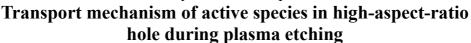
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## I. Introduction

The demand for microfabrication technology has been increasing as semiconductor devices become three-dimensional (3D) structures. In particular, plasma etching processes for 3D structure are required with high aspect ratio holes and without their shape abnormalities. [1] Hot neutrals generated by charge transfer on sidewalls surface in a hole play an important role for improvement of etching rate. Furthermore, the etching rate had been significantly improved at lower substrate temperature region, which suggests that this is due to a unique transport and adsorption mechanism of active species on the surface in the hole. However, there have been few experimental reports of the transport mechanisms of reactive species from the gas phase to the surface and in the holes. Simulation-based studies are actively uncovering particle transport and reactions inside these holes, which are difficult to measure.[2] The models use approximate values for the sticking probability of radicals on sidewalls, which is often set based on the number of unpaired electrons of radicals. We have developed a new measurement method to quantitatively determine the sticking probability of radicals on sidewalls of HAR interior using quadruple mass spectrometer (QMS). This method paves way for establishing effective measurement methods of the sticking probability and contributing accuracy of the simulation-based studies involving particle transports of HAR features.

### II. Method and Experimental

Passing probability of radicals through cylindrical pipes with aspect ratios of 1, 5, and 10 was calculated by a Monte Carlo simulation.[3] Ballistic transports and the Bernoulli scheme on reflection at interior wall were assumed. Typically, ten million particles were traced until convergence.

A mixed gas of C<sub>4</sub>F<sub>8</sub>/Ar/O<sub>2</sub> was introduced into a capacitively coupled plasma (CCP) apparatus A QMS was installed on the CCP apparatus. By varying the aspect ratio of the orifice at the QMS entrance,

radicals passed through orifices with different aspect ratios in measurements. This method is named Aspect Ratio-Resolved Mass Spectrometry (ARMS). Transmission amounts of CF, CF<sub>2</sub>, CF<sub>3</sub>, and  $C_2F_4$  were measured by the ARMS method.

The passing probabilities were calculated. The results indicate that the passing probability of radicals through a cylindrical pipe decreases with increasing aspect ratios.

# III. Results

For the same aspect ratio, particles with a higher sticking probability exhibit a lower passing probability. The sticking probability for representative radicals were determined by fitting the trends of aspect ratios of each by the simulation results. The sticking probability for the CF<sub>3</sub> radical was estimated to be 0.006. Similarly, the sticking probabilities for other representative neutral particles, CF, CF<sub>2</sub>, and C<sub>2</sub>F<sub>4</sub>, were estimated on the polymer film deposited inside the orifice. From the estimated sticking probabilities, it was calculated that the rate at which CF, CF2, and CF<sub>3</sub> reach the bottom of a hole with aspect ratio of 100 decreases by 10<sup>-5</sup>. Furthermore, it was quantitatively estimated that the composition of the polymer film formed by the C<sub>x</sub>F<sub>y</sub> particles on the sidewall becomes F-rich the deeper region into the hole.

# IV. Conclusion

This method paved way for establishing effective measurement methods of the sticking probability and contributing accuracy of the simulation-based studies involving particle transport of HAR features.

#### References

- [1] T. Ueyama et al., Jpn. J. Appl. Phys., 56, 06HC03 (2017)
- [2] S. Huang et al., J. Vac. Sci. Technol. A, 37, 031304 (2019)