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NO_x (x=1 or 2) / F_2 混合ガスの高温下 Si ケミカルドライエッチング Si chemical dry etching in NO_x (x=1 or 2) / F_2 gas mixture at elevated temperature

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[Introduction] Si chemical dry etching can be used to texture the solar panel surface to reduce light reflections from the surfaces to increase the amount of light absorbed and converted into electricity [1]. We have previously reported that single crystal Si (100) can be etched using NO/F₂ gas mixture at the vertical etch rate, E_v , of ~ 5 µm/min utilizing F atoms generated by the reaction of F₂ + NO \rightarrow FNO + F at room temperature [2]. This E_v was comparable to that by XeF₂ [3]. In this study, we have evaluated E_v , etched profiles, and etched morphology of Si not only in NO/F₂ gases but also in NO₂/F₂ gases while modulating the substrate temperature and the total flow rate, f_{tot} .

[Experimental] 5 mm × 15 mm samples were cleaved from a p-type Si (100) wafer covered by 100-nm-thick SiO₂ mask with 8 μ m × 8 μ m square openings. Ar/NO_x (x = 1 or 2) /F₂ at f_{tot} of 50 to 250 sccm were introduced into the process chamber while maintaining the process pressure at 600 Pa throughout the process time of 300 s.

[Results and Discussion] Figure 1 shows cross-sectional images of the etched Si. When Si was etched in NO/F₂ gas mixture at f_{tot} of (a) 109 and (b) 218 sccm at 300 °C, Ev and the etched profile did not change significantly. This indicates that chemically dissociative adsorption was not influenced on the surface etching reactions, in concerning that the residence time affects the chemical composition of such species as F₂, NO, F, and FNO. On the other hand, when Si was etched in NO₂/F₂ gas mixture, E_v was (c) ~2.3 nm/min at f_{tot} of 109 sccm, and (d) ~17 nm/min for 218 sccm at 300 °C. E_v using NO₂/F₂ gas were more than 3 orders of magnitude slower than that using NO/F₂. The low E_v is due to the difference in rate coefficient, k, where the k of NO₂ + F \rightarrow FNO + F is much smaller than that of NO + F₂ \rightarrow FNO₂ + F at 300 °C [4, 5]. Furthermore, we estimated total energies of F produced by the reaction of NO_x (x=1 or 2) + F by calculating with B3LYP/6-311G+(d) in *Gaussian 09*. Consequently, selection of the reactions of NO_x (x = 1 or 2) / F₂ will expand potential applications.



Fig.1 Cross-sectional SEM images after chemical dry etching of Si in Ar/NO/F₂ at total flow rates of (a) 109 sccm (b) and 218 sccm, and in Ar/NO₂/F₂ at total flow rates of (c) 109 sccm, and (d) 218 sccm. Etching was performed while maintaining the substrate temperature at 300 °C and the pressure at 600 Pa.

[References] [1] Koynov *et al.* Appl. Phys. Lett. **88** (2006) 203107. [2] Tajima *et al.* JSAP Spring 17p-A7-14; Fall 13a-F7-4 (2012). [3] Ibbotson *et al.*, J. Appl. Phys. **56** (1984) 2939. [4] Turnipseed *et al.*, J. Phys. Chem. **95** (1991) 6569, [5] Perrine *et al.*, J. Chem. Phys. **21** (1953) 2202.