Plasma Science and Technology
Room 315 - Session PS2-WeA

Low Global Warming Potential and Sustainability in Plasma Processing

Moderators: Hisataka Hayashi, Daikin Industries, Ltd., **Phong Nguyen**, Air Liquide

4:15pm **PS2-WeA-9 Impact of Low-GWP GST Etch Chemistries on PCM Device Performance and Reliability**, ***Luxherta Buzi,*** IBM Research*; Yohei Takakura, Kazunori Horiguchi,* DAIKIN INDUSTRIES, LTD.*; Aya Kagimura,* DAIKIN INDUSTRIES, LTD., Japan*; Asit Ray, Amlan Majumdar, Lynne M. Gignac, Matthew BrightSky, Jaylynn Sheppard,* IBM Research*; Yasuhiro Nojiri, Hisataka Hayashi,* DAIKIN INDUSTRIES, LTD., Japan*; Eric Joseph, Robert L. Bruce,* IBM Research

PCM is an emerging non-volatile memory technology for AI and Storage Class Memory applications due to its low power consumption, high density, and fast switching capability. Optimization of GST etch chemistry and process integration while minimizing structural and compositional damage is critical for reliable PCM device operation and long-term endurance. GST is commonly etched using halogen-based plasmas, where hydrofluorocarbons are often employed for sidewall passivation and profile control. However, due to the ongoing phase-out of high global warming potential (GWP) gases, development of low-GWP alternatives is becoming increasingly important for future PCM manufacturing.

In this work we report on the development and integration of GST reactive ion etch (RIE) processes using DIN01, a proprietary low-GWP chemistry, combined with Xe and Ar gas mixtures with and without passivating additives. DIN01/Xe and DIN01/Ar processes demonstrated good elemental composition and were successfully implemented on integrated PCM hardware. Electrical characterization showed excellent wafer yield, strong within-chip yield, fast SET speed, and high cycling endurance. PCM etch processes using DIN01/Xe gas mixtures exhibited superior electrical performance over DIN01/Ar mixtures.

Transmission electron microscopy (TEM) and chemical analysis were performed on DIN01/Xe etched devices and compared to a conventional PCM etch gas mixture. After approximately 20 programming cycles, similar electrical behavior and chemical evolution were observed for both process schemes without evidence of significant trace of gas residue. However, optimization is required to address poor etch selectivity to the SiN hard mask that leads to tungsten redeposition and oxidation in DIN01-patterned structures.

These results demonstrate that DIN01-based GST etch processes can successfully enable integrated PCM device operation and high yield while maintaining structural integrity and long-term device reliability.

4:30pm **PS2-WeA-10 A Low-GWP Molecule for High-Performance Plasma Etching**, ***Phong Nguyen,*** *Nathan Stafford, Xiangyu Guo,* Air Liquide

In recent years, several countries and semiconductor manufacturing companies have announced targets for net-zero carbon emission by 2050 or earlier. Plasma etch processes are responsible for a high percentage of a semiconductor manufacturer's scope 1 emissions. Dielectric plasma etch applications are pervasive in the manufacturing process, and are a significant contributor to these scope 1 emissions. These processes typically employ high global warming potential (GWP) fluorocarbon gasses such as C4F8. . Not only is C4F8 a high GWP gas, in addition hard to abate high GWP chemistries such as CF4 maybe formed in the plasma fragmentation process.

To address this challenge without sacrificing process capabilities, we introduce a novel low-GWP molecule (intrinsic GWP ~0) designed as a robust alternative to legacy etchants. This alternative chemistry is engineered to permit advanced plasma etch performance while providing a friendly abatement profile that substantially reduces overall direct CO2-equivalent emissions, whether evaluated post pump with no dedicated PFC abatement technology or post abatement systems designed to abate a portion of the PFC.

Characterization of the etch characteristics is done using an Ellipsometer for thickness and selectivity assessment. Furthermore, the plasma etch chamber emission gas stream is analyzed and quantified by Fourier Transform Infrared Spectroscopy (FTIR). Complementary to FTIR analysis, Quadrupole Mass Spectrometry (QMS), is implemented to help identify emission species in the chamber through studying the positive ion fragments present inside the plasma.

Results demonstrate that this novel molecule matches legacy etching rates while delivering improved selectivity to amorphous carbon (a-C) mask materials. The combination of analysis via QMS and FTIR gives us a better understanding of the etching process, confirming that this novel molecule yields beneficial deposition-promoting positive ions and crucially lacks the CF3 fragmentation pathways responsible for excessive CF4 generation. In addition, this novel chemistry has shown improved etch performance with lower CO2 equivalent emission than the current baseline.

4:45pm **PS2-WeA-11 Machine-Learning-Assisted Investigation of CF_3–X (X=H, I) Plasma Kinetics In Semiconductor Manufacturing for Etch Effectiveness and Environmental Sustainability**, ***Chi-Yun Lin,*** UCLA*; Junpin Yao, Mansour Moinpour, James Nehlsen,* EMD Group*; Elizaveta Kossoy,* Merck Group*; James Hie,* EMD Group*; Aditya Nandy, Jane Chang,* UCLA

Hydrofluorocarbons (HFCs) gases are commonly used in semiconductor manufacturing to etch silicon dioxide, an essential insulator in integrated circuits, either from chamber wall deposits or patterned features. CHF_3 plasma is utilized for its high etch rate (ER), comparable to CF_4, and favorable anisotropic etching characteristics, though its high global warming potential (GWP_{100}) of 12400 and long atmospheric lifetime (LT) of 222 have prompted its phasedown by the EPA. CF_3I has a lower atmospheric lifetime (<0.005) and GWP_{100} (<1), which are 4-5 orders of magnitude smaller than those of HFCs, making it a promising alternative gas.

This work investigates CF_3X-based plasmas (where X = H, I) in etching SiO_2 with a focus on machine learning to extract meaningful kinetic parameters for modeling. $CHF_3/O_2/Ar$ plasma was first used to evaluate the reduce and abate strategies. O_2 serves a dual role: process-gas additive to reduce the usage of CHF_3 for improving SiO_2 etching and abatement reactant for reducing high-GWP fluorocarbon emissions. The experimental and modeled SiO_2 etch rate increased with measured emission of SiF_4 (kg-CO_2e) and the modeled ratio of fluorine flux to oxygen flux (Γ_F/Γ_O), reaching above 150 nm/min under selected conditions. The corresponding downstream composition was converted to $MMTCO_2e$ for CHF_3, CF_4, and C_2F_6. After introducing O_2 to downstream abatement, the modeled $MMTCO_2e$ decreased by approximately a few orders of magnitude relative to the untreated emission.

$CF_3I/O_2/Ar$ was evaluated as a lower-GWP alternative. A differentiable surface-kinetic model was developed to infer the unknown iodine adsorption and abstraction probabilities, using experimental SiO_2 etch rates as the ground truth, while modeled ion fluxes and etch rates served as known inputs. Descriptor information from CF_3X (X = F, Cl, Br, and I), including C–X bond dissociation energy, Si–X bond strength, and electronegativity, was used to define physically reasonable bounds for the unknown iodine-related surface kinetics. Automatic differentiation through the ODE solver reduced the average absolute percent error from 23% for the initial assumption to 12.5% after applying new surface kinetic by AI/ML inference. As the SiO_2 etch rate increases from 50–80 nm/min to above 100–130 nm/min, the corresponding measured and modeled emission for CF_3I and CF_4 decreases by an order of magnitude in $MMTCO_2e$.

Overall, selected $CF_3I/O_2/Ar$ operating conditions showed the SiO_2 etch rate increased by approximately 70% while the estimated emission impact reduce by an order of magnitude, indicating that higher etch performance can be achieved with lower greenhouse-gas-equivalent emissions.

5:00pm **PS2-WeA-12 A Low GWP and Low Emission Gas for Trench and Hole SiO_2 Etching**, ***Scott Biltek,*** *Nathan Stafford, Phong Nguyen, Angéla Christin,* Air Liquide

Over the past few years, numerous countries and semiconductor manufacturing entities have unveiled their commitments to achieving net-zero carbon emissions by 2050 or even sooner. A substantial fraction of direct emissions (as CO_2e) in semiconductor manufacturing stems from plasma etch processes. Standard gases for dielectric etching such as C_4F_8, CH_2F_2, CHF_3 or CF_4 typically have high global warming potential (GWP) or emit high GWP byproducts after plasma fragmentation and recombination processes. While low GWP etch gases exist, it is challenging to find alternative gases that provide comparable etch process performance, with limited recipe development, that significantly decreases the direct CO_2e etch process emissions.

In previous work we have presented a novel low GWP etching gas as a replacement for C_4F_8 in high power, high aspect ratio etching[1]. In this work we revisit that gas as a replacement for C_4F_8 in lower power SiO_2 etches for

both trench and contact hole applications. In both applications, we once again demonstrate matching etch performance with minimal recipe modification (simply replacing C_4F_8 flow with an appropriate replacement gas flow rate). Due to the high efficiency in the dissociation of the replacement gas, this etch performance is achieved at a significantly lower flow rate relative to C_4F_8. In addition to the low intrinsic GWP_{100} of the low GWP gas (<50) compared to C_4F_8 (~10,200), we also show significant (~80%) reduction in GWP_{100} of the final post plasma exhaust emissions as measured via fourier transform infrared spectroscopy (FTIR). In combination with past results, this strongly indicates the broad compatibility of this low GWP gas with current C_4F_8 plasma etch processes.

[1] - Biltek, Scott, et al. "Low GWP and Low Emission Gases for High Aspect Ratio Etching." AVS 70th International Symposium & Exhibition, Nov. 2024, Tampa, FL. Conference Presentation.

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