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Decomposition Mechanism of CF_4 by Long DC Arc Plasma

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Carbon tetrafluoride, CF_4, is mainly used as the dry etching gas in the semiconductor industry. CF_4 has a high global warming potential about 6,500, and is difficult to be decomposed. Various decomposition treatment methods are currently being used. A combustion and a catalyst degradation are widely implemented, while these methods possess some problems. The combustion method has insufficient temperature, which leads to non-negligible emissions of NO_x and SO_x. Catalytic degradation is high cost process due to the replacement of catalysts, resulting from the poisoning of catalysts by sulfur and HF [1].

Abatement processing with thermal plasmas has been implemented in industrial fields due to their advantages of high temperature and high chemical activity. Long DC arc has a long electrode gap distance of 300 mm. This configuration leads to sufficiently long residence time for decomposition of harmful target [2]. The purpose of this study is to decompose CF_4 by long DC arc and to investigate decomposition mechanism.

The setup consists of a power supply, a plasma torch, and a scrubber. The arc current was 10 A. Nitrogen at 25 L/min was used as the plasma gas, while CF_4 was injected at 0.5 L/min. Steam was introduced as the additive gas, and the flow rate was changed from 0.0 to 2.0 L/min. This is because H, O, and OH radicals dissociated from H_2O molecular inhibit recombination of CF_4 outside the discharge area. Molar ratio of H/F was changed as 0.0, 0.5, 1.0 and 2.0.

The produced gases were analyzed by a gas chromatograph (GC) and a quadrupole mass spectrometer (QMS) to investigate the destruction and removal efficiency (DRE) and the composition of the produced gases.

Figure 1 shows the relationship between the H/F molar ratio and DRE. The DRE was 0% without steam addition. This is because C and F radicals are easily recombined to CF_4 after thermal decomposition. The maximum DRE of 97% was achieved with the steam flow rate of 2.0 L/min. High flow rate of steam leads to strong oxidation atmosphere, therefore C and O combine to form stable CO and CO_2. In addition, highly reactive F radicals were recovered by forming HF.

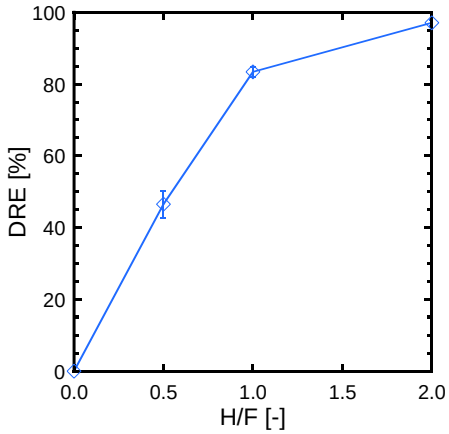

Figure 1 Effect of H/F ratio on the DRE. CF_4 flow rate: 0.5 L/min, H_2O flow rate: 0.0, 0.5, 1.0, and 2.0 L/min.

Figure 2 shows the mass spectra of the produced gases. The peaks of CF_3^+ were decreased with the increase of H/F ratio. NO^+ peak was detected only at H/F=2.0. A strong oxidizing atmosphere promoted the decomposition of CF_4 and generation of nitrogen oxides.

The recombination mechanism of CF_4 after plasma decomposition is discussed here on the basis of thermodynamic consideration. Recombination temperature of HF is 4,740 K, while that of CF is 4,670 K, estimated from the temperature dependence of Gibbs free energy change. This small difference of recombination temperatures suggests that the recovery of F radicals by H is difficult due to the competitive reaction of CF recombination. In contrast, the recombination temperature of CO is 7,600 K. This fact indicates that the recovery of C by O radical is a key reaction to suppress CF_4 recombination.

CF_4 was successfully decomposed by long DC arc with sufficient steam addition. The DRE was increased with an increase of the H/F molar ratio and oxidizing atmosphere. Long DC arc system is expected to play an active role in the semiconductor industry due to the ability to decompose alternative PFC gases completely.

References

[1] S.H. Chen, et al., J. Fluorine Chem. **217**, 41-49 (2019).
[2] S. Choi, et al., J. Chem. Eng. Jpn, **46**, 201-208 (2013).

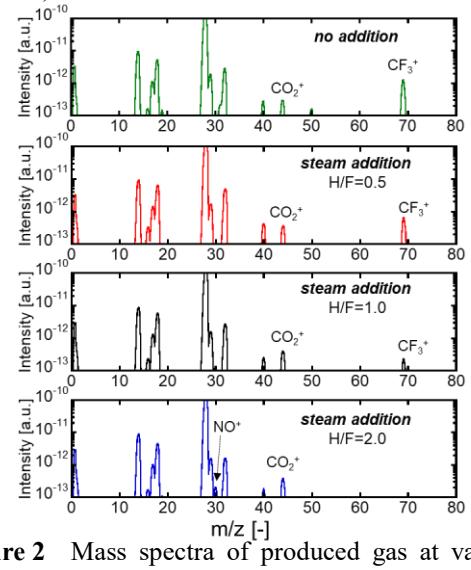

Figure 2 Mass spectra of produced gas at various H/F ratio; H/F=0.0, 0.5, 1.0, and 2.0.