Transactions of the Materials Research Society of Japan 29 [3] 759-762 (2004)

Chromogenic Responses Induced by Electric Field in Phthalocyanine Derivative LB Films

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Abstract Langmuir-Blodgett (LB) films of mixtures of arachidic acid (AA) and aluminum 1,4,8,11,15,18,22,25-octabutoxy-29H,31H-phthalocyanine triethyl siloxide were accumulated on ITO substrates. The morphology of AA LB films strongly depended on the flatness of ITO substrates. The Hetero LB films which were accumulated alternately the mixture and pure AA had very flat surfaces and highly aligned molecules with AA buffer layers on flat ITO. The absorption spectra of the films were reversibly changed by applying electric fields in the solid chromogenic cell.

Key words: chromogenic materials, phthalocyanine derivative, LB films, absorption spectrum

1. INTRODUCTION

As chromogenic materials, several transition metal oxides[1] and also some organic materials[2] have been studied in an electrochromic (EC) system. These conventional EC responses were slow and short in the life because of chemical redox reactions. On the other hand, Bucher and Kuhn[3] have reported an EC phenomenon produced by electric fields applied to the single dye molecule. The EC response speed was very high although the amount of color change was small.

We have also proposed a new mechanism of color changes induced by electric fields. In the model the distribution of electrons is changed intra molecules by applying electric fields.

The purposes of this work are to prepare films with aligned organic dye molecules and to investigate chromogenic properties experimentally.

The alignment of the molecules is a very important issue to realize our model, since electric fields are applied to one direction. As well known a Langmuir-Blodgett (LB) technique[4] has been widely used to prepare ultrathin films with high aligned functional molecules. We have focused at a phthalocyanine derivative and prepared its LB film as the candidate of highly aligned dye molecules. But we didn't obtain highly aligned phthalocyanine LB films to realize large color change in the past work[5]. In this report, we paid attention the flatness of surfaces of ITO substrates and a configuration of the film structure to obtain LB films with high alignment. It will be appeared in this paper that the obtained films were investigated with respect to the layered structure and typical chromogenic properties.

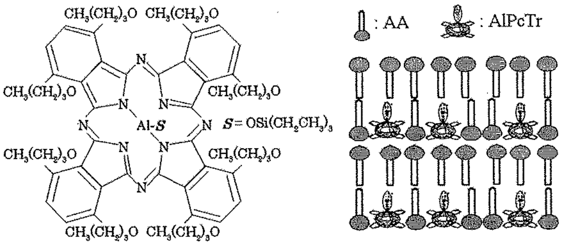
2. EXPERIMENTAL

We fabricated LB films by a Kuhn type of apparatus.[6] The phthalocyanine derivative used was aluminum 1, 4, 8, 11, 15, 18, 22, 25 -octabutoxy- 29H, 31H-phthalocyanine triethyl siloxide (AlPcTr). The molecular structure was schematically shown in Fig. 1.

Since the AlPcTr is not an amphiphilic molecule, an arachidic acid (AA, $CH_3(CH_2)_{18}COOH$) was used in order to stabilize the Langmuir film (L-film) on the subphase. We prepared a chloroform solution of AlPcTr at a concentration of 0.64 mmol / l and AA at 3.2 mmol / l. The AlPcTr was a commercial product of Aldrich-Chemical Co., Ltd., and the AA was obtained from Wako Pure Chemical Industries, Ltd.

After spreading the solution, a L-film of AlPcTr / AA was kept on a water subphase at pH = 10.3 containing 2 mmol / l $CaCl_2$ and 0.1 mmol / l NaOH. The subphase temperature was maintained at 290K. The films were transferred onto the substrates at a constant surface pressure (24 mN / m) through vertical dipping / lifting strokes. The stroke speed was 12 mm / min.

The substrates used were two kinds of ITO glasses (Kinoene-Kogaku-Kougyou Co., Ltd, and Sumitomo Heavy Industries, Ltd) cut to the size of 1.0 cm^2. Each the sheet resistance of the ITO glasses was 10, 20 Ω / cm^2, respectively. The accumulation of the LB films was done by the three kinds of processes; strokes for pure AA, only AlPcTr&AA (Y-type), and alternated dipping / lifting strokes for AlPcTr&AA and AA. The



AlPcTr   Hetero LB films

Fig.1. Molecular structures of the phthalocyanine derivative (AlPcTr) and the schematic Hetero LB films.

latter case was named as Hetero LB films in Fig. 1.

The surface morphology of the obtained films was observed by an atomic force microscopy (AFM) (Seiko Instruments Inc.). The accumulated structures of the obtained films were investigated by a reflected X-ray diffraction (XRD) (Rigaku Co., Ltd). The solid cell to measure the absorption spectra in the reflection mode has a configuration of Glass / ITO / Insulator / LB films / Counter Electrode. The insulator was AA film as the buffer layers. The counter electrode used was Au film. Surface area of counter electrode was about 27mm^2. The absorption spectra of the reflection were measured by a double beam spectrometer (Shimadzu Co., Ltd).

3. RESULTS AND DISCUSSION

Figure 2 shows top-view AFM images of the rough ITO substrates (a-1) and very flat ITO substrates (a-2). The surface morphology of rough ITO has Ra, surface roughness of approximately 5.4 nm. Island grains with the size of *ca.* 200 nm were observed. The Ra of flat ITO's was *ca.* 0.5 nm. The observed surfaces were atomically flat and very smooth.

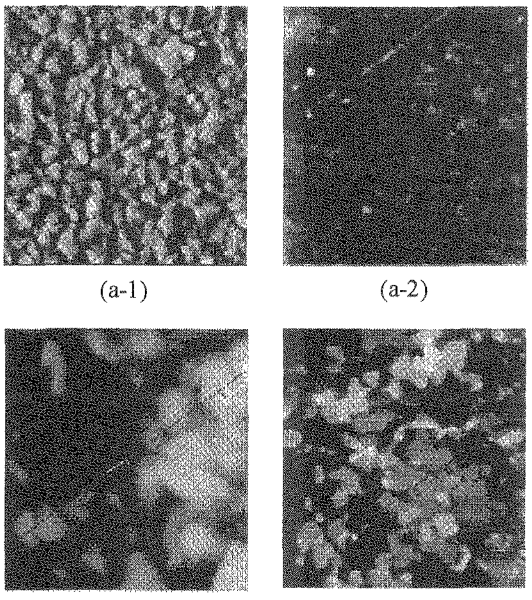
The figures (b-1) and (b-2) show the result of AA LB films on rough and flat ITO, respectively. The surface of AA / rough ITO was quite rough. The morphology of AA LB films revealed cohesive structure on rough ITO. The observed surfaces of AA / flat ITO were very smooth. So it was concluded that the accumulation process was well done. From the value of Ra the AA LB films on flat ITO was estimated flatter by decuple than on rough ITO.

Figure 3 shows the typical XRD pattern of AA LB films on each the ITO. A lattice spacing of the obtained AA films evaluated from XRD peaks was about 5.4 nm. The intensity of AA LB films on flat ITO was one hundred times stronger than on rough ITO. In this case this result suggested that the molecule plane was poor on rough ITO, also we expected that the molecular planes of the arachidic acid were aligned parallel to the film plane on flat ITO.

Figure 4 shows the AFM images of AlPcTr&AA (Y-type) LB films and Hetero LB films on flat ITO. Even if flat ITO was used, the surface morphology was rough in the case of only Y-type films. The molecular length of arachidic acid and AlPcTr was different. So the film doesn't show well alignment to substrate planes. On the other hand, the Hetero films stratificated well. We expect that the films accumulated were stabilized and became flat by sandwiching of AA films.

Figure 5 shows the typical XRD pattern of Y-type LB films (c-1) and Hetero LB films (c-2), respectively. The Hetero LB films indicate intensive peaks of (001), whereas small peaks appeared in the Y-type LB films. This result reveals that Y-type LB films were not well stratified parallel to the film plane.

Figure 6 shows AFM images of (d-1) Hetero LB films / flat ITO, (d-2) Hetero LB films / AA / flat ITO. As buffer layers, Arachidic Acid LB films were inserted between ITO and hetero films (d-2). The case of (d-1) is the result without buffer layers. The surface of the accumulated Hetero LB films was so flat with buffer layers. Another LB films were poor in flatness. Since the substrate surface became hydrophobic by preparing


(a-1) (a-2)

(b-1) (b-2)

Fig.2. AFM images of the ITO substrate and AA / ITO. The scanned area is 2μm□. (a-1) rough ITO, Ra: 5.4 nm, (a-2) flat ITO, Ra: 0.5 nm, (b-1) AA / rough ITO, Ra: 45 nm, and (b-2) AA / flat ITO, Ra: 2.7 nm.

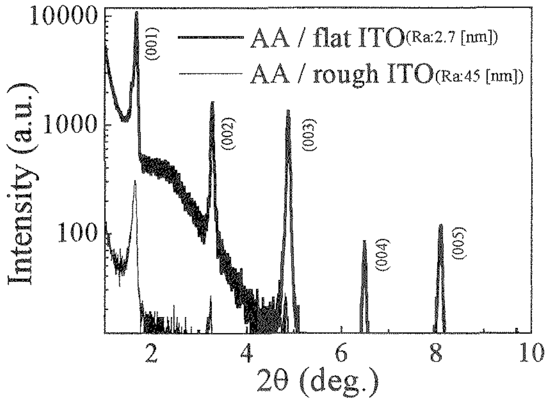


Fig.3. XRD patterns of the AA LB films on different types of ITO's.

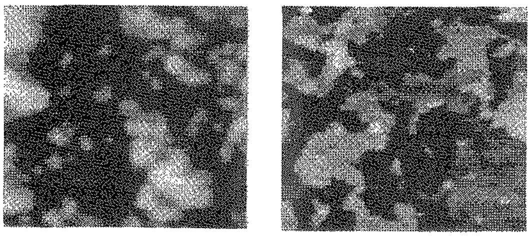

(c-1) (c-2)

Fig.4. AFM images; (c-1) Y-type / flat ITO, Ra: 10.5 nm, (c-2) Hetero LB films / flat ITO, Ra: 2.4 nm. The scanned area is 2μm□.

buffer layers and the continued accumulation was performed smoothly, the film surfaces were very flat. Also in the cross-sectional profile, the step height indicated by an arrow was about 5.8 nm. This height was confirmed to be the size of a couple of AA molecules, namely the bilayered structure was achieved.

Figure 7 shows XRD pattern of Hetero LB films / flat ITO, Hetero LB films / AA / flat ITO. The both films revealed periodic reflections and the remarkable difference in the XRD pattern was not found.

Figure 8 shows comparison of Ra vs. the number of layers. The Ra of the AA films was the value of 2-3 nm and was kept stabilized from 20 layers. The Hetero LB films revealed the same tendency to the AA films. This figure suggests a Hetero LB films are so flat and stable. In other films, the roughness of ten or more layers increased in proportion to the number of layers. Conclusively these results reveal that the LB films should be accumulated in the conditions of the Hetero structure and flat substrates.

The solid chromogenic cell was prepared by the accumulation of Au thin film electrodes as shown in Fig. 9. The reproducibility was not good because of leakage current between ITO substrates and Au electrodes. In this stage only a few cell was available for the observation of chromogenic responses.

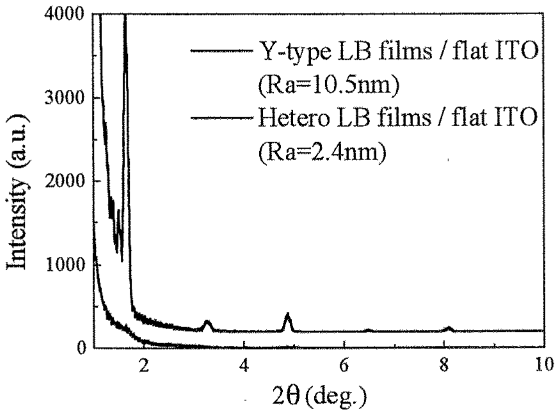
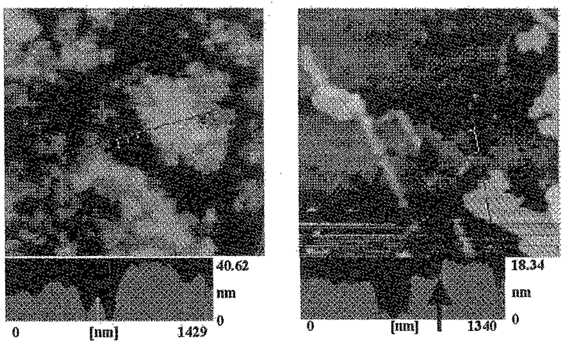


Fig.5. XRD patterns of Y-type LB films / flat ITO and, Hetero LB films / flat ITO.



(d-1) (d-2)

Fig.6. AFM image and line profiles; (d-1) Hetero LB films / flat ITO, Ra: 5.6 nm, (d-2) Hetero LB films / AA / flat ITO, Ra: 1.6 nm. The scanned area is 2μm□.

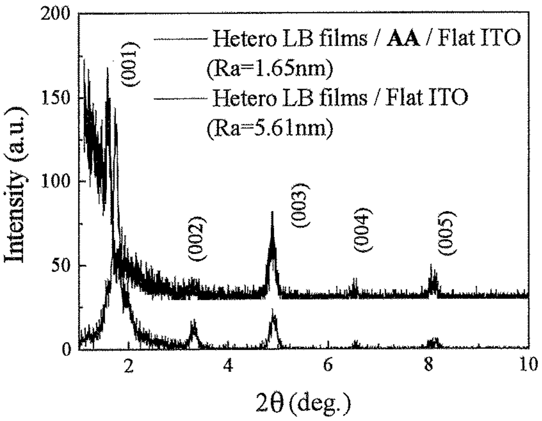


Fig.7. XRD pattern of Hetero LB films / ITO, Hetero / AA / ITO.

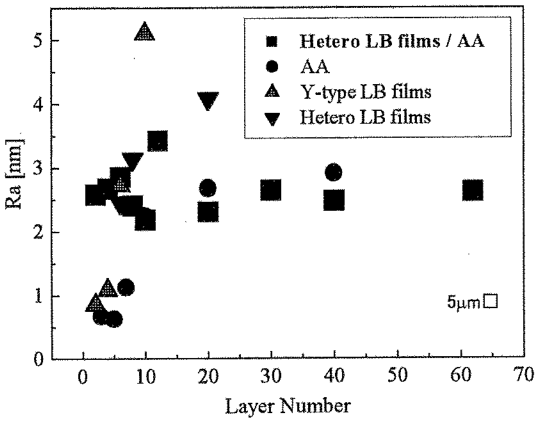


Fig. 8. Comparison of Ra of the various LB films vs. the number of layers.

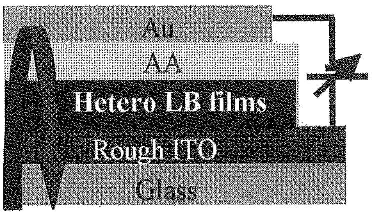


Fig.9. The schematic configuration of the solid chromogenic cell.

Figure 10 shows the color changes observed in the cell of the Hetero LB films on rough ITO. The spectrum of the original green state has the $\lambda_{\max}$ of *ca.* 756 nm. The color changed slightly when voltage of above 3 V was applied. The spectrum had the $\lambda_{\max}$ at *ca.* 766 nm. When voltage above -3 V was applied, the spectrum was almost same to the case of 3 V. When voltage was 0 V, the spectrum turned back the original

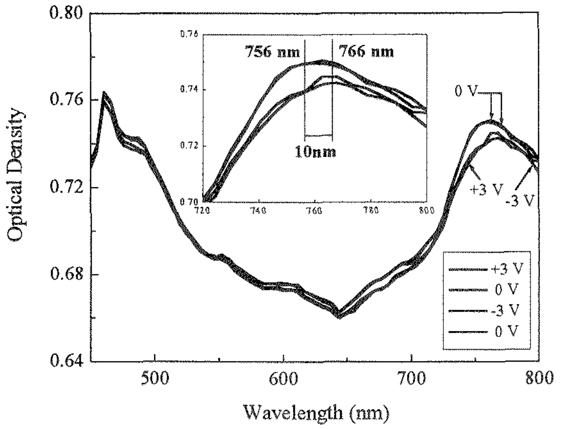


Fig. 10. Color changes observed in the Hetero LB films / rough ITO the solid cell by applying voltages.

state and the reversible color changes were confirmed. The shift of the absorption peak was, however, about 10 nm and not so large. We think that the comparatively small changes of the cell color were caused by an inferior alignment of molecules. The observed phenomena were still restricted and not enough to discuss the mechanisms of the color changes in relation to the LB film structure. The investigation for the cell with high alignment of AlPcTr molecules is a future subject.

4. SUMMARY

We prepared successfully extremely flat AlPcTr&AA LB films with highly aligned molecules. The surface morphology of the AA films was compared with the two types of ITO; rough ITO with Ra of about 5.4 nm and flat ITO with one of about 0.5 nm. The morphology of AA LB films strongly depended on the flatness of the ITO substrates. The surface morphology of only AlPcTr&AA films, however, was rough even by using flat ITO. The Hetero LB films had very flat surfaces and highly aligned molecules with buffer layers on flat ITO.

We confirmed the reversible color changes, chromogenic responses induced by applying electric fields in the Hetero LB films. As a future subject the more definite color changes are achieved in the LB films which are prepared in the optimized preparation conditions.

ACKNOWLEDGEMENTS

The authors wish to thank Advanced Materials Research Center in their College for helps by physical analyses.

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(Received October 14, 2003; Accepted November 25, 2004)