Drawing Fine Patterns with Cross-Linkable Polymer Langmuir-Blodgett Film

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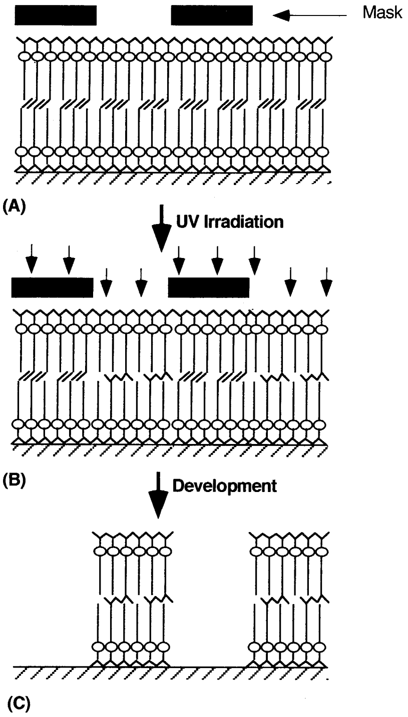
(Received April 22, 1996)

Langmuir-Blodgett (LB) films of copolymer (**1**) consisting of *N*-dodecylacrylamide (DDA), and cross-linkable group, *N*-ω-acryloylundecyl-4-vinylpyridinium salt has been prepared. On UV irradiation, the cross-linking reaction occurs efficiently giving uniform two dimensional cross-linked polymer LB films with a high stability against solvents. The photolithographic property of the LB film are applicable to a new type of high resolution negative photoresists.

Recently, polymerizable monomer LB films[1-5] and self-assembly monolayers[6,7] have been greatly investigated for the application to high resolution lithographic resists. Since such resists have molecularly ordered structures and ultrathin films, the theoretical resolution of lithographically defined features can be as small as a few nanometers. However, high degree of polymerization has to occur at the monomer ultrathin films in order to render the LB films insoluble with UV irradiation.

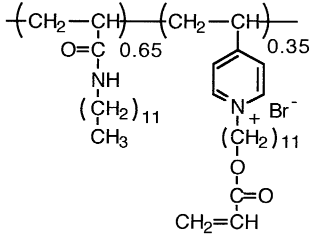
Polymer LB films have been received much attention from viewpoints of thermal and mechanical stability compared with conventional LB films such as long-alkyl chain fatty acids. We have, previously, reported that the preformed DDA polymer has an excellent spreading behavior and forms stable polymer LB films.[8] Furthermore, we have also succeeded in introduction of various functional groups such as aromatic chromophores[9] and chiral groups[10] into the polymer LB films as a comonomer of DDA. Introduction of cross-linkable groups into polymer LB films is expected to provide higher thermally and mechanically stable two-dimensional polymer films,[11,12] and ultra fine negative resists.[13] In the case of the cross-linkable preformed polymer LB film, a few percentage polymerization by UV irradiation can make the film insoluble. This advantage results in high sensitivity of the photoresist. In this report, we describe synthesis of a cross-linkable amphiphilic copolymer **1** and the photolithographic property of the LB films with UV irradiation.

The schematic illustration of cross-linking reaction of polymer LB films with UV irradiation is shown in Scheme 1. We begin by placing the photomask in contact with a LB film of copolymer **1** on a silicon wafer (Scheme 1, A). The entire assembly is then exposed to UV light, which induces cross-linking reaction in the unmasked regions of the LB film (Scheme 1, B). Next unreacted portions of the resist is selectively dissolved in organic solvents (Scheme 1, C). Selective developing is possible because the cross-linked polymer LB film is sufficiently insoluble. Thus two-dimensionally patterned polymer films can be formed in the LB films.



Scheme 1.

The copolymer **1** was prepared as follows; the copolymer of DDA with vinylpyridine was prepared by free radical polymerization in benzene at 60 °C with 2, 2'-azobis(isobutyronitrile). The fraction of vinylpyridine in the resulting copolymer was quaternized with 11-bromo-1-undecanol in 2-propanol under reflux. Finally, copolymer **1** was obtained by the reaction of acryloyl chloride with hydroxyl group in the quaternized copolymer in the presence of triethylamine in chloroform at room temperature. The copolymer **1** was washed with water to remove unreacted acryloyl chloride and triethylamine and then purified by precipitation. The mole fraction of acryloyl group in the copolymer **1** was determined to be about 0.35 by ^{1}H NMR spectrum and elemental analysis data. A chlorofom solution of copolymer **1** was spread on the surface of water in Langmuir trough (FSD-110, USI) to measure surface pressure (π) - area (A) isotherm of the monolayer. The π-A isotherm showed the formation of a stable condensed monolayer with a high collapse pressure (50 mN m^{-1}) as same as that of DDA homopolymer.[8] The monolayer was transferred onto a silicon wafer as a Y-type film with a transfer ratio of unity.



$$\left(\mathrm{CH_2{-}CH}\right)_{0.65}\left(\mathrm{CH_2{-}CH}\right)_{0.35};\ \mathrm{CH}:\ \mathrm{O{=}C{-}NH{-}(CH_2)_{11}{-}CH_3};\ \mathrm{CH}:\ \mathrm{C_5H_4N^{+}Br^{-}{-}(CH_2)_{11}{-}O{-}C({=}O){-}CH{=}CH_2}$$

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UV irradiation with Xenon-filled lamps was carried out on a LB film of copolymer **1** with 39 layers thickness through a photomask under N_2 atmosphere. After 0.5 h irradiation, the LB film was immersed in chloroform solvent for a few minutes to develop the pattern of the LB film. The microscopic photograph

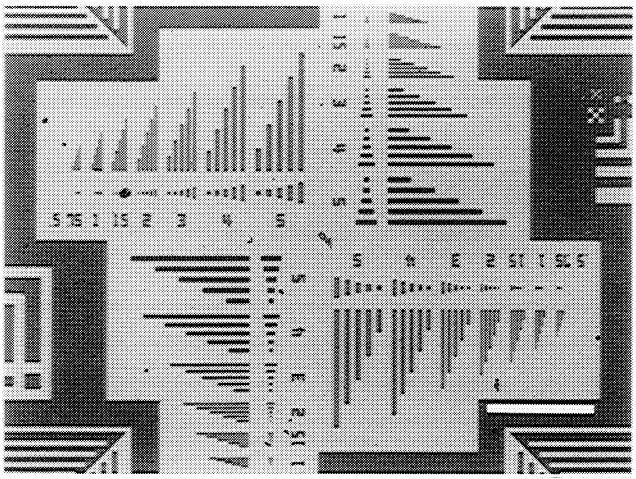

Figure 1. Optical micrograph of a negative test pattern of LB film of polymer **1** with 39 layers on silicon wafer. Film parts appear dark. Scaling bar indicates 100 µm.

for the pattern of cross-linked LB film is shown in Figure 1. Lines of 0.75 µm width were clearly visible. Evidently, the LB film of copolymer **1** has a high resolution for lithographic resists. The microscopic photograph showed that the surface of cross-linked LB films is uniform with no crack. It means that any contraction of the LB film with UV irradiation does not occur. There was a large difference in solubility between no cross-linked and the cross-linked LB film. After exposure to UV light, the LB films were not dissolved in chloroform and remain on the Si wafer, whereas the cast films were dissolved in chloroform. Apparently, it indicates that highly ordered structure, that is acryloyl groups are ordered and become neighboring in the LB film as shown in Scheme 1, is essential to form cross-linkage between acryloyl groups. An efficient cross-linking reaction with UV irradiation is attributable to high orientation of the LB film.

Figure 2 shows UV absorption spectra for LB multilayers of copolymer **1** with various exposing times with Xenon lamp. The absorbance around 250 nm due to the π-π* transition decreased with irradiation time. Although the absorbance did not completely disappear at 90 min of UV irradiation, the exposed polymer LB film had been already insoluble in chloroform. It suggests that a few percentage proceedings of cross-linking reaction is enough to render the polymer LB film insoluble.

In conclusion, cross-linkable amphiphilic copolymer forms a stable monolayer on the water surface and is transferred onto a solid support with a transfer ratio of unity giving a Y-type LB film. The LB film of copolymer **1** becomes insoluble with UV irradiation because of cross-linking of acryloyl group. UV irradiated LB films form an ordered two-dimensional polymer. Further investigation for lithographic properties of LB film of copolymer **1** is in progress.

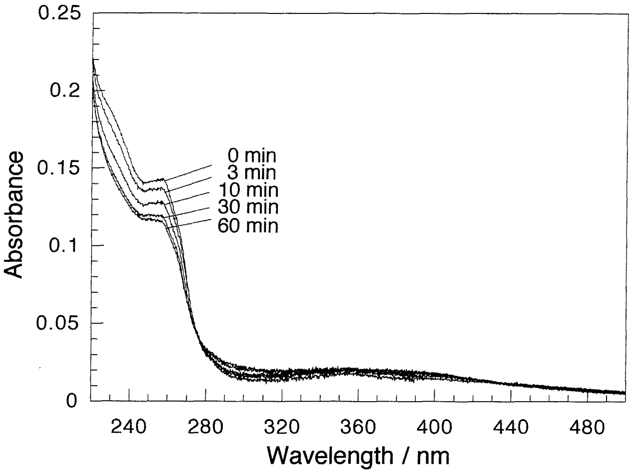

Figure 2. UV adsorption spectra of LB films of copolymer **1** with 99 layers on quartz slide with various irradiation time of Xenon light.

This work was partially supported by a Grant-in-Aid for Scientific Research on Priority-Area-Research "Molecular Superstructures - Design and Creation -" from the Ministry of Education, Science and Culture, Japan (No.07241204).

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