Positive-Tone Imaging of Photo-Decomposable Polymer LB Films

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We describe the lithographic properties of poly(*N*-isopentylmethacrylamide-*co*-*t*-butyl 4-vinylphenyl carbonate) [p(iPMA-*t*BVPC)] which has a structure that is subject to the main chain scission and to deprotection of *t*-butoxycarbonyloxy group by deep UV irradiation. The positive-tone patterns of the p(iPMA-*t*BVPC) LB film with 60 layers could be obtained by deep UV light irradiation, followed by development with alkaline aqueous solution. The resolution of the pattern was 0.75 µm, which is the resolution limit of the photomask employed. The photopattern formation with the copolymer [p(iPMA-*t*BVPC)] LB film was more sensitive than the homopolymer poly(*N*-isopentylmethacrylamide) [p(iPMA)] LB film. The etching resistance of the p(iPMA-*t*BVPC) LB film deposited for the pattern of the gold film is also investigated.

The continuing trend toward higher circuit density in microelectronic devices has motivated research efforts in a variety of high-resolution lithography techniques, including electron beam (EB), X-ray, and deep UV technologies. These new technologies also demand highly sensitive resist materials system in order to be of practical use.

The Langmuir–Blodgett (LB) technique makes it possible to prepare an ultra-thin film with controlled thickness and well-defined molecular orientation at a molecular size.[1,2] Because of this superior feature, we have tried to use the polymer LB film as a new type of resist material applicable to high-resolution lithographic technique.[3,4]

In previous studies,[5–7] we have found that *N*-octadecylacrylamide forms a uniform LB film with a highly ordered structure, and yielded a fine negative pattern by photopolymerization. Furthermore, we have also succeeded in the preparation of preformed polymer LB film that has a cross-linking group.[8] By the cross-linking reaction with deep UV and electron beam irradiation we obtained a fine negative pattern consisting of a two-dimensional network. All of these polymer LB films resulted in negative-tone photopatterns. On the other hand, we also obtained positive type photopatterns using poly(*N*-tetradecylmethacrylamide) LB films without any development process (self-development).[9,10] It was found that the higher sensitivity could be obtained by changing the alkyl side chain to the short-branched type.[11] In addition, the deprotection reaction of *t*-butoxycarbonyloxy group has also been used in positive patterning of polymer LB films.[12] Combining these interesting properties, the improvement of not only the sensitivity but also the imaging quality can be expected. In this work, we prepared the copolymers of photodegradable *N*-isopentylmethacrylamide (iPMA) with *t*-butyl 4-vinylphenyl carbonate (*t*BVPC) (Fig. 1) aiming at the fabrication of a new type of positive resist which can employ both main chain scission and polarity change caused by *t*-butoxycarbonyloxy group deprotection.

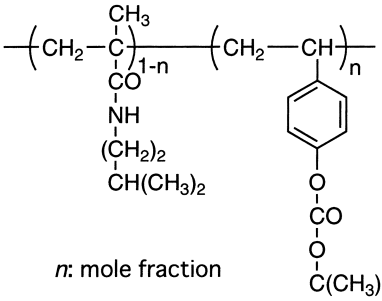

Fig. 1. Chemical structure of p(iPMA-*t*BVPC).

Experimental

The copolymer poly(*N*-isopentylmethacrylamide-*co*-*t*-butyl 4-vinylphenyl carbonate) [p(iPMA-*t*BVPC)] was prepared by free-radical copolymerization of iPMA monomer with *t*BVPC monomer in toluene at 60 °C. The measurement of surface pressure (π)–area (A) isotherm and the deposition of monolayers were carried out with a Langmuir trough system (FSD-50 and 51, USI). The measurement was performed at 15 °C with a compression speed of 14 cm^2/min. The rate of the deposition was 10 mm/min at both up and down strokes. Deionized pure water (Milli-QII, MILLIPORE) was used as the subphase. The copolymer was dissolved in chloroform at a concentration of ca. 1 mM and the solution was spread on the water surface. The glass, quartz, and silicon slides on which the LB film was deposited were treated in boiling concentrated HNO_3 solution, following by the washing with water, and were made hydrophobic with trichlorooctadecylsilane. UV absorption measurements were carried out with a Hitachi U-3000 UV-vis spectrophotometer. Molecular weight was determined with a Toyo Soda gel permeation chromatography (GPC) using a polystyrene standard. The IR spectra were measured with a JASCO-IR 230 spectrometer. Deep UV irradiation was carried out with a deep UV lamp (UXM-501MA) through an IR-cut filter. The thickness of each LB film was determined with surface profilometry using a Sloan Dektak 3ST.

Results and Discussion

Formation of the Copolymer LB Films. The *t*BVPC content of the copolymer was determined to be 39% by ^{1}H NMR [p(iPMA-*t*BVPC39)]. The molecular weight of p(iPMA-*t*BVPC39) was also determined to be $M_n = 2.05 \times 10^4$ and $M_w/M_n = 1.78$. The π–A isotherm of p(iPMA-*t*BVPC39) has a steep rise in surface pressure and high collapse pressure, showing the formation of the condensed monolayer on the water subphase (Fig. 2). The p(iPMA-*t*BVPC39) monolayer could be transferred onto a solid substrate with a transfer ratio of almost unity. Figure 3 shows the UV absorption spectra of the deposited p(iPMA-*t*BVPC39) LB film as a function of the number of layers. The absorbance at 193 nm apparently increases linearly with the number of layers deposited, indicating that the regular deposition of the copolymer monolayer occurs.

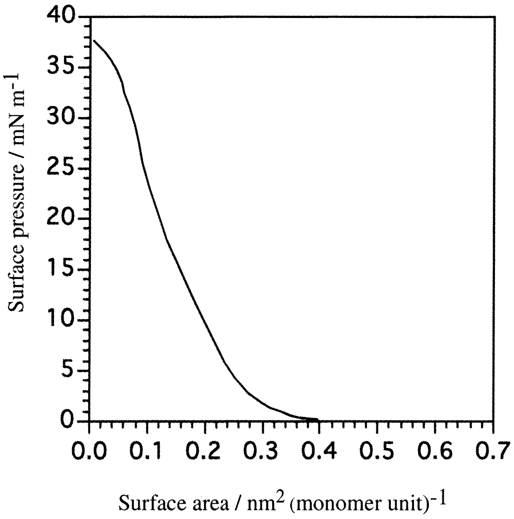

Fig. 2. Surface pressure–area isotherm of p(iPMA-*t*BVPC39) measured at 15 °C.

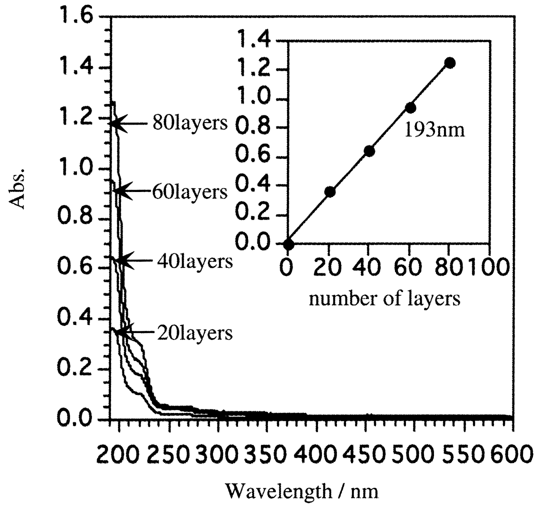

Fig. 3. UV absorption spectra of p(iPMA-*t*BVPC39) LB films as a function of deposited layers. Inset; the plots of the absorbance at 193 nm vs the number of LB films deposited.

Photopatterning. The p(iPMA-*t*BVPC39) LB film with 60 layers was directly exposed to the deep UV light (86 mW/cm^2) through a photomask in the air for 60 min and then developed with 1% tetramethylammonium hydroxide (TMAH) aqueous solution. As shown in Fig. 4, we obtained a clear positive-tone pattern with a resolution of 0.75 µm, which is the resolution limit of the photomask employed in the present work. Among the photopatterns of the LB films (20, 40, 60, and 80 layers), the LB film with 60 layers gave the finest resolution under the present condition. Therefore, the subsequent experiments for the sensitivity were carried out with the 60 layers of p(iPMA-*t*BVPC39) LB films.

To estimate the sensitivity of lithographic property for the LB film, the residual thickness of the LB films in the exposed portion was measured as a function of the exposure time (Fig. 5). The normalized film thickness decreases with exposure time, that is, the copolymer in the LB film is effectively decomposed by deep UV irradiation and removed completely

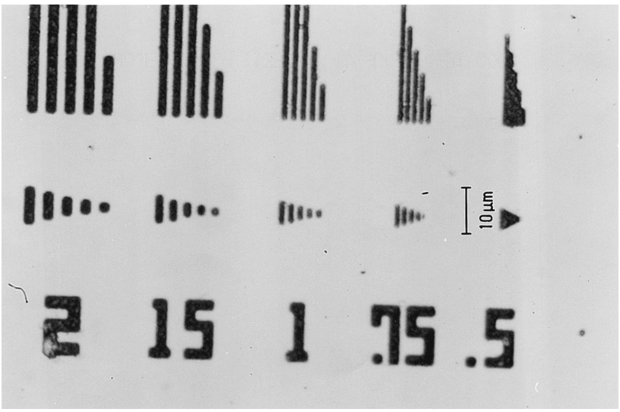

Fig. 4. An optical micrograph of p(iPMA-*t*BVPC39) LB film with 60 layers irradiated with deep UV light for 60 min in the air followed by the development with 1% TMAH aqueous solution for 20 s.

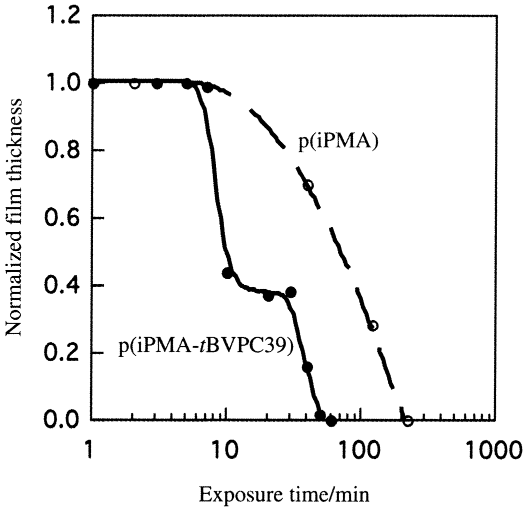

Fig. 5. The sensitivity curves of p(iPMA-*t*BVPC39) LB film and p(iPMA) LB film on silicon wafer.

with development of alkaline solution. It should be noted that the p(iPMA-*t*BVPC39) LB films are more sensitive than the homopolymer [p(iPMA)] LB film (Fig. 5).[11] Moreover, there are apparently two steps in the decrease in the thickness of the p(iPMA-*t*BVPC39) LB film, while the monotonic decrease in the thickness was observed in the sensitivity curve of all poly(alkylmethacrylamide) LB films which undergo main chain scission.[11] Since the light intensity at 193 nm ($\lambda_{\max}$ of the copolymers) from the deep UV lamp was very weak and was not able to be estimated exactly, the quantitative analysis of the sensitivity of the LB films could not be determined. From the shape of the sensitivity curve of p(iPMA-*t*BVPC39) LB films, however, it is noticeable that there are two steps in the process of photodecomposion; the deprotection of *t*-butoxycarbonyloxy group is predominant in the initial region and consequently the main chain scission due to the iPMA fragmentation occurs. The detailed analysis, e.g., the effect of the mole content of *t*BVPC group on the lithographic properties, is now in progress.

Photodecomposition of Copolymer LB Films. The photopattern formation in the copolymer LB films was investigated for the photodecomposition mechanism. To obtain the significant change in the experimental data, p(iPMA-*t*BVPC39) LB film with 80 layers were used for the UV and IR spectra, and p(iPMA-*t*BVPC39) cast film was utilized for GPC measurements. First, the absorption spectra change of p(iPMA-*t*BVPC39) LB film with 80 layers under deep UV irradiation was observed (Fig. 6). The absorption band at 193 nm is assigned to the amide group and the carbonyl group of *t*-butoxycarbonyloxy group. The decrease in the absorbance at 193 nm indicates that the main chain scission and/or deprotection of *t*-butoxycarbonyloxy group occurs by UV light irradiation, leading to the formation of volatile low molecular weight compounds such as carbon dioxide and isobutylene.[14]

In addition, the GPC measurement of the p(iPMA-*t*BVPC39) cast film was carried out to confirm the molecular weight change during the deep UV irradiation. As clearly shown in Fig. 7, the molecular weight decreased with irradiation time, and the curve became broader, indicating that the molecular distribution is larger than that of the initial state. These findings suggest that the main chain scission also takes place.

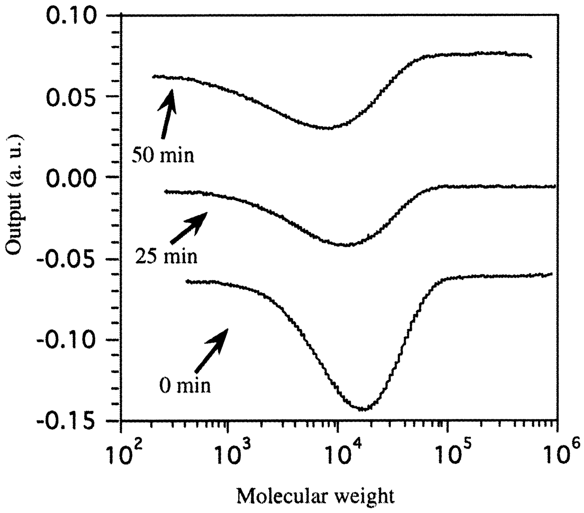

Fig. 7. GPC curves of p(iPMA-*t*BVPC39) cast film as a function of exposure time of deep UV light.

The absorbance at 3250 cm^{-1} in the IR spectra of the LB film, assigned to the stretching vibration of hydroxy group, was increased after irradiation (Fig. 8), which is evidence that the hydroxy group was produced immediately by the irradiation.[15] The band at 1750 cm^{-1}, which is assigned to the carbonyl group, is attenuated by the deep UV irradiation. This also means that the *t*-butoxycarbonyloxy group is removed from the side chain to give a phenol group[13] which can be dissolved in alkaline solution. Morever, the absorbance at 2910 cm^{-1} assigned to the alkyl group is drastically decreased after 30 min irradiation. This implies that the LB film is more dissolved in alkaline solution due to the change of the molecular weight. Although the difficulty still remains in distinguishing the dif-

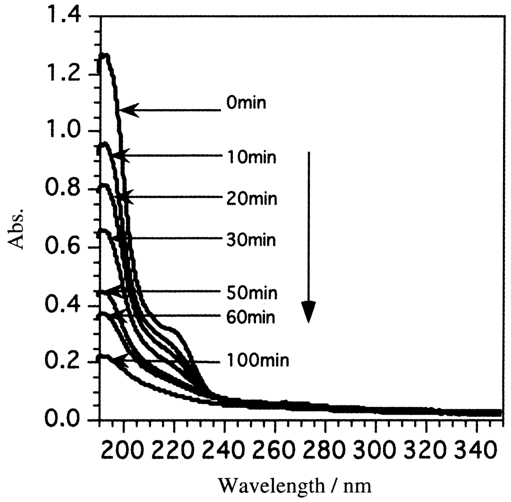

Fig. 6. The changes of UV absorption spectra of p(iPMA-*t*BVPC39) LB film with 80 layers by deep UV irradiation at ambient air.

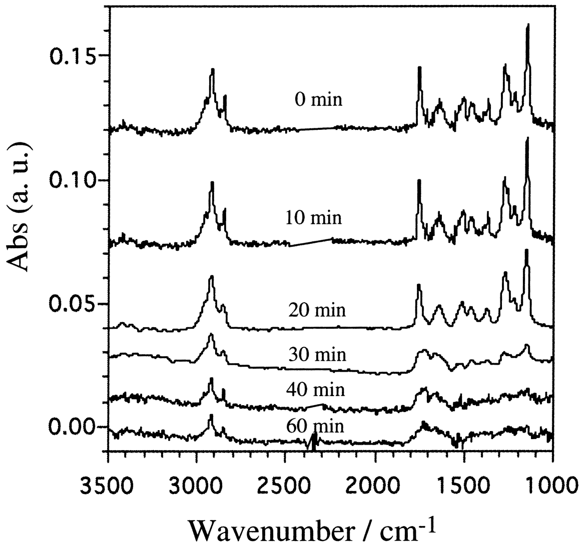

Fig. 8. The change in IR spectra of p(iPMA-*t*BVPC39) LB film with 80 layers by deep UV irradiation.

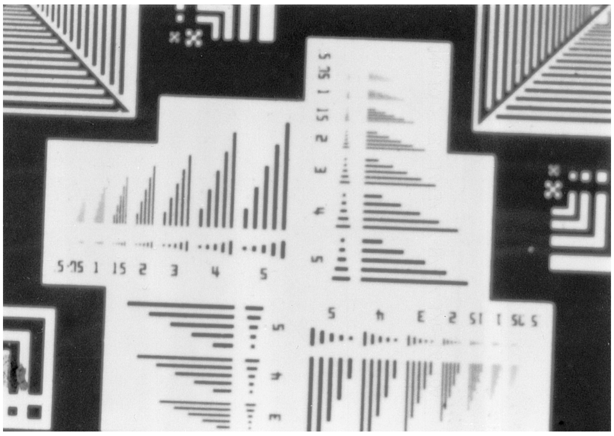

Fig. 9. Etched pattern of the gold film on the glass substrate.

ference between main chain and side chain scissions, these findings support the above discussion on the sensitivity curve for p(iPMA-*t*BVPC39) LB film.

Etching Resistance. The p(iPMA-*t*BVPC39) LB film with 20 layers was deposited on a gold substrate, and then irradiated through a photomask with deep UV light, followed by development with alkaline solution. The patterned substrate was immersed into a mixed solution of ammonium iodide, iodide, ethanol and water (etchant). Finally the LB film on the gold was removed with chloroform. Figure 9 shows the patterns of the gold film after the etching process, giving 1.5 µm resolution. This indicates that the copolymer p(iPMA-*t*BVPC39) LB film with at least 20 layers has a high etching resistance for the etchant. Further studies of lithographic properties and optimization of the copolymer p(iPMA-*t*BVPC39) LB film are now in progress.

Conclusion

The copolymer [p(iPMA-*t*BVPC39)] was prepared by free radical copolymerization. The copolymer has a structure which can be subjected to decomposition in main chain scission and side chain cleavage. The polymer forms a stable monolayer on the water subphase and the monolayer can be transferred onto a solid substrate. On irradiation with deep UV light on the LB film, the positive tone patterns could be printed after development with an alkaline aqueous solution. We also investigated the etching property of the underlying gold. The p(iPMA-*t*BVPC) LB films with 20 layers have a high etching resistance with a resolution of 1.5 µm. From the results we expect that the new copolymer [p(iPMA-*t*BVPC)] can be used in the lithographic process in future.

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