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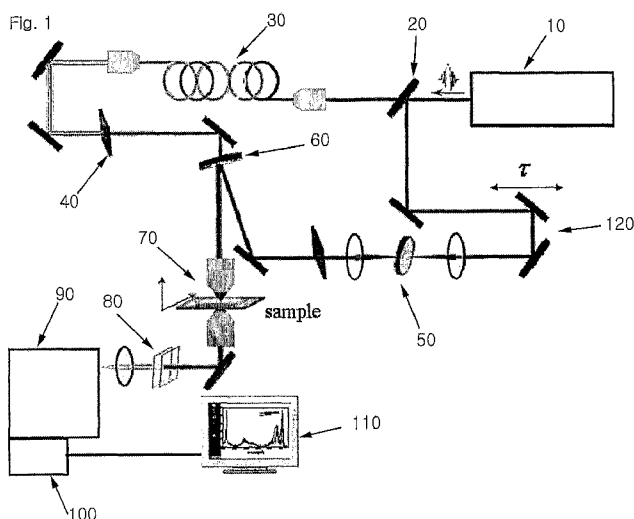
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(54) Title: SPECTRAL ANALYZER FOR MEASURING THE THICKNESS AND IDENTIFICATION OF CHEMICALS OF ORGANIC THIN FILMS USING CARS MICROSCOPY



(57) Abstract: The present invention relates to a spectral analyzer using a CARS microscopy which can measure the thickness and identification of kinds of chemicals of organic thin films at high spatial precision using a non-destructive method. The spectral analyzer using the CARS microscopy according to the present invention measures the wavelength and intensity of the coherent anti-stokes Raman scattering (CARS) signals scattered by irradiating Stokes beam and pump beam to the thin films to measure the thickness of the thin films and to analyze the chemicals. The spectral analyzer using the CARS microscopy according to the present invention is based on a vacuum spectroscopy corresponding to a vibration mode of a molecule by using a CARS microscopy that is one of third-order non-linear optical phenomena, making it possible to analyze each component, measure the components non-invasively and in real time, and overcome a general diffraction limitation of spatial resolution.

【DESCRIPTION】**【Invention Title】**

SPECTRAL ANALYZER FOR MEASURING THE THICKNESS AND
IDENTIFICATION OF CHEMICALS OF ORGANIC THIN FILMS USING CARS
5 MICROSCOPY

【Technical Field】

The present invention relates to a spectral analyzer for
measuring the thickness and identification of chemicals of
10 non-invasive organic thin films, which can non-invasively
measure the thickness of the organic thin films and at the
same time, identifying a structure of compounds forming the
organic thin films by using a coherent anti-stokes Raman
scattering (CARS) method that is one of third-order non-linear
15 optical phenomena.

【Background Art】

Recently, the importance of polymer and organic monomer
thin films has been increased in industry. Particularly, it
can be understood that in the fields of a semiconductor
20 industry, such as an integrated circuit device, a use of a
multi-type substrate of mobile products having various forms
and a packaging of the multi-type substrate, and a display
device that is developed and produced using a thin film of a
polymer or an organic molecule having relatively small

molecular weight, as well as in the field of producing the exterior decor of a car and an external appearance of a mobile phone, a high-quality coating and a precision control of the thickness of the polymer thin films are important component technologies, which determine performance and external appearance of products. Further, as the availability of the polymer in various forms, which includes proteins having biological characteristics in a recent bio and medical fields, is increased, the importance of polymer and organic monomer thin films is being increased day by day. For example, it has been known that the characteristics, such as a biologically useful polymer in a template that is used for a tissue-engineering based regeneration of a skin, etc., considered to be crucial in view of a regenerative medicine and the thickness of the thin film of the polymer and molecular materials for processing a surface of an implant having various forms, or the like, affect the whole development and the performance of products.

As methods for performing the measurement and performance evaluation of the polymer thin film having the above-mentioned importance, there have been known a method of directly measuring a vibration mode of a molecule, such as a Fourier Transform Infrared Spectroscopy (FT-IR), a linear Raman spectroscopy, etc., a measurement method using electron

transition in a molecule, such as absorption or light emission, an optical interference method and an ellipsometry method based on an optical change in refractive index and phase difference by an object thin film, or the like. Among those, 5 the FT-IR, which has been the most widely known traditionally, uses the absorption phenomenon of an electromagnetic wave (light) in an infrared band by the vibration in the organic molecule. The FT-IR is very sensitive to a change in a chemical structure of a molecule, but it is not proper to 10 improve spatial resolution to a micron size or to measure the very thin film due to the use of the infrared rays. The measurement method based on the absorption or the light emission by the electron transition is very excellent as a measurement method of the spatial resolution and the change in 15 the thickness if the organic materials have sufficient photoluminescence quantum efficiency. Furthermore, the emission spectral feature is not usually sensitive to the change in the chemical structure of the organic molecule, in particular, the polymer. Therefore, the measurement method can 20 be very usefully used when the chemical structure of the polymer is known or when the polymer thin film is formed of a single chemical; otherwise, its applications are very limited. The measurement technology developed on the basis of the light refractive index (light interference method and ellipsometry)

is the technology of determining the thickness of the thin film having the most excellent precision among currently known technologies when the chemicals is one and the refractive index is accurately known, but since the measurement
5 technology cannot analyze the chemicals of the organic molecule by itself, it cannot be applied to the a case where the thin file is formed of two kind of chemicals. Meanwhile, the linear Raman spectroscopy (FT or cw, continuous wave) has advantages that the spatial resolution can reach an optical
10 diffraction limitation and the chemicals can be analyzed, or the like. Due to its much lower sensitivity, however, its applications are very limited when the thin film is very thin. In order to overcome the problem of the sensitivity, an attempt to achieve the advanced technology, such as a surface
15 enhanced Raman spectroscopy (SERS) has recently been made actively, but the applications of the SERS is limited due to the characteristic that the dependency of the signal intensity with respect to the thickness of the polymer thin film is different for each sample.

20 A study on a CARS, which is one of third-order non-linear phenomenons, has considerably been progressed after it is used for a diagnosis study on a combustion engine, such as Taran, etc. from 1970s. A linear Raman scattering means that an electric dipole induced into a molecule by light is combined

to a vibration movement of the molecule to generate and scatter light having a new frequency. The CARS irradiates laser having two different wavelength of pump beam and stokes beam to a medium to make intensity of anti-stokes beam scattered in a sample to be measured large and to give the anti-stokes beam directivity. When the difference between the frequency of the pump beam and the frequency of the stokes beam is accurately equal to the frequency of the Raman activity, the signal of the CARS is generated. A microscopy using the CARS in 1980s is first developed by Duncan. During about 20 years from the development the CARS microscopy technology is improved to be able to measure a three-dimensional image in real time and increases the resolution to a half wavelength or less.

Recently, a supercontinuum multiplex CARS apparatus using one laser is developed. The applications of the CARS are currently being expanded to, in particular, the biological field based on the above-mentioned advantages.

20 [Disclosure]

[Technical Problem]

The present invention proposes to solve the above-mentioned problems. An object of the present invention provides an apparatus for measuring the thickness and

identification of chemicals of non-invasive organic thin films using a CARS microscopy, which can non-invasively measure the thickness of the polymer and at the same time, identify a structure of chemicals and overcome the spatial resolution and the light diffraction limitation forming the organic thin films by using a CARS method that is one of third-order non-linear optical phenomenons. In particular, the present invention provides a spectral analyzer for analyzing of each chemical forming the thin film and measuring the thickness of the thin films, in the thin films formed of a multi layer or a mixture.

【Technical Solution】

In order to achieve the above-mentioned objects, the spectral analyzer using the CARS microscopy of the present invention which can measure the thickness and identification of kinds of compounds (chemicals) of organic thin films at high spatial precision using a non-destructive method. The spectral analyzer using the CARS microscopy according to the present invention measures the wavelength and intensity of the coherent anti-stokes Raman scattering (CARS) signals scattered by irradiating stokes beam and pump beam to the thin films to measure the thickness of the thin films and to analyze the chemicals.

The spectral analyzer using the CARS microscopy according

to the present invention can analyze all the thin films regardless of kinds of thin films, such as an organic thin film, an inorganic thin film, etc. Specifically, as the analyzable thin films, there may be thin films containing
5 compounds selected from a single molecular organic compound, an organic polymer compound, a bio material, or a mixture thereof, wherein the thin film includes all the stacked form of a single layer or more than two layers. In particular, the spectral analyzer using the CARS microscopy according to the
10 present invention is suitable for analyzing the stacked type thin films and can simultaneously measure the chemicals forming each layer and the thickness of each layer in the stacked type thin films.

In the spectral analyzer using the CARS microscopy
15 according to the present invention, the used pump beam is a single line beam and the stokes beam is a wideband line beam. In particular, the stokes beam uses a beam in a near-infrared band.

The spectral analyzer using the CARS microscopy according
20 to the present invention is based on a principle that when the difference between the frequency of the pump beam and the frequency of the stokes beam is accurately equal to the frequency of the Raman activity, the CARS signals are generated, the CARS signal light is irradiated by laser having

two different wavelength of pump beam and stokes beam to a medium to make intensity of anti-stokes beam scattered in a sample to be measured large and to give the anti-stokes beam directivity, the CARS signals, the CARS signal measures an inherent Raman frequency for each material due to the chemical structure of the material, and the thin film and the object material are measured by the microscopy based on the thickness dependency with respect to the theoretical CARS signal intensity proportional to a square of the thickness of the object material and third-order optical susceptibility in the frequency to be able to non-invasively measure the chemicals and the thickness of the thin film while having the very excellent measurement sensitivity of the chemicals and the thickness of the thin film.

A theoretical expression of the CARS signal, which is one of the third-order non-linear optical phenomenons, is as follows under a state where the pump beam and the stokes beam inducing the CARS signals have a cylindrical form and a phase matching condition of the third-order non-linear optical phenomenons is satisfied.

$$I_3 = \frac{\omega_3^2}{n_1^2 n_2^2 n_3^2 c^4 \epsilon_0^2} I_1^2 I_2 | \chi_{CARS} |^2 I^2 \left(\frac{\sin \frac{\Delta k l}{2}}{\frac{\Delta k l}{2}} \right)^2 \quad (1)$$

In the equation, I_3 is the CARS signal intensity, ω_3 is a

frequency of the CARS signal, n_1 is the refractive index in the pump beam wavelength of the medium through which the pump beam is progressed, n_2 is the refractive index in the stokes beam wavelength of the medium through which the stokes beam is progressed, n_3 is the refractive index in the CARS signal wavelength of the medium through which the CARS signal is progressed, c is the speed of light in the medium, ϵ_0 is the dielectric constant in vacuum, I_1 is the intensity of the pump beam, I_2 is the intensity of the stokes beam, χ_{CARS} is the non-linear third-order decay rate, and l is the thickness of the sample.

Since it is assumed that the pump beam and the stokes beam are aligned on the same line, the phase matching condition is approximately satisfied. In other words, it becomes $\Delta k \approx 0$. Therefore, a sin function value of the equation (1) may approach to a unit value when the thickness l of the sample is relatively small. In conclusion, it can be appreciated from the equation (1) that the intensity of the CARS signal is proportional to a square of the third-order non-linear susceptibility and the thickness of the sample

Meanwhile, a Raman band corresponding to the vibration mode (vibrator in molecule, molecular vibration, or photon of material having a lattice structure, etc.) for the material of the object to be measured can be determined by the existing

obtainable database or the Raman spectroscopy in the case of a new material. Therefore, the characteristic signal band can be discriminated from the CARS signal of the present invention. In other words, the Raman frequency can be measured by the
5 inherent frequency of the material in view of the characteristic of the CARS signal and the chemicals can be discriminated and measured by using the frequency (Raman frequency) of the measured CARS signal. Also, the intensity of the Raman signal can measure the chemicals forming each thin
10 film and the thickness of the material to be measured by comparing the signal intensity in the Raman frequency for each compound, which are previously established, with the measured value in the thickness of the specific thin film, such that can be measured.

15 In the spectral analyzer using the CARS microscopy according to the present invention, an irradiation apparatus of the stokes beam and the pump beam to the thin film may include: a light source 10 that generates the stokes beam and the probe light; a beam splitter 20 that splits a beam
20 generated from the light source 10; a photonic crystal fiber 30 that passes a portion of the beam split by the beam splitter 20 and has the stabilized beam distribution in a wideband; a low pass filter 40 that passes the stabilized beam by the photonic crystal fiber 30 and passes a low-frequency

beam to generate the stokes beam in a near-infrared band; a narrow band pass filter 50 that passes the remaining beam split by the beam splitter 20 and makes the wavelength of the remaining beam narrow to passes the pump beam which makes the medium molecule of the polymer sample into an excited state; a notch filter 60 that spatially combines the stokes beam passing through the low pass filter 40 with the pump beam passing through the narrow band pass filter 50; and a scan device 70 that generates the CARS signals by scanning the beam combined by the notch filter 60 onto the polymer sample.

The irradiation apparatus may further include an optical delay 120 that is installed at a front end and a rear end of the narrow band pass filter 50 to temporally delay the optical paths of the stokes beam and the pump beam so that the optical paths are matched to each other. The narrow band pass filter 50 passes the pump beam having a range where the wavelength of the beam is 10 to 1.0nm. Preferably, the splitter 20 splits a portion of the split beam and the remaining beam at a ratio of 3~4:7~6. The length of the photonic crystal fiber 30 is 30 to 40cm.

Also, a measurement apparatus of the scattered coherent anti-stokes Raman scattering (CARS) signal may include: a short pass filter 80 that interrupts the scanned stokes beam and pump beam and passes the short CARS signal; a spectrograph

90 that makes the CARS signal passing through the short pass filter 80 into monochrome and spectroscopy; a detector 100 that detects the CARS signal spectroscoped by the spectrograph 90; and an analyzer 110 that converts the CARS signal detected from the detector 100 into an electrical signal and simultaneously analyzes the kind of the polymer and the thickness of the polymer thin film using the converted electrical signal. The detector 100 may adopt a photomultiplier tube (PMT) that amplifies and detects light.

10 **【Advantageous Effects】**

The spectral analyzer using the CARS microscopy according to the present invention can non-invasively measure the thickness of the thin film and the chemicals forming the thin film and obtain the precision three-dimensional shape using the high spatial resolution exceeding the optical diffraction limitation, which is one of the CARS advantages being the third-order nonlinear optical phenomenon even in the case of the thin film having a spatial shape. The advantages can remarkably improve the quality of products by monitoring the process in real time in the industry using various thin films, such as the polymer thin film, etc., in the near future.

In particular, the apparatus according to the present invention can measure the thickness even at a laser of 1 wavelength or less and can measure the thickness in real time

as well as obtain the information of the thickness in connection with a three-dimensional volume, such as a micro channel, a micro device using the polymer film.

【Description of Drawings】

5 The above and other objects, features and advantages of the present invention will become apparent from the following description of preferred embodiments given in conjunction with the accompanying drawings, in which:

FIG. 1 is a schematic view showing a spectral analyzer
10 using a CARS microscopy according to the present invention, which can analyze chemicals forming thin films and the thickness of the thin film;

FIG. 2 is a graph showing a dependency on a film coating frequency of the thickness of the thin films determined by
15 locally etching the thin films using an ultrafast laser and measuring it using an atomic force microscope in order to absolutely measure the thickness of a poly-methyl metacrylate (PMMA) thin film having various thicknesses;

FIG. 3 is a graph showing results that show the
20 spectroscopic spectrum of the CARS signal according to the thickness of the poly-methyl metacrylate (PMMA) thin film manufactured in FIG. 2;

FIG. 4 is a graph showing results that performs a log-log plot on the CARS signal intensity with respect to the

thickness of the PMMA thin film; and

FIG. 5 is a graph showing a spectroscopy distribution of the measured CARS signal in the PMMA, polyvinyl, and polystyrene thin film.

5

[Detailed Description of Main Elements]

10: LIGHT SOURCE 20: BEAM SPLITTER

30: PHOTONIC CRYSTAL FIBER

40: LOW PASS FILTER

10 50: NARROW BAND PASS FILTER

60: NOTCH FILTER

70: SCAN DEVICE

80: SHORT PASS FILTER

90: SPECTROSCOPE

15 100: DETECTOR

110: ANALYZER

120: OPTICAL DELAY

【Best Mode】

20 Hereinafter, a spectral analyzer for measuring the thickness and identification of chemicals of non-invasive organic thin films using a CARS microscopy according to the present invention having the above-mentioned configuration will be described in detail with reference to the accompanying

drawings.

In order to show the implementation example of the spectral analyzer using the CARS microscopy according to the present invention, a polymethyl metacrylate (PMMA) polymer
5 thin film coated on a glass substrate as one example is manufactured by using a CARS microscopy technology, the absolute thickness of the PMMA polymer thin film is non-invasively measured by an atomic force microscope, and the thickness of the thin film is measured by confirming the
10 dependency on the CARS signal.

FIG. 1 shows a configuration view of a CARS microscopy manufactured using one laser.

As shown in FIG. 1, an apparatus of simultaneously measuring the kind and thickness of the non-invasive polymer
15 thin film using the CARS microscopy according to the present invention includes: a light source 10 that generates the stokes beam and the probe light; a beam splitter 20 that splits a beam generated from the light source 10; a photonic crystal fiber 30 that passes a portion of the beam split by
20 the beam splitter 20 and has the stabilized beam distribution in a wideband; a low pass filter 40 that passes the stabilized beam by the photonic crystal fiber 30 to make the passed beam into the stokes beam; a narrow band pass filter 50 that passes the remaining beam split by the beam splitter 20 to pass the

pump beam; a notch filter 60 that spatially combines the stokes beam passing through the low pass filter 40 with the pump beam passing through the narrow band pass filter 50; a scan device 70 that generates the CARS signals by scanning the beam combined by the notch filter 60 onto the polymer sample; a short pass filter 80 that interrupts the stokes beam and the pump beam of the scanned beam and passes the short CARS signal; a spectrograph 90 that makes the CARS signal passing through the short pass filter 80 into monochrome and spectroscopy; a detector 100 that detects the CARS signal spectroscopied by the spectrograph 90; and an analyzer 110 that converts the CARS signal detected from the detector 100 into an electrical signal and simultaneously analyzes the kind of the polymer and the thickness of the polymer thin film.

The light source 10, which is a laser light source, uses a Ti: sapphire laser (Coherent, Mira 900). The laser is operated at a repetitive rate of 76MHz and its pulse width is about 140fs, its power is about 1.2W, and its central wavelength is 780nm. The pump beam and the probe light (or stokes beam source) necessary for obtaining the CARS signal are obtained by the following method using the beam splitter 20 that can split the laser basic beam at a intensity ratio of 3~4:7~6 as follows. The laser basic beam split at the intensity ratio of 3:7 using the beam splitter 20 will be

described herein.

First, the stokes or probe light source can be obtained by using the laser beam having the intensity of 30% of two split beams. Meanwhile, since the stokes beam source should
5 have the wideband spectrum, the split light source is first focused on the photonic crystal fiber (PCF) 30 by using an objective lens (Nikon, NA=0.4, X20) to obtain supercontinuum light having the wideband wavelength. In order to obtain the wideband stabilized beam distribution in the present invention,
10 the length of the photonic crystal fiber is optimized and the length of the PCF is determined to have about 30 to 40cm based on the result. In order to minimize the interference with the final CARS signal, the stabilized beam, that is, the low frequency beam of the supercontinuum light is passed by the
15 photonic crystal fiber 30 and passes through the low pass filter 40 that makes the low frequency beam into the stokes beam of a near-infrared band, making it possible to obtain only the beam of the near-infrared band. The beam of the near-infrared band is used as the stokes beam in the CARS.

20 The remaining beam split by the beam splitter 20, that is, a laser beam having a beam split to about 70% of the Ti:Sapphire laser basic beam power passes by using the narrow band pass filter 50 that makes the wavelength of the remaining beam and passes the pump beam which makes the medium molecule

of the polymer sample into an excited state, thereby making the spectroscopy distribution of the basic light source narrow from about 10 nm to about 1.0 nm and using it as the pump beam source. The notch filter 60 is used to spatially combine the
5 stokes beam passing through the short pass filter 40 and the pump beam passing through the narrow band pass filter 40. Also, in order to obtain the CARS signal, the stokes beam and the pump beam should temporally be matched to each other. To this end, the optical delay 120 that can reduce the difference in
10 the optical paths of the pump beam is installed. The optical delay 120 is installed at a front end or a rear end of the narrow band pass filter 50.

The stokes beam and the pump beam that are temporally and spatially matched well as described above are focused on a
15 sample through the objective lens (Nikon, NA=0.9, X100) of the scan device 70, thereby generating the CARS signal. The CARS signal, which is generated forward, is focused by installing another objective lens. The light focused through the second objective lens should necessarily be split since there are the
20 CARS signal as well as the stokes light source and the pump light source together. To this end, the CARS signal is transmitted to the spectrograph 90 that makes only the CARS signal into monochrome by using the short pass filter 80 that interrupts the focused stokes beam and pump beam and passes

the short CARS signal, such that the CARS signal is spectroscoped, and the spectroscoped CARS signal in a single line is detected by a detector, such as a CCD, a photomultiplier tube (PMT), or a high-speed photodiode, or the like and the detected CARS signal is converted into the electrical signal and the electrical signal is transmitted to the PC, making it possible to process the signal.

The polymer thin film having various thicknesses used as the examples of the present invention is manufactured by coating a film on a slider glass using the polymethyl methacrylate (PMMA) as described below. In particular, the reason of using the the PMMA is because due to the colorlessness and transparency of the polymer thin film, the PMMA has excellent advantages, such as excellent optical characteristics, excellent weather-resistant as compared to other resins, very high hardness, and easiness of adhesive printing, etc. to produce a huge ripple effect on the industry in the various forms such as an optics and a substrate for an electronic element. First, the PPMM (Mw 120,000) power is put in toluene to be 5wt% and is then melted for about 10 hours while stirring at about 40C° using a magnetic bar. Meanwhile, the slider glass used as the substrate is washed with an ultrasonic wave for about 20 minutes under acetone and methanol, respectively, and is then dried. The PMMA thin film

on the substrate can be obtained by performing a spin coating for 15 seconds under a speed of 2000 rpm. After the coating, the PMMA thin film is put in a drier under a dry atmosphere and is dried for two hours at a temperature of 80°. The above-mentioned coating and dry processes are repeated, making it possible to obtain the PMMA thin film having various thicknesses. In the present invention, the coating and dry processes are repeated in total, such that a total of 18 PMMA thin film thicknesses can be manufactured and used.

As described above, the existing thickness measurement methods, such as the ellipsometry, etc. depend on the relative change in the optical characteristic of the object thin film and the chemical characteristic of polymer. Therefore, the present invention locally etches the thin film, which is manufactured to overcome the problems, to measure the absolute thickness and to be used for an illustration. In particular, the present invention etches only a very local region using an ultrafast laser, not using the chemical etching and uses the etched local region. Also, as already known, threshold fluence is $2.6\text{J}/\text{cm}^2$ of the ultrafast laser process of the PMMA thin film and the threshold value of the slide glass is $3.5\text{J}/\text{cm}^2$, such that the fluence of the laser is controlled to be able to selectively etch the PMMA thin film without any damage to the glass substrate. A surface profile around the

selectively etched region is measured by an atomic force microscope and the difference in the height of the surface of the non-processed PMMA thin film and the height of the completely etched glass surface is determined, making it possible to absolutely determine the PMMA thickness.

FIG. 2 is a graph showing a dependency on a film coating frequency of the thickness of the thin films determined by locally etching the thin films using an ultrafast laser and measuring it using an atomic force microscope in order to absolutely measure the thickness of a poly-methyl metacrylate (PMMA) thin film having various thicknesses, FIG. 3 is a graph showing results that show the spectroscopic spectrum of the CARS signal according to the thickness of the poly-methyl metacrylate (PMMA) thin film manufactured in FIG. 2, FIG. 4 is a graph showing results that performs a log-log plot on the CARS signal intensity with respect to the thickness of the PMMA thin film; and FIG. 5 is a graph showing a spectroscopy distribution of the measured CARS signal in the PMMA, polyvinyl, and polystyrene thin film.

FIG. 2 shows the thickness of the thin film according to a repetitive number of the coating process of the PMMA thin film. The reason why the increase rate of the thin film with respect to the frequency of the coating relatively approaches a straight line is that the characteristic of the PMMA thin

film having various thicknesses manufactured through the present process is relatively constant. The thinnest film thickness of the film is 368nm and the thickest film thickness is 3726nm.

5 FIG. 3 shows a spectral distribution of the CARS signal detected by the developed CARS measurement apparatus according to the PMMA thin film sample having various thicknesses manufactured as above. In the measurement of the present illustration, the CARS signal is obtained in a wavelength of 10 624nm to 674nm obtained by irradiating the pump beam having a wavelength of 780nm and the stokes beam having a wavelength of 924nm to 1040nm being a wideband beam to the PMMA polymer thin film. The CARS signal is measured by well aligning the film thickness at the position where the laser beam is focused 15 through the microscope lens. It can be appreciated that as the thickness of the PMMA thin film is increased, the intensity of the CARS signal is constantly increased. In FIG. 3, it is well matched in that it is well separated into a combination band in connection with O-CH₃ of the PMMA polymer, a symmetric 20 stretching of (CH₂) group at 2842 cm⁻¹ and 2925 cm⁻¹ widely known and a CH symmetric stretching vibration of O-CH₃ and C-CH₃ at 2953 cm⁻¹, and an asymmetric stretching vibration of CH bond of O-CH₃ and C-CH₃ group showing at 3000 cm⁻¹. Also, the lower portion of FIG. 3 shows a Raman signal measured at one sample.

It may be determined that the spectral distributions measured by two different measurement apparatuses are the same when considering the difference in the spectroscopic degradability. The thin film sample and the CARS signal are measured by the
5 CCD camera by using the measurement apparatus of the thin film using the CARS proposed in the present invention. The measured data is shown in FIG. 3.

FIG. 4 shows a result that a log function value of the spectrum intensity, which the spectrum width is 38cm^{-1} based on
10 2950cm^{-1} being the maximum value of the CARS signal, plots on a Y-axis and the log value of the thickness of the PMMA sample plots on an X-axis. It can be appreciated from the intensity and thickness of the measured signal that the measured thin film thickness is linearly changed well from 380 nm, which is
15 the minimum value, to 2170 nm in the case of the PMMA sample. Meanwhile, FIG. 3 shows a phenomenon where the CARS signal is saturated beyond a square function at $2.17\mu\text{m}$ or more. Qualitatively viewing this phenomenon, a beam waist in the course of a focus process of the pump and stokes beams
20 irradiated when measuring the CARS signal is finite beyond an infinitely long cylindrical form, such that when the thickness of the object sample is larger than the finite beam waist, the CARS signal is not increased any more. Quantitatively viewing this phenomenon, when the laser beam is focused through the

objective lens, the length of the beam waist, that is, the length of Rayleigh is expressed by $z_0 = k\omega_0^2/2$. If this is theoretically derived by using characteristics of optical components in the CARS measurement apparatus of FIG. 1 used in
5 the example of the present invention, the value is about 812nm. It is expected that the CARS intensity will be proportional to the square of the thickness up to 1624nm that is a point having the maximum value of the laser intensity of $1/e^2$ along the optical axis and is two times the above value. The
10 theoretically expected value approximately matches the experimental value but is not an accurate value. The reason is because the numerical aperture (NA) value of the signal focusing lens is 0.55, not 0.9 and also, the refractive indexes of air, slider glass, PMMA are different from each
15 other. The CARS intensity matches an approximate theory in the region prior to the saturation state, such that the thickness can accurately be measured to a half wavelength or less by the CARS intensity. When the present invention configures the spectral apparatus capable of making the beam waist long based
20 on the above-mentioned theory, the embodiment of the present invention can be expanded to the thickness of the polymer thin film even thicker than the linear region shown in the embodiment of the present invention. In other words, when an objective lens being a half of the case of the embodiment of

the present invention due to a small NA value is used, the linearly changeable thin film thickness, that is, the very thick thin film thickness of $(1624 \times 2) \text{ nm}$, that is 3248 nm can also be measured.

5 FIG. 5 shows spectrums where each chemical for some cases among the most widely used polymer thin films is split and analyzed by the CARS spectroscopy. In other words, viewing the CARS signal for three different kinds of organic polymer thin films of polystyrene, PMMA, poly-vinyl, the CARS band
10 corresponding to the inherent vibration of each chemical is clearly split in the approximately same region. As a result, the split and analysis can be performed based on the CARS band.

 Those skilled in the art will appreciate that the conceptions and specific embodiments disclosed in the
15 foregoing description may be readily utilized as a basis for modifying or designing other embodiments for carrying out the same purposes of the present invention. Those skilled in the art will also appreciate that such equivalent embodiments do not depart from the spirit and
20 scope of the invention as set forth in the appended claims.

【Industrial Applicability】

 The spectral analyzer using the CARS microscopy according to the present invention can non-invasively measure the

thickness of the thin film and the chemicals forming the thin film and obtain the precision three-dimensional shape using the high spatial resolution exceeding the optical diffraction limitation, which is one of the CARS advantages being the
5 third-order nonlinear optical phenomenon even in the case of the thin film having a spatial shape. The advantages can remarkably improve the quality of products by monitoring the process in real time in the industry using various thin films, such as the polymer thin film, etc., in the near future.

10 In particular, the apparatus according to the present invention can measure the thickness even at a laser of 1 wavelength or less and can measure the thickness in real time as well as obtain the information of the thickness in connection with a three-dimensional volume, such as a micro
15 channel, a micro device using the polymer film.

【CLAIMS】**【Claim 1】**

A spectral analyzer using a CARS microscope characterized in that it measures the thickness of thin films and analyzes
5 chemicals by measuring the wavelength and intensity of a coherent anti-stokes Raman scattering (CARS) signal scattered by irradiating a stokes beam and a pump beam to the thin films.

【Claim 2】

The spectral analyzer according to claim 1, wherein the
10 thin film is an organic thin film or an inorganic thin film.

【Claim 3】

The spectral analyzer according to claim 2, wherein the thin film contains compounds selected from a single molecular organic compound, an organic polymer compound, a bio material,
15 or a mixture thereof.

【Claim 4】

The spectral analyzer according to claim 1, wherein the thin film is stacked at more than two layers having different compounds from each other.

20 【Claim 5】

The spectral analyzer according to claim 1, wherein the scattered CARS signal intensity is proportional to a square of the thickness of the thin film.

【Claim 6】

The spectral analyzer according to claim 5, wherein the stokes beam uses a beam in a near-infrared band

【Claim 7】

The spectral analyzer according to claim 5, wherein the
5 CARS signal strength is measured at a Raman frequency of the thin film.

【Claim 8】

The spectral analyzer according to claim 1, wherein the pump beam is a single line beam

10 【Claim 9】

The spectral analyzer according to any one of claims 1 to 8, wherein an irradiation apparatus of the stokes beam and the pump beam to the organic thin film includes:

a light source 10 that generates the stokes beam and the
15 probe light;

a beam splitter 20 that splits a beam generated from the light source 10;

a photonic crystal fiber 30 that passes a portion of the beam split by the beam splitter 20 and has the stabilized beam
20 distribution in a wideband;

a low pass filter 40 that passes the stabilized beam by the photonic crystal fiber 30 and passes a low-frequency beam to generate the stokes beam in a near-infrared band;

a narrow band pass filter 50 that passes the remaining

beam split by the beam splitter 20 and makes the wavelength of the remaining beam narrow to passes the pump beam which makes the medium molecule of the polymer sample into an excited state;

5 a notch filter 60 that spatially combines the stokes beam passing through the low pass filter 40 with the pump beam passing through the narrow band pass filter 50; and

 a scan device 70 that generates the CARS signals by scanning the beam combined by the notch filter 60 onto the
10 polymer sample.

【Claim 10】

The spectral analyzer according to any one of claims 1 to 8, wherein a measurement apparatus of the scattered coherent anti-stokes Raman scattering (CARS) signal includes:

15 a short pass filter 80 that interrupts the scanned stokes beam and pump beam and passes the short CARS signal;

 a spectrograph 90 that makes the CARS signal passing through the short pass filter 80 into monochrome and spectroscopy;

20 a detector 100 that detects the CARS signal spectroscoped by the spectrograph 90; and

 an analyzer 110 that converts the CARS signal detected from the detector 100 into an electrical signal and simultaneously analyzes the kind of the polymer and the

thickness of the polymer thin film using the converted electrical signal. The detector 100 may adopt a photomultiplier tube (PMT) that amplifies and detects light.

【Claim 11】

5 The spectral analyzer according to claim 9, further including an optical delay 120 that is installed at a front end and a rear end of the narrow band pass filter 50 to temporally delay the optical paths of the stokes beam and the pump beam so that the optical paths are matched to each other.

10 【Claim 12】

The spectral analyzer according to claim 11 wherein the narrow band pass filter 50 passes the pump beam having a range where the wavelength of the beam is 10 to 1.0nm.

【Claim 13】

15 The spectral analyzer according to claim 9, wherein the splitter 20 splits a portion of the split beam and the remaining beam at a ratio of 3~4:7~6.

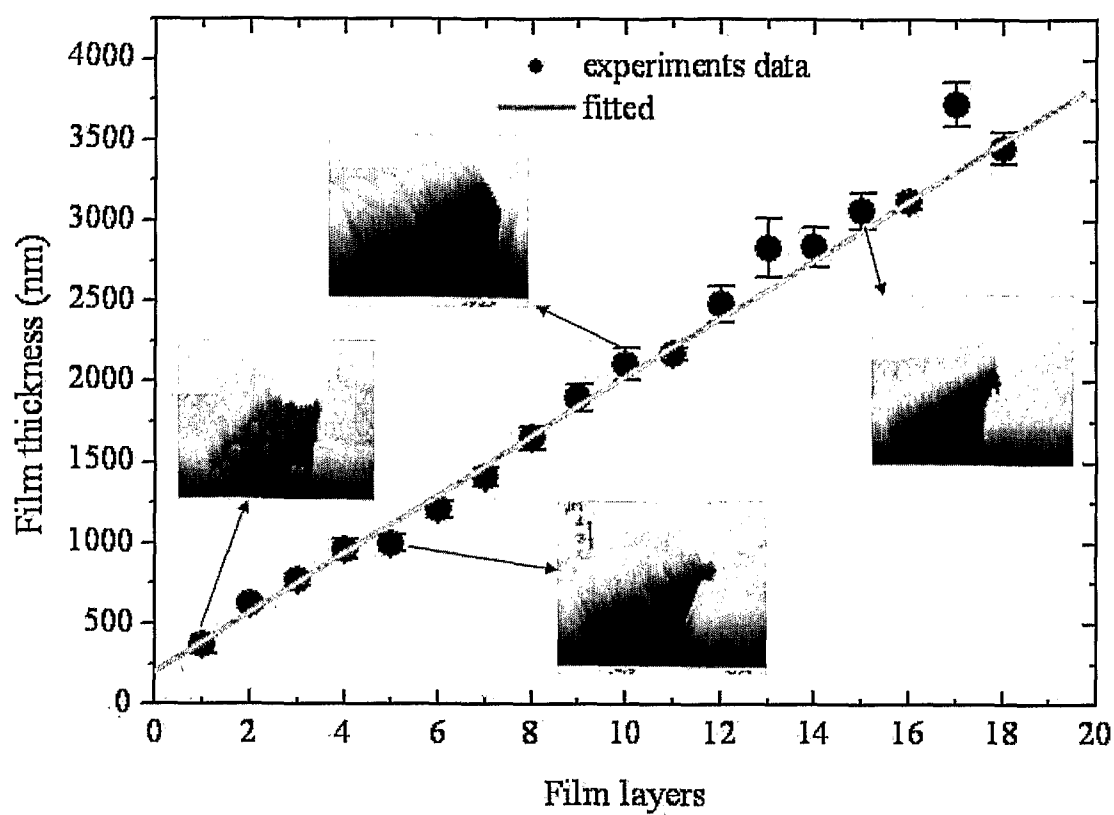
【Claim 14】

20 The spectral analyzer according to claim 9, wherein the length of the photonic crystal fiber 30 is 30 to 40cm.

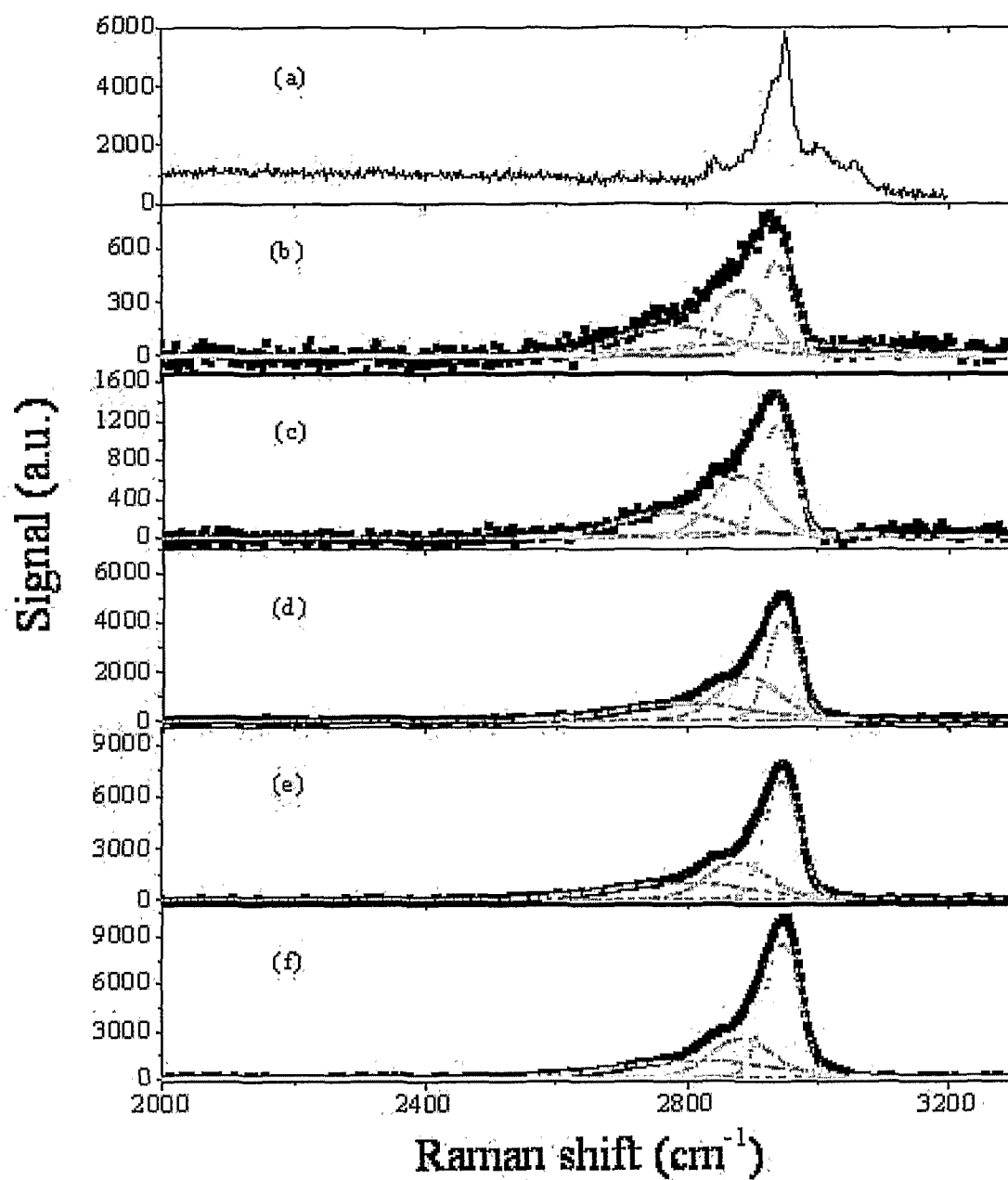
【Claim 15】

The spectral analyzer according to claim 10, wherein the detector 100 is a photomultiplier tube (PMT) that amplifies and detects light.

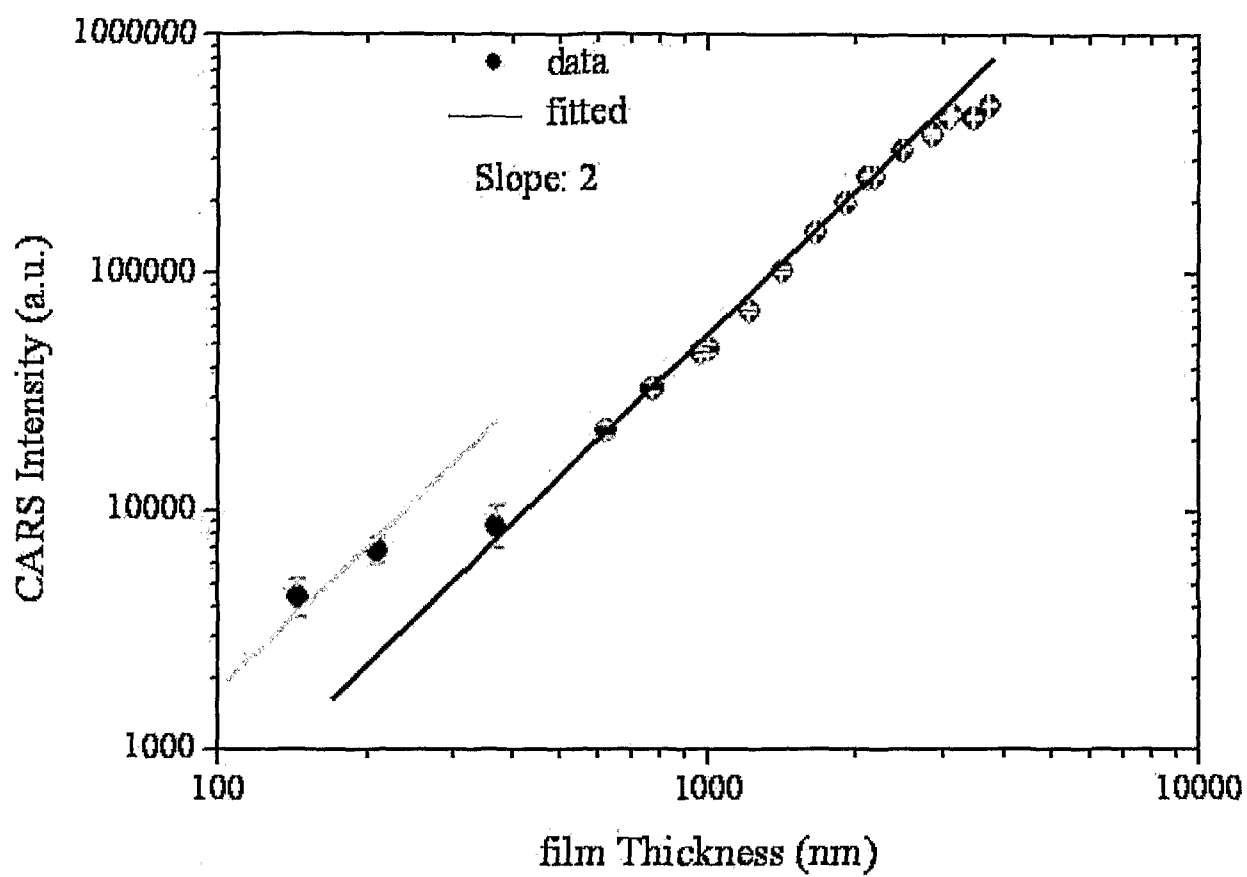
[Fig. 2]



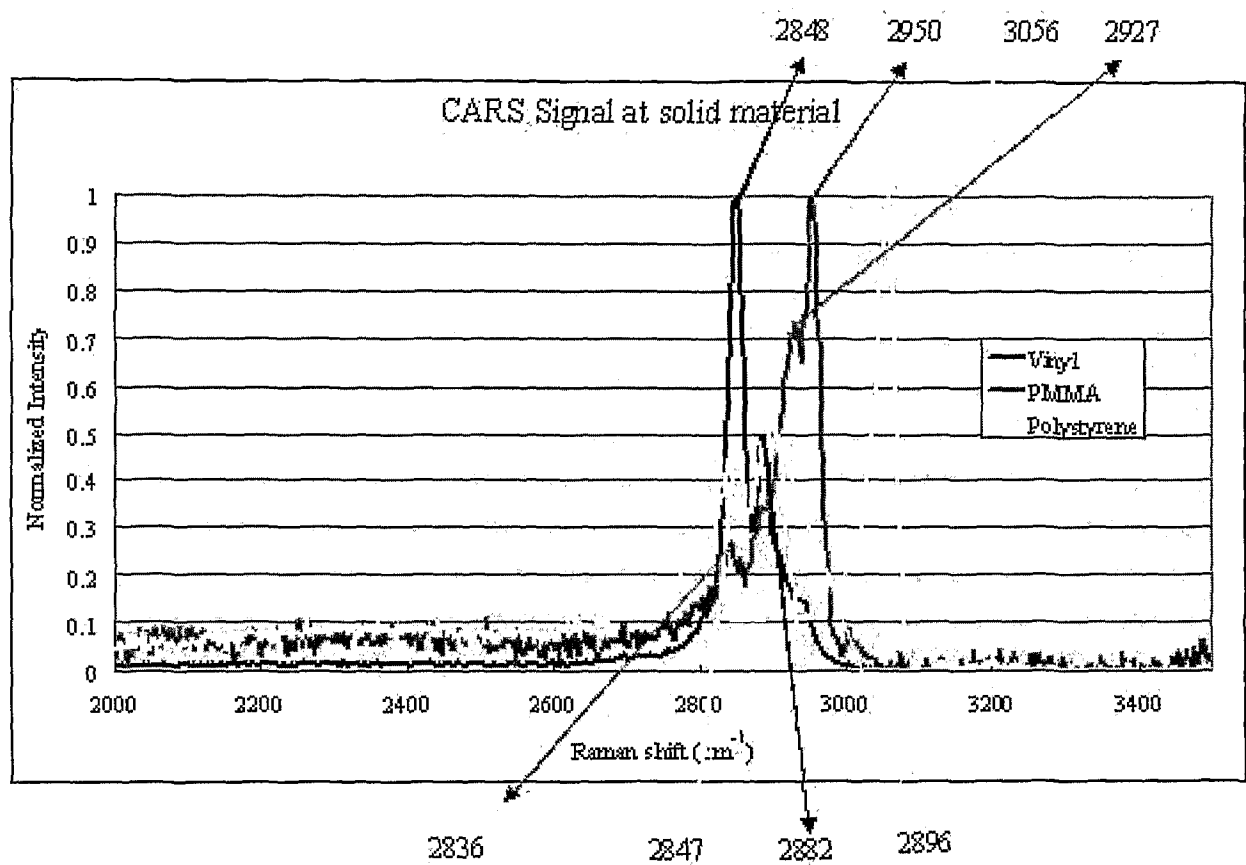
[Fig. 3]



[Fig. 4]



[Fig. 5]



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2008/005229**A. CLASSIFICATION OF SUBJECT MATTER****G01B 11/06(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 8 G01B 11/06

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean Utility models and applications for Utility models since 1975

Japanese Utility models and applications for Utility models since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

KIPASS & keywords: "spectral", "analyzer", "measure", "thickness", "film", "organic", "cars", "microscopy"

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	US6657708B1(Drevillon et al.) 02 DEC 2003 see fig 1, claim 1, column 4-6	1-8, 10 9, 11-15
Y A	JP05288681A(Osaka gas co.Ltd) 02 NOV 1993 see abstract, claim 1	1-8, 10 9, 11-15
A	JP09213652A(SHARP corp) 15 AUG 1997 see the entire documents	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

18 DECEMBER 2008 (18.12.2008)

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

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