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Synergistic Application of XPS and TOF-SIMS for Accurate Trace Element Analysis in Electronic and Automotive Materials

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ABSTRACT

This paper presents a comprehensive study on the combined application of X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS) for the identification and quantification of trace elements in surface analysis. Two detailed case studies are examined:

- The detection and quantification of selenium (Se) on LED lead frames, and
- The analysis of boron (B) and phosphorus (P) residues on automotive aluminum components after surface cleaning.

XPS provides reliable quantitative data and chemical state information, but is limited by spectral interferences and a detection limit of approximately 0.1–1.0 at%. TOF-SIMS offers superior sensitivity (ppm level) and mass specificity, but lacks inherent quantitative capability without standards. By integrating TOF-SIMS for qualitative confirmation prior to XPS quantification, we overcome the limitations of each technique, avoid analytical misjudgements, and obtain accurate quantitative results. This synergistic approach enhances analytical confidence and is applicable to surface contamination studies in microelectronics, automotive, and related high-value manufacturing industries.

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Introduction

In failure analysis and material characterization, Time-of-flight secondary ion mass spectrometry (TOF-SIMS) and X-ray photoelectron spectroscopy (XPS) have been widely used [1-3]. Generally, the advantage of TOF-SIMS is that its detection limit can reach ppm (parts per million) level or lower. It is particularly suitable for the analysis of trace elements or components. However, in the absence of standard samples, TOF-SIMS is currently unable to provide quantitative analysis. The analytical advantage of XPS is that it can perform quantitative analysis without standard samples, but the detection limit of XPS is much higher than that of TOF-SIMS, which is about 0.1-1.0 at% (depending on the elements analysed) [4]. However, the qualitative analysis of some trace elements is sometimes difficult using XPS, especially for elements with complex characteristic peaks or low atomic numbers.

Therefore, we propose the joint application of TOF-SIMS and XPS. In this paper, these two analytical techniques are applied to two distinct material systems:

- LED frame materials for selenium analysis, and
- Automotive aluminum parts for boron and phosphorus residue analysis.

The combination makes full use of their respective advantages-TOF-SIMS for high-sensitivity detection and XPS for accurate quantification—thereby improving the reliability of trace element analysis.

Analytical Instruments and Experimental Conditions

In this study, XPS and TOF-SIMS techniques are used for joint application in failure analysis and material characterization.

XPS Surface Analysis

XPS is used to analyse the surface composition. The model used for XPS analysis is Scanning XPS Microscope PHI Quantera II (Aluminium source at 1486.6 eV) from Japan. The sputtering rates were calibrated against silica (SiO_2) standards for depth profiling.

TOF-SIMS Surface Analysis

TOF-SIMS is used to further confirm the presence of trace elements and ensure the accuracy of XPS quantitative analysis results. The model used for TOF-SIMS analysis is ToF. SIMS from Germany [5]. The primary ion beam used is Bi^+ with an energy of 25 keV, a pulse current of 1 pA, a scan time of 100 µs per cycle, a total analysis time of 100 s, and a mass range of 1–800 amu.

Case Study 1: Selenium Analysis in Led Lead Frames

Initial XPS Analysis and Ambiguity

When XPS is used to analyse the surface of LED lead frames, the method can be confusing for trace element characterization. For example, Figure. 1 shows XPS spectra collected on an LED lead frame:

(A) full spectrum scan, and

(B) high-resolution narrow spectrum scan in the 120–190 eV range. In Figure. 1(B), three distinct peaks are observed at 137 eV, 161 eV, and 177 eV. Automated peak identification software suggested these correspond to Pb 4f, S 2p, and Zr 3d, respectively.

However, based on customer feedback and knowledge of LED manufacturing, the lead frame should be Pb- and Zr-free. This discrepancy prompted further investigation.

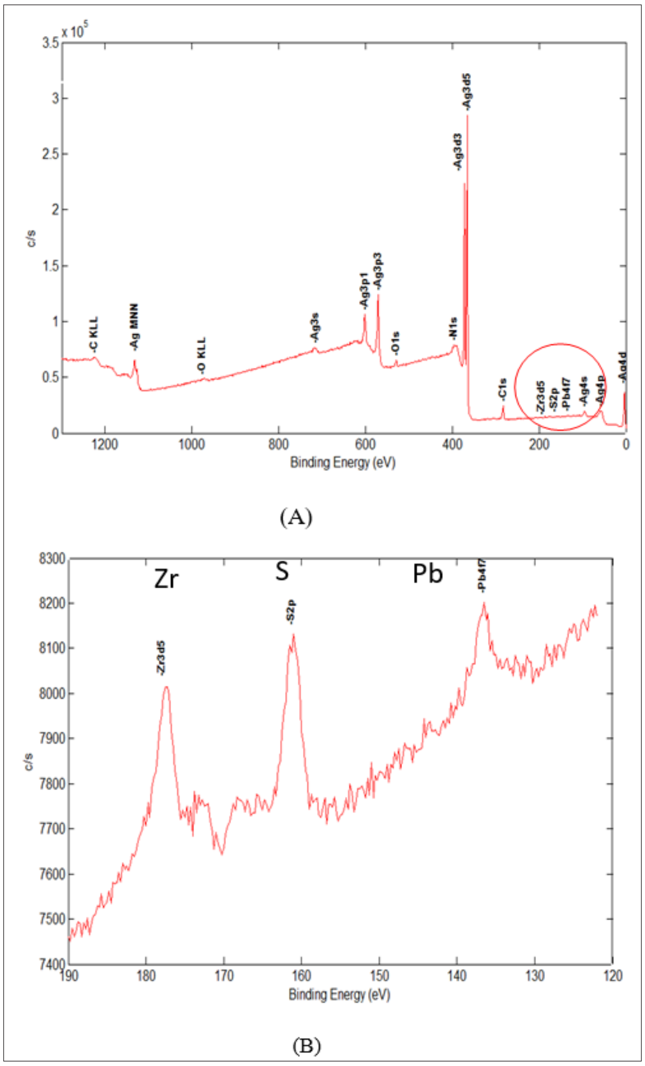

Figure 1: XPS Spectrum Collected on the LED Lead frame :
(A) Full Spectrum scan
(B) High Resolution Narrow Spectrum Scan, Scanning Range 120-190eV. The XPS Software Automatically Identified these Peaks as Lead (Pb), Sulphur (S) and Zirconium (Zr) Elements, but Pb and Zr were Suspected

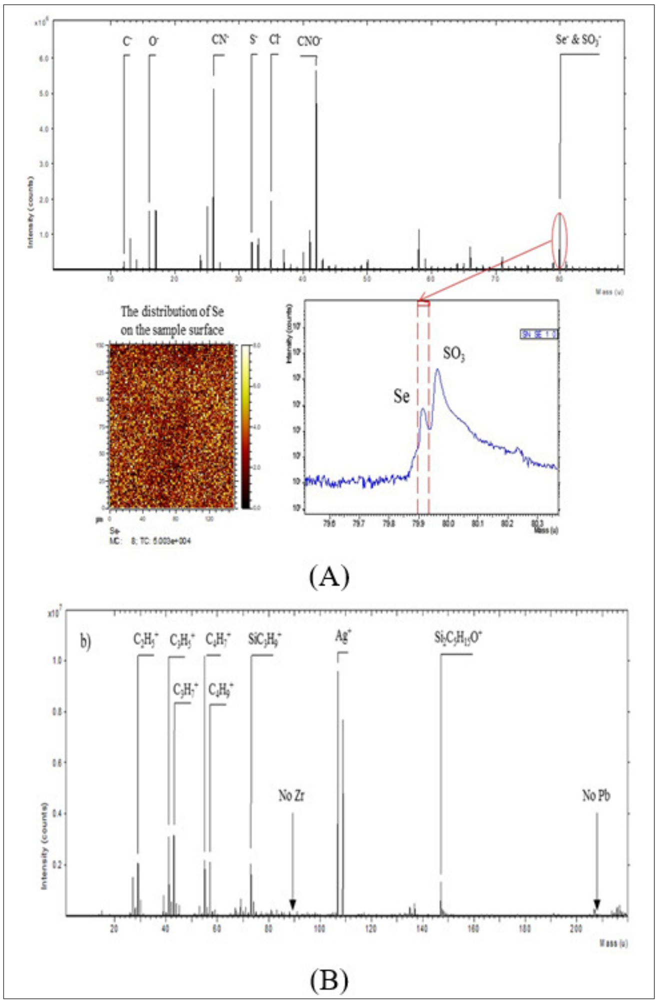

Figure 2: TOF-SIMS Analysis Results
(A) Negative Ion Mass Spectrum Confirmed the Presence of Se (79.916u) and S (31.972u) Elements and
(B) Positive Ion Mass Spectrum Collected on LED Lead Frame Excluded the Presence of Pb (207.977u) and Zr (89.905u) on the Sample Surface

BTOF-SIMS Confirmation

To resolve the ambiguity, TOF-SIMS analysis was performed. The results are shown in Figure. 2. The negative ion mass spectrum (Figure. 2A) confirmed the presence of Se^- (79.916 u) and S^- (31.972 u). The positive ion mass spectrum (Figure. 2B) showed no signals for Pb^+ (207.977 u) or Zr^+ (89.905 u), effectively ruling out their presence.

Revised XPS Interpretation and Quantification

With TOF-SIMS confirmation, the XPS peaks were reassigned:

- 137 eV → Se LMM2 Auger peak
- 161 eV → Overlap of S 2p and Se 3p
- 177 eV → Se LMM1 Auger peak

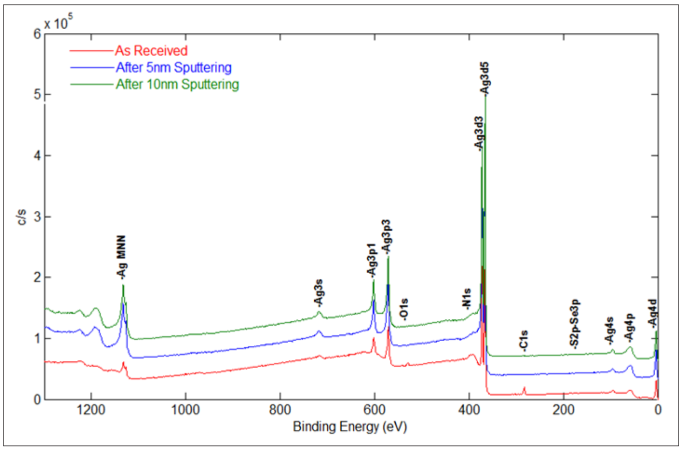

Figure 3: XPS Spectrum Collected on the LED Lead Frame for a Full Spectrum Scans at as Received, after 5nm and 10nm Sputtering

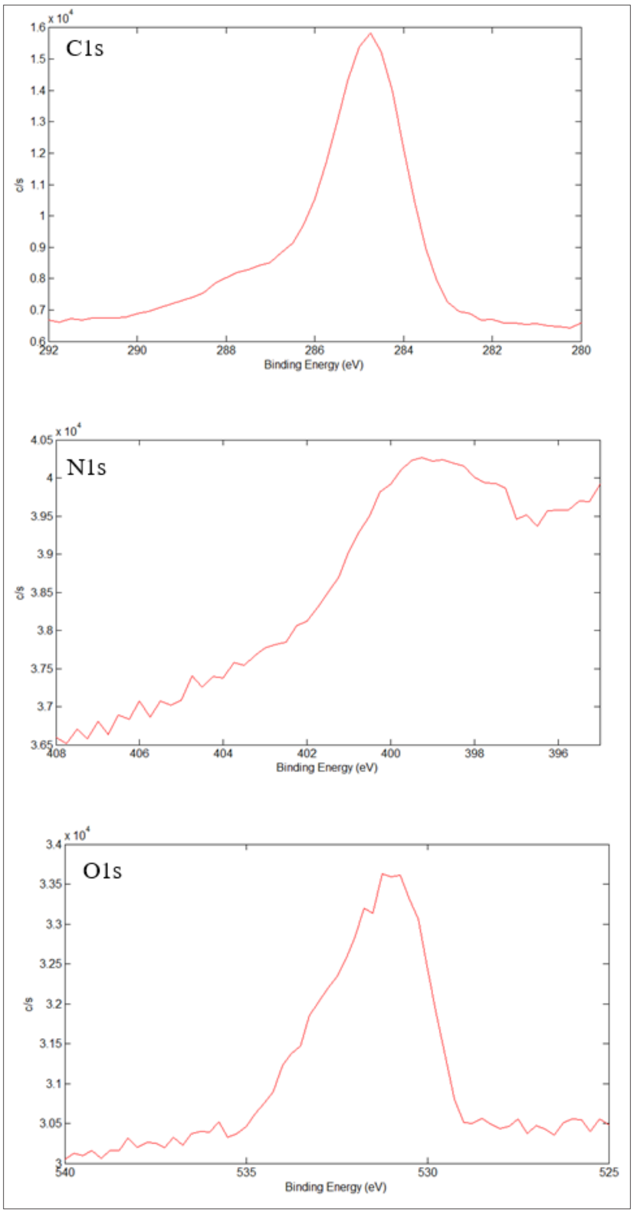

Figure 4: XPS Spectrum Narrow Scan of Elements C, N and O on the LED Lead Frame Sample

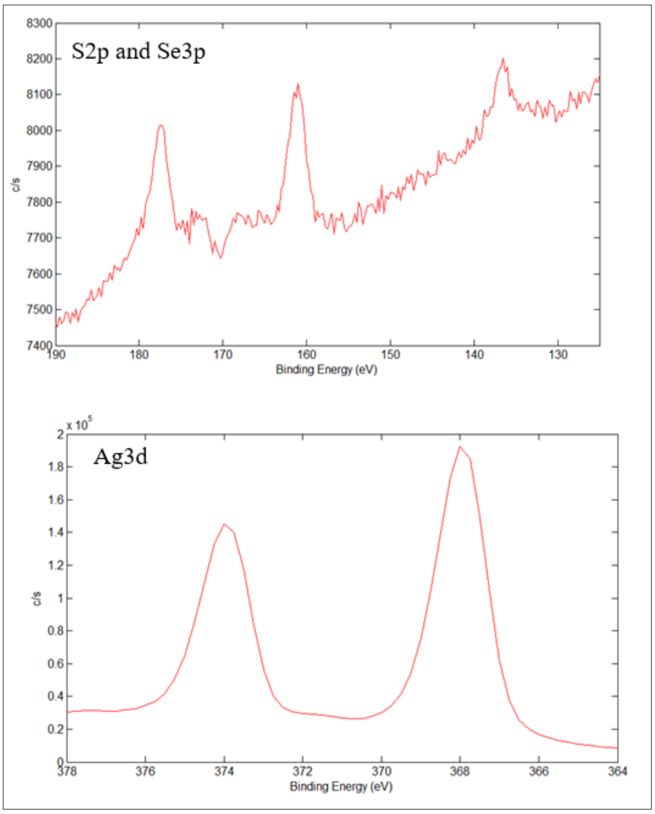

Figure 5: XPS Spectrum Narrow Scan of Elements S, Se and Ag on the LED Lead Frame Sample

Subsequent quantitative XPS analysis was performed using the following equations:

$$X_A = \frac{\text{Peak Area}(A)/\text{RSF}(A)}{\sum_i \text{Peak Area}(i)/\text{RSF}(i)} \quad (1)$$

For Se and S overlap correction:

$$\frac{\text{Peak Area(Se/LMM2)}}{\text{RSF(Se/LMM2)}} = \frac{\text{Peak Area(Se/3p3)}}{\text{RSF(Se/3p3)}} \quad (2)$$

$$\text{Peak Area(S/2p)} = \text{Peak Area(Se+S)} - \text{Peak Area(Se/3p3)}$$

The quantitative results are summarized in Table I. Full-spectrum and narrow-scan XPS data are shown in Figure. 3 (full spectrum after sputtering) and Figure. 4-5 (narrow scans for C/N/O and S/Se/Ag, respectively).

Table 1: XPS Quantitative Analysis Results of Led Lead Frame (As Received)

LED frame Elements	C	N	O	S	Se	Ag
Atomic %	44.9	3.1	9.0	0.3	0.1	42.6

Case Study 2: Boron and Phosphorus Analysis in Automotive Aluminum

XPS Analysis and Spectral Overlap Challenge

XPS was used to analyse residual elements after cleaning of aluminum automotive parts. Figure 6 shows XPS spectra:
(A) full spectrum scan, and
(B) high-resolution scan in the 130–210 eV range. A prominent peak near 190 eV was observed. Automated identification

suggested contributions from both B 1s (189 eV) and P 2s (188 eV). However, B 1s and P 2s peaks overlap closely, making discrimination difficult at low concentrations. Additionally, the P 2p peak at 130 eV overlaps with an Al 2p satellite, further complicating analysis.

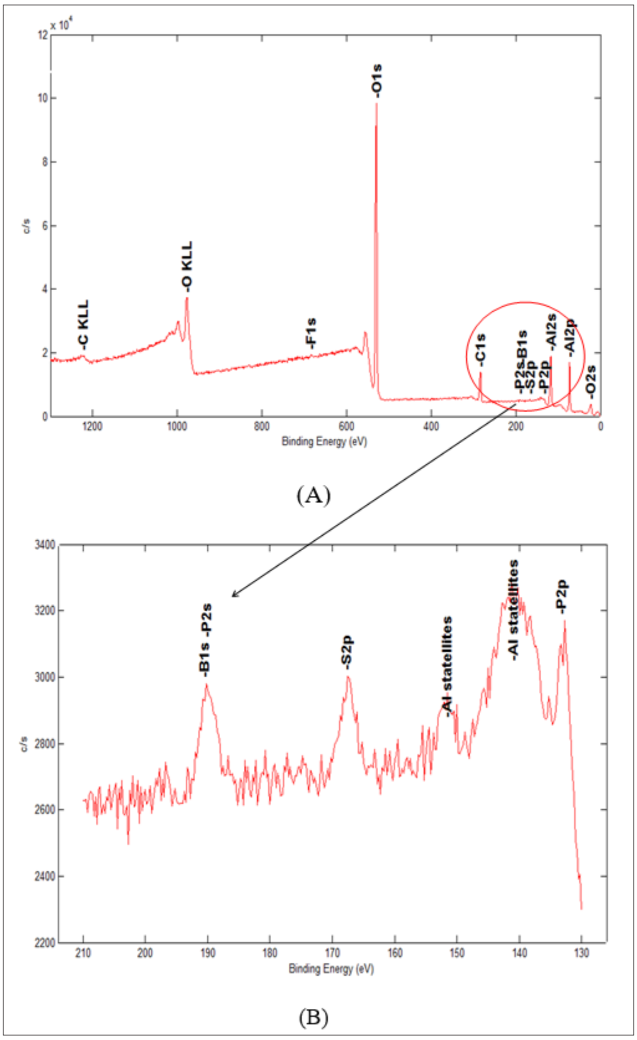

Figure 6: XPS Spectrum Collected on the Sample
(A) Full Spectrum scan
(B) High Resolution Narrow Spectrum Scan, Scanning Range 130-210eV. The XPS Software Automatically Identified these Peaks as Boron (B) and Phosphorus (P), which need to be Confirmed by TOF-SIMS

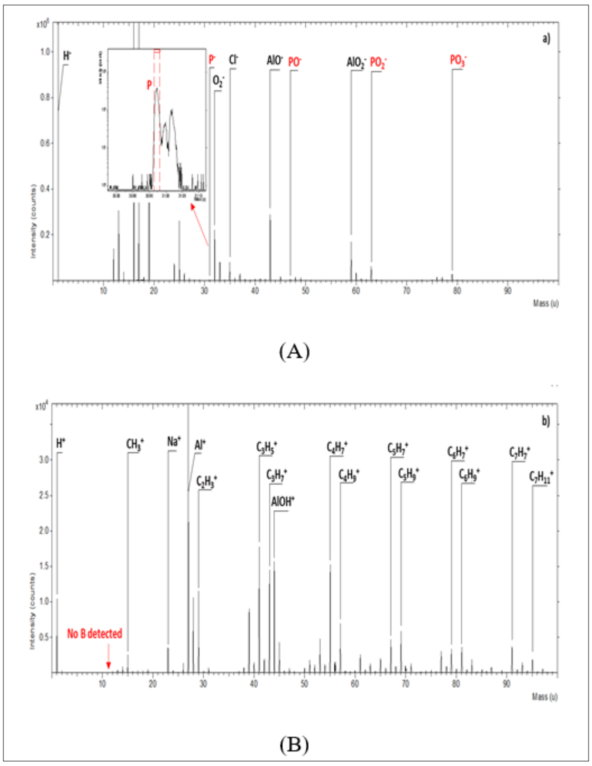

Figure 7: TOF-SIMS Analysis Results
(A) Negative Ion Mass Spectrum Confirmed the Presence of Element P; and
(B) Positive Ion Mass Spectrum Confirmed no Presence of Element B on the Sample Surface

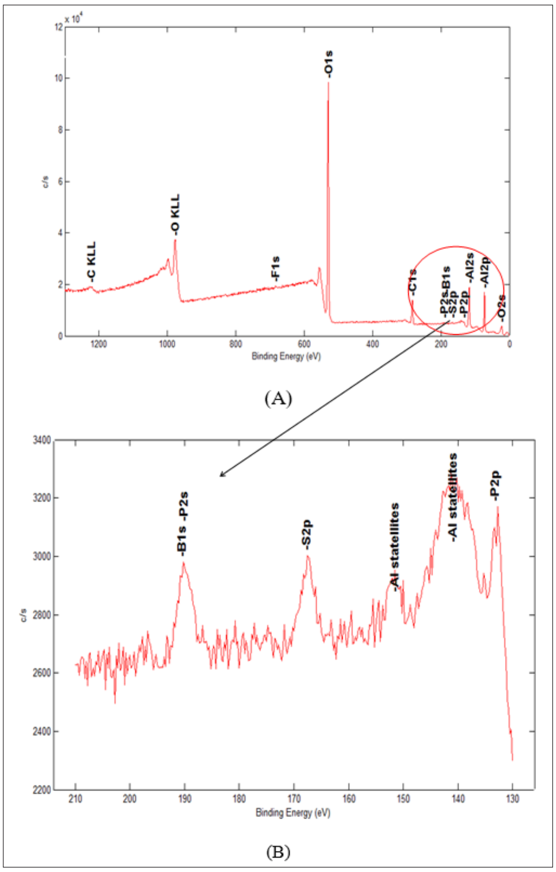

Figure 8: XPS Spectrum Collected on the Sample
(A) Full Spectrum scan

(B) High Resolution Narrow Spectrum Scan, Scanning Range 130-210eV. The XPS Software Automatically Identified these Peaks as Boron (B) and Phosphorus (P), which need to be Confirmed by TOF-SIMS

TOF-SIMS Discrimination
TOF-SIMS analysis was performed to clarify the composition. Results are shown in Figure. 7. The negative ion spectrum (Figure. 7A) confirmed the presence of P^-. The positive ion spectrum (Figure. 7B) showed no B^+ signal, indicating the absence of boron. Thus, the XPS peak near 190 eV is attributed solely to P 2s.

XPS Quantification of Phosphorus
Using TOF-SIMS confirmation, XPS quantitative analysis was performed. The results for an automotive sample (S1) are shown in Table II. The narrow-scan XPS spectrum confirming only P near 190 eV is shown in Figure. 8.

Table 2: XPS Quantitative Analysis Results of an Automotive Part Sample after Cleaning Process (As Received, at%)

Ele.	C	N	O	F	Al	P	S
S1	17.0	0.3	60.9	0.3	20.8	0.5	0.2

Discussion
The Two Case Studies Demonstrate a Consistent Analytical Workflow:
- Initial XPS screening identifies potential trace elements but may suffer from spectral overlaps.
- TOF-SIMS confirmation unambiguously identifies presence/absence based on mass spectrometry.
- Revised XPS quantification uses corrected peak assignments for accurate results.
- This approach is particularly valuable for:
- Elements with overlapping XPS peaks (e.g., Se/Pb/Zr, B/P)
- Low-concentration traces near the XPS detection limit
- Light elements (e.g., B, P) where XPS sensitivity is poor

The combination leverages TOF-SIMS's sensitivity (ppm level) and XPS's quantitative capability, minimizing the risk of misjudgement.

Conclusions
XPS is often used for quantitative trace element analysis, but its accuracy can be compromised by spectral interferences and detection limits. TOF-SIMS, with its high sensitivity and mass specificity, serves as an ideal confirmatory tool. By combining both techniques, we can avoid misidentification and obtain reliable quantitative data. This paper successfully applied the XPS/TOF-SIMS combined approach to analyze Se in LED lead frames and B/P in automotive aluminum, demonstrating its effectiveness in real-world failure analysis and surface characterization. The methodology is widely applicable to other materials and industries where trace element analysis is critical [6-10].

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