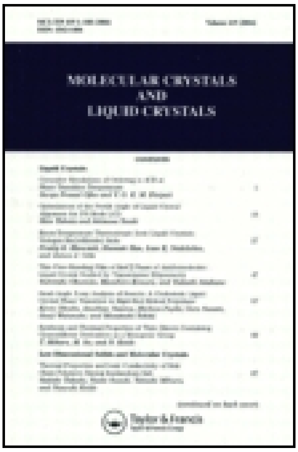

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Fluorescent Image Patterning with Copolymer LB Film Having Anthracene Chromophore

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Fluorescent Image Patterning with Copolymer LB Film Having Anthracene Chromophore

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In this article, we described a way to direct method of generating fluorescent image pattern with a copolymer (poly(*N*-neopentyl methacrylamide-*co*-9-anthrylmethyl methacrylate)) [p(nPMA-AMMA)] LB film. It was found that the copolymer [p(nPMA-AMMA)] LB film irradiated by deep UV light (at 254 nm or 365 nm) gives fluorescent image pattern with a resolution of 1.5μm. It is of interest that the fluorescent image pattern was produced only by deep UV irradiation without any development treatments.

Keywords polymer; LB film; fluorescent image; pattern

1. INTRODUCTION

Recently various resist materials have been developed to realize a high-resolution lithography for higher circuit density. As one approach to improve the resolution in photolithography, the use of ultra-thin films such as Langmuir-Blodgett(LB) film or Self-assembled monolayers(SAM) has been proposed. The LB technique is one of the most effective methods that can be used to form well-defined ultra-thin film with controlled thick-

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ness and molecular orientation. Therefore, LB films are expected to realize an ultra-high resolution photo lithography [1-5]. As for the application of LB films to photoresist materials, Barraud et al. obtained fine negative patterns by electron beam polymerization of ω-tricosenoic acid LB film [6]. Ringsdorf et al. studied the photopolymerization of octadiene and docosadiene derivative LB films [7]. Furthermore, Fu et al. investigated fine negative patterns of PMMA LB films by electron beam irradiation [8].

We have continued to investigate the resists using a series of polymer LB films consisting of *N*-alkylacrylamide. For example, fine negative-tone patterns with a resolution of 0.1μm were clearly figured by the polymerization of *N*-octadecylacrylamide monomer LB film by deep UV or electron beam irradiation [9]. Furthermore, we found that fine positive-tone patterns were obtained from the effective photodecomposition of poly(*N*-alkylmethacrylamide) LB films and the copolymer [poly(dodecylacrylamide-*co*-*tert*-butyl-4-vinylphenyl carbonate)s] LB films [10-15].

In this paper, we designed a new copolymer composed of *N*-neopentylmethacrylamide (nPMA) and 9-anthrylmethyl methacrylate (AMMA) monomers. The nPMA LB film is known to show the photodecomposition of both the main chain scission and the side chain scission by deep UV irradiation from the previous study [14]. On the other hand, the anthracene group is cross-linked with light irradiation at 365 nm and gives an insoluble fragment [16]. The lithographic properties of the copolymer [p(nPMA-AMMA)] were investigated from the viewpoint of fluorescent image photopatterning.

2. EXPERIMENTAL

The copolymer [p(nPMA-AMMA)] (Figure 1) was prepared by free-radical polymerization of *N*-neopentylmethacrylamide (nPMA) with 9-anthrylmethyl methacrylate (AMMA) in toluene at 60°C. Glass, silicon, and quartz slides on which LB films were deposited were initially cleaned by a UV-O_3 cleaner (NL-UV253, Nippon Laser Electronics) and then made hydrophobic with n-octyltrichlorosilane. Measurement of surface pres-

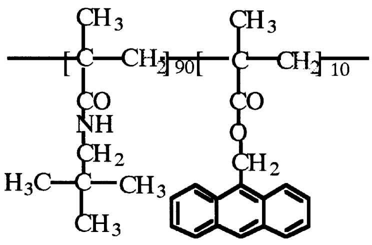

FIGURE 1 Chemical structure of p(nPMA-AMMA).

sure (π) - area (*A*) isotherms and deposition of monolayers were carried out at 15 °C with a Langmuir trough system (FSD-50 and 51, USI) with a compression speed of 14 cm^2/min. The rate of the deposition of monolayers was set at 10 mm/min at both up- and down-strokes. Deionized pure water (milli-QII, millipore) was used as the subphase. UV absorption spectra were recorded with a Hitachi U-3000 UV-vis spectrophotometer. The molar ratio of the anthracene in the copolymer was determined to be 10mol% from the UV absorption spectra. The molecular weight was determined ($Mn=1.60 \times 10^4$ ($Mw/Mn=1.50$)) with a Toyo Soda gel permeation chromatography (GPC) using a polystyrene standard. Deep UV irradiation was carried out with a deep UV lamp (UXM-501MA, USHIO). The thickness of LB film was determined with surface profilometry using a Sloan Dektak 3ST and X-ray diffraction (XRD) with a M18XHF^{22}-SRA (λ=0.1541 nm, Cu-Kα). All measurements were carried out at room temperature. The photopatterns were observed with an OLYMPUS VANOX-T Microscopy.

3. RESULTS AND DISCUSSION

3.1. Monolayer behavior of p(nPMA-AMMA)

The copolymer [p(nPMA-AMMA)] was spread on the water subphase from a chloroform solution (*ca.* 1mM) to measure the pressure (π) – area (*A*) isotherm (Figure 2). The copolymer monolayer has a collapse pressure of *ca.* 33 mN/m and the curve stands up sharply. We can conclude

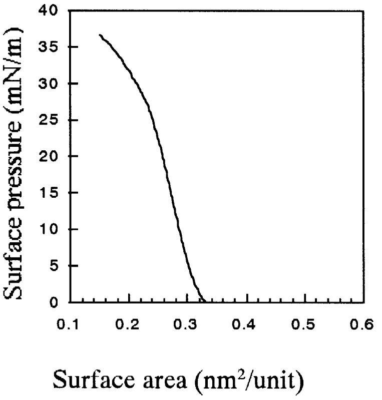

FIGURE 2 Surface pressure (π) - area (A) isotherm of p(nPMA-AMMA) at 15°C.

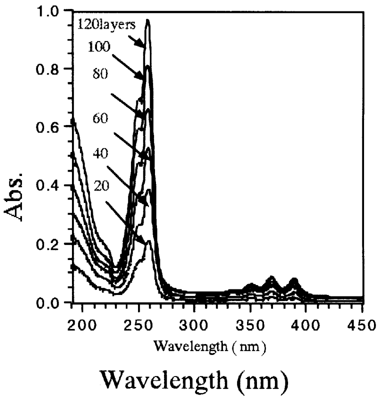

FIGURE 3 UV spectra of p(nPMA-AMMA) LB film as a function of deposited layers.

that the copolymer forms a condensed monolayer on the water surface. The thickness of monolayer of the LB film was 1 nm obtained from XRD measurement. The surface area occupied by each repeat unit of the copolymer was calculated to be 0.31 nm^2/monomer for nPMA unit and 0.45 nm^2/monomer for AMMA unit, respectively. The values are consistent with the results for the polymer reported in a series of the *N*-alkylacrylamide copolymer in our previous studies. The monolayers could be transferred onto solid supports as Y-type LB films with a transfer ratio of almost unity at both downward and upward strokes.

The UV absorption spectra of the copolymer LB films on quartz were measured as a function of the number of deposited layers (Figure 3). The maximum absorbance is linearly increased with the number of deposited layers, indicating the regular deposition of p(nPMA-AMMA) monolayer onto the solid substrate.

3.2. Fluorescent image of p(nPMA-AMMA) LB films

The photolithographic properties of the LB film using a monochromatic

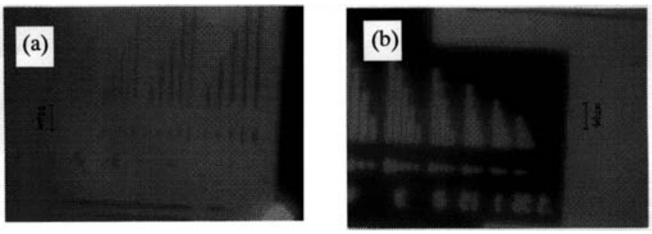

FIGURE 4 (a) Fluorescent image patterns of p(nPMA-AMMA) LB film with 80 layers on a silicon wafer after irradiation at 254 nm. (b) Fluorescent image patterns of p(nPMA-AMMA) LB film with 80 layers on a silicon wafer after irradiation at 365 nm. The bar represents 50 μm.

light were investigated. When the p(nPMA-AMMA) LB film with 80 layers is irradiated by deep UV light at 254 nm, the fluorescent image with a resolution of 5 μm was obtained (Figure 4(a)). These findings suggest that the photodecomposition of nPMA and/or AMMA took place by deep UV irradiation at 254 nm, i.e., potitive-tone patterns, resulting in the luminescent image from unexposed regions. In the case of spin-coat film, however, we were not able to obtain fine image patterns in the same condition.

On the other hand, when the p(nPMA-AMMA) LB film with 80 layers was exposed at 365 nm, of which the absorbance is assigned to π-π* transition of anthracene group, the photocross-linking reaction occurred at exposed regions. The fluorescent image was also yielded with a resolution of 1.5 μm (Figure 4(b)). In the case of the spin-coat film, the resolution obtained was 5 μm. This indicates that the photo-induced cross-linking reaction between anthryl groups in the LB films took place more easily than that of in spin-coat film. Furthermore, it should be mentioned that these processes used in this study do not necessitate any development processes.

4. CONCLUSION

We have prepared a novel copolymer(p(nPMA-AMMA)) LB films having anthraence group for fluorescent imaging. The anthraence groups could be decomposed or linked with etch other by different wavelength irradiation to form fluorescent image patterns without any development. The simple and straight-formed strategy described above should be useful in the design of new imaging materials.

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