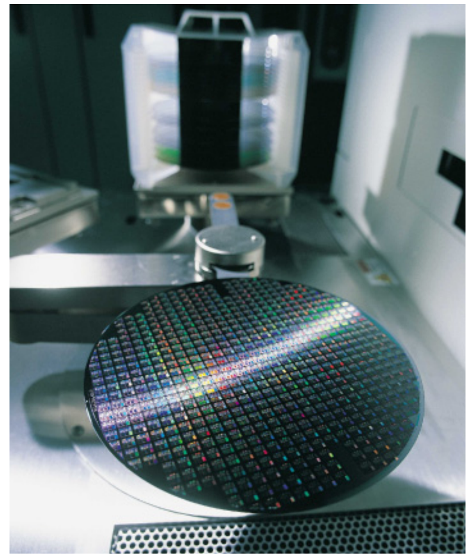
4.3.2 SEMICONDUCTOR INDUSTRY: SUBSTITUTES FOR HIGH GWP GASES

Technology Description

Semiconductor manufacturers perform plasma etching and cleaning processes that use gaseous chemicals including perfluorocarbons (e.g., CF_4, C_2F_6 and C_3F_8), nitrogen trifluoride (NF_3), HFC-23 (CHF_3), and sulfur hexafluoride (SF_6). Collectively termed high global-warming potential (GWP) gases, these chemicals are potent greenhouse gases; one metric ton of SF_6 is equivalent to 23,900 Mt of carbon dioxide in terms of its potential effect on global warming. In addition, many high GWP gases have extremely long lifetimes in the atmosphere (3,000-50,000 years). For the past 15 years, through international efforts to decrease ozone-depleting substances in the atmosphere, industry has been engaged in activities to reduce emissions and find alternatives. One method of decreasing the emissions of high GWP gases from the semiconductor industry is to substitute a different chemical or process for the high GWP gases. Replacing high GWP gases with environmentally benign substitutes for chemical vapor deposition clean and dielectric etch processes is a preferred option when viewed from the perspective of EPA's pollution prevention framework. Alternatives to the high GWP gases, such as SF_6, CF_4, C_3F_8, c-C_4F_8, and C_2F_6, are sought. To significantly lower emissions of high GWP gases, investigators seek gases that do not have high GWPs (and, if they do, are eliminated during the production process) and do not form byproducts with significant GWPs, particularly CF_4 and CHF_3. Important etch process performance criteria are etch rate, etch profile, etch selectivity, and control of the critical dimension. In this option, investigators seek alternative highly fluorinated compounds that either are not high GWP gases themselves or are highly utilized during plasma etching and do not form byproduct high GWP emissions.



PFCs, HFCs, NF_3, and SF_6 are used to construct intricate semiconductor products on silicon wafers such as this one. (Reprinted with permission of Greenleaf Publishing.)

System Concepts

- Replacements are not favored if they increase cleaning times (which adversely affects fabrication productivity), form high GWP byproducts such as CF_4 and CHF_3, or pose new health and safety hazards.
- In dielectric etch processes, fluorine is required to etch the desired features into the dielectric materials, and carbon is required to passivate newly etched surfaces by gas formation of C_xF_y polymers that are then deposited to retard etching. Generally accepted models state that the boundary between net etching and deposition is a function of the fluorine:carbon ratio in the discharge. Plasmas rich in fluorine favor etching over deposition and those rich in carbon favor deposition over etching.

Representative Technologies

- Replacing C_2F_6 with C_4-compounds, e.g., switching to c-C_4F_8 and c-C_4F_8O
- Replacing C_2F_6 with NF_3 using in situ plasma cleaning.
- Replacing C_2F_6 with a remote fluorine source that dissociates NF_3 in an upstream plasma source.
- Replacing C_2F_6 with ClF_3.
- Hydrofluorocompounds, unsaturated fluorocompounds and iodofluorocompounds are attractive etch gas candidates because they have lower GWPs.
- C_3F_8 is a potential drop-in replacement for C_2F_6 in some chemical vapor deposition clean and etch processes because its high utilization during etch may offset its high GWP.
- Using NF_3, a high-GWP gas with high process utilization, in mixtures of a noble gas with unsaturated hydrocarbons of varying degrees. Examples of unsaturated hydrocarbons are ethyne or acetylene (C_2H_2), ethylene (C_2H_4), propyne (C_3H_4) and ethane (C_2H_6).

Current Research, Development, and Demonstration
RD&D Goals • To identify the *chemical* and *physical* mechanisms that govern chemical vapor deposition chamber cleaning and etching with perfluorocarbons and non-perfluorocarbons as well as govern process performance so that emissions of high GWP gases may be significantly reduced without either adversely affecting process productivity or increasing health and safety hazards. **RD&D Challenges** • Developing conceptual models that guide the identification of candidate substitutes and substitute classes. • Finding substitutes that do not form CF_4 (or other high-GWP gases such as CHF_3). • Finding substitutes that do not require costly process requalification. **RD&D Activities** • Evaluations at the Massachusetts Institute of Technology (MIT) simulated process conditions, and at semiconductor facilities (with participation of equipment manufacturers and gas suppliers) actual representative process conditions (AMD, Motorola, and Texas Instruments). • Discovery of the in situ dilute NF_3 cleaning process. • Development of the remote NF_3 cleaning process.
Recent Progress
• Use of C_3F_8 will reduce high GWP emissions, in terms of carbon dioxide equivalent, by 60% relative to the standard C_2F_6 process. • A switch to C_4 -fluorocarbons reduces emissions by 90% relative to the standard C_2F_6 process. • Industry familiarity with the use of fluorocarbon compounds, excellent process performance and chemical cost savings make these alternatives attractive options. c-C_4F_8 is already in widespread fabrication use for high-density plasma oxide etching, reducing the usual procedures for chemical and supplier qualification by the industry. • NF_3 dilute clean process reduces high GWP emissions by 85% relative to the standard C_2F_6 process. • Remote NF_3 cleaning process reduces high GWP emissions by more than 99% relative to standard C_2F_6 process.
Commercialization and Deployment Activities
• C_3F_8 is reported in commercial applications at fabricating facilities owned by AMD, Motorola, and Texas Instruments. • IBM and Novellus have commercialized and deployed dilute NF_3 cleaning processes. • AMAT and ASTeX have deployed remote NF_3 cleaning processes. • The etch gas research underway, and completed thus far, is described as proof-of-concept. There are no reports of commercial use. **Market Context** • Identification of a cost-effective PFC substitute could have wide applicability in the semiconductor industry.