# 4.3 EMISSIONS OF HIGH GLOBAL-WARMING POTENTIAL GASES 4.3.1 SEMICONDUCTOR INDUSTRY: ABATEMENT TECHNOLOGIES





Figure 1. Litmas Blue Plasma Abatement Device

Figure 2. Hitachi Catalytic Oxidation System

Semiconductor manufacturers perform plasma etching and cleaning processes that use gaseous chemicals including perfluorocarbons (e.g., CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub> and C<sub>3</sub>F<sub>8</sub>), nitrogen trifluoride (NF<sub>3</sub>), HFC-23 (CHF<sub>3</sub>), and sulfur hexafluoride (SF<sub>6</sub>). Collectively termed high global-warming potential (GWP) gases, these chemicals are potent greenhouse gases; one metric ton of SF<sub>6</sub> 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 abate the emissions before they reach the atmosphere. Abatement of high GWP gases from the exhaust gas stream in semiconductor processing facilities may be achieved by two mechanisms: 1) thermal destruction and 2) plasma destruction. Thermal destruction technology may be applied to chamber-cleaning and etching processes within a fab (a local point-of-use [POU] application) or fab wide (an end-of-pipe [EOP] application). A POU device controls emissions as they emerge from an individual tool, while an EOP device is installed further "downstream," where it can abate emissions from a group of tools – or the entire fab – prior to the exhaust reaching the stack. Two thermal destruction technologies are being pursued: combustion systems and catalytic systems. In plasma-based systems, plasmas are formed from the effluent stream from etch or clean processes using either radio frequencies (low pressure streams) or microwaves (streams at atmospheric pressure). Destruction of high GWP gases that use plasmas offer system designers a broad range of conditions: oxidizing, reducing, and combinations of oxidizing and reducing conditions.

# **System Concepts**

• In POU applications, thermal-destruction systems may be configured to accept exhaust from multiple etch/chemical vapor deposition chambers. High GWP emissions are oxidized in a natural gas-fired burner or over an electrically heated catalyst before the combustion products are removed by the on-site waste treatment systems.

- Burner and catalytic systems require pretreatment of inlet streams to reduce the loads of unused deposition/etchant gases and particles that can block burners or clog catalysts.
- Hydrofluoric acid formed in thermal destruction systems may be removed via POU scrubbers to prevent exceeding scrubber design limits.
- Plasma abatement technologies rely on the basic idea that larger exhaust molecules are broken into fragments in the plasma and then recombine in new ways, in the presence of other fragments formed from the dissociation of other gases added to the plasma, to form a new set of exhaust gases that may then be removed by existing waste-treatment systems.
- Plasma abatement systems for high GWP gases typically require very little floor space, because they are mounted off the floor directly on the foreline to the dry pump that feeds exhaust to scrubbing systems.

## **Representative Technologies**

- The Edwards TPU 4214 (oxidation with advanced burner technology) is applicable for all high GWP emissions.
- The Hitachi system (catalytic oxidation technology) is applicable to CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, c-C<sub>4</sub>F<sub>8</sub> and SF<sub>6</sub>.
- Investigators at Texas A&M patented an approach that used radio frequency and microwave surface wave plasmas. They now favor microwave technology that has proven more effective and holds the potential for exploiting low-cost magnetron technology.
- Litmas, Inc., has two systems. The first, "Blue," uses an inductively coupled radio frequency plasma source to transform high-GWP exhaust gases from etchers. The second technology from Litmas, "Red," transforms the exhausts from plasma-enhanced chemical vapor deposition chambers using microwaves.
- AMAT's Pegasys™ POU unit integrates cold-plasma abatement technology with popular etchers, which makes the abatement unit transparent to process engineers.

### **Current Research, Development, and Demonstration**

#### RD&D Goals

- To lower high GWP emissions from waste streams by more than 99%, while minimizing (1) NO<sub>x</sub> emissions to levels at or below emissions standards, (2) water use and burdens on industrial wastewater-treatment systems, (3) fabrication floor space, (4) unscheduled outages and (5) maintenance costs.
- To apply plasma technology to develop a cost-effective POU abatement device that lowers exhaust stream concentrations of high GWP gases by two to three orders of magnitude from etchers and plasma-enhanced chemical vapor deposition chambers; and transforms those gases into molecules that can be readily removed from air emissions using known scrubbing technologies.

#### **RD&D** Challenges

- Optimal combustion conditions to achieve destruction efficiencies for all high GWP gases, minimal energy consumption, and water use.
- In low-pressure applications, convincing skeptical process engineers that back-streaming from the plasma system does not threaten etch-process performance.
- Achieving more than 99% destruction efficiencies for all high GWP gases, particularly CF<sub>4</sub> and SF<sub>6</sub>.
- Develop a cost-effective POU abatement device that lowers exhaust-stream concentrations of high GWP gases by two to three orders of magnitude, and transforms these gases into molecules that can be removed with current scrubbing technologies.

# **RD&D** Activities

• Evaluations/reviews of approximately 13 thermal-destruction systems have been completed. Evaluations and demonstrations performed under fabrication operating conditions with Litmas and Texas A&M plasma systems produced favorable results.

#### **Recent Progress**

- The Edwards TPU 4214 (oxidation with advanced burner technology) achieves more than 99% destruction efficiency.
- The Hitachi system (catalytic oxidation technology) achieves destruction efficiencies of more than 99% for CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, c-C<sub>4</sub>F<sub>8</sub> and SF<sub>6</sub>.

- Litmas, Inc., reports emission reductions from 97% to 99% for its "Blue" POU device.
- AMAT's capacitively coupled device (Pegasys II™) claims typically more than 95% reduction in emissions.
- Recent reports indicate that the surface wave device offers emissions reductions of more than 99% for a large range of tested waste streams.
- The Pegasys and Litmas radio frequency POU units appear affordable, with reasonable capital and operating costs, assuming that the existing hydrofluoric acid scrubber system (including ductwork) can handle the increase in hydrofluoric acid from these abatement units.
- The AMAT and Litmas radio frequency POU units have a small footprint, are easy to install, and are applicable to 200- and 300-mm etch tools.

#### **Commercialization and Deployment Activities**

- The Edwards TPU 4214 is the only thermal-destruction device in commercial use and represents a favored POU solution for chemical vapor deposition cleaning processes.
- AMAT's and Litmas' systems are commercially available and reported in use.
- AMAT's (Pegasys II<sup>TM</sup>) interfaces with AMAT's 200 and 300mm dielectric oxide etchers.
- Litmas' "Blue" technology has successfully completed long-term impact tests on etch process performance.
- Litmas' "Red" technology reported by Litmas to be in use on plasma-enhanced chemical vapor deposition chambers.
- There are no reports of commercial application of the surface wave plasma device. Research continues at Texas A&M.

#### **Market Context**

• Thermal and plasma destruction technologies can have broad applicability across the semiconductor industry.