

Raman Microscopy as an Aid in Failure Analysis – Examples From the Lab

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Raman spectroscopy, much like the more familiar infrared spectroscopy, reveals chemical information of materials under investigation as a result of molecular vibrations. The result of these techniques, the spectrum, is a chemical “fingerprint” allowing for material identification. While infrared microscopy is well known and well established in the industrial laboratory setting, Raman microscopy has only recently begun a resurgence as a result of technological advances. These include advances in lasers, optical filters (notch filters), and CCD detector technologies.

Why choose Raman microscopy? The answers are many. For our labs, perhaps the greatest advantage is related to “spot size.” Infrared and Raman microscopy are both diffraction limited with respect to spatial resolution, however, because of the wavelengths of the exciting energy in both cases, infrared microscopy is limited to a spot size of about 10 microns (this only under best-case scenario), while Raman spectra can be routinely collected from samples with a size of about 1 micron. Another impressive advantage, as compared to infrared microscopy, is that the background or substrate that a material of interest resides upon is typically of little consequence. This results from the fact that the requirement of a reflective background, such as for the collection of reflectance spectra, is not necessary with Raman microscopy. An indirect result is that spectra can be collected most times “as is” without modification, or without the often tedious sample preparation associated with infrared analyses. Another advantage unique to this technique is the ability to “see through” materials as a result of the instrument’s confocal capabilities. This means that buried layers of a laminate can be examined simply by focusing into the sample, or that the contents of a bottle may be analyzed without opening it. Additionally, because the selection rules governing what makes a material a good candidate for Raman microscopy are in essence the converse of infrared microscopy, the techniques are naturally complementary and Raman microscopy allows for analysis of materials inaccessible by other means. Also, as is the case with infrared spectroscopy, database matching is a valuable tool for materials identification. Interpretation of spectra is performed in an identical fashion as that of infrared spectroscopy so an operator well-versed in infrared analysis can make the transition to Raman spectroscopy with ease.

It should be pointed out that this method, like all others, has limitations: for example, fluorescence can make the collection of spectra impossible with certain samples. Multiple laser configurations can mitigate this limitation. Also, because the excitation source is energetic, sample decomposition, interfering with collection of spectra, is possible. However, the unique capabilities offered by Raman microscopy make it a natural adjunct to other existing laboratory methods.

The remainder of this article will highlight examples encountered by us, the Failure Analysis Labs, Raytheon, McKinney, TX., where Raman spectroscopy has proven to be a valuable technique. In fact, in many cases, without this method, we would not have been able to unequivocally identify specimen constituents without the strong spectral data provided by this form of microscopy.

The Ubiquitous Cross Section:

One of the most common chores for the failure analyst is the preparation of cross-section specimens. Cross section specimens are

suitable for the examination of the construction of layered assemblies and prepare the way for investigations using a variety of other analytical techniques, including optical and electron microscopy. As will be shown, Raman microscopy synergistically complements other forms of microscopy—especially with regard to materials identification.

Frequently, the identification of materials revealed by the cross sectioning process is required. Infrared microscopy is incapable of performing these analyses because of both beam size limitations and background interference concerns. The elemental information provided by SEM/EDS methods, while providing a list of elements present and their concentrations, lacks the ability to provide bonding information, which would allow the analyst to identify molecular compounds. Raman microscopy is particularly well suited to address these concerns. The following example highlights these capabilities.



Example cross-section.

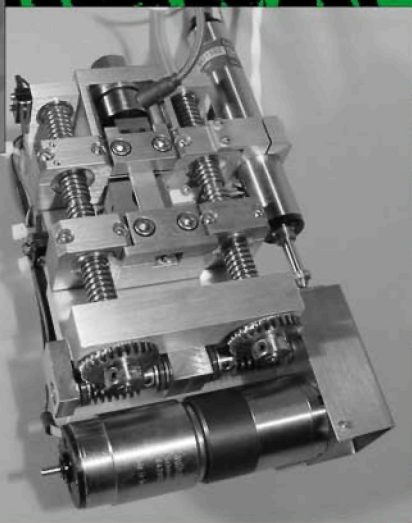
The lab was asked to investigate the above cross section with regards to material identification as well as to verify the presence of cracking. Optical examination revealed that the expected well-ordered layering of materials did not occur and insights into material distribution were requested. The following spectra were obtained from the areas labeled in the image.

Cracking was verified by noting that the potting material used in the sectioning process was observed filling crack voids (some area widths as small as 1 micron were characterized) and the presence of a hard anodized aluminum was confirmed on the outer layer of the part. The unknown residue was shown to be composed of polyimide. This material is associated with the inner fiberglass portion of the part. Finally, the area labeled “Area 1” was shown to be consistent with a urethane that was expected in this region.

This example highlights the unique ability of Raman microscopy to collect high quality vibrational spectra and identifying molecular species from spots as small as 1 micron in diameter without any additional specimen preparation other than making the cross section.



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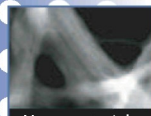
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Depth profiling:

While multi-layer laminates and similar types of samples are more commonly investigated using the confocal capabilities of Raman microscopy, I have chosen a seemingly more mundane example. As a result of this investigation, a longstanding failure mechanism associated with wafer fabrication was corrected.

During manufacture of a particular wafer, an outer polyimide layer is plasma etched prior to the application of an additional layer of the same polyimide. In a seemingly random fashion, bonding failures occur during the application of this second polyimide layer – sometimes the bonding is exceptional and at other times horrendous. The lab was approached to help determine the failure mechanism.

Initial theories included the formation of a carbon ash residue as a result of the etch procedure, as well as an expected metallic contamination. As a result, initial investigations were carried out using SEM/EDS methods. The result of these investigations was that no differences between etched and unetched samples were noted. As carbon ash is an excellent Raman scatterer, Raman microscopy was chosen to test this assumption. As shown below unexpected results were obtained.

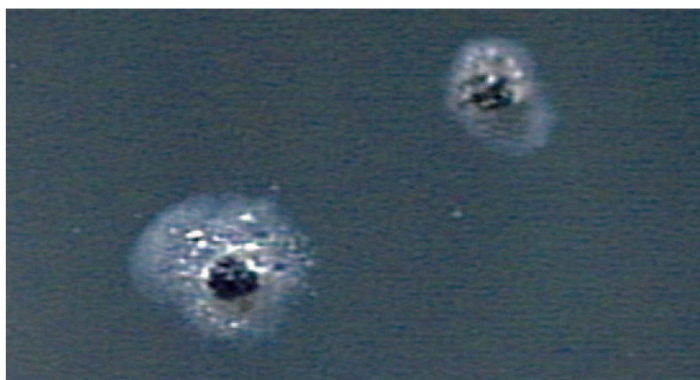


Top spectrum focused above surface, bottom focused into surface.

The upper spectrum is that of alumina collected when 532 nm irradiation is applied. This was unexpected but not a complete surprise as the wafer substrate in this case is alumina. Note that in the bottom spectrum the alumina peaks are greatly diminished and bands associated with polyimide are observed. This is a clear indication that alumina is contaminating the surface of the polyimide. In this case, SEM/EDS methods did not detect this as the levels of contamination were below EDS detectability limits. However, as alumina is a very strong Raman emitter, with 532 nm irradiation, it was detected. Additionally, the contamination was shown to be confined to the surface.

That confounded background:

The final example highlights the fact that in most cases, the background on which a material under investigation resides is usually less of a problem when using Raman microscopy as opposed to other methods.



Laser burn spots on optics.

The lab was presented with life-test failures associated with artifact formation on the optics of a laser assembly. These artifacts were forming during the early stages of life testing and degraded the laser output to an unacceptable level.

SEM/EDS investigation revealed the presence of silicon, oxygen, and carbon in the artifact areas, and only silicon and oxygen on the surrounding surface. As a result, and as is often the case with such data, it was assumed that these areas contained organic contamination of some sort. Infrared spectroscopy was not considered as the artifact's size was far smaller than the minimum IR analysis size, plus the background behind the deposit made reflectance microscopy problematic. The sample could not be removed to attempt transmission methods. This seemed the perfect candidate for Raman microscopy. The following spectra were recorded.

The blue spectrum was recorded from the center dark area of the artifact. It is indicative of the formation of carbon decomposition products (a material not observable using infrared methods). This suggests that the material responsible for the artifact was decomposed by the heat absorbed in the artifact due to the firing of the laser. Assuming that the source of the carbon might still be identified, we obtained spectra from the very edges of the artifact where any residual of the causative deposit may be so thin that it did not absorb enough laser heat to be decomposed. The center spectrum is typical of those collected in these regions.



Center of residue, blue, edge of residue, purple, reference silicon spectrum, red.

The unmistakable symmetric and anti-symmetric C-H stretches of the methyl groups of dimethylsiloxane, also known as silicone, are obvious (the bottom spectrum is a reference spectrum of silicone). This is conclusive data that the source of the residue that created the artifact is silicone. The previously mentioned SEM/EDS analyses, absent any molecular information, were incapable of identifying silicone, as the deposits reside on a fused silica background, and infrared methods could not be used for the reasons previously stated.

Further investigation revealed the source of the residues as a silicone lubricant used within the laser housing. Outgassing of volatile silicone with concurrent artifact creation as a result of the laser firing was shown to be the cause of the failures. Corrective actions were instituted to address these failures.

The above examples are just a few of many we have encountered in which Raman microscopy has proven to be a valuable tool for failure analyses. While no analytical technique is all-encompassing, Raman microscopy is a natural complement to many more commonly encountered methods such as micro-FTIR and SEM/EDS. In all the cases listed above, and many others we have encountered, analyses could not have been as fully addressed without this capability; supposition and educated guesses would have been the result. For our labs, small spot size is probably the most important advantage offered by this technique, however, ease of use, depth-profiling capabilities, an expanded range

of sample types, the collection of diagnostic molecular information, and others have also proven to be of great value.

Experimental:

All Raman spectra were collected using a Nicolet(tm) Almega(tm) XR dispersive Raman microscope from Thermo Electron Corporation, equipped with 532 nm and 785 nm high brightness lasers. The Nicolet Almega XR was configured with a trinocular and a software-controlled motorized microscope stage for precise location and examination of the sample features under investigation. ■

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