RENISHAW
apply innovation™

Indentation and Raman spectroscopy combined

Combine the power of inVia™ with nanoindentation measurements and directly correlate mechanical and tribological properties with chemical information such as crystallinity, polymorphism, phase and stress/strain.

Raman spectroscopy is a powerful technique commonly used to study the composition, uniformity, strain, stress and disorder of materials. However, it does not directly characterise physical, mechanical and tribological properties.

Renishaw and Hysitron have combined an inVia confocal Raman microscope with a TI 950 TriboIndenter, producing a system with the capability to directly correlate mechanical property measurements with comprehensive chemical analyses, *in situ*.

Collect high quality correlated data from your samples

- Nano-scale indentation, scratch and wear analysis
- Determine local, mechanical and tribological properties
- *In situ* SPM for surface topography imaging
- Raman spectroscopy for chemical and structural properties

One combined system

Using Renishaw's fibre optic technology, inVia can couple to a range of nanoindentation systems, such as the TI 950 TriboIndenter® from Hysitron. Such pairings result in a combined instrument that provides greatly enhanced characterisation capabilities.

For maximum efficiency, you can analyse the same location on the sample by indentation and Raman spectroscopy without needing to transfer and orient samples between instruments. The inVia and nanoindenter can also be used independently and simultaneously, without any compromise in individual performance.

A TI 950 TriboIndenter (Hysitron, Minneapolis, Minnesota, USA, www.hysitron.com) coupled to an inVia confocal Raman microscope via a separate fibre optic probe.

Gain greater insights into mechanical properties and deformation behaviour at the nanoscale and microscale

Diamond-like carbon (DLC) is a class of metastable amorphous materials with many attractive mechanical, chemical, tribological, optical and electrical properties. These properties vary depending on the relative abundance of sp^3 versus sp^2 bonding in their structures. DLC films can rival diamond in terms of mechanical performance, such as high wear resistance, very low coefficient of friction, high hardness and high elastic modulus.

The following study of diamond-like carbon films demonstrates the power of this combined Raman/indenter system.

Raman and nanoindentation studies of three DLC films

Three DLC films (a, b and c) were studied. All were deposited on silicon wafers using different deposition techniques. Raman point spectra were acquired from each film, and then nanoindentations made to generate indentation curves that reveal the hardness and the modulus of each film. The variations in the indentation curves of the three DLC coatings correlate with the differences observed in each Raman spectrum (Figures 1 and 2).

Sample c is the thinnest DLC film (40 nm), making this sample the softest of all three, as the indentation is sampling the softer silicon substrate as well as the harder DLC film. This also produces the ‘elbow’ in the unloading portion of the indentation curve (Figure 2). The thinness of the coating of sample c is confirmed by the presence of a silicon feature in the Raman spectrum; this is from the substrate, and appears because light can penetrate the thin DLC coating of sample c. This feature is absent in the other spectra because of the much thicker coatings involved.

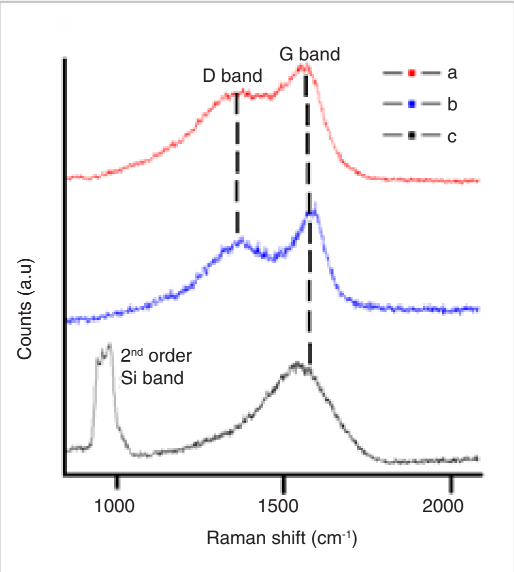

Figure 1. Raman spectra of DLC samples a, b and c.

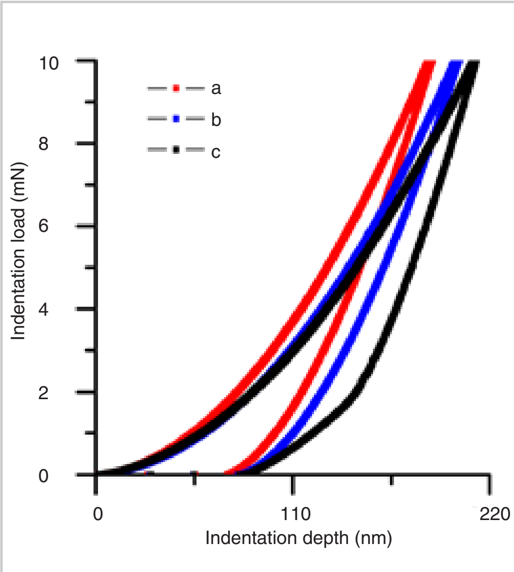

Figure 2. Indentation curves for samples a, b and c. A maximum normal force of 10 mN was used for each sample.

Raman and SPM imaging of a wear pit

The behaviour of the coating was investigated further by performing a wear test on sample c (Figure 3). The wear pit was generated by traversing a Berkovich indenter five times over the surface at a 1 Hz rate, with a 500 μN normal force. The wear feature can be seen in the optical image (Figure 3A), in the scanning probe microscopy (SPM) image (Figure 3B), and in the Raman image (Figure 3C). Raman spectra are also shown for three key positions on the sample: inside the wear pit, at its edge, and on virgin material away from the pit.

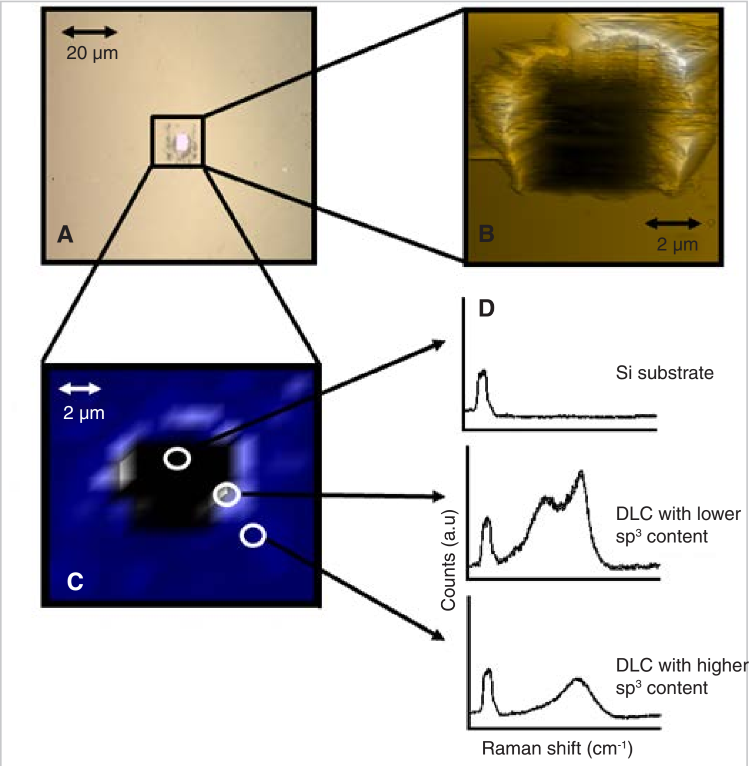

Figure 3. (A) Optical white light and (B) scanning probe microscopy (SPM) images of a wear pit on sample c. (C) In situ Raman image showing the distribution of the disordered (D band at 1360 cm^{-1}) and graphitic (G band at 1580 cm^{-1}) carbon band areas as well as the second order silicon band area at 960 cm^{-1}. The colour code is as follows: 1360 cm^{-1} D band (white), 1580 cm^{-1} G band (blue) and 960 cm^{-1} (black) second order silicon band. (D) Corresponding Raman spectra extracted from three different locations, as indicated on the Raman image.

The lighter appearance of the centre of the optical image (A), and the height change in the SPM image (B), suggest that the film has been removed and the silicon substrate exposed in the pit. The Raman spectrum (D) confirms this, as it exhibits features from silicon, but not carbon.

Debris is visible at the edges of the pit, with a corresponding increase in height shown in the SPM image. Comparison of the Raman spectra from the edge of the pit and virgin material reveals an additional peak present in the debris spectrum, associated with disordered carbon. This indicates that wear has not just moved coating material to the edge of the wear pit, but deformation has changed it from an sp^3 dominated structure to a more defective graphitic sp^2 structure.

Experimental conditions

Hysitron's TI 950 TriboIndenter and Renishaw's inVia confocal Raman microscope are coupled using Renishaw fibre optic probes. These are directly mounted to Hysitron's granite bridge, for stability. Using this configuration, you can acquire from the sample: an optical white light image; an SPM image; Raman point spectra; Raman images; and nano- and micro-indentation data, all without having to transfer the sample between instruments.

Raman spectroscopy: the Raman measurements were made with 514 nm excitation (Ar^+ ion laser), with a 50× ultra-long working distance objective lens. Raman point spectra were acquired on each DLC film. The wear pit image was generated by point mapping.

Nanoindentation: indentation was performed in continuous measurement regime (CMX) at maximum indentation load of 10 mN. This generated the depth profiles of storage modulus and indentation hardness of the DLC films. For the wear pit, the 40 nm DLC film on sample c underwent nanoWear™ testing at a constant normal force of 500 μN. The Berkovich probe passed five times over the surface at a reciprocating rate of 1 Hz. The 6 μm × 6 μm topographic image was post-scanned *in situ* using scanning probe microscope (SPM) mode.

Renishaw plc

Spectroscopy Products Division
New Mills, Wotton-under-Edge,
Gloucestershire GL12 8JR
United Kingdom

T +44 (0) 1453 524524
F +44 (0) 1453 524901
E raman@renishaw.com

www.renishaw.com/raman

RENISHAW
apply innovation™

Conclusions

These studies show that indentation and Raman spectroscopy provide complementary mechanical and chemical information that scientists and engineers can use to better understand diamond-like carbon films. With the combined Renishaw/Hysitron instrument you can make measurements in situ, at the same location, thereby studying not only the spatial variation in coating properties, but also changes associated with microscopic features such as wear pits. The combined instrument also saves you time by removing the need to transfer and orient samples between instruments.

Acknowledgements

We thank Prof. Virginia Lea Ferguson for hosting our team at University of Colorado, Boulder, and giving us time on her instrument.

Sample courtesy of Prof. Yeau-Ren Jeng and Dr Mehdi Rouhani, NCCU Taiwan

Contact your local Renishaw office or agent now for further details or download inVia product details from **www.renishaw.com/invia**

inVia. The ideal Raman-indentation analysis tool

- Combine inVia with nanoindentation measurements
- Nano-scale indentation, scratch and wear analysis
- Determine local, mechanical and tribological properties
- *In situ* SPM for surface topography imaging
- Raman spectroscopy for chemical and structural properties

Laser safety

Class 3B laser product. Visible and invisible laser radiation. Avoid exposure to beam.

The Renishaw inVia confocal Raman microscope.

Renishaw. The Raman innovators

Renishaw manufactures a wide range of high performance optical spectroscopy products, including confocal Raman microscopes with high speed chemical imaging technology, compact process monitoring Raman spectrometers, structural and chemical analysers for scanning electron microscopes, solid state lasers for spectroscopy and state-of-the-art cooled CCD detectors, for both end-user and OEM applications.

Offering the highest levels of flexibility, sensitivity and reliability, across a diverse range of fields and applications, the instruments can be tailored to your needs, so you can tackle even the most challenging analytical problems with confidence.

A worldwide network of subsidiary companies and distributors provides exceptional service and support for its customers.

Please visit www.renishaw.com/nanoindentation for more information.