ANALYSIS OF CLEANROOM AIRBORNE MOLECULAR CONTAMINATION BY TOF-SIMS

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Introduction

As devices become smaller and technology pushes the physical limit of device size, process parameter and contamination controls must become more stringent. Although the current level of concern of manufactures of semiconductor devices for organic species is typically low, the SEMI roadmap expects the tolerances for organic contamination will become tighter [1a]. As the tolerances for organic contamination are reduced, it will become more important to identify and control sources of airborne molecular contamination (AMC). In this work, the contribution of cleanroom construction materials to the ambient levels of carbon on silicon wafers will be studied. Inorganic airborne contamination also will be investigated.

Experimental

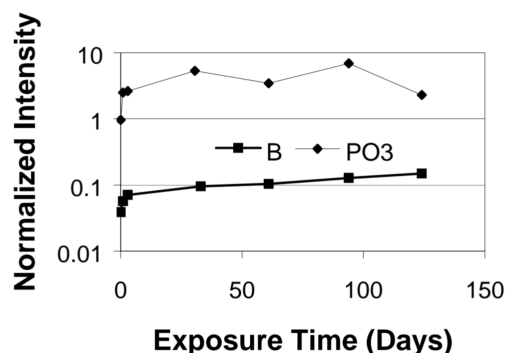
A newly installed class 10 cleanroom was used for this study. The cleanroom was constructed to house a Total Reflection X-ray Fluorescence (TXRF) instrument. During the course of the experiment the cleanroom was in use, although no process chemicals were used. A series of 100 mm silicon wafers were stored in an open wafer carrier exposed to the cleanroom for varying periods of time. Cumulative exposures of up to six months and sequential exposures of three days were performed. The cumulative exposure experiments used wafers that were introduced into the cleanroom at the start of the experiment and removed at prescribed dates. Sequential exposures were performed by introducing the wafer into the cleanroom at a given start date and removing it after three days. All data shown were normalized to the substrate signal, silicon.

Experiments were performed on a Physical Electronics TRIFT I system with a mass resolution of approximately 7000 at m/z 41. All experiments were performed with a cooled sample stage at ~-50C. Details of the cold stage experiment can be found elsewhere [2a]. The center of the wafers were analyzed. Three replicates were made for each measurement to ensure reproducibility, and the average of the three locations were plotted. Typical standard deviations were ~20%.

Results and discussion

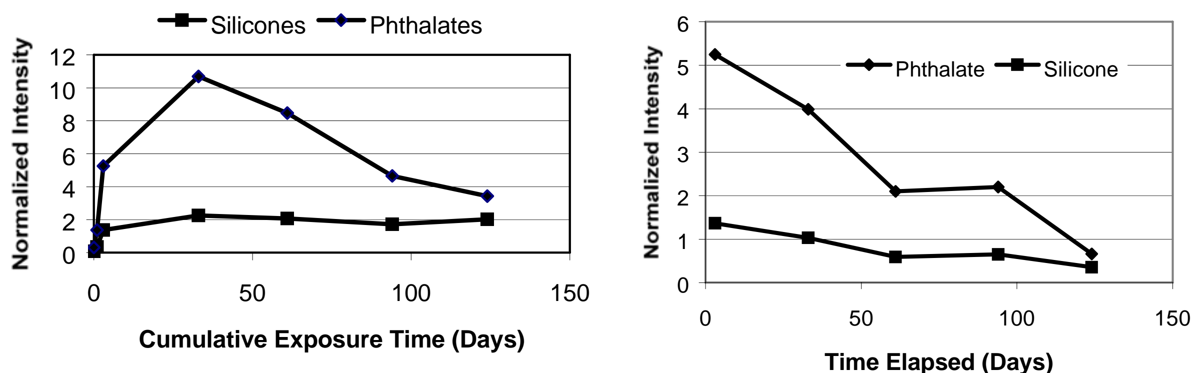
Figure 1 shows the normalized intensities of boron and phosphorus (measured as phosphite, PO_3^-) as a function of exposure time to the cleanroom ambient. Measurement of the phosphite ion is complicated by an interference from $^{30}SiO_3H$. Both of these species show an increase in concentration as a function of exposure time, particularly in the first three days. After this time the levels stabilize, although the phosphite ion signal fluctuates.

Figure 1: Normalized intensities of ^{11}B and PO_3 as a function of cumulative exposure time.



This fluctuation may be due to actual changes in the phosphorus concentration in the cleanroom. However, a spectral interference from $^{30}SiO_3H$ increases the uncertainty of the measurement, and this may account for the observed fluctuation. Normal B levels in the atmosphere have been used to explain the increase in B intensity on similar samples[3a].

Figure 2 shows the cumulative and sequential exposures results for silicone and phthalate species. Phthalates (measured as the phthalate cation, $C_8H_5O_3$) are plasticizers that outgas from a variety of polymers (particularly PVC) and are well known to strongly adhere to the surface of silicon wafers [5a]. Silicones are common polymers with a wide range of industrial uses. The cumulative exposure data in Figure 2 shows the phthalate signal increasing to a maximum intensity after 30 days, while the silicone signal increases in the first three days and then reaches equilibrium. The sequential exposure data shows a general decrease in the levels of these species as the experiment progresses, with the phthalate decreasing more rapidly than the silicone signal. The decreased intensities of the sequential exposure experiments indicate the airborne levels of these species are decreasing with time, as has been observed by previous researchers[4a]. The sequential exposure data is consistent with the outgassing of the new cleanroom construction materials. The outgassing rate is initially high and, as the construction materials are depleted of volatile species, the amount of airborne contamination deposited on the wafers decreases. These two sets of data



also show that the levels of phthalates and silicones on the wafers decrease (measured in the cumulative experiment) as the airborne levels of these materials decrease (as seen in the sequential experiment). This phenomenon is

Figure 2: Relative levels of Silicones and phthalates after cumulative (left) and sequential (right) exposures.

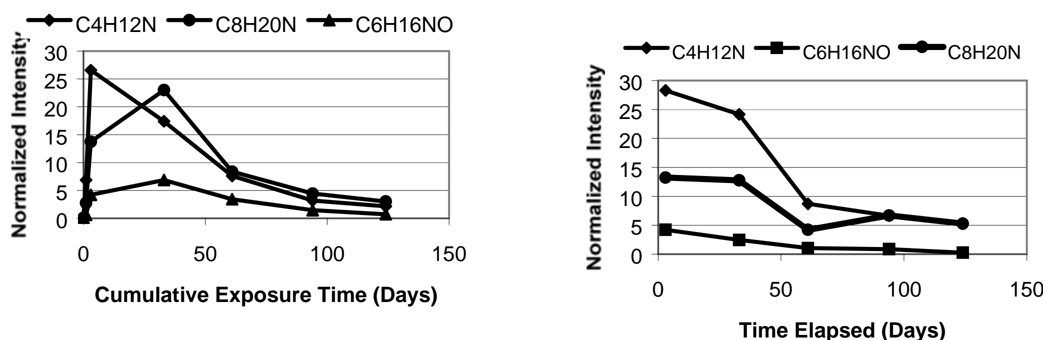


Figure 3: N-containing organic contaminants after cumulative (left) and sequential (right) exposures.

consistent with an equilibrium adsorption process: as the level of atmospheric contamination is reduced, material adsorbed on the wafers is removed to re-establish the equilibrium state.

A similar but more pronounced trend is observed for the nitrogen-containing species monitored in Figure 3 ($C_4H_{12}N$, $C_8H_{20}N$ and $C_6H_{16}NO$). The rapid rise and then fall off in these intensities in the cumulative experiments is related to the decaying signal observed in the sequential experiments. The initial elevated levels of these species in the cleanroom air lead to the rapid increase in adsorption observed in the first stages of the cumulative experiment. Over time, the outgassing of these compounds decreases and the equilibrium level of the amine species on the wafers also decreases.

Individually, the species exhibit somewhat different behavior. For example, the time required to reach a maximum concentration on the wafers is different for the $C_8H_{20}N$ and $C_4H_{12}N$ ions. The lower molecular weight amine species ($C_4H_{12}N$) reaches a maximum concentration more quickly in the cumulative exposure data (after three days), while the higher mass ion's intensity increases up to the 30 day measurement. While the chemistry of these species is similar and their adsorption onto Si would be expected to be similar, the observed difference is likely due to variations in vapor pressure and outgassing rates based on molecular weight.

Figure 4 shows the trend for carbon (measured as C_2^-). This species can be used to track general organic levels of the wafer. The overall carbon signal is seen to increase rapidly initially and then stabilize. In contrast to the other organic species shown, the overall carbon levels do not decrease significantly as a function of time. This is consistent with the expectation that a silicon wafer exposed to the atmosphere will reach a saturation level of contamination, after which the levels will remain relatively constant. In Figure 5, halogen levels are seen to increase rapidly in the first three days and remain relatively constant for the remainder of the experiment. This would be expected for species that bind strongly to the wafer surface.

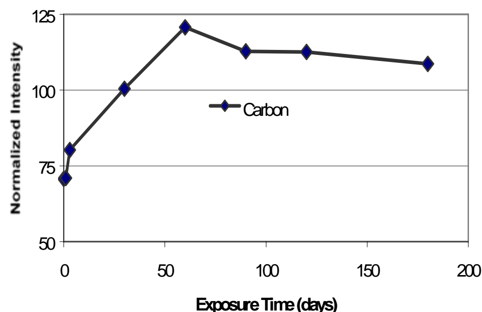
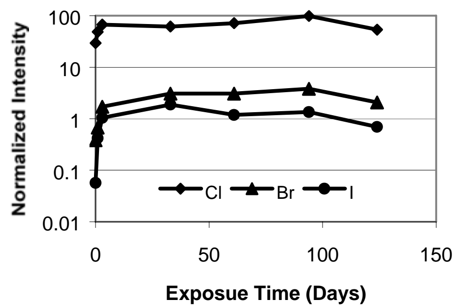


Figure 4: Carbon (measured as C_2^-, left) and halogens (right) levels after cumulative exposure.



Conclusions

Outgassing of a newly constructed cleanroom was investigated by TOF-SIMS. Both organic and inorganic contaminants were detected. Many of the organic contaminants were found to have a higher outgassing rate at the beginning of the experiment and then decreased in intensity later in the experiment.. The long-term accumulation of AMC on the wafers showed a consistent relationship with the sequential measurements, indicating an equilibrium adsorption process with the atmospheric contamination.

References

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