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Preparation of Poly(*N*-alkylmethacrylamide) Langmuir−Blodgett Films for the Application to a Novel Dry-Developed Positive Deep UV Resist

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ABSTRACT: The monolayer behaviors of poly(*N*-alkylmethacrylamides) with various pendant substituents, octyl (POMA), dodecyl (PDDMA), tetradecyl (PTDMA), hexadecyl (PHDMA), or octadecyl (PODMA), on the water surface and the properties of the Langmuir−Blodgett (LB) films were investigated. Among those polymers, PTDMA formed the most stable condensed monolayer. The PTDMA monolayer can be transferred successively onto solid supports such as quartz, glass, and silicon slide, giving Y-type uniform polymer LB films. It was found that PTDMA LB film could be effectively decomposed by deep UV irradiation and produced directly a positive fine pattern with high resolution without any development process. The sensitivity of the PTDMA LB film was remarkably enhanced with decreasing number of layers. This lithographic property of the LB film is expected to be applicable to a new type of positive photoresist for a deep UV excimer laser.

Introduction

Deep UV, X-ray, high- and low-energy electron beams have been proposed as possible exposure systems for the next generation high-resolution lithography.[1] In photolithography the resolution is limited by resist absorption and light diffraction related to the resist development processes. Moreover, the resist resolution limiting effects generally become more serious with increasing resist thickness. Therefore, to improve the resolution of resists, the use of ultrathin resists has been proposed.[2,3]

The Langmuir−Blodgett (LB) technique has been approved as an effective way to form a defect-free and molecularly ordered ultrathin film with controlled thickness and orientation.[4,5] Because the LB technique can overcome the weakness of spin-coat films in which molecules are distributed randomly, recently the polymer LB films have been investigated for the application to high-resolution lithographic resists with electron beams or X-ray beams to expose the resist layers deposited on substrates and then with a development process to remove the exposed portions (positive type) or the unexposed portions (negative type) selectively.[6−9]

Previously, we have succeeded in the preparation of fairly uniform polymer LB films using acrylamide polymers having long alkyl chains.[10] Furthermore, we also succeeded in producing the fine patterns by the polymerization of alkylacrylamide monomer LB films[11,12] and the cross-linking reaction in polymer LB films[13] with UV irradiation and electron beams.[14] All of these LB films resulted in negative photoresists.

In this paper, we describe a new type of positive photoresist by using poly(*N*-tetradecylmethacrylamide) (PTDMA) LB film without any development process (we call it dry development). A high resolution of 0.75 μm, which is the highest resolution of the photomask employed in this study, was clearly drawn. The PTDMA LB film has an absorption maximum at 194 nm and no absorption in a region of wavelength longer than 240 nm, of which property is desired for a deep UV resist for excimer lasers.

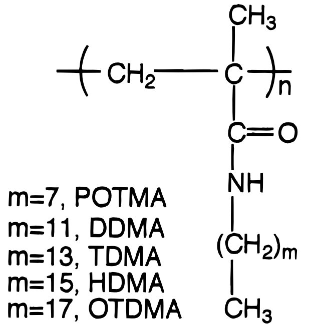

Figure 1. Molecular structure of poly(*N*-alkylmethacrylamides).

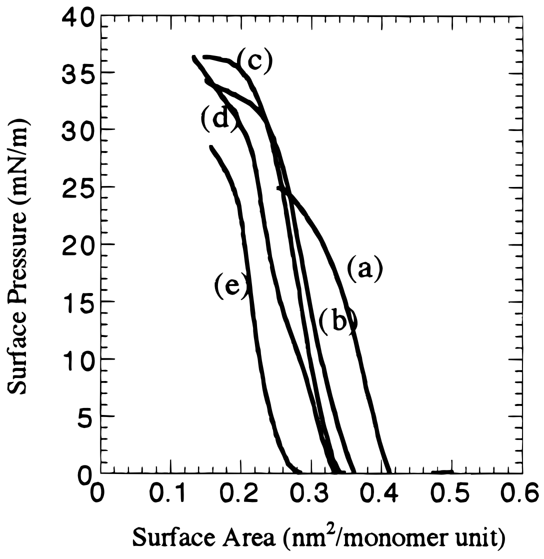

Figure 2. Surface pressure−area isotherms of poly(*N*-alkylmethacrylamides) [(a) POTMA, (b) PDDMA, (c) PTDMA, (d) PHDMA, and (e) POTDMA] on the water surface at 20 °C.

Experimental Section

Materials. All of *N*-alkylmethacrylamide monomers (alkyl substituents: *n*-octyl (OTMA), *n*-dodecyl (DDMA), *n*-tetradecyl (TDMA), *n*-hexadecyl (HDMA), and *n*-octadecyl (OTDMA))

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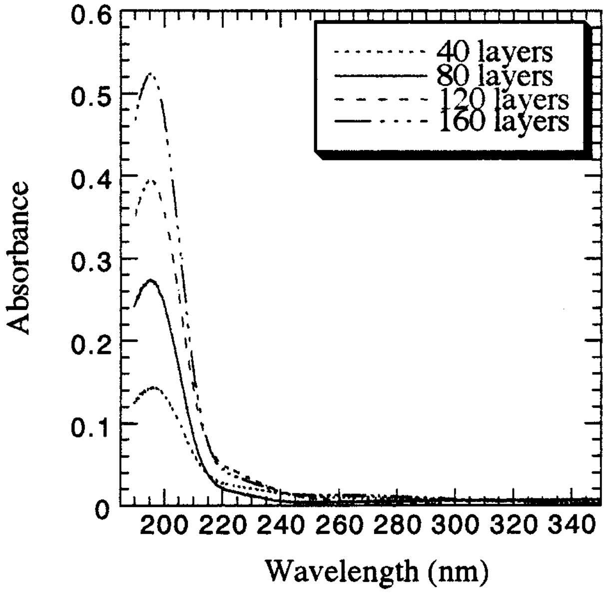

Figure 3. UV absorption spectra of PTDMA LB films.

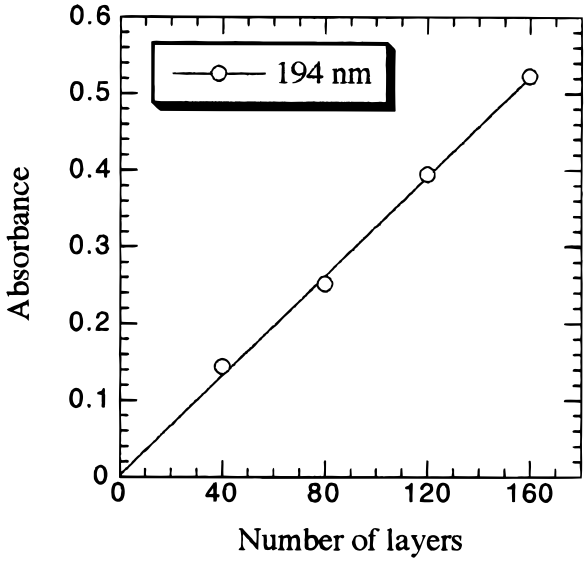

Figure 4. Linear relationship between the absorbance at 194 nm and the number of layers for PTDMA LB film.

were synthesized by the reaction of methylacryloyl chloride and the corresponding alkylamine in the presence of triethylamine in chloroform and purified by column chromatography and recrystallization. Poly(*N*-alkylmethacrylamides) with various alkyl substituents (Figure 1) were prepared in dried benzene at 60 °C by free-radical polymerization using AIBN as a thermal initiator. The homopolymers were purified by dissolution in chloroform, filtering, and precipitation into a large excess of acetonitrile and subsequently dried under vacuum at room temperature. The molecular weights and polydispersities for POTMA, PDDMA, PTDMA, PHDMA, and POTDMA are 3.17×10^3 ($M_w/M_n = 1.57$), 1.48×10^4 (1.90), 7.60×10^3 (1.82), 6.76×10^3 (1.69), and 9.66×10^3 (1.74), respectively.

Monolayer and Multilayer Formation. Measurement of surface pressure (π)−surface area (A) isotherms and deposition of monolayer were carried out with a computer-controlled Langmuir trough (FSD-110, USI) at a compression speed of 14 cm^2/min. Distilled, deionized water with a resistivity higher than 17 MΩ cm^{-1} was used as the subphase. Chloroform used for spreading monolayers on the water surface was of spectroscopic grade. Quartz and silicon substrates for the deposition of monolayers were cleaned in a boiling concentrated HNO_3 and made hydrophobic with *n*-octadecyltrichlorosilane.

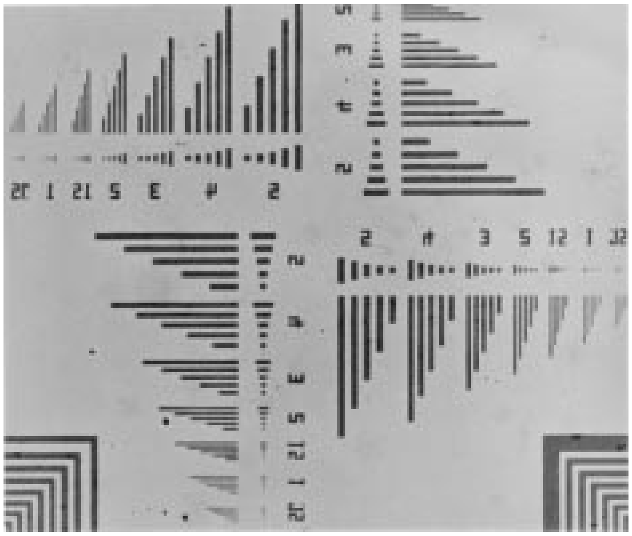

Figure 5. Optical micrograph of positive fine patterns with PTDMA LB film (30 layers) on a silicon wafer after UV irradiation without development.

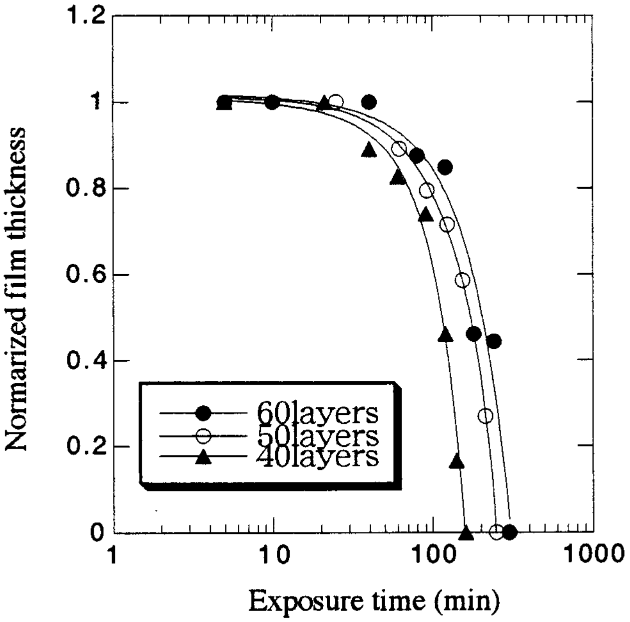

Figure 6. Plots of normalized film thickness of PTDMA LB films with different layers remaining after UV irradiation vs exposure time.

Measurement. Molecular weights were determined by a Toyo Soda gel permeation chromatography (GPC) using a polystyrene standard. UV absorption measurements were carried out with a Hitachi U-3000 UV−vis spectrophotometer. The thickness of LB films was determined by a Sloan Dektak 3ST surface profile. Deep UV irradiation was carried out with a high-pressure Hg lamp (UXM-501MD) using a water filter.

Results and Discussion

Monolayer Behavior on the Water Surface and LB Film Formation. The π−A isotherms for the monolayers of poly(*N*-alkylmethacrylamides) with various alkyl chain lengths at 20 °C show a steep rise in surface pressure and have a relatively high collapse pressure (Figure 2). Apparently, the isotherms are changed with alkyl chain lengths. The pressure curves stand up more sharply with increasing alkyl chain length from POTMA to PTDMA, and the collapse pressures also increase, while the POTDMA monolayer

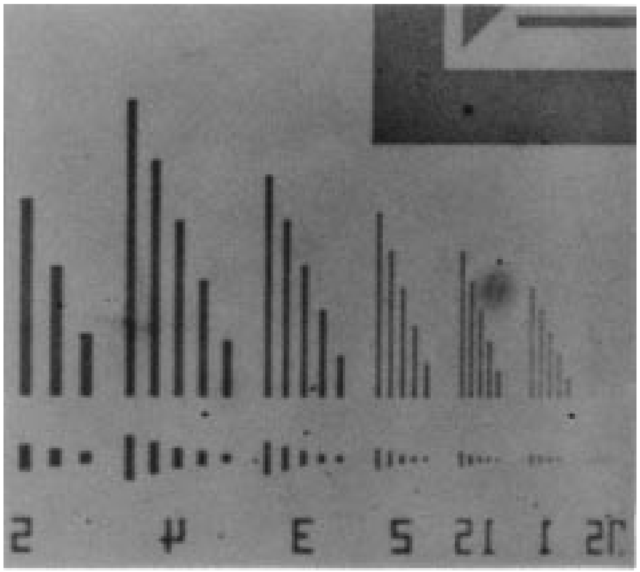

Figure 7. Optical micrograph of negative patterns with PDDA LB films (30 layers) on a silicon wafer after the development by toluene solvent.

became unstable and their collapse pressure decreased, which may be attributed to strong hydrophobicity of octadecylalkyl chains. As a result, PDDMA, PTDMA, and PHDMA form a condensed monolayer. In the previous work, we investigated the monolayer properties of poly(alkylacrylamide) series, where dodecylacrylamide polymer forms the most stable monolayer having a collapse pressure of ca. 50 mN/m. Compared with the series of polyacrylamide monolayers, the polymethacrylamide monolayers show lower surface pressure. This difference is due to the methyl group attached the polymer main chains.

The limiting surface area per monomer unit was determined by extrapolating the linear portion of steep rise in the $\pi-A$ isotherms to zero surface pressure. The surface area of PTDMA was estimated to be 0.32 nm^2, which is slightly larger than that of PDDA (0.28 nm^2), indicating that the methyl group at the polymer main chain disturbs a tightly molecular packing on the water surface. Among polymethacrylamide monolayers investigated, the PTDMA monolayer showed the steepest rise in the surface pressure and the highest collapse pressure in the $\pi-A$ isotherms, indicating that PTDMA forms the most stable condensed monolayer; therefore, the subsequent experiments were carried out mainly with the poly(*N*-tetradecylmethacrylamide).

The condensed monolayer of PTDMA on the water surface was transferred onto hydrophobic solid supports such as glass, quartz, and silicon wafer as a Y-type LB film under a surface pressure of 20 mN/m with a transfer ratio of 0.96 in both downward and upward strokes. The UV absorption spectra of the LB film were measured as a function of the number of deposited layers (Figure 3). The maximum absorbance at 194 nm is proportional to the number of layers at least up to 160 layers (Figure 4). The linear relationship between the absorbance and the number of layers suggests that a regular deposition of the PTDMA monolayer takes place. The absorbance of one monolayer (D) was obtained to be 3.27×10^{-3} from the slope of the straight line in Figure 4. Moreover, the molar extinction coefficient (ϵ) of PTDMA was determined to be 6.38×10^3 (mol/L)$^{-1}$ cm^{-1} from the equation $D = 1.66 \times 10^{-7}\epsilon S$, where S is molecular density (molecules/nm^2).

Drawing Fine Patterns by UV Irradiation. Deep UV light from a high-pressure Hg lamp was irradiated in air on PTDMA LB films with 30 layers through a photomask where a test pattern is figured. After 70 min irradiation, the LB film of exposed portion completely decomposed, while the unexposed portion remained on the substrate. So the fine positive pattern was efficiently produced without any development (we call it dry development). The microscopic photograph of the fine patterns is shown in Figure 5, where a line width of 0.75 μm can be clearly drawn.

The LB film thickness of the exposed portion as a function of exposure time was measured to estimate the sensitivity as positive resist (Figure 6). Obviously, the normalized film thickness decreases with increasing exposure time, and the UV irradiation on the LB film caused effective decomposition of the polymer. The sensitivity was remarkably enhanced with decreasing number of layers. Since the light intensity at 194 nm ($\lambda_{\max}$ of PTDMA) from a high-pressure Hg lamp is very weak and cannot be estimated, the quantitative sensitivity could not be determined. From the shape of plots in Figure 6, however, the contrast of the LB films[15] can be determined to be 3.16, 3.51, and 4.24, respectively. It is of great interest that only irradiation on the LB films forms a fine pattern. On the other hand, deep UV irradiation on a spin-coat film of PTDMA (2000 rpm, a thickness of 1000 nm) was carried out; however, we cannot get any fine patterns under the same conditions.

Deep UV irradiation on a poly(*N*-dodecylacrylamide) (PDDA) LB film as an example of acrylamide polymer LB film was also carried out with the same method. No

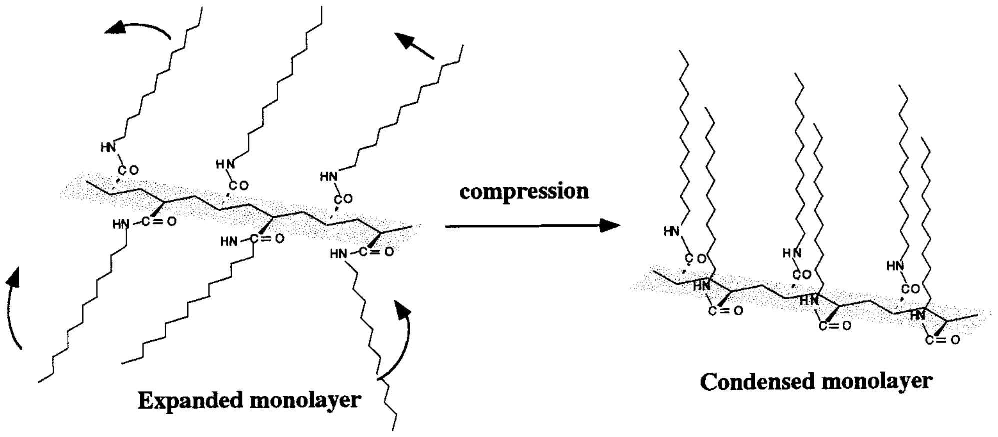

Figure 8. Schematic illustration of conformational change in the condensed monolayer.

positive pattern was obtained by only irradiation. After development by an organic solvent, we obtained a negative pattern instead of the positive pattern. Figure 7 shows a negative test pattern which was produced by irradiation on the PDDA LB film (30 layers) for 70 min followed by the development with toluene; the resolution was of 1.0 μm line and space. This result implies that the acrylamide polymer, which does not have a methyl group at the main chain, is not effectively decomposed by deep UV irradiation; oppositely, a cross-linking reaction between the PDDA main chains takes place.

The mechanism of the positive-type patterning by PTDMA LB film is not clear in the present work. However, on the basis of the observation that irradiation on acrylamide (not methacrylamide) polymer LB film produces no pattern, we can say that the decomposition of the main chains is a key reaction. The pendant side chains of the polymer stand up compactly with respect to the main chain in the monolayer on the water surface by compression to form the condensed monolayer (Figure 8).[10] The condensed monolayer is transferred onto solid supports giving an LB film where a stress energy is produced around the main chain. The polymer in the LB film is subject to bond scission, so the excellent fine pattern can be formed, compared with the patterning using a spin-coat method in which molecules distribute randomly or polyacrylamide LB film where a cross-linking reaction mainly occurrs. This lithographic property of the LB films having a high resolution is expected to be applicable to a new type of positive photoresists for deep UV excimer laser. Research on the mechanism of the decomposition reaction and further lithographic properties of PTDMA LB films is in progress.

In conclusion, poly(*N*-tetradecylmethacrylamides) (PTDMA) formed the most stable condensed monolayer on the water surface, and the monolayer can be transferred successively onto solid supports such as quartz, glass, and silicon slide, giving Y-type uniform polymer LB films. Deep UV irradiation (around 200 nm) with a high-pressure Hg lamp on the PTDMA LB film produced directly a positive fine pattern with high resolution. It is very interesting that a fine positive pattern due to the decomposition of the polymer LB film appeared clearly without any development process. The sensitivity of the PTDMA LB film was remarkably enhanced with decreasing number of layers. This lithographic property of the LB film is expected to be applicable to a new type of positive photoresist for a deep UV excimer laser.

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