A New Type of Dry-developed Positive Deep UV Resist Using Polymer Langmuir-Blodgett Films

Yinzhong Guo, Fei Feng, and Tokuji Miyashita*
Institute for Chemical Reaction Science, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577

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It is described that poly (*N*-tetradecylmethacrylamide) (PTDMA) LB films can produce directly a new type of positive fine pattern by decomposing effectively with Deep UV without any development (dry-developed resist).

As a means of organizing molecular assemblies, Langmuir-Blodgett (LB) films have been approved an effective way to deposit ultrathin films with the controlled thickness and orientation.[1,2] Recently polymer LB films have been investigated for the application to high resolution lithographic resist with the electron beam or X-ray beam to expose the resist layer deposited on substrates and then with development process to remove the exposed portions (positive type) or the unexposed portions (negative type) selectively.[3-6]

Previously, we have succeeded in the preparation of fairly uniform polymer LB films using acrylamide polymers having long alkyl chains.[7] Furthermore, we also succeeded in producing the fine patterns by the polymerization of alkylacrylamide monomer LB films[8,9] and the cross-linking reaction in polymer LB films[10] with UV irradiation. All of these LB films resulted in negative photoresists.

We will describe in this paper a new type of positive photoresist using poly (*N*-tetradecylmethacrylamide) (PTDMA) LB film (Figure 1) 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 absorption maximum of PTDMA LB film is 194 nm, of which property is desired for a Deep UV resist for 193 nm KrF excimer laser.

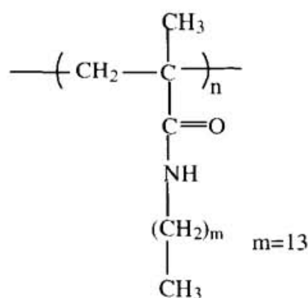

Figure 1. Chemical structure of poly(*N*-tetradecylmethacrylamide).

N-Tetradecylmethacrylamide (PTDMA) monomer was polymerized in dried benzene at 60 °C by using AIBN as an initiator. The homopolymer was purified by dissolution in chloroform, filtering, and precipitation into a large excess of acetonitrile and subsequently dried under vacuum at room temperature. The molecular weight (M_n) and polydispersity are 7.6 $\times 10^3$ and 1.82, respectively.

First, the monolayer behavior of PTDMA on the air-water surface and the formation of LB films were investigated. The polymer was spread from a chloroform solution onto the pure water (Milli-Q II, Millipore) surface in Langmuir trough (FSD-110. USI). The surface pressure(π)-area (A) isotherms at 20 °C (Figure 2) show a steep rise in surface pressure and a relatively high collapse pressure. In the previous study, polyacrylamides were found to form stable monolayers where hydrogen bonding based on the amide structure is working as an self-assembling factor.[11,12] A similar interpretation is also possible in the present case. The limiting surface area per monomer unit of the monolayer is determined to be 0.32 nm^2, which is slightly larger than that of polyalkylacrylamide,[11,12] because of the exist of methyl group at the polymer main chain. The monolayer on the water surface can be transferred onto a hydrophobic silicon wafer as Y-type LB films by the vertical dipping method under a surface pressure of 20 mN/m. The transfer ratios for the down- and upstroke are almost unity.

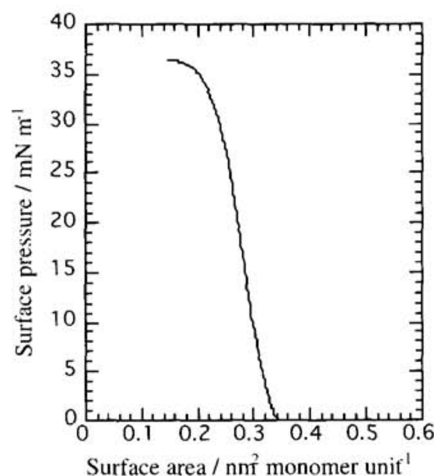

Figure 2. Surface pressure (π) - area (A) isotherm of poly(*N*-tetradecylmethacrylamide) at 20 °C.

Deep UV light from a high pressure Hg lamp (UXM-501MD) was irradiated on PTDMA LB films with 30 layers through a photomask in air to draw a fine pattern. After 70 min irradiation, the LB films of exposed portions were completely decomposed, while the unexposed portions remained on the substrate. So the fine pattern was efficiently produced without any development (we call it dry development). The microscopic photograph of the PTDMA LB films pattern is shown in Figure 3, where a line width of 0.75 μm can be clearly drawn. It is of great interest that only irradiation on LB films forms a fine pattern. The LB film thickness as a function of exposure time was measured to obtain the

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sensitivity as positive resist (Figure 4). Obviously, the normalized film thickness decreases with increasing exposure time, and the UV irradiation caused effective decomposition of the LB films. Since the light intensity at 194 nm (λmax) from the Hg lamp is very weak, the quantitative sensitivity could not be determined. From the shape of plots in Figure 4, however, the contrast[13] of the LB films can be determined to be 3.16.

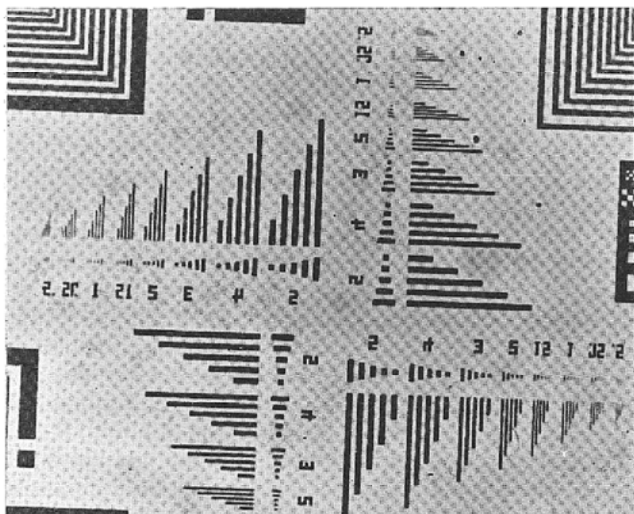

Figure 3. Optical micrograph of a PTDMA LB film positive fine pattern with 30 layers on silicon wafer.

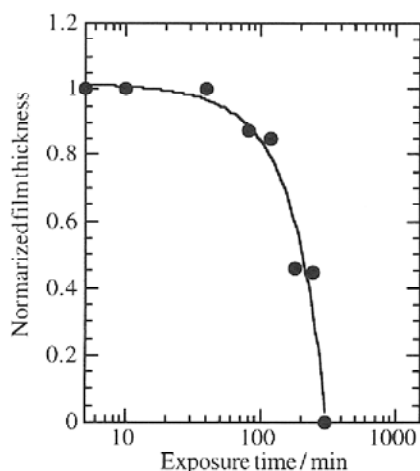

Figure 4. Normarized thickness of irradiated PTDMA LB film (60 layers) as a function of exposure time.

The mechanism of the positive-type patterning is not clear in the present work; however, we can say that the decomposition of the main chains is a key reaction. Irradiation on polyalkylacrylamide (not methacrylamide) LB films produces no pattern and after development by organic solvent, negative patterns appeared. The side chains of the polymer stand up with respect to the main chain by compression to form the condensed monolayer, where a stress energy is produced around the main chain. The polymer monolayer is subject to bond scission, so the excellent fine pattren can be formed, compared with the patterning using a spincoat method in which molecules distribute randomly. 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.

In conclusion, poly (*N*-tetradecylmethacrylamide) (PTDMA) formed a stable condensed monolayer on the water surface and can be transferred onto a solid support with the transfer ratios of unity giving Y-type LB films. This LB films can produce directly a new type of fine pattern by decomposing effectively with Deep UV without any development. The mechanism of the decomposition reaction and the further lithographic properties of PTDMA LB films are in progress.

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