An Evaluation of 1,3,3,3-Tetrafluoropropene as a Low Global Warming Potential Silicon Dioxide Etch Gas at the Cornell NanoScale Facility

CNF Project Number: Cornell NanoScale Facility Staff Research
User(s): Aaron Windsor, Robert G. Syvret, Jeremy Clark, and Ron Olson

Affiliation(s): Cornell NanoScale Facility, Cornell University; EFC Gases & Advanced Materials

Primary Source(s) of Research Funding: National Science Foundation under Grant No. NNCI-2025233

Contact: windsor@cnf.cornell.edu

Research Group Website: https://www.cnf.cornell.edu/

Primary CNF Tools Used: Oxford Plasmalab System100 ICP RIE system, SUSS MicroTec Gamma cluster tool, ASML PAS 5500/300C DUV Wafer Stepper, Oxford PlasmaLab 80+ RIE System, SCE-110-RF Anatech Plasma Etcher, FilMetrics F50-EXR Optical Measurement System, Zeiss Ultra Scanning Electron Microscope, B2 Thermal Oxide LPCVD Furnace Tube

Abstract:

Currently, fluorocarbon (FC) and hydrofluorocarbon (HFC) gases are the primary choice for high aspect ratio etching of dielectric materials. The reason for this is that among the known and commonly used gases, one has access to a wide range of F:C ratios, e.g. from 4:1 in CF_4 to 1:1 in CHF_3, as well as great structural diversity including straight-chain and cyclic saturated alkanes (e.g., CH_2F_2 and C_4F_8), unsaturated alkenes (e.g., C_3F_6 and C_5F_8) and dienes (e.g., C_4F_6). These diverse characteristics provide a wealth of tunable options related to the aggressiveness of radical species generated in a plasma environment as well as, in some cases, important protective deposition properties of the resulting plasma fragments. Furthermore, each of the FC and HFC gases are readily available in high purity. However, despite all the positive attributes of FC and HFC gases, most have in common a serious downside, and that is related to their chemical and thermal stability. Most of the FC and HFC gases have a high global warming potential (GWP) and are damaging to the environment, and as a result, they are targeted for phase down and possibly eventual elimination through regulatory vehicles such as the U.S. AIM Act of 2021 [1].

One potential alternative to the use of FC and HFC gases is the use of low-GWP hydrofluoroolefins (HFOs). These HFOs have been developed by the fluorochemical industry and commercialized over the last decade or longer to replace high-GWP environmentally damaging refrigerants such as HFC-134a and foam expansion agents such as HFC-245fa. Amongst the known low-GWP HFOs one can find a range of F:C and H:C ratios. Thus, this group presents a potentially viable and environmentally friendly alternative to the use of legacy FCs and HFCs [2]. After promising initial tests etching blanket SiO_2 with the HFO 1,3,3,3-Tetrafluoropropene ($C_3H_2F_4$), the logical next step was to attempt real-world etches of patterned micron and submicron lines. This work will compare SiO_2 etches using the environmentally friendly alternative $C_3H_2F_4$ with saturated alkane legacy gases trifluoromethane (HFC-23, CHF_3) and difluoromethane (HFC-32, CH_2F_2).

Experimental:

Approximately 500 nm and 1000 nm of wet thermal oxide were grown on 100 mm diameter, 550 μm thick, single side polished, P-type prime silicon wafers. All dielectric etches were done on an Oxford PlasmaLab 100 inductively coupled plasma (ICP) reactive ion etch (RIE) system. Both $C_3H_2F_4$ and CH_2F_2 were individually introduced through the gas ring just above the wafer on the electrode.

An automated SUSS MicroTec Gamma cluster tool and an ASML PAS 5500/300C DUV Wafer Stepper were used for all photolithography processing. Wafers were coated with approximately 62 nm of DUV 42P antireflective coating (ARC) followed by approximately 600 nm of DUV 210 positive photoresist, baked at 135°C for ninety-seconds and developed with AZ MIF 726 developer for sixty-seconds. Patterned etched features consisted of eight 5000 μm lines with widths between 5 μm and 300 nm. 40 μm x 400 μm "L" shaped corners were added to the CAD for the profilometer measurements. After development, each wafer was etched with an Oxford PlasmaLab 80+ RIE System to remove the ARC. A ten-minute oxygen plasma chamber clean and two-minute etch on a bare silicon wafer was done to season the chamber before etching with the process gas. For comparison, all three

Table 1: $C_3H_2F_4$ Silicon Dioxide Etch Rates			
Etch Time (seconds)	Average SiO_2 Etch Rate (nm/min)	Average Resist Etch Rate (Angstrom/second)	Average Selectivity
45	208.9	6.5	5.37
120	206.3	5.7	6.04
150	212.6	6.2	5.79
240	210.8	5.2	6.84

Table 2: SiO_2 etch comparison between gases		
Two-Minutes		
Etch Gas Groups	Average SiO2 Etch Rate (nm/min)	Selectivity
$C_3H_2F_4$	206.3	6.04
CHF_3/O_2	182.5	1.51
CH_2F_2	158.7	2.24
Four-Minutes		
Etch Gas Groups	Average SiO2 Etch Rate (nm/min)	Selectivity
$C_3H_2F_4$	210.8	6.84
CHF_3/O_2	181.3	1.55
CH_2F_2	158.4	2.63

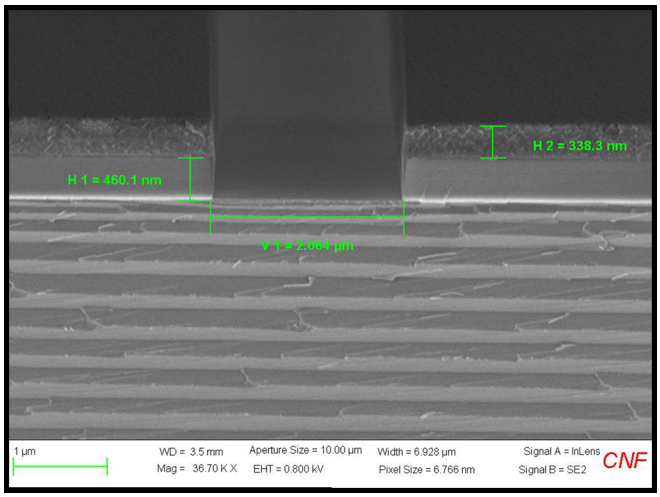

Figure 1: 2000 nm silicon dioxide line etched with $C_3H_2F_4$ for 160 seconds. SEM image was taken at a 70-degree angle. The actual calculated thicknesses are approximately Height #1 (SiO_2) = 487nm and Height #2 (Photoresist)= 359 nm.

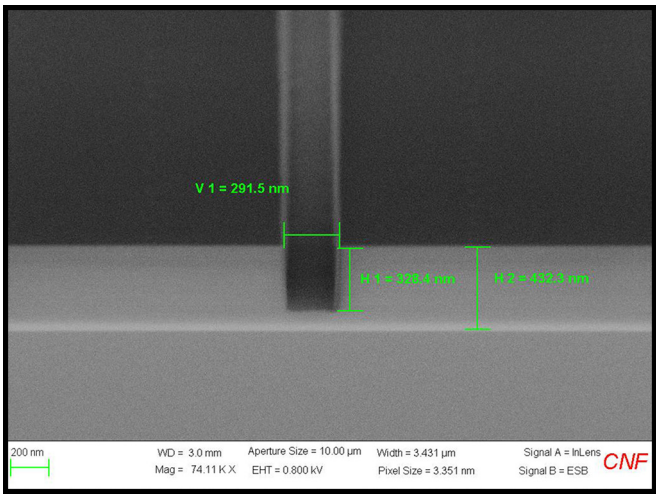

Figure 2: 300 nm silicon dioxide line etched with $C_3H_2F_4$ for 120 seconds. The photoresist was stripped. SEM image was taken at a 70-degree angle. The actual SiO2 calculated thicknesses are approximately Height #1 = 348 nm and Height #2 = 458 nm.

gases etched patterned wafers for two and four minutes. Feature etch rates/selectivity were determined using a KLA Tencor P-7 Stylus Profilometer by measuring an automated programed sequence of twenty step heights across the wafer. The three step heights measured were the height of the DUV 210 resist after the ARC etch, the step height after the dielectric etch, and the step height of the etch after the resist was stripped in an oxygen plasma using a SCE-110-RF Anatech Plasma Etcher. The selectivity was determined by the ratio between the SiO_2 and photoresist etched. Cross-sectional etch profiles were observed using a Zeiss Ultra scanning electron microscope (SEM).

Results:

Four separate $C_3H_2F_4$ patterned etches between forty-five and two hundred forty seconds established consistent etch rates and etch selectivity for DUV 210 resist (Table 1). When compared to the two legacy gases (Table 2), $C_3H_2F_4$ had the highest etch rate for SiO_2. The desired selectivity between the oxide and the resist was much higher than etches using trifluoromethane and difluoromethane. Cross-sections of all $C_3H_2F_4$ patterned SiO_2 etches appear to have smooth, vertical sidewalls, without signs of resist undercutting (Figure 1). There was evidence of RIE lag for the narrower features (Figure 2). Overall, these etch tests demonstrated that $C_3H_2F_4$ is a viable alternative for reactive ion etching SiO_2.

References:

[1] Environmental Protection Agency. (2024, January). Final Rule – Phasedown of Hydrofluorocarbons: Establishing the Allowance Allocation and Trading Program under the American Innovation and Manufacturing (AIM) Act. EPA. https://www.epa.gov/system/files/documents/2021-09/hfc-allocation-rule-nprm-fact-sheet-finalrule.pdf.

[2] Cynthia B. Rivela, Carmen M. Tovar, Mariano A. Teruel, Ian Barnes, Peter Wiesen, María B. Blanco, CFCs replacements: Reactivity and atmospheric lifetimes of a series of Hydrofluoroolefins towards OH radicals and Cl atoms, Chemical Physics Letters, Volume 714, 2019, Pages 190-196, ISSN 0009-2614, https://doi.org/10.1016/j.cplett.2018.10.078.