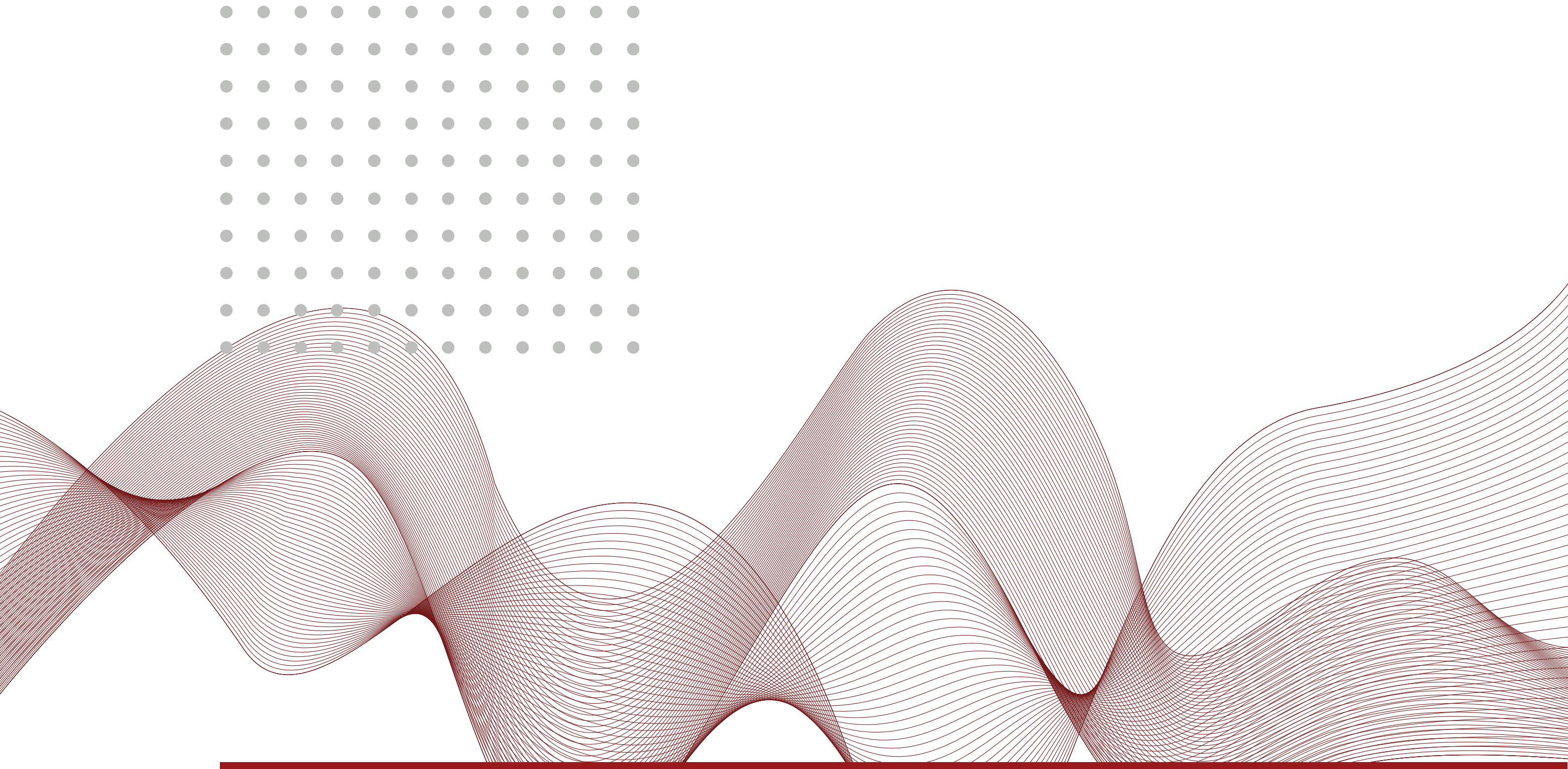

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Plasma Atomic Layer Etching of SiO_2 and Si_3N_4 with Low Global Warming $C_4H_3F_7O$ Isomers

Reference
Yongjae Kim, Hojin Kang, Changkoo Kim and Heeyeop Chae, ACS Sustainable Chem. Eng. 2023, 11, 6136−6142https://doi.org/10.1021/acssuschemeng.2c05186

Introduction

Atomic layer etching (ALE) is an important process for creating nano scale patterns as ALE can remove layers with atomic-scale precision, excellent uniformity, and atomic level surface roughness. ALE processes are typically operated with self-limiting cyclic processes that consist of surface modification and removal steps in a cycle accomplished via a variety of surface reactions. The conventional Perfluorocarbons used in ALE cycle have a very high global warming potential (GWP). The current study features a low-GWP C4H3F7O isomer plasmas for ALE process on SiO2 and Si3N4.Impedans made Octiv VI probe was used to measure bias potential on the substrate and build up a relationship between the etch rate and bias voltages.

Experimental setup

The cyclic ALE was studied in an inductively coupled plasma (ICP) reactor with a source power of 13.56 MHz and a bias power of 12.56 MHz, as shown in Figure 1 where the bias voltage was measured using a VI probe (Impedans, Octiv Poly). This study uses three isomers of C4H3F7O which are heptafluoropropyl methyl ether (HFE-347mcc3), heptafluoroisopropyl methyl ether (HFE-347mmy) and Perfluoropropyl carbinol (PPC) and argon plasma for fluorination and etching steps.

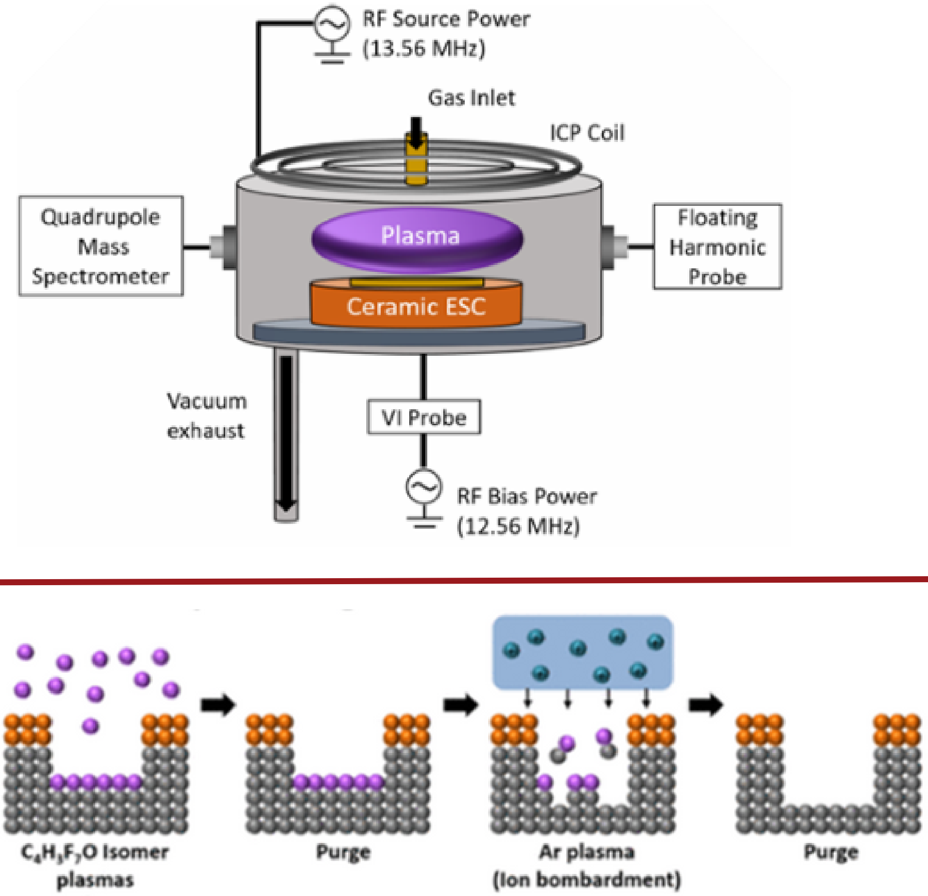

Figure 1 (above) Schematic of the ICP reactor and (below) atomic layer etching process

Results

As shown in Figure 2, the etch per cycle (EPC) of SiO2 was investigated as a function of the bias voltage of the Argon plasma. Depending on the ion energy during the etching step, three distinct regions were identified: the incomplete etch region, the ALE window region, and the physical sputtering region. At a bias voltage of less than 50 V, an incomplete etch region was observed for all of the C4H3F7O isomers. At bias voltages ranging between 50−60 V, the ALE window regions or constant EPC were observed in all C4H3F7O isomers. The physical sputtering region was observed at 60V, which is comparable to the previous SiO2 etching result using Ar plasma.

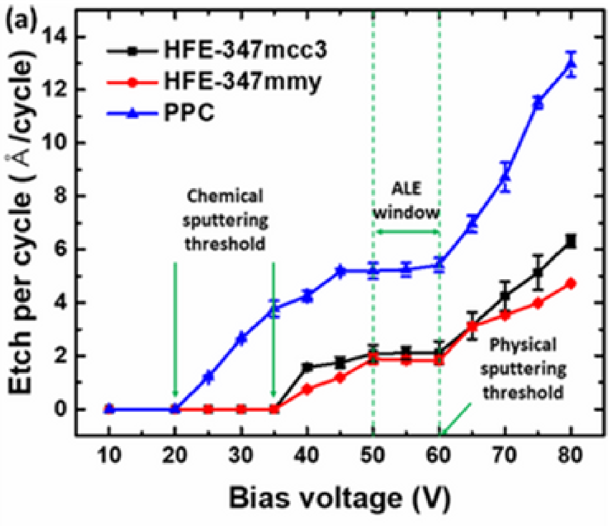

Figure 2 Etch per cycle of SiO2 in the fluorination step using C4H3F7O isomers as a function of bias voltage.

The EPC of Si3N4 for C4H3F7O isomer plasmas was also investigated as a function of Ar plasma bias voltage, as shown in Figure 3. The chemical sputtering threshold energy of Si3N4 was determined to be 15 V for the PPC plasma and 25V for the HFE-347mcc3 and HFE-347mmy plasmas. The ALE window regions were observed at bias voltages ranging from 50−60 V, as in the case of SiO2. Because of the hydrogen content, all C4H3F7O isomers have a higher EPC of Si3N4 than SiO2.

Results

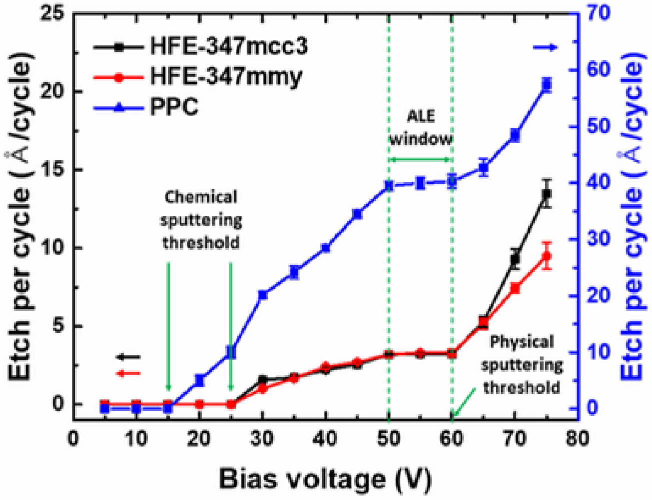

Figure 3 Etch per cycle of Si3N4 using C4H3F7O isomers in the fluorination step as a function of bias voltage in the etching step using Ar plasma. The etch per cycle of HFE-347mcc3 and HFE-347mmy is shown on the left y-axis, and that of PPC is shown on the right y-axis.

In the ALE process, high selectivity is one of the most critical factors in the etching process, and it is affected by the precursor, fluorocarbon film thickness, ion energy, and etching time. As shown in Figure 4, the etch selectivity of SiO2/poly-Si and Si3N4/poly-Si was investigated depending on the C4H3F7O isomer plasmas used in the fluorination step. The high etch selectivity of SiO2/poly-Si can be applied to the SiO2 etching process of fin field-effect transistor fin formation, and the high etch selectivity of Si3N4/ poly-Si can be applied to the Si3N4 spacer etching process.

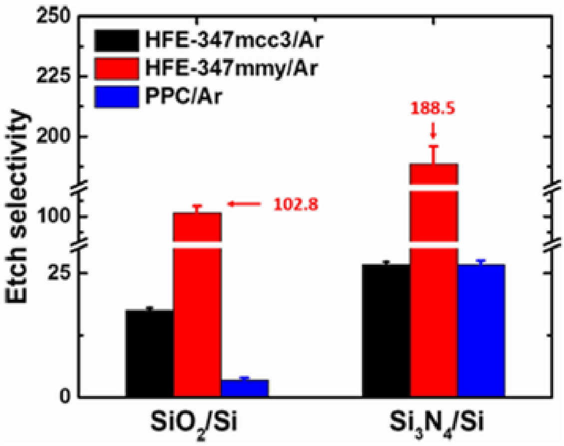

Figure 4 Etch selectivity of SiO2/poly-Si and Si3N4/poly-Si depending on the precursor in the fluorination step.

Summary

In this study, an ALE process for SiO2 and Si3N4 was developed and characterized as a cyclic process consisting of surface fluorination and etching steps using low-GWP C4H3F7O isomer plasmas. Owing to the hydrogen contained in the C4H3F7O isomers, the chemical sputtering threshold energy of Si3N4 is observed to be 5−10 V lower than that of SiO2. The ALE window region was identified in all C4H3F7O isomers at bias voltages ranging from 50−60V and the EPC of Si3N4 was higher than SiO2. The C4H3F7O isomers can be used to reduce the global warming effect in the ALE process while also achieving high etch selectivity of SiO2/poly-Si and Si3N4/poly-Si.