



**Global Warming: A White Paper on the Science, Policies and
Control Technologies that Impact the U.S. Semiconductor
Industry**

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Global Warming: A White Paper on the Science, Policies and Control Technologies that Impact the U.S. Semiconductor Industry

Technology Transfer # 93112074A-TR

SEMATECH

March 30, 1994

Abstract: This report gives an overview of the current global warming picture as it relates to the semiconductor industry. Specifically, it addresses the interrelationship of the greenhouse effect, global warming, and perfluorocarbons; discusses global warming and climate modeling; and refers to the relevant national and international environmental policies. The report also outlines some of the emission reduction strategies being considered by the semiconductor industry and presents a table of abatement technologies by manufacturer.

Keywords: Environmental Safety, Policies, Gases, Chemical Containment Systems

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Disclaimer

This paper was compiled by Linda C. Marinilli (EPA Region I) while she was an intern at SEMATECH. This paper is her perspective on global warming issues on the semiconductor industry. However, no official support or endorsement by the Environmental Protection Agency or any other agency of the federal government is intended or should be inferred.

Acknowledgements

I would like to thank the many people who helped make this paper possible, including:

- The EPA Women’s Executive Leadership (WEL) Program that made my temporary assignment at SEMATECH possible.
- My supervisor, Suzanne Parent, who has allowed me to choose my own road.
- The library staff at SEMATECH, including Barbara Denton, Micheal Harper, Joan Conger, and Zoe Dyle, who by relentless efforts in a very short period of time gathered many pieces of pertinent information.
- Michael Mocella, Nicholas Nazarenko, and Sharon Gidumal at DuPont and Peter Maroulis, Andrew Woytek, Udo Virmalo, Robert Ridgeway, and Joseph Gentile of Air Products for their help in understanding the semiconductor industry and global warming.
- For the many kindnesses from all those at SEMATECH, including Ray Kerby, Donna Kleinert, Eric Koehler, John Cole, Jack Stankus, Marie Adams, Robin McShaffry, and Jeanne Cranford.
- Linda Chao, for being a gracious hostess.
- My friend, Bruce Kristal, for his support and thought-provoking questions.
- My family—Mom, Dad, brother Joseph, and sister-in-law Grace for their love and continued support.
- Phyllis Pei, my host supervisor at SEMATECH, who had the ability to make such an assignment a reality. For her vision, faith, determination, commitment and example I am extremely grateful.

Dedication

This paper is dedicated to the memory of my niece, Catherine Grace Marinilli.

1 EXECUTIVE SUMMARY

Data collected since 1958 have shown that atmospheric concentrations of carbon dioxide, a “greenhouse gas,” have increased, raising the question of whether the temperature of the Earth’s atmosphere will likewise increase. Additionally, certain trace gases in the atmosphere that also absorb infrared radiation from the Earth have extremely long lifetimes—on the order of thousands of years. Some of these gases are used in semiconductor manufacturing. This paper gives an overview of global warming and discusses some of the emission reduction strategies being considered by the semiconductor industry.

While some scientists are skeptical about the phenomenon of global warming and its potential impact on the global climate, it is a fact that a variety of chemicals with extremely long lifetimes are being emitted into the atmosphere every year. Their respective long-term effects and interactions with other pollutants are as yet unknown.

Federal regulations do not now mandate specific compliance measures for chemicals that might contribute to global warming, relying instead upon voluntary reporting and reduction initiatives. One such effort is the U.S. Climate Change Action Plan, which aims at reducing carbon dioxide and other “greenhouse gases” by the year 2000. The plan targets specific market sectors with noncompulsory programs to reduce or eliminate substances that contribute to global warming. The U.S. semiconductor industry is seeking ways to reduce emissions through alternative process chemicals, process optimization, recovery methods, and abatement equipment.

1.1 Conclusions

Some scientists find the evidence for impending global warming convincing, while others view the notion with skepticism. Regardless of whether global warming is occurring, it is a fact that every year chemicals with extremely long lifetimes are being emitted into the atmosphere. Because the long-term effect of these substances on the atmosphere and global climate is not known, the U.S. semiconductor industry is researching ways of changing its processes to decrease, if not completely eliminate, these long-lived gases. Maybe the Earth’s atmosphere and climate can effectively handle the increased input of such gases without global warming or other deleterious effects on the planet.

On the other hand, maybe the long-term effects will be harmful. Since it will take another decade or longer to answer this question, a concerted effort to reduce emissions of global warming agents appears to be the most prudent and environmentally responsible course of action.

Although the semiconductor industry’s use of PFCs is minimal compared to the amounts released by the aluminum smelting industry, the semiconductor industry is proactively attempting to find ways to reduce their emissions. The overall environmental impact of chemical substitution, control methods, and process optimization will have to be carefully evaluated to ensure that these efforts result in a net benefit to the environment and the semiconductor industry.

2 INTRODUCTION

Some scientists speculate that the Earth's atmosphere is getting warmer because of increasing levels of so-called "greenhouse gases." Others question the reality of this phenomenon. The purpose of this paper is to present a current snapshot of the global warming issue, particularly with respect to the U.S. semiconductor industry.

There is a natural greenhouse effect known to keep the mean temperature of the Earth's atmosphere at about 15°C (60°F). The primary gases responsible for this are water vapor and carbon dioxide (CO₂). In 1958, Dr. David Keeling began to measure the atmospheric concentration of carbon dioxide found over Mauna Loa, Hawaii. The data collected show seasonal fluctuations but also indicate a very clear upward trend of CO₂ concentrations over the past 35 years.

The question that naturally arose was that if CO₂ was helping to keep the Earth's atmosphere warm because of its capacity to absorb radiation and if its concentration was ever-increasing, would the amount of radiation trapped by the Earth's atmosphere also increase? And would this radiation increase the temperature of the Earth's atmosphere to an extent that would significantly change the global climate?

Over the past 20 years, other gases have been detected in the atmosphere. These have been found not only to absorb infrared radiation from the Earth but also to possess extremely long lifetimes—on the order of thousands of years. Speculation continues on the impact of these trace gases, the perfluorocompounds (PFCs).

The overwhelming source of these PFCs is aluminum smelting. However, a small percentage (5-10%) of these PFCs is also produced for the manufacture of semiconductors. The possibility that PFCs may be contributing to global warming has prompted the U.S. semiconductor industry to seek ways to reduce emissions through alternative process chemicals, process optimization, recovery methods, and abatement equipment.

This paper covers the scientific data related to global warming and U.S. policies toward it. Some abatement technologies are also discussed.

3 SCIENCE

3.1 The Greenhouse Effect and Global Warming

A simple definition of a greenhouse gas is one that is transparent to incoming solar radiation but traps long-wave infrared radiation. The primary greenhouse gases are water vapor and carbon dioxide. Ozone (O₃), methane (CH₄), and nitrous oxide (N₂O) are also considered greenhouse gases, but they contribute only 5% to the greenhouse effect [1]. They trap heat in the atmosphere by absorbing infrared radiation from the Earth. Because of the presence of greenhouse gases in the atmosphere, the Earth's average temperature is higher than it would be if these gases were absent. This phenomenon is known as the greenhouse effect (see Figure 1).

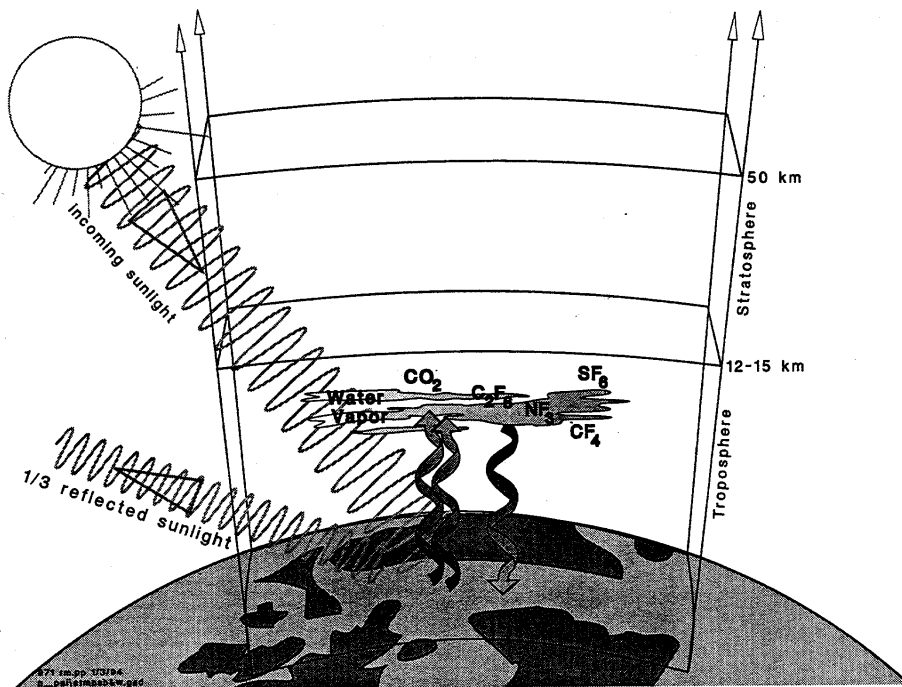


Figure 1 Greenhouse Effect

The greenhouse effect derives its name from the operation of greenhouses. Both the atmosphere and the greenhouse glass allow the sun's short-wave radiation to pass through freely, but they trap the outgoing long-wave radiation. In contrast to greenhouses, however, the atmosphere allows the heated air to be cooled by natural convective mixing.

The sun emits radiation, primarily in the form of heat and light, in wavelengths between 0.15 and 4.5 microns. These include the short-wave ultraviolet, visible, and near-infrared ranges. Short-wave radiation passes freely through the atmosphere to Earth. Approximately two-thirds of the radiation from the sun is absorbed by the Earth, warming it, while one-third is reflected back into space in the form of longer-wavelength infrared radiation (primarily between 8 and 50 microns). (See Figure 2.)

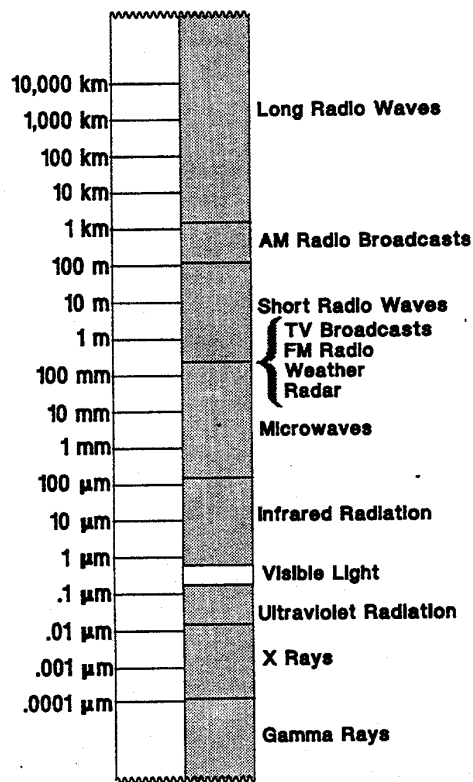


Figure 2 Electromagnetic Spectrum

Nitrogen, oxygen, and argon make up over 99% of the Earth's atmosphere. These gases absorb very little infrared radiation. Other gases, however, such as water vapor, CO_2 , O_3 , CH_4 , N_2O and chlorofluorocarbons (CFCs), present in concentrations of parts per million or less—while transparent to short-wave radiation from the sun, absorb the long-wave infrared radiation coming from the Earth (see Figure 3).

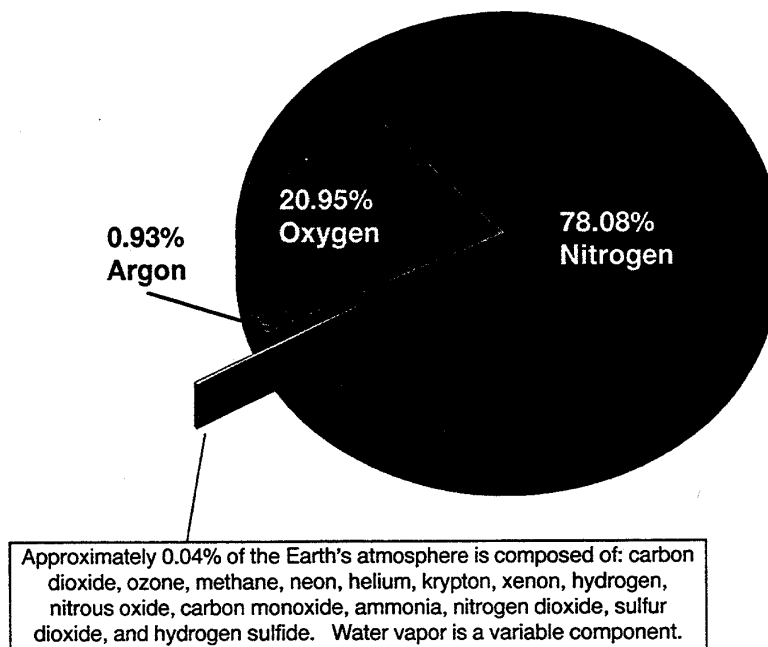
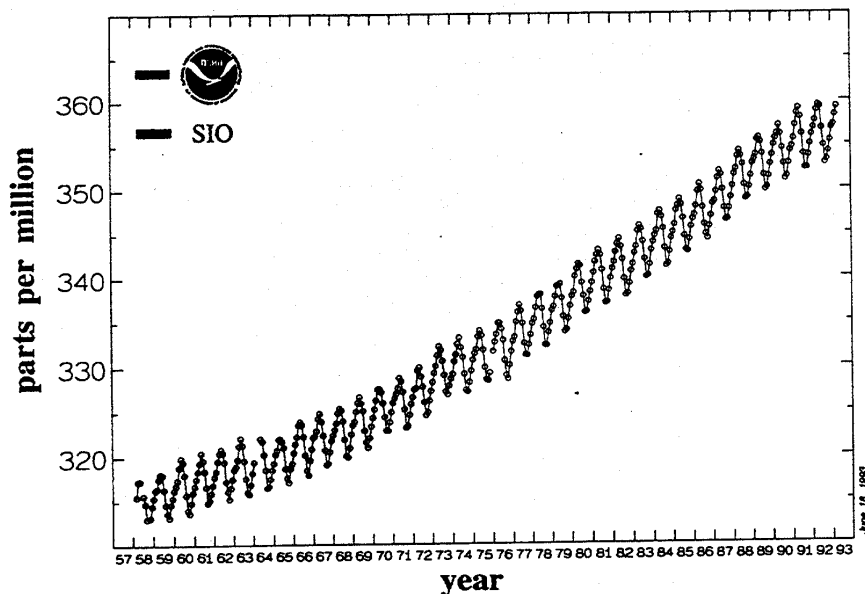


Figure 3 Gaseous Composition of the Atmosphere

Some of this long-wave infrared radiation reflected from the Earth is trapped by the greenhouse gases, which become heated and reflect the radiation back to Earth. This raises the temperature of the troposphere (the Earth's lower atmosphere). These infrared absorbing substances act as a blanket around the Earth, maintaining the global mean surface temperature at 15°C (60°F). Without water vapor and CO₂, the Earth's average surface temperature would be -18°C (0°F)—about 33°C colder. Therefore, an energy balance of global radiation results, since heating by incoming short-wave radiation is offset by cooling from outgoing long-wave infrared radiation.

Data collected over the last century show an increase in the amount of atmospheric CO₂ from a pre-industrial (mid-18th century) level of 280 parts per million by volume (ppmv) to a level of 353 ppmv in 1990. If the CO₂ emissions produced by accelerated rates of fossil fuel consumption and deforestation continue at the present rate, CO₂ concentrations by the year 2050 could be twice as great as the pre-industrial era concentrations [2]. Figure 4 shows the increase in atmospheric concentration of CO₂ over Mauna Loa, Hawaii, from readings that Dr. David Keeling began taking in 1958.



Atmospheric carbon dioxide mixing ratios. Data prior to May 1974 are from the Scripps Institution of Oceanography, data since May 1974 are from the National Oceanic and Atmospheric Administration. Principal Investigators: Pieter Tans, NOAA/CMDL Carbon Cycle Group, Boulder, Colorado, (303) 497-6676, and Charles D. Keeling, SIO, La Jolla, California, (619) 534-6001.

Figure 4 Mauna Loa Monthly Mean Atmospheric CO₂ Concentration

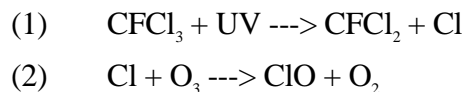
Since it is known that CO₂ is a greenhouse gas, the increasing quantities raise the question of how much the temperature would increase if the trend continued. There is conjecture that anthropogenic (derived from the activities of man) sources of other chemicals such as CH₄ and N₂O may also contribute to this warming. This additional warming is known as the enhanced greenhouse effect or, more popularly, global warming.

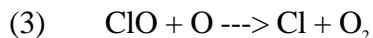
Global warming becomes a concern in that these infrared absorbing gases and others are increasing in the atmosphere. Can the Earth maintain its energy balance with these increasing concentrations or will the heat begin to accumulate and produce an increase in the Earth's surface temperature?

3.2 Global Warming and Ozone Depletion

In the early 1930s, organic compounds were developed containing one or more carbon atoms, along with chlorine and fluorine, to serve as nonexplosive, nontoxic household and commercial refrigerants. Soon these CFCs were being used in many other aspects of everyday life, including insulation, aerosol sprays, and fire extinguishers. Because of their relative inertness, CFCs are able to pass through the troposphere and into the stratosphere (which contains the Earth's protective layer of ozone).

In 1974, Dr. Sherwood Rowland and Dr. Mario Molina published a paper that presented a theoretical chemical model for the ozone-destroying effects of CFCs [3]. At the top of the stratosphere, where ultraviolet radiation is intense, CFC molecules begin to dissociate and release energetic chlorine atoms. These chlorine atoms then react with ozone (O₃) to release a molecule of oxygen, resulting in ozone depletion. The following is the proposed mechanism:





It is believed that reactions (2) and (3) continue almost indefinitely, meaning that one Cl atom can destroy many ozone molecules. This theory was confirmed in 1985 when scientists associated with the British Antarctic Survey, who had been studying the atmospheric chemistry above Antarctica since 1957, found that springtime levels of ozone had decreased by nearly 40%, while ultraviolet radiation had increased tenfold [4]. The hole in the ozone layer had been found.

So how does this affect global warming? The ozone layer in the upper stratosphere blocks the penetration of radiation from the sun. With a thinning protective ozone layer, the Earth is hit by more of the sun's radiation. Also, the CFC molecules, which destroy the ozone layer, absorb the Earth's outgoing long-wave radiation between 7 and 13 microns. This range normally contains the wavelengths at which infrared radiation can pass through the atmosphere back into space. The CFCs essentially block the release of infrared radiation and thereby disrupt the heat balance of the Earth.

Ozone is also a greenhouse gas. Warming by CFCs may be offset by cooling from stratospheric ozone depletion; diminished amounts of ozone decrease the amount of solar and long-wave radiation absorbed. The net effects of ozone depletion on global warming depend on where in the atmosphere the ozone is destroyed.

3.3 Quantifying Global Warming

Most of the chemicals that are released into the atmosphere as a result of human activities or natural processes are either converted to other forms or completely removed from the atmosphere within a few years. Most of these chemicals react with the major oxidants in the atmosphere or are photolyzed at wavelengths greater than 190 nanometers (nm) [5]. (Photolysis is the breaking of a molecule into smaller fragments by the absorption of photons with energies greater than the dissociation energy of the molecule.) A few chemicals, however, do not react to any significant extent in the atmosphere. How long they persist and what effects they may produce in the future become important questions.

The calculated change in outgoing thermal radiation from the Earth attributable to a change in a greenhouse gas (if nothing else changes) is called radiative forcing. A factor that alters the balance of incoming and outgoing radiation from the Earth is called a radiative forcing agent. Reaction rates identify the time required for one chemical to react with another to decompose. The lifetime of a chemical is based on its reactivity or reaction rate coefficients. Reaction rate coefficients for the greenhouse gases are very small. Therefore, these chemicals react extremely slowly in predicted atmospheric reactions. Reaction-rate coefficients coupled with a model incorporating chemistry and atmospheric transport yield calculated lifetimes or atmospheric residence times.

Both the atmospheric lifetime of a chemical and its infrared absorption spectrum are used to calculate global warming potentials (GWPs). The concept of relative GWPs has been developed to take into account the differing times that gases remain in the atmosphere. This index defines the time-integrated warming effect resulting from an instantaneous release of unit mass (1 kg) of a given greenhouse gas in today's atmosphere, relative to that from 1 kg of carbon dioxide [6]. For example, a kilogram of methane produces the same amount of global warming over a 100-year period as do 11 kilograms of CO₂, hence methane has a GWP₁₀₀ of 11 [7].

The following equation is used to calculate GWP:

$$GWP_T = \frac{\int_0^T a_i c_i dt}{\int_0^T a_{CO_2} c_{CO_2} dt}$$

where:

a_i = the instantaneous radiative forcing resulting from a unit increase in the atmospheric concentration of trace gas, i

c_i = the concentration of trace gas, i , remaining in the atmosphere at time, t , after the release of unit mass at $t = 0$

t = the number of years over which the calculation is performed

The corresponding values for CO_2 are in the denominator. Therefore, the GWP is the ratio of the time-integrated radiative forcing of a trace gas to that of an equal mass of CO_2 . The GWP depends on the infrared absorption spectrum and the atmospheric lifetime of a particular substance. “The concept of the GWP has been developed for policy makers as a measure of the possible warming effect on the surface-troposphere system arising from the emission of each gas relative to CO_2 . The indices are calculated for the contemporary atmosphere and do not take into account possible changes in chemical composition of the atmosphere [8].” In other words, GWPs are a means to begin to quantify the possible effects of these trace gases in the atmosphere. The absorption capabilities of greenhouse gases may change the balance of the Earth’s absorbed solar radiation and outgoing infrared radiation.

3.4 Climate Modeling

Because global warming could potentially alter the Earth’s climate, scientists have been trying to predict the effects of this phenomenon using mathematical models. These models attempt to quantify or explain the Earth’s response to global warming and to predict the consequences of such warming. Climate models are mathematical formulations of atmosphere, ocean, and land surface processes that are based on classical physical principles [9]. The models range from simple one-dimensional models to complex three-dimensional ones with hundreds of equations. The simplest models reduce a three-dimensional spatial representation of the atmosphere to one dimension, usually the vertical (altitude). Two-dimensional models represent both altitude and latitude, while three-dimensional models generate equations for altitude, latitude, and longitude.

The most common three-dimensional models are the Numerical Weather Prediction (NWP) models, Chemical Transport models (CTMs), and General Circulation models (GCMs). NWPs are used to forecast daily weather; GCMs, to determine current and future climate under several atmospheric perturbations; CTMs, to study the long-range transport of trace gases. Most of these models are used to determine the temperature increases that would occur if CO_2 levels were doubled. In studies of climate change resulting from increased greenhouse gas concentrations, the models usually take into account simple representations of the oceans, land surface temperatures, and soil moisture.

Only a few models have been developed that can link all the main components of the climate system in a comprehensive way. Many of these complex models require a great deal of scarce, high-

end computer resources. As will be discussed in more detail, feedback mechanisms in the climate system introduce nonlinearities that account for many of the difficulties in predicting climate change. The fundamental processes driving the global climate system are heating by incoming short-wave solar radiation and cooling by outgoing long-wave infrared radiation into space.

The most common models used are variations of the GCMs and predict an increase in average global surface temperature ranging from 1.9 to 5.2°C for a doubling of the CO₂ concentration in the atmosphere. Most of the estimates lie between 3.5 and 4.5°C [10]. According to a report by the Intergovernmental Panel on Climate Change (IPCC), the wide disparity in these estimates stem from the difficulty of simulating clouds. However, all models predict that a doubling of the CO₂ concentration will result in the following:

- A warming of the Earth's surface and the troposphere, along with a cooling of the stratosphere.
- A warming in higher latitudes in late autumn and winter.
- Increased precipitation in high latitudes and the tropics throughout the year and in mid-latitudes in winter.
- A general increase in soil moisture in northern, high latitude continents in winter.

Critics cite the fact that these models do not incorporate all the dynamics of the Earth's climate and are not precise enough to determine regional changes.

3.5 Global Warming Chemicals

As stated previously, a greenhouse gas allows short-wave solar radiation to pass freely through the atmosphere **to** the Earth while trapping long-wave infrared radiation emitted **from** the Earth. The absorption of infrared radiation by these substances keeps the Earth's average surface temperature at an inhabitable level of 15°C (60°F). However, the addition of new greenhouse gases to the atmosphere and the increasing concentrations of existing gases may be disturbing this heat balance. Substances that are the main natural greenhouse gases are water vapor, CO₂, CH₄, N₂O, and tropospheric O₃. CFCs are also considered greenhouse gases. Aerosols (small particles) in the atmosphere can also affect climate because they can both reflect and absorb radiation.

Normally, most chemicals released into the atmosphere are converted to other chemicals or are destroyed after several years. These chemicals either react with the oxidants in the atmosphere or are photolyzed. However in 1979, Dr. Ralph J. Cicerone discovered that carbon tetrafluoride (CF₄), a PFC, was extremely stable in the atmosphere and could have an atmospheric lifetime of over 10,000 years. He concluded that the principal environmental effect of CF₄ could be the trapping of outgoing planetary infrared energy [11]. In the past several years, other PFCs have come to be known as global warming gases because of their infrared radiation absorption spectra, their stability, and their relatively long residence times in the atmosphere. These PFCs include gases used in semiconductor manufacturing such as CF₄, hexafluoroethane (C₂F₆), Freon 38 (C₃F₈), sulphur hexafluoride (SF₆), and nitrogen trifluoride (NF₃). The properties of PFCs and other greenhouse gases are shown in Table 1.

Table 1 Properties of Greenhouse Gases

Chemical	Yearly Global Emissions (metric tons)	Atmospheric Concentration (ppbv)	Lifetimes (years)	GWP (100-year)	Major Industrial Sources
CF₄	27 x 10 ³ (a)	70 x 10 ⁻³ (b) (c)	>50,000 (d)	10,900 (e)	aluminum
C₂F₆	27 x 10 ² (a)	2 x 10 ⁻³ (c)	>10,000 (d)	11,500 (e)	aluminum
NF₃	45	0.017 x 10 ⁻³ (j)	<179 (j)	24,200 (j)	semiconductor
SF₆	2.5-5.0 x 10 ³ (f)	2.5 x 10 ⁻³ (f)	3,200 (d)	21,000 (f)	insulation of electrical equipment
C₃F₈	<50	N/A	>10,000	N/A	
CO₂	26,000 x 10 ⁶ (g)	353 x 10 ³ (h)	120 (i)	1 (i)	
CH₄	300 x 10 ⁶ (g)	1.72 x 10 ³ (h)	10.5 (i)	11 (i)	
CFC-11	300 x 10 ³ (g)	0.28 (h)	55 (i)	3400 (i)	
CFC-12	400 x 10 ³ (g)	0.48 (h)	116 (i)	7100 (i)	
N₂O	6 x 10 ⁶ (g)	3.10 x 10 ² (h)	132 (i)	270 (i)	

- a) U.S. Environmental Protection Agency, Global Climate Change Division, November 1993.
- b) Penkett, et al., Journal of Geophysical Research, (86), 1981, p.5172.
- c) Fabian, P. et al., Journal of Geophysical Research, (92), 1987, p.9831.
- d) Ravishankara, A.R., S. Solomon, A.A. Turnipseed, and R.F. Warren, "Atmospheric Lifetimes of Long-Lived Halogenated Species," Science, Vol. 259, 8 January 1993, p.196.
- e) Abrahamson, Dean, and Valdimar K. Jonsson, "Iceland, Aluminum, and the Greenhouse Effect," Aluminum Association Report, October 1991, p.3.
- f) Ko, Malcolm K.W., Nien Dak Sze, Wei-Chyung Wang, George Shia, Aaron Goldman, Frank J. Murcray, David G. Murcray, and Curtis P. Rinsland, "Atmospheric Sulfur Hexafluoride: Sources, Sinks, and Greenhouse Warming," Journal of Geophysical Research, (98), p.10499.
- g) Intergovernmental Panel on Climate Change (IPCC), Working Group I, "Climate Change, The IPCC Scientific Assessment," 1990, Table 2.9 (1990 emissions), p.61.
- h) Ibid., Table 2.5, p.54.
- i) Intergovernmental Panel on Climate Change (IPCC) "Climate Change 1992: The Supplementary Report to the IPCC Scientific Assessment", Table A2.1, p. 56
- j) Estimates provided by Air Products & Chemicals, Inc.

3.6 Sources of Global Warming Chemicals

Though water vapor has the greatest greenhouse effect, its concentration in the troposphere is determined internally within the climate system. Water vapor increases in response to global warming and further enhances it [12]. Carbon dioxide is produced by burning fossil fuels and deforestation. Natural sources of methane are the oceans, freshwater, wetlands, flooded fields, and methane hydrate destabilization. Anthropogenic sources of methane are rice paddies, cattle, biomass burning, landfills, coal seams, and leakage from natural gas pipelines. The increase in nitrous oxide concentrations is presumably due to human activities; it is likely that agriculture plays a part [13].

Ozone concentration changes in the stratosphere and the troposphere are attributed to human activities as well. Natural sources of aerosols are explosive volcanic eruptions, while the anthropogenic source is the burning of fossil fuels that produces sulfur dioxide and contributes sulfate particles to the troposphere. Emissions of CFCs began with their invention in the 1930s.

The most significant anthropogenic source of CF_4 and C_2F_6 is aluminum smelting. CF_4 and C_2F_6 are produced during electrolytic reduction of alumina (Al_2O_3) dissolved in a molten cryolite (Na_3AlF_6) bath. In 1987, Fabian et al estimated yearly global emissions of CF_4 and C_2F_6 to be 28,000 tons and 3,200 tons respectively [14]. This translates to 1.6 kg of CF_4 and 0.2 kg of C_2F_6 produced per ton of primary aluminum production. Cicerone cites several other industrial processes that are likely sources of CF_4 , either because CF_4 has been detected in the process or because C, F, and heat are available:

- The electrolytic generation of fluorine (F_2), especially in carbon or graphite electrode systems
- The analogous reduction of uranium tetrafluoride (UF_4) or uranium hexafluoride (UF_6)
- The use of fluorspar in steelmaking (although CF_4 production from CaF_2 seems disfavored thermodynamically)
- The burning of polyfluoroethylenes
- Rocket fuel combustion
- Inadvertent production in fluorocarbon manufacture.

Direct, intentional industrial production of CF_4 amounts to only 10 to 60 tons per year [15]. The principal sinks for CF_4 are:

- Vacuum ultraviolet (VUV) radiation in the high mesosphere and ionosphere
- Possible (but unlikely) reactions with electronically excited oxygen atoms and with vibrationally excited hydroxyl (OH) molecules in the stratosphere and above
- Several ionospheric processes
- Pyrolysis in high-temperature combustion.

Such long lifetimes ensure that relatively small sources will increase the atmospheric CF_4 burden and that CF_4 will remain ubiquitous in the atmosphere [16].

The major source of sulfur hexafluoride (SF_6) is leaking insulated electrical equipment. SF_6 's high dielectric strength and unique arc-quenching ability make it ideally suited for safe, reliable gas-insulated high-voltage circuit breakers, substations, transformers and transmission lines. The major sources of SF_6 emissions are leaks through seals and gaskets and venting when the gas-filled equipment is opened for servicing. Other lesser sources include blanketing or degassing of molten reactive metals and tracer gas emissions.

3.7 Feedbacks in the Global Climate

For scientists to effectively model climate changes based on concentrations of greenhouse gases, they must be able to determine what the present concentrations are and what future concentrations will be. Though they can estimate emissions of these chemicals, they also must be able to identify those mechanisms that remove them from the atmosphere, alter them, or increase their concentrations. This can lead to positive or negative feedbacks. A positive feedback enhances the greenhouse effect, while a negative feedback reduces it. Both positive and negative feedbacks need to be taken into account when modeling future climate change.

Clouds can give both positive and negative feedback in the climate system. They can cool the Earth's surface by reflecting solar radiation back into space. However, they can also trap outgoing radiation from the Earth, thereby causing a rise in surface temperature. Aerosols act in a similar way. They can reflect incoming solar radiation, thereby decreasing Earth's surface temperature. However, these particles can also serve as cloud condensation nuclei, with the same result as with clouds.

As warming occurs, water evaporation increases. Since water vapor is a greenhouse gas, its presence contributes to more warming. A rise in temperature can also melt snow and ice, resulting in less solar radiation being reflected. This can also lead to increased warming as more solar radiation is absorbed by the Earth's surface.

3.8 What If Global Warming Is Not Happening?

Since accurate records of Earth's climate go back only about 100 years, many scientists see no evidence of anthropogenic global warming. While it is true that the average global temperature has increased from between 0.3 and 0.6°C over the last 100 years [17], this circumstance could be attributed to natural climate variability rather than to greenhouse warming. But even with our limited understanding of climate system dynamics, it is a fact that atmospheric carbon dioxide levels have increased from 280 ppmv prior to 1750 to 353 ppmv by 1990. The question then is how much CO₂ (or other "greenhouse gases") can build up in the atmosphere before any climate warming (if at all) occurs?

Although scientists have begun to model the Earth's climate to predict the effects of global warming chemicals, these models have not been effective. Some experts say that it will be 10 years before a model accurate enough to characterize the Earth's climate will be developed. Most models predict a rise in the Earth's temperature as a result of a doubling of CO₂ in the atmosphere. Regardless of whether global warming is occurring, thousands of pounds of chemicals—with calculated lifetimes of many thousands of years—are being emitted into the atmosphere. Another question then raised is what will be the effect (if any) of these chemicals in 10, 100, or 10,000 years?

Although it is estimated that the amount of PFCs used in the semiconductor industry is between 5 and 10% of the total annual PFC emissions, the semiconductor industry is taking a proactive approach to demonstrate responsible stewardship of the PFCs used in manufacturing.

4 ENVIRONMENTAL POLICY

4.1 Intergovernmental Panel on Climate Change (IPCC)

The Intergovernmental Panel on Climate Change (IPCC) was jointly established in 1988 by the World Meteorological Organization and the United Nations Environment Programme. In its summary of climate change, the IPCC reported it was certain that a natural greenhouse effect exists and that

emissions resulting from human activities are substantially increasing the atmospheric concentrations of the greenhouse gases carbon dioxide, methane, CFCs, and nitrous oxide. These increases will enhance the greenhouse effect, resulting on average in an additional warming of the Earth's surface. The main greenhouse gas, water vapor, will increase in response to global warming and further enhance it [18].

Furthermore, the summary states that the effectiveness of certain gases in changing climate can be estimated. Over half of the greenhouse effect can be attributed to CO₂. Also, inasmuch as the atmospheric concentrations of CO₂, N₂O, and the CFCs do not adjust quickly to changes in emissions, reductions in emissions of these gases would need to be over 60% to stabilize their present day concentrations. Further, the IPCC predicts that the global mean temperature could increase by about 0.3°C per decade during the next century if the current situation continues unchanged. The IPCC also predicts an average global mean sea level rise of about 6 cm per decade during the next century resulting from thermal expansion of the oceans and the melting of land ice.

4.2 United Nations Conference on Environment and Development (UNCED)

The United Nations Conference on Environment and Development (UNCED), also known as the Earth Summit, was held June 3-14, 1992, in Rio de Janeiro, Brazil. The conference brought together representatives from 150 nations, 1400 nongovernmental organizations, and 8,000 journalists.

The Earth Summit produced five documents:

- Rio Declaration of Principles
- Convention on Climate Change
- Biodiversity Treaty
- Treaty on Forest Principles
- Agenda 21

Two of these documents relate to global warming issues, among other topics. The Rio Declaration contains 27 principles intended to guide nations in their obligations to environmental protection and development. The Convention on Climate Change produced a document that requires industrialized countries to develop, update, and publish national inventories of anthropogenic emissions of greenhouse gases, most importantly CO₂. The document established a goal to return CO₂ emissions to earlier levels by the turn of the century. One hundred fifty-three nations signed the Climate Convention Treaty. The U.S. signed the treaty only after it was weakened during several pre-summit meetings in which enforceable target emission levels were abandoned for unenforceable, broad aims [19].

Agenda 21 is essentially an action plan for the twenty-first century that includes most global environment and development issues, including mechanisms to transfer technology and funds from developed countries to developing countries and to provide safe drinking water and sanitation for

people who are in need. The target reductions addressed in the Climate Change Convention provided the framework for the U.S. Climate Change Action Plan. This Climate Change Action Plan, or an updated version if necessary, will form the cornerstone of the U.S. National Action Plan required by the Climate Convention [20].

4.3 U.S. Climate Change Action Plan

On October 19, 1993, President Clinton and Vice President Gore announced the Climate Change Action Plan, which was designed to reduce emissions of CO₂ and other greenhouse gases to their 1990 levels by the year 2000. The plan, consisting of almost 50 new or expanded programs, establishes public-private partnerships with key industries across all sectors of the economy to reduce greenhouse gases. The programs involve the manufacturing, transportation, forestry, and agriculture industries as well as homes and office buildings.

These programs are targeted in specific sectors to stimulate markets for technologies that reduce emissions of CO₂, CH₄, N₂O, and halogenated compounds that contribute to global warming. The plan also reduces emissions of CO₂ by protecting forests, which are greenhouse gas “sinks” that store carbon removed from the atmosphere [21]. According to the plan, 1990 emissions were 1,367 million metric tons of carbon equivalent (MMTCE). (All gases are converted to MMTCE by using GWPs.)

Without the action plan, emissions of greenhouse gases are projected to increase by about 7% to a level of 1,568 MMTCE in the year 2000. While a few of the President’s initiatives would be mandatory, the plan calls for voluntary participation by industry. According to a White House press release dated October 19, 1993, and a similar one from the EPA, the President’s Climate Change Action Plan will:

- Stimulate over \$60 billion in private investment in technologies and services that allow for economic growth without harming the environment.
- Form a new partnership with industrial motor manufacturers to work with the Department of Energy to increase the efficiency of motor systems.
- Form partnerships with coal mine and landfill operators, farmers, and gas companies to reduce methane leaks.
- Expand the EPA’s “Green Lights” program, which assists companies in converting to energy-efficient lighting.
- Form more “Golden Carrot” partnerships to accelerate the commercialization of advanced energy-efficient appliances.
- Narrow the uses allowed for hydrofluorocarbons (HFCs), which can substitute for ozone-depleting CFCs but are themselves a factor in global warming.
- Form a new partnership with aluminum producers to identify emission reduction opportunities and to reduce PFC emissions by up to 50%.

Action #40 of the plan directs the EPA to “restrict the use and emissions of high GWP chemicals by encouraging product stewardship for long-lived gases and using section 612 of the clean Air Act Amendments of 1990 to narrow uses of high GWP CFC substitutes, such as HFCs and PFCs, based on an overall risk assessment [22].” The EPA is also directed to create partnership programs with manufacturers of long-lived HFCs and PFCs. Under this partnership program, companies will commit to not selling those chemicals for emissive uses and to ensuring that users of long-lived gases handle the material in an environmentally responsible manner—by capturing and destroying the gas rather than emitting it into the atmosphere [22].

5 TECHNOLOGY

5.1 Semiconductor Industry

Silicon, the basic raw material for the semiconductor industry, is an ideal material because of its electrical properties. Through various process steps, the silicon wafer is made into a packaged chip.

The semiconductor industry has used PFC materials in integrated circuit manufacturing for over 20 years. The most common are the gases C_2F_6 , CF_4 , and SF_6 [23]. NF_3 is being used to some extent as a deposition chamber cleaning gas and as an etch gas. PFC gases provide the fluorine necessary to etch silicon, silicon dioxide, and silicon nitride films used in the production of advanced MOS and bipolar circuits. The stable nature of the PFC feed gas eliminates the need for special handling and delivery equipment when used in radio frequency (RF)-based plasma systems. Dissociation of the PFC gas in an RF field under low-to-moderate process pressures provides the free fluorine and CF radicals necessary to initiate and sustain thin film etching. Figure 5 describes where in the semiconductor manufacturing process certain PFCs are used.

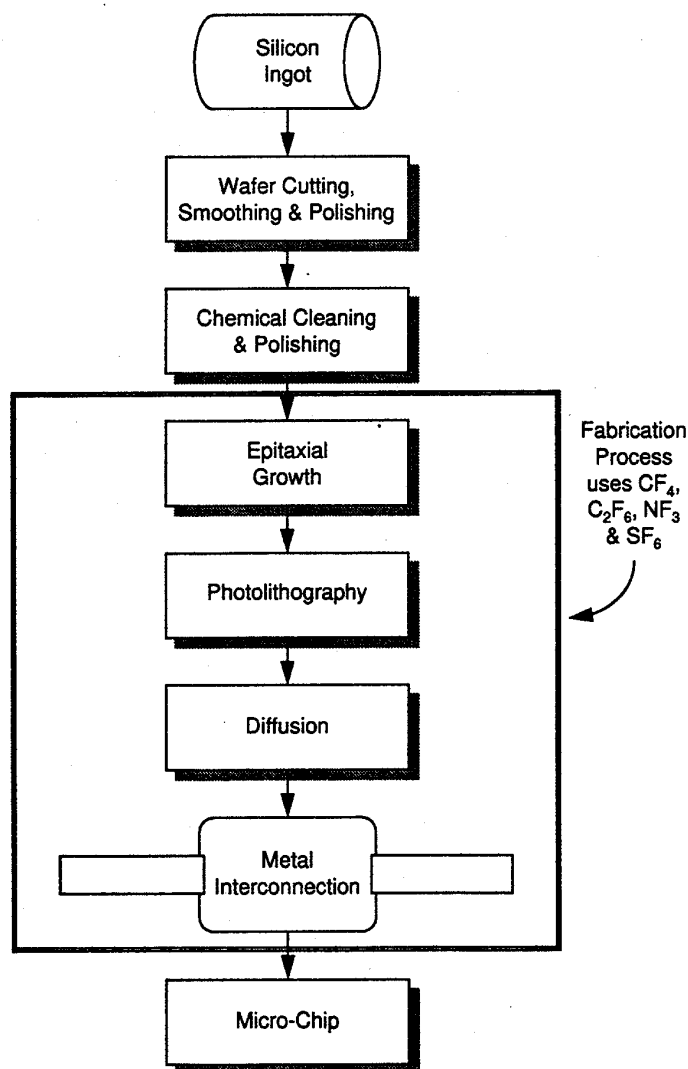


Figure 5 Semiconductor Process Flow Diagram

Until recently, the majority of PFC gases used in the semiconductor industry were in plasma etching tools for etching photoresist masked patterns on device wafers. However, the success of plasma enhanced chemical vapor deposition (PECVD) systems in depositing of dielectric films has created a new and larger application for PFC materials. Specifically, this application involves the use of C_2F_6 , NF_3 , and CF_4 in plasma etch cleaning of PECVD reactors after deposition. As in etching resist-patterned circuitry, the gas is used as a source of fluorine in an RF discharge. Rather than etch patterns on integrated circuits, the fluorine etches extraneous silicon dioxide, nitride, and tungsten films from reactor process chamber fixtures. In situ cleaning of PECVD tools results in a more reproducible and predictable deposition process with improved particulate performance and increased production availability [24].

PFCs are used in the semiconductor industry in dry etch applications; some are also used in a plasma-based process for chemical vapor deposition (CVD) chamber cleaning. CVD is used to reproducibly deposit the high quality, defect-free dielectric films required for various passivation layers. Plasma etching processes are needed for pattern delineation and planarization for very large scale integrated (VLSI) circuits [25]. C_2F_6 is commonly used in cleaning CVD chambers because it is a good source of fluorine. Also, it is relatively nonflammable and nontoxic because of its stability and very low reactivity.

As shown in Figure 6, PFC emissions caused by the semiconductor industry are a very small percentage (5 to 10%) of global emissions. For example, compare the estimated 230 tons per year used by the U.S. semiconductor industry to the 25,000 to 50,000 tons emitted per year globally and about 6,800 tons per year emitted in the U.S. by the aluminum smelting industry.

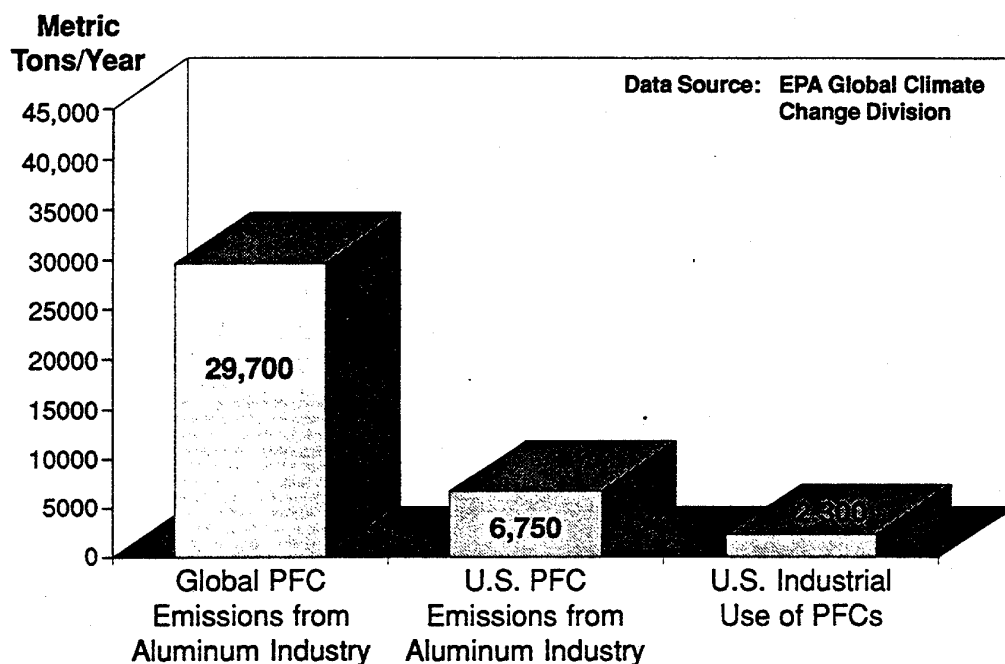


Figure 6 Estimates of PFC Emissions and Use

5.2 DuPont's C₂F₆ Sales Policy

At this time, the major impetus to reduce or remove PFCs from use is DuPont's restrictive sales policy toward C₂F₆, which DuPont markets under the tradename of ZYRON 116. DuPont wants users of DuPont-supplied C₂F₆ to hold emissions to 1990 levels by the end of 1996 and take interim steps to support this goal.

According to its sales policy, DuPont will:

- Limit C₂F₆ sales to those customers not demonstrably evaluating emission reduction systems.
- Sell C₂F₆ without restrictions to customers with emission reduction systems in place, on order, or under demonstrable evaluation.
- Sell no C₂F₆ to anyone not having emission reduction systems in place by the end of 1996 [26].

In summary, DuPont's sales policy permits only those facilities with a means to control emissions of C₂F₆ to buy the chemical. Those facilities with no means or intention of reducing emissions will not be able to purchase it.

5.3 Emission Control Alternatives

Because of the long atmospheric lifetimes of PFCs, the unknown long-term fate of these compounds in the atmosphere, and DuPont's C₂F₆ sales policy, semiconductor manufacturers are looking in the short term toward abatement systems to control PFC emissions. In the long term, the industry hopes to eliminate these chemicals entirely and find suitable substitutes. Semiconductor manufacturers may also be able to recycle or capture emissions for reclamation and reuse and to lower overall emissions by process optimization.

Several options are available for reducing or eliminating PFC emissions. Some companies plan to destroy the chemical through thermal or plasma decomposition. Small combustion units are currently being used for the abatement of various exhaust gases, and similar combustion units have been tested for the abatement of C₂F₆ with either natural gas or hydrogen fuel. These units have shown high destruction-removal efficiencies but require large amounts of fuel. The thermal decomposition of C₂F₆ has been shown to be up to 90% efficient in controlled conditions; however, the combustion products have included high levels of hydrogen fluoride (HF) vapor. Table 2 lists manufacturers, equipment, and people to contact about PFC abatement methods.

Table 2 Abatement Technologies

Company/Manufacturer	Unit Name	Technology	Contact	Phone Number
Alzeta Corporation	Edge	combustion	David Bartz	(408) 727-8282
DAS GmbH	Escape	combustion	Jochem Steuber Robert Burkhardt Mark Lamberton (US)	011-49-814125828 (714) 436-3100
Delatech Inc.	CDO	combustion	Rock McKinley	(408) 262-1631
MG Industries	Guardian	combustion	Ram Ramachandran	(215) 736-5235
Electrochemical Technology Corp.	Dry Scrub	plasma-based	Don Sanservino	(408) 744-0447
Process Technology Limited	PRC	plasma-based	Rick DesBrisay	(506) 446-5200
DuPont	N/A	recovery/pro- moted thermal	Mike Mocella	(302) 892-0870
Edwards High Vacuum International	GRC	recovery/pro- moted thermal	Peter Mawle Howard Mastropeiro (US)	011-44-275810246 (408) 946-4707
Novapure Corporation	N/A	recovery	Dave Ruede	(203) 790-0048
Westate Products	N/A	recovery	Jim Huelster	(602) 998-0508
Novellus	N/A	conservation	Clark S. Stone	(408) 432-5240
Applied Materials	N/A	replacement	J. Leong	(408) 235-6136
DuPont	N/A	replacement	Mike Mocella	(302) 892-0870
Vector Technology	N/A	combustion	Frank Deak	(408) 727-1966

Other companies are studying plasma decomposition units. Varying plasma process conditions allow 40 to 80% of reactive gases to pass through the CVD process chamber without being reacted. The radio-frequency (RF) plasma generated in these decomposition units breaks down the residual PFCs not consumed in the manufacturing process. Several companies plan to recover PFCs from process effluents for reprocessing or destruction. This involves trapping/adsorbing the more reactive non-PFC components from PFC-containing process streams, leaving a PFC-rich stream, as well as schemes for direct PFC adsorption.

Still other facilities plan to use PFCs more efficiently in CVD chamber cleaning, thereby reducing PFC emissions. Hardware is being developed for etch endpoint detection to reduce the use of PFCs in cleaning processes. Scientists are also working to find substitutes for chemicals currently in use. Replacement compounds such as C_2HF_5 and $C_2H_2F_4$ are still fluorine-rich but have shorter lifetimes and may serve as alternatives in some instances.

6 CONCLUSION

Some scientists find the evidence for impending global warming convincing, while others view the notion with skepticism. Regardless of whether global warming is occurring, it is a fact that every year chemicals with extremely long lifetimes are being emitted into the atmosphere. Because the long-term effect of these substances on the atmosphere and global climate is not known, the U.S. semiconductor industry is researching ways of changing its processes to decrease, if not completely eliminate, these long-lived gases. Maybe the Earth's atmosphere and climate can effectively handle the increased input of such gases without global warming or other deleterious effects on the planet.

On the other hand, maybe the long-term effects will be harmful. Since it will take another decade or longer to answer this question, a concerted effort to reduce emissions of global warming agents appears to be the most prudent and environmentally responsible course of action.

Although the semiconductor industry's use of PFCs is minimal compared to the amounts released by the aluminum smelting industry, the semiconductor industry is proactively attempting to find ways to reduce their emissions. The overall environmental impact of chemical substitution, control methods, and process optimization will have to be carefully evaluated to ensure that these efforts result in a net benefit to the environment and the semiconductor industry.

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