Application Notes AN MIC416

Diamond Layers Analysis by Raman and FTIR Spectroscopy

The exciting properties of diamond layers

Diamond has many outstanding physical and chemical properties and has fascinated humans for thousands of years. It is the hardest material known in nature, has the highest room-temperature thermal conductivity and is virtually chemically inert.

Despite these amazing material properties, it was only used as a gemstone or cutting tool for centuries. More recently, however, the application of thin diamond coatings directly onto workpieces has opened the door to exciting and new technical applications.

Chemical vapor deposition changed the game

The application of diamond layers on non-diamond substrates has been possible since the early 1980s thanks to advances in chemical vapor deposition (CVD).

CVD processes produce uniform coatings with high hardness and good adhesion, but require very high temperatures. Thus, only temperature resistant substrates can be coated with a true, crystalline diamond coating.

Fortunately, an amorphous diamond-like carbon (DLC) coating can be used instead, which does not require high temperatures and can be applied to almost any material.

Keywords	Instrumentation and Software
Diamond like carbon (DLC)	LUMOS II FTIR microscope
Chemical vapor deposition	SENTERRA II Raman microscope
Hard coating of tools	OPUS Software
Drills and cutters	OPUS/3D

About diamond layers and DLC films

Both diamond and DLC films are innovative coating systems that share the characteristics typically associated with a macroscopic diamond. They combine excellent wear resistance and micro-hardness with an extremely low coefficient of sliding friction, reaching or even exceeding the values of Teflon (PTFE).

It is therefore predestined for use on moving parts that are subject to particularly heavy wear. Typical applications include the coating of drills, milling tools, gear wheels, shafts, bearings and razor blades. Their exceptional properties make diamond and DLC coatings a great choice for improving thermal conductivity, biocompatibility and corrosion resistance of treated materials.

The chemistry behind DLC

Chemically, both CVD diamond and DLC are carbon materials with different sp^3-to-sp^2 ratios and different contents of hydrogen and other foreign atoms. These synthesis-dependent factors heavily influence the chemical and physical properties of a diamond and DLC coatings and must therefore be closely observed.

While a higher sp^3 content makes the carbon harder, an increased hydrogen content will have an inverse effect and reduce its hardness. Naturally, another important factor is coating's thickness, as a thicker coating is more robust and therefore more effective.

Analytical tools for DLC film analysis

In the field of optical spectroscopy, there are two techniques that provide a broad range of information about DLC and diamond films, namely Fourier-Transform-Infra-Red (FTIR) and Raman spectroscopy.

FTIR spectroscopy can be used for the layer thickness-determination of such films.[1] For smaller structures in the micrometer range, FTIR microscopes provide excellent results and enable reliable layer thickness determinations.

The FTIR investigations in this application note were peformed by the LUMOS II FTIR imaging microscope shown in Figure 2a.

Raman spectroscopy is one of the most powerful tools for carbon allotrope analyses.[2] It allows differentiating the numerous carbon types and provides essential structural information, e.g. the important sp^3/sp^2 ratio. Furthermore, Raman microscopy is able to acquire Raman spectra in the submicrometer range.

The Raman investigations in this application note were peformed by the confocal SENTERRA II Raman microscope shown in Figure 2b.

Figure 1: The carbide cutter (bottom left) with an cross section embedded in resin (top right).

Sample description

The following measurements were performed on a milling cutter used for roughing and finishing machining of carbon fiber reinforced polymer (CFRP). It is made from solid carbide and was coated with a thin layer of diamond via a hot-filament CVD (Figure 1).

Although these coatings can significantly increase the service life of coated materials, it is important to choose the right manufacturing parameters in order to obtain a reliable high product quality. As mentioned before, the most relevant parameters are layer thickness and the sp^2/sp^3-ratio, which are both easily determined by vibrational spectroscopy.

In the following, we will show the analysis of the cutter with both Raman and FTIR microscopy. For the Raman analysis of the layer cross-section, the cutter was embedded into resin and cut (see Figure 1, upper right corner).

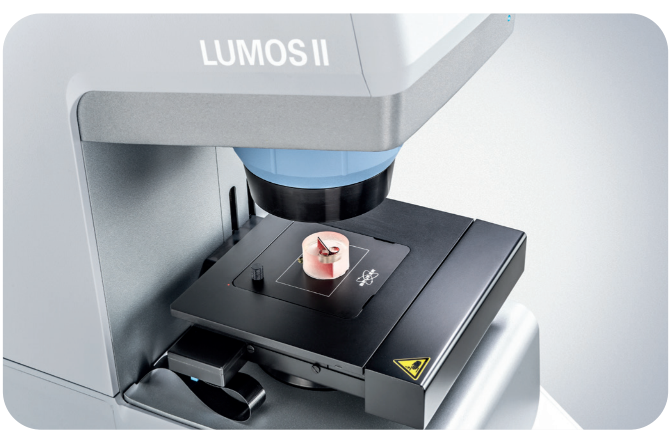

Figure 2a: LUMOS II FTIR imaging microscope focuses heavily on an intuitive user experience, peak efficiency and excellent visual and spectroscopic performance.

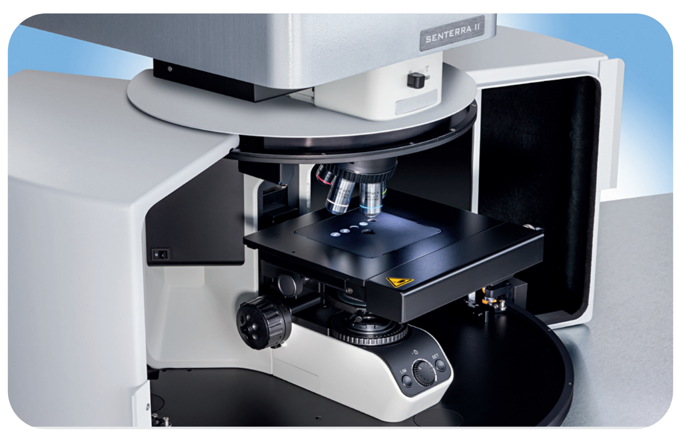

Figure 2b: SENTERRA II confocal Raman imaging microscope. It is completely automated and features an impressive permanent calibration (SureCAL™) that keeps the device calibrated even after changing the grating or switching between lasers.

Diamond layer thickness determination by FTIR

Reflection measurements on optically transparent thin films lead to so-called interference-induced fringes. These are caused by light being reflected both from the surface of the coating layer and from the substrate below the coating.

As a result, the light reflected off the substrate travels a longer path, which leads to optical retardation. Wavelength-dependent interference then leads to a sinusoidal baseline of the spectrum.

The thickness of the CVD diamond layer was determined by measuring nine FTIR spectra, one measurement point on each edge of the above described cutter. The measurements were performed in reflection, with an MCT detector and a scan time of about 4 seconds per spot.

FTIR Spectra

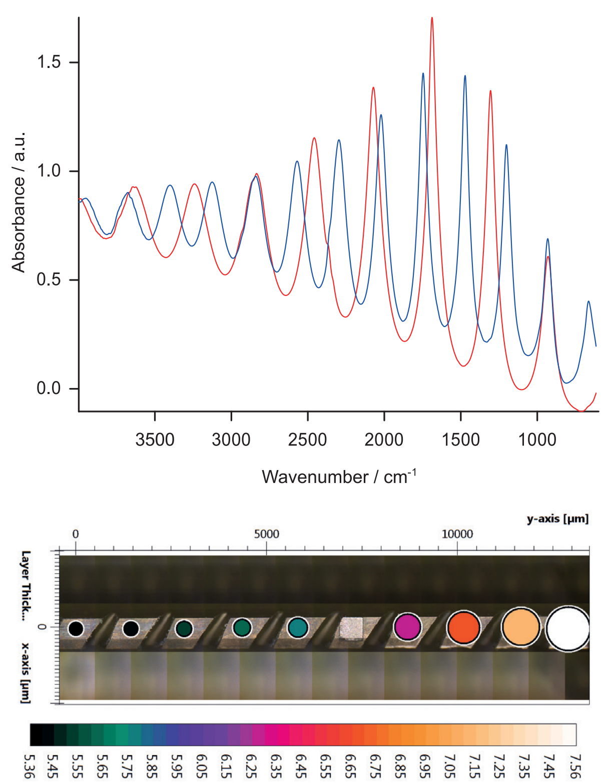

Figure 3: FTIR spectra with fringes (a) and chemical image of the cutter with color coded layer thickness (b).

Figure 3a shows fringes of two different spectra. The red spectrum was measured at the tip of the cutter, the blue one closer to the shaft.

Figure 3b shows the microscopic image of the cutter together with the color and size coded sample thickness information that was automatically calculated via OPUS.

The brighter and larger the dots, the higher the thickness of the layer. A closer look at the results reveals a range between 5.4 and 7.5 µm, showing a gradually increase in thickness in the direction of the cutter's tip.

What is sp, sp^2 and sp^3 hybridization?

In chemistry, orbital hybridization is the concept of mixing atomic orbitals into new hybrid orbitals suitable for the pairing of electrons in valence bond theory.

- sp hybridized carbon atoms are found in triple bonds (e.g. acetylene or other alkynes).
- sp^2 hybridized carbon atoms exhibit double bonds and are of linear (CO_2) or planar (graphite) geometry.
- sp^3 hybridized carbon atoms show a tetrahedral geometry, e.g. in diamond, CH_4 and polyethylene.

Diamond film quality assessment by Raman

The Raman spectra of carbon generally show a G-band ("Graphite"-band, around 1575 cm^{-1}) and in many cases also a defect related D band ("Defect"-band, around 1355 cm^{-1}). Whereas the G band arises from stretching any pair of sp^2 sites (planar rings or chains), the D-mode is the breathing mode of sp^2 sites in rings.[3]

In contrast, diamond only exhibits one band at 1332 cm^{-1} that originates from the sp^3 hybridized, tetrahedral carbon lattice. The relative intensity of the diamond-band to the intensity of the G-band can thus be used as a coarse measure for the quality of the diamond coating.[4]

Figure 4 shows two example spectra measured by 532 nm excitation on two different locations on the cutter. It is obvious that the magenta colored spectrum contains a higher amount of sp^3 carbon, since the diamond-band of the dark-blue spectrum is considerably lower.

Raman Spectra

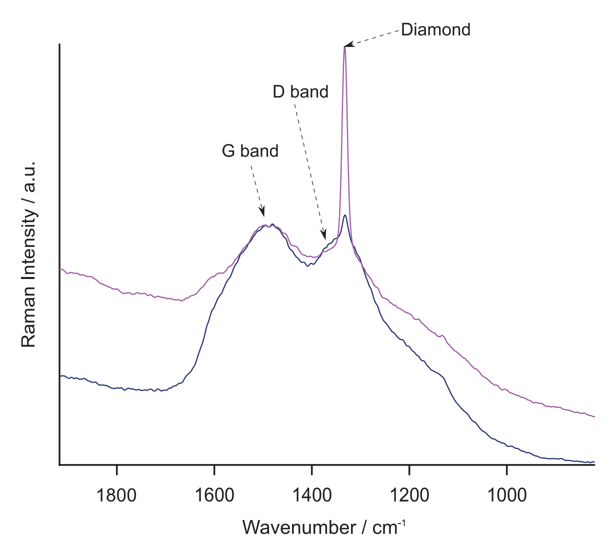

Figure 4: Selected Raman spectra of the cutter's diamond coating with a high (magenta) and low (dark blue) sp^3 content.

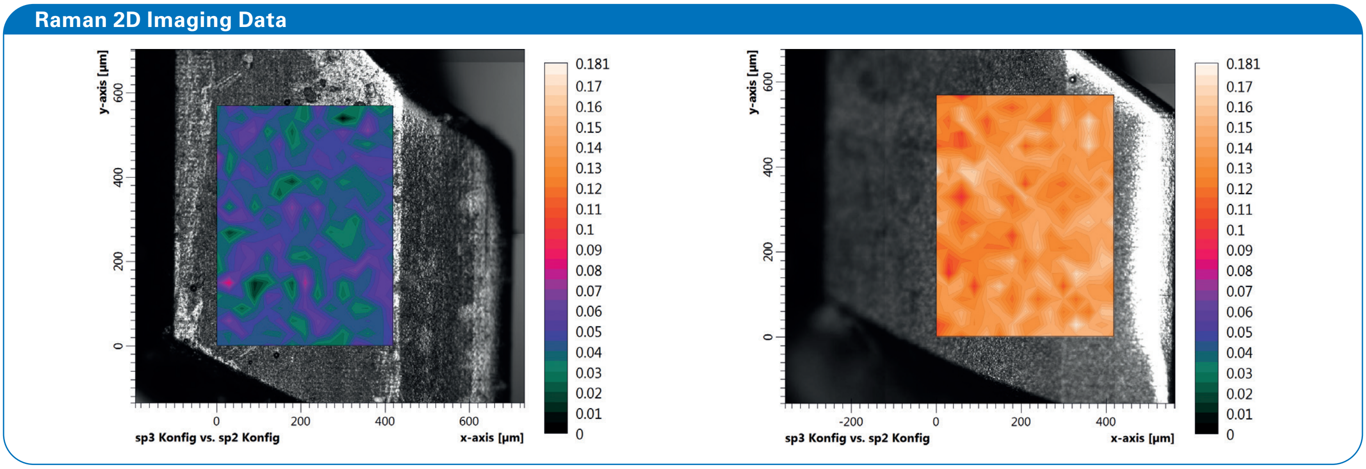

Figure 5: Comparison of the sp³ content of two different samples via chemical imaging.

Raman comparison of different coating procedures

For comparison, chemical images of two differently coated samples were measured by scanning a larger area on the surface with the Raman laser.

Both samples were subsequently evaluated the same way by integration both the diamond band (sp³ carbon) and the G-band (sp² carbon) using the ratio (sp³/sp²) as a measure.

The result is shown in figure 5. The sp³ content is color coded: the brighter the color the higher the sp³ content. It is evident, that the sample on the right has higher sp³ content and is thus expected to be harder.

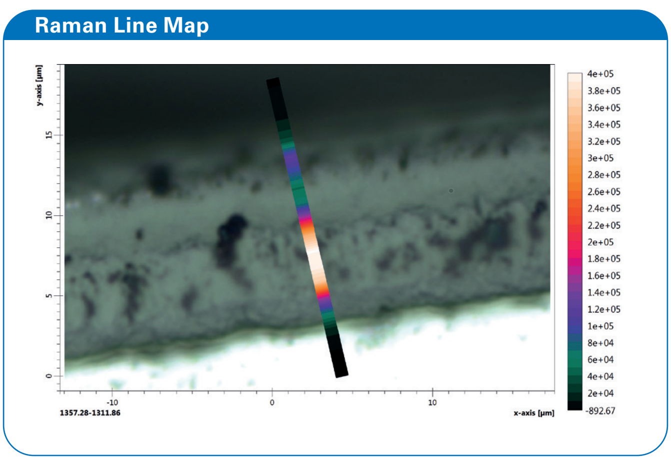

Figure 6: Line scan through the cross section of the cutter visualizing the sp³-content.

Finally, Figure 6 shows the cross-section of the diamond layer from the sample with the lower sp³ content. Different zones can already be recognized by the visual image. The analysis of the sp³/sp² ratio verifies the assumption, that the coatings's distribution is not homogeneous and that there are different areas of varying sp³ content.

Summary

Raman and FTIR micro spectroscopy provide important information about DLC quality related parameters. such as the sp²/sp³ ratio or the film's thickness.

Especially Raman microscopy is suitable to differentiate the different types of carbon allotropes. Both methods can be used to generate chemical images that provide two-dimensional information about the chemical and/or physical properties of the sample.

References

[1] Bruker Application Note AN MIC415, *Quality Control of DLC Layers* **2017**.
[2] Bruker Application Note AN R535, *Analysis of Graphene with Raman Spectroscopy* **2019**.
[3] J. Filik, *Spectroscopy Europe* **2005**, 17(5).
[4] L. Golunski, M. Sobaszek, M. Gardas, M. Gnyba, R. Bogdanowicz, M. Ficek, P. Plotka, *Act. Phys. Pol. A.* **2015**, 128, 136.

Bruker Scientific LLC
Billerica, MA · USA
Phone +1 (978) 439-9899
info.bopt.us@bruker.com

Bruker Optics GmbH & Co. KG
Ettlingen · Germany
Phone +49 (7243) 504-2000
info.bopt.de@bruker.com

Bruker Shanghai Ltd.
Shanghai · China
Tel.: +86 21 51720-890
info.bopt.cn@bruker.com

www.bruker.com/optics