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A molecular-level photodiode was fabricated using a phase separation technique. The separated phase of a stacked layer of flavin (sensitizer (S))-ODTCS (octadecyl trichlorosilane) mixture and PFCA (nonadecafluoro-decanoic acid) was constructed and observed by AFM. Based on this structure, a submicron scale electron donor (D)/S/relay (R)/acceptor (A) molecular photodiode was fabricated on the silicon wafer substrate by the LB method. The morphology of the device was confirmed by AFM. The photodiode effect of the molecular device was observed using STM. The molecular scale photodiode and photoswitching effect could be verified.

Keywords: phase separation technique; Langmuir-Blodgett (LB) film; atomic force microscopy (AFM)

INTRODUCTION

Currently, miniaturization of device and highly integrated circuit design is major interest for the development of electronic device. To realize the artificial photodiode as a molecular-scale device, molecular patterning using phase separation technique was performed. In the molecular patterning, two kinds of methods are mainly used. The one is direct patterning or lithography using AFM tip and the other is phase separation

technique[1]. Molecular patterning using phase separation technique is one step process. When mixed solvent of hydrocarbon and fluorocarbon are spread on the surface of water, hydrocarbon domains are formed. Since the attraction forces between hydrocarbons are stronger than that between fluorocarbons, hydrocarbon layers form island like domain and fluorocarbon layers form sea like domain. In this study, the molecular patterning was performed using phase separation technique for the fabrication of molecular-scale photodiode.

EXPERIMENTAL DETAILS

The octadecyltrichlorosilane (ODTCS) and nonadecafluorodecanoic acid (PFCA) were used as hydrocarbon and fluorocarbon, respectively. Ferrocene(1-1'-ferrocene-N-dioctadecylcarboxamide), flavin (7,8-dimethyl -10-dodecylisoalloxazine), viologen (N-allyl-N'-[3-propylamido-N",N"-di (n-octadecyl)]-4,4'-bipyridiniumdibromide) and TCNQ (N-docosylquinol inium tetracyanodimethan) are used as an electron donor (D), sensitizer (S), relay (R) and acceptor (A) unit, respectively. The deposition of LB film was carried out using a circular Langmuir trough (type 2022, Nima Tech., England). To observe AFM (PSI AutoProbe CP, USA) images of LB films, mica was used as a substrate. For the STM image of the hetero LB film, silicon wafer was used as a substrate. Tungsten wires were electrically etched for STM tips in 1 M KOH solution with inducing voltage and rinsed with ethanol.

RESULTS AND DISCUSSION

The 2:1 mixed solvent of ODTCS and PFCA in the chloroform was spread on the subphase. After drying chloroform (30 min), monolayer of mixed LB film was fabricated on the mica substrate using horizontal dipping method. LB film was annealed in the oven for 12 hours at 70 °C to harden the hydrocarbon layer. Annealed LB film was sonicated in the ethanol

solution for 5 minutes, so the PFCA layer was removed and the patterned structure of ODTCS was constructed. Domains of ODTCS were clearly formed and each domain has about 0.25 μ m radius. The height of domain is about 150 ~ 200 Å so it is thought that the domain is not a monolayer of ODTCS but stacked layers of ODTCS. The molecular patterning using hydrocarbon and fluorocarbon was confirmed. Based on this structure molecular patterned D/S/R/A hetero LB film was fabricated.

Monolayer of D LB film was deposited on the silicon wafer substrate. Onto this layer the mixed LB film of S:ODTCS:PFCA = 0.2:1:2 was fabricated using horizontal dipping method. LB film was annealed in the oven at 45 °C for 4 hours for hardening the hydrocarbons and sonication was performed using ethanol for 5 minutes. The average radius of domain is about 0.15 μ m and the average height from valley to top is ca.150 Å. On the patterned layer of D/S-ODTCS, R and A LB layers were fabricated. First, R monolayer is deposited during upstroke and A monolayer was deposited during downstroke sequentially. Fig. 1 shows the expected structure of D/S/R/A LB films. The weak head-tail interaction will reduce the amount of the viologen which are directly deposited on the D layer.

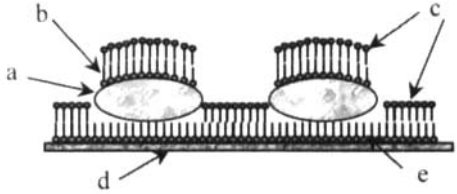

FIGURE 1. Structure of Molecular Photodiode; a, S/ODTCS; b, R; c, A; d, Si wafer; e, D.

Fig. 2(a) shows the AFM image of D/S/R/A hetero LB film. The average height from valley to top is ca. 180 Å. The height of domain in the D/S/R/A structure increased by 30 Å than in D/S structure. No adhesion of the R molecules to the D layer might lead the increase of average height of domain. To obtain the photodiode effect in the D/S/R/A hetero LB films STM images were shown. Fig. 2(b) and (c) show the STM image of

D/S/R/A hetero LB film in the dark (without light) state and photo (irradiation of light) state when sample bias was 0 V and tip bias was 0.8 V. In the STM, the difference of the current density can be represented by the difference of height. In the STM image of photo state LB film, the domain structure could be observed. The height of domain was about 400 Å which is extremely higher (about 10 times) than that in the dark state. When we applied the tip bias as a negative voltage, the observed signals were very unstable, so images cannot be obtained. Based on the results it could be concluded that the photoinduced electron transport and directional flow of electron from D to A was successfully occurred in the molecularly patterned domain and molecular photodiode and photoswitching effect could be obtained.

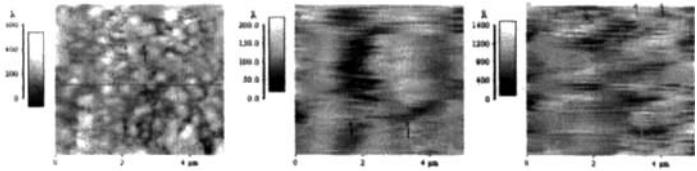

FIGURE 2. AFM and STM image of D/ODTCS-S/R/A hetero LB film; a, AFM ; b, STM in dark condition; c, STM with light irradiation.

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