

Etching Fused Silica with Low Global Warming Potential HFO-1234ze(E)

CNF Project Number: MENG CNF

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Primary CNF Tools Used: ABM Mask Aligner, AJA Sputter 1, AJA Sputter 2, Glen 1000 Resist Strip, KLA P7 Profilometer, Oxford 100 ICP, PT 720-740 RIE, Zeiss Supra SEM, Zeiss Ultra SEM

Abstract:

The semiconductor industry is currently having to reevaluate reactive ion etch processes to comply with the yearly reductions of hydrofluorocarbons (HFCs) mandated by the American Innovation and Manufacturing (AIM) Act. This, along with global supply chain concerns, has increased interest in the use of alternative etch gases, more specifically, replacing high global warming potential (GWP) gases such as difluoromethane (CH_2F_2), trifluoromethane (CHF_3) and other HFC legacy gases used for etching dielectrics. After demonstrating that the low GWP, hydrofluoroolefin, HFO-1234ze(E) (trans-1,3,3,3 tetrafluoropropene) is an effective etch gas for reactive ion etching thermal silicon dioxide (SiO_2), this work focuses on etching 10-20 μm deep microfluidic channels in amorphous SiO_2 , fused silica (FS). Early etch trials were promising but etches deeper than 1 μm would result in polymer deposition in the channels. By increasing the DC bias applied to the electrode, channels could be etched beyond 1 μm . At a DC Bias of 70 V, channels were etched over a depth of 9 μm with a chromium hard mask selectivity of 45:1.

Summary of Research:

The optical transparency of FS has always been an attractive option for high resolution microfluidic and micro-optic devices, but fabricating microstructures with FS is challenging, especially reactive ion etching deep channels. Hydrofluorocarbons (HFCs) such as CH_2F_2 and CHF_3 have been used in the past for reactively ion etching SiO_2 , but with the emergence of the American Innovation and Manufacturing (AIM) Act, semiconductor manufacturers are mandated to reduce their production and consumption of HFCs by 85% by 2036 (1-3). Our current geopolitical climate has further complicated the use of HFCs by creating global supply chain issues for semiconductor materials and gases. Combined, these issues have driven research into exploring possible replacements for HFC etch

gases. The CNF currently uses a CH_2F_2 recipe for deep FS etches. The ICP power is set at only 1500 W which lowers the etch rate (100nm/min) but maintains good chromium mask selectivity (43:1) for deeper etches. In the past, a CHF_3/O_2 was used but this recipe involved heating the power electrode from 10° C to 50° C. This recipe had a higher etch rate of 188nm/min, but a much lower chromium mask selectivity ($\approx 20:1$).

One potential alternative for the use of HFC gases is the use of low-GWP hydrofluoroolefins (HFOs) (4). HFOs are chlorine free, unsaturated organic compounds composed of carbon, hydrogen, and fluorine with at least one carbon double bond ($\text{C}=\text{C}$). Unlike the HFCs and other saturated halohydrocarbon refrigerants, HFO double bonds are molecularly less stable and have a significantly shorter atmospheric lifetime. (5)

In 2025, HFO-1234ze(E) (trans-1,3,3,3 tetrafluoropropene) was shown to be an effective etch gas for wet thermal oxide. (6) This work will be focused on etching between 10-20 μm microfluidic channels into FS using HFO-1234ze(E) and the effects DC bias has on etch rate, mask selectivity and wall angle.

Experimental

An AJA sputtering tool was used to deposit a 200nm chromium hard mask on four-inch FS wafers. The hard mask was patterned on an ABM contact aligner using Shipley 1813 photoresist. The chromium mask was reactively ion etched in a Plasmatherm 740. After removing the resist, the FS was etched on an Oxford PlasmaLab 100 ICP380 system using the same SiO_2 HFO etch recipe used in the 2025 paper (Table 1) with only the DC bias minimum changing. Channel depths were measured on a KLA P7 profilometer after each five-minute etch until the hard mask began to disappear. All final channel depths were measured after removing the remaining chromium by soaking in Transene 1020AC chromium etch.

Chamber Pressure	4 mTorr
HFO-1234ze(E)	20 sccm
Helium	80 sccm
Minimum DC Bias	30V
Forward Power	60W
ICP Power	3000W
Electrode Temperature	10° C

Table 1: Original SiO₂ Etch Recipe for HFO-1234ze(E).

Conclusions and Future Steps:

The initial five-minute etch using the original 2025 HFO recipe etched over 1µm of FS with an etch rate of 201.8nm/min. A channel depth of 3.1µm was achieved before the mask was etched through. For the next trial, the DC bias minimum was lowered from 30V to 20V with similar results after five-minutes of etching, but subsequent etches resulted in the channels filling with brown polymer. The polymer was removed in a high-power oxygen plasma, but the polymer would redeposit when the HFO recipe was run again. From literature, the polymer layer forms in the beginning of the etch as fluorine anions bond and passivate the SiO₂ surface. (7,8) Ions from the plasma then interact with the fluorinated surface resulting in polymer/FS removal. The ion energy can be influenced by increasing the DC bias of the etch. DC bias is the voltage difference between the plasma and the wafer surface that accelerates positive ions towards the power electrode and substrate. The Oxford 100 manual states that the RF generator toggles between the forward power and DC bias settings. (9) DC bias effects not only etch rate, but selectivity and the degree of sidewall angle. The original recipe's DC bias minimum was set at 20V so by increasing DC bias, the ion surface interactions should also increase, removing polymer and increasing etch channel depth. Table 2 illustrates the affect DC Bias had on FS etch depth and chromium mask selectivity. Both etch depth and selectivity increased as the DC bias increased up to 70V. At 70V, the channel depth was 9.1µm with a selectivity of 45:1. Above 70V, the selectivity decreased. This decrease could be due to insufficient neutral passivation or substrate heating which will reduce selectivity. (8) It is important to note that with all the DC bias changes, the etch rates were consistently ≈ 200nm/min. This demonstrates that the DC Bias effected the mask selectivity and not the FS etch rate. In addition, the

DC Bias (Volts)	Maximum Etch Depth (µm)	Selectivity to Chromium Mask
20	1.0	5:1
30	3.1	16:1
50	6.2	31:1
70	9.1	45:1
100	5.9	29:1
130	5.9	29:1

Table 2: The effects of DC Bias on fused silica channel etch depth etched and selectivity.

improved selectivity enabled deeper FS etches. A cross-section of the 70V DC bias etch measures a sidewall angle of the is 74.6° (Figure 1).

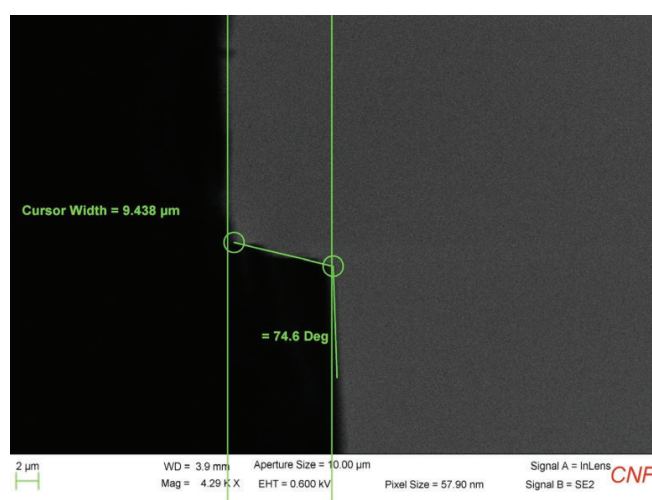


Figure 1: Cross-section of a 9µm fused silica channel etched with HFO-1234ze(E) (*trans*-1,3,3,3- tetrafluoropropene) with a DC bias minimum of 70V.

This work has demonstrated that HFO-1234ze(E) is an effective etch gas for FS. The established recipe has a higher etch rate and better selectivity than CH₂F₂ and CHF₃. The effects of increasing the ion bombardment/DC Bias are critical for etching beyond 1µm. Deeper etches may be achieved with different and/or thicker hard masks. In their 2015 paper, Pedersen and Huff were able to etch 100µm FS holes with a 20µm electroplated nickel hard mask. (7) Future work will examine the effects of including oxygen and argon into the plasma chamber that has on edge depth and sidewall angle.

References:

- [1] A. Windsor, J. Clark, G. McMurdy, E. Joseph, R. Syvert, R. Olson and J. Cha, J. Vac. Sci. Technol. B 43, 2 (2025).