loss but is subject to other interpretations. It was not possible to measure the concentration of this ion in the bulk sample, since AES is a surface-sensitive technique and RBS cannot distinguish sodium ion against a silicon background. The observed loss of sodium may thus represent either volatilization of NaX or migration of sodium ion away form the surface and into the bulk of the silica or into precipitates of iodide-rich material. In the case of a similar gel containing CsCl[12], the chloride clearly volatilized independently of the cesium ion, which remained in the gel.

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Laser-Assisted Vacuum Deposition of 10-(1-Pyrenyl)decanoic Acid: In Situ Fluorescence Observation of the Process

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Laser irradiation effects on the deposition process (laser-assisted deposition) of 10-(1-pyrenyl)decanoic acid (PyC$_{10}$) were investigated by measuring in situ fluorescence spectra during deposition. Fluorescence spectra of films prepared by laser-assisted deposition were different from those of normally deposited films and depended upon laser fluence. A difference in the absorption spectrum among these films was also observed. Laser irradiation effects on normally deposited films of PyC$_{10}$ (irradiation after deposition) were investigated for comparison. On the basis of these results, the high potential of laser-assisted vacuum deposition is discussed.

Introduction

Important factors that determine the vacuum-deposition process for organic compounds are both interaction among deposited molecules and interaction between the molecules and substrate surface. Substrate temperature, deposition rate, and surface property of substrates were examined as a parameter that determines the formation mechanism of organic deposited films. In the case of epitaxial growth of semiconductor films, recently the effect of the light irradiation on the surface-growing process has been studied as a new parameter.[1,2] The light- or laser-assisted epitaxy has induced a change of morphology, an increase in growth rate, and so on. Thus, it is of interest to investigate a light irradiation effect during deposition of organic compounds, in particular, organic compounds containing π-electronic groups. For example, it has been reported that UV-light-assisted vacuum deposition of spiropyran compounds gave a 100% amorphous film and that reversible photochromism was observed in the deposited film.[3]

Recently, we prepared vacuum-deposited films of ω-(1-pyrenyl)alkanoic acids (PyC$_n$, where n represents the number of methylenes in the substitution), a type of pyrene derivative, and studied on their fluorescence properties in connection with the deposition mechanism and the resulting chromophore association in the film.[4-7] We also reported interesting phenomena of fluorescence spectral changes of these deposited films caused by irradiation with an excimer laser.[8] This spectral change was caused by a nonlinear photochemical process with respect to irradiation intensity. A similar phenomenon was also observed for cast films of PyC$_n$ and for Langmuir-Blodgett (LB) films of a mixture of PyC$_n$ and arachidic acid.[9,10] Thus, we found that a thermalization process from higher excited singlet states of pyrenyl chromophores is responsible for the fluorescence spectral change induced by excimer laser irradiation and leads to a common local structure among cast, vacuum-deposited, and LB films.[10]

Furthermore, we applied the fluorescence spectroscopic method to in situ observation of the vacuum-deposition process of 10-(1-pyrenyl)decanoic acid (PyC$_{10}$) and discussed the formation mechanism of excimer sites in deposited films on the basis of the observed thickness-dependent fluorescence spectra.[11] Thus, the fluorescence spectroscopy was shown to be an effective and powerful method for elucidating the formation process of vacuum-deposited film, as was an investigation on the formation process of monolayers on water subphase.[12]

Pyrene is one of the representative compounds of which photophysical data are well documented.[13] The fluores-

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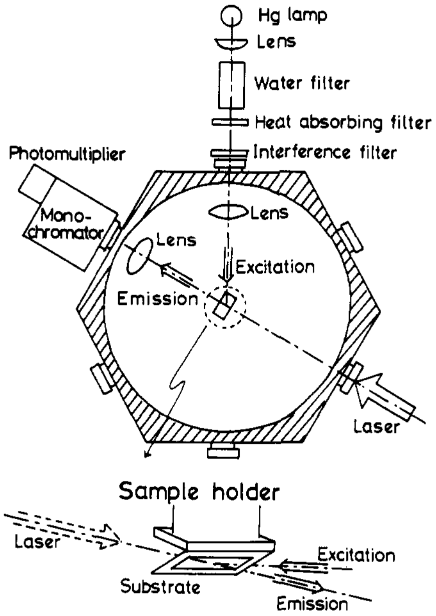

Figure 1. Optical set for fluorescence spectroscopy and laser irradiation.

cence of pyrene has been widely used as a microenvironmental probe because of its unique excited-state properties such as the long lifetime of the singlet excited state. In concentrated solution and molecular assemblies, pyrene and its derivatives form excimers formed between the ground- and excited-state pyrene. Furthermore, it is known that some pyrene molecules doped in poly(methyl methacrylate) film form a dimer and nonfluorescent aggregates.[14] Thus, pyrene and its derivatives are some of the compounds liable to form aggregates.

In the present work, we investigated excimer laser irradiation effects on the deposition process of PyC_{10} (laser-assisted vacuum deposition) by measuring in situ fluorescence spectra during deposition. This compound has both hydrophilic and hydrophobic groups and, thus, a self-assembling property.

Experimental Section

PyC_{10} (Molecular Probes) was used as received. Hydrophilic quartz plates were used as a substrate. To avoid influence by impurities that may be contained in the sample, initial and final stages of evaporation of PyC_{10} were excluded for deposition purposes.

Fluorescence spectra were observed by means of a home-made fluorescence spectrometer attached to the vacuum-deposition chamber (Figure 1). The spectrometer consists of a 300-W high-pressure mercury lamp, a water filter (7 cm), a heat-absorbing filter, an interference filter, a monochromator (Jobin-Yvon H-10), and a photomultiplier. In situ measurements were done using the following cycle: deposition on a substrate, cessation of deposition by insertion of a shutter between a sample boat and the substrate, measurement of the fluorescence spectrum, and recommencement of deposition on substrates. In the case of laser-assisted deposition, the laser was used on substrates only during deposition in the cycle (the direction of the laser beam is shown in Figure 1). By comparing fluorescence and absorption spectra between deposited films prepared with and without the in situ fluorescence measurement and observing the films under a fluorescence microscope, we confirmed that both interruption of deposition and excitation light irradiation for fluorescence measurement did not affect the properties and morphology of deposited films. Laser irradiation was performed with repetition rate of 1 Hz by using a Lambda-Physik EMG101-MSC excimer laser with XeF (351 nm). The full width at half-maximum (fwhm) was 15 ns. The irradiation power was measured with a Gentec ED-200 power meter.

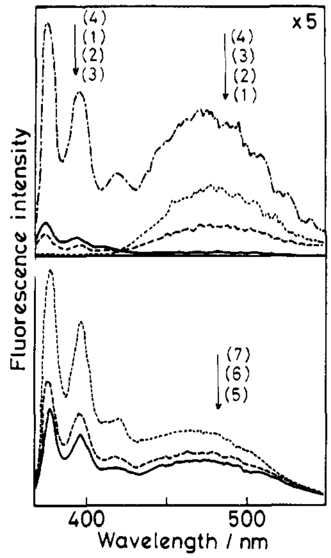

Figure 2. Fluorescence spectral change of PyC_{10} deposited film observed during deposition on a hydrophilic substrate at 19 °C. Film thickness: (1) 0.17, (2) 0.78, (3) 2.43, (4) 3.82, (5) 4.72, (6) 5.81, and (7) 10.8 nm.

Absorption spectra were measured with a Shimadzu MPS-2000 multipurpose spectrometer after taking out the sample from the chamber.

In the case of normal deposition (without laser irradiation), the average thickness of films was estimated as follows:[11] A linear relation between absorbance measured after deposition and the average film thickness, directly determined by using a calibrated quartz crystal oscillator, was confirmed. Since the deposition rate was controlled to be constant (ca. 0.1 nm/min), the average thickness of films can be calculated. For laser-assisted deposition, however, the average thickness of films could not be calculated. The reasons are as follows: Films prepared by laser-assisted deposition showed different absorption spectra from those prepared by normal deposition (vide infra). Furthermore, we cannot reject a possibility that laser irradiation under vacuum induces desorption of molecules on substrates. Therefore, for laser-assisted deposition, the time after starting the deposition was used as a measure of the thickness.

Results and Discussion

In Situ Fluorescence Observation of the Deposition Process. Figure 2 shows a fluorescence spectral change observed during normal deposition of PyC_{10} (without laser irradiation). Four deposition stages are observed. At the initial stage of deposition, pyrene monomer fluorescence was observed (the first stage). This fact indicates that the compound is deposited as a single molecule, not as clusters. With deposition, the monomer fluorescence decreased, and a broad and structureless fluorescence with a peak at ca. 480 nm appeared in addition to the monomer fluorescence and then increased (the second stage). This broad spectrum is assigned to pyrene excimer fluorescence, judging from the spectral shape and the peak position. By further deposition, pyrene monomer fluorescence disappeared, and only excimer fluorescence became observable (the third stage). Afterward, a structured fluorescence was observed again in the shorter wavelength region (less than 400 nm), and at the same time a broad excimer fluorescence increased with a peak shift from 480 to ca. 470 nm (the fourth stage). The peaks of the structured fluorescence were shifted by 1–2 nm to longer wavelength compared

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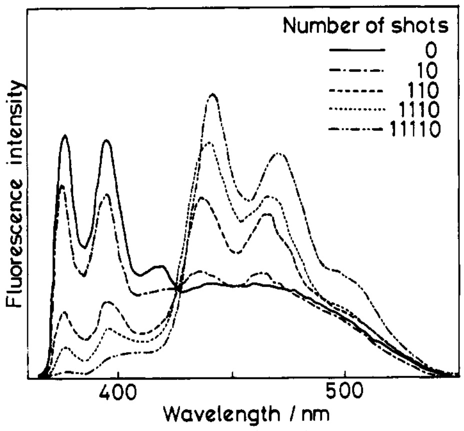

Figure 3. Fluorescence spectral change induced by laser irradiation with a fluence of 0.65 mJ/cm^2. The number of laser shots is given in the figure. Film thickness is 12.0 nm.

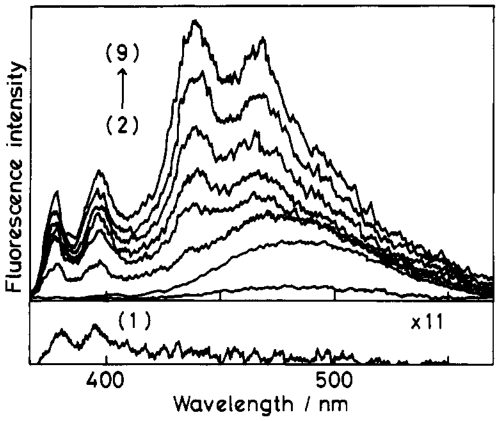

Figure 4. Fluorescence spectral change of PyC$_{10}$ deposited film observed during laser-assisted deposition with a fluence of 0.07 mJ/cm^2. Time after a starting the deposition: (1) 5, (2) 15, (3) 30, (4) 45, (5) 65, (6) 85, (7) 105, (8) 130, and (9) 150 min.

with those of the monomer fluorescence at the first stage of deposition. Hence, this structured fluorescence is considered to be attributed to a dimer of pyrenyl chromophores. This type of the dimer was reported for LB films of a mixture of PyC$_{16}$ and stearic acid.[15] Thus, normally deposited films show both dimer and excimer fluorescence. These thickness-dependent fluorescence spectra suggest that fluorescent sites in the bulk are different from those in the layer near the substrate.

Fluorescence Spectral Change Induced by Laser Irradiation on Normally Deposited Films (Irradiation after Deposition). When deposited films (in the fourth stage mentioned above) in the vacuum-deposition chamber were irradiated with an excimer laser, a remarkable fluorescence spectral change was observed, as shown in Figure 3. Irradiation with 10 laser shots with a fluence of 0.65 mJ/cm^2 resulted in both a decrease in the dimer fluorescence intensity and an appearance of shoulders in the longer wavelength region. With an increase in the number of laser shots, the dimer fluorescence intensity decreased furthermore, and a new vibrational structured fluorescence with peaks at ca. 441 and 470 nm and a shoulder at ca. 500 nm appeared and increased. A similar fluorescence spectral change was observed for laser irradiation with a fluence from 0.02 to 0.68 mJ/cm^2.

The absorption spectrum, which gives information about the main aggregate of pyrenyl chromophores, was measured in air after the sample film was removed from vacuum chamber. The absorption spectrum of irradiated films was same as that of unirradiated films (vide infra, Figure 8). This fact indicates that laser irradiation after deposition induces the structural change of fluorescent sites but not a structural change of the main pyrenyl aggregates responsible for the absorption spectrum.

As mentioned above, laser irradiation on deposited films after deposition caused the change of the local structure of fluorescent sites. However, this local change did not affect the aggregate structure of the main pyrenyl chromophores responsible for absorption spectrum. Hence it is very interesting to investigate how laser irradiation during deposition (laser-assisted deposition) induces fluorescence and absorption spectral changes and structural changes of the pyrenyl aggregate in the film.

In Situ Fluorescence Observation of the Laser-Assisted Vacuum-Deposition Process. Typical fluorescence spectral changes observed during deposition of PyC$_{10}$ with laser irradiation (laser-assisted deposition) are shown in Figures 4–6. Since an exact average thickness of films is unknown, as described in the Experimental Section, the time after a starting the deposition is indicated. The spectral change depended upon the laser fluence remarkably, although it was independent of laser fluence in the case of irradiation on films after deposition.

Laser-Assisted Deposition with Low Fluence. In the case of laser-assisted deposition with low fluence (0.07 mJ/cm^2; Figure 4), pyrene monomer fluorescence was observed first, and a broad excimer fluorescence with a peak at ca. 480 nm appeared and increased. By further deposition, both dimer fluorescence below 400 nm and new one with shoulders in superposition with the excimer fluorescence appeared. Further deposition resulted in both an increase in the dimer fluorescence intensity and a distinct appearance of vibrational structured fluorescence with peaks at ca. 440 and 470 nm, and these fluorescence intensities increased. The structured fluorescence in the longer wavelength region is considered to be the same as that observed for films irradiated with the laser after deposition (Figure 3), judging from both the spectral shape and peak positions.

A series of time-resolved fluorescence spectra were measured to measure minor components more selectively. In the late-gated spectrum, a contribution of excimer fluorescence was observed clearly. This indicates that the sites giving the excimer fluorescence are still contained. That is, the pyrenyl aggregate responsible for the structured fluorescence is considered to be formed on the layer with excimer sites, judging from the spectral change during deposition. In other words, excimer sites in the layer deposited near substrates at the initial stage of deposition do not change to the aggregate giving the structured fluorescence by further laser-assisted deposition.

Laser-Assisted Deposition with Medium Fluence. For a medium fluence of 0.54 mJ/cm^2 (Figure 5), a very weak pyrene monomer fluorescence appeared at the initial stage. At the next stage, the monomer fluorescence disappeared, and excimer fluorescence appeared with a peak at ca. 480 nm. By further deposition, the excimer fluorescence increased, and the fluorescence peak shifted slightly to the shorter wavelength (470 nm). This fluorescence spectral change is quite different from that with the low laser fluence (Figure 4). That is, dimer and the structure fluorescence were never observed even at any position stage. Moreover, we should notice that laser irradiation with nearly the same fluence (0.65 mJ/cm^2) on normally deposited films resulted in the structured

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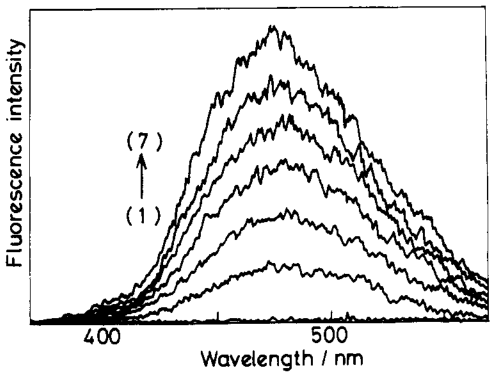

Figure 5. Fluorescence spectral change of PyC_{10} deposited film observed during laser-assisted deposition with a fluence of 0.54 mJ/cm^2. Time after a starting the deposition: (1) 5, (2) 30, (3) 45, (4) 65, (5) 85, (6) 105, and (7) 130 min.

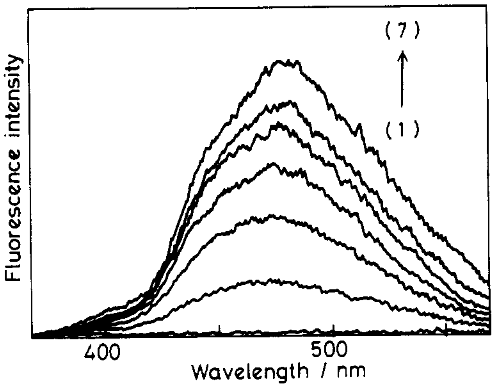

Figure 6. Fluorescence spectral change of PyC_{10} deposited film observed during laser-assisted deposition with a fluence of 2.1 mJ/cm^2. Time after a starting the deposition: (1) 5, (2) 15, (3) 30, (4) 45, (5) 65, (6) 105, and (7) 130 min.

fluorescence in the longer wavelength region, as shown in Figure 3.

Laser-Assisted Deposition with High Fluence. The fluorescence spectral change with a high fluence of 2.1 mJ/cm^2 was similar to that with a medium fluence, as shown in Figure 6. One different observation in the fluorescence spectral change is a peak wavelength of excimer fluorescence observed at the early stage of deposition. That is, a peak of the excimer fluorescence observed for high laser fluence was at ca. 470 nm. This peak wavelength is shifted to shorter wavelength compared with that (ca. 480 nm) observed for laser-assisted deposition with medium and low fluence and normal deposition. This result suggests that interaction between a PyC_{10} molecule and the surface of substrates induces excimer fluorescence with a peak at 480 nm. When the laser fluence is very high, however, the interaction is overcome by the laser irradiation effect, and thereby the excimer site giving the fluorescence with a peak at 470 nm is formed even in the layer near the interface. The excimer fluorescence spectrum of films prepared with a high fluence is slightly broader than that with medium fluence. This suggests the presence of excimers with various overlap between two pyenyl chromophores in films prepared by laser-assisted deposition with a high fluence.

Comparison of a Fluorescence Spectrum between Films Irradiated with the Laser during Deposition and Films Irradiated with the Laser after Deposition. To make clear a difference in the fluorescence spectrum between films prepared by laser-assisted deposition and films irradiated with laser after deposition, the ratio of fluorescence intensity observed at 438 nm to that at 463 nm (I_{438}/I_{463}) for films prepared by both methods are plotted against the laser fluence in Figure 7. For films showing structured fluorescence in the longer wavelength region, this intensity ratio is the same as that of the first to the second vibrational bands of the structured fluorescence. Values of ca. 1.25 and 0.55 of the ratio correspond to spectral shape of the structured fluorescence and excimer fluorescence, respectively. For irradiation after deposition, the intensity ratios are almost independent of the laser fluence and have a constant value of ca. 1.25.

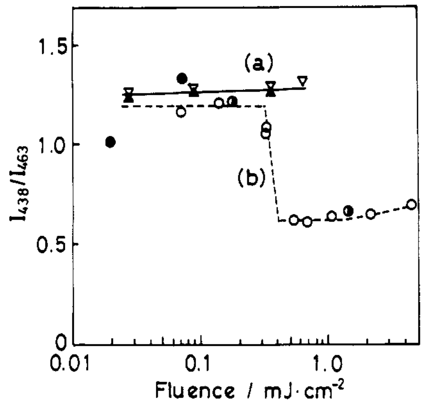

Figure 7. Fluorescence intensity ratio (I_{438}/I_{463}) as a function of laser fluence. (a) PyC_{10} deposited film irradiated with laser after deposition: ▲, 7800; ▽ 11000 shots. (b) PyC_{10} films prepared by laser-assisted deposition: ○ 7800; ◑, 8400; ●, 8700 shots.

In the case of laser-assisted deposition, the ratio for a laser fluence of less than 0.3 mJ/cm^2 is close to the constant value of ca. 1.25 observed for films irradiated after deposition. This fact indicates that laser-assisted deposition with a fluence less than 0.3 mJ/cm^2 produces films with the aggregate that is responsible for the structured fluorescence. Films giving excimer fluorescence (I_{438}/I_{463} ratio of 0.55) are prepared by laser-assisted deposition with a fluence higher than 0.5 mJ/cm^2. A slight increase in the ratio for a fluence higher than ca. 2 mJ/cm^2 is due to the presence of various excimers mentioned above.

Thus, films prepared by laser-assisted deposition are classified into the following two types by fluorescence spectra: One of these types of films shows both dimer fluorescence below 400 nm and structured fluorescence with their peaks beyond 430 nm. Another shows only excimer fluorescence.

Absorption Spectra of Films Prepared by Laser-Assisted Deposition. Absorption spectra of films prepared by laser-assisted deposition with various fluence are shown in Figure 8. For comparison, absorption spectra of the deposited film, the film irradiated with the laser after deposition, and a methanol solution of PyC_{10} are also shown in Figure 8. Spectra of these films were measured in air after the films were removed from the vacuum-deposition chamber. The absorption spectrum gives information on the main pyrenyl aggregates, while the fluorescence spectrum gives information on minor fluorescent sites of pyrenyl chromophores because of energy migration among pyrenyl chromophores.

The absorption spectrum of PyC_{10} in methanol solution consists of ^1L_b, ^1L_a, ^1B_b, and ^1B_a bands characteristic of 1-substituted pyrene. Compared with this spectrum, deposited films of PyC_{10} showed broad and red-shifted bands. The absorption feature of deposited films was ascribed to an aggregate of pyrenyl chromophores, where component molecules were considered to interact with each other along the long axis of the pyrenyl chromophores.[5] Since no fluorescence spectrum corresponding to this absorption

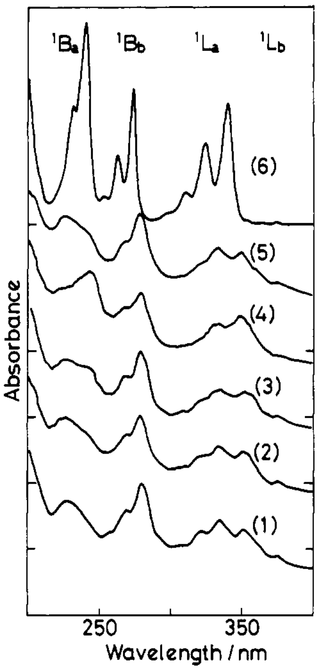

Figure 8. Absorption spectra of PyC_{10} films prepared by laser-assisted deposition. Laser fluence: (1) 0 (that is, normal deposition), (2) 0.07, (3) 0.32, (4) 0.54 mJ/cm^2. (5) Reference spectrum of PyC_{10} deposited film irradiated by laser with a fluence of 0.65 mJ/cm^2 after deposition; (6) reference spectrum of a methanol solution.

spectrum was observed, this aggregated state is considered to be nonfluorescent.[5]

Although absorption spectra of films prepared by laser-assisted deposition with a fluence less than 0.32 mJ/cm^2 are similar to that of films prepared by normal deposition, spectra of films prepared with fluence higher than 0.54 mJ/cm^2 are different from it. The large difference in the absorption spectrum is observed for ^1L_a and ^1B_a bands, of which the transition dipoles are polarized along the long axis of the pyrenyl chromophore. These results indicate that the interaction between pyrenyl chromophores along the long axis in films prepared by laser-assisted deposition is different from that in films prepared by normal deposition. That is, the laser-assisted deposition forms a new aggregate structure. This aggregate is a main component in films and responsible for the absorption spectrum.

As described above, laser irradiation on deposited films after deposition does not induce the change of the absorption spectrum even by using a high laser fluence, with which the irradiation induces the change of the absorption spectrum in the case of laser-assisted deposition.

Effect of Laser Irradiation on Deposited Films after and during Deposition. The results obtained are summarized in Figure 9. The laser irradiation during deposition (laser-assisted deposition) forms a new aggregate structure, which is never formed by the laser irradiation after deposition. This was revealed by the difference in the absorption spectrum between films prepared by laser-assisted deposition and films irradiated with the laser after deposition. The difference in the fluorescence spectrum indicated that fluorescent sites in films prepared by laser-assisted deposition are quite different from those in normally deposited films and were never created by laser irradiation after deposition.

The laser irradiation on films after normal deposition has nothing to do with molecular migration on the surface of substrates. Thereby, this does not induce the change of the main aggregates structure responsible for the absorption spectrum but does induce the change of the local structure from dimer sites to the fluorescent site responsible for the structured fluorescence with peaks beyond 440 nm. These results indicate that main aggregate structures that were formed once by normal deposition are too tight to change to the other structures by the thermal energy of deactivation from higher excited states formed by laser irradiation after deposition.

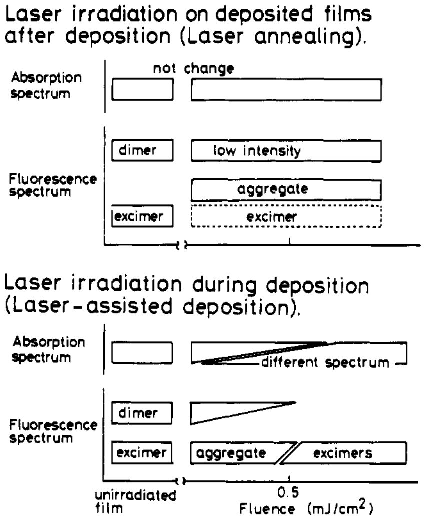

Figure 9. Identification of aggregated states of pyrenyl chromophores.

On the other hand, laser-assisted deposition resulted in a different aggregate structure depending upon the laser fluence. For low fluence, a pyrenyl aggregate that shows structured fluorescence with peaks beyond 440 nm was formed, and the aggregate is considered to be a minor component because the absorption spectrum is quite similar to that of films prepared by normal deposition. For high fluence, the main aggregate responsible for the absorption spectrum is different from those of normally deposited films. Fluorescence spectra of the films are also quite different from those of normally deposited films. Laser irradiation during deposition excites not only deposited molecules but also migrating ones. Molecules in the excited state have an ability to interact with the ground-state molecules. Thermalization energy from the excited state activates the molecular migration on substrates. These effects are considered to induce the formation of new aggregates. That is, laser irradiation during deposition assisted self-assembling and induced new aggregate structures in deposited films.

The present results indicate that a new type of pyrenyl aggregate was formed only by excimer laser irradiation during deposition, although it was difficult to obtain direct information on the geometrical structure of the pyrenyl aggregates. This suggests a possibility that new functional materials can be created by laser-assisted vacuum deposition. Fluorescence spectroscopy is considered to be a powerful analytical method for investigating the molecular aspects of the vacuum deposition process.

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