CASE STUDY

Discoloration on Gold Plating

Separating Cosmetic Defects from Reliability Concerns with AFM, PiFM, and TOF-SIMS

Introduction

Gold plays a critical role in modern electronics because of its electrical conductivity and corrosion resistance. In this case study, a customer noticed mysterious dark spots appearing across a gold surface intended for electrical contact. The key question was simple: were these spots merely cosmetic blemishes, or evidence of contamination that could compromise wire bond reliability? The investigation combined conductive atomic force microscopy (AFM), photo-induced force microscopy (PiFM), and time-of-flight secondary ion mass spectrometry (TOF-SIMS) to correlate morphology, conductivity, and chemistry at the nanoscale.

The Challenge

Under visible-light microscopy, the gold surface exhibited scattered dark spots. The primary concern was whether these regions represented a contaminant layer that could interfere with electrical performance or bond reliability. Traditional optical inspection alone could not determine whether the contrast originated from surface chemistry differences, oxidation or residue, or nanoscale topography effects.

To answer this question, Covalent scientists developed a correlative workflow using:

- **Conductive AFM** for nanoscale topography and electrical mapping,
- **PiFM** for localized chemical identification,
- **TOF-SIMS** for large-area surface chemistry mapping.

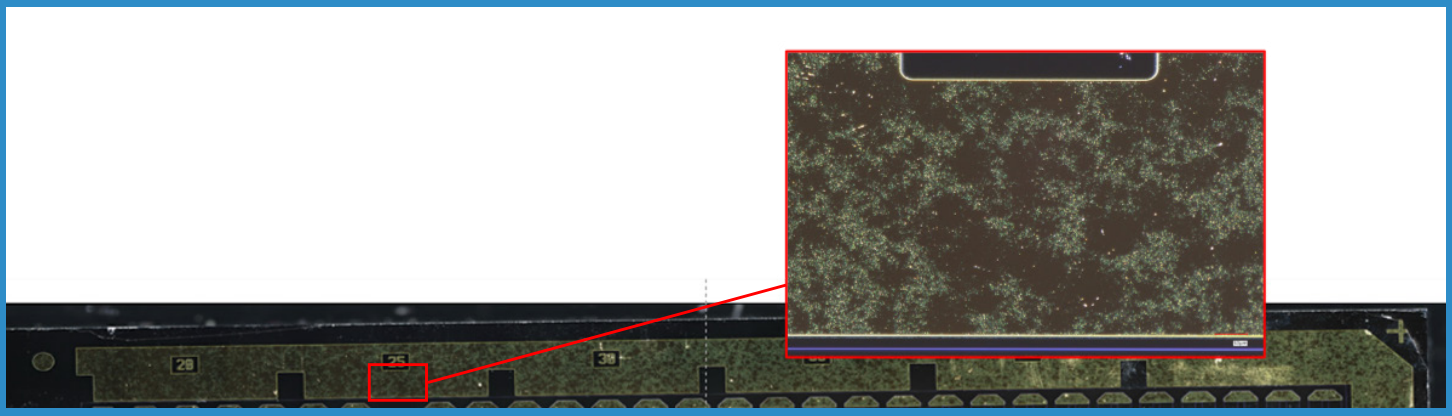


Figure 1: Optical microscopy images of gold plating on device.

What is Time of Flight Secondary Ion Mass Spectroscopy (TOF-SIMS)?

Time-of-flight secondary ion mass spectrometry is a powerful analytical technique that combines two key ideas: mass spectrometry and time-of-flight analysis.

First, let's discuss the SIMS principle. A solid surface is bombarded by keV-energy ions, which we call "primary ions." Some of that energy is transported to the surface, allowing surface particles to overcome the binding energy. Most emitted particles are neutral, but a small proportion are positively or negatively charged; these are the ones we analyze and call "secondary ions." Once we have our secondary ions, we need to figure out what they are. That's where the TOF analyzer comes in.

The idea behind this is simple: if you give ions of different masses the same energy, they will move at different speeds. Lighter ions will travel faster, and heavier ones will move slower. So, we use an electrostatic field to accelerate all the ions to the same energy level, then let them travel through the analyzer. As they move toward the detector, we measure how long each ion takes to arrive - this is their "time of flight." By knowing this time, we can calculate the ion mass with incredible precision.

Because each chemical species produces a characteristic set of ions, TOF-SIMS can be used to identify the chemical composition of a surface. TOF-SIMS can detect positively and negatively charged ions as a function of the voltage applied to the analyzer. Positive mode is particularly useful for detecting metals and organic fragments, while negative mode enhances the detection of halogens and oxides. Collecting both datasets provides a more complete picture of surface chemistry and contamination. The measurement is performed by rastering the ion beam across the sample and collecting a mass spectrum at every pixel, which allows the generation of high-resolution chemical maps.

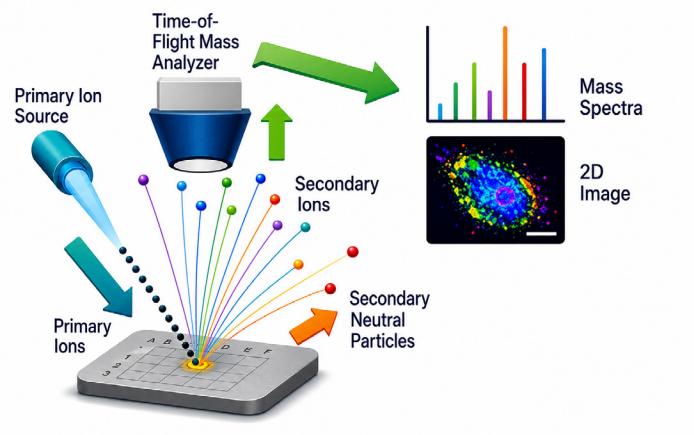


Figure 2: Diagram showing TOF SIMS functionality.

What is Atomic Force Microscopy (AFM)?

AFM is a high-resolution imaging technique that uses an extremely sharp probe to physically scan across a sample surface and measure its topography. As the tip moves over hills, valleys, and other surface features, tiny deflections of the cantilever are detected by a laser and converted into a three-dimensional map of the surface. Because AFM does not rely on light, it can resolve features down to the nanometer scale—thousands of times smaller than the width of a human hair. In addition to topography, specialized AFM modes can measure properties such as electrical conductivity, mechanical stiffness, adhesion, and surface chemistry, making AFM a powerful tool for correlating nanoscale structure with material performance.

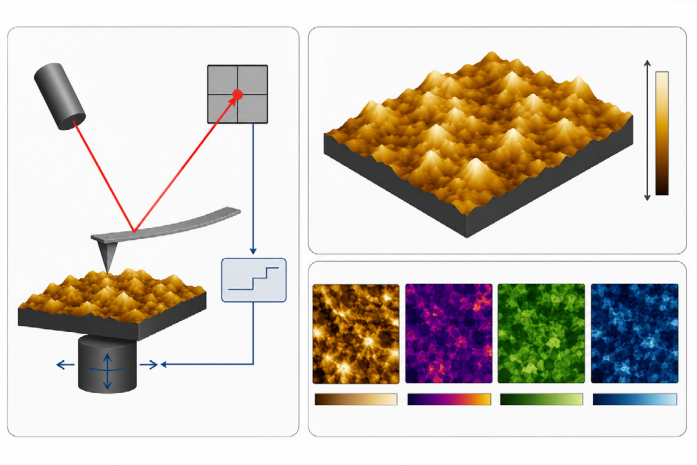


Figure 3: Diagram showing AFM functionality.

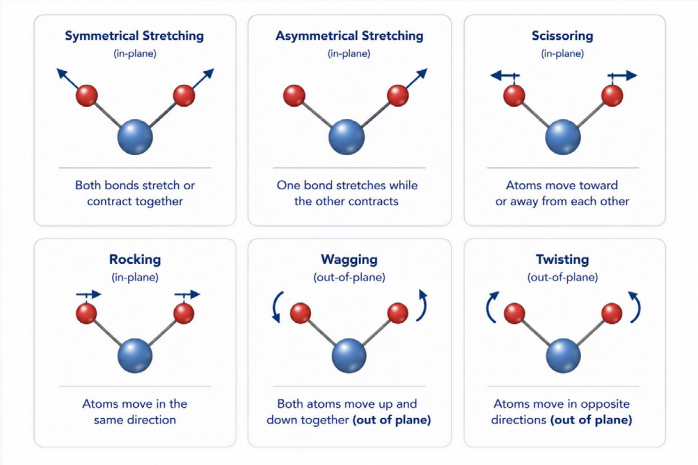


Figure 4: Different chemical bonds absorb infrared (IR) light at specific wavelengths, causing them to vibrate in characteristic ways such as stretching, scissoring, rocking, and twisting. By measuring which wavelengths are absorbed, techniques such as PiFM can identify the chemical species present and map their distribution with nanoscale spatial resolution.

What is Photo-Induced Force Microscopy (PiFM)?

Photo-induced force microscopy (PiFM) combines the nanoscale imaging capabilities of atomic force microscopy with the chemical specificity of infrared spectroscopy. A tunable infrared laser is focused on a metal-coated AFM tip, creating a highly localized electromagnetic field that interacts with molecules directly beneath the tip. By measuring the resulting photo-induced forces, PiFM can identify the specific chemical bonds which absorb incoming energy by vibrating in certain ways such as scissoring and stretching.

With this energy absorption information, chemical maps can be generated with spatial resolution down to a few nanometers- far beyond the diffraction limit of conventional infrared microscopy. This unique combination of topographical and chemical information makes PiFM a powerful tool for identifying contaminants and correlating nanoscale chemistry with surface features.

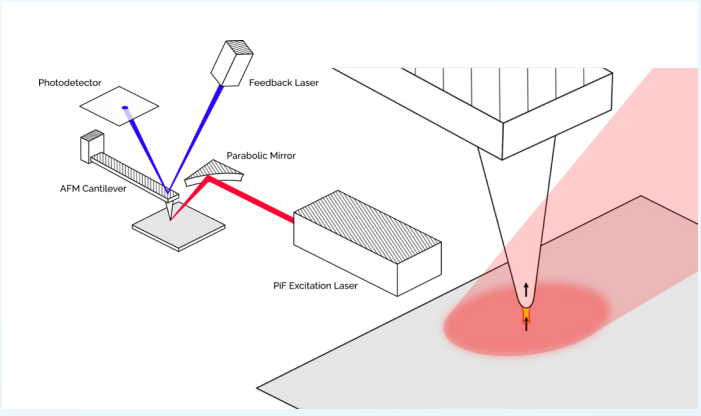


Figure 5: Diagram demonstrating PiFM functionality.

Why One Technique Wasn't Enough

TOF-SIMS, AFM, and PiFM are complementary surface analysis techniques because they combine broad chemical sensitivity with nanoscale spatial resolution and molecular idnetification. TOF-SIMS excels at detecting trace surface contamination and mapping the distribution of molecular fragments and elements across relatively large areas with extremely high sensitivity. AFM provides nanometer-scale topographical information and can be extended to measure properties such as electrical conductivity, enabling direct correlation between surface structure and material performance. PiFM complements this by providing localized infrared chemical identification at the nanoscale, allowing researchers to distinguish specific chemical functionalities and correlate them directly with topographical features observed by AFM. Together, these techniques provide a powerful correlative workflow for understanding complex surface contamination that would be difficult to fully characterize with any single technique alone.

With the analytical toolkit assembled, the investigation turned to the dark spots themselves. In this study, AFM revealed 10–20 nm surface islands and associated conductivity differences, PiFM identified localized siloxane-rich regions consistent with silicone-based contamination, and TOF-SIMS mapped contamination across larger surface areas.

Results on our Client's Sample

The first surprise came from the AFM data. The dark spots that stood out under the optical microscope were not raised defects at all—in fact, they were relatively flat. Instead, the brighter regions contained nanoscale islands roughly 10–20 nm tall. While far too small to be resolved optically, these features were large enough to influence how light scattered from the surface, creating the apparent discoloration.

Conductive AFM measurements showed that the nanoscale islands exhibited higher electrical conductivity than the surrounding background regions. This result was particularly important for the customer's wire bonding concern because despite not being flat, the raised areas were not obviously electrically insulating contamination features.

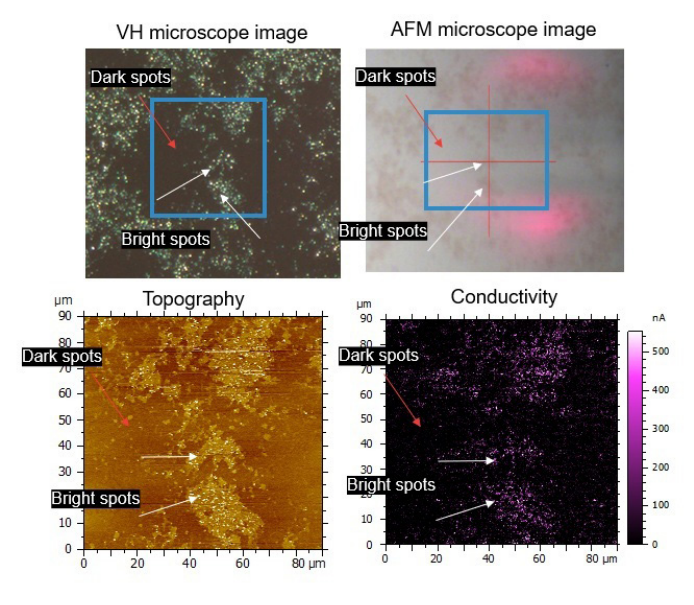


Figure 6: Topography and conductivity AFM results on gold sample.

When AFM is operated in phase mode, it measures how much energy is lost as the tip interacts with the sample surface. Regions with higher energy dissipation are typically associated with softer or more adhesive materials, while regions with lower phase are generally more rigid. Our AFM results revealed

that higher phase was observed on the islands compared to off the islands, indicating the presence of a soft or sticky contaminant layer on the surface.

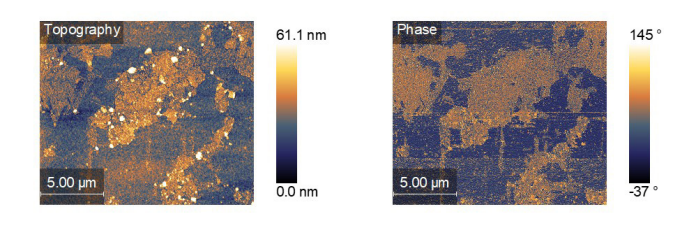


Figure 7: AFM results demonstrating phase distribution on sample. This allows us to quantify the softness or adhesion properties of our sample surface.

PiFM Identifies Localized Chemical Differences

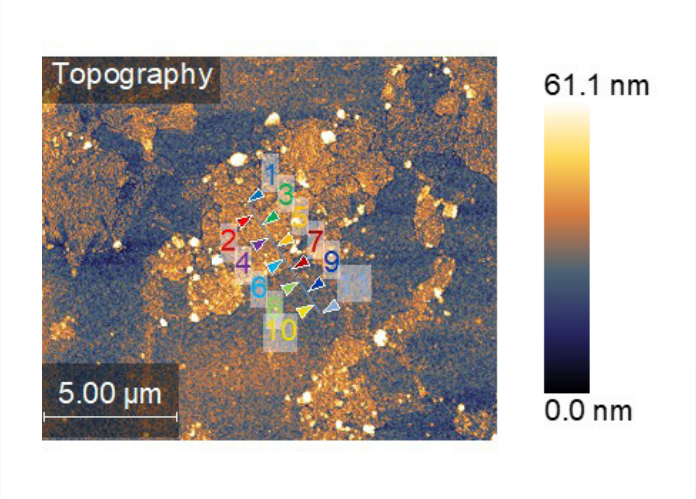


Figure 8: A line scan was conducted across the island and onto the background.

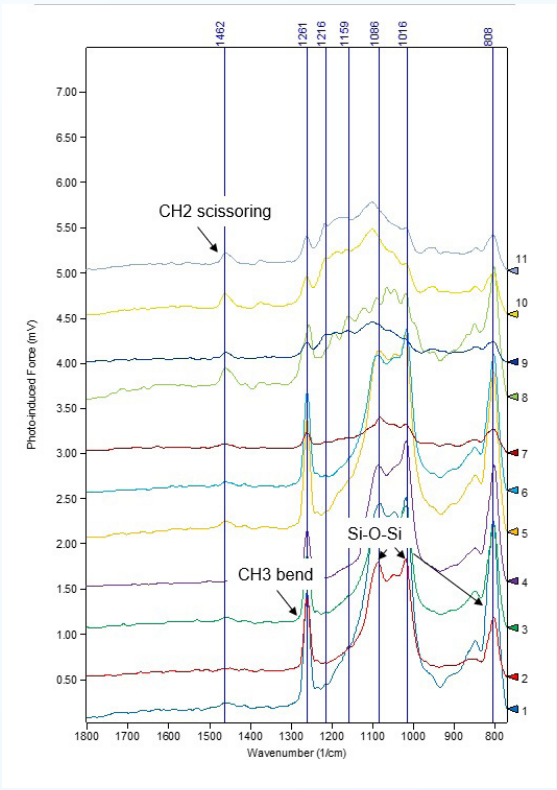


Figure 9: PiFM spectra collected from the indicated points across the sample surface. The x-axis shows the infrared wavenumber (cm-1), which corresponds to the characteristic vibrational energy of specific chemical bonds. The y-axis shows the photo-induced force (mV), which is proportional to the local infrared absorption measured by the PiFM probe. Higher signal intensity indicates stronger absorption at that wavenumber and therefore a greater relative abundance of the corresponding chemical at the analyzed location. Vertical markers highlight key vibrational bands used to distinguish the surface chemistry of the dark and bright regions.

The islands exhibited increased absorption near ~1090–1100 cm^{-1}, corresponding to the stretching vibrational mode of Si-O-Si (siloxane) while the regions surrounding the islands exhibited increased absorption near 1462 cm^{-1} corresponding to the scissoring vibrational mode from CH_2 . This finding revealed that the islands and surrounding regions were chemically distinct despite appearing similar under optical inspection, providing evidence that multiple contamination mechanisms may be present on the surface.

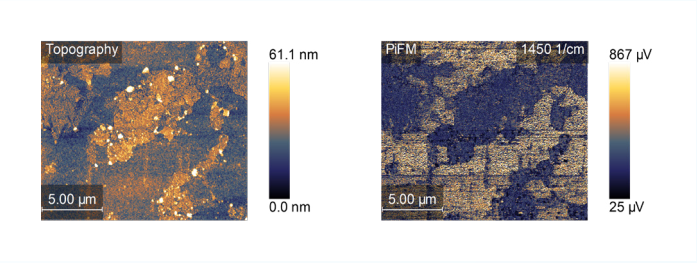


Figure 10: AFM data (left) side by side with PiFM data (right). The bright regions in the AFM map indicate areas with raised topography while the bright regions in the PiFM map indicate areas that have an abundance of CH2

TOF-SIMS Maps Surface Contamination Across Larger Areas

TOF-SIMS measurements were performed on the sample in both negative mode and positive mode which indicated the presence of Cl, F, Br, I, S, Ca, K, Na, Ti, Fe, Al, Ag, Sn, and Cu.

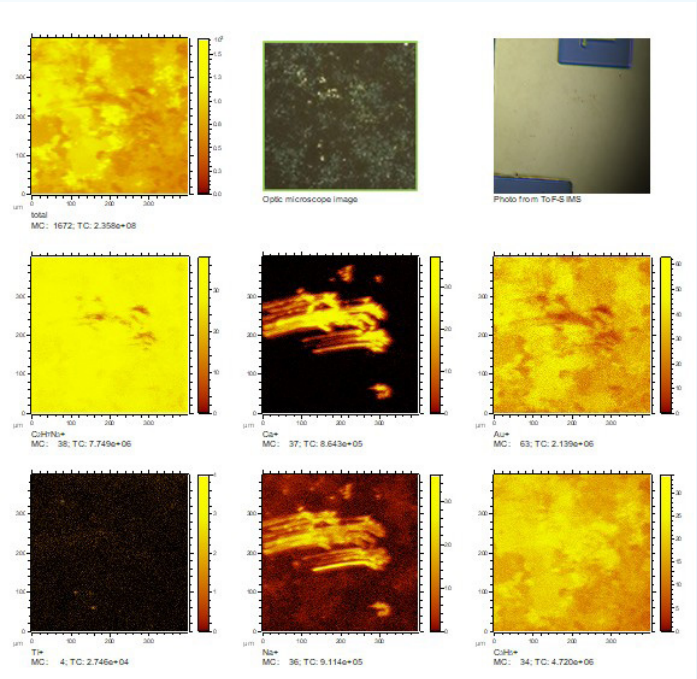


Figure 11: TOF-SIMS maps on sample in positive mode.

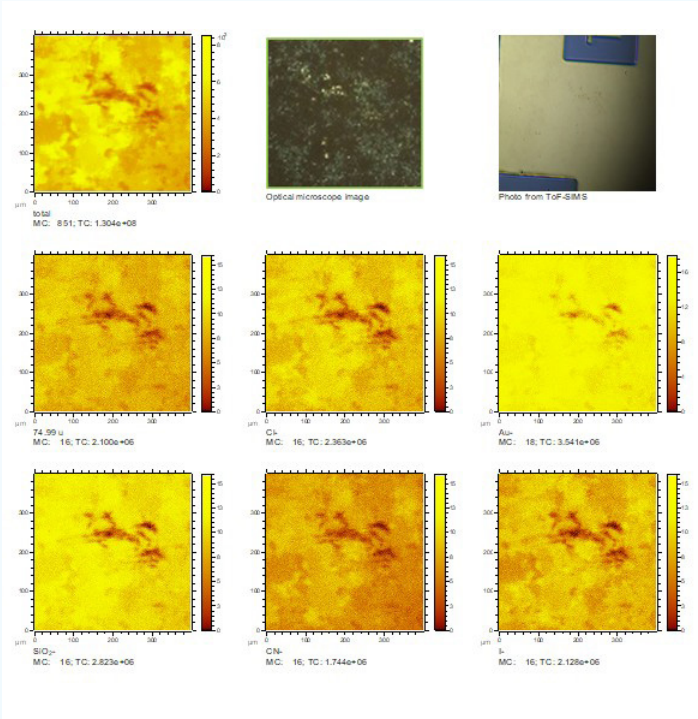


Figure 12: TOF-SIMS maps on sample in negative mode.

Despite detecting surface contamination, TOF-SIMS did not show a strong correlation between the visible dark/bright spots and regions with chemistry differences. This was somewhat unexpected because the optical image suggested the dark spots might correspond to chemically distinct regions. Instead, the TOF-SIMS maps suggested that surface roughness was a contributing factor to discoloration across the analyzed regions. This highlights an important analytical lesson: visible discoloration on metallic surfaces does not necessarily correspond directly to chemically unique regions and vice versa.

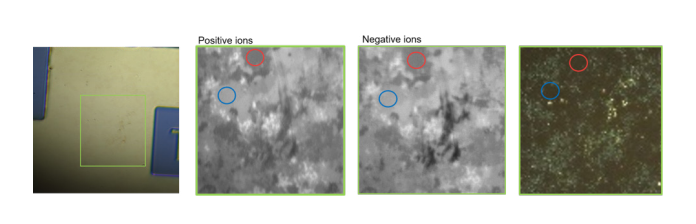


Figure 13: TOF SIMS Ion images (middle) compared with optical microscope images (right). The colors of the circles indicates indicate regions of the sample imaged in different modes. These images show there is no correlation between chemically different regions and visible discoloration on the sample surface.

The final piece of the puzzle came from the TOF-SIMS mass spectra. When spectra collected from the sample were compared to a reference spectrum for PDMS (Polydimethylsiloxane), a series of characteristic silicon-containing organic fragments appeared at matching mass-to-charge ratios. This provided strong evidence that at least part of the surface contamination originated from PDMS, or a closely related silicone material commonly found in oils, greases, sealants, and other manufacturing environments.

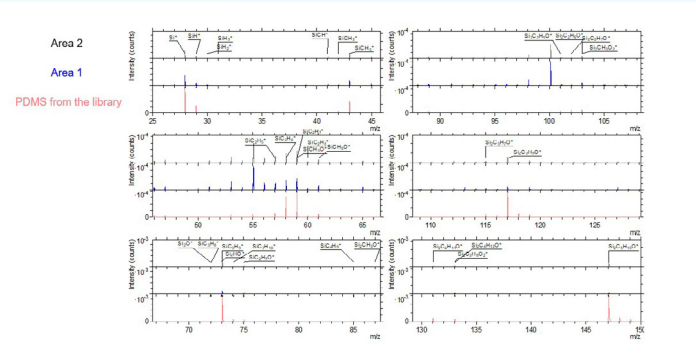


Figure 14: Positive mode TOF-SIMS mass spectrum on both regions of the sample compared to the known spectrum from PDMS.

Taken together, the PiFM results suggested that PDMS-like material was concentrated on the raised islands, while the surrounding background regions exhibited enhanced CH_2 absorption, indicating a chemically distinct material. PDMS is a silicone-based polymer commonly found in oils, greases, sealants, and other manufacturing materials. Because it transfers easily and can be present in trace amounts, it is one of the most frequently encountered surface contaminants.

Why a Correlative Workflow Matters

No single technique alone could fully explain the origin of the dark spots. By combining AFM topography, conductive AFM, PiFM nanoscale chemistry, and TOF-SIMS large-area chemical imaging, the study built a much more complete understanding of the surface.

The results suggest the optical contrast likely arose from a combination of nanoscale topography and localized siloxane/PDMS contamination.

Conclusion

What began as a simple question about a few dark spots ultimately revealed a much more complex surface story.

Conductive AFM revealed nanoscale conductive islands only 10–20 nm tall, PiFM identified localized siloxane/PDMS-related chemistry, and TOF-SIMS mapped broader contamination and trace surface species across the gold surface. Together, these techniques showed that the observed dark spots were not simply isolated chemical defects, but rather a complex combination of topography, contamination, and surface roughness effects.

For advanced electronics and wire bonding applications, this type of multi-technique workflow provides a powerful way to distinguish cosmetic surface artifacts from potentially performance-limiting defects. Ultimately, the investigation transformed an ambiguous visual defect into actionable engineering insight, helping the customer determine whether the observed dark spots were merely cosmetic or a genuine threat to wire bond reliability.

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