



Real-time / *In-situ* Electron Spin Resonance Analysis of Chemical Reactions on Silicon-Nitride with CF₄ Gas Plasma

Nagoya Univ. ^{○(PC)} Y. Miyawaki, H. Wang, Y. Kondo, K. Ishikawa, K. Takeda, H. Kondo, M. Sekine, and M. Hori

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

Introduction -The fluorocarbon plasmas have been used in reactive ion etch processes for fabricating the high-aspect-ratio contact-hole (HARC) on SiO₂. There are needs of highly selective etch of SiO₂ over photoresist, SiN and Si; vertical profiles for deep hole; and suppression of RIE lag. Among these needs, C₅F₈ is able to improve selectivity of SiO₂ over SiN than C₄F₈ and used for the HARC etch process. When the C₅F₈ gas is used, high selectivity of SiO₂ to SiN and Si was not achieved, and the etching reaction of SiN and Si was not clarified. In this study, for understanding the etching reaction of SiN, we investigated active species on SiN surface for chemical reactions in the processes, and measured the DBs by using the real-time / *in-situ* electron-spin-resonance (ESR) to elucidate CF₄ plasma induced surface reactions.

Experimental result and discussion -To understand the etching reaction of SiN, we have used the real-time / *in-situ* ESR apparatus ^[1]. Plasma was generated by supplying 2.45 GHz microwave power of typically 50 W. A CF₄ gas flew a quartz tube and a total pressure was kept to approximately 100 Pa. At the position of ESR cavity, SiN film on a quartz rod inside the quartz tube was inserted. By this means, DB formed via the SiN surface reactions was measured by the real-time / *in-situ* ESR. Figure 1 shows the ESR spectra of (a)

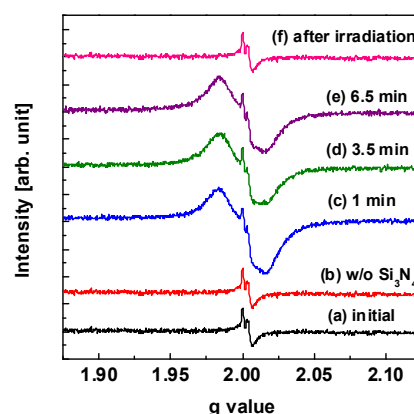


Fig. 1 ESR spectra of (a) initial, (b) during CF₄ plasma irradiation without SiN film for 1 min, (c) with SiN film for 1 min, (d) 3.5 min, (e) 6.5 min, and (f) after CF₄ plasma irradiation with SiN film.

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after CF₄ plasma irradiation with SiN film. During CF₄ plasma irradiation (b and c), the broad ESR signals due to a-C DBs in a fluorocarbon films were clearly observed with SiN film, but the broad ESR signals were not observed without SiN film. With the passage of plasma irradiation time, the peak intensity around g value of 2.0 – 2.012 slightly decreased. After plasma irradiation (d), the broad ESR signals were not observed on SiN film. At the same time, we investigated the ESR spectra around g value = 1.19 – 1.25, due to F atoms, and the ESR signals of F atoms disappeared after plasma irradiation. From this result, on SiN film surface, a-C DBs were formed by CF₄ plasma irradiation. In other words, a-C DBs were formed on SiN surface by F atoms reaching to SiN surface.

[1] K. Ishikawa *et al.*, J. Phys. Chem. Lett. **2**, 1278 (2011).