to enhance the SiN film etching.

Consequently, in actual etching, not only the densities of CHF_2^+ and CH_2F^+ ions but also the densities of H, F, CHF_2, and CH_2F radicals affect the selective etching of various dielectrics. Thus controlling the ion density ratio may help to improve the performance of plasma etching. The results of the present study demonstrated a new concept for achieving highly precise control of plasma processing.

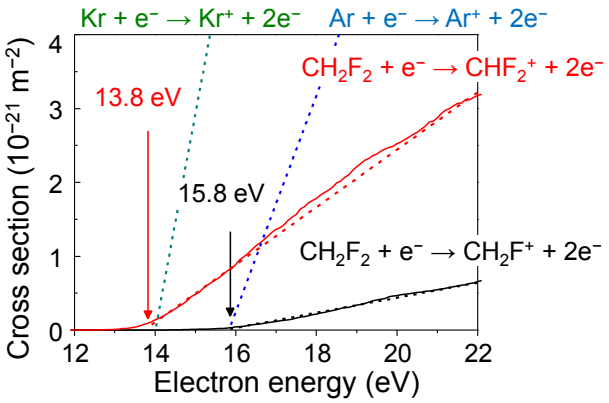

Figure 1 Cross-section of dissociative ionization for a CH_2F_2 molecule.

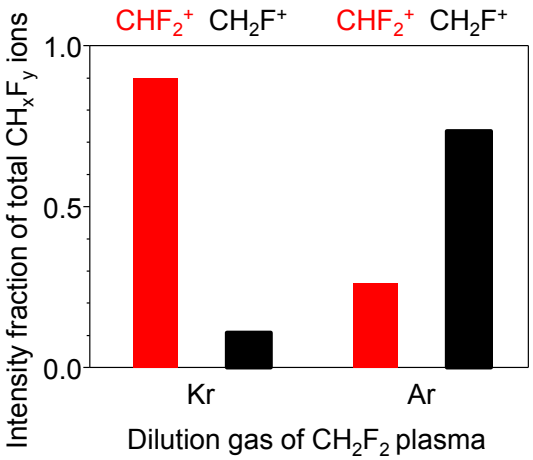

Figure 2 Individual CH_2F^+ and CHF_2^+ ion fraction on total $CH_xF_y^+$ ion density at Kr- and Ar-diluted CH_2F_2 plasma.

References

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