

CHAPTER 10: CONTAMINATION MONITORING AND FAILURE ANALYSIS BY ToF-SIMS

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INTRODUCTION:

Contamination, often at very low levels, is a common cause of device and product failures. The success of ToF-SIMS as a failure analysis (FA) tool is tied to its ability to easily detect contaminants on surfaces. Typically, when attempting to determine causes of failure, investigators want to have the most information possible, and ToF-SIMS can providing a wide range of information about surface chemistry. Specific capabilities of ToF-SIMS, namely its ability to identify molecular contamination in the top monolayer, excellent detection sensitivities, submicrometer lateral resolution and survey capability, allow it to address problems that might otherwise be difficult or impossible to solve. For these reasons, ToF-SIMS is a valuable tool in many surface analysis laboratories.

The types of industries using ToF-SIMS indicate the versatility of the technique. Applications have been shown in the semiconductor, hard disk drive, optics, glasses, petroleum, chemical, polymer, automotive, paper, flat panel display, adhesive, pharmaceutical and biomedical industries, among others. Although the levels of contamination and types of failures observed in each of these areas are vastly different, they all require controlled surface characteristics for optimum product performance.

This chapter will cover several types of failure analysis and the importance of contamination monitoring in various types of applications. It will investigate several examples where ToF-SIMS provides useful failure information from a range of samples. FA can describe an extremely broad range of problems including: general contamination studies (organic and inorganic), debonding, delamination, discoloration, particle analysis, changes in resistivity, changes in wettability, incomplete etching, over etching, void formation, changes in electron emission, additive segregation and others. While it is not possible to cover all of these

subjects, a number of representative types of problems ToF-SIMS has successfully addressed are discussed.

Sample Handling

The high sensitivity and surface selectivity of ToF-SIMS make it particularly susceptible to inadvertent contamination from sample handling, storage and mounting. Handling practices used in conjunction with other surface analysis techniques can introduce impurities detectable by ToF-SIMS. Of course the level and type of foreign material originating from handling may or may not interfere with the analysis at hand, but it is good practice to avoid procedures that can introduce additional contamination whenever possible. Sample handling is discussed in detail in an earlier chapter; however, the ability of improper sample handling to distort results during FA and contamination monitoring merits a brief review.

Most samples to be analyzed must be stored and/or shipped at some point, and the storage and shipping conditions are common sources of sample contamination. For example, plastic bags and shipping boxes may transfer additives onto samples, resulting in contamination levels so severe as to completely mask the surface of interest. Cleanroom wipes, lens tissue or high quality aluminum foil can work well as sample packaging, but particular brands should be analyzed for impurities prior to use. The use of single-sided adhesive tape should always be avoided, since these are sources of silicones. Some double-sided tapes do not contain silicones and can be successfully used away from analytical surfaces.

To keep a surface in a pristine state, nothing should come in contact with the sample's surface. In situations where a sample must be marked to locate a specific feature it is better to use a ceramic or diamond scribe rather than an ink marker. Though on certain samples scribes may generate particles, the solvents in markers can migrate to the area of interest carrying ink components that more often interfere with an analysis.

Often FA samples come from environments that are far from pristine. It is therefore tempting to try to clean the sample with a solvent. While this may prove successful, it can introduce additional contamination. The success of solvent cleaning is dependent on both the contaminants that need to be

removed and the sample. Silicones can sometimes be successfully removed with a hexane or methylene chloride wash, but blanks should always be run to confirm the purity of the solvents.

Detecting molecular contamination is often of interest when performing ToF-SIMS analyses, particularly if the mode of failure is a delamination, change in wettability, or similar problem. Organic compounds can have significant vapor pressures in the ToF-SIMS ultra-high vacuum (UHV) environment. Using a cooled sample stage can greatly reduce the vapor pressure of volatile compounds. In Figure 1, the effect of using a cold stage during the analysis of an organic solvent is shown. The two spectra are from silicon wafers exposed in a covered Petri dish containing a drop of 2-amino-1-butanol (bp 172-174°C). The top spectrum is obtained from wafer under standard, ambient temperature conditions. In the bottom spectrum, the effect of using a cold stage with the sample temperature maintained at approximately -50°C is shown. Even though the aminobutanol is relatively high boiling, at ambient temperature the compound is not detected at notable levels. Although the use of a cold stage is more cumbersome than ambient temperature analysis, for the analysis of unknown molecular contamination its use can be the difference between success and failure.

Methodologies

The versatility of ToF-SIMS often means that the operator has choices in the approach to solve the problem. Typical instrumentation allows for optimizing the tradeoffs in mass resolution, beam diameter, delivered primary ion current and analysis area. Also choices regarding elemental profiling and variations of sample preparation need to be made. It is obvious that some of these choices are limited by the problem at hand. In many cases it may be that either mass or spatial resolution is the characteristic of greatest importance, but more often it is necessary to work in the gray area between the extremes. Sometimes the analytical approach can be modified to take advantage of the technique's strengths and avoid its limitations.

A typical example of altering the analysis approach to better fit the strengths of the technique is when determining the composition of many small particles. Although current instruments have beam diameters that are on the order of 100 nm, the analysis of particles in this size range is problematic. The analysis of

even micrometer-sized organic particles is limited by the quickly reached static SIMS limit. Primary ion beam current and mass resolution are typically far from maximized when operated in the highest lateral resolution mode. The net effect is a decreased detection sensitivity and difficulty in resolving mass interferences. An alternative to attempting to analyze a single submicrometer particle is to analyze a large region of a sample that contains many particles. The spectral data from the particle-rich region can be compared to data acquired from a control sample or a control region on the same sample. The advantage of this method is that it plays into a strength of ToF-SIMS (high sensitivity) and avoids its weakness (limited spatial resolution and the static SIMS limit). Details of how and when this approach works must be determined on a case by case basis. The basic requirements are for a high density of particles in an area of the sample that can be located, and a control sample or control region of a sample for comparison. The necessary density of the particles is the parameter that is somewhat unquantified, but is related to the ion yield of the contaminant and the fraction of the area covered by the particles.

Analysis of buried interfaces for contamination can be difficult. If the analysis is limited to the identification of inorganic contamination, it is possible to depth profile through the uppermost layer(s) until the desired interface is reached. An example of this method is shown in Figure 2. A stack composed of 40 nm polysilicon/40 nm polysilicon/Si was analyzed in order to identify contaminants at each of the interfaces. The mass spectrum obtained was a composite of all of the individual cycles of the profile. At the conclusion of the data analysis, the mass spectrum was investigated to determine what elemental contaminants were detected. The resulting contaminant profiles could be recreated from the raw data stream file. As is evident from this example, the advantage of ToF-SIMS for this type of analysis is that no elements need to be chosen *a priori*, reducing the chance that a contaminant will be missed.

An alternative to profiling through the uppermost layers of a multilayer stack is to perform a typical surface analysis on samples earlier in the manufacturing process, before the top layers are deposited. This is one of the only viable methods if the detection of organic contamination is of interest. An example of this method to look at ultra-thin integrated oxynitrides has been reported by J.J. Lee and co-workers.¹

Another potential problem for ToF-SIMS is the analysis of insulating materials such as glass, ceramics and plastics. Many industries, including the biotechnology, polymer and flat panel display areas, rely heavily on these materials. Unfortunately, insulating samples such as these often develop a charge build-up on their surfaces during analyses. This phenomena results from the bombardment of the surface with significant amounts of positively charged particles and the emission of secondary electrons. This charge build up results in a non-uniform electrical field at the sample surface. This non-uniform field alters the kinetic energy of the secondary ions. The secondary ion energies are important as the spectrometer only accepts ions within a certain energy range. Sample charging often dramatically reduces the mass resolution of the peaks and can be so severe that no useful signal is obtained from the sample. This problem is typically most pronounced when acquiring negative ion spectra.

A number of methods can be employed to minimize sample charging of insulating samples. The most common method is by bombarding the sample with a beam of low energy (<70 eV) electrons to compensate for the positive bias.² The low energy compensating electrons are typically pulsed so that there is no extraction field present while the charge compensation is occurring. Also, a grounded metal grid or a perforated metal plate can be placed over the sample to bleed away the charge build-up. It should also be noted that a thin contaminant layer on the insulator could also minimize charging. In any event, this is an area critically in need of additional research to more fully utilize the tremendous capabilities of ToF-SIMS on insulating samples.

One key element of more mature failure analysis tools such as FTIR and GC/MS are their extensive databases. When characterizing molecular contamination, the power of a technique can be limited by its spectral database. Although ToF-SIMS can often provide a probable empirical formula of an ion signal in a spectrum, this is not as valuable as providing the chemical origin of signal. As industries realize the power of ToF-SIMS as a characterization tool, individual companies as well as instrument vendors have begun to construct their own spectral libraries. For example, the Surface Spectra Static SIMS Library³ contains over 500 compounds. The major manufacturers of ToF-SIMS instruments also provide databases with their software.

These packages typically include search routines allowing the analyst to compare unknowns to the reference spectra. However, searching for specific characteristic ions is often more useful than attempting to correlate the entire acquired spectrum with a reference spectrum. This is because ToF-SIMS is not a separatory technique. Thus, spectra most often contain signals from many species including the contaminant(s) of interest, adventitious contamination (*i.e.*, Na and O) and the substrate. Thus, unknown spectra are usually much more complex than those found in reference libraries. Search routines are not yet sufficiently advanced to compensate for these factors.

Databases need to be expanded and search routines improved in order for ToF-SIMS to fully realize its potential in contamination identification. Companies are best suited to determine which compounds need to be added to their libraries, as they know the materials used in their various manufacturing processes. Attempting to create a single database of spectra for all industries is likely to have limited success. Further, search routines must be developed which more effectively use iterative processes to allow sequential identification of compounds.

FA Examples

The following demonstrations of ToF-SIMS usefulness in FA and contamination problem solving are not meant to be exhaustive. Rather, they are examples showing where ToF-SIMS has provided useful information in solving general types of problems. Some examples discussed do not represent actual failure analyses, but rather show approaches that can be utilized for failure analyses and contaminant monitoring in various industries.

No chapter on failure analysis by ToF-SIMS can be written without some mention of silicones. The most common type is polydimethylsiloxane (PDMS), but there are countless other chemical formulae for this class of compounds. Silicones go by several names including siloxanes, silicon oils, dimethicone and many proprietary trade names. These materials have many uses, including paper treatments, mold release agents, fiber lubricants, textile modifiers, water repellents, defoaming agents, anticaking aids, corrosion inhibitors, emulsifiers, lubricants, viscosity modifiers in personal care products, adhesives and countless others. Silicones have very low surface tensions and viscosities, making them extremely mobile on

surfaces. Thus, they are observed on many samples as indirect contamination. It will not take long for a novice ToF-SIMS analyst to become familiar with the distinctive pattern of positive ion mass peaks at m/z 28, 43, 73, 147, 207 and 281. The real difficulty lies in that, although PDMS may be the cause of failure, it is also possible that these compounds were introduced in shipment, storage or during handling and played no role in the device failure. Unfortunately, there is no hard and fast rule about when the presence of silicones should be considered important and when it can be safely ignored though the use of appropriate control and reference samples can aid in determining their importance on specific samples. A number of examples exist in the literature where PDMS is the cause of failure, particularly concerning delamination.⁴

Adhesives

Adhesives are often required to retain their holding characteristics for long periods of times under extreme environmental conditions. They play a critical role in many industries including aerospace, semiconductor, data storage, automotive and biotech. Understanding the adhesive failure mechanisms is crucial in developing adhesives and pretreatment preparations that provide the required adhesive properties. Failure can occur at the adhesive-substrate interface (adhesion failure) or within the adhesive itself (cohesive failure). Adhesion failure modes investigated by ToF-SIMS have included water ingress, cathodic delamination and segregation of components within the adhesive system.^{5,6,7}

In an example of adhesion failures applications, Davis and Watts used ToF-SIMS in conjunction with XPS to study the effects of pretreatment with yttrium hydroxide as an adhesion promoter on the durability of iron joints.⁶ After adhering the two iron bars with a two-part amine-cured epoxy adhesive, the joints were exposed to water for varying periods of times before shearing. Joints not exposed to water exclusively displayed cohesive failure. Joints exposed to water exhibited areas displaying cohesive failure as well as areas of adhesive failure. The percentage of interfacial (adhesive) failures increased with increasing exposure times. In addition, interfacial failure occurred in two discernable modes. The first consisted of areas where separation between the adhesive and metal layer was initiated while in solution as indicated by the elevated iron oxide levels. The second adhesion failure mode occurred closer to the cohesive failure region. This area had comparatively low iron oxide concentrations, indicating that the disbonding occurred

after the sample was removed from the water bath. ToF-SIMS and XPS line scans were performed across the failure zones. Both techniques found elevated levels of Na and Ca in the second adhesion failure region. Localization of these alkali and alkaline earth ions have been used as proof of cathodic delamination.

The primary role of ToF-SIMS in this analysis was to determine conclusively whether the apparent interfacial failure did, in fact, occur at the interface. ToF-SIMS analysis of the adhesive failure region detected a number of species characteristic of the adhesive on one side of the failure. These characteristic ions included nitrogen-containing signals such as $C_5H_8NO^+$ and CN^- , both from the amine curing agent, and peaks typical of siloxanes. None of these signals were detected on the metal side of the interfacial failure zone. These observations confirmed that the failure was adhesive and not cohesive.

In a related study,⁵ ToF-SIMS and XPS were used to examine adhesion failure in a phosphated hot-dipped galvanized steel joint adhered with an epoxy adhesive and aged for 12 months at 95% relative humidity. ToF-SIMS images found distinct complementary regions consisting of Mg^+ and characteristic adhesive signals. Fitzpatrick *et al.*, proposed that the Mg^+ regions, ranging from 100-150 μm in diameter, act as cathodic cells which weakened the adhesive at the metal/adhesive interface. Thus, electrochemical activity was in part responsible for the adhesive failure. The complementary adhesive regions within the initiation zone indicated that water ingress occurred resulting in adhesive weakening, another source of adhesive failure.

Adhesive failure can also occur in comparatively simple systems such as labels adhered to containers with glues. Keller and Hug recently demonstrated the use of ToF-SIMS to identify the cause of failure of self-adhesive labels on glass vials in a pharmaceutical application.⁸ Analysis of surfaces from both "good" and "bad" vials revealed high levels of PDMS on vials in which the labels would not stick. PDMS was also found to be the contaminant in another study on adhesive labels [Zimmerman, 1995 Tappi J.]. In this work, ToF-SIMS analysis was performed on labels exhibiting surface spotting and on control labels without spotting. Significantly higher levels of PDMS were found on the labels with spotting problems than on the control labels. In order to determine the source of the PDMS, both the adhesive and the

adhesive release liner were analyzed. These tests concluded that the release liner was the source of the contaminant.

Paint and Coatings

The automotive industry has shown significant interest in determining the cause of paint failures on metal surfaces and plastic composites. Modern automotive paints are complex, consisting of multiple layers of coatings each present to perform a specific task such as protection (the clear coat) or coloring (the base coat). Since each of these coatings have notably different chemistries, ToF-SIMS has proven useful to characterize and evaluate them in several different ways. Obviously, delaminations of paint layers analogous to those described above can be investigated by ToF-SIMS. Paints must adhere to the adherend surfaces for long periods of time and often under extreme conditions (*e.g.*, hot and cold temperatures, rain and snow, salt conditions). An additional investigated area is the distribution of additives within the paint system. A variety of additives are often employed in these systems, including antioxidants, light stabilizers and other modifiers to improve performance characteristics. The distribution of the additives within a particular layer is often critical in its performance.

One plastic composite of particular interest is a thermoplastic olefin (TPO). This type of plastic is used in many automotive moldings. Researchers have found that applying a primer consisting of a chlorinated polyolefin polymer (CPO) can increase paint adhesion to TPO. While adhesion increases, the mechanism by which this happens is uncertain. Prater, *et al.*, used a combination of ToF-SIMS and fluorescence microscopy to study the mechanics of the CPO adhesion promoter on TPO.⁹ A TPO/CPO system was cross-sectioned using a microtome and analyzed using ToF-SIMS. Both ToF-SIMS images and line scans of Cl⁻, an ion characteristic of the CPO, found a sharp interface between the CPO and TPO. Diffusion of the CPO within the TPO was therefore concluded to be less than a few micrometers. These results strongly suggest that the adhesion-promoting characteristic of CPO is an interfacial phenomenon. This result is contrary to earlier hypotheses suggesting the promotion occurs through diffusion and molecular entanglement of the CPO into the TPO.

Gerlock, *et al.*, have performed studies using ToF-SIMS to map the resistance of paint systems to photo-oxidation.^{10,11} In these experiments, paint systems were exposed to UV light in an $^{18}\text{O}_2/\text{N}_2$ atmosphere. Cross-sections of the paint systems were then prepared and analyzed by ToF-SIMS. Line scans of $^{18}\text{O}^-$ across the cross-section reveal the presence of ^{18}O -labeled photoproducts within all the coating layers. In their most recent study, they exposed a paint system consisting of a clearcoat with and without Mel-A on top of a red acrylic/melamine basecoat to 2000 hr of UV light in an $^{18}\text{O}_2/\text{N}_2$ atmosphere. Mel-A is an ultraviolet light absorber. The base coat surface of the system without Mel-A in the clearcoat exhibited much higher $^{18}\text{O}^-$ ion intensities. However, some $^{18}\text{O}^-$ intensity was also observed on the system utilizing Mel-A. It was concluded that this photo-oxidation was initiated by visible light that is not absorbed by the clearcoat/Mel-A system.

A similar experiment was performed on two paint systems (A and B) that had been exposed for 5 years in Florida. The 5-year old samples were subjected to an additional 1000 hr of UV exposure in the $^{18}\text{O}_2/\text{N}_2$ atmosphere. Two colors from each system were studied. The $^{18}\text{O}^-$ line scans from the two systems samples showed oxidation at the basecoat for both colors, indicating that the clearcoat had failed. Line scans for the two system B samples revealed no oxidation at the basecoat. The system B clearcoat was superior to the system A clearcoat.

These types of experiments allow auto makers to directly analyze the various layers of their paint systems with high sensitivity, and by using the ^{18}O isotope, to distinguish between the oxygen natively present in their organic coating system and oxygen introduced during the photo-oxidation experiment. These characteristics allow manufacturers to shorten their paint exposure experiments and improve their time to market.

When applying coatings to surfaces, stringent cleaning is often necessary. Even low levels of contaminants will affect the adhesive properties of the coating resulting in unintentional delamination of the coating. In one study by Brenda, *et al.*, ToF-SIMS was used to help determine the cause of delamination of aluminum drops on trucks coated with a refinishing paint.¹² ToF-SIMS analysis on the

backside of a delaminated paint chip displayed spectra dominated by Cl^- and complex Al_xO_y ions. From these results, they concluded that chloride from road salt began the corrosion process.

Coating technology is not limited to the area of automobiles or other high technology industries. Doring, *et al.*,¹² used ToF-SIMS to study delamination problems on the interior side of an aluminum can. Many metal cans used in food packaging are coated with polymeric linings to protect both the food and can surfaces. Spectra on the backside of a delaminated coating chip revealed the presence of fatty acid glycerols. Spectra obtained from cans directly after the final rinse step (immediately prior to coating) also displayed these signals. Thus, incomplete rinsing of the Al surface resulted in the observed delamination.

Another common coating failure examined by ToF-SIMS is the presence of craters. Cratering can occur in coatings deposited as liquids in the presence of contaminants. Surface contamination can lead to a change in wettability of the sample being coated, leading to the uneven application of the layer. Cratering is not simply a cosmetic issue, since the crater will often extend to the substrate and can severely reduce the effectiveness of the applied coating. In one study, ToF-SIMS spectra indicated the presence of dioctylphthalate and/or ethylhexyl phthalate on the surfaces of a coating (Brenda et al) displaying craters. The contaminant was traced to a PVC waterline in the electrochemical coating system.

Additives in Rubbers and Polymers

Additives are not only a crucial element in paints. They are also heavily used in many types of rubbers and polymers. These additives can take the form of antioxidants and light stabilizers. These additives are critical in allowing polymers/rubbers to maintain their properties over the lifetime of a product. A number of researchers have demonstrated ToF-SIMS utility in detecting additives in polymers^{-13,14,15,16,17} Both the concentrations and the distributions of these additives are critical in allowing materials to maintain their properties.

Recently, imaging ToF-SIMS was used to map the distribution of Chimassorb 944FDTM in polyethylene.¹⁸ Chimassorb is a hindered amine light stabilizer (HALS) produced by Ciba Geigy that is added to polyethylene to control its photoinduced decomposition. The compound has a repeat unit with a mass of

598.54 D. The M+H ion of the oligomer was detected at the nominal mass-to-charge of 599; however, the signal intensity of this ion was insufficient to obtain useful images. The additive fragment ion at m/z 58 ($C_3H_8N^+$) could be used for imaging, as this signal was present at sufficiently low intensities in the polyethylene reference. Polyethylene samples containing additive weight percent concentrations from 0.1% to 2.0% were imaged over a $180\ \mu\text{m} \times 180\ \mu\text{m}$ area. Ion images of the m/z 58 signal for a 2% sample displayed 3-5 μm additive agglomerations in one sample and 10 μm features in another. Ion images of the 0.25% sample showed fewer and smaller agglomerations. Samples of the 0.1% showed no localization of the additive.

This work and those discussed in the related references demonstrate ToF-SIMS capabilities in addressing additive-related problems. A rubber or polymer may fail in the field due to heterogeneous distribution of its additives, or the additives may migrate to or away from the surface. Both of these scenarios will degrade the properties of the additives.

Interesting work by Lang, *et al.*, involved ToF-SIMS and XPS analysis on PET [poly(ethylene-terephthalate)] from two different suppliers.¹⁹ The PET from one supplier had much higher levels of the antioxidant additive Irgafos 168 and the lubricants octylarachidate, octylstearate and octylpalmitate. In addition, the intensities of PET fragment ions varied significantly between the two sources. The dramatic differences between spectra from the two PET samples demonstrate the importance of using reference spectra of materials from suppliers specific to a process.

Paper

The surface characteristics of paper are strongly tied to its performance. Wettability, absorptivity and color are a few of the traits that directly affect the print quality of documents. Additives called sizing agents are used to control the surface properties of papers and to improve their machinability. Often other additives are added to “fix” the sizing to the paper. Previously, analyses were performed to determine the concentration of sizing agents and other additives at the bulk level using conventional techniques; however, ToF-SIMS provides a valuable method for actually determining the distribution of these agents

on the surface of the paper.^{20,21} Contaminants on paper surfaces are also important since they can affect print quality, decrease surface energy and change the wettability of inks.

Ozaki and Sawatari used ToF-SIMS to examine the distribution of L-750, a soap-type rosin sizing agent, in paper.²² The main component of this particular rosin is abietic acid. Characteristic ions of the rosin were $C_7H_7^+$, $C_7H_{12}O_2^+$, $C_{15}H_{27}O_2^+$ and $C_{20}H_{30}O_2^+$, with the C_7H_7 or tropylium ion signal having sufficient intensity to allow imaging on the paper. The C_7H_7 ion intensity increased with increasing levels of the rosin (0% to 2%). This check is essential when using an ion, such as the tropylium ion, that has many sources. The ion images showed a relatively even distribution of the sizing agent over the paper surface. These samples were then modified with osmium tetroxide for electron probe microanalysis (EPMA). EPMA images of the paper found that although the entire surface of the paper was coated with a film of the sizing agent, there were additional 5-10 μm droplets that were not observed in the ToF-SIMS analysis. These results are a good example of how sampling depth can effect observed results. ToF-SIMS is a true surface analysis tool used to characterize the top several monolayers of a sample, while EPMA extracts data from 5-10 μm into the sample. Neither data set is wrong, although in this case the EPMA information is more useful and complete.

Other researchers have been active in this field as well. Brinen and Kulick published research on a bleached sulfite paper that required abnormally high levels of sizing agent to attain the intended degree of sizing.²³ They performed ToF-SIMS analysis on paper exposed to acetone in a chromatography chamber. Exposure resulted in three areas having various levels of sizing. Spectra from areas exhibiting low sizing levels contained greater intensities of higher mass signals such as $C_{21}H_{44}NO^+$, $C_{22}H_{42}O_2^+$, $C_{26}H_{52}O_2^+$ and $C_{31}H_{64}NO^+$. Ion images of these species showed that they were present as droplets 5-30 micrometers in diameter. Levels of these species were much lower on the areas exhibiting good sizing characteristics and no localizations were observed. Analysis of the pitch (organic extractables) from the pulp of the paper found high levels of the $C_{21}H_{44}NO^+$ and $C_{26}H_{52}O_2^+$ species. This observation suggests that pitch components such as $C_xH_{2x+1}NO$ compounds, fatty acids and/or other species may be responsible for the poor sizing characteristics of the paper.

Problems with paper do not always focus upon sizing agents, especially for specialty papers such as those coated for use in printing color graphics. Typically, these papers are coated with latex to improve their printing properties; however, problems with the latex or underlying paper can result in problems such as mottling (uneven print density). One study used ToF-SIMS to compare coated paper from stocks exhibiting good and bad printing characteristics.²⁴ Surface calcium levels were significantly higher on the paper that exhibited mottling. Ion images revealed localized areas of Ca on the problem paper, with complementary areas containing low latex coverages. The images from the good paper showed essentially uniform coverages of both calcium and latex.

Microelectronics and Data Storage Industries (chips, hard drives, equipment manufacturers)

High technology industries are particularly susceptible to failures caused by contamination, often at low levels. As devices get smaller and processes get more complex, the possibility of contaminants having an adverse affect on a product's performance increases proportionately.

AMC

Often, the source of device failure is not a specific defect, but rather due to a layer of contamination over the entire sample. Airborne molecular contamination (AMC) is one problem area that cold stage ToF-SIMS is well qualified to tackle. AMC consists of organic and inorganic compounds. No other surface analytical technique can provide specific and sensitive identification for all these species. In addition, TOF-SIMS spatial resolution allows data to be obtained from different areas of the sample (*e.g.*, center, edge and backside of wafers).

AMC can originate from a range of sources, including construction materials, processing chemicals, cleanroom furniture and people. Many materials such as plastics undergo outgassing of volatile organics into the atmosphere, with the extent and type of outgassing varying widely for different materials. The effects of airborne molecular contamination, both organic and inorganic, can include defective epitaxial growth, deterioration of gate oxides, unintentional doping, uneven oxide growth, unintended

hydrophobization, changes in surface wettability, corrosion, hazing of optics, decreased metal pad adhesion and silicon carbide formation.²⁵

Many companies attempt to identify outgassing sources before they become problematic. Procedures vary, but they often follow one of two scenarios. In the first, silicon wafers are placed at various positions in a cleanroom for specific periods of time. The wafers are then analyzed by ToF-SIMS and perhaps GC/MS to identify adsorbed species. By repeating this process over time, the level of airborne molecular species can be monitored. This data essentially provides engineers a chart of the contaminants in their rooms, permitting better identification of sources when problems arise.

The second scenario involves a more controlled attempt to identify specific contaminants. In these experiments, Si wafers are used as witness plates in the presence of heated materials. Heating results in larger levels of species outgassing from the materials than at ambient conditions, thus shortening the exposure times necessary to obtain detectable levels of material on the wafer. After exposure, the wafers are analyzed by cold stage ToF-SIMS. Repeating this procedure on a variety of materials allows the user to construct a library of outgassing sources. Information on potential sources of a contaminant is often much more useful than simply providing a list of contaminants.

Goodman, *et al.*, described a specific example of the use of Si wafers to monitor contaminants, by tracking contaminant levels in a newly constructed class 10 cleanroom over a six-month period.²⁶ Both cumulative exposures and sequential exposures were performed. The cumulative experiments consisted of introducing a number of Si wafers at the beginning of the experiment and removing individual wafers at designated time intervals over the lifetime of the experiment. In the sequential experiments, wafers were introduced for one and three day intervals on a monthly basis throughout the experiment.

Figure 3 shows relative levels of silicones and phthalates on the wafers over the course of the experiment. Phthalates are common plasticizers used in many plastics while silicones are a common type of polymer. Both species undergo a rapid increase in the cumulative experiment and then level off. The phthalate undergoes decay after reaching the maximum level. The sequential exposures show high levels on wafers exposed during the initial stages of the experiment, while those exposed at later stages have decreasing

levels. This observation is consistent with those from other researchers in similar experiments,²⁷ and can be explained by the observation that new materials initially undergo higher levels of outgassing. After a period of time, outgassing rates decrease as species are removed and not replenished. The decrease in the phthalates in the cumulative experiments after reaching a maximum value indicates that this species undergoes an equilibrium adsorption process. Here, when the level of atmospheric contamination is reduced, material adsorbed on the wafers is removed to re-establish the equilibrium state. Similar behavior was observed with the some nitrogen containing species ($C_4H_{12}N^+$, $C_8H_{20}N^+$ and $C_6H_{16}NO^+$); however, lower molecular weight species ($C_4H_{12}N^+$) reached a maximum level at an earlier point. The difference may be due to variations in vapor pressure and outgassing rates based on molecular weights.

Other work has compared the use of ToF-SIMS to thermal desorption gas chromatography/mass spectrometry (TD-GC/MS) as a tool for measuring organic contamination on Si wafers. TD-GC/MS involves heating the wafer to desorb the adsorbed organics. The volatile species are trapped and then analyzed by conventional GC/MS. Schnabel, *et al.*, showed that the two techniques tended to provide complementary information.²⁸ Compounds with low volatility and high polarity were more easily detected with ToF-SIMS while TD-GC/MS was the preferred technique for compounds of high volatility and low polarity. ToF-SIMS exhibited excellent sensitivities for many compounds such as tris(2-chloroethyl)phosphate ($<10 \text{ pg/cm}^2$) and cyclodecamethylpentasiloxane ($<5 \text{ pg/cm}^2$). Compounds such as aminobutanol, tetramethylammonium hydroxide and Irganox 1010 were detected by ToF-SIMS and not with TD-GC/MS. However, hydrocarbons such as octadecene could not be detected with ToF-SIMS.

A major advantage of TD-GC/MS is that it is a separation technique, which can greatly simplify the interpretation of spectra compared to ToF-SIMS interpretation. In addition, the spectral libraries available to TD-GC/MS users are much larger. However, ToF-SIMS has its own advantages such as superior mass resolution and its ability to look at a wide array of species (metals, inorganic and inorganic compounds) in specific regions of the sample.

Karen, *et al.*, also found the sensitivity of ToF-SIMS for polar compounds to be superior to that of GC/MS.²⁹ In their experiments, Si wafers were exposed to air both inside and outside a cleanroom.

Significant levels of phthalates ($C_8H_5O_3^+$, m/z 149), as well as N-containing species such as $C_3H_8N^+$ (m/z 58), $C_5H_{12}N^+$ (m/z 86), $C_6H_{16}N^+$ (m/z 102) and $C_{12}H_{28}N^+$ (m/z 186), were observed on both wafers. The species were generally higher on the wafer exposed to the atmosphere outside the cleanroom. Sulfur-containing species such as SO_3^- (m/z 80) and HSO_4^- (m/z 97) were also detected in significant levels on these wafers. Levels of all of these species were much smaller on a wafer not exposed to either of the atmospheres. In their experiments, they estimated the detection limit of typical alkyl amines by ToF-SIMS to be approximately 10^8 to 10^9 molecules/cm². The detection of low levels of amines is particularly important since these species can poison acid-catalyzed photoresists.

Metals

In general, ToF-SIMS is not considered to be a quantitative technique because relative sensitivity factors (RSFs) that are matrix dependent must be determined for each compound or element of interest. Since it can be difficult to obtain well-characterized standards that are needed to develop RSFs, a limited number of species and matrices have been investigated. Much of the earliest quantitative work involves the measurement of surface metal contaminants on silicon substrates.^{30,31,32} Recently, several new papers discussing the topic have been published.^{33,34,35} This renewed interest is driven by semiconductor devices that continue to shrink in size. With smaller devices, the ability to detect lower levels of contamination becomes critical, and the detection limits achievable with standard measurement techniques are becoming inadequate to meet the requirements.³⁶

In comparisons with other surface metal analysis tools, ToF-SIMS can offer several advantages that make it worthy of evaluation for this application. For example, it provides better detection limits than Total Reflection X-ray Fluorescence (TXRF), which is perhaps the most common tool currently used for surface metal measurements. In addition, unlike TXRF, ToF-SIMS can detect elements with atomic numbers below Si, and it can be used to analyze significantly smaller areas since the TXRF spot size is approximately 1 cm². In comparisons with SurfaceSIMS or Vapor Phase Decomposition (VPD) combined with another technique (*e.g.*, TXRF, ICP-MS, AAS), the reported detection limits of TOF-SIMS are generally similar (typically approximately 10^8 atoms/cm² for metals such as Fe, Ni and Cu).

However, SurfaceSIMS is not a survey technique, and VPD techniques can only effectively be used on whole, unpatterned silicon wafers.

Recent work by Mowat, *et al.*, sought to correlate metal quantitation on wafers by ToF-SIMS to three other techniques, TXRF, SurfaceSIMS and Vapor Phase Deposition Atomic Absorption Spectroscopy (VPD-AAS).³⁷ Table 1, which shows a comparison of K, Cr and Fe data obtained by the four techniques from a single wafer, indicates a reasonable agreement among them. In a second experiment, ToF-SIMS and SurfaceSIMS data on approximately 90 wafers were compared. This work showed good correlations between the two techniques for Al, Na and Ca (correlation coefficients = 0.90-0.99). However, correlation coefficients for K ($r=0.51$) and Cr ($r=0.56$) were much worse. Further experiments are necessary to explore this discrepancy.

Zanderigo, *et al.*, have also reported comparisons of ToF-SIMS, VPD-AAS, TXRF, ICP-MS and GFAAS data from Na, Al, Fe and Cu contaminants on Si wafers.³⁸ In this work, the focus was on the development of a protocol for uniform sample preparation and on comparisons of the various analytical techniques to determine which would provide the best comparison to determine ToF-SIMS detection limits. The discussion covers some of the difficult issues related to the preparation of good reference samples, including the requirement for uniform contaminant deposition and the possible value of matching the chemistry of the contaminant to anticipated samples. The method the authors chose to use was spin coating, though they describe previous work that used sputtering (Schnieders, *et al.*³¹) and ion implantation (Douglas and Chen³³) to prepare standards used to determine RSFs and detection limits.

The variability in detection limits obtainable by ToF-SIMS under standard analytical conditions are also discussed by Mowat, *et al.*³⁷ The source of this variability is apparent from the equation used to determine metal concentrations:

$$\text{Metal Concentration} = (\text{Metal Counts}/^{30}\text{Si Counts}) \times \text{Relative Sensitivity Factor}$$

It is clear that the detection limit depends on the number of ³⁰Si secondary ions that are counted. For instance, Fe detection limits were found to vary from 2.9×10^8 to 8.4×10^8 atoms/cm² for a total of 90 wafers analyzed under identical conditions. One major reason that the intensity of the silicon peak can vary

significantly from wafer to wafer is a difference in the level of adsorbed molecular species. The presence of peaks for 'adventitious' or 'atmospheric' hydrocarbon species in ToF-SIMS spectra is well known to any user of the technique. High levels of molecular contamination tend to reduce the signal intensity of ^{30}Si (and the contaminant metal).

An example from a semiconductor equipment manufacturing process highlights another benefit of ToF-SIMS in surface metal measurements, namely, its ability to analyze small areas.³⁹ Copper is replacing aluminum as the next generation interconnect wiring for semiconductors due to its lower resistivity. Patterning of copper features currently relies on chemical-mechanical planarization (CMP) during the processing. Unfortunately, CMP is a relatively dirty process. Debris may originate from slurry abrasives, polishing pads, pad conditioners and the polished materials. This debris can result in catastrophic failures of the device.

Copper residue in the dielectric regions is another critical problem for interconnect structures. If present in these regions at the gate level, device failure will occur. In this particular work, the level of metal contamination on the dielectric after two different cleaning processes was compared to evaluate the relative effectiveness of the cleans. Table 2 shows a comparison of residual copper concentrations on the silicon oxide substrate in a copper patterned area on the two samples. Copper concentrations on the oxide dielectric have been calculated in an area with Cu lines spaced 10 μm apart. Four lines were analyzed for each clean. The average Cu concentration was 6.6×10^{15} and 3.7×10^{13} atoms/cm² for cleans A and B, respectively. This indicates that clean B was significantly more effective than clean A.

Further work must be done to optimize experimental conditions and determine and standardize RSFs, but ToF-SIMS is already a useful complementary technique to other tools used for these measurements. With excellent detection limits, survey capability and ability to obtain quantitative data from small areas, ToF-SIMS is a valuable tool for surface metal measurements and should become more important in the future.

Other Examples

Not all contaminants in semiconductor processes are the result of foreign material that is deposited on a sample. Another source of contamination is the failure to completely remove a material used during processing. A common example of this type is residual photoresist. Photoresists are used as masks during doping and dry etching processes; however, these processes can significantly modify the chemistry of the photoresist itself, making it difficult to fully remove the mask with traditional O₂ plasma techniques. ToF-SIMS can be used to evaluate the chemical nature of the residual resist, allowing engineers to construct systems that will more efficiently remove the material. ToF-SIMS can also be used to characterize the resist films both before and after they have been subjected to doping and dry etching procedures.^{40,41} Understanding the chemical changes produced during these procedures is also useful to design better means of photoresist removal.

Other work has shown that residues left behind during plasma ashing to remove photoresists are not always completely organic in nature.⁴² Hues and Davin deposited aluminum films on silicon oxide. Metal lines were then formed by delineating with photoresist, and etching the device in a BCl₃/Cl₂ plasma. All organic residue should be removed by an O₂ plasma ashing. However, ToF-SIMS analysis on the ashed surface indicated that some residual organic species and aluminum were present on the sidewalls. The presence of metals is a problem because they will form oxides during the plasma ashing that will be difficult to remove. In addition, the metal oxides can prevent the complete removal of the resist during ashing. The combination of these processes can ultimately result in an increase in effective line width, which is a particular problem at smaller device dimensions.

ToF-SIMS is also a useful tool during process development. In this manner, potential detrimental contaminants are discovered before devices are produced. In one example, Martin, *et al.*, describe attempts to develop an improved wet cleaning process.⁴³ Wet cleaning processes are used to remove species such as particles, metals and organic matter. Often, a process designed to remove one type of species may result in the unintentional deposition of another. For example, the common SC-1 clean that uses a mixture of ammonia, hydrogen peroxide and water to remove particles and organic matter can deposit metals in the process. In the work, the researchers attempted to minimize metal deposition by adding chelating agents such as Dequest 2060s and cTRAMP to the SC-1 solution. The cTRAMP was used to prevent the

precipitation of Fe, Cu and Zn onto the surface, while Dequest 2060s was useful for minimizing Fe and Ni concentrations. ToF-SIMS analysis detected no sign of these phosphonic acid-containing chelating agents as residues on the wafers. As part of this work, TXRF was used to quantitate contaminant metals on the wafers, though ToF-SIMS could have been used for this measurement as well.

In another example, ToF-SIMS was used to determine the nature of defects originating during the $\text{Cl}_2/\text{HBr}/\text{He}/\text{O}_2$ etching of SiO_2 .⁴⁴ Micrometer-sized defects were found to increase in number after removal from the etching environment, and then decrease after approximately 20 hours in the ambient. Initial analysis by Auger spectroscopy and SEM-EDS was unsuccessful because the defects were not stable in the electron beam, but the defects could be analyzed by ToF-SIMS. Images and mass spectra from the defects showed intense peaks at m/z 18 in the positive ion spectrum and at m/z 79 and 81 in the negative ion spectrum. These most likely arise from an ammonium salt, NH_4Br .

Glasses

The topic of glasses overlaps with a number of industries already discussed, since they are used extensively in the microelectronic and automotive industries. During processing of many types of glass, the products are often moved or manipulated using rubber suckers and then stored on paper. Both the suckers and paper can produce stains on the glass surfaces that can cause subsequent problems with wettability and adhesion. The contaminants can also result in surface defects when applying thin films to the glass.

ToF-SIMS has been used to investigate both sucker and paper contamination on glasses. In one study, glass was exposed to five different types of suckers, including silicone rubber, nitrile rubber, fluorine-containing rubber, urethane rubber and chloroprene rubber.⁴⁵ ToF-SIMS analyses were performed on both the sucker stain and on the rubber sucker itself. Characteristic peaks were observed for four of the five rubbers; however, these peaks were only detected on the corresponding glass samples for the nitrile (*e.g.*, CN^+ and $\text{C}_3\text{H}_4\text{N}^+$) and fluorine-containing rubber suckers (*e.g.*, CF_3^+ and $\text{C}_3\text{H}_2\text{F}_5^+$). The silicone rubber sample did not produce characteristic peaks, since the standard silicone species were detected in all of the rubber samples. Thus, silicone originating from the silicone rubber could not be separated from common silicone contamination.

This study also examined stains left by paper contacting glass in an oven at 60°C for 48 hours. SEM analysis of the paper stain found small, micrometer-sized particles on the surface. ToF-SIMS analysis was then performed on the paper stain area, on an area not in contact with the paper, and on the paper itself. The paper spectrum contained a series of low-mass organic ions up to m/z 160 with an empirical formula of $C_xH_yO_z^+$. Sodium and silicon signals dominated both glass spectra; however, when the control glass spectrum was subtracted from the paper-stained glass, an organic fingerprint essentially identical to that on the paper reference was observed. Ion images of these species revealed micrometer-sized localizations that were consistent with the SEM results, and further demonstrating that the stains result from the paper itself. The authors note that their results demonstrate the need for a reference library of materials that can be used to better identify contaminant sources.

Biomedical/Pharmaceutical

The biotechnology area can cover a broad range of areas, including medical devices such as catheters, artificial joints, contact lenses and stents, as well as biosensors, biochips and pharmaceuticals. Surface analysis is important in all of these areas because it impacts characteristics such as adhesion, absorption and biocompatibility. ToF-SIMS can be a vital tool in development processes, to evaluate the success of procedures such as surface treatments and to determine if contaminants are being introduced in products. Both of these factors are critical in determining the eventual success and regulatory approval of the device. Contamination issues are particularly important, since they have relevance for both successful fabrication processes and for possible cytotoxicity when the product is in use.⁴⁶

An example of the utility of ToF-SIMS is reported in an application that involves the integration of biotechnology and microelectronics in a new field termed bioelectronics.⁴⁷ Bioelectronics has potential applications in areas such as cell-based biosensors and biological neural networks. In order for bioelectronics to develop, it must first be demonstrated that spatially controlled cell adhesion is possible. Mahohliso, *et al.*, used ToF-SIMS during initial bioelectronic development to evaluate micropatterned samples consisting of Teflon AF and 5 μm wide SiO_2 strips that were designed for cell attachment. Teflon AF has a low dielectric constant that makes it useful to the microelectronic industry, as well as a low

surface energy that inhibits adhesion of cells to its surface. The micropatterned samples were prepared by putting a coating of Teflon AF on SiO₂. An aluminum-patterned layer was placed on top of the Teflon AF, and the exposed Teflon AF was then plasma etched to expose SiO₂. After the Al was removed using wet etching, initial studies showed an undesirable attachment of cells onto the surfaces of the Teflon AF. ToF-SIMS analysis of the Teflon AF found evidence of a primary amine fragment at m/z 32 (CH₆N⁺). These types of species have been demonstrated to promote cell adhesion. After baking the polymer system to a temperature above its glass transition temperature, this amine fragment was no longer detected, and cell adhesion no longer occurred on the Teflon.

Later research by the same authors carried the study one step further.⁴⁸ In this case, an oligopeptide used to enhance cell adsorption was attached to gold microelectrodes isolated by Teflon AF. ToF-SIMS analysis of the sample detected fragment ions (*e.g.*, m/z 70, C₄H₈N⁺) and a molecular ion (m/z 966, C₂₀H₆₄O₁₃N₁₃S) from the oligopeptide on the gold, but not on the Teflon-coated surfaces. This is important, since attachment of even low levels of the oligopeptide on the Teflon could promote cell adhesion. ToF-SIMS images were also used to evaluate defects observed on some of the microelectrodes. Spectra from the defects were consistent with Teflon AF, indicating that the etching process used during fabrication was incomplete.

A recent review by Léonard and Mathieu extensively describes the use of ToF-SIMS in studies to characterize biomaterials.⁴⁹ Applications include areas such as combinatorial synthesis, actual imaging of cells and liposomes, quantification studies and efforts to create bioactive surfaces. More recent studies used ToF-SIMS to monitor solid phase peptide syntheses.^{50,51} Others have used ToF-SIMS to detect femtomole quantities of organic species within an array of silicon nanovials which could ultimately aid in pharmaceutical drug discovery.⁵² In more direct ToF-SIMS applications to the pharmaceutical industry, Cassidy, *et al.*, attempted to alter the handling properties of polystyrene particles by adsorbing poloxamers on their surfaces.⁵³ While some of these topics do not necessarily fit into the areas of failure analysis and contamination monitoring in the strictest sense, they are mentioned to demonstrate ways in which ToF-SIMS may function in this role in the future.

Conclusions

While ToF-SIMS may not yet be considered a mature technique, the examples discussed here clearly demonstrate its utility in many different applications. ToF-SIMS instrumentation and software are continuing to advance in order to keep up with the technological demands of the industries it serves. Advances in quantification, sensitivity, mass resolution and database availability offer a promising future for the technique as an important surface analytical tool. The use of ToF-SIMS should increase as scientists and engineers from additional fields acquire an understanding of the capabilities of the technique.

REFERENCES:

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- ¹ L. Wu, J.J. Lee, H-H Tseng, D. Sieloff, D. O'Meara, P. Tobin, in 'Secondary Ion Mass Spectrometry SIMS XII,' A. Benninghoven, P. Bertrand, H-N. Migeon, H.B. Werner, Eds., 2000, p. 477.
- ² B. Hagenhoff, D. van Leyen, E. Niehuis, A. Benninghoven, *J. Vac. Sci. Technol.* **A7**, 3056 (1989).
- ³ J.C. Vickerman, D. Briggs (Eds.), 'Static SIMS Library,' Surface Spectra, Manchester (1999).
- ⁴ A. T. Cheung *Proc. -Electron. Compon. Technol. Conf., 49th*, 816 (1999).
- ⁵ M.F. Fitzpatrick, J.F. Watts, J.S.G. Ling, *Polym. Mater. Sci. Eng.* **81**, 417 (1999).
- ⁶ S.J. Davis, J.F. Watts, *J. Mater. Chem.* **6**(3), 479 (1996).
- ⁷ A.M. Taylor, J.F. Watts, H. Duncan, I.W. Fletcher *J. Adhesion* **46**, 145 (1994).
- ⁸ B.A. Keller, P. Hug, *Anal. Chim. Acta*, **393**, 201 (1999).
- ⁹ T.J. Prater, S.L. Kaberline, J.W. Holubka, R.A. Rytz *J. Coat. Technol.* **68**(857), 83 (1996).
- ¹⁰ J.L. Gerlock, T.J. Prater, S.L. Kaberline, J.E. deVries, *Polym. Degrad. Stab.* **47**, 405 (1995).
- ¹¹ J.L. Gerlock, T.J. Prater, S.L. Kaberline, J.L. Dupuie, E.J. Blais, D.E. Rardon, *Polym. Degrad. Stab.* **65**, 37 (1999).
- ¹² M. Brenda, R. Döring, U. Schernau *Prog. Org. Coatings* **35**, 183 (1999).

-
- ¹³ R.W. Linton, P.O. Mown, A.M. Belu, J.M. Desimone, M.O. Hunt Jr., Y.Z. Menciloglu, H.G. Cramer, A. Benninghoven, *Surf. Interface Anal.* **20**, 991 (1995).
- ¹⁴ R. Dietrich, *Fresenius J. Anal. Chem.* **361**, 692 (1998).
- ¹⁵ F. Andrawes, T. Valcarcel, G. Haacke, J. Brinen, *Anal. Chem.* **70**(18), 3762 (1998).
- ¹⁶ F.R. Lang, U. Pitton, H.J. Mathieu, D. Landolt, E.M. Moser, *Fresenius' J. Anal. Chem.* **358**(1-4), 251 (1997).
- ¹⁷ M.P. Mawn, R.W. Linton, S.R. Bryan, B. Hagenhoff, U. Jürgens, A. Benninghoven, *J. Vac. Sci. Technol.* **A9**(3), 1307 (1991).
- ¹⁸ M.J. Walzak, N.S. McIntyre, T. Prater, S. Kaberline, B.A. Graham, *Anal. Chem.* **71**, 1428 (1999).
- ¹⁹ F.R. Lang, Y. Pitton, J.J. Mathieu, D. Landolt, E.M. Moser, *Fres. J. Anal. Chem.* **358**, 251 (1997).
- ²⁰ J.S. Brinen, S. Greenhouse, N. Dunlop-Jones, *Nord. Pulp Pap. Res. J.* **6**, 47 (1991).
- ²¹ J.S. Brinen, *Nord. Pulp Pap. Res. J.* **1**, 123 (1993).
- ²² Y. Ozaki, A. Sawatari, *Nord. Pulp Pap. Res. J.* **12**(4), 260 (1997).
- ²³ J.S. Brinen, R.J. Kulick, *Int. J. Mass Spectrom. Ion Proc.* **143**, 177 (1995).
- ²⁴ P.A. Zimmerman, D.M. Hercules, H. Rulle, J. Zehnpfenning, A. Benninghoven *Tappi J.* **78**(2), 180 (1995).
- ²⁵ P.J. Smith, P.M. Lindley, in 'Characterization and Metrology for ULSI Technology,' AIP Conf. Proceedings 449, D.G. Seiler, *et al.*, Eds., Woodbury, NY, 1998, p. 133.
- ²⁶ G. Goodman, P. Schnabel, L. McCaig, P. Lindley, T. Schuerlein, in 'Secondary Ion Mass Spectrometry SIMS XII,' A. Benninghoven, P. Bertrand, H.N. Migeon, H.W. Werner, Eds., Wiley, Chichester, 2000, p. 817.
- ²⁷ K. Takeda, T. Nonaka, Y. Sakamoto, T. Taira, K. Hirono, T. Fujimoto, N. Suwa, K. Otsuka *IEST Proceedings, Contamination Control, IEST 556* (1998).

-
- ²⁸ P. Schnabel, D. Nehr Korn, G. Goodman, P. Lindley "Analysis of Organic Contamination on Wafer Surfaces by ToF-SIMS" Presented at Semicon Europa 2000, April 12, 2000.
- ²⁹ A. Karen, K. Ozawa, A. Ishitani, in 'Secondary Ion Mass Spectrometry SIMS XI,' G. Gillen, R. Lareau, J. Bennett, F. Stevie Eds., Wiley, Chichester, 1998, p. 229.
- ³⁰ B. Schueler *Microcontam. Conf. Proc.* 783 (1994).
- ³¹ A. Schnieders, R. Mollers, M. Terhorst, H.G. Kramer, E. Niehuis, A. Benninghoven, *J. Vac. Sci. Technol. B* **14**, 2712 (1996).
- ³² P.K. Chu, B.W. Schueler, F. Reich, P.M. Lindley *J. Vac. Sci. Technol. B* **15**, 1908 (1997).
- ³³ M.A. Douglas, P.J. Chen *Surf. Interface Anal.* **26**, 984 (1998).
- ³⁴ P. Lazzeri, A. Lui, L. Moro, L. Vanzetti *Surf. Interface Anal.* **29**, 798 (2000).
- ³⁵ H. De Witte, S. De Gendt, M. Douglas, T. Conard, K. Kenis, P.W. Mertens, W. Vandervorst, R. Gijbels *J. Electrochem. Soc.* **147**, 1915 (2000).
- ³⁶ "The National Technology Roadmap for Semiconductors," Semiconductor Industry Association (1997).
- ³⁷ I.A. Mowat, T. Schuerlein, J. Metz, R. Brigham and D. Huffaker in 'Cleaning Technology in Semiconductor Device Manufacturing VI,' R.E. Novak, J. Ruzyllo, T. Hattori, Eds., The Electrochemical Society, Pennington, NJ, 2000, p. 569.
- ³⁸ F. Zanderigo, S. Ferrari, G. Queirolo, C. Pello, M. Borgini *Mat. Sci. Eng.* **B73**, 173 (2000).
- ³⁹ J. Li, D.J. Hymes, J. de Larios, I.A. Mowat, P.M. Lindley *Micro* **17**(3), 35 (1999).
- ⁴⁰ R. Saito, Y. Ichinohe, M. Kudo, *Appl. Surf. Sci.* **142**, 460 (1999).
- ⁴¹ R. Saito, Y. Ichinohe, M. Kudo, in Secondary Ion Mass Spectrometry SIMS XI, G. Gillen, R. Lareau, J. Bennett, F. Stevie, Eds., Wiley, Chichester, 1998, p.505.
- ⁴² S.M. Hues, C.M. Davin, in Secondary Ion Mass Spectrometry SIMS XI, G. Gillen, R. Lareau, J. Bennett, F. Stevie, Eds., Wiley, Chichester, 1998, p.225.

-
- ⁴³ A.R. Martin, M. Baeyens, W. Hub, P.W. Mertens, B.O. Kolbesen *Microelectronic Eng.* **45**, 197 (1999).
- ⁴⁴ J. Zhao, D. F. Reich, T. T. Nguyen, L. Zhao, T. Z. Hossain *J. Vac. Sci. Technol. A* **18**(1), 207 (2000).
- ⁴⁵ A. Hattori *J. Non-Crystal. Sol.* **218**, 196 (1997).
- ⁴⁶ J. Black, *Biological Performance of Materials*, 2nd ed.; Marcel Dekker Inc.: New York, 1992, Chapter 16.
- ⁴⁷ S.A. Makohliso, L. Giovangrandi, D. Léonard, H.J Mathieu, M. Ilegems, P. Aebischer *Biosensors Bioelectron.*, **13** 1227 (1998).
- ⁴⁸ S.A. Makohliso, D. Leanoard, L. Giovangrandi, J.J. Mathieu, M. Ilegems, P. Aebischer *Langmuir* **15**(8), 2940 (1999).
- ⁴⁹ D. Léonard, H.J. Mathieu *Fres. J. Anal. Chem.* **365**, 3 (1999)
- ⁵⁰ J.L. Aubagnac, C. Enjalbal, C. Drouot, R. Combarieu, J. Martinez *J. Mass Spectrom.* **34**, 749 (1999).
- ⁵¹ C. Enjalbal, D. Maux, G. Subra, J. Martinez, R. Combarieu, J.L. Aubagnac *Tetra. Lett.* **40**, 6217 (1999).
- ⁵² R.M. Braun, A. Beyder, J. Xu, M. C. Wood, A. G. Ewing, N. Winograd *Anal. Chem.* **71**(16), 3318 (1999).
- ⁵³ O.E. Cassidy, G. Rowley, I.W. Fletcher, S.F. Davies, D. Briggs *Inter. J. Pharm.* **182**, 199 (1999).

Tables

Table 1: Comparison of K, Cr and Fe concentrations on a silicon wafer

Table 2: Comparison of Cu concentrations after two different cleaning processes

Figure Captions:

Figure 1: Spectra obtained from silicon wafers exposed to 2-amino-1-butanol under ambient temperature conditions and using a cold stage.

Figure 2: Retrospective depth profile of contaminants detected in spectrum from 40 nm polysilicon/40 nm polysilicon/ Si structure.

Figure 3: Relative levels of silicones and phthalates on wafers after cumulative and sequential cleanroom exposures over a six-month period.