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In situ Observation of Deep UV Patterning in Polymer LB Films by Surface Plasmon Spectroscopy

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The paper describes in situ observation of the photopattern formation in polymer Langmuir-Blodgett (LB) film by surface plasmon spectroscopy. The copolymers (p(DDA/tBVPC)) of *N*-dodecylacrylamide (DDA) which is known to form a stable monolayer with a photo-degradable monomer, *tert*-butyl-4-vinylphenyl carbonate (*t*BVPC), form a stable monolayer and LB film. When the copolymer LB films were irradiated by deep UV light in air, the photodecomposition took place, consequently the thickness in the LB film was gradually decreased. On the other hand, there were no significant changes in the thickness with the irradiation at the argon atmosphere. It was found that the molecular oxygen plays a decisive role in yielding the positive-tone pattern in the p(DDA/*t*BVPC) LB films.

Keywords polymer; LB film; pattern; surface plasmon

1. INTRODUCTION

Recently light optical techniques based on surface plasmon resonance have been intensively exploited in wide variety of scientific fields. In particular, specific adsorption processes, for instance, between streptavidin and biotin, and between alkylthiol derivative and gold substrates have been paid much attention [1]. However, the technique has been rarely utilized for the investigation of desorption processes observed in photolithography [2].

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A series of polymer Langmuir-Blodgett (LB) films based on *N*-alkylacrylamide form highly oriented and condensed monolayer assemblies [3]. We have found that positive-tone patterns could be yielded with deep UV irradiation toward polymer LB films which consist of *N*-dodecylacrylamide (DDA) and a photodecomposable group, *tert*-butyl-4-vinylphenyl carbonate (*t*BVPC) as a comonomer [4]. In the current article, the formation of the positive-tone pattern is investigated in the polymer LB film by surface plasmon spectroscopy. The transient thickness during the irradiation could be precisely determined by analyzing the *in situ* data as a function of irradiation time.

2. EXPERIMENTAL

The synthesis of p(DDA/*t*BVPC) (Figure 1) has been published elsewhere [4]. The copolymer in which the content of *t*BVPC group was 53 % was utilized.

A silver layer was thermally evaporated on glass substrates in vacuum, and then the p(DDA/tBVPC53) LB films with 40 layers were deposited on the substrate. They were coupled with a BK-7 prism through index matching oil.

Angle-dependent reflectvities, i.e., surface plasmon curves were obtained by monitoring the reflected light intensity from the coupler as a function of incident angle. To observe the photopattern formation, a deep UV lamp (USHIO) was utilized. The sample was irradiated by the light of 20 mW/cm^2 in air at room temperature. It took *ca.* 1 min to obtain the angle-dependent reflectivities with a range of 20°.

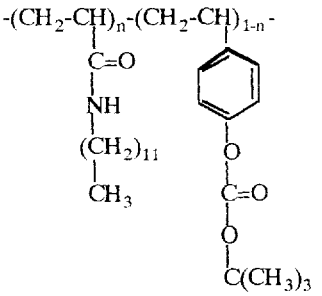

FIGURE 1 Chemical structure of p(DDA/*t*BVPC)

3. RESULTS AND DISCUSSION

From the surface plasmon curves of p(DDA/*t*BVPC53) LB films as a function of deposited layers, we could determine the refractive index and the thickness of p(DDA/*t*BVPC53) LB films; 1.508 and 1.3 – 1.4 nm per monolayer.

Figure 2 shows the time course of the angle-dependent reflectivities during deep UV irradiation. As the time proceeds, the resonance peak shifts toward smaller angles. Althogh it takes about 12 h to complete the photodecomposition, the LB film could be photodecomposed by deep UV irradiation under air condition.

From the comparison of the experimental data with the theoretical curve, the transient thickness of the LB film could be precisely determined as shown in Figure 3, where we assumed constant refractive index. As shown in Figure 3, the thickness gradually decreases at the beginning, then the rates increases over 60 min. On the other hand, the irradiation on the sample under the argon atmo-

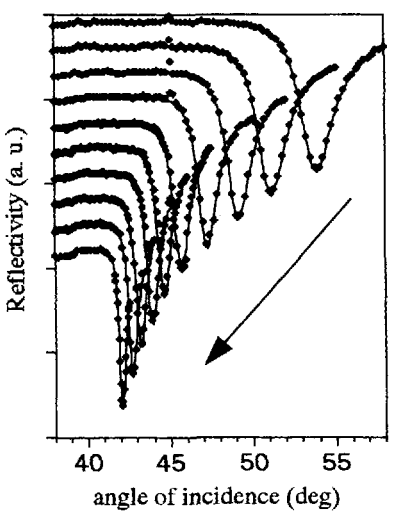

FIGURE 2 Surface plasmon curves of p(DDA/tBVPC53) with 40 layers as a function of irradiation time: (from right) 0, 65, 95, 135, 195, 255, 315, 405, and 765 min.

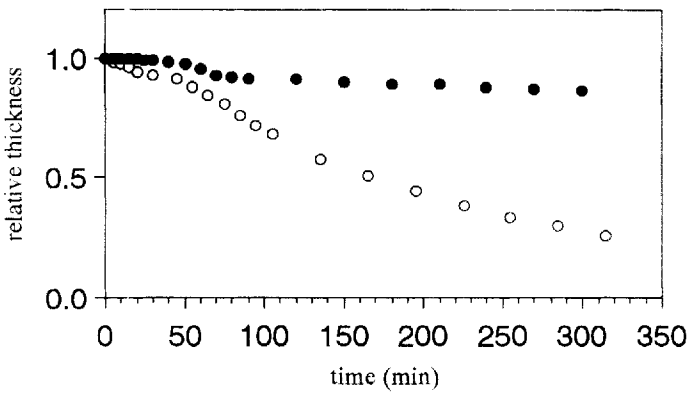

FIGURE 3 Time course of the thickness during deep UV irradiation: (open circle) in air and (closed circle) in argon atmosphere.

sphere results in no significant change in the thickness. This is different from the result published by Rühe and coworkers [2]. In this case, the existence of the molecular oxygen is prominent for the positive pattern formation.

In conclution, we demonstrate that the *in situ* observation yielded by surface plasmon measurement provides us with detailed understanding of photopatterning in polymer LB films. The optimization of the mechanism and the experiments are now in progress.

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