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Supplementary information

Clean SiO_2 Atomic Layer Etching based on Physisorption of High Boiling Point-Perfluorocarbon

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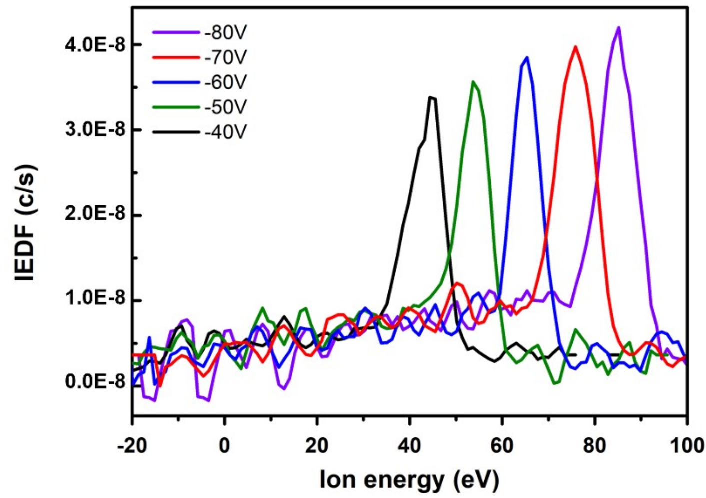

Fig. S1 IEDFs of Ar^+ ions (input 60 MHz bias voltage of - 40 ~ - 80 V)

Fig. S1 shows the Ar^+ ion energy distribution function (IEDF) at the center of the substrate using an RFEA (retarding field energy analyzer; Impedance, Semion) with the Ar plasma (bias voltage of -40 ~ -80 V). During the measurements, monoenergetic Ar^+ ion distributions were observed because a high bias frequency of 60 MHz was used to minimize the energy split of IEDF for anisotropic etching of SiO_2. It is believed that the monoenergetic distribution of the Ar^+ ions can control the fluorocarbon layer deposited on the SiO_2 and Si_3N_4 precisely during the HBP ALE process.

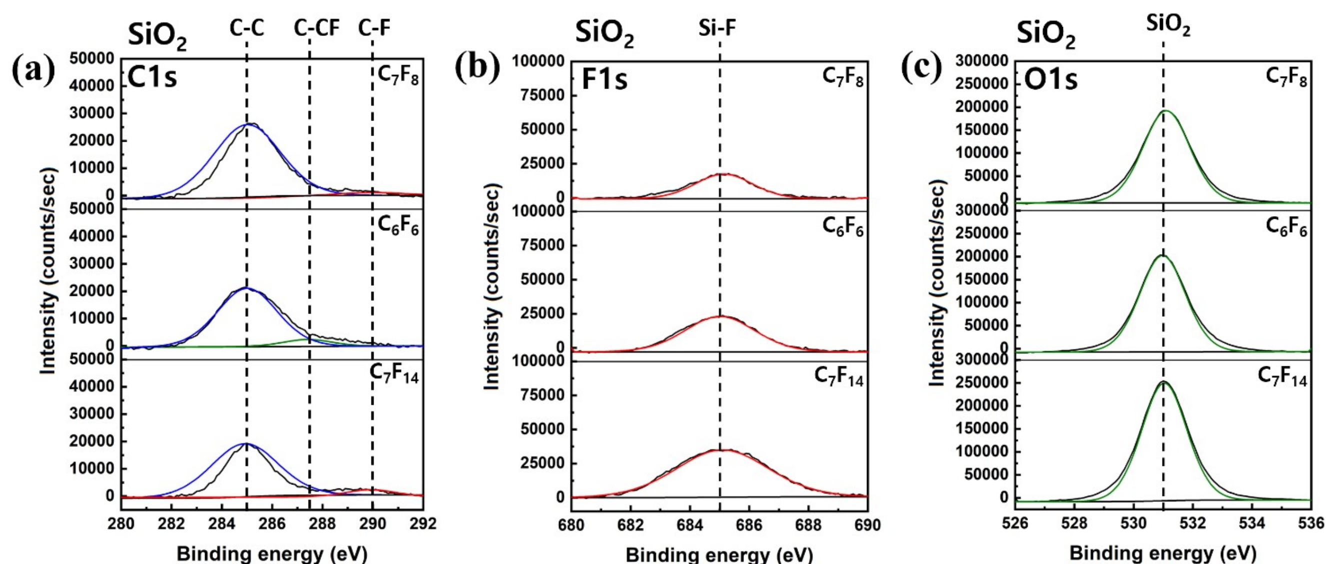

Fig. S2 (a) C1s, (b) F1s, and (d) O1s XPS narrow scan spectra of SiO_2 surface after ALE process (for 70 cycles) using C_7F_{14}, C_6F_6, and C_7F_8 at the optimized process conditions. The temperature of all substrates was maintained at -15 °C.

The binding states of carbon, fluorine, and oxygen on the surfaces of SiO_2 after the ALE processes investigated using XPS. SiO_2 samples were etched at the following conditions; for C_7F_{14} with the bias voltage of -50 V, for C_6F_6 with bias voltage of -70 V, and for C_7F_8 with the bias voltage of -80 V while the adsorption time and the desorption time were maintained at 10 s and 5 s, respectively. Other process conditions are the same as those in Fig. 3. As shown, no significant differences in bonding states on the etched surfaces of SiO_2 were observed for F and O bonding peaks among different PFC gases except for C bonding states.

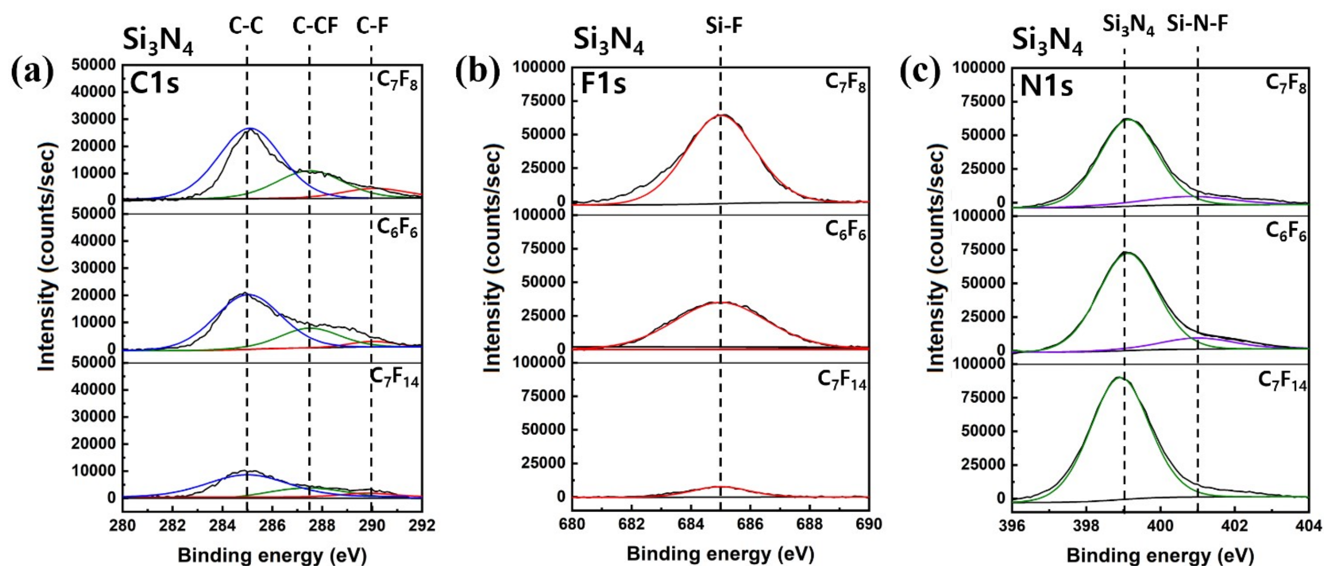

Fig. S3 (a) C1s, (b) F1s, and (d) N1s XPS narrow scan spectra of Si_3N_4 surface after ALE process (for 70 cycles) using C_7F_{14}, C_6F_6, and C_7F_8 at the optimized process conditions. The temperature of all substrates was maintained at -15 °C.

The binding states of carbon, fluorine, and nitrogen on the surfaces of Si_3N_4 after the ALE processes investigated using XPS. Si_3N_4 samples were etched at the following conditions; for C_7F_{14} with the bias voltage of -50 V, for C_6F_6 with bias voltage of -70 V, and for C_7F_8 with the bias voltage of -80 V while the adsorption time and the desorption time were maintained at 10 s and 5 s, respectively. Other process conditions are the same as those in Fig. 3. As shown, no significant differences in bonding states on the etched surfaces of Si_3N_4 were observed for F and N bonding peaks among different PFC gases except for C bonding states.

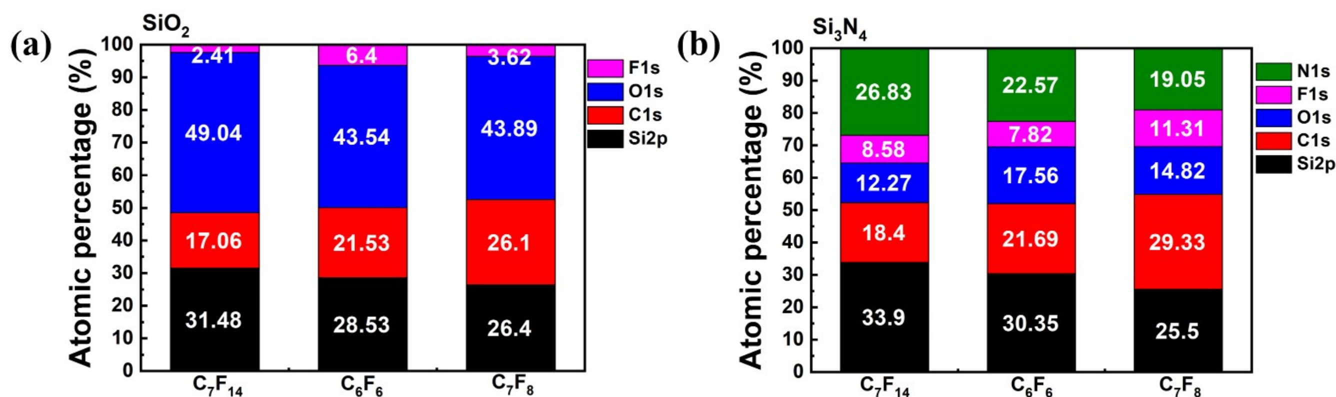

Fig. S4 Atomic percentages of (a) SiO_2 and (b) Si_3N_4 surface measured by XPS after C_7F_{14}, C_6F_6, and C_7F_8-ALE processes (70 cycles) at the optimized process conditions. The temperature of all substrates was maintained at -15 °C.

Atomic percentages of silicon, oxygen, carbon, fluorine, and nitrogen on the surfaces of Si_3N_4 after the ALE processes investigated using XPS. SiO_2 and Si_3N_4 samples were etched at the following conditions; for C_7F_{14} with the bias voltage of -50 V, for C_6F_6 with bias voltage of -70 V, and for C_7F_8 with the bias voltage of -80 V while the adsorption time and the desorption time were maintained at 10 s and 5 s, respectively. Other process conditions are the same as those in Fig. 3. As shown, the increase of carbon percentage on the etched SiO_2 surface and the increase of carbon and fluorine percentages on the etched Si_3N_4 surface were observed due to the thicker fluorocarbon layer formation in the sequence of C_7F_{14}, C_6F_6, and C_7F_8.

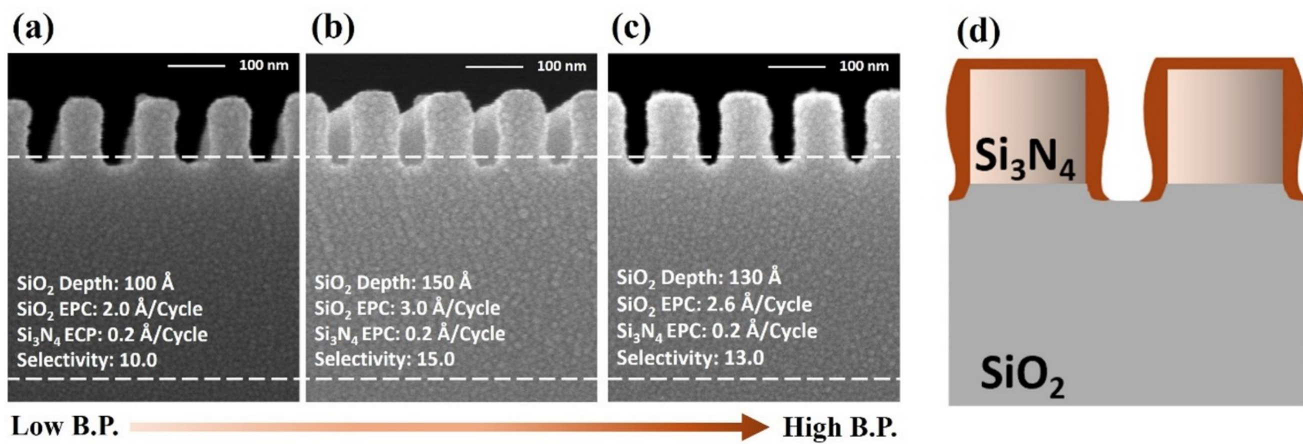

Fig. S5 SEM cross-sectional images of the Si_3N_4 masked SiO_2 sample after the ALE processes for (a) C_7F_{14}, (b) C_6F_6, and (c) C_7F_8 with the optimized process conditions in Fig. 4. (d) Schematic drawing showing a polymer formed at the sidewall of Si_3N_4 mask during the ALE cycles. The number of ALE cycles were 50 cycles. The temperature of all substrates was maintained at -15 °C.

When the ALE processes were performed for 50 cycles using the previously optimized conditions in Fig. 4 using C_7F_{14}, C_6F_6, and C_7F_8, due to the fluorocarbon deposition not only on the top of the Si_3N_4 masked SiO_2 but also on the sidewall of the Si_3N_4 mask, the SiO_2 EPC was decreased to 2.0 Å/cycle for C_7F_{14}, 3.0 Å/cycle for C_6F_6, and 2.6 Å/cycle for C_7F_8, and Si_3N_4 mask was thickened due to the deposition of fluorocarbon layer on the sidewall.