Molecular Implantation by Pulsed Laser Irradiation Using Self-Organized Polymer Honeycomb Templates

Masahiro Goto*
Materials Reliability Center, National Institute for Materials Science,
1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan,

Olaf Karthaus
Chitose Institute of Science and Technology, Bibi 65-758, Chitose 066-8655, Japan,

Yuriy Pihosh, Akira Kasahara, and Masahiro Tosa
Materials Reliability Center, National Institute for Materials Science,
1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
(Received 25 August 2008; Accepted 10 October 2008; Published 22 October 2008)

The transfer of a polymeric micropattern onto a poly(methyl methacrylate) film surface was achieved by the pulsed laser irradiation of Coumarin 6 molecules using self-organized polymer honeycomb templates. The molecular implanted areas were analyzed by fluorescence microscopy and fluorescence spectroscopy. It was found that the implantation patterns were affected by the configuration of the sample, the template, and the atmospheric conditions. This technique is applicable to the production of molecular patterns on a centimeter-scale region of polymer film surfaces by a simple process. [DOI: 10.1380/ejssnt.2008.222]

Keywords: Surface photochemistry; Laser methods; Photochemistry; Laser molecular implantation; Honeycomb template; Polymer film

I. INTRODUCTION

The micropatterning of functional organic molecules onto polymer films has received much interest because of its wide range of applications including photonic-band-gap materials [1–4], nonlinear optical devices and surface-emitting lasers [5]. A promising method of fabricating such micropatterns is the laser molecular implantation (LMI) technique [6], which enables the implantation of molecules onto a polymer film over an area with a diameter of several micrometers by a single laser shot. In combination with a computer-controlled mechanical stage, it is possible to fabricate molecular dot patterns over a centimeter-order area [7]. This method, however, takes more than 3 hours to fabricate one sample. It is obvious that this lengthy process is not suitable for industrial application. If templates can be used with the LMI process, a molecular pattern with a centimeter-order area can be realized by a single laser shot. Recently, we have attempted to implant organic molecules onto polymer films by using metal templates. However, it was difficult to remove the metal template from the polymer film after the laser irradiation, because the template adhered to the polymer film.

On the other hand, ordered micrometer-sized honeycomb-like porous polymer films grown by self-assembly were successfully produced by Francois et al. in 1994 [8]. The hole size of the honeycomb films is controllable and the fabrication process of the films is quite simple. The cost of fabricating such honeycomb films is reasonable, then the films are disposable.

In this paper we describe our attempt to implant organic molecules through a honeycomb polymer film template with different configurations of samples and templates either in air or in water.

II. EXPERIMENTAL

The details of the setup used for laser molecular implantation have been described previously [7]. A schematic illustration of the setup is shown in Fig. 1. Chlorobenzene (Wako Co.) solutions of poly(butyl-methacrylate) (PBMA) (Aldrich Co.) containing 4 wt% Coumarin 6 (C6) (Aldrich Co.) were spin-coated onto a conventional 170-µm-thick borosilicate glass microscope slide cover plate (Matsunami Co.) for use as a source film with a thickness of several hundred nanometers. The absorption spectrum of the source film is shown in Fig. 2. Neat polymer films of PBMA were prepared in the same way and were used as target films. Honeycomb films were prepared by the evaporation of a polysulfone solution under high humidity; a similar procedure is described in the literature [9]. The honeycomb film was covered with an adhesive tape in which a central hole with a diameter of about 2 cm was cut. Lifting the tape leads to the cleavage of the top layer of the honeycomb film, which then can be used as a mask. The source, mask and target films were placed in contact with each other and the gap between them was varied by changing the induced compression load between the source and target, as shown in Fig. 1(a) (high load) and Fig. 1(b) (low load). The gap was filled with distilled water (Wako Co.) (see Fig. 1(c)). A single pulse of the laser light (440 nm wavelength, 4 ns pulse length) was focused onto the surface of the source film, and the molecules in the source film were photo excited by the laser light. After that, the excited molecules were ejected from the source to the target, which is known as the LMI phenomenon [6], through the honeycomb mask. After the molecular implantation, the implanted areas were observed using a fluorescence microscope equipped with a digital camera to record and store images. The laser
III. RESULTS AND DISCUSSION

Figure 3 shows the results of the molecular implantation using the setup shown in Fig. 1(a). In this case, the source, mask and target films were placed in close contact. A photograph of the honeycomb film is shown in Fig. 3(a). Figure 3(b) shows a photograph of the source film after the laser irradiation. Three molecular implantation areas of about 3 μm diameter can be recognized. C6 molecules were implanted onto the PBMA target film through the honeycomb mask. The shape and size of the implanted C6 areas were measured from fluorescence images using 1/e of the peak value of the fitted Gaussian intensity distribution. The laser fluence used for the molecular implantation was 680 J/cm² [Fig. 3(c)], 1.09 kJ/cm² [Fig. 3(d)] or 1.36 kJ/cm² [Fig. 3(e)]. The implanted region was divided into 3 or 4 areas by the mask. The diameter of the implanted areas slightly increased upon increasing the laser fluence from about 2.5 to 3 μm. The size of each implanted area was almost the same as the ablated area of the source film. The distance between the implanted areas also increased upon increasing the laser fluence from about 2 to 7 μm. It was found that the ejected molecules were not implanted perpendicularly through the mask but at an oblique angle. Figure 4 shows the results for the setup shown in Fig. 1(b). The gaps between the source and the mask and between the mask and the target were both 1±0.15 μm. The honeycomb film was then used as the mask, as shown in Fig. 4(a). The ablated area shown in Fig. 4(b) has a diameter of about 10 μm. C6 molecules were effectively implanted onto the PBMA target films, as shown in Figs. 4(c) and (d). The diameter of the separated implantation areas was about 10 μm. The distance between the implanted areas slightly increased upon increasing the laser fluence from 550 J/cm² with about 20 μm at [Fig. 4(c)] to 700 J/cm² with about 25 μm [Fig. 4(d)]. The implantation phenomena were quite similar to those obtained using the setup in Fig. 1(a). However, for the setup in Fig. 1(b), the number of implanted molecules was larger than that for the setup in Fig. 1(a). We consider that molecules were able to pass through the honeycomb mask because of the gap containing air.

Figure 5 shows fluorescence images of the implanted C6 molecules obtained using the sample geometry shown in Fig. 1(c). In this case, the gap between the films was filled with water. Quite recently, Goto et al. discovered a new phenomenon of a laser-induced molecular microjet in water and succeeded in implanting some molecules using...
FIG. 3: (a) Optical microscope image of the honeycomb film mask and (b) source film. (c) Fluorescence microscope images of implanted Coumarin 6 molecules prepared with a single pulse of 680 J/cm² laser light; (d) 1.09 kJ/cm²; (e) 1.36 kJ/cm² in the case of short distance configuration of the source and target films in air.

FIG. 4: (a) Optical microscope image of the honeycomb film mask and (b) source film. (c) Fluorescence microscope images of implanted Coumarin 6 molecules prepared with a single pulse of 550 J/cm² laser light; (d) 700 J/cm² in the case of long distance configuration of the source and target films in air.

this molecular microjet in water [10–13]. In the present experiment the honeycomb film was placed in the water-filled gap. The distance between the source and the target was about 6 µm. Separated molecular implanted areas were observed at a laser fluence of 180 J/cm² [Fig. 5(a)], which were similar to those obtained by implantation in air. However, we were able to implant molecules using a weaker laser fluence in this case. As the laser fluence increased to 340 J/cm² [Fig. 5(b)], the molecular implanted areas became connected to each other, which revealed that the honeycomb mask had started to decompose. Furthermore, a single molecular implantation spot was observed at a laser fluence of 550 J/cm² [Fig. 5(c)]. The diameter of the implanted area was about 3 µm, which was much smaller than that of the ablated area of the source film. By increasing the laser fluence to 700 J/cm², the diameter of the implanted spot increased to about 6 µm [Fig. 5(e)].

We found that the honeycomb film was destroyed by the molecular jet in water [10–13] and that some of the molecules in the jet passed through the honeycomb film. We consider that the size of the implanted molecular area was decreased using the honeycomb mask. If a neat polymer film was used as a mask instead of the honeycomb film, the mask cannot be removed from the target film after the implantation. The honeycomb films are suitable for LMI in water and can be used to reduce the size of the implanted area.

Fluorescence spectra of the implanted C6 molecules in the target films as well as those of the source films are shown in Fig. 6. The spectral peak of the implanted molecules appears at the same position as that of the source film, which confirms that the C6 molecules were implanted without being decomposed.

This molecular implantation technique using honeycomb film masks may be applied to the fabrication of patterned molecular structures over a large area by a simple method with a low cost.
FIG. 5: (a) Fluorescence microscope images of implanted Coumarin 6 molecules prepared with a single pulse of 180 J/cm$^2$ laser light; (b) 340 J/cm$^2$; (c) 550 J/cm$^2$; (d) 700 J/cm$^2$ in water case.

IV. CONCLUSIONS

Laser molecular implantation using a honeycomb film as a mask was observed under different experimental conditions. The effects of the laser fluence, sample configuration and the material filling the gaps between the source, mask and target on the implanted area and pattern were studied. This method will be useful for the fabrication of patterned molecular structures over a large area by a simple method with a low cost.

Acknowledgments

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

[1] S. John, Phys. Today 44, 32 (1991).
[2] E. Yablonovitch, J. Opt. Soc. Am. B 10, 283 (1993).
[3] J. D. Jannopoulos, R. D. Meade, and J. N. Winn, Photonic Crystals (Princeton, New York, 1995).
[4] S. Noda, M. Imada, and A. Chutinan, Nature 407, 608 (2000).
[5] C. M. Wu et al., IEEE Photon Tech. Lett. 4, 960 (1992).
[6] H. Fukumura, H. Kohji, Y. Nagasawa, and H. Masuhara, J. Am. Chem. Soc. 116, 10304 (1994).
[7] M. Goto, J. Hobley, T. Oishi, A. Kasahara, M. Tosa, K. Yoshihara, M. Kishimoto, and H. Fukumura, Appl. Phys. A 79, 157 (2004).
[8] G. Widawski, B. Rawiso, and B. Francois, Nature 369, 387 (1994).
[9] O. Karthaus, N. Maruyama, X. Cieren, M. Shimomura, H. Hasegawa, and T. Hashimoto, Langmur 16, 6071 (2000).
[10] M. Goto, Y. Pihosh, A. Kasahara, and M. Tosa, Jpn. J. Appl. Phys. 45, 966 (2006).
[11] Y. Pihosh, M. Goto, M. B. Gaifullin, A. Kasahara, and M. Tosa, J. Photochem. Photobio. A: Chemistry 193, 42 (2008).
[12] Y. Pihosh, M. Goto, A. Kasahara, and M. Tosa, Thin Solid Films 516, 2507 (2008).
[13] M. Goto, Y. Pihosh, A. Kasahara, and M. Tosa, Appl. Phys. Exp. 1, 067010 (2008).