Moiré Pattern of Bilayered Fatty Acid Monolayers Based on Dark Field Imaging

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Moiré patterns of bilayered fatty acid monolayers prepared by the Langmuir-Blodgett method were successfully observed on the basis of dark field imaging by using transmission electron microscope for the first time. The moiré lines of the bilayered fatty acid monolayers prepared by the continuous compression method were warped and discontinuous, whereas that prepared by the multi-step creep method were straight and continuous. These differences apparently reflect their crystallographical regularities.

The ultimate functions such as electro-conductive, optical guide or molecular permeation properties of Langmuir-Blodgett (LB) films can be attained by using a defect-free or a defect-diminished monolayer being the precursor of the LB film.[1] In order to prepare such a structually high quality monolayer, it is indispensable to evaluate the structural defects in the monolayer. An atomic force microscopy (AFM) is an effective technique to directly evaluate the structural defects, and has been applied to observe edge dislocation[2] in fatty acid monolayer and point defect[3] in alkylsilane monolayer. However, AFM is not a useful and powerful technique to evaluate the type and density of defects in the monolayer on a wide-area of micrometer order. Moiré pattern is observed in the dark field image on transmission electron microscopic (TEM) observations as an interference fringe when the two thin layers are superposed with a small orientation or a small spacing difference of layered crystals. Therefore, the moiré pattern technique allows us to evaluate defect types and densities on a wide-region.[4-6] In this letter, the moiré pattern technique was extended to investigate the molecular packing regularity in the fatty acid monolayer for the first time.

A stearic acid monolayer was prepared by the multi-step creep method,[7] and also, a barium arachidate monolayer was prepared as follows; A benzene solution of arachidic acid with a concentration of 3×10^{-3} mol l^{-1} was spread on the water subphase containing 3×10^{-5} mol l^{-1} of $BaCl_2$ and 4×10^{-4} mol l^{-1} of $KHCO_3$ and then, compressed to a surface pressure of 20 mN m^{-1} at an area change rate of 2×10^{-3} nm^2 $molecule^{-1}s^{-1}$ at the subphase temperature, T_{sp} of 293 K. Each monolayer was transferred onto a hydrophilic SiO substrate by the vertical dipping method to prepare bilayered monolayers for TEM observation. The hydrophilic SiO substrate was prepared by vapor-deposition of SiO onto a collodion thin film with which an electron microscope grid was covered on a glass slide. Bright field image, dark field image and electron diffraction (ED) pattern of the bilayered monolayer were taken in radiation time of 3s, 13s and 1s, respectively, with a Hitachi H-7000 transmission electron microscope which was operated at an acceleration voltage of 75 kV and a beam current of 0.5 μA. The electron beam, objective aperture and selective area aperture were 10 μm, 20 μm and 400 μm in diameter, respectively.

Figures 1(a), 1(b) and 1(c) show the ED pattern, the bright field image and the dark field image, respectively, which were taken in the same region of the bilayered stearic acid monolayers prepared by the multi-step creep method. The dark field image was formed by using the (1 0) diffraction spot shown by an arrow in the ED pattern. The ED pattern exhibited sharp

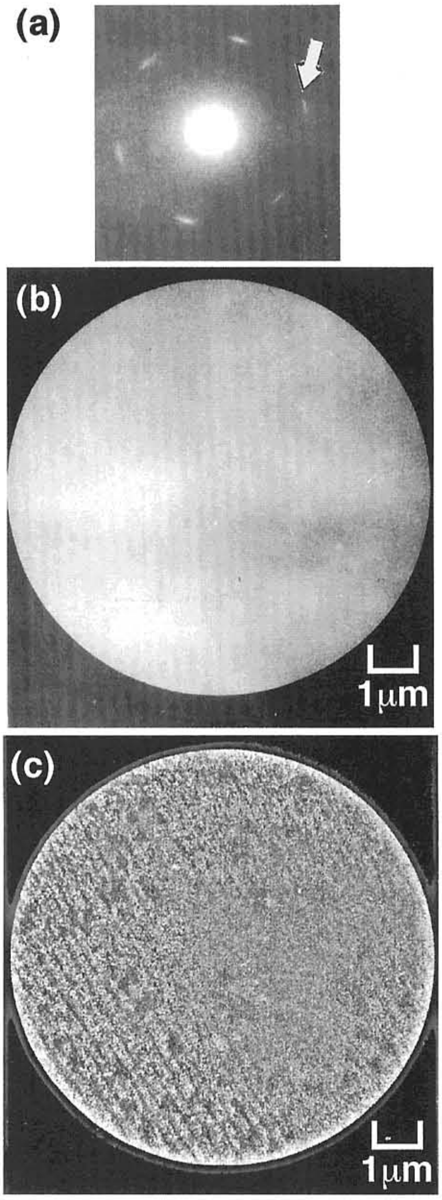

Figure 1. (a) ED pattern, (b) bright field image and (c) dark field image of the bilayered monolayers prepared by the multi-step creep method.

crystalline hexagonal spots along an azimuthal direction. This apparently indicates that the crystallographic axes in the crystalline domains orient in fairly similar directions over the observed region of about 10 μm. The bright field image shown in Figure 1(b) was homogeneous, indicating that two morphologically homogeneous monolayers were overlappingly transferred onto the substrate. On the other hand, many parallel lines were observed in the dark field image, as shown in Figure 1(c). It is reasonable to consider that the observed parallel lines were not attributed to the surface morphology but the inner structural origin in the bilayered monolayers. Furthermore, such parallel lines were not observed for a dark field image of the single monolayer. Also, since the direction of the interference fringe shown in the dark field image of Figure 1(c) was parallel to the reciprocal vector of (1 0) diffraction spot of Figure 1(a), it is reasonable to conclude that the interference fringe observed in the dark field image is a rotation moiré pattern. The orientational misfit angle, θ of the two overlying monolayers was calculated from the equation, $D = d / \theta$, where D and d were the observed spacing of

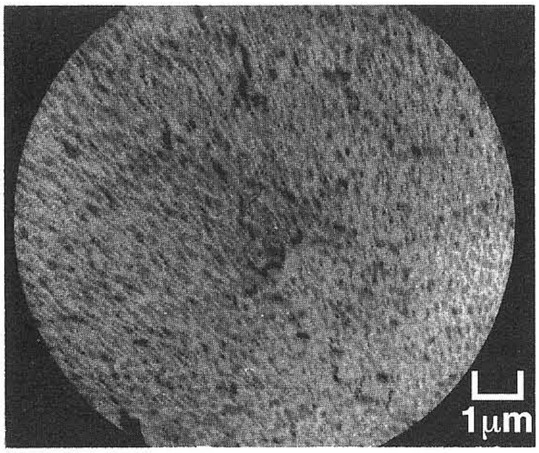

Figure 2. Dark field image of the bilayered monolayers prepared by the continuous compression method.

the moiré lines (200 nm) and the (1 0) lattice spacing (0.42 nm), respectively. The calculated magnitude of θ was 2.1×10^{-3} rad. Since the magnitude of θ for the bilayered monolayers is comparable to that for high density polyethylene single crystal,[5] it is also reasonable to conclude that the interference fringe observed in the dark field image is the moiré pattern.

Figure 2 shows the dark field image of bilayered barium arachidate monolayers which were prepared by the continuous compression method at a constant speed. As shown in Figure 2, the moiré lines of the bilayered monolayers prepared by the continuous compression method were warped and discontinuous in comparison with that prepared by the multi-step creep method. The multi-step creep method provide the large-area and defect-diminished crystalline monolayer owing to an effective sintering at the interfaces among the crystalline domains during its compression process, in the case of T_{sp} just below the crystalline relaxation temperature.[7] Therefore, the difference in the moiré patterns of the bilayered monolayers prepared by the multi-step creep and the continuous compression methods might arise from the difference in their crystallographical regularities.

The moiré pattern only for inorganic thin film[4] and polymer single crystal[5,6] has been observed. The present report is the first example of moiré pattern observation for organic monolayer. Also, it is concluded from the moiré pattern-molecular packing relationships for the fatty acid monolayers that the moiré pattern technique on dark field imaging is fairly effective to evaluate the structural defects over a wide region at the crystalline monolayer.

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