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Laser molecular implantation into polymer solids induced by irradiation below ablation threshold

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Abstract

Polymer films involving fluorescent molecules such as anthracene, diphenyl anthracene or pyrene (source films) were overlaid with neat polymer films (target films), and irradiated with nanosecond pulsed laser from the rear of the target films. Fluorescent patterns of these molecules were found at the surface of the target films even when the laser fluence was less than the ablation threshold of the source films. The amount of ejected molecules from the source film was estimated from the reduction of fluorescence intensity. It was found that the lower the glass transition temperature of the source film, the higher the amount of ejected molecules. The thickness of the implanted layer at the surface of the target film was obtained by means of total internal reflection fluorescence spectroscopy. The amount of molecular aggregates was found to increase with increasing the number of laser shots. The mechanism of the penetration and aggregation of the fluorescent molecules by repetitive irradiation was discussed in connection with photothermal temperature jump and thermally activated diffusion in polymer solids.

Keywords: Laser implantation; Ablation; Activated diffusion; Polymer; Fluorescence

1. Introduction

Laser ablation of polymer films which do not absorb laser light has been demonstrated by the addition of laser absorbing sensitizers [1–5]. This ablative photo-etching requires a certain laser fluence called ablation threshold, and no substantial change of the surface has been considered to occur with one-shot irradiation below the ablation threshold until recently. However, various kinds of time-resolved measurements have revealed transient changes even below the ablation threshold: (i) the ejection of intact sensitizer molecules by time-of-flight mass spectrometry [6], (ii) photothermal transient expansion and contraction of the irradiated polymer surface by nanosecond interferometry [7,8] and (iii) fast diffusion of sensitizer molecules in the irradiated polymer by nanosecond absorption spectroscopy [9]. The temperature rise at the irradiated surface around ablation threshold has been estimated to be 300 °C [4,6], which necessitates that a single sensitizer molecule absorbs on average more than several photons since the sensitizer molecule should feed thermal energy to the surrounding non-light-absorbing polymer chains [6]. This multi-photonic absorption by the sensitizer without its decomposition can be explained by the repetition of internal conversion and photo-excitation in the excited singlet or triplet manifold of the sensitizer [10]. The light absorption mechanism is supported by the fact that the absorbance of a polymer film transiently varies during a single laser pulse depending on the laser intensity and the sensitizer which is doped in the film [11–13]. Based on these studies, we have succeeded in transferring light-absorbing molecules between two polymer films in contact by using pulsed laser irradiation, and named this phenomenon 'laser molecular implantation' [14,15]. It should be noted that the implantation means that light-absorbing molecules move without accompanying the transfer of the surrounding polymer, and diffuse into a surface layer several tens of nanometers thick.

The application of the laser molecular implantation would be widely available, since it does not require a common solvent for a dopant and polymer. Various kinds of functional organic molecules may be space-selectively fixed on polymer films by laser irradiation, being used as devices like electrodes or optrodes for sensors, micro optical or electronic circuits, and analytical instruments integrated on microtips. Many factors related to this phenomenon, however, remain unclear such as the molecular structures suitable for dopants, the necessary conditions for polymer, the laser pulse width and intensity etc. These factors are closely related to the whole mechanism of the implantation process including the light absorption and electronic energy relaxation of dopant mole-

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cules in polymer solids. Hence, comprehensive understanding of the mechanism from a molecular point of view is indispensable for the application.

At present a few intact dopants have been confirmed to be implanted into polymer films under certain irradiation conditions [14,15]. When the number of laser shots was kept constant, fluorescence spectra of pyrene implanted in poly(methyl methacrylate) (PMMA) changed depending on the laser fluence [14]. This spectral change is ascribed to the formation of molecular aggregates like dimer in the implanted layer, since the concentration of pyrene in the layer is expected to increase with the laser fluence [15]. The thickness of the implanted layer at the surface of the polymer films was also found to increase with the number of laser shots when diphenyl anthracene was implanted into poly(ethyl methacrylate) (PEMA), whereas it remained nearly constant for PMMA [15]. This result suggests that molecules implanted in a polymer film may move further by repetitive irradiation of laser pulse. Although the effect of the repetitive irradiation on the implanted molecules seems to be a key for understanding the mechanism of the implantation, it still remains obscure since no systematic experiment has been reported yet. The repetitive irradiation would affect both the amount and concentration of the implanted molecules at the polymer surface, which makes its effect complicated. In this report, both the fluorescence and absorption spectra of implanted molecules will be measured for studying the effect of the repetitive irradiation. The implantation mechanism will also be discussed by separating the implantation process to the following three steps: (i) ejection of dopant molecules from a source polymer film, (ii) their penetration into a target polymer film and (iii) formation of molecular aggregates in the target film.

2. Experimental

Poly(methyl methacrylate) (PMMA) (Aldrich, secondary standard, Mw = 103 000), poly(ethyl methacrylate) (PEMA) (Aldrich, secondary standard, Mw = 340 000) or poly(butyl methacrylate) (PBMA) (Aldrich, secondary standard, Mw = 320 000) was dissolved in chlorobenzene or chloroform together with a desirable amount of pyrene, anthracene or diphenyl anthracene (DPA), and spin-coated on glass plates for the preparation of source films. The amount of the dopants were adjusted to yield a few wt.% of the dopants in polymer solid after complete drying of the films. The same polymers without any dopants were also spin-coated and used as target films for implantation. The thickness of these polymer films was measured by a depth profiler (Sloan Dektak^3), being around 2.5 μm in most cases.

As Fig. 1 illustrates, a source film was overlaid with a target film and irradiated with an excimer laser (Lambda Physik, LEXTRA 200) from the rear of the substrate of the target film. The wavelength of the laser was set to 248 nm for pyrene, and 351 nm for anthracene and DPA implantation.

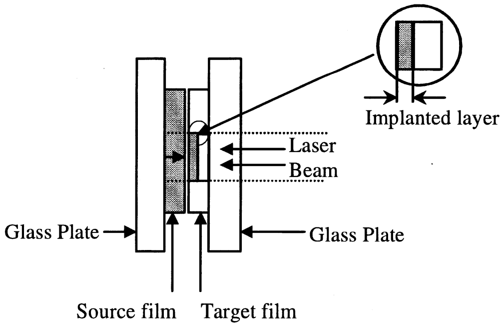

Fig. 1. Experimental arrangement for irradiation of a sample to perform the laser molecular implantation.

The pulse duration (full width at half maximum) was about 20 ns for either wavelength. The repetition rate was kept less than 1 Hz. The irradiated area of the surface of either target and source films was observed under a fluorescent microscope (Olympus, BX 50), and its absorption and fluorescence spectra were measured by a conventional spectrophotometer (Shimadzu, UV-3100) and spectrofluorimeter (Hitachi, F-4500). For estimation of the thickness of an implanted layer, the variable angle total internal reflection technique was employed as described elsewhere [15].

3. Results and discussion

3.1. Evidence of implantation

The irradiated area of target films became fluorescent as shown in Fig. 2. The repetitive irradiation just below the ablation threshold sometimes resulted in the formation of small emissive particles at the target film surface. Clear implantation patterns without these particles could be made with the repetitive irradiation sufficiently below the ablation threshold of a source film or with limiting the irradiation to two or three laser shots just below the threshold. The example

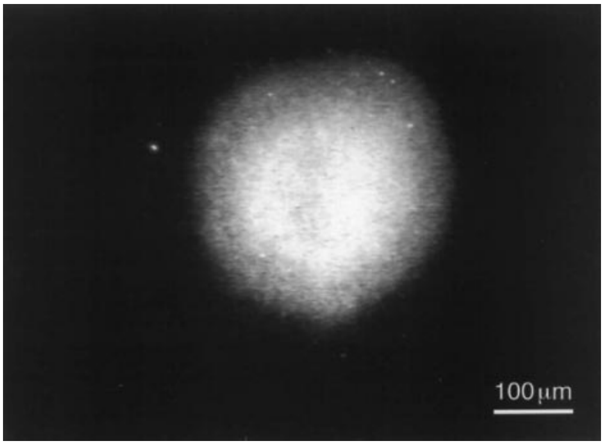

Fig. 2. Fluorescence image of a PMMA target film after the implantation of pyrene. The source film was pyrene-doped PMMA. Irradiation conditions: laser fluence, 100 mJ cm^{-2}; wavelength, 248 nm; number of laser pulse, 5 shots.

of the clear pattern produced below the threshold, which did not exhibit any trace of polymer adhesion at the target surface, will be shown elsewhere [16]. In general, the ablation threshold decreases with increasing the number of laser shots owing to the 'incubation effect' that means a partial decomposition of polymer matrix caused by its transient heating [6,9], mechanical distortion [7,8] and photochemical reactions [17–19]. This incubation effect should be taken into account when a clear implantation pattern is required. In this paper, the ablation threshold for the first shot was about 110 mJ cm^{-2} for pyrene-doped films irradiated with 248 nm and about 520 mJ cm^{-2} for DPA-doped films irradiated with 351 nm.

The fluorescence spectra of the produced patterns on target films were very similar to those of the source films for anthracene and DPA. As an example, the result for DPA with different laser shots is shown in Fig. 3(a). This result indicates that fluorescent molecules were transferred without their decomposition to the target films. When pyrene was implanted into PEMA target films, the longer wavelength part of its fluorescence spectra increased with the number of shots as shown in Fig. 3(b). The implanted surfaces emitting this type of fluorescence were scraped and dissolved into ethanol, after which the fluorescence changed to the normal monomer fluorescence of pyrene. The ethanol solution was also separated on a thin-layer chromatography plate, showing no reaction product by the implantation as long as the laser fluence was lower than the ablation threshold. Thus, the fluorescent species emitting the longer wavelength part is assigned to molecular aggregates that can emit excimer-like fluorescence. The formation mechanism of the molecular aggregates by repetitive irradiation will be discussed later. It should be noted that the excimer-like emission was not due to the molecules involved in the polymer particles adhered on the target film. These particles generated by laser ablation showed the fluorescence of pyrene monomer rather than that of the excimer.

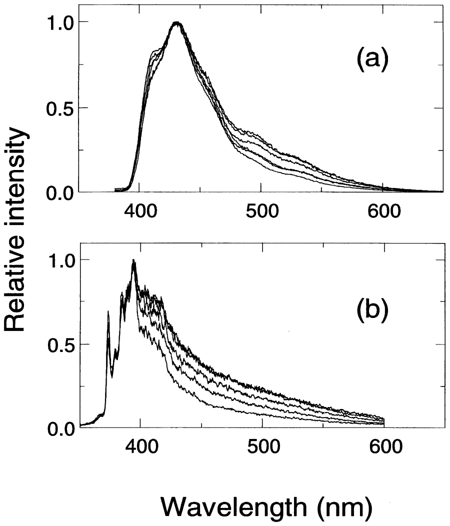

Fig. 3. Normalized fluorescence spectra of target films after implantation by various number of laser shots (from the top to bottom: 30, 25, 20, 15, 10 and 5 shots): (a) the source film was DPA-doped PMMA, the target film was PEMA, the laser fluence was 490 mJ cm^{-2}; (b) the source film was pyrene-doped PMMA, the target film was PEMA, the laser fluence was 100 mJ cm^{-2}.

The results above demonstrated that aromatic molecules can be laser-implanted without decomposition even under intense laser irradiation. The irradiated surface just below the ablation threshold would reach a temperature around 600 K several tens of nanoseconds after an excitation laser pulse [6,8,10], and then be cooled down to room temperature by thermal conduction within 1 ms [8]. This suggests that light-absorbing molecules can endure if they do not undergo photoreaction by laser irradiation nor thermal reaction in this time range. Actually, some polycyclic aromatic hydrocarbons have been expected to be quite stable even at high temperatures above 1000 K [20].

3.2. *Ejection of molecules*

Here we consider the ejection mechanism of molecules from a source film by laser irradiation. Fig. 4 shows decreases in the intensity of anthracene fluorescence (ΔF) for PMMA, PEMA and PBMA source films by laser irradiation. The decreases were due to the ejection of anthracene molecules from the films, clearly indicating that the ejected amount increased with laser fluence. The amount of ejected molecules was found to be in the order of PBMA > PEMA > PMMA, which indicates that the lower the glass transition temperature (T_g) of the polymer, the higher the ejection amount would be. This result implies that the ejection would be caused by a thermally activated diffusion process, since the diffusion coefficient of small molecules in a polymer increases with temperature and its absolute value is high in polymer of low T_g. The diffusion coefficient of diacetyl in PMMA has been reported to change step-like more than 3 orders of magnitude at T_g [21]. However, this marked change of the diffusion coefficient at T_g was found to take place only when the concentration of small molecules is less than 0.5% [22]. In our cases, the concentration of dopant in source films are higher

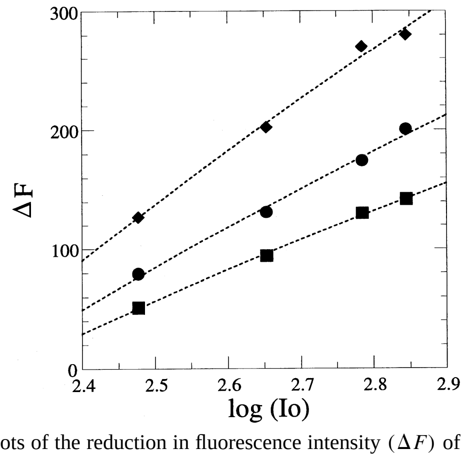

Fig. 4. Plots of the reduction in fluorescence intensity (ΔF) of anthracene in source films versus laser fluence (I_0) after one shot irradiation. The film materials were PBMA (◆), PEMA (●), and PMMA (■).

than 1%. Hence it may be considered that the diffusion coefficient is represented by a simple Arrhenius-type equation displaying no obvious change at T_g. Here, we assume the temperature dependence of the diffusion coefficient D_m for small molecules in polymers as follows:

$$D_m = D_m^0 \exp(-\epsilon/kT) \quad (1)$$

where D_m^0 and ϵ are the amplitude factor and activation energy, respectively. When a source polymer film is irradiated with a laser pulse and heated up by complete photothermal conversion, the temperature distribution in the polymer film $T(x)$ just after the laser pulse is given by:

$$T(x) = (\alpha I_0/\rho C)\ \exp(-\alpha x) + T_r \quad (2)$$

where x denotes the depth from the film surface, α the absorptivity at the laser wavelength, ρ the density of the polymer, C the specific heat capacity and T_r the room temperature. It should be noted that α is assumed to be constant for a first approximation although it varies during the laser pulse depending on the laser fluence and the photo-absorbing molecules [11–13].

Practically there are two extreme cases depending on the thickness of the source film d and its α as shown in Fig. 5: (a) high absorbance limit, $\alpha d > > 1$ and (b) low absorbance limit, $\alpha d \approx 0$. In (a), most of the laser energy is absorbed at the surface. Therefore, only molecules at the thin surface layer will be ejected from the film, the analysis of which would be rather complicated. In (b), the whole film will be heated up to a high temperature, which leads to a simple analysis. By combining Eq. (1) and Eq. (2), the diffusion of the embedded molecules in the film can be represented by:

$$\ln D_m = \ln D_m^0 - [\epsilon/k\{(\alpha I_0/\rho C) + T_r\}] \quad (3)$$

The flux of molecules (J_m) passing through the surface of the source film, would be expressed by Fick's first law of diffusion as the product of D_m and the concentration gradient of the molecules. If the gradient remains constant during a certain time period Δt and the molecules diffuse only in this period, the amount of ejected molecules ΔF which was monitored by the reduction of the fluorescence intensity would be written as:

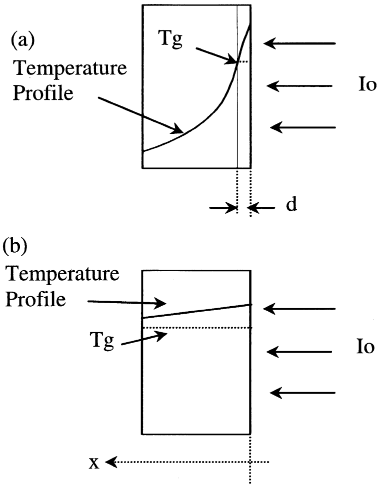

Fig. 5. Schematic drawing of temperature distribution in source films just after laser irradiation: (a) high absorbance limit, (b) low absorbance limit. The heat diffusion process in the film was ignored.

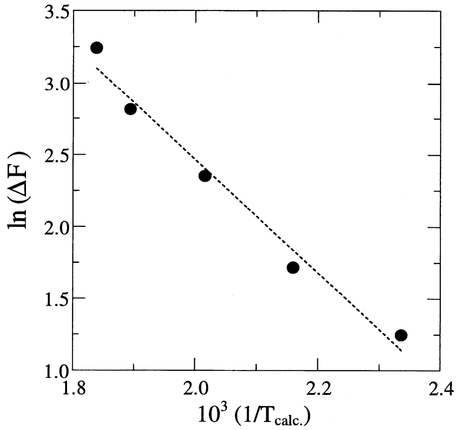

Fig. 6. Plot of logarithmic changes (ΔF) of anthracene fluorescence versus calculated temperature (T_{calc}) from Eq. 3 and Eq. 4. The best fit line giving 76 kJ mol^{-1} of the activation energy for the diffusion coefficient in PMMA is also indicated.

$$\ln \Delta F = \ln \gamma \Delta t D_m^0 - (\epsilon/kT_{calc}) \quad (4)$$

where γ is constant including the ejection efficiency and $T_{calc} = (\alpha I_0/\rho C) + T_r$ is introduced for simplification. According to this equation, the result of anthracene in PMMA was analyzed and plotted as shown in Fig. 6. The slope of the plot gives 76 kJ mol^{-1} as the value of ϵ. This value seems to be reasonable as the activation energy of the diffusion process of aromatic molecules in polymer solids, since it is comparable to the reported values of ~100 kJ mol^{-1} for triphenylene and coronene in PMMA [23]. Obviously, the analysis here would be too simplified, however it has showed that the thermal activated diffusion process would play a key role in the ejection process.

3.3. Penetration of molecules

As shown in Fig. 3, the fluorescence spectra of pyrene implanted into target films changed with repetitive irradiation, while those of DPA scarcely did. Hence DPA was employed for quantitative measurement of the implanted layer by using the total internal reflection fluorescence. In the vicinity of the implanted polymer surfaces, a step function was assumed to represent the concentration profile of DPA. Subsequently, the estimated intensity of total internal reflection fluorescence as a function of the incident angle was plotted and compared with the experimental values described elsewhere [15]. The estimated thickness of the implanted layers was plotted against the number of laser shots as shown in Fig. 7. The result indicates that the thickness increased with the number of laser shots for the PEMA films, reaching to 170 nm after 20 shots, whereas it remained around 50 nm for the PMMA films. It is obvious that laser irradiation allows

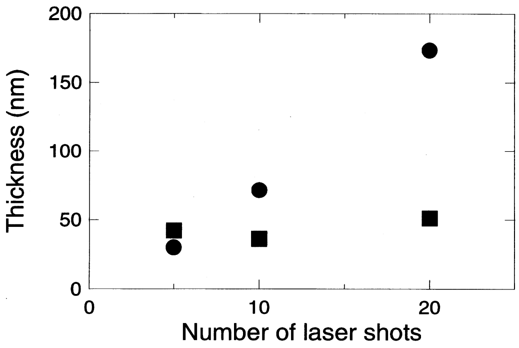

Fig. 7. The estimated thickness of the implanted layer at the target films of PMMA (■) and PEMA (●) as a function of the number of laser shots. The laser fluence was 490 mJ cm^{-2} and the source films were DPA-doped PMMA films for the both cases.

DPA molecules to move into deep regions in PEMA target films.

Since the distribution curve of the implanted molecules at the surface is known to be represented by a step function rather than Gaussian and Lorentzian [15], the diffusion of molecules into target films may not be explained by simple diffusion of molecules. Here the difference between the source and target films should be taken into account. In the case of a source film, the whole film is doped with light-absorbing molecules and can be heated up to a certain temperature as shown in Fig. 5. On the contrary, a target film does not involve any light-absorbing molecules before the first shot of laser irradiation. In this case, only the implanted layer can be heated up by laser irradiation and molecules would move into a deep layer where no dopant has existed before. Therefore, the Arrhenius-type activated diffusion may not occur at the front of the implanted layer. As an alternative, a step-like change of the diffusion coefficient at T_g mentioned before [21,22] would be responsible for this process. In a system where the Arrhenius plot of diffusion constant has a break point at T_g, the diffusion constant increases markedly with a temperature above T_g since the activation energy is generally higher in the rubber state than in the glass state [22,24]. Fig. 8 shows a model to explain an increase in the implanted layer thickness with repetitive irradiation. The first shot of the laser would implant molecules in a very thin layer around 30 nm. These molecules would convert photon energy into intra- and inter-molecular vibrational energy and heat up the surrounding polymer domains by the following shots of the laser. If we assume that the diffusion of heat is faster than that of molecules, a certain depth of the polymer surface would reach above its T_g, thus the molecules would move until the front where the mobility of the molecules suddenly falls off.

3.4. Formation of molecular aggregates

In the case of pyrene implantation, the excimer-like fluorescence became prominent by increasing the number of laser shots, indicating the formation of aggregates in the layer as shown in Fig. 3(b). One simple explanation might be an increase of the concentration of pyrene in the implanted layer with increasing the number of shots. If a certain amount of molecules are injected into the layer shot by shot, this could result in an increase in the concentration of pyrene, thus aggregates could be formed. On the contrary, the absorbance of pyrene in the implanted layer was constant although the excimer-like fluorescence increased as shown in Fig. 9. This

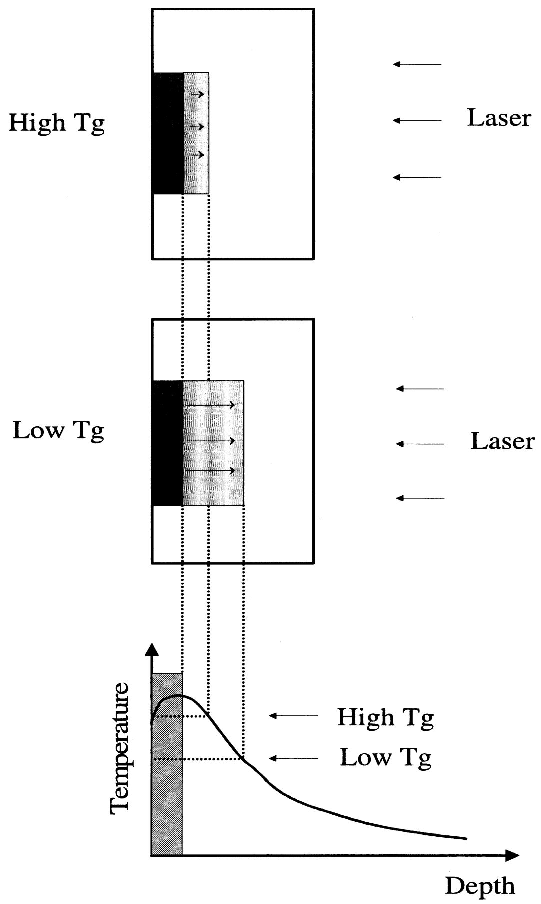

Fig. 8. Description of the penetration mechanism at the surface of target films in terms of a transient temperature rise at the surface layer.

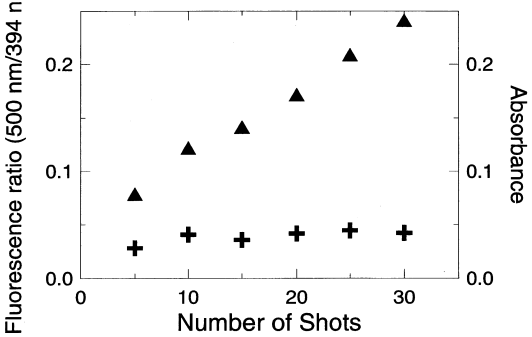

Fig. 9. The ratio of the fluorescence intensity at 500 nm to that at 394 nm (▲) as a function of the number of laser shots, showing the formation of excimer-like aggregates in PEMA target films. The absorbance at 337 nm (+) was also plotted for showing the total amount of the implanted pyrene in the films. The laser fluence was 100 mJ cm^{-2} and the source was pyrene-doped PMMA.

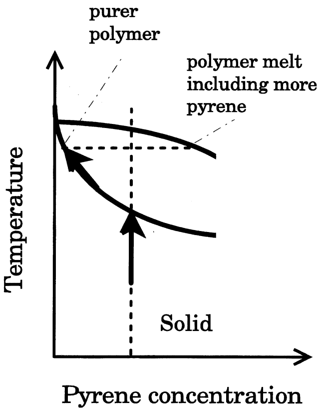

Fig. 10. Conceptual phase diagram for a dopant-polymer system at a low limit of dopant concentration.

means that the amount of molecules in the implanted layer would not change so much, but pyrene molecules would move in the implanted layer, resulting in the formation of their aggregates.

This may be explained by the repetition of melting and sudden cooling of the system which consists of polymer and dopant molecules. As illustrated in the conceptual phase diagram in Fig. 10, when a polymer system involving a certain amount of dopant is heated up, purer polymer solid and partially melted polymer involving a higher concentration of dopant molecules is yielded. If the system cools down rapidly, the purer polymer solid would solidify without dopants, resulting in the generation of domains which involve more dopants. This process is similar to the fractional crystallization, and its repetition will amplify inhomogeneity of the distribution of dopants in polymer. This would be a result of repetitive heating and cooling of polymer including a small amount of dopant molecules.

4. Conclusion

The mechanism of laser molecular implantation was studied by fluorescence and absorption spectroscopy. Fluorescent patterns of implanted molecules were also found at the surface of the target films even when the laser fluence was less than the ablation threshold of the source films. The amount of ejected molecules from the source film was estimated from the reduction of fluorescence intensity. It was found that the lower the glass transition temperature of the source film, the higher the ejected amount. The thickness of the implanted layer at the surface of the target film was obtained by means of total internal reflection fluorescence. The molecular aggregates were found to increase with increasing the number of laser shots. The mechanism of the penetration and aggregation of the fluorescent molecules by the repetitive irradiation was discussed in connection with photothermal temperature jump and thermally activated diffusion in polymer solids.

Acknowledgements

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