Current State of Technology: Perfluorocompound (PFC) Emissions Reduction

International SEMATECH
Technology Transfer # 98053508A-TR

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Abstract: This report summarizes the status of research and development efforts undertaken by the semiconductor industry to reduce emissions of perfluorocompounds (PFCs). Strategies include process optimization, alternative chemistries for chamber cleans and etch in both installed based and future tools, capture/recovery, and abatement. The appendix describes 41 technologies that have been examined.

Keywords: Perfluorocompounds, Global Climate Change, Plasma Chemical Vapor Deposition, Chamber Cleaning, Process Optimization, Emissions Reduction

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1 EXECUTIVE SUMMARY

This report summarizes the status of research and development efforts undertaken by semiconductor manufacturers, process tool suppliers, gas and chemical suppliers, equipment suppliers, and research organizations to reduce emissions of perfluorocompounds (PFCs). PFCs and hydrofluorocarbons (HFCs) are used in plasma processes in the semiconductor industry to etch substrates and clean the inside of deposition tool chambers. Carbon and fluorine contained in PFCs and HFCs are essential when etching high aspect ratio device features because, in addition to etching, they form polymers, which provide etch selectivity and anisotropy. PFC emissions reduction research sponsored by the semiconductor industry has been performed over several years in four general areas: process optimization, alternative chemistries, capture/recovery, and abatement.

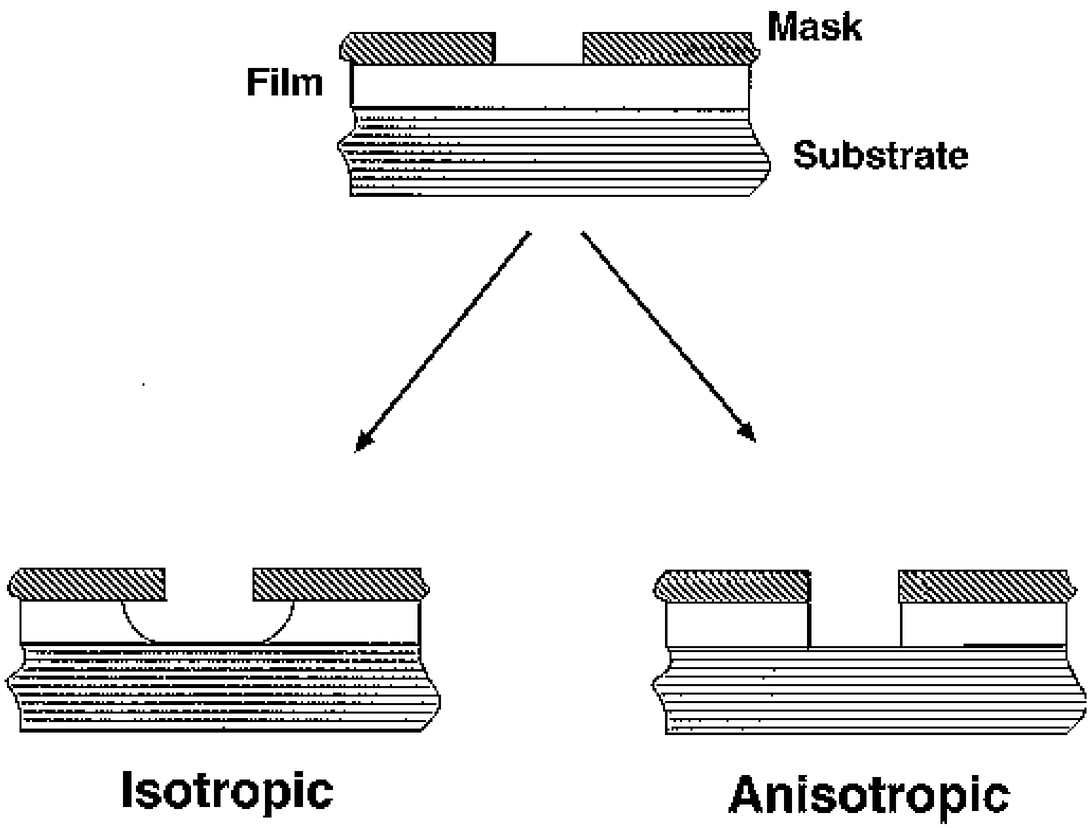
Results to date have shown that no single measure will resolve the PFC emissions problem because of the great variety of tools and processes using PFCs and the varying age and infrastructure of semiconductor manufacturing facilities. In certain circumstances, process optimization of chamber cleans can reduce PFC emissions by 10–50%; however, optimization is not a viable solution for existing etch processes. Some alternative chemicals have promise in reducing the global warming impact of emissions; however, extensive process qualification is required before these chemicals can be widely employed. Capture/recovery systems are currently being evaluated; however, no evaluation has reached the stage to show that recycling PFCs back into the semiconductor manufacturing process is feasible. In addition, PFC supplier issues surrounding product take back for recycled material have not been resolved. Abatement technologies are passing through various stages of development; however, existing fabs may not have the space or infrastructure necessary to support their widespread installation and byproducts from these systems may cause detrimental environmental effects.

A major issue associated with all of the options explored to date is the difficulty of integrating changes into an operating environment. Many of the options generate other environmental problems that can overload existing control systems or require additional control systems. Options requiring production process changes must go through requalification steps to ensure that product quality is maintained. The many types of processes employed in the industry and the variety of products manufactured by the industry make process requalification a major effort.

Although significant progress has been made in understanding the applicability and limitations of PFC emissions reduction technologies, continued development of multiple solutions encompassing the four areas of process optimization, alternative chemistries, capture/recovery, and abatement is necessary to ensure cost-effective and environmentally sound solutions.

2 BACKGROUND

Perfluorocompounds (PFCs) and hydrofluorocarbons (HFCs) are used in the semiconductor industry for plasma cleaning deposition chambers and for plasma etching. Because PFCs and HFCs have long atmospheric lifetimes and are strong infrared absorbers, they have been included in the basket of gases identified in Kyoto [1] that are subject to emissions reduction requirements during 2008–2012. PFCs were embraced by the semiconductor industry for their process performance and low impact on employee safety. Etching high aspect ratio wafer features requires a source of fluorine ions and radicals as well as carbon. Carbon is necessary to form F-C polymers, which are deposited on feature walls to ensure anisotropic etching (see Figure 1) and to provide etch selectivity. PFCs contain the necessary ratio of carbon to fluorine to etch substrates and deposit polymer. Chemistries such as F_2 and HF cannot be used by themselves for high aspect ratio plasma etching because they do not contain the carbon necessary for polymer deposition.



Note: In semiconductor manufacturing, anisotropic etching is the desired process. For plasma etching, the etch gas molecule must contain both carbon and fluorine to give this result.

Figure 1 Illustration of the Difference Between Anisotropic and Isotropic Etching

PFCs share similar chemical properties as the chlorofluorocarbons (CFCs); however, in contrast to the CFCs, which are used for their physical properties, the PFCs are important to the semiconductor industry for their chemical properties. Consequently, finding suitable replacements for the PFCs is much more difficult.

In the spring of 1996, members of the semiconductor industry signed memoranda of understanding (MOU) [2] with the U.S. Environmental Protection Agency (EPA) agreeing to endeavor to reduce the normalized rate of PFC emissions from U.S. semiconductor manufacturing operations through a combination of strategies including process optimization, alternative chemistries, recycle, and abatement. The companies also agreed to undertake a 24-month research and development effort to identify solutions that would benefit the environment and satisfy the industry's manufacturing requirements. This report documents results of the industry's research and development effort.

The information presented in this report is current as of April 1998. Work is ongoing in many areas and the performance and status of various technologies will change over time. This report is not intended to be an all-inclusive, comprehensive summary of all the PFC emissions reduction activities to date. There may be significant activities that the authors were not aware of because the developers of the technology did not disclosing such information for competitive or other confidentiality reasons. In addition, the authors' knowledge of activities in Europe and Asia was limited. The appendix includes technology descriptions for the processes that have been examined.

3 TECHNOLOGY AREA DEVELOPMENT

PFC emissions reduction options can be divided into four technology areas listed in order of preference:

1. Process optimization
2. Alternative chemistries
3. Capture/recovery
4. Abatement

Each of these four technology areas has experienced significant development in the past two years.

3.1 Process Optimization

At semiconductor fabrication facilities (fabs), both plasma etch and chemical vapor deposition (CVD) chamber clean processes emit PFCs. Process optimization development work to date has focused primarily on chamber cleans for two reasons. First, most PFC emissions were thought to have come from chamber clean processes, although emissions from etch processes are substantial and will increase as future technology changes. Second, chamber clean processes are easier to change without affecting wafer yield, since anisotropic etching is not an issue. Within the scope of chamber cleans, process optimization can reduce PFC emissions through the use of endpoint detectors and/or through process parameter variation to find the point optimum for PFC utilization. In some cases, optimization can yield emission reductions (from chamber cleans) on the order of 10–50%. Optimization is part of the solution for existing fabs and is encouraged; however, to obtain significant reductions in PFC emissions, process optimization must be complemented by solutions from other technology areas.

3.2 Alternative Chemistries

A great deal of work has recently focused on developing alternative chemistries, mostly for chamber cleans and etch in 200 and 300 mm tools. Although many candidates are currently being investigated by DuPont, Allied Signal, 3M, Air Products and Chemicals, Massachusetts Institute of Technology (MIT), and others, only some replacements show immediate promise for the installed tool base. Octofluoropropane, C_3F_8, has undergone extensive development work in Novellus dielectric deposition tools and is supported by Novellus and 3M (the supplier of C_3F_8) as a replacement for C_2F_6 cleans. C_3F_8 has the potential to reduce emissions (expressed in million metric tons of carbon equivalents [MMTCE]) by more than 50%; however, Novellus has announced that they are developing an optimized C_2F_6 clean for dielectric films that results in emissions reductions equivalent to those achieved using C_3F_8. In developing alternative chemistries, the industry is aware that the use of non-PFC chemistries in plasma processes may result in PFC byproducts.

3.2.1 Chamber Clean: Installed Tool Base

Although previous efforts to develop NF_3 clean processes have had limited success [3], IBM is currently re-examining the use of NF_3 in Applied Materials tools. In addition, Novellus, IBM, and MIT have announced work on development of an NF_3 clean process for 200 mm plasma enhanced (PE) CVD dielectric and tungsten tools. Although NF_3 cleans for installed Novellus and Applied Materials tools are being developed, equivalent tool performance compared to existing C_2F_6 processes has not yet been shown. Issues such as process drift, lower tool uptime, and impact on consumables are still a concern.

Applied Materials has developed a chamber clean process that uses a remote NF_3 plasma as a replacement for C_2F_6 based cleans in certain newer generation tools such as the DxZ chamber, sub-atmospheric (SA0 CVD and high density plasma (HDP) tools. The remote plasma NF_3 cleans that Applied has developed for SACVD and HDP tools are production-worthy. Applied Materials and Novellus are both developing NF_3 cleans for their next generation tool sets that appear to be capable of achieving > 90% reductions in MMTCE compared to existing C_2F_6 processes. Although process requalification costs are still a concern, alternative CVD chamber clean chemistry will play a significant role in the industry's overall strategy.

3.2.2 Chamber Clean: Future Tools

Many tool suppliers are developing tools that can take advantage of the characteristics of NF_3 as a potential replacement for C_2F_6 as a chamber clean gas. Certain tool suppliers have developed a chamber clean process that uses ClF_3 for metal processes. (ClF_3 is not an effective process for in situ dielectric cleans.) It is capable of reducing PFC emissions of the chamber clean process to practically zero MMTCE. This gas, while effective in reducing global warming emissions, introduces many safety issues that the U.S. semiconductor industry would like to avoid, if possible.

3.2.3 Etch: Installed Tool Base

Generally, etch processes (except those using SF_6) have fewer emissions (MMTCE) than chamber clean processes. Contrary to the chamber clean situation, etch processes take place in the presence of the product, and anisotropic etching and etch selectivity are of primary importance. The etch gas is used in process steps that dramatically impact product yield and product reliability. To safeguard these elements requires a very comprehensive, lengthy, and thorough qualification of any process change. These factors have led the industry to focus on future etch tools as the higher priority.

3.2.4 Etch: Future Tools

Work is under way by several research organizations and tool suppliers to develop etch chemistries for future generation tools. Most efforts are still very early in the development process. Tokyo Electron Limited is working on C_5F_8 as a C_4F_8 substitute. In general, most efforts are looking at PFCs and HFCs with shorter atmospheric lifetimes and lower 100-year global warming potentials.

3.3 Capture/Recovery

Several of the major gas suppliers have developed systems for PFC capture/recovery that are now in alpha and/or beta site pilot testing. Capture of PFCs as an end-of-pipe solution can be applied to both chamber clean and etch tools. The capture can be for either repurification and reuse of the etch gas or for a concentration step before abatement. In each case, considerable pretreatment is required ahead of the actual capture step to remove harmful materials such as pyrophorics, corrosive gases, and particulate matter. Pretreatment systems can also be designed to remove unwanted PFCs (e.g., the ones that are difficult to recover but easy to abate). In ongoing testing at Intel and Texas Instruments, pretreatment is proving more difficult than anticipated. Following pretreatment, the PFCs are captured and concentrated to greater than 95%. Once captured and concentrated, the PFC can be packaged for subsequent off-site or on-site repurification or disposal. The pilot scale systems target and recover C_2F_6, CF_4, and SF_6 very well; NF_3 and CHF_3 are more difficult to recover but can be removed by the pretreatment system. The combined pretreatment and recovery pilot system can provide > 90% reduction of all PFCs.

Some suppliers of PFCs are developing plans to take back the recovered PFCs for either reuse or other form of disposition. In fact, DuPont has announced a “take-back” policy for the PFC it manufactures that states, “In support of recovery options, DuPont commits to develop a disposition offering for recovered ZYRON® 116 (C_2F_6).” Other gas suppliers are investigating on-site and off-site repurification of recovered PFCs, but no one has submitted any formal “take-back” plans. Although very little data exist, recovered PFCs from pilot testing of various systems consist of about 80–85% C_2F_6, 10–15% CF_4, with a balance of small amounts of other PFCs, HFCs, and N_2. To make repurification to virgin material quality economically attractive, a C_2F_6 concentration of > 90% is desirable. As fabs employ recovery systems and a clearer picture of the total available market for reuse and/or other alternative uses is established, market forces may help define the value of the recovered PFCs. However, a widespread industry shift away from C_2F_6 as a chamber clean gas to NF_3, for example, may have negative implications for PFC recovery. Because reducing fab emissions to the recovery system reduces the potential benefit derived from the recovery system, this technology is not complementary with the higher order emission reduction options such as process optimization and alternative chemistries. Also, many existing fabs may not have the space to install capture/recovery technology.

3.4 Abatement

Abatement technology development can be applied to PFC emissions from both chamber cleans and etch processes. Certain abatement technologies may be better suited for one or the other. Abatement systems can be applied locally as point-of-use (POU) devices or fab wide as end-of-pipe (EOP) devices. Several commercially available POU abatement devices can effectively abate some of the PFCs, but only one combustion-based system has so far been proven effective in abating all PFCs to >90%. The typical combustion device uses significant quantities of water (up to 8,600 gallons per day per device) and creates waste water that requires treatment for fluorides in the fab's industrial waste treatment (IWT) system. Many sites do not have the IWT capacity to handle widespread installation of such abatement devices. In addition, some devices require gas distribution systems in the fabs for oxygen and natural gas (a gas not commonly used in fabs).

Research and development work is underway aimed at more novel abatement approaches (plasma, absorption, adsorption, etc.); however, no novel technologies that will treat all PFCs are yet commercially available. Abatement systems vary in capability and capital/operating costs, but all are very expensive relative to some of the solutions discussed above.

3.5 Applicability of Technologies

Several factors affect the applicability of PFC emissions reduction technologies; of those, the age and size of the fab are most important. For older fabs and smaller labs/fabs, chamber clean process optimization may be the best way to reduce PFC emissions because space constraints, aging infrastructure, and the size of PFC emissions reduction equipment may preclude utilization of alternative chemistries, recovery, or abatement. In selected cases, process optimization of chamber cleans can result in a 10–50% reduction in PFC usage. However, for fabs processing 150 mm or smaller wafers, optimization of tools has so far been limited.

For existing 200 mm fabs, alternative chemicals in chamber cleans or capture/recovery of both etch and CVD emissions appears to be the most cost-effective means of achieving significant emissions reductions. Alternative chemistries can reduce emissions about 20–50%. Since 200 mm equipment may still be under warranty or subject to a supplier service contract, fabs may have to work with tool suppliers to implement alternative chemistries. New processes using alternative chemistries must be developed by tool suppliers, and if NF_3 is not plumbed to a tool, its cost as an alternative chemistry may be prohibitive. Again, as in the case of process optimization, significant time and dollars may be required to develop and requalify alternative chemistry processes.

For future fabs, purchasing process equipment that optimizes PFC use and/or uses alternative chemistries may be the best option. It is anticipated that PFC usage and emissions may increase in 300 mm etch tools since process performance and tool throughput, not PFC emissions, are the driving forces in etch technology development.

Technology alternatives vary for CVD and etch. For CVD equipment that uses silane as a deposition gas, POU combustion abatement systems may be a preferable alternative since POU abatement is already required for silane. For installed base ≤ 150 mm CVD tools, process optimization may be the only cost-effective alternative since tool suppliers are not designing retrofits for these tools and/or developing alternative processes. Newer CVD tools (e.g., high density plasma, etc.) using NF_3 will significantly lower PFC emissions. For installed etch tools, the cost of process requalifications may preclude widespread adoption of alternative chemistries or process optimization. Small POU plasma abatement devices that are installed after the turbo pump but before the vacuum pump may be a cost-effective means of abating installed etch tool PFC emissions; however, many existing fabs do not have the space or infrastructure to support installation of any abatement devices. In future etch tools and processes (5–10 years out), alternative chemistries may be a viable means of significantly reducing emissions. Table 1 summarizes potential PFC emission reduction options by wafer size.

Table 1 Potential PFC Emission Reduction Options

Tool Type	≤ 150 mm	200 mm	300 mm
CVD	Process Optimization Alternative Chemistries Limited Abatement	Process Optimization Capture Alternative Chemistries	Alternative Chemistries Process Optimization Capture
Etch	Limited Solutions	Process Optimization Capture Alternative Chemistries	Capture Alternative Chemistries Process Optimization

4 CONCLUSIONS

This report summarizes the research and development efforts undertaken by semiconductor manufacturers, tool suppliers, gas and chemical suppliers, equipment suppliers, and researchers. Results have shown that no single measure will resolve the PFC emissions problem because of the great variety of tools and processes using PFCs; thus, the industry will continue to explore and push for development of multiple approaches and solutions. While emissions reductions are achievable in certain instances, reducing absolute emissions in the near term will be difficult because

1. A large installed base of tools exists that is not amenable to abatement and process changes.
2. The technologies that can achieve the greatest reductions in PFC emissions are being developed for future tools and for newer facilities, because that is where they can be most readily applied.

Although significant progress has been made, multiple solutions encompassing all four technology options—process optimization, alternative chemistries, capture/recycle and abatement—will need to be developed. Currently, most solutions are still in the development phase and have both technical and economic hurdles that must be overcome before they can be considered viable.

5 REFERENCES

[1] Kyoto Protocol, Climate Change Conference, Kyoto, Japan, Dec. 1-10, 1997.

[2] U.S. EPA Memorandum of Understanding for the PFC Emission Reduction Partnership for the Semiconductor Industry.

[3] Laurie Beu and Paul Thomas Brown, “Motorola’s Plans for Controlling PFC Emissions” Global Semiconductor Industry Conference on PFC Emissions Control, Monterrey, CA, April 7–8, 1998.

APPENDIX A
Technology Summaries

A.1 PROCESS OPTIMIZATIONS

A.1.1 Optimization of Novellus C_2F_6 W-CVD and PECVD Chamber Cleans

Description

Novellus has a multi-phase program underway to optimize their standard C_2F_6/O_2 cleans for both silicon oxide and silicon nitride PECVD chamber cleans and tungsten CVD chamber cleans. Most of the optimization has focused on 200 mm tools and involved endpoint detection as well as studying the effect of process variables such as C_2F_6 flow, C_2F_6/O_2 flow ratio, and pressure on etch rate and emissions.

Project Status

PECVD

For SiO_2, the optimized process achieved a 5–10% reduction (MMTCE) in emissions for the low pressure clean step and a 63% reduction for the high pressure clean step. The etch rate also improved slightly. The process is being alpha-tested at customer sites to determine if the new C_2F_6 process is production worthy. For SiN, a reduction of 43% was achieved, but only at the expense of an unacceptable decrease in throughput of 31%.

W-CVD

Using bias voltage endpoint detection, Novellus was able to determine the actual end of the chamber clean to reduce gas flow and achieve a 15–30% emissions reduction. By optimizing the flow ratio of C_2F_6/O_2, they were able to develop a stable process with an emissions reduction of 30%. The alpha testing of this process is currently on hold pending completion of the alternative chemistry tests with dilute NF_3.

Applicability

Assuming these processes become production worthy, they will be applicable to old and new fabs using 200 mm wafers for Novellus Concept Two tools.

Pros and Cons

The benefits of implementing these optimized processes are minimal additional capital costs and potential chemical cost savings of as much as 50% over the standard C_2F_6 process. However, the cost of endpoint detection for each chamber can represent a significant cost. Also widespread conversion of tools to these processes will require considerable process requalification that varies from company to company and fab to fab

Reference

Ken Aitchison, Director of Chemical Systems for Novellus, Presentation at PFC Emissions Reduction PTAB, SEMATECH, March 4–5, 1998.

A.1.2 Optimization of Applied Materials PECVD Chamber Cleans

Description

Applied Materials' efforts to optimize the dielectric chamber clean process to reduce PFC emissions started several years ago. First, they optimized the standard two-step clean process by using improved endpoint detection and adding a plenum pumping plate kit. Then, they developed a new high power radio frequency (RF) source and 200 mm lamp heated retrofit kit for the P5000 tools. Most recently, they released a new symmetrically designed chamber (DxZ), available on Centura and P5000 mainframes.

Project Status

The processes using endpoint detection and the plenum plate have been released to the tool users, with 50% and 60% reductions in C_2F_6 usage, respectively, over the standard two-step process. The DxZ high power RF process has been released, and the retrofit kit will be available in 3Q 98, with a 75% reduction in PFC usage and 15% greater throughput reported. The newly designed DxZ chamber has been released, claiming an 85% reduction in PFC usage over the standard two-step process.

Applicability

The endpoint detection is applicable to all P5000 TEOS and PSGCVD systems in the installed tool base. The plenum plate kit is suitable only for 4" to 8" lamp-heated standard and universal chambers. The new high power RF retrofit kit will be available for the installed tool base P5000 lamp-heated systems. The new DxZ chamber will be available for new chamber purchases on Centura and P5000 mainframes.

Pros and Cons

The benefit of the endpoint detection and plenum pumping plate kit are lower PFC usage and emissions as well as increased throughput resulting from the reduced clean time. However, an endpoint detector and/or plenum plate retrofit on each chamber represents significant costs. The kit price per chamber ranges between $4K–5K. Also implementation of these process changes requires an additional process qualification at each fab. The new high power retrofit kit for the installed base P5000 lamp-heated systems costs $50K/chamber, but the reported 15% increase in throughput may justify the cost. The benefits associated with the new DxZ chamber can be realized only by purchasing the new chamber, a major capital outlay. However, Applied Materials reports 30% faster cleans than the lamp-heated chambers.

Reference

Communication from Jerry Schoening, ESH Director, Applied Materials to Larry Novak, VP, Radian International in reference to this report, April 1998.

A.1.3 Optimization of a Dielectric Etch Process at STMicroelectronics

Description

STMicroelectronics and Lam Research optimized the dielectric etch process on a commercial etch tool (Lam 4520) using blanket and patterned SiO_2 films grown from TEOS on 150 mm p-type silicon wafers. The process uses a mixture of CF_4 and CHF_3 diluted with argon. RF power, pressure, gap, and total PFC flow were the process parameters that were studied in statistically designed experiments. The CF_4/CHF_3 ratio was kept constant, and no tool hardware changes were made. The results showed that the etch gas flow could be reduced by 50% with a similar reduction in emissions (using global warming potentials [GWPs] at infinity). The new process had etch rates, uniformity, and photoresist selectivity equivalent to the process of record.

Project Status

STMicroelectronics was pleased with the results and plans to incorporate the optimized process in their manufacturing lines. Before this process becomes generally available to the semiconductor industry, Lam Research will have to validate the process at their facilities and issue the new process as an alternative, approved process for the Lam 4520 tool.

Applicability

The optimized process is applicable only to the dielectric etch process and only for the Lam 4250 etch tool, one of many different makes and models of etch tools typically used in a fab.

Pros and Cons

Switching to the optimized process will reduce PFC emissions as well as save chemicals. The plasma does generate more CF_4 byproduct from the feed gas, but a net 50% reduction in PFC emissions is still apparently possible. Since any change in process parameters on an existing manufacturing line can impact yield and product reliability dramatically, this process will require extensive qualification at each company before it can be implemented, even after validation by the tool supplier.

References

F. Illuzi, M. Molgg, L. Colombo, L. Atzei, "Etching Process Optimization: A Way to Reduce PFC Emissions," *Proceedings of the Fourth International ESH Conference*, Milan, Italy, 1997, Vol.2, Session 7.

A.2 ALTERNATIVE CHEMISTRIES

A.2.1 AMD Studies of a C_3F_8-Based PECVD Clean

Technical Description

This project evaluated C_3F_8 as a potential chamber cleaning gas substitute for the standard C_2F_6 clean in a Novellus Concept Two SEQUEL reactor for the PECVD dielectric process.

Project Status

C_3F_8 is a viable replacement to C_2F_6; it is currently being used in AMD's Fab 25 manufacturing processes for 200 mm wafers as well as for 150 mm wafer sizes in Novellus Concept One PECVD reactors in a manufacturing environment.

Project goals were achieved. The recipe has been released to the industry through Novellus. Evaluation concluded that the C_3F_8 process

- Uses less gas by volume (60% less etch gas and 30% less oxygen)
- Has a slightly faster etch rate than the C_2F_6
- Reduces net PFC emissions by 60–70%

Test results showed that neither tetraethyl ortho silicate (TEOS) film characteristics nor chamber condition degraded; additionally, the lots showed no significant statistical differences in terms of device parameters, die yield, and reliability performance when processed with the C_3F_8.

Applicability

This technology is applicable to newer fabs if they have sufficient space to accommodate new gas configurations. This particular project was performed on 200 mm wafers for a CVD process; however, AMD has since migrated this process to 150 mm tools.

Pros and Cons

C_3F_8 is an interim solution since the C_3F_8 process produces CF_4 byproducts. Widespread conversion will need to be evaluated fab by fab. Qualification requirements are extensive and will also have to be performed fab by fab. Capital costs of implementation could be high depending on the fab's individual gas configuration set-up.

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Sherwood, G. "C_3F_8 for CVD Cleaning," Presented at the MIT Technology Transfer Course, December 1995.

Sun, S. *Evaluation of C_3F_8 as a Cleaning Gas in a Novellus Concept Two SEQUEL Tool*, SEMATECH Technology Transfer #97053282A-TR, Austin, TX, May 31, 1997.

Sun, S. "Evaluation of C_3F_8 as a cleaning gas in a Novellus Concept Two SEQUEL Tool," Presented at the SEMATECH ESHC002 PTAB meeting, Austin, TX, February 26, 1997.

Sun, S., Zazzera, L. "Reducing PFC Emissions Using C_3F_8-Based PECVD Clean," *Semiconductor International*, Vol. 2, February 1998.

A.2.2 Motorola/3M/Texas Instruments Evaluation of C_3F_8 as a Cleaning Gas

Description

This project evaluated C_3F_8 as a potential chamber cleaning gas substitute for the standard C_2F_6 clean in a Novellus Concept One reactor for PECVD dielectric (TEOS, silicon nitride, PSG, (polysilicon glass) and BPSG (boron polysilicon glass)) processes.

Project Status

At Motorola, C_3F_8 has proven to be a viable replacement for C_2F_6 and is currently being used in a Motorola manufacturing fab. Project goals were achieved. Evaluation concluded that the C_3F_8 process

- Uses less gas (24% less etch gas and 31% less oxygen by mass)
- Is the same duration as the standard C_2F_6 clean process
- Reduces net PFC emissions measured as MMTCE by approximately 50%

Test results showed no degradation of PECVD reactor hardware after processing approximately 150,000 wafers.

Applicability

This process is suitable for existing fabs with an installed base of Novellus Concept One reactors for PECVD dielectric processes. This particular project was performed on < 150 mm wafers. Texas Instruments evaluated C_3F_8 in a 150 mm Novellus Concept One reactor for oxynitride deposition. Film uniformity problems were identified and not resolved, preventing implementation of a C_3F_8 clean.

Pros and Cons

C_3F_8 is an interim solution, which produces CF_4 byproducts. Widespread conversion will need to be evaluated fab by fab and process by process. Qualification requirements are extensive and will also have to be performed fab by fab. C_2F_6 distribution in existing fabs is often from one cylinder to a number of different tool sets. Use of C_3F_8 will require splitting that distribution unless all tools are converted to C_3F_8 at once. Current Novellus efforts to optimize C_2F_6 cleans and to use alternative cleaning chemistries should be factored into decision making.

For tools other than the Novellus Concept One, extensive experiments will need to be performed to determine the potential to implement C_3F_8 processes.

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R. Kachmarik, McLaughlin, Tousignant, and Zazzera. “Comparative Analysis of PECVD Cleans for Some Commonly Deposited Films,” Presented at SEMICON SW 97 Partnership for PFC Reductions Conference, October 13, 1997.

A.2.3 Chemical Mechanical Planarization (CMP)

Description

Chemical mechanical planarization is a relatively new unit process that replaces some PFC-using etch steps. CMP is used to planarize wafer topography for improved photolithography capability in smaller geometry integrated circuits. Another use for CMP replaces tungsten etchback steps that also traditionally use PFCs. Process tools using chemical slurries containing suspended solids combine chemical etch reactions with mechanical removal to create a level wafer surface or remove blanket-deposited films.

Project Status

CMP processes are used today in manufacturing in many semiconductor facilities fabricating advanced semiconductors.

Applicability

CMP is an extremely complex and expensive process to implement. The technical requirements of the manufacturing process will usually drive the implementation, which has the serendipitous effect of reducing PFC requirements. It generally can not be retrofitted to mature processes. Therefore, the applicability is limited to newer, advanced processes only.

Pros and Cons

CMP reduces PFC requirements for fabrication of circuitry with ever-increasing complexity and more layers of metal and dielectric that require more planarization steps and more tungsten etchback steps. However, it is extremely expensive and complicated to implement. It requires expensive process tooling and slurry delivery systems. It replaces PFC emissions with slurry waste that might create regulatory or waste treatment issues and is also a water-intensive process.

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Iscoff, R. “CMP Takes a Global View,” *Semiconductor International*, Cahners Publishing, May 1994, p. 74.

A.2.4 Chlorine Trifluoride Chamber Clean

Description

Chlorine trifluoride (ClF_3) is used in the Japanese semiconductor industry as a cleaning agent for quartz furnace tubes and tungsten and tungsten silicide chambers. ClF_3 has no ozone depletion or global warming potential.

Project Status

The process is in place in specialized applications and in a minimum number of locations in the U.S. Although domestic use is not extensive, there are some chamber clean installations.

Applicability

Because ClF_3 is extremely reactive, it should clean chambers; however, it may be so reactive that the chambers will degrade or aluminum will become ionized, causing deposits on the next cycle of wafers. Indications are that it works for removing films of polysilicon and silicon nitride, but not silicon oxide. Since it cannot be used for dielectric films, its ability to replace PFCs will be limited.

Pros and Cons

ClF_3 is consumed in the reactor and none of the byproducts have a global warming potential. It is so reactive that some companies are reluctant to use it because of safety and handling concerns. A leak would result in a very dangerous situation. It will be expensive to set up a feed system; special handling is required (e.g., fluorine-passivated stainless piping). POU treatment and special exhaust lines will be required. Capital and operating costs are unknown at this time; however, extensive process qualification would be required.

Reference

Pierce, A. M., Taylor, M., Sauer, J., and Rupert, D., “Safe Usage of ClF_3: Supply, Vacuum Service, and Exhaust Management,” *Solid State Technology,* September 1997, pp. 107–114.

A.2.5 DuPont Studies of Highly Fluorinated Ethers as PFC Alternatives for PECVD Oxide Chamber Cleaning

Description

Studies were performed on two classes of compounds, the perfluoroalkyl perfluorovinyl ethers I and the hydrofluoroethers II.

I: F2C=C(F)OCxF(2x+1), x = 1-3

II: F[CF(CF3)CF2O]nCHFCF3, n = 1

The tests were performed in the laboratory of Professor H. Sawin (MIT) in a lab scale reactor designed to mimic the performance of commercial oxide PECVD tools, including the deposition of PETEOS oxide, and the subsequent in situ cleaning process.

Project Status

The laboratory studies did not provide sufficient incentive to carry these results to further pre-commercial testing.

Applicability

The focus of these studies was on chamber cleaning, with applications to both installed base and new tools that have the conventional parallel-plate (capacitively coupled) configuration.

Pros and Cons

The compounds I have very low atmospheric lifetimes (days to weeks). Compounds II are somewhat higher (estimated at a few years). Cleaning rates roughly comparable to the currently used C_2F_6 were found. CF_4 emissions typical of a carbon-based cleaning gas were seen. These results did not justify further work, given the anticipated greater cost of the new gases, the uncertain availability of high purity gas (quantities available are sufficient, but not in purities typical of the industry's specialty gases), and other trends in chamber clean process optimization.

References

Further information on these studies can be obtained from M. Mocella, DuPont (michael.mocella@usa.dupont.com). These studies were reviewed at a 1997 SEMI-sponsored PFC seminar, Alternative Gases for PECVD Chamber Cleaning, H. H. Sawin, H. Chae, and M. T. Mocella, *Proceedings of the SEMICON Southwest 97*, A Partnership for PFC Emissions Reductions, Poster Session, paper #2 (1997).

A.2.6 Hydrofluorocarbons (HFCs) as Alternative Chemistries in Selected Plasma Etch Applications

Description

These MIT studies focused on substituting HFCs (generic formula CxFyHz) for various plasma etch processes in an Applied Materials 5000 etcher, a Lam Research HDP etcher, and an Applied Materials Centura 5300 HDP etcher.

Project Status

Initial proof-of-concept studies were carried out in 1994 by MIT and Lam Research in an Applied Materials Precision 5000 etch tool at MIT using pentafluoroethane (C_2F_5H, GWP100 = 2800) and 1,1,1,2-tetrafluoroethane (CF_3-CFH_2, GWP100 = 1300). Patterned oxide substrates were etched, and high aspect ratio submicron features were successfully patterned with both gases. Similar experiments were also carried out in a high density Lam etch tool at Lam, also with good results. However, significant amounts of CHF_3 (GWP100 = 11,700) were required in these processes and no emissions data are available.

In 1995–1996, additional proof-of-concept work was carried out on an Applied Materials Precision 5000 etch tool at MIT with six HFC chemistries. Blanket thermal oxide and LPCVD nitride films were etched. The first three compounds were found to be effective etchants in the regime explored; the latter three were found to polymerize heavily, but could be made to etch under appropriate conditions. No emissions data are available.

On the basis of preliminary data, 2H-heptafluoropropane was selected for an alpha test in collaboration with Motorola in 1997. Blanket TEOS oxide, PECVD nitride, I-line resist, and patterned TEOS oxide wafers were etched in an Applied Materials Centura 5300 HDP high density etch tool at Motorola’s Advanced Products Research and Development Laboratory (APRDL). 2H-heptafluoropropane was found to be capable of reducing emissions about 60% compared to a C_3F_8-based reference process in a high aspect ratio via etch application.

A follow-up study was carried out in 1998, on the same tool at Motorola’s APRDL. A high aspect ratio TEOS via etch process was developed that matched, and in some cases exceeded, the performance of a referenced C_3F_8-based process for the same application. Earlier findings that significant PFC emission reductions were attainable with this compound were confirmed.

Applicability

This technology may be applicable to future advanced etch tools and processes, for wafer diameters of 200 mm and larger. Chemical substitution for etch applications is generally not retrofittable into installed base equipment and processes.

Pros and Cons

These studies are still in very early development and have been investigated in limited applications and equipment. HFCs possess similar handling characteristics as well as process behavior as PFCs. Emissions data indicate that measurable, though significantly lower, quantities of global warming products (including PFCs such as CF_4) are emitted by the HFC-based etch processes studied (compared to typical PFC processes). The emissions reductions relative to existing processes are likely to be significant, but not by orders of magnitude and may not achieve the high PFC emissions reductions desired. A current concern is the fact that 2H-heptafluoropropane is not TSCA-listed.

References

V. Mohindra, H.H. Sawin, M.T. Mocella, J.M. Cook, J. Flanner, and O. Turmel, "Alternatives to Perfluorocompounds as Plasma Processing Gases: SiO_2 Etching Using C_2F_5H and $C_2F_4H_2$," *Proceedings of the Tenth Symposium on Plasma Processing*, Proceedings Volume 94–20 of the Electrochemical Society, 1994, pp. 300–310.

B. A. Tao, S.M. Karecki, L.R. Reif, "Alternative Chemistries to Perfluorocompounds for Dielectric Plasma Etching," *Proceedings of the Electrochemical Society: 11th International Symposium on Plasma Processing*, 96–12, p. 424 (1996).

S.M. Karecki, B.A. Tao, L.R. Reif, L. Beu, T. Sparks, V. Vartanian, "Use of 2H-heptafluoropropane, 1-iodoheptafluoropropane, and 2-iodoheptafluoropropane for a High Aspect Ratio Via Etch in a High Density Plasma Etch Tool," to be published in *Journal of Vacuum Science and Technology A*, July/Aug 1998.

M.C. Olefin, "Alternative Etch Chemistries and Optimization Studies for Dielectric Reactor Cleaning," Global Warming Symposium (SEMATECH), 1994.

J.E. Nullity, P.S. Trammel, "Self-Aligned Contact (SAC) Dry Etch Process for 0.5 µm SRAM Technology," *Proceedings of the American Vacuum Society*, 41st National Symposium, 1994.

A.2.7 MIT Studies on Iodofluorocarbons as Alternative Chemistries for CVD Tools

Description

These MIT studies focused on investigation of the iodofluorocarbon family (generic formula CxFyIz) as PFC alternatives in etch and chamber clean processes using an Applied Materials Precision 5000 etch tool, a Novellus Speed Dielectric Deposition tool, and an Applied Materials Centura 5300 HDP high density etch tool.

Project Status

Proof-of-concept tests were carried out at MIT in 1996 and 1997 in an Applied Materials Precision 5000 etch tool using several iodofluorocarbon compounds. Blanket thermal oxide and LPCVD nitride films were etched. It was found that in the Precision 5000 etcher, iodotrifluoromethane and 1-iodoheptafluoropropane etched both oxide and nitride films quite readily. Iodotrifluoroethylene and 2-iodoheptafluoropropane, on the other hand, etched oxide films but, under the conditions tested, were found to be quite selective to nitride. Iodopentafluoroethane was found to exhibit oxide and nitride etch rates intermediate to those of iodotrifluoromethane and 2-iodoheptafluoropropane. No emissions data are available for these tests.

In 1996, MIT and Novellus performed limited proof-of-concept chamber clean tests using iodotrifluoromethane and iodopentafluoroethane at Novellus. In the regimes tested, significant molecular iodine was deposited in the chamber with both chemistries.

MIT and Motorola performed testing on iodotrifluoromethane, 1-iodoheptafluoropropane, and 2-iodoheptafluoropropane based on preliminary data from MIT. Blanket TEOS oxide, PECVD nitride, I-line resist, as well as patterned TEOS oxide wafers were etched in an Applied Materials Centura 5300 HDP high density etch tool at Motorola's Advanced Products Research and Development Laboratory (APRDL). All three compounds showed very high emissions reductions (up to 95%) compared to a C_3F_8-based reference process in a high aspect ratio via etch application. Iodotrifluoromethane did not prove viable from a process standpoint; however, both isomers of iodoheptafluoropropane yielded encouraging results. Very high etch rates (in excess of 10,000 Å/min for some features) were obtained. No evidence of molecular iodine deposits in the process chamber was found with either iodoheptafluoropropane isomer. Further development work is required to achieve performance targets equivalent to those of standard C_3F_8 processes. Additional testing is scheduled for 1998.

Applicability

This technology may be applicable to future advanced etch tools and processes for 200 mm and larger wafers. Chemical substitution for etch applications is generally not retrofittable into installed base equipment and processes.

Pros and Cons

These studies are still in very early development and have been investigated in limited applications and equipment. Some iodofluorocarbons are liquids at room temperature and can only sustain lower flowrates. IFCs are expected to have negligible Global Warming Potentials, and all of the data indicates that substantially lower quantities of global warming products (including PFCs such as CF_4) are emitted by the IFC-based etch processes studied (versus typical PFC processes).

References

Karecki, Pruette, Reif. "Plasma Etching of Silicon Dioxide and Silicon Nitride with Non-perfluorocompound Chemistries: Trifluoroacetic Anhydride and Iodofluorocarbons," *Proceedings from the Materials Research Society*, Symposium Proceedings 447: Environmental, Safety, and Health Issues in IC production, 1997, pp. 67–74.

A.2.8 Texas Instruments' Studies on Iodofluorocarbons as Alternative Chemistries for CVD Tools

Description

This study focused on an investigation of CF_3I as a PFC alternative in chamber clean processes using an Applied Materials 3300 IIA parallel plate PECVD dielectric deposition tool.

Project Status

Texas Instruments reported investigating CF_3I as a replacement for PFCs in PECVD chamber clean and etch processes. The testing was performed in the Chemical Operations Department at Texas Instruments' Dallas facility, using an Applied Materials 3300 IIA parallel plate PECVD batch reactor for the experiments. CF_3I was chosen because of its structural similarity to PFCs, its environmentally benign characteristics, and its availability. The experiments showed that CF_3I can successfully be used to etch dielectric films and that it does not destroy common PECVD chamber material.

Emissions testing was carried out in March 1997. Fourier transform infrared (FTIR) characterization of the byproducts under different process conditions revealed that high utilization efficiency of CF_3I would be achieved at an RF power level of 1500 W and that the extent of CF_4 and C_2F_6 formation in a CF_3I /O_2 plasma was significantly lower than a traditional process employing C_2F_6/O_2 mixtures. Future testing is planned to evaluate the performance of the new chemistry on actual process tools for both chamber cleaning and wafer patterning and to evaluate other iodofluorocarbons, such as C_2F_5I. (The experimental group that did this work is now part of Air Liquide Electronics Chemicals and Services, Inc.)

Applicability

This technology may be applicable to future advanced etch tools and processes for 200 mm and larger wafers. Chemical substitution for etch applications is generally not retrofittable into installed base equipment and processes.

Pros and Cons

These studies are still in very early development and have been investigated in limited applications and equipment. Other IFC studies have reported the possibility of buildup of molecular iodine in chamber cleaning applications. Some iodofluorocarbons are liquids at room temperature and can sustain only lower flowrates. IFCs are expected to have negligible global warming potentials, and all of the data indicate that substantially lower quantities of global warming products (including PFCs such as CF_4) are emitted by the IFC-based etch processes studied (as opposed to typical PFC processes).

References

Levy, Zaitsev, Aryusook, Ravindranath, Sigal, Misra, Kesari, Rufin, Sees, and Hall, "Investigation of CF_3I as an Environmentally Benign Dielectric Etchant," Accepted for publication in the *Journal of Materials Research,* 1998.

Misra and Magel, "X-ray Photoelectron Spectroscopy of Aluminum Alloys Exposed to CF_3I Plasma," Accepted for publication in *Materials Letters*, 1997.

Misra, Sees, Hall, Levy, Zatisev, Aryusook, Ravindranath, Sigal, Kesari, and Rufin, "Plasma Etching of Dielectric Films Using the Non Global-Warming Gas C_3FI," Accepted for publication in *Materials Letters*, 1997.

A.2.9 University of Bari Studies of CF_3I-Based Etchants as a Substitute for CF_4 in a Lam Rainbow 4520 Replica

Description

This project evaluated the feasibility of using iodofluorocarbons (CF_3I) as a substitute for the standard CF_4 etchant in a silicon dioxide dry etch process.

Project Status

In 1997, proof-of-concept bench tests were carried out by the University of Bari in collaboration with Lam Research and STMicroelectronics to evaluate CF_3I in an oxide etch process. A Lam Rainbow 4520 replica with a parallel plate reactor was used. Preliminary results indicate that emissions were reduced four to six times compared to standard processes.

Applicability

Iodofluorocarbons are applicable to silicon dioxide dry etch processes in a Lam Rainbow 4520 using 150 mm wafers.

Pros and Cons

Members of the iodofluorocarbon family share the generic formula CxFyIz. Their handling properties vary. The iodofluoroalkanes possess somewhat higher acute toxicities (although still low relative to other gases used as etchants such as Cl_2 and HBr) than perfluorocarbons. Many, though not all, iodofluorocarbons are liquids at room temperature. None are flammable or corrosive. Iodofluorocarbons photolyze readily once released into the atmosphere and are expected to have lifetimes on the order of days; their global warming potential values are expected to be negligible. Byproducts of CF_4 in the effluent, although present in lower concentrations, are still a concern. Significant process qualification testing will be required to ensure equivalent process performance to the standard CF_4/CMF_3 processes for SiO_2 etching. At the same mass flow rate, CF_3I has a somewhat lower etch rate and a slightly greater tendency to form polymers than CF_4.

References

Fracassi, F., “Environmental Impact of Fluorocarbon and Iodofluorocarbon Containing Glow Discharge for SiO_2 Etching,” Presented to the International Environment, Safety and Health Conference, Milan, Italy, June 1997.

A.2.10 Applied Materials µClean Technology for DxZ PECVD Dielectric Chamber Clean

Description

This process is a remote microwave clean using 100% NF_3 as a replacement for the standard C_2F_6/ NF_3 clean. It is used on Applied Materials DxZ PECVD dielectric chambers. The NF_3 is dissociated in a microwave plasma outside the reactor. The dissociated species flow into the reactor to clean the chamber. No plasma is required inside the chamber.

Project Status

Proof of concept has been verified at Applied Materials on TEOS oxide, silane oxide, and silicon nitride for up to 1 mm films. The proof of concept yielded the following results:

- Shorter clean times than standard process
- Reduced hardware damage
- > 95% conversion efficiency of NF_3 (up to > 99%) resulting in almost zero PFC emissions
- Reduced frequency of required wet cleans
- No adverse effects on film quality

Initial alpha testing at Motorola had some problems with particle generation because the unit was misfigured, but NF_3 conversion efficiency was high (up to 94%) for the baseline process. Further developments by Applied Materials have resulted in a unit that can clean up to 3 mm thick oxide films with no particle generation; endpoint detection feasibility was also demonstrated. The testing will be repeated at Motorola with the improved unit.

Applicability

The technology is applicable to all 200 mm DxZ PECVD dielectric chambers, most of which already have NF_3 plumbed to them if they are running the standard Applied Materials NF_3-doped C_2F_6 clean. This technology will also be available for 300 mm platforms (new tools) and SACVD and HDP tools, but it is limited to specific Applied Materials tools.

Pros and Cons

The microwave is a compact, lid-mountable unit that will add to the capital cost of the tool. Because most DxZ PECVD dielectric chambers already have NF_3 plumbed to the chamber, no new gas cabinets or configurations will be required. Technology virtually eliminates PFC emissions by having nearly 100% conversion of NF_3. Clean times are reduced, thus allowing for increased throughput. The remote plasma should reduce hardware damage in the chamber.

However, 100% NF_3 generates more air pollutants (e.g., F_2, HF, etc.). This may result in abatement (scrubber and wastewater treatment) issues for existing fabs. Qualification requirements for this technology may be extensive and will have to be performed fab by fab.

References

Applied Materials MicroClean Technology for DxZ Chamber Clean for PFC Emissions Reduction: Preliminary Evaluation, SEMATECH Technology Transfer #98023458A-ENG, February 1998.

A.2.11 Dilute NF_3 as an Alternative Chemical for Applied Materials PECVD Chamber Cleans

Description

Dilute NF_3 (using helium as the diluent) has been proposed by IBM as an alternative chamber clean chemistry for C_2F_6. Work is being done at IBM to develop an NF_3 clean on an Applied Materials 5000 PECVD tool. Previous efforts by Motorola, Intel, and Applied Materials to develop dilute NF_3 cleans on the Applied Materials platform have had limited success.

Project Status

Proof-of-concept testing has been done at IBM. Process development is in the early stages. Applied Materials is currently reviewing the IBM data and is comparing the results to their previous efforts to develop a dilute NF_3 clean process.

Applicability

This technology may be applicable to all wafer sizes for CVD chamber clean (primarily dielectric PECVD, although some testing has been done on tungsten CVD); however, results appear to be dependent on chamber design. The technology may not be readily applicable to old fabs where space requirements limit installation of the necessary NF_3 and He supply lines and cabinets. According to IBM, all Applied Materials 200 mm tools, including those that are lamp-heated, are candidates. Applied Materials is reviewing 200 mm tool results. The < 200 mm tools still require process development and evaluation; this is a significant effort.

Pros and Cons

A 90+% reduction in emissions from 1995 cleaning processes has been seen. However current issues, such as process drift, increased tool downtime, and the long-term impact on consumables, have to be resolved before this process is ready for implementation. If these issues cannot be overcome, most fabs cannot implement the technology. Another implementation issue is the distribution of NF_3 gas to the tools. Existing fabs may not be plumbed for NF_3, which can be a significant cost (NF_3 requires different piping and cabinets than C_2F_6 and toxic gas monitoring). In addition, the necessary space may not be available. Assuming this technology becomes production worthy, it will produce low global warming emissions and may eliminate major solids problems with tungsten cleans (WOFx). IBM estimates this process will have a lower cost than the optimized C_2F_6 clean process for Applied Materials tools. The chemistry change will require significant qualification in the fab (IBM estimates 18 months). Some additional safeguards may be necessary to address toxicity of NF_3, especially since the primary byproducts of this process are SiF_4 and unreacted NF_3 (in the use of dielectric processes).

References

Tamayo, Hines, Pinto. "IBM PFC Gas Emission Reduction Status." Presented at the SEMI Meeting, A Partnership for PFC Emissions Reduction, October 1997.

Tamayo, Hines, Pinto, Miller, Izor. "IBM PFC Gas Emissions Reduction Status." Presentation at the SEMATECH PFC Emissions Reduction PTAB Meeting (ESHC005), March 1998.

Pruette, Karecki, Reif. "Update on Alternative Chemistries Work at MIT." Presentation at the SEMATECH PFC Emissions Reduction PTAB Meeting (ESHC005), March 1998.

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H. Denton, “An effective In-Situ Clean for PECVD to Reduce PFC Emissions,” Conference Proceedings from SEMICON/Southwest 1996, Partnership for PFC Emissions Reduction Conference, October 14, 1996.

A.2.12 Dilute NF_3 as an Alternative Chemical for Novellus Concept One PECVD Chamber Cleans

Description

Dilute NF_3 (using helium as the diluent) has been proposed by IBM as an alternative chamber clean chemistry for C_2F_6. NF_3 chamber clean viability work has been done at MIT on a Novellus Systems PECVD Concept One reactor, followed by process development at Novellus Systems.

Project Status

Proof-of-concept testing has been done at IBM, Novellus, and MIT; development is continuing at IBM and Novellus. Beta testing is underway at IBM.

Applicability

For Novellus, 200 mm tools are in beta testing. Preliminary results are promising; this technique may become a Novellus process for 200 mm tools in 1998. Novellus is also reviewing 300 mm and < 200 mm applications.

Pros and Cons

A 90+% reduction in emissions from 1995 cleaning processes has been seen. Assuming a manufacturing-worthy process is developed, an implementation issue is the distribution of NF_3 gas to the tools. Existing fabs may not be plumbed for NF_3, which can be a significant cost (NF_3 requires different piping and cabinets than C_2F_6 and toxic gas monitoring). In addition, the necessary space may not be available. The chemistry change will require significant qualification in the fab (IBM estimates 18 months). Some additional safeguards may be necessary to address toxicity of NF_3, especially since the primary byproducts of this process are SiF_4 and unreacted NF_3 (in the use of dielectric processes). Assuming this technology becomes production worthy, it will produce low global warming emissions and may eliminate major solids problems with tungsten cleans (WOFx).

References

Tamayo, Hines, Pinto. "IBM PFC Gas Emission Reduction Status." Presented at the SEMI Meeting, A Partnership for PFC Emissions Reduction, October 1997.

Tamayo, Hines, Pinto, Miller, Izor. "IBM PFC Gas Emissions Reduction Status." Presentation at the SEMATECH PFC Emissions Reduction PTAB Meeting (ESHC005), March 1998.

Pruette, Karecki, Reif. "Update on Alternative Chemistries Work at MIT." Presentation at the SEMATECH PFC Emissions Reduction PTAB Meeting (ESHC005), March 1998.

H. Denton, “An Effective In-Situ Clean for PECVD to Reduce PFC Emissions,” Conference Proceedings from SEMICON/Southwest 1996, Partnership for PFC Emissions Reduction Conference, October 14, 1996.

A.2.13 NF_3-Based Chamber Clean for Lam Research PECVD

Description

Lam's DSM 9900 has reduced PFC emissions as an integral part of the tool design. Lam is migrating to low pressure, high density inductively coupled reactor technology using NF_3 as the source gas.

Project Status

The tool is currently being beta-site evaluated by two semiconductor manufacturing companies. NF_3 is the standard gas offering for this tool.

Applicability

This technology is appropriate for chamber cleaning for SiO_2, and SiOF gap fill (PECVD processes) in new fabs using 200 mm wafers. This is a new tool and is not part of the installed base.

Pros and Cons

The tool is undergoing an extensive qualification process. It uses NF_3 for the chamber clean. Facilitization requires NF_3 plumbing and installation according to local code requirements. As a tool-based technique, it cannot be retrofitted to existing fabs. Possible byproducts include HF and F_2. NF_3 is a toxic gas and appropriate monitoring devices must be used to ensure its safe use. Exhaust gas scrubbers are strongly recommended.

References

Maille, J., "A Partnership for PFC Emissions Reduction," Presented at the SEMATECH PFC Workshop, February 1996.

A.2.14 NF_3-Based Chamber Clean Processes for Novellus Tungsten CVD and PECVD

Description

This project evaluated NF_3 as a potential chamber cleaning gas substitute for the standard C_2F_6 clean for Novellus Concept Two W-CVD and Novellus Concept One PECVD and Concept 2 PECVD tools were developed using NF_3 as the source gas.

Project Status

These processes are under development at Novellus Systems and are currently being alpha tested. Project goals are to develop a chamber clean process for Novellus CVD tools with the following characteristics:

- Equivalent or higher etch rate than the standard C_2F_6 process
- PFC emissions reductions greater than 40% compared to the standard C_2F_6 process
- No negative process impact (hardware, film properties, etc.)

Applicability

This recipe is currently being evaluated for 200 mm and 300 mm tool sets. It is applicable to Novellus Concept Two W-CVD and Novellus Concept 1 and Concept 2 PECVD tools. It is possible that it could be retrofitted to both old and new fabs.

Pros and Cons

Implementation will require some capital investment including mass flow controller changes, some software modifications, as well as NF_3 plumbing and installation according to local code requirements. Byproducts include residual NF_3 (10–20% of input levels) and F_2. Wide-spread conversion will need to be evaluated fab by fab. Qualification requirements are extensive and will also have to be performed fab by fab. Capital costs of implementation could be high depending on the fab’s individual gas configuration set up.

NF_3 is a toxic gas, and appropriate monitoring devices must be used to ensure safe use. Exhaust gas scrubbers are strongly recommended.

References

Aitchison, K., “Combined Approaches to Zero-Emitting Processes,” Presented at the SEMICON West meeting, 1997.

A.2.15 NF_3-Based Chamber Clean Processes for Novellus High Density Plasma (HDP) CVD Tools

Description

Chamber clean processes for Novellus HDP CVD tools were developed using NF_3 as the source gas.

Project Status

This process is currently in use on all installed Novellus HDP CVD tools, primarily 200 mm. Calibrated measurements by quadrupole mass spectrometry (QMS) have shown that > 90% of the NF_3 is consumed in the chamber. The high efficiency clean process was developed as an integral part of the system development and was one of the success criteria for the product. Project goals were achieved.

Applicability

The HDP CVD tool is a new generation tool that can be used in old or new fabs depending on the need for 200 mm and 300 mm wafer sizes.

Pros and Cons

NF_3 is the standard chamber clean process for Novellus HDP CVD tools. There is no further implementation necessary. Facilitization requires NF_3 plumbing and installation according to local code requirements. Byproducts include residual NF_3 (10% of input levels) and F_2. Since this is the standard process, additional qualification efforts are not necessary. NF_3 is a toxic gas; therefore, appropriate monitoring devices must be used to ensure safe use. Exhaust gas scrubbers are strongly recommended.

References

Aitchison, K., “Combined Approaches to Zero-Emitting Processes,” Presented at the SEMICON West meeting, 1997.

A.2.16 Toshiba Studies on Oxygenated Perfluorocarbons

Description

The project involved testing several PFC alternative chemistries to the PFC gases for etch processes. The most promising of the chemicals identified from this study are HFE-227 ($CF_3OCHFCF_3$), HFE-329 ($CF_3CF_2OCF_2CHF_2$), and HFO-Z1 (C_5F_8).

Project Status

Lab scale studies were performed at Toshiba in Japan. Two parallel plate etching systems (TE-5000S from Tokyo Electron Yamanashi Limited) and one etching system (I-1400SH from ANELVA Corp.) were used in the experiments.

Applicability

These chemicals would completely replace PFCs in etching activities; however, all three gases had unacceptable deposition characteristics.

Pros and Cons

Besides not being acceptable from a performance standpoint, the toxicity characteristics of gases and byproducts are not known.

References

Yoshida, Y., “Study on the Possibility of Alternative Gas to PFC,” Presented to the International Environment, Safety, and Health Conference, Milan, Italy, June 1997.

A.2.17 Triflouroacetic Anhydride (TFAA) as an Alternative Chemistry in Oxide Chamber Clean

Description

Several studies investigated trifluoroacetic anhydride (TFAA) as an alternative chemistry for dielectric etch and chamber cleaning in an Applied Materials Precision 5000 etch tool, a Novellus Concept One 200 PECVD dielectric deposition tool, and an Applied Materials Precision 5000 dielectric PECVD deposition tool.

Project Status

In 1996, proof-of-concept tests with TFAA were carried out at MIT in an Applied Materials Precision 5000 etch tool with blanket thermal oxide and LPCVD nitride films. TFAA was found to have nitride etch rates comparable to those of C_3F_8 throughout the parameter space studied, whereas its oxide etch rates were generally slower. Trends with respect to the process parameters that were varied were generally similar to those observed with C_3F_8. No emissions data are available from these tests.

In 1997, TFAA was evaluated in a dielectric PECVD chamber clean application in a Novellus Concept One 200 PECVD tool at MIT. A silane oxide process was used for the deposition cycle. FTIR and QMS were employed to quantify emissions. The only global warming gas identified in the effluent was CF_4. Relative to a C_2F_6 reference process, approximately five-fold emissions reductions were attained with equivalent clean times and eight-fold reductions were attained with slightly longer clean times. Generally, TFAA was found to be effective as a chamber clean chemistry in the Concept One. However, because the material has a high boiling point and is a liquid at room temperature, problems were experienced when attempting to deliver the high flows required.

In 1996, TFAA was evaluated for chamber cleaning in an alpha-test in an Applied Materials Precision 5000 dielectric PECVD tool located in Motorola’s Semiconductor Technologies Laboratory (STL). A plasma-enhanced TEOS oxide process was used for the deposition cycle. QMS, electron impact mass spectroscopy (EIMS), and chemical ionization mass spectroscopy (CIMS) were used to analyze the effluent. Chamber effluent from a representative TFAA process was reported to contain less than 1% C_2F_6 and 9–27% CF_4. Both clean times and etch rates were found to be at least comparable to those of a standard two-step C_2F_6 process normally run on the tool. The net global warming impact of the representative TFAA process was estimated to be less than 4% of that of a one-step C_2F_6-based clean. Overall, both process and emissions characteristics of TFAA in this application were found to be encouraging, warranting a recommendation for further study.

Applicability

This technology may be applicable to future advanced etch tools and processes for 200 mm and larger wafers. Chemical substitution for etch applications generally cannot be retrofitted into installed base equipment and processes. Chemical substitution for dielectric deposition chamber cleaning in installed base equipment is generally regarded as time-consuming and costly; it may not be economically feasible for many facilities and processes.

Pros and Cons

These studies are still in very early development and have been investigated in limited applications and equipment. TFAA is expected to have negligible lifetime and GWP values. TFAA can be corrosive if exposed to moisture; this can present a potential health and safety issue. In addition, because of its high boiling point, the use of TFAA in high flow applications, such as the Novellus Concept One chamber clean, may be difficult without heated lines and/or liquid inject. Introduction of this compound into a production environment for a chamber clean application would require the resolution of facilities issues associated with the delivery of TFAA to the tool. In some cases, the need for alternate piping would prohibit the use of this technology.

Although significant emissions reductions (compared to typical PFC processes) were obtained when TFAA was evaluated in dielectric PECVD chamber clean applications, some global warming byproducts are still produced using this process.

References

S. Soggs, B. Bryant, B.A. Boeck, S. Rogers, R. Vrtis, L. Mendicino, “Trifluoroacetic Anhydride as an Alternative Plasma Clean Chemistry,” *Proceedings from the SEMI Technical Program: A Partnership for PFC Emissions Reduction,* Austin, TX, pp. 71–80 (1996).

S. M. Karecki, L. C. Pruette, L. R. Reif, “Plasma Etching of Silicon Dioxide and Silicon Nitride with Non-Perfluorocompound Chemistries: Trifluoroacetic Anhydride and Iodofluorocarbons,” *Proceedings of the Materials Research Society,* Symposium Proceedings 447: Environmental, Safety, and Health Issues in IC Production, R. Reif, M. Heyns, A. Bowling, A. Tonti, eds., pp. 67–74 (1997).

J. Langan, S. Rogers, R. Ciotti, B. Felker, S. Karecki, L. Pruette, R. Reif, “Investigation of Alternative Chamber Clean Chemistries for PFC Emissions Reduction in the Novellus Concept One Reactor,” *Proceedings from the SEMI Technical Program: Perfluorocompound (PFC) Technical Update*, San Francisco, CA, p. H-1 (1997).

A.2.18 Low Global Warming Potential (GWP) Alternatives from AlliedSignal

Description

Four chemicals with lower GWPs than conventional PFC compounds have been demonstrated to work for etch/clean applications. The molecules were selected for the combination of the desirable physical properties, low environmental impact, favorable plasma performance, and commercial availability.

Compound	Toxicity	Flammable	Lifetime (yrs)	GWP (100 yr)	BP (°C)	TSCA Inventory
FC(O)C(O)F Oxalyl fluoride	Medium	No	~0	~0	-3.0	Yes
$CF_3CH_2CHF_2$ HFC-245fa	Low	No	7	790	15.3	Pending
$CF_3CH_2CF_3$ HFC-236fa	Low	No	209	6,300	-1.1	Yes
IF_5 Iodine pentafluoride	High	No	~0	~0	99	Yes

Status

Proof of concept testing in a Plasma Therm etcher with Astex ECR source has been completed at Allied Signal's Microelectronics & Technology Center. Discussions are underway with several organizations to test the molecules in state of the art production equipment and monitor emissions. The compounds are available in commercial quantities (IF_5), large scale pilot quantities (HFC-245fa, HFC-236fa), or approaching the pilot stage (oxalyl fluoride).

Applicability

Because of the propensity to polymerize under some conditions, the HFC molecules are more useful for etching than for CVD chamber cleaning. Oxalyl fluoride and IF_5 do not leave residues and have utility for both etching and chamber cleaning.

Pros and Cons

Compound	Pros	Cons
FC(O)C(O)F	Unoptimized etch rates comparable to CF_4 No polymerization observed in plasma chamber Decomposes in aqueous scrubbers CO_2, CO are major etch byproducts (after acid trap/pump)	Additive gases useful to modify selectivity More reactive than PFCs
$CF_3CH_2CHF_2$	High selectivities relative to CF_4 Low toxicity (rat LC_{50} ~ 200,000 ppm)	Polymerization occurs under some conditions Small quantities of CF_4 plasma byproduct
$CF_3CH_2CF_3$	High selectivities may be possible Low toxicity (rat LC_{50} ~ 189,000 ppm)	Polymerization occurs under some conditions Small quantities of CF_4 plasma byproduct
IF_5	Least reactive interhalogen compd. (ClF_3, ClF_5,...) Low vapor pressure reduces hazards Decomposes in aqueous scrubber Safely manufactured for 30 years Commercially available in large volumes	Strong oxidizer, corrosive Liquid injection system may be necessary

References

Additional details have been presented at the following meetings:

PFC Leadership Group, Santa Clara, February 1998.

SEMATECH PFC PTAB Group, Austin, March 1998.

U.S. Environmental Protection Agency Global Semiconductor Industry Conference on Perfluorocompound Emissions Control, Monterey, April 1998.

For additional information contact Matthew Luly, Allied Signal, 716-827-6299.

A.3 CAPTURE AND RECYCLE

A.3.1 Edwards Perfluorocompound Recovery

Description

The Edwards technology segregates the PFC exhaust streams using a mechanism in the pumping system that communicates with the process tool to divert PFC-laden tool exhaust before the nitrogen pump purge. This results in an initial exhaust stream PFC concentration of greater than 30%. The diverting mechanism is synchronized with the gas change. The Edwards recovery unit has a dry bed reactor that removes acid gases. A cryogenic condenser collects the PFC gases, rejecting non-condensable gases. Thawing the condenser creates a substantially pure PFC product, with more than 90% concentration. Further off-site purification, done by BOC Edwards, would be necessary to achieve 99.995% C_2F_6 purity.

Project Status

An initial Edwards prototype unit was evaluated in their England research lab on simulated gas flows (The results were published at SEMICON/Southwest 1997). The equipment was then operated at the Texas Instruments Dallas fab on a full-scale production tool. The same prototype alpha unit collected PFCs from an Applied Materials P5000 TEOS tool. The production test verified the initial lab data. The Edwards approach is being evaluated for economic viability, high capture and purity, low risk, and high reliability. Texas Instruments and Edwards are currently evaluating the next steps.

Applicability

The Edwards capture and recovery unit can be applied to fabs with the newest Edwards IH80 dry pump and with space for a 1- to 2-inch segregated PFC exhaust line. The CVD cleaning steps maximize the PFCs captured and recovered in the TEOS process evaluated.

Pros and Cons

New fabs can implement this technology more easily than existing fabs. A liquid nitrogen source, a segregated PFC line, and space in the sub-fab or on the property are the three major items to facilitize this system. The new IH80 dry pump has to be qualified first for the fab processes. Moderate capital and operating cost are expected compared to other PFC recovery technologies. This system could provide a PFC product to be purified on-site or off-site.

Reference

Gilliland, T. and Seeley, A., “Edwards Perfluorocompound Recovery at Texas Instruments,” Presented to the SEMI meeting, October 1997.

A.3.2 Praxair's PFC Recovery System

Description

Texas Instruments and Praxair are currently testing this process (first half of 1998). Tests will continue through the second quarter of 1998 and will have a cost of ownership study completed by the third quarter of 1998. Praxair offers the first system based entirely on known patented technology. The unit contains Ecosys wet scrubbers for corrosives removal and an Ecosys dry scrubber for hydride removal. A molecular sieve dryer is also used for water removal.

Exhaust gases are continuously passed through a capture column in which a cryogenic wash liquid absorbs PFCs. The PFCs are stripped from the wash liquid, and then the concentrated PFCs are batch distilled using a cryogenic distillation tower. High purity PFCs are obtained from various distillation stages. Recovered C_2F_6 and SF_6 are expected to be extremely pure. Due to similar boiling points, CF_4 and NF_3 are more difficult to separate. The recovered products are predicted to achieve 99.999% C_2F_6 and SF_6.

Project Status

Texas Instruments (Dallas) is the first test location. The system is a full-scale prototype and will be available for permanent installation when testing proves successful. The system is currently commissioned and will be tested through June 1998. Process exhaust from 20 chambers in the Texas Instruments research fab has been routed to the unit installed outside. These chambers include PECVD tetraethyl ortho silicate, nitride deposition, and oxide etching.

Applicability

The Praxair system is believed to be more suitable for larger facilities with over 15,000 lbs of PFC purchased per year. Segregated piping will be a simpler installation for new facilities and likewise for the recovered product gas distribution center.

Pros and Cons

The disposition of the captured and purified stream will depend on the economics and product purity. The cost of ownership of this technology will become clearer after this evaluation. It is hoped that this process will produce a positive return on investment. Inside the sub-fab, the process exhaust requires segregated piping delivered to preferably a central location on the site. Part of the current test plan includes certifying the purity of recovered PFCs and then evaluating the material in chamber cleaning at a tool supplier. The acceptance of the recovered PFC product in lieu of virgin material by process engineers will be a major hurdle.

References

Giannini, R., "Praxair's System for Fab-wide Capture and Purification of Semiconductor Manufacturing PFC Emissions," Presented at the SEMICON/Japan conference, November 1997.

Gilliland, T., "Praxair and Edwards Perfluorocompound Recovery and Reuse Evaluations at Texas Instruments," Presented at the SEMI meeting, 1997.

Gilliland, T. and Hoover C., "Texas Instruments' Evaluation of Praxair's PFC Recovery System," Presented at the SEMATECH S-69 PTAB meeting, October 1997.

A.3.3 Air Liquide's PFC Capture Technology

Description

Air Liquide's process was designed to capture and concentrate PFCs from the exhaust of wafer etch tools and PECVD chamber cleaning operations. The unit first pretreats exhaust with a dry scrubber, water scrubber, and a filter. The exhaust is then sent through a compression stage, followed by a separation stage. The two-stage separation, using membrane technology, removes the bulk of the nitrogen from the stream.

Project Status

The first alpha unit was tested at Intel on a single PECVD tool. The first prototype unit was tested at Texas Instruments in Dallas. The prototype unit has since been shipped to Air Liquide's Japanese division for testing at a major semiconductor fab. Negotiations with several large semiconductor companies are underway to perform further testing in Japan and Europe. The tests at Texas Instruments spanned more than 2,000 hours, with 800 hours of actual tool operation. The prototype was able to treat the exhaust from four chambers of three Applied Materials Precision 5000 PECVD reactors.

Applicability

The prototype captured and concentrated C_2F_6, CF_4, and SF_6 at efficiencies > 95%. Capture efficiencies for CHF_3 and NF_3, however, were < 50%, although the amount captured was concentrated to > 95% (using bottled gas feed). These efficiencies were consistent over a wide range of flow rates and inlet PFC concentrations. Removal of reactive gases before contact with the membranes is required. Membrane life has not been determined, but no degradation was detected following the testing at Texas Instruments.

Pros and Cons

The units can handle only four reactor chambers. The units are fairly large (10 feet wide, four feet deep, and six feet tall). Once collected and concentrated, the PFCs must be piped to a cylinder filling unit. Units are adaptable for indoor or outdoor installation. Membranes require that all particulate and corrosive gases be removed by pretreatment to ensure long life.

The recovered PFC mixture must be cryogenically separated and purified and tested extensively to confirm process compatibility. In a recent article, Air Liquide indicated that off-site purification was the best economical choice, despite the shipping costs involved.

References

Cummins, Gilliland, Kesari, Richards, and Trilli, *Evaluation of Air Liquide's Perfluorocarbon (PFC) Capture Technology*, SEMATECH Technology Transfer #97013229A-TR, Austin, TX, February 28, 1997.

Cummins, Dupuis, Fleming, Kesari, Miner, and Trilli, "The Future of Perfluorocarbon Capture and Recycling: Membrane Technology," *Semiconductor International* (July 1997), pp. 265-272.

A.3.4 Air Products Large Scale PFC Capture System

Description

In this process, both PECVD chamber clean and etch process exhaust are first routed through a scrubber, HEPA filter, coalescing filters (to remove water), ozone destructor, and compressor. They are then passed through a semi-permeable polymer membrane that separates the PFCs from other gases and vapors. A booster compressor would be used to fill containers with the concentrated mixed PFCs for off-site purification.

Project Status

A full-scale version of the system has been installed at a commercial fab in California. This prototype system is designed to process exhaust gas from over 20 tools. The system is undergoing qualification testing.

Applicability

Preliminary tests achieved 95% C_2F_6 recovery at a concentration of 95% C_2F_6 in the captured product.

Pros and Cons

The system is designed to handle emissions from a large number of tools. Collection piping to the system and fab floor space will be of concern to existing fabs. The collected and concentrated PFCs will have to be shipped back to Air Products and Chemicals or others for reuse and/or recycle. Economic issues may lead to the destruction of some or all PFCs instead of recycle as a last resort.

References

Carson, Christian, Crossland, Hsiung, Ridgeway, and Yang, “Large Scale PFC Capture System,” Presented to the SEMI meeting, October 1997.

Air Products and Chemicals, “PFC Recovery and Recycle Systems,” Promotional brochure.

A.3.5 MEGASORB Pressure Swing Adsorption Unit

Description

This process was designed to extract and concentrate PFCs from tool exhaust. The alpha pilot system consisted of five pieces of equipment: a Delatech unit that combined thermal decomposition/oxidation and wet scrubbing, a caustic wet scrubber, a compressor, a molecular sieve dryer, and a pressure swing adsorption (PSA) unit. The PSA unit was tested on the exhaust from four tool chambers. The system consisted of four beds of polymeric adsorbent; two beds were pressurized to absorb the PFCs, while two were regenerated by releasing the pressure and flushing with nitrogen. Because the beds are sequentially pressurized and depressurized, this mode of operation is referred to as pressure swing adsorption.

Project Status

The system was tested at Texas Instruments' Dallas facility. The pilot unit operated on test gases for a design of experiment period and on process exhaust for several hundred hours. The process is no longer under development since other forms of PFC recovery technology appear to be more effective than PSA.

Pros and Cons

The system was successful at capturing over 99% of all the PFCs emitted from the process tools during wafer production; however, desorption of the PFCs from the beds required large volumes of nitrogen, resulting in low concentrations of the PFCs in the recovered gas stream. The second stage of the process, as originally envisioned, would have involved further concentration and the circulation of a large amount of PFCs across a condensing/flash unit. Power costs were estimated to be high as well as requirements for liquid nitrogen for cooling. Advances in membrane technology caused this technology to be abandoned.

References

Gilliland, Richards, Culp, Christian, Ridgeway, Hall, and Behrens, *Evaluation of a MEGASORB Pressure Swing Adsorption Unit Designed to Capture PFCs*, SEMATECH Technology Transfer #96123221A-ENG, Austin, TX, December 31, 1996.

A.3.6 BOC/IMEC/TI Study of PFC Capture Using Pressure Swing Adsorption

Description

A BOC/Texas Instruments study at IMEC in Belgium evaluated pressure swing adsorption as a technique to capture and concentrate PFCs from tool exhaust.

Project Status

The technology was effective in recovering PFCs from tool exhaust. However, the concentration of the PFCs in the product was typically very dilute (approximately 1%). The system was not effective in capturing and concentrating the PFCs simultaneously. Consequently, the project was terminated; no further development of this technology is planned.

Applicability

This technology would have be an end-of-pipe system, collecting the exhaust from a number of tools and then processing the combined stream. Other forms of PFC recovery appear to be more effective than pressure swing adsorption.

Pros and Cons

This technology requires similar pretreatment of the tool exhausts as the membrane technology. Implementation and facilitization would be similar. Capital and operating costs have not been quantified.

Reference

J.A.B. Van Hoeymissen, M. Daniels, N. Anderson, W. Fyen and M. Heyns, “Gas Stream Analysis and PFC Recovery in a Semiconductor Process,” *ESH Issues in IC Production, Materials Research Society, Symposium Proceedings*, Dec. 4–5, 1996.

A.4 ABATEMENT/DESTRUCTION

A.4.1 CS-CLEANSORB Dry-Bed Treatment System

Description

The CLEANSORB system consists of a granulated dry bed adsorption system that operates at elevated temperatures (500–600°C). The tool exhaust gases to be treated form stable salts with the reactor granules. CS Systems, the manufacturer of the device, retrieves the spent CLEANSORB column for refilling with fresh material. The CLEANSORB system is commercially available for NF_3 abatement.

Project Status

The high temperature (500–600°C) NF_3 abatement system is commercially available. Materials are being developed for treating CF_4 or C_2F_6.

Applicability

Since the capacity of the bed for reacting PFCs is limited, this system is best suited for low flow, point-of-use applications

Pros and Cons

The spent solids are not regenerated. Disposal of the spent solids as well as space issues are of concern. The footprint of a dual canister system is about 2 feet by 3 feet. Capital cost and the cost of the refill canisters are a concern. The Cleansorb system with heat recovery uses little electricity (200 W) during normal operation.

A.4.2 Kanden F-Torr-T Dry Bed Conversion

Description

The marketing literature states that the process treats PFCs by chemically converting them into calcium fluoride. Exhaust gases are delivered to the top of the decomposition reactor, where they encounter the reagent at an elevated temperature and are converted to SiF_4, CO_2, etc. The decomposed gases are cooled and exhausted from the equipment. A separate wet treatment converts the gases into CaF_2.

Project Status

Unknown.

Applicability

The literature reports destruction efficiencies of all PFCs to be above 98% at temperatures of 1200°C. These efficiency levels are for non-diluted gases; efficiencies for low concentration gas data are not reported in the literature.

Pros and Cons

Unknown issues include the disposition of the solid waste, HF emission levels, water requirements, cost of ownership, performance efficiency in an operating environment, and capability to destroy silane and ammonia or other reactive gases.

References

Kanto-Denka Kogyo Corp, Marketing literature for the Kanden F-Torr-T waste gas treatment system, 1994.

A.4.3 Guild/Novellus Catalytic Oxidation Technology

Description

This technology employs a proprietary catalyst to oxidize PFCs in the presence of air and moisture to abate PFCs. The unit is installed downstream of a vacuum pump and requires pre-scrubbing to remove compounds that could deposit solids in the catalyst bed. Operation occurs at atmospheric pressure in 300–500°C. The scrubbed pump exhaust is mixed with humidified air in a static mixer before passing through the catalyst bed. Before being exhausted from the unit, the gas stream passes through a heat exchanger for heat recovery. The device converts the fluorine to HF.

Project Status

Proof-of-concept and alpha scale tests have been performed. The goals of this program were to demonstrate >95% destruction for CF_4, C_2F_6, C_3F_8, and NF_3. These goals were met in the benchscale reactor as well as a full-scale device. Testing in a manufacturing environment has not been done.

Applicability

Both CVD cleaning and etch process exhausts may be treated by this method as long as pre-scrubbing is adequate. All wafer sizes are candidates as well as both old and new fabs.

Pros and Cons

This system operates at atmospheric pressure downstream of the pump; it has no effect on the process. The system requires a 30” x 32” footprint, electrical service (9 kW in continuous operation), 40 cfm of room air, and a downstream scrubber. As is the case with all end-of-pipe abatement equipment, the ability to install it in a sub-fab will be depend on space. HF byproducts must be sent to a scrubbed exhaust. The system still requires considerable testing beyond the benchscale evaluations performed to date. Lifetime of the catalyst is unknown. Care must be to taken to prevent poisoning of the catalyst by ensuring that the pre-scrubber is operating properly.

References

Roy Brown, Joseph Rossin (Guild Associates), Kenneth Aitchison (Novellus Systems),“Catalytic Oxidation for the Control of Perfluorocarbon Emissions During Semiconductor Manufacturing Operations,” presented at A Partnership for PFC Emissions Reductions, SEMICON Southwest, October 13, 1997.

A.4.4 Delatech Controlled Decomposition/Oxidation (CDO) Unit

Description

The Delatech unit employs thermal decomposition/oxidation followed by wet scrubbing. Exhaust gases from one or more processes are introduced to the top of the unit through separate inlet lines. It uses hydrogen as fuel, which is injected into the tool exhaust at entry to the combustion zone. The exhaust stream is then mixed with oxygen or air at the beginning of the thermal reaction zone. The combustion section consists of a cylindrical INCONEL liner surrounded by a heating element. The liner serves as the ignition source. Following thermal reaction, the exhaust stream passes to the primary cooling/scrubbing section of an integral scrubber where it is cooled and particulate and water soluble gases are removed. The effluent stream then passes through the secondary packed bed scrubbing system to remove residual particulates and water soluble gases (HF).

Project Status

The process is available commercially for C_2F_6 abatement.

Applicability

It is applicable to all PECVD chamber cleaning applications using C_2F_6.

Pros and Cons

This system is commercially available (C_2F_6 only). The integral scrubber may be overloaded with HF and solids in some applications. The system uses fab floor space and consumes hydrogen as fuel. It requires significant amounts of fresh water (6–8 gpm) and creates significant quantities of HF containing wastewater. The point-of-use device can handle up to four reactor chambers.

References

Beu, Ridgeway, Filipak, Boeck, Ford, Pearce, Moore, and Storch, *Results of Delatech Controlled Decomposition/Oxidation (CDO) Unit Testing for Perfluorocompounds (PFC) Emission Abatement Applications – Interim Report*, SEMATECH Technology Transfer #94092543A-ENG, Austin, TX, October 31, 1994.

Beu and Ford, *Delatech Controlled Decomposition/Oxidation (CD)) Unit – Cost of Ownership (COO) Report*, SEMATECH Technology Transfer #95012674A-ENG, Austin, TX, January 31, 1995.

A.4.5 Ecosys Phoenix IV

Description

The Phoenix IV is a methane-fueled active flame oxidizer designed to abate C_2F_6. The unit consists of an inlet head, combustion chamber, and stirring/mixing jets for mixing the methane fuel and the process exhaust gases. Exhaust cooling is accomplished by drawing in cleanroom air to dilute the heated air.

Project Status

The unit is commercially available (C_2F_6 only).

Applicability

It is applicable to all CVD cleaning emissions containing C_2F_6.

Pros and Cons

The device has good destruction efficiency for C_2F_6, but not CF_4. The unit has high water usage and questionable solids handling capability.

References

Walling, Tran, and Ridgeway, *Evaluation of an Edwards TPU4214 and an EcoSys Phoenix IV for CF4 Abatement*, SEMATECH Technology Transfer #97073319A-TR, Austin, TX, September 30, 1997.

Anderson, L., “Vector Technology’s Phoenix Combustor,” Presented to the Global Warming Symposium, Dallas, Texas, June 1994.

A.4.6 Edwards Thermal Processing Unit (TPU)

Description

Edwards TPU uses combustion to convert PFCs to water-scrubbable byproducts. The TPU operates in a high-fire mode, using increased fuel flow and higher temperatures to achieve PFC combustion. When no PFCs are flowing, the unit goes into low-fire mode to conserve fuel. There are now several models of TPUs, depending on the process tool, the process recipe, and the application selected.

Project Status

Dating back to 1995, three SEMATECH-related projects have characterized the TPU for PFC abatement in differing applications. Each of the projects required significant engineering development resources before project objectives were achieved.

1. The TPU 4200 was beta tested for C_2F_6 abatement on an Applied Materials P5000 PECVD at Texas Instrument's Semiconductor Process Development Laboratory in Dallas, Texas. In high-fire mode, the TPU demonstrated > 90% efficiency at abating C_2F_6, 99% efficiency at abating NF_3, and 77–85% efficiency at removing SF_6. Abatement of CF_4 was very low.
2. The TPU 4200 was also beta tested for C_2F_6 abatement in a Novellus Concept One tungsten CVD application at Hewlett-Packard in Corvallis, Oregon, demonstrating > 90% efficiency at abating C_2F_6 in high-fire mode after significant process-specific modifications to handle the tungsten process byproducts.
3. The TPU 4214, a modified version of the TPU 4200, was beta tested for CF_4 abatement at Motorola's MOS-10 Irvine facility on an Applied Materials P5000 PECVD, demonstrating > 90% CF_4 removal efficiency in high-fire mode after significant optimization.

Edwards TPUs are commercially available products that are now used in select applications in several semiconductor manufacturing fabrication operations. The POU units are normally designed to handle three to four chambers for a total flow of 200 slpm.

Applicability

Edwards TPUs may theoretically be used in select applications for older and newer fabs and tools for all wafer diameters. However, the capital costs and utility requirements, such as natural gas availability and fresh water capacity, are significant. In addition, further development may be required for TPU use in untested applications. Finally, the facility must be able to tolerate or treat the added wastewater containing fluoride generated from PFC combustion.

The TPU may be most easily justified in some fabs for those CVD processes that use flammables or pyrophorics that require point-of-use treatment for safety reasons or for those processes that generate large quantities of solids that tend to plug exhaust lines.

Pros and Cons

The Edwards TPU is one of the few commercially available abatement systems that has demonstrated and documented effective PFC abatement in several semiconductor processing applications. It may be retrofitted to some older tools, fabs, and processes.

It should not require significant unit process recipe changes or process tool modifications if TPU flowrate limitations are met.

The system may require significant engineering development resources to qualify the TPU on untested applications. Each of the SEMATECH projects demonstrated that the performance and maintainability of the TPU differ depending on the process tools and recipes. It also requires significant utilities, most notably natural gas (> 78 cubic feet per hour per TPU) and water (>8,600 gallons per day per TPU). Water recirculation is an option to reduce wastewater volume, but will add complexity and require additional cost, resources, and space to design and implement. It converts the PFC waste into other byproducts that may be regulated and require additional treatment. When PFCs are combusted, they generate fluoride in the wastewater at significant levels (> 1000 ppm during chamber cleans for some current applications). Natural gas combustion byproducts include CO_2 and CO emissions with a GWP impact that will limit the GWP reduction benefit for small PFC-emitting applications. Only the CF_4 abatement TPU testing showed significant NOx emissions in high-fire mode (~6 lb/yr).

Combustion and water scrubbing are continuously running in low-fire mode even when not processing wafers. The system also has relatively high capital and operating costs, which vary depending on the cost and availability of space, natural gas, water, and wastewater treatment capacity.

References

Walling, Tran, and Ridgeway, *Evaluation of an Edwards TPU4214 and an EcoSys Phoenix IV for CF_4 Abatement*, SEMATECH Technology Transfer #97073319A-TR, Austin, TX, September 30, 1997.

Gilliland, Cummins, Ridgeway, *S69 Evaluation of an Edwards/Alzeta Thermal Processing Unit Designed to Abate PFCs*, SEMATECH Technology Transfer #95113010B-ENG, Austin, TX, December 22, 1995.

Van Gompel, J. and Walling, T., “A New Way to Treat Process Exhaust to Remove CF_4,” *Semiconductor International,* September 1997, pp.95–100.

Mawle, P., “PFC Gases Emission Reduction: CF_4 – The Difficult One to Treat,” Presented to the International Environment, Safety, and Health Conference, Milan, Italy, June 1997.

A.4.7 Guardian Burn Box

Description

The Guardian system is a thermal destruction device. Process exhaust is combined with intake air in the combustion chamber flame zone. The exhaust is then sent to a point-of-use scrubber.

Project Status

The system is commercially available (C_2F_6 only).

Applicability

The system can be used on all C_2F_6 CVD tools.

Pros and Cons

Although commercially available for C_2F_6 abatement, it provides minimum CF_4 treatment. The system requires large volumes of cleanroom air and a separate scrubber system. The steps needed to implement the system are the dedication of floor space, cleanroom air, natural gas, and a large water scrubber. Byproducts of the combustion process can impact scrubber performance. Safety and environmental concerns must also be addressed with this system.

References

Hayes, M., “Abatement of PFC Emissions Utilizing a Direct Flame Waste Gas Processor,” Presented to the Global Warming Symposium, Dallas, Texas, June 1994.

A.4.8 Japanese PFC Abatement Technologies

Description

This overview, presented by Hitachi at the 1997 ESH Conference in Milan, gave an overview of available Japanese abatement/destruction technologies. The table below summarizes the information presented.

Vendor	Equipment	Abatement Method
Koike Sanso Kogyo	Guardian	Combustion
Taiyo Toyo Sanso	Toxoclean	Combustion
Japan Pionics	Phoenix Thermal Oxidizer	Combustion
Nippon Edwards	TPU	Thermal Destruction
SEIKA HI-TECH/Kanken-Techno Co.	KT-100	Thermal Destruction
Kanto Denka	Kanden	Thermal Chemical Destruction
Nippon Sanso	Vega-G	Thermal Chemical Destruction
Showa Denko	Clean Ace	Thermal Chemical Destruction
Tomoe Shoukai	Thermal Swing Method	Thermal Chemical Destruction
Mitsui Touatsu Kagaku	Plasma	Plasma

Reference

Yabuhara, Y., "Recent Advances in PFC Emission Reduction Technologies," Presented to the International Environment, Safety and Health Conference, Milan, Italy, June 1997.

A.4.9 MIT Microwave Plasma Tubular Reactor

Description

MIT's microwave tubular reactor operates at low pressure and would treat the tool exhaust upstream of the vacuum pump. In the benchscale experiments, the PFCs flowed through a 1-inch tube housed in a microwave power applicator. Air was used to cool the tube, which reached 200°C during the experiments. The exhaust from the tool was sent to a water scrubber.

Project Status

Current status of the technology is unknown because of confidentiality issues. However, laboratory testing has been done, and the following results were recorded:

- PFCs can be abated using a plasma process that achieves a high neutral gas temperature (> 1200K). As the gas temperature increases, COF_2 and F radical production is strongly favored over CF_4 production.
- Since these high temperatures are not compatible with conventional plasma processing conditions, CF_4 will be formed.
- CF_4 is the most thermodynamically favored product in most carbon-fluorine discharges at low neutral temperatures.

Applicability

This type of device is mounted in the foreline of the vacuum pump; it is probably best suited for treating emissions from etch tools. Potentially, existing tools could be retrofitted with such a device.

Pros and Cons

Conceptually this is a good form of abatement, but it is unproven in a manufacturing setting at this time.

References

Mohindra, Chae, and Sawin, "Study of PFC and CFC Emissions and Abatement for Plasma Processes," Prepared 1997.

Mohindra, Chae, and Sawin, "Abatement of Perfluorocompounds in a Microwave Tubular Reactor Using O_2 as an Additive Gas," Presented to the MIT Technology Transfer Class, December 1995.

Mohindra, Chae, and Sawin, "Destruction of PFC/CFCs in a Microwave Tubular Reactor," Prepared March 1995.

A.4.10 Microwave Impinger Plasma Destruct

Description

Motorola developed and patented a microwave plasma destruction unit. The unit exposes incoming waste gas to microwave energy and directs it to a hot impinger plate for inelastic collisions in the region of the plasma at the surface of the impinger.

Project Status

Testing of a proof-of-concept unit was performed at Motorola fabs in Phoenix and Austin. Project goals were not achieved.

Applicability

Not applicable.

Pros and Cons

The project did not proceed past proof-of-concept testing.

References

Proposal for SEMATECH: Motorola Microwave Impinger Plasma Unit Evaluation, Statement of Work, Motorola, July 7, 1994.

Global Warming Symposium, Irving, Texas, June 18, 1994.

A.4.11 Evaluation of ETC's DryScrub

Description

The Electrochemical Technology Corporation's (ETC's) Dry Scrub is a commercially available device, consisting of a vacuum chamber containing a spiral electrode, powered by a radio frequency power supply. The Dry Scrub was designed to extend vacuum pump life by extracting reactive components from CVD tool exhausts. When used as a PFC abatement device, the plasma is off during deposition to prevent build-up of solids and on during chamber cleaning when PFC gases are flowing.

Project Status

Proof-of-concept testing was completed at Motorola where the unit was installed on an Applied Materials P5000 PECVD chamber using TEOS based chemistry. Project goals were not achieved. The Dry Scrub, as it is currently designed, demonstrated only 24–85% destruction efficiency for C_2F_6 and 21–87% destruction efficiency for NF_3. C_2F_6 abatement resulted in the creation of 0.38 to 1.24 molecules of CF_4 for every molecule of C_2F_6 abated.

Applicability

Not applicable.

Pros and Cons

Adequate destruction efficiencies were not achieved with the Dry Scrub system. When abating C_2F_6, significant amounts of CF_4 were produced.

References

Beu, Bocek, Smith, Soggs, Ford, Hartig, Moore, Ridgeway, Chiu. *Evaluation of ETC's DryScrub for Abating Perfluorocompound Emissions.* Technology Transfer #96013062A-TR. Austin, TX:SEMATECH. January 31, 1996.

A.4.12 NSF/SRC Inductively Coupled Plasma Abatement of PFCs and HFCs

Description

An inductively-coupled high density plasma point-of-use abatement system was used to abate C_2F_6, CF_4, and CHF_3 into gases that can be easily scrubbed using existing technology. This system operation occurs before the nitrogen dilution step in the dry pumps enabling reaction of a highly concentrated stream.

Project Status

Proof-of-concept testing has been performed at University of California at Berkeley.

Applicability

It can be used in old fabs depending on space requirements, for all wafer sizes. Etch tools are also candidates.

Pros and Cons

The technology is in early development; integration issues and capital costs are unknown. It has not been tested using the exhaust from an etch reactor. Abatement efficiency is unknown.

References

Graves, “Point-of-Use Plasma Abatement of HFC and PFC Emissions,” Presented to NSF/SRC Engineering Research Center of Environmentally Benign Semiconductor Manufacturing, Second Year Annual Review, February 1998.

A.4.13 RF Environmental Systems, Inc./Texas A&M University/Motorola Surface Wave PFC Abatement Device

Description

Tool exhaust before dilution by the pump nitrogen purge enters a dielectric discharge tube, where a wave launcher produces a surface wave plasma. The PFCs, including CF_4, are destroyed in the plasma reactor and only simple, low molecular weight byproducts are created that are either harmless or easily scrubbed and neutralized.

Project Status

The unit has been evaluated at Texas A&M using actual silicon dioxide etch process chemistries; the device has demonstrated high (>95%) destruction and removal efficiency. The same unit evaluated at Texas A&M will be tested for proof-of-concept at Motorola's research and development laboratory in Austin, Texas, on a commercial silicon dioxide etch tool.

Applicability

It can be used on all commercial tools used in the etching of silicon dioxide for wafer patterning (150, 200, and 300 mm).

Pros and Cons

Surface wave plasma technology allows large plasma volumes and short residence times for higher PFC destruction efficiency with low power usage. In addition, surface wave plasma permits broadband impedance matching, a wide domain of operating frequencies, and great plasma stability and reproducibility over a wide range of operating conditions. The plasma generator also does not require frequent tuning based on variations in input gas composition. The addition of hydrogen and oxygen to a mixing chamber before the microwave reactor chamber prevents PFC fragment recombination into other possibly longer-lived PFCs such as CF_4. Testing at Texas A&M has indicated virtually no microwave leakage; only low levels of toxic gases are created, which can be easily scrubbed. Qualification would entail analytical techniques such as FTIR and MS to demonstrate destruction removal efficiency.

As now configured, the device has footprint (0.6 m^2) and utility requirements that make implementation difficult and facilitization expensive in a research fab. The overall height of the device (> 3 meters) makes it virtually impossible to implement in any manufacturing fab due to severe space limitations. The large number of air cooling hoses required for heat dissipation from the plasma reactor require manifold construction both for air delivery and for exhaust collection before being transferred to heated process exhaust.

References

Wofford, Hartz, and Bevan, "Surface Wave Plasma Abatement of Perfluorocompounds," Presented to the SEMATECH ESHCOO5 PTAB meeting, March 1998.

Wofford, Hartz, and Bevan, "Surface Wave Plasma Abatement of Perfluorocompounds," Presented to the SEMATECH ESHCOO2 PTAB meeting, October 1997.

Bevan, "Surface Wave Plasma PFC Abatement," Presented to the SEMATECH ESHCOO2 PTAB meeting, May 1996.

A.4.14 Silent Discharge Plasma (SDP) for Abatement of PFCs

Description

Silent discharge plasma (SDP) treatment is an advanced oxidation process that relies on free radical chemistry at ambient temperatures and pressure to oxidize gas phase contaminants. Within the SDP, myriad micro-arcs similar to tiny lightening bolts, each lasting only a few nanoseconds, produce energetic electrons. While the bulk of the gas remains at ambient temperatures, the high temperature electrons efficiently dissociate oxygen and water to produce large concentrations of free radicals. The desired chemistry is very similar to thermal oxidation, except that the radicals are produced by electron dissociation of water and oxygen, not by thermal dissociation.

Project Status

The technology was actually developed and evaluated for the destruction of dilute air emissions containing volatile organic compounds (VOCs). In conjunction with the benchscale tests of this technology at Los Alamos National Laboratories, some experiments were conducted on bottled C_2F_6 and CF_4 to determine its applicability to the abatement of PFCs. These tests showed that the destruction efficiency for C_2F_6 and CF_4 was 95% and 45%, respectively. These results were not favorable enough to continue the development of this technology for PFC destruction.

Applicability

The technology was intended as a point-of-use abatement device downstream of the vacuum pump. There were indications that it would have a large footprint, limiting its use in existing, older fabs, which tend to have very congested sub-fabs. In new fabs, floor space and cost of ownership may also limit the applicability of this technology.

Pros and Cons

Inherently, plasma-based destruction devices appear to have a lower cost of ownership and lend themselves to point-of-use control of emissions. However, some of the advantages of such devices disappear because this technology operates at atmospheric pressure and would treat the tool emissions after dilution by the nitrogen introduced by the vacuum pump. Another drawback is that the plasma is not energetic enough to destroy CF_4.

Reference

Silent Discharge Plasma (SDP) for Point-of-Use Abatement of Volatile Organic Compound (VOC) Emissions: Final Report (ESHC003), SEMATECH Technology Transfer #97023244A-ENG.

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