SVC Topics

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Reactive Plasma Stripping

Vacuum systems are used to remove unwanted gases and vapors from a processing chamber before backfilling with the desired processing gases.

Vacuum systems are also used to control the partial pressures of processing gases in atmospheric pressure chemical vapor deposition (AP-CVD), and in vacuum processes such as: subatmospheric CVD (SA-CVD), plasma enhanced CVD (PECVD), high-density plasma CVD (HDP-CVD), plasma etching, sputter deposition, evaporation, ion plating, and arc deposition. In these processes, a portion of the material being deposited, or byproducts, often ends up on non-removable surfaces in the vacuum chamber ("vacuum surfaces"). The deposits can affect the performance of the vacuum system and can flake off, putting particulate contamination in the system. These deposits can be removed by wet-chemical cleaning, but this means disassembling the system and handling aggressive chemicals such as hydrofluoric acid (HF).

An alternative to wet cleaning is to clean the surfaces by reacting the materials with an "activated" reactive gaseous material to form a volatile reaction product that is pumped away by the vacuum system. The simplest reactive cleaning process is the removal of hydrocarbons by reaction with oxygen from an oxygen (or air) plasma discharge to form CO and CO_2.[1] Hydrocarbons can also be removed by reaction with a hydrogen plasma to form more volatile hydrocarbons, such as methane. Plasma "activation" typically means dissociation of the molecular compound to form a reactive atomic or molecular species. For oxygen, the dissociation can form atomic oxygen, which then rapidly reacts with diatomic oxygen to form ozone (O_3), a chemically reactive species. The activation can take place in the region to be cleaned (*in situ*) or the cleaning can be in a separate ("remote") region from the plasma-activation region.

Plasmas containing perfluorocompounds (PFCs), such as CF_4, C_2F_6, C_3F_8 (C-F molecules), NF_3, and SF_6, provide activated fluorine for removing silicon, silicon oxides, silicon nitrides, and many metals.[2] When etching silicon, oxygen is sometimes added to the plasma to oxidize the silicon for more rapid removal by the fluorine. Plasmas of BCl_3 provide activated chlorine for removing aluminum. The reactive gases are often mixed with argon, which has metastable excited states with energies greater than the dissociation energy of the reactive molecule. This aids activation of the molecular species.

The reactive molecular species are activated by bond scission, which produces a complex range of fragments of the original molecule. The simplest action is to produce atomic fluorine. Bond strengths of common reactants are: $NF_3 \Longrightarrow NF_2 + F$ (59 kcal/mole), $CF_4 \Longrightarrow CF_3 + F$ (130 kcal/mole) and $C_2F_6 \Longrightarrow C_2F_5 + F$ (127 kcal/mole). One consideration in the choice of activation configurations (remote vs. *in situ*) is the lifetime of the activated species.

Activated species from NF_3 have a longer lifetime than activated species from C-F molecules. By using NF_3 in an optimized remote, high-power, microwave reactor configuration, operating at several Torr pressure, the most effective activation (>95% dissociation) of the reactant gas can be achieved.[1,2]

Reactants	Reactor Type	Film	Cleaning Material/Technique
$SiH_4 : O_2/N_2$	AP-CVD	SiO_2, Si_3N_4	HF/manual wet clean, ClF_3/un-activated gaseous clean
SiH_4	AP-CVD	poly-Si	HF/manual wet clean
TEOS : O_3	AP-CVD	SiO_2	HF/manual wet clean
TEOS : O_3	SA-CVD/thermal	SiO_2	C_2F_6, C_3F_8, NF_3/*in situ* plasma, NF_3/remote plasma
WF_6	SA-CVD/thermal 50-100 Torr	W	C_2F_6, C_3F_8, NF_3/*in situ* plasma, NF_3/remote plasma
$SiH_4 : O_2/N_2$	PECVD 0.1-10 Torr	SiO_2, Si_3N_4	C_2F_6, C_3F_8, NF_3/*in situ* plasma, NF_3/remote plasma
TEOS : O_2/N_2	PECVD 0.1-10 Torr	SiO_2, Si_3N_4	C_2F_6, C_3F_8, NF_3/*in situ* plasma, NF_3/remote plasma
$SiH_4 : O_2$	HDP-CVD 0.005-0.010 Torr	SiO_2	C_2F_6, C_3F_8, NF_3/*in situ* plasma, NF_3/remote plasma

TEOS = tetraethoxysilane

The Global Warming Potential

The Global Warming Potential Infinite time (GWP•) is a measure of the ozone-depleting capability of a gas, and takes into account its lifetime in the atmosphere and its IR adsorption properties. The GWP• of gases are relative to carbon dioxide as the standard ($CO_2 = 1$). The GWP• for the PFCs are: $CF_4 = 850{,}000$, $C_2F_6 = 230{,}000$, $C_3F_8 = 130{,}000$, $SF_6 = 230{,}000$, and $NF_3 = 18{,}000$. Therefore, PFCs can pose a waste-disposal problem when used in large amounts. NF_3 is the better material from a GWP• standpoint.

The effluent from the plasma cleaning process consists of a complex mixture of unused reactants, fragments of reactant molecules, and reaction products. These species can polymerize downstream of the reaction region, giving further cleaning problems. In C-F plasma cleaning, oxygen is often added to the plasma to reduce polymer formation. Products from NF_3 cleaning seem to be less prone to polymerization than those from the C-F cleaning species. Adding oxygen to the NF_3 plasma will generate NO_X, which is a hazardous air pollutant (HAP).

Some of the waste materials are soluble in water and can be removed by wet "scrubbers." Some of the materials are not water soluble and must be removed by other means. These include: reaction with other gases before or after the mechanical vacuum pumping stage to produce water soluble compounds, or cryogenic condensation after the pumping stage. For example, F_2 can be converted into water-soluble HF by thermal reaction with hydrogen at 600-900°C. It is best to reduce the amount of gaseous materials that must be treated and removed. This makes it attractive to clean using the remote plasma activation reactors since they can be designed to maximize activation and thereby reduce the amount of reactant gases needed to clean a system.

Reactive plasma cleaning is widely used in the semiconductor industry to clean atmospheric and sub-atmospheric CVD reactors that are used to deposit silicon, silicon oxide, and silicon nitride, as well as some metals. The table shows some common CVD precursors, CVD reactor configurations, deposited species, and cleaning techniques.

Reactive plasma cleaning is used in PVD processing for *in situ* cleaning of substrate surfaces in the deposition chamber to remove recontamination that has occurred after the primary cleaning step, as well as to clean vacuum surfaces. Reactive plasma cleaning is typically done in a pressure range of a few Torr to 10^{-2} Torr, using DC- or RF-generated plasmas. The cleaning rate is roughly proportional to the gas pressure. For example, in reactive PVD deposition of carbon-containing materials, oxygen plasma cleaning is used to remove the "sooty" deposit on vacuum surfaces formed by the gas-phase decomposition and nucleation of the carbon-containing precursor vapor. Oxygen plasma cleaning can also be used to remove hydrocarbon oil contamination from vacuum surfaces. Plasma "cleaning" can also be used to convert a mobile contaminant, such as silicone oil, to an immobile contaminant, such as SiO_2, by reaction with activated oxygen.[1]

Reactive gaseous cleaning can also take place without the presence of a plasma. For example, molecular fluorine can be activated by thermal decomposition of the fluorine molecule to atomic fluorine on a hot tungsten surface (thermal activation) (F_2 ==100% ==> 2F at 1100°C). Oxygen can be "activated" by decomposition of the oxygen molecule by ultraviolet radiation (photodissociation). ***P&SF***

Footnotes

1. Care must be taken when using oxygen plasma cleaning, particularly at higher pressures, in hydrocarbon-oil-sealed vacuum-pumped systems. Compression of pure oxygen in contact with the oil can cause an explosion (diesel effect). This can be avoided by using "artificial air" ($20\%O_2 : 80\%N_2$) in the plasma or by diluting the oxygen before it reaches the vacuum pump. Other alternatives are to use oil-free ("dry") vacuum pumps or use oxygen-compatible oil, such as Fomblin™, in the vacuum pump.
2. Contact Air Products Technical Information Center (800/752-1597) for technical information on process gases.
3. Adapted from second reference.

Bibliography

S. Radoux, S. & J.G. Langan, "Remote NF_3 Chamber Clean Virtually Eliminates PFC Emissions from CVD Chambers and Improves System Productivity," *Semiconductor FabTech*, 9th ed. p. 107, (1998/99).

W. Hobler, X. Chen & M. Naddy, "Reducing PFC Emissions from CVD Reactors." *Vac ThinFilm*, **2**(2) 26 (1999).