Direct Observation of Edge Dislocation in Lignoceric Acid Monolayer Based on Atomic Force Microscopy

Tisato Kajiyama,* Yushi Oishi,[†] Kazuaki Suehiro,[†] Fuminobu Hirose, and Taishi Kuri
Department of Chemical Science and Technology, Faculty of Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812
[†]*Department of Applied Chemistry, Faculty of Science and Engineering, Saga University, 1 Honjo-machi, Saga 840*

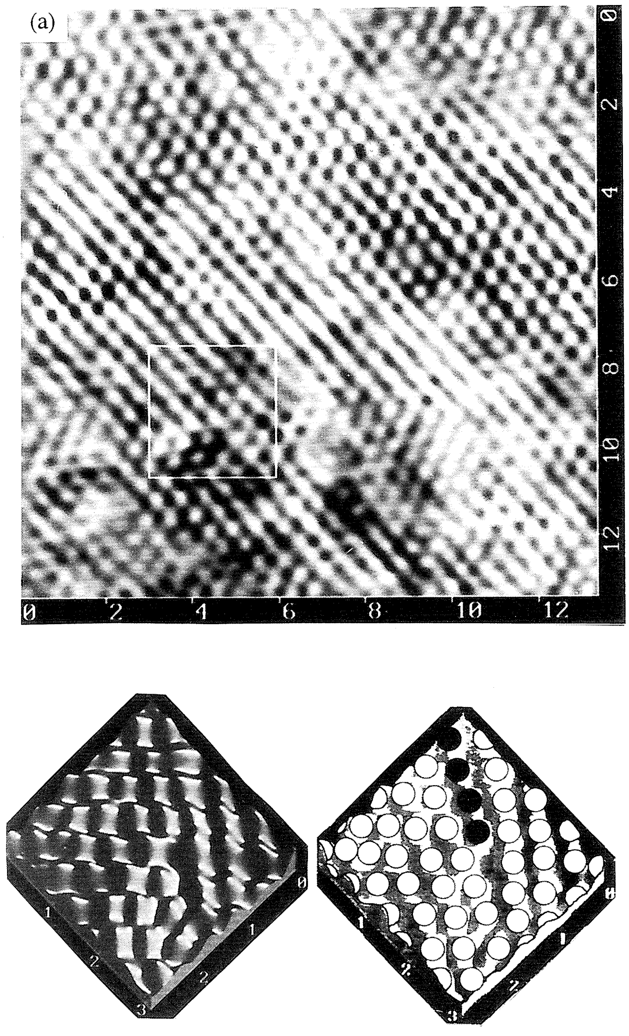
(Received December 16, 1994)

Structural defect in lignoceric acid monolayer was investigated with an atomic force microscope(AFM). A molecular-resolution AFM image exhibited us the first direct observation of edge dislocation in the lignoceric acid monolayer.

The ultimate functional properties, for example, electroconductive and optical 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 high quality monolayer, it is indispensable to evaluate the number and types of structural defects in the monolayer. An atomic force microscope(AFM) allows us to characterize the surface structure of organic monolayers to observe the state of molecular arrangement in the monolayer and the multi-layered LB film.[2-4] The crystal defects only for multilayered LB films have been observed by using an AFM.[3] In this letter, the crystal defect of edge dislocation in the lignoceric acid monolayer on a mica surface has been successfully observed for the first time.

In order to obtain an AFM molecular image of the fatty acid monolayer, it is indispensable to prepare the monolayer with a high mechanical stability.[4] In the case of a continuous compression method, the mechanically stable fatty acid monolayer can be prepared at a low surface pressure. Mechanical stability of the monolayer depends also on the degree of thermal molecular motion in the monolayer because a molecular aggregation strength increases with decreasing the degree of thermal molecular motion. Then, the mechanical stable monolayer used in this study was prepared as follows. A benzene solution of lignoceric acid($CH_3(CH_2)_{22}COOH$) with a concentration of 1 X 10^{-3} mol/l was spread on the water surface at a subphase temperature, T_{sp} of 293 K. Since T_{sp} is below the crystalline relaxation temperature, $T\alpha_c$ and the melting temperature, T_m of the lignoceric acid monolayer($T\alpha_c$ = 329 K, T_m = 345 K), the monolayer is in a crystalline state with a low degree of thermal molecular motion.[5] The lignoceric acid monolayer was prepared at a low surface pressure of 5 mN/m by a continuous compression method at a rate of 1.7 X 10^{-3} nm^2/molecule·sec and then, transferred onto a freshly cleaved mica(Okabe Mica, Fukuoka, Japan) by a vertical dipping method. The transfer ratio was unity, implying that mica substrate was completely covered with the monolayer. The AFM image of the monolayer was obtained with a SFA300(Seiko Instruments, Industry) in air, using a silicon nitride tip on a cantilever with a spring constant of 0.022 N/m. The applied force on scanning was about 10^{-10} N. In order to reduce the noise component in raw AFM images, a digital filtering treatment for the Fourier-transformed image was carried out by keeping only the spatial frequencies corresponding to the spots of the Fourier-transformed image.

Figure 1(a) shows the AFM image for the lignoceric acid monolayer on a scan area of 13.5 X 13.5 nm^2. The Fourier-transform spectrum of the AFM image revealed that the brighter portions in Fig. 1(a) were arranged in a hexagonal array with the (1 0) spacing of 0.43 nm. This magnitude agrees with the spacing of 0.43 nm which was estimated from the electron diffraction pattern of the lignoceric acid monolayer and also, is quite different from the 0.46 nm spacing of a mica substrate.[4] It is, therefore, reasonable to conclude that the brighter portions in the AFM



(b) (c)

Figure 1. Filtered AFM images of lignoceric acid monolayer on scan area of (a) 13.5 X 13.5 nm^2, (b) 3 X 3 nm^2 and (c) a schematic representation of Fig. 1(b).

image represent the individual methyl group of lignoceric acid molecule in the monolayer and also, that lignoceric acid molecules are regularly aligned with a hexagonal array. A periodic hexagonal array was extended over ~10 nm. The image in Fig. 1(b) corresponds to a magnification (3 X 3 nm^2) of the marked zone shown in Fig. 1(a). Fig. 1(b) apparently exhibits a discontinuous molecular array in the crystal lattice. That is, a typical edge dislocation can be observed in the center portion of the image, in which an additional molecular array is inserted between two molecular arrayes coming down, as schematically shown by opened and closed circles in Fig. 1(c). The observation of edge dislocation in monolayer is due to the usage of the mechanically stable monolayer prepared by the continuous compression to a lower surface pressure. However, we cannot estimate the edge dislocation density in the monolayer at present time because we have no information about molecular arrangement in a wider region than μm^2 obtained with AFM. The dislocation density in monolayer may depend on preparation conditions of monolayer on the water surface and, may decrease by using regularization methods of monolayer structure, for example, the multi-step creep[6] and the cooling crystallization[7] methods.

The crystal defect such as edge dislocation in the lignoceric acid monolayer was directly observed with an AFM. The direct observation of edge dislocation in the monolayer was succeeded in for the first time, resulting from the possible preparation of the mechanically stable monolayer.

References and Notes

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