NO_2 を用いた Si 系材料の低速ケミカルドライエッチング中の表面反応

Surface reaction during the slow Si etching using F_2 and NO_2

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【**Introduction**】We have been investigating Si chemical dry etching using the F generated from the reaction of $F_2 + NO_2 \rightarrow F + FNO_2$ to remove the plasma-induced damaged layer around the gate electrode [1-3]. Previously we evaluated the gas phase reaction of F_2 and NO_x (X = 1, 2) using the density functional theory and found that generation of F was significantly low when NO_2 was used instead of NO due to the restriction of the reaction space by the presence of two oxygen[3]. Furthermore, the reproducible Si etching by $F_2 + NO_2$ is challenging since the NO_2 tend to be lost by the reaction of $2NO_2 \leftrightarrow N_2O_4$. [4] Our preliminary results show that maintaining the gas line and the chamber wall temperature is much critical when Si etching was performed using NO_2 instead of using NO. In this study, we varied the chamber wall and the substrate temperature separately and evaluated the change in etch rate and the surface reaction to obtain the reproducible ~nm/min slow etching.

【**Experimental**】p-type and non-doped Si(100) 10 x 10 mm^2 samples were prepared and placed in the Pyrex tube etching apparatus. The total of 107 sccm of Ar/10%F_2 + NO_x were introduced to the etching apparatus and the pressure was maintained at 600 Pa during the process time of 30 ~ 60 min. The chamber was heated at 80 °C while the substrate temperature was varied from 150 ~ 350 °C. The vertical etch rate, E_V, was measured by scanning electron microscopy (SEM) and the surface chemical bonding structure was measured by Fourier transform infrared spectroscopy (FTIR).

【**Results & Discussion**】Figure 1(a) shows the preliminary results of the E_V with respect to the substrate temperature. The E_V obtained from the Si that was exposed to F_2 and NO_2 was in the range of 10 nm/min to 200 nm/min when the substrate temperature was varied from 150 °C to 350 °C. This E_V value was one to two order of magnitude smaller than the E_V obtained from the Si exposed to F_2 + NO. Figure 1(b) shows the FTIR spectra measured from the non-doped Si samples exposed in $F_2 + NO_x$. Si-F stretching peak was not observed but Si-O stretching peak position shifted to the low wavenumber and the peak width became broad when Si was exposed in F_2 and NO_2, indicating that the possible formation of Si-NO bond at the surface. Further investigation of the molecules present at the Si surface exposed in $F_2 + NO_2$ are in progress.

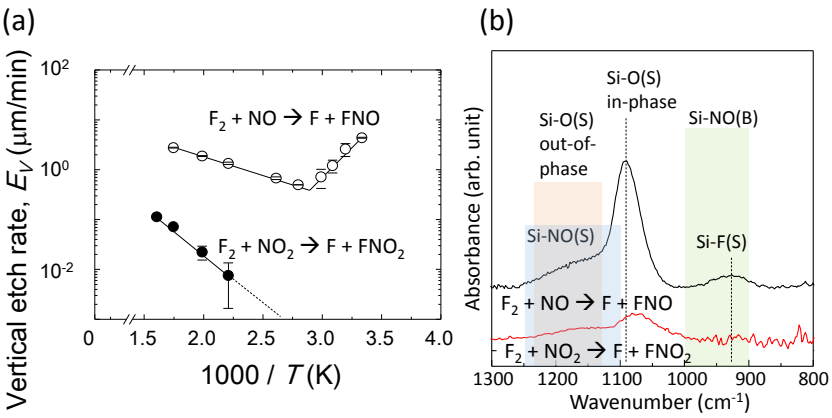

Fig. 1 The vertical etch rate, E_V (a) and the FTIR spectra (b) obtained from the Si etched in F_2 and NOx (X =1, 2) gases.

【**Reference**】 [1] Tajima *et al*. J. Phys. Chem. C **117** (2013) 5118. [2] Tajima *et al*. J. Phys. Chem. C **117** (2013) 20810. [3] Tajima *et al*. J. Phys. Chem. A 2015 in review. [4] L'Air Liquide, "Gas Encyclopededia," Elsevier, p.1065.

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