Low Global Warming Potential Gases for the Reduction of Greenhouse Gas Emission in Plasma Etching Processes

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Heeyeop Chae, Prof., Ph.D.

School of Chemical Engineering,
Sungkyunkwan University **(SKKU)**

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The 17 th ROK-USA Forum on Nanotechnology:
Environmental Implications of Semiconductor Manufacturing

Heeyeop Chae

Heeyeop Chae

Chem Eng.
(ChemE)
& Institute of
Nano Tech.
(SAINT)

SKKU

- Education
  - B.S. in Chemical Engineering, Seoul National University
  - M.S. in Chemical Engineering, Seoul National University
  - Ph.D. in Chemical Engineering, M.I.T.
- Work Experience
  - Sungkyunkwan University (SKKU) (2004 ~ Present)
  - Applied Materials, Sr. Process Engineer (2000 ~ 2004)
  - AIST, Japan, Visiting Scholar(2010, 2017)
- Research Activities
  - **Plasma Monitoring and Data Analysis Algorithm**
  - **Atomic Layer Etching (ALE) and Atomic Layer Deposition (ALD)**
  - **Reduction of Greenhouse Gases in Plasma Processing**
  - **Quantum Dots and Quantum-Dot Light Emitting Diodes**
- Publications: 150 papers and 20 patents
- Lab: 60 alumni, 20 students in the group
- Societies
  - Korea Vacuum Society, Vice President (2021~2022)
  - Korea Semiconductor Conference, Patterning Committee Chair
  - Korea Institute of Chemical Engineers, Fellow
  - Korea Information Display Society, QD&PV Committee Char
  - AVS Organized ALD/ALE Organization Committee Member
  - Guest Editor for Thin Solid Films, Associate Editor for KJChE
- Email: hchae@skku.edu
- Homepage: https://npl.skku.edu

Outline

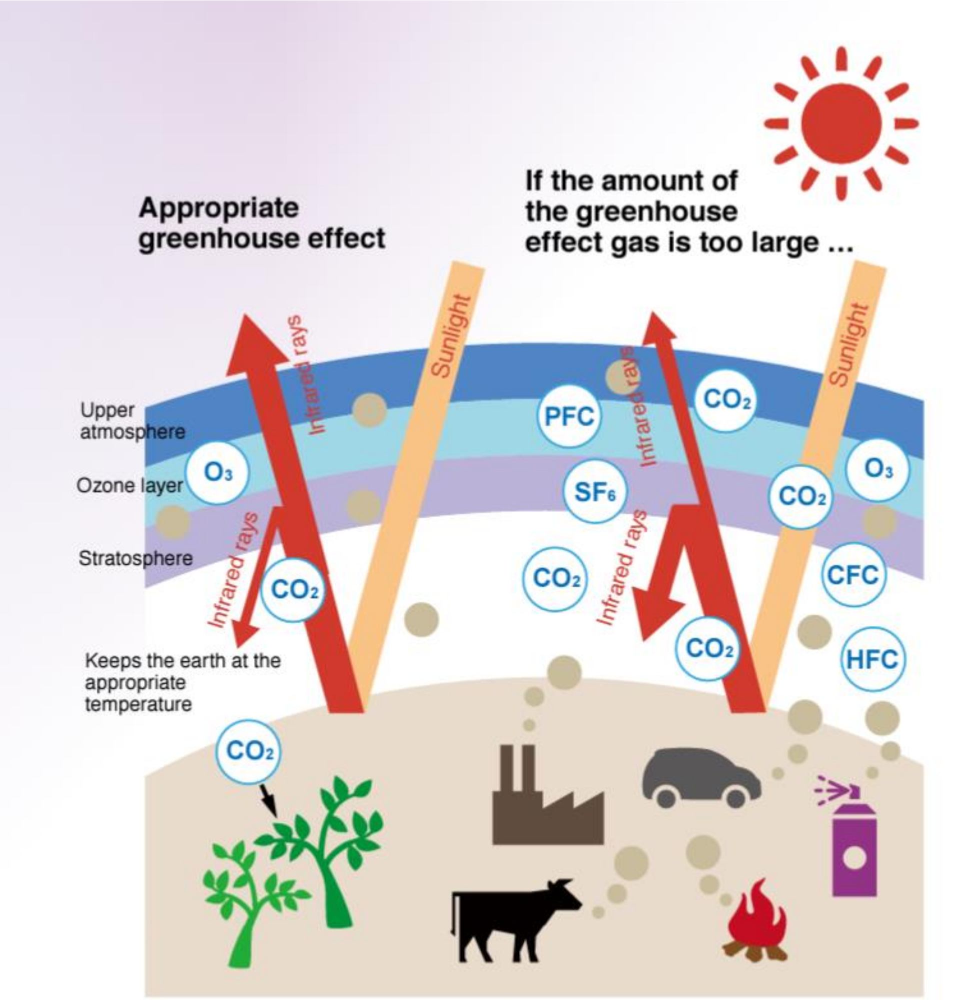
- Introduction:
    - Greenhouse Gases in Semiconductor Industry
    - Reduction of Greenhouse Gas Emission

- Alternative gases for the reduction of greenhouse gas emission
    - Fluoroether and fluoroalcohol screening
    - Plasma etching
    - Atomic Layer Etching (ALE)

- Summary / Potential Collaboration

Introduction

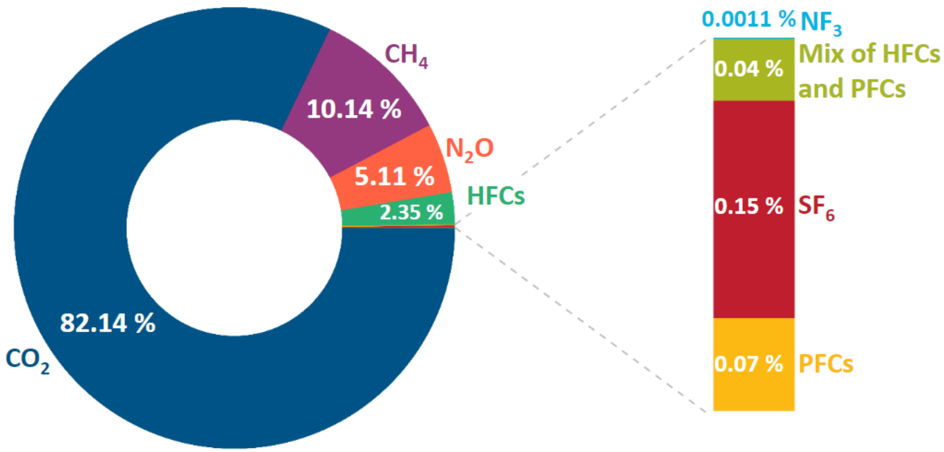
Greenhouse Effect and Gases



Greenhouse effect gases:
CO_2, methane gas (CH_4), monoxide dinitrogen (N_2O), CFC, HCFC, HFC, PFC, SF_6, NF_3, others
(CFCs and the HCFCs are not subject to the Kyoto Protocol.)

https://www.nedo.go.jp/content/100900128.pdf

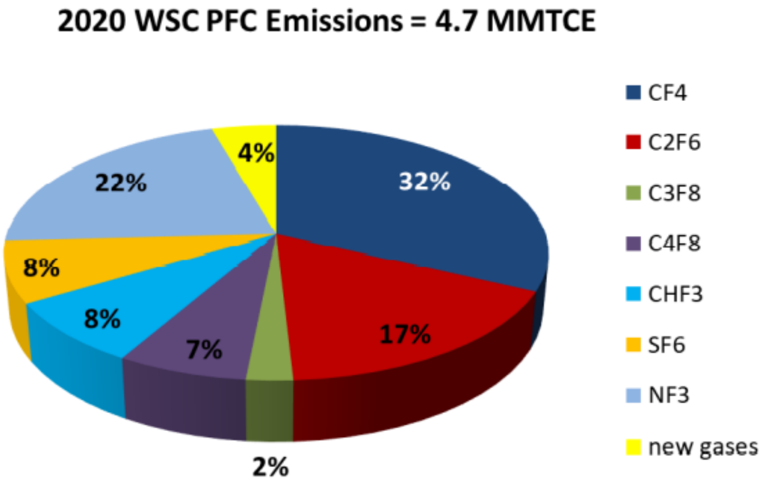
Greenhouse Gas Emissions by Gas

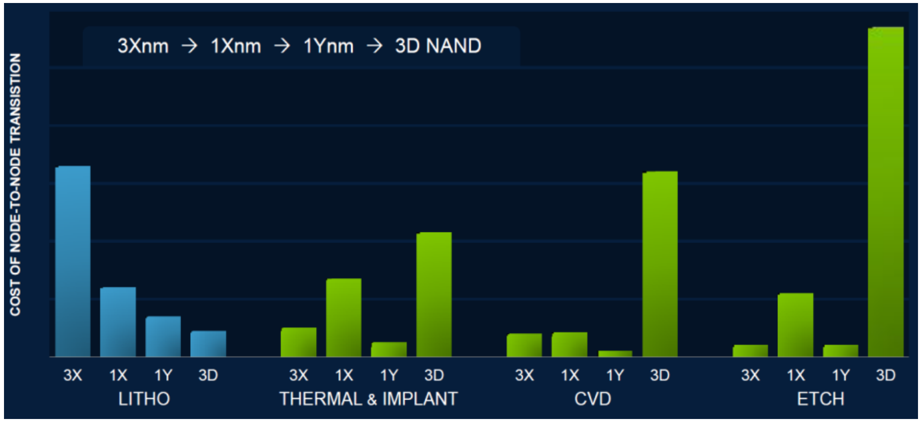


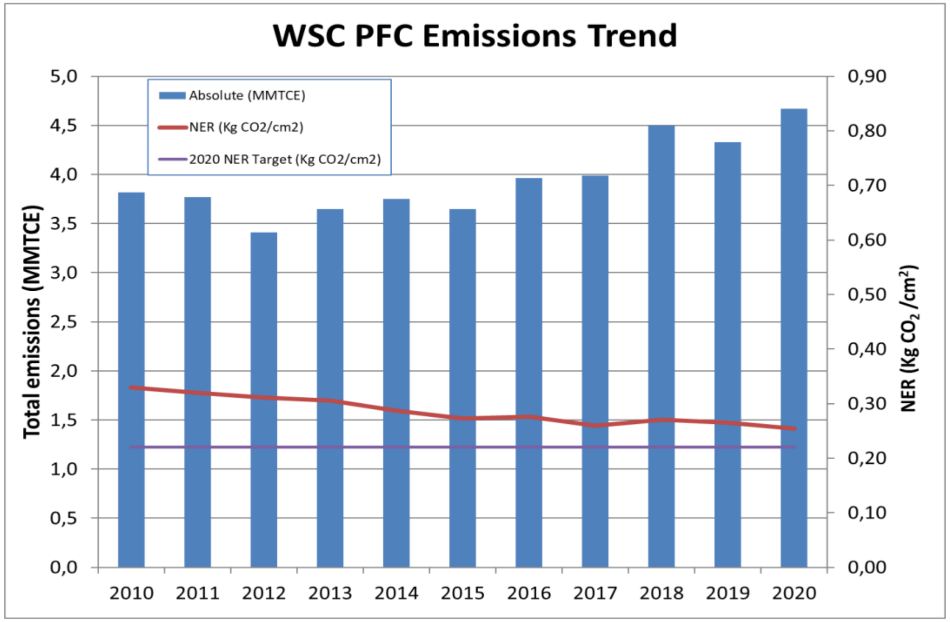
*Data on emissions from the aggregated EU inventory reported to the UNFCCC in 2019.

Greenhouse Gas	GWP	Lifetime (yr)
CO_2	1	Variable
CH_4	21	12.2
NO_2	206	120
HFCs	140 - 11,700	1.5 - 264
PFCs	6,500 - 9,200	3,200 - 50,000
SF_6	23,000	3,200

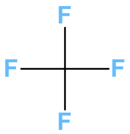
Greenhouse Gas Emission in Semiconductor Industry

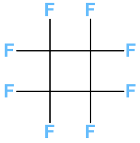


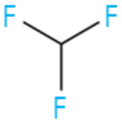




- Molecular structure: Examples

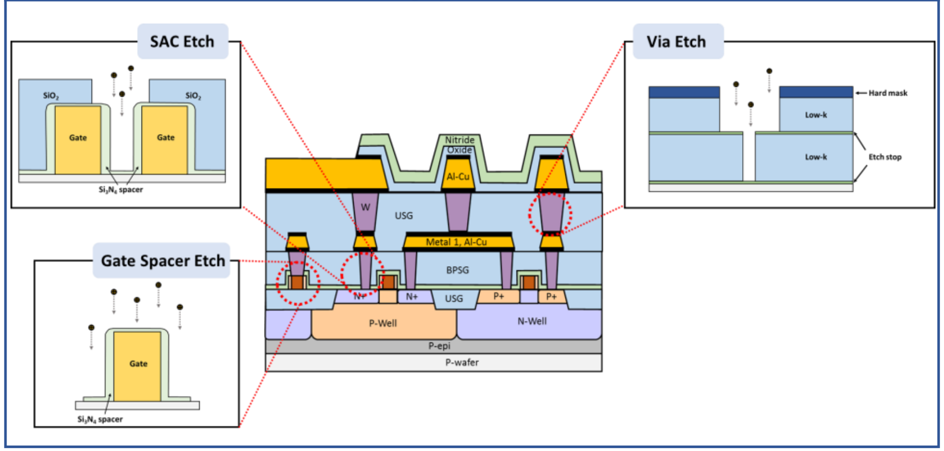




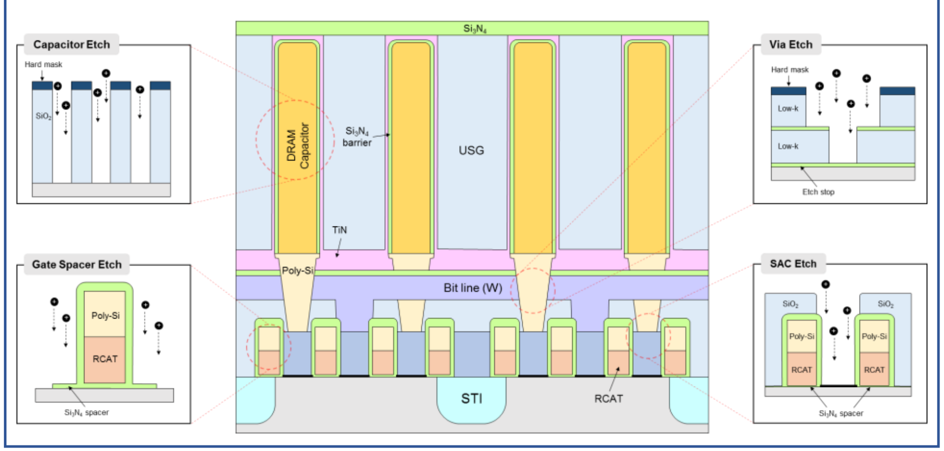


Etching Processes and Semiconductor Devices

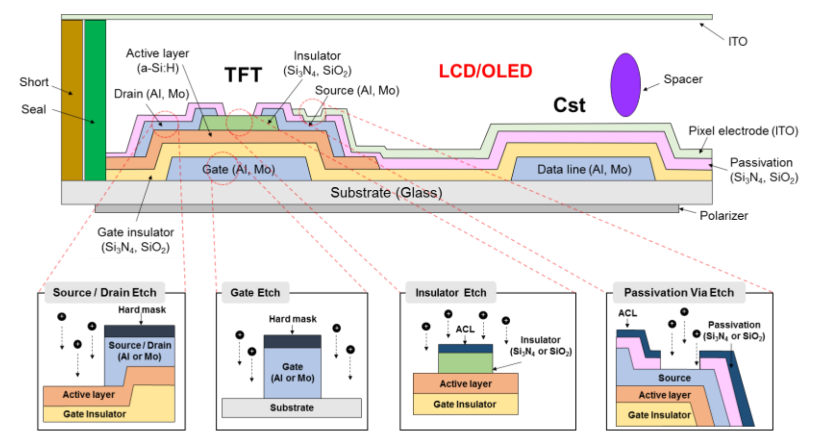
Logic Device



DRAM

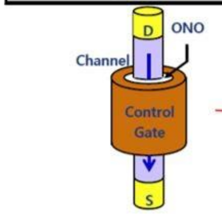


Display Panels



3D NAND

3D cell (Vertical String)



Charges stored in FG
Charges in/out through the tunnel oxide.

- Poly-Si channel
- SONOS (Si / Oxide / SiN / Oxide / SiN)
- All-around gate
- Channel-last process
- 1 step litho (hole)

http://gigglehd.com/zbxe/613729€
Micron
Wednesday, August 10, 2011

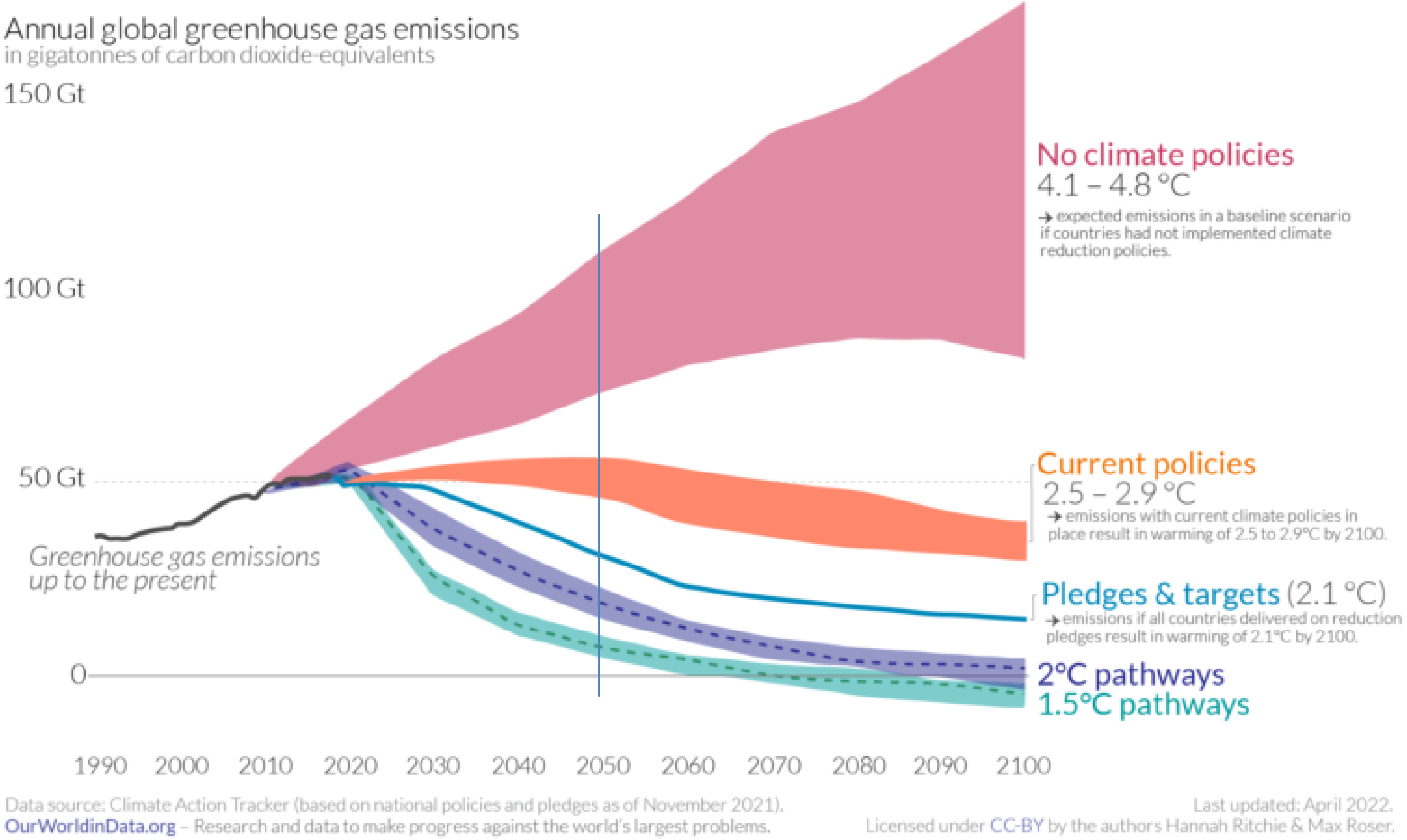
SAC Etch: C_4F_8, C_4F_6

Via Etch: C_4F_8, C_4F_6

Gate Spacer Etch: CF_4, CHF_3

3D NAND: C_4F_8, C_4F_6

Global Greenhouse Gas Emission & Warming Scenarios



Annual global greenhouse gas emissions
in gigatonnes of carbon dioxide-equivalents

→ expected emissions in a baseline scenario if countries had not implemented climate reduction policies.

→ emissions with current climate policies in place result in warming of 2.5 to 2.9°C by 2100.

→ emissions if all countries delivered on reduction pledges result in warming of 2.1°C by 2100.

Data source: Climate Action Tracker (based on national policies and pledges as of November 2021).
OurWorldinData.org – Research and data to make progress against the world's largest problems.

Last updated: April 2022.

https://ourworldindata.org/co2-and-greenhouse-gas-emissions

- Is this reduction possible?

Success Story: Ozone Layer Fully Recovered

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Ozone layer recovery is on track, due to success of Montreal Protocol

© NASA | The ozone layer, a thin shield of gas, is seen from space.

9 January 2023 | Climate and Environment

The Earth's ozone layer is on track to recover within four decades, a UN-backed panel of experts said on Monday.

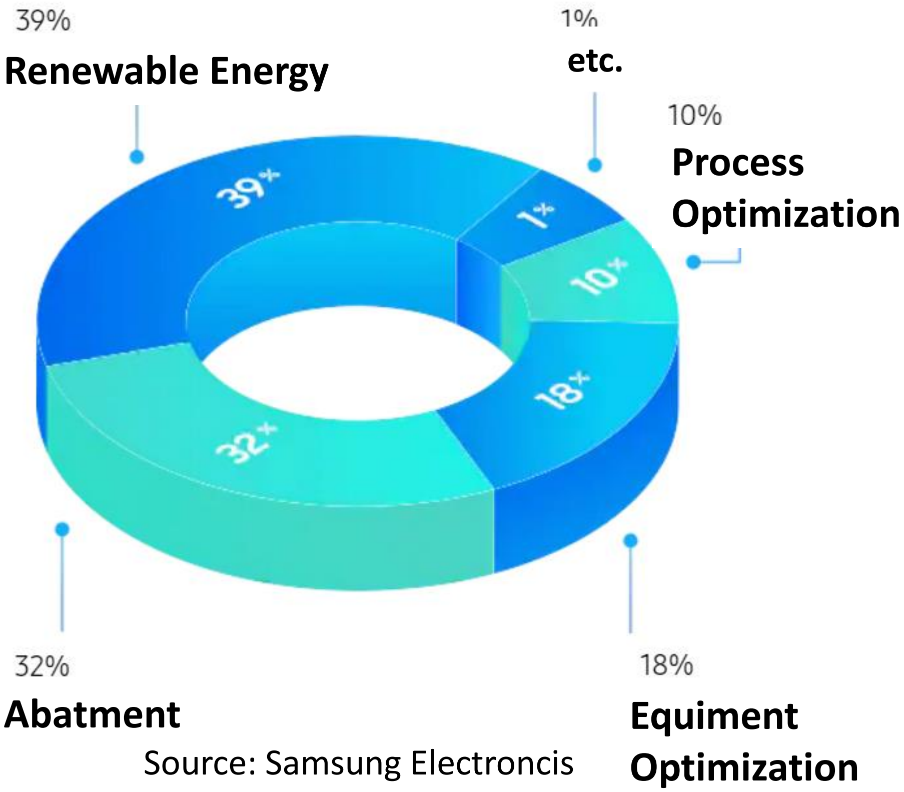
- In the 1980s, scientists discovered harmful hole in the ozone layer.
- The **Montreal Protocol** signed in 1987.
- **Scientists, policymakers, and governments worked together** to control and phase out ozone-depleting substances. And it is working.
- **The ozone layer is on track to fully recover** in our lifetime and help to avoid global warming by 0.5°C.
- Ozone layer recovery is **an environmental success story** and has helped curb the effect of climate change.
- This sets **a powerful precedent** for climate action.

(UN, World Meteorological Organization)

How to Reduce Greenhouse Emission

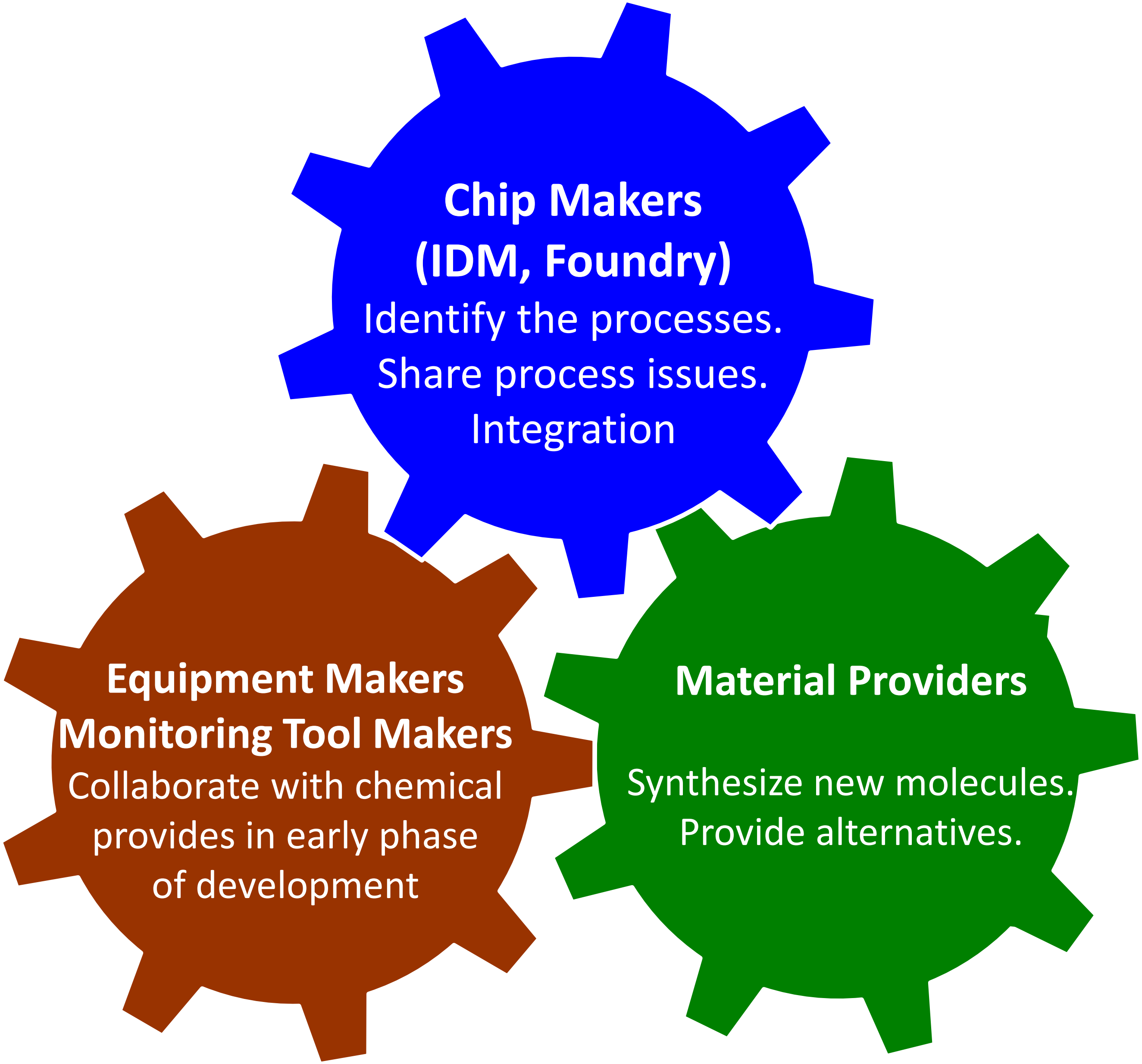
- Ways to reduce greenhouse emission
  - Process optimization
  - Recovery & Recycle
  - Abatement
  - **Alternative gases**

▶ Greenhouse reduction in SEC (2020): Mostely reduced by process optimization and abatement



Source: Samsung Electroncis

Cooperation of Major Players is Required



Chip Makers (IDM, Foundry)

Identify the processes.
Share process issues.
Integration

Equipment Makers
Monitoring Tool Makers

Collaborate with chemical provides in early phase of development

Material Providers

Synthesize new molecules.
Provide alternatives.

Alternatives for GHG in Plasma Etch Processes

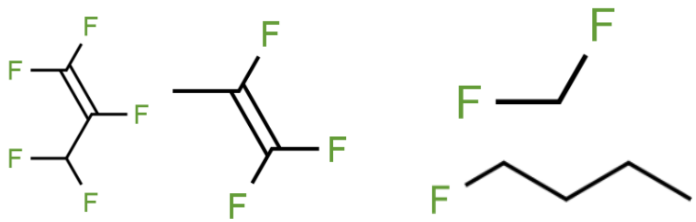
ACS Sustainable Chem. 10, 10537 (2022)

J. Vac. Sci. Technol. A, 38(2), 022606 (2020)

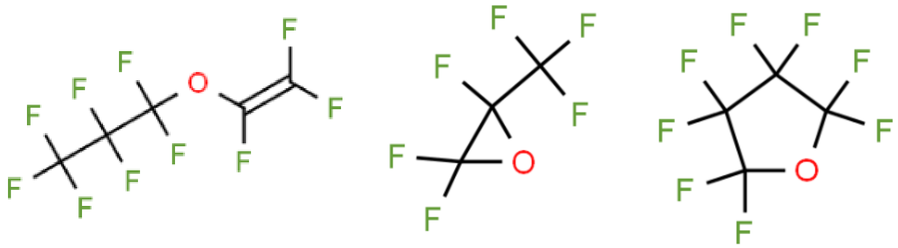
How to Reduce GWP: Structure and Examples

- Double bonds or cyclic

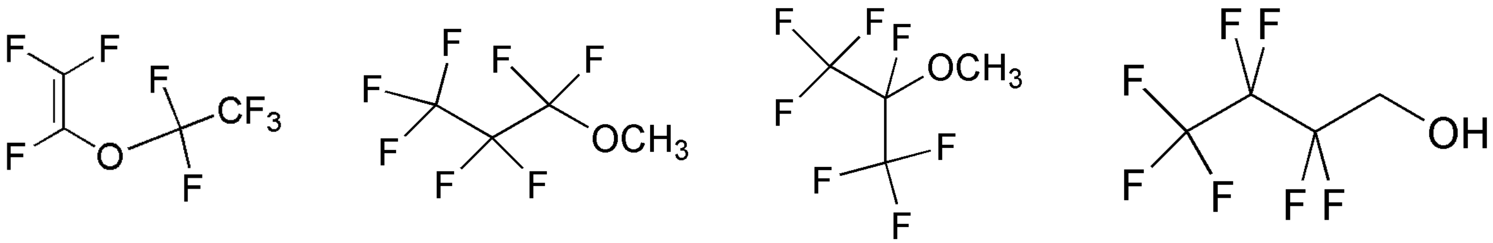
- Hydrogen: Formation of HF



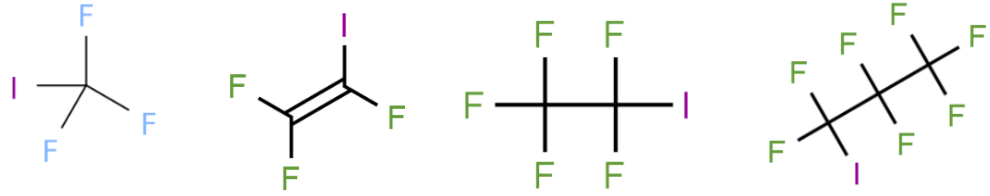
- Oxygen: Formation of CO, CO_2 and, COF_2



- Hydrogen/Oxygen



- Iodine: Easily decompose



Things to Consider for Alternatives

Low GWP

Boiling Point

Gas Properties

Alternative Gases

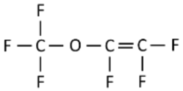
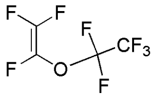
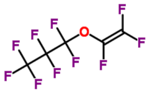
Time/ Expense

Gas Recombination

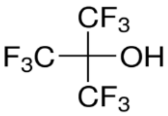
Process Results

Examples of Alternatives: Fluoroether & Fluoroalcohol

Perfluorinated fluoro-ether (R_F-O-R_F)

Molecular Formula	Chemical Name	Chemical Structure	C/(F+O-H)	b.p. (℃)	GWP
CF_3OCFCF_2 (HFE-216)	1,1,2-trifluoro-2-(trifluoromethoxy)ethane (trifluoromethyl Trifluorovinyl Ether)		0.43	-23	< 1
$CF_3CF_2OCFCF_2$	Perfluoro ethyl vinyl ether		0.44	~0	3
$CF_3CF_2CF_2O\text{-}CFCF_2$	Perfluoro propyl vinyl ether		0.45	35~36	3

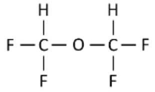
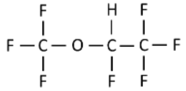
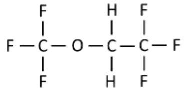
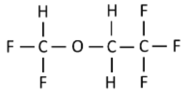
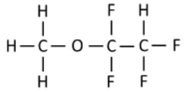
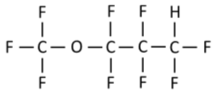
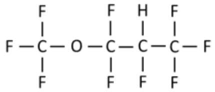
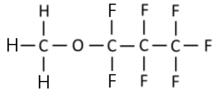
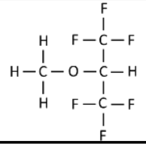
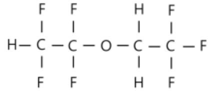
Perfluorinated fluoro-alcohol (R_F-OH)

Molecular Formula	Chemical Name	Chemical Structure	C/(F+O-H)	b.p. (℃)	GWP
$(CF_3)_3COH$	Nonafluoro-tert-butanol		0.44	45	

SKKU

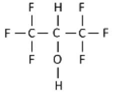
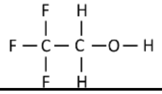
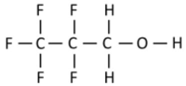
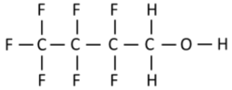
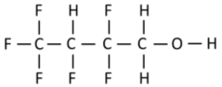
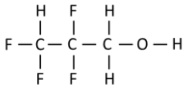
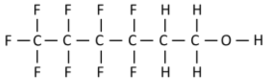
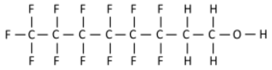
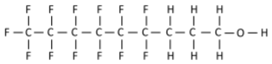
Candidates for Altenatives: Fluoro-ether

Partially fluorinated fluoro-ether (R_F-O-R_H, R_F-O-$R_{F\text{-}H}$, $R_{F\text{-}H}$-O-R_H, $R_{F\text{-}H}$-O-$R_{F\text{-}H}$)

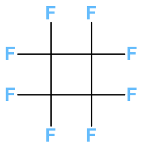
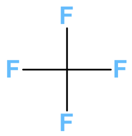
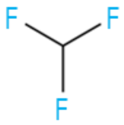
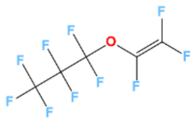
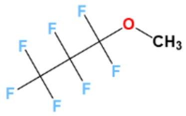
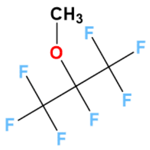
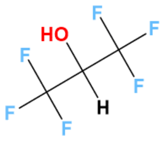
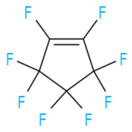
Molecular Formula	Chemical Name	Chemical Structure	C/(F+O-H)	b.p. (℃)	GWP
CHF_2OCHF_2 (HFE-134)	1,1,3,3-Tetrafluorodimethyl ether		0.67	4.7	6,320
$CF_3OCHFCF_3$ (HFE-227)	1,2,2,2-Tetrafluoroethyl trifluoromethyl ether 97%		0.43	-9	1,540
$CF_3CH_2OCF_3$ (HFE-236fa)	2,2,2-Trifluoroethyl trifluoromethyl ether		0.60	5.6	487
$CF_3CH_2OCHF_2$ (HFE-245fa2)	2,2,2-trifluoroethyl difluoromethyl ether		1	29	649
$HCF_2CF_2OCH_3$ (HFE-254cb1)	1,1,2,2-tetrafluoroethyl methyl ether (Tetrafluoroethyl methyl ether)		3	36	353
$CF_3OCF_2CF_2CHF_2$ (HFE-329mcc2)	1,1,2,2,3,3-hexafluoro-1-(trifluoromethoxy)propane		0.44	24~34	890
$CF_3OCF_2CHFCF_3$ (HFE-329me3)	1,1,1,2,3,3-Hexafluoro-3-(trifluoromethoxy)propane		0.44	-	4,550
$CF_3CF_2CF_2OCH_3$ (HFE-347mcc3)	1,1,1,2,2,3,3-Heptafluoro-3-methoxypropane (Heptafluoropropyl methyl ether)		0.8	34	530
$(CF_3)_2CHOCH_3$ (HFE 347mmy)	1,1,1,3,3,3-Hexafluoro-2-methoxypropane (Heptafluoroisopropyl methyl ether)		0.8	50	353
$HCF_2CF_2OCH_2CF_3$ (HFE-347pcf2)	1,1,2,2-tetrafluoroethyl-2,2,2-trifluoroethyl ether		0.8	50	889

Candidates for Altenatives: Fluoro-alcohol

- **Partially fluorinated fluoro-alcohol (R_F-CHOH, R_F-CH_2OH, R_F-CH_2CH_2OH, $R_{F\text{-}H}CH_2OH$, $R_{F\text{-}H}CH_2CH_2OH$)**

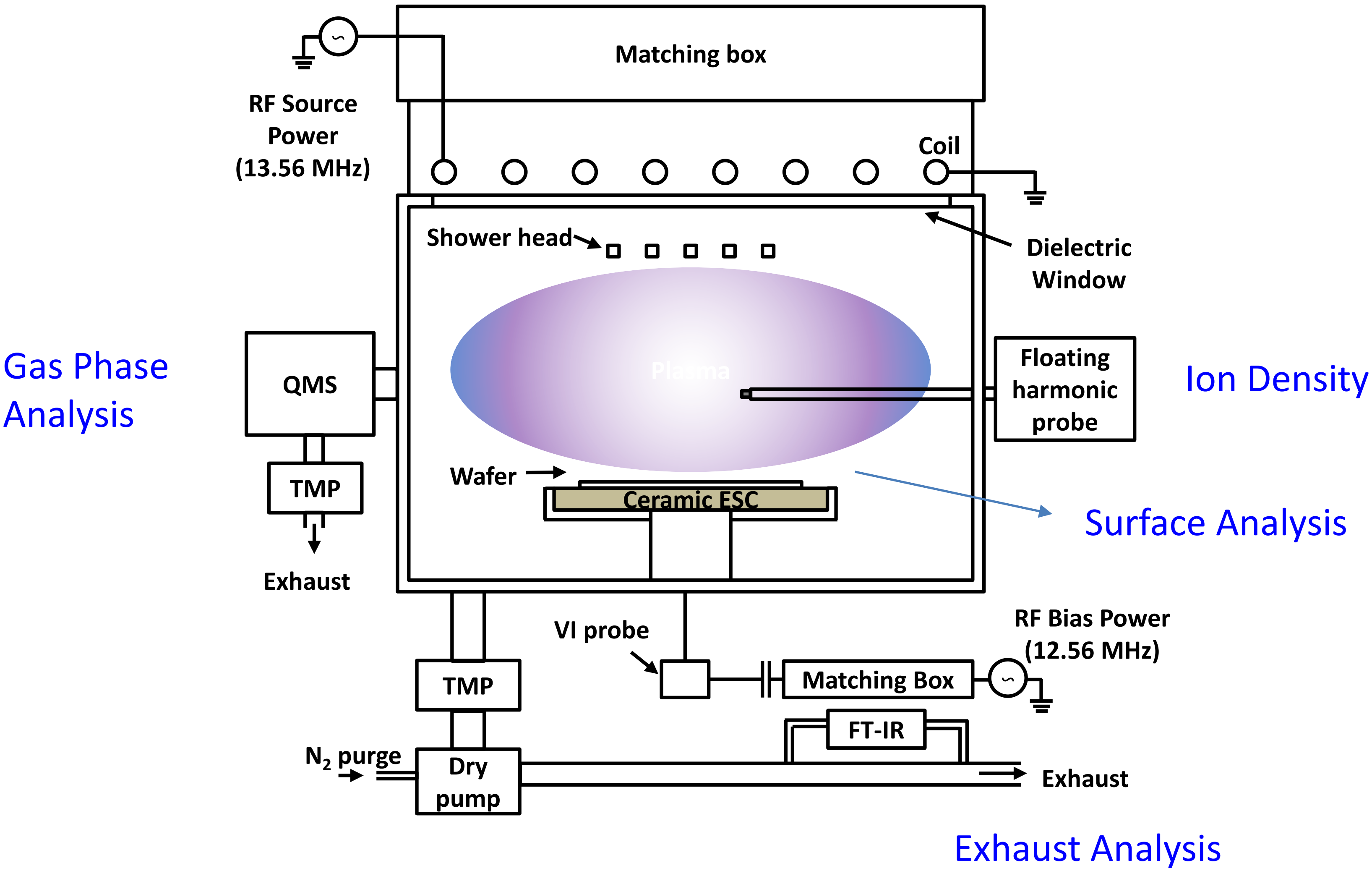
Molecular Formula	Chemical Name	Chemical Structure	C/(F+O-H)	b.p. (℃)	GWP
$(CF_3)_2CHOH$	1,1,1,3,3,3-Hexafluoro-2-propanol (Hexafluoroisopropanol)		0.6	59	190
CF_3CH_2OH	2,2,2-Trifluoroethanol (Trifluoroethyl alcohol)		2	74	57
$CF_3CF_2CH_2OH$	2,2,3,3,3-Pentafluoro-1-propanol (Pentafluoropropylalcohol)		1	81	40
$CF_3(CF_2)_2CH_2OH$	Perfluoropropyl carbinol (2,2,3,3,4,4,4-Heptafluoro-1-butanol)		0.8	95	25
$CF_3CHFCF_2CH_2OH$	Hexafluorobutanol (2,2,3,4,4,4-Hexafluoro-1-butanol)		1.33	114	17
$CHF_2CF_2CH_2OH$	Tetrafluoropropyl alcohol (2,2,3,3-Tetrafluoro-1-propanol)		3	107	13
$CF_3(CF_2)_3(CH_2)_2OH$	2-perfluorobutylethanol (1H,1H,2H,2H-Perfluorohexanol)		1	140	-
$CF_3(CF_2)_5(CH_2)_2OH$	2-(Perfluorohexyl)ethanol (1H,1H,2H,2H-Perfluorooctanol)		0.89	88 (27 mmHg)	-
$CF_3(CF_2)_5(CH_2)_3OH$	3-(perfluorohexyl)propanol (4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononan-1-ol)		1.29	80 (10 mmHg)	-

Alternatives and Physical Propoerties (Examples)

	Greenhouse Gases (PFC/HFC)			Low GWP				
Name	Octafluoro-cyclobutane	Tetrafluoro-methane	Trifluoromethane	PPVE	HFE-347mmc3	HFE347mmy	HFIP	Octafluoro cyclopentene
Formula	C_4F_8	CF_4	CHF_3	$CF_3CF_2CF_2OC_2F_3$	$CF_3CF_2CF_2OCH_3$	$(CF_3)_2CHOCH_3$	$(CF_3)_2CHOH$	c-C_5F_8
Chemical Structure								
MP (℃)	-40.1	-183.6	-155.2	-70	-122.5	-107	-4	-70
BP (℃)	-6	-127.8	-82.1	35~36	34	29	59	37.5
GWP	**9,540**	**6,630**	**11,700**	**3**	**530**	**343**	**190**	**7**
C/(F+O-H)	0.5	0.25	0.5	0.455	0.8	0.8	0.6	0.625

Plasma Generation and Silicon Oxide/Nitride Etching

ACS Sustainable Chem. 10, 10537 (2022)



Gas Phase Analysis

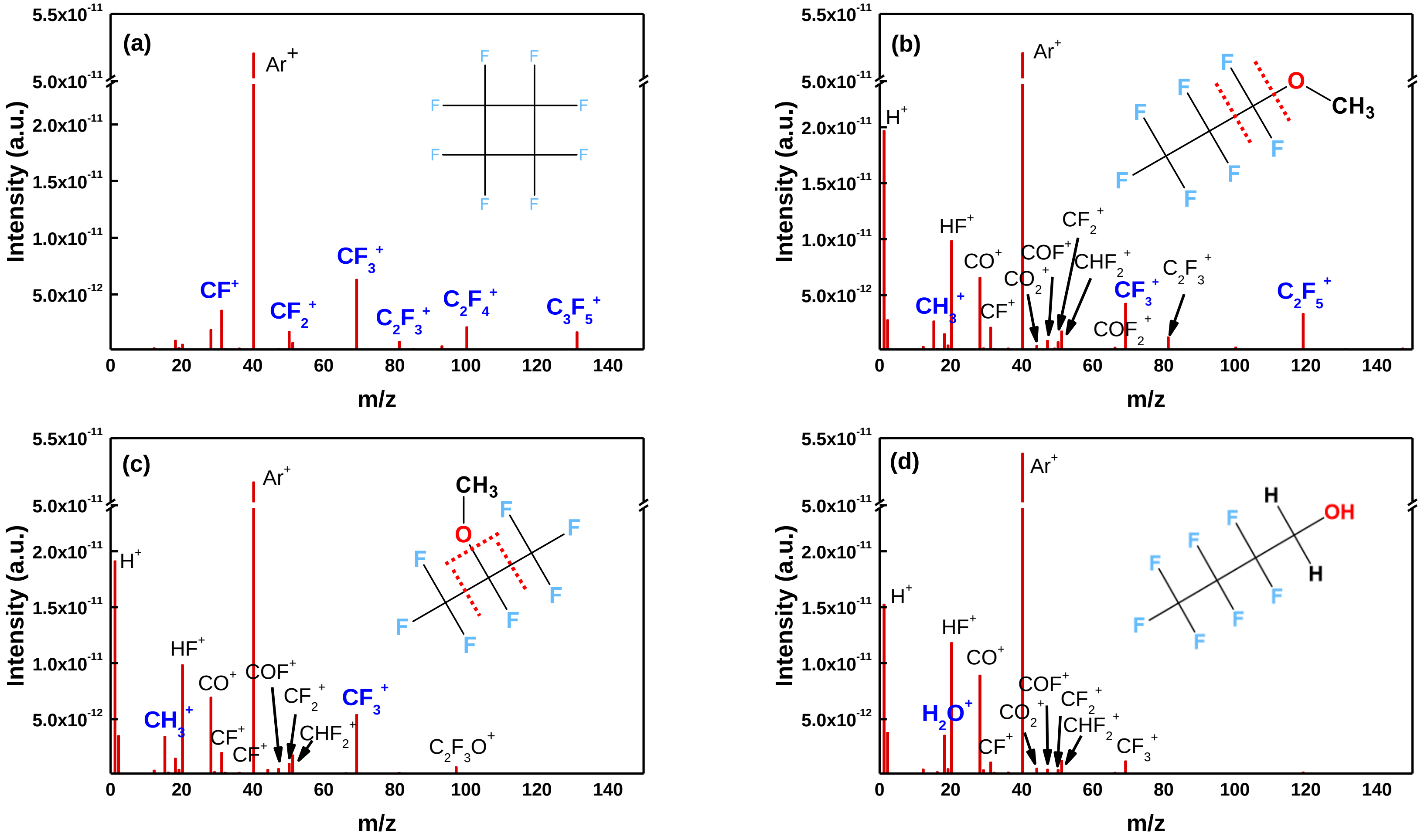
Ion Density

Surface Analysis

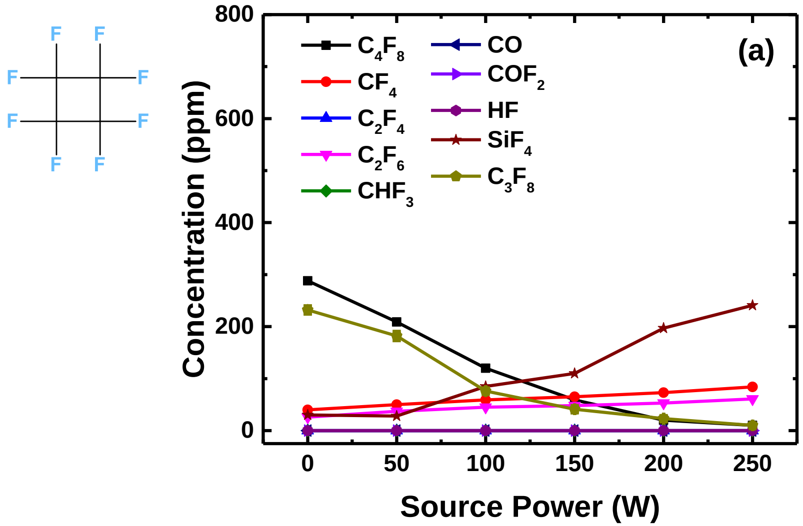
Exhaust Analysis

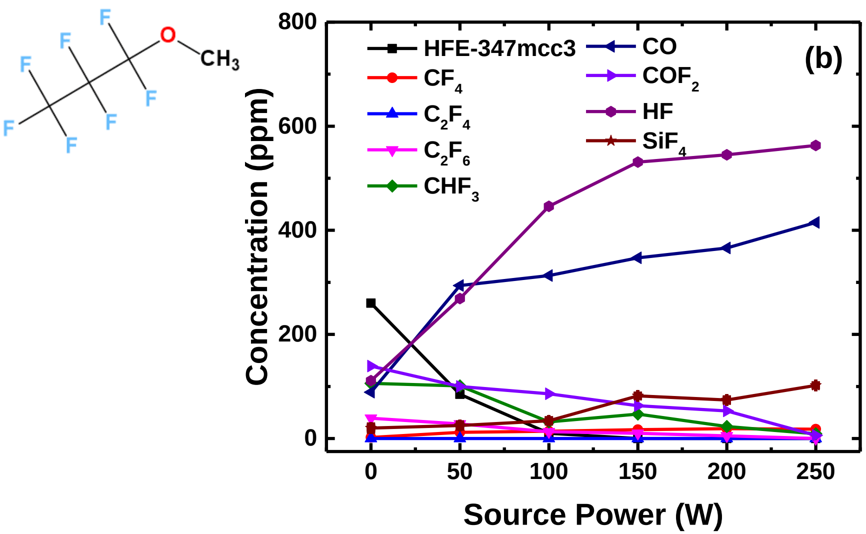
Plasma Etching w/ Low-GWP Gases: Plasma Phase

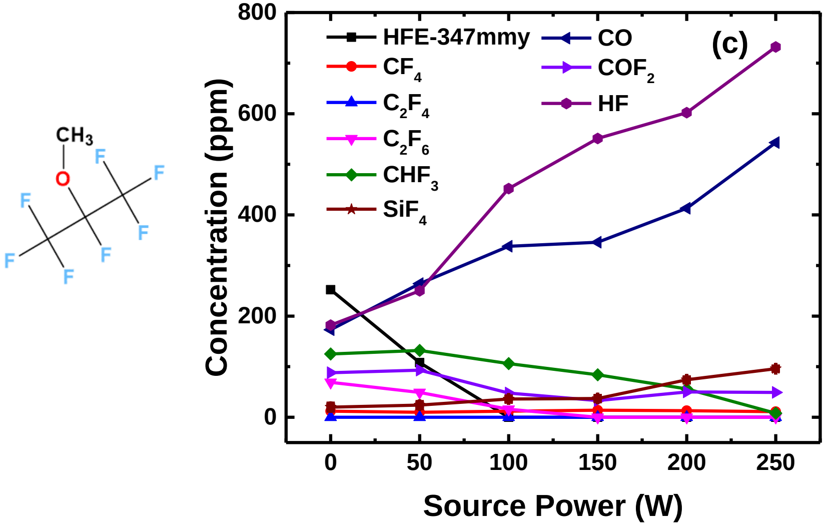
❖ **At 50W, 700V**

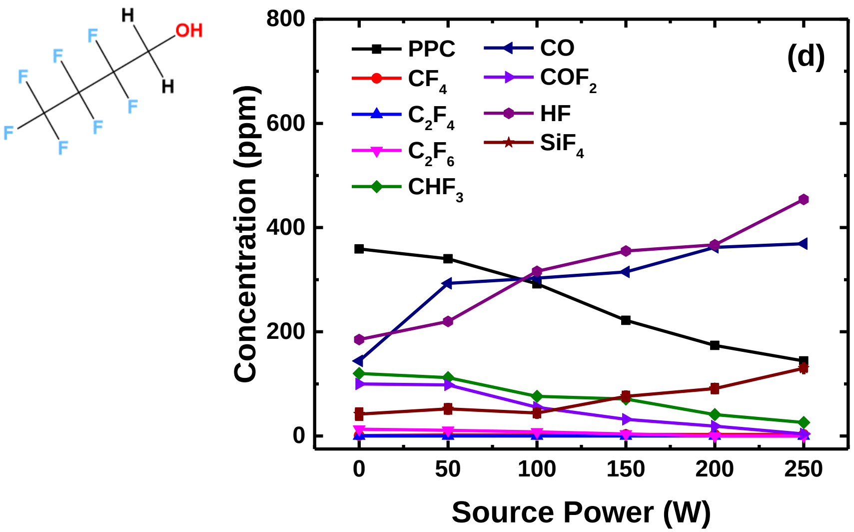


Plasma Etching w/ Low-GWP Gases: Exhaust Analysis









Silicon Oxide Etching w/ Fluoroethers and Fluoroalcohols

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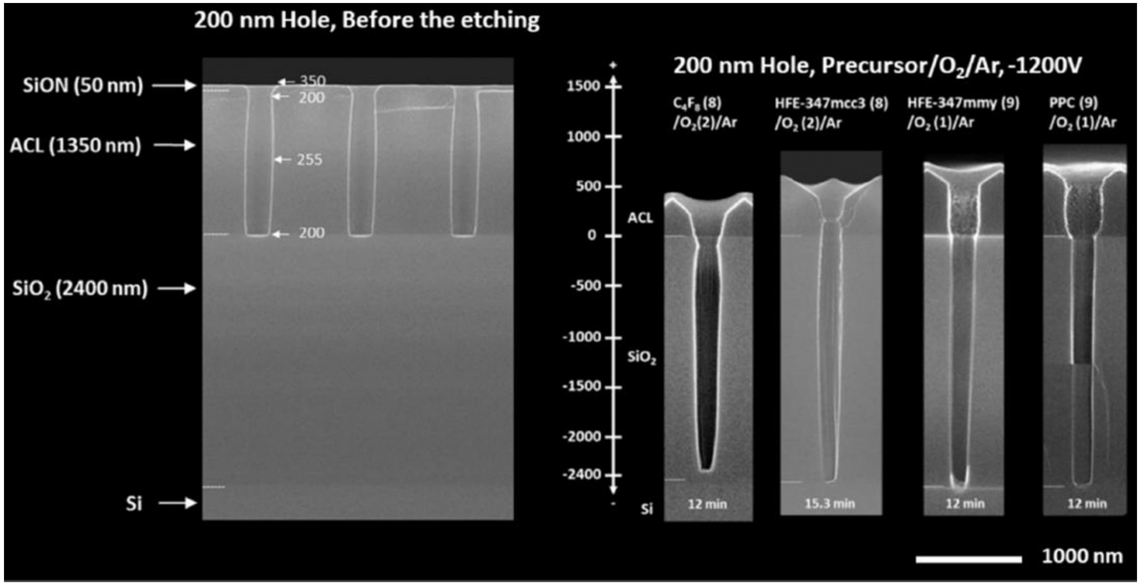
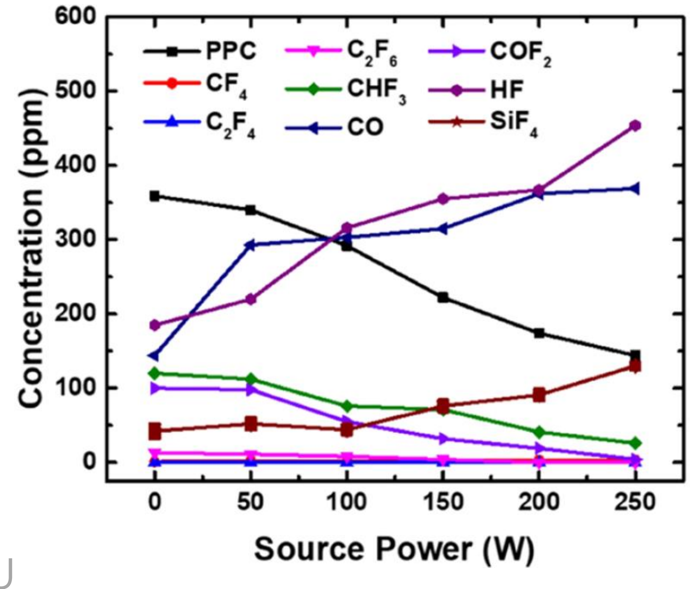
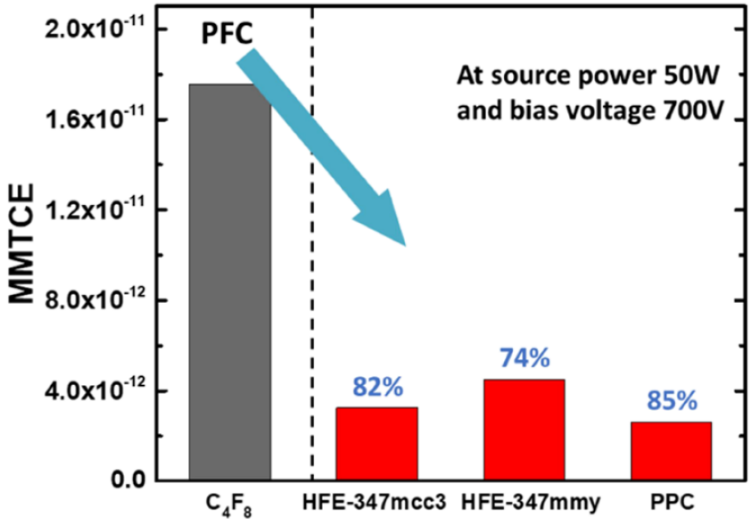
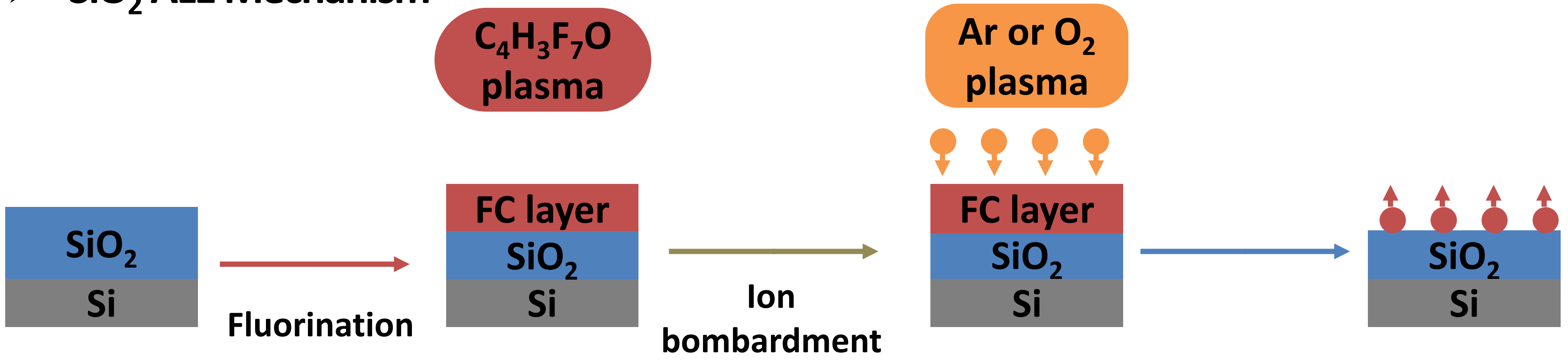






ALE with $C_4H_3F_7O$ Isomers

- **SiO_2 ALE Mechanism**



$C_4H_3F_7O$ plasma

Ar or O_2 plasma

SiO_2

Si

Fluorination

FC layer

SiO_2

Si

Ion bombardment

FC layer

SiO_2

Si

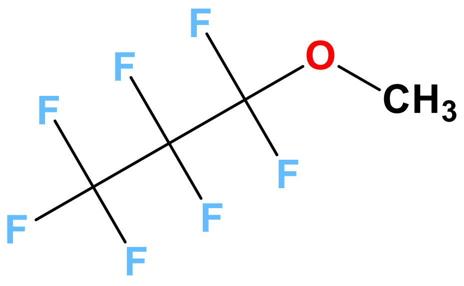
SiO_2

Si

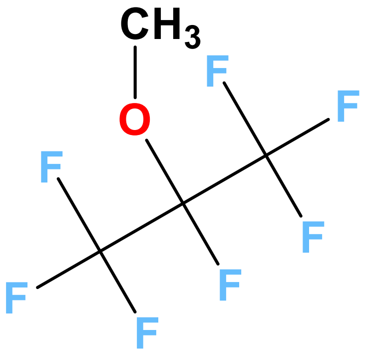
Product	Boiling point (°C)
SiF_4	-86

- **$C_4H_3F_7O$ Isomers used as precursor**

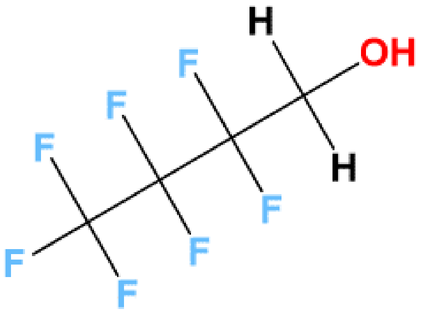
Heptafluoropropyl methyl ether **(HFE-347mcc3)**



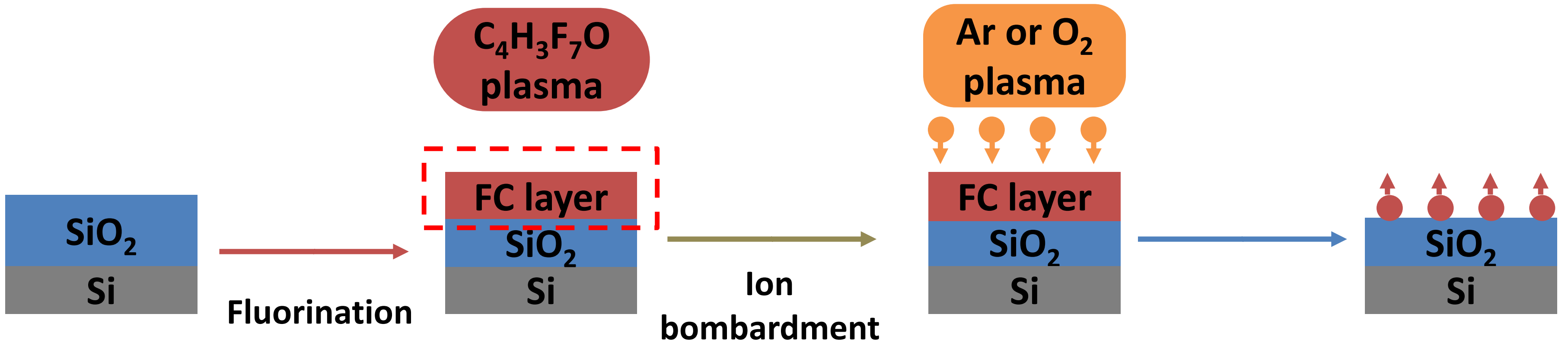
Heptafluoroisopropyl methyl ether **(HFE-347mmy)**



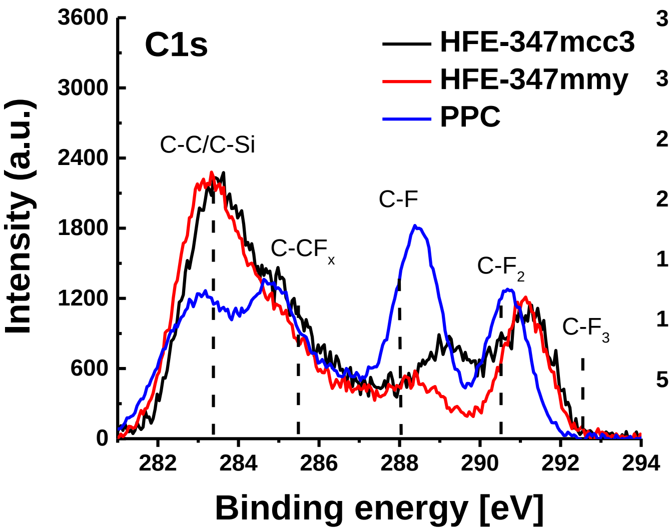
Perfluoropropyl carbinol **(PPC)**

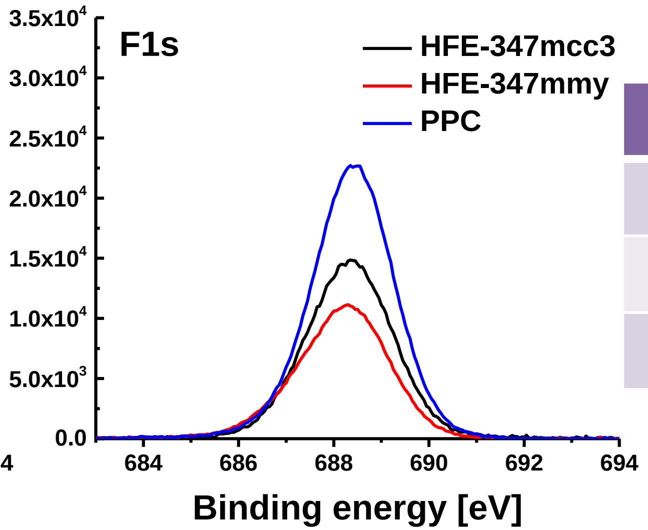


ALE with $C_4H_3F_7O$ Isomers



J. Vac. Sci. Technol. A, 38(2), 022606(2020)





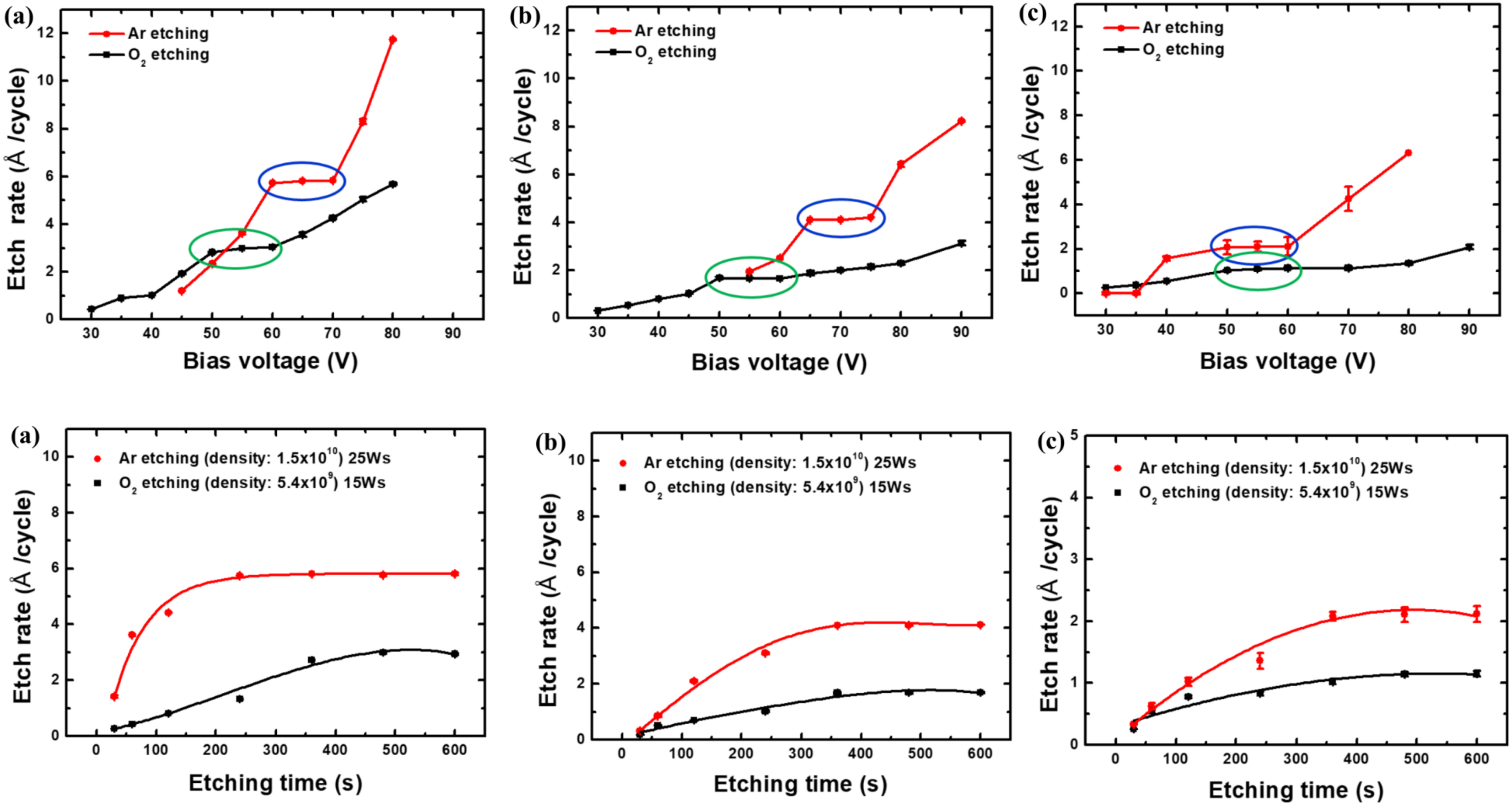
Precursor	F1s/C1s Ratio
HFE-347mcc3	1.266
HFE-347mmy	1.048
PPC	1.516

- The thickness of the FC layer was maintained at **0.5nm**.
- HFE-347mcc3 and HFE-347mmy precursors generate mainly C-C and C-Si bonds.
- PPC precursor generate more C-F bonds than C-C and C-Si bonds.

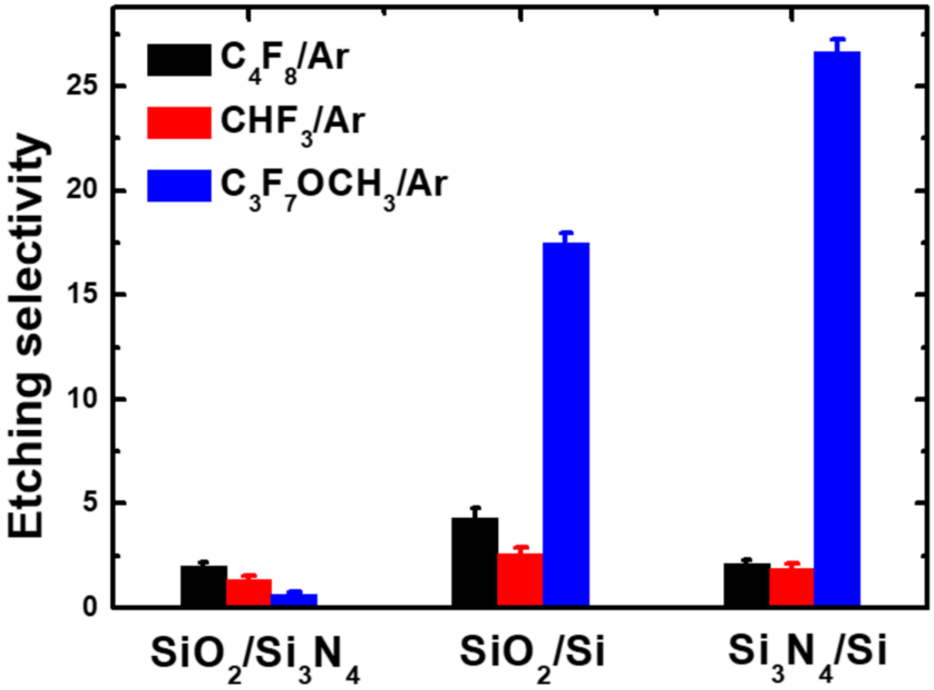
ALE with $C_4H_3F_7O$ Isomers: ALE Window and Self-Limiting

J. Vac. Sci. Technol. A, 38(2), 022606(2020)

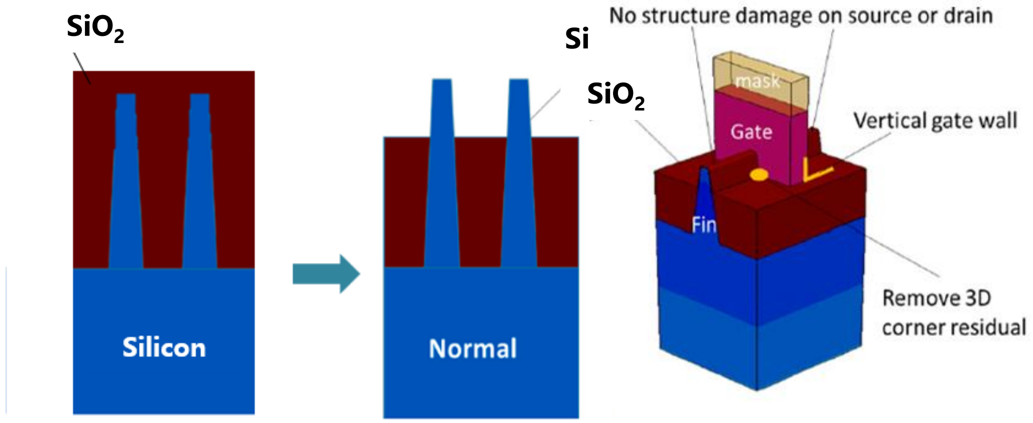
C_4F_8 CHF_3 $C_3F_7OCH_3$



ALE with $C_4H_3F_7O$ Isomers: High Selectivity over Si



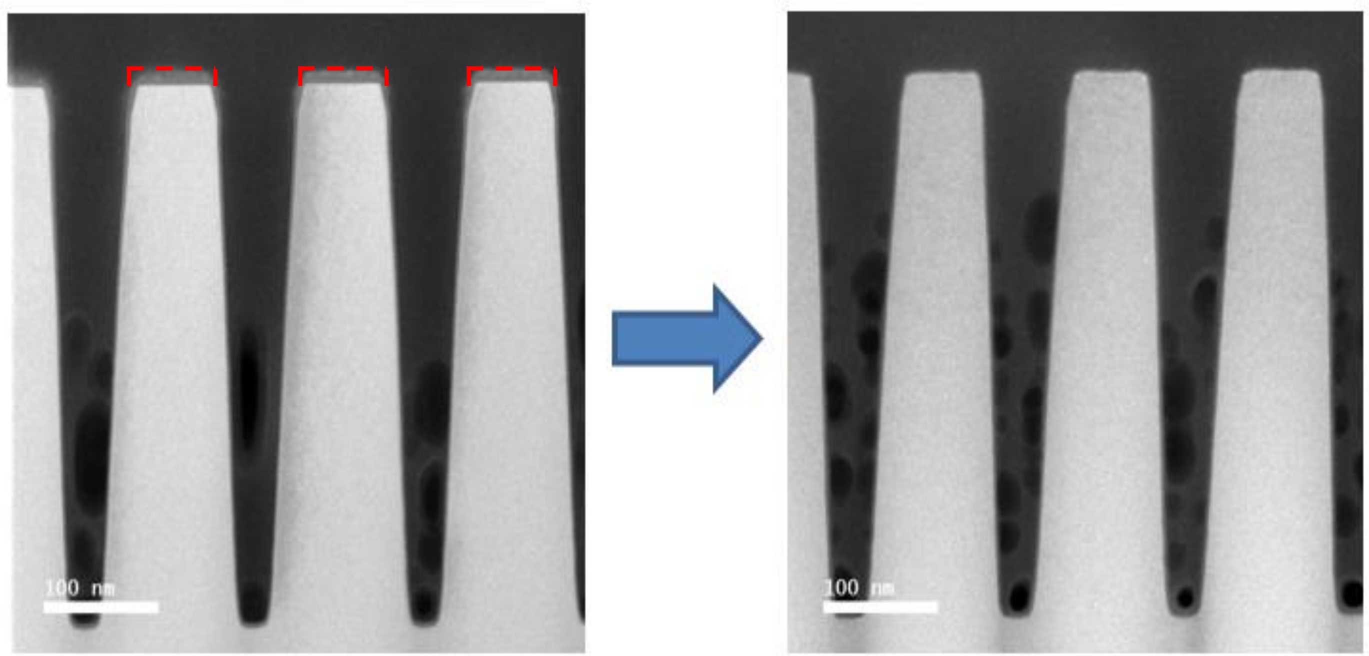
J. Vac. Sci. Technol. A, 38(2), 022606(2020)

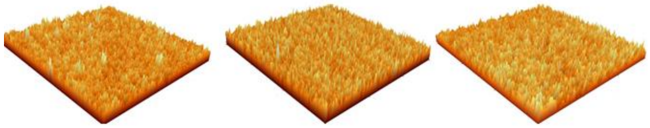


Appl. Sci. 7, 1047, (2017).

ALE with $C_4H_3F_7O$ Isomers applied to SiO2 Removal

✓ Oxide Removed





	Ref. SiO_2	Wet Cleaning	Dry Cleaning
Roughness(nm)	0.092	0.113	0.10

- After dry cleaning process, SiO_2 layer is removed
- After dry cleaning process, surface roughness is lower than wet cleaning

ROK Government Projects for Carbon Neutrality (2023)

- Etching Processes
  - Alternative gases having GWP less than 150 for the replacement of carbon-rich PFC Gases
  - Alternative gases for the replacement of high GWP HFC Gases
  - Alternative gases for the replacement of fluorine-rich PFC Gases
- Deposition Processes
  - Alternative gases for the replacement of dielectric CVD chamber cleaning
  - N_2O reaplacement
- Process Optimization
  - Monitoring and simulation technologies for greenhouse gas emission

→ ROK government plans to support ~200 mil. USD for the carbon neutrality projects in semiconductor processes for the next 8 years.

Summary / Collaboration

- Strong demand in the reduction of greenhouse gas emission in semiconductor industry due to drastically increasing steps and volume
- Fluorine-containing gases (PFCs, HFCs) are major contributors to greenhouse gas emission
- Active searches for new chemistries required
  - Examples: fluoroether, fluoroalcohol, cyclyic fluorocarbons,….
- Cooperation required among device makers, chemical/gas providers, equiment makers and monitoring tool makers
- **Potential collaboration between ROK and USA for building database of new chemistries for the reduction of greenhouse gas emission**
  - **Ex: Plasma database in NIST (USA) and Database in alternative gases (ROK)**

Thank You for Your Attentions!!

hchae@skku.edu

Cooperation of Major Players is Required

Chip Makers
(IDM, Foundry)
Identify the processes.
Share process issues.
Integration

Equipment Makers
Monitoring Tool Makers
Collaborate with chemical
provides in early phase
of development

Material Providers

Synthesize new molecules.
Provide alternatives.

Acknowledgement

- Research Funding
  - Korea Institute of Energy Technology Evaluation and Planning (KETEP)
  - National Research Foundation of Korea (NRF)
  - Korea Institute for Advancement of Technology (KIAT)

- Graduate students
  - Yongjae Kim (SKKU)
  - Seoun Kim (Samsung Electronics)
  - Hojin Kang (SKKU)

- Collaborators
  - Prof. Chang-Koo Kim (Ajou University)
  - Prof. Jihyun Kim (Seoul National University)
  - Prof. Geun Young Yeom (SKKU)

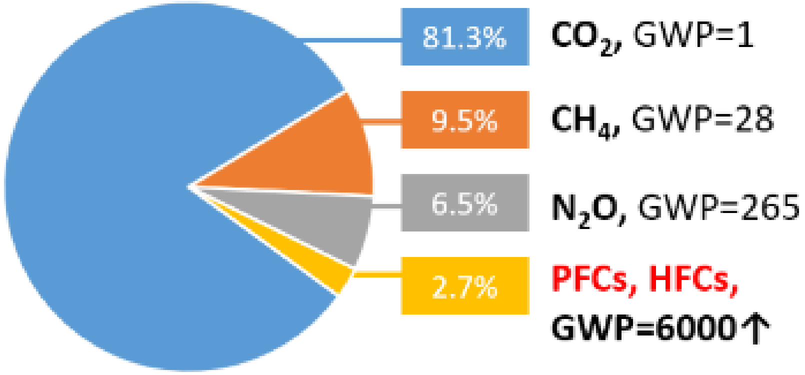
Internationl Projects Completed

- DuPont (USA) – PFC reduction
- Advance Energy (USA) – plasma source evaluation
- Air Liquide (France) – precursor study
- BASF (Gernamy) - thin film development
- Kaneka (Japan) – thin film encapsulation

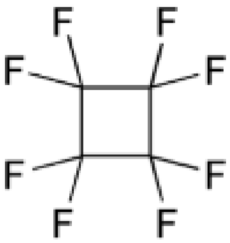
Plasma Etching with Low-GWP Molecules

ACS Sustainable Chem. 10, 10537 (2022)

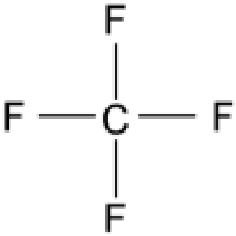
- **Major Greenhouse Gases**



- **PFC Gases**

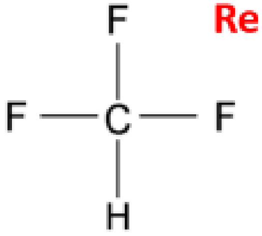


c-C_4F_8
GWP: 10,592



CF_4
GWP: 7,349

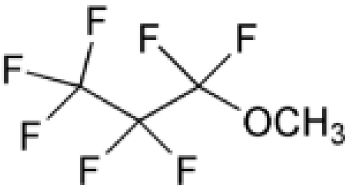
- **HFC Gas**



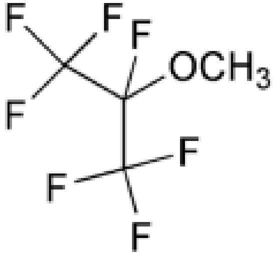
CHF_3
GWP: 12,400

Replace

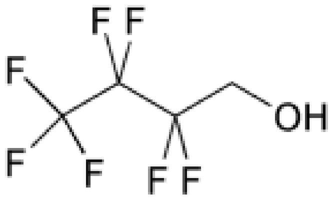
- **Low-GWP Gases**



n-$C_4H_3F_7O$
GWP: 530



i-$C_4H_3F_7O$
GWP: 343

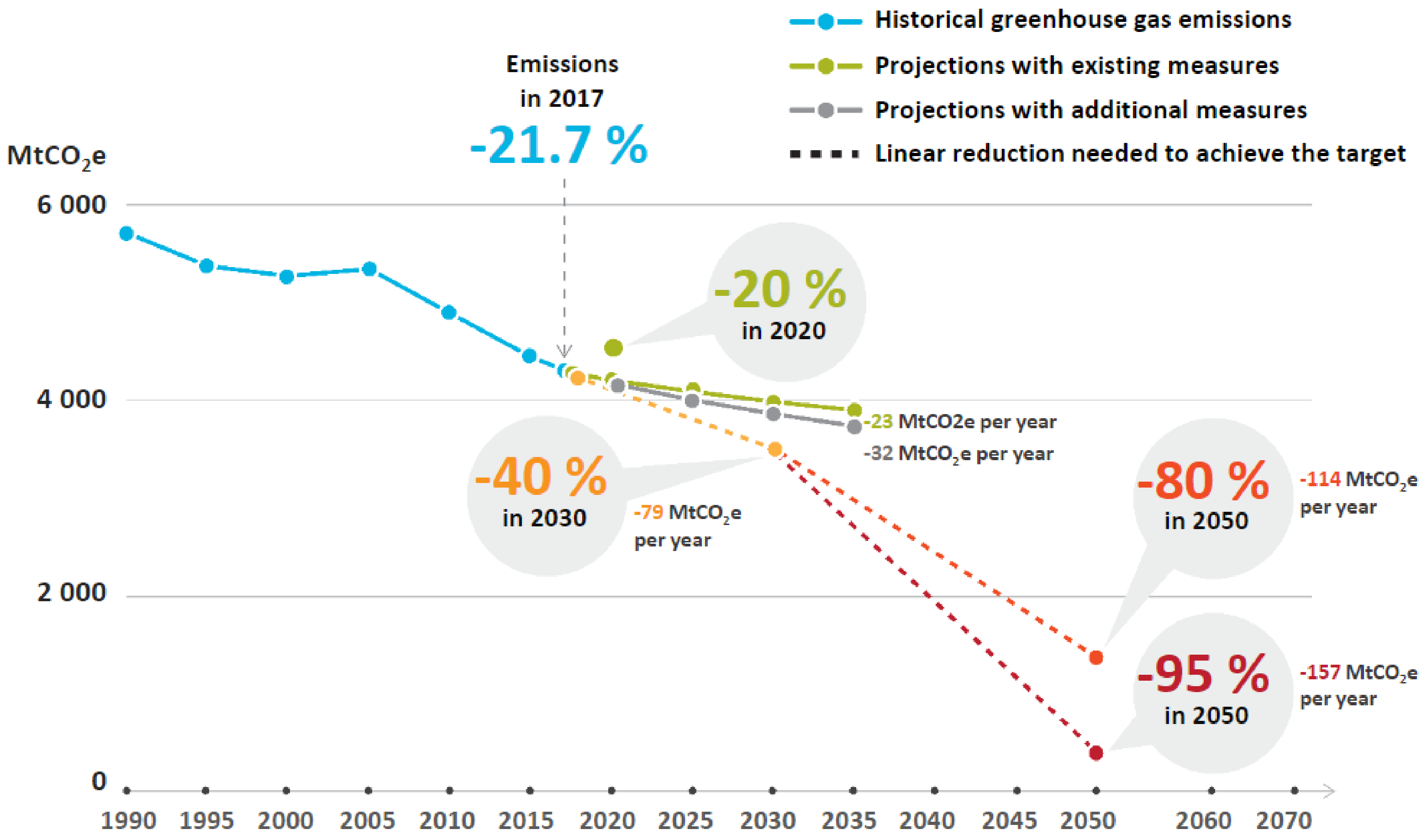


$CF_3CF_2CF_2CH_2OH$
GWP: 25

Global Warming Potential of Gases

Name	Chemical Formula	Atmospheric Lifetime (years)	GWP_{100}
Carbon monoxide	CO	50-200	3
Carbon dioxide	$\mathbf{CO_2}$	**50-200**	**1**
Carbonyl fluoride	COF_2	50-200	1
Trifluoromethane	CHF_3	222	**12,400**
Tetrafluoromethane	CF_4	50,000	**7,349**
Tetrafluoroethylene	C_2F_4	<1	**<1**
Hexafluoroethane	C_2F_6	10,000	**12,340**
Octafluorocyclobutane	C_4F_8	3,200	**10,592**
Perfluoropropyl methyl ether (HFE-347mcc3)	$n\text{-}C_4H_3F_7O$	5	**530**
Perfluoroisopropyl methyl ether (HFE-347mmy)	$i\text{-}C_4H_3F_7O$	3.7	**343**
Perfluoro propyl carbinol (PPC)	$CF_3CF_2CF_2CH_2OH$	0.55	**25**

Reduction Target



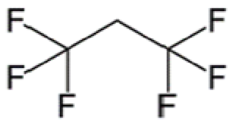
*European Court of Auditors

- Is this reduction possible?

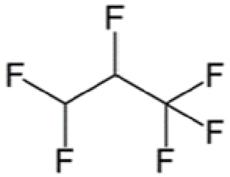
Research in SKKU

Yeom's Group

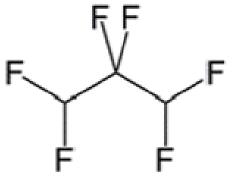
Appl. Surf. Sci. 600, 154050 (2022)



1,1,1,3,3,3-hexafluoropropane
(HFC-236fa)



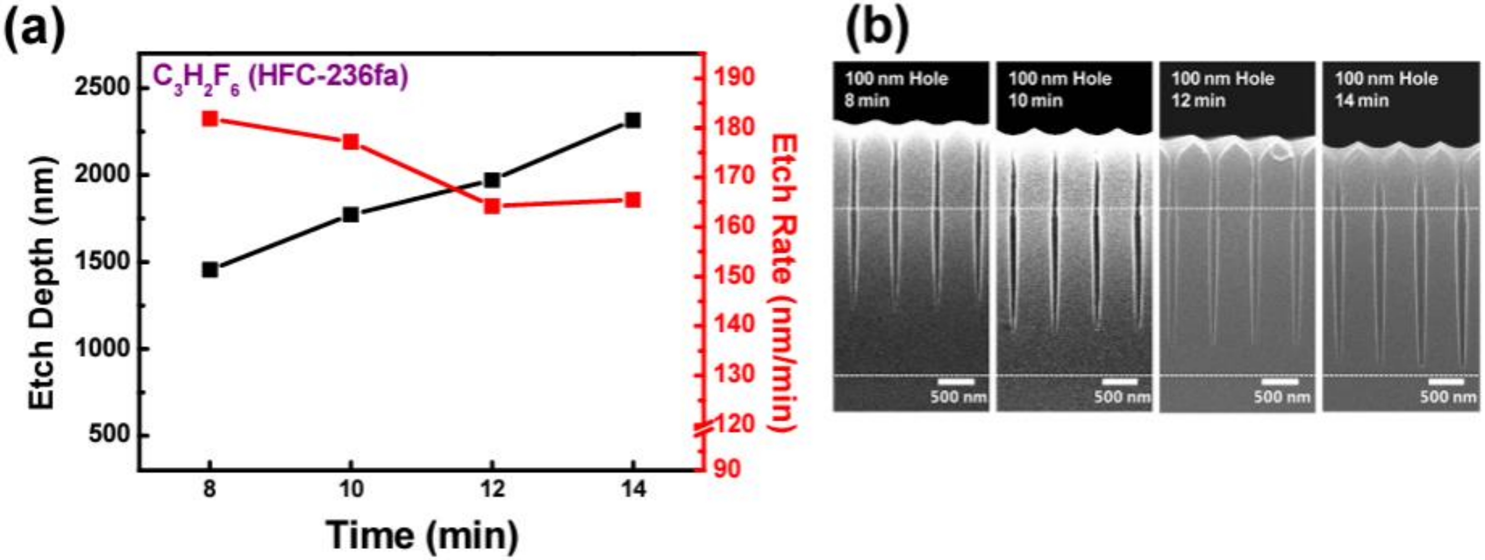
1,1,1,2,3,3-hexafluoropropane
(HFC-236ea)



1,1,2,2,3,3-hexafluoropropane
(HFC-236ca)

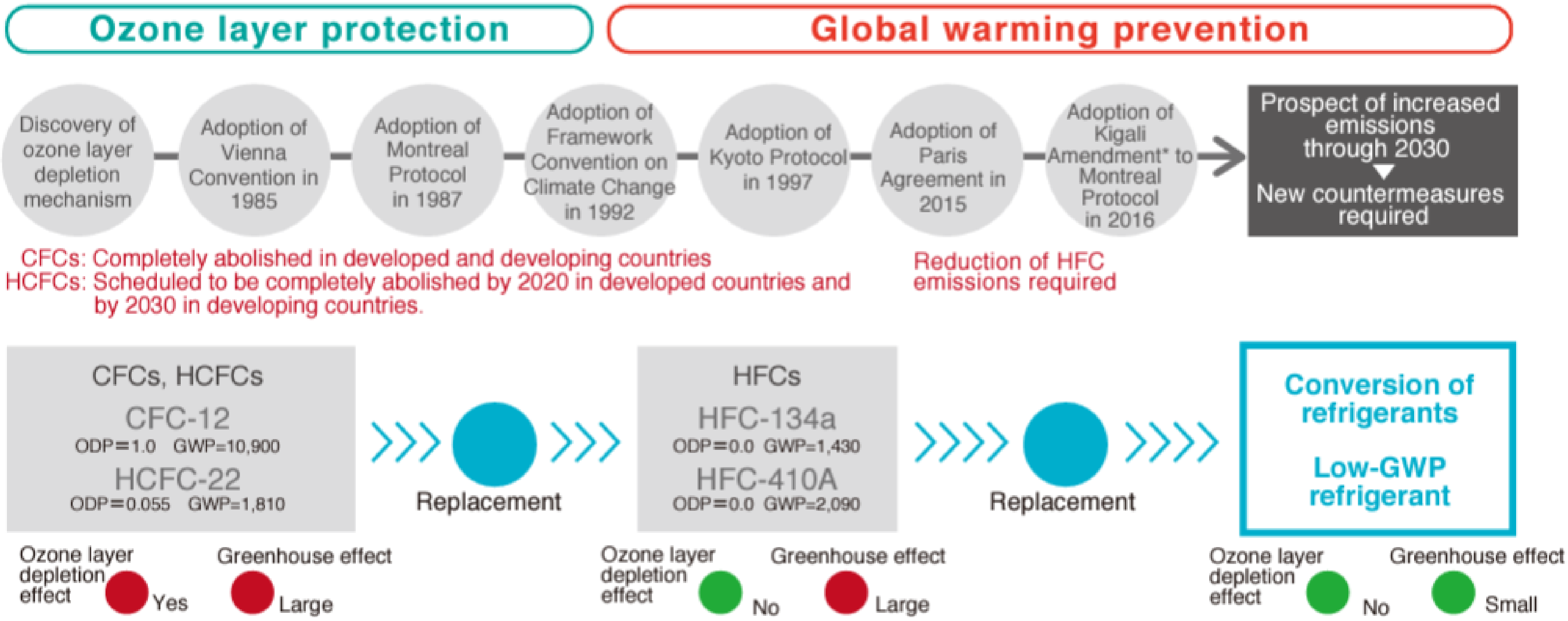
← Faster Etch Rate

Higher Polymerization →



Activities for Reduction of GHG Emission in Semiconductor Industry

Activites in Japan: NEDO



Ozone layer protection

Global warming prevention

Discovery of ozone layer depletion mechanism

Adoption of Vienna Convention in 1985

Adoption of Montreal Protocol in 1987

Adoption of Framework Convention on Climate Change in 1992

Adoption of Kyoto Protocol in 1997

Adoption of Paris Agreement in 2015

Adoption of Kigali Amendment* to Montreal Protocol in 2016

Prospect of increased emissions through 2030
▼
New countermeasures required

CFCs: Completely abolished in developed and developing countries
HCFCs: Scheduled to be completely abolished by 2020 in developed countries and by 2030 in developing countries.

Reduction of HFC emissions required

CFCs, HCFCs
CFC-12
ODP=1.0 GWP=10,900
HCFC-22
ODP=0.055 GWP=1,810

Ozone layer depletion effect ● Yes
Greenhouse effect ● Large

Replacement

HFCs
HFC-134a
ODP=0.0 GWP=1,430
HFC-410A
ODP=0.0 GWP=2,090

Ozone layer depletion effect ● No
Greenhouse effect ● Large

Replacement

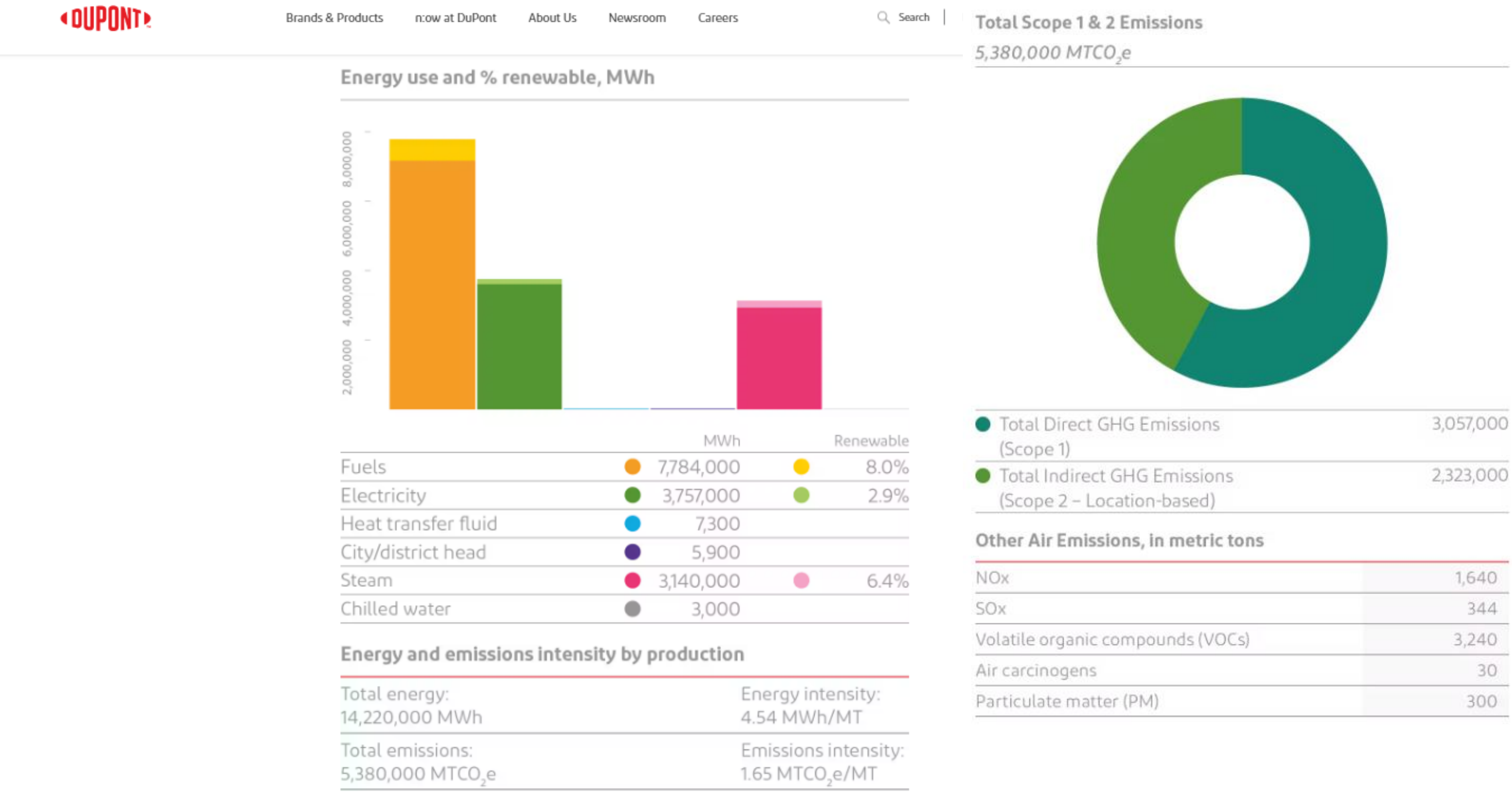
Conversion of refrigerants

Low-GWP refrigerant

Ozone layer depletion effect ● No
Greenhouse effect ● Small

Ozone-depleting potential (ODP): This term refers to the relative strength of the depletion effect affecting the ozone layer when the strength of CFC-11 is fixed at 1.0.
*Kigali is the name of the capital city of Rwanda where the 28th Meeting of the Parties to the Montreal Protocol (MOP28) took place.
The agreement is called the Kigali Amendment since it was concluded at this meeting.

Activities in USA



Energy use and % renewable, MWh

		MWh		Renewable
Fuels	●	7,784,000	●	8.0%
Electricity	●	3,757,000	●	2.9%
Heat transfer fluid	●	7,300		
City/district head	●	5,900		
Steam	●	3,140,000	●	6.4%
Chilled water	●	3,000		

Energy and emissions intensity by production

Total energy: 14,220,000 MWh	Energy intensity: 4.54 MWh/MT
Total emissions: 5,380,000 $MTCO_2e$	Emissions intensity: 1.65 $MTCO_2e/MT$

Total Scope 1 & 2 Emissions

5,380,000 $MTCO_2e$

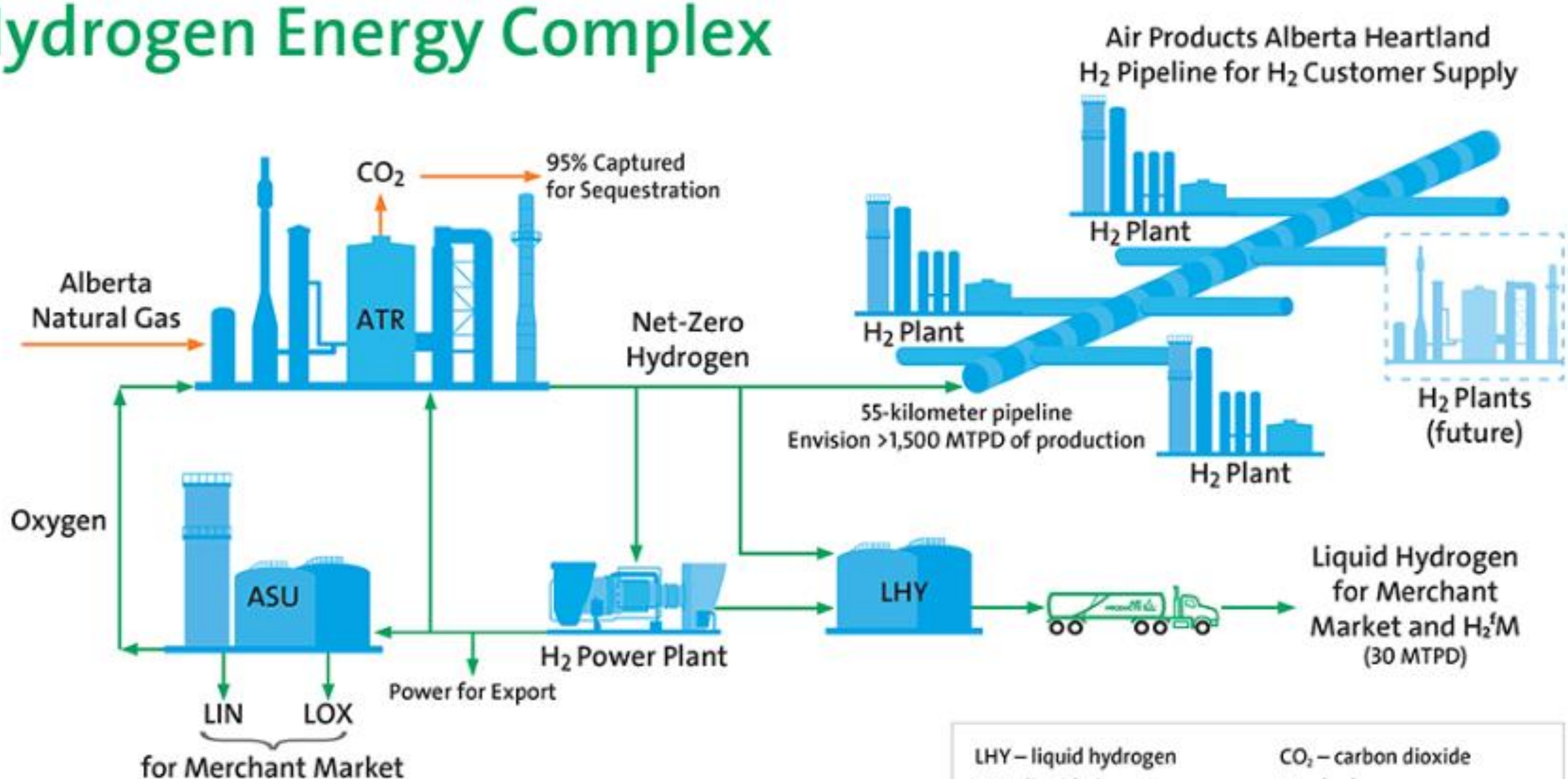
●	Total Direct GHG Emissions (Scope 1)	3,057,000
●	Total Indirect GHG Emissions (Scope 2 – Location-based)	2,323,000

Other Air Emissions, in metric tons

NOx	1,640
SOx	344
Volatile organic compounds (VOCs)	3,240
Air carcinogens	30
Particulate matter (PM)	300

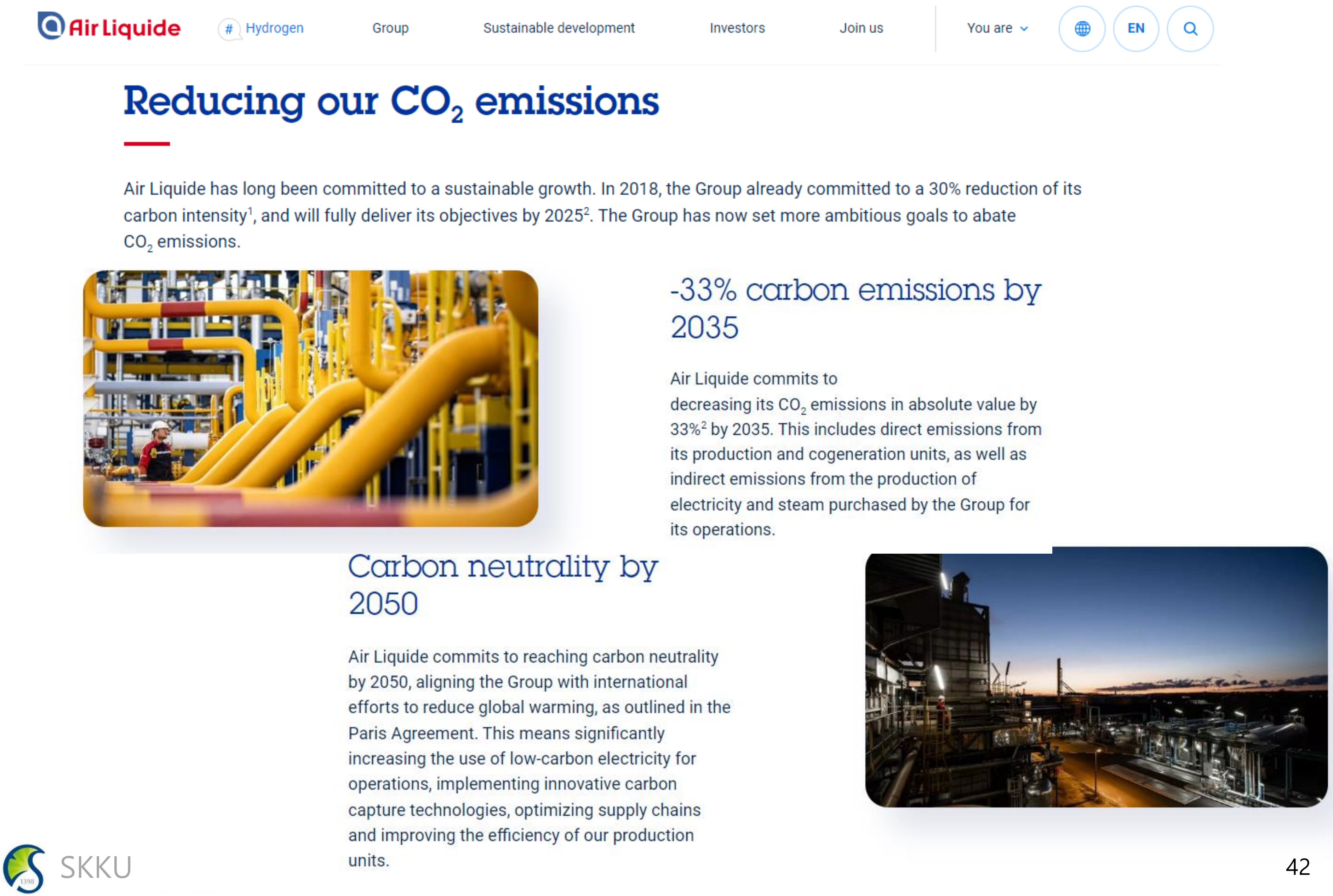
Activities in Europe: Air Products

Air Products' World-Scale Net-Zero Hydrogen Energy Complex



LHY – liquid hydrogen
LIN – liquid nitrogen
LOX – liquid oxygen
ATR – autothermal reformer
CO_2 – carbon dioxide
H_2 – hydrogen
H_2^fM – hydrogen for mobility

Activities in Europe: Air Liquide



Reducing our CO_2 emissions

Air Liquide has long been committed to a sustainable growth. In 2018, the Group already committed to a 30% reduction of its carbon intensity[1], and will fully deliver its objectives by 2025[2]. The Group has now set more ambitious goals to abate CO_2 emissions.

-33% carbon emissions by 2035

Air Liquide commits to decreasing its CO_2 emissions in absolute value by 33%[2] by 2035. This includes direct emissions from its production and cogeneration units, as well as indirect emissions from the production of electricity and steam purchased by the Group for its operations.

Carbon neutrality by 2050

Air Liquide commits to reaching carbon neutrality by 2050, aligning the Group with international efforts to reduce global warming, as outlined in the Paris Agreement. This means significantly increasing the use of low-carbon electricity for operations, implementing innovative carbon capture technologies, optimizing supply chains and improving the efficiency of our production units.

Activities in US: Air Product

Current "Third by '30" Carbon Intensity Goal
Scope 1 and 2

2021 reduction of 4%

Significant improvement later in decade as key projects come onstream

New "Third by '30" Carbon Intensity Goal
Scope 3

Reduce intensity by **1/3 from 2015 baseline**

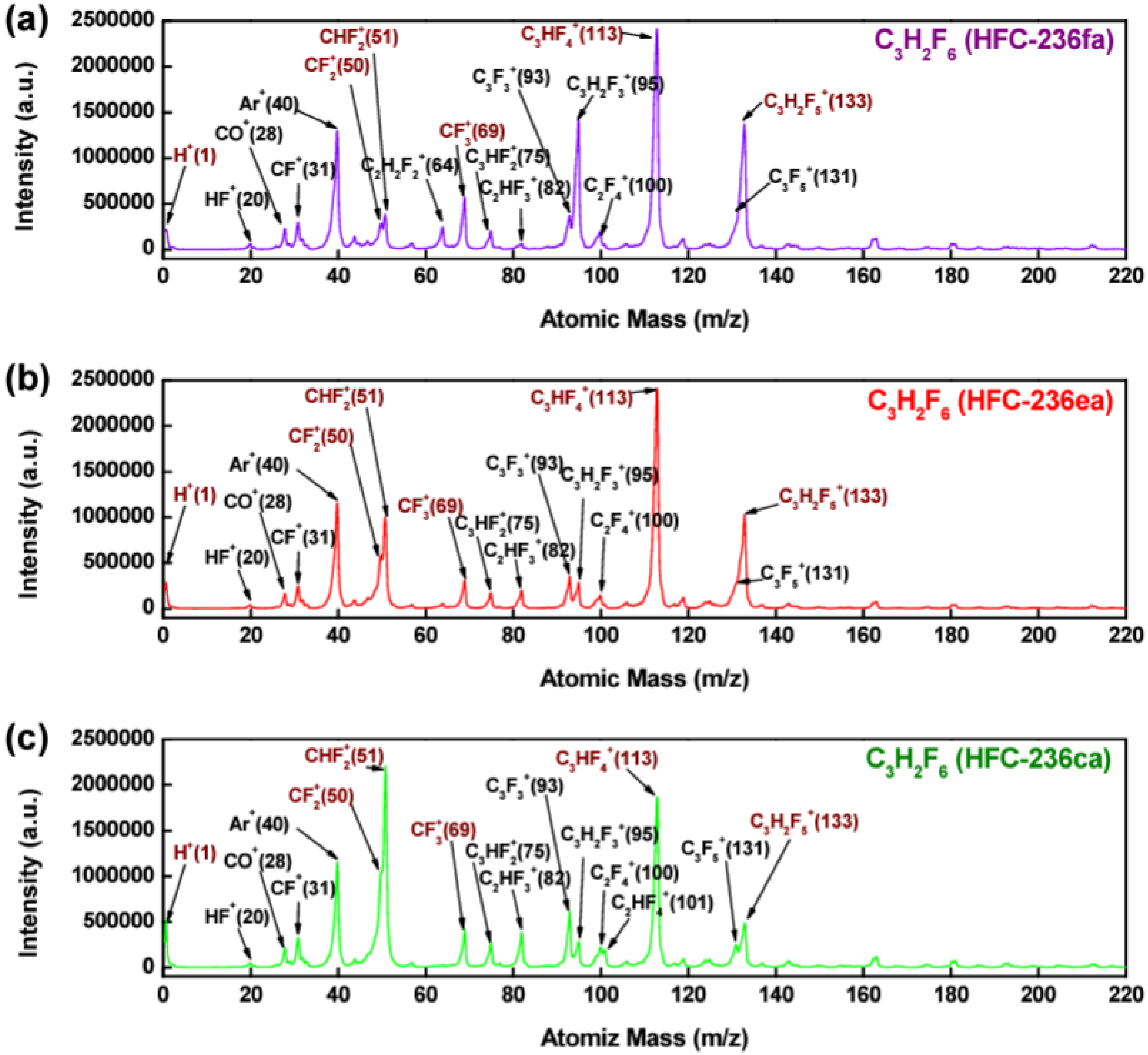
Scope 3 categories include upstream energy, use of sold products and investments

- **Third by '30 Scope 3 goal**
- **Net Zero by 2050**
- **$15B in capex for Energy Transition**
- **Engage on Science-Based Targets**
- **Climate benefits of zero- and low- carbon H_2**

Research in SKKU

Yeom's Group

Appl. Surf. Sci. 600, 154050 (2022)



Questions

- 대체가스: 합성 vs. 정제,
- 배출제어: POU vs. 총괄처리?, 에너지 효율
- 인증평가: 우리나라 규제 강도의 정도, Tier 1~4, Scope 1~3
- 소자/현장: 저전력반도체, 공정별 사용량 정보 공유 여부? RE100?
  - 협력 저해 요인, 리스크 적은 공정부터 적용, Coolant
- 기타: 공급망/운송의 문제(Scope 3)

Evaluated Precursors

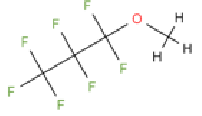
Partially fluorinated

Ether

Heptafluoropropyl methyl ether (HFE-347mcc3)

B.P (℃)	GWP	C/(F+O-H)
34	530	0.8

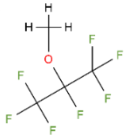
$C_4H_3F_7O$



Heptafluoroisopropyl methyl ether (HFE-347mmy)

B.P (℃)	GWP	C/(F+O-H)
29	353	0.8

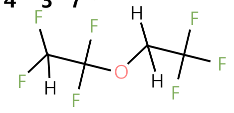
$C_4H_3F_7O$



1,1,2,2-tetrafluoroethyl-2,2,2-trifluoroethyl ether (HFE-347pcf2)

B.P (℃)	GWP	C/(F+O-H)
50	889	0.8

$C_4H_3F_7O$

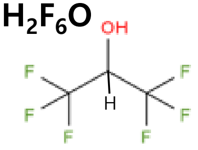


Alcohol

Hexafluoroisopropanol (HFIP)

B.P (℃)	GWP	C/(F+O-H)
59	190	0.6

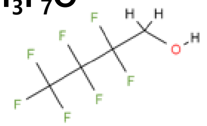
$C_3H_2F_6O$



Perfluoropropyl carbinol (PPC)

B.P (℃)	GWP	C/(F+O-H)
95	16	0.8

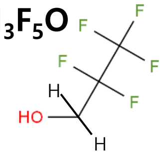
$C_4H_3F_7O$



Pentafluoropropanol (PFP)

B.P (℃)	GWP	C/(F+O-H)
80	42	1

$C_3H_3F_5O$



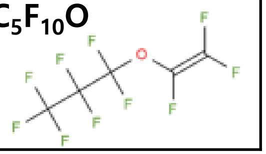
Perfluorinated

Ether

Perfluoropropyl vinyl ether (PPVE)

B.P (℃)	GWP	C/(F+O-H)
35	3	0.45

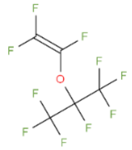
$C_5F_{10}O$



Perfluoroisopropyl vinyl ether (PIPVE)

B.P (℃)	GWP	C/(F+O-H)
35	3	0.45

$C_5F_{10}O$

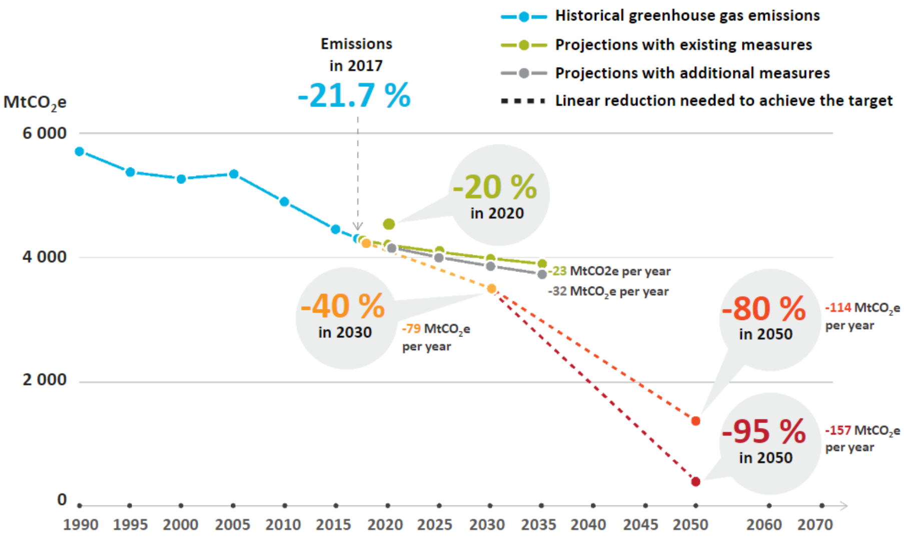


PFCs 저감이 필요한 이유

- **PFCs (Perfluorocompounds)**

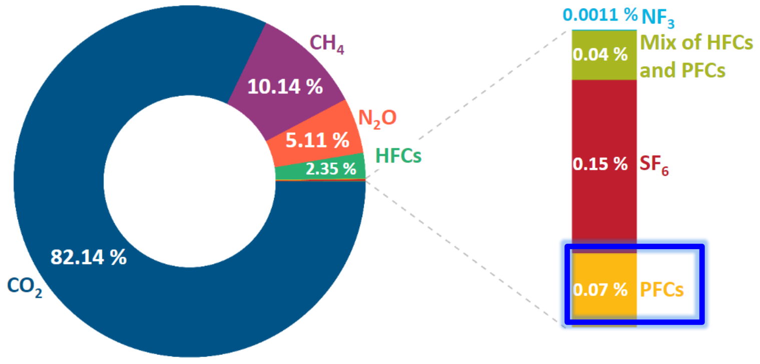
: 반도체·디스플레이 산업에서 주로 발생되는 Greenhouse gas로 총 배출량 중 약 0.07%이나, 지구온난화지수(GWP)가 높고 Lifetime이 길어 저감 필요.

Greenhouse Gas Emission Trend and Future Emission Reduction Targets



*European Court of Auditors

Greenhouse Gas Emissions by Gas



*Data on emissions from the aggregated EU inventory reported to the UNFCCC in 2019.

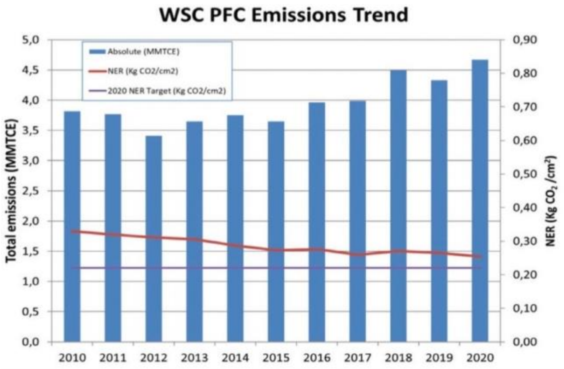
Greenhouse Gas	GWP	Lifetime (yr)
CO_2	1	Variable
CH_4	21	12.2
NO_2	206	120
HFCs	140 - 11,700	1.5 - 264
PFCs	6,500 - 9,200	3,200 - 50,000
SF_6	23,000	3,200

PFCs 저감 방안 및 연구시 고려 사항

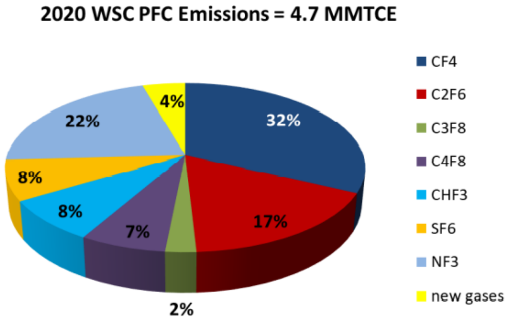
- 현재 산업에서 공정 최적화 및 처리 기술 효율화로 PFCs 저감 진행 중
- PFCs 대체 물질이 산업에 적용되기 위해선 기존 물질과 동일한 Device 성능 확보가 절대적

→ 연구시 대체 Gas의 Low GWP 와 더불어 Etch Profile, Selectivity, Rate 등에 중점 예정

PFCs Emissions Trend



*NER(Normalized Emission Rate
:실리콘 기판 면적당 온실가스 배출량, kg CO_2/cm^2)



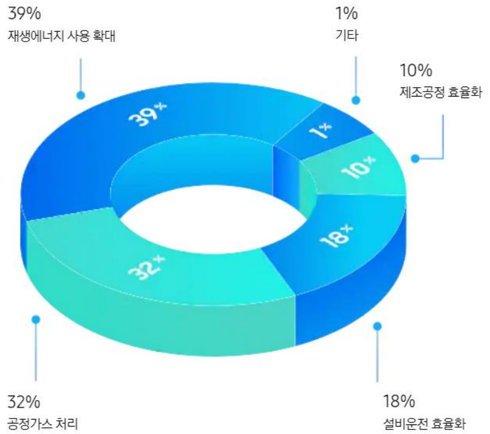
PFCs 저감 방안 및 실제 산업 성과

PFCs 저감 방안

대체 물질 개발	회수 및 재사용
공정 최적화	처리 기술

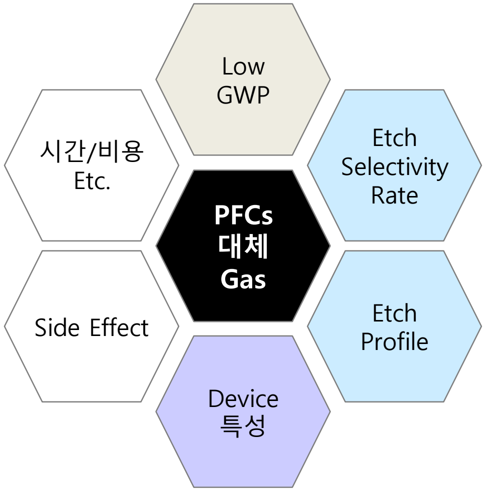
▶ 삼성전자 2020년 PFCs 감축 비율

: 공정 최적화 및 처리 기술의 감축 비중↑



PFCs 대체 물질 개발시 고려 사항

▶ C_2F_6, C_3F_8 → C_4F_8 or NF_3 대체 물질 사례처럼 기존 PFCs Gas와 Device 특성 동일 or 개선 필요



선행 연구

- **수많은 Low GWP Gas에 대해 연구 진행중이며,**
- **Hole Pattern 시료로 Profile 확보하고 다양한 분석 방법 Tool을 활용하여 Gas별 유의차를 해석하고 이해하여 예측하는 것이 목표.**

No.	Precursor	Target Material	Process	Plasma	Analysis							Sample	Etch Rate	Selectivity	Remarks
					VI-Pro.	XPS	FT-IR	QMS	SEM	OES	Etc.				
1	C6F6	SiO2	RIE	ICP/CCP		●			●	●		Hole Pattern ACL/SiO2/Si	~400nm/m @ICP ~267nm/m @CCP	~6.5 @ICP ~23 @CCP	ICP: etch parameter 잘 control하면 etch rate high, anisotropic profile.
2	c-C4F8, c-C5F8, C7F8	SiO2	RIE	ICP		●				●		SiO2/Si3N4, SiO2/ACL	C4F8>C5F8>C7F8	C7F8>C5F8>C4F8	C가 많을수록 (F/C Ratio 감소) SiO2 etch rate 감소, selectivity 증가
3	C3F7OCH3, C4F8, CHF3	SiO2 Si3N4	ALE	ICP	●	●					●	SiO2, Si3N4	C4F8>CHF3 >C3F7OCH3	C3F7OCH3 >CHF3>C4F8	F/C Ratio↓ low etch rate, high selectivity C3F7OCH3 ALE Window: 55-60V
4	C3F7OCH3 (HFE-347mmc3), C5F10O (PPVE)	SiO2	RIE	ICP		●				●	●	SiO2	347mmc3>PPVE (2.5배@bias -400V)	-	Low bias: FC layer 두께+ratio High bias: F/C ratio만 etch 속도 제어
5	C4F8, HFE-347mmc3, HFE-347mmy, PPVE	SiO2 Si3N4 Poly-Si	RIE	ICP			●	●			●	SiO2, Si3N4, Poly-Si	막질別 상이 SiO2 PP>C4>HF Si3N4 y>c>P>C Poly-Si P>C>c>y	막질別 상이 SiO2 mc(18)>my(13) Si3N4 mc(24)<my(18)	PPVE: O 존재하여 CO 형성 C-C peak↓ -mmc, mmy: H 존재하여 hydrocarbon film 형성 → C-C,C-H peak↑
6	C3F6O, C4F8	SiO2	RIE	df-CCP		●	●		●	●		Hole Pattern SiO2/ACL	C3F6O>C4F8	C4F8>C3F6O	C3F6O: Etch profile more anisotropic
7	C4H3F7O (HFE-347mmy, HFE-347pcf2)	SiO2	RIE	ICP							●	SiO2	347mmy>347pcf2	-	CF2 radical 형성에 따른 FC Layer 증가 Ion 입사각에 따른 Etch rate: 50-60º Best
8	C5F10O (PPVE, PIPVE)	SiO2	RIE	ICP					●		●	Hole Pattern SiO2/ACL	PPVE>PIPVE	-	Ion 입사각에 따른 Etch rate: 40-60º Best
9	C3H2F6O (HFIP), C4F8	SiO2	RIE	ICP		●			●	●	●	Hole Pattern SiO2/ACL	HFIP>C4F8	-	HFIP: O 존재→O radical→FC Layer 두께↓ Etch depth: HFIP>C4F8
10	C4F8, HFE-347mmc3, HFE-347mmy, C4H3F7O (PPC)	SiO2 Si3N4 Poly-Si	RIE	ICP	●	●	●	●	●			SiO2, Si3N4, Poly-Si Hole Pattern SiO2/ACL	막질/Source Power 別 상이 Pattern P,y>C4>c	막질/Source Power 別 상이 Pattern: C4>P,y>c	
	C4F8, C6F6 + α	SiO2	RIE	ICP	●	●	●	●	●	●	●	Hole Pattern SiO2/ACL			

SKKU

Cooperation Required

- Device makers
  - Identify the gases
  - Share process issues as much as possible

- Chemical/gas makers
  - Provide alternatives gases

- Equipment/reactor makers
  - Collaborate with chemical provides in early phase of development

- Monitoring/analysis tool makers
  - Assess greenhouse emission
  - Real-time monitoring