Airborne Molecular Contamination and Effects on Process Yield in Electronics Manufacturing

The issue of particle control with the use of HEPA and ULPA filters has long been an essential part of the fabrication process for integrated device semiconductors as well as the disk drive and liquid crystal display industries. Although very efficient for removing particles down to a critical size of 0.05µm, filter technology is not as efficient in removing molecular contamination with average dimensions of 2-30Å. The presence of such Airborne Molecular Contamination (AMC) within the processing areas has played a more significant role as device geometries for integrated circuits and disk drives have shrunk and glass panels for liquid crystal displays have grown much larger. As these manufacturing trends have evolved, ever-shrinking concentrations of AMC have been shown to play a critical role in yield processes for all of these fabrication processes.

In recognition of growing concerns about AMC effects, a SEMI working group established the F21-95 standard in 1995. Now known as the F21-1102 standard, the 4 classes of AMC were defined as molecular acids (MA), molecular bases (MB), molecular condensables (MC or Organics) and molecular dopants (MD). Since the creation of the F21-95 standard, a number of studies and tests have been performed to help monitor and in effect limit the amount of AMC within various process disciplines. In this brief review article we will discuss the sources of AMC and the effects that AMC can produce to limit process yield.

Overview of Contaminants Sources and Yield Effects

Molecular Acids (MA)

Molecular Acids in the form of atmospheric contaminants are comprised primarily of hydrofluoric acid, hydrochloric acid, sulfuric acid, and nitric acid. The primary sources for each of these MA are the process chemicals used in the manufacturing areas. Acid contamination can spread throughout manufacturing by poor airflow design and recirculation of acid fumes into other process areas. Another source of molecular acids can be outside pollution. The use of chemical filters in process sensitive areas or at the air intake (primarily for removal of NO_x and SO_x compounds) has a considerable benefit for removing MA and limiting associated problems.

At concentration levels of parts per billion molar (ppbM), the presence of MA can cause yield problems. These effects include the corrosion of aluminum and copper films, hazing of surfaces – both for products and process tools, as well as a host of electrical faults at the chip level. The interaction of acids and molecular bases in air can produce small sized particles that can fall on product surfaces. Important to all silicon-based processing, hydrofluoric acid is an especially critical MA due to its widespread usage and its deleterious nature. The aggressive nature of HF with SiO_2 is critical for the thinner gate oxides now in play with integrated device manufacturing. An ancillary issue with HF is the presence of HF attacking the borosilicate glass in HEPA filters thereby releasing boron as an airborne contaminant and causing unwanted p-doping of silicon based processes.

Molecular Bases (MB)

Molecular bases includes ammonia, amines (including trimethylamine from exchange resins, morpholine from humidifer systems and amines present in photoresist strippers) and amides (for example NMP). Ammonia is far and large the MB found most often due its presence in process chemicals (via NH_4OH), photoresist chemicals (via HMDS), and its widespread use as an electronic specialty gas (especially for TFT-LCD manufacturing). Similar to MA, careful control of MB via proper air handling is critical for limiting the presence of MB in critical process areas.

The effects of MB are in some cases similar to those of MA in that aluminum or copper corrosion and salt formation as a result of combination with MA in air can occur. In addition, a time-dependent haze due to MB can occur on wafers, disks, and displays. Base-specific yield effects include T-topping of chemically-amplified DUV photoresists. Moreover, lithography processes are susceptible to MB effects due to the large amount of ammonia byproducts in lithography chemicals and lithography process areas. The presence of MB at ppb levels is an area of concern for causing any of these effects especially in the latest technology manufacturing processes.

Molecular Condensables (MC)

Molecular condensables in air can be caused from a number of sources found throughout the processing areas. Common examples and sources are shown in the table below. These organic compounds have boiling points typically greater than 150 °C and can adsorb and irreversibly bind to product and tool surfaces.

Condensable	Example Compounds	Source Examples
Plasticizers	TXIB, DOP	Floor tiles, vinyl materials, gloves,
Antioxidants	BHT	FOUPs, pods, sealants,
Phosphates	TEP, TEB	Fire retardent in filter potting compounds
Silicones	Both linear and cyclic	Sealants, o-rings, lubricants

Beyond establishing proper air handling for MC control, it is imperative that materials used in cleanrooms, components used in air handling systems, and those materials that come into contact with the manufactured product all should be tested for outgassing potential MC contamination.

Yield problems caused by MC are well documented and occur at a host of different process steps. Although too exhaustive for this summary article, several examples include: Phthalates, silicones, and plasticizers that can desorb and cause delamination problems for thin films and photoresists in semiconductor and disk drive manufacturing. Phthalates that have been shown to affect gate oxide integrity and can also decompose to form silicon carbide. Finally, optic and mask hazing due to silicones has become more problematic with the shift to lower wavelength/higher energy systems (193 nm).

Molecular Dopants (MD)

The two dopants of dominant interest and most wide-spread use are boron and phosphorus compounds. Various implant molecules and CVD compounds are sources for both boron and phosphorus, however two inherent sources of boron and phosphorus come from materials used within the fab. The borosilicate glass present in HEPA and ULPA filters is a source for boron compounds. Some shedding of boron over time can occur naturally, but improved control of this boron contamination source can be accomplished a) by strict control of hydrofluoric acid vapors in the air handling system and b) substitution of boron-free filter material. Phosphorus compounds are also found in and around filtration systems as the flame retardants in potting compounds. These compounds can contain organophosphates that can outgas and condense on product surfaces.

The yield issues for MD are unwanted n-doping (phosphorus) and p-doping (boron) of silicon. These effects are known to be problematic at levels around 10 pptM, and products will become more sensitive as thinner junctions in advanced devices will produce inherently higher dopant concentrations.

Benefits of Controlling Airborne Molecular Contamination

The benefits of controlling AMC are numerous and far outweigh the cost of implementing control methods and performing baselining studies when considering the impact AMC may have on process success. Yield declines due to AMC have been well documented, and complete factory shutdowns, costing millions of dollars, do occur.

It is important to note some of the benefits of controlling AMC:

- Improved yield and process control
- Improved product reliability
- Ability to "copy exact" processes between factories such that new factories and processes ramp up more quickly
- AMC data information allows the engineer to set rational, cost-effective specifications
- Establishing AMC data and specifications by process allow quicker recoveries from contamination events.

Conclusions

In this article we have provided a summary view of AMC sources and the general yield effects within the electronics fabrication industries. It is vital, especially as manufacturing of electronic devices move to both smaller features (semiconductors and disk drives) as well as larger areas (TFT-LCD) that proper control and monitoring of AMC is performed. A properly defined monitoring program can be limited in scope, and yet still provide important information for establishing baseline data of molecular contamination. It is this baseline information that is vital to understanding normal levels of contamination and also allows a comparison with AMC data found during a troubleshooting event. Without baseline data no comparison can be made and events that harm product yield are much more difficult to find, understand, and eventually correct.

AMC is by definition contamination species found in air. An important extension of AMC are the contamination species that eventually find their way to the silicon wafer or hard disk drive or liquid crystal display. This Surface Molecular Contamination (SMC) can transfer from airborne species directly to contamination on the product surface or may be transferred indirectly via wafer handling or robotics from process tools or material contaminated by SMC. SMC is important to monitor and control as the eventual process problem and yield issue is one that occurs on the manufactured surfaces, and is not simply an airborne issue. Roadmap definitions and contamination levels were first defined in the 2003 International Technology Roadmap for Semiconductors for surface molecular organics (SMOrg), surface molecular dopants (SMD), and surface molecular metals (SMM). These surface related issues will only become more important as technology generations continue to advance.

Finally, it is important to note that many yield incidents involving AMC (or SMC) can only be diagnosed with a thorough understanding of the chemicals, gases, materials and the air handling systems in use. All of these parameters can interact independently or in conjunction to promote contamination and process problems. The simple effect of haze or spots on a processed surface could be due to a number of issues. These include elevated concentrations of silica or TIC in rinse DIW. Alternatively, MA, MB, or MC in air could cause this hazing via MA or MB corrosion of the surface, MA and MB reaction to form particles that form on the surface or MC condensation. Each of these gas phase pollutants can be transported to processing areas via insufficient or inefficient air handling. Still many other sources could be investigated and turn out to be the final root cause of a simple effect of hazing or spotting on the processed surface, be it silicon wafers, hard disk drives, or liquid crystal displays. As shown by just this simple example, there are many opportunities for AMC to contribute to process yield issues in the modern fabrication environment.