Analysis of F loss during the chemical dry etching of Si using NO and F\textsubscript{2} gases (II)

O. Tajima\textsuperscript{1}, T. Hayashi\textsuperscript{1}, K. Ishikawa\textsuperscript{1}, M. Sekine\textsuperscript{1}, M. Sasaki\textsuperscript{2}, K. Yamakawa\textsuperscript{3}, and M. Hori\textsuperscript{1,3}

\textsuperscript{1}Satomi Tajima, Toshio Hayashi, Kenji Ishikawa, Makoto Sekine, Minoru Sasaki, Koji Yamakawa, and Masaru Hori, Nagoya Univ., Toyota Tech. Inst., Katagiri Engineering Co., Ltd.

E-mail: stajima@plasma.engg.nagoya-u.ac.jp

**Introduction** We have been developing a large-scale Si chemical dry etching apparatus using the reaction of F\textsubscript{2} + NO → F + FNO for the MEMS sacrificial layer etching and the Si surface morphology modification of solar panels. Maintaining the F density at the proximity of the Si surface is critical to conduct a reliable etching process. However, the F is lost in the gas phase, at the Si surface, and on the chamber wall. In our previous study, we reported the existence of the critical number of collisions in the gas phase, \( n \), to obtain the maximum F density.[1] In this study, we evaluated the F loss at the Si surface by varying the sample size of the wafer. We also calculated the possible chemical reaction between the Si surface and molecules present in the gas phase by density functional theory (DFT) to elucidate the contribution of the etched product to the Si etching at the downstream of the nozzle.

**Experimental** Various sizes of Si samples in the range of 6 x 10 mm\textsuperscript{2} ~ 10 x 100 mm\textsuperscript{2} were prepared. Those samples were exposed to Ar/NO/10\%F\textsubscript{2} for 5 min while maintaining the pressure at 600 Pa and varying the distance from the gas mixing point to the sample surface, \( d \), from 30 to 70 mm in the etching apparatus shown in Fig. 1(a). The vertical etch rate, \( E_v \), was measured by scanning electron microscopy (SEM) and plotted with respect to the \( d \). Also, we performed the DFT calculation to evaluate the chemical reaction between SiF\textsubscript{4}, FNO, and Si with CAM-B3LYP/6-311+G(d,p) in Gaussian 09 program. The detailed calculation procedure was described elsewhere.[2, 3]

**Results & Discussion** Figure 1(b) shows the relationship between the \( E_v \), measured from two different sizes of Si samples (named as Sample A: 6 x 10 mm\textsuperscript{2}, Sample B: 10 x 50 mm\textsuperscript{2}), \( n \), and \( d \). The \( E_v \) measured at \( d = 30 \sim 33 \) mm were almost the same for two different samples. \( E_v \) up to \( d = 33 \) mm from the Sample A and up to \( d = 40 \) mm from the Sample B were proportional to the \( n^{-1} \sim 1/d^2 \). \( E_v \) dropped sharply at the downstream and did not have any correlation with respect to \( n \) and \( d \). As the sample size increased, the \( E_v \) became high at the downstream. This phenomenon was opposite from the previous study of stating the loading effect[4] so that the etched product may promote the etching process at the downstream. Preliminary DFT calculation results show that the SiF\textsubscript{4} could react with two FNO to form SiF\textsubscript{4}(FNO)\textsubscript{2} (see Fig 1(c)). This molecule and Si would form SiF-FNO and SiF\textsubscript{2}-FNO. A SiF\textsubscript{4}-FNO could be formed by reacting the incoming F to complete the etching process. The SiF\textsubscript{4} may act as a FNO scavenger from the gas phase. The further investigation of this calculation result is in progress.


**Acknowledgement** This research was partially funded by Seeds Validation, Feasibility study stage of A-step, JST, Grant-in-Aid for Challenging Exploratory Research 25600123 funded by MEXT/JSPS, Japan, and Sumitomo Seika Chemicals Co, Ltd.