MONITORING OF CLEANROOM AIRBORNE MOLECULAR CONTAMINATION BY TIME-OF-FLIGHT SIMS

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Biographies

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Abstract

Airborne molecular contamination (AMC) that can deposit on product and processing equipment is a growing concern in cleanrooms. Using a newly installed class 10 cleanroom in our laboratory, we have investigated the deposition of AMC on witness wafers. Since it was expected that more outgassing of construction materials would occur immediately after the cleanroom came on-line, a goal of the work was to evaluate how quickly this outgassing rate changed with time. Silicon wafers were exposed to the cleanroom environment for varying periods of time and were subsequently analyzed using Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). Because TOF-SIMS can be used to directly analyze wafer or product surfaces, it provides information about the types of AMC that adsorb onto surfaces of interest. In addition, ionic species such as halides and metals can be detected simultaneously. Molecular species, including silicones, phthalates, fatty acids, organic amines and alcohol amines are observed on the wafers. The relative intensities of most of these organic species reached a maximum approximately 1-2 months after the cleanroom came on-line. After that time, the intensities of these species actually decreased. Inorganic species detected included sulfur oxides and halides, along with the dopant species boron and phosphorus. These species typically reached an equilibrium concentration after 1-2 months, but did not show the same decrease that was noted for the organic compounds.

Keywords

Airborne molecular contamination, AMC, microelectronic devices, cleanrooms, TOF-SIMS.

Introduction

Understanding the effects of AMC in cleanroom environments is of increasing concern as technologies develop. These contaminants can produce a variety of effects that are important in all types of cleanrooms, including those used in semiconductor processing, disk drive manufacture, and biomedical device production. With the decreasing size and increasing complexity of new products and devices, the importance of identifying and then isolating or eliminating AMC presents a substantial challenge.

In the semiconductor field, the National Technology Roadmap for Semiconductors has proposed that airborne molecular contamination is the next technical challenge for the semiconductor industry[1]. As the linewidths of microelectronic devices shrink toward 0.1 μm, contaminants that have not traditionally been a processing problem become issues. In order to achieve low defect rates in the next generation devices, the technical ability to identify, isolate and eliminate AMC becomes increasingly important.

AMC can result from many sources, including materials used in construction, compounds from fab processes, and outgassing from the local environment. Some of the known effects it can include[2]: changes in oxide quality

or growth rate, unintentional boron or phosphorus doping, adhesion effects, and effects on deep UV photoresists.

The term ‘AMC’ covers a wide range of contaminants, including volatile organic compounds, as well as some organometallic and inorganic species. Because the range is so broad, it is essential that any discussion of AMC include methods for identifying particular contaminants. This is important in order to evaluate the effects of a particular contaminant, to trace it back to a source, and to provide a means for eliminating the contaminant if necessary.

Methods that provide a general quantification of AMC tend to serve a limited purpose, since many types of contamination have never been shown to cause particular processing problems. In fact, molecules that introduce problems in one process often are unimportant in others because the relevant processing parameters are different. For example, boron or phosphorus compounds that are significant problems in some semiconductor processes because they can unintentionally dope silicon[3] may be insignificant in a disk drive manufacturing process.

When assessing analytical techniques to be used for AMC evaluation, it is also useful to understand the difference between evaluating contaminants that deposit directly on surfaces and those found in cleanroom air. Takeda, *et al*., discuss this point when they identify differences between compounds detected by air sampling methods and those found on witness wafers left in semiconductor fabs.[4]

In the work discussed here, TOF-SIMS is used to analyze witness wafers stored for varying times in a newly constructed class 10 cleanroom on-site in our laboratory. Short-term experiments were used to monitor AMC on a daily and weekly basis. Longer-term experiments were used to show gradual changes in AMC over the course of several months. This paper covers a four-month period and summarizes changes in molecular and elemental contamination levels noted over that time.

Surface Analysis Technique

In TOF-SIMS, mass spectra are obtained by detecting either positive or negative ions generated directly from the surface of a sample. The analysis is performed under ultra-high vacuum (UHV, 10^{-8} to 10^{-10} torr) conditions. After a sample is introduced into the instrument, a pulsed, primary ion source is used to bombard the surface of interest. This bombardment causes the emission of molecular and atomic species, including some that are ionized. These secondary ions are electrostatically accelerated into a field-free drift region. At the end of the drift region the mass of each ion is determined from its flight time[5]. A complete spectrum is generated by accumulating secondary ions over a period of time.

There are several advantages of TOF-SIMS that make it amenable to the study of AMC. First, because it is a survey technique, both molecular and elemental species (including dopants) can be monitored simultaneously. Second, the technique has excellent sensitivity for low levels of contaminants. It is also particularly useful for low volatility or thermally unstable contaminants that can be difficult to analyze by desorption techniques such as Ion Mobility Spectrometry (IMS) or Gas Chromatography-Mass Spectrometry (GC-MS). Finally, the high mass resolution of the mass spectrometer can provide unambiguous identification of many chemical species.

Relevant limitations of TOF-SIMS in AMC analyses are related to difficulties with absolute quantification and to the effect of the UHV environment. Quantification is difficult because ion yields for individual organic compounds vary considerably. It is difficult to prepare the standard samples for each compound of interest that are needed for quantification. At present, except in limited cases, it is only possible to make comparisons of the concentrations of particular species among a series of samples by comparing relative intensities. In other words, the relative intensities of a species ‘B’ can be compared among wafers, but it is not possible to directly compare intensities of species B to another species, ‘A’.

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,[6] as was done in this work.

Experimental

The cleanroom used for this work was certified as class 10 and was built to house a Total Reflection X-ray Fluorescence (TXRF) instrument for use in the analysis of semiconductor wafers. The experiments were begun immediately after final certification of the cleanroom. During the experiment, the cleanroom was in use.

Silicon wafers (100) were placed in an open wafer carrier and exposed to a class 10 cleanroom environment. For the cumulative exposure (long term) experiments, wafers were exposed for lengths of 1 day, 3 days and 1, 2, 3 and 4 months. Shorter-term experiments were conducted each month using 3 day exposures with a fresh set of wafers. A blank wafer, *i.e*., with no exposure time, was also studied to provide a baseline. The wafers were removed from the cleanroom in clean Fluoroware™ containers and analyzed by TOF-SIMS.

TOF-SIMS data were acquired on a Physical Electronics TRIFT I time-of-flight spectrometer. The spectra were acquired using a cold stage attachment. The cold stage was used to maintain the temperature of the sample below -50C during the analysis. Data were obtained using a $^{69}Ga^{+}$ liquid metal ion gun (LMIG) primary ion source operated at a potential of 15kV and a continuous current of 2 nA. Both positive and negative ion spectra were acquired with an energy slit and contrast diaphragm in place. The mass resolution (M/ΔM; full width, half maximum) was greater than 7000 at m/z 41. All spectra were integrated for 4 minutes from a raster area of 80 μm x 80 μm. Three positive and three negative ion spectra were acquired from each of the wafers in order to confirm the reproducibility of the data.

The total number of secondary ions detected for various species were integrated and then normalized to the substrate signal, silicon. For the cumulative exposure experiment, the normalized intensities were plotted versus exposure time. In the short-term experiment, the intensities of replicate 3-day exposures were plotted versus the total time elapsed in the study.

Results

Cumulative exposure experiments: Figures 1-4 show data for various inorganic and organic species accumulated on witness wafers over the course of four months. Error bars showing the variation in the three replicate measurements on each wafer are shown only in Figure 1.

In Figure 1, the relative intensities of $^{11}B^{+}$ and PO_3^- are shown as a function of exposure time. As discussed previously, these species serve as markers for B- and P-containing compounds that can be unintentional dopants in wafers. PO_3^- was monitored because it has a higher ionization yield than P^-. It should be noted that the oxide has a mass interference with $^{30}SiO_3H^-$ that cannot be fully resolved, but the relative intensity comparison is comparable. As shown in Figure 1, the normalized intensities of both boron and PO_3^- increase most significantly during the first three days of exposure. After this time, boron continues to adsorb on the wafers, but at a much slower rate, while the intensity of the phosphorus species is fairly constant, with minor fluctuations over successive months.

Other elemental species detected on the wafers are the halides (F, Cl, Br and I) and various sulfur oxide species. The normalized intensities of F^-, Cl^-, and SO_3^- (sulfite) are shown as a function of exposure time in Figure 2. These results indicate that chlorine and sulfur oxides, as well as bromine and iodine, are deposited most rapidly on the wafers during the first three days of exposure. After that time, the Cl, Br, and I show only small changes, with minor fluctuations in concentration over successive months. In contrast, the adsorption of sulfite on the wafers continues after three days, though at a much slower rate. Interestingly, fluorine behaves somewhat differently from the other species discussed to this point, since its relative intensity remains relatively constant over the course of the experiment.

A number of organic or carbon-containing species are observed on the wafers. Data from several of these are shown in Figures 3 and 4. Dioctylphthalate (DOP, or one of its structural isomers such as diethylhexylphthalate) and polydimethylsiloxane (PDMS) have often been detected on wafers[4], and these species are also observed on the samples in this experiment (Figure 3). DOP is a common plasticizer used in a wide range of polymers, while PDMS is known to outgas from silicone sealants, though it has a number of industrial uses[7].

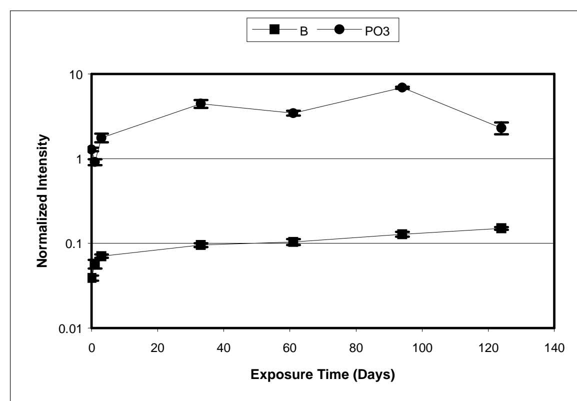

Figure 1. Normalized intensities of ^{11}B and PO_3^- as a function of cumulative exposure time. Error bars are for replicate measurements on each wafer.

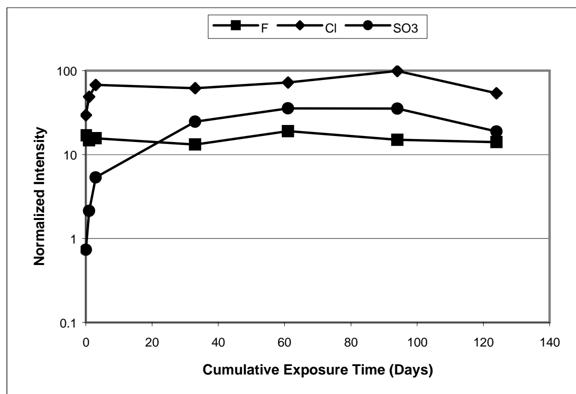

Figure 2. Normalized intensities of F^-, Cl^-, and SO_3^- as a function of cumulative exposure time.

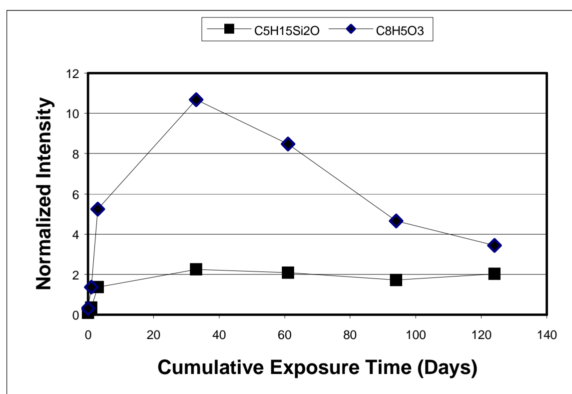

Figure 3. Normalized intensities of $C_5H_{15}Si_2O^+$ (from PDMS) and the phthalate cation, $C_8H_5O_3^+$, as a function of cumulative exposure time.

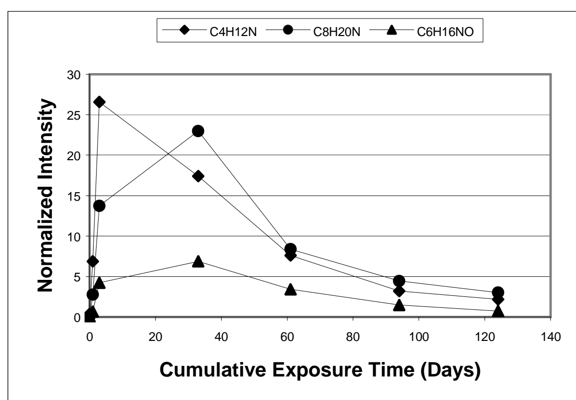

Figure 4. Normalized intensities of $C_4H_{12}N^+$, $C_8H_{20}N^+$ and $C_6H_{16}NO^+$ plotted vs. cumulative exposure time.

In Figure 3, PDMS is monitored using the normalized intensity of $C_5H_{15}Si_2O^+$, and DOP deposition is tracked by the phthalate cation, $C_8H_5O_3^+$. The phthalate ion is also a fragment of other phthalic acid esters (e.g., dibutylphthalate), but on these wafers, it tracked the behavior of ions unique to DOP.

As noted for most of the inorganic species discussed previously, the highest deposition for both DOP and PDMS occurs over the first three days of the experiment. However, unlike most of the inorganic ions, the molecules continue to be deposited on the wafers at notable levels up to the one month measurement. After one month, the behavior of the two species becomes significantly different: PDMS maintains a fairly steady concentration on the wafers, while the DOP concentration falls by a factor of more than two over the following three months.

Other molecular compounds observed in the spectra are organic amines, amino alcohols and fatty acids. The amines in particular are often seen in TOF-SIMS spectra from wafers, and they can be of significant interest since low levels of these compounds can have serious adverse effects on deep UV resists[2].

The deposition behavior of three of these species, two amines and an amino alcohol, is shown in Figure 4. Again, these results indicate that the fastest deposition on the wafers occurs during the first three days of exposure in the cleanroom. However, as noted for the other molecular species, the behavior of individual compounds can vary significantly after this initial period. For the lower molecular weight nitrogen-containing compounds (e.g., the $C_4H_{12}N^+$ species in Figure 4), a rapid decrease in the amount of deposited material is observed after the first three days. This loss of material is approximately 30% between three days and one month, and by four months, the levels of amine detected are similar to those at the beginning of the experiment. Higher molecular weight amines and alcohol amines show a similar decrease after four months, but these species typically continue to deposit on the wafers through the one month measurement (see $C_8H_{20}N^+$ and $C_6H_{16}NO^+$ in Figure 4).

Fatty acids observed on the wafers include myristic ($C_{14}H_{27}O_2^-$) and palmitic ($C_{16}H_{31}O_2^-$) acid anions. These compounds deposited on the wafers in a pattern similar to that observed for the low-molecular weight amines, with an initial rapid deposition over three days, and then a loss of material over the succeeding four months.

Short-term experiments: The three-day exposure data compares results from fresh wafers exposed to the cleanroom for three days at the beginning of the experiment (time zero) and after one, two, three, and four months. These results indicate the change in deposition rate for different compounds as the cleanroom materials outgas.

The data are summarized in Figures 5-8. In each of the figures, the species shown are analogous to those in Figures 1-4 of the cumulative experiment. Error bars with typical variations in the three measurements from each wafer are shown only on Figure 5.

In general, these results are consistent with those discussed from the cumulative experiments. For most of the inorganic or dopant species, levels deposited on the wafers remain constant over a four month period. This is particularly clear for boron (Figure 5) and fluorine (Figure 6), which also show the most consistent cumulative behavior. Phosphorus (as PO_3^-, Figure 5) and chlorine (Figure 6) deposition fluctuates slightly over the course of the experiment, but these species do not show a steady trend. The sulfite ion is an exception in this group, since its initial deposition rate drops significantly after the first set of measurements (Figure 6).

The organic/molecular species tracked exhibit more varied behavior over the course of the experiment, as they did in the cumulative results. In general, however, the deposition rate for all of the organic species decreases over the four month period.

PDMS and DOP deposition is highest in the initial three day measurement (Figure 7). Both of these species show a steady decrease through the first and second months, level off in month three, and then exhibit a further decrease in month four. Generally, this is consistent with results of the cumulative experiments, though the intensity drop for DOP in the previous data is much stronger than that observed for PDMS.

The nitrogen-containing organic species (amines and alcohol amines) also have the highest deposition in the initial measurements and generally decline over successive months. The correlation to the cumulative data is clearest for the low-molecular weight amines, where the deposition also declines after the initial measurement (compare Figures 4 and 8). For the alcohol amines and higher molecular weight saturated amines, the correlation is more complicated since the cumulative deposition on the wafers reaches a maximum at one month.

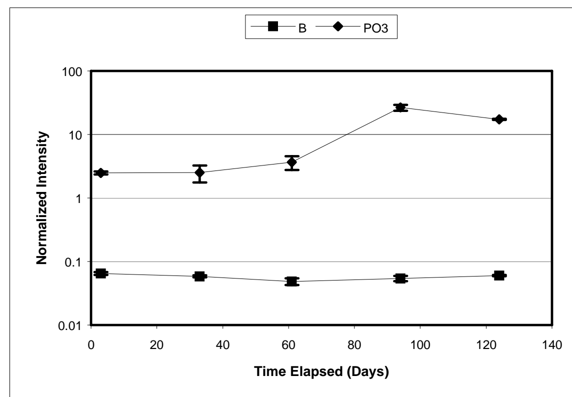

Figure 5. Normalized intensities of 3-day exposures of B^+ and PO_3^- as a function of elapsed time. Error bars are for replicate measurements on each wafer.

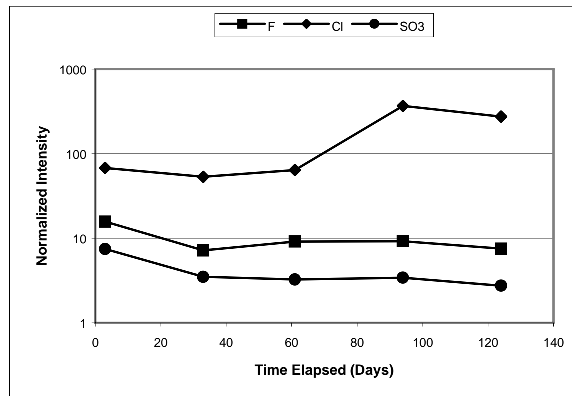

Figure 6. Normalized intensities of 3-day exposures of F^-, Cl^- and SO_3^- as a function of elapsed time.

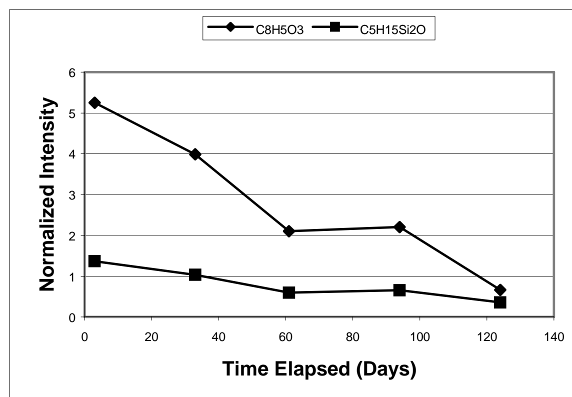

Figure 7. Normalized intensities of 3-day exposures of $C_5H_{15}Si_2O^+$ (from PDMS) and the phthalate cation as a function of elapsed time.

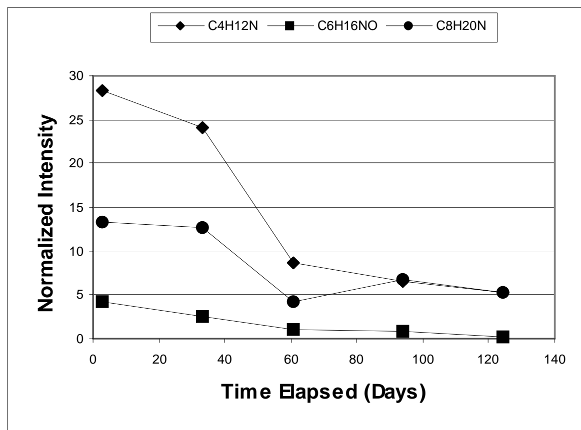

Figure 8. Normalized intensities of 3-day exposures of $C_4H_{12}N^+$, $C_8H_{20}N^+$ and $C_6H_{16}NO^+$ plotted vs. elapsed time.

Discussion

As discussed previously, the types of contaminants detected on the witness wafers can be broadly divided into inorganic and organic/molecular categories. The deposition behaviors of species from these two categories seen in both the long- and short-term experiments are considerably different.

For the inorganic species, short-term experiments indicate that the deposition of all ions investigated with the exception of sulfur (monitored as SO_3^-) remains fairly constant over the course of the four month experiment (Figures 5 and 6). Several of these species, including Cl^- and PO_3^-, reach a relatively constant level fairly quickly (3 days), and then fluctuate to varying degreees around that level (Figures 1 and 2). These results indicate that outgassing of the inorganic species does not track the outgassing behavior of the organic compounds. The variation that is observed for specific inorganic ions may be because the cleanroom was in use during this period, meaning that additional sources of these species could be introduced at various times.

In contrast to the behavior of the inorganic species, the deposition rate for all of the organic compounds (as well as sulfite) generally declines after the initial measurements through the four month point. For all of the compounds shown in Figures 7 and 8, the highest deposition levels are observed at the initial three-day measurement (time zero). The sharpest declines in deposition occur between time zero and the second month, indicating that most of the outgassing of organic species that occurs in a new cleanroom takes place in the first one to two months. This is consistent with results reported by other researchers[4]. After this initial period, the outgassing levels of organic contaminants are significantly lower.

The cumulative behavior of the organic/molecular species is somewhat more complicated (Figures 3 and 4). While the deposition rate reaches a maximum for all of the species at time zero, specific compounds or classes of compounds reach maximum concentrations at different times. For example, the highest levels of DOP and the higher molecular weight amines are reached at one month. In contrast, low molecular weight amines and fatty acids are highest at time zero (initial three-day measurement). PDMS is the most unique of this group: its concentration increases from time zero to month one, and then remains relatively constant for months one through four. Sulfite, which may be a fragment or decomposition product of an organic sulfur compound or from an inorganic, reaches a maximum at the two to three month point, even though its deposition level is highest at time zero (Figure 5).

These results suggest that molecular species rapidly adsorb onto the wafers upon exposure to the cleanroom. The normalized intensity of each species increases until an equilibrium is reached between the wafer surface and cleanroom environment (generally in 3-30 days). After this initial period, the behavior of individual species varies depending on the specific chemistry of the compound, its interaction with the silicon substrate, and the level of replenishment from the cleanroom environment. For example, previous work has shown that DOP will replace other AMC on wafers over a six day monitoring period due to its high sticking coefficient on wafers[4]. Over a longer term monitoring period, the depletion of DOP in the cleanroom air (as indicated by the short-term data) results in the loss of DOP from the surface as it re-equilibrates with the surrounding environment.

Conclusions

Several general observations can be made as a result of this work: (1) Both inorganic and organic species that deposit from the cleanroom environment can be identified on wafers by TOF-SIMS. (2) The highest deposition of contaminants occurs in the first several days after the wafers are introduced to the cleanroom. (3) The deposition of organic species from a new cleanroom is significantly higher in the first one to two months of operation. (4) Cumulative results indicate

that organic species depositing on wafers establish an equilibrium that allows them to be readily removed from the wafers as the level of contaminants in the cleanroom is reduced over time.

Future Directions

Two new sets of experiments are now underway in cleanrooms. The first investigates the substrate dependence of the deposition process by comparing contaminants that deposit on copper surfaces to those observed on silicon. The second evaluates contamination deposited in a class 1 cleanroom that has been constructed using a number of different materials from those in this work. A parallel effort also is being made to establish a library of data from various cleanroom materials that can be used to trace contaminants to possible sources.

References

[1] Special Report, *Cleanrooms*, 21-25, (1998).

[2] Smith, P. and Lindley, P., CP449, *Characterization and Metrology for ULSI Technology: 1998 International Conference*, Seiler, D.G., et al, eds., American Institute of Physics, 1998, pp 133-139.

[3] Stevie, F.A., Martin, E.P., Kohora, P.M., Cargo, J.T., Nanda, A.K., Harrus, A.D., Muller, A.J., and Krautter, H.W., *J. Vac. Sci. Technol.*, **A9**, 2813-2816 (1994).

[4] Takeda, K., Nonaka, T., Sakamoto, Y., Taira, T., Hirono, K., Fujimoto, T, Suwa, N., and Otsuka, K., *IEST Proceedings, Contamination Control*, IEST, 1998, pp 556-561.

[5] Schueler, B.W., *Microsc. Microanal. Microstruct.*, 3, 119-139 (1992).

[6] Strossman, G., Lindley, P., and Bowers, W., *Secondary Ion Mass Spectrometry (SIMS XI)*, Chichester, England: John Wiley & Sons, 1998 pp. 699-702.

[7] Thames, S.F., in ‘Applied Polymer Science,’ Tess and Poehlein, eds., ACS Symposium Series 285, ACS, Washington, DC, 1985, pp 1129-1139.