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Journal of Photochemistry and Photobiology A: Chemistry 183 (2006) 292–296
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Process during laser implantation and ablation of Coumarin 6 in poly (butyl methacrylate) films

Y. Pihosh *, M. Goto, T. Oishi [1], A. Kasahara, M. Tosa

Materials Engineering Laboratory, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

Available online 5 July 2006

Abstract

Coumarin 6 (C6) molecules were implanted into poly butyl methacrylate (PBMA) polymer films following excitation using a pulsed dye laser coupled with a microscope. The mechanism of this microscopic laser induced molecular implantation method (LIMIT) is discussed on the basis of experimental parameters affecting the implanted area's size. The C6 molecules were ejected from a C6 source film facing a PBMA target film with various interface distances between them. The area size variation was observed in terms of the density distribution of the ejected C6 molecules in the plume and the plume shape was estimated at different laser fluences. The size and the shape of the ejected C6 molecules are discussed in terms of the processes taking place in the plume. Based on the obtained results, the implantation method was optimized so that the formation of extended fine-art quality green-color fluorescent patterns consisting of C6 molecular dots could be demonstrated.

Keywords: Laser molecular implantation; Coumarin 6; Fluorescence molecule; Polymer; Micro-pattering

1. Introduction

The laser induced molecular implantation technique (LIMIT) of organic molecules has been successfully adapted in a number of important practical applications such as surface microfabrication of polymer thin films [1,2] and manufacturing of molecular devices [3]. The method has already been applied to fabricate photo-switching devices [4] as well as to demonstrate laser induced mixing of two different chemicals in a polymer solid [5]. It is also a desirable method for the fabrication of devices where functional organic molecules can be arranged in a spatially selective manner in or on a substrate [6]. LIMIT can be achieved by tightly contacting a doped polymer "source" film and an un-doped polymer "target" film. High-power laser pulses guided to the contacting film interface lead to evaporation of a matter from the "source" surface in a relatively mild condition so that the stoichiometry of the material is preserved in the interaction. As a result, a high velocity jet of particles (a plume) is ejected normal to the "source" surface. The plume expands away from the surface with a strong forward-directed velocity distribution for the collective particles. The ablated species condense on the "target" substrate placed opposite the "source". This method has been successfully applied to laser transfer of several molecules having various functionalities [6,7], however the mechanism of the elementary processes in the irradiated source material, leading to ablation, as well as the interactions in the plume occurring after the plume ejection, are not yet understood well. The laser induced pressure and a phase explosion due to overheating of the irradiated material are considered to be key processes that determine the laser ablation dynamics [8]. The simulation of laser ablation of a molecular solid performed using a breathing sphere model [9] has shown that the dynamics of the ablation provide different ejection conditions for molecular particles of different size as well as their distribution under the irradiated surface [10,11]. The results suggested that the total velocity distribution of the ejected particles can be described by the distribution of the axial (normal to the surface) and radial (parallel to the surface) velocity components. In contrast to the axial velocities, the radial velocities do not contain a contribution from the jet velocity and appear to be associated with the thermal motion in the plume, which is well described by Maxwell–Boltzmann distribution function, considering single temperature of the plume. However, a modified Maxwell–Boltzmann distribution function taking into account the range of jet velocities has also been introduced to describe the axial velocity distribution [10]. Thus, the complete velocity

* Corresponding author. Tel.: +81 29 859 6533; fax: +81 29 859 2501.
E-mail address: Yuriy.Pihosh@nims.go.jp (Y. Pihosh).
[1] Presented address: National Institute of Advanced Industrial Science and Technology, Research Institute for Environmental Management Technology, Metals Recycling Group 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan.

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doi:10.1016/j.jphotochem.2006.05.020

distribution can be described with a single set of parameters, namely by the temperature of the plume and the maximum jet velocity. The expansion of the plume in both radial and axial directions can be simulated taking into account the duration of the laser pulse, the laser fluence, as well as the size and position of the ejected particles under the surface of the "source" film. In the present work, we provide experimental results on the dynamics of the expansion of the C6 plume formed using LIMIT.

2. Experimental

LIMIT was used for implantation of C6 into poly butyl methacrylate (PBMA) films. The experimental set up, described previously [6], consisted of a pulsed dye laser (4 ns pulse, 440 nm wavelength, coumarin dye laser pumped by an LSI–VSL-337ND–S nitrogen laser), and an X–Y translation stage as shown in Fig. 1. A selection of different ND filters was used to control the laser pulse intensity.

Source films of C6/PBMA with a concentration of 4 wt% and neat target PBMA films were prepared by dissolving the corresponding components (PBMA and C6) in monochlorobenzene (from Wako). These were spin-coated to cover glasses of about 170 μm thickness using a conventional spin coater. The prepared source C6/PBMA films with thickness several hundred nm were brought into contact with the neat target PBMA films, as shown in Fig. 1.

A single focused laser pulse was applied to the sandwich structure inducing molecular transfer from the source to the target film. The laser pulse energies were 0.43 and 0.86 nJ/pulse. The exact position of the implanted area was pre-determined by computer control of the X–Y stage. Molecular dot formation was investigated using different distances between the source and target surfaces (D_{SS}) and different laser focus positions. The distance between interfaces was measured using an optical microscope and could be varied by changing the pushing force applied to both sides of glasses as shown in Fig. 1. The implanted films obtained were observed using a universal fluorescence microscope (Olympus, model-IX70) equipped with a high-resolution conventional digital camera. The size of each dot was estimated by fitting the intensity profile with a Gaussian distribution function. The reported dot diameters were derived from the full width of the function at half of its height.

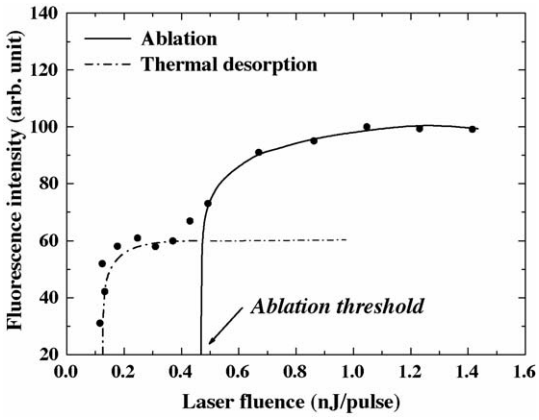

Fig. 2. Dependence of the fluorescent intensity of C6 dots on laser fluence.

3. Results and discussion

The formation of the plume of the laser ejected C6 molecules could be examined by comparing the dot size when the target PBMA film was introduced at different distances (D_{SS}) above the source C6 film surface. Thus, the size distribution of deposited C6 molecular dots can be used to estimate the shape of the ejected plume. In this way, the plume shape was examined at two laser fluencies. The influence of the laser fluence on the C6 dot formation was investigated earlier [12]. The fluorescent intensity of the deposited dots was assumed to be proportional to the quantity of the ejected material is shown in Fig. 2 and was monitored as a function of the laser fluence. The ablation threshold was determined to be 0.47 nJ/pulse. The fluorescent patterns along with the density profiles of C6 dots deposited at different distances above the source film at a laser fluence, which was close to the ablation threshold of 0.43 nJ/pulse, are shown in Fig. 3. Well-formed C6 dots having Gaussian density profiles were observed until the distance above the surface of the source film exceeded 100 μm. The plume shape derived from the radii of the dots of different distances from the surface is presented in Fig. 4. The expansion of the plume toward to the target film has an obvious linear character.

The results of the plume formation at a laser fluence of 0.86 nJ/pulse are shown in Fig. 5. In this case, a more complex structure of the plume is obvious. In contrast to the shape of

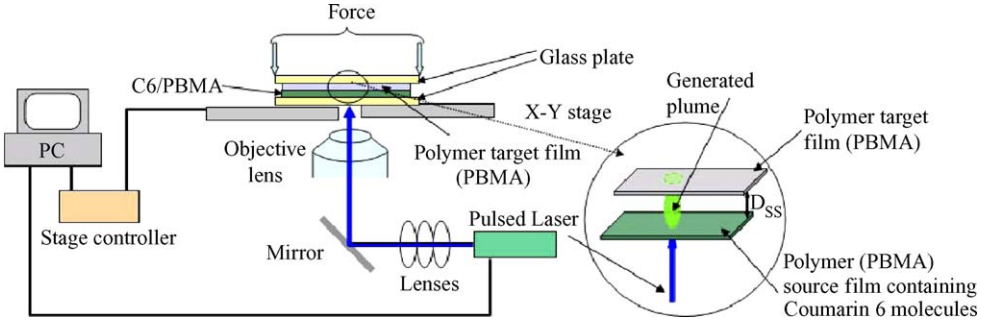

Fig. 1. Schematic illustration of the experimental set up used for molecular implantation of (PBMA, poly (butyl methacrylate); C6, Coumarin 6).

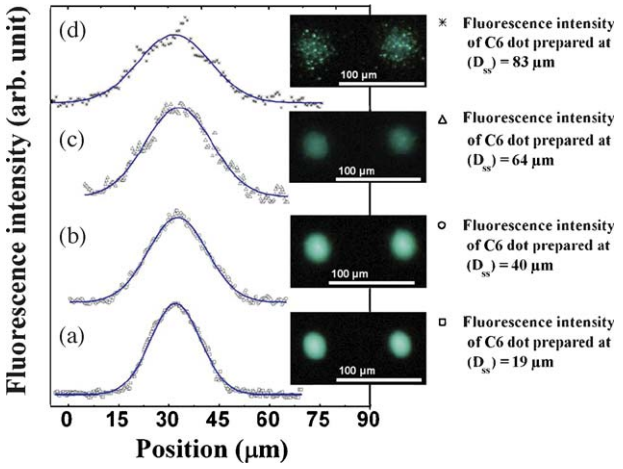

Fig. 3. Fluorescent patterns and fluorescent intensity distribution of C6 dots deposited at 0.43 nJ/pulse at different distances from the source film surface: (a) 19 μm; (b) 40 μm; (c) 64 μm; (d) 83 μm.

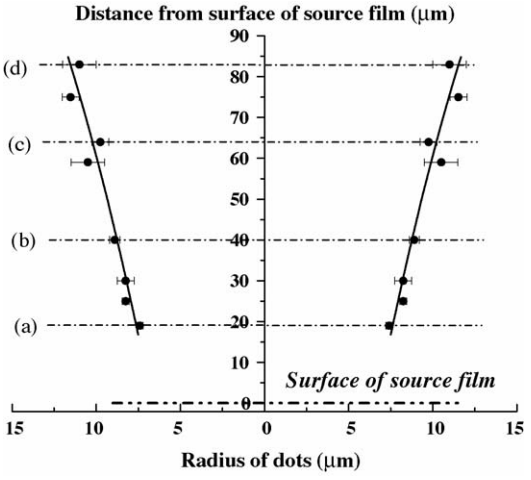

Fig. 4. Derived cross section of plume excited at laser fluence 0.43 nJ/pulse.

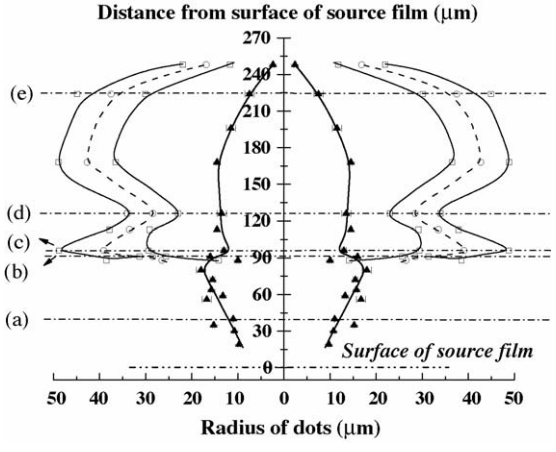

Fig. 5. Derived cross section of plume excited at laser fluence 0.86 nJ/pulse. (▲), shape of plume of the C6 dots; (□), shape of halo; (◯), center of halo).

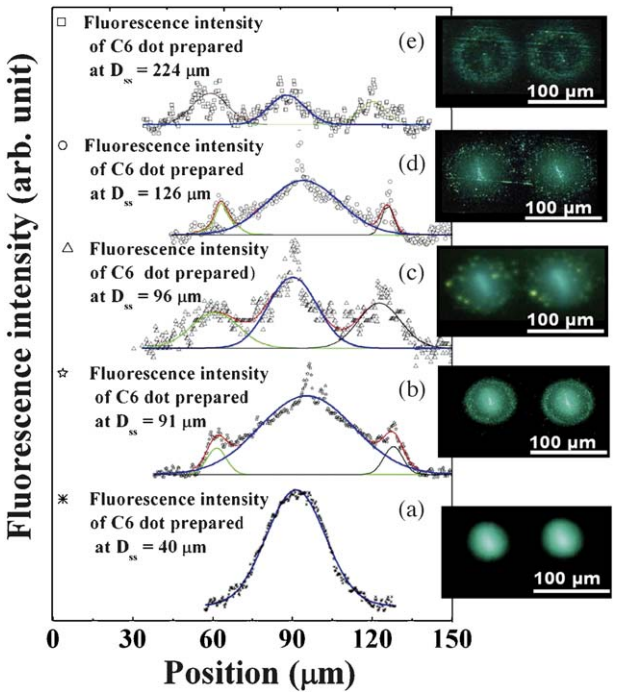

Fig. 6. Fluorescent patterns and fluorescent intensity distribution of C6 dots deposited at 0.86 nJ/pulse at different distances from the source film surface: (a) 40 μm; (b) 91 μm; (c) 96 μm; (d) 126 μm; (e) 224 μm.

plume, formed after excitation at a laser fluence of 0.43 nJ/pulse, the plume resulting at higher fluence appears to be double folded. The lower part of the plume, located from the proximity of the surface to 100 μm above the surface, has wider density distribution than the upper part of the plume. Furthermore, a halo of low density formed around the upper part of the plume. The plume cross sections (a–e) derived from the fluorescent patterns of C6 dots along with the density profiles are presented in Fig. 6 for different distances of target film from the source film surface. One can see that the dots obtained when the distance between source and target films was small were homogeneous and the density profile could be well described by Gaussian distribution (Fig. 6(a)). In contrast to these, dots obtained at greater distances from the surface had non-homogeneous density distributions. Halo patterns appeared at distances greater than 90 μm from the source film surface (Fig. 6(b–e)). The intensity profile revealed three peaks in the density distribution. The main peak is surrounded by two peaks of lower intensity as seen from Fig. 6(b and c). For the dots, which were prepared at a distance of 224 μm, the main peak and the halo peaks have similar intensity as shown in Fig. 6(e).

The explanation of the evolution of the plume shape at higher laser fluence is not yet completely clear. The double folded shape of the plume could be caused by the contribution of two fluxes of C6 particles of different size. In contrast to the smaller particles, larger particles are reported to have radial velocity components that are much higher and this may be the reason of increased plume spreading [8]. The part of the plume responsible for the side peaks was possibly formed by a flux of bigger particles which tend to be slower perpendicular to the

surface than smaller particles [8]. However, the origin of the particles of different sizes is also not clear. The bigger particles can be excited from the deeper layers within the source film whereas the smaller particles may have their origin from its surface. Alternatively, the smaller particles could be a product of the disintegration of the bigger ones within the plume [8,13]. From the view of possible particle disintegration, the formation of halo patterns is rather interesting. The presence of the halo patterns formed around organic molecular dots has been reported earlier [14]. These authors associated the origin of the halo with the impact fracture of the large particles at the target film. However, no halo patterns were observed at distances closer to the surface of the source film (see for example Fig. 6(a)). We speculate that the origin of the halo pattern formation could be the result of disintegration of big particles of C6 at distances about 90 μm above the source film surface. The appearance of the halo probably results from the disintegration of big particles at the edge of the plume, during its forward movement in the plume, due to the overheating of the ablated species at high laser fluencies [8,13]. The increase of the internal temperature with increasing particle size has been reported elsewhere [8]. Since thermal energy is the source of the potential energy required for disintegration of overheated material and also the origin of the kinetic energy of the plume expansion, the disintegrating species can be accelerated in both radial and axial directions inside the plume. Once the disintegration starts at 90 μm above the source surface it continues during the motion of the plume toward the target film. The described results imply that target distance from the source film surface should not exceed 90 μm in order to get well-formed C6 dots at high fluence.

Another mechanism is possible that may occur in parallel with the previously discussed one or even pre-dominate. Namely, if condensed material ejected in the centre of plume is more forward-directed then solid and liquid will push through the gas phases producing a turbulent medium. Turbulent gas flows may push material laterally outwards in a non-linear fashion, since the gaseous material will ebb and flow within the shock wave, which may have turbulent wakes as a function of time and distance. Further the solid material in the centre can potentially even break through the advancing shock wave.

Besides the distance of the target from the source film surface, the variation of the laser focal plane can drastically influence the size of the deposited dots. The influence of the laser focus point on the size of C6 dots was studied in both, forward and backward, directions from the source film surface. The results obtained at laser fluences of 0.43 and 0.86 nJ/pulse are presented in Fig. 7(a and b), respectively. Taking into account the dots size variation in the surface proximity region of ±40 μm in both, toward and backward, directions from the source surface the dots size range was estimated as 26.4 ± 3.6 and 20.0 ± 9.5 μm for laser fluencies of 0.43 and 0.86 nJ/pulse, respectively. This means that the laser focus variation in the surface proximity region can result in 14 and 47% error to the dot size deposited at laser fluencies of 0.43 and 0.86 nJ/pulse, respectively, within the ±40 μm range.

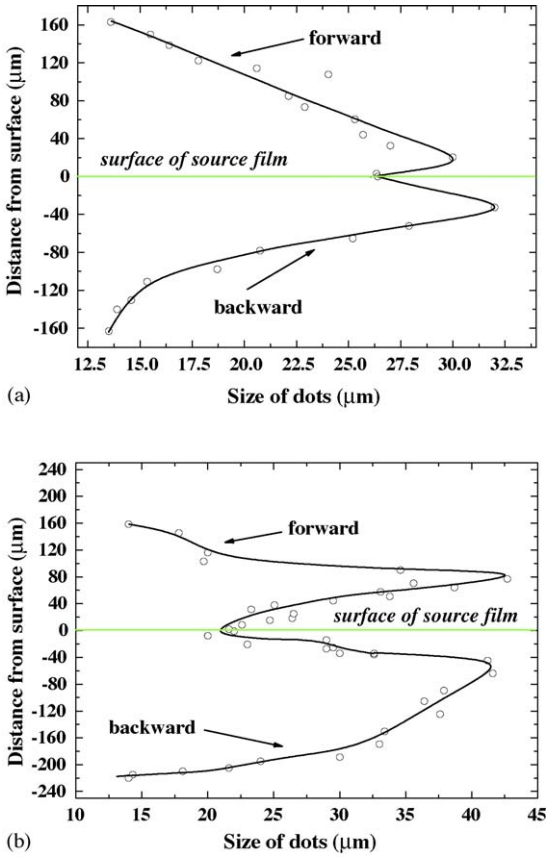

Fig. 7. Evolution of the C6 dot size as a function of the laser focus fluctuations for laser fluences of 0.43 (a) and 0.86 nJ/pulse (b). C6 dots size variation is presented for focus fluctuation in both directions: toward the target and backward the source film surface.

Using suitable parameters for the formation of implanted dots, high quality patterns can be produced. Fig. 8 shows the fluorescence image of one from the "Thirty-six Views of Mount Fuji" by Katsushika Hokusai [15] formed by C6 dots implanted into a PBMA matrix. The green dots were produced by optimized implantation of C6 from 4 wt% C6/PBMA source film at laser fluence of 0.33 nJ/pulse. The size of the C6 dots was about 10 μm when distance between source and target surface

Fig. 8. Fluorescent image of one from the Thirty-six Views of Mount Fuji created by Japanese painter Katsushika Hokusai (1760–1849) formed by laser-implanted C6 dots onto PBMA substrate film.

was 4 ± 0.5 μm. This technique is applicable for fabricated of novel photonic crystal in the future.

4. Conclusions

A pulsed dye laser ($\tau = 4$ ns, $\lambda = 440$ nm) was used to implant C6 into poly butyl methacrylate polymer films. The dependence of the implanted dot sizes on the distance between the source and the target films was discussed in terms of the plume shape of the laser ejected C6 particles. The shape of the plume was explored at different laser fluences. The disintegration of big particles in the plume at 0.86 nJ/pulse was suggested, which can be explained by overheating of the particles ablated at high laser fluence. The influence of the laser focus variation on the C6 dots size was estimated. Successful application of the experimental results has been demonstrated by the production of a green image of one from the "Thirty-six Views of Mount Fuji".

Acknowledgements

The present work is supported by the Grant-in-Aid for Scientific Research (KAKENHI) in Priority Area "Molecular Nano Dynamics" from Ministry of Education, Culture, Sports, Science and Technology.

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