

## **Supercleanrooms - Design for Molecular Contamination Control**

### **Contents**

- Purpose
- Introduction
- Sources of molecular contamination
- Effects of molecular contamination
- Reduction of molecular contamination
- Evaluation of molecular contaminants
- Materials to be avoided in cleanrooms
- Guidelines for selection of cleanroom materials

### **Purpose**

The purpose of this paper is to study the next level of air quality so that the future generation of cleanrooms can efficiently produce more sophisticated products. This means considering air contaminants on a molecular scale. This paper attempts to take the current information published on molecular contamination and concentrate on the causes and effects of offgassing, then propose practical guidelines to control molecular contamination. However, until there is an accepted industry standard for testing of materials for offgassing and this data becomes available, the full extent of offgassing will not be completely defined.

### **Introduction**

Currently cleanrooms are classified by the total particle mass in the cleanroom air. However there is now a standard, SEMI F21-95, which classifies the 'Airborne Molecular Contaminant Levels in Cleanrooms'. This is particularly applicable for 'Supercleanrooms' which are generally referred to as Class M2.5 (10) or better. This level of cleanliness is generally required for semiconductor devices with line geometry finer than 0.5  $\mu\text{m}$ . This is also referred to as 'ultraclean technology' where the presence of molecular contaminants can have a significant effect on the quality of the product.

Surprisingly, the abundance, by mass, of molecular contaminants per unit volume of air is many orders of magnitude greater than the total particle mass in a typical cleanroom. Also the molecular contaminants have far greater diffusivities and attach themselves to surfaces more easily than particles. Consequently, the arrival rate of molecular contaminants at clean surfaces, on a mass basis, greatly exceeds the arrival rate for particles. Furthermore, tests have shown that the level of molecular contamination is higher in the cleanroom than in an office building or even in outside air.

To meet the requirements of supercleanrooms the level of molecular contaminants has to be lowered considerably. This requires identifying the sources of the contaminants, evaluating the harmful contaminants and specifying acceptable molecular contaminant levels.

The main premise of this paper is offgassing which is the discharge of vapors from a substance. These vapors are either dissolved in the substance and are offgassed due to their volatility or are trapped in the substance and migrate to the surface. Molecular contaminants from offgassing include organic compounds such as hydrocarbons, amines and organosilicon as well as inorganics such as chlorine, fluorine, boron and sulfur. In the cleanroom these are also referred to as volatile pollutants.

### **Sources of molecular contamination**

- Material offgassing (or outgassing)
- Outside air
- Leaching
- Processes in cleanroom
- Cleaning agents
- Cleanroom personnel

### **Effects of molecular contamination**

The following are some of the problems associated with molecular contamination:

- T-topping of photoresists
- Boron doping
- Phosphorous doping
- Etch rate shifts
- Si<sub>x</sub> formation following preoxidation clean
- Threshold voltage changes
- Nucleation irregularities
- Poor adhesion during metallization
- Oxide growth
- Oxide etching, voltage breakdown
- HEPA filter degradation
- Wafer and stepper optics hazing

### **Reduction of molecular contamination**

The following design concepts assist in preventing molecular contamination:

- Avoid use of materials which do not meet offgassing criteria.
- Minimize the amount of materials used which unavoidably offgas.
- Improve wafer cleaning procedures e.g. the RCA cleaning method, incorporate ozonized ultrapure water treatment or use megasonics.

- Encapsulate or cover materials that offgas.
- Avoid exposure of cut edges.
- Use minienvironments.
- Reduce the amount of fugitive or corrosive gases emitted from the manufacturing process.
- Use DI water and not steam for humidification.
- Establish and maintain correct protocol procedures and QA for preparation, installation and commissioning of all cleanroom materials.
- Maximize amount of prefabrication that can be done outside of cleanroom.
- Ensure sealants, gels and adhesives have properly cured before entering cleanroom.
- Design tool layout to isolate or deter molecular contamination in sensitive tool areas.
- Isolate and/or filter fugitive emissions from the process.
- Use chemical filters to filter outside makeup air.
- Use chemical filters to filter recirculated cleanroom air.
- Use gas phase adsorber cells close to the tools.
- Use inert gas e.g. nitrogen for blanketing or purging.
- Avoid unnecessary painting or finishing in the Clean Zone.
- Perform any necessary painting outside the cleanroom and allow sufficient drying time.
- Reduce air velocity across materials that offgas or avoid exposure to airstream.
- Use condensation traps.
- Desorb gases from materials prior to installation eg heating, ultraviolet radiation, plasma scrubbing.

### **Evaluation of molecular contaminants**

The following is a list of contaminants which have been identified in the cleanroom air. Although some of the effects on the cleanroom process have been evaluated not all effects are known. Therefore, some offgas compounds are listed with no specifically known effects.

#### Amines

Sources: HMDS used in the lithographic process, steam humidification, water based epoxies, paints, TMAH, NMP

Some photo resists, especially the deep UV photo resists, are very sensitive to trace levels of amines. As little as 600 parts per trillion of reactive amine such as NMP, HMDS or ammonia can disable the image processing. Contamination effects can be reduced by,

- Reducing the offgassing of fugitive amines.
- Using chemically treated carbon filters to remove the amines.
- Reduce the amount of silanes that react with amines which form silicon nitrides on the wafer surface.
- Reduce the amount of chlorine that react with amines which form ammonium chloride on the wafer surface.

- Reformulate amine containing compounds.

#### Aromatics (benzene, styrene, toluene, xylene)

Sources: Paints, sealants, polymers, outside air.

#### Boron

Sources: HEPA filters, flame retardant in some materials, outside air.

Boron exists in both volatile and particulate contaminants. Tests have shown that the cleanroom can contain more than twice the amount of volatile boron than general laboratory air. The main source of boron is from the air and from the borosilicate glass used in HEPA filters. Trace levels of hydrofluoric acid will etch the borosilicate fibers and release boron. Boron is a fast diffuser and has an affinity for the oxide that forms on bare silicon making it particularly problematic. Boron contamination on silicon surfaces can lead to unintentional p-type doping of lightly doped n-type layers. Boron contamination can be reduced by,

- Eliminate the use of boron in the filter material.
- Use potassium hydroxide impregnated filters to collect volatile boron.
- Reduce the amount of hydrofluoric acid gas exhausted into the air which reacts with borosilicate in the filters.
- Use a more stable flame retardant i.e. antimony, bismuth

#### Highly volatile organic compounds (solvents, alcohol's)

Sources: Paints, adhesives, plastics, polymers

Highly volatile organic compounds such as methanol, acetone and low molecular weight alkanes quickly produce a monolayer on clean surfaces but their high volatility prevents accumulation much beyond a monolayer and so they cause little problem. As a general rule organics with low boiling points do not pose detrimental effects. Many polymers offgas significant quantities of low molecular weight hydrocarbons and solvents but these compounds have not been detected on the wafer surface.

#### Phosphorus and Phosphates

Sources: Triethylphosphate (TEP) in HEPA filter polyurethane sealant, tape, capacitor covers, paint, filter media

TEP is used as flame retardant in polyurethane sealant. Offgassing of organic phosphorus compounds from the sealant containing TEP is orders of magnitude higher than from any of the other sources. TEP diffuses into the silicon bulk and causes undesirable electrical effects. It is particularly harmful because of the relatively large amount of offgas produced. Phosphorus acts as a dopant and is detrimental to the silicon wafer surface at low ppm levels.

#### Phthalates

Sources: Polymers, urethane water-proofing, wire coatings, soft plastics

The primary source of phthalates are plasticizers and stabilizers in various polymers used in construction materials. These are long chained molecules which should be avoided on the wafer surface.

Aliphatics (nonane, decane, undecane)

Sources: Paint, adhesives, petroleum products, outside air

Usually present in very small quantities and so doesn't present a problem.

Aromatics (toluene, xylene, ethylbenzene, styrene)

Sources: Paints, adhesives, solvents

Methylene chloride (dichloromethane)

Source: paint stripper

In general this compound does not cause any problems.

Formaldehyde and other aldehydes

Sources: particle board, plywood, urea-formaldehyde foam insulation

Butyl and Cellosolve acetate

Sources: Process chemicals, outside air

Chlorofluorocarbons (freon)

Sources: Air conditioners, foaming agents

Iron

Sources: Corrosion product in air handling system

Magnesium, sodium

Sources: Outside air, air conditioning system

Polymer additives (BHT, DOP)

Sources: BHT and DOP are present in polymers as antioxidants and plasticizers, respectively.

Tests carried out on commonly found additives in polymers such as butylhydroxytoluene (BHT) and di-octylphthalate (DOP) in the absence of moisture, do not lead to degradation haze. Although the effect on hazing is minimal their deposition is extensive and the potential for defect generation in wafer bonding is significant. Hence, these compounds are only harmless if moisture is excluded.

### Siloxanes

Sources: Sealants, silicone gels, urethane water-proofing, wire coatings, polymers

The source of siloxanes is primarily the offgas products of silicone sealants and silicone gels. Siloxanes are of particular concern because of the relatively large amount that can be offgassed. Siloxane contamination can be reduced by the following:

- Minimize the amount of curing done in the cleanroom. Hence maximize the amount of prefabrication outside of the cleanroom.
- Manufacture sealants and silicone gels with minimum number of short chained siloxanes.

### Acid gases

Sources: Process chemicals

These gases are particularly harmful especially HCL and HF as they are strong oxidizing agents. They react with HEPA filters and metals producing other gases. They also react to form salts on the wafer surface. Their presence should be eliminated as much as possible.

### **Materials to be avoided in cleanrooms**

The following products should be avoided in the cleanroom based on offgas criteria:

- Urea-formaldehyde foam insulation
- Pressed wood products
- Plywood
- Particleboard or hardboard
- Gypsum board
- Neoprene
- Fluorocarbon dry lubricant
- Premium grease
- Fiberglass
- Materials that contain amines.
- Materials that contain phosphorus and phosphate compounds including TEP and DOP.
- Materials that contain sulfur.
- Materials that contain chlorine and fluorine.
- Materials that contain boron.
- Soft plastics that contain high levels of phthalate or other plasticizers.
- Materials that contain flame retardants such as boron or organophosphorous (TEP).

### **Guidelines for selection of cleanroom materials**

In general other than untreated metal products e.g. aluminum, carbon steel and stainless steel there are few materials that are guaranteed to meet offgassing criteria without being tested. As a crude rule the harder the material the better and the softer the material the more likely it is to offgas. Since a lot of manufactured materials are proprietary it is not always known what all the components are and hence the requirement for testing. The major contributors to offgassing are those compounds that are close to a fluid state e.g. sealants, adhesives, gels. If

preferred cleanroom materials do not meet the offgassing criteria it may be possible to work with the manufacturer to reformulate the material and eliminate the undesirable component. The following is a guideline for selection of cleanroom materials:

- Avoid phosphorous compounds in polyurethane materials.
- Select hard, high density plastics e.g. high density polyethylene, polypropylene, PVDF, polycarbonate, ABS, EPDM, PTFE, PFA (Teflon), nylon rather than soft plastics e.g. vinyl chlorides (PVC). Expanded PTFE (Gore-tex) is a low offgassing material. There are some hard PVC and CPVC materials e.g. molded pipe fittings which are acceptable.
- Avoid polymers which contain significant amounts of plasticizers and other materials with BHT antioxidants.
- Silicone based gels should be halogen free and processed to minimize offgassing of short chained siloxanes.
- Urethane gels should be stabilized to avoid offgassing at maximum ambient temperature.
- Petroleum based gels e.g. Protopet demonstrate zero offgassing.
- Silicone sealants should be stabilized to meet offgassing criteria eg type S-11, Dow Corning 739 and 790.
- In general, avoid glues and adhesives.
- Acetone or acetic acid based adhesives or sealants are acceptable. Should preferably be alcohol based.
- Preferred sealants are acrylic or butyl rather than silicone or urethane.
- Alkoxy Cure Silicone sealant, Tosseal 80 SC (Toshiba Silicone) is acceptable.
- Preferred adhesive is acrylic. Avoid use of epoxy.
- For cleaning use isopropyl alcohol and non-ionic, non-phosphate detergent. Do not use any ammonia based products.
- For wire coating select hard material e.g. Teflon and not soft material e.g. PVC.
- Preferred coating is amine free, water based synthetic polymer
- Avoid acrylic latex or oil-based enamel paints. Preferable use polyester powder coatings which are electrostatically applied and thermally treated. Paints should be amine free.
- If paint thinners are used they should be water or low molecular weight solvents e.g. toluene or acetone.
- Avoid or minimize use of boron silicate in filters.
- Use laminate Formica or metallic e.g. powder coated aluminum for flooring rather than vinyl.
- Preferably use cathodically applied and baked epoxy coatings.
- Preferred structural material is anodized aluminum. Also acceptable is powder coated aluminum and nickel plated alloy.
- Preferred gasket materials are Teflon, expanded PTFE, EPDM and EPT.
- Preferred lubricants are Teflon based grease or oil. Krytox is acceptable.