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The chemistry of volatile waste from silicon wafer processing

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The semiconductor industry uses extremely pure gases and vapours to produce solid-state devices based on silicon wafers of great chemical and physical sophistication under very clean conditions. However, the waste volatiles from the processes pose a serious environmental threat. This article attempts to show how an increasing armoury of chemical methods is being applied to abate any pollution and to highlight areas where ideal solutions to problems have yet to be found.

1 Introduction

The production of semiconductors for use as computer chips has grown phenomenally in the last twenty five years and the semiconductor industry is now very large and of major economic importance. The industry is rightly regarded as "high tech" with its use of ultra-pure materials handled and processed under very clean conditions using sophisticated equipment. It is still dominated by semiconductors based on silicon and a new "Fab", a unit for the large scale production of silicon chips through processing of 200 mm diameter silicon wafers, will cost upwards of $1 bn. Even higher costs are predicted when the industry moves on from its current recession to make chips on 300 mm diameter wafers.

Chemistry plays a part in the industry in a variety of ways: in the production of ultra-pure, single crystal, silicon ingots which are cut into wafers; in the choice and design of chemicals which can dope, etch or coat wafers to help achieve an intricate architecture with millions of individually accessible sub-micron domains from which the final chips are cut; in developing methods to make ultra-pure forms of the chemicals used to process silicon under vacuum or in liquid media at atmospheric pressure. Many of these chemical aspects of the semiconductor industry have been reviewed.[1,2]

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Peter Timms graduated from Oxford and spent two years in industry gaining experience with high temperature chemistry. This shaped much of his subsequent work in synthetic main group and transition element chemistry at Oxford, Rice, Berkeley and at Bristol where he is a Reader in Inorganic Chemistry, and led him to become involved with pollution control in the semiconductor industry through a successful use of hot solids to destroy waste gases. He is a consultant to BOC Edwards.

Table 1 Some of the gases and vapours used in semiconductor processing (number in parentheses show approximate amounts in metric tons per annum used by the semiconductor industry)

Hydrides	Fluorides	Other inorganics	Organo-derivatives
SiH_4 (300)	CF_4 (800), C_2F_6 (400)	SiH_2Cl_2	$Si(OEt)_4$ (150)
Si_2H_6 (2)	C_3F_8	BCl_3 (200)	$B(OMe)_3$
GeH_4	CHF_3 (160)	HCl (1000)	$P(OMe)_3$
B_2H_6 (2)	$(CF_3CO)_2O$	HBr (40)	$(Me_2AlH)_2$
NH_3	NF_3 (190)	Cl_2 (100)	$Bu^t{}_3Al$
PH_3 (13)	SF_6 (50)	O_2, NO, N_2O (300)	Me_3Ga
AsH_3 (7)	ClF_3 (50)		[Cu(Hfac)-(TMVS)][a]
	WF_6 (40)	H_2, H_2O_2	

[a] Hfac = Hexafluoroacetonate, TMVS = trimethylvinylsilane.

Table 2 Some volatile products formed during semiconductor processing

SiF_4 $SiCl_4$ $(SiOCl_2)_n$ $(SiH_2NH)_n$
HF COF_2 C_2F_4 C_4F_8 $AlCl_3$ WOF_4
NH_4Cl NH_4F $(NH_4)_2SiF_6$

Less obvious is the fact that the ultra-clean semiconductor industry has a significant waste disposal problem arising from its use of a wide range of gases and vapours in low pressure processing of wafers. It is the chemical challenge of how to deal with this gaseous waste which is the topic of this perspective.

2 The range of process gases and their reaction products

Table 1 shows a list of gases and vapours used in processing of semiconductors. This is a list which changes with time under the pressure of new process developments on the one hand and environmental considerations on the other. For example, the demands of semiconductor device miniaturisation are dictating a change from aluminium to copper as the main metal for electrical and heat conduction and this is spurring the use of volatile metal–organic precursors of copper. A few years ago, tetrachloromethane and other carbon–chlorine compounds would have been in the list for plasma etching of aluminium. These are no longer used both on account of the Montreal agreement on the release of ozone depleting substances and because of a perceived risk of dioxin production from a malfunction of equipment employing thermal methods to destroy these gases.

Table 2 shows some additional gases and vapours which arise from the use of the compounds of Table 1 in semiconductor device processing using plasma etching or chemical vapour deposition. For example, plasma etching of silicon using perfluoroalkanes mixed with oxygen at low pressure generates SiF_4, COF_2 and traces of perfluoroalkenes which are far more dangerous than the starting materials.

Each vacuum chamber where processing of wafers occurs will be using some of the gases or vapours in Table 1 in short bursts, interspersed with permanent gas purging and cleaning operations. The percentage of each process gas which is used effectively varies widely with the nature of the process and the design of equipment but currently figures of 25 to 50% consumed are typical.

Approximate values for the amounts in metric tons of some of the compounds which are used annually in the industry are included in parentheses in Table 1. It follows from above that the waste gases will contain 25–50% of these amounts so that, overall, there will be many tons of waste to deal with. To put these quantities into context, the waste CF_4 from the semiconductor industry is <10% of the amount produced as a by-product of extracting aluminium by electrolysis in fluoride containing melts with carbon anodes. On the other hand, the semiconductor industry is probably the major producer of waste containing Group 14 and 15 hydrides, or fluorides such as NF_3, ClF_3 and WF_6, or some metal–organic compounds. In the last category, as has been mentioned there is a great potential for growth of copper precursors which could generate tons per annum of waste in a few years times.

3 Methods of dealing with gaseous waste

3.1 Destruction or recycling?

It might seem that the hazardous gaseous waste from semiconductor processing could be dealt with in either of two ways. It could all be destroyed and converted into products which are much less hazardous or it could be collected, fractionated and the useful components recycled. The latter would seem to be the obvious environmentally friendly approach. Unfortunately, recycling is not an easy option for the reasons given below and destruction is currently the dominant technology.

The semiconductor industry is based around the use of very pure substances mainly because the intrinsic properties of silicon are affected beneficially or adversely by such low concentrations of additives. So all gases used in processing are extremely pure, at least 99.995% and upwards to 99.99999%. This purity is achieved by gas manufacturers by very careful selection of source materials to avoid compromising impurity elements as far as possible since these elements are often very hard to remove completely from the process gas. Gases recovered after use in semiconductor processing are likely to contain a broader spectrum of impurities than is compatible with their easy and economic reconversion to very high purity starting materials. So it is often more expensive to recycle gases than to use new gases and destroy what is unused in wafer processing. Of course, future legislation may force the industry into recycling but at present only a few opportunities for economic recycling can be seen. Examples include some of the perfluoroalkanes, compounds so stable that they could be put through vigorous purification procedures to remove possible impurities (see section 4) and some metal–organic compounds which are so expensive to synthesize that recovery and recycling may be economically attractive.

3.2 Where destruction takes place

Fig. 1 shows a schematic of a vacuum chamber for semiconductor processing and its associated pumping equipment. The waste gases can be intercepted for destruction/recycling at any point between the main exit valve on the vacuum process chamber and the exhaust ducts of the Fab.

At the present time the great majority of waste destruction is done at essentially atmospheric pressure, *i.e.* after the pumps and before the waste gases enter the ducts. This region is chosen because it is simple to work at atmospheric pressure and because any chemistry carried out on waste there is well removed from the process chamber which is so sensitive to contamination. Fig. 1 indicates a local waste destruction system, specific to one process chamber. Local destruction is usually preferred over using a centralised destruction system which would abate the waste output from the many different process chambers in a Fab. There are several reasons for this. First, local systems reduce the risk of accidentally mixing chemically incompatible waste streams. Secondly, the local system can be designed to cope with a particular group of waste components. Thirdly, it is usually easier to destroy waste products before they have become too diluted by other gas streams. Finally, if a local waste abatement system fails, it has less effect on the running of the Fab than if there is a problem with a centralised system.

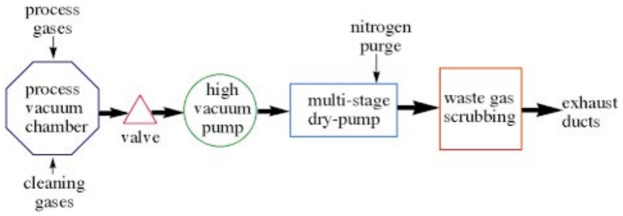


Fig. 1 Schematic showing where waste volatiles from semiconductor processing are commonly treated to remove environmentally harmful products.

When waste gases are destroyed at atmospheric pressure it means that all the waste has had to pass through the vacuum pumps, commonly a combination of a turbomolecular or Roots pump to raise the pressure to *ca.* 10^{-2} mbar, backed by a foreline pump to take gases from *ca.* 10^{-2} mbar to atmospheric pressure. The industry began using conventional oil filled rotary pumps to back the higher vacuum pumps but this was largely abandoned for two reasons. Using hydrocarbon pump oils there were often chemical reactions between the oil and the waste gases and vapours. This resulted in corrosion, pump seizure and even the risk of fire. When hydrocarbon pump oils were replaced by chemically inert perfluorinated oils (*e.g.* Fomblin) there was still a risk of retention of compounds in the oil which could react in dangerous ways with other compounds subsequently pumped through the oil. There was a rapid move towards multi-stage “dry-pumps” employing a series of close-tolerance mechanical rotors with no lubricant. The final stages of these pumps are normally purged with nitrogen to reduce the likelihood of reactions between waste products depositing solid residues (which could jam the pump) as the pressure in the gas is increased, but this has the disadvantage of giving a waste stream highly diluted by nitrogen.

3.3 Required levels of destruction

While the semiconductor industry would like to have a “zero emissions” policy this is very hard to achieve in practice. A more realistic aim is to require that the effluent gas stream from each device used to destroy waste contains no species at a concentration above its “threshold limiting value” (t.l.v.). The range of t.l.v. values for the compounds of Tables 1 and 2 is large. Some values are <1 ppm, particularly among the hydrides; values in the range 3–10 ppm are typical among the acid gases but values >1000 ppm are found for a few compounds like sulfur hexafluoride and the perfluoroalkanes. Scrubbing gases so that their t.l.v. values are not exceeded is an attainable target with many commercial destruction devices working completely to specification. However, various factors, including operating errors, can contribute to situations when gases at much above their t.l.v. are released from the scrubbing device. Mostly these gases enter the exhaust ducts of the whole Fab where they experience such considerable dilution that the emission from the Fab may be below the t.l.v. of each compound. Analysis of the gaseous effluent composition is easily achieved using mass spectrometry but less costly devices are needed for continuous monitoring of the output from individual scrubbing devices. Techniques include infrared detectors, paper-tape detectors using colorimetry to detect reactions between reagents on the tape and effluent gases, and electrochemical detectors. Spot sampling of the concentrations of individual gases using Draeger (or equivalent) tubes is also used as an additional check.[3]

3.4 Types of methods of destruction[4]

Any inorganic chemist looking at the compounds listed in Tables 1 and 2 might reasonably ask, "What is the problem?" For, apart from some of the perfluorinated compounds, disposal of the compounds does not seem to be too difficult. The first challenge is that the destruction system must be able to cope successively with a range of waste from the different process stages such as chemical vapour deposition, etching and cleaning. The second challenge is the jump from laboratory conditions, where experiments tend to be short term and under the control of chemists, to the situation in a Fab which works virtually continuously under the control of process engineers. So any destruction system has to be capable of running with the minimum of attention.

Three main types of methods for destroying waste gases are currently in use based on (i) water based absorbents, (ii) solid absorbants or (iii) combustion. Very limited use is made of plasmas for scrubbing as described in section 5.3. In ideal situations, methods (i) and (ii) will lead to total removal of environmentally harmful components of a gas stream whereas method (iii) always requires some follow-up treatment. For example, combustion of halides will leave hydrogen halides in the gas stream which have to be subsequently taken out by liquid or solid absorbents.

3.4.1 Water based absorbents. Treating waste gas streams with water or aqueous solutions of bases is widely used for removing acid gases in many industries. Looking at the molecules listed in Tables 1 and 2, it is clear that this method is not universally applicable for waste from semiconductor processing as several of the gases shown will either not react at all or not quickly enough to be useful. Nevertheless, water-based scrubbers of various designs to maximise the contact of gas with water or with solutions of bases (mainly KOH or aqueous ammonia but seldom NaOH because sodium is a feared impurity in silicon based semiconductors) have important uses where only a limited range of gases have to be scrubbed. A problem in their use arises from hydrolysis of dichlorosilane, silane, tetraethyl orthosilicate or other silicon containing compounds which generates silica, as this comes out of solution as a suspension capable of restricting gas or liquid flow and of blocking many types of filters.

Direct coupling of a vacuum system to a water-based scrubber calls for careful design of fail-safe systems. The industry has known costly accidents when the contents of a water based scrubber have been sucked back through the pumps into the process chamber! Water treatments are also used to follow-up combustion processes which convert the least reactive compounds into simple molecules which can be absorbed by water or base. All silicon compounds are converted into SiO_2 in the flames and this solid creates the problems described above when it is collected in a wet scrubber and its concentration builds up in recirculating wash water.

Many Fabs have a large water scrubber on their exhaust ducts before exit to atmosphere. This may be in addition to local exhaust scrubbers and is intended to catch not only waste breaking through local systems but also vapours of many kinds which enter the ducts from diverse operations throughout the Fab.

A general problem with water based scrubbing is the eventual disposal of large volumes of used wash liquor. Sometimes this can be put into municipal sewers at controlled rates but sometimes costly processing of the wash liquor has to be carried out on site before release. The semiconductor industry is quite familiar with waste wash liquors, because aqueous chemistry is also used for a variety of etching and cleaning operations on wafers which produce an effluent containing HF, NH_4HF_2, HNO_3, H_2O_2 and other chemicals. In this effluent and in the effluent from wet scrubbing of vapours the fluoride ion concentration is currently of greatest concern to regulatory authorities in Europe and the USA and the industry is seeking to find better methods for control of aqueous fluoride emissions.

3.4.2 Solid absorbents. Solid absorbents are more versatile than water based liquid absorbents as they can be used either at room temperature or at elevated temperatures. Absorbents for room temperature use will be considered first.

Activated charcoal or molecular sieves which physically absorb vapours only delay the problem of destroying waste and there can be dangerous reactions with these solids (see section 4.2). However, they do find uses in systems designed to avert catastrophic release of dangerous gases in the event of leakage from cylinders housed in gas cabinets and in final stages of chemical absorber systems.

Calcium hydroxide is a commonly used solid base either by itself or intimately mixed with a few percent of sodium hydroxide (or potassium hydroxide) as porous, granular soda lime. Soda lime is a versatile material, the simple acid-absorbing properties of which can be extended by many different additives, *e.g.* with addition of oxidants such as sodium or potassium permanganate it can also destroy germane, phosphine and arsine. It is fairly cheap and disposal of part-used material gives only limited environmental problems. The disadvantages associated with its use are that it cannot attack all perfluorinated compounds, particularly NF_3, SF_6 or perfluorocarbons, and that typically $<30\%$ of the theoretical capacity of a soda lime absorber can be used before its reactivity is reduced enough to allow vapours to breakthrough at unacceptably high concentrations.

A quite different range of solids used to purify gases, especially hydrides and organometallics, was described in a lengthy patent by Tom *et al.*[5] Polyvinylphenoxylithium on alumina or other high surface inorganic support was recommended for destroying Group 13 alkyls and silane and chlorosilanes. Dibutylmagnesium on alumina, calcium fluoride or polytetrafluoroethylene was recommended for destroying Group 15 hydrides and alkyls (except NH_3), and Group 16 and 17 hydrides. Supported $KMnO_4$ was recommended as a back-up oxidant for hydride scrubbing. An acid ion-exchange resin was proposed for ammonia scrubbing. The patent specified conditions under which the heat of reaction with waste gases could be removed from the solids. This technology was licensed and some is still in use (NovaPure Dry Scrubber). The much higher cost of the reagents compared with simple bases like soda lime is offset by the fact that they react very quickly with waste gases so that short contact times and almost complete usage of the reagents is possible before substantial breakthrough occurs.

3.4.3 Hot solids. Using heated solids gives increased possibilities for destroying waste gases for a number of reasons. First and most obvious is that the rate of reaction increases. Secondly, solid-state diffusion effects may help counter coating of the surface of a solid by reaction products. Thirdly, thermal decomposition of gases, particularly some hydrides, may occur on hot solids irrespective of any particular reaction between the solid and the gas.

Hot soda lime is not an ideal absorber of waste gases as its efficiency at room temperature depends critically on water absorbed in the structure which is lost on heating. More effective is solid CaO which is a very powerful base. The reactivity of CaO varies greatly with the way in which it is formed. Perhaps the highest reactivity CaO has been prepared by Klabunde and

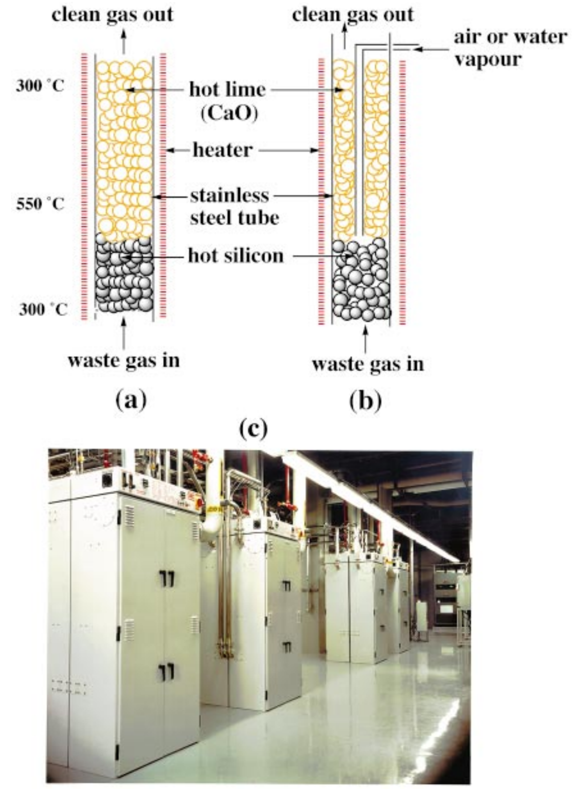


Fig. 2 (a) The normal form of the Gas Reactor Column (GRC). (b) A special form of GRC with an inlet to add air or water vapour to improve destruction of some compounds. (c) A bank of GRCs enclosed in cabinets in a Fab (Photograph courtesy of Texas Instruments, Dallas, USA).

co-workers[6] by vacuum dehydration of $Ca(OH)_2$ prepared under carefully controlled conditions. The surface area of such powdered material can be up to 120 $m^2\ g^{-1}$ and it has been proposed for a number of applications.[7] More practicable for large scale use is granular CaO of surface area of 2–5 $m^2\ g^{-1}$, prepared commercially by heating selected limestone in a rotary lime kiln to 900–1100 °C. At 500 °C a column of such granular lime will react with high efficiency with many gases.

The reactivity of granular lime is exploited in the Gas Reactor Column, marketed by BOC Edwards.[8,9] As shown in Fig. 2(a), the column is a vertically mounted stainless steel tube (the replaceable "cartridge", commonly 150 mm diameter, 1.5 m long) electrically heated from the outside, which contains in the bottom third granular metallurgical grade silicon and granular CaO in the upper two thirds. It is designed to be used with gas streams which contain waste gases mixed with a large excess of nitrogen at flow rates which give a residence time of *ca.* 6 s for molecules passing through the packed zone. The silicon acts both as a heat transfer medium and a reactant. It reacts efficiently with free halogens or ClF_3 forming silicon tetrahalides and, rather less completely, with NF_3, SF_6 and with hydrogen halides. Reaction of ClF_3 with silicon is highly exothermic but, provided the amount of gas is controlled, this is a recommended, safe method for destroying the compound.[10] The calcium oxide stage then reacts with silicon tetrahalides forming calcium halides and calcium silicate and it is a powerful reagent for destroying nearly all the compounds of Tables 1 and 2 except the perfluoroalkanes. Silane and diborane undergo both thermal decomposition to the elements and some reaction with the CaO as a base. The column has the ability to retain small amounts of phosphorus or arsenic formed by thermal decomposition of PH_3 or AsH_3, but if large amounts of these gases are to be absorbed, air can be blown into the column at the bottom of the lime stage as shown in Fig. 2(b), allowing complete oxidation of P or As to calcium phosphate or arsenate on the lime. In favourable cases, up to 60% of the theoretical capacity of the lime part of the cartridge can be used before an acid gas such as silicon tetrachloride, introduced at a concentration of 1% (10 000 ppm) in nitrogen, breaks through at unacceptable concentrations. This is a higher percent usage of the CaO than has been reported for commercial lime by other users.[11] The reason is probably the long period over which the lime is being treated when the gas stream contains only 1% of an acid gas. This allows solid-phase diffusion to occur to a greater extent than if the column is exposed to a higher concentration of an acid gas for correspondingly less time. A bank of Gas Reactor Columns in use in the Texas Instruments Fab in Dallas, USA, is shown in Fig. 2(c). Over the next few years, the existing Gas Reactor Column will need to be resized to cope with the higher gas flows associated with processing of larger diameter silicon wafers.

A good feature of the Gas Reactor Column is that spent cartridges are often acceptable as landfill as the waste gases they have trapped have been converted mainly into calcium salts which are either water insoluble or, if soluble like calcium chloride, are not too harmful. If a cartridge is contaminated with arsenic (as calcium arsenate) it is classified as a special waste the disposal of which is strictly controlled. Dealing with waste arsenic in solid or aqueous effluents is an unsolved problem for the industry. The situation would become worse if the industry wanted to make more use of gallium arsenide as a semiconductor.

The use of heated layered silicates for perfluoroalkane destruction is discussed in section 4.2.4.

3.4.4 Destruction in flames and related methods. Incineration of waste is a well established process in many industries and it has been adapted to the needs of the semiconductor industry. Combustion devices which are used range from very simple burners to more sophisticated inwardly fired burners. Successful use of combustion has to overcome a number of problems. First, the flame into which the waste stream is to be injected must provide sufficient enthalpy and sufficient mixing of gases that the waste gases all become hot and are all exposed to reactive flame components for sufficient time to bring about complete chemical decomposition and oxidation. This is difficult because the large excess of nitrogen mixed with the waste gases from semiconductor processing tends to cool a flame. Secondly, combustion can only convert waste into the most stable, oxidised forms of the elements it contains. So the off-gases from combustion may contain HF, HCl, SO_2 and other acidic gases which must be absorbed in water in an adjacent scrubber. Thirdly, combustion of silicon, boron, phosphorus or metal compounds will create solid oxide residues which must not be allowed to block the burner. Finally, the combustion temperature must be kept as low as possible to minimise NO_x formation and the flame made sufficiently oxidising to yield CO_2 not CO, so the effluent gases after water scrubbing are as environmentally acceptable as possible.

A range of commercial burners have been developed which meet the above requirements to a greater or lesser extent. Many involve passing the waste gases (usually heavily diluted by nitrogen as mentioned above) through the centre of a hydrogen or methane plus air or oxygen flame. Such flames tend to have a wide range of temperatures within them and the residence time of the waste gases in the hottest parts is short. Most waste gases undergo complete decomposition/oxidation/hydrolysis to products which can be washed out in a water scrubber. However, to achieve complete destruction of CF_4 requires the highest flame temperatures (see section 4.1.3) and, under these conditions, the amount of NO_x also formed can be quite high. The flame temperature can be kept lower if the residence time in the flame can be increased. This has been effectively achieved by passing the waste gases through the hot zone of an inward fired burner as in the Thermal Processing Unit[12] made by BOC

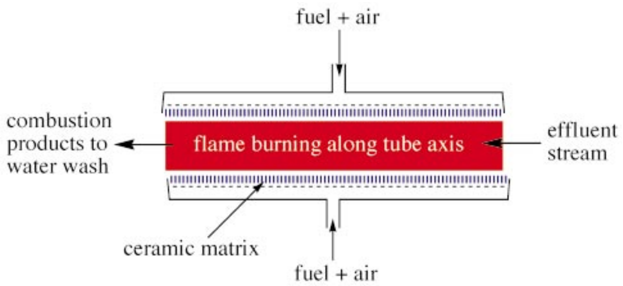


Fig. 3 Schematic of an inward fired burner which can convert all waste volatiles into simple combustion products.

Edwards. As shown in Fig. 3, a mixture of methane (or other hydrocarbon fuel) is forced through a porous ceramic matrix lining of the cylindrical combustion chamber and ignited to create a structureless flame just above the surface of the matrix which fills the cylinder with hot gas. Waste gases are blown axially through this hot gas and combustion and decomposition products are fed into a high efficiency water scrubber. The temperature can be controlled in the range 800–1100 °C by varying the fuel/air/oxygen ratios.

An alternative approach to passing waste gases through a flame is to pass them through a heated tube in the presence of air or oxygen. Thermal oxidation may then occur with development of a flame only with high concentrations of oxidisable wastes gases, particularly silane. Pioneers of this simple but useful approach have been Delatech Inc. in the USA. An inconel tube is used (in one model, 15 cm diameter and 90 cm long) heated electrically to 900–1000 °C. An inlet manifold feeds air, nitrogen and the waste gas stream down the hot tube, with the flows being designed to try to prevent blocking of the inlet manifold or the tube by solid oxidation products, *e.g.* silica. A wet scrubber immediately following absorbs solid and gaseous products. The system is fairly successful with air-oxidisable gases such as SiH_4, PH_3, $Si(OEt)_4$ or BCl_3, and, with the addition of hydrogen, it will destroy NF_3 and C_2F_6 but not CF_4. The main problem with the method is blocking of the lower part of the tube although this can be overcome in part with a mechanical scraper device.

4 The problem of perfluorocarbons

4.1 Thermodynamics and kinetics

The perfluorocarbons have a well established role in plasma-based dry etching and process chamber cleaning operations and are very effective. They are safe because they are of low toxicity but are environmentally damaging on account of their effectiveness as greenhouse gases and their long atmospheric lifetimes.[13] So the only problem with their use is the difficulty of destroying any that remains unused and is pumped out of the process chamber with other waste gases.[14,15]

The inertness of simple perfluorocarbons arises from a combination of co-ordinative saturation and strong C–F bonds. This is most extreme with tetrafluoromethane which is the least reactive of known molecular compounds with an extraordinary resistance to attack by dissociative or associative mechanisms. Unlike many other highly fluorinated compounds, CF_4 has little affinity for thermal electrons[16] or F^-[17] but its proton affinity is comparable with that of CH_4 or CO_2.[18] It is also a thermodynamic and kinetic sink compound which is formed as a by-product from treating perfluorinated or highly fluorinated carbon compounds, *e.g.* CHF_3 or $(CF_3CO)_2O$, with oxygen in plasmas. So, whenever highly fluorinated carbon compounds are used the problem of dealing with CF_4 still has to be faced.

The reactivity of perfluoroalkanes containing C–C bonds is definitely higher than that of CF_4. Among the compounds in current use in the semiconductor industry, reactivity decreases down the series $C_3F_8 > C_2F_6 > CF_4$, in proportion to the number of C–C bonds. The reactivity of C_3F_8 and C_2F_6 is still very low as none of the methods for attacking perfluorinated organic compounds reviewed by Saunders involving electron transfer reactions from organometallic compounds[19] or from hot sodium oxalate[20] is applicable to their rapid destruction. However, as described below, methods have been developed which allow destruction of these compounds as components of waste gas streams containing a large excess of nitrogen.

4.2 Methods for destroying perfluoroalkanes

4.2.1 Reaction with alkali metals at elevated temperatures. Perfluorocarbons are sensitive to attack by Group 1 metals as is evident from ease of activating the surface of Teflon by attack with sodium in liquid ammonia. A Japanese patent describes destruction of CF_4 by sodium in liquid ammonia at −33 °C but this is not a method that could readily be used in conjunction with an effluent stream from semiconductor production.[21]

The rate of reaction of CF_4 with gaseous Na, K, Rb and Cs atoms has been measured at temperatures around 500 °C. The results show some inconsistencies but all suggest that the rate constant for the endothermic, primary defluorination, eqn. (1),

$$CF_4 + M(g) \longrightarrow CF_3^{\bullet} + MF(g) \qquad (1)$$

is *ca.* 10^3 times less than for the corresponding exothermic reaction involving CF_3Cl or 10^5 times less than for SF_6.[22] Nevertheless, the complete defluorination of CF_4 by sodium vapour is highly exothermic and Dufaux and Zachariah[22] have destroyed CF_4 to >96% completion in a flame created by mixing it with a two-fold excess of sodium vapour pre-heated to temperatures >700 °C.

The destruction of perfluorocarbons present in low concentrations in nitrogen streams, simulating the conditions of the effluent from semiconductor processing, has been explored at Bristol.[24] When a gas stream containing 1% CF_4 in N_2 was passed over dispersed sodium metal supported on alumina reaction was first detectable at 420 °C and, with a contact time of *ca.* 6 s, destruction of the CF_4 was >99% complete at 595 °C. Comparable figures for C_2F_6 were 370 and 510 °C respectively. It was concluded that the reaction was occurring mainly on the surface of molten sodium not with sodium vapour, which is consistent with the reported low reaction rate of sodium atoms with CF_4.

However, the use of metallic sodium or potassium as liquid or vapour to destroy waste gases from semiconductor processing raises such serious safety issues that it is extremely unlikely to be acceptable to the industry. An alternative, safer approach is to pass the waste gas stream containing perfluorocarbons over heated mixtures which can generate sodium or potassium. Before electrolysis became the dominant route for making metallic sodium or potassium, numerous thermal processes were proposed by which the metals were liberated by high temperature reduction of their compounds.[25] At Bristol, a range of such mixtures have been studied including $Na_2SiO_3/Si/CaO$, NaF/Si/CaO, NaF/Al and corresponding mixtures using potassium salts.[24,26] They have been used to remove perfluorocarbons from nitrogen streams containing 1% CF_4 or C_2F_6 at temperatures of 500–800 °C, which are substantially lower than the temperatures proposed to liberate alkali metals on a laboratory or manufacturing scale.[25] The NaF/Si/CaO mixture heated to 700 °C proved particularly effective as the NaF was engaged partly in a catalytic role as in eqns. (2) and (3). Adding reaction (2) and (3) gives (4) with elimination of the “catalyst” NaF. In

$$4NaF + Si + 3CaO \longrightarrow 4Na + CaSiO_3 + 2CaF_2 \qquad (2)$$

$$CF_4 + 4Na \longrightarrow 4NaF + C \qquad (3)$$

$$CF_4 + Si + 3CaO \longrightarrow CaSiO_3 + 2CaF_2 + C \qquad (4)$$

practice, it was found that in order to maintain the level of CF_4 destruction at >98% and to make effective use of >50% of the available Si and CaO, a NaF : Si : CaO mole ratio of 1 : 1 : 2 was best. The calculated equilibrium vapour pressure of sodium over the mixture at 700 °C is *ca.* 5 mbar, but the observed transport of sodium in a pure nitrogen stream was very slight. This implies that the rate of production of free sodium from the solid-phase reactions was quite low and that CF_4 was involved in reactions on the solid surfaces not just with liberated sodium vapour.

4.2.2 Catalytic destruction of perfluorocarbons over hot iron. Other electropositive metals in Groups 2–4 cannot be used to destroy perfluoroalkanes diluted with nitrogen as all the metals form nitrides when hot which do not then seem to react readily with perfluoroalkanes. The tendency to nitride formation diminishes across the transition series and at Bristol heated iron has been useful for destroying perfluoroalkanes.[24] By adding hydrogen and an oxidising gas such as O_2, H_2O or CO_2, iron can be used as a catalyst for conversion of perfluorocarbons into carbon oxides and HF. Temperatures about 950 °C are required to get >99% reaction with C_2F_6 and about 1050 °C for CF_4. The rate determining step is the fluorination of the metal by the perfluorocarbon; subsequent reduction of the fluoride by hydrogen to give HF and the metal and oxidative removal of carbon from the metal surface are processes which occur easily above 700 °C.

4.2.3 Flame destruction. Destruction of perfluorocarbons other than CF_4 in air/hydrocarbon or air/hydrogen flames at temperatures of >1000 °C occurs fairly readily through thermal breaking of the C–C bonds and attack on the molecules by flame generated radicals. The comparable reactions with CF_4 are significantly slower so that higher temperatures and/or longer residence time in the flame are needed to achieve near total destruction and this increases the likelihood of generating significance amounts of NO_x. The greatest success in flame destruction of CF_4 has been obtained with an inward fired burner (Fig. 3 and section 3.4.4) but even with this design extra fuel and oxygen have to be added completely to destroy CF_4. In all cases, HF is a reaction product which has to be scrubbed out of the off-gases from the combustion.

4.2.4 Destruction on active sites in heated oxides. Both CF_4 and C_2F_6 will react with hot silica but the reactions are not very fast below 1000 °C so this is not a practicable method of destroying these gases.[27,28] A quite different approach to destroying CF_4 or C_2F_6 is to use high surface area, layered silicates to retain and destroy the perfluoroalkanes.[29,30] Full details of the chemistry of these products which are available commercially from CS Clean Systems have not been published but it is claimed that they are successful and, remarkably, that they destroy CF_4 at a lower temperature than that for C_2F_6. Activated layered clays and silicates are reported irreversibly to absorb CF_4 at above 300 °C while temperatures of above 500 °C are required for C_2F_6. The fluorine is said to be retained as metal fluorides from Group 1 and 2 and transition metal ions originally present or intercalated into the structure, with carbon dioxide and some water as the only volatile products. The capacity of the system for CF_4 or C_2F_6 is not given but the paper implies that it is fairly low.[30]

A similar effect has been observed in experiments at Bristol in which it was shown that chromatographic grade alumina will destroy CF_4 at 450–500 °C and C_2F_6 at 500–550 °C. The capacity of the alumina for destroying either gas is very small, *ca.* 2% of the theoretical assuming that the alumina could all be converted into AlF_3. Pretreatment of the alumina with acids or the use of acid-treated Al_2O_3/TiO_2 mixtures caused a slight lowering of the temperature of reaction but caused little change in the absorptive capacity of the solid.[31]

This observed greater ease of destruction of CF_4 than C_2F_6 is contrary to the order of their reactivity under all other situations. The implication is that there are specific sites on the oxide surfaces which hold CF_4 more strongly than C_2F_6 so that it can undergo an overall reaction to yield a metal fluoride (*i.e.* AlF_3 on alumina or aluminium, iron or other metal fluorides from metal cations in the activated clays or layered silicates), carbon dioxide (or an alkali carbonate) and some water (from hydroxyl groups on the oxide). It is still unclear if this reaction is triggered by proton transfer at a superacid site, by Lewis-acid interactions between lone pairs on the fluorine atoms and a metal cation, or by some other mechanism.

4.3 Other perfluorinated compounds

The other two perfluorinated compounds which are used and which can be difficult to scrub because of their low reactivity are NF_3 and SF_6. They are both used for plasma activated etching and NF_3 is widely used for the cleaning stage of plasma enhanced chemical vapour deposition processes. While both gases show considerable kinetic stability and are entirely untouched by room temperature wet scrubbing processes, NF_3 is the less thermodynamically stable. Violent explosions can arise if NF_3 is absorbed at low temperatures in charcoal or in molecular sieves and then the solid is warmed, through formation of $N_2 + CF_4$ or of $N_2 + SiF_4 + AlF_3$. The gases can be destroyed safely on proprietary solid absorbents based on activated layered silicates or aluminosilicates (CS Clean Systems) at temperatures of >150 °C,[30] or in the BOC Edwards Gas Reactor Column through contact with silicon and CaO at 450–550 °C.[8] The reactivity of NF_3 towards the hot silicon can be improved by precoating the silicon with copper which acts catalytically through the cycle shown in eqns. (5) and (6).

$$Cu + 2NF_3 \longrightarrow CuF_2 + 2NF_2 \qquad (5)$$

$$2CuF_2 + Si \longrightarrow 2Cu + SiF_4 \qquad (6)$$

Further reaction of NF_2 with the silicon or copper occurs much more readily so complete destruction of NF_3 can be achieved.

The relative ease of flame destruction of perfluorocompounds decreases in the order $NF_3 \gg C_2F_6 > SF_6 \gg CF_4$. So, destruction of NF_3 occurs easily in flames; SF_6 is more difficult and is only achieved with efficient burner designs. The combustion products from SF_6 are HF, SO_2 and SO_3 which are easily removed by post-flame scrubbing but with NF_3 the flame conditions have to be carefully controlled to prevent too much NO formation as this is not trapped in water based scrubbers.

4.4 Recovery of perfluorinated compounds

The inertness of the perfluoroalkanes and SF_6 and to a lesser extent NF_3 makes them attractive targets for recycling. Details of a recycling system have been published.[32] This involves complete removal of reactive waste products from the processing using conventional wet and dry scrubbing, followed by low temperature condensation and fractionation of the perfluorinated compounds which have passed through the scrubbing stages. The fractionation is aided by a cryogenic "wash liquid" such as C_3F_8 (mp −148, bp −37 °C). Pure compounds can be recovered in high yield which is a remarkable achievement. However, the effluent gases have to be extensively pre-purified to remove all compounds apart from the perfluorinated compounds so the cost-of-ownership of the system is likely to be higher than for competitive systems which destroy everything including the perfluorinated compounds.

5 Disposing of silanes

5.1 Processes using silanes

Silane, SiH_4, is consumed in large quantities by the semiconductor industry for deposition by thermal or plasma methods of "polysilicon" (polycrystalline or amorphous silicon), of boron or phosphorus doped silicon, of silica, of tungsten silicide and in numerous other applications. Bulk deliveries of up to three tons of ultra-high purity compressed gaseous silane are available to users in the USA. Dichlorosilane, SiH_2Cl_2, is also used as a source of polysilicon and, in conjunction with ammonia and nitrogen, for depositing silicon nitride usually by Low Pressure Chemical Vapour Deposition. The problems that the residual silanes cause when pumped out of the process chambers are considered below.

5.2 Silane; a pyrophoric gas that is hard to oxidise

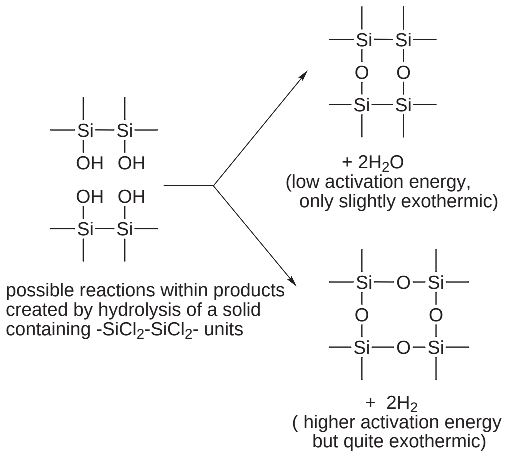
Silane is well known to be pyrophoric so its destruction by controlled oxidation or combustion does not appear difficult. However, the reaction of silane with oxygen is a very complex process. The classic study of Emeleus and Stewart[33] on the upper and lower explosion limits of silane and oxygen showed that silane and oxygen in a 1 : 2.3 mol ratio at a total pressure of *ca.* 0.6 bar do not react appreciably even when kept at 70 °C for many days. Yet at a slightly higher partial pressure of silane or at a slightly higher temperature an explosion occurred immediately. Much more detailed studies have been done since, extensively reviewed by Koda.[34] Many of the species contributing to a radical chain oxidation as well the kinetics of their reactions have been documented. Nevertheless, the initiation of the reaction of oxygen with silane seems to require the intermediacy of reactive surfaces or of traces of gaseous radicals otherwise it does not occur. This makes silane/air mixtures treacherous, with spontaneous ignition/explosion likely but not certain. It also means that when silane at concentrations of <2% in nitrogen is brought into contact with air there is no ignition as radical quenching predominates.

There is available "burn-box" technology in which effluent SiH_4/N_2 mixtures are brought into contact with a large volume of air with the intention of allowing either controlled, spontaneous combustion or air oxidation without combustion. The idea works to some extent. High concentrations of silane will ignite and burn safely within the box but lower concentrations of silane pass through and are released without ignition into the atmosphere where oxidation/hydrolysis will occur very slowly.

Many other of the methods described in section 3 can be used successfully, the main complication being the solid oxidation or decomposition products generated. Thus, injection of SiH_4 into a flame generally results in complete decomposition but premature decomposition depositing silicon in the inlet tubes and excessive deposition of silica on burner components can occur. Silane can be destroyed rapidly by bases such as supported polyvinylphenoxylithium[5] or less rapidly and completely with sodium or potassium hydroxide solutions[35] but these create the problems described in section 3.4.1. Soda lime will also readily destroy SiH_4 but its capacity is rather limited. Silane is completely destroyed in the Gas Reactor Column although blocking may eventually occur as silane is largely thermolysed at 450–550 °C to powdered silicon which can build up on the hot silicon or CaO stages.

5.3 Explosive by-products

Deposition of polysilicon by thermal or plasma enhanced chemical vapour deposition using SiH_2Cl_2 or $SiHCl_3$ in the presence of hydrogen, followed by cleaning processes using HCl gas, leads to the formation of a complex mixture of solid and gaseous by-products. The solids carried out of the process chamber collect in the pumps or in the immediate exhaust from the pumps. Initially, the solids contain Si–Si, Si–H and Si–Cl bonds but they may be exposed subsequently to limited amounts of oxygen and water. Mostly, the solids are simply a nuisance but on rare occasions they explode violently. The chemistry of these explosions is still a matter of conjecture but a clue may come from old literature on hydrolysis of polychlorosilanes; for example, hydrolysis of Si_3Cl_8 is said to give an explosive solid, fancifully named as "silico mesooxalic acid".[36] This is likely to be a partial condensation product of $Si_3(OH)_8$, which may owe its explosive power to an exothermic internal oxidation which is a possible alternative to the expected elimination of water in species containing both Si–Si and Si–OH bonds. The process is shown schematically below. Further energy could be derived from oxidation of Si–H bonds by water liberated from condensation of Si–OH groups. When the right amount of hydrolysis of the primary solid has occurred the final solid could have the potential to explode, liberating hydrogen which may in turn be ignited in contact with air.



5.4 Problems with the SiH_2Cl_2/NH_3 reaction

The reaction of SiH_2Cl_2 with NH_3 under chemical vapour deposition conditions gives excellent layers of insulating silicon nitride. However, the waste products are messy because ammonium chloride and solid complexes of SiH_2Cl_2 and NH_3 are formed and may condense in and block vacuum pumps or the pipework on the atmospheric pressure side of the pumps. The problem has been addressed in two ways. The DryScrub Systems device, which is one of the few examples of low pressure scrubbing, is positioned between the process chamber and the dry-pump. It exposes the effluent vapours to a powerful plasma between concentric aluminium electrodes. Silicon nitride is deposited on the electrodes, completing the reaction which began in the process chamber. The residual gaseous pollutant is then HCl. The system needs to be stripped down periodically to clean the silicon nitride deposit off the electrodes. Corrosion of the aluminium electrodes by HCl and other chlorine-containing species is a longer term problem. The second solution is simply a water cooled trap on the outlet to the dry-pump which finally condenses and collects the solids. If stoichiometric mixtures of SiH_2Cl_2 and NH_3 are used in the process all the final products are solids and no further scrubbing than the cold trap is required.

6 Concluding observations

Methods of controlling the waste volatiles from the semiconductor industry may not yet appear to compare in sophistication to the chemistry of wafer processing. In part, this is a consequence over the years of a lower research effort by the industry and its suppliers on pollution control than on wafer production, for the profits of the industry are generated from sales of processed wafers. Despite its elegance, much of the highly developed process chemistry is quite inefficient in its use of valuable chemicals. When the industry moves into the next scale of production processing 300 mm instead of 200 mm silicon wafers it is committed to increase the efficiency of the process chemistry as well as further reducing emissions of all environmentally harmful gases and to promote recycling where practicable.

There are undoubtedly many opportunities for research on both process chemistry and emission control. However, because of the way the semiconductor industry has developed, there are perhaps now easier opportunities for developing new methods of emission control.

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