

Fine Pattern Drawing in Polymer Hybrid Thin Film Assemblies

Tokuji Miyashita / Institute of Multidisciplinary Research for Advanced Materials, Tohoku University/
2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

1. Introduction

Recently, bottom-up approaches for constructing ordered nanoscale structures in organic molecular assemblies have been of interest and various techniques for preparation of organic ultrathin films have been studied. Organic thin films are attractive materials for their processability, ease of functionalization, their light weight, flexibility, and so on. However their processing technologies in nanoscale are immature and the development is expected. Various organic films, for example, a spin-coating film, self-assembled monolayers (SAM), grafting polymers, and layer-by-layer alternative adsorption via electrostatic interactions, have been investigated. We have tried to prepare various polymer thin films with Langmuir-Blodgett technique. It is found that *N*-alkylacrylamide polymer forms a two-dimensional net-work on the water surface and gives a condensed polymer monolayer (Figure 1). We are able to build-up the monolayer on a solid support and then obtain a polymer nano-sheet assemblies with nm-scale thickness and ordered structure. Free-standing film of polymer nano-sheet assemblies can be also fabricated^{1), 2)}.

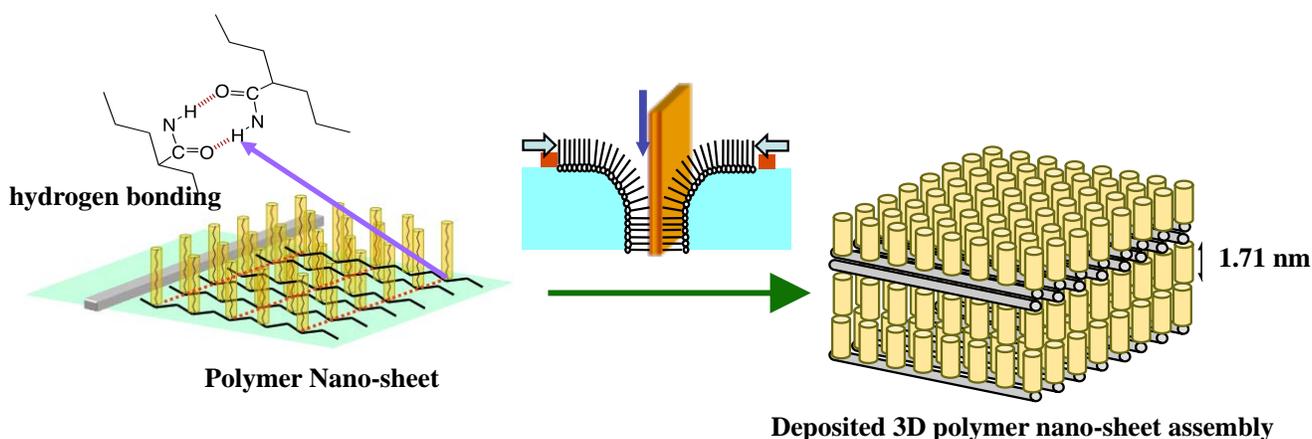


Figure 1 Fabrication of polymer nano-sheet assemblies with Langmuir-Blodgett method

On the other hand, fine pattern drawing using polymer hybrid thin films has been received much attention not in lithography for semiconductor fabrication, also printable and flexible soft electronics such as organic TFT, organic LED, molecular imaging sensor etc. In this talk, fine pattern drawing and material modification using radiation technique on polymer thin film assemblies, hybrid polymer of silsesquioxanes are introduced.

2. A New type of Thin Film Lithography based on Polymer Nano-sheet Assemblies

Recently, a lithographic technique using scanning probe microscopy (SPM) has been reported, where

novel lithographic materials giving subnanosize surface flatness. 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. Because of this superior feature, polymer LB films have been investigated for the application to high-resolution lithographic technology with deep UV, electron beam, and X-ray beam in order to construct the state-of-art nano-structure on solid substrates with development process to remove the exposed portion (positive type) or the unexposed portion (negative type) (Figure 2)³⁾⁻⁷⁾. First, we would like to show the outline of the fine patterning using these polymer thin films.

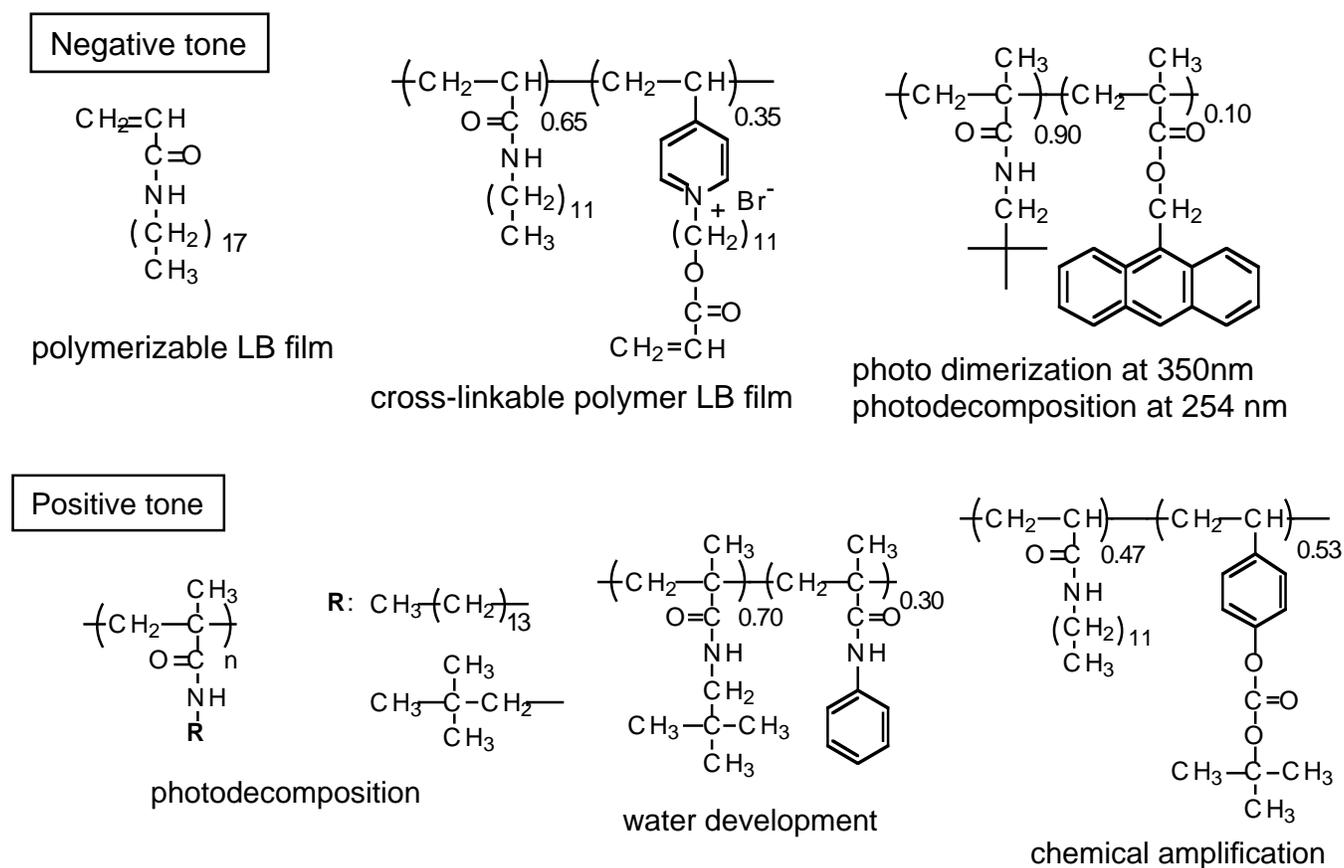


Figure 2 Nano-sheet films (LB films) for negative and positive lithography

3. SiO₂ Ultrathin Film Formation Using Silsesquioxane Copolymer Nano-sheet Assembly

A high-quality silicon dioxide (SiO₂) thin film has been important material in the field of electronics and optoelectronics. Thermally oxidized SiO₂ films are now commercially available and are generally grown or annealed at high temperatures (about 1,000 °C) to yield high quality. A low-temperature preparation process of SiO₂ film is urgently desired for flexible electronics devices. Herein, we discuss a novel way of SiO₂ film fabrication at room temperature using polymer nano-sheet (LB film) assemblies containing polyoctahedral silsesquioxane (POSS)⁸⁾.

The precursor hybrid material, poly(*N*-dodecylacrylamide-*co*-3-methacryloxypropyl-T8-heptaphenyl POSS), p(DDA/SQ) was synthesized by free radical polymerization (Figure 3). The copolymers are spread onto water surface from a chloroform solution

to measure monolayer behaviors. The surface pressure – area (π - A) isotherms of p(DDA/SQ)s show a steep rise in surface pressure and high collapsed pressure indicating stable monolayer formation. The p(DDA/SQ) monolayers can be transferred onto solid substrates as Y-type LB film with a transfer ratio of almost unity. The layer structure of p(DDA/SQ)s was confirmed using XRD measurements. The Bragg peak corresponds to bilayer periodicity for p(DDA/SQ) LB film, indicating 1.67 nm monolayer thickness. Uniform LB film deposition was confirmed using UV absorption spectra; that is, the absorbance increased linearly with the number of deposited layers.

In conclusion, hybrid inorganic-organic materials containing silsesquioxane (POSS) were manipulated using Langmuir-Blodgett techniques. The POSS units were distributed uniformly in the polymer LB films. The surface densities of POSS units were calculated as 0.54 nm^{-2} for the p(DDA/SQ) monolayer, indicating that the POSS units were separated using an averaged center-to-center distance of 1.5 nm. The films show a well-defined layer structure (ca. 3.4 nm bilayer periodicity) and surface smoothness (0.4 nm at $1 \mu\text{m}^2$) as well as high LB film deposition capability (ca.400 layers).

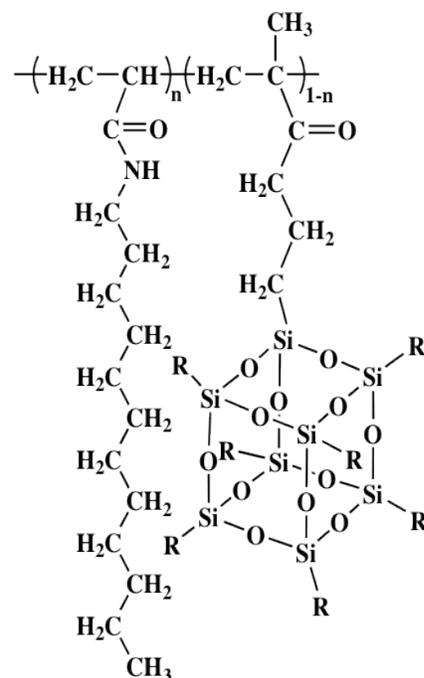


Figure 3 Chemical structure of p(DDA/SQ)

3.1 Photoirradiation on the hybrid nanosheet films (SiO_2 thin film formation)

The p(DDA/SQ) nano-sheet was deposited onto a substrate by vertical dipping method with a surface pressure at 30 mN/m by LB technique. The p(DDA/SQ) nano-sheets were irradiated so as to prepare SiO_2 film. The AFM image indicates that the photoirradiated film is quite flat (RMS 0.6 nm in $10 \times 10 \mu\text{m}^2$). The resulting film thickness by photoirradiation was one-fifth smaller than that of the pristine films, irrespective of the number of the hybrid nano-sheet. This predictable decrease in thickness can be explained by selective removal of organic moieties from photoirradiated nano-sheet. The density of the photooxidized SiO_2 film was also determined to be 2.24 g/cm^3 . The value is quite comparable to that of thermally oxidized SiO_2 film. Furthermore, the mechanical properties of hybrid nano-sheets before and after photoirradiation were investigated by nanoindentation. The hardness and modulus of the films were changed considerably from 0.1 and 2.6 GPa to 1.7 and 32.2 GPa , respectively. These dramatic changes in the density and mechanical properties are caused by the change in chemical structure by photochemical reaction as well as the dissociation of organic moieties in hybrid nano-sheet. Namely, it implies that Si-O-Si network structure based on SiO_2 can be created by photooxidation.

FT-IR spectra of p(DDA/SQ) nano-sheet with photoirradiation at room temperature show that the bands at 2853 and 2923 cm^{-1} ascribed to symmetric and asymmetric vibrations of the C-H groups decreased and then disappeared with photoirradiation. The sharp absorption peak at 1130 cm^{-1} based on Si-O-Si cage structure also decreased with photoirradiation. Corresponding to the decrease of 1130 cm^{-1} absorption peak, the increase in absorbance at 1065 cm^{-1} was observed. The peak position is exactly the same as that of a Si-O-Si network structure of conventional SiO_2 film. This change in the peak is ascribed to transform the cage structure into the network structure by photoirradiation. The experimental results provide a plausible mechanism for photochemical reaction induced by deep UV irradiation. The energy of deep UV lamp is great enough to any of the bond energies in p(DDA/SQ) and that results in photo-cleavage in the hybrid nano-sheet. After cleavage of the bond, an extremely reactive Si, O₂ and O

species will immediately react to each other to form silicon dioxide and a small amount of silanol.

The pattern drawing based on photooxidized SiO₂ film was also examined. Figure 4 shows the AFM images of photopatterned SiO₂ films. The SiO₂ film emerges in negative tone mode. The line width is exactly the same as that of the photomask. The direct writing of SiO₂ patterns with high resolution will offer a wide range of possibilities for practical applications.

In summary, we have demonstrated the fabrication of photo-induced high-quality SiO₂ film from p(DDA/SQ) hybrid nano-sheet. The present method is available at room temperature and quite simple; the photooxidation process requires no initiator and annealing process involving post baking. We were able to obtain an ultrathin SiO₂ film with 1.6 nm thickness so far, and that was confirmed to be high quality from the results above. The film thickness is predictable and easy to reproduce; it strongly depends on the amount of SQ in hybrid nano-sheet. Thus the SiO₂ thickness can be easily determined by controlling the precursor hybrid nano-sheet deposited. This approach will be a practical way to develop flexible optical and electrical devices.

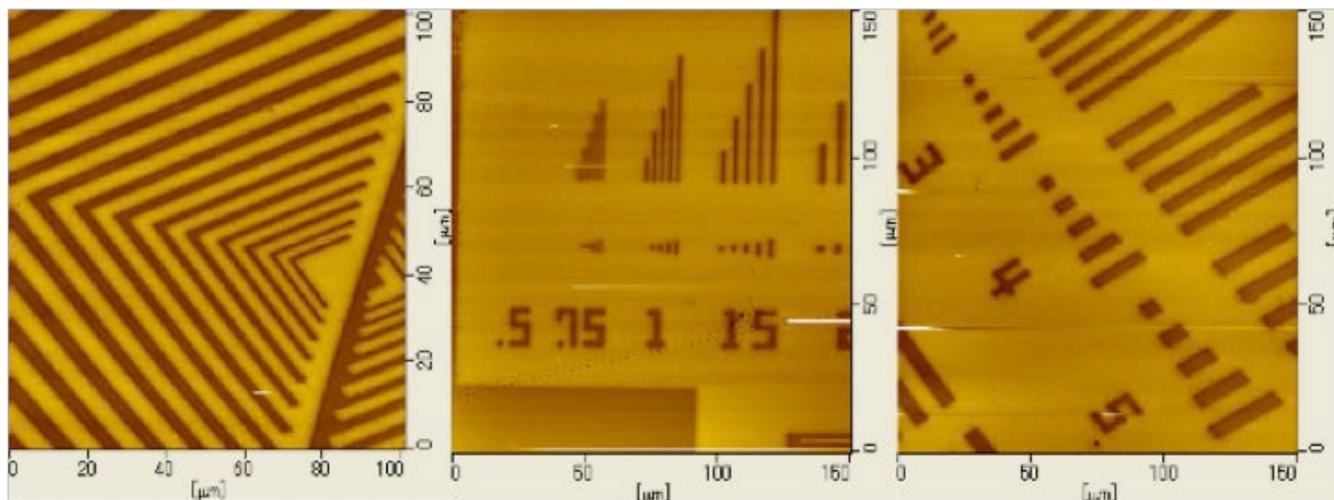
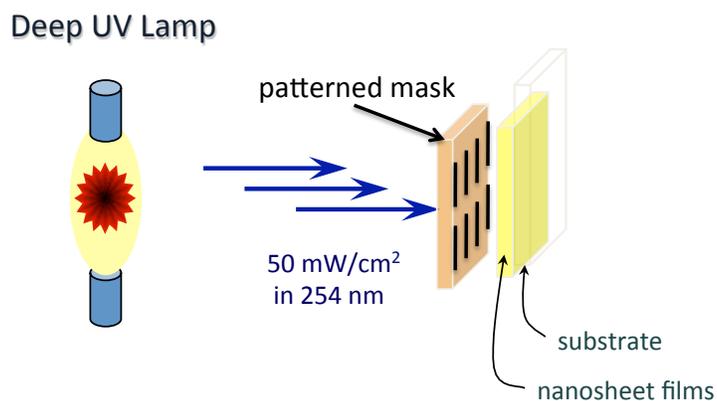


Figure 4 AFM image of SiO₂ pattern prepared by photooxidation polymer nano-sheet film

References

- 1) M. Mitsuishi, J. Matsui, T. Miyashita, *Polymer Journal*, **38**, 877-896 (2006).
- 2) M. Mitsuishi, J. Matsui, T. Miyashita, *Journal of Materials Chemistry*, **19**, 325—329 (2009).
- 3) Aoki T. Miyashita, *Advanced Materials*, **9**, 361-364 (1997).
- 4) Y. Guo, F. Feng, T. Miyashita, *Chemistry Letters*, **27**, 1269-1270 (1998).
- 5) Y. Guo, F. Feng, T. Miyashita, *Bulletin of the Chemical Society of Japan*, **72**, 2149-2153 (1999).
- 6) T. Li, M. Mitsuishi, T. Miyashita, *Bulletin of the Chemical Society of Japan*, **74**, 1757-1760 (2001).
- 7) Y. Kado, M. Mitsuishi, T. Miyashita, *Advanced Materials*, **17**, 1857-1861 (2005).
- 8) Y. Kim, Feng Zhao, M. Mitsuishi, A. Watanabe, T. Miyashita, *Journal of the American Chemical Society*, **130**, 11848-11849 (2008).