Surface Preparation for Film and Coating Deposition Processes

3.1 Introduction

Surface preparation [1] includes surface treatments (surface modification) to change the properties of the surface in a desirable way [2] as well as cleaning, which is the reduction of surface contamination to an acceptable level. One objective of any surface preparation procedure is to produce as homogeneous a surface as possible. Reproducible surface preparation, as well as the associated handling and storage techniques, are obtained by having

and following appropriate written specifications and procedures. In order to have reproducible surface preparation processes it is generally necessary to have a reproducible and homogeneous starting surface.

Surface modification can include surface treatments such as roughening or smoothing the surface, making a harder surface by plasma treatment, or by activating a polymer surface by plasma treatment. Care must be taken to ensure that the surface preparation processes do not change the surface in an undesirable or in an uncontrolled manner.

Cleaning is used so that desirable processing and film/coating properties can be obtained. As a practical matter a 'clean' surface is one that contains no significant amounts of undesirable material; thus what constitutes a clean surface depends on the requirements. The requirements range from those concerned with monolayer coverage and atomically clean surfaces, to gross cleaning such as used for fusion welding. General contamination such as a hydrocarbon surface layer can cause a low nucleation density of the depositing film on a surface, cause poor overall adhesion of a film to a surface, and prevent good electrical contact in the case of deposited electrical contacts. Local contamination (film or particle) can result in locally poor adhesion of a film to a surface giving pinholes in the film. Figure 3.1 shows how pinholes are formed in deposited thin films by particulate contamination on the surface, inclusions in the surface or by surface features. Cleaning should address local surface conditions such as porosity, embedded particles, steps, roughness, etc., that affect film properties, produce pinholes, and local loss of adhesion.

External cleaning takes place outside the deposition system as a separate process in a controlled environment. It includes gross cleaning to remove large amounts of contaminants often by removing some of the substrate surface, and specific cleaning, which is directed toward removing a specific contaminant such as particulates, or hydrocarbons. A clean processing environment, and proper handling and storage after the external cleaning are important to minimize recontamination of the cleaned surface before it is placed in the deposition chamber. For example, to control recontamination by particulates, a filtered air cleanroom can be used. Problems with recontamination are lessened if the cleaning procedure is integrated into the deposition line, the prepared surfaces are used immediately, and/or if there is a final in situ cleaning process in the deposition system.

The objective of cleaning processes is to facilitate the fabrication of an acceptable product in the most reproducible and economical way. Cleaning processes should be as simple and effective as possible in order to meet the processing requirements. Elaborate cleaning processes are often expensive and self-defeating. Often there is a tradeoff between the various stages of the cleaning process, handling/storage, and previous as well as subsequent processing. This can mean that simple changes in one stage make complex changes in another step unnecessary. The processing sequence as a whole should be considered when developing a cleaning process.
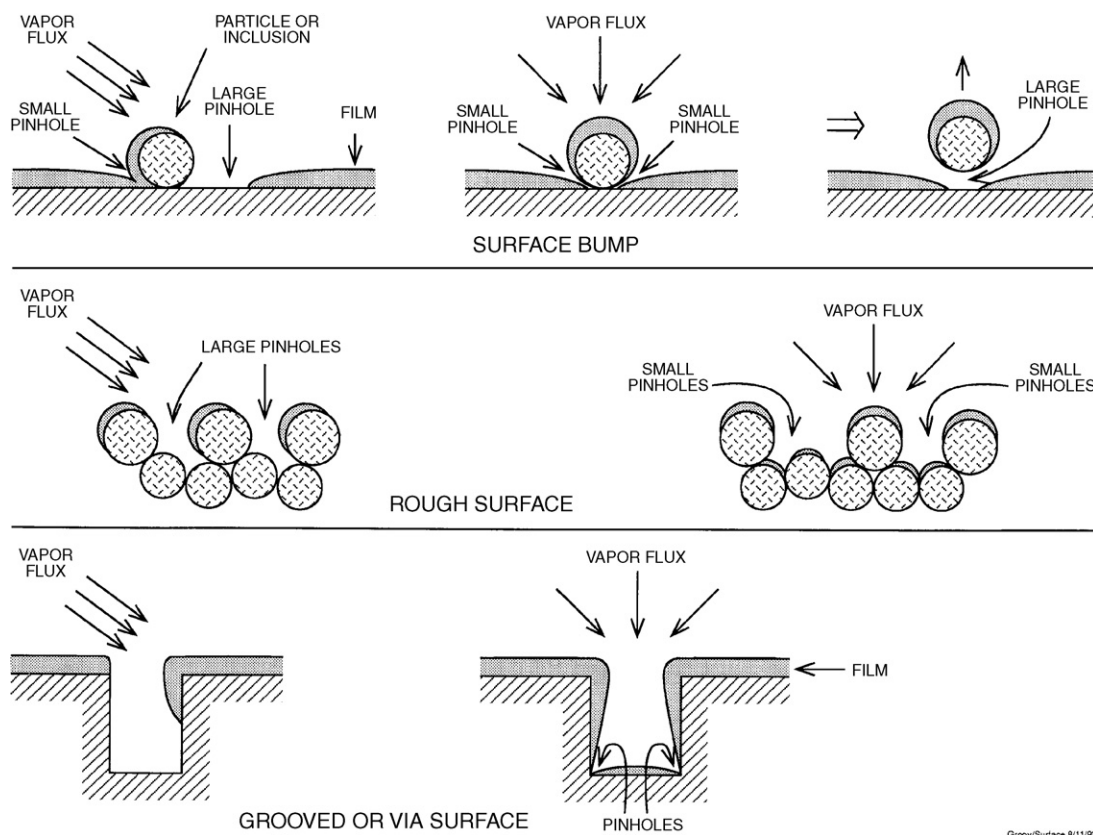
Figure 3.1: Pinhole formation. [From Society of Vacuum Coaters Education Guides to Vacuum Coating Processing (2009) – Atomistic Film Growth and Resulting Film Properties – Pinholes, with permission.]

3.2 External Cleaning

3.2.1 Gross Cleaning

In general, gross cleaning takes some of the substrate surface with it and can change the surface chemistry or morphology in an undesirable manner. After the gross contamination is removed, it is important to control the type and amount of contaminants to which the surface is exposed.

3.2.1.1 Stripping

In some cases, such as removing deposited film material from fixtures, or reprocessing parts with defective coatings, large amounts of undesirable material must be removed from a surface and the process is called stripping. Stripping is usually done by mechanical abrasion or by chemical etching.

3.2.1.2 Abrasive Cleaning

The removal of gross contamination by abrasive cleaning includes the use of:

- abrasive surfaces, e.g. sandpaper, emery paper, steel wool, Scotch-brite[TM] and Soft-scour[TM] scouring pads

- abrasive powders in a paste or fluid carrier, e.g. SiC, Al_2O_3, diamond, precipitated calcium carbonate ($CaCO_3$), CeO, and Snow-Floss[TM] (diatomaceous earth with the calcium carbonate removed, leaving a friable silica network)

- impacting particles entrained in a high-velocity gas or liquid stream: vapor honing, glass bead blasting, liquid honing, grit blasting, sand blasting, etc.

- abrasives combined with an etchant to provide chemical–mechanical abrasion and polishing.

Abrasive particles can be used wet or dry. Commercially available abrasive particles include:

- aluminum oxide

- diamond

- cerium oxide

- glass beads

- crushed glass

- silicon carbide

- fractured cast iron grit

- sodium bicarbonate

- silica sand.

Dry glass bead blasting is a commonly used cleaning technique but, as with other grit abrasive techniques, can leave shards of glass embedded in soft surfaces. The amount of grit embedded depends on how long the glass beads have been used, i.e. how much they have been fractured. Water-soluble particles can be used for abrasive cleaning and allow easy removal of the water-soluble embedded particles. For example, the Prophy-jet[TM] dental abrasive unit uses 5 μm sodium bicarbonate (baking soda) particles entrained in a high-velocity water stream.

Grit blasting uses grit such as fractured cast iron, alumina, or silica, of varying sizes and shapes accelerated in a gas stream to deform and gouge the surface. Particles can be entrained in a high-velocity gas steam by using a siphon system or a pressure system such as used in sand blasting equipment. In addition to removing gross contamination, grit blasting roughens

the surface. The Society of Automotive Engineers (SAE) has specifications on grit size and type, e.g. SAE Specification J444 for cast iron grit in the range G10 (2820 µm maximum size) to G325 (120 µm maximum size), which gives the percentage by weight allowed on standard screens. Bombardment of a surface by grit is like shot peening and places the surface in compressive stress which may produce unacceptable distortion of the surface. Blasting can also be done with plastic media, which is less damaging than the harder grits; however, it can leave organic contamination on the surface.

Wet blasting uses an air-blasted slurry of fine abrasives in chemically treated water. It is sometimes called liquid honing since it is usually used when dimensional tolerances have to be maintained. Abrasion cleaning can be very mild, such as the use of CeO polishing slurry in a high-throughput wash system to preclean glass before the standard wash cycle [3].

3.2.1.3 Wet Chemical Etching

Chemical etching can be used to remove surface material along with the contaminants. This is a very useful technique for getting the surface into a known condition. Pickling is a term used to denote the removal of the large amounts of oxides (scale) that are formed on metals during the metal fabrication process. The process generally involves an alkaline clean before acid pickling in order to get uniform wetting and etching. For example, aluminum and aluminum alloys can be pickled by immersion in various combinations of sulfuric, nitric, hydrofluoric, and chromic acids; copper and copper alloys can be pickled in combinations of sulfuric and oxidizing acids, and iron and steel are pickled in sulfuric or hydrochloric acid solutions. Chemical etchants can be highly selective in their action. This can result in preferential etching of grain boundaries and when etching a two-phase system. Mild pickling is called a bright dip. Acid cleaning of metals can have the detrimental effect of introducing hydrogen into the surface and embrittling metals and ceramics [4]. If hydrogen embrittlement is a concern, either do not use an acid or the etched part should be high-temperature vacuum fired after etching.

Etching removes surface layers such as oxides, eliminates or blunts surface cracks in brittle materials, and removes difficult-to-remove contaminates. Common etchants for glass include sodium or ammonium bifluoride (100 g of ammonium bifluoride salt to 800 ml deionized water), trisodium phosphate, which is a mild etchant, and hydrofluoric acid, which is a very strong etchant. Hydrofluoric (HF) acid solution is a common etchant for silicon and can leave a silicon surface either hydrogen-terminated or hydroxyl-terminated. The silicon surface is hydrophobic if hydrogen-terminated and hydrophilic if hydroxyl-terminated.

When using etchants for cleaning, care must be taken to prevent selective removal of surface constituents that are important to further processing. For example, etching glass-bonded alumina ceramics in HF results in selective removal of the glass [Ca–Mg–Al–Si–O] phase which can weaken the ceramic surface and result in poor adhesion. Etchants can change the

surface chemistry. For example, acid etching a soda lime glass surface, which is normally basic, leaches the sodium from the surface and makes the surface acidic, which changes its wetting properties [5].

Sometimes chemical etching does not remove some constituents from a surface and leaves a smut that must be removed by another etching step. For example, etching copper-containing aluminum alloys with NaOH leaves a copper smut and/or a silicon smut on the surface. The copper smut can be removed by an HNO_3 etch and a copper/silicon smut can be removed with a HNO_3/HF etch. In some cases an etchant can be devised that etches all the constituents uniformly. For example, in etching Al:Cu:Si alloys a concentrated nitric acid (100 ml) plus ammonium bifluoride (6.8 g) etch is used. The etching mechanism is solution of the copper, oxidation of the aluminum and the silicon, then etching of the resulting oxides. The etchant actually etches silicon more rapidly than the aluminum.

3.2.2 Specific Cleaning

3.2.2.1 Solvent Cleaning

Some contaminants can be removed from surfaces by solvents that dissolve (take into solution) the contaminant. Polar solvents such as water and water–alcohol mixtures are used to dissolve ionic materials that are polar contaminates. Non-polar solvents such as the chlorinated hydrocarbon (chlorofluorocarbon (CFC)) solvents are used to remove non-polar contaminates such as grease. Often there is a mixture of solvents used to dissolve both polar and non-polar contaminates. Solvents can vary greatly as to their ability to dissolve contaminants and their effectiveness needs to be determined by determining the solubility parameter for specific contaminants. The solubility parameter is the maximum (saturation) amount of a specific contaminant that can be dissolved in a specific amount of the solvent. Many non-chlorinated hydrocarbon-based or petroleum-based materials are used as solvents.

Chlorinated hydrocarbon non-polar solvents such as trichloroethylene are often preferred to hydrocarbon-based or petroleum-based solvents because of their lower flammability (i.e. higher flashpoint as determined by ASTM D-1310-63). However, there is concern with the toxicity, carcinogenic properties, and ozone-depleting action of some of the materials and they should be used in closed recirculating systems.

Chlorinated solvents can react with water to form HCl, which can react with metals, particularly aluminum, producing corrosion. For example, chlorinated solvents can react with Al, Mg, Be, and Zn (white metals) to form inorganic salts. Often stabilizers are added to the chlorinated solvents to reduce their tendency to react with water and form acids. If stabilizers are not used the pH of the cleaner should be monitored to keep a pH in the 6–7 range [6]. If there is a possibility of solvent trapping due to incomplete rinsing, particularly in stressed metal joints, chlorinated solvents should not be used since chloride residues enhance stress
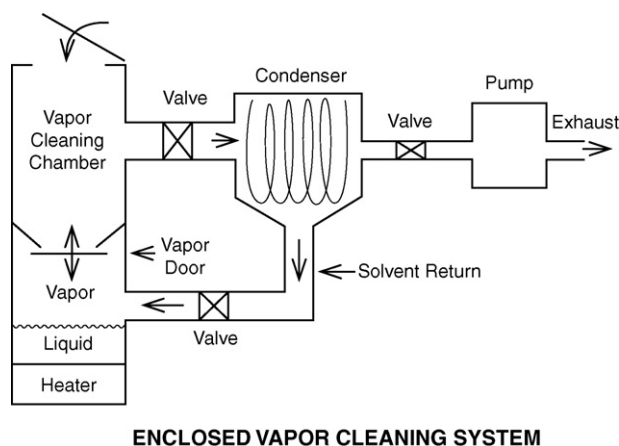
ENCLOSED VAPOR CLEANING SYSTEM

Figure 3.2: Recycling with VOCs. [From SVC Education Guides to Vacuum Coating Processing (2009) – Surface Preparation: Enclosed and Closed-Loop Cleaning Systems, with permission.]

corrosion. Cleaners containing chlorine-based oxidants can present the same stress corrosion problem.

Volatile organic compounds (VOCs) are those that have boiling points below 138 °C. The discharge of VOCs into the environment is regulated by local, state, and federal laws. In order to comply with these regulations it may be necessary to recycle the material by condensation of the vapors or to thermally destroy the vapors by burning before they are released into the atmosphere. Figure 3.2 is one such recycling system. Many clothes dry-cleaning establishments use VOCs with intensive recycling.

Some solvents for removal of greases are: *N*-methyl-2-pyrrolidone-based solvents such as GAF NMP™ and GAF M-PYROL™ (22–24), terpene-based solvents such as Bioact EC-7™ and Genesolv 2000™, and *n*-propyl bromide (nPB), as well as the Fluoroinerts™, which do not contain chlorocarbon bonds. Reports indicate that the terpenes may be as effective as CFCs in many instances, although they have a greater tendency to leave residues. Terpenes suffer from the fact that they have low flash points (about 49 °C) and reduced lower explosive limits (LELs).

Supercritical fluids (SCF) can be used as solvents. There is a good correlation between the ability of a simple solvent to dissolve materials and its density. Solvents can be densified most easily when they are in the supercritical state, i.e. no distinction between the liquid and vapor state. Carbon dioxide (CO_2) has been shown to have a Hildebrand solubility parameter that can vary from 0 in the gas to 10 under high-pressure supercritical conditions. Values of 6–8 are typical, which is about the same as hexane and carbon tetrachloride. Supercritical CO_2 fluid (SCF-CO_2 – critical point 31 °C, 74 bar pressure) has the advantage that it is stable, has low

toxicity and minimal cost, and is a solvent for many organic materials. Liquid CO_2 is used in some clothes dry-cleaning systems.

3.2.2.2 Alkaline Cleaners

Alkaline cleaners (generally silicate and phosphate based) are saponifiers which convert organic fats to water-soluble soaps. Alkaline cleaners have a pH of about 11 and are generally used hot. After using alkaline cleaners the surface should be neutralized by an acid dip before the water rinse since alkali salts adhere strongly to surfaces. Clean oxide surfaces strongly adsorb hydrocarbons, and detergents or solvents normally do not completely remove the hydrocarbons; alkaline or oxidative cleaners must be used to remove the remaining hydrocarbons. For example, carbonized hydrocarbon contaminants on glass can be removed by cleaning in a saturated water solution of KOH at 75 °C. Strong alkaline cleaners can etch aluminum and oxide surfaces, particularly glasses, so solution strength (pH), temperature, and exposure times should be carefully controlled.

Alkaline cleaners are used to clean the oil and oxide off steel drills. After rinsing in an acid rinse they are rinsed in a final rinse containing a flash rust inhibitor to protect the surfaces from oxidation as they dry.

3.2.2.3 Detergent (Soap) Cleaners

Detergent cleaning is a comparatively mild cleaning technique. In detergent cleaning, the detergent surrounds particles, taking them into suspension without actually dissolving the material. This action is assisted by wetting agents and surfactants that loosen the particles from the surface. Liquid dishwasher soap is an excellent detergent for many applications such as cleaning polymer surfaces. A major problem with soaps is that metal ions, such as the calcium and magnesium, which are found in hard water, make the soaps insoluble thus leaving a residue. Deionized (DI) water should always be used for residue-free detergent cleaning. Many detergents contain phosphates that can be environmentally harmful and subject to pollution regulations.

3.2.2.4 Solution Additives

When cleaning a surface with a fluid, the surface energies [7] of both the solid and the liquid, as well as the interfacial energy between the two, are important in the wetting and spreading of the fluid on the surface and the ability to displace particles and other contaminants from the surface. Wetting agents reduce the surface energy of fluids. Table 3.1 shows the effect of some additives on the surface tension of water.

Surfactants are the generic name for surface-active agents that reduce the interfacial energy of materials in contact. Surfactants used with water have both hydrophobic (water-hating) and hydrophilic (water-loving) groups. They dissolve in water by virtue of their hydrophilic groups and lower the surface energy of water to about 30 mJ/m^2. The surfactant collects at the

Table 3.1: Surface tension of fluids

Material	Temperature	Surface tension (in air)
Pure H_2O	18 °C	= 73.05 mJ/m^2 (dyne/cm)
	50 °C	= 67.91
	100 °C	= 58.9
n-Propanol	25 °C	= 23.32
H_2O + 30 vol% *n*-propanol	18 °C	= 26.9
Ethyl alcohol	30 °C	= 21.5
H_2O + 50 vol.% ethyl alcohol	30 °C	= 27.5
1000 g H_2O + 34 g NH_4OH	18 °C	= 57.05
1000 g H_2O + 17.7 g HCl	20 °C	= 65.75
1000 g H_2O + 14 g NaOH	18 °C	= 101.05
1000 g H_2O + 6 g NaCl	20 °C	= 82.55

interface between immiscible substances, such as oil and water, and lower the interfacial energy. Surfactants should only be used in deionized water.

In solutions pH adjusters are used to aid in the cleaning action. In general, it is found that basic solutions clean better than acidic solutions if chemical etching is not involved. The pH of the cleaning solution is often adjusted to the basic side using ammonia or ammonium hydroxide.

Chelating agents keep the normally insoluble phosphates, which are formed in hard water detergent cleaning, in solution. Glass cleaning solutions use chelating agents such as ethylene diamine tetraacetic acid (EDTA) and citric acid with salts containing hydroxyl and amine substitutes.

### 3.2.2.5 Wet Reaction Cleaning

Reactive cleaning uses liquids, gases and vapors or plasmas to react with a contaminant to form a volatile or soluble reaction product. Reactive cleaning liquids are often oxidizing solutions. Many acid-based systems can be used as oxidants. One system commonly used in the semiconductor industry is the 'piranha solution', i.e. hot (50 °C) concentrated sulfuric acid plus ammonium persulfate. The addition of the solid ammonium persulfate to the hot sulfuric acid produces peroxydisulfuric acid which reacts with water to form H_2SO_5 (Caro's acid), which further decomposes to form free atomic oxygen. The ammonium persulfate should be added just before the immersion of the substrate into the solution. The effectiveness of this oxidation technique can be shown by first placing a piece of paper in the hot sulfuric acid where it is carbonized, then adding the ammonium persulfate and watching the carbon disappear. This treatment is sometimes followed by a brief dip in a 10:1 solution of water and HF or immersion for 20 minutes in a hot solution of hydrogen peroxide and ammonium hydroxide in the ratio H_2O:H_2O_2 (30%):NH_4OH (29%) at 80 °C. Another similar oxidizing solution uses stabilized sulfuric acid–hydrogen peroxide.

A hot chromic–sulfuric acid cleaning solution prepared from potassium dichromate and sulfuric acid provides free oxygen for cleaning but has a tendency to leave residues and the surface must be rinsed very thoroughly.

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

Nitric acid can also be used as the oxidizing agent. Nitric acid together with an oxide etchant such as hydrofluoric acid or ammonium bifluoride can be used to simultaneously oxidize and etch oxidizable material such as the silicon in some aluminum alloys.

Hydrogen peroxide is a good oxidizing solution for cleaning glass. Often boiling 30% unstabilized H_2O_2 is used. The most common hydrogen peroxide has been stabilized, which reduces the release of free oxygen. Unstabilized H_2O_2 must be stored in a refrigerator to slow decomposition. Hydrogen peroxide is sometimes used with ammonium hydroxide, to increase the complexing of surface contaminants, and is used at a ratio of:

8 (30% H_2O_2):1 (NH_4OH):1 (H_2O)
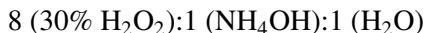
However, the decomposition rate of the unstabilized H_2O_2 is greatly increased by combination with ammonium hydroxide.

In cleaning silicon, the ammonical hydrogen peroxide solution may be followed by an acid rinse and this procedure is called the RCA cleaning procedure. This solution has also been shown to be effective in removing particulate contamination from a surface. The wettability of silicon in an alkaline solution is very dependent on the prior surface preparation (such as etching) and shows a profound hysteresis with the number of wetting cycles. A technique called the modified RCA cleaning technique is performed using the following steps:

1. H_2SO_4:H_2O_2 at a ratio of 4:1
2. HF:DI water 1:100
3. NH_4OH:H_2O_2:DI water 1:1:5
4. HCl:H_2O_2:DI water 1:1:5
5. DI rinse.

Oxidative cleaning can be performed using chlorine-containing chemicals. For example, a water slurry of sodium dichloroisocyanurate (i.e. pool chlorine), which has 63% available chlorine, can be used to scrub an oxide surface to remove hydrocarbon contamination. This combines mechanical scrubbing with oxidation and improves the cleaning properties.

Anodic oxidation in an electrolysis cell can be used to clean surfaces. For example, carbon fibers, which are formed by the pyrolysis of polymer fibers, have a weak surface layer. This

layer can be removed by anodically oxidizing the surface in an electrolytic cell, followed by hydrogen firing. This treatment increases the strength of the carbon fiber and improves the bond when the fiber is used as part of a composite material.

3.2.2.6 Reactive Gas Cleaning

Reactive gas cleaning relies on the formation of volatile reaction products of the contaminant. Oxidation cleaning is usually accomplished using oxygen, chlorine, fluorine, ozone, NO, etc. If non-volatile products result from oxidation (e.g. silicone oil to silica), then a residue is left on the surface. Oxidation cleaning can be used on surfaces where surface oxidation is not a problem.

Reactive gas cleaning uses a reaction with a gas at high temperature to form a volatile material. For example, air firing of an oxide surface oxidizes all of the hydrocarbons and they are volatilized. High-temperature air fire is an excellent way to clean surfaces that are not degraded by high temperature. For example, alumina can be cleaned of hydrocarbons by heating to 1000 °C in air. Some care must be taken in furnace firing in that particulate generation from the furnace liner may be a source of undesirable particulates and sodium from the insulating material may be an undesirable contaminant for semiconductor device fabrication. Self-cleaning kitchen ovens clean by oxidation at about 425 °C.

The use of oxidation at atmospheric pressure by ozone (O_3) created by ultraviolet (UV) radiation, which also causes bond scission of the hydrocarbon contaminants, has greatly simplified the production, storage, and maintenance of hydrocarbon-free surfaces [8, 9]. The UV is produced by a mercury vapor lamp in a quartz envelope so that both the 1849 Å and the 2537 Å radiation is transmitted. The mercury lamps can be custom made to a variety of shapes for specific applications. Ozone adsorbs UV so the substrates should be as close as possible to the UV source. UV radiation intensity should be maintained to about 1–10 mW/cm^2 at the substrate surface. In the UV/O_3 chamber the air may be stagnant or flowing. If flowing air is used, the air should be filtered.

Typical exposure times for cleaning are from a few minutes to remove a few monolayers of hydrocarbon contamination to hours or days or weeks for storage of cleaned surfaces. The UV/O_3 cleaning technique has the advantage that it can be used as an in situ cleaning technique. The UV/O_3 cleaning technique is also useful for cleaning holes (vias) in surfaces. In a correctly operating system, ozone can be detected by smell when the chamber is opened. The smell is similar to that of the air after a lightning storm and indicates that the ozone concentration is less than 10 ppm bv. Higher concentrations of ozone deaden the olfactory nerves and are harmful.

SAFETY: OSHA has set a limit of 100 ppb of ozone in the air over an 8-hour day, 6 days per week. At these levels some irritation and discomfort will be noted. A level of 10 ppb is more reasonable.

3.2.2.7 Reactive Plasma Cleaning

Reactive plasma cleaning is a variation of reactive plasma etching (RPE) that can be done in a plasma system separate from the deposition system. Reactive plasma cleaning uses a reactive species in the plasma to react with the surface to form a volatile species which leaves the surface at much lower temperatures than those necessary for reactive gas cleaning. The additional requirement on reactive plasma cleaning is that it does not leave a residue. Oxygen (from pure ('medical') air), hydrogen (pure or as 'forming gas'), fluorine (from SF_6, CF_4, CHF_3, C_2F_6, C_3F_8, or SF_6), and chlorine (from HCl, CCl_4 or BCl_3) are the most widely used reactive gases. The reactive plasma cleaning/etching technique is typically specific and can be used to selectively remove the oxide from the surface and then have a low etch rate for the substrate material. Most metals are more easily cleaned using fluorine gas rather than with chlorine, since the fluorides are generally more volatile than the chlorides. An exception is aluminum, which is commonly etched using BCl_3.

Oxygen (or air) plasmas are very effective in removing hydrocarbons and absorbed water vapor from surfaces. The reaction of the oxygen with carbon on the surface can be monitored using a mass spectrometer to monitor the CO and CO_2 produced. Figure 3.3 shows a plasma cleaning system.
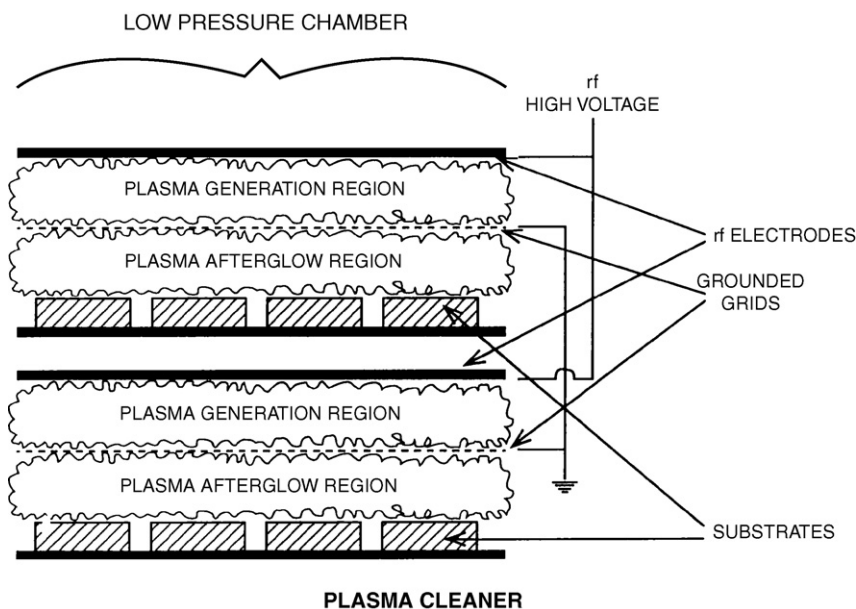
Figure 3.3: Plasma cleaning chamber. [From SVC Education Guides to Vacuum Coating Processing (2009) – Surface Preparation: Plasma Cleaning, with permission.]
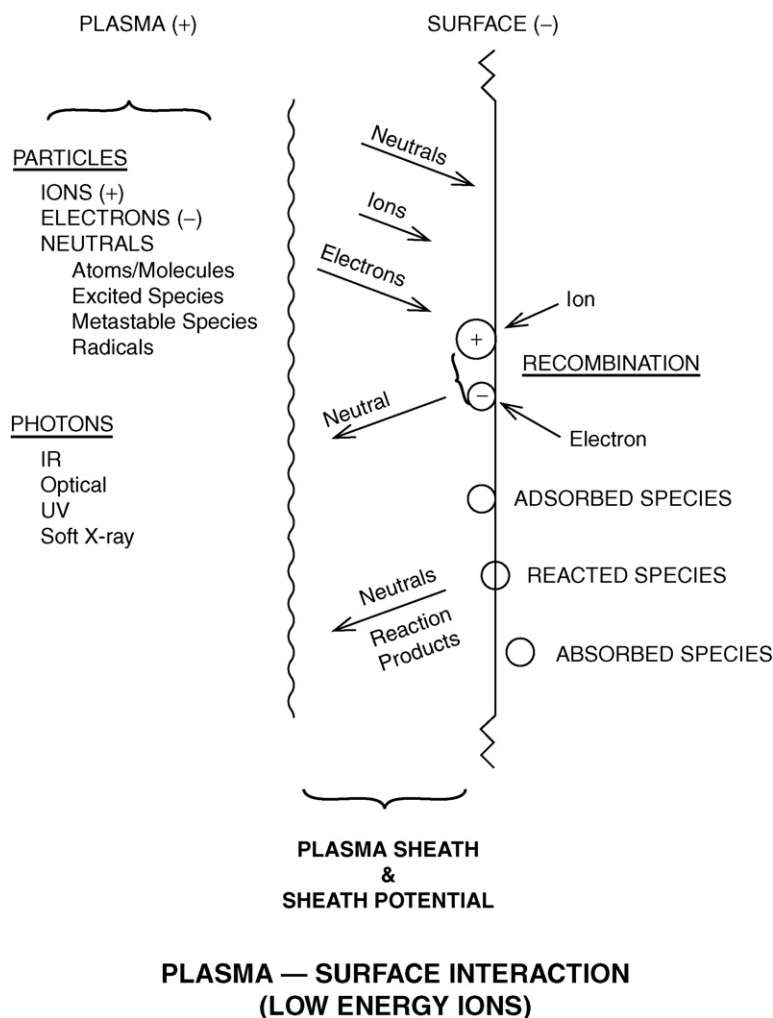
Figure 3.4: Plasma–surface interactions. [From SVC Education Guides to Vacuum Coating Processing (2009) – Surface Preparation: Plasma Cleaning, with permission.]

Figure 3.4 shows the processes that occur on a surface exposed to a plasma. The surface attains a potential (sheath potential) that is negative with respect to the plasma and ions are accelerated from the plasma to the surface. For the case of a cold plasma which has low-energy particles this sheath potential will only be a few volts. When the plasma particles are more energetic or the electrons are accelerated to the surface, the sheath potential can be tens of volts. In addition to being bombarded by ions the surface in contact with the plasma will be bombarded by activated species, excited species, and thermal species. Ions and excited species will release their energies of ionization or excitation when they impinge on the surface. For

example, when a singly charged argon ion impinges on a surface it will give up its kinetic energy attained by acceleration through a potential and its ionization energy, which is 15.7 eV.[1] Locally this release of energy will generate a high local temperature. This process is sometimes called ion scrubbing.

Often mixtures of gases are used for etching and cleaning. Oxygen is often added to the fluorine system to promote the formation of atomic fluorine and thus increase the etch rate of silicon. One of the most common gas mixtures to etch silicon is 96% CF_4 with 4% O_2. A mixture of HF and H_2O can be used to removed SiO_x from silicon. Helium is often added as a diluent and to increase the thermal conductivity of the plasma, thus reducing the temperature rise of the surface during etching. Numerous gases and gas mixtures are available for RPE.

Etching and cleaning with compound gases should be used with caution since the decomposition products (B, C, Si) can react with or deposit on the surface, thereby changing the chemical composition or contaminating the surface. When using a carbon-containing chemical, e.g. CCl_4 or CF_3 in the plasma, a residual carbon contaminate often remains [10]. Using chlorine, HCl, or SF_6 avoids this problem. Exposure to reactive plasmas can leave a reacted/chemisorbed layer of halogen species. This layer can be very important to the sensitization of the surface to atomic nucleation or the wetability of organic species to a surface. RPE of silicon in CCF_4 plasmas has been reported to create a very thin fluoride layer that passivates the semiconductor surface to oxidation.

Reactive plasma cleaning is typically performed at gas pressures of 100–500 mtorr, usually using an RF-excited plasma as shown in Figure 3.3. The reactive gas can be oxygen or air (21% O_2) for cleaning surfaces that can withstand oxidation, or can be hydrogen or forming gas (90% N_2:10% H_2) for those that require a non-oxidizing environment. The surfaces to be cleaned are often placed in a region outside the plasma generation region (i.e. remote plasma region) as shown in Figure 3.3. As depicted in Figure 3.3 the plasma leaks from the plasma generation region through a grid electrode into the cleaning region.

Hydrogen plasmas can be used to remove hydrocarbon contamination when oxygen plasmas are unacceptable. This technique has been used to clean vacuum surfaces (stainless steel) in nuclear fusion reactors [11]. Hydrogen plasma cleaning using a remote plasma cleaning reactor can reduce the temperature necessary for hydrogen reduction of oxides. Such hydrogen plasmas have been shown to remove the oxide on silicon at 500 °C, rather than dry hydrogen

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[1]   An electron volt (eV) is the amount of energy attained by the acceleration of a singly charged particle (ion, ionized particle, or electron) through a potential of 1 volt. One eV is equivalent to a thermal temperature of about 11,000 °C.

firing at 900 °C. Hydrogen plasmas have been used to clean metals and semiconductor materials.

SAFETY: For reactive cleaning by oxidation, pure air (medical air) is generally used, although oxygen–gas mixtures such as O_2–Ar may be used. Be very careful if pure oxygen is used because compression of the oxygen in contact with hydrocarbon oil can cause an explosion (diesel effect) in a mechanical pump.

3.2.3 Application of Fluids

Fluids are often used in cleaning processes. There are a number of ways to apply the fluids to the surface to be cleaned. Fluid baths should be continuously filtered and monitored so as to replace or replenish the active ingredients as they are used or become contaminated. In cases of heavy oil contamination, the surface of the solution should be skimmed as contaminants such as oils rise to the surface. One method of doing this is to skim the surface with oil-absorbent (oleophilic) toweling.

3.2.3.1 Immersion

Probably one of the most widely used cleaning techniques for stubborn contaminants is soaking. Soaking involves extended times and therefore may not be a desirable technique for production. This may change in the future when less aggressive cleaning methods must be used because of environmental concerns. Immersion of a surface in a stagnant solution is generally a poor technique since the contaminants that are taken into solution are concentrated near the surface and must diffuse away. Mechanical disturbance uses agitation, wiping, brushing, or scrubbing in a fluid environment to break up the stagnant fluid layer near the surface, loosen particles, and aid in carrying contamination away from the surface. Care must be taken to ensure that any material that is used in a fluid does not produce particulates and is compatible with surfaces it contacts. When using any mechanical rubbing, care should be taken to prevent contamination by abrasive transfer from the rubbing media. Gentle pressure should be used.

A variety of brush materials is used in fluids, including: polypropylene, Teflon™ and Nylon™. If wiping or scrubbing with a cloth is used, care should be taken that the cloth is lint free and desized by multiple washing before use. Special particulate-free sponge materials are available for wiping. In semiconductor technology mechanical scrubbing combined with high-pressure fluid jets (2000–3000 psi) and spinning are standard cleaning procedures.

3.2.3.2 Spraying

Liquid spray pressures can be low, at less than 100 psi, or high at several thousand psi. Spraying parameters include the type of fluid, pressure, angle of incidence, and volume of fluid. Liquid sprays should be directed at an oblique angle to the surface. Spray systems often

use copious amounts of material so the fluid should be recycled. The fluid should be monitored by residue analysis, and when it is contaminated above a given level it should be replaced. With increasing concern about solvent vapors, many of the newer spray systems are self-contained with condensers to trap the solvent vapors as shown in Figure 3.2. Some systems allow the purification of the solvents by distillation. It should be noted that spraying can induce resonant vibrations that can cause component failure or deterioration.

3.2.3.3 Vapor Condensation

Vapor degreasers operate by putting a cold part in the hot vapor above a liquid solvent contained in a sump. The solvent condenses on the surface and flows off into the sump. Cleaning action only occurs during the condensation process. When the part reaches a temperature at which the solvent does not condense, cleaning stops and the part should be removed. Parts should never be immersed in the sump fluid. Fluid in the sump should be changed when it becomes contaminated. Vapor degreasers have, in the past, been open to the atmosphere so solvent vapors escape into the atmosphere. New designs use closed chambers and condensers to capture the vapors and return them to the solvent reservoir, as shown in Figure 3.2.

3.2.3.4 Ultrasonic Cleaners

Low-frequency ultrasonic cleaning relies on the jetting action of collapsing cavitation bubbles in contact with a surface to provide a high-pressure jet of fluid against the surface [12]. Ultrasonic cleaning is often a good way to remove loosely adhering particles after a grinding or abrasive procedure and can be used with solvents to remove adsorbed contaminants. The cavitation bubbles are formed by the tension wave portion of an ultrasonic wave in a fluid medium. The ultrasonic wave is produced by magnetostrictive or electrostrictive transducers(s), typically operating at 18–120 kHz, and at an energy density of about 100 W/gallon of fluid. The ultrasonic cleaner size can be from 5 gallons for a small cleaner up to very large systems using many transducers.

The size of cavitation bubbles in the fluid depends on the vapor pressure, surface energy, and temperature of the fluid. For example, water at 60 °C and 40 kHz has a cavitation bubble size of about 3 μm. The jet pressure from the collapsing bubble can be as high as 300 psi. The cavitation jetting is more energetic for cooler media and when there are no gases in the bubble to hinder its collapse. The ultrasonic energy density decreases with distance from the transducer; therefore the cavitation energy is greatest near the transducer surface. Acoustic streaming results in an overall movement of fluid away from the transducer surface (bottom of the tank). This brings contaminants that have settled to the bottom of the tank up into the cleaning region. Therefore the cavitating fluid should be continuously filtered.

When using a fixed-frequency transducer nodes and antinodes are formed (standing waves) in the fluid, which produce variations of cavitation energy with position. These standing wave

patterns can be modified by reflection of the pressure waves from surfaces in the tank. This variation in cavitation with position can be overcome somewhat using swept-frequency generation. A typical system uses 40 ± 2 kHz. If frequency sweeping is not used or there are large variations of cavitation energy with position, the parts should be moved from one region to another in the tank during cleaning. The ultrasonic frequencies are above the hearing range of the human ear and the audible noise that is heard from an ultrasonic cleaner is due to vibration of surfaces in the cleaner.

Variables in ultrasonic cleaning include:

- amplitude and frequency of pressure wave (energy density, standing wave pattern)
- nature of the transducer fluid (density, viscosity, surface tension, vapor pressure)
- nature of the cleaning fluid if different from the transducer medium
- surfaces in the transducer medium that must transmit the pressure waves
- flow and filtering of the cleaner fluid
- temperature of fluid
- gas content of the fluid
- energy of cavitation implosion (temperature, pulse height of ultrasonic wave)
- cavitation density changes with position in tank
- cavitation density changes with time
- shape of the pressure pulse
- nature of ultrasonic cycle train (quiet time, degas time, cycles per train)
- geometry of the system and associated fixtures.

The temperature of the transducer/cleaning media is important, not only to degas the fluids but to enhance cleaning and maximize cavitation. For example, when using water with detergents and surfactants the optimal temperature for ultrasonic cleaning is in the range of ~ 55–$65\,°C$.

The intensity with which cavitation takes place depends on the properties of the fluid. The energy required to form a cavitation bubble in a liquid is proportional to the surface tension and the vapor pressure. Thus the higher the surface tension of the fluid, the greater the energy required to form a bubble, and the greater the energy released on collapse of the bubble. Water, for instance, with its surface tension of about 70 dynes/cm, is difficult to cavitate. However, with a surfactant, the surface energy can be lowered to 30 dynes/cm and cavitation is easier.

Cavitation is enhanced with increasing temperature; however, the jetting energy is lessened at higher temperatures. Gases dissolved in the fluid enter the cavitation bubble and reduce the jetting energy. Solvents in particular are susceptible to dissolved gases.

Ultrasonic erosion or deformation of aluminum foil or an aluminum metallized glass surface can be used to determine the cavitation power that a surface is exposed to in the ultrasonic solution. A general rule is that ultrasonic cavitation should generate ten holes in a 1×2 inch area on aluminum foil of 1 mm thickness in 10 s. The cavitation intensity can be studied by observing the cavitation damage on a series of aluminum foils with increasing thickness. The damage changes from hole-generation to dimpling to pitting to no damage, with foil thickness. The cavitation intensity of an ultrasonic cleaner should be plotted as a function of position with fixtures and substrates in position since reflections from surfaces can change the cavitation energy distribution. The cavitation pattern should be checked periodically, particularly if the fixturing is changed. Some work has been done using sonoluminescence to visually monitor cavitation intensity [13].

Fixturing is very important in ultrasonic cleaning to insure that all surfaces are cleaned. In general, the total area of parts, in cm^2, should not exceed the volume of the tank, in cm^3. Parts should be separated and suspended with the surface to be cleaned parallel to the stress wave propagation direction. The parts must not trap gases which prevent wetting of the surface by the cavitating fluid. Metal or glass holding fixtures of small mass and an open structure should be used. Energy-adsorbing materials such as polyethylene or fluoropolymers should not be used in fixturing since they adsorb the ultrasonic energy.

Often the cleaning fluid is filtered in a flowing system that exchanges 25–50% of its volume per minute. This is particularly desirable when the system is used continuously. An overflow tank system can be used to continuously remove contaminants that accumulate on the fluid surface. A cascade ultrasonic system with perhaps three stations of increasing solvent or rinse water purity can be used in the cleaning process.

Ultrasonic cleaning must be used with care since the jetting action can produce high pressures that cause erosion and introduce fractures in the surface of brittle materials. For example, in high-power laser applications it has been shown that extended ultrasonic cleaning of glass surfaces increases the light scattering from the surfaces indicating surface damage. Ultrasonic agitation has been shown to create particles by erosion of the container surface. The erosion of stainless steel creates 500 times as many particles as the erosion of Pyrex^{TM} glass containers. In all cases studied, particles of the container material were produced on prolonged use. Resonance effects may also mechanically damage devices in an ultrasonic cleaner. Ultrasonic cavitation can also be a source of pitting and adhesion loss of thin films. Surface damage can be controlled by adjusting the energy density of the cavitation and/or controlling the time of application. Ultrasonic jetting is good for removal of large particles but less efficient as the particle size decreases into the submicrometer range.

High-frequency ultrasonic cleaning in the 400 kHz range does not cause cavitation. Instead, the action is a train of wave fronts that sweep across a smooth surface producing disruption of the viscous surface boundary layers on the substrate surface by viscous drag. The resulting pressure is less than 50 psi and does not hurt fragile surfaces. A high-frequency ultrasonic transducer can be focused to restrict the area of impact and allow lateral fluid flow from the area of concentration.

Megasonic cleaning uses high-frequency (> 400 kHz) transducers to produce non-cavitating pressure waves. The megasonic agitation system is applicable to smooth surfaces, particularly for removing particles, but does not work on configured surfaces where the surface is shadowed from the pressure wave. The megasonic cleaning system is widely used in silicon wafer processing.

3.2.3.5 Removal of Particulate Contamination

Particulate contamination (including surface inclusions and irregularities) are a major source of pinholes in deposited films. The ability to remove particles from a surface depends on the size, shape, and composition of the particle, as well as the surface to which it adheres [14].

Removal: Mechanical
Removal of particulate contaminants from a surface is best done by mechanical disturbance in a flowing fluid environment. The mechanical disturbance should be done in a fluid environment containing detergents and wetting agents and the fluid should be continually filtered. There are a variety of brush materials. Camelhair and mohair are used for dry brushing. Polypropylene, Teflon, and Nylon are used for wet brushing. Mechanical scrubbing is often combined with high-pressure fluid jets (2000–3000 psi) as a standard cleaning procedure for particles in the semiconductor industry. Commercial particle cleaning solutions are available.

A mechanical particle removal technique is the use of high-purity CO_2 'snow', formed and blown from a gaseous CO_2 cylinder. The snow mechanically scrubs the particles from the surface without leaving residuals, if the CO_2 gas is pure, or harming the surface. This technique is also reported to remove fingerprints and silicone from silicon wafers and to be as effective as solvent cleaning for the removal of hydrocarbons in many cases. The CO_2 snow technique is also used to clean the surface of aluminum coated astronomical mirrors. A major processing variable is the purity of the compressed CO_2 gas.

Removal: Blow-Off
Blow-off techniques have the advantage that they can be done after the substrates have been placed in fixtures and even in a deposition system. The best means of blow-off is to use filtered gas from a liquid nitrogen tank. The gas is filtered with a 0.2 μm or smaller filter in the nozzle and the nozzle should allow ionizing of the gas with a radioactive or electrostatic source.

Ionized gas should be used when blowing off insulator/organic surfaces to prevent electrostatic charge build-up on the insulator surface that attracts particles.

Blow-off of particulates is often done with dusters using canned pressurized gases. One environmentally friendly duster uses pressurized (and flammable) difluoroethane. Residuals from the blow-off gases should be checked, particularly with the spray can in the inverted position where liquid sprays out instead of vapor.

Removal: Spraying

The fluid sprays are generally effective for removing large particles but are not effective on submicrometer-sized particles. The jetting action by the collapsing cavitation bubble acts as a high-pressure fluid spray that displaces the particle. Ultrasonic jetting is good at removing large particles but as the particle size decreases to submicrometer the cleaning effectiveness decreases.

Removal: Megasonic

The fluid drag associated with a pressure wave moving over a smooth surface in megasonic cleaning creates turbulence that knocks particles loose from the surface. If the surface is not smooth, particles can accumulate in depressions on the surface.
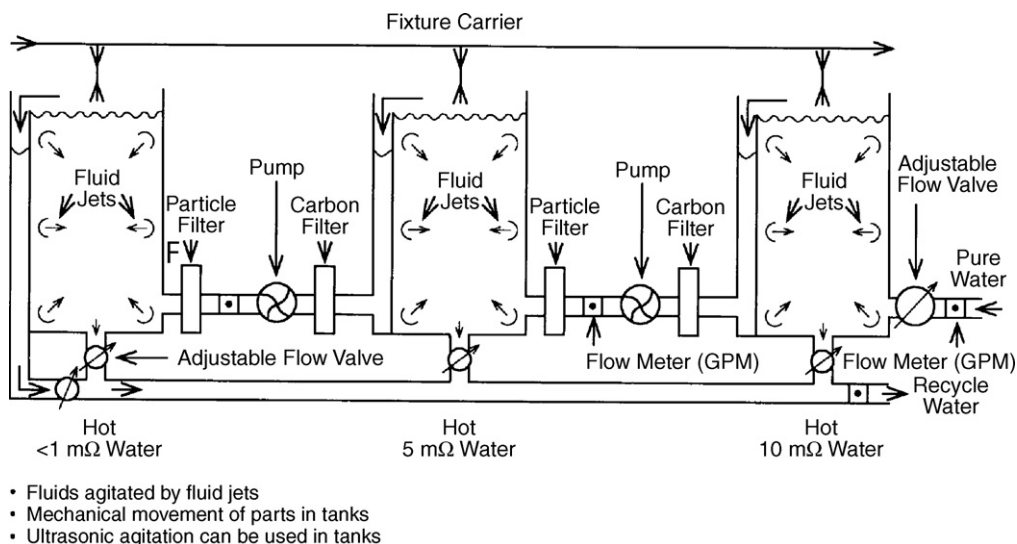
Removal: Contact Cleaning

Particles can be removed from surfaces by covering the surface with a liquid polymer, allowing it to solidify then stripping the polymer from the surface. This technique is used by the optics industry to remove particles from mirror surfaces and protect surfaces from abrasion during assembly. There are many variations on strip coats, with various coatings leaving differing residues on stripping and having differing corrosion compatibility with surfaces.

Another technique for contact cleaning uses an elastomer material that picks up the particles. This technique has been used for continuously cleaning a polymer film in web coating [15].

3.2.4 Rinsing

After any wet cleaning process the surface should be thoroughly rinsed in an ultrapure liquid, usually water, before allowing to dry. This avoids leaving residues on the surface. The most common rinsing technique is to use successive rinses (cascading rinsing) in ultrapure water until the rinse water retains a high resistivity (> 12 megohm). This is called rinse to resistivity. After rinsing the surface should be dried as quickly as possible since the residual water film on the surface will cause particles to stick to the surface and on drying the particles will stick very tenaciously. Figure 3.5 shows a cascade rinse system and Figure 3.6 shows an in-line cleaning system.

Figure 3.5 labels:

Fixture Carrier

Pump — Pump — Adjustable Flow Valve

Fluid Jets — Particle Filter — Carbon Filter — Fluid Jets — Particle Filter — Carbon Filter — Fluid Jets

F

Pure Water

Adjustable Flow Valve — Flow Meter (GPM) — Flow Meter (GPM)

Recycle Water

Hot <1 mΩ Water — Hot 5 mΩ Water — Hot 10 mΩ Water

• Fluids agitated by fluid jets
• Mechanical movement of parts in tanks
• Ultrasonic agitation can be used in tanks

CASADE (CONTERFLOW) RINSE TANKS

Figure 3.5: Cascade rinse system. [From SVC Education Guides to Vacuum Coating Processing (2009) – Surface Preparation: Cleaning Lines, with permission.]

Figure 3.6 labels:

Rack Carrier

Splash Shield — Splash Shield

Skim — Spray Nozzels — Air Jets

Fluid Jets — To Storage

Hot Alkatine Immersion Cleaning | Hot Alkatine Spray Cleaning | Hot Soft Water Immersion Rinse | Hot Acid Immersion Cleaning | Hot Pure Water Spray Rinse | Hot Air Blow Dry | Hot Air-Dry Tunnel

• Fluids agitated by fluid jets
• Mechanical movement of parts in tanks
• Fluids continuously recirculated anb filtered for particulates and organics
• Alkaline electrolytic cleaning can be used instead of alkaline immersion cleaning
• Ultrasonic agitation can be used in fluid tanks

TYPICAL CLEANING LINE-FOR NON-RUSTING METAL PARTS

Figure 3.6: In-line cleaning system. [From SVC Education Guides to Vacuum Coating Processing (2009) – Surface Preparation: Cleaning Lines, with permission.]

3.2.4.1 Ultrapure Water

Ultrapure or deionized (DI) water (18 megohm-cm resistivity) is used for rinsing since it leaves a minimum of residues. Water purity is measured using a conductivity cell that measures the ionic concentration in the water. Spontaneous dissociation of the water molecule limits the resistivity of water to 18 megohms between electrodes spaced 1 cm apart. Conductivity measurements do not measure the organic or biological contamination and some type of residue analysis must be used to measure these impurities. There are a number of techniques for determining the nature of the contaminants.

Typical semiconductor specifications for ultrapure water for endpoint use are:

- resistivity – 18 megohm-cm continuous at 25 °C
- particle count – less than 500 particles (0.5 μm or larger) per liter
- bacteria count – less than one colony (cultured) per cm^3
- organics – less than one part per million
- total electrolytes – less than 5 parts per billion NaCl equivalent
- quantity requirements
- peak-level usage.

High volumes of ultrapure water are made by:

- pretreatment – pH adjustment, coagulation, filtration
- reverse osmosis – semipermeable membrane (pore size of 10^{-3} to 10^{-4} μm) which rejects salts, dissolved solids (90–98%), and organics (99%), and requires 150–600 psi feedwater
- degasification – removes dissolved CO_2
- ion exchange (anion and cation) – ion-exchange resins remove ions by exchanging H^+ for cations and OH^- for anions
- absorption materials (activated carbon) – remove organics
- filtration – removes particulates and biological matter – 0.2 μm for bacterial, 1.0 μm prefilter
- ultraviolet radiation or ozone bubbling – kills bacteria on filters
- endpoint filtration – 0.2 μm.

Smaller amounts of ultrapure water can be prepared by the same process using steps beginning with the ion-exchange process.

Ultrapure water should be stored or distributed in plumbing or containers using uPVC (unplasticized) or a fluoropolymer such as Teflon, or HALAR^{TM} with heat bonding or welding instead of glue bonding. In distribution systems the water should be continuously flowing or allowed to flow before use and the electrical conductivity measured at the point of use. Ozone may be injected into the water in the distribution system to continuously remove organics by oxidation.

3.2.5 Drying, Outgassing, and Outdiffusion

3.2.5.1 Drying

Drying is the vaporization of water or other fluid adsorbed on the surface or absorbed in the bulk. Porous and rough surfaces retain fluids more readily than do smooth surfaces and are more difficult to dry since the fluids are trapped in capillaries. Oxide layers on metals are often porous and retain fluid molecules readily. Drying by removal or displacing the water has the advantage that when the water is removed it takes the bulk of the potential residues with it, whereas vaporization of large amounts of fluid concentrates the potential residues giving a water spot of residue. After fluid cleaning and rinsing it is important to dry the surface quickly to prevent the water film from collecting particles. Drying can be done in the following ways.

Drying: fluid

Anhydrous alcohol, such as isopropyl alcohol (IPA), anhydrous ethyl alcohol denatured with acetone or methanol, or a commercial drying agent are good drying agents. They displace the water and when the surface is removed from the fluid the surface dries rapidly. Drying fluids should be residue free and should be discarded or recycled as they take up water, either from the drying process or from the ambient. The water content of the drying fluid can be monitored by its specific gravity or by monitoring the infrared adsorption peak for water.

One of the best drying techniques is an alcohol vapor dry where the cold surface is immersed in the vapor above a heated anhydrous alcohol sump. The cold surface condenses the alcohol vapor that flows off into the sump taking water and particulates with it. When the surface becomes hot, condensation ceases and the hot surface, when withdrawn, dries rapidly. This should be done in a closed recirculation system as is shown in Figure 3.2.

Drying: mechanical

Surfaces may be dried by spinning at a high velocity (> 2000 rpm). The equipment for high-velocity spinning is common in the semiconductor industry where spinners are used to coat surfaces with photoresist. Spin drying tends to leave liquid along the outside edges of the

substrate which can produce contamination in this area unless copious amounts of pure fluids are used. This technique can leave a thin layer of water on the surface.

Drying: blow-off

Fluids can be blown from the surface using a low- or high-velocity gas stream. This technique has the advantage that the fluid takes most of the potential residues with it as it is blown from the surface. When using nitrogen as the blow-off gas, it is best to obtain the nitrogen from the vapor above liquid nitrogen in a Dewar flask next to the workstation and transport the nitrogen through fluorocarbon or stainless steel tubing. When blowing, a nozzle with a 0.2 μm or smaller particulate filter should be used in the nozzle. In addition, when drying insulator surfaces the gas should be ionized to prevent charge build-up on the surface. The gas can be ionized with an electrostatic (corona), laser or nuclear (Polonium-210) ionizer. Electrostatic ionizers can arc and produce particulates. Nuclear ionizers are not sold any more but can be leased.

A high-velocity jet of gas can be shaped to blow-off a moving surface. The jet is often shaped into a long, thin configuration and this 'air knife' is used to remove fluid from a moving surface such as a large glass plate. Exiting the air knife the gas velocity can be as high as 35,000 fpm (feet per minute). The jet should hit the oncoming wet surface at about a 30° angle. At the trailing edge a droplet will form and spread back over the surface when the jet has passed, so the water on the surface should be ultrapure. The size of the droplets can be reduced by reducing the surface tension of the water by the addition of alcohol. This technique leaves a thin layer of water on the surface so subsequent heat drying may be necessary.

Drying: thermal

Water can be removed from a surface by evaporation. The most common means is to use vacuum baking or gas drying in a hot oven. The vacuum environment aids in evaporation but a circulating gas dryer is most often used. This technique suffers from the fact that the residue is concentrated as the water dries, leaving a water spot unless the water is very pure.

SAFETY: See CRC Handbook of Laboratory Safety (2000) [16]; A Comprehensive Guide to the Hazardous Properties of Chemical Substances (2007) [17].

3.2.5.2 Outgassing

Volatile material from the bulk of the material is removed by outgassing. Outgassing involves the diffusion of the material to the surface and vaporization from the surface. Heating should be such as not to decompose the material. The material can be heated in a hot oven or by microwave absorption which heats the water directly. The outgassing rate is increased by heating in a vacuum. A common mistake is to not allow sufficient time for outgassing the material. The time–temperature environment for outgassing should be determined using weight-loss measurements or by analysis of the outgassing ambient. Often outgassing can take
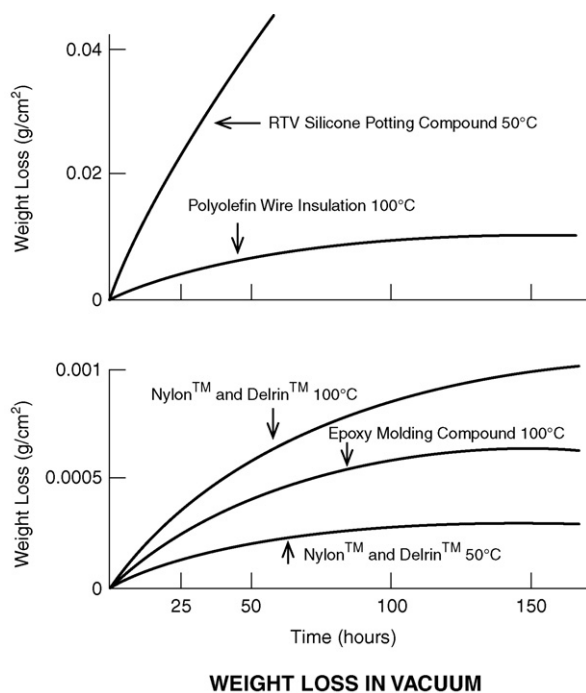
WEIGHT LOSS IN VACUUM

Figure 3.7: Typical ougassing curves. Note the long times needed for outgassing. [From SVC Educational Guides to Vacuum Coating – Surface Preparation: Cleaning Lines, with permission.]

hours or days, particularly if the material is thick and/or the temperature is low. Figure 3.7 shows some typical outgassing curves.

3.2.5.3 Outdiffusion

Outdiffusion is the diffusion of material to the surface that is not volatilized. This material must be removed by surface cleaning techniques. In some cases where there is a lot of such material in the bulk, the surface may have to be cleaned many times before an acceptable contaminant level is attained.

In some cases the diffusing material may be sealed in using a surface barrier layer (basecoat) such as a UV curing polymer.

3.3 Evaluating and Monitoring of Cleaning

In order to have a reproducible cleaning process it is necessary to have process documentation that is followed faithfully.

3.3.1 Cleaning Tests

The best monitoring technique for cleaning is the ability of the process to provide surfaces that can be processed in an acceptable manner. The testing of a surface invariably results in contamination of the surface, so tested surfaces generally cannot be used for subsequent processing. In some cases witness sample surfaces can be tested for certain properties to determine surface conditions. These tests include the following.

3.3.1.1 Test: Sheeting

The cleanliness of smooth surfaces can be determined during the rinse operation by observing the wetting and sheeting of water on the surface. Sheeting is the flow of the water over the surface as it drains, giving a smooth water surface. If there is hydrophobic contamination on the surface the water will avoid that area and the sheet of water will break up. This test is often called the water break test [18].

3.3.1.2 Test: Contact Angle

A common check on the cleaning of a glass surface uses the contact angle of a liquid drop on the surface of the cleaned glass. If the surface is clean it has a high surface energy, and the liquid wets and spreads over the surface. In the case of water on a clean glass surface the contact angle is less than 5° as measured with a contact angle goniometer [7]. This technique must be used with some care since, if a hydrophilic contaminant, such as a soap residue, is present, the contact angle may be low even though the surface is contaminated. For sensitive characterization of surface energies, liquids of various surface tensions can be used. Liquids of 30–70 dynes/cm (as per ASTM D-2578) are available. Advancing and receding contact angle behavior can be studied using systems that add or remove fluid or tilt the substrate.

The surface energy of a surface can be determined using liquids having various surface energies and determining the contact angle (ASTM D-2578-84). When using the dyne test make sure that the dyne solutions do not dissolve the surface layer or chemically react with the surface. The dyne test can also be performed using marking pencils having various dyne inks.

3.3.1.3 Test: Nucleation

A smooth clean surface will give uniform nucleation of a vapor on the surface. A common test is to breathe on the surface and look at the nucleation pattern. This is called the black-breath test [18]. For example, nucleation of water on the mirror in a shower room will show up the swipes where the mirror surface has not been cleaned very well.

3.3.1.4 Test: Adsorption and Desorption Behavior

Absorption of a tracer material such as a fluorescent dye or radiochemical (e.g. MESERAN^TM technique) can be used to detect the presence of many contaminants. Evaporative rate analysis
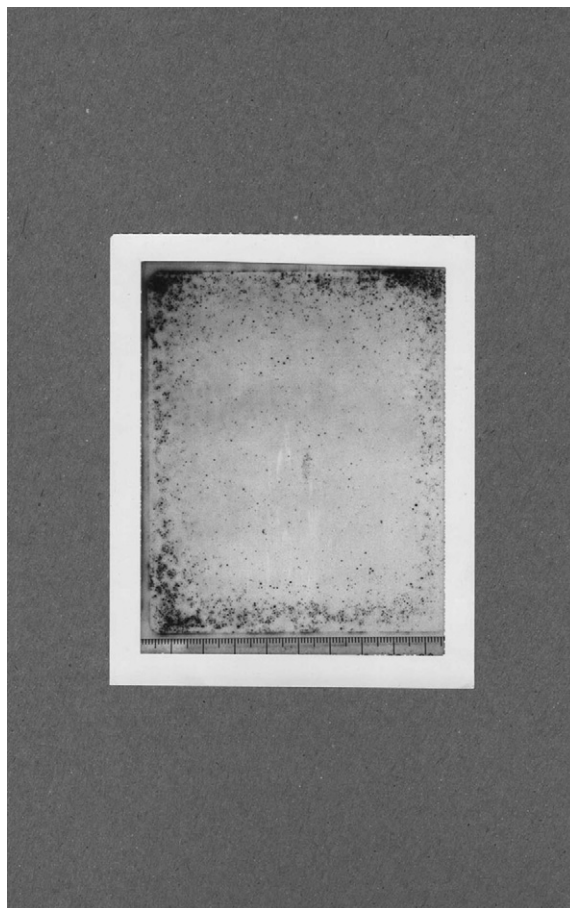
Figure 3.8: ^{85}**Kr autoradiography of a cleaned 94% alumina surface. The black areas are where retained contamination has absorbed the** ^{85}**Kr. Centimeter scale.**

may be used to characterize surfaces and contaminants. Figure 3.8 shows the adsorption of the radioisotope ^{85}Kr on a fused alumina surface as determined by autoradiography [19]. Residual contamination after cleaning adsorbs the ^{85}Kr, which then exposes the film use in autoradiography.

3.3.1.5 Test: Friction and Marking

A clean glass surface has a high coefficient of friction that can be detected by feel (squeaky clean). If the surface feels slick then it is probably contaminated. One type of friction test is the marking test where materials having various surface energies are rubbed on a surface. There is adhesion and abrasive transfer if the surface is of higher surface energy than the marking material. For example, indium writes on clean glass.

3.3.1.6 Test: Extraction and Analysis

Contaminant material may be extracted from a surface and analyzed. Ionic contamination changes the electrical conductivity of water and the conductivity can easily be monitored. Non-ionic materials can be determined by residue analysis.

3.3.1.7 Test: Surface Analytical Spectroscopies

Surface spectroscopies such as Auger electron spectroscopy (AES), ion scattering spectroscopy (ISS), secondary ion mass spectroscopy (SIMS), and X-ray photoelectron spectroscopy (XPS) can be used to characterize contamination levels on very small areas. Problems with the use of these techniques for cleaning evaluation include the small area analyzed and the potential for recontamination before the analysis can take place. When only a small area is analyzed the true contamination condition of the total surface can be misjudged. The surface spectroscopies are quite useful in detecting and identifying heavy elemental contaminants that cover a surface, particularly in the semiconductor industry.

3.3.2 Particle Detection on Smooth Surfaces

Particulate contamination on smooth surfaces such as polished silicon wafers can be detected by observing scattered light with an optical microscope or by using a scanning laser microscope which integrates all the scattered light. Laser scattering is a sensitive technique and is capable of detecting particles as small as 0.2–0.15 μm in diameter with a probability of 90–50% respectively. Using angle-resolved light scattering it is possible to obtain compositional and morphological data on the particle. Scanning interferometry can also be used to detect particles on smooth surfaces. Ultraviolet luminescence can be used to detect some types of particles.

Particles on surfaces can be observed using scanning electron microscopy (SEM) and in special cases transmission electron microscopy (TEM). Compositional analysis of inorganic particles can be done using the SEM in the EDAX mode (SEM/EDAX) and by small area electron diffraction in the TEM.

3.3.3 Particle Detection on Rough Surfaces

Particles on rough surfaces can only be detected by extraction techniques. For example, a strippable coating or tape can be applied and removed taking the particles with them. A particle count can then be made and the particles identified. The particles can be removed from the surface by ultrasonic cleaning, collected, and identified.

3.4 Recontamination in the Ambient Environment

An integral, and often neglected, aspect of cleaning, is that of handling and storage before the next processing step or usage. Handling and storage during processing and after cleaning are major sources of contamination and recontamination. It is not unusual to see a carefully cleaned substrate placed into a plastic bag where it is recontaminated by the polymer – either by the volatile constituents in the polymer or by abrasive transfer. The best procedure is to integrate the cleaning line with the deposition process so as to eliminate or minimize handling and storage. For example, in metallizing compact discs (CDs) the molded disc is taken directly from the molding machine into the deposition system, where it is individually metallized with a cycle time of less than 3 s. Another example is the metallizing of mirrors, where the glass is scrubbed, rinsed, and dried in-line with the metallizing system [3].

3.4.1 Ambient Environment

Clean surfaces are very reactive and easily recontaminated. Recontamination can occur from the adsorption of vapors, collection of particles, contact with other surfaces, or reaction with reactive gases. Important aspects of cleaning are the conditions existing in the processing area, the handling of the surfaces, and storage of the cleaned part. Dust is a particular concern in many instances since particulates on the substrate surface will result in pinholes in the deposited film. Figure 3.9 shows the recontamination of a clean gold surface in a very clean environment, a typical cleanroom environment, and a machine shop environment as determined
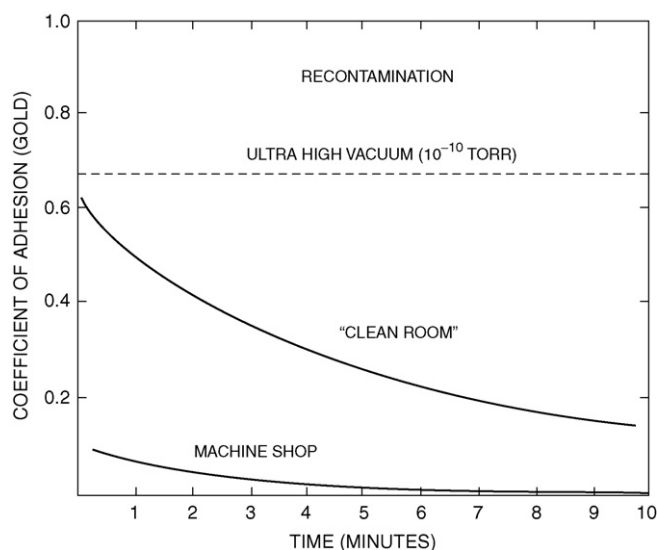

Figure 3.9: Recontamination of cleaned gold surfaces in several environments [20].

by coefficient of adhesion measurements between gold surfaces [20]. The recontamination is primarily by the adsorption of hydrocarbon vapors on the clean gold surfaces.

Avoidable contaminants in the processing area include large and small particulates, some vapors, and some reactive gases such as chlorine. The least expensive action that should be taken to reduce contaminants in the processing area is to remove as many sources of contaminants as possible. This can mean good housekeeping, separation of contaminant-producing processing from the cleaning area, elimination of particulate-producing materials, and elimination of vapor-producing materials such as many molded plastics and vinyl coverings. Personnel doing the cleaning should not use particulate-producing products such as mascara or body powders.

Vapor contamination is generally not controlled in the processing environment except by ventilation, construction, and segregation of vapor-producing processes such as soldering, etching, and electroplating from the clean area. Vapor-producing and aerosol-producing processes should be performed in ventilated work areas such as chemical hoods. Some filter systems use activated carbon to filter organic vapors. Activated carbon is an amorphous material with a high surface area (500–1500 m^2/g). For use in gases, it has a pore size of 12–200 Å. Activated carbon has a high affinity for the absorption of organic molecules. It is better for adsorbing non-polar molecules than polar molecules. Catalytic agents (Cu, Ag, Cr) in the activated carbon can be added to improve the absorption of complex organic molecules and are used in gas mask filters.

Another action that can be taken to reduce contamination is to contain contaminant-producing sources as much as feasible. Humans and their clothing shed large amounts of particulates that are pumped out through the loose weave of the clothing as the person moves about. The use of head coverings, facial hair coverings, and coats or coveralls (bunny suits) of tightly woven long-fiber cloth will contain the particulates somewhat. In particular, the hair and mouth should be covered since the head is often over the surface being processed.

Cleanrooms and clean areas are generated by using mechanical filtering of the air along with control of the air flow pattern [21, 22].

3.4.2 Handling

It is preferable to handle surfaces using fixtures or tools; however, in many cases the surfaces must be handled directly and gloves may be used. Gloves may be of a woven fabric or of a polymer film that is either molded to shape or heat welded from flat sheet. Polymer gloves for general use are often powdered to make donning the gloves easier, but for cleaning applications unpowdered gloves must be specified in order to avoid particulate contamination. Glove lengths can vary from wrist-length to elbow-length.

There are a number of choices for polymer glove material, including latex rubber, nitrile rubber, vinyl, polyethylene, and fluorocarbon materials such as Teflon, as well as polymer blends such as latex–nitrile–neoprene–natural rubber blends for use with acids. All glove material should have low extractables for the chemicals with which they may come into contact. Vinyl gloves are comfortable and are often used in handling surfaces. A problem with the vinyl is that when in contact with alcohol, a common wipe-down material and drying agent, the alcohol extracts phthalate plasticizers from the vinyl. Those extractables on the glove surface can then contaminate surfaces. It is generally best not to have vinyl gloves in the cleaning area.

Unplasticized polyethylene gloves are compatible with alcohol and most cleaning chemicals and are good gloves for clean handling. A disadvantage of polyethylene gloves is that they are rather awkward and uncomfortable and operators will readily discard them when they are not required. Latex or nitrile rubber gloves are often used in suiting-up for the cleanroom. A problem is that is they are then used all day long, thereby transferring contamination from one place to another. When handling clean surfaces an unplasticized polyethylene glove should be put on over the latex glove and then discarded when the handling is over. A disadvantage of the polymer gloves is that the soft polymer can be easily transferred to a clean surface by abrasive transfer. Abrasive transfer is dependent on the materials and the adhesion and friction between the surfaces. Another disadvantage of the polymer gloves is that they are slippery and it may be desirable to use fabric gloves such as Nylon when handling large or heavy parts.

Desized and lint-free Nylon or Dacron™ woven fabric gloves are used when friction in handling is desirable or abrasive transfer from softer polymer gloves is a problem. Woven fabrics will wick oils from the skin to the glove surface, so polyethylene or latex gloves or finger cots should be used under the fabric gloves.

3.4.3 Storage

Cleaned surfaces should be stored in a non-recontaminating environment. Often surfaces to be stored are held in clean fixtures to reduce the necessity for handling the surfaces directly. The fixtures must be compatible with the storage environment. Non-contaminating storage environments can be passive or active.

3.4.3.1 Storage: Passive

Passive storage environments are those which have been carefully cleaned. A commonly used passive environment is a clean glass container such as a Petri dish. Clean surfaces can be stored by wrapping them in a clean material. Wrapping the surfaces in clean Nylon fabric or clean aluminum foil works well. Usually it is best to avoid wrapping in paper or polymer wrap because of contaminants in the material and abrasive transfer of contaminants. A simple

method of passive storage is to place cleaned surfaces in contact with one another. This has been called wafer bonding in the semiconductor industry.

Cleaned parts may be stored under liquids to exclude reactive gaseous agents. Metals stored in anhydrous liquids such as anhydrous alcohol or anhydrous acetone do not reoxidize as rapidly as if they were exposed to the atmosphere. Storage of surfaces in degassed (boiled) water decreases the oxidation of the surface compared to water containing dissolved air (cold water).

In some cases the surface condition can be preserved by covering the surface with a liquid polymer, allowing it to solidify and then stripping the polymer from the surface when the surface is to be used. This technique is used by the optics industry to protect optical surfaces from abrasion and particulate contamination during assembly. Various strippable coatings leave differing residues on stripping and have differing corrosion compatibility with surfaces.

3.4.3.2 Storage: Active

Active storage environments are those where the contaminants are continually removed from the storage environment by adsorption or reaction. Hydrocarbon adsorption can be on freshly oxidized aluminum or activated carbon. Hydrocarbon contaminants can be continually removed by having an oxidizing atmosphere. A UV/O_3 cleaning cabinet provides such an environment [8, 9]. The UV/O_3 cleaning chamber is by far the best technique for storing surfaces where surface oxidation is not a problem.

For some storage applications moisture is the main contaminant to be considered and an actively desiccated environment is desired. Common desiccants include:

- silica gel

- phosphorous pentoxide (P_2O_5)

- magnesium perchlorate ($Mg[ClO_4]_2$).

Phosphorous pentoxide is probably the most effective desiccant material. It should be used to reduce particle formation. Desiccants must be used with care since they tend to be friable and produce particulates. It is best to isolate the desiccants from the storage chamber by means of a particle filter.

3.5 In Situ Cleaning

In situ cleaning is done in the deposition system and is intended to remove the small amount of contamination that has developed since the external or primary cleaning process was performed. The most common in situ cleaning techniques for PVD processing are as follows.

3.5.1 Sputter Cleaning

At low gas pressures of 1–10 mtorr the mean free path for particle collision is long and the ions from a plasma can be accelerated to high energies before they impinge on a surface. Figure 3.10 shows the effect of this energetic particle bombardment on the surface and near-surface region of a material [23]. The energy and momentum transferred from the bombarding particle to surface atoms creates a collision cascade in the near-surface region. Much of this energy becomes heat but some energy can be transferred to surface atoms causing them to be physically ejected. This non-thermal vaporization is called physical sputtering or just sputtering.

Sputter cleaning uses sputtering to remove the surface layer, which includes the contaminants. Sputtering has been called the universal etch since conceptually everything can be removed by the sputtering process. However, certain types of surface contamination, such as inorganic particles and inclusions, are difficult to remove by sputtering. Electrically conductive surfaces can be sputtered using an applied DC potential. The sputtering potential on electrically insulating surfaces must be applied with an RF field, a pulsed DC, or by generating a high self-bias on the surface.

Often a major problem with sputter cleaning is to have a uniform bombardment over the surface to be cleaned. In areas where the bombardment is low, contaminates may accumulate by redeposition from areas being cleaned. Sputter cleaning configurations can be tailored to
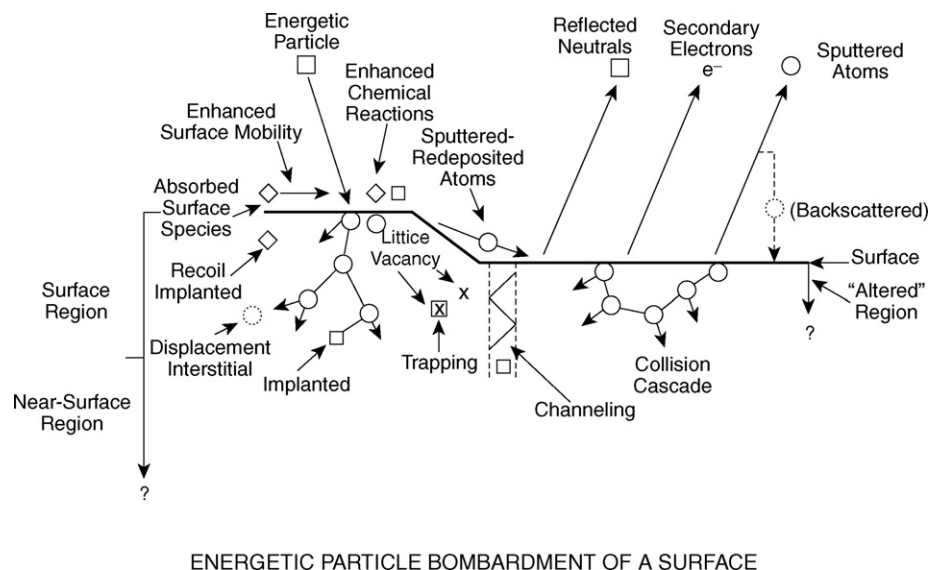

ENERGETIC PARTICLE BOMBARDMENT OF A SURFACE

Figure 3.10: Processes that occur on a surface and in the near-surface region of a surface being bombarded by energetic atomic-sized particles [23].

the surface being cleaned in much the same way as are sputtering targets in the physical vapor deposition (PVD) process of sputter deposition (see Chapter 5).

During sputter cleaning the bombarding gas can become incorporated into the surface and subsequently released on heating. In thin film deposition technology this can cause loss of adhesion of films deposited on the bombarded surface. To avoid this problem, the substrate should be heated during bombardment or before film deposition to prevent or remove gases included in the substrate surface. Sputtering from a plasma environment has the disadvantage that contamination, such as oxygen, in the plasma becomes activated and can react with the surface being cleaned. One way to avoid this problem is to sputter clean the surface in a good vacuum using an ion source (ion gun) where the ions are formed in a plasma and then extracted and accelerated through a grid electrode system into the processing chamber. Both inert (e.g. argon) and reactive (e.g. oxygen) ions can be formed in ion guns.

This cleaning process can be easily integrated into the deposition process so as to have no time for recontamination between the cleaning and the deposition process, as in the ion plating process (Chapter 6).

Often a major problem with sputter cleaning is to have a uniform plasma over the surface to be cleaned. If the plasma is not uniform the surface will not be cleaned uniformly. In areas where the bombardment is low, contaminates may accumulate by redeposition from areas being cleaned.

3.5.2 Ion Scrubbing

Ion scrubbing of a surface occurs when a surface, which is in contact with an inert gas plasma, develops a wall sheath and is bombarded by inert gas ions accelerated across this wall sheath, where it gives up its kinetic energy as well as its energy of ionization. The plasma-surface effects are shown in Figure 3.4. The ion energy is generally too low to cause surface damage or physical sputtering but does aid in desorption of the adsorbed surface contaminants.

3.5.3 Reactive Plasma Cleaning

When there is a reactive gas such as oxygen or hydrogen in the plasma, ion scrubbing can cause chemical reactions that create a volatile compound of the contaminant. This plasma cleaning process using air or oxygen is widely used in the optical coating industry for substrate preparation in the vacuum deposition system using a DC air discharge. When generating a DC plasma in a system for cleaning purposes, the cathode should be hidden from the surface to be cleaned and the discharge pressure should be high enough to prevent high-energy reflected neutrals from bombarding the surface, i.e. 10 mtorr or higher.

A glow bar is a high-voltage cathode used for generating a plasma for plasma cleaning at a gas pressure of a few micrometers up to several torr. A glow bar often can be found in deposition
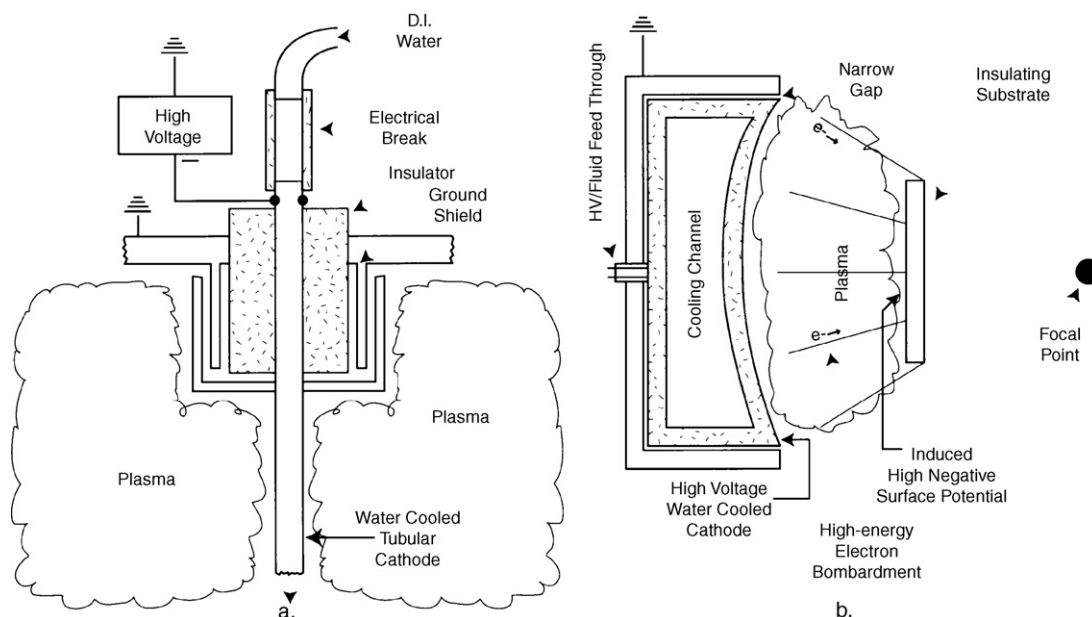
Figure 3.11: (a) Shielded high-voltage feedthrough for use with a glow bar. The gaps between the shields should be less than the cathode dark space distance. (b) Watercooled shaped glow discharge cathode where the active surface is defined by the conformal ground shield. The focused and accelerated electrons from the cathode increase the shield potential at the substrate surface. [From SVC Educational Guides to Vacuum Coating – Surface Preparation: Glow Bars for Plasma Cleaning, with permission.]

systems, such as in optical coating facilities using thermal evaporation, where the deposition takes place in a good vacuum. Figure 3.11 shows a feedthrough design for a glow bar and a shaped cathode design for plasma cleaning.

Low-energy ion bombardment can be used to clean surfaces without electronic damage of semiconductor materials. The ions may be accelerated to the surface under an applied potential or a self-bias. The low-energy ion bombardment can be obtained from high-pressure plasmas, in downstream processing with low biases, and with low-energy ion beams. In silicon technology low-energy (2 ev) bombardment is effective in removing adsorbed contaminants but is unable to remove the oxide.

In a simple DC diode (non-magnetically confined) discharge, electrons are accelerated away from the cathode. These establish the plasma, but also many of the electrons reach high energies and bombard any surface on which they impinge. Thus, the glow bar provides three possible cleaning mechanisms: (1) plasma cleaning, which occurs on all surfaces in contact with the plasma; (2) electron bombardment of surfaces facing the cathode; and (3) on an

electrically floating or electrically insulating surface the electron bombardment can generate a self-bias that accelerates ions to the surface (see Chapter 6, Figure 6.9).

Figure 3.4 shows the cleaning processes that occur at the surface in contact with a plasma. Photon irradiation, hot gases and energy from de-excitation and deionization can cause volatile species to desorb from the surface, while the UV radiation can cause chemical bond scission and volatilization of some species. The sheath potential accelerates positive ions from the plasma and these energetic species can ion scrub the surface to remove contaminants. Reactive species from the plasma can react with the contaminants on the surface, forming volatile reaction products that leave the surface. For example, oxidized hydrocarbons will volatilize as CO, CO_2, and H_2O. Reaction with no volatilization will leave a residue on the surface. For example, if silicone oil is present on the surface, an oxygen plasma will oxidize the oil to SiO_2, which will remain on the surface as a residue.

If a hydrogen plasma is used for cleaning, the hydrocarbon contaminants are hydrogenated to more volatile hydrocarbon species such as acetylene (C_2H_6). The amount of volatile species formed by reactive plasma cleaning can be monitored using a differentially pumped mass spectrometer.

Other reactive gases, such as those containing fluorine or chlorine, can be used to remove oxide layers from materials. For example, a CF_4 plasma is used to preferentially remove silicon oxide from silicon. The addition of oxygen to the CF_4 plasma allows rapid etching of silicon since the oxygen plasma continuously reacts with the silicon surface to form the oxide. When using reactive gases for plasma cleaning, care should be taken that the vacuum pumping oils are compatible with the gases being used. For example, pure oxygen should never be pumped using hydrocarbon oils in an oil-sealed mechanical pump, as an explosion can occur.

Reactive plasma cleaning is typically done at gas pressures where the plasma particle density is high and the mean free path for collision is small. Under these conditions it is impossible to accelerate ions to high kinetic energies in an electric field.

Reactive plasma cleaning and sputter cleaning can often be integrated into the processing line. Reactive plasma cleaning using an oxygen plasma is more rapid than the ultraviolet/ozone cleaning (UV/O_3) cleaning process, although the processes are very similar.

SAFETY: When using an electrically isolated metal chamber, be sure to turn off the plasma power supply before venting the chamber. If you do not, the chamber may lose its ground as the chamber is vented, allowing the O-ring to expand. The plasma will attempt to take the now electrically floating surface to the cathode potential, giving a high voltage on the metal chamber. To prevent this, the chamber can be grounded at all times or the plasma supply turned off before the chamber is vented.

3.6 Recontamination in the Deposition System

Particulates in a deposition system are generated during use from a variety of sources, including:

- general and pinhole flaking of deposited film material on walls and fixtures

- wear debris from surfaces in contact, i.e. opening and closing valves

- debris from maintenance and installation, i.e. insertion of bolts, wear of handtools, motor tools, and from personnel and their clothing

- unfiltered gas lines

- particulates brought in with fixtures and substrates

- particulates brought in with processing gases and vapors

- particulates formed by gas-phase nucleation of vaporized material or decomposed chemical vapor precursors.

Film build-up on walls and fixtures may flake as it becomes thick, particularly if the film material has a high residual stress. For example, sputtering $TaSi_2$ produces a large number of particulates because the deposited material is brittle and is generally highly stressed. One way to alleviate the problem somewhat is to occasionally overcoat the brittle deposit with a softer material such as aluminum. Pinholes form in films on surfaces producing flakes and this source of particulates is called pinhole flaking. Liners which may be easily removed and cleaned or discarded to prevent deposit build-up should be used. Heating or mechanical vibration of surfaces contributes to flaking and wear.

The control of particulate contamination in a system is very dependent on the system design, fixturing, ability to clean the system, and the gas source/distribution system. The use of dry lubricants decreases wear and particle generation. In particular, bolts used in the vacuum chamber should be silver plated to prevent wear and galling. Some types of plasma etching processes generate large amounts of particulates.

Hydrocarbon vapors in the deposition chamber can originate from the vacuum pumping system. Pump oil and lubricant vapors can backstream into the system. Backfill gases can contain oil vapors from the ambient environment. This type of contamination can be detected by placing a clean glass slide in the system, going through the pumping (and heating) sequence, and then checking the wetting angle on the glass surface. If vapor contamination is suspected or detected the system can be cleaned using an air plasma discharge.

The most common vapor in a good vacuum system is water vapor. The water molecule is highly polar and is strongly adsorbed on clean metal and oxide surfaces. Water vapor often

presents a major variable in many PVD processes. Water and water vapor in the vacuum system affect the pumpdown time and the contamination level during the deposition process. Water vapor is much more difficult to pump away than a gas because the water vapor molecule has a long residence time on a surface compared to the gas molecule. Thus, if many adsorption–desorption collisions are necessary for the water molecules to reach a pump, the time to reduce the chamber pressure to a given base pressure will be long compared to an open system.

The best procedure for eliminating water vapor in the vacuum chamber is to prevent its introduction in the first place. This can be done by: (1) backfilling with a dry gas; (2) reducing the time the system is open to the ambient; (3) maintaining a flow of dry gas through the system while it is open; (4) keeping the chamber walls and surfaces warm to prevent condensation; and (5) drying and warming the fixtures and substrates before they are introduced into the chamber. Large volumes of dry gas can be obtained from the vaporization of liquid nitrogen (LN_2) usually from above the LN_2 in a tank (1 liter of LN_2 produces 650 liters of dry gas at STP), by compression and expansion of air, or by using high-volume air dryers. Gas dryers dry gas by desiccants, refrigeration, or membrane filtering.

When introducing substrate materials that can absorb moisture, such as many polymers, the history of the material may be an important variable in the amount of water vapor released by outgassing in the deposition chamber, as shown in Figure 3.7. In this case the history of the material must be controlled and perhaps the materials outgassed before they are introduced into the deposition chamber. In some web coaters, the web material is unwound in a separately pumped vacuum chamber before it is introduced into the deposition chamber. This isolates the deposition chamber from most of the water vapor released during the unrolling operation.

Contamination from the processing gas can come from an impure gas source or contamination from the distribution line. Distribution lines for gases should be of stainless steel or a fluoropolymer to reduce contamination. Gases can be purified near the point of use using cold traps to remove water vapor or purifiers to remove reactive gases. Purifiers may be hot metal chips or cold catalytic nickel surfaces and should be sized to match flow requirements. Reactive gases can come from the ambient processing environment around the system.

Often the process itself introduces contamination into the deposition system. This contamination can be associated with removable surfaces such as fixtures, the source material, the substrate material, or with processes related to the deposition process itself such as ultrafine particles from vapor-phase nucleation of the vaporized source materials. Surfaces and materials that are to be introduced into the deposition system should be cleaned and handled commensurate with the contamination level that can be tolerated.

3.7 Some Surface Modification Processes

3.7.1 Ex Situ Surface Modification

3.7.1.1 Surface Morphology

Basecoats: polymer

Polymer basecoats such as the UV curing epoxies are used not only to flowcoat and smooth a surface but also to seal in materials that can outgas or outdiffuse from a polymer substrate.

Surface chemistry

There are several ways to treat polymer surfaces and increase their surface energy or modify the functional groups on the surface to make them more amenable to adhesive bonding to another polymer or to a metal. These treatments include flame treatments, corona (atmospheric) treatments, and plasma treatments. In vacuum coating technology, flame or corona treatments are the most common external treatments, while plasma treatments are the most common for in situ treatment in the deposition system [24].

Surface hardness

In addition to changing the surface morphology and chemistry, the hardness of the near-surface region can be changed by diffusion. Diffusion hardening can be done by high-temperature pack cementation or by plasma-enhanced gaseous diffusion (e.g. ionitriding) [25–27]. Table 3.2 gives some typical values of hardness and thicknesses (case depth) formed by high-temperature diffusion [2].

Surface barrier layers

Float glass is generally a soda lime glass and is a common substrate material. A problem with float glass in some cases is the diffusion of sodium out of the glass and into the film during

Table 3.2: Hardening of surfaces by diffusion [2]

Treatment	Substrate	Microhardness	Case thickness (kg/mm^2)
Carburizing	Steel: low C, medium C, C–Mn Cr–Mo, Ni–Mo, Ni–Cr–Mo	650–950	50–3000
Nitriding (ion)	Steel: Al, Cr, Mo, V, or W Austenitic stainless	90–1300	25–750
Carbonitride	Steel: low C, medium C, Cr Cr–Mo, Ni–Cr–Mo	550–950	25–750
Boriding	Steel: Mo, Cr, Ti, cast Fe Cobalt-based alloys Nickel-based alloys	1600–2000	25–500

processing. To avoid this problem a barrier layer of silica can be deposited by spray pyrolysis on the air side of the glass on the float glass line.
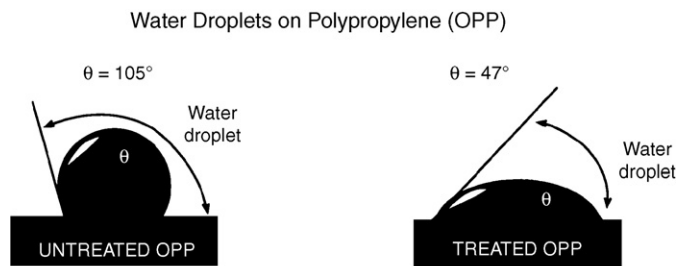
Basecoats: inorganic

An example of an inorganic basecoat to increase the functionality of a coating is the use of a diamond-like carbon (DLC) basecoat to increase the scratch resistance of a decorative coating on a soft substrate [28].

3.7.2 In Situ Surface Modification

There are several techniques to modify surface in the deposition system. They include:

- Plasma immersion ion implantation deposition (PIIID), where a metallic cathode is immersed in a plasma and pulsed momentarily to a high voltage (50–100 kV) [29, 30]. Ions are accelerated from the plasma and before there is an arc the pulse is terminated. When using nitrogen and a high part temperature this process is similar to ionitriding

- Plasma anodization is a method of growing a very coherent oxide layer on the surface of some metal compounds and silicon [31, 32]

- A plasma may be used to change the functional groups on the surface of a polymer to change the surface energy and make the surface more acidic or more basic. This can change the contact angle on the treated surface, as shown in Figure 3.12

- Polymer evaporation and flow coating. The deposition of a film of liquid polymer on the substrate surface is similar to flow coating and can be used to reduce the number of surface defects in vacuum web coating [33, 34].

Plasma treatment by nitrogen plasmas (N_2 or NH_3) can produce functional groups such as imine (C=N), amide (N–C=O) or amine C–N) groups [35, 36], which can aid in

Water Droplets on Polypropylene (OPP)

$\theta = 105°$

Water droplet

θ

UNTREATED OPP

$\theta = 47°$

Water droplet

θ

TREATED OPP

EFFECT OF CORONA TREATMENT ON WETTING

Figure 3.12: Contact angle. [From SVC Education Guides to Vacuum Coating Processing (2009) – Surface Preparation: Surface Energy, Wetting Agents, and Surfactants, with permission.]

metal–polymer adhesion. Oxygen-containing plasmas are used to produce covalent bonds (C–O–C), where the oxygen can bond to oxygen-active metals [37].

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