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NOとF_2を用いたSiケミカルドライエッチング中のF失活過程の解析(II)

Analysis of F loss during the chemical dry etching of Si using NO and F_2 gases (II)

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【Introduction】 We have been developing a large-scale Si chemical dry etching apparatus using the reaction of F_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^2 ~ 10 x 100 mm^2 were prepared. Those samples were exposed to Ar/NO/10%F_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_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^2, Sample B: 10 x 50 mm^2), n, and d. The E_V measured at d = 30 ~ 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} ~ $1/d^2$. 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_4 could react with two FNO to form $SiF_4(FNO)_2$ (see Fig 1(c)). This molecule and Si would form SiF-FNO and SiF_3-FNO. A SiF_4-FNO could be formed by reacting the incoming F to complete the etching process. The SiF_4 may act as a FNO scavenger from the gas phase. The further investigation of this calculation result is in progress.

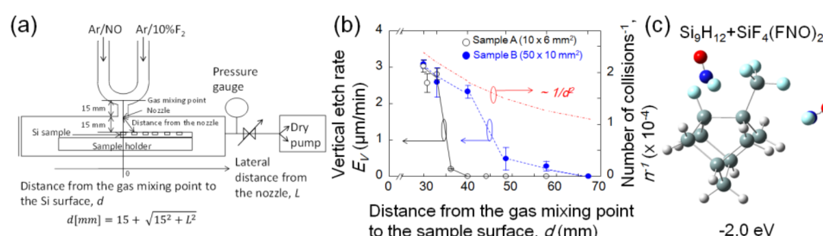

Fig. 1 (a) The Si etching apparatus, (b)The relationship between the vertical etch rate, E_v, the number of collisions, n, and the distance from the gas mixing point to the sample surface, d. (b) The chemical bonding structure of Si_9H_{12}+$SiF_4(FNO)_2$.

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