

Hydrofluorocarbon ion density of argon- or krypton-diluted CH₂F₂ plasmas: generation of CH₂F⁺ and CHF₂⁺ by dissociative ionization in charge exchange collisions

Quadrupole mass-spectroscopic analysis – in rare gas (M) diluted CH₂F₂ plasma – has revealed selective formation of CH₂F⁺ ion for Ar dilution and CHF₂⁺ ion for Kr dilution. Ion densities of CH₂F⁺ and CHF₂⁺ were determined by dissociative ionization pathways in channels of charge exchange collisions, *i.e.*, CH₂F₂ + M⁺ → CH₂F⁺ + F· + M* and CHF₂⁺ + H· + M* in CH₂F₂ plasmas. In Ar-diluted plasmas, CH₂F⁺ ions predominated due to dissociative ionization between Ar⁺ (*ca.* 15.8 eV) and C-F appearance energy (*ca.* 16 eV) to form CH₂F⁺. In contrast, for Kr-diluted plasmas, C-H appearance energy (*ca.* 13.8 eV) predominated to produce a larger amount of CHF₂⁺ ions due to a similar channel for charge exchange collisions between Kr⁺ (*ca.* 14 eV) and CH₂F₂. In accordance with the analytic results, the addition of Ar and Kr gas to CH₂F₂ plasmas provided control over the fraction of CH₂F⁺ and CHF₂⁺ ion densities.

Hydrofluorocarbons have H atoms in place of F atoms in fluorocarbon gases. Dissociation reactions involving C–H and C–F bonds are of interest for controlling the density of reactive species: F atoms, produced by dissociation of the C–F bond, are a main etchant for Si, while H atoms, produced by dissociation of the C–H bond, promote the deposition of polymers on a substrate surface. For processing accuracy, a balance of species for etching and deposition is believed to be important and to be closely related to the dissociation processes in gas-phase. However, the variety and densities of the ions and radicals generated in hydrofluorocarbon plasmas have not been fully elucidated.

The experiments were performed with a dual frequency capacitively coupled plasma (CCP) etching reactor, installed a quadrupole mass spectrometer (QMS; Hiden Analytical, EQP) at the chamber wall. A 100-μm diameter aperture was installed in the QMS entrance. A mixture of Ar or Kr gas with CH₂F₂ gas was introduced into a chamber, and plasmas were sustained by applying the very high frequency (VHF) power to the electrode.

Positive ion mass spectrometric measurements revealed that the dominant positive ions were CH₂F⁺ and CHF₂⁺. In the ionization pathway generated for CH₂F⁺ and CHF₂⁺ ions, two channels are involved: CH₂F⁺ through C-F bond dissociation or through C-H bond dissociation. The reaction schemes for the dissociative reactions in electron collisions are given by CH₂F₂ + e⁻ → CH₂F⁺ + F + 2e⁻ (threshold at 15.8 eV), and → CHF₂⁺ + H + 2e⁻ (13.8 eV). The counter fragments of charge-neutral H and F atoms were generated simultaneously through these dissociation mechanisms. A larger ion density for CH₂F⁺ in the Ar-diluted plasma, other dissociation processes but the electron collisions need to be considered. Charge exchange collisions between rare gas ions and CH₂F₂ molecules occurred, because the appearance energies were located close to that for Ar (16 eV) and Kr (14 eV).

We concentrate our continuous study in elucidation of the dissociative reactions in plasma through the gas-phase diagnostics utilized the mass-spectrometric measurements.

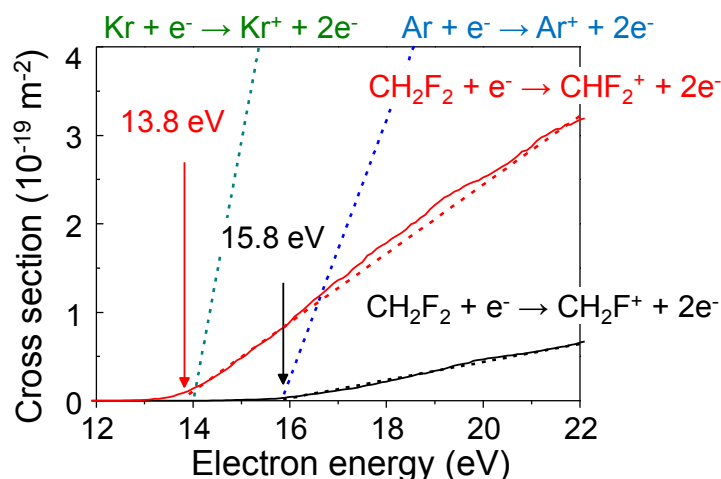


Fig 1. Cross section for dissociative ionization for a CH_2F_2 molecule

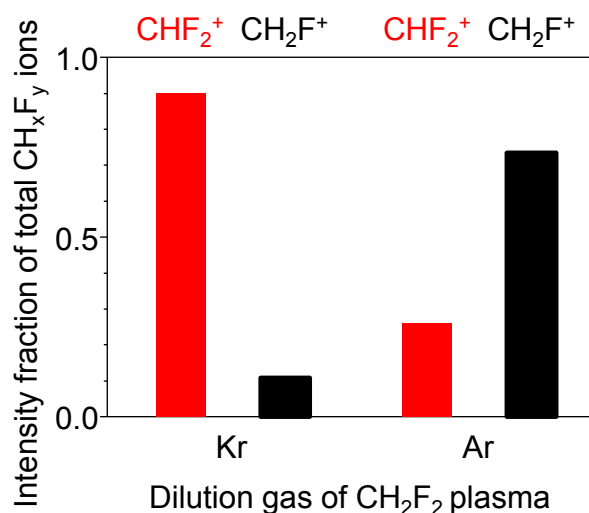


Fig 2. Individual CH_2F^+ and CHF_2^+ ion fraction on total CH_xF_y^+ ion density at Kr- and Ar-diluted CH_2F_2 plasma

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Paper Reference:

Yusuke Kondo *et al.*, (2015) "Hydrofluorocarbon ion density of argon- or krypton-diluted CH_2F_2 plasmas: generation of CH_2F^+ and CHF_2^+ by dissociative-ionization in charge exchange collisions" *J. Phys. D: Appl. Phys.* **48** 045202. doi:10.1088/0022-3727/48/4/045202

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