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# A New Replica Method for Electron Microscopic Observation of Langmuir-Blodgett Film with Plasma Polymerized Film by Glow Discharge

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A new replica method for transmission electron microscopy with plasma polymerized film by glow discharge was originally developed. The method was found to be applicable for the surface observation of Langmuir-Blodgett film.

The structure of Langmuir-Blodgett (LB) films has been the subject of continuous studies since the discovery made by Blodgett.[1] Only a few years after the discovery of built-up films (LB films), evidence was obtained indicating that LB films do not necessarily form a "two-dimensional single-crystal" as was often assumed.[2,3] The remarkable development of electron microscopy technique seems to allow us to study microstructure of LB film system, without any artifact such as staining, for example, up to a resolution of 100 nm.[4] One of the authors (A. T.) has devised a new replica method for transmission electron microscopy (TEM) with plasma polymerized film by glow discharge. We have published several reports on its application.[5,6] In this article, we demonstrate the feasibility of the new method for the surface characterization of LB film.

The apparatus for plasma polymerization consists of a high voltage power supply, a vacuum chamber containing a hydrocarbon vapour (e.g., naphthalene, methane, and ethylene), and electrodes of anode disk and a cathode of the specimen base. Figure 1 illustrates the trial equipment of plasma polymerization replica device. The apparatus is now commercially available from Ushio (Model PNR-110). The surface replication of a sample by plasma polymerization in negative glow phase on the cathode was carried out by gassing at 0.05-0.1 Torr and glow discharging at 1.5-3.0 kV D.C. Ionized hydrocarbon molecules diffused onto the complex surface configuration of a sample and deposited as a three dimensionally polymerized film. As exemplified in Fig. 2, the film

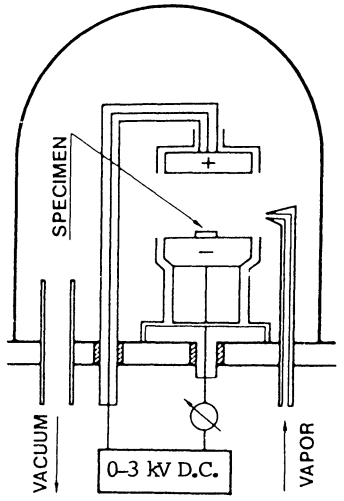


Fig. 1. Equipment of plasma polymerization replica device.

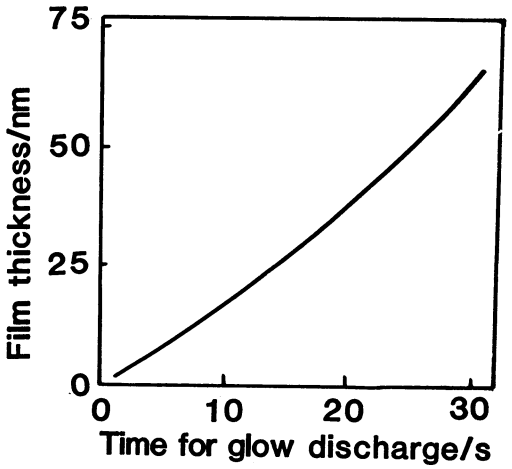


Fig. 2. Relationship between the plasma polymerized film-thickness and the time for glow discharging at 2.5 kV D.C.

thickness is able to be well-controlled.

In our previous report,[6] we were able to visualize a gold particle (10 nm diameter) without any granular texture by using the plasma polymerized film as a supporting film. This fact seems to suggest that the resulting plasma polymerized film on the complex surface has uniform thickness without any granular texture in it. It was also found that the film was chemically very stable, resistant against heat and mechanically extremely strong. In this study, the plasma polymerized film prepared on an LB film-covered glass plate was treated with hydrofluoric acid in order to dissolve the organic film-coated glass for TEM examination of the resultant replica film. In addition, it was found that the electron density of the replica film was proportional to the electron beam path through the film, probably due to the generally accepted fact that the strength of diffuse scattering of electron beam is proportional to the electron beam path. The electron beam path through the film was strongly dependent on the ultra-local diffuse-scattering pattern of the replica film.[7] As a final result, the surface replica might be able to give the fine three-dimensional image with adequate contrast. Since the plasma polymerization process was devised to give no heat- and sputtered ion-damage on a specimen and the resultant film was amorphous in texture, this new method gave a more real image of the specimen with higher resolution. The new replica method is applicable for the surface-structure studies of inorganic and organic materials.[5] In order to demonstrate the fact that the method gives a more real image of the specimen with higher resolution, (a) the high resolution image of an MgO crystal on a glass plate and (b) the high magnification image of a freeze-fractured rod outer segment in retina of a rat are represented in Fig. 3. As seen in a circle of the replica image of an MgO crystal, the resolution is found to be less than 4 nm.[7] The image of the rod outer segment suggests that the surface of the biomaterial was not damaged during the course of glow discharge-induced polymerization.[7]

In this study, an LB film system of spiropyran (6-nitro-3',3'-dimethylspiro-(2H-1-benzopyran-2,2'-indoline)) with a long hydrocarbon chain was used as a test sample for demonstrating the feasibility of the new replica method in the LB film studies. The chemical structure of the dye surfactant is shown in Fig. 4. Chloroform solution of the amphiphilic dye was prepared at the concentration of $1.0 \times 10^{-4}$ mol·l$^{-1}$ as a spreading solution. The subphase temperature was always maintained at 18 °C during the course of LB-film preparation. An aliquot of the spreading solution was carefully delivered onto a surface of $CdCl_2$ solution ($5.0 \times 10^{-4}$ mol·l$^{-1}$), whose pH was adjusted to 6.1 ± 0.1 by the addition of $NaHCO_3$ ($5.0 \times 10^{-5}$ mol·l$^{-1}$). Deposition of a monolayer from the aqueous subphase onto a glass plate was carried out according to the same manner as used in our earlier report.[8]

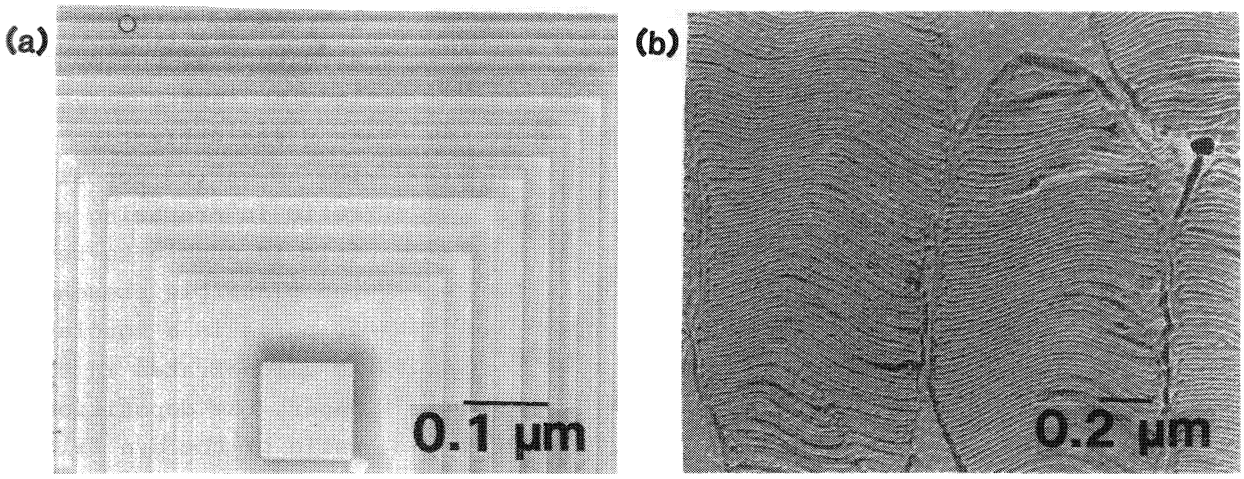


Fig. 3. The replica images of (a) an MgO crystal and (b) a freeze-fractured rod outer segment in retina of a rat.

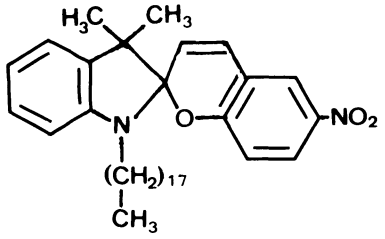


Fig. 4. The chemical structure the dye surfactant employed in this study.

The deposition ratio estimated for each LB film preparation examined in this study was found to be nearly unity, when the deposition was carried out at a surface pressure of 20 mN/m.

A glass plate, on which an LB film of the dye surfactant was prepared, was put on the cathode (see Fig. 1), followed by evacuation of the reaction vessel. Naphthalene gas of high purity was introduced into the glass-made vessel, and DC high voltage was applied between two electrodes (2.5 eV), generating glow discharge for 20 s. The calibration curve exemplified in Fig. 2 should be obtained for each equipment of plasma polymerization replica device because the rate for deposition of plasma polymerized film was found to be strongly dependent on the plasma polymerized conditions. In this study, the calibration curve shown in Fig. 2 was obtained. By digesting the LB film-coated glass plate away with 5% hydrofluoric acid solution, a single replica stage film could be obtained. Each replica film thus prepared was examined with a JEOL 100 S or 1200 EX electron microscope.

Figure 5 shows the typical TEM of the replica film prepared from a glass plate, on which three dye-monolayers were deposited for each side. As seen herein, the surface of the dye film was not flat. As pointed out by the arrows in Fig. 5, some pores in the dye monolayer were observed. The time resolved visible absorption spectroscopic observation of a monolayer of the dye surfactant on the aqueous subphase revealed[9] that when an aliquot of the spreading solution was delivered onto the butter solution, the amphiphilic dye molecules might form the numerous two-dimensional islands and those islands originally formed might contact to form a large two-dimensional film after the gradual decrease of the surface aqueous area, on which the dye molecules were placed with chloroform. On the basis of the spectrophotometric observation described above, we assume that if the islands might be too rigid to form a single two-dimensional monolayer after the plausible molecular re-arrangement on the aqueous subphase, the formation of some pores should be

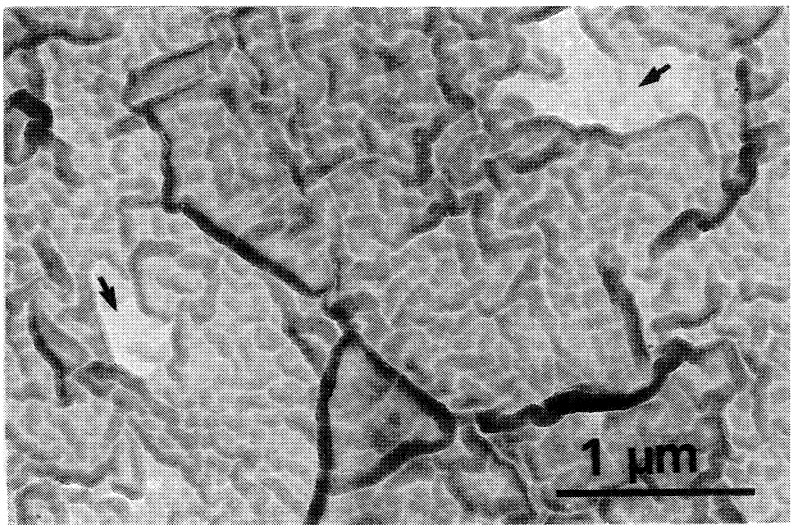


Fig. 5. Transmission electron micrograph of the replica film. For further explanations, see the text.

introduced into the structure of the monomolecular layer.

The estimation of the so-called deposition ratio in preparing an LB film is unable to reveal the plausible presence of pores in a monolayer. As demonstrated in this paper, the deposition ratio of the dye film with numerous pores, some of which is shown in Fig. 5, was found to be nearly unity. Therefore, the electron microscopic observations of the LB-film surface seem to be essentially necessary to study of the LB-film structure. The new replica method seems to assist the progress in the LB-film studies.

We have already performed to observe the surface of various kinds of LB films by TEM coupled with the new replica method and have been able to accumulate numerous informations on the structure of the built-up films. We would like to stress here that the new replica method combined with TEM is a powerful tool for the surface characterization of the extremely small and thin samples such as the LB film system. Since it has been found that the thickness of plasma polymerized film is able to be well controlled, the equipment of plasma polymerization replica device may be applicable for the preparation of ultra-thin insulator film.

References

1) K.B. Blodgett, J. Am. Chem. Soc., 60, 1007 (1935).
2) K.B. Blodgett and I. Langmuir, Phys. Rev., 51, 964 (1937).
3) L.H. Germer and K.H. Stokes, J. Chem. Phys., 6, 280 (1938).
4) A. Fischer and E. Sackman, Nature, 313, 299 (1985).
5) A. Tanaka, M. Yamaguchi, and T. Hirano, Proc. 46th Annual Meeting of the Electron Microscopy Society of America, 1988, 414.
6) T. Araki, Y. Sugawara, N. Hirao, T. Iwamoto, M. Yoshiura, and K. Iriyama, Chem. Lett., 1989, 329.
7) A report on the visualization of the fine three-diemnsional image with some other related results will be published from the theoretical point of view by K. Iriyama and A. Tanaka.
8) K. Iriyama, M. Yoshiura, Y. Ozaki, T. Ishii, and S. Yasui, Thin Solid Films, 132, 229 (1985).
9) K. Iriyama, manuscript in preparation.

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