TOF SIMS Analysis for Sn_xO_y Determination on Lead-Free HASL PCB's

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Abstract

During the production of Lead-Free Hot Air Solder Leveling (LF HASL), non-wetting issues in several components were found including BGA pad. The common visual aspect of the suspicious pads was the typical yellowish and bluish color. However, during traditional Scanning Electron Microscopy/Electron Dispersive X-Ray Spectroscopy (SEM/EDX) analysis for wetting issues only a small increasing of copper was found but not related to the problem. Because of that, Time-Of-Flight Secondary Ion Mass Spectroscopy (TOF SIMS) analysis was proposed; using this technique, we could achieve better surface analysis in which we found the root cause on non-wetting just in nanometers of penetration.

With this non-common tool, the results showed something not detected before: the yellowish were zones with different thick oxide layers (about 250 nm) undetectable by SEM/EDX -four times higher than a normal oxide thickness. Consequently, solder paste flux was not able to clean that oxide thickness and joints were not formed properly. The oxide is expected to be Sn_2O_3 and not SnO_2, the most common tin oxide. In this part, we would also conclude the activation level of solder paste flux depends on the type of oxide. With this information, an investigation was conducted to remove the oxide layer as much as possible, so a solder paste with a flux more suitable to eliminate it was implemented and a cleaning process was designed to reduce it. These actions decreased the defects. In conclusion, TOF-SIMS analysis is a tool to understand better the solderability topics in Electronics Industry.

Introduction

1. Scanning Electron Microscope and (SEM/EDX) for analysis

SEM uses a focused beam of high-energy electrons to generate a variety of signals at the surface. When the primary electron beam interacts with the specimen, the electrons lose energy with a repetitive and absorption volume known as interaction volume. It sizes will depends on the electron´s released energy, the atomic number, and the specimen density. The energy exchange between the primary beam and the sample electrons released energy results in the reflection of electrons with high energy and electromagnetic radiation that are detected by a specialized screen that collects the information. The imaging is created by multiple scanning on the surface. Figures 1.a & 1.b show the principle of SEM interaction with the surface and the internal functionality of the equipment. SEM can analyze secondary and backscattering electrons depending on the type of detector. The first ones generated by a primary beam are collected by a Faraday cathode with +/-300 Volts and interact with the photographical medium to obtain the image. The 3D appearance comes from the number of electrons generated. The backscattered electrons are ejected with an angle greater than 90 degrees; their reflection occurs as results of several collisions, and the generated image shows contrast due to the variations of the elements content in the specimen.

EDX is a tool used together with the SEM to get the spectrum of elements. To obtain the information from the electrons, it is needed an interaction of some source of X-ray excitation and the sample´s surface. The EDX principle is that every element has its unique "atomic structure" and the element atom emits a particular X-ray energy peak. In order to release this energy from the atom, an energy beam (X-ray or electrons) is conducted into the studied atom, reaching internal energy levels bound to the nucleus; the beam excites the electron and removes it from the shell. This "missing" electron is replaced by another electron coming from an external level; this "jumping" electron releases X-ray energy (the difference between a higher energy level to a lower energy level). The energy is measured and it is possible to determine its composition.
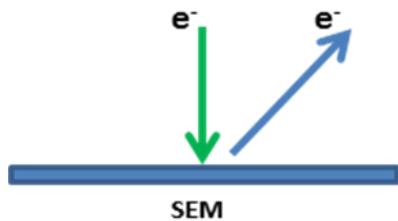
Figure 1.a   Figure 1.b

Figure 1.a SEM schematic showing the ion attack to release surface ions.
Figure 1.b SEM schematic for beam signal
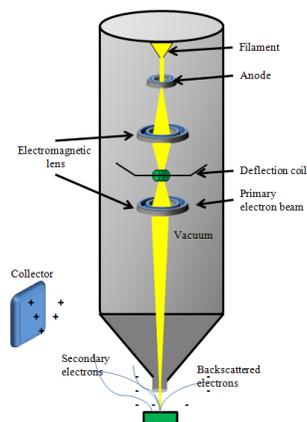
2. TOF-SIMS for analysis

Time-Of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) uses a primary ion beam to desorb and ionize species from a surface, see Figure 2. The resulting secondary ions are accelerated into a mass spectrometer, which measures the ions time-of-flight from the sample surface to the detector.

TOF-SIMS has three types of analysis modes: 1) mass spectra acquired to determine the atoms and molecular elements of a surface; 2) images to visualize the distribution of individual species on the surface; and 3) depth profiles to determine the distribution of different chemical species as a function of depth from the surface, analyzing every thin layer for its characterization. This profile allows to determine only one or two atomic layers; the ions and molecules desorption is caused by a "collision cascade" that it is started by hitting the surface with ions normally Ga (but it could be used Bi or C to increase the efficiency). Ions are generated, focused and transported to the target in the form of ion packages with well-defined arrival times. The detached elements are extracted into the TOF analyzer using high voltage potential and these have different velocities depending on their mass to charge ratio ($KE=1/2mv^2$). The mass and the profile are used to determine the elements or components, which are contained in the analyzed area.
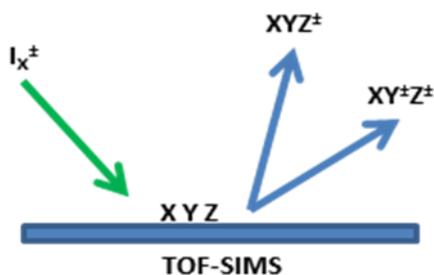

Figure 2.a   Figure 2.b

Figure 2.a. TOF-SIMS schematic that shows the ions desorbed from the surface.
Figure 2.b. "Collision cascade"
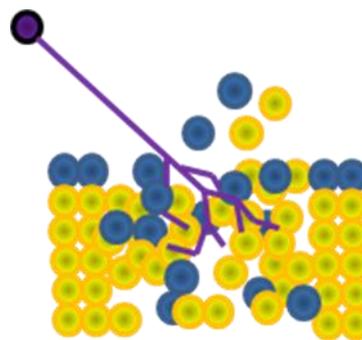
The following table, Table 1, shows the main characteristics between both techniques. SEM is the most affordable, common and known tool for surface characterization; however during the failure analysis the researcher should consider the advantages and disadvantages of the technique application and its detection limits, depth and lateral resolution. In the Figure 3, both techniques are set in a detection table that illustrates the analysis coverage.

Table 1 SEM & TOF-SIMS techniques comparison: Application

	Type of results	Type of analysis	Signal Detected	Elelments detected	Organic information	Depth resolution	Imaging / mapping
SEM	Quantitative	Stains, surface roughness, morfology, feature size, buried defects, particles, layers	Secondary and backscattered electrons and X-ray	B- U	NA	1 to 5 microns (EDS)	Yes
TOF-SIMS	Matrix (semi-quantitative)	Particles, residues, low concentration, metallic and dopand surface contamination, "survey technique"	Secondary ions, atoms, molecules	H-U	Molecular ions to mass 10K	1 monolayer	Yes
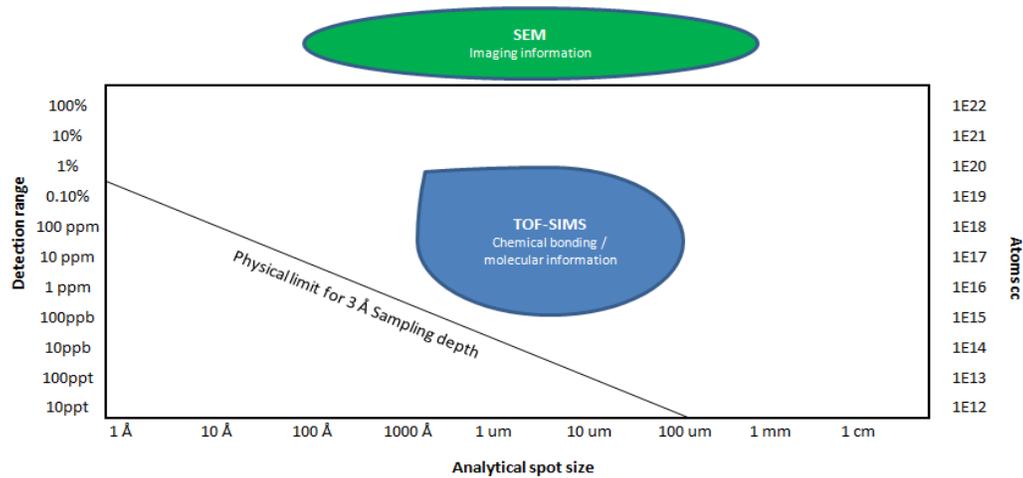
Figure 3. SEM & TOF-SIMS techniques comparison: Range of detection

Case of Study

A printing circuit board with LF HASL finish showed poor solderability in random areas. It was analyzed in order to find the origin of the non-wetting. The initial hypothesis was low HASL thickness; however, after the measurements, the pads had acceptable level of thickness (> 2 µm). The investigation was conducted to find another source of "contamination". Figure 4 shows the issue.
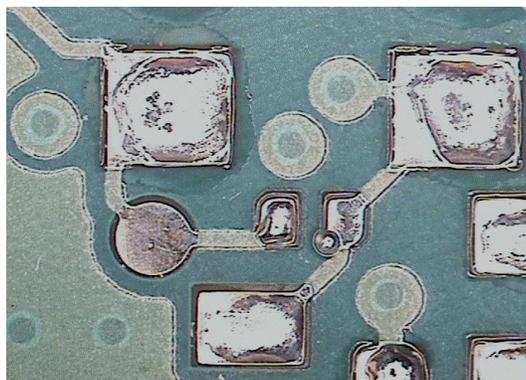
Figure 4. Non-wetting areas on LF HASL

a) Stage 1: Metallographic comparison

In Figures 4a, 4b, and 4c, the comparison of the pads with discoloration and a "normal" LF HASL pad is shown. Yellowish aspect was seen using stereoscope microscope, but dark areas and also brown spots were found with the metallographic microscope. Therefore, a second hypothesis was some kind of intermetallic or foreign materials were present on the surface.
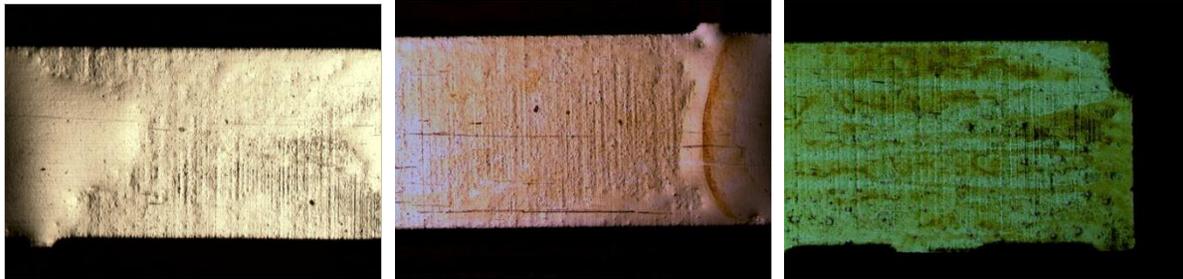

Figure 4.a	Figure 4.b	Figure 4.c

Figure 4.a, 4.b & 4.c These images were taken with a metallographic microscope: a normal LF pad (a), and two problematic pads (b & c) using two different polarized lens. These show dark areas and brown spots.

b) Stage 2: SEM/EDX

After the metallographic inspection, the next step for further investigation was SEM/EDX analysis. In the good PCBs, the common concentration of impurities was found and the surface looked smooth and homogenous; the only significant difference respecting to "bad" parts was that higher copper concentration was found without any surface abnormality. Although Cu could form oxides that are hard to be clean by fluxes, the Oxygen concentration was low and in some areas, no oxygen percentage was detected. Nevertheless, the areas with higher visual discoloration presented more surfaces with non-wetting. The oxygen (related to possible oxides) content was approximately the same percentage in both samples (not problematic – problematic PCB's); additionally Nitrogen content could come from the HASL environment, because HASL is performed in a nitrogen atmosphere, see Figures 5 and 6.

The SEM has a depth resolution of 1 to 5 um, and the material that was provoking issues the PCBs pads could be less than 0.1 um thick. Sometimes the failure is detected by the human eye, but not visible for the SEM microscope, if you cannot see failure in SEM you cannot analyze it. In Figures 5 and 6 "Normal" and problematic pads are shown; the elements found on the surface are considered typical on a HALS Lead Free PCB finish.

An analysis in the upper surface layers (less than 1 um thick) is required to check if there are any others wetting inhibitors which are not "visible" to SEM/EDX.
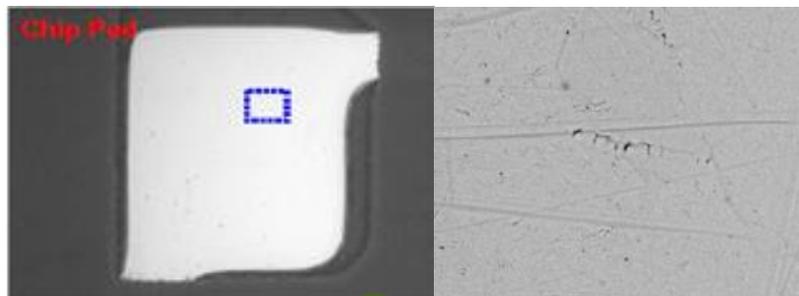

|	C	O	Si	Br	Sn
Reference sample	3.3	8.8	1.2	0.6	86.5

Figure 5. "Normal" PCB pads under SEM/EDX
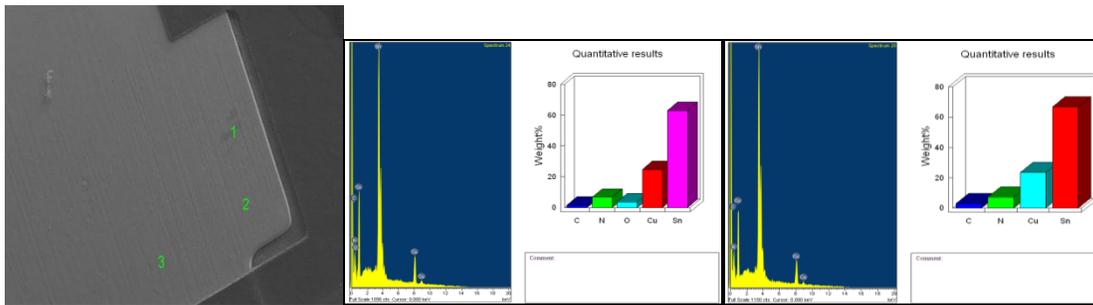
Figure 6. Problematic PCB pads under SEM/EDX

c) Stage 3: TOF-SIMS

The analysis consisted in a sputter erosion of the surface (approximate 100 um^2) reaching approximately 100 nm of lateral resolution. Two different ion beams are used for data acquisition. A sputter beam (e.g. O_2^+ or Cs^+) is applied to erode the sample while a second ion beam (analysis beam e.g. Bi_1^+) is used for to chemically characterize the resulting crater bottom. It is possible to have two different type of information: the first atomic layer, which recompiles information from the primary ions and the depth profile, which obtain data from inner layers.

In TOF-SIMS investigation using spectrometry mode (first atomic layer), a total mass spectrum of the surface region is acquired. These spectra are usually recorded with high resolution and used a low number of primary ions; the limited number of primary ions guarantees that detected signals are representative of the original composition of the sample surface (static SIMS limit).

A "normal" pad was included in the study in order to compare the results and locate the main differences between the surface that was inhibiting the soldering and the one without wetting issues. Figures 7.a & 7.b are showing the "normal" pad spectrometry and. Figures 8.a & 8.b show a "bad" pad. Both of them had similar elements on the surface; however, some of them were higher concentrations on problematic pads. Some of following elements found in the samples could be initiators or catalysts of wetting problems.
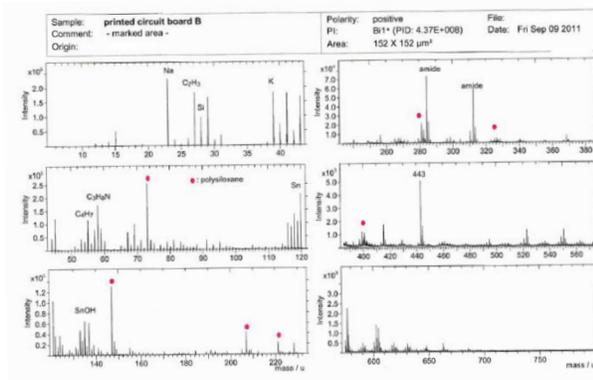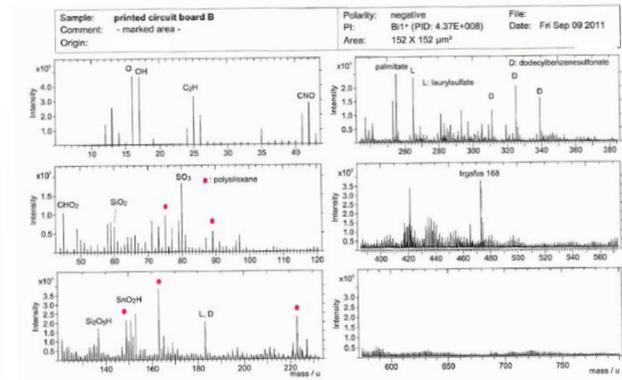
Figure 7.a   Figure 7.b

Figures 7.a & 7.b Mass Spectrum: Positive-Negative Secondary Ion Polarity: "Normal" pad

The most significant ions detected in the "bad" and "normal" pads spectra (see Figures 7 & 8) are indicative of the following elements and compounds on the sample surface:

- Sn and Sn oxides
- Aliphatic hydrocarbons
- N-containing hydrocarbons especially amides, e.g., Kemamide
- O-containing hydrocarbons, e.g. fatty acid residues
- Polysiloxane
- Laurylsulfate
- Dodecylbenzenesulfonate

N-containing hydrocarbons would come from flux residues. Laurylsulfate and Dodecylbenzenesulfonate are compounds that would come from detergents residues, all of these components could come from PCB manufacturing. Moreover, most of the above substances seem to be contaminant from handling and packaging than genuine components of the pad, such as, fatty acid residues. Polysiloxanes can be detected only on the top layer of atoms. The presence of these compounds, therefore, can be rooted in processes after HASL application.
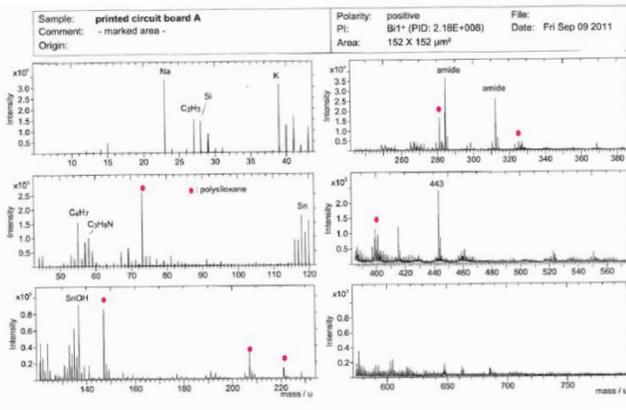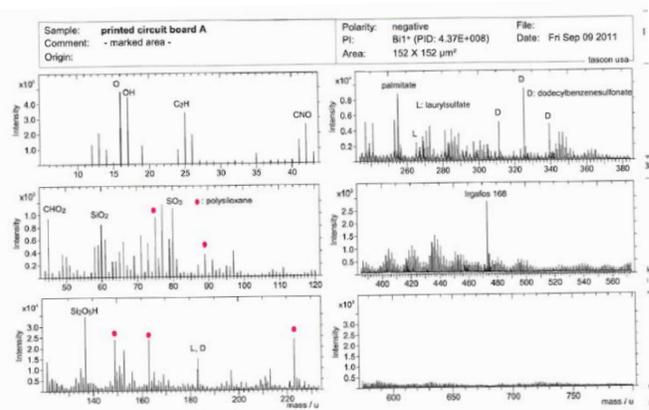

Figure 8.a   Figure 8.b

Figures 8.a & 8.b Mass Spectrum: Positive-Negative Secondary Ion Polarity: Problematic pad

In some cases, depth profile shows only the distribution of elements because the massive sample erosion causes a destruction of molecular structures. In addition, in a few selected cases, organic information can be obtained. Although the resulting intensities are not inherently quantitative, comparing semi-quantitative analysis of chemically similar samples are possible after a suitable normalization. As it was mentioned, Cs in the surface is sputtered as positive ion Cs+, which easily attaches to other sputtered particles forming Cs-cluster ions. Elements M are generally detected as MCs+. Electronegative elements are simultaneously detected as MCs2+.
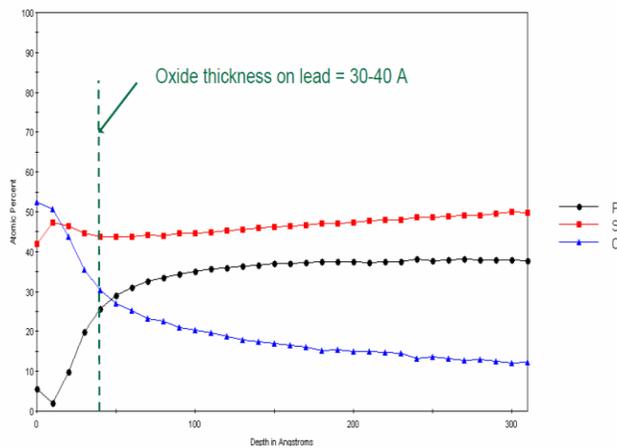
Figure 9

Figure 9. Common oxide layer on SnPb finishes

Some of the wetting issues could be explained by the thick Sn-oxide layer of about 250 nm. In SnPb components, the common oxide thickness is in average 40 nm, see Figure 9 above. Over that number, serious wetting issues would appear according to investigation done in SnPb metallizations.

According to the generated graphics, both "normal" & problematic pads are covered with a tin oxide layer; however, the second ones have a significantly thicker layer. Additionally, as shown in the top layer spectra, it has a significant amount of Ca and also higher Cl content was found on them; it is known Cl under some circumstances can be an oxidation accelerator. This element would be explained why the Sn-Oxide layer is bigger when Cl is present. See figures 10 & 11. It is interesting to observe that the higher amount of copper on the discolored zones below oxide layer, although its presence cannot completely explain the discoloration due to the fact Sn oxide can also create this effect.
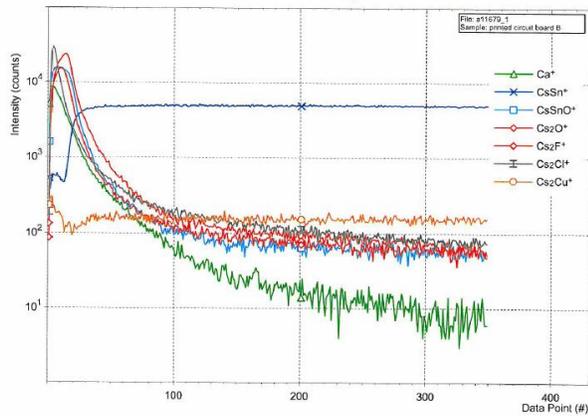
Figure 10.a
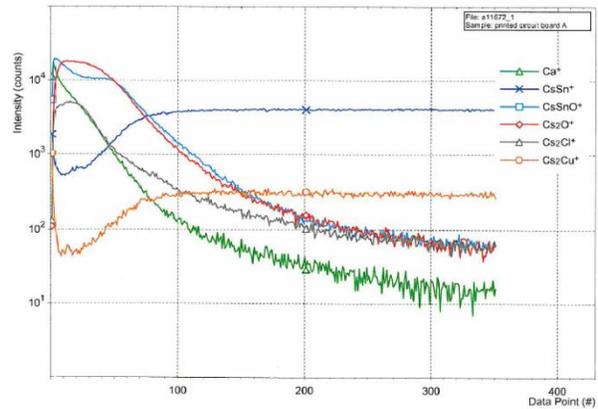
Figure 10.b

Figure 10.a "Normal" pad depth profiling & Figure 10.b Problematic pad depth profiling

According to the surface element finding; the idea of removing this layer of wetting inibitors was proposed: "washing" the pads applying detergents, DI water and brushing them. This cleaning would improve the surface conditions.

Stage 4: Analysis after cleaning
In order to close the hypothesis than a mechanical removing of these oxides could improve the wetting; SEM/EDX & TOF-SIMS analysis were performed. The results demonstrated that the thick oxide layer was eliminated or significantly reduced.

Figures 11.a to 11.d corroborated the low oxide and Cu content on the surface; however, this information could be corroborated with TOF-SIMS because SEM is showing only average deep layers of the pad.
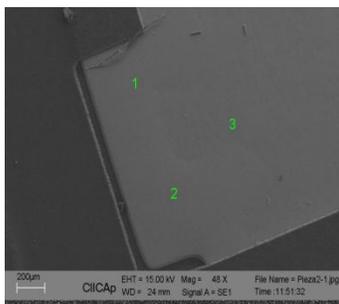
Figure 11.a
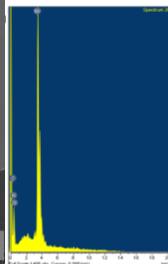
Figure 11.b
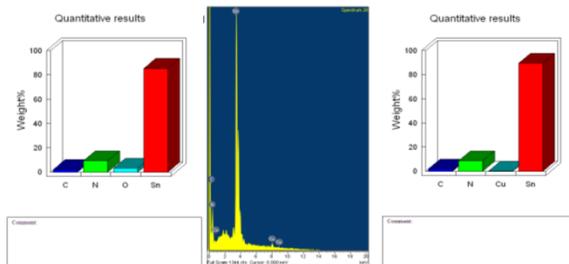
Figure 11.c
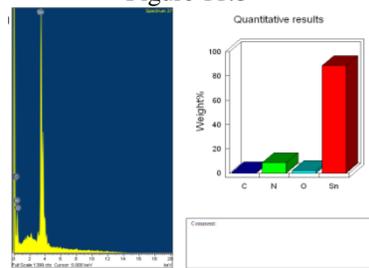
Figure 11.d

Figures 11.a to 11.d SEM analysis show the surface condition after special cleaning. The Cu and oxides are significantly reduced.

The use of detergents and water during cleaning increased the content of some other elements on the primary ion layer Figures 12.a & 12.b. Ions of the following compounds were detected:

- Sn and Sn oxide
- Na, Mg, Al, K, Cr, Mn, Mn. Fe, Ni, Cu, Zn, Pb; Cl, Br, I
- N-containing hydrocarbons especially amides, e.g., Kemamide
- Sulfates
- Phosphates, especially Irgafos 168
- Laurylsulfate
- Dodecylbenzenesulfonate
- Flourocarbons

Nevertheless, the presence of these components in the spectra does not mean that the surface will be altered in wetting. The percentage of them will determine the level of possible wetting change. It should be noted that the values are only semi-quantitative and absolute concentrations cannot be derived from the data.
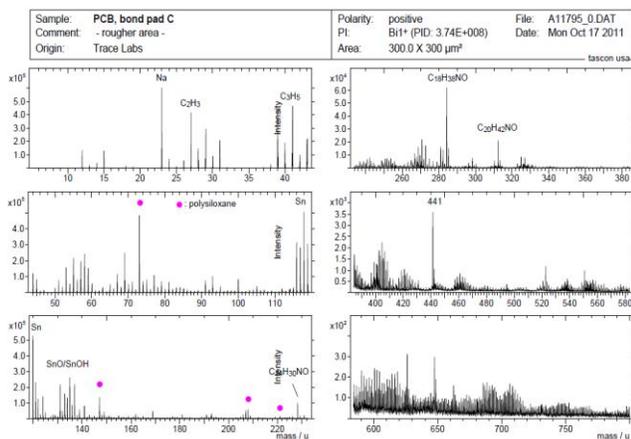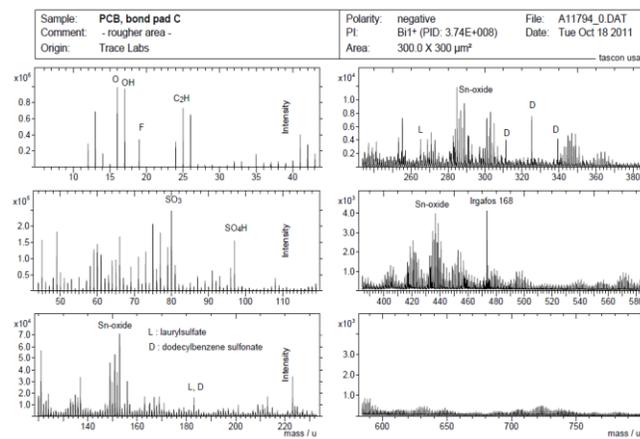
Figure 12.a   Figure 12.b

Figures 12.a & 12.b Mass Spectrum: Positive-Negative Secondary Ion Polarity: "Cleaned" pad

In the depth profiling graphics, the oxide layer reduction is noticed. Even some other elements were added during the washing; the impact on the oxides was demonstrated. Also, consider than the F content after cleaning increased. Compare Figures 10 with Figures 13.
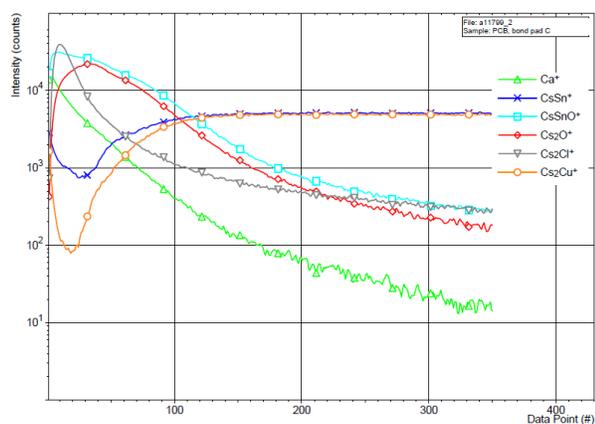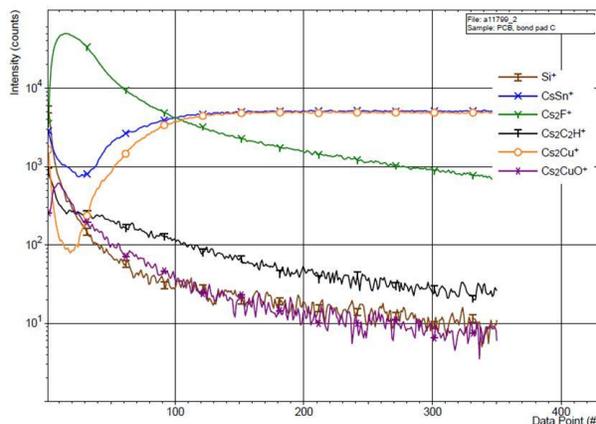
Figure 13.a   Figure 13.b

Figures 13.a & 13.b TOF-SIMS analysis (Note: the sputter rate in these analyses is four time slower than that of the depth profiles in Figure 10)

Conclusions

Wetting issues are related to oxidation or oxide layers on the surface of metallizations. However, its detection and quantification are hard because oxide layer is too thin (less than 1 micron) in many cases. This type of thickness can be shadowed by the presence on the element in deeper layers when SEM/EDX is used to analyze. In our case, a LF HASL PCB presented several wetting issues. Several analyses were made but the one which gave important insights was TOF SIMS. This tool can sputter and remove material layers measured in atomic thickness and determine the presence of inorganic and organic compound in orders of ppm or lower. The results showed the oxide layer was thicker in problematic areas compared to "good" ones. Cleaning actions were carried over to eliminate this oxide layer therefore. A good reduction of its presence and reduction of wetting issues were obtained.

References

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- Microelectronic Failure Analysis: Desk Reference 2002 supplement by ASM International
- Physical Principles of Electron Microscopy: An Introduction to TEM, SEM, and AEM written by R.F. Egerton
- Scanning Electron Microscopy: Physics of Image Formation and Microanalysis written by Ludwig Reimer
- Secondary Ion Mass Spectroscopy of Solid Surfaces written by Valentin Tikhonovich Cherepin

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Technique comparison: TOF-SIMS vs SEM/EDX

- **SEM**: Excites the electrons with external electron beam and collect them

- **EDX**: Removes the inner layers electrons to create energy differentiate when it is replaced
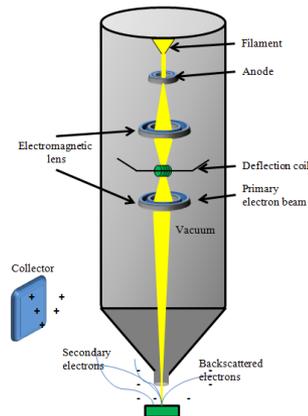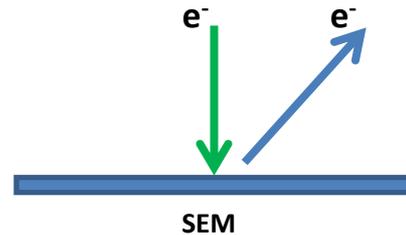
- **ToF-SIMS**: Collection of

- detached atoms & ions from outer material layers using external electron beam
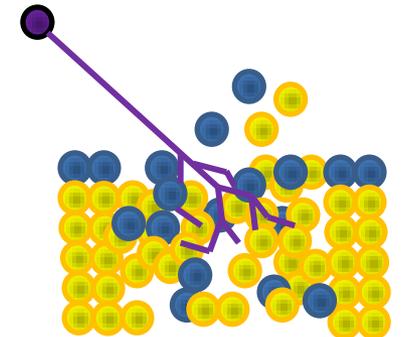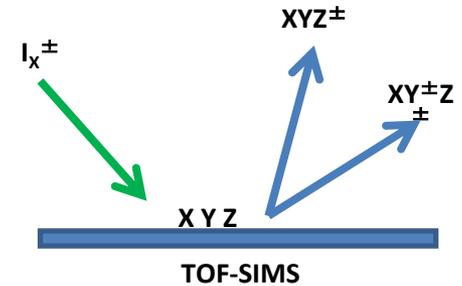
Technique comparison: TOF-SIMS vs SEM/EDX

- **SEM**: Imaging technique, topographic images, surface profile
- **EDX:** Spectra
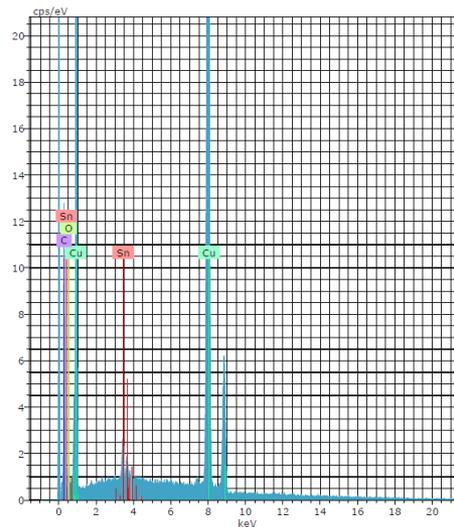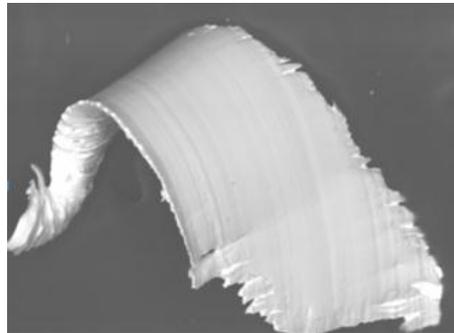
- **ToF-SIMS:** Spectra, image with the distribution of individual species on the surface, depth profiles



CsSnO
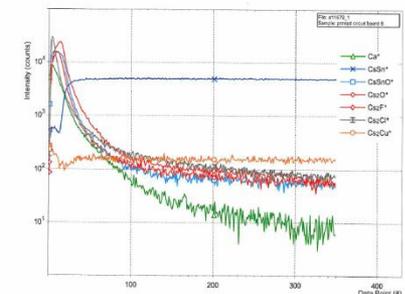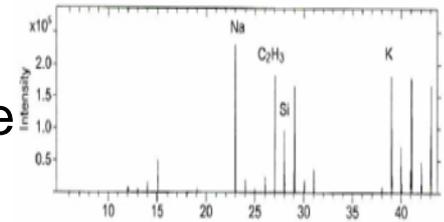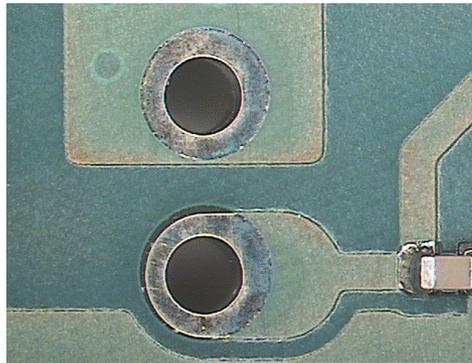
Case of study

Yellowish and bluish color
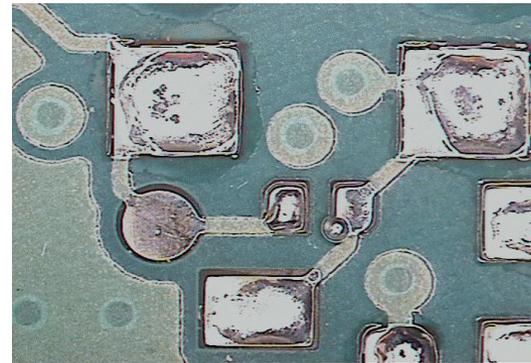
Dewetting

- Boards with LF HASL finish showed poor solderability in random areas.

- The initial hypothesis was low HASL thickness; however further investigation found another source of "contamination".

Case of study
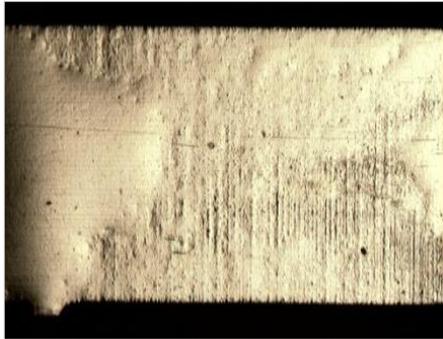
Normal LF pad
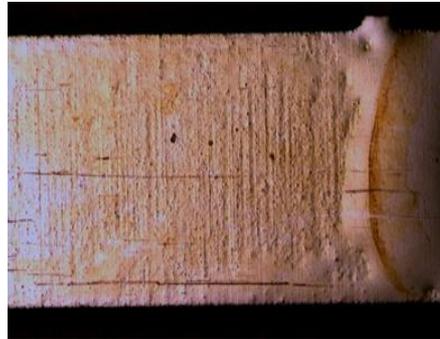
Problematic pad, polarized light
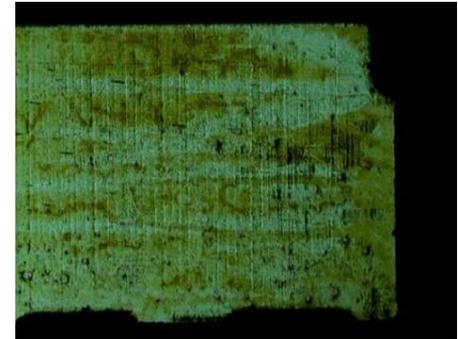
Problematic pad, dark field

- Images generated with a metallographic microscope show dark areas and brown spots on PCB surface.

- These contaminations could be organic or inorganic inhibitors. SEM technique is the most recommended tool to further analysis.

SEM/EDX Analysis: "Good part"
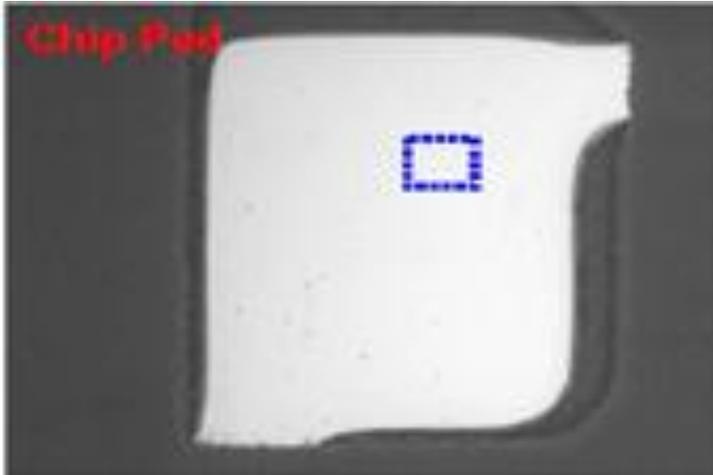
	C	O	Si	Br	Sn
Reference sample	3.3	8.8	1.2	0.6	86.5

- In the good PCBs, only the common concentration of impurities was found and the surface. It looked smooth and homogenous.

- The highlight elements in the sample are Br and O. These two could diminish the wetting properties.

SEM/EDX Analysis: "Bad part"
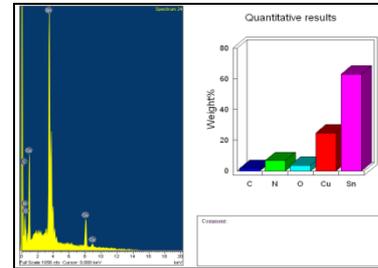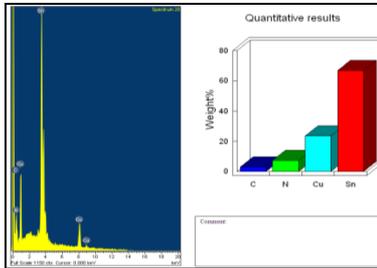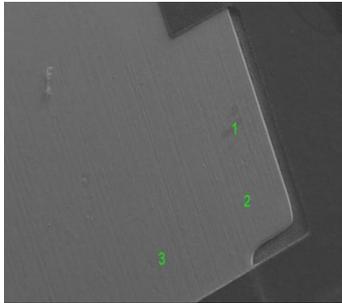
- The significant difference respecting to "good" parts was a higher copper concentration.

- Cu could form oxides that are hard to clean by fluxes. The Oxygen concentration was low, and in some areas, no oxygen percentage was detected. These results were not expected!

SEM/EDX Analysis

- The areas with higher visual discoloration presented more surfaces with non wetting. However, in SEM/EDX, the difference between both samples was minimal.

- The oxygen (related to possible oxides) content was approximately the same percentage in both samples (not problematic – problematic PCB's).

- Sometimes the failure is detected by the human eye, but not visible for the SEM microscope. Basically if you cannot see failure in SEM, you cannot analyze it!.

TOF-SIMS Analysis

- Spectrometry mode:
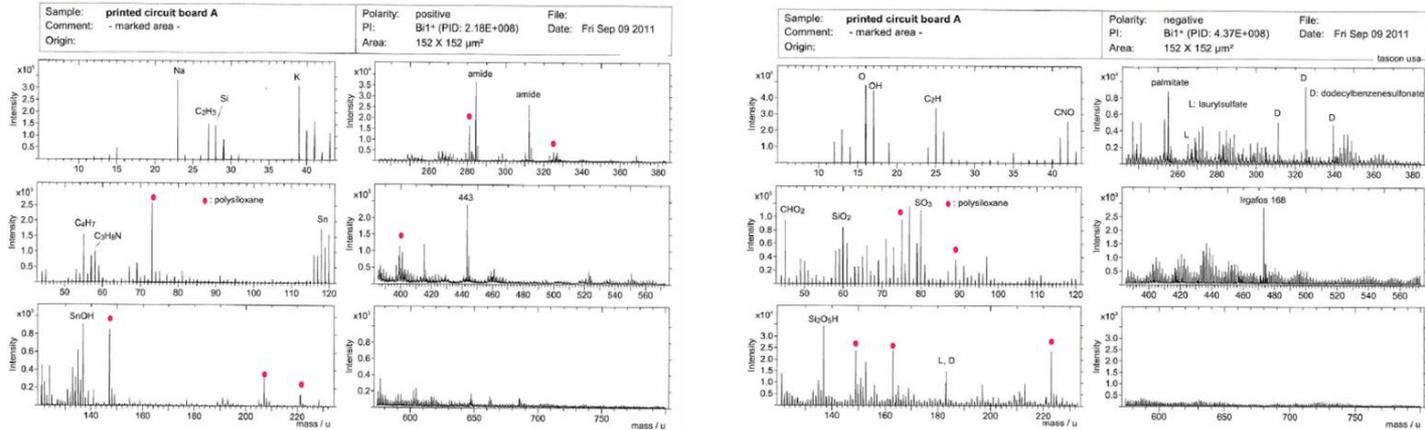
Spectrometry on "bad" pads

- The most significant ions detected in the problematic and "normal" pads spectra are the following elements and components:
  - Sn and Sn oxides
  - Aliphatic hydrocarbons
  - N-containing hydrocarbons especially amides, e.g., Kemamide
  - O-containg hydrocarbons, e.g. fatty acid residues
  - Polysiloxane
  - Laurylsulfate
  - Dodecylbenzenesulfonate

ToF-SIMS Analysis

- N-containing hydrocarbons would come from flux residues.

- Laurylsulfate and Dodecylbenzenesulfonate are compounds that would come from detergents residues. <u>All of these components could come from PCB manufacturing</u>.

- And the other mentioned substances seems to be contaminant, such as, fatty acid residues, from handling and packaging better than original components of the pad.

- Polysiloxanes can be detected only on the top layer of atoms.

- The presence of these compounds, therefore, can be rooted in processes after HASL application.

TOF-SIMS Analysis

- Depth profiling mode:
  - Some of the wetting issues could be explained by the thick Sn-oxide layer about 250 nm thick. In SnPb components, the common oxide thickness is in average 40 nm. Over that number, serious wetting issues could appear.
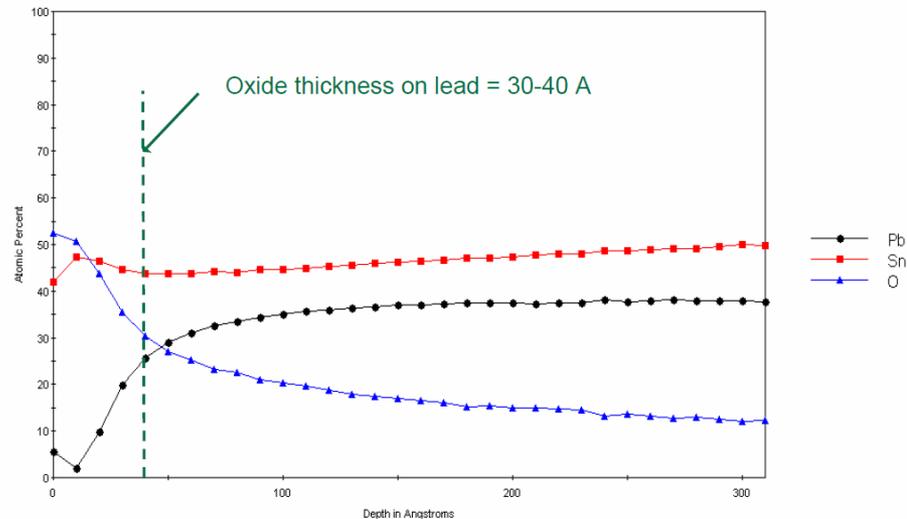

Common oxide layer on SnPb finishes

TOF-SIMS Analysis
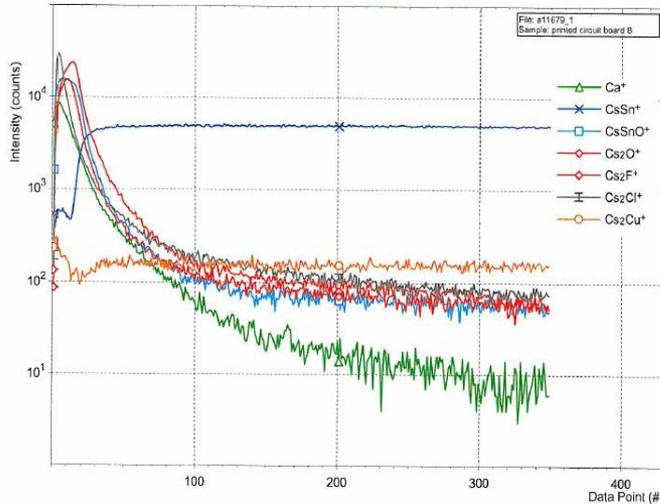


"Good" pad
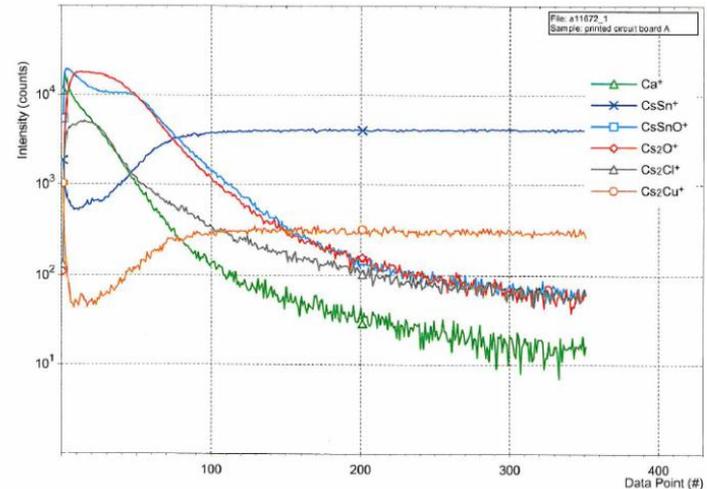
Problematic pad

- According to graphics, both "normal" & problematic pads are covered with a tin oxide layer.

- The "bad" has a significantly thicker oxide layer. And, significant amount of Ca and higher Cl content are shown in the top layer spectra. It is known Cl under some circumstances can be an oxidation accelerator.

Analysis conclusions

- According to the surface element findings; the idea of removing this layer of wetting inhibitors was proposed: "washing" the pads applying detergents, DI water and brushing them. This cleaning would improve the surface conditions.

Analysis after cleaning

- A mechanical removing method was applied to clean these oxides, this could improve the wetting on surface.
- SEM/EDX & TOF-SIMS analysis were performed on "cleaned" PCBs.
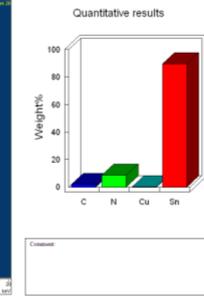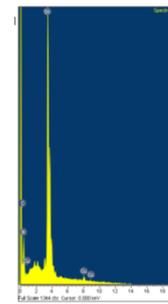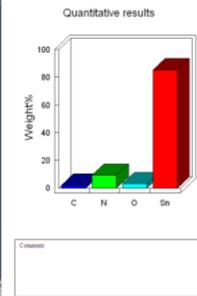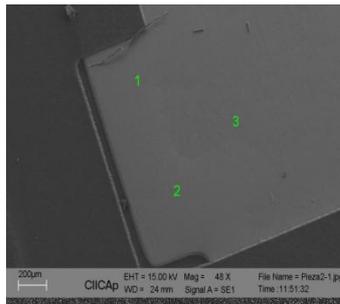
SEM on problematic pad after proposed cleaning

- Lower oxide and Cu percentage was detected.

Analysis after cleaning
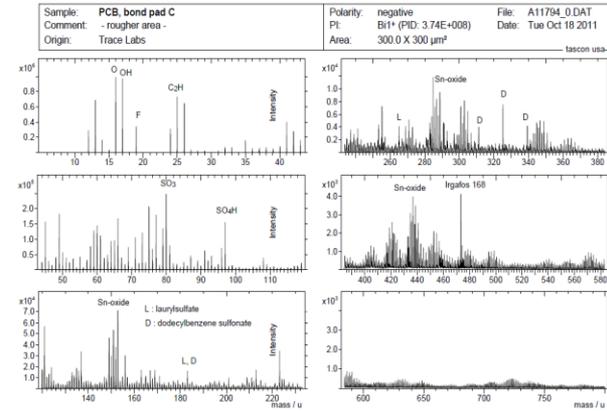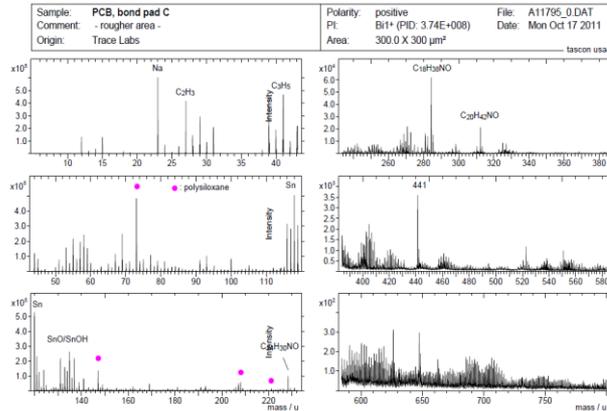
Spectrometry on cleaned pads

- The use of detergents and water during cleaning increased the content of some other elements on the primary ion layer:
    – Sn and Sn oxide
    – Na, Mg, Al, K, Cr, Mn, Mn. Fe, Ni, Cu, Zn, Pb; Cl, Br, I
    – N-containing hydrocarbons especially amides, e.g., Kemamide
    – Sulfates
    – Phosphates, especially Irgafos 168
    – Laurylsulfate
    – Dodecylbenzenesulfonate
    – Flourocarbons

Analysis after cleaning

- The presence of mentioned components in the spectra does not mean that the surface will be altered in wetting.

- The percentage of them will determine the level of possible wetting change. It should be noted that the values are only semi-quantitative and absolute concentrations cannot be derived from the data.

Analysis after cleaning
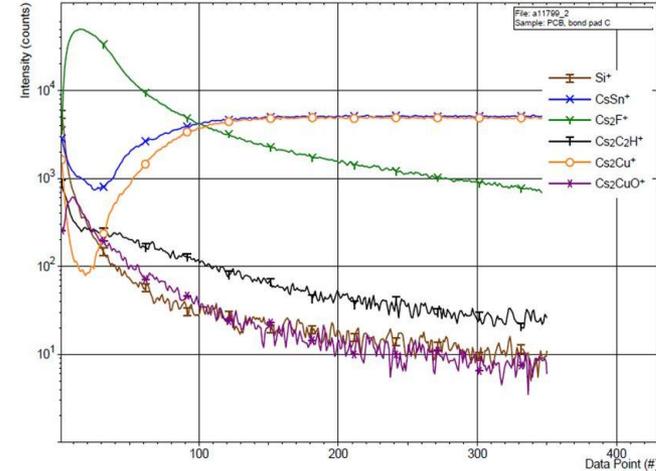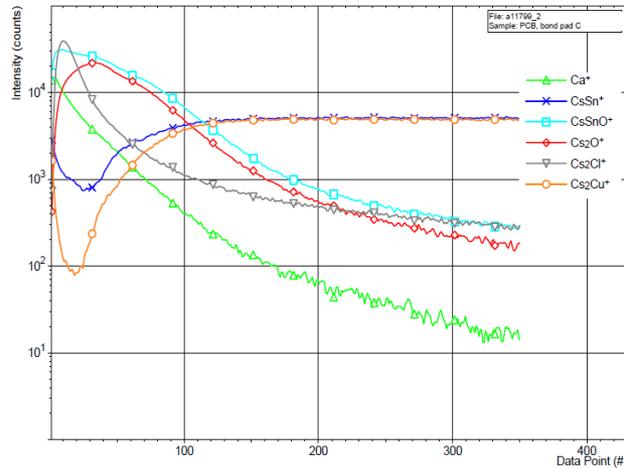
Depth profiling on cleaned pads

- In the depth profiling graphics, the oxide layer reduction is noticed.

- Even some other elements were added during the washing; the impact on the oxides was demonstrated. Also, consider that F content increased after cleaning.

Conclusions

- Wetting issues are related to oxidation or oxide layers on the surface of metallization.

- Oxide detection and quantification are hard because oxide layer is too thin (less than 1 micron) in many cases. This type of thickness can be shadowed by the presence on the element in deeper layers when SEM/EDX is used to analyze.

- In this case, LF HASL PCB presented several wetting issues. Several analyses were made but the one which gave important insights was TOF SIMS. This tool can sputter and remove material layers measured in atomic thickness and determine the presence of inorganic and organic compound in orders of ppm or lower.

- The results showed the oxide layer was thicker in problematic areas compared to "good" ones. Cleaning actions were carried over to eliminate this oxide layer therefore. A good reduction of its presence and reduction of wetting issues were obtained.