

# ANALYSIS OF ORGANIC CONTAMINANTS IN GASES USING NON-VOLATILE RESIDUE (NVR) MONITORS AND TIME-OF-FLIGHT SECONDARY ION MASS SPECTROMETRY (TOF-SIMS)

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## 1. INTRODUCTION

Increasing capabilities in semiconductor and hard disk technologies are often tied to more stringent requirements for surface cleanliness, particularly in the processing environment. As cleanliness requirements become more important, organic/molecular contamination has become the focus of renewed interest in the evaluation of existing processing problems and in new process development.

One area of concern as a source for organic contaminants is the chemicals supplied for various processing steps. In particular, a need has been identified to measure low levels of non-volatile residue (NVR) contaminants in process gases used in the microelectronics industry.

Current techniques for evaluating contamination in these gases are limited in that they: (1) require relatively large volumes of gas to be used for the testing process, and (2) provide information only about specific types of contamination (e.g., hydrocarbons). More useful methods to evaluate gas contaminants are required to have good sensitivity to low (sub-monolayer) levels of contamination, to provide specific chemical information that will allow a compound to be traced to its source, and to operate under conditions that will permit the analysis of a wide range of materials.

This work describes a technique for gas contaminant analysis that combines a sensitive Non-volatile Residue (NVR) monitor to *quantify* levels of contamination with Time-of-flight Secondary Ion Mass Spectrometry (TOF-SIMS) to *identify* the detected contaminants. The NVR monitors are based on SAW (surface acoustic wave) devices, sensitive piezoelectric microbalances that can detect submonolayer levels of airborne molecular contamination.<sup>1</sup> TOF-SIMS, with its excellent sensitivity and ability to provide fingerprint spectra that can be compared to reference materials, has proven to be valuable in providing specific chemical identification of many types of contaminants. However, because it is a high vacuum ( $10^{-8}$ - $10^{-10}$  torr) technique, it has primarily been useful for less volatile contaminants. This work has been performed on a TOF-SIMS system equipped with a cold stage to permit evaluation of more volatile organic species.

For these analyses, a set of SAW devices has been exposed to cylinders of

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a common gas used in microelectronics applications. The cylinders, provided by two different suppliers, are to be evaluated for contamination.

## 2. EXPERIMENTAL

The SAW-based NVR monitor used in this work was a modified version of a commercial instrument designed by Femtometrics to measure ambient contamination in aerospace and microelectronic cleanroom facilities. A series of SAW sensors was cleaned by plasma treatment, then exposed to small quantities (approximately 50 g) of gas from various cylinders (Table 1). The deposition of material on each SAW was monitored, and then TOF-SIMS analyses were performed within 24 hours.

TOF-SIMS data were obtained on a Physical Electronics TFS I instrument<sup>2</sup> equipped with a temperature-controlled sample stage. For these experiments, the stage was pre-cooled with liquid nitrogen to provide a sample temperature of approximately -50C. . Each SAW device was mounted in a modified holder that was designed to permit re-use of the sensor after the analysis. The sample and holder were placed in a dry nitrogen atmosphere and cooled to approx. -70C using liquid N<sub>2</sub>. The sample was introduced into the instrument under dry N<sub>2</sub>. Positive and negative ion spectra were acquired using a bunched <sup>69</sup>Ga<sup>+</sup> Liquid Metal Ion Gun (LMIG) primary ion beam operated at 15 kV.

*Table 1.* SAW devices analyzed by TOF-SIMS

SAW Sample	Description
control	plasma-cleaned only (no gas exposure)
N <sub>2</sub> blank	exposed to dry nitrogen gas
supplier #1, “dirty”	semiconductor gas, known contamination
supplier #1, “clean”	semiconductor gas, “clean” cylinder
supplier #2, “clean”	semiconductor gas, “clean” cylinder

## 3. RESULTS AND DISCUSSION

SAW data from the four cylinder-exposed samples described in Table 1 indicates that only the N<sub>2</sub> cylinder (N<sub>2</sub> blank) did not deposit significant levels of contamination on the sensor. SAW traces from the three samples treated with cylinders of the microelectronics gas all reveal significant levels of contaminant deposition.

TOF-SIMS analysis results are consistent with the SAW data and also serve to identify specific contaminants on each of the samples. Spectra from the N<sub>2</sub> blank, where no significant deposition was observed on the SAW, are quite similar to spectra from the control sample (Figure 1).

Positive ion spectra from the SAW device exposed to a microelectronics gas cylinder known to be contaminated with hydrocarbons (supplier #1, “dirty”)

clearly show a series of  $C_{25}$ - $C_{35}$  hydrocarbon peaks in the mass range from 300-500 Da. This sample also highlights the importance of the cold stage in the TOF-SIMS work, since spectra of the SAW acquired under room temperature conditions do not contain this series of peaks (Figure 2).

While results from the “dirty” cylinder are generally as predicted, the more interesting data from an applications perspective are those from the two cylinders described as “clean.” Spectra from the gas supplier #1 “clean” sample contain a series of peaks typical of chlorotrifluoroethylene (CTFE), a material used as a sealant in many applications. Figure 3 shows a region of a positive ion spectrum from this sample. In Figure 4, a positive ion spectrum from gas supplier #2’s “clean” sample contains significant peaks for dioctyl phthalate (DOP).

Figure 1. Comparison of positive ion spectra from control (top) and  $N_2$  blank (bottom) SAW samples.

Figure 2. Comparison of positive ion spectra obtained with (top) and without (center) cold stage from the gas supplier #1 “dirty” SAW.

Figure 3. Positive ion spectrum from the gas manufacturer #1 “clean” SAW.

Figure 4. Positive ion spectrum from the gas manufacturer #2 “clean” SAW.

#### 4. SUMMARY

The chemical specificity of TOF-SIMS can be a valuable tool for the identification of contaminants in many types of processing steps. With a cold stage, the increased range of contaminants that can be observed makes the technique more useful for the analysis of organic/molecular contamination. Combining TOF-SIMS' sensitivity and chemical identification capabilities with the quantification possible with SAW-based NVR monitors provides a very powerful contamination analysis tool.

## **REFERENCES**

1. W.D. Bowers, R.L. Chuan, T.M. Duong, *Rev. Sci. Instrum.*, **62**, 1624 (1991).
2. B.W. Schueler, *Microsc. Microanal. Microstruct.*, **3**, 119 (1992).