Fluorocarbon Gases for Advanced Dielectric Etch Applications: A Chemical Manufacturer's Perspective

Michael Mocella

DuPont Electronic Gases

michael.mocella@usa.dupont.com

No one ever asks ...

Why are my dielectric etch gases so cheap?

But the reason is ...

Fluorocarbon etch gases have been either large-volume industrial products, or co-products in such processes

Products	**Co-products**
CH_2F_2	CF_4 (from CF_2Cl_2)
$C_2H_2F_4$	CHF_3 (from CHF_2Cl)
C_2HF_5	C_2F_6 (from C_2F_5Cl)
C_3F_6	C_4F_8 (from Teflon®)

The current challenge

- Damascene processing requires high selectivity etching of silicon dioxide versus closely-related compounds (especially silicon nitride)
- This requires precise control of the relative fluoropolymer formation rates on the films
- It is commonly believed that compounds with F/C ratios of 2 and below best serve this requirement

Summary of options at F/C ≤ 2

- PFCs (perfluorocompounds)
- HFCs (hydrofluorocompounds)
- OFCs (oxyfluorocompounds)
- UFCs (unsaturated fluorocompounds)

Availability & economics of these gases may not follow the traditional (existing product/co-product) model

PFC options

Compound	Availability	Applications
C_2F_6 (116)	Commercial, product	numerous – see Application Guide*
c-C_3F_6 (C216)	Not commerical	
C_3F_8 (218)	Commercial, co-product	JVST B, 14, 3470 (1996); JVST A, 14, 1092 (1996)
c-C_4F_8 (C318)	Commercial, co-product	numerous – see Application Guide*

* www.dupont.com/zyron

HFC options

Compound	Availability	Applications
CH_2F_2 (32)	Commercial, product, flammable	numerous – see Application Guide*
CH_3F (41)	Commercial, product, flammable	US 6,025,255; US 5,942,446; US 5,906,948
CH_2FCF_3 (134a)	Commercial, product	multiple – see Application Guide*
H_3CCF_3 (143a)	Commercial, product, flammable	
H_3CCHF_2 (152a)	Commercial, product, flammable	JJAP, 39, 4666 (2000)
$F_3CCH_2CF_3$ (236fa)	Commercial, product	US 6,183,655; US 6,120,697
$CF_3CH_2CHF_2$ (245fa)	Commercial, product	US 6,120,697
$F_3C(CHF)_2CF_2CF_3$ (4310meee)	Commercial, product	

* www.dupont.com/zyron

OFC options

Compound	Availability	Applications
$CF_3CF(O)CF_2$ (HFPO)	Manufactured, product; toxic	US 5,928,963
(CF3)2CO (HFA)	Manufactured, product; highly toxic	
C_4F_8O	Commercial, co-product	
$C_2F_2O_2$ (oxalyl fluoride)	Potentially	JECS, 148, G141 (2001); WO 99/34429

A substantial number of fluorocompounds containing ether (C-O-C) and carbonyl (C=O) linkages are reported in Japanese studies

UFC options

Toxicity concerns are typically larger for this class versus the others

Compound	Availability	Applications
C_2F_2	No, unstable	
C_2F_4 (TFE)	Manufactured, product; reactivity	US 5,874,013; JVST B, 18, 166 (2000); JVST A, 14, 2127 (1996); R. Chatterjee et al, SEMICON Southwest 2001 PFC Seminar
$CF_3CF=CF_2$ (HFP)	Commercial, product	multiple – see Application Guide*
$CF_3OCF=CF_2$ (PMVE)	Manufactured, product	CA 134, 230651
F2C=CFCF=CF2	Commercial, co-product	US 6,174,451
(CF3)C=CH2	Commercial, product	
c-C_5F_8	Commercial, intermediate	US 6,159,862; US 6,069,092
$F_3CC(F)=C(F)CF_2CF_3$ (PF2P)	Manufactured, intermediate	* www.dupont.com/zyron

Conclusions

- Many compounds available at F/C ≤ 2
- Compound uniqueness versus process development flexibility/options?
- The attributes of optimum compounds for advanced dielectric etch are not well understood or predictable
- Empirical process development seems likely to continue as a dominant process specification methodology