AIRsight™ Infrared/Raman Microscope

Application News

Nondestructive Analysis of Diamond-Like Carbon (DLC) Film Using AIRsight Infrared/Raman Microscope

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User Benefits

- The AIRsight Infrared/Raman microscope enables analysis of carbon materials, which cannot be analyzed with an infrared microscope.
- Use of the curve-fit function makes it possible to evaluate film quality from various viewpoints, such as the crystallinity and hydrogen concentration of DLC films.

■ Introduction

Diamond-like carbon (DLC) films are amorphous hard films consisting of carbon and hydrocarbon, and are a material that occupies an intermediate position between graphite, which is characterized by sp^2 bonding, and diamond, which has sp^3 bonding. Because DLC films have a number of excellent features, they are used in all types of familiar products. For example, DLC films are formed on the edge of cutting tools and surface of bearings owing to their excellent wear resistance and low friction property. DLC films are also used on the inner surface of easily-oxidized beverage containers, utilizing their outstanding gas barrier property. Because DLC films are used in such a wide range of applications, the carbon bonding state and hydrogen concentration in the film are adjusted to modify the film properties as required by the intended application. However, when producing or receiving DLC products, it is important to measure and control the bonding state and hydrogen concentration, as these properties may also cause variations in the properties of the film.

Raman spectroscopy is used as a quality control technique for DLC films because the bonding state and structure of carbon materials can be captured with good sensitivity. In comparison with X-ray photoelectron spectroscopy (XPS), which is another DLC film analysis method, Raman spectroscopy offers the advantages of simple preparation for measurements and nondestructive measurement with minimal danger of damaging the sample. An example of analysis of a DLC film by XPS may be found in Application News No. K78 [1].

The Shimadzu AIRsight Infrared/Raman microscope, which is an integrated instrument including both an infrared microscope and a Raman microscope, supports analysis of various parts and materials, such as carbon materials, with a single instrument. Fig. 1 shows the appearance of AIRsight. AIRsight not only mutually compensates for the strengths and weakness of infrared spectroscopy and Raman spectroscopy, but also enables highly accurate qualitative analysis by making it possible to measure the same sample by both methods [2]. Moreover, because AIRsight is a microsystem, pinpoint measurement of micro regions of parts that appear externally to be defective and other target positions is possible. This article introduces an example in which the Raman measurement function of AIRsight Infrared/Raman microscope was used to analyze DLC films deposited on silicon wafers.

Fig. 1 Appearance of AIRsight™

■ Raman Spectrum Evaluation Items for DLC Films

Table 1 presents a summary of the evaluation items investigated in this experiment and their related properties. Fig. 2 shows the indices that were used here, where Item I is the intensity from the corrected baseline to the top of the peak, N is the intensity from zero intensity to the corrected baseline, and FWHM is the half-width.

Table 1 Raman Spectrum Evaluation Items for DLC Films

Item	Content	Related properties	Reference
I(D)/I(G)	Intensity ratio of the D band (around 1350 cm^{-1}) and G band (around 1550 cm^{-1}).	Disorder of the crystal structure (sp^3/sp^2 ratio)	(3)
FWHM (G)	Half-width of the G band	Crystallinity (sp^2 bond), Young's modulus, density	(4)
log(N(G)/I(G))	Ratio of baseline and intensity at the position of the G band	Hydrogen concentration	(5)

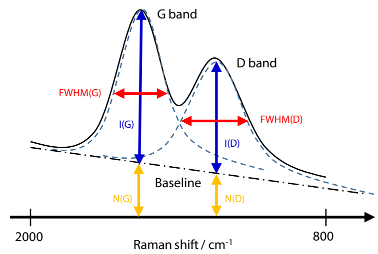

Fig. 2 Schematic Diagram of Raman Spectrum Evaluation Items for DLC Films

I(D)/I(G) is an index expressing the disorder of the crystal structure. In the Raman spectrum of a DLC film, the G (Graphite) band appears at around 1550 cm^{-1} and the D (Disorder) band appears at around 1350 cm^{-1}. The G band originates from the vibration of all sp^2 bonds, including both the chain type and cyclic type, whereas the D band derives from the vibration of sp^3 bonds, which occur as a result of disordering of the crystal structure. The disorder of the crystal structure can be evaluated quantitatively by evaluating the intensity ratio of the G band and the D band obtained by waveform separation of the Raman spectrum of the DLC film.

The half-width of the G band (FWHM(G)) is an index that represents the crystallinity of the sp^2 bonds, and it is known that FWHM(G) generally becomes wider if the degree of amorphousness increases. Therefore, it is possible to evaluate the crystallinity of a DLC film by confirming the half-width. Since it has also been reported that FWHM(G) has a positive correlation with density and Young's modulus, it can be said that this is an effective index for estimating the mechanical properties of films by a noncontact approach.

log(N(G)/I(G)) is an index of the hydrogen concentration. If a DLC film that contains hydrogen is measured by Raman spectroscopy, the baseline will rise by the equivalent of the N(G) value in Fig. 2 due to the effect of fluorescence. However, it should be noted that the fluorescence intensity is also influenced by other arbitrary conditions, such as laser intensity, in addition to the hydrogen concentration. It is possible to evaluate the hydrogen concentration by eliminating the influence of these arbitrary conditions by taking the ratio of the Raman disorder intensity I(G) and the intensity of the fluorescence component N(G).

■ Measurement Sample and Measurement Conditions

For this experiment, two types of silicon wafers on which DLC films were formed were prepared as the measurement samples. Film-forming was done by chemical vapor deposition (CVD) in both cases, using CH_4 or C_2H_2 as the respective feedstock gases. In order to investigate possible variations in the film quality, the samples were measured at two positions, that is, near the center (Center) and near the outer edge (Periphery). Table 2 shows the measurement conditions.

Table 2 Measurement Conditions

Instruments	: IRTracer™-100, AIRsight
Raman Spectrometry	
Accumulation	: 100
Exposure Time	: 1.0 sec
Objective Lens	: 50x
Excitation Wavelength	: 532 nm
Detector	: CCD

■ Data Analysis Using Curve-Fit Function

As a standard feature, the software AMsolution used to control AIRsight includes a "curve-fit" function which separates the overlapping peaks of the infrared spectrum and the Raman spectrum on the software. Table 3 shows the setting conditions for curve fitting in this experiment. Once the conditions are set, the software carries out all subsequent calculations automatically and outputs the result of the optimum peak separation, held to within the maximum allowable error. In addition, the position and intensity, half-width, and peak area of the separated peaks can also be calculated, making it possible to conduct analyses such as intensity comparisons and the like. Fig. 3 is an example of the Raman spectrum of a DLC film in which a data analysis was carried out using the curve-fit function. This figure shows the results of the data analysis of the Raman spectrum measured near the sample center for the silicon wafer on which the DLC film was deposited using the CH_4 gas. From Fig. 3, it can be understood that the D band and the G band of the DLC film can be separated by a simple operation by using the curve-fit function.

The Raman spectra at near the periphery of the above-mentioned sample and at near the center and periphery of the silicon wafer with the film formed using C_2H_2 gas were also measured in the same manner, but due to space limitations, the results will be omitted here.

Table 3 Setting Conditions for Curve Fitting

Peak Positions	: 1350 cm^{-1}, 1551 cm^{-1}
Half-width	: 100 cm^{-1}
Parameter Fixing	: Not fixed
Function	: Gaussian
Baseline Order	: 1st order
Wavenumber Range	900 - 1800 cm^{-1}
Maximum Error	: 0.01

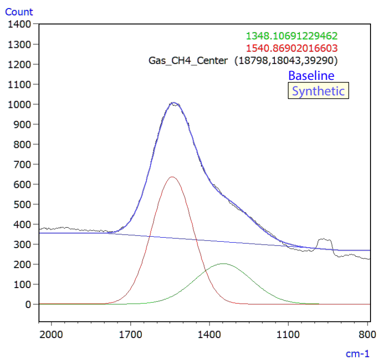

Fig. 3 Results of Curve Fitting

■ Results of Film Quality Evaluation

The Raman spectra were separated from the measured Raman spectrum by using the curve-fit function, and the film quality of the DLC films was evaluated based on the obtained values of intensity, half-width, and other features, as shown in Table 4. It was found that the respective evaluation indices were in good agreement at the two measurement positions with both of the feedstock gases CH_4 and C_2H_2 prepared for this experiment. Accordingly, it is considered possible to form uniform films without variations due to location. Comparing the samples prepared using the different feedstock gases, in particular, differences in FWHM(G) and log(N(G)/I(G)) were noticeable. Based on this fact, it can be inferred that the silicon wafer prepared using the CH_4 feedstock gas was superior in crystallinity in comparison with the wafer prepared using C_2H_2, and the hydrogen concentration of the CH_4 film was higher.

Table 4 Results of Film Quality Evaluation

	I(D)/I(G)	FWHM(G)	log(N(G)/I(G))
CH_4_center	0.32	182.17	-0.29
CH_4_periphery	0.32	181.40	-0.28
C_2H_2_center	0.34	190.85	-0.44
C_2H_2_periphery	0.34	190.25	-0.44

■ Conclusion

In this article, film quality evaluation of the DLC films was introduced as an example of evaluation of carbon materials, which is a strong point of Raman spectroscopy. Although the properties of DLC films are changed depending on the disorder of the crystal structure and the hydrogen concentration, a quantitative evaluation of film quality was possible by using the micro-Raman measurement function of the Shimadzu AIRsight infrared Raman microscope. In comparison with other analytical techniques, in these measurements there was no sample damage and information concerning the bonding state of carbon and the concentration of hydrogen could be acquired without complicated sample preparation or setup for the measurements. In the analysis, the overlapping peaks of the D band and the G band of the DLC film could be separated simply by the curve-fit function of AMsolution. Although this article introduced an example of an analysis of DLC films, which is a particular strength of Raman spectroscopy, because the AIRsight microscope realizes infrared/Raman spectroscopy in one instrument, it can also be used in quality evaluations of a diverse range of other materials.

<Reference>
(1) Application News No. K78: Analysis of DLC (Diamond Like Carbon) by XPS.
(2) Application News No. 01-00394-JP: Contaminant Analysis of Pharmaceuticals (Tablets) Using the AIRsight Infrared Raman Microscope.
(3) G. Adamopoulos, J. Robertson, N.A. Morrison & C. Godet: Hydrogen Content Estimation of Hydrogenated Amorphous Carbon by Visible Raman Spectroscopy, J. Appl. Phys., 96 (2004) 6348.
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(5) Ken-ichi Miura & Morimasa Nakamura: Analysis of Hydrogen Concentration in DLC Films by Raman Spectroscopy, J. Surf. Finish. Soc. Jpn., 59 (2008) 203.

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