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Lateral Molecular Space Control of LB Films by Introducing Spacer Molecules

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Lattice constant of LB films were controlled by introducing "Spacer Molecules" such as pyrrole or fullerene into arachidic acid LB films. The appropriate buffer layers which satisfy lattice matching between the different monolayers were successfully formed. The observation using an atomic force microscope clearly showed that the LB films are highly ordered in the lateral direction even after introducing spacer molecules. The spatially controlled LB films were also found to be applied for a novel gas sensor with a molecular size recognition.

Keywords: Langmuir-Blodgett film; fullerene; spacer; atomic force microscope; sensor; molecular recognition

INTRODUCTION

Lattice matching between monolayers is one of the important factors to develop a functional device using hetero structure of LB films by piling up different molecules layer-by-layer. In this study, the lattice constant of LB films were controlled by introducing "Spacer Molecules" such as pyrrole(Py)^[1-4] or fullerene (C₆₀) into arachidic acid (C₂₀) LB films for the purpose of producing appropriate buffer layers which satisfy lattice matching between the different monolayers. This concept is schematically shown in Fig.1. The molecular arrangement of the larger molecules in the upper layer is expected to be improved by adjusting the lattice constant of the lower layers.

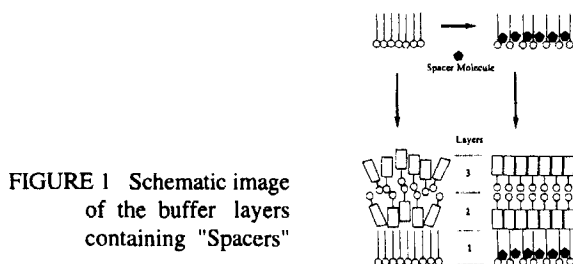


FIGURE 1 Schematic image of the buffer layers containing "Spacers"

EXPERIMENTAL

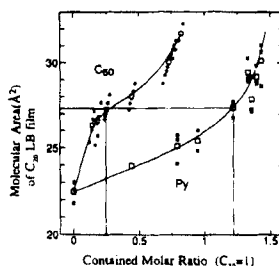
The change of the molecular area of C_{20} molecules was studied as a function of an increasing quantity of spacer molecules. Several variations in the composition of the spreading solution containing Py were prepared^[1-4]. All of them contain 10%(v/v) ethanol and 5mM C_{20} in benzene solutions. For the solutions containing C_{60} , the molar ratios were ($C_{20} : C_{60}$) 1:0, 1:0.05, 1:0.1, 1:0.2, 1:0.55, 1:0.75 and 1:1. The concentration of C_{20} was always 0.03mg/ml. The C_{20} LB films containing Py were transferred to the substrate at a surface pressure of 25mN/m at 23°C, whereas those containing C_{60} were transferred to the substrate at 14°C. The benzene solution containing 3.3mM fluorocarbon (hepta-decafluorononadecanoic Acid (Wako Chemicals), $CF_3(CF_2)_7(CH_2)_{10}COOH$, denoted as FOM) was prepared for the spreading solution used to build up layers with a larger molecular area. For the deposition of FOM LB films, $5 \times 10^{-5}M$ $AlCl_3$ was dissolved in the water subphase^[5] and the film was deposited at the pressure of 35mN/m at 23°C. Transfer of a monolayer to the substrate was made with a moving-wall type LB trough (Nippon Laser & Electronics Lab., NL-LB240-MWC). The resistivity of the subphase pure water was 18M Ω cm. The change in the molecular area of the C_{20} LB film was estimated from a quartz crystal micro balance (QCM)^[6,7] and atomic force microscopy (AFM).

RESULTS & DISCUSSIONS

Observation by atomic force microscopy (AFM) showed that the molecular area (A) of C_{20} molecules in the LB films can be controlled from 22 to 32Å² by increasing the number of spacer molecules. The results are shown

in Fig.2. The extent of the change was almost the same for both Py and C_{60} as the spacer. It was also found that when larger molecule, C_{60} was used as the spacer, the molecular area was controlled by less quantity than when smaller molecule, Py was used. This was caused by the difference of the volume exclusion effect between C_{60} and Py. These experimental results showed good agreement with the results of computer simulation based on molecular mechanics.

FIGURE 2 Change of Molecular Area as the increase of "Spacer Molecules".

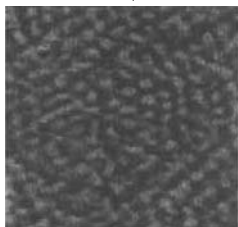


In order to examine the effect as buffer layers of the LB films containing spacer molecules, the molecular arrangements of 2 layers of fluorocarbon LB films were formed by two different methods. One was formed on 11 layers of pure C_{20} LB film and the other was formed on the C_{20} LB film which contains Py molecules 1.5 times as many as C_{20} molecules. Mica substrates were used for both. The AFM observation showed that the molecular arrangement characteristics of 2 layers of fluorocarbon LB films ($A=33\text{\AA}^2$) formed on a C_{20} LB film containing spacer molecules (LB2, $A=32\text{\AA}^2$) was greatly superior to that formed on a pure C_{20} LB film (LB1, $A=20\text{\AA}^2$). The results are shown in Fig.3. These results showed that spatially controlled LB films can act as excellent buffer layers for piling up larger molecules on a substrate which has a different lattice constant with the molecules, because the lattice constant of the C_{20} LB film can be controlled by introducing spacer molecules. Similar results were obtained when C_{60} was used as the spacer.

The highly ordered structure of the laterally space controlled LB films were also proved by the experimental results that they can be used for the molecular size recognition of gas molecules^[8]. Several kinds of gas molecules with different molecular weight were easily recognized by the spatially controlled LB films formed on the electrode of QCM. The results are shown in Fig.4. The gas adsorption characteristics of spatially controlled LB were much

superior to the LB films without spacer molecules. It was also found that the characteristics were improved as the increase of spacer molecules in the LB films.

(a) LB1



(b) LB2

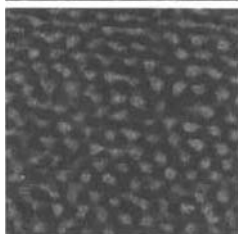


FIGURE 3 AFM images of the fluorocarbon LB films formed on LB1 and LB2.

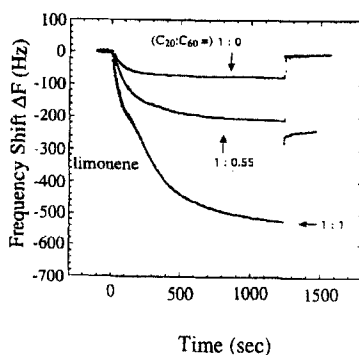


FIGURE4 Response characteristics of the LB films containing C_{60} to the gas molecules.

CONCLUSION

LB films are highly ordered in the lateral direction even after introducing spacer molecules and they can be applied to buffer layers for the LB films with larger molecules, novel gas sensor or chemical sensor with a molecular size recognition.

Acknowledgements

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