LASER IMPLANTATION AND ABLATION PROCESS OF MOLECULES INTO POLYMER FILMS

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ABSTRACT. Coumarin 6 (C6) molecules has been successfully implanted into poly butyl methacrylate (PBMA) polymer films by means of a pulsed dye laser. This mechanism of the microscopic laser induced molecular implantation method (LIMIT) is discussed on the basis of experimental parameters affecting the implanted area size. C6 molecules were ejected from C6 source film facing PBMA target film at various interface distances between them. The area size variation has been observed in terms of the density distribution of the ejected C6 molecules in the plume and the plume shape was estimated at different laser fluencies. The size and the shape of the ejected C6 molecules have been discussed with respect to the processes having place in the plume. Basing on the obtained results the formation of the green-color fluorescent patterns consisting of C6 molecular dots was demonstrated.

Introduction

Laser induce molecular implantation method (LIMIT) of organics 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 electronic devices [3]. The method has already been applied to fabricate photo-switching devices [4], to demonstrate laser-induced mixing of two different chemicals in a polymer solid [5] and is desired for the fabrication of the devices where functional organic molecules can be arranged in a spatially selective manner in or on the substrate [6]. The more recent patterning method of LIMIT, involving tightly contacted a doped polymer “source” film and un-doped polymer “target” film, could be successfully applied to laser transfer of several molecules having various functionalities [6-7]. High-power laser pulses lead to evaporation of a matter from a “source” surface such that the stoichiometry of the material is preserved in the interaction. As a result, a high velocity jet of particles (plume) is ejected normal to the “source” surface. The plume expands away from the surface with a strong forward-directed velocity distribution of the different particles. The ablated species condense on the “target” substrate placed opposite to the “source”. However a 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 still under investigation. The laser induced pressure and a phase explosion due to overheating of the irradiated material are considered as the 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 clusters 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 clusters 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 well described by Maxwell-Boltzmann distribution function considering single temperature of the plume.
However, modified Maxwell-Boltzmann distribution function taking into account the range of jet velocities has been introduced to describe the axial velocity distribution \[10\]. Thus, the complete velocity distribution can be describe 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 duration of the laser pulse, laser fluence, size and position of the ejected clusters under surface of the “source” film.

In the present work we provide experimental results on the dynamic of the expansion of the Coumarin 6 plume.

**Experimental**

Laser molecular implantation method (LIMIT) was used for implantation of Coumarin 6 (C6) into poly-(butyl methacrylate) (PBMA) films. The experimental setup 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 laser pulse intensity. The source films of Coumarin 6/PBMA (C6/PBMA) with concentration 4 wt % and target (PBMA) films were prepared by dissolving the corresponding components (PBMA and C6) in monochlorobenzene (from Wako). These were transferred to cover glasses of about 150 µm thickness using a spin coater. The prepared source C6/PBMA was brought into contact with 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 films. The laser pulse energy was 0.43 nJ/pulse and 0.86 nJ/pulse. The exact position of the implanting area was pre-determined by computer control of the X-Y stage. Dots formation has been investigated at different distances between source and target surfaces and laser focus positions. The distance between interfaces varied with respect to the puling force applied to both side 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 digital camera. The size of each dot has been estimated fitting the intensity profile with a Gaussian distribution function. The reported dot diameter was ascribed to the full width of the function at half of its height.

**Results and discussion**

A formation of the plume of the laser ejected coumarin 6 molecules can be examined when target PBMA film is introduced at different distances above the source C6 film surface. Thus, a distribution of the sizes of deposited C6 molecular dots describes the shape of the ejected plume. By this way, the plume shape was examined at two laser fluencies. An influence of the laser fluence to the C6 dots was investigated earlier \[12\]. The fluorescent intensity of deposited dots proportional to the yield of the ejected material is shown in Fig. 2 as a function of laser fluence. The ablation threshold was detected at 0.47 nJ/pulse. The fluorescent patterns along with the density profiles of C6 dots deposited at different distances above the source film at laser fluence close to the ablation threshold, 0.43 nJ/pulse, are shown in Fig. 3. Well formed C6 dots having Gaussian density profile were detected till the distance above the surface of the source film exceed 100 µm. The shape of plume derived from the radiuses of the dots of different distances from the surface is presented in Figure 4. An expansion of the plume toward to the target film has well recognized linear character. The results of the plume formation at laser fluence of 0.86 nJ/pulse are presented in Figure 5. A complex structure of the plume is well recognized. In contrast to the shape
of plume excited by the laser fluence of 0.43 nJ/pulse, the plume of the higher fluence appears as double folded. The lower part of the plume, located from the proximity of the surface to the 100 µm above the surface, has wider density distribution than the upper part of the plume. Furthermore, a halo of low density region is formed around the upper part of the plume. Plume cross sections (a) – (e) reflected by the fluorescent patterns of C6 dots along with the density profiles are presented in Figure 6 for different distances of target film from the source film surface. One can see the dots obtained at small distance between source and target films are homogeneous and the density profile can be well described by Gaussian distribution (Fig.6a). In contrast to these, dots obtained at higher distances from the surface show non-homogeneous density distribution. A halo patterns appears above 90 µm from the source film surface (Fig.6b-e). The intensity profile revealed three peaks in the density distribution. The main peak is surrounded two peaks of lower intensity as is seen from Fig. 6b-c. For the dots prepared at distance of 224 µm the main peak is dominated and ring-like dots shown in Fig. 6e are formed. The evolution of the plume shape at higher laser fluence is not completely clear. Double folded shape of the plume is probably caused by the contribution of two fluxes of C6 clusters of different size. The lower part of the plume is probably formed by flux of bigger clusters which tend to be slower and are closer to the source film surface. In contrast to the smaller clusters, they have the radial velocity component much higher that can be a reason of higher plume spreading [8]. However, the origin of the clusters of different sizes is not clear. Bigger clusters can be excited from the deeper layer of the source film when the smaller from its surface, although they can be a product of the disintegration of the bigger ones in the plume [8, 13]. From the view of possible cluster disintegration, the formation of halo patterns is rather interesting. Presence of the halo patterns formed around organic molecular dots has been reported earlier [14]. The authors associated the origin of the halo with the impact fracture of the large clusters to the target film. However, no halo patterns formation is seen at distances closer to the surface of the source film (see for example Fig.6a). We suppose the reason of the halo pattern formation can be found in the disintegration of big clusters of C6 at distances about 90 µm above the source film surface. The appearance of the halo probably results from the disintegration of big clusters at the edge of the plume in process of its forward movement in the plume due to the overheating of the ablated species at high laser fluences [8, 13]. Increase of the internal temperature at increasing size of the clusters has been reported elsewhere [8]. Since thermal energy is transformed to the potential energy of disintegration of overheated material and to the kinetic energy of the plume expansion, the disintegrated species can be accelerated in both radial and axial direction in the plume. Once the disintegration starts at 90 µm above the source surface it survives 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.

Besides the distance of the target from the source film surface, fluctuation of the laser focus can drastically influent size of the deposited dots. Influence of the laser focus fluctuation to the size of C6 dots has been studied in both, toward and backward, directions from the source film surface. The results obtained at laser fluences of 0.43 nJ/pulse and 0.86 nJ/pulse are presented in Fig. 7a and Fig. 7b respectively. Taking into account dots size fluctuation in surface proximity region of ±40 µm in both toward and backward directions from the source surface the dots size range has been estimated as following: 26.4 ± 3.6 µm and 20.0 ± 9.5 µm for laser fluences of 0.43 nJ/pulse and 0.86 nJ/pulse respectively. It means that the laser focus fluctuation in the
surface proximity region can bring 14% and 47% error to the dot size deposited at laser fluences of 0.43 nJ/pulse and 0.86 nJ/pulse, respectively. Since the fluorescence emission of C6 is located in the green part of the visible spectrum it is possible to produce patterns consisting of C6 molecules. Using suitable parameters for the formation of implanted dots high quality patterns can be produced. Figure 8 shows the fluorescence image of one from the Thirty-six Views of Mount Fuji formed by C6 dots implanted into a PBMA matrix. The green dots were produced by 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.

Conclusions

A pulsed dye laser (τ = 4 ns, λ = 440 nm) has been used to implantation of C6 into poly (butyl methacrylate) (PBMA) polymer films. The dependence of the implanted dot sizes on distance between the source and the target films has been discussed in terms of the plume shape of laser ejected C6 clusters. The shape of the plume has been explored at different laser fluences. The disintegration of big clusters in the plume at 0.86 nJ/pulse has been explained by overheating of the clusters ablated at high laser fluence. The influence of the laser focus fluctuation to the C6 dots size has been estimated. Successful application of the experimental results has been demonstrated by production of a green image of one from the Thirty-six Views of Mount Fuji from Japanese painter Katsushika Hokusai (1760-1849) [15].

REFERENCES

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

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

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<tr>
<th>Laser fluence (nJ/pulse)</th>
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- **Ablation**
- **Thermal desorption**

Ablation threshold
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.

Distance from surface of source film (μm)

Fig. 4 Modeled plume excited at laser fluence 0.43 nJ/pulse.
Fig. 5 Modeled plume excited at laser fluence 0.86 nJ/pulse. (Δ – 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.
Fig. 7 Evolution of the C6 dot size in dependence on the laser focus fluctuations for laser fluence 0.43 nJ/pulse (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.
Fig. 8  Fluorescent image of one from the Thirty-six Views of Mount Fuji from Japanese painter Katsushika Hokusai (1760-1849) formed by laser-implanted C 6 dots onto PBMA substrate film