

Semiconductor Technology from A to Z

Dry Etching

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Dry etch processes

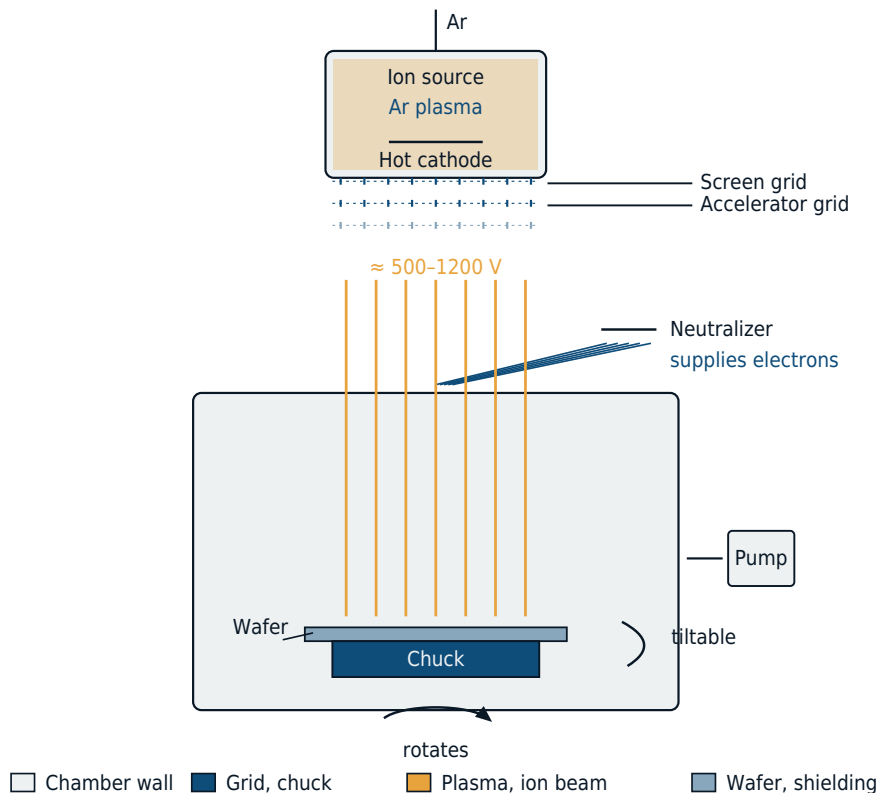
Ion beam etching

Ion beam etching (IBE) is a purely physical dry etch process. Here, argon ions are directed onto the wafer as a collimated ion beam with an energy of 1–3 keV. Due to the energy of the particles, they knock material out of the surface. The ions are generated in a source separated from the process chamber and extracted through a grid system; the working pressure is below 0.1 Pa, so that the ions retain their direction all the way to the wafer. The wafer is held perpendicular or tilted relative to the ion beam in the process chamber, and the etch proceeds in a completely anisotropic manner. The selectivity is only low, since the accelerated ions do not distinguish between materials. The gas and the material knocked out are extracted by the pump system; however, particles also deposit on the chamber walls and on vertical edges of the wafer itself, since the removed material does not transition into the gaseous state.

To prevent particle deposition, a reactive gas is introduced into the chamber in addition to argon. This gas reacts with the argon ions, resulting in a physical etch process with a chemical character. The gas then reacts partly with the surface, but also with the material knocked out by the physical component, to form a gaseous reaction product. If the reactive gas is already added within the ion source, this is called reactive ion beam etching (RIBE); if it is introduced only in front of the wafer, it is called chemically assisted ion beam etching (CAIBE).

Ion Beam Etching Reactor

A collimated ion beam removes material purely physically



The grid system accelerates the argon ions into a focused beam; the neutralizer supplies electrons so the wafer doesn't charge up. Because no reactive gas is involved, almost any material is removed purely mechanically – but this etch lacks the chemical selectivity of reactive ion etching.

With this process, almost all materials can be etched. Due to the perpendicular irradiation, removal at vertical edges is very low (high anisotropy).

Because of its low selectivity and low etch rate (low ion density in the beam), ion beam etching no longer plays a role in patterning silicon and silicon compounds. It is, however, indispensable for materials that do not form volatile reaction products and are therefore hardly etchable by chemical means:

- magnetic layer stacks, such as the tunnel elements of MRAM memory cells made of CoFeB and MgO, as well as read heads and magnetic field sensors
- noble metals such as platinum, iridium, and ruthenium
- piezoelectric and ferroelectric layers such as PZT
- lithium niobate and similar crystals in integrated photonics

The tiltable, rotating substrate holder is a significant advantage here: the angle of incidence can be used to set the sidewall angle of the structure and to remove redeposited material from the sidewalls – for layer stacks made up of many different materials, a result that cannot be achieved with plasma chemical processes. Since insulating substrates would charge up under ion bombardment,

the source operates with a neutralizer that adds electrons to the beam.

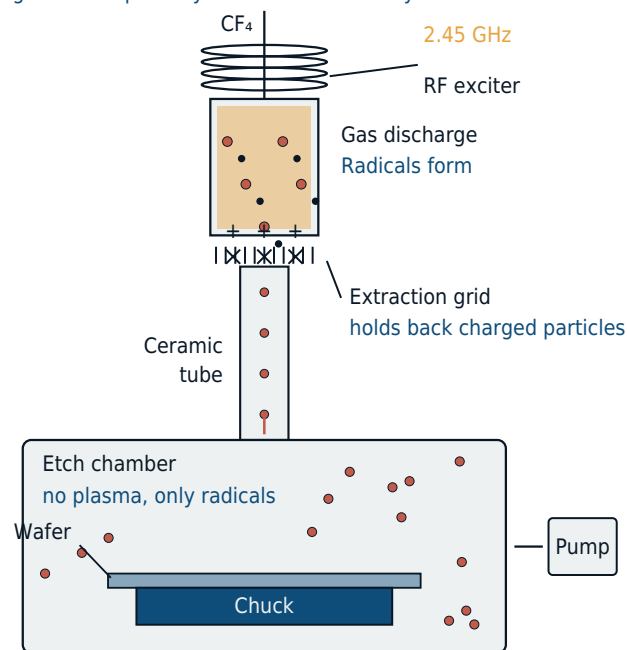
Plasma etching

Plasma etching is a purely chemical etch process (chemical dry etching, CDE). Its advantage is that the wafer surface is not damaged by accelerated ions. Because of the freely moving gas particles, the etch profile is isotropic, which is why plasma etching is mostly used for removing entire layers at a high etch rate.

One type of equipment used for plasma etching is the downstream reactor. Here, a plasma is generated by impact ionization through the application of a high-frequency voltage (e.g. 2.45 GHz). The space where the gas discharge occurs is separated from the wafer, and the gas reaches the wafer via a ceramic tube.

CDE Downstream Reactor

The gas discharge burns separately from the wafer - only radicals reach it

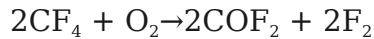


■ Gas discharge ■ Radicals + charged particle ■ Chuck ■ Wafer

Because the plasma burns separately from the wafer, no accelerated ions strike the wafer - only uncharged but highly reactive radicals do. Etching therefore remains damage-free, but isotropic: it attacks in all directions.

In the gas discharge zone, various species are formed through collisions between the gas molecules, including radicals. Radicals are molecules with a broken bond, made highly reactive by an unpaired outer electron. As a neutral

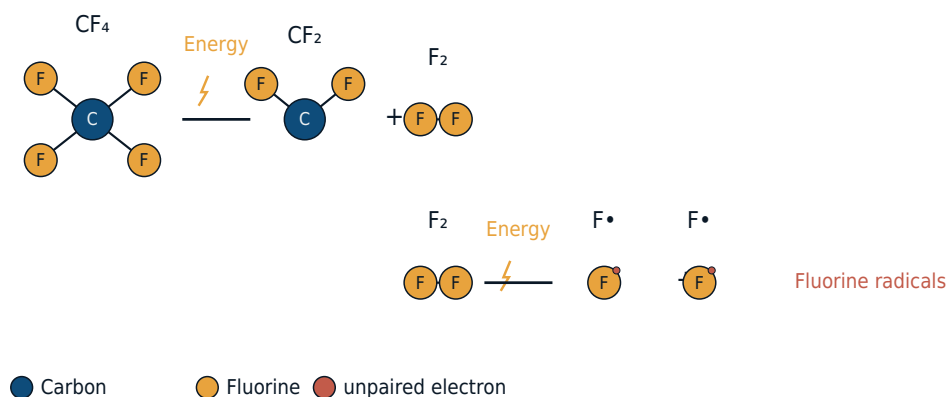
gas, tetrafluoromethane CF_4 (also known as carbon tetrafluoride), for example, is introduced and broken down by the alternating voltage into CF_2 and a fluorine molecule F_2 . Fluorine can likewise be split off from CF_4 by adding oxygen:



The fluorine molecule can then be split into two individual fluorine atoms by the energy present in the gas discharge zone: fluorine radicals (radicals are uncharged particles; a single fluorine atom has nine protons in its nucleus and nine electrons in its electron shell).

Formation of Fluorine Radicals

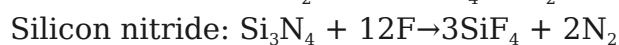
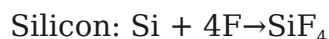
Energy in the gas discharge splits CF_4 in two steps



A radical is an uncharged particle with an unpaired outer electron – this makes it highly reactive. Fluorine can also be released using added oxygen: $2\text{CF}_4 + \text{O}_2 \rightarrow 2\text{COF}_2 + 2\text{F}_2$.

In addition to the neutral radicals, further particles are formed, some of them charged (CF_4^+ , CF_3^+ , CF_2^+ , ...), which are all carried together through the gas tube to the etch chamber. Charged particles are either intercepted by an extraction grid or recombine back into neutral molecules on the way. The fluorine radicals, too, are partly recombined again. Nevertheless, enough radicals reach the etch chamber, where they react with the wafer surface. Neutral particles do not take part in the reaction and, like the resulting reaction products, are extracted by the pump system.

Examples of layers etched using the CDE process:



Present-day relevance

Purely chemical dry etching is unsuitable for patterning layers, because the

isotropic profile undercuts the mask. As a remote or downstream process – the plasma burns separately from the wafer, and only long-lived neutral radicals reach it – it fulfills clearly defined tasks in manufacturing, however:

- Resist removal (ashing): oxygen radicals burn off the photoresist after etching or implantation into CO_2 and H_2O .
- Chamber cleaning: nitrogen trifluoride NF_3 is dissociated in an upstream plasma source; the fluorine radicals remove deposits from process chambers without the chambers having to be opened.
- Selective etchback: radical processes based on NH_3 and NF_3 remove native oxide and thin nitride layers without causing damage – even inside contact holes, which a directional etch can only reach with difficulty.
- Channel release: in nanosheet or gate-all-around transistors, silicon-germanium is removed isotropically and selectively against silicon in order to release the channel layers. Here, the isotropy that is a nuisance in patterning is deliberately exploited.

Reactive ion etching

In reactive ion etching (RIE), the etch characteristics – selectivity, etch profile, etch rate, uniformity, reproducibility – can be precisely adjusted through the gases used and the process parameters (generator power, pressure, electrode spacing, gas flow). Both an isotropic and an anisotropic etch profile are possible. This makes RIE, a chemical-physical etch process, the most important etch process for patterning various layers in semiconductor manufacturing.

Inside the process chamber, the wafers sit on an electrode fed with an alternating voltage (RF electrode). Impact ionization generates a plasma containing free electrons and positively charged ions. When the RF electrode is at a positive voltage, electrons accumulate on it and, due to the work function, cannot leave it during the positive half-cycle; the electrode thus charges up negatively to as much as 1000 V (bias voltage). The slow ions, which could not follow the fast alternating voltage, now move toward the negatively charged electrode carrying the wafers.

If the mean free path of the ions is long, the particles strike the wafers at nearly perpendicular incidence due to their velocity. Material is thereby knocked out of the surface by the accelerated ions (physical etching), while some particles also react chemically with the substrate. Vertical sidewalls are not struck, so no removal occurs there and the etch profile remains anisotropic. The selectivity is not very high because of the physical removal component, and in addition the wafer surface is damaged by the accelerated ions. This damage later has to be repaired by thermal treatment.

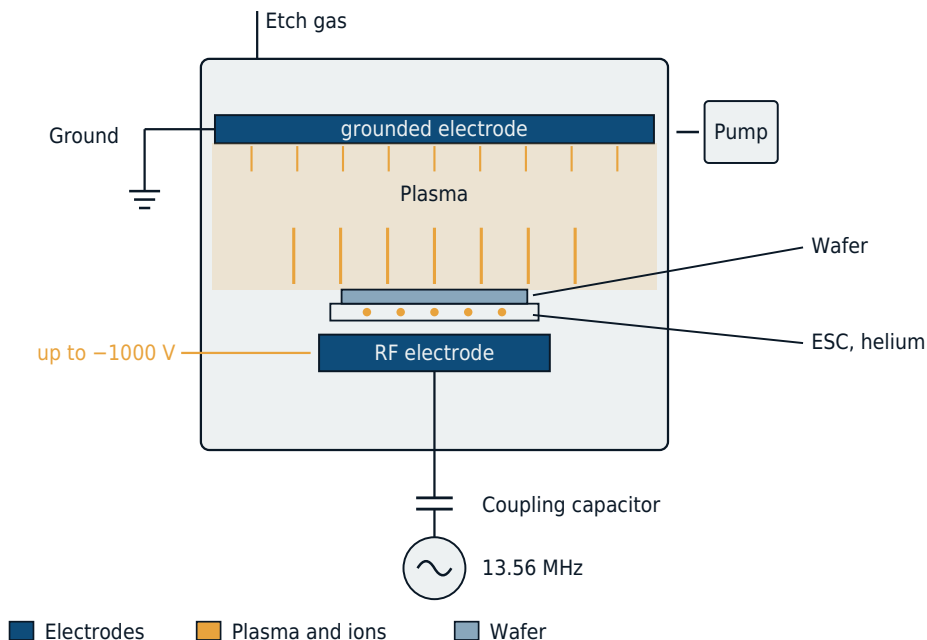
The chemical component of the etch occurs through the reaction of free radicals with the wafer surface and with the physically removed material, so that this material, unlike in ion beam etching, cannot redeposit on the chamber walls or on the wafers. As the pressure is increased, the mean free path of the particles decreases, so that many collisions occur between particles on their way to the wafer, continuously changing their direction. Directional etching of the wafer surface then no longer occurs; the etch process takes on a more chemical character, the etch profile becomes isotropic, and the selectivity increases.

The hexode design etched several wafers simultaneously on a six-sided carrier. Such batch tools are today only of historical interest, because uniformity and endpoint can no longer be controlled with sufficient precision across many wafers.

Today, etching is carried out exclusively on a single-wafer basis in a parallel-plate configuration. The wafer rests on an electrostatic chuck (ESC), which holds it flat and thermally couples it to the temperature-controlled electrode via helium on the wafer backside. This allows wafer temperatures to be set from about $-100\text{ }^{\circ}\text{C}$ up to over $100\text{ }^{\circ}\text{C}$ - temperature is one of the most effective control parameters for selectivity and profile.

Reactive Ion Etching

Parallel-plate design: the wafer sits on the RF electrode

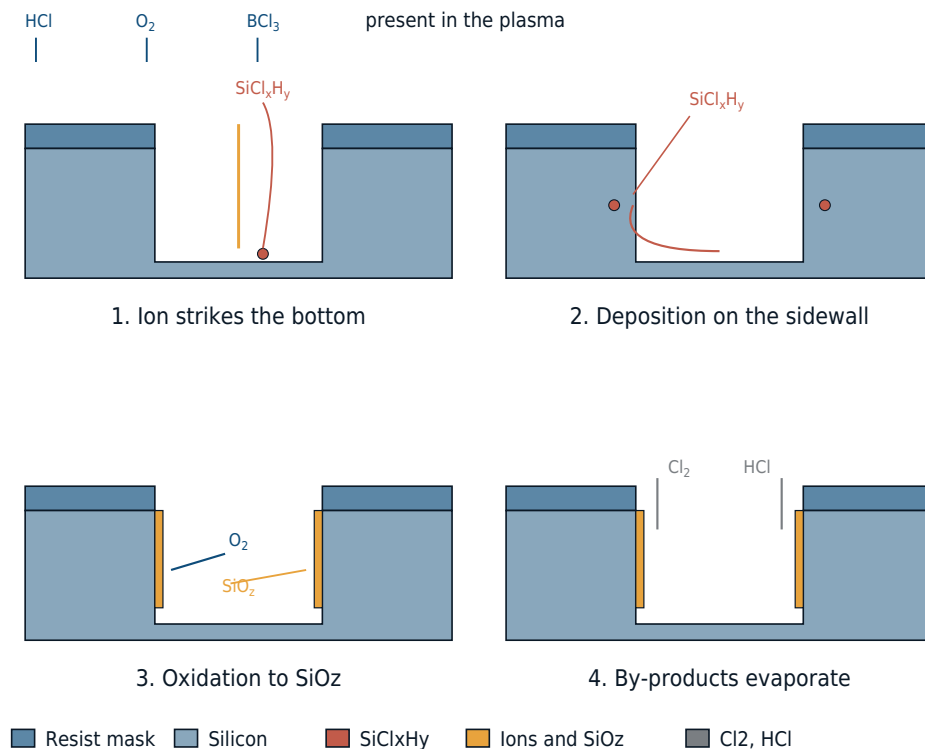


Because the lower electrode is smaller than the upper one, it charges negatively relative to the plasma. This accelerates the positive ions perpendicular to the wafer, removing material directionally - the etch profile becomes anisotropic.

An anisotropic etch profile is achieved in silicon etching through passivation of the sidewalls. Here, oxygen in the process chamber reacts with silicon released from the wafer surface to form silicon dioxide, which grows on the vertical sidewalls. An oxide layer on horizontal surfaces is removed by ion bombardment, allowing the etch to proceed further into the depth.

Mechanism of Sidewall Passivation

Four steps from ion bombardment to the protective oxide layer



Ion bombardment releases SiCl_xH_y from the silicon at the trench bottom. Some of it deposits on the sidewalls and oxidizes there with O₂ to form SiO₂. Cl₂ and HCl evaporate, leaving the oxide layer behind as protection – at the bottom, the vertical ion bombardment immediately removes it again.

The etch rate depends in every case on the pressure, the power of the RF generator, the process gases, the gas flow rate, and the wafer or electrode temperature.

Anisotropy increases with rising RF power, decreasing pressure, and decreasing temperature. The uniformity of the etch is determined by the gases, the electrode spacing, and the electrode material. If the electrode spacing is too small, the plasma is not distributed evenly within the chamber, leading to non-uniformity. As the spacing increases, the etch rate decreases, since the plasma is spread over a larger volume. Carbon was formerly used as the electrode material: since fluorine and chlorine gases also remove carbon, the electrode causes a uniform loading of the plasma, so that the wafer edge is not stressed

more than the wafer center. Today, electrodes made of silicon, silicon carbide, or quartz are common; the chamber parts facing the plasma are coated with yttrium oxide or aluminum oxide to prevent particles and metallic contamination.

Further developments of reactive ion etching

The classic RIE reactor couples plasma density and ion energy through the same electrode: more power simultaneously means more etch rate and more damage. Today's generations of equipment decouple these two quantities and extend the process in several directions.

High-density plasma sources

In inductively coupled plasma (ICP, also TCP) tools, a coil above a dielectric window generates the plasma; in ECR tools, a microwave in a magnetic field does so. The ion energy is set separately via a bias generator at the wafer electrode. The result is high etch rates at low ion energy, i.e. less damage, at pressures well below 1 Pa.

Multi-frequency tools

For etching dielectrics, capacitively coupled reactors operate with two or three generators of different frequencies on the same electrode, in order to set ion density, ion energy, and energy distribution separately. For deep structures, bias voltages of several kilovolts are used.

Pulsed plasma

If the supplied power is pulsed in the kilohertz range, charge buildup in deep structures decays between pulses. This reduces profile defects such as bowing and notching and improves selectivity.

Deep etching (DRIE, Bosch process)

In deep reactive ion etching, very short etch steps using SF_6 alternate cyclically with passivation steps using C_4F_8 . This produces trenches with aspect ratios above 30:1 and depths of several hundred micrometers. The cyclic sequence leaves a wavy sidewall (scalloping). The main applications are micromechanical devices (MEMS) and through-silicon vias.

Cryogenic etching

At wafer temperatures around -100°C , reaction products condense on the cold sidewalls and passivate them, while ion bombardment keeps the bottom clear. This yields smooth, vertical sidewalls without scalloping. For several years, this process has also been used in volume production for etching the memory holes in 3D NAND flash: at depths of around $10\text{ }\mu\text{m}$ and aspect ratios above 50:1, the low temperatures allow etch chemistries that do not work at room temperature, and roughly double the etch rate of conventional dielectric processes.

Atomic layer etching (ALE)

Surface activation and removal are split into separate, self-limiting half-steps and repeated cyclically. The removal per cycle is on the order of one atomic layer, controlled via the number of cycles. ALE is used wherever individual nanometers determine functionality, such as in releasing

channels and etching gate structures.

Selectivity and etch rate can be strongly influenced by the etch gases used. For silicon and silicon compounds, chlorine and fluorine are primarily employed.

Etch gases used in dry etching

Processes do not necessarily run with a single gas mixture and constant etch parameters throughout. Native oxide on polysilicon, for example, can first be removed with a high etch rate and low selectivity. The polysilicon is then etched with high selectivity to the underlying layer. Real-world recipes therefore consist of several steps with different gas mixtures, powers, and pressures.

The following table gives an overview of gases used in dry etching.

Layer	Process gases	Remark
SiO ₂ , Si ₃ N ₄	CF ₄ , O ₂	F etches Si, O ₂ removes carbon (C)
	CHF ₃ , O ₂	CHF ₃ acts as a polymer, increased selectivity against Si
	CHF ₃ , CF ₄	
	CH ₃ F, CH ₂ F ₂	improved selectivity of Si ₃ N ₄ against SiO ₂
	C ₂ F ₆ / SF ₆	
	C ₃ F ₈	increased etch rate compared to CF ₄
	C ₄ F ₆ , C ₄ F ₈ + O ₂ , Ar	standard chemistry for deep structures (contact holes, memory holes in 3D NAND); the carbon-rich molecules form a polymer layer on the mask and sidewall, O ₂ controls its thickness
	BCl ₃ , Cl ₂	no contamination by carbon (C)
Poly-Si	SiCl ₄ , Cl ₂ / HCl, O ₂ / SiCl ₄ , HCl	
	HBr / Cl ₂ / O ₂	improved selectivity against photoresist and SiO ₂ ; standard chemistry for gate structures
	SF ₆	high etch rate, good selectivity against SiO ₂
	NF ₃	high etch rate, isotropic
	HBr, Cl ₂	
monocrystalline Si	HBr, NF ₃ , O ₂	higher selectivity against SiO ₂
	BCl ₃ , Cl ₂ / HBr, NF ₃	
	SF ₆ / C ₄ F ₈ SF ₆ , O ₂	deep etching: cyclic in the Bosch process, or at low temperatures in the cryogenic process

	Cl_2	isotropic etching
	BCl_3	only low etch rate, additionally binds residual moisture and native Al_2O_3
Al alloys	$\text{BCl}_3 / \text{Cl}_2 / \text{CF}_4$	anisotropic etching
	$\text{BCl}_3 / \text{Cl}_2 / \text{CHF}_3$	improved sidewall passivation
	$\text{BCl}_3 / \text{Cl}_2 / \text{N}_2$	higher etch rate, no carbon contamination
W, TiN, Ti	$\text{SF}_6 / \text{NF}_3$	etchback of tungsten in contact holes
	$\text{Cl}_2, \text{BCl}_3$	barrier and metal gate layers

Historically, bromine-containing chlorofluorocarbons such as CF_3Br were also used for monocrystalline silicon. As ozone-depleting substances, they are banned under the Montreal Protocol and have been replaced in manufacturing by HBr mixtures.

Metallization: why copper is not etched

Etching of aluminum alloys has become less important with the transition to copper interconnects. Copper does not form compounds with chlorine or fluorine that are volatile at process temperature and can therefore practically not be dry-etched. Instead, in the damascene process, the trench is first etched into the dielectric, copper is then deposited, and the excess is removed by chemical mechanical polishing. Aluminum continues to be patterned for bond pads as well as in power and analog technology.

Climate impact of the process gases

The perfluorinated etch and cleaning gases are chemically extremely stable – precisely the property that makes them useful in the process. In the atmosphere, they are therefore barely broken down and act as very potent greenhouse gases. According to the sixth IPCC report, the 100-year global warming potentials are around 7,400 for CF_4 , around 12,400 for C_2F_6 , around 14,600 for CHF_3 , around 17,400 for NF_3 , and around 25,000 for SF_6 . Based on current estimates, CF_4 remains in the atmosphere for several tens of thousands of years.

On the manufacturing side, the exhaust of every tool is treated individually (point-of-use abatement), either thermally, catalytically, or in a plasma torch. Reactive gases such as NF_3 are broken down by more than 99 %, but CF_4 only partially; moreover, it is also formed as a decomposition product of other fluorine compounds. The contribution is therefore reduced primarily at the process level itself: by replacing C_2F_6 with NF_3 for chamber cleaning, lower gas flows, shorter etch times, and processes such as cryogenic etching with a higher etch rate. Regulatorily, these substances are covered by the EU regulation on fluorinated greenhouse gases; in addition, a restriction on PFAS is being discussed under REACH, with exemptions and long transition periods so far for

semiconductor manufacturing.

Special Case: Bosch Process (Deep Reactive Ion Etching)

An important advancement of reactive ion etching is the Bosch process (DRIE), which uses a cyclic alternation of etch and passivation steps to achieve extremely high aspect ratios with nearly vertical sidewalls – significantly more than continuous etching could achieve.

Since it is used primarily in microsystems technology to pattern deep trenches and to singulate MEMS devices, it is described in detail in the Micromechanics section: [DRIE: Deep Reactive Ion Etching](#).