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Development of High Sensitivity Techniques for Characterizing Outgassing of Polymeric Construction Materials for Microenvironments

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Abstract

Further reductions in particulate contamination in semiconductor device manufacturing environments will be required to meet the future challenges of producing

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devices with decreased dimensions. Using pods (microenvironments) to provide very clean environments on a local (wafer level) scale is an alternative that may reduce the technological demands and cost (capital and operating) of providing comparable contamination levels in an entire clean-room manufacturing facility. It has been demonstrated that pods can provide wafer environments that have lower and less variable levels of particulate contamination than conventional clean-room manufacturing environments. However, there have also been indications that outgassed constituents from polymeric pod materials can condense on wafers during storage. These condensed contaminants may impact device processing, device properties, and device performance.

Pods can be constructed of several polymeric materials. In addition, microenvironment manufacturers can choose from several different formulations from the same polymer family. A standard technique to evaluate outgassing of polymers is needed so that: (1) manufacturers can make reliable comparisons of the outgassing potential of materials being considered for use and (2) microenvironment users can make judgements on the relative outgassing threats from different manufacturers' products.

The goal of the work that is summarized below has been to develop standard high sensitivity (10-100 ppb) testing techniques for evaluation of outgassing from polymeric pod materials in a temperature range from 30°C-75 °C. This paper will briefly review outgassing data from polycarbonate materials that was obtained using thermal desorption combined with detection using gas chromatography/mass spectroscopy with volatile pre-concentration or using a flame ionization detector (FID). Although the focus of this program has been on developing techniques to evaluate pod materials of construction, the techniques that have been evaluated may be useful for characterizing outgassing from other polymeric materials found in cleanrooms.

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Key Words

Polymers, Outgassing, Volatile Organic Compounds (VOCs), Pods, Microenvironments, Polycarbonate, Gas Chromatography/Mass Spectroscopy (GC/MS), Flame Ionization Detection (FID)

Introduction

The objective of the work presented below was to develop a high sensitivity technique to detect outgassing at low temperatures ($T \leq 75^\circ\text{C}$) from polymers used to construct wafer pods. Polycarbonate materials were chosen for technique development because polycarbonates are widely regarded as being the cleanest of the materials present in the pods (microenvironments). The techniques that were examined for low temperature outgassing detection were gas chromatography/mass spectroscopy (GC/MS) with volatile pre-concentration and GC with flame ionization detection (FID) for total organics detection. These techniques were chosen as test methods for measuring polymer outgassing since they are very sensitive to volatile organic compounds (VOCs), are widely available, are easy to implement, and use common, relatively inexpensive analytical equipment.

Examples of data collected using each technique will be presented below. The use of cryo-focusing to pre-concentrate the volatile organic compounds (VOCs) and thus enhance the sensitivity of the GC/MS outgassing testing technique played an important role in determining what compounds were outgassing near the temperatures at which the materials are normally used. Outgassing spectra collected at temperatures (150°C) that were far in excess of the normal use temperature were distinctly different than the lower temperature spectra. Results collected using the FID technique indicated that VOCs may migrate from the bulk of the polymers to the surface before outgassing at low temperatures.

Background

In the last few years work has been published (1-3) that suggests that polymeric wafer enclosures can be the source of organic contamination on wafers. Miller and coworkers (1) conducted tests that demonstrated that the contact angle of water on Si wafers increased with increasing storage time in pods. Chemical analysis of the condensed species responsible for the increase in contact angle revealed that some of the contaminants

were additives from the polymers used to construct the pods while other contaminants could be traced to other cleanroom wafer processing sources.

Budde and Holzapfel (2) have shown that plasticizers and antioxidants condensed on Si samples stored in polypropylene wafer boxes. Their work also demonstrated that there were large variations in outgassing from different lots of polyamide and polypropylene materials used to make wafer boxes.

More recently, Budde and coworkers (3) evaluated the outgassing from two different brands of carbon-filled polypropylene wafer boxes using GC/MS with cryofocussing. Their analysis of the contamination from the polymers and contamination on Si samples stored in the boxes showed that there was not a one-to-one correlation between the amount of outgassing from the polymers and the amount of contamination that was detected on Si wafers stored in the boxes. In fact, in this study, the least amount of contamination was detected on the Si samples that were stored in the box constructed out of the polymer that outgassed the most. This work suggests that the chemical nature of both the outgassed VOCs and the potential condensation sites (Si, Al, silicon oxide, and other surfaces) on processed wafers must be considered when assessing potential impact of condensed organic contamination.

Description of Outgassing Testing Procedure and Results

Samples/Sample Preparation

Samples were used as-received from the manufacturers who provided samples for the tests. Some samples were resin pellets (raw material used in polymer molding), while others were obtained from shavings generated by slow drilling of processed polymer sheets. Before use, all sample tubes (approximately 0.25 inches diameter x 6 inches long, stainless steel) and associated analysis end-caps were heated to the same temperature as the experimental run and analyzed on the GC/MS until no detectable impurities remained (the background levels have not been quantified accurately but are estimated to be less than 10 ppb). Approximately 0.1 grams of sample was weighed and placed in the sample tube. One end of the sample tube was equipped with a stainless steel screen to keep the sample in the tube. Both ends of the tubes were then fitted with analysis caps for the autosampler.

Cryofocussed Gas Chromatography/Mass Spectroscopy (GC/MS) Technique Description and Results

Samples were placed in sample tubes in a temperature controlled oven. Sample temperatures ranged from 50 °C to 150 °C. The outgassed VOCs from the sample were swept from the sample tube to the cold finger by a helium carrier gas. The cryofocussing unit used in this test is the PE ATD 50 with a multisampling capability. The cold finger was filled with TENAX 60/80 adsorbent resin. The cold finger collected the VOCs at -30 °C for a specified amount of time, 30 minutes typically. Then, the cold finger was heated rapidly (up to 300 °C) sending the collected sample to the Perkin Elmer 8500 GC/MS where the various constituents were separated by the GC and analyzed by the mass spectrometer. The GC column was a DB-5, 30 meter, 0.25 mm diameter with a 0.25 mm stationary phase, and the oven program included a starting temperature of 45 °C and a 10 °C/min ramp up to 300 °C. This combination of column type, diameter, ramp rate, etc., were found to provide good separation of outgassed compounds. The upper temperature value was somewhat arbitrary but was found to work well for cleaning out the column before the next run. Background runs were made before and after each sample scan using the same parameters as the samples to ensure no contamination was present in the cold finger, GC column, or the MS from the previous sample.

Initial testing was conducted at relatively high temperatures (150 °C) where most polycarbonate outgassing and other studies (e.g., thermal degradation) have been performed and where outgassing is known to occur in easily measurable amounts. As the analytical methods were refined, results at temperatures as low as 50 °C were achieved. Testing temperatures in this range are a much closer approximation to the normal environmental conditions the wafer pods or boxes will experience.

Figure 1 shows two plots of GC/MS data collected during two different tests on the same polycarbonate material. The data is plotted as the total ion count (from the MS) (y axis) versus the GC column elution time (x axis). The peaks are generally associated with compounds. However one compound may generate several peaks due to fractionation caused by sampling. Data in Figure 1a was obtained by conducting an outgassing test as described above. The peaks are reasonably intense, well separated, and well defined, thus facilitating compound identification. For comparison, a test was conducted in which the

polycarbonate material was soaked for three days in high purity acetone. Following soaking, a small portion of the acetone was injected directly into the GC column for analysis. The plot in Figure 1b shows the results of this low-temperature solvent extraction test. Only one peak, due to acetone, was observed in the spectrum.

Comparison of the spectra in Figures 1a and 1b show that the GC/MS with cryofocussing, pre-concentration of the VOCs is very sensitive to low temperature outgassing from the polymers.

Figures 2a, 2b, and 2c show spectra collected from the same polycarbonate material at outgassing temperatures of 50 °C, 75 °C, and 100 °C, respectively. These plots show that the number and type of compounds that outgass from polymers can be significantly influenced by the temperature at which outgassing occurs. These results emphasize the importance of conducting outgassing tests at temperatures that are representative of the actual use temperature of the polymer.

Flame Ionization Detector (FID) Technique Description and Results

In this technique, the samples were placed directly in a sample tube (same tube as used for the cryofocussed GC/MS technique). The sample holder was located in the oven of a gas chromatograph (HP5890II) instead of the chromatographic column. The sample tube was connected to the helium carrier and the FID using a four-way valve which allowed the isolation of the sample loop while keeping the carrier flowing through the FID during sample loading. During data acquisition, the valve was turned so that carrier gas flowed through the sample tube and to the FID.

Two types of sample loading/preparation techniques were tried. In the first method, the sample tube was evacuated for a short period (approximately 15 seconds) to remove any room air from the tube. In the second method, no evacuation was performed and the room air was analyzed with the outgassed gases. The first method was not as repeatable as the second. The exact reason for the lack of repeatability has not yet been determined but could have been due to many factors including contaminants from the vacuum pump and hardware, and variable pump-down pressures causing variable off-gassing of the polymer.

Figure 1
 Gas Chromatography/Mass Spectroscopy (GC/MS) Spectra. The Y axis corresponds to total ion count from the MS and the spectra are normalized so the most intense peak has an intensity of 100%. The X axis corresponds to the GC column elution time. Figure a) shows spectra collected from an acetone solvent extraction test on polycarbonate. Figure b) shows the results of a GC/MS test conducted at 75 °C with cryofocussing.

Figure 2
GC/MS spectra collected (using cryofocussing) from polycarbonate samples tested at a) 50 °C, b) 75 °C, and c) 100 °C. The Y axis is normalized so that the most intense peak has an intensity of 100%.

A constant rate sample temperature ramp (40 °C/minute) was used for testing. A typical chromatogram for the constant temperature ramp is shown in Figure 3. The constant rate ramp produced one large peak with a peak width on the order of 5 minutes wide. The maximum in the FID signal corresponded to a temperature of approximately 100 °C. The area under the peak was proportional to the amount of VOCs emitted from the sample. The peak corresponded to the total organic outgassing of the sample for that run. The peak was not due to a separation of the compounds since there was no GC column after the sample tube. Consequently, the FID measured the total hydrocarbon content of the outgassed constituents. The peak is very wide (approximately 5 minutes wide) due to the large sample volume, the "slowness" of the heating rates for the sample, and the bulk outgassing characteristics of the polymer.

In preliminary sensitivity studies, this technique detected approximately 10 ng of toluene, though further work is needed to determine the sensitivity precisely. In an initial set of sensitivity studies, a polymer sample was spiked with a standard solution of toluene in acetone by injecting it directly on the polymer. The sample was then sealed in the tube and analyzed using TD-FID. The increase in peak height was difficult to distinguish from the off-gassing of the polymer and the dissolving of the polymer by the solvents. As a result, the spike was added to a cleaned, empty sample tube to ensure the peaks measured resulted from the VOCs being added to the tube.

There is evidence that in the polycarbonate samples many of the impurities may have diffused from the bulk and then off-gassed. Fig. 4 shows a plot of repeated runs, where the temperature was ramped to 150 °C and then returned to room temperature on the same polycarbonate sample. The amount of outgassing is low at first, but increases to a maximum after about 2 or 3 runs, and finally decreases as the impurities are depleted from the polymer.

Conclusions

Results have been presented from two outgassing testing techniques used to measure the outgassing from polycarbonate materials. Both techniques were able to detect outgassing from the polymers at low temperatures. The GC/MS with cryofocussing technique is being developed as a standard technique

for identifying the chemical identity of VOCs while the TD/FID technique is being developed as a screening technique for monitoring total hydrocarbons in polymer materials. Although the latter technique does not provide chemical identification of the VOCs, it may be useful as a quality control measurement for raw and processed pod materials.

Issues regarding sample preparation and sample storage are now being addressed in more detail. The low temperature outgassing testing is expected to be sensitive to surface contamination of the polymer test sample. While higher temperature outgassing allows for diffusion of VOCs from the bulk of the samples, a larger fraction of the VOCs are expected to originate at the surface or in the near-surface region of the samples tested at low temperatures.

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Figure 3

Typical TD/FID data scan using a constant temperature ramp rate. The plot shows the large peak width of approximately five minutes. The peak corresponds to the total amount of hydrocarbons outgassed.

Polycarbonate Sample, Ramping to 150 C

Figure 4

Outgassing as a function of the number of times the sample was run using TD/FID testing. Data for three different samples of the same type of polycarbonate are shown.

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