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IDENTIFICATION OF SURFACE CONTAMINANTS USING
INFRARED MICRO-PROFILING*

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Infrared micro-profiling is the combination of infrared microspectroscopy with precise microscope stage movements. It can provide molecular and spatial information for a variety of samples as small as 10 μm in diameter. To illustrate the technique different contaminant materials, including a cellulose acetate fiber, oils deposited in a fingerprint, and a thin film of solder flux residue, were infrared micro-profiled. An integrated absorbance data reduction technique commonly used in gas chromatography/FT-IR applications was applied to the micro-profiling data. This technique organizes the vast amount of data generated, enabling the user to plot the results in 3-dimensional projections, allowing extraction of relevant spatial information. A method of coadding spectra from different pixel elements, providing higher quality spectra without increasing data acquisition time, is presented. This procedure improves spectral signal-to-noise which aids in the identification of unknown contaminants.

INTRODUCTION

Infrared spectroscopy (IR) is a vibrational spectroscopic technique used for the nondestructive identification of molecular species. It provides information about the molecular structure of a compound by determining the frequency and quantity of light it absorbs in the infrared region. The resultant IR absorption spectrum is characteristic of the compound. It is one of the compound's physical properties, like its boiling point or density. In fact, with the exception of optical isomers, no two compounds have identical infrared absorption spectra. The molecular information that IR spectroscopy provides distinguishes it from other analytical techniques such as x-ray fluorescence, atomic absorption, and emission spectroscopy, that yield information about elemental composition. In general, due to quantum selection rules and vibrational absorption frequencies, IR spectroscopy is used for the identification of

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organic materials. However, many inorganics also exhibit IR detectable molecular vibrations and therefore can be identified by this technique¹.

IR spectroscopy can be performed on molecular species in any physical state. Therefore, gases, liquids, and solids can all be easily sampled. However, IR spectroscopy may not be as useful for the identification of dilute solutions of less than millimolar concentrations due to low absorbance intensity. Complex mixtures can be difficult to identify due to the large number of absorption bands present in the spectrum. Also, metals and metallic alloys cannot be identified using IR spectroscopy since these materials are not infrared active.

Dispersive spectrometers were among the first commercially available infrared spectrometers. These instruments compare a beam of infrared light transmitted through or reflected by a sample to a parallel beam not exposed to the sample. The infrared spectrum is obtained and recorded by scanning successive frequencies. However, with the ready availability of powerful, but affordable computers, many research and analytical laboratories now use Fourier-transform infrared spectrometers. These spectrometers examine the entire frequency range of infrared light simultaneously by interferometry. The pathlength of two beams of infrared light is varied with time during each scan. A time dependent pathlength difference between the two beams cause phase shifts of one beam relative to the other. When the two beams combine, a constructive and destructive interference pattern, known as an interferogram, is formed. A Fourier transform is used to mathematically change the time dependent interferogram into a frequency dependent spectrum. The result is a measure of the intensity reaching the detector as a function of frequency. This is equivalent to a single beam spectrum obtained with dispersive infrared spectroscopy. However, Fourier-transform infrared spectroscopy (FT-IR) is an improvement over dispersive infrared spectroscopy. It can increase spectral quality while reducing acquisition time by examining all frequencies simultaneously. For more information about FT-IR, the reader is referred to the comprehensive text on the subject by Griffiths and de Haseth².

Microscopy/FT-IR became a reality after the development of high sensitivity detectors, high-intensity infrared sources became commercially available, and improvements were made in the throughput efficiency of infrared spectrometers. These instruments make it possible to examine samples as small as 10 μm in diameter. The size limitation is a physical constraint based on the diffraction limit of light in the infrared region. However, a contaminant of this size may be considered macroscopic in the microelectronics industry. Miniaturization of semiconductor devices has created a demand for the detection and identification of contaminants in the tenths of microns range. In our laboratory, though, microscopy/FT-IR has proven itself extremely useful for detecting contaminants on microelectronic components that have originated from processing equipment, personnel, and storage facilities because many such contaminants are larger than the 10 μm limit.

Infrared micro-profiling further enhances microscopy/FT-IR. It combines infrared microspectroscopy with controlled microscope stage movements and can be used to both locate and help identify chemical species. Like traditional IR microspectroscopy, IR micro-profiling can be used to examine contaminants present as particles, droplets, smears, fibers, crystals, inclusions, bubbles, or additives¹. Recently, it was used to map, chemically identify and spatially resolve, a fiber contaminant on a microelectronic device³. It has also been used to identify individual polymers present in a multilayer polymer structure⁴,

and a fluid inclusion⁵. As will be shown, the usefulness of IR micro-profiling includes the ability to detect contaminants not visible with standard optical microscopy. Furthermore, even though data collection time is increased, the "hands-on" time of the spectroscopist is greatly reduced.

During IR micro-profiling, a complete infrared spectrum is obtained at each stage position or pixel element. This creates a large number of spectra that must be manipulated so that relevant information can be extracted to produce a spatial image. One approach for examining the data is to create infrared maps that show the spectral regions of interest for each pixel organized on a grid scaled to the sampled area⁵. Another approach is to compress the raw spectral data to a single intensity value at each pixel and plot it as a function of position in an axonometric projection. This allows efficient examination of the data collected using a 3-dimensional representation of the image. The compression can be accomplished by measuring the intensity of a single absorption frequency, by integrating the total absorbance over a specified spectral range, or by a procedure known as Gram-Schmidt reconstruction³.

Three examples will be presented to illustrate the usefulness of IR micro-profiling for contaminant identification. The examples are a cellulose acetate fiber, a fingerprint, and a thin film of rosin-based solder flux. Three-dimensional axonometric projections of the images will be presented. These result from compression of the spectral data at each pixel to a single value by integrating the absorbance over a spectral range containing absorption frequencies characteristic of the contaminant. A brief discussion will also be presented on coaddition of spectra from different pixel elements that contain spectral information of the contaminant. This procedure improves spectral quality, increases the signal-to-noise ratio, S/N, and provides a good quality resultant spectrum for subsequent library searches that helps in the identification of unknown contaminants.

EXPERIMENTAL

Infrared spectra were obtained using a Spectra-Tech (Stamford, CT) IR-PLAN infrared microscope interfaced to a Nicolet 7199 FT-IR (Madison, WI). The IR-PLAN is an adaptation of an Olympus (Lake Success, NY) research grade optical microscope. It allows the operator to visually align and mask the sample area before IR spectroscopy is performed. The spectra reported here were all obtained with the microscope in reflectance mode. Infrared radiation was focused at the sample by a totally reflecting 15X Cassegrainian objective (numerical aperture, N.A., 0.58). Redundant AperturingTM was used to collect spectra of high spatial purity and photometric accuracy⁵. The system is equipped with a narrow band mercury-cadmium-telluride (MCT) detector having a 0.25 x 0.25 mm element and a spectral range of 4000-800 cm⁻¹. The microscope was coupled with a Spectra-Tech motorized micropositioning stage that provided movement in two dimensions. X and Y stage step sizes were varied from 20 to 80 μ m with a spatial precision of 1 μ m. A square aperture with adjustable blades masked each pixel area consistent with the step sizes.

The collection of infrared data and movement of the motorized stage was fully automated. A Nicolet 1280 computer, with a Fast Fourier Transform (FFT) co-processor, was interfaced to a stage controller which moved the stage an assigned distance after each spectrum was collected. Coadditions of 64 scans/spectrum at 8 cm⁻¹ resolution and Happ-Genzel apodization were collected at each pixel with an acquisition time of 20 seconds/spectrum. The total data acquisition time for collecting 400 spectra for each of the three examples to be presented was approximately

2.5 hours. For image reconstruction, each spectrum was reduced to a single intensity value by integrating the infrared absorbance in a specified spectral region and plotting it as a function of spatial location. The 3-dimensional axonometric projections were made by transferring the integrated Nicolet absorbance files to a DOS based PC. The data were loaded into a 3-dimensional array and plotted using Axum™, a technical graphics and data analysis software package commercially available from TriMetrix Inc. (Seattle, WA).

RESULTS AND DISCUSSION

To illustrate the capabilities of IR micro-profiling, a single cellulose acetate fiber on a gold coated glass slide was mounted on the microscope stage. A square 20 x 20 μm aperture masked each pixel area with X, Y stage step sizes of 20 μm . Four hundred 400 pixels were collected. Data were collected, processed, and stored sequentially on the Nicolet computer disk. After examining individual spectra it was determined that the C-H stretching region, 2800 - 3000 cm^{-1} , was distinctive to the fiber and would be the spectral region used for integration. The integrated intensity values were plotted as a function of pixel position in an axonometric projection, Fig. 1. The pixels that exhibit infrared absorptions in the spectral region of interest can be seen to move diagonally along the projection from the lower left to the upper right corner. Figure 1 can be used to estimate the fiber's diameter, 40 μm , and length, 450 μm . However, visible inspection of the sample under 150X magnification indicated that the entire length of the fiber was not profiled. This is confirmed by the significant image intensity at the upper right edge of the figure.

Naturally occurring hand oils can easily be deposited on electronic components and their presence may adversely affect the component's performance. Therefore, a sample fingerprint on a gold coated glass slide was IR micro-profiled to further illustrate the usefulness of the technique. The print was visually inspected at 150X magnification. The oily regions of the print were approximately 240 μm wide and separated by approximately 100 μm of clean, non-oil deposited areas. To adequately map the entire print with a 100 x 100 μm aperture and 100 μm step size would have resulted in the generation of over a million spectra and required over 8 months for data collection with our current system. Therefore, it was decided that only the upper left portion of the print would be imaged. A square 80 x 80 μm aperture was used to mask each pixel area concomitant with 80 μm stage movements. This resulted in the collection of 400 pixels. After the data were collected, processed, and stored, individual spectra were examined. Since all oils deposited were of interest, the entire C-H stretch region, 2800 - 3000 cm^{-1} , was again chosen as the spectral region to be integrated. Any absorbance intensity in this region was considered diagnostic for the presence of oils. The integrated intensity values for each pixel are plotted as a function of position in the axonometric projection, Fig. 2. Pixels corresponding to infrared spectra that contain absorptions in the C-H stretch range can be seen as ridges in the projection that form four concentric curves. The valleys indicate regions of no IR absorption in the diagnostic range, i.e. no oils deposited. These results illustrate that IR micro-profiling can be used to generate a visual image characteristic of a contaminant based on the chemistry of the contaminant. Furthermore, if sufficient computer disk space and data collection time had been allocated, the entire fingerprint could have been mapped.

Rosin-based solder flux is used in some electronics applications. However, the complete removal of flux after its use may be imperative to assure no subsequent reaction or degradation of printed circuit board or

component materials. Therefore, to determine the effectiveness of IR micro-profiling in detecting the presence of solder flux, a thin film of Kester 197 Solder Flux (Litton/Kester Solder, Des Plaines, IL.) was applied to a copper coupon. It was dried and the coupon was then mounted on the microscope stage. Four hundred pixels were collected over a $400 \times 400 \mu\text{m}$ area, mapped with $20 \mu\text{m}$ step sizes and $20 \times 20 \mu\text{m}$ square aperture. The data were collected, processed, and stored. Examination of individual spectra revealed that absorbances characteristic of the compound were present in both the carbon-hydrogen, C-H, and carbonyl, C=O, stretch regions at $2800\text{--}3000$ and $1700\text{--}1800 \text{ cm}^{-1}$, respectively. Therefore, either region could be used for integration. Data reduction and the generation of 3-dimensional projections of both regions yielded similar results. Figure 3 shows the axonometric projection of the integrated IR intensities as a function of pixel position for the C-H stretch region. Pixels with infrared absorption in this region are present in the upper left corner of the projection. The large intensity values on the edge suggests that the contamination continues past the area imaged. This was confirmed by a visual inspection of the sample under $150\times$ magnification. Also, a spot that was not optically visible and measuring approximately 120 by $80 \mu\text{m}$ can be seen centered at $(175, 300 \mu\text{m})$. This confirms that IR micro-profiling is useful for the location and identification of small contaminants that are not visibly apparent.

Identification of an unknown contaminant is often performed by matching the infrared spectrum of the unknown with that of known reference material. The ability to match spectra is a direct function of their quality. One measure of quality is the spectrum's S/N. This can be improved during data collection by either increasing the number of scans per spectrum at each pixel or by increasing pixel size. However, increasing the number of scans at each pixel could make the technique time prohibitive. Furthermore, increasing the pixel size would decrease spatial resolution. Therefore, we examined spectral averaging of data from multiple pixels as a post data collection technique to obtain a higher quality resultant spectrum. This technique is commonly used in gas chromatography/FT-IR applications where a single compound eluates from a gas chromatographic (GC) column over a period of time. A number of infrared spectra may be collected in the time it takes a single compound to leave the column. This results in low absorption intensity spectra due to the relatively low sample concentration associated with each spectrum. Spectra corresponding to a single compound eluting from the GC column are coadded to produce a single spectrum of higher S/N. It has been established that coadding spectra with integrated intensity values equal to or greater than 40% of the largest value results in an increased S/N⁷. This same approach was followed in coadding spectra from various pixel elements. Spectrum A in Fig. 4 is the spectrum of the highest intensity integrated absorbance pixel from the solder flux residue in Fig. 3. The major features of the spectrum indicate that the solder flux is a carboxylate salt with the absorption frequencies related to the O-H stretching vibration at 3380 cm^{-1} , C-H stretch at 2923 and 2860 cm^{-1} , and C=O stretch between 1715 and 1680 cm^{-1} . The sinusoidal type wave present between 2800 and 1850 cm^{-1} is characteristic of interference fringes that appear in spectra of thin samples with parallel sides. These fringes can be eliminated if thicker samples and/or samples with nonparallel sides are used. Spectrum B, Fig. 4, results from averaging spectra that correspond to pixels with integrated absorbance values greater than 40% of the maximum intensity after baseline correction. Examination of Spectrum B reveals that the fringing pattern is no longer apparent and the spectrum appears less noisy than Spectrum A. Reduction of the fringing pattern is due to variance in sample thickness across the mapped area; in some spectra no fringing pattern is present, in others the pattern has a different period. Therefore, averaging these spectra reduces overall

fringe amplitude. Decrease in noise level is confirmed by a decrease of 64% in the root-mean-square (rms) noise between 2200 and 2000 cm^{-1} .

CONCLUSIONS

Infrared micro-profiling is a nondestructive technique that is useful for the location and identification of various types of contaminants common to the microelectronics industry. Furthermore, it can be used to detect contaminants that are not optically apparent. The large amount of spectral information that is generated can be successfully managed by compressing spectra for each pixel element to a single intensity value and plotting these values as a function of pixel position. Therefore, the availability of versatile and flexible software facilitates the usefulness of micro-profiling. Also, spectral quality can be improved, as measured by reducing rms noise 64%, by coadding spectra from different pixel elements with integrated absorbance values exceeding 40% of the maximum intensity.

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Figure 1. Axonometric projection of cellulose acetate fiber infrared micro-profiled using a 20 μm aperture, 20 μm step size.

Figure 2. Axonometric projection of finger print on gold slide infrared micro-profiled using an 80 μm aperture and 80 μm step size.

Figure 3. Axonometric projection of rosin-based solder flux on copper coupon infrared micro-profiled using a 20 μm aperture, 20 μm step size.

Figure 4. Infrared spectra A) corresponding to highest intensity pixel element in Figure 3, B) of averaged spectra in Figure 3 (see text).

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