Application Note Booklet

Raman Spectrometer

RAMAN SPECTROMETER

CONTENTS

Measurement of buried foreign material by Raman Spectrophotometer NRS-4100

Introduction

Currently, the infrared microscope is used extensively as one of the identification approaches for micro foreign materials. Since in microscopic infrared spectroscopy, there is a huge database, which works very well on the identification of foreign materials, while the infrared microscope has several problems for the measurement such that the spatial resolution is limited to only a few micrometer and the sample preparation is necessary if the foreign material is buried in the sample. Therefore, the Laser Raman spectrophotometer is now often used for measurement of foreign materials in combination with infrared microscope. Raman spectroscopy is a method to analyze molecular structure by molecular vibration as well as infrared spectroscopy, but there are following advantages in Raman spectrophotometer.

(1). The spatial resolution is as small as 1 µm by using visible laser.
(2). The Raman spectrophotometer allows quick and easy measurement of the sample with non-destructive manner without sample pretreatment
(3) For inorganic samples, it is easy to indentify because of the easy measurement in low wavenumber range.

The potential of measuring foreign materials by using Raman spectrophotometer is expanding, and JASCO has developed a new laser Raman spectrophotometer, NRS-4100 with compact design and ease of use to be used together with FTIR. In this application note, the features of NRS-4100 and identification of foreign materials buried in the polymer film are illustrated.

Fig. 1 NRS-4100

Features

The NRS-4100 as shown in Fig. 1 is a Raman Spectrophotometer, incorporating high performance spectrograph, sample compartment, detector and laser light source in a space as small as 60 cm square, which can be installed on the ordinary laboratory bench other than anti-vibration bed, with no extra space because the door of sample compartment moves up and down for open/close. In addition, the NRS-4100 meets the laser safety standards of Class 1. Maximum three lasers such as 457nm and 785nm as well as 532nm can be mounted, and the spatial resolution is as small as only 1 µm in XY and 1.5 µm in Z direction, enabling the high spatial resolution and fluorescence minimization, which are important for the foreign material measurement.

The "Measurement assist function" aids the user in setting up the NRS-4100 for sample measurement; a simple sequence guide takes you through setup and optimization of measurement parameters with helpful advice and tips, such as a warning if you have the laser intensity set too high. The new "Sample Search" function is used with the automated XYZ stage. A new algorithm developed by JASCO (patent pending) analyzes the microscopic image and automatically selects measurement position(s) based on the size, contrast and/or color of the target material described by the user, then simply click the measurement button to execute spectral measurements of the automatically identified sample positions. Spectra Manager II includes a wealth of user-selectable options for data analysis, as well as the usual tools like opening single or multiple spectra, zooming, normalization, a variety of arithmetic data processing functions, there is a variety of Raman specific tools and analysis functions.

Fig. 2
Measurement assist function

System configuration

- NRS-4100 Raman Spectrometer w/ 532 nm laser (100 mW)
- Automatic imaging system

Foreign material measurement/Analysis

The foreign material buried in the multi layer substrate (Glass/Adhesion layer/Transparent film) shown in Fig. 3 was measured. It is difficult to measure such foreign material by using infrared microscope, because it is difficult to cut the foreign material in section due to the presence of glass and the adhesion layer may be picked up together. On the other hand, Raman spectrophotometer with the confocal optical system can obtain the spectrum of laser focused point selectively. As a result, it is possible to measure the inside of the sample in non-contact and non-destructive manner without lousy sample pretreatment. In this report, the position where the target foreign material is located was measured in the depth direction (Z axis direction) and also each layer's information was obtained. The major spectrum obtained from each layer is shown in Fig. 4.

Measurement parameters

Ex wavelength: 532 nm   Grating: 900 gr/mm   Exposure time: 5 sec. (Accumulation: 2 times)
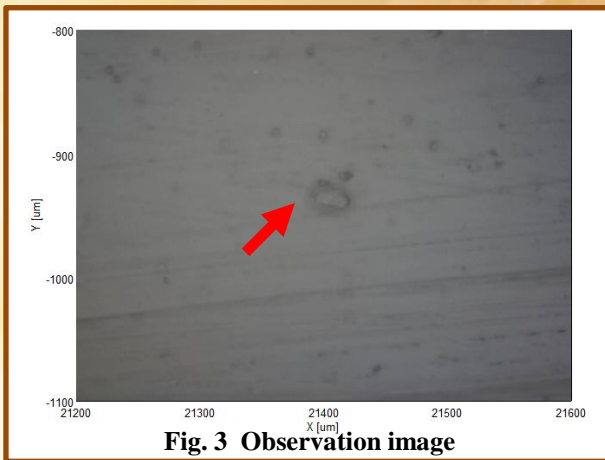
Fig. 3 Observation image
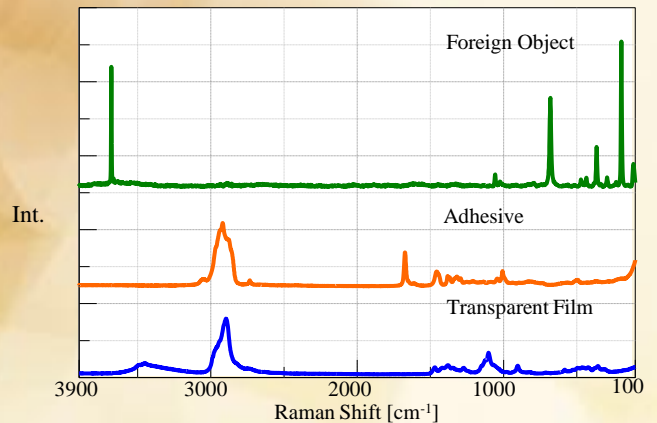
Fig. 4 Spectrum for each layer

In the obtained spectrum of the foreign material, the C-H peak at around 300 cm^{-1} is not shown, and so it is quite different from the spectrum of transparent film and adhesion layer. In order to analyze the result in further details, the spectrum of foreign material was tried to be identified by using database as shown in Fig. 5, and it was found to be talc (hydrated magnesium silicate). In addition, it is known that the transparent film is made of cellulose and the adhesion layer is made of terpene resin.

Fig. 5 Search result of the database

Evaluation of cosmetics by Raman micro-spectroscopy

Introduction

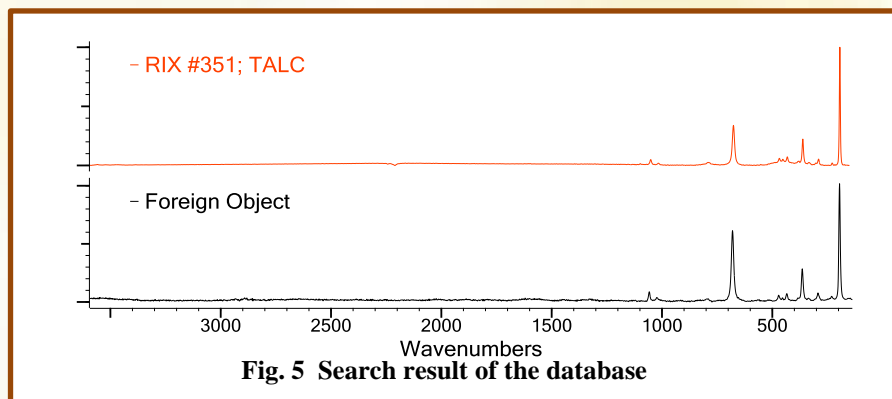Raman spectroscopy can be used to analyze the molecular or crystalline structure based on various molecular vibrations. The technique has been applied to analyses of various kinds of organic and inorganic materials such as polymers, chemicals, biological materials, semiconductor or various nanomaterials including graphene and carbon nanotubes.

Due to miniaturization, performance improvement and cost reduction of lasers and other optical devices, the price point of Raman spectrometers has been steadily declining. As a result, Raman spectroscopy is now being used for materials analysis in many fields such as quality control for pharmaceuticals and in the food industry. In comparison with infrared spectroscopy, there are several advantages in Raman as non-contact, non-destructive , easy sample preparation and small measuring spot down to approx. 1 micron.

An additional (and important) advantage, is that measurement in the low wavenumber range can be easily achieved to obtain precise information on inorganic samples. Cosmetic preparations consist of organic and inorganic materials. This application note shows the method for identification and discrimination of the components in eye shadow samples using Raman micro-spectroscopy NRS-4100.

Fig. 1 NRS-4100

Experimental

Two kinds of eye shadow products (manufactured by Company A and Company B) were coated onto a metal plate. And these samples were measured with JASCO NRS-4100 Raman micro-spectrometer (Fig. 1) to get mapping images of it. These data were analyzed and identified by using a search database.

System configuration

	Model	Description	P/N	Remarks
Main Unit	NRS-4100	NRS-4100-532 Raman Spectrometer	6882-J021A	532 nm laser
Option	RXY-4100	Auto Stage Imaging System	6882-J178A	

Measurement conditions

|					
Excitation wavelength:	532 nm	Grating:	900 gr/mm	Laser power:	3.2 mW
Objective lens:	100x	Sampling area:	35 x 35 mm	Measurement points:	35 x 35 with 1 mm interval

Results and discussion

Fig. 2 shows observation image of each eye shadow and Fig. 3 shows the spectra of the main components of each eye shadow (black spectra are calculated using a PCA model analysis and red spectra are the results of the database search). Fig. 4 presents the color mapping images of each eye shadow. The visual differences in the particle size or the color of the two kinds of eye shadow cannot be found in the visual observation image (Fig. 2).
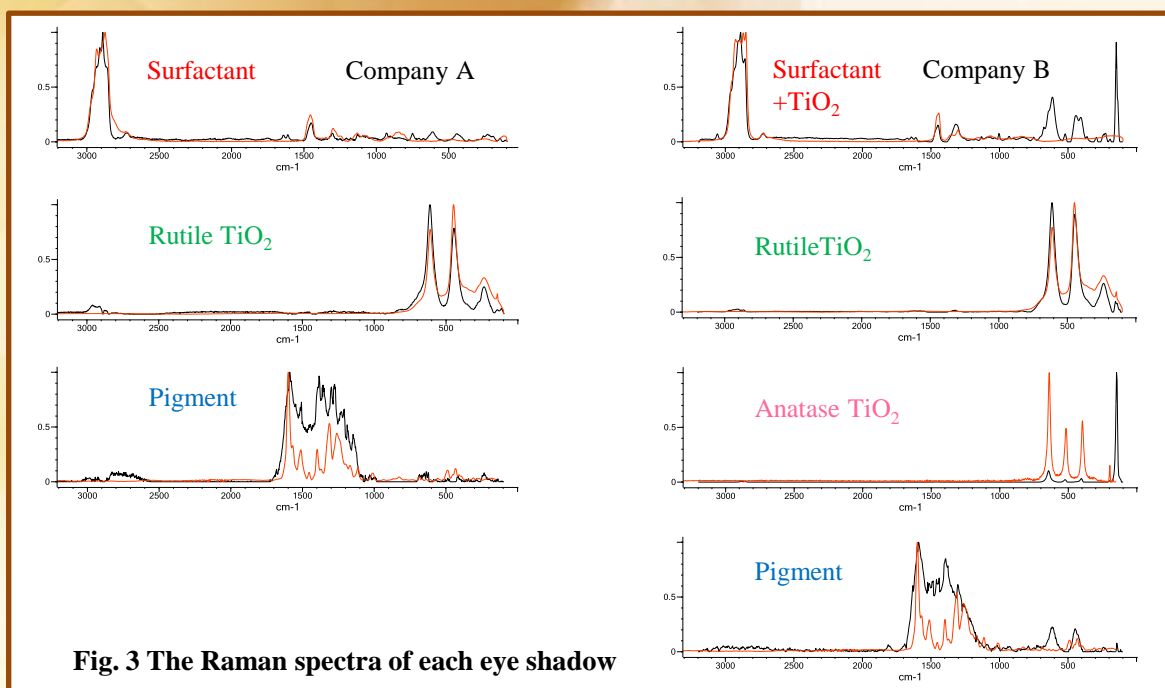
The difference between the two kinds of eye shadows can be easily recognized by the spectra difference shown in Fig. 3. The eye shadow made by company A contains a surfactant, rutile TiO_2 and pigment. Another sample contains anatase TiO_2 in addition to a surfactant, rutile TiO_2 and the pigment.

Fig. 4 shows the color mapping images of the component distribution for each eye shadow formulation. The differences in component dispersion can be reviewed in the mapping images.

Raman microscopy easily highlights the composition differences in chemical formulations that cannot be discerned by optical or infrared microscopy. As an example, the dispersion of inorganic crystals that demonstrate polymorphism can be easily measured by colored mapping images of the spectral peaks. Raman micro-spectroscopy is effective for measurement of composite materials like cosmetics that contain organic and inorganic material dispersed in discrete micron-sized locations within the chemical formulation.
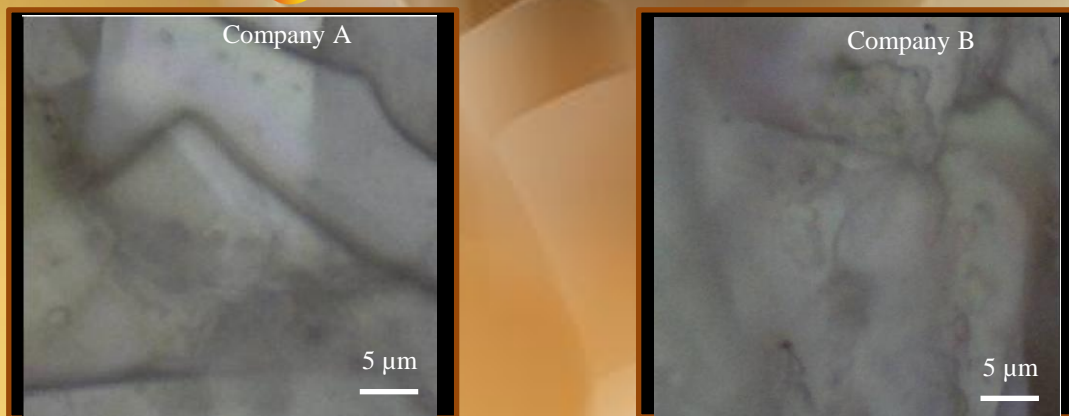
Fig. 2 The microscopic visual observation image of each eye shadow

Fig. 3 The Raman spectra of each eye shadow

Red: Surfactant
Green: Rutile TiO$_2$,
Blue: Pigment

Red: Surfactant
Green: Rutile TiO$_2$,
Pink: Anatase TiO$_2$
Blue: Pigment
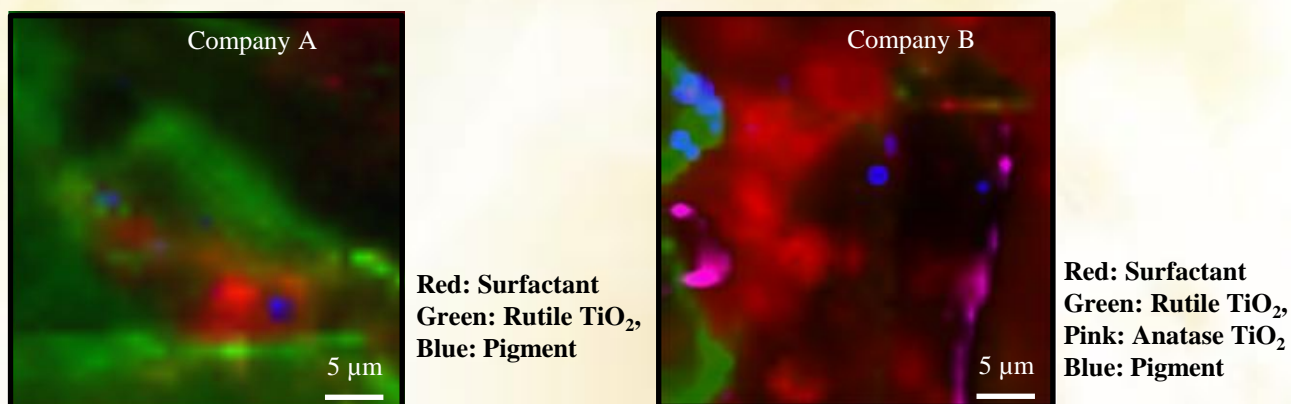
Fig. 4 The color mapping image of each eye shadow application

Minimizing fluorescence using a 457nm laser excitation wavelength

Introduction <Benefits of Raman Spectroscopy>

Raman spectroscopy is a popular method for analyzing molecular structure and is considered a complementary technique to infrared spectroscopy. Recently, Raman has been attracting the attention of FT-IR users because it offers several important advantages over FT-IR. Raman spectroscopy is a non-contact and non-destructive technique and measurements can be made with little to no sample preparation. Samples can be measured with a spatial resolution as small as 1µm and depth profiling can also be easily performed on transparent samples. However, in some cases, good quality analysis by Raman spectroscopy can be adversely affected by interference from fluorescence.

The JASCO NRS series of Raman spectrometers have several fluorescence compensation features, which fluorescence elimination algorithm is patented.

This application shows the evaluation of NRS-4100 (Figure 1) mounting 457 nm laser for the measurement of samples that exhibit fluorescence, to determine if this can be a better alternative to red and NIR lasers such as 785 or 1064 nm excitation.

Fig. 1 Raman Spectrometer

Methods for minimizing fluorescence

Both Raman scattering and fluorescence are phenomena where the wavelengths of light emitted from a sample are different from the wavelength of the input excitation light. If the wavelengths of Raman scattering and fluorescence overlap, it is impossible to obtain good Raman spectra. The NRS series Raman instruments have three different functions for reducing or eliminating these fluorescence effects.

1. The fluorescence correction algorithm (JASCO patent) on Spectra Manager II software. for minimizing fluorescence effect.
2. The high spatial resolution in the confocal optical system for the case that fluorescence is emitted from the surrounding exogenous conditions.
3. When the sample itself emits fluorescence, the most effective method is to change the wavelength of the excitation laser. The wavelengths of Raman scattering do not change even if the excitation wavelength is changed, while the fluorescence wavelengths are dependent on the excitation wavelength. Therefore, it is possible to minimize or even eliminate the overlap of the Raman scattering and fluorescence by changing the excitation wavelength. As Raman spectra are displayed as a shift value from the excitation wavelength, Raman peaks always appear at the same position independent of the excitation wavelength and so Raman spectra with substantially minimized fluorescence can be obtained. An additional benefit of using the 457 nm laser is that the intensity of Raman scattering is inversely proportional to the fourth power of excitation wavelength, therefore by using a shorter wavelength laser as the excitation source, Raman scattering intensity can be substantially increased while minimizing fluorescence.

**Fig. 2 457 nm laser spot
(a blue-purple-color)**

The 457 nm laser as shown in Figure 2 has a shorter wavelength than the 532 nm laser and offers two important advantages; the same CCD detector can be used as with the 532 nm laser and the Raman scattering intensity can be up to 1.8 times higher when using a laser of equal power output.

System configuration
 - NRS-4100 Raman spectrometer /532 nm laser (100 mW) /785 nm laser (100 mW) / 457 nm laser
 - Laser switching mechanism
 - 900 and 400 gr/mm grating

Measurement and Analysis

A fiber sample was measured using the laser excitation wavelengths of 457 nm, 532 nm and 785 nm; measurement parameters are outlined in table 1. The spectra in Figure 3 demonstrate that using excitation wavelengths at both 532 nm and 785 nm result in strong fluorescence which completely obscures any peaks of the Raman spectrum. However, by using an excitation wavelength at 457 nm, the fluorescence interference exhibited by the other excitation lasers is quite reduced. The spectrum obtained using the 457 nm laser and the fluorescence correction software resulted in data which could be compared to a database library spectrum and the measured sample was correctly identified as a nylon-6 fiber (Figure 4).

Table 1: Excitation Wavelength Measurement Parameters

Wavelength [nm]	Grating [Line/mm]	Measurement time[sec]	Number of scans
457	900	30	2
532	900	5	12
785	400	30	2
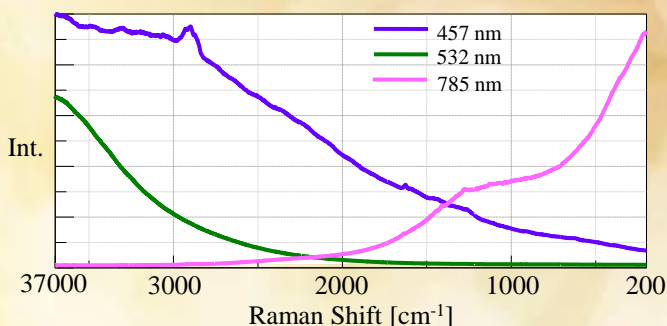
Fig. 3 Overlaid spectra for three laser excitation wavelengths
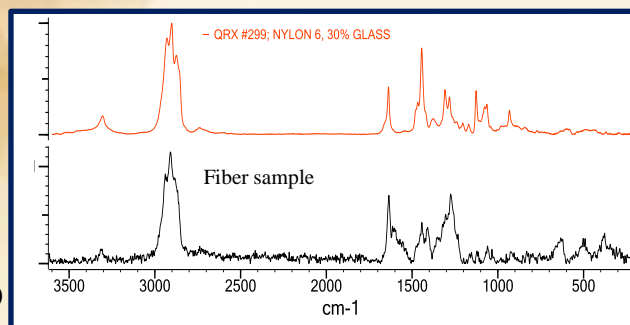
Fig. 4 Database Search Result

Summary

A nylon sample fiber was measured using the 'standard' 532 and 785 nm excitation wavelengths and the results for both lasers demonstrate a strong fluorescence emission. However, using the shorter (higher energy) 457 nm laser excitation, which has significantly higher Raman scattering intensity, proves to be an extremely effective method to minimize the effects of fluorescence.

In addition to the nylon test fiber, we used the three-laser NRS-4100 Raman spectrometer (582 nm, 457 nm and 785 nm) to evaluate a range of samples that exhibit strong fluorescence, such as polyimide and biological materials and found that the 457 nm excitation wavelength offers spectra with much lower fluorescence than the 'standard' combination of 532 nm and 785 nm laser excitation wavelengths.

Measurement of scattered foreign materials by using the Measurement Assist function and the Sample Search function

Introduction

Recently, foreign material analysis by Raman Spectroscopy is frequently performed (ref.: JASCO Raman application data 260-AN-0010). This is because Raman spectroscopy is a method which enables to obtain the information on molecular structure as well as IR spectroscopy. In addition, it has several features to allow non-destructive and non-contact measurement without sample preparation, measurement in depth direction with about 1µm of spatial resolution, and easy identification of the inorganic material because of easy measurement in low wavenumber range. However, some of the users who analyze the foreign material by micro FT/IR are saying that it is difficult to do by the Raman system. Therefore, JASCO developed a special measurement tool on the software of NRS-4100 with intuitive user interface which make it possible to use with ease for user friendly purpose. For example, it has the functions such as "Measurement Assist" function which enables the easy measurement by supporting at wizard form from focus adjustment to condition setting/measurement, "Real time data processing" for executing the automatic operation such as peak detection, or "User advice" function (patented) for performing in real time basis the operation procedure or advice for spectra. This time, utilizing the functions of newly-developed software for NRS-4100, the measurement of scattered foreign materials was implemented rapidly and easily as reported below.

System configurations

- NRS-4100 Raman spectrometer w/ 532 nm laser (100 mW)
- Automatic imaging system

Sample search function

In measurement program of NRS-4100, "Sample search" function is provided which determines the measurement position automatically from size or contrast of observation image when the automatic stage is mounted. The screen of "Sample search" function is shown in Fig. 1, in which the search was implemented so that only foreign materials that is larger than given size were detected. The measurement points were displayed in observation image, and then as a view of search result the images of determined sample position were displayed. It is also possible to select only the desired position from the result view and to implement the mapping measurement of whole sample region based on searched shape.
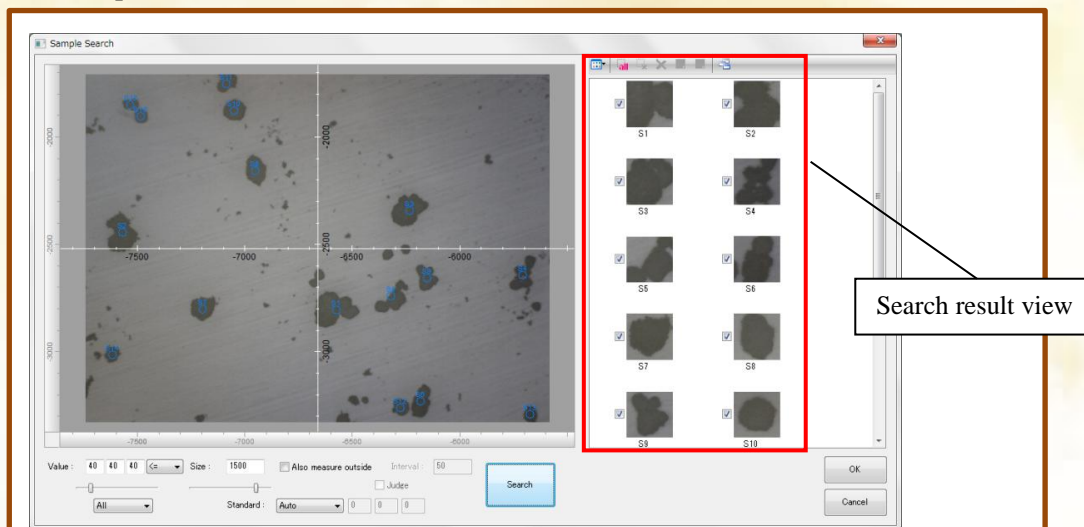

Fig. 1 Image of sample search function

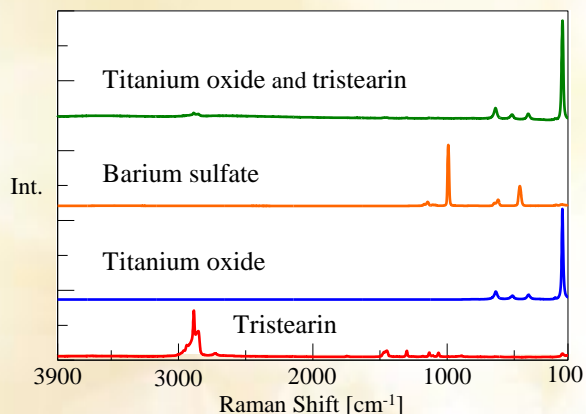## Application of the "Measurement assist" function

The concept of "Measurement assist" function that JASCO developed is to enable anyone to implement Raman measurement easily, by guiding at wizard form the several measurement conditions that are essential to Raman measurement. The screen is configured enabling to operate intuitively using slide bar or tabular form.

This time, the sample search result performed in Fig. 1 was regarded as a measurement point, and then the scattered foreign materials on substrate were measured. The foreign materials at 16 positions detected from sample search result were regarded as measurement points. In the setting screen of "Measurement assist" function, the measurement condition setting can be assisted by displaying each point where the measurement condition needs to be set following the "User advice" function, which is shown in Fig. 2.
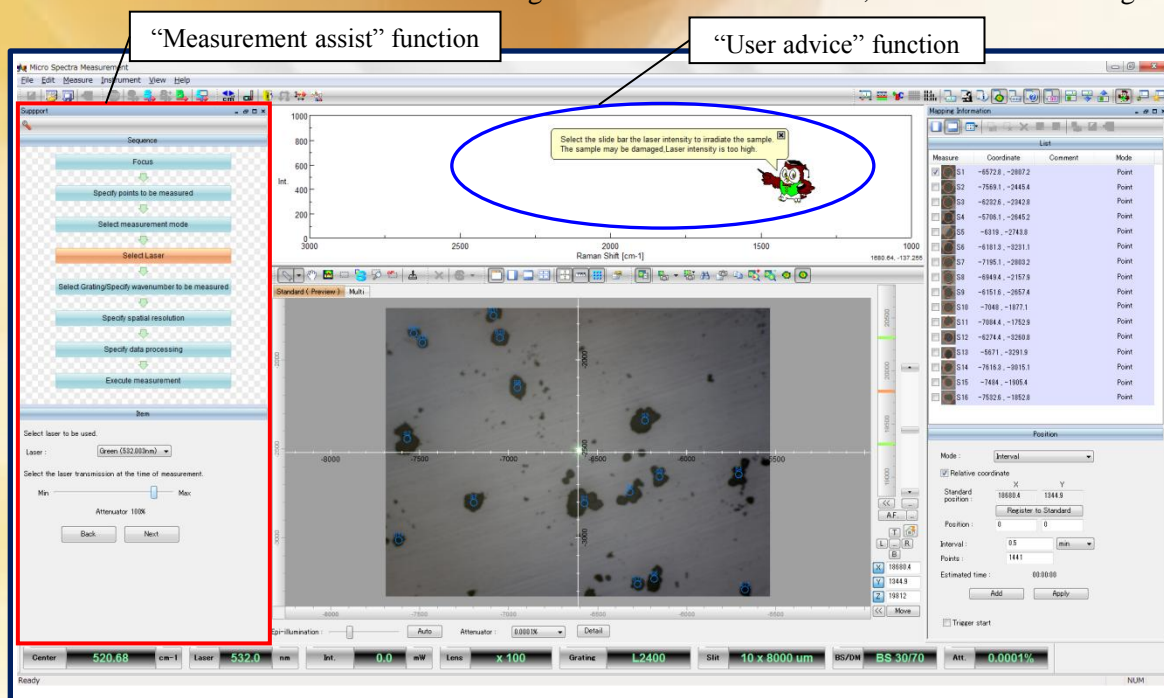
Fig. 2 Measurement screen when using "Measurement assist" function
(with displaying the "User advice" function)

Three spectra and their mixture spectra were observed as obtained spectra of foreign material. The typical spectra are shown in Fig. 3. From the characteristic of spectra at 16 points, it was determined that 10 points of them are for titanium oxide (anatase type), 2 points of them are for barium sulfate, 2 points of them are for tristearin, and 2 points of them are for the mixture of titanium oxide and tristearin. It is also possible to analyze such as more specific scattering condition by the mapping measurement of the mixture.

Fig. 3 Spectra of foreign materials

Summary

Thus, by using the "Measurement assist" function or "Sample search" function of NRS-4100, it is possible to perform smoothly a sequence of measurement starting from determination of sample position to measurement condition setting and measurement.

Evaluation of crystallization in micro part on plastic (polyethylene terephthalate) bottle

It is reported that the full width at half maximum (FWHM) and crystallization (density) of the carbonyl group. ［C=O］(1730cm^{-1}) of polyethylene terephthalate (PET) have the good correlation. [1].

In comparison to other analytical methods, the measurement procedure in Raman spectrometry is simple, easy and, it is effective for the measurement of micro part. In this application, the distribution of crystallization on cross-section of plastic (PET) bottle was measured.

<Sample preparation>

The A and B part shown in the photo of plastic bottle were cut and then, the cross-section of each part was prepared by a slicer (Model HW-1 Variable angle slicer, JASCO Engineering Co., Ltd.), since the mapping measurement in micro area requires the smooth sample surface.

The multi-point measurement was carried out in 50 microns step from outside to inside of cross-section.

<Measurement conditions>

Excitation wavelength: 532 nm
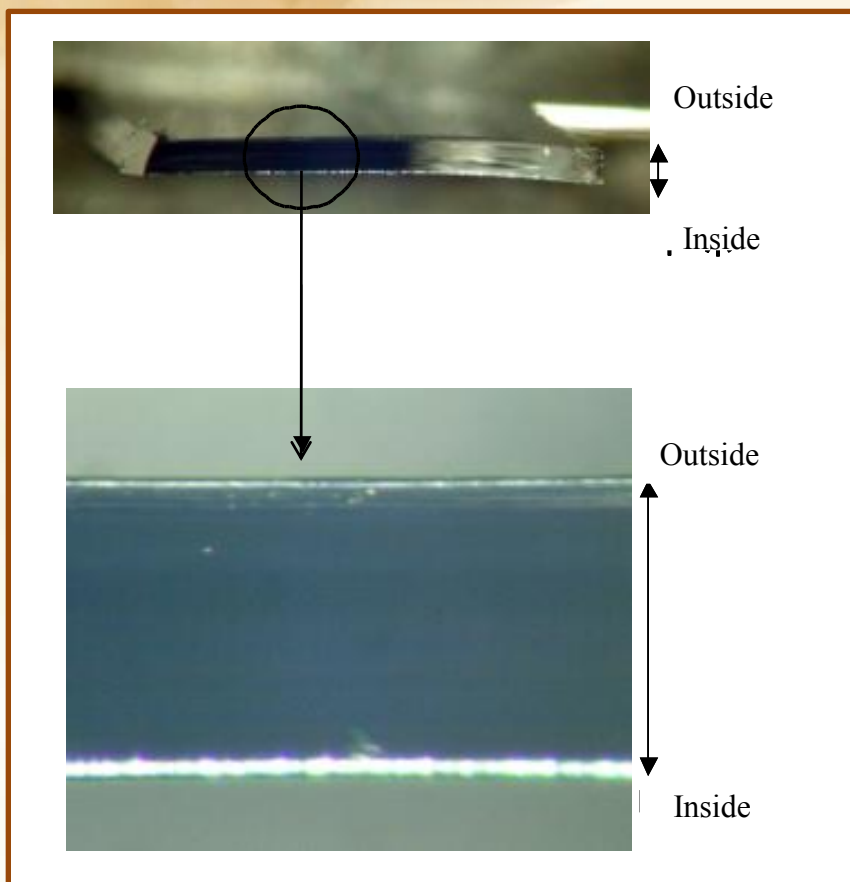Objective; ×100, beam diameter; 1 micron
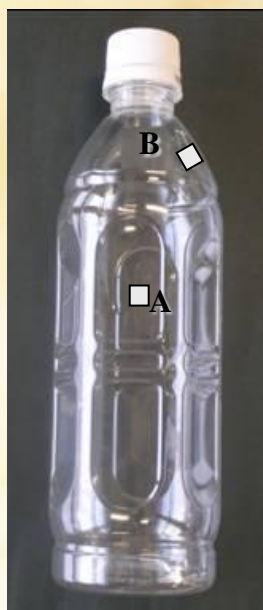
PET Bottle

Fig. 1. Sampling part and its cross-section

Results

The FWHM of carbonyl group in each sampling part is shown in Fig. 2. Since the FWHM and crystallization shows the negative correlation, the crystallization becomes higher when the FWHM becomes narrower. The results indicate that the distribution of crystallization in A and B part is different. In the evaluation of physical properties of plastic (PET) bottle, the crystallization is an important factor. Therefore, the micro Raman spectrometry is an effective analysis method especiallyfor the measurement of micro part.

Raman Spectrum of PET

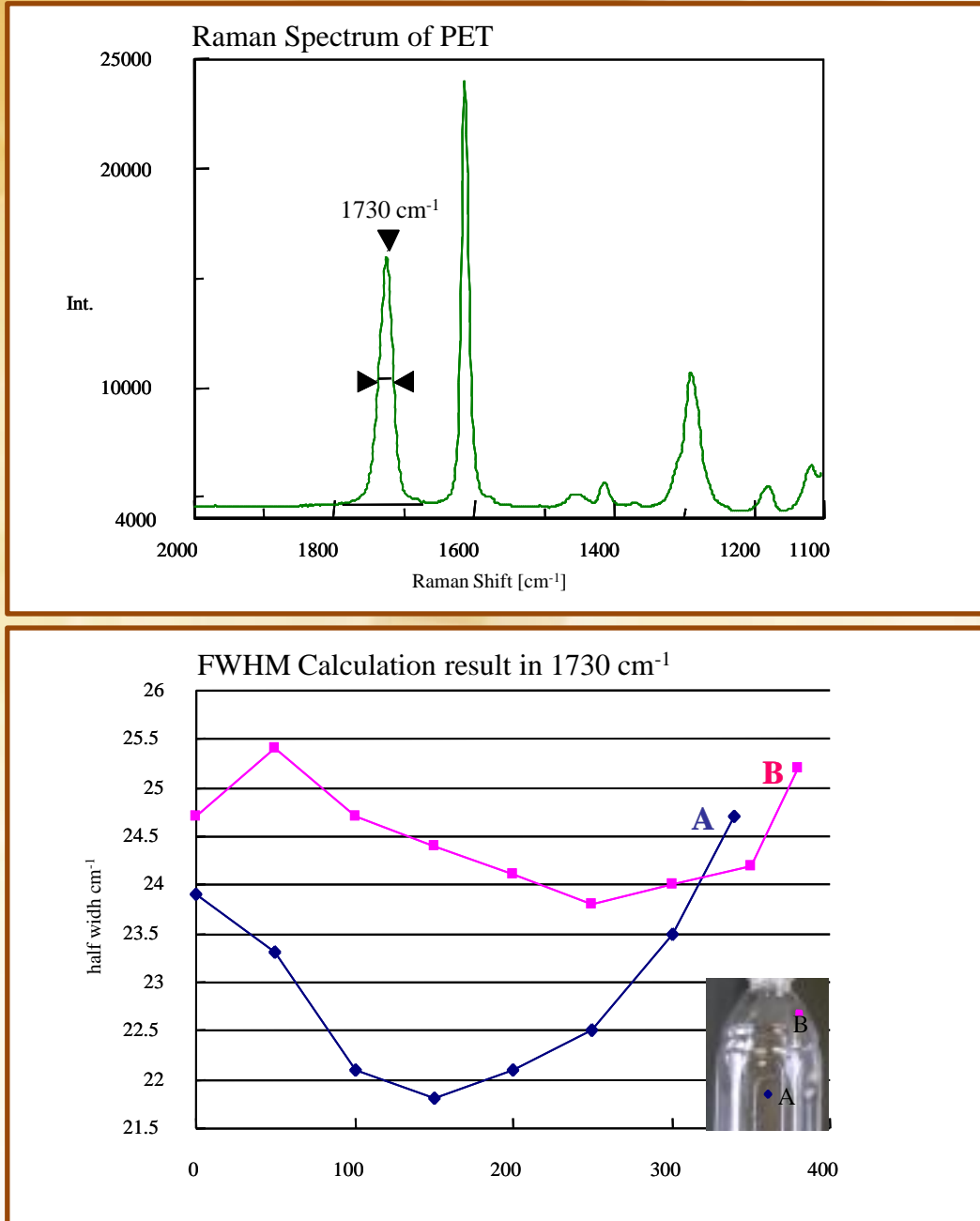$1730 \ cm^{-1}$

FWHM Calculation result in $1730 \ cm^{-1}$

Fig. 2. FWHM of carbonyl group and Raman spectra of PET

Spatial Resolution and DSF in Micro Raman Spectrometer

Raman micro-spectroscopy has been widely used due to the ability to provide rapid and non-destructive measurements of micron sized samples. Also, Raman spectroscopy can provide similar information as compared to FT-IR micro-spectroscopy offering enhanced capabilities for the analytical laboratory. A primary advantage of Raman micro-spectroscopy is better spatial resolution as compared to FT-IR micro-spectroscopy. Comparatively, the minimum spatial resolution for FT-IR measurements is about 10 µm, while Raman can easily achieve a spatial resolution of 1 µm.

In this note, the spatial resolution of micro Raman spectroscopy, its general definition, and evaluation methods will be described as well as an explanation of the Dual Spatial Filtration (DSF) system that is a standard feature of the JASCO NRS-5000/7000 series micro-Raman spectrometers.

Definition of Spatial Resolution

A laser, of a specific wavelength, is used as the excitation source for Raman micro-spectroscopy. As the laser beam spot size on the sample is reduced, the spatial resolution on the XY plane becomes higher. When light having a constant intensity distribution is introduced into an objective lens, the diffraction pattern shown as Figure 1 appears. The bright center area is called the 'Airy-disk' and, its size "d" can be determined by the wavelength "l" and the numerical aperture "N.A." (equation 1). The "d" term refers to the diffraction limit that determines the spatial resolution of an optical microscope.
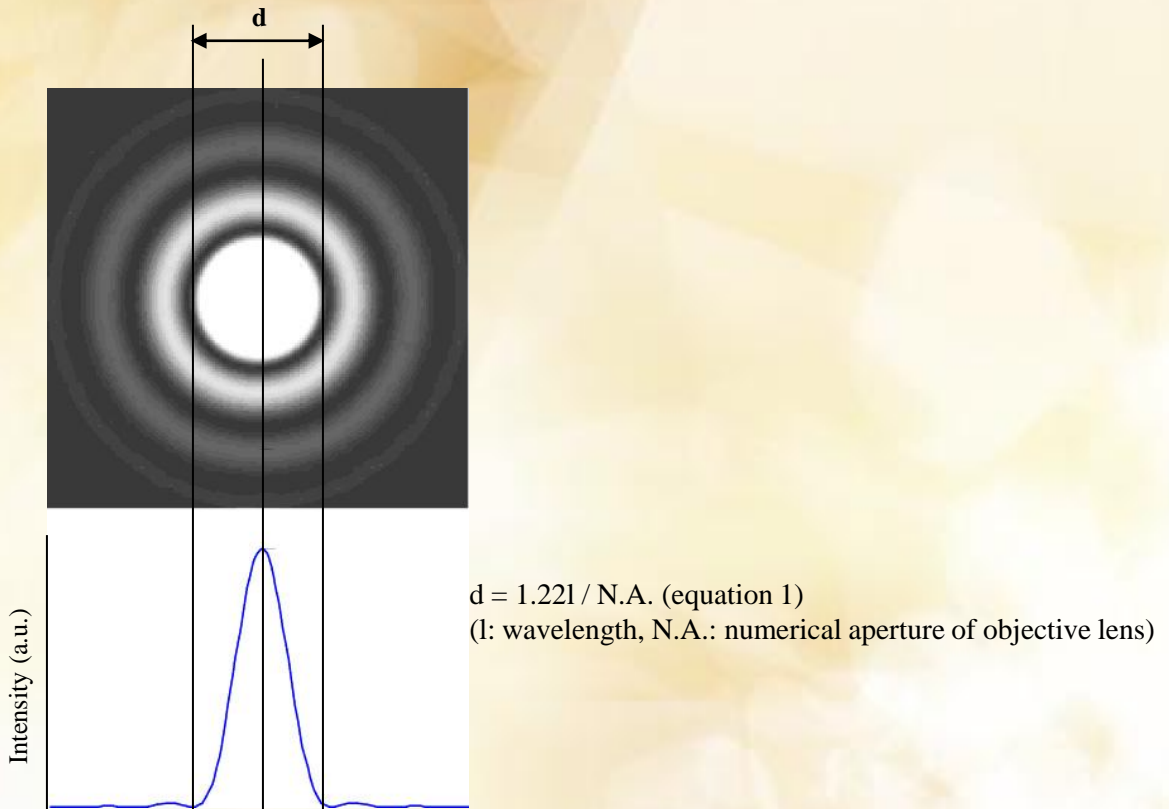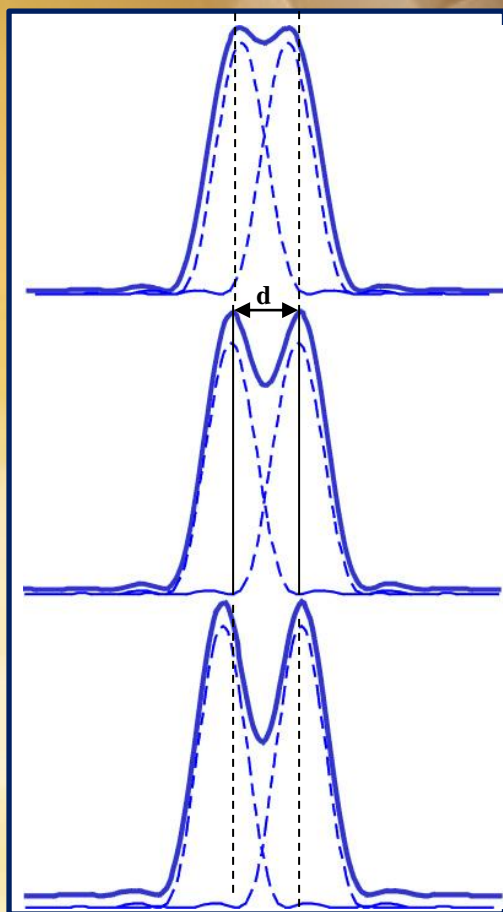

d = 1.22l / N.A. (equation 1)
(l: wavelength, N.A.: numerical aperture of objective lens)

Figure 1: Airy-disk resulting from diffraction with a circular aperture.

(a) The distance between two points is smaller than "d".
» The two points are not separated.

(b) Rayleigh criterion
d = 0.61l/N.A

(c) The distance between two points is larger than "d".
» The two points are separated.

Figure 2: Spatial resolution defined by the Rayleigh criterion

On an XY plane, the definition of spatial resolution is based on the distance between two points close to each other, the 'Rayleigh criterion'. In the standard configuration of the JASCO NRS-5000/7000 (532 nm laser, the 100X objective lens with a N.A. = 0.90), the laser spot size at the diffraction limit is calculated as "d" = 720 nm and the spatial resolution according to the Rayleigh criterion is then equal to 360 nm.

As equation 1 suggests, if the laser wavelength is getting shorter (lower wavelength), the spatial resolution then becomes higher. Also, if an objective lens such as an oil-immersed lens having a larger N.A. is used, one can expect a comparative increase in the spatial resolution.

However, the definition based on FWHM (full width at half maximum) of the intensity of the interference ring has also been recognized. Therefore, in the comparison of spatial resolution for the Raman micro-spectrometers prepared by different manufacturers, the definition of 'spatial resolution' which has been applied should be confirmed. For the NRS-5000/7000 series, each of the values calculated from the two different definitions is shown in Table 1.

**Table 1: Spatial resolution on an XY plane**

	Equation	532 nm, N.A＝0.90 configuration	355 nm, N.A＝1.4 configuration
Rayleigh criterion	$0.61\lambda/N.A$	360 nm	154 nm
FWHM	$0.51\lambda/N.A$	301 nm	129 nm

Evaluation of Spatial Resolution in Confocal Optics

Theoretically, one can calculate the spatial resolution for confocal optics as shown in Table 1, however, the actual value for optical microscopes may become larger due to lens aberrations, the intensity distribution of the incident laser light to the objective lens, etc. The actual spatial resolution can be evaluated by measuring the distance for the Raman intensity profile when it changes from 10 % to 90% by the measurement of a sample having a sharp edge as illustrated in Figure 3.

This evaluation method was applied to the NRS-5000/7000 series instruments with the standard configuration of a 532 nm laser and an objective lens of N.A. = 0.9, resulting in a very close value of 370 nm compared to the theoretical value of 360 nm, as calculated according to Table 1.
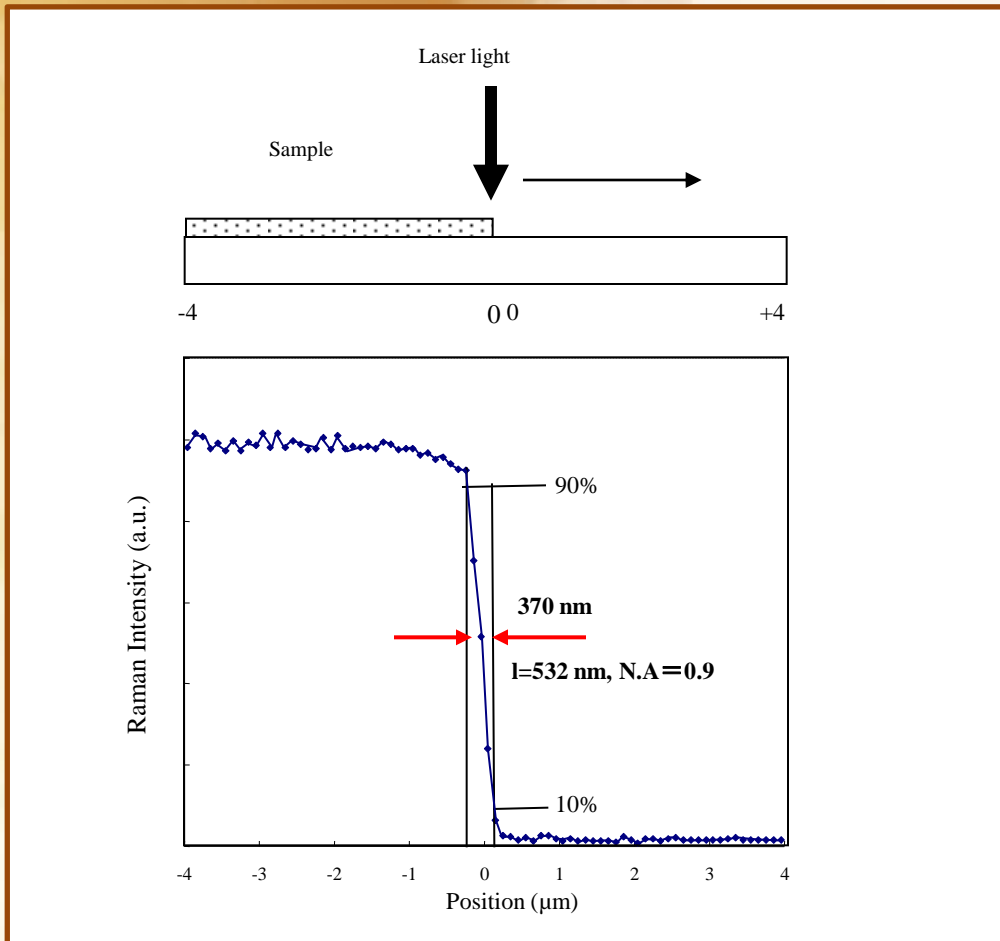
Figure 3: Measured spatial resolution in NRS-5000/7000
(532 nm laser , objective lens 100x)
(upper – illustration for measurement of silicon sharp edge; lower –
Raman intensity profile of silicon peak)

Resolution in Depth in Confocal Optics

In a confocal optical system, a pin hole aperture is located at a reciprocal focal point of the optical system. Therefore, light rays coming from points other than the focus of the objective lens are eliminated.

The depth resolution (Z resolution) "dz" can be determined by the excitation wavelength "l", the refractive index "n" of the substrate and the numerical aperture "N.A." of the objective lens (equation 2).

$$dz = \frac{0.88 * \lambda}{n - \sqrt{n^2 - NA^2}} \qquad \textbf{(equation 2)}$$

Inserting the values of "l"=532nm, "n" =1 (atmosphere) and N.A.=0.90, a calculated "dz" of 830 nm is obtained.

The actual depth resolution can again be estimated by measuring the FWHM of the Raman intensity profile for a silicon crystal when it is scanned in the Z direction.
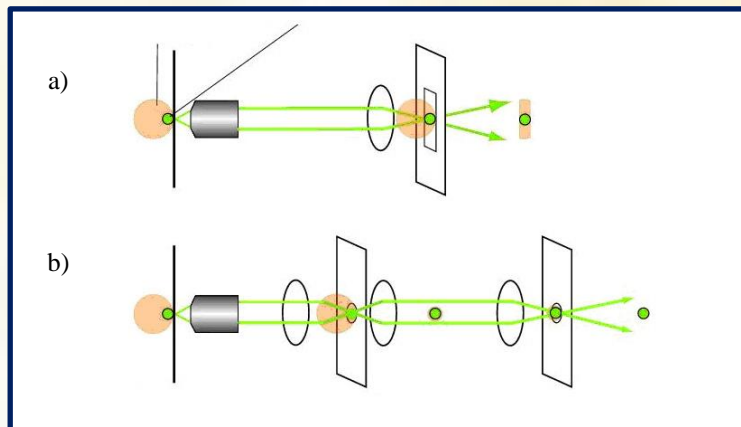
In a standard confocal optical system, available with most of the commercially available micro Raman spectrometers, a 1.5 to 2.0 µm of FWHM is expected. In the NRS-5000/7000, a FWHM of 1 µm can be expected that is much closer to the theoretical value as shown in Figure 4. This number can be achieved by the use of an improved confocal aperture optimized for Raman spectroscopy.

FWHM=1mm

Z position (mm)
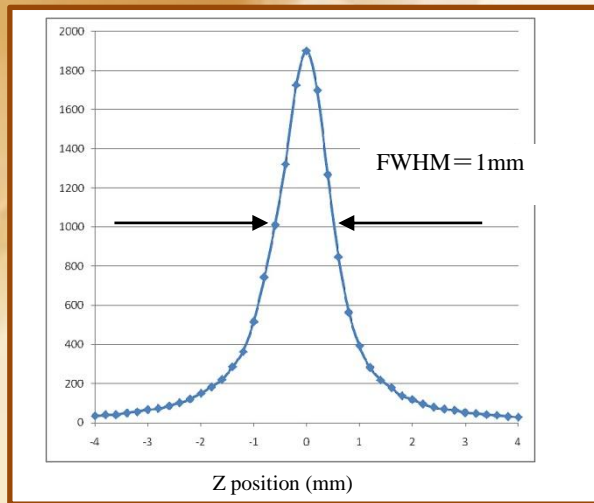
Figure 4: Raman intensity profile of silicon in Z depth profiling
(532 nm laser, objective lens 100x, N.A=0.9)

Dual Spatial Filtration(DSF)

The standard Dual Spatial Filtration (DSF) optical system in the NRS-5000/7000 instruments has a dual aperture system for confocal optics. Therefore, the DSF system can eliminate any stray light that was not removed using the first aperture. The DSF method can improve the Z resolution and at the same time, one can expect an improvement of the spatial resolution for the XY plane.


Figure 5: (a) standard confocal optics with pinhole aperture; (b) JASCO DSF confocal optics

The stamdard single aperture system ('a' of Figure 5) and the JASCO DSF optics ('b' of Figure 5) were applied to the measurement of oxidized titanium (TiO2) particles on a silicon substrate. The Raman imaging of the peak intensity profile for both results are shown in Figure 7. As seen in the figure, the spatial resolution in the XY plane was improved by use of the DSF optics (right image in Figure 7) and, the image intensity profile was closer to the microscope image of the sample (Figure 6).
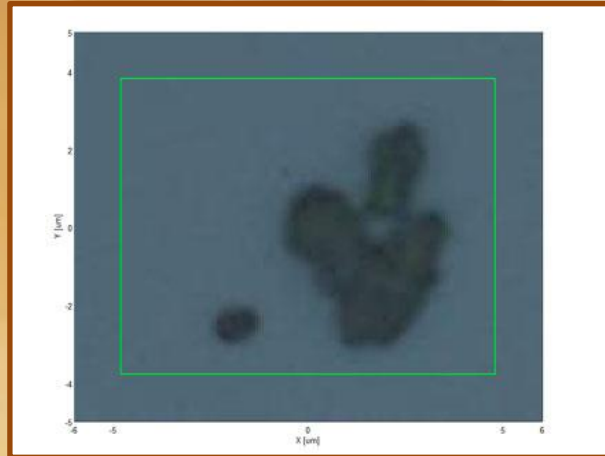
Figure 6: Microscope image of a TiO2 particle on a silicon substrate.
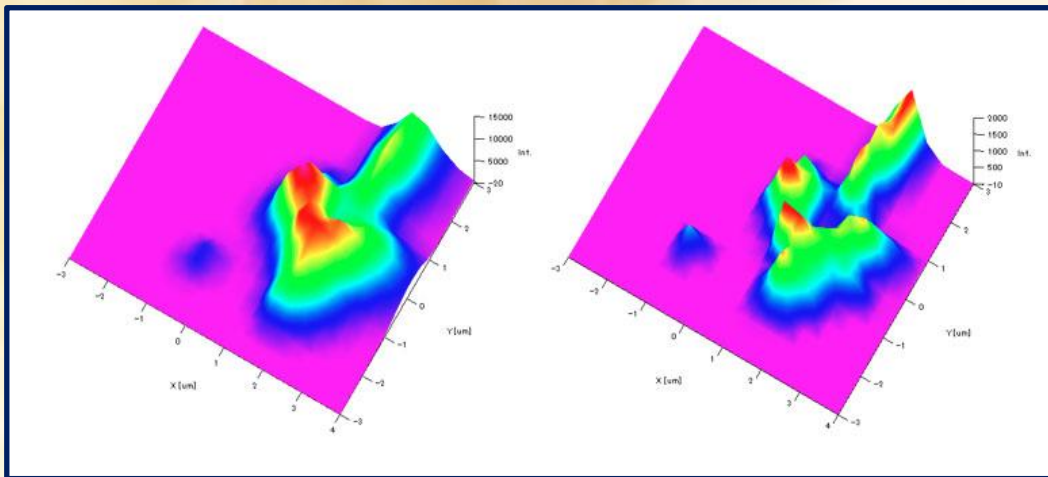
Figure 7: Raman imaging of a TiO2 particle on a silicon substrate
(Intensity profile of the TiO2 peak height)
(left; by ordinary confocal system ('a' of Figure 5), right; the JASCO DSF system ('b' of Figure 5)

Also, the single aperture confocal system and the DSF system were applied to the non-destructive Z scan of a polyvinyl-alcohol (PVA) layer of a polarizer film to observe the change of the Raman peak intensity of an iodide compound (25 μm thickness) that is sandwiched in the PVA layers. (Figure 8)

Theoretically, the intensity of the iodide compound peak will rapidly increase when reaching the iodide compound layer then, rapidly decrease when again reaching the PVA layer as shown in the blue dashed line in the Raman intensity profile displayed as Figure 8.

The results demonstrate that the profile by the DSF optics (solid red line in Figure 8) is closer to the theoretical profile than the standard confocal system (solid green line in Figure 8). These results clearly indicate that the DSF optical system can greatly improve the Z resolution of the confocal optical system.
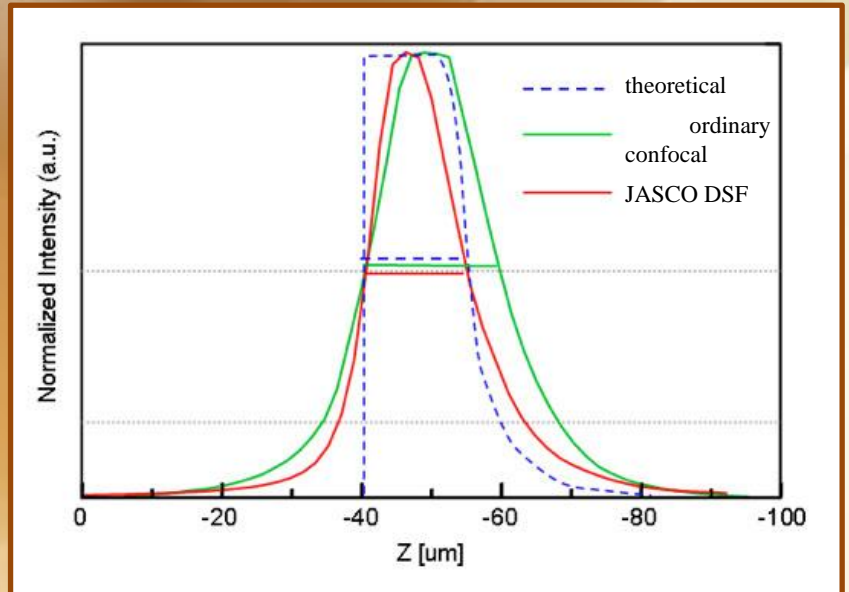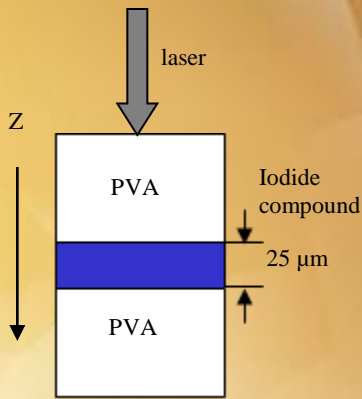
Figure 8: Z scan profile of polarizer film (PVA)
(left: cross section of multi-layer; right: peak intensity profile of an iodide compound)

Conclusion

As outlined above, the NRS-5000/7000 offers a high spatial resolution close to the theoretical diffraction limit. Also, the maximum performance in the confocal optical system can be realized by use of the DSF optical system. If high spatial resolution is not required for specific experiments, the larger pin hole aperture can be used such that better energy throughput can be obtained for better S/N results.

NOTE

The measurement position in the Z scan becomes shallower (thinner) than the actual sample position (thickness) due to the influence from the refractive index of the substrate. In the case of a 25 µm thickness of the iodide compound layer, the apparent thickness will be approximately 15.3 µm when the refractive index is 1.64. In the NRS-5000/7000, a [Refractive Index Correction] function is available in the mapping data analysis program so that a correction for the difference between the true and measured values can be performed.

Reference

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# Raman and Photoluminescence Measurements of Glass and Quartz Materials

This note is intended to provide important information for users of Raman spectroscopy, specifically discussing measurements using microscope slide glass, cover glasses or glass tubes for holding the Raman sample.

A fluorescence free glass is commercially available, however, it can still cause very weak fluorescence. Even though it is very weak, it may significantly disturb the intended Raman measurement, specifically when changing the laser excitation wavelength. To estimate the influence from substrate fluorescence, the Raman and fluorescence spectra of simple microscope slide glass and quartz materials were measured using the laser excitation wavelengths of 532 and 785 nm. The Raman and fluorescence spectra of the various samples are displayed as Figure 1 (horizontal axis – wavelength; vertical axis – Raman shift).

For the measurement of slide glass using 532 nm excitation, a Raman peak in the low wave number region was observed in addition to the Fluorescence peaks centered at 693 and 880 nm. Using the 785 nm excitation, the slide glass sample offered a fluorescence peak of 880 nm. Using 532 nm excitation, the observed peaks of the slide glass may not disturb the Raman spectral measurement (Raman shift: 0 to 4000 cm^{-1}).
However, the fluorescence peak of 880nm at 785 nm excitation may overlap the Raman shift around 1385 cm^{-1} and, it may significantly disturb measurements due to the very strong intensity of the fluorescence as compared to the Raman spectrum. On the other hand, for the quartz materials, only the Rayleigh band was observed at both 532 and 785 nm excitations and there was almost no influence from fluorescence. These results suggest that the quartz glass must be used for the measurement especially at 785 nm excitation. It is our suggestion that only quartz be used for the majority of Raman measurements, wherever possible. It may be feasible, however, to use glass as a rounded surface (HPLC vials, NMR tubes, capillary tubes, etc.) if measurements using only 532 nm excitation are to be attempted.
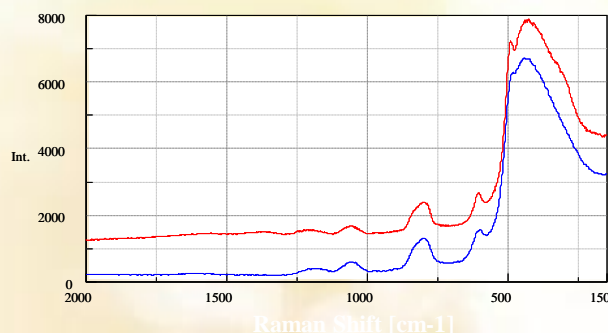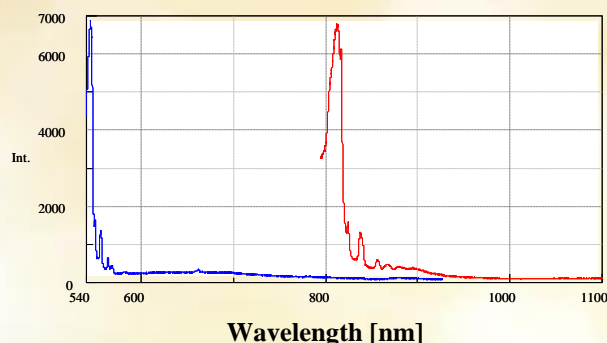
Slide glass
（Excitation: 532nm, 7875 nm）
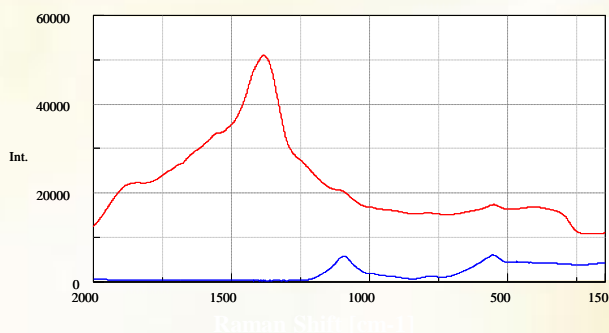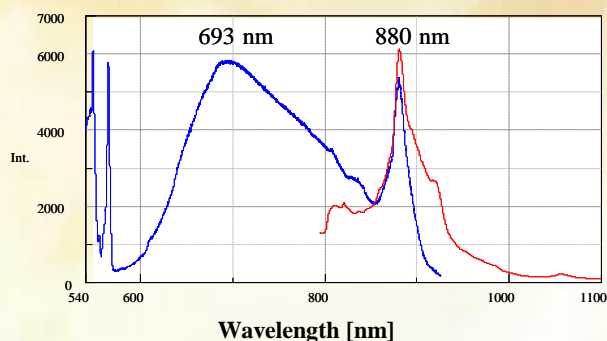
Quartz glass
（Excitation: 532 nm, 785 nm）

2D correlation spectroscopy using 2 kinds of IR and Raman spectra obtained by time course measurement (Analysis of instant adhesive in cure process) -AN

1. Introduction

2D correlation spectroscopy was proposed in the 1980s as an analytical method for the changes of IR spectra with time. Although 2D correlation spectroscopy is usually used to analyse one kind of spectra obtained by time course measurement, In this experiment, 2D correlation spectroscopy was applied to 2 kinds of time-course spectra such as IR and Raman. Instant adhesive was used as a model sample and the changing of the spectrum in cure process was observed. The obtained spectra of both IR and Raman were analyzed by 2D correlation program run on Spectra Manager.

2. Experimental

Commercially available instant adhesive was used as a sample. One of the main components, cyanoacrylate, is reacted with water in the air and the molecules are polymerized, and it becomes hardened (Figure 1). IR spectrum was obtained by thin-film method using KBr windows. The spectrum was obtained by time course measurement with FT/IR-4100 for 60 seconds at intervals of 2 seconds. Raman spectrum was obtained with NRS-3100. A drop of the instant adhesive was put on a glass slide and thinly spread, and it was measured with an objective lens of ×20 for total 60 seconds at intervals of 2 seconds. (Excitation wavelength: 532 nm).
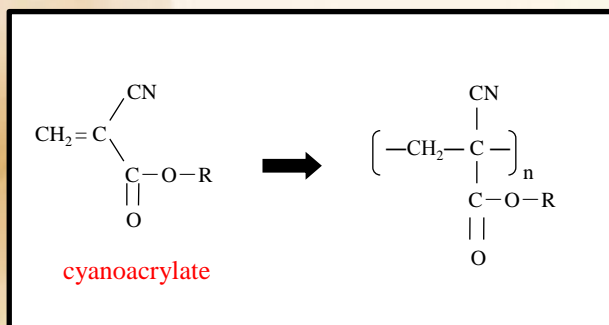

Figure.1: Reaction of instant adhesive in cure process

3. Results and Discussion

The obtained IR and Raman spectra by time course measurement were shown in Figure 2 and Figure 3 respectively.
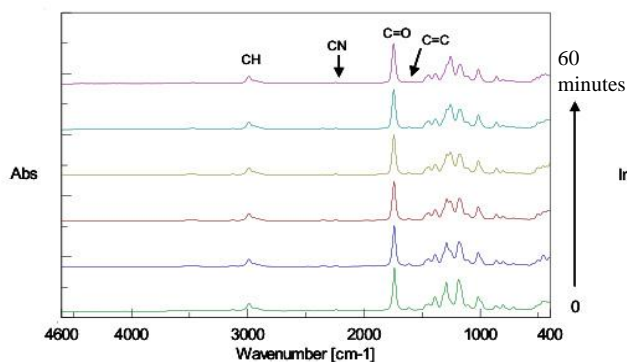

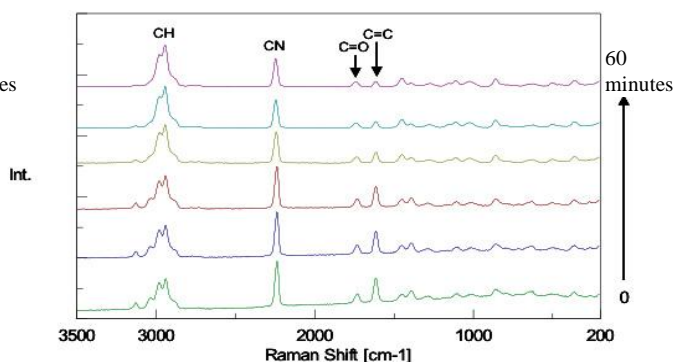**Figure2. IR absorption spectra**

Figure3. Raman scattering spectra

By comparing Figure 2 with Figure 3, it is seen that the intensity of Raman peak attributed to C=C double bond at 1620 cm^{-1} was decreased (polymerization in progress), while any clear change of IR spectra is not seen with time because the peak intensity was too weak. On the other hand, the peaks in the IR spectra in fingerprint region are changed with time while there is no distinguished change in the peaks in the Raman spectra in such region. Next, the results of simultaneous correlation of the IR and Raman spectra changes with time are shown in Figure 4 and Figure 5 respectively.


Figure 4. Simultaneous correlation spectrum with only IR

Figure 5. Simultaneous correlation spectrum with only Raman
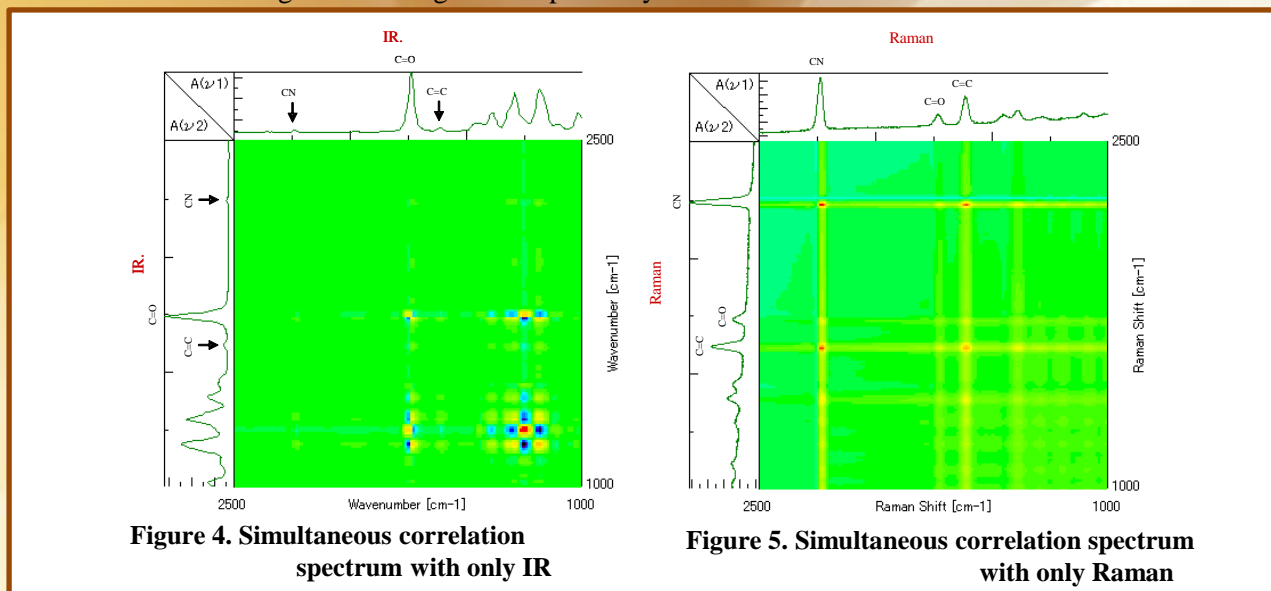
From the simultaneous correlation of IR shown in Figure 4, there is a correlation seen between the peaks from 1100 cm^{-1} to 1400 cm^{-1} in the fingerprint region and the peak of C=O at 1735 cm^{-1} whose significant difference was not seen in Figure 2. In the simultaneous correlation of Raman shown in Figure 5, there is a correlation seen between the peak of C=C double bond at 1620 cm-1 and the peak of C=O at 1735 cm^{-1}. In other words, it is estimated that the peaks of IR spectrum largely changed with time in the fingerprint region from 1400 cm^{-1} to 1100 cm^{-1}, the peaks of C=C double bond having strong activity on Raman and the peaks of C=O might be correlated with one another.

In order to analyze them in integrated manner, simultaneous correlation analysis was carried out by combining IR spectra with Raman (Figure 6). At the intersection point of the peak of C=C in Raman and the peak of C=O in IR, the peak of C=O in low-wavenumber side in blue (minus) and the one in high-wavenumber side in red (plus) are correlated. It is considered that the peak of C=O is shifted to high-wavenumber side with time as the peak of C=C is monotonically decreased with time as shown in Figure 7. In addition the peak of C=C in Raman and the peak in the region from 1400 cm^{-1} to 1100 cm^{-1} also have correlation. Just like C=C in Raman against C=O in IR, the same correlation is seen for CN group, and accordingly, it is found that the peak intensity of CN group is deceased without shift of the peak.

Figure 6. Simultaneous correlation spectrum with IR and Raman
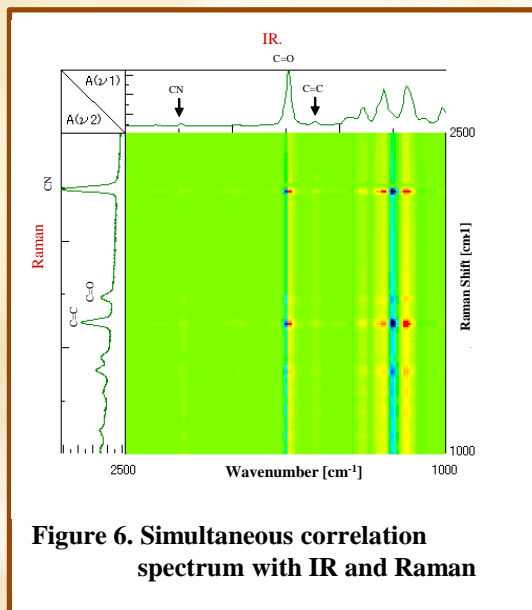
As explained above, in accordance with the transformation of structure from C=C to C-C by the polymerization reaction, it is presumed that the conformation of functional group not related to the polymerization such as C=O and CN are also changed. Although the results obtained by IR and Raman were used for analysis this time, the combination of the results obtained by other spectroscopic (NIR, UV, VIS, CD etc.) technique and the results by Raman and IR would expand the possibilities for various analysis such as attribution of peaks, lattice vibration and the relation among color, chiral information and intramolecular vibration.
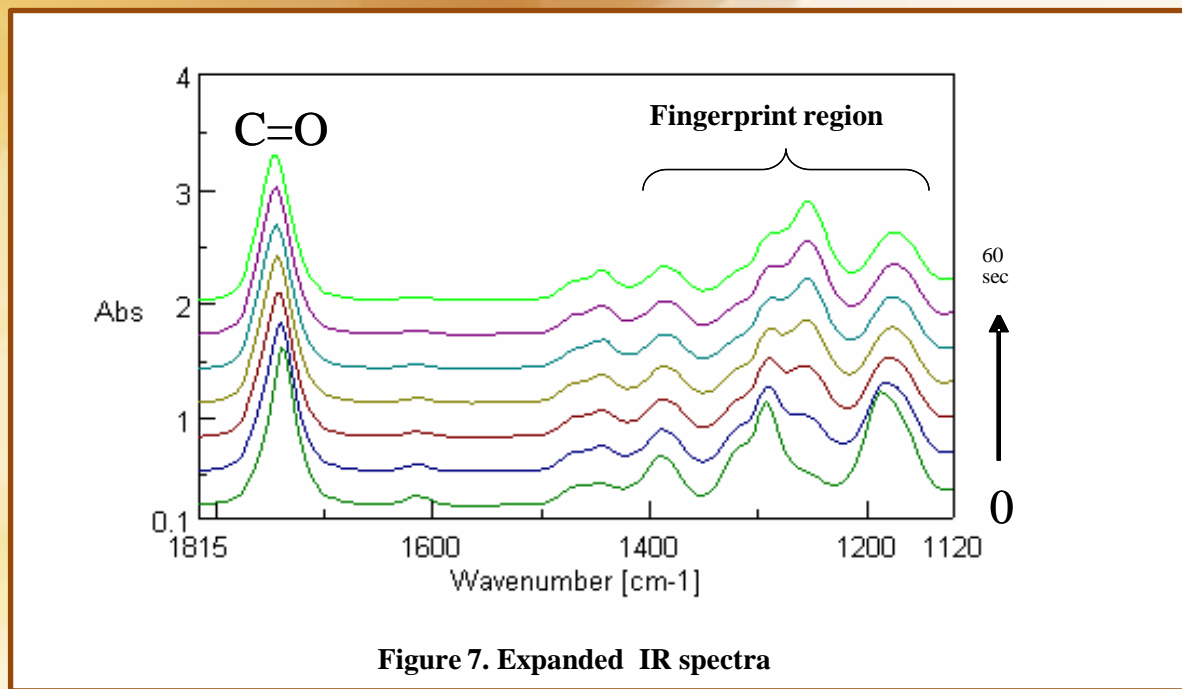
Figure 7. Expanded IR spectra

Determination of ortho and para hydrogen ratio by using Raman spectroscopy - Application to fuel cell -

<Introduction>

Hydrogen molecule which is now attracting attention as energy source of fuel cell, has two different nuclear spin isomers such as ortho hydrogen (the same direction pair) and para hydrogen (the opposite direction pair). Both ortho and para hydrogen show the same chemical property, while their physical property such as specific heat is different from each other, and since the conversion between ortho and para needs extremely long time, each molecule tends to be handled as different from the other. The abundance ratio of ortho-para in hydrogen gas in ambient temperature is stable as approx. 3: 1, but when it is cooled to liquid state, most hydrogen molecule becomes para hydrogen. However a part of ortho hydrogen also becomes to liquid state, and ortho-para conversion in liquid hydrogen after long time may generate heat, which may affect to storage efficiency. Therefore when hydrogen gas is liquefied industrially, ortho-para conversion catalyst is necessary. In this experiment, we will describe, as an example, simple evaluation of ortho-para abundance ratio by using Raman spectroscopy which is one of the vibrational spectroscopy methods.

<Experimental>

Laser Raman spectrophotometer NRS-3100 was used for the measurement. 10 cm gas cell with NaCl window which is usually used for FTIR was evacuated by rotary pump, and then hydrogen gas with pressure lower than one atmosphere was encapsulated directly into the gas cell from hydrogen gas cylinder. The gas cell is mounted as shown in Figure 1, and the measurement was done using the objective lens with long working distance by focusing the beam inside of the cell (Excitation wavelength; 532 nm, Laser power at sample point; approx. 10 mW).
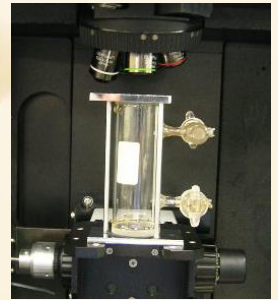
Fig. 1 Sample compartment

<Results and discussions>

Figure 2 shows the obtained Raman spectrum of hydrogen gas. The peaks due to rotational transition were seen in the spectrum in the range from 350 to 1100 cm^{-1}. The system temperature was estimated from Stokes anti-Stokes ratio using equation (1) to be as approx. 300K.

$$\frac{l_{\text{anti-stokes}}}{l_{\text{stokes}}} = \exp\left(-\frac{h v}{kT}\right) \quad (1)$$

Ortho-para abundance ratio is calculated from each partition function equation (2) of ortho and para hydrogen by adding the peak height of ortho and para hydrogen in the rotation spectrum and supposing T = 300K in the equation (2), and then the ratio, approx. 7:3 was obtained. The hydrogen molecular rotation constant B in equation (2) was referred to B'=. 59 cm^{-1} which was calculated from the equal distance of rotation line 4B.

$$Z = \underset{J}{S} \, P_j \exp\left(-\frac{B J(J+1)}{kT}\right) \quad (2)$$

B: Rotation constant, J: Rotation quantum number
$P_J = g_J(2J+1)$
g_J : Each abundance ratio of ortho and para hydrogen

Compared to the standard ortho-para ratio of hydrogen in the ambient temperature, 3:1, the ratio of para hydrogen was higher. From this result, it can be recognized that ortho hydrogen was already converted to para hydrogen when hydrogen in the cylinder was liquefued and filled. This time, ortho-para ratio was obtained from the rotation spectrum, but when the rotation spectrum in the wavenumber region in the vicinity of peaks of rotation spectrum is affected from unnecessary light such as fluorescence generated from window, the abundance ratio can be calculated from vibration-rotation spectrum (which is) separated from the change of rotation energy by high resolution measurement of the vibration spectrum region around 4160 cm^{-1}.
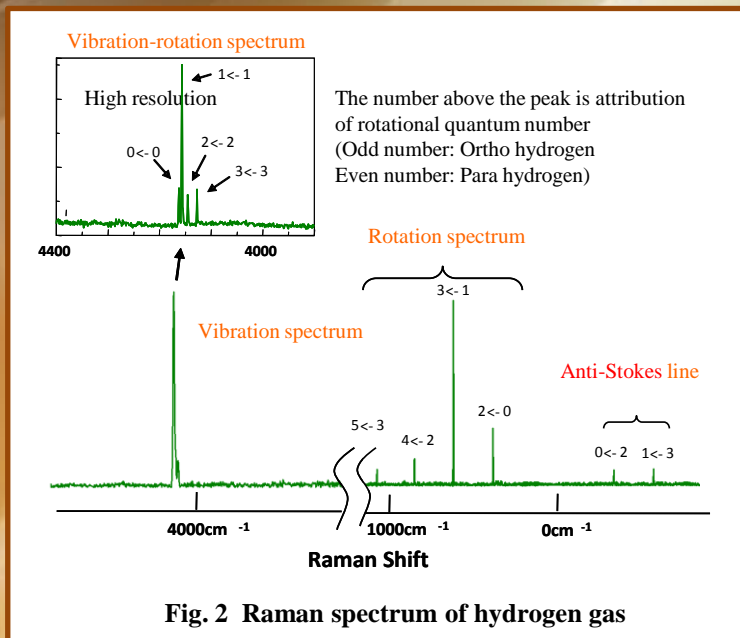

Fig. 2 Raman spectrum of hydrogen gas

<Comment>
The reason why the difference of the direction of nuclear spin such as ortho and para hydrogen is evaluated by Raman spectroscopy (vibration spectroscopy), can be explained by quantum-mechanics. The wave function of whole hydrogen molecule can be expressed as the product of each wave function of electron, vibration, rotation and nuclear spin as shown in the equation (3).

$$\phi_{Total} = \phi_{electron}\phi_{vibration}\phi_{rotation}\phi_{nuclear\ spin} \quad \text{--- (3)}$$

Equation (4) and (5) show the energy of molecular vibration and rotation respectively calculated from the characteristic value of Schrodinger equation.

Figure 3. energy level of ortho-para hydrogen

Vibration energy $E = (v + 1/2) h\nu$ v =0.1.2... (4)
Note, $\nu = (1/2\pi)(k/\mu)^{1/2.}$ (v: vibrational quantum number, k: force constant, μ: reduced mass)

Rotation energy $E = BJ(J+1)$ $B = h/(8\pi^2 Ic)$ $J = 0.1.2...$ (5)
(B: rotational constant, J: rotational quantum number, I: inertia moment, for diatomic molecule, $I = \mu R^2$ (μ: reduced mass, R: distance between nucleus)

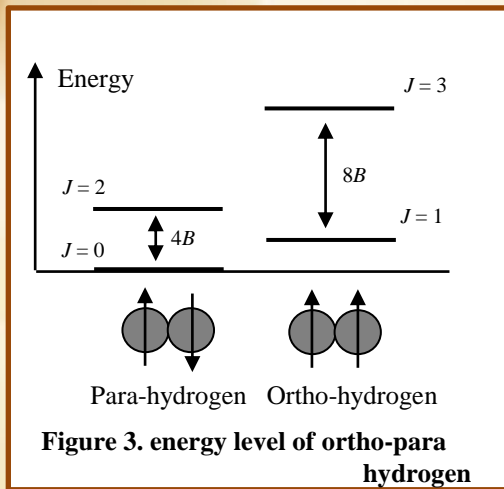Figure 3 shows the energy level of hydrogen molecule using quantum number of rotation J. Generally in electronic ground state, wave function of electron and vibration is symmetric to the displacement of nucleus. On the other hand, wave function of nuclear spin has both symmetric and asymmetric cases to the displacement, and the each case is called as ortho and para. Wave function of rotation must be symmetric in order to satisfy the Pauli exclusion principle. Therefore ortho hydrogen exists only when rotation level J is odd (asymmetric), and para hydrogen exists only when rotation level J is even (symmetric). Nuclear spin information such as ortho and para hydrogen can be obtained from rotation spectrum (or vibration rotation spectrum) of hydrogen molecule. However, in case of Deuterium molecule (D2), Deuterium atom is Bose particle, so that the relationship between odd - even and ortho - para is contrary to hydrogen molecular case, resulting interesting phenomenon that the shape of rotation spectrum changes drastically.

Qualitative analysis of colorant by Raman Spectroscopy

<Introduction>

In order to progress Archeology, to study art history and to repair the works of art, it is generally very important to know and analyze what kind materials our ancestors used historically as colorant. Raman spectroscopy is a very useful technique especially for non-destructive analytical tool for qualitative analysis of archaeological ruins and works of art, because the measurement range is much wider than IR spectroscopy, enabling the measurement of not only organic colorant but also inorganic colorant that has absorption peaks in low wave number range below 400 cm⁻¹. It is considered to be difficult in general to obtain good Raman spectrum of the material which has fluorescent characteristic in UV region such as colorant, but it is possible to avoid this fluorescence emission effect without changing the excitation wavelength but keeping away from the absorption band because such materials have strong and sharp absorption peaks in visible region.

In this experiment, 12 different color water paint colorants were used as samples, which were excited by the lasers with 3 different wavelengths for comparative study.

<Experimental>

Instrument: JASCO NRS-5100 Laser Raman spectrometer
Samples: 12 different color water paint colorants
Objective lens: ×20
Excitation wavelength: 532 nm, 63 3nm, 785 nm

<Result and discussion>

Fig.1 shows the spectral data obtained in this experiment. As the result, Raman spectra of White, Yellow, Black colorants samples show the similar level S/N even excited by any of 3 different excitation wavelength. Spectra of Red, Lemon, Indigo blue, Scarlet, Brown and Ocher colorant samples show better S/N when excited by longer wavelength such as 785 nm, On the other hands, the better spectrum of Blue colorant sample was obtained when excited by the shorter wavelength such as 532 nm and also good spectra were obtained for Green, Yellow colorant samples excited by 633 nm. Table 1 shows colorant components of each samples as the result of this analysis. Generally, the color is recognized as the complementary color of absorbed light (Fig.2). As an example, Red colorant sample is considered to irradiate strong fluorescence when excited by 532 nm because it absorbs selectively the light between green and blue region. However, the Green colorant sample which is expected to absorb Red light has actually shown the best S/N condition when excited by 633 nm in Red region.

The cause of this phenomenon can be considered that Raman peak of Phthalocyanine compound(Fig.3) as the component of Green colorant sample is enhanced selectively by Red laser due to Resonance Raman effect. In addition the shapes of spectra of Green, Blue and Indigo Blue samples are different depending on excitation wavelength, which can be considered that the group vibration of Chromophore derived from absorption is enhanced selectively due to Resonance Raman effect. As well as Phthalocyanine, Chlorophyll and Hemoglobin which have similar chemical structure to Phthalocyanine are known as typical compounds that have Resonance Raman effect characteristics depending on excitation wavelength. Any spectra of Organic colorant which obtained in this experience could not be found in the liberally after searching. This is because the ratio of peak intensity is considered to be different depending on the excitation wavelength, which makes the spectra different from library data obtained by FT-Raman (1064 excitation) and Colorant components contain various crystal polymorph. Physical characteristics such as hue and anti-corrosion are different depending on the type of crystal Polymorph.

As shown in the above, Raman spectroscopy is one of the very useful analysis tool not only for colorant analysis, but also for evaluation of crystal polymorph and patent application for the cutting edge materials such as the luminescence material of Organic EL, absorbing colorant of Blue-Ray disk, and functional colorant as photovoltaic materials of Dye Sensitized Solar Cell.
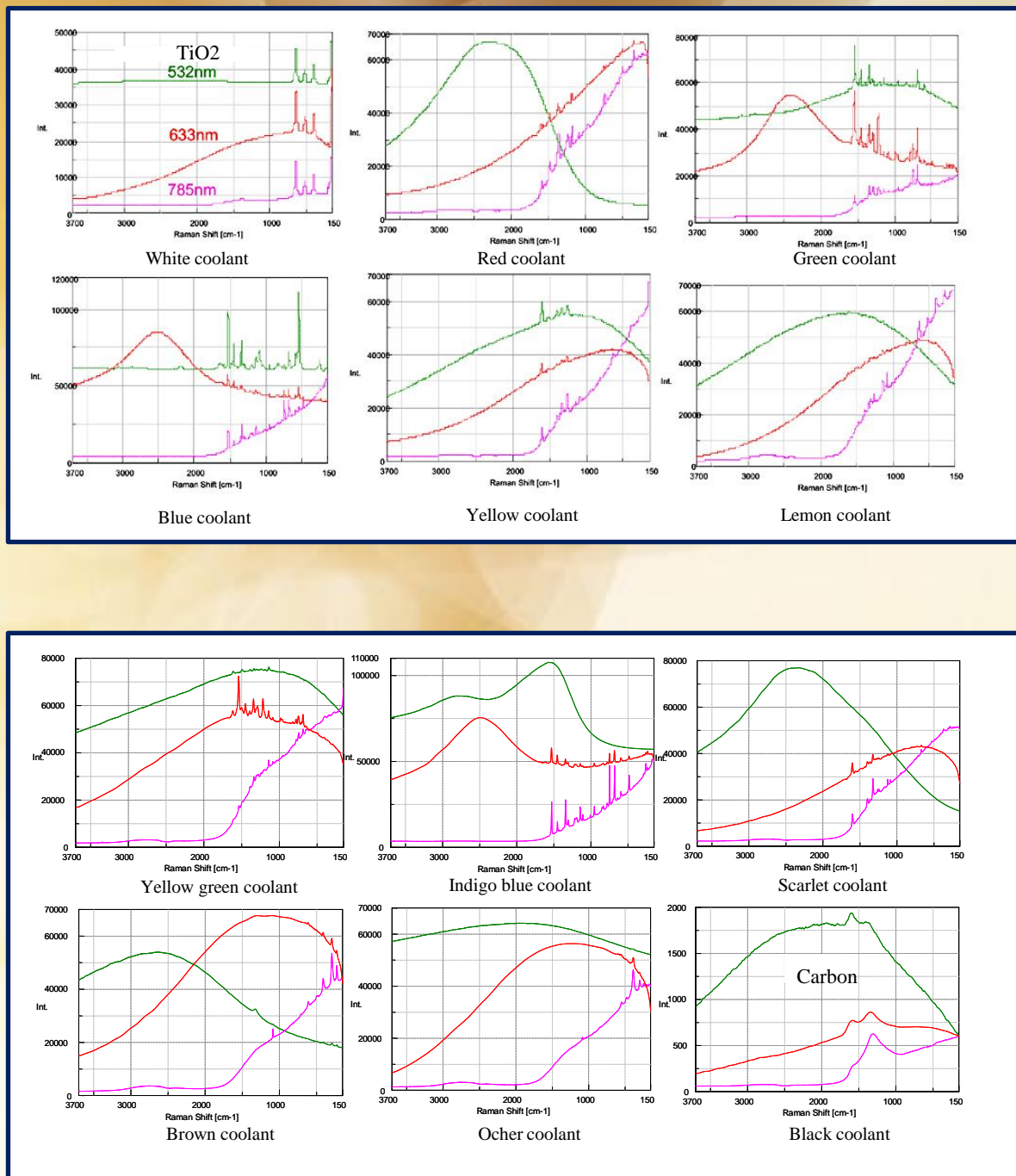
Fig1. Spectra data of colorant samples

Colorant sample	White	Red	Green	Blue	Yellow	Lemon
Component	Titanium Oxide	Heterocyclic organic	Phthalocyanine	Phthalocyanine	Heterocyclic organic	Heterocyclic organic
Colorant sample	Yellow Green	Indigo Blue	Scarlet	Brown	Ocher	Black
Component	Phthalocyanine	Phthalocyanine	Heterocyclic organic	Inorganic	Inorganic	Carbon

Table 1. Analysis result of Colorant component

Fig 2. Wheel of hue

Fig3. Phthalocyanine complex
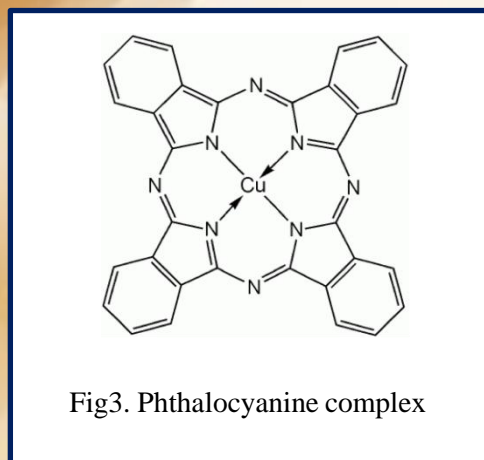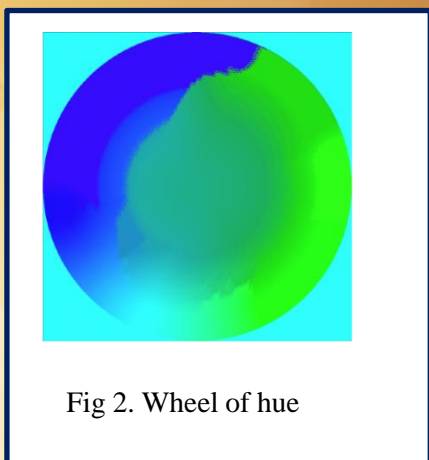
Discernment of the vermillion ink by Raman spectroscopy

Introduction

Raman spectroscopy is a technique to analyze the molecular structure from molecular vibrations as well as infrared spectroscopy. There are several advantages of RAMAN such that much smaller microscopic area can be measured, measurement in low wavenumber range can be easily implemented, a sample can be measured by non-destructive and non-contact method, and precise information on inside of a sample can be obtained selectively. Therefore, RAMAN has been used in the analysis of many fields, such as semiconductor and pharmaceutical as well as chemistry. Recently, more applications to the field of a criminal investigation are now expected. For example, RAMAN is applied to multilateral judgment of a very small piece of evidence and moreover, to identification of the poisonous , deleterious substances and illegal drugs from outside of the container. As explained, Raman spectroscopy is now effectively utilized in a criminal investigation, however there are following two points to be noted for measurement. One is the disturbance by the fluorescence from a sample, and the other, the possible damage to the sample by laser irradiation. The effective method of avoiding fluorescence is changing an excitation wavelength, or improvement in spatial resolution. If an excitation wavelength is changed into longer wavelength such as 785 nm or 1064 nm rather than 532 nm of standard, generally fluorescence will be decreased. Moreover, by narrowing down the laser beam size or using a confocal optical system, the spatial resolution of the xy-direction and even the z-direction improves, and then the influence of fluorescence can be eliminated. In order to avoid damage of the sample by the laser, it is important to set the optimum laser intensity by using attenuator.
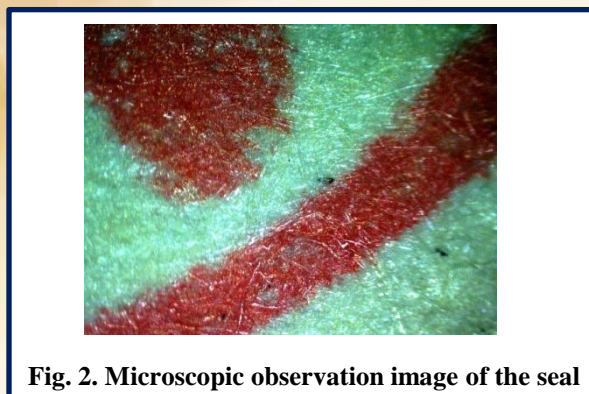

Fig. 1. NRS-5100

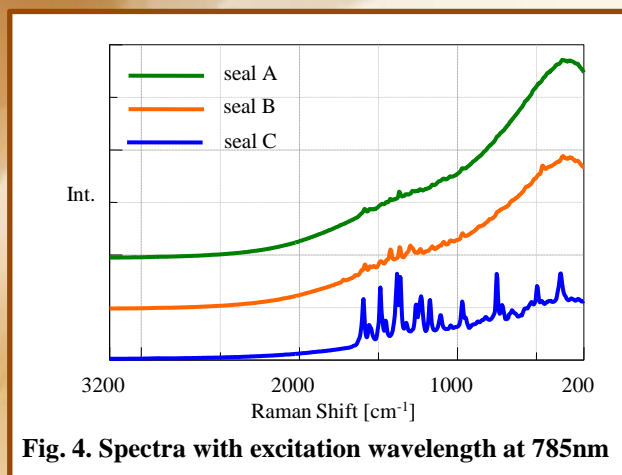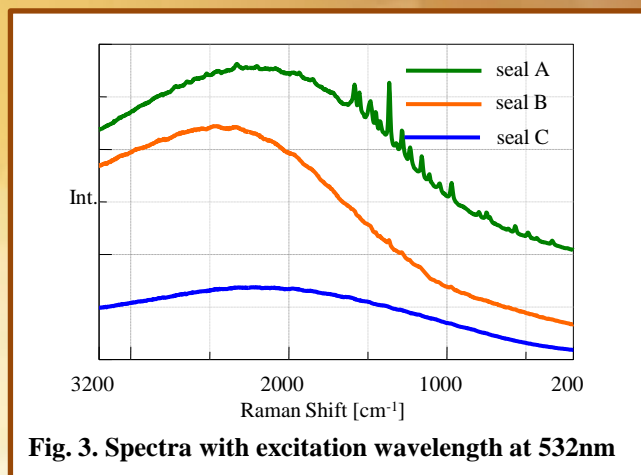**Fig. 2. Microscopic observation image of the seal**

As one of the cases which could be identified by Raman spectroscopy, here is a report on the identification of the imprint of a seal placed, which is essential for official documents in Japan. Vermillion ink pad containing the inorganic pigments such as cinnabar and the other ink pad containing organic pigments are generally used for imprint. Both materials can be easily discriminated by the Raman spectra in the low wavenumber range. If the ink material can be specified, it will be quite helpful for investigative information.

Measurement by 532nm laser

Using JASCO Laser Raman spectrophotometer, NRS-5100 (Fig. 1), the seals (Fig. 2) on three different papers were measured by standard 532nm laser. In order to avoid the damage to a sample, the laser intensity was raised gradually to be optimized. Moreover, since the fluorescence from vermillion ink or from its surrounding was very strong when measured without using a confocal optical system, it was very difficult to identify Raman peaks. Therefore, in order to increase spatial resolution, the measurement was implemented using the confocal optical system. Fig. 3 shows the measurement result. As can be seen, the Raman peaks were confirmed in the spectrum of A Seal, though it was affected by fluorescence. In the spectrum of a Seal B, some small peaks were slightly seen, but it was impossible to see the peaks at all on the spectrum of a Seal C.

Measurement by 785nm laser

In order to avoid the influence of fluorescence, 785 nm laser was used for measurement. Fig. 4 shows the measurement result. The Raman peaks are seen in the spectrum of Seal A, but the fluorescence is dominant, but the effect from fluorescence was reduced greatly in the spectra of Seal B and Seal C as compared with using 532 nm laser. If the optimum conditions are selected, such as a suitable laser wavelength, better spatial resolution and proper laser intensity, good Raman spectra can be obtained even for a sample like vermillion ink which generates the large background of fluorescence.

Fig. 3. Spectra with excitation wavelength at 532nm

Fig. 4. Spectra with excitation wavelength at 785nm

Analysis of the results

In order to analyze the measurement results in details, the measured three spectra (Seal A:excitation wavelength 532 nm, Seal B and C: excitation wavelength 785 nm) were processed by fluorescence correction and normalization in software and shown in Fig. 5. Concentrating on the wavenumber range of 2000-600 cm^{-1}, three different peaks have appeared, and all peaks could be identified. These peaks are due to the resin that contains organic pigment. On the other hand, in the low wavenumber range (red frame in Figure 5) where the peaks due to inorganic substances are expected to appear, a peak is hardly seen in the spectrum of a Seal A as compared with the spectra of Seal B and Seal C. Therefore, it is assumed that organic pigments are used primarily in ink of Seal A, while Seal B and Seal C contain inorganic pigment in the resin of vermillion ink pad. If the standard spectral data of multiple vermillion ink pad and other ink are available, by comparing the obtained spectra of imprint with such standard data, the type of ink and the vermillion ink pad used in imprint can be identified.
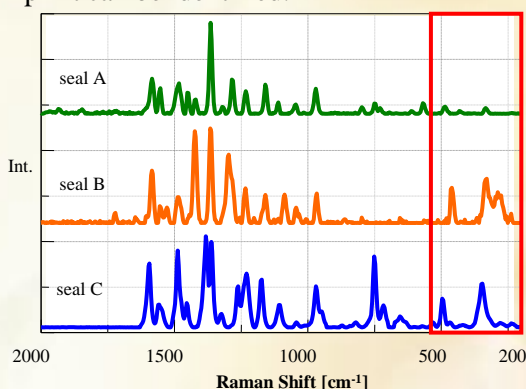

Fig. 5. Spectra after fluorescence correction (normalized view)

As mentioned above, in Raman spectroscopy a sample can be measured in a non-contact method with very simple operation. It is an analysis technique to demonstrate it as a powerful tool, when the amount of sample is limited and non-destructive analysis is required.

Evaluation of Single-Walled Carbon Nanotube (SWNT) by Raman Spectroscopy for inorganic and high function materials

Raman spectroscopy is widely used for the evaluation of carbon materials and can be applied to analysis of single-walled carbon nanotube(SWNT) in order to obtain useful information on carbon nanotube. SWNT shows metallic and also semiconducting characters due to different electronic structure in accordance with chirality and tube radius. Accordingly, by exciting its molecules with the energy corresponding to electronic transition (Resonance Raman Scattering), information about chirality and tube radius can be obtained. Fig. 1 shows Raman spectra of two SWNTs with different synthesis method (Sample A and B). In Raman spectra, three specific bands are seen. G-band observed around 1600cm-1 corresponds to vibrational mode assigned to graphite. In metal SWNT, BWF (Breit-Wigner-Fano) type spectrum is observed in the lower wavenumber range of G-band. D-band which attributes to defect is often utilized in the evaluation of crystallization. In addition, the band appearing in the low wavenumber region corresponds to the mode called RBM (Radial Breathing Mode), which correlates nanotube stretching diametrically. The peak position is inversely proportional to the tube diameter. From the equation shown in Fig.1, diameter can be estimated by peak position.

532 nm Excitation（2.33 eV）
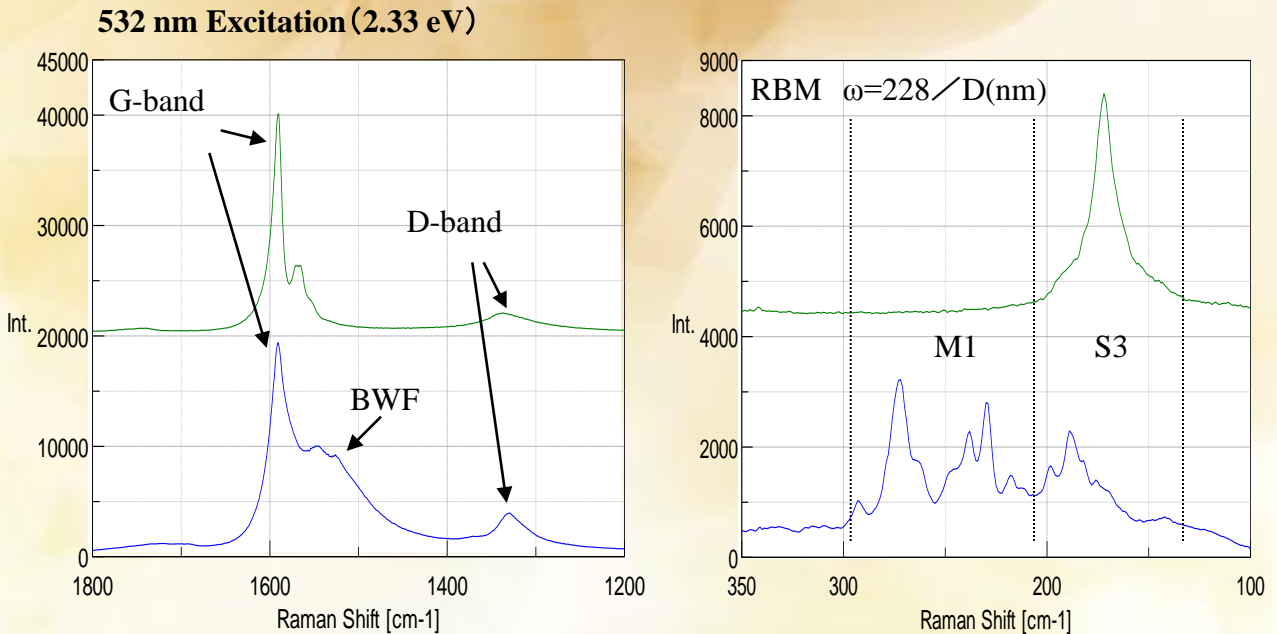
Figure 1 Resonance Raman spectra of SWNT (above: sample A, below: sample B)
(M1 : resonance of metallic SWNT, S3 : resonance of semiconducing SWNT)

Fig. 2 shows excitation wavelength dependence of SWNT (Sample B) Raman spectra. Using Resonance Raman Scattering, SWNT measurement can be done selectively for specific chirality and tube radius, depending on the excitation wavelength. Therefore, the shape of Raman spectra changes drastically depending on the selected excitation wavelength. It is assumed that 532 nm excitation is mainly in resonance with metallic SWNT, 633 nm with both metallic and semiconducting SWNT, and 785 nm with semiconductor SWNT respectively.
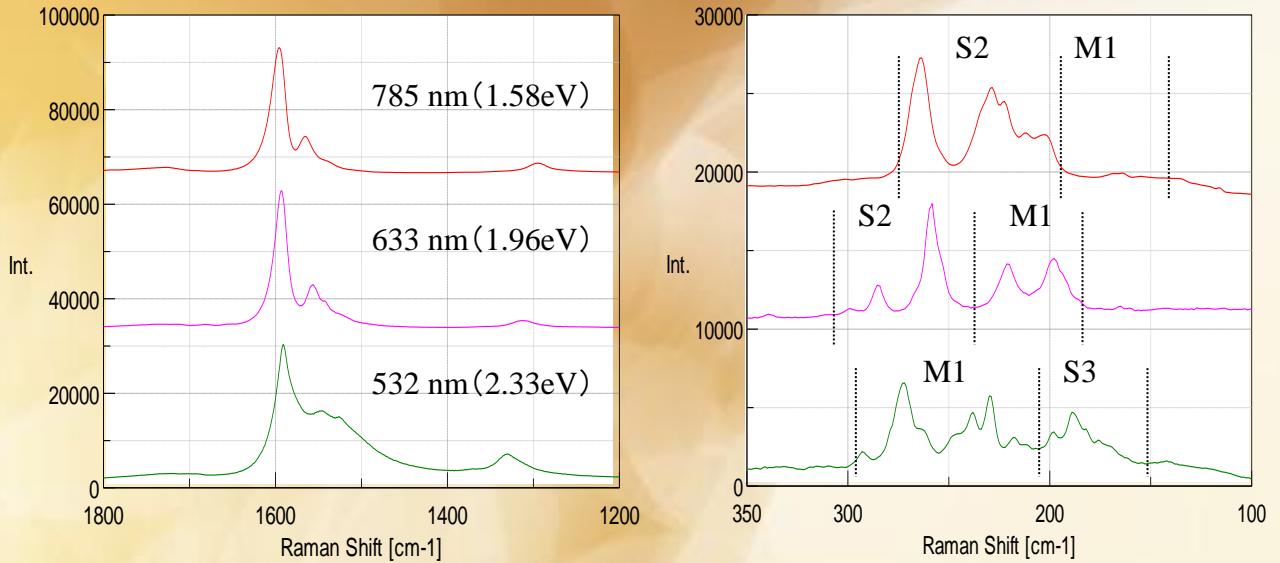
Figure 2 Raman spectrum of SWNT (excitation wavelength dependence)
(M1; resonance of metallic SWNT, S2,S3; resonance of semiconducing SWNT)

As in the above, the usefulness and measurement examples by Raman spectroscopy for single-walled carbon nanotube have been described. The best features for Raman spectroscopy are capabilities of simple and non-destructive measurement, even in the air environment.

Distribution Estimation of Polymorphism of Coral Skeleton Component by Mapping Measurement

<Introduction>

The biogenic mineral of the gallstone, seashell, coral and so on is in many cases made of calcium carbonate. There are two kinds of crystal polymorphism such as calcite and aragonite due to the difference of the crystal structure. The aragonite is more thermally unstable than the calcite at ordinary temperature and pressure, and when heated, the aragonite changes the phase to the calcite. The crystal formation depends on the organism species. On the other hand, in some cases, the calcite and aragonite are formed contiguously in the same species.

According to the recent research, if the Mg^{2+} is taken in the calcite crystal as an impurity, the solubility of the calcite is increased, resulting the inhibition of the crystal growth. On the other hand, the aragonite cannot take in the Mg^{2+} in the crystal lattice due to the ionic radius, therefore the solubility is not changed. There are a lot of Mg^{2+} in the sea water these days, so the aragonite is formed more in the sea due to the relation of the crystal formation in the sea and kinetic aspect of the dissolution.

Figure 1 Observation image of 5x Objective lens

In Raman spectroscopy, it is easier to measure in the low wavelength range, and it is possible to identify the polymorphism by peak pattern of the lattice vibration of the crystal appearing in the low wavenumber range. This time, the coral larva was transferred to the laboratory, then it was grown under the condition of some sea ingredient composition with adjusted the concentration of the each ions for easy growth of the calcite skeleton. The process of the skeletal formation of the calcite was measured by using the mapping measurement with Raman spectroscopy.
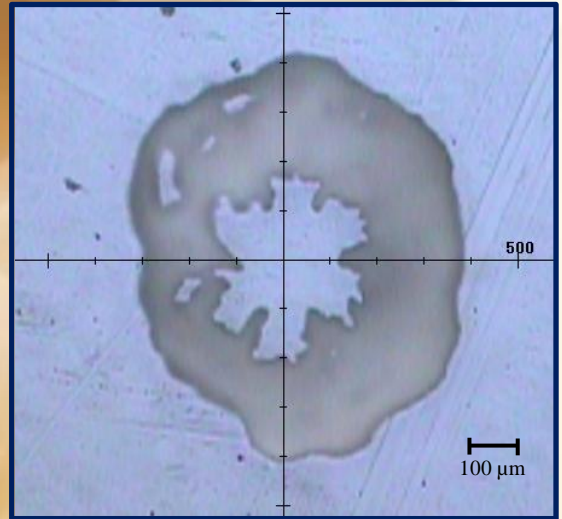
<Experimental>

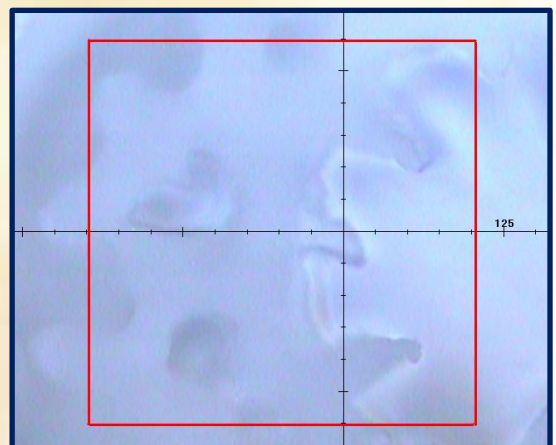|	
Instrument:	NRS-5100
Objective lens:	20x
Interval:	10 µm
Measurement points:	31 x 31, total 300 x 300 µm
Ex wavelength:	532 nm
Laser power at sample point:	about 10 mW
Measurement time:	about 1 hour
Sample:	1 seed coral

Figure 2 Observation image of 20x objective lens (300 x 300 um in the red square)

<Results and discussions>

The peak due to the symmetrical stretch vibration specific to carbonate ion was observed at 1090 cm^{-1} from the result of the mapping measurement. In the wavenumber region below 300 cm^{-1}, the difference of the peak patterns due to the lattice vibration depending on the crystal configuration difference between the calcite and aragonite was seen as shown in Figure 3. The peak specific to the calcite is 285 cm^{-1} and to the aragonite, 210 cm^{-1}. Those peaks are shown as colored-coded plot in Figure 4. As a result, it can be said that 2D image of crystal growth of the aragonite and calcite was visualized.
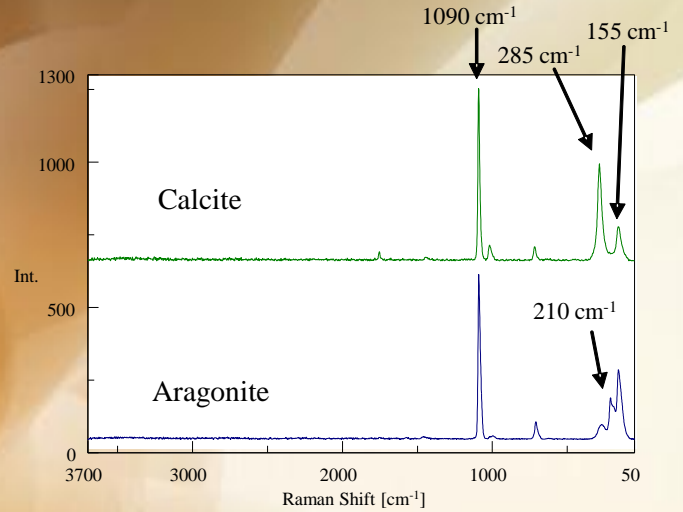

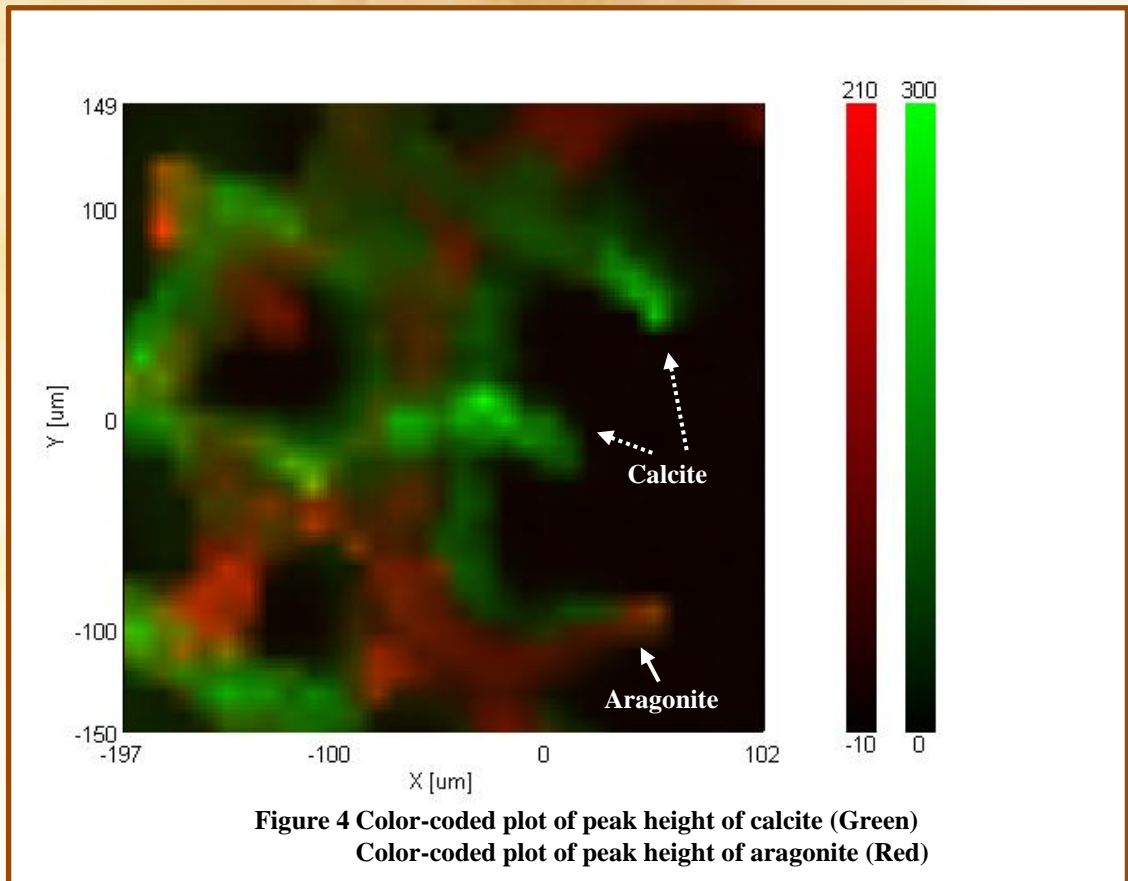**Figure 3 Raman spectrum of calcite and aragonite**

Figure 4 Color-coded plot of peak height of calcite (Green)
Color-coded plot of peak height of aragonite (Red)

Evaluation of semiconductor materials by Raman spectroscopy
- Crystal polymorphism and carrier density of Silicon power semiconductor device -

Introduction

Raman spectroscopy is widely used for evaluating chemical composition, orientation, crystallization, density, stress, temperature of semiconductor materials, and also for various structure-property evaluation such as impurity concentration, defect of semiconductor materials and composition ratio of mixed crystal semiconductor. Hall effect measurement with formed electrode is applied for evaluating electrical characteristics of carrier density in general, while Raman spectroscopy is also utilized for estimating carrier density of group III-V semiconductor. In this application data, we would like to show several measurement results using monocrystal SiC by Raman spectroscopy, such as determination of polymorphism and calculation of carrier density.

Experimental

<Evaluating crystal polymorphism>
1: Background

It is well known that SiC crystal has more than 200 different types of polymorphism depending on atomic arrangement and these each polymorphism has different physical property. Among such many types of polymorphism, there are the most valuable ones starting from 4H polymorphism which has the biggest band gap and also high mobility and the trials have been attempted to grow crystals selectively as one of hot topics and challenge in field. Raman spectroscopy can evaluate and determine the type of polymorphism by analysis of peak patterns due to lattice vibration of crystals, appearing in low wavenumber region where the measurement is quite difficult by IR spectroscopy.

Fig. 1 Raman Spectra of 6H-SiC and 4H-SiC

2: Experiment and result

Two kinds of SiC monocrystal with 0.33 mm thickness that have been prepared by vacuum sublimation method under the different conditions have been measured with 532 nm excitation and backscattering position. As the result of this experiment, by comparing measured spectra in the range of 150-200 cm^{-1} and 700- 800cm^{-1} with reference spectra in published paper[1], two samples were determined to be 6H and 4H polymorphism respectively.

<Evaluating carrier density>

1: Background

In manufacturing process of semiconductor materials, it is not unusual to dope some impurity material to pure semiconductor to increase the concentration of free election and electron hole as carrier. Regarding n-type compound semiconductor, Raman spectroscopy is applied as an easy method to estimate the carrier density.

In polar semiconductor such as GaN, GaAs, SiC, longitudinal wave and transverse wave due to lattice vibration of crystal can be observed separately in Raman spectra. Collective oscillation of free electron which exists in n-type semiconductor as carrier is called as Plasmon, which is longitudinal wave similar to sound wave. This plasma oscillation is the same kind of wave as the longitudinal wave due to lattice vibration, LO phonon and therefore they interact with each other. This interaction is magnified due to the concentration of carrier and this relevancy makes peak position of longitudinal wave due to lattice vibration shift to higher wavenumber side. Such peak shift is named as L_+ and L_- and shown in Fig. 2. In evaluation of SiC, only the peak of L_+ can be observed by using of Raman spectroscopy. It is known that this peak shifts to higher wavenumber side with broadening peak shape when carrier concentration is increased, and accordingly, the absolute carrier concentration is evaluated by the peak position.
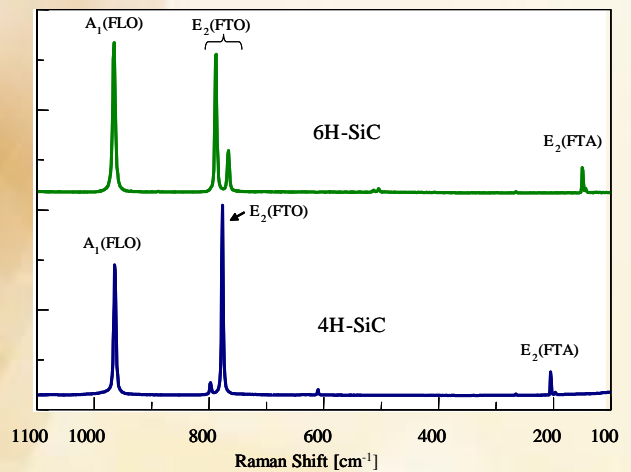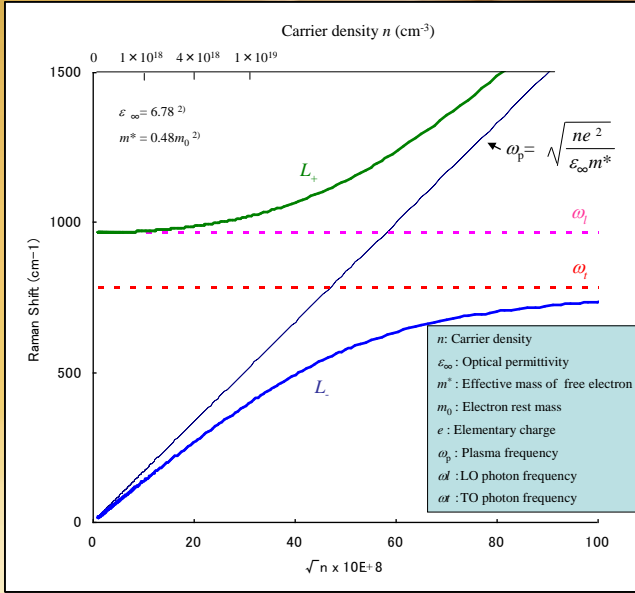
Carrier density n (cm^{-3})

$\varepsilon_\infty = 6.78$ [2]
$m^* = 0.48 m_0$ [2]

$\omega_p = \sqrt{\dfrac{ne^2}{\varepsilon_\infty m^*}}$

L_+

ω_l
ω_t

L_-

n: Carrier density
ε_∞ : Optical permittivity
m^* : Effective mass of free electron
m_0 : Electron rest mass
e : Elementary charge
ω_p : Plasma frequency
ωl : LO photon frequency
ωt : TO photon frequency

Raman Shift (cm^{-1})

$\sqrt{n}$ x 10E+8

Fig. 2 Carrier concentration change vs. wavenumber shift
(L_+ and L_-) in combined mode of Plasmon and phonon

Fig. 2 shows that the energy level of Plasma oscillation, collective oscillation of free electron in semiconductor increases with increase of carrier concentration in compound semiconductor. Peak is shifted through interaction between LO phonon, longitudinal wave due to lattice vibration and Plasmon by resonance phenomenon which is generated under the condition that plasma frequency is close to the energy of lattice vibration. However, any peak shift cannot be observed for TO phonon, since TO photon, transverse wave due to lattice vibration does not have any such interaction.

2. Experimental and result

Samples in this experiment are 3 kinds of 4H-SiC monocrystal which have been grown to 0.33 mm thickness by several different conditioned sublimation method. Each sample is measured using JASCO NRS-5100 Raman Spectrometer with 532 nm excitation and backscattering position.
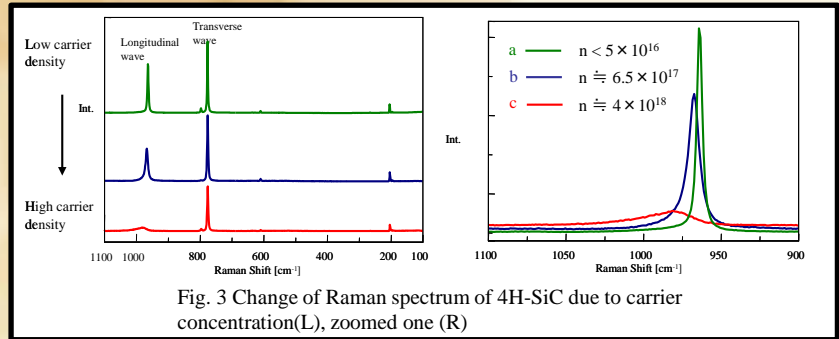

Fig. 3 Change of Raman spectrum of 4H-SiC due to carrier concentration(L), zoomed one (R)

Fig. 3 shows that peak wavenumber of longitudinal wave is different for each sample. The absolute carrier concentration can be estimated by inputting central wavenumber of each peak to theoretical curve which indicates the relationship between carrier concentration and LO phonon - Plasmon connection mode as shown in Fig. 4.

As shown in Fig.3, carrier concentration is getting higher in the order of a – b – c, and the higher carrier concentration is, the broader the peak shape becomes, while peak is shifting to higher wavenumber side.

As a conclusion, Raman spectroscopy makes it possible to evaluate sample in micron level spatial resolution which is difficult by the technique for Hall measurement, to analyze surface by imaging and also to evaluate depth profile with ease as non-destructive method.
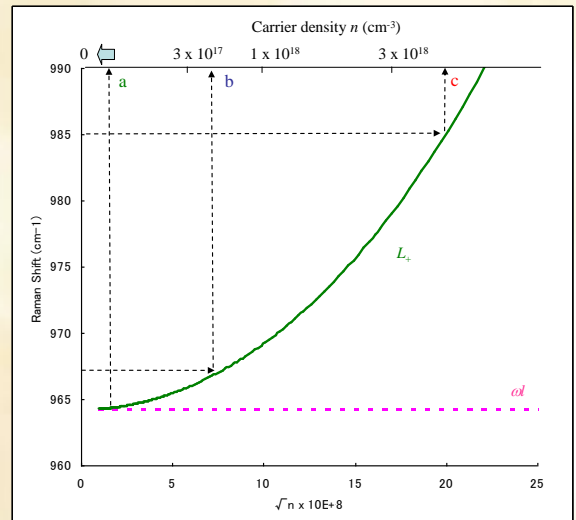
Fig. 4 Carrier concentration calculation
from central wavenumber

Reference
1) S. Nakashima, and H. Harima, *Phys . Stat . Sol* . (a) **162**, 39 (1997).
2) H. Harima, S. Nakashima, and T. Uemura, *J . Appl . Phys* ., **78**, 1996 (1995).
Samples in this evaluation had been provided from Prf. Inushima and Mr. Ohta of Course of Electrical and Electronic System in Tokai University.