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

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Primary CNF Tools Used: Oxford Plasmalab System 100 ICP RIE system, FilMetrics F50-EXR Optical Measurement System, B2 Thermal Oxide LPCVD Furnace Tube

Abstract:

Silicon dioxide (SiO_2) is one of the most common dielectric materials in the semiconductor industry. Not only is SiO_2 an excellent insulator for integrated circuits and transistors, but it is also an effective hard mask and can be easily patterned at the microscale. While the ability to reactively ion etch (RIE) precise anisotropic features is vital for the future of the industry, many of the etch gases used are reactive hydrofluorocarbons (HFCs) which are considered greenhouse gases (GHGs). These gases hinder the earth's ability to cool down by absorbing/redirecting shortwave radiation from the sun and reflecting longwave radiation admitted from the earth's surface. For the past fifty years, climate scientists have been concerned that GHGs may have varying effects on the warming of the planet. In 1987, the Montreal Protocol was finalized to phase out the use and consumption of ozone depleting gases (OFCs) such as chlorofluorocarbons (CFCs) and bromofluorocarbons (halons) [1]. HFCs were once developed as replacements for OFCs but were later found to be warming the atmosphere at a faster rate than carbon dioxide [2] which is why in 2016, the Kigali Amendment was adopted to the Montreal Protocol to include limits on their use worldwide. Most recently, the United States Congress has taken further steps to reduce HFCs by enacting the American Innovation and Manufacturing (AIM) Act. This grants the U.S. Environmental Protection Agency (EPA) the authority to phase down eighteen HFC gases they consider having high Global-Warming Potentials or GWP.

The Aim Act wants the production and consumption of HFCs to be reduced by 40% between 2024–2028 and 85% by 2036 [1,3].

To reduce their consumption of HFCs while expanding chip manufacturing throughout the United States, the semiconductor industry is seriously exploring the next generation of lower GWP gases for etching semiconductors and dielectrics such as SiO_2.

The hydrofluoroolefin (HFO) 1,3,3,3-Tetrafluoropropene ($C_3H_2F_4$) has been recommended as a substitute gas for etching SiO_2. HFOs are considered a promising environmentally friendly replacement for CFCs, halons, hydrochlorofluorocarbons (HCFCs) and HFCs as refrigerants and for other industrial processes [4]. These gases have high gas phase reactivity along with exchange values (numerically equivalent of 100-year GWP) much lower than legacy etch gases such as trifluoromethane (HFC-23, CHF_3) and difluoromethane (HFC-32, CH_2F_2) [5].

This work will investigate the viability of the unsaturated fluorocarbon $C_3H_2F_4$ for etching SiO_2 when directly exchanged for difluoromethane, a known saturated fluorocarbon etch gas (both gases supplied by Electronic Fluorocarbons). Repeated blanket SiO_2 films were etched with both gases as a direct comparison of etch rates and uniformity on 100 mm wafers. Difluoromethane etches were done before and after repeated $C_3H_2F_4$ etches to examine possible unwanted side effects this HFO may have on the etch chamber and/or future etches.

Experimental:

Approximately 500 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) RIE system that has dependable etched SiO_2 at the Cornell NanoScale Facility for over fifteen years. The etch parameter for both gases are illustrated

Table 1: Etching Parameters for Silicon Dioxide

$C_3H_2F_4$ or CH_2F_2	20 sccm
Helium	80 sccm
ICP	3000 W
RIE	60 W
Chamber Pressure	4 mTorr
Electrode Temperature	10 °C

Table 2: 100mm Silicon Dioxide Etch Trials

Etch Gas Groups	Average SiO2 Etch Rate (nm/min)	Standard Deviation (nm/min)
First CH_2F_2	135.26	0.5
$C_3H_2F_4$	160.85	1.1
Last CH_2F_2	133.46	0.65

in Table 1. Both $C_3H_2F_4$ and difluoromethane were individually introduced through a gas ring just above the wafer on the electrode. Helium is applied for backside wafer cooling.

Blanket silicon dioxide thicknesses were mapped on twenty-four wafers and divided into three, eight wafer groups. The first group of eight wafers were etched consecutively with difluoromethane for ninety seconds and mapped again for thickness. The second group of eight wafers were etched for ninety seconds with $C_3H_2F_4$ and the third group of eight wafers were etched again with difluoromethane. Before all three etch groups, a ten-minute oxygen plasma chamber clean and seasoned for two-minute with either difluoromethane or $C_3H_2F_4$. Full wafer mapping and mean etch rates were calculated by measuring film thicknesses before and after etching using a FilMetrics F50-EXR Optical Measurement System. Each wafer map was measured at twenty-five points with 10 mm edge exclusion and aligned to the wafer's flat. The final average etch rates were calculated by the average of the mean etch rates for all eight wafers in a group.

Results:

The full wafer etch test demonstrated that $C_3H_2F_4$ is an equivalent etch gas for SiO_2. The average mean etch rate is higher than difluoromethane (Table 2). The standard deviation was higher for $C_3H_2F_4$ than both difluoromethane runs. Further, the average etch rate was slightly lower and the standard deviation slightly higher for the last difluoromethane etch group than the first etch group. This demonstrates that a ten-minute oxygen clean is effective for cleaning the chamber after 720 seconds of $C_3H_2F_4$ etching and the unsaturated fluorocarbon does not display any obvious detrimental effects to the etch chamber or later etch processes. This first test was promising, but more work needs to be done in the future.

References:

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