Submicron Non-contact Simultaneous Infrared and Raman Spectroscopy for Challenging Failure Analysis

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Abstract

We introduce a new infrared (IR) technique that provides submicron spatial resolution by making use of an infrared-visible, pump-probe arrangement that also offers a simultaneous Raman measurement in formerly challenging failure and contamination analyses. These challenges are typically due to the lack of spatial resolution and sample preparation restrictions from conventional FTIR, plus auto-fluorescence (AF) from Raman spectroscopy. Such a combined Optical PhotoThermal InfraRed (O-PTIR) and Raman instrumentation offers spatial resolution improvement over conventional IR measurements by 30 times at 1000 cm⁻¹. The technique also improves sensitivity to exceptionally small quantities (≥400 femtogram) in reflection mode by sensing the photothermal response arising from absorbing infrared radiation (Fig. 1) [1]. The AF-free O-PTIR technique also delivers constant spatial resolution over the entire mid-IR range due to the use of a fixed wavelength probe beam at 532 nm [2]. Simultaneous Raman confirms and complements the O-PTIR measurements in cases with low AF. We will illustrate three examples that will highlight the advantage of the novel technique commonly observed in the failure and contamination analysis community.

Introduction

IR spectroscopy has been a workhorse analytical tool for the past 50 years [3]. Modern infrared spectroscopic instruments are widely popular due to its high versatility for and good adaptability towards a wide range of application fields and the systems’ user-friendliness. This method is based on exciting and detecting of molecular vibrations of functional groups within a given molecule. A functional group would likely have multiple infrared absorption frequencies depending on the mode of vibrations [4], which corresponds to the band positions in an infrared spectrum. For instance, the methylene (-CH₂-) group in a polyethylene molecule would typically absorb around 2918/2848 cm⁻¹ for its antisymmetric and symmetric stretching motions; concurrently its scissoring mode would have an absorption band around 1468 cm⁻¹ [4]. Complex molecules will have many functional groups which would have discrete absorption bands at multiple frequencies in the mid-infrared region and their positions will be slightly shifted by its neighboring groups due to chemical shifts or coordination effects [4]. The vibrational modes of each molecule are slightly different from one another, in spite of similar chemical structure [3]. Therefore, their infrared absorption spectra are unique, thus enable the identification of unknowns in contaminants, monitoring processes, and failure analysis.

The versatility of the Fourier transformed infrared (FTIR) technique is limited by the intrinsic wavelength of IR beam, which spans the spectroscopic range from 4000 to 500 cm⁻¹ (2.5 – 20 µm). For transmission mode FTIR spectroscopy, radiation is focused on the sample and the unabsorbed infrared radiation passes through the infrared absorber and is focused to the IR detector (Figure 2). Therefore, infrared wavelengths define the practical diffraction limited spatial resolution, which varies between 2.5 and 20 µm across the mid-IR spectral range [5]. Often times, FTIR needs to be operated in reflection mode for semiconductor and microelectronics specimen due to their opaque sample characteristics; these samples cannot be easily thinned for transmission mode operations. The sharp corners and rough surface topography will lead to optical and scattering artefacts. As the result, these spectra are challenging to interpret with derivative-shaped bands at strong absorption bands [6], which are not directly searchable in commercially
available infrared spectral databases. Such databases are constructed of spectra obtained from transmission and attenuated total reflection (ATR) modes.

![FTIR Microscope](image)

**Figure 2. Basic operation schematic of a FTIR microscope**

Organic, carbon-containing contamination and foreign matter (FM) are often analyzed with conventional FTIR due to its ease-of-use and the availability of large commercial infrared database for identifying unknowns. Conventional FTIR can give a good signature of the organics in conjunction with a focal plane array (FPA) detector to provide microscopic chemical analysis down to 20 µm that parallels to the spatial resolution mentioned above. Certainly, the use of germanium ATR accessories could improve practical spatial resolution in the fingerprint region to about 4 µm at 1723 cm⁻¹ (5.8 µm) [7] but would vary depending on the wavenumber; in addition, the ATR probe needs to make good and complete contact with sample surfaces, leading to permanent sample damages and potential sample cross-contamination [3]. Frequently, this option is not feasible either due to the presence of a hard and rough surface and/or the blocked access to the FM by neighboring structures. Smaller FM would be referred to Raman spectroscopy due to the shorter excitation wavelength, which also significantly improves the spatial resolution to about 1 µm, as limited by Rayleigh criterion [7].

Raman spectroscopy complements FTIR spectroscopy by observing the interaction of polarizable vibrational modes with a monochromatic laser excitation [8]. The wavelength of excitation can be from ultraviolet to visible to near-infrared. The incident light projects perpendicularly to the sampling surface, with only a small number the back reflected photons being Raman shifted. [8]. These Raman active modes are typically the strongest for the symmetric modes, such as the carbon-carbon double bond stretching mode (~1600 cm⁻¹) and the breathing mode of aromatic rings (~1000 cm⁻¹). The Raman-shifted radiation containing these discrete Raman lines are reflected back to a charged coupled device, e.g., array camera, to generate plots in a typical spectral range of 200 – 4000 cm⁻¹. Unlike infrared spectroscopy, the positions of these discrete lines in the Raman spectra are representative of their corresponding vibrational modes and are routinely used for identifying unknowns to complement results from infrared spectroscopy or when infrared spectroscopy could not provide spectroscopic data due to sampling limitations and/or restrictions.

![Theoretical Spatial Resolution Comparisons](image)

**Figure 3. Spatial resolution comparison between conventional FTIR, QCL-equipped IR microscope and the O-PTIR pump-probe infrared microscope [2].**

Raman data are typically collected in a non-contact, reflection mode manner, that is highly desirable for the microelectronic failure and contamination industry due to good compatibility with existing sample preparation methods, such as chemomechanical polishing (CMP) and focus ion beam (FIB). While this is an attractive attribute afforded by Raman analysis, sample very frequently demonstrate auto-fluorescence (AF) upon irradiation of visible light, leading to significantly elevated baselines that can obscure Raman spectral features and can even saturate the detector all-together. AF is an optical phenomenon; any given material may fluoresce upon excitation without adding targeted fluorescent materials due to the minute presence of fluorophores within the specimen [9,10,11]. Fluorophores could be extraneous organic [12] and inorganic matters [13] that could be sensitized within the ultraviolet-visible wavelengths. Minor impurities in the polymer may also contribute to the AF behavior of colorless polymers [14]. In particular, plastics are well-known to express auto-fluorescence when illuminated by visible laser [15,16]. These fluorescence baselines can overshadow the weak Raman signals. Even colorless materials, such as polyethylene terephthalate and polyethylene, would yield a background fluorescent response under illumination without additional fluorophores.

Colored material would emit strong AF that would saturate the detector, even at short integration times under the illumination of shorter visible wavelengths, such as 488 nm and 532 nm. It is sometimes possible to reduce AF by using longer excitation wavelengths, but that would result in significantly lower Raman
scattering intensities [3,9]. Increasing excitation power could increase signal intensity and could reduce AF intensity by photobleaching mechanism, but this significantly increases the risk of sample photodamage [17]. Photobleaching could take significant amount of time in the order of a few minutes to few hours to effectively reduce the fluorescent effects from chromophores [10]. Furthermore, some organic dyes have strong Raman scatterers, such as copper phthalocyanine (CuPC) in the solder masks of printed circuit board (PCB) [18], which Raman shift intensities are quite strong [19] and would dwarf the Raman scattering cross-sections from other components. Finally, commercially available Raman spectral databases cover much fewer compounds than the infrared variant by roughly 10x [20], making identification of unknowns more challenging.

In essence, the O-PTIR technique directly measures the photothermal effect of absorption of infrared light at the localized region, leading to an ultra-sensitive technique that could detect ~0.4 picograms of matter (e.g., a single 900 nm diameter PS) [1]. In contrast, FTIR spectrometry determines the infrared absorption spectrum of a given material by comparing the remaining infrared radiation after passing through (in transmission mode) or reflected from the sample to the background spectrum. The sensitivity of transmission mode FTIR of approximately 100 picogram [23] is at least two hundred times less than the O-PTIR technique. For matter as small as 0.4 picograms or less in a diameter of ~0.9 µm, the optical changes in transmission mode FTIR would have been too small to be discernable within the spectral noise. Furthermore, it is also challenging to position the internal reflection element (IRE) of the FTIR’s ATR accessory to make sufficient contact with these spheres; high pressure crystal-sample contact increases risks of probe damage and the spheres could be rejected upon contact. Finally, only a small amount of infrared light from the Globar source in standard FTIR spectrometers could reach the single infrared pixel element of the FPA-equipped microscope; therefore, the small signals would make the resulting spectra noisy [5].

O-PTIR spectra are not affected by AF, nor from dispersive scattering artefacts in spite of its reflection mode operation. The detection architecture makes use of a room temperature photodiode detector, which is low noise and unaffected by the longer wavelength autofluorescence. As a result, reflection-collected O-PTIR spectra are comparable to thin film FTIR transmission spectra and thus directly searchable against commercially available digital libraries of IR spectra. Subsequently, unknowns can be readily identified without requiring customized infrared spectral libraries of compounds. To increase the definitiveness of the spectral search,

Figure 4. High level schematic of the O-PTIR technique

For modern material and contamination analysis, new analytical approaches are required to reach a spatial resolution in the submicron regime. The variable spatial resolution across the spectral range can also add significant challenges to the analysis. The mRage+R instrument (Photothermal Spectroscopy Corp., USA) takes advantage of the novel infrared-visible pump-probe approach to produce IR spectra with submicron spatial resolution. Figure 1 illustrates the working principle of the O-PTIR technique, which is significantly different than the conventional FTIR spectroscopy. First, the wavelength tunable quantum cascade laser (QCL) emits an infrared laser beam that is pulsed and is combined co-linearly with a constant wave visible laser at 532 nm. These two beams are focused to their diffraction limited spot size with a high NA reflector-based Cassegrain objective. The impinging infrared laser radiation would be partially absorbed by the matter when the wavelength resonates with the vibrational mode of the organic matter. This excitation process causes the area under the infrared spot to heat up; and subsequently, the localized material expansion along with changes in the refractive indices, collectively known as the photothermal effects [21,22]. This absorption process conforms to the infrared absorption profile of the material, like that of the conventional FTIR spectrometry. As the pulsed infrared laser is switched into the “off” state, the photothermal effect would be off as well [22]. The absolute amplitudes between the “on” and “off” photothermal effects would be captured by the co-located constant wave visible beam and plotted against the wavenumber being emitted by the QCL laser over its tunable range (Fig. 4). The resulting O-PTIR spectra resemble the band shapes and positions like that of conventional FTIR spectra. Since the detection mechanism relies on the visible laser instead of the pump source (infrared radiation), the spatial resolution of the O-PTIR technique is hence defined by the shorter wavelength visible laser instead of the longer wavelength infrared laser beam. At 532 nm, the diffraction limited spot size of the visible beam corresponds to approximately 416 nm [1,2], which leads to a 30-times improvement in spatial resolution than conventional FTIR microscope at 1000 cm⁻¹ (Fig. 3). Furthermore, this submicron spatial resolution is independent of the infrared wavelength, making the O-PTIR technique a de facto submicron method.
simultaneous O-PTIR and Raman spectra taken at the same spot can be searched simultaneously or separately as necessary.

**Discussion**

Figure 5. A defect spot where the solder could not wet the metal pad due to the presence of organic contamination.

The simultaneous O-PTIR and Raman technique provides clarity in chemical identification of contaminants that were previously impossible with conventional FTIR spectroscopy. Fig. 5 illustrates a common open connection due to a non-wetting metal pad. The separation is roughly 1 µm, which would be impossible with the resolving power of conventional FTIR techniques. Using O-PTIR imaging, the defective solder joint appears to have significant amount of contamination from a FM with a strong absorption at 1672 cm$^{-1}$ (Spectrum A), which is consistent with the carboxylates typically found in the flux [24,25]. These spectra differ from a typical underfill, which is composed of mostly silica filled epoxy (Spectrum B).

Despite making the measurements in non-contact reflection mode, O-PTIR spectra provide clear chemical details of the failure mode. Spectra collected from the gap, as represented by the black and gray-colored spectra, have a strong and broad IR absorption band consistent with carboxylates at 1672 cm$^{-1}$. In addition, the surrounding area also has strong 1672 cm$^{-1}$ hotspots (black and gray markers in Fig. 5A and corresponding O-PTIR spectra in Fig. 6A), correlating with the spectral features. A possible material containing a carboxylate group could be rosin-based fluxes, which are commonly embedded in solders to reduce oxidation of the metal alloys at high soldering temperatures. The corresponding Raman spectra (Fig. 6B, Spectra A-R and B-R) have a distinct spectral feature around 1370 cm$^{-1}$, which is consistent with disordered carbon-like material [26] and correlates well with the strong baseline offset in the O-PTIR spectra. Such strong baseline offsets in the infrared spectra are typically observed in material loaded with carbon [27]. Strong AF in many of Raman spectra is still notable, highlighting the inherent value of the O-PTIR technique complementing the simultaneous Raman spectra. A few micrometers away from the contamination, spectra are consistent with a normal silica-filled epoxy underfill (teal and green markers). Such simultaneous submicron O-PTIR and Raman spectroscopic measurements provide confirmatory and complementary chemical analysis in a non-contact, far-field mode in an effective manner previously unattainable with separate conventional infrared and Raman instrumentation.

Figure 6. Simultaneous O-PTIR and Raman spectra with color-coded to the corresponding markers in Figure 2.

Open connections can have drastically different chemical compositions than we have seen in the first case. In our second failure analysis example, Fig. 7 shows an O-PTIR image taken at 1660 cm$^{-1}$ illustrating the position of the FM, which spreads...
widely over the metal pad with a thickness of 1 – 2 µm. O-PTIR spectra of the layer reveal functional groups consistent with proteinaceous amides (Fig. 8). These O-PTIR spectra are clearly differentiated from the silica-epoxy based underfill material. One of the red spectra with amide absorption appears to have notable amount of the epoxy absorption as indicated with three red arrows (1512, 1245 and 1180 cm⁻¹). Their relative intensities are exceedingly stronger than the epoxy absorption in the silica-filled underfill. Therefore, the O-PTIR spectra has likely resolved a spatially varying composition within the thin layer of proteinaceous FM. Finally, the direct search compatibility of O-PTIR spectra in commercially available databases (Fig. 9) reveals the FM is likely to be protein based. In stark contrast, strong bands in FTIR spectra collected in non-contact reflection mode generally possess distorted band shapes [3, 28] that could lead to misidentification of FM. Here, spectral matching of the FM’s O-PTIR spectrum display expected band shapes that compare well with ideal transmission mode FTIR spectra for a positive identification. Based on this new information enabled by the O-PTIR technique at submicron spatial resolution without AF interference, processes or sources of contamination can be effectively identified and eradicated.

In the final example, we have a FM that could be large enough for FTIR but then failed to produce an interpretable nor searchable infrared spectrum due to the close proximity of FM to nearby ball grids (Fig. 10). The ball grids are highly scattering for the infrared radiation. The FM also has a rough surface texture, which prevent effective collection of infrared radiation in reflection mode. The adjacent sphere-like surfaces would also prevent the microscope’s attenuated total reflection (ATR) internal reflection element (IRE) from making contact with the particle surface with high risk of damaging the IRE. The non-contact, far-field reflection mode operated O-PTIR readily collected the infrared spectra of the particles (Fig. 11). Both the amide-I and amide-II bands are clearly observed at 1656 and 1542 cm⁻¹, which are consistent with polyamides [4]. Since the O-PTIR analysis requires no physical contact, the pristine chemical condition of the contamination is preserved for further investigations and confirmation purposes.

**Figure 7.** Overlaid O-PTIR infrared image taken at 1660 cm⁻¹ and the corresponding optical image.

**Figure 8.** Corresponding O-PTIR spectra taken within the region where strong O-PTIR absorption could be observed near the metal pad with an open-circuit.

**Figure 9.** Spectral searching of O-PTIR spectrum taken in the region with strong 1660 cm⁻¹ and 1540 cm⁻¹ absorption bands

**Figure 10.** Optical image illustrating the limited accessibility of the particulate in between the ball grid array.

**Conclusion**

Using the submicron spatial resolution O-PTIR and Raman technique, process engineers can now probe the chemical identity of FM by simply polishing the specimen to preserve the spatial information or presenting the specimen in question directly to the O-PTIR system. Furthermore, specimen too small (less than 20 µm) for FTIR, too difficult to reach with an ATR probe, or significantly interfered by strong AF in Raman can now be accessed with submicron spatial resolution, non-contact O-PTIR spectroscopy. Such results are unattainable by conventional FTIR or Raman microspectroscopic methods.
The simultaneous infrared and Raman combined technique at the same time, same spot and at the same resolution will revolutionize failure and contamination analysis strategy toward a highly efficient analytical process, thereby improving efficiency and product yields.

![Figure 11. O-PTIR spectra of the particle as highlighted in Figure 10.](image)

### References


