

Raman Microspectroscopic Study on Polymerization and Degradation Processes of a Diacetylene Derivative at Surface Enhanced Raman Scattering Active Substrates. 2. Confocal Raman Microscopic Observation of Polydiacetylene Adsorbed on Active Sites

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Confocal Raman microscopic measurements were performed at room temperature on the Langmuir–Blodgett (LB) monolayer of 10,12-pentacosadiynoic acid (DA) prepared on surface enhanced Raman scattering (SERS) active Ag island films, two-dimensional (2D) Raman images of which exhibit bright and dim spots on a dark background. The measurements performed by focusing the excitation laser light (488 nm) on the dark background indicate the prompt appearance of the Raman bands (1515 and 2115 cm^{-1}) due to polydiacetylene (PDA) in the red phase and subsequent diminution of the Raman bands. On the other hand, the spectra observed by focusing the excitation laser spot on the dim and bright spots exhibit almost random fluctuations, giving rather narrow Raman bands in the 1620–1000 cm^{-1} region, which appear and disappear temporarily with varying intensities under the continuous irradiation at 488 nm. Broad Raman bands appear around 1580 and 1360 cm^{-1} , which are ascribable to amorphous carbon, at a later stage of the observation, the intensities from the bright spot being more than 100 times stronger than those from the dim spot. The narrow bands are ascribed to a series of carbonaceous intermediates such as polyenes, graphite sheets with various sizes, and folded or reorganized forms of the sheets including carbon nanotubes and fullerenes, which are formed during the conversion of PDA to amorphous carbon. The random spectral fluctuation was interpreted by considering that the intermediates undergo thermally activated diffusion and get temporarily in contact with the SERS-active site, resulting in the enhancement of their Raman bands and the fluctuation.

Introduction

As reported in the preceding paper,¹ the thermal polymerization of the LB films of 10,12-pentacosadiynoic acid (DA) proceeds at an appreciably enhanced rate on surface enhanced Raman scattering (SERS) active substrates under the irradiation of the excitation laser light at 532 nm. At room temperature, the polymerization occurs promptly upon the laser irradiation and subsequent bleaching of polydiacetylene (PDA). At low temperatures below $-50\text{ }^{\circ}\text{C}$, the bleaching is appreciably suppressed. The analyses of the polymerization kinetics based on the SERS spectra, measured at the temperature range of -50 to $-60\text{ }^{\circ}\text{C}$, indicated that there exist at least two surface reactions; that is, one of the reactions consists of the formation of PDA in the blue phase and its subsequent conversion to the red phase, and another reaction consists of the direct formation of the red phase and its bleaching. The first process was considered to proceed at sites with relatively low SERS activity, and the second was considered to proceed at the site with high SERS activity (or so-called “hot spots”^{2,3}). These reactions were probed at the same time because the Raman microspectroscopy in the previous paper employed a rather broad excitation laser spot with a diameter of ca. 10 μm . Confocal microscopic measurements on the LB monolayer of DA (DA-LB($n = 1$)) prepared at the SERS-active substrates with the excitation laser focused on bright spots of the 2D Raman microscopic image

of the sample surfaces, however, give spectral features, which exhibit almost random fluctuation, quite different from those reported by the preceding paper and ascribable to conversion of PDA to amorphous carbon. The random fluctuation or “blinking” of the SERS spectra associated with the formation process of amorphous carbon has been reported by several authors.^{2,3} Kudelski and Pettinger² observed the Raman spectra of carbon films deposited on SERS-active substrates, which exhibit remarkably fluctuating lines ascribable to vibrations of carbonaceous groups. The fluctuation evidences a surface chemistry producing a variety of carbon chain configurations, which get temporarily in contact with the “hot spots”, that cause large surface enhancements. Moyer et al.³ also performed confocal microspectroscopy measurements of Raman scattering from carbon nanocrystallites adsorbed on an isolated Ag nanoparticle, reporting a blinking effect of Raman lines associated with carbon atoms forming carbon domains. The blinking was explained as a result of a thermally induced diffusion of the carbon nanoparticles through a SERS-active “hot spot” on the Ag nanoparticle.

As explained in the present paper, the observation of the fluctuating spectral features for DA-LB($n = 1$)/Ag island/ITO and DA-LB($n = 1$)/Ag island/mica under various conditions (excitation laser power and kinds of substrates) actually proved that the spectral changes are associated with the conversion process of the DA monolayer to amorphous carbon via the formation of PDA, and the fluctuation is interpreted as a result of the formation of intermediate carbonaceous species such as polyenes, graphite sheets with various sizes, folded species of

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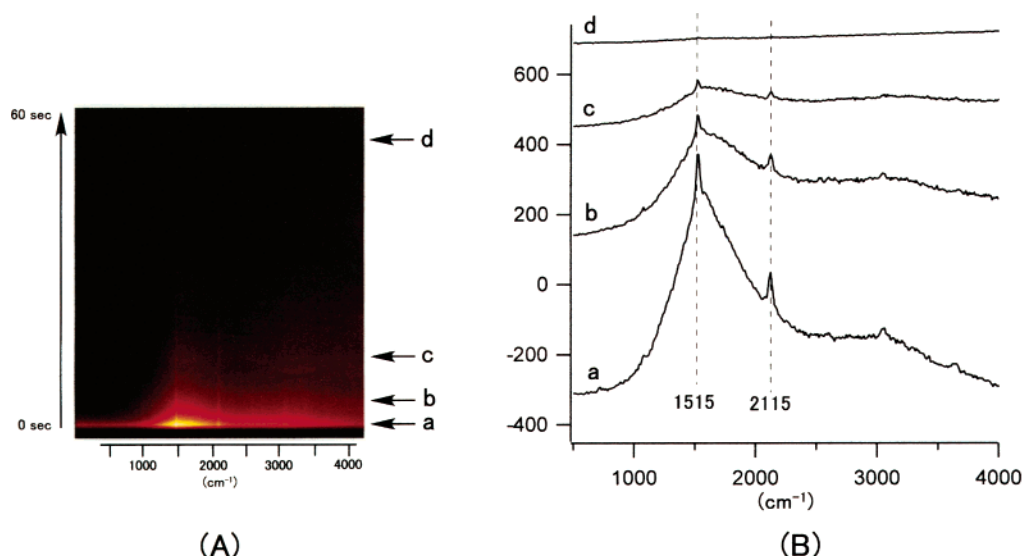


Figure 1. SERS spectral changes as a function of irradiation time observed for DA-LB($n = 1$)/Ag island/ITO by focusing the excitation laser light (power, $50 \mu\text{W}$; wavelength, 488 nm) on the dark background: (A) 2D image of the spectral changes; (B) the SERS spectra read from the points indicated in the 2D image. See text.

the sheets (e.g., carbon nanotubes and fullerenes), and the thermally activated diffusion of the intermediates through a hot spot on SERS-active substrates. Although each Raman band comprising the fluctuating Raman spectra cannot always be assigned to a certain chemical species, the results give new aspects of the thermal degradation or the conversion to amorphous carbon of PDA on the SERS-active substrates.

Experimental Section

Preparation of SERS-Active Substrates. The SERS-active substrates are the same as those explained in the preceding paper.¹

Preparation of Monolayer Films of DA on SERS-Active Substrates. Samples used in the present paper were prepared by the method explained in the preceding paper;¹ the number of the LB layer was fixed at one. The same notations of the samples as those in the previous paper are also used, that is, DA-LB($n = 1$)/Ag island/ITO and DA-LB($n = 1$)/Ag island/mica.

Measurements. A confocal Raman microspectrometer (Tokyo Instruments Co. Ltd., Nanofinder 30) was used for measurements. With a microscope objective lens ($40\times$, 0.55 NA), a focused laser spot size is calculated to be about 500 nm . The Raman spectra were acquired mainly with 488 nm excitation, and the laser power at the sample spot was $50\text{--}100 \mu\text{W}$.

Results and Discussion

Spectra Observed from a Dark Background on DA-LB($n = 1$)/Ag Island/ITO. As Figure 2A of the preceding paper shows,¹ the two-dimensional (2D) Raman microscopic image of DA-LB($n = 1$)/Ag island/ITO consists of bright and dim spots on the dark background. The SEM image (not shown in this paper) of the sample surface indicates that the surface giving the dark backgrounds is also covered by small Ag grains. Figure 1A is a two-dimensional (2D) image of Raman spectral change observed by focusing the laser spot (power at the sample spot, $50 \mu\text{W}$; wavelength, 488.0 nm) on the dark background of DA-LB($n = 1$)/Ag island/ITO. The abscissa in Figure 1A corresponds to the wavenumber; the ordinate corresponds to the time of measurement (each spectrum was acquired with 1

s of the integration time), and the brightness in the image corresponds to Raman intensity. Figure 1B exhibits the spectra read from the 2D image at the points indicated by a–d. Upon irradiation of the excitation laser light, the spectrum exhibits Raman bands at 1515 and 2115 cm^{-1} due to PDA in the red phase^{4,5} in addition to emission backgrounds centered around 1500 and 3000 cm^{-1} . These spectral features disappear within several seconds after the onset of irradiation, as can be seen from the 2D image in Figure 1A and the spectra read from points a–d. The spectral changes indicate the immediate formation of PDA in the red phase and subsequent degradation of PDA. The 2D image, measured with the reduced laser power of ca. $10 \mu\text{W}$ at the sample spot (not shown in this paper), exhibits Raman bands near 2080 and 1480 cm^{-1} due to PDA in the blue phase^{4,5} with emission backgrounds centered around 1500 and 3000 cm^{-1} , the subsequent shift of the former two bands to 1515 and 2115 cm^{-1} accompanying the diminution of the backgrounds, and finally, the disappearance of the Raman bands; the disappearance is much retarded compared to the result in Figure 1A. The 2D images of the SERS spectral changes from the dark background of DA-LB($n = 1$)/Ag island/mica are more or less similar to those observed for the ITO substrate. As reported in the preceding paper,¹ the surface process taking place on the dark background (with relatively low SERS activity) at the temperature range of -50 to $-70 \text{ }^\circ\text{C}$ was presumed to be the formation of the blue phase and its conversion to the red phase. Thus, the above-mentioned surface processes probed by the confocal Raman microscopic measurement for the dark background corroborates the conclusion of the preceding paper. The disappearance of the Raman bands due to the red phase is ascribable to degradation of PDA at the higher temperature of the substrate compared to those employed by the preceding paper, and the absence of Raman bands associated with the degradation product (amorphous carbon), contrasting to the spectra from the dim and bright spots explained in the following sections, is due to the low SERS activity of the substrate.

Spectra Observed from a Dim Spot on DA-LB($n = 1$)/Ag Island/ITO. Figure 2A exhibits the 2D image of the SERS spectral changes observed by focusing the excitation laser at 488 nm (ca. 500 nm in diameter with a power of $100 \mu\text{W}$ at the sample spot) on one of the dim spots of DA-LB($n = 1$)/Ag

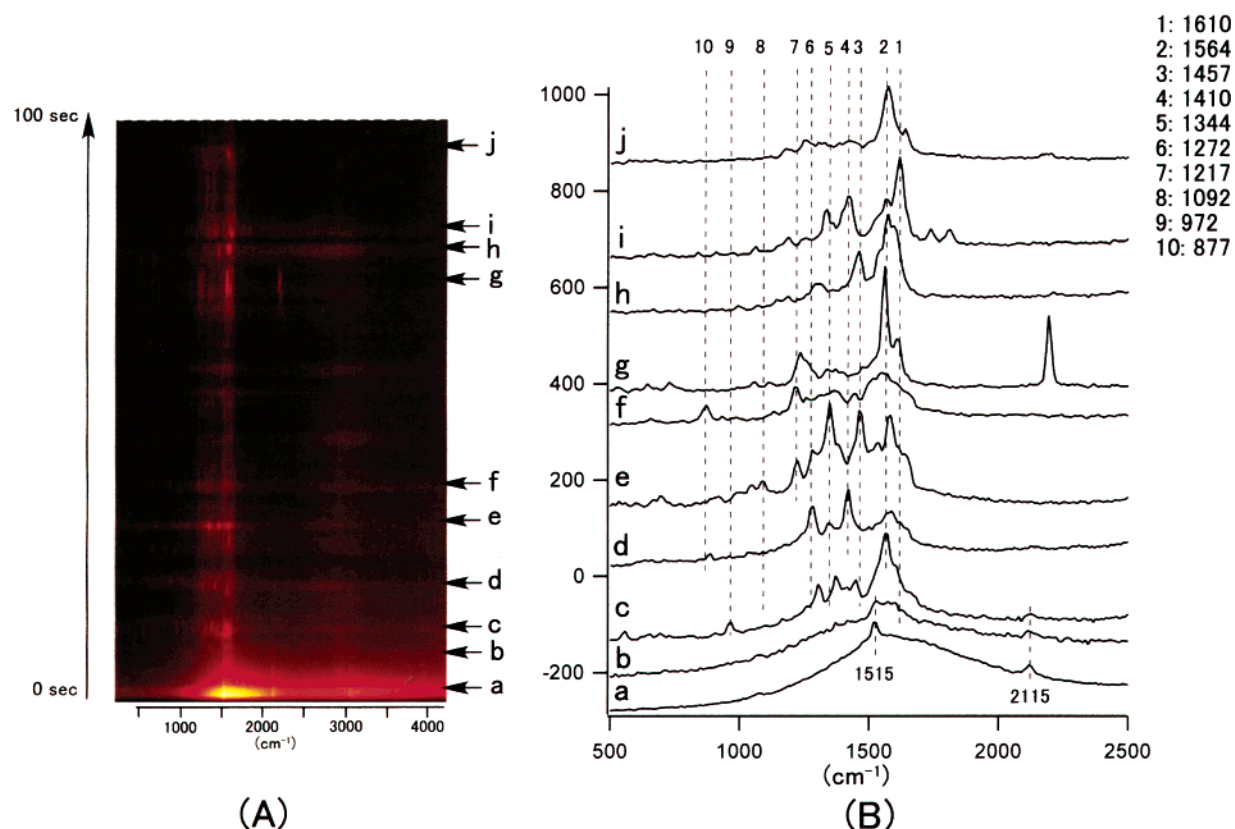


Figure 2. SERS spectral changes as a function of irradiation time observed for DA-LB($n = 1$)/Ag island/TTO by focusing the excitation laser light (power, $100 \mu\text{W}$; wavelength, 488 nm) on one of the dim spots: (A) 2D image of the spectral changes; (B) the SERS spectra read from the points indicated in the 2D image. The inserted list in (B) indicates the wavenumbers of prominent peaks. See text.

island/TTO, and Figure 2B shows the SERS spectra read from the 2D image at the indicated points a–j. As in the case of the spectra from the dark spot (Figure 1), the emission background and Raman bands at 1515 and 2115 cm^{-1} due to PDA in the red phase appear upon irradiation of the excitation laser and disappear within several seconds after the irradiation. Subsequent spectral changes are quite different from those of the spectra from the dark spot, exhibiting almost random fluctuations in overall spectral features which last until several hundred seconds of the laser irradiation. As Figure 2B shows, each spectrum consists of broad bands around 1560 cm^{-1} and a distinct set of intense but rather narrow Raman bands and shows discernible fluctuations in the form of sudden appearance and disappearance of narrow Raman lines mainly in the region of 1000 – 1620 cm^{-1} . The fluctuation is similar to that observed for carbon materials deposited on electrochemically roughened Ag substrates by Kudelski and Pettinger,² although they did not assign each component of the fluctuating features except for those due to amorphous carbon. According to the authors, the average spectra obtained by numerical addition of a series of the fluctuating spectra are more or less similar to that of amorphous carbon giving two broad bands around 1580 and 1340 cm^{-1} ; the former band is due to the in-plane E_{2g} zone center mode of graphite, and the latter is due to a disorder-induced band.^{6,7} The spectrum observed at a later stage of the observation in Figure 2 (e.g., the spectrum j in Figure 2B) gives a prominent peak at 1564 cm^{-1} , which corresponds to the peak 1582 cm^{-1} observed for the graphite crystal. Thus, the overall spectral changes in Figure 2 are also interpreted as a result of the conversion from PDA to carbon materials including graphite and amorphous carbon. The sharp peaks observed in Figure 2B are more abundant compared to those reported by Kudelski and Pettinger,² indicating that they actually trace a series of carbonaceous

compounds formed during the conversion from PDA to amorphous carbon. Expected intermediates are polyenes with various conjugation lengths, graphite sheets (or two-dimensional (2D) graphenes) with various sizes, folded and reorganized species of the graphite sheets including carbon nanotube-like materials and fullerene-like compounds, and carbon nanocrystallites. Polyenes as thermal degradation products of polymers such as poly(vinyl chloride) exhibit prominent Raman bands near 1100 and 1500 cm^{-1} associated mainly with C–C and C=C stretching vibrations, respectively; the frequency of the latter band ranges from 1464 cm^{-1} for the conjugation length $n = 50$ to 1530 cm^{-1} for $n = 10$.⁸ An infinite monolayer of hexagonally ordered carbon atoms (a graphene sheet) gives a phonon dispersion curve of the in-plane stretching E_{2g} mode from ca. 1590 cm^{-1} at the Γ point (the wave vector $q = 0$) to ca. 1200 cm^{-1} at the M point, and it is possible that finite size graphene sheets give rise to Raman bands corresponding to the optical branch associated with $q \neq 0$.⁹ Carbon nanotubes give prominent Raman bands near 1580 cm^{-1} , the frequency of which depends on the tube radius (r) being observed as triplet bands at 1591 , 1568 , and 1549 cm^{-1} for $r = 0.55 \text{ nm}$, as a doublet at 1589 and 1570 cm^{-1} for $r = 0.65 \text{ nm}$, and as a singlet at 1586 cm^{-1} for $r = 1 \text{ nm}$.^{10,11} C_{60} fullerene exhibits a prominent band at 1470 cm^{-1} in addition to a relatively weak band at 1428 and 1575 cm^{-1} , and C_{70} fullerene exhibits a series of distinct and narrow bands including 1186 , 1231 , 1448 , and 1569 cm^{-1} components.¹² Thus, each carbonaceous compound gives rise to rather narrow and prominent one or two Raman bands in the 1100 – 1600 cm^{-1} region. Although each narrow Raman band observed in Figure 2B cannot be explicitly assigned to one of the expected intermediate species, the overall correspondence between the listed Raman bands and those in Figure 2B indicates that the carbonaceous intermediates are formed during the

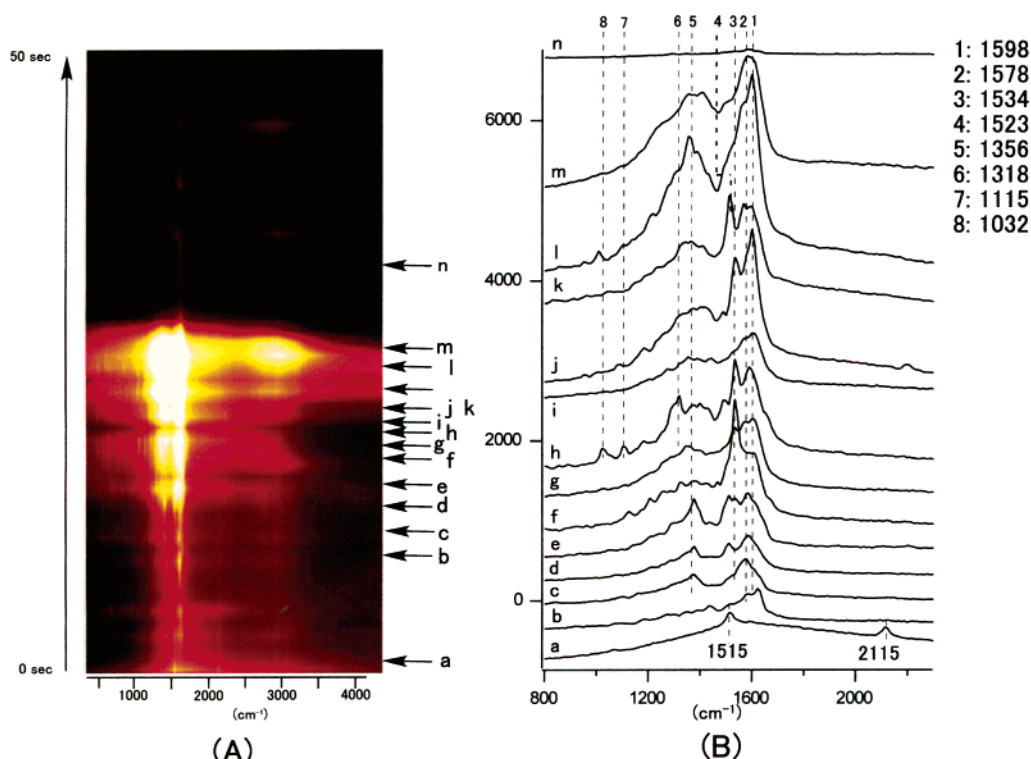


Figure 3. Spectral changes as a function of irradiation time observed for DA-LB($n = 1$)/Ag island/ITO by focusing the excitation laser light (power, $100 \mu\text{W}$; wavelength, 488 nm) on one of the bright spots (so-called "hot spot"): (A) 2D image of the spectral changes; (B) the SERS spectra read from the points indicated in the 2D image. The inserted list in (B) indicates the wavenumbers of prominent peaks. See text.

conversion, continue thermally activated diffusion, and get temporarily in contact with the SERS-active spots, resulting in the fluctuating spectral features given in Figure 2. The SERS spectral changes observed for DA-LB($n = 1$)/Ag island/mica are similar to those in Figure 2. The changes observed by using a reduced or an increased excitation laser power (10 and $100 \mu\text{W}$) are again similar to those in Figure 2. These results indicate that the spectral fluctuation observed during the conversion of PDA to amorphous carbon does not depend on the kind of substrates and the laser power in the range of $100\text{--}10 \mu\text{W}$.

Spectra Observed from a Bright Spot of DA-LB($n = 1$)/Ag on the SERS Active Substrates. The SERS spectral changes observed by focusing the excitation laser light (power, $100 \mu\text{W}$; wavelength, 488 nm) on one of the bright spots on DA-LB($n = 1$)/Ag island/ITO are illustrated in Figure 3. As in the case of the SERS spectra from the dim spot explained in the preceding section, PDA in the red phase is formed promptly upon laser irradiation, giving the Raman bands at 1515 and 2115 cm^{-1} due to the polymer. Subsequent spectral changes are different from the previous observations at several points; that is, the formation of amorphous carbon layer proceeds rapidly, giving the broad Raman bands around 1578 and 1356 cm^{-1} after ca. 27 s of the laser irradiation (spectrum m in Figure 3B), and the huge enhancement of the Raman bands are observed. (Note that the intensity ratio of the Raman band near 1570 cm^{-1} due to the amorphous carbon observed for spectrum m in Figure 3B to that for the spectrum j in Figure 2B is estimated to be about $1421/127$.) The Raman bands due to the amorphous carbon accompany a broad band centered around 3000 cm^{-1} , as can be seen from the 2D Raman spectral pattern at point m in Figure 3A. These results suggest that the bright spot from which the spectra are observed corresponds to the so-called "hot spot" of the substrate^{2,3} and that the formation of the amorphous carbon is highly enhanced at the spot. The SERS enhancement

of carbonaceous materials on Ag islands has been reported by many authors and applied to highly sensitive probing of surface chemistry taking place at graphite surfaces.^{2,3,7,13} The broad Raman band around 3000 cm^{-1} has also been observed for carbon nanoparticles adsorbed on an Ag island by Moyer et al.³ and interpreted as the typical second-order Raman band of graphite; according to the authors, the band is a result of the sum frequency of the two intense first-order bands occurring at 1578 and 1356 cm^{-1} . The Raman spectra, observed in the time range of 0 to ca. 27 s of the irradiation in Figure 3, exhibit fluctuations in frequencies and intensities, indicating that the intermediate species formed in the conversion to the amorphous carbon undergo thermal diffusion through the hot spot. The extent of the fluctuations is reduced in comparison with that in Figure 2, corresponding to the rapid conversion to amorphous carbon at the hot spot. In addition to the broad bands around 1360 and 1580 cm^{-1} , which are ascribable to amorphous carbon and/or more or less ordered graphites, several relatively narrow Raman bands observed during the conversion can be assigned to certain species; that is, narrow peaks at 1534 cm^{-1} (spectra f, h, and j in Figure 3B) and those near 1115 cm^{-1} (spectra f and h in Figure 3B) may be ascribable to $\text{C}=\text{C}$ and $\text{C}-\text{C}$ stretching vibrations of polyenes, respectively, the frequency of the former band being dependent on the average conjugation chain length, as already explained.⁸ The $\text{C}=\text{C}$ stretching band shifts from 1534 to 1523 cm^{-1} (spectra j and k in Figure 3B), suggesting the elongation of the conjugation length of the polyenes. Thus, the polyene species are formed as intermediates during the conversion from PDA to amorphous carbon. Carbon sheets, formed on the hot spot, may undergo folding and/or rearrangement of the carbon atoms, resulting in agglomeration of carbon atoms forming the amorphous carbon domains. A sharp peak at 1598 cm^{-1} , observed for spectra j and l in Figure 3B, may be assigned to carbon nanotubes formed as a result of the folding process because, as already explained, they give a

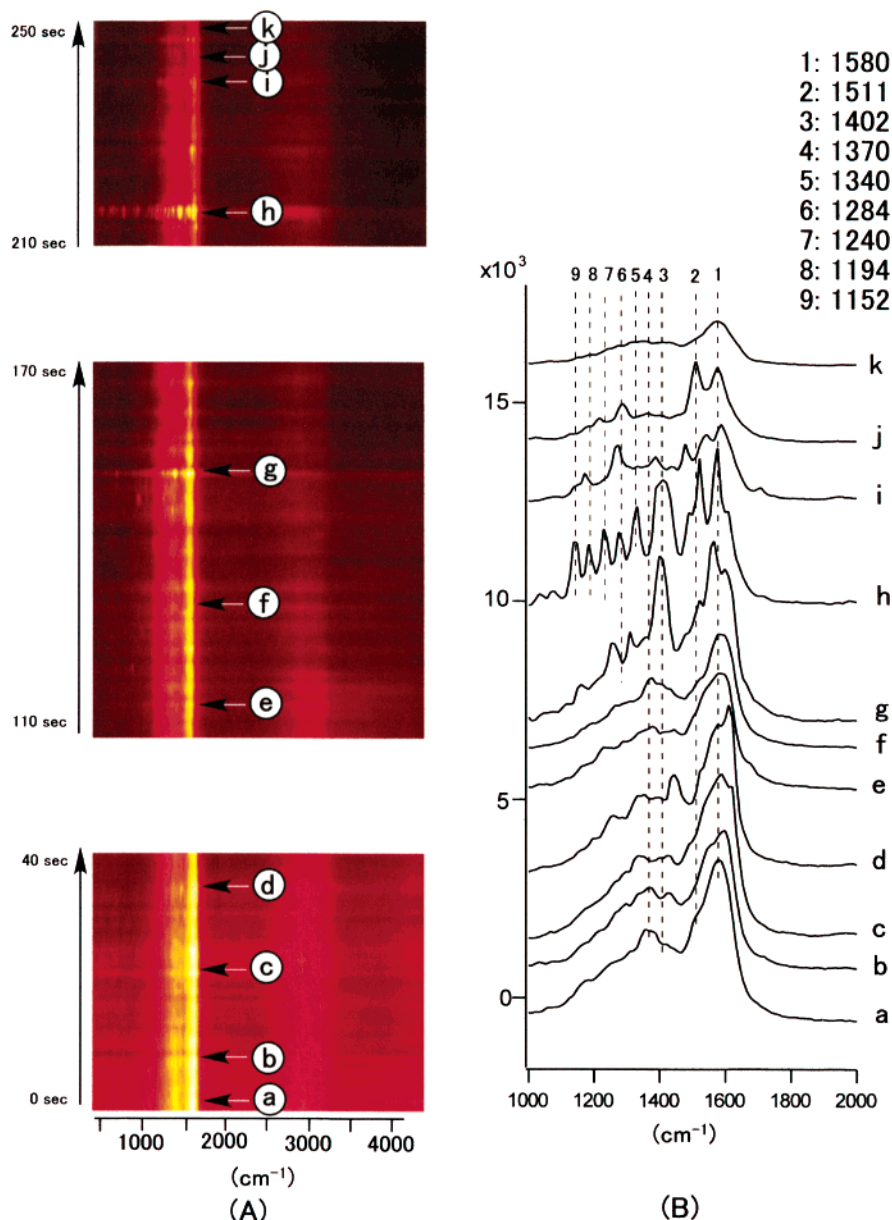


Figure 4. Series of the spectral changes as a function of irradiation time observed for DA-LB($n = 1$)/Ag island/mica by focusing the excitation laser light (power, $100 \mu\text{W}$; wavelength, 488 nm) on one of the bright spots (so-called “hot spot”): (A) 2D image of the spectral changes; (B) the SERS spectra read from the points indicated in the 2D image. The inserted list in (B) indicates the wavenumbers of prominent peaks. See text.

prominent Raman band around 1592 cm^{-1} .^{10,11} The agglomerated carbon domain may be sometimes detached from the hot spot as a result of a thermally activated diffusion. The abrupt disappearance of the huge spectral features after an irradiation time of ca. 27 s in Figure 3A can be explained as a result of the agglomerate leaving from the hot spot.

In contrast to the abrupt spectral diminution observed in Figure 3, the spectra observed from the bright spot of DA-LB($n = 1$)/Ag island/mica sometimes keep the enhanced spectral features characteristic of the amorphous carbon. Figure 4 illustrates another series of the SERS spectral changes observed for the hot spot, where spectral fluctuations take place for a long time after the completion of the amorphous carbon. The spectra retain the spectral feature consisting of the strong and broad bands around 1580 and 1350 cm^{-1} due to the amorphous carbon and, in addition to the two bands, exhibit temporarily fluctuating narrow bands, as can be typically seen in spectrum h in Figure 4B. The result suggests that amorphous carbon sheets in contact with the hot spot continue configuration rearrange-

ments (e.g., folding and refolding of the sheets) and thermal diffusion, resulting in the continuous fluctuation.

The results, explained in this section, clearly indicate that the polymerization of DA-LB and conversion of PDA to amorphous carbon are greatly accelerated at the hot spot of the SERS-active substrates. As explained in the preceding paper,¹ the polymerization is initiated mainly through two-photon or multiphoton processes, which should be enhanced through huge electromagnetic fields generated at the hot spot.^{14–16} PDA and polyenes, which are the intermediates of the conversion to the amorphous carbon, exhibit absorption maxima near 488 nm . Then, in addition to the two-photon and multiphoton processes, the enhanced absorption due to the overlap between the excitation laser wavelength and the maxima may accelerate thermal and/or photofragmentation of PDA forming the amorphous carbon.^{15,16} To get more explicit conclusions about the mechanism, however, we should observe the dependence of the rate of the amorphous carbon formation on the power and wavelength of excitation lasers.

Conclusion

The confocal Raman microspectroscopic measurements, performed with the excitation laser spot focused on the dark background as well as on the bright spot of the 2D Raman microscopic image of the DA-LB monolayer on the SERS-active Ag island films, exhibit different spectral behaviors; that is, the spectra from the dark background gives the Raman bands due to PDA in the red phase and its subsequent diminution, indicating the polymerization of the DA monolayers and its degradation, while spectra from the bright spot exhibit almost random fluctuation, where narrow Raman bands temporarily appear and disappear with varying intensities in the 1620–1000 cm^{-1} range. After a certain period of the excitation laser irradiation, intense and broad Raman bands appear around 1580 and 1360 cm^{-1} , characteristic of amorphous carbon. Thus, the fluctuations are ascribed to carbonaceous intermediates including polyenes, graphite sheets with various sizes, and folded and rearranged forms of the sheet such as carbon nanotubes and fullerenes. The intermediates continue thermally activated surface diffusion and get temporarily in contact with the SERS-active spot, so-called “hot spot”, giving rise to enhancement of Raman bands, resulting in the random fluctuations. Similar Random fluctuations have been observed for carbon layers on SERS-active Ag islands by other groups.^{2,3} Thus, the fluctuations are a general phenomenon associated with the formation of amorphous carbon on the SERS-active Ag islands. Although each narrow Raman band in the fluctuating spectra cannot be explicitly assigned to one of the predicted intermediates, the results presented in the present paper provide us with new aspect of the surface chemistry associated with the formation process of carbonaceous compounds from PDA on the SERS-active

substrates. In this context, time-resolved SERS measurements in the nanosecond and picosecond time ranges are of interest to clarify the surface chemistry.

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