Identifying the Types and Potential Sources of Airborne Molecular Contamination: A Multi-Technique Approach

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Abstract:

In this study we use TOF-SIMS, GC/MS and FTIR for the identification of different types of condensable airborne molecular contaminants that outgas from cleanroom materials. The materials under investigation include construction materials (*e.g.*, floor tiles, filters and sealants), cleanroom furniture, garments and utensils. The transfer of contaminants onto silicon wafers that are brought in contact with the materials is also investigated. In these experiments, each of the materials produces a fingerprint that can be used to identify potential sources of contamination. The longterm objective of these studies is to generate an extensive database that makes it possible to link contaminants observed on wafers to potential sources within the cleanroom environment.

1. Introduction:

The term Airborne Molecular Contamination (AMC) covers a wide range of contaminants present in the cleanroom air. These contaminants can be in form of gases or aerosols. Their chemical nature can be organic or inorganic, and includes acids, bases, polymer additives, organometallic compounds and dopant-containing species. The main sources of AMC are process chemicals, construction materials, and the local environment. The range of the chemical nature of AMCs results in a large number of potential processing problems. Reported are cases of uncontrolled boron and phosphorus doping, etch rate shifts, changes in the wafers electrical properties, fab corrosion, silicon carbide formation following pre-oxidation clean, stepper optics hazing, threshold voltage shifts, HEPA filter degradation and more [1 - 3]. However, the effects of specific AMCs on individual processing steps are not very well understood. Furthermore, correlations between process yield and the concentrations of individual AMCs are either rare or not published at the current stage. The latter are particularly challenging to obtain since AMC-related defects are mostly caused by the deposition of extremely low levels of contaminants on failed components.

As line widths of microelectronic devices approach 0.1 micrometer and below, controlling AMC becomes a critical processing issue [1]. This can only be accomplished if the technical ability is

gained to fully identify the types and sources of AMCs and if the concentrations present in cleanroom and fab environments can be measured [4-6, 10]. Furthermore the chemistry between AMCs and process components needs to be understood in great detail. This in particular must also include “new materials” such as copper or low k dielectrics. Once these issues are solved, material selection and cleanroom design may allow elimination of contaminants that interfere with ongoing processes.

For the purpose of material selection for future fabs and cleanrooms the outgassing of molecular contaminants from each of the materials that are going to be used will have to be considered. Among the substances that are typically observed to outgas from cleanroom materials, those contaminants that are condensable on critical process components are generally assumed to be more likely to cause problems than highly volatile contaminants such as small nonpolar hydrocarbon molecules. The ideal analytical technique for evaluating outgassing from cleanroom materials would specifically identify each of the outgassing components and quantify the amounts of contaminants that outgas. In addition, extremely high detection sensitivity is required.

In the work presented here TOF-SIMS, GC/MS and FTIR are used in order to identify potential sources of AMCs that outgas from materials typically present in cleanrooms. Materials under investigation include construction materials, cleanroom furniture, garments and utensils. In these experiments each of the materials provides a fingerprint that can be used to identify potential sources of cleanroom contamination. The amounts of contaminants that outgas from specific materials are not only due to their chemical composition, but also to the environment (temperature, humidity, chemistry) they are exposed to in the cleanroom and to the surface area they provide for transfer of contaminants into the vapor phase. The surface area can widely be enlarged when a material is spread over the cleanroom due to contact transfer (*e.g.*, a person in a cleanroom is touching equipment or product with gloves). Therefore it seems valuable to study the transfer of contaminants onto surfaces that are brought in contact with these materials as well. The longterm objective of this study is to generate an extensive database that will allow us to link observed condensable AMCs with potential sources in the cleanroom environment.

2. Experimental

Sample preparation:

“Condensed volatiles”: In order to study outgassing, the material under investigation was placed in a vial. The vial was heated at ~85˚C for 24 hours, and outgassing species were collected on a silicon wafer placed on top of the vial. The wafer temperature was slightly above room temperature. Control samples with an empty vial were prepared.

“Contact”: In order to study the transfer of contaminants by contact, a sample of the material was placed onto a clean Si wafer and a 5 lb weight was placed on top of it for 2 hours. In both experiments, the cleanliness of the wafers used was controlled by TOF-SIMS.

TOF-SIMS: Data from the wafers were acquired on a Physical Electronics TRIFT I time-of-flight spectrometer [7]. The instrument was equipped with a cold stage operated at –70C. A $^{69}Ga^{+}$ liquid metal ion gun (LMIG) primary ion source was operated at a potential of 15kV and a continuous ion current of 2 nA. Mass spectra were obtained by detecting either positive or

negative ions generated by ion bombardment of the sample. The data acquisition time was 4 minutes.

The analysis was performed under ultra-high vacuum (UHV, 10^{-8} to 10^{-10} torr) conditions. Under standard UHV conditions, volatile compounds present on wafers are susceptible to removal before the analysis is performed, *i.e.*, during pump down or before the analysis is completed. This is particularly relevant for many organic compounds that constitute AMC. This problem can be reduced or eliminated by using a cold stage [8], as was done in this work.

FTIR: Spectra from the wafers were acquired using Nicolet Magna-IR 550 Spectrometer. The instrument was operated in transmission mode. The spectral range was 4000 to 450 cm^{-1}. The resolution was set to 4 cm^{-1}.

GC/MS: The cleanroom samples were outgassed for 24 hours at 85°C using a non-equilibrium, Dynamic Headspace Analysis System. The samples were placed in a chamber through which dry nitrogen gas was passed at a flow rate of 30mL/minute. The effluent was collected on a charcoal trap from which the organic components were extracted using carbon disulfide. The components were separated and identified by Gas Chromatography/Mass Spectrometry (GC/MS) using the following conditions: (1) All samples were analyzed on a Trio 1000 GC/MS (Fisons Instruments) using an mass selective detector (MSD); (2) the GC column was a 30 mm X 0.25 mm DB-5MS (J&W Scientific) 1 micrometer film thickness; (3) the column head pressure was 25 psi; (4) the oven temperature range was 35°C (5 min.) to 150°C @ 10°C/min.; to 300°C @ 20°C/min.; 300°C (5 min.).

Both contact and outgassing measurements for each sample were performed using all three analytical methods. The relative strengths and weaknesses of each of the methods are summarized in Table 1.

Table 1 Summary of advantages and disadvantages of TOF-SIMS, GC/MS and FTIR

Technique	Advantages	Disadvantages
GC-MS	• gas chromatograph separates components • mass spectra from individual components • libraries available for identification • useful for volatile contaminants	• insensitive for low-volatile contaminants • limited information about inorganics
FTIR	• direct surface analysis w/o vacuum • good for volatile or non-volatile contaminants • extensive libraries of spectra for identification	• detection limits for AMC-type contamination is poor • inability to separate components from a mixture complicates spectra interpretation • limited information about inorganics
TOF-SIMS	• high sensitivity • good for low volatile contaminants • high mass resolution for identification • parallel molecular and elemental detection	• vacuum conditions cause problems for volatile contaminants (cold stage can reduce this problem) • inability to separate components from a mixture complicates spectra interpretation

3. Results:

In this section data from the “condensed volatile” and “contact” experiments of selected cleanroom materials are presented. The examples provided represent a part of our ongoing investigation of cleanroom materials.

Components of a cleanroom chair: Figures 1 to 4 show FTIR, GC/MS and TOF-SIMS data acquired from a "condensed volatile" sample of the seat cover of a chair that was specified for cleanroom use.

All three methods detect triphenyl phosphate as a major component outgassing from the seat cover. Figure 1 shows the GC/MS chromatogram and the corresponding mass spectrum obtained from the eluent (upper panel). The mass spectrum obtained from the eluent matches the library spectrum of triphenyl phosphate (lower panels). Figure 2 shows an FTIR spectrum with absorption bands in the fingerprint region of the spectrum that are characteristic of triphenyl phosphate. Diagnostic absorption bands include those at 1589 cm^{-1}, 1485 cm^{-1}, 1184 cm^{-1} and 959 cm^{-1}. Figure 3 shows a negative ion TOF-SIMS spectrum. Signals characteristic of triphenyl phosphate include m/z 249 ($C_{12}H_{10}PO_4^-$) and m/z 305 ($C_{16}H_{18}PO_4^-$).

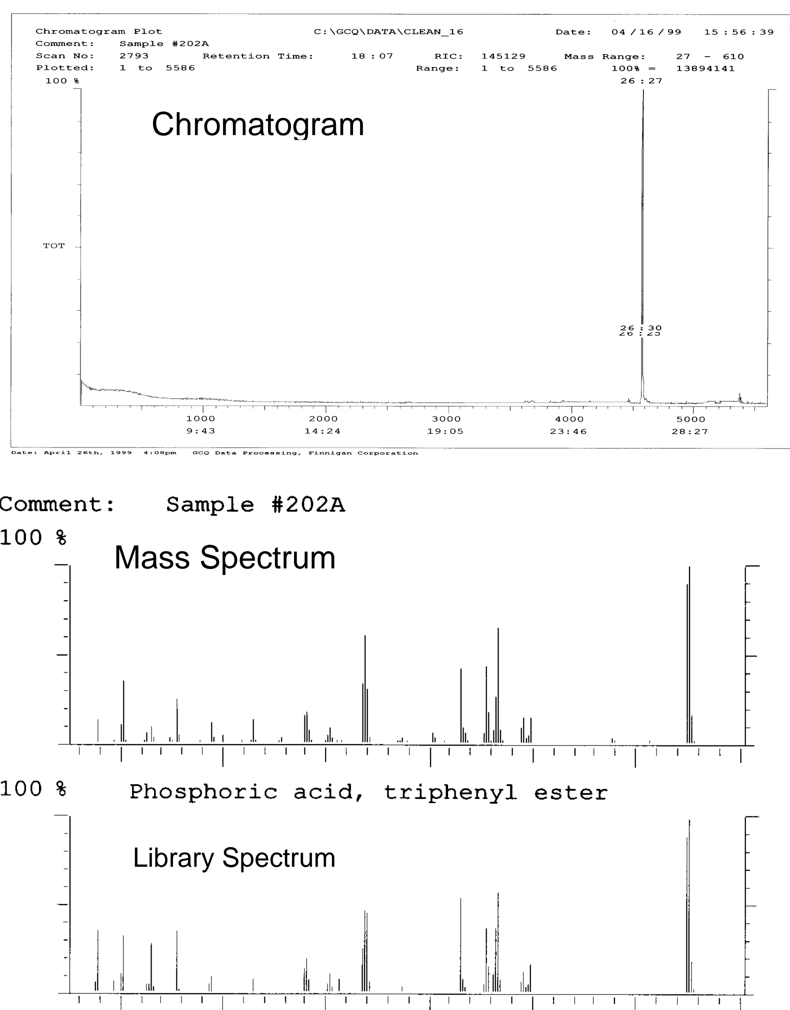

Figure 1 GC/MS analysis of condensable contaminants outgassing from a seat cover of a cleanroom chair: chromatogram (upper panel), mass spectrum obtained from the eluent, and library spectrum of triphenyl phosphate (lower panels).

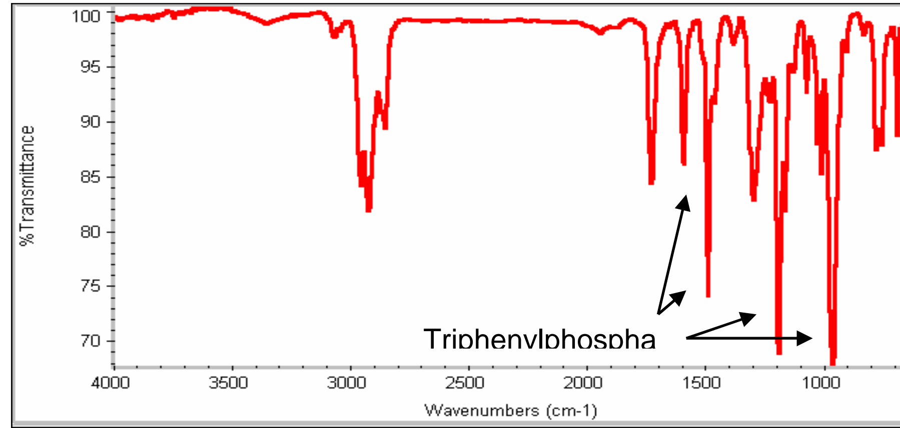

Figure 2 FTIR spectrum of condensable contaminants outgassing from a seat cover of a cleanroom chair.

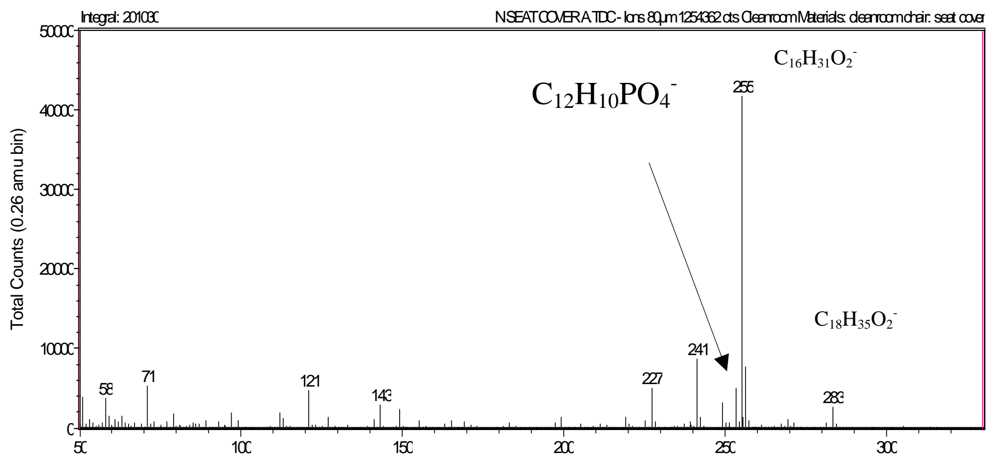

Figure 3 TOF-SIMS negative ion spectrum of condensable contaminants outgassing from a seat cover of a cleanroom chair.

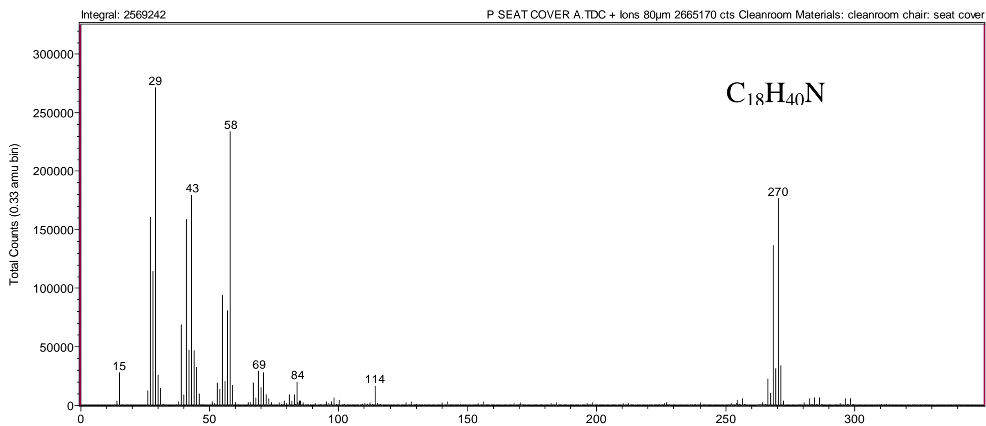

Figure 4 TOF-SIMS positive ion spectrum of condensable contaminants outgassing from a seat cover of a cleanroom chair.

FTIR and TOF-SIMS data suggest that other organic species are present in the condensed volatile mixture from the seat cover besides triphenylphosphate. The absorption bands at 1728 cm^{-1} and around 3000 cm^{-1} in the FTIR spectrum may be due to the presence of an organic ester. Combining positive and negative ion TOF-SIMS data (Figures 3 and 4) reveals the presence of fatty acids, fatty acid amides, amines, and phthalate plasticizers.

Detection of contaminants transferred by contact onto a silicon wafer was only successful by TOF-SIMS. Figures 5 and 6 show positive and negative ion spectra obtained. Triphenylphosphate is also observed to be transferred by contact. In addition, fatty acid amides and amines are observed in the spectra.

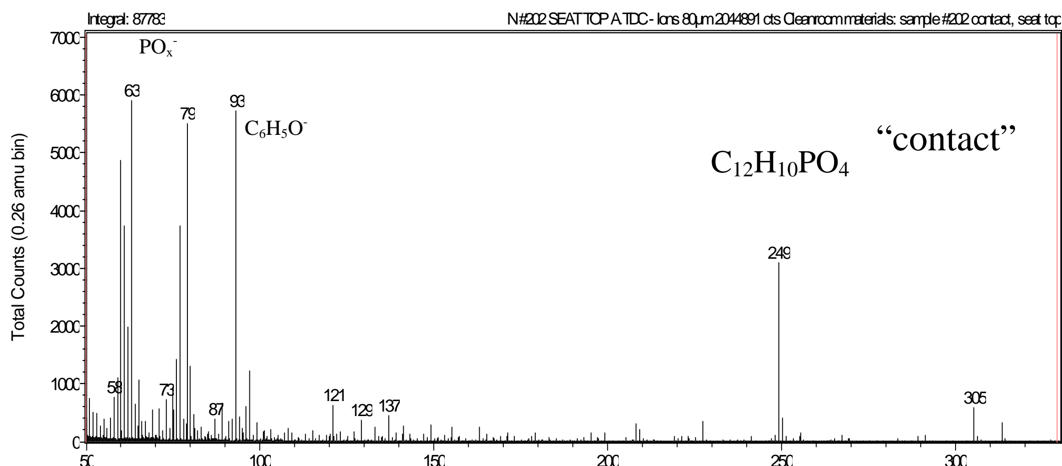

Figure 5 TOF-SIMS negative ion spectrum of contaminants transferred by contact from a seat cover of a cleanroom chair.

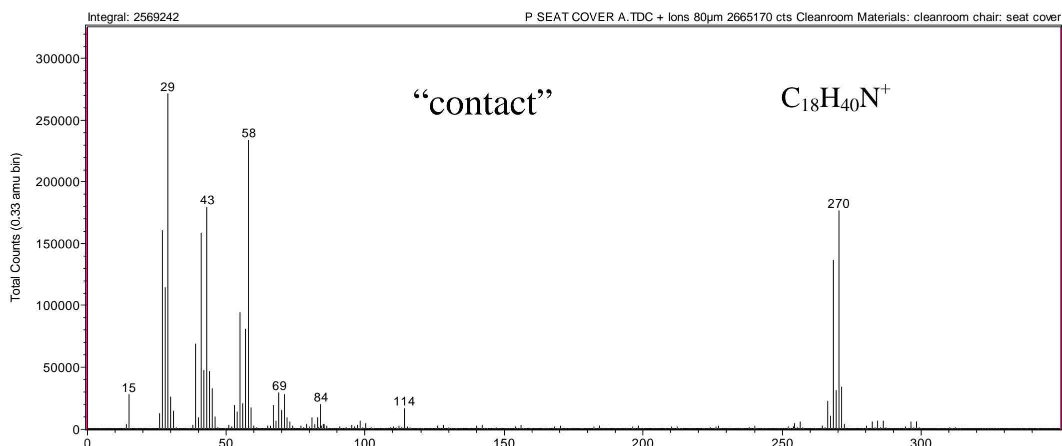

Figure 6 TOF-SIMS positive ion spectrum of contaminants transferred by contact from a seat cover of a cleanroom chair.

Table 2 summarizes the results for different parts of a cleanroom chair. The letter indicates the technique by which a contaminant was detected, the color of the letter indicates whether a contaminant has been detected as condensable AMC (black) or by contact transfer on a wafer (red). The specification into different groups of contaminants is somewhat arbitrary and simplified to provide an overview.

Table 2 Summary of results from a cleanroom chair

Contaminants	seat bottom	foam seat int.	seat cover	wheel
plasticizer: phthalates, adipate, etc.	**TF**		**T**	
antioxidants: BHT etc.				
amines		**TTFG**	**TT**	
fatty acid amides			**TT**	
other **CxHyNO**			**T**	**T**
organophosphates	**TTF**	**G**	**TTFG**	
fatty acids				**T**
other **organic acids**				
siloxanes		**T**		**T**
fluorocarbons				
esters			**F**	
CxHySOz				
hydrocarbon oils				
aromatic CxHyOz				
inorganic contaminants				

T, **F**, **G** (**T**OF, **F**TIR, **GC/MS**)

Results from cleanroom gloves: Table 3 summarizes results from seven gloves specified for cleanroom use. As in Table 2, the letter indicates the technique by which a contaminant was detected, the color of the letter indicates whether a contaminant has been detected as a condensable AMC (black) or by contact transfer on a wafer (red).

As evident from Table 3, gloves can be a source of many different contaminants including plasticizers, antioxidants, antistatics, lubricants, oils, surfactants and inorganic species. The number of different kinds of contaminants detected varies greatly between different kinds of gloves. For example, glove #1 shows a much lower overall number of detected contaminants than glove #2. The latter is a latex glove while glove #1 is a nitrile glove.

Table 3 also suggests that a larger number of contaminants is detected by TOF-SIMS than by FTIR or GC/MS. This is a consequence of the higher detection sensitivity of TOF-SIMS for condensable contaminants.

Table 3 Summary of results from different cleanroom gloves

contaminants	glove 1	glove 2	glove 3	glove 4	glove 5	glove 6	glove 7
plasticizer: phthalates, adipate, etc.		**T**					
antioxidants: BHT etc.		**T**				**T**	**G**
Amines	**T**	**TT**	**T**	**T**	**T**	**TTF**	**T**
fatty acid amides	**T**	**T**	**T**			**TF**	
other **CxHyNO**	**T**	**TT**	**F**	**TF**		**T**	**F**
Organophosphates							
fatty acids		**TT**	**TTG**	**TG**	**T**	**TTF**	**G**
other **organic acids**			**F**	**FF**	**F**		**F**
Siloxanes	**T**	**T**			**TF**		**TTF**
Fluorocarbons	**T**		**T**				
Esters			**F**	**F**	**F**		**F**
Organosulfates, -sulfonates etc.		**T**		**T**			**T**
hydrocarbon oils							**F**
aromatic CxHyOz							**T**
inorganic contaminants: metals, salts etc.	**F**	**FT**	**F**			**T**	**T**

T, **F**, **G** condensed volatiles (**T**OF, **F**TIR, **GC/MS**) **T**, **F**, **G** contact (**T**OF, **F**TIR, **GC/MS**)

Results from a floor tile

Table 4 summarizes results from a floor tile as an example for a construction material. Construction materials are of particular interest since they often provide a large surface area for outgassing of contaminants. FTIR and TOF-SIMS detect plasticizers and a hydrocarbon oil from the floor tile. In addition, amines and fatty acids are observed by TOF-SIMS. GC/MS does not detect any contaminants outgassing from the floor tile.

Table 4 Summary of results from a floor tile

contaminants	floor tile
Plasticizer: phthalates, adipate, etc.	**TT F**
Antioxidants: BHT etc.	
Amines	**T**
fatty acid amides	
Other **CxHyNO**	
Organophosphates	
fatty acids	**T**
Other **organic acids**	
Siloxanes	**T**
Fluorocarbons	
Esters	
Organosulfates, -sulfonates etc.	
Hydrocarbon oils	**TF**
Aromatic CxHyOz	
Inorganic contaminants: metals, salts etc.	

T, **F**, **G** condensed volatiles (TOF, **F**TIR, **GC/MS**) **T**, **F**, **G** contact (**T**OF, **F**TIR, **GC/MS**)

4. Discussion

The results summarized in Tables 2 to 4 suggest that an analysis of outgassing condensable contamination from cleanroom materials may be incomplete without using TOF-SIMS. TOF-SIMS detects significantly more contaminants than GC/MS or FTIR. This is mainly due to the extremely high sensitivity of TOF-SIMS compared to GC/MS or FTIR. In addition, the group of condensable contaminants is less suited for a GC/MS analysis since amines, amides and acids are known to show a low recovery in GC/MS. The latter group of substances accounts for a major part of the overall contaminants observed. Furthermore TOF-SIMS data were acquired in both, positive and negative ion mode adding to the overall information extractable from TOF-SIMS data. GC/MS data were acquired only in positive ion mode.

The outgassing temperature of the cleanroom materials was chosen such that even FTIR, which was anticipated to be the least sensitive among the three techniques, could potentially detect species deposited on the wafers. In some cases visible residues on the wafers were observed. For a TOF-SIMS analysis the outgassing temperature could have been significantly lower. The ability of TOF-SIMS to detect airborne molecular contaminants from materials outgassing at room temperatures has been demonstrated [9].

The group of condensable contaminants this study is focussed on may ultimately be the most interesting molecular form of airborne cleanroom contamination since any failure mechanism requires contaminants to adsorb and stick (for an appreciable time) onto components that fail. The results from the contact experiments demonstrate that TOF-SIMS also allows evaluation of contact transfer in great detail. The spread of contaminants across a cleanroom by contact may also increase its airborne levels since the surface area for an exchange with the gas phase can be greatly enlarged.

The data collected in this project is being used to build a library providing links between cleanroom materials and molecular contamination they may release into the cleanroom environment. However, TOF-SIMS is not quantitative for these types of contaminants and samples, so it does not allow a quantitative comparison of different cleanroom materials. The latter is crucial for replacing materials in order to lower the overall levels of contamination in a cleanroom. GC/MS on the other hand does allow quantification on contaminants it detects. To provide quantitative methods with high sensitivity will be of extreme importance for future contamination control. Quantification of TOF-SIMS data is not a principle problem. However, it requires calibration experiments for each individual contaminant and some knowledge on how coadsorption effects ion yields of individual species.

The requirements for future contamination control may also change with the use of new materials. It is conceivable that the affinities of these materials to certain forms of airborne molecular contamination are different from that of silicon. In addition to line width and feature sizes, the materials processed will also determine levels of airborne molecular contamination that can be tolerated in a cleanroom environment.

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