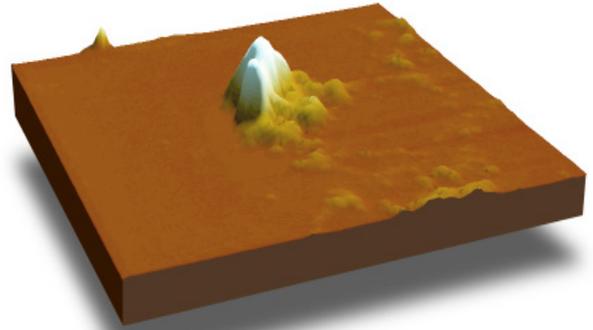


# Characterization of organic nano-contaminants and advanced semiconductor materials by AFM-IR

- nanoIR spectroscopy unambiguously identifies organic nano-contaminants, nanoscale semiconductor features and thin films
- Tapping AFM-IR provides <10 nm chemical mapping spatial resolution with simultaneous mechanical property mapping
- nanoscale IR spectroscopy directly correlates to bulk FTIR libraries for easy material identification



**Image:** AFM height image of an organic contaminant on a silicon wafer.

## Abstract

Organic nano-contaminants are a serious defectivity issue for semiconductor and data storage companies where current characterization techniques have limited capabilities. This note describes the application of the nanoIR2-FS™ to the measurement of such defects and other semiconductor materials. The nanoIR2-FS system is based on a scientific breakthrough technique of acquiring IR spectra at spatial resolutions down to 10 nm, enabling researchers to obtain nanoscale chemical fingerprints of their material. The spectra generated using Anasys Instruments' patented AFM-IR™ technique directly correlates with traditional FTIR spectra, and are thus comparable to standard FTIR libraries. In addition to chemical analysis, the nanoIR2-FS provides complementary mechanical, electrical, thermal, and structural property information with nanoscale spatial resolution.

## Key words

AFM-IR | Nanoscale IR spectroscopy | Organic contamination | Defect analysis | Low-k dielectric | Silicon wafer

## Introduction

Scanning Electron Microscopy coupled with Energy Dispersive X-ray spectroscopy (SEM/EDX) is the industry standard in surface analysis, and offers nanometer scale spatial resolution with semi-quantitative elemental analysis. While this elemental analysis offers useful chemical insight into surface defects and contaminations, it is fairly limited in identifying organic materials.

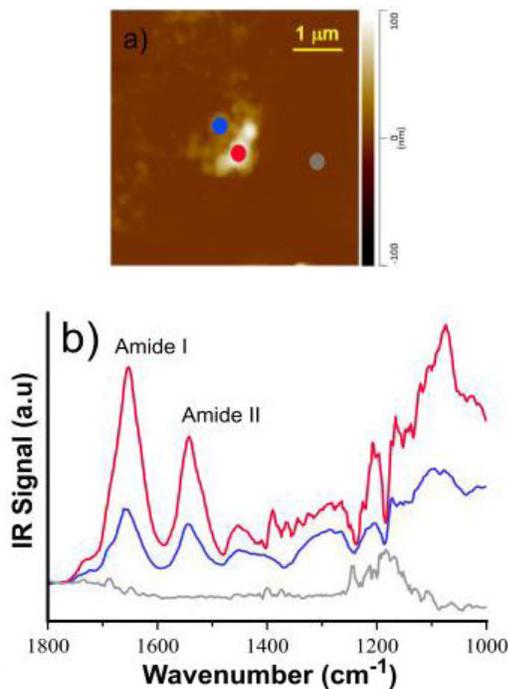
Infrared (IR) spectroscopy is a powerful technique for chemical characterization of organic species that cannot be readily identified by SEM/EDX.

However, traditional IR spectroscopic techniques are limited by Abbe diffraction laws to spatial resolutions between 3 – 10 μm, depending on the technique used.

Atomic Force Microscopy (AFM) is a widely used nanoscale imaging technique which provides the user with a high spatial resolution topographic map of a sample surface. Until now, the major drawback of AFM was its inability to chemically characterize the material underneath the tip. When combined with an IR source, the resulting AFM-IR technique breaks the diffraction limit of conventional IR spectroscopy by orders of magnitude, while still preserving high resolution imaging capabilities of AFM.

## Nanoscale organic contaminants

To demonstrate nanoscale chemical characterization capabilities on the nanoIR2-FS, contaminated silicon wafers were prepared using known materials typical of those found in semiconductor fabrication environments and analyzed. For each sample, high resolution tapping mode AFM images were acquired to locate the contaminants, followed by respective AFM-IR measurements.

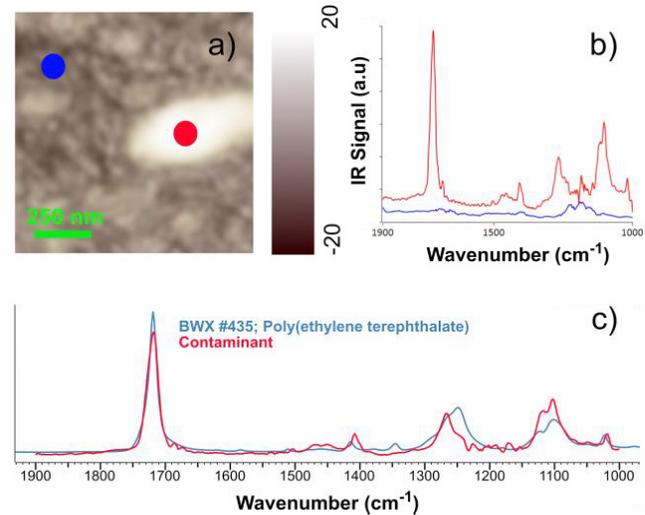


**Figure 1.** (a) AFM height image of human skin residue on silicon wafer. (b) Corresponding AFM-IR spectra; Amide I and II bands are indicated.

The AFM height image (Fig. 1a) illustrates the thickness variation (20-100 nm) of the contaminant residue (human skin tissue) on the wafer. After locating a point of interest in the AFM image, the probe is positioned in the desired location, and the laser wavelength is scanned to acquire the AFM-IR spectra (Fig. 1b). Spectra were then collected at sites with varied sample thickness. As expected, the observed IR intensities differed with sample thickness; however, the overall signal to noise ratio is sufficient to accurately identify the material, even at 20 nm thickness, reflecting the excellent sensitivity in detection of thin samples.

New **FASTspectra** capabilities on the nanoIR2-FS enable faster acquisition of spectra over the full IR tuning range, allowing for a reduction in spectral acquisition time by a factor of 10. This is accomplished by the laser source sweeping over its range, while the cantilever oscillation amplitude is measured simultaneously with the wavelength change, illustrated in figure 2.

In order to demonstrate the correlation to conventional FTIR spectra, the AFM-IR spectra collected were compared against a common FTIR database (KnowItAll, Bio-Rad Inc.). The ~30 nm tall contamination residue was positively identified as polyethylene terephthalate (PET), a polymer typically used in polyester fabrics (Fig. 2c).

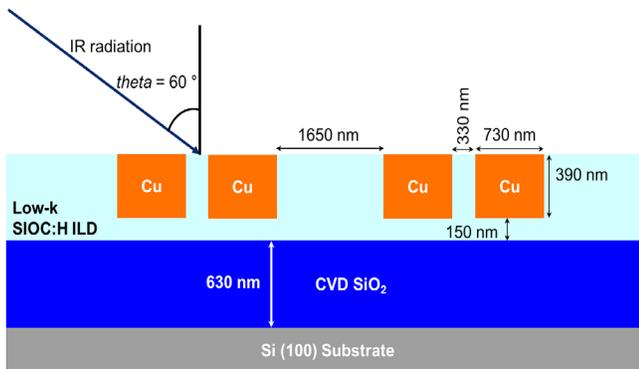


**Figure 2.** (a) AFM height image of a wafer with organic residue. (b) AFM-IR spectra on (red) and off (blue) the contaminant. (c) Positive bulk FTIR database identification of the surface contaminant as PET.

## Process induced defects<sup>1</sup>

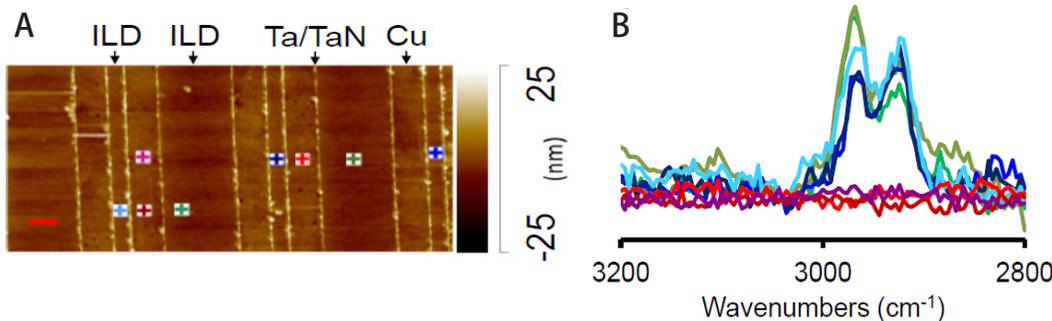
Low-k a-SiOC:H/Cu interconnects are a useful example of the susceptibility of contamination during manufacturing, due to the sensitivity low-k a-SiOC:H exhibits in response to slight chemical modifications induced during fabrication. The structure of the interconnect device designed for this experiment is shown in figure 3. The average width of the low-k a-SiOH:C varies from 1650 nm to 330 nm, well under the spatial resolution limits of conventional IR spectroscopy, testing the capabilities of AFM-IR.

Figure 4 shows the AFM topography image of the low-k a-SiOH/Cu structure; the markers on the image represent the locations for subsequent AFM-IR measurements. Each AFM-IR spectrum was collected from a different portion of the interconnect, including both exposed regions of the a-SiOC:H dielectric, as well as Copper. Spectra were also collected from narrow (390 nm) and wide (1650 nm) regions of the a-SiOC:H interconnect domains.

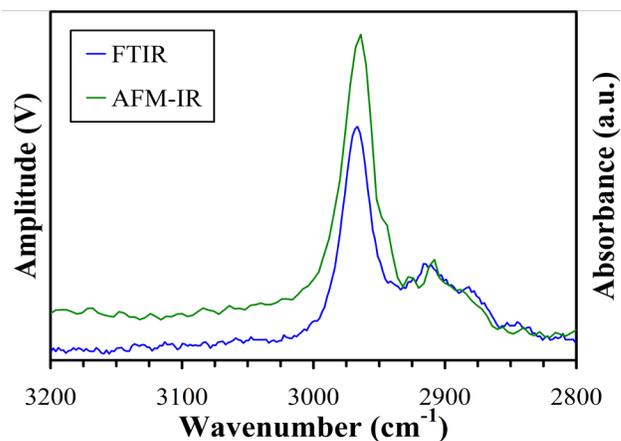


**Figure 3.** Schematic diagram of the cross section of the Low-K SiOC:H-Copper interconnect structures fabricated for this experiment.

Close inspection of the spectra (Fig. 4b) reveals subtle differences in the C-H stretch region of the narrow and wide regions of the a-SiOC:H dielectric. The asymmetric methyl CH<sub>3</sub>-stretching vibration at 2968 cm<sup>-1</sup> exhibited reduced intensity relative to the asymmetric methylene CH<sub>2</sub>-stretching vibration at 2924 cm<sup>-1</sup> for the narrow regions of the a-SiOC:H dielectric. For the wide regions of the a-SiOC:H dielectric, the ratio of peak intensity for the CH<sub>3</sub>/CH<sub>2</sub> modes was closer to that observed by both bulk FTIR and AFM-IR of an



**Figure 4.** (a) AFM height image of the interconnect structure. (b) AFM-IR spectra (2800 cm<sup>-1</sup> – 3200 cm<sup>-1</sup>) of corresponding regions on the interconnect structure.

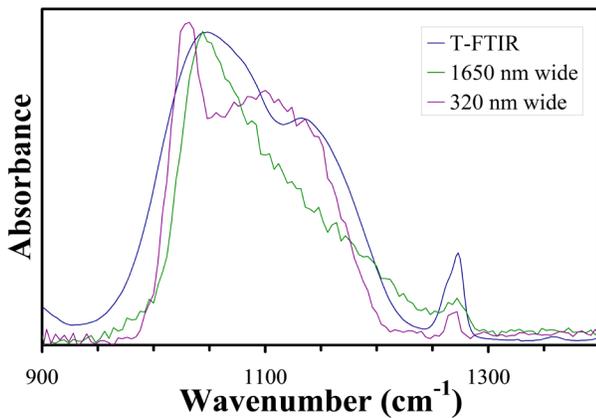


**Figure 5.** Bulk Transmission FTIR and AFM-IR of C-H stretching band from 1 micron thick layer of a-SiOC:H.

unpatterned a-SiOC:H dielectric control sample (Fig. 5).

In order to confirm the differences observed in the C-H spectral regions of narrow vs wide a-SiOC:H regions aren't due to other phenomena such as optical effects, AFM-IR spectra were also collected for the Si-O-Si stretching region.

Focusing on figure 6, comparative differences were also observed in the AFM-IR spectra of the Si-O-Si stretch from the wide versus narrow regions of the a-SiOC:H dielectric similar to the C-H stretch. The primary observation is the relative difference in absorbance for the Si-O-Si cage mode at 1050 cm<sup>-1</sup>, that is more prominent in the narrow regions of the a-SiOC:H dielectric relative to the wide regions. Relative to the bulk transmission FTIR spectra of the unpatterned a-SiOC:H dielectric, the cage mode for the 320 nm wide patterned a-SiOC:H region is also downshifted to lower wavenumbers and the network Si-O-Si stretching mode appears to have a more narrow line width.



**Figure 6.** AFM-IR spectra of the asymmetric Si-O-Si stretch and symmetric Si(CH<sub>3</sub>)<sub>x</sub> deformation mode from both narrow (390 nm) and wide (1650 nm) regions of the a-SiOC:H dielectric. Note: a bulk transmission FTIR spectrum of the unpatterned a-SiOC:H dielectric is also included for comparison.

These combined results support the suggestion that the significant modification of the a-SiOC:H chemical structure occurs in the narrow regions of the a-SiOC:H/Cu interconnect structure relative to the wide regions. Numerous investigations of low-k a-SiOC:H materials have shown a tendency for these materials to lose terminal methyl (CH<sub>3</sub>) groups during the plasma etching, ashing, and CMP steps utilized to fabricate inlaid Cu wiring. The loss of such terminal organic groups in low-k a-SiOC:H dielectrics typically results in the formation of new chemical bonds and a more SiO<sub>2</sub> like composition.

In this regard, the decreased intensity of the CH<sub>3</sub> mode (Fig. 6) in the narrow regions of the a-SiOC:H dielectric is consistent with the loss or modification of terminal CH<sub>3</sub> groups during the plasma etch and ashing processes utilized to pattern the dielectric. It is also consistent with the greater absorbance observed for the Si-O-Si cage mode in the narrow a-SiOC:H regions.

## Conclusions

AFM-IR spectra collected from common types of nanoscale contamination were able to be easily identified as biological material from the presence of the amide absorption bands; additionally, any spectra of unknown materials generated using AFM-IR can be readily searched in a conventional FTIR database for easy identification.

AFM-IR also excels in the characterization of nanoscale defects induced during fabrication processes. Low-k a-SiOC:H/Cu interconnect structures with features of ~330 nm were examined. Significant chemical differences were observed for narrow low-k regions when compared to thick regions. Due to the broad spectral range available for AFM-IR, these differences were observed in both the Si-O-Si and CH stretching regions, unlike conventional IR spectroscopy where limited spatial resolution cannot uncover these subtleties.

Nanoscale infrared spectroscopy via AFM-IR shows great potential as a characterization tool for the identification of nanoscale organic contaminants and defects in the nanoelectronics industry. It offers superior sensitivity and spatial resolution when compared to previous industry standard bulk characterization techniques.

## References

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info@anaysinstruments.com      Tel: +1 (805) 730 3310  
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