Characterization of Organic Contaminants Outgassed from Materials Used in Semiconductor Fabs/Processing

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Abstract. As ULSI technology continues to advance, semiconductor manufacturers are facing new contamination control and monitoring challenges, including airborne molecular contamination (AMC). AMC is being recognized as one of the yield limiting factors in newer generation microelectronics fabrication processes. A major AMC source, materials’ outgassing can introduce a variety of organic contaminants into semiconductor fabs, impacting many processes. This paper provides a brief overview of typical organic outgassing contaminants, their sources, process impacts and analytical techniques used to detect these species. In addition, outgassing study results for polycyclodimethylsiloxanes and several other contaminants using thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS) analysis are employed to demonstrate the relationships among (1) outgassing level and outgassing time (linear), (2) outgassing quantity and the inverse of outgassing temperature (logarithmic), and (3) outgassing quantity and material surface area (linear). A new method, based on gas diffusion conductivity detection, for ammonia and volatile amines’ outgassing analysis is also presented.

INTRODUCTION

Understanding the effects of Airborne Molecular Contamination (AMC) on microelectronic fabrication processes is of increasing concern as ULSI technology continues to develop. SEMI F2-951 standard “Classification of Airborne Molecular Contaminant Levels in Clean Environments” specified AMC in four classes – molecular acids (MA), molecular bases (MB), molecular condensables (MC), and molecular dopants (MD) [1]. Molecular condensables are organic contaminants that may adversely impact many semiconductor processes. The 2002 International Technology Roadmap for Semiconductor (ITRS-02) indicates organic contamination on silicon wafers after critical cleans should be below 2.6E13 carbon atoms/cm² for 130 nm technologies. The value drops to 1.5E13 for 90 nm technologies [2]. As one of the major sources of molecular condensables, materials’ outgassing can contribute to organic contamination from a variety of cleanroom materials including filters, sealants, walls, adhesives, floor tiles, paints, wafer carrier and packaging materials, as well as consumables such as garments, gloves, tapes and cleaners.

Material’s outgassing is also a source of airborne base contamination in semiconductor cleanrooms. As lithography continues to progress to deeper DUV wavelengths, the resists employed in semiconductor processing are increasingly sensitive to airborne bases. The current ITRS specification for total bases in lithography is 750 pptM (parts per trillion Molar) [2]. Therefore, better understanding of materials’ outgassing behaviors is necessary for cleanroom material selection and the control of both molecular base and molecular condensable concentrations in microelectronic Fab environments.

EFFECTS OF MOLECULAR CONDENSABLES AND ANALYTICAL METHODS FOR MATERIALS’ OUTGASING

Effects of Outgassed Organic Contaminants

Organic contaminants can affect semiconductor processing in a variety of ways. Tamaoki, et al.,
reported that organic contamination on the initial SiO\textsubscript{2} surface caused degradation in the polysilicon layer resulting in breakdown field strength reduction [3]. Kasi, et al., found that significant organic contamination (10\textsuperscript{14}-10\textsuperscript{15} \text{C atoms/cm}^\text{2}) could cause serious degradation in MOS devices grown on hydrogen-passivated silicon (Si) [4]. Both oxide and nitride film growth and quality can be affected by organic contamination as well. Licciardello, et al., reported that plasticizers such as dioctyl phthalate (DOP) could react with HF-etched surfaces to generate carbon-rich hydrophobic surfaces that retarded silicon oxide growth [5]. Saga et al., found that wafers contaminated with butylated hydroxytoluene (BHT) and dibutyl phthalate (DBP) experienced gate oxide integrity (GOI) degradation and low-pressure CVD nitride growth retardation [6,7]. Organophosphorus contaminants such as triethyl phosphate (TEP) and tris(chloropropyl) phosphate (TCPF) flame retardants can cause serious unintentional doping of Si device wafers resulting in yield losses [8,9]. FTIR and GC studies have shown that polycyclohexyl-2-siloxanes outgassed from sealants of silicone polymers form particles [10]. Organic contaminants and photo resist outgassing can present contamination and haze problems in DUV lithography [11].

**Analytical Methods for Materials’ Outgassing Measurements**

Both direct and indirect techniques may be used for materials’ outgassing measurements. Direct methods commonly used in the microelectronic industry include material weight loss analysis and thermal desorption gas chromatography-mass spectrometry (TD-GC-MS, also referred as dynamic headspace GC-MS). Weight loss measurements are an excellent method to determine total mass loss due to outgassing of volatiles and semi-volatiles. They provide useful information for assessing physical property changes such as shrinkage during the curing process of a sealant material. TD-GC-MS combines the superior separation ability of GC and the powerful unknown identification and quantification ability of mass spectrometry. The TD-GC-MS technique allows for qualitative and quantitative analysis of volatile and semi-volatile compounds outgassed from different materials used in semiconductor fabs and processes.

Indirect measurements of outgassed volatiles and semi-volatiles can be made by exposing witness Si wafers to materials of interest and subsequently analyzing the outgassed or adsorbed species by TD-GC-MS or Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS), respectively. One of the benefits of indirect outgassing measurements is that they provide a means to study the adsorption behavior of outgassed organic species on Si wafer surfaces [12,13]. A drawback of the indirect measurement is that it does not provide a complete picture of the total outgassed organic contaminants.


**CHARACTERIZATION OF OUTGASSED ORGANIC CONTAMINANTS USING TD-GC-MS**

**Detection of Organic Contaminants Outgassed from Cleanroom Materials**

Because of its good qualitative and quantitative capabilities, TD-GC-MS was used in all of the organic outgassing characterization experiments and wafer surface organics’ analyses described here. Fig. 1 shows a block diagram of a TD-GC-MS system. For materials’ outgassing analysis, a piece of selected material was placed in an outgassing thermal desorption tube and analyzed on a TD-GC-MS system (Fig.1A). Method B in ASTM F1982-99 standard [15] was used for wafer surface organic analysis (Fig. 1B).

![FIGURE 1. Block diagram of TD-GC-MS system.](image-url)
Fig. 2A shows a TD-GC-MS outgassing chromatogram of a silicone-based cleanroom sealant. Fig. 2B shows the TD-GC-MS chromatogram for a witness wafer that was exposed to one gram of the sealant shown in Fig. 2A. After three days of exposure at room temperature, the same types of polycyclo(dimethyl)siloxanes were detected on the witness wafer surface with dodecamethyl cyclohexasiloxane as the most abundant contaminant (peak 4 in Fig. 2B). The total polycyclo(dimethyl)siloxane level of 6 ng/cm$^2$ (~2.5E14 carbon atoms/cm$^2$) was significantly higher (>10 times) than the ITRS-02 requirement for 130 nm technologies. Another major outgassing compound, acetic acid was not detected on the wafer surface, suggesting that acetic acid did not deposit there. Fig. 2C demonstrates the powerful contaminant identification capability of TD-GC-MS technique. The chemical structure of the contaminant eluted from the GC column at 10.9 min.
was identified to be dodecamethyl-cyclohexasiloxane by matching the unknown spectrum (top panel in Fig. 2C) with the standard dodecamethyl-cyclohexasiloxane spectrum (bottom panel in Fig. 2C) stored in the MS spectral library.

Fig. 3 shows the detection of triethyl phosphate (TEP), a commonly used flame retardant. Approximately 49 μg/g of TEP outgassed from a cleanroom pop-out sealant material at 50 °C (Fig. 3A). A witness wafer exposed to the pop-out sealant at room temperature showed a surface TEP level of 5.8 ng/cm² (~2E13 P atoms/ cm²), well above the critical level that can cause unintentional phosphorus doping of Si wafers and yield loss [17]. Once again, TEP was positively identified by the MS detector (Fig. 3C).
Outgassing Characterization

Several polymer materials known to outgas organic contaminants commonly seen in semiconductor Fab cleanroom environments were selected as part of a study designed to understand outgassing behavior as a function of time, temperature, material surface area and weight. Organic contaminants tested included polycyclodimethylsiloxanes, dibutyl phthalate (DBP), butylated hydroxytoluene (BHT), 2-ethyl-1-hexanol, methylstyrene and naphthalene.

As shown in Fig. 4, a linear relationship was observed between the concentration of various polycyclodimethylsiloxanes outgassed at 50 °C and outgassing time. Outgassing rates for different compounds were estimated from the slopes of outgassing concentration vs. outgassing time plots. Similar results were also obtained for DBP and BHT. Data for tests conducted at 75 °C also showed a linear relationship with higher slope values, indicative of higher outgassing rates at 75 °C verses 50 °C.

The influence of outgassing temperature on outgassing concentration is shown in Fig. 5. A linear relationship was observed between the logarithm of outgassing quantity and the inverse of outgassing temperature (1/T) for polycyclodimethylsiloxanes, DBP and BHT. These results are in agreement with the findings reported by Takeda, et al., in their paper, which demonstrated a method of estimating outgassing rates of contaminants of interest based on their vapor pressure [18].

Fig. 6 and Fig. 7 illustrate the relationship among surface area, sample weight and outgassing quantity. As shown in Fig. 6, outgassing levels of polycyclodimethylsiloxanes are proportional to the sample surface area when the sample weight remains constant. However, outgassing is independent of sample weight when the surface area remains constant (Fig. 7). Similar behavior was observed for methylstyrene, 2-ethyl-hexanol and naphthalene.
Siloxane Outgassing Dependence on Sample Surface Area
(outgassing condition: 50°C, 15 min)

![Graph](image)

**FIGURE 6.** Outgassing quantity vs. material surface.

Outgassing Dependence on Sample Weight (50°C, 15min)

![Graph](image)

**FIGURE 7.** Outgassing quantity vs. material weight.

Based on the results of these material outgassing characterization experiments, the following conclusions may be drawn for the contaminants studied under the conditions outlined above: 1) there is a linear relationship between outgassing concentration and outgassing time; 2) outgassing rate can be estimated from the slope of the outgassing concentration vs. outgassing plot; 3) there is a linear relationship between the logarithm of the outgassing quantity and the inverse of outgassing temperature (1/T); and 4) outgassing quantity is proportional to the material surface area and independent of material weight when surface area remains constant, suggesting that outgassing is a surface phenomenon. However, due to the large number of variables in the physical properties and chemical composition of materials used in cleanroom construction and operation, the authors believe that materials’ outgassing can be far more complicated than the limited findings reported in this paper.

### AMMONIA/AMINES’ OUTGASSING

**Ammonia/Amines’ Impact**

The impact of airborne molecular base (MB) contamination on the performance of chemically amplified (CA) resist has been a long-standing problem in semiconductor lithography [20-21]. MB can neutralize the photo-generated acid during the time delay between the exposure and post-exposure bake (PEB), generating insoluble products that cannot be dissolved by the developer solvent. A lip, known as “T-topping”, forms at the top of the developed resist profile. Extreme cases of “T-topping” cause bridging between adjacent patterns. Among numerous possible MB contamination sources, materials’ outgassing is a common one. Volatile molecular bases can outgas from cleanroom materials such as ceiling tiles, sealant, paints, adhesives, cleaning solutions and process chemicals, among others. Screening new cleanroom materials for NH3/amines outgassing before using them in the cleanroom and/or DUV bay may substantially reduce the likelihood of MB contamination.

**Gas Diffusion-Conductivity Ammonia/Amines’ Outgassing Analysis**

The typical TD-GC-MS technique used for condensable organics outgassing is generally not suited for detecting ammonia (NH3) and very volatile amines, which have poor recovery in TD-GC-MS due to their high volatility. Therefore, a new materials’ NH3/amines’ outgassing method based on gas diffusion conductivity detection has been developed. Fig. 8 shows a schematic diagram of this NH3/amines’ outgassing technique. Detection limits of less than 1 part per billion (ppb or ng/g) can be achieved using this method.

FIGURE 9. NH3/amines' outgassing of two cleanroom sealants. A. Sealant A; B. Sealant B; C. SEM image of "T-topping" caused by NH3/amines' outgassing of sealant A.

Fig. 9 shows the NH3/amines' outgassing of two cleanroom sealants. Sealant A outgassed 723 ng/g NH3/amines at room temperature (Fig. 8A) and caused significant "T-topping" defects in E0 delay photo resist tests (Fig. 8C). The NH3/amines' outgassing level of sealant B was < 5 ng/g and this sealant had no impact on the photo resist develop process.

In time-dependent outgassing studies, three (3) days of curing were required for the NH3/amines' outgassing level from sealant A to drop to the single ppb range (Fig. 10A). The initial quantity of NH3/amines outgassed was in excess of 700 ppb. The outgassing level dropped to 30 ppb after an 8-hour cure.

FIGURE 10. NH3/amines' outgassing of and deposition on witness wafer surfaces. A. Time dependent NH3/amines' outgassing of sealant; B. Surface NH4+ on witness wafers exposed to sealant A; C. Correlation of witness wafer surface NH4+ and sealant outgassing levels.
In order to understand the adsorption behavior of outgassed NH₃/amines on Si wafers as a function of curing time, clean Si wafers were exposed to samples of sealant A that had been cured for different lengths of time. Each wafer was subsequently extracted with deionized (DI) water and the extract analyzed by ion chromatography (IC) [22] in order to determine the ammonium (NH₄⁺) content. The wafer exposed to fresh sealant A for one (1) hour at room temperature showed a very high surface NH₄⁺ concentration of 2600E10 NH₄⁺ ions/cm² (Fig. 10B). By contrast, the wafer exposed to a sealant A sample that has been cured for 69 hours exhibited a surface NH₄⁺ concentration close to that of the control wafer, which had no sealant exposure. The linear relationship between witness wafer surface NH₄⁺ concentration and NH₃/amines’ outgassing measurements for sealant A appears in Fig. 10C.

The results from the time-dependent outgassing studies and wafer exposure tests have demonstrated that the gas diffusion-conductivity based technique provides a sensitive method for materials’ NH₃/amines’ outgassing measurements. The combination of this technique with the widely used TD-GC-MS method allows for a more complete screening of cleanroom materials for potential airborne base and condensable contamination, respectively.

**SUMMARY**

Microelectronic fabrication processes with decreasing device geometries are increasingly susceptible to AMC. Many AMC contaminants found in semiconductorfabs come from outgassing of cleanroom materials. Outgassed contaminants can adversely affect many processes, resulting in yield loss, shortened tool life and reduced long-term device reliability. The large variety of cleanroom materials and numerous outgassing contaminants combined with the complexity of process steps makes understanding detrimental levels of particular contaminants in individual processes very challenging. Screening materials for condensables’ and NH₃/amines’ outgassing prior to bringing them into fabs can be used as a first-line-of-defense against molecular contaminants such as organo-phosphorus, siloxanes, plasticizers and ammonia/amines. As processes and chemistries change, requirements for monitoring, control and analysis of materials’ outgassing will continue to evolve. Cooperative efforts among manufacturers of integrated circuits, materials and analytical tools are needed to better understand the impact of molecular contaminants and to properly define specifications applicable to the new ULSI technology.

**ACKNOWLEDGMENTS**

The authors thank Yaacov Maoz of Intel Fab 18 for providing the “T-topping” defect SEM image, Zari Pourmontamed of Intel California Materials Technology Department for collecting the time-dependent NH₃/amines’ outgassing results, and Joseph O’Sullivan of Intel Facilities Technology Development for providing valuable technical inputs.

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