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Preparation of Self-Assembly Monolayer by C60 Derivatives

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A self-assembly monolayer (SAM) of C_{60} derivatives with alkanethiol at the end of long alkyl chain was tried to be prepared. Substrates used were Au (111) films on organic resin sheets. The covering ratio of C_{60} derivatives which was evaluated from the results of the XPS peak intensity for C-C bond energy was saturated in the specimens soaked for about 15hr in a 0.01mM benzene solution of C_{60} derivatives at room temperature. The microstructures observed by AFM or TEM revealed that ultrathin films exactly covered on Au substrates.

Key words: C_{60} derivatives , self-assembly monolayer, covering ratio , TEM

1. Introduction

Since the discovery of C_{60}[1) and the development of mass production of Fullerenes[2), they have been widely studied in the field of materials science because of great interests in its fascinating physical and chemical properties. We have been studying about a new type of electronic devices in which conductivity among C_{60} molecules are controlled by switching polymerization reactions. For such a study ultrathin or monolayered C_{60} films are essential. Recently Shi et al.[3) reported a noble wet-process, self-assembly monolayer (SAM) for a preparation of a C_{60} derivatives monolayer. They used C_{60} derivatives with alkanethiol at the end of long alkyl chain.

We tried to prepare the SAM of almost similar C_{60} derivatives by following Shi's process. Figure 1 shows a schematic molecular structure of a C_{60} derivatives used in this work. Structures of the obtained SAM were evaluated by X-ray photoelectron spectroscopy (XPS), Atomic Force Microscopy (AFM) and/or Transmission Electron Microscopy (TEM).

2. Experimental

2.1 Preparation process of SAM

A schematic self-adsorption process on Au substrates by C_{60} derivatives is showed in Fig. 1. The length of C_{60} derivatives is calculated to be 2.2nm by space-filling model. C_{60} derivatives form a stable monolayer by the interaction between Au-S and by van der Waals' force among alkyl chains. According to the previous report[3), C_{60} derivatives form SAM to have the nearest neighbor distance of about 1nm on Au substrates.

The equipment used is shown in Fig. 2. Au (111) films on organic resin sheets (Auro Sheet : Tanaka Kikinzoku Kogyou Co.) were used as a substrate. The Au substrates were soaked in a 0.01mM benzene solution of C_{60} derivatives for 2 - 48hr at room temperature. After

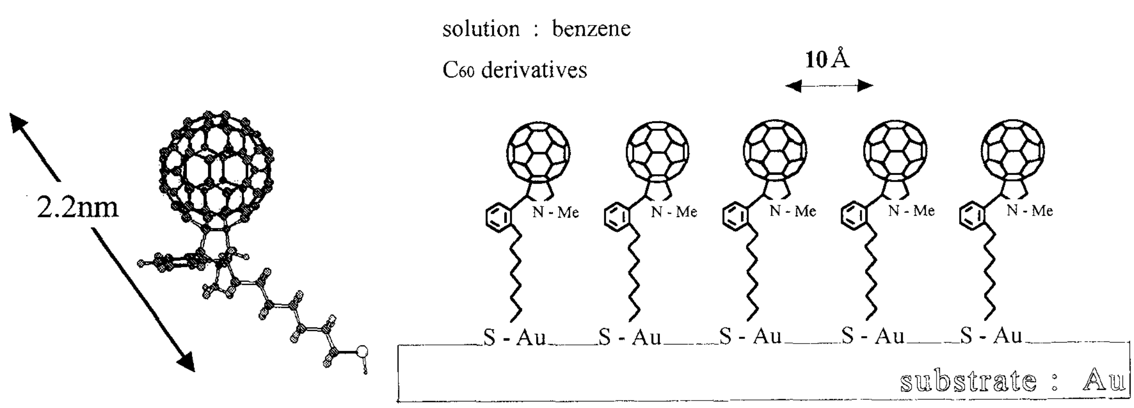


Fig .1 Molecular structure of C_{60} derivative and schematic self - assembly monolayer.

the soaking non-adsorbed C_{60} derivatives were washed out by benzene and the specimen was dried by N_2.

2.2 Synthesis of C_{60} derivatives

The C_{60} derivatives with a long alkyl chain were synthesized by the similar method as the previous report[3]. Figure 3 shows a schematic process of synthesis reactions. The samples were purified by the HPLC with Buckyprep column (Nacalai Tesque Co.) and toluene as an eluent, and characterized by FAB-MS and H-NMR spectroscopy.

Figure 4 shows an optical absorption spectrum of 0.01mM benzene solution of C_{60} derivatives and 0.01mM benzene solution of pure C_{60}. The λmax of C_{60} derivatives in benzene solution revealed red-shifts comparing with that of C_{60}.

3. Results and Discussion

3.1 Analysis by XPS

Figure 5 (a) shows the depth profile of C_{1s} peak intensity in the SAM by soaking for about 42hr. The XPS peak intensity for C-C bond energy of 285eV in etching time from 0.00min to 0.03min represents carbons adsorbed on surfaces. After more etching the bond energy shifts to lower than 285eV, that of C_{60}. This result means the existence of C_{60} molecules on substrates.

The covering ratio of C_{60} derivatives was evaluated from the result of the intensity of the C_{1s} peak of SAM comparing with that of an evaporated C_{60} thin film. As shown in Fig. 5 (b) the value of the covering ratio increased as increasing the soaking time until about 10hr and almost saturated at about 15hr soaking. The result means that absorbing reactions saturated by a self-assembly mechanism.

3.2 Observation of specimen surfaces by AFM

Figure 6 (a) and (b) shows AFM image of Au film surfaces and SAM surfaces, respectively. The undulation of Au surfaces were 2 - 6nm, while the undulation of the SAM was comparatively small to be about 3nm. The remarkable change of the surface conditions was observed. The drastic change of topographic properties on the SAM surfaces may result in effectively smooth surfaces by the

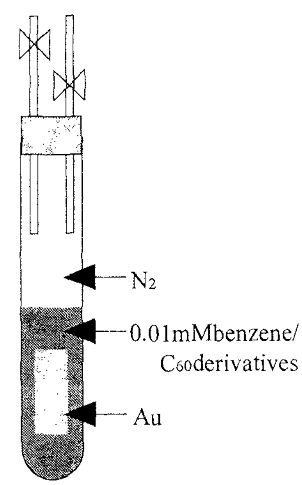


Fig .2 Schematic equipment for a SAM preparation.

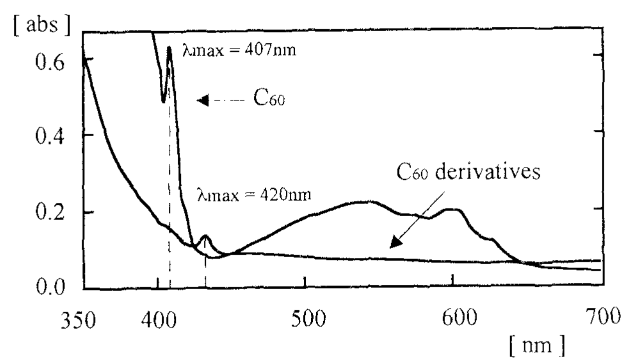


Fig. 4 Optical absorption spectrum of C_{60} derivatives and pure C_{60} in 0.01mM benzene solution.

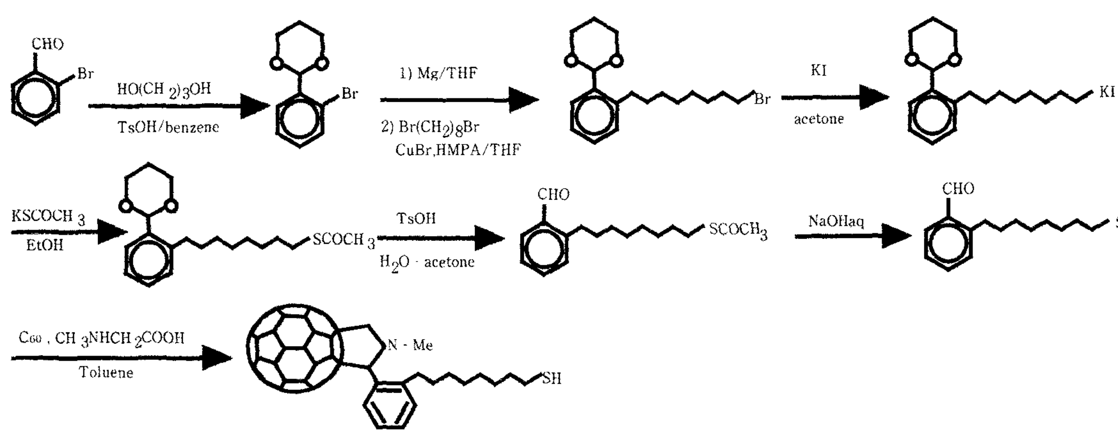


Fig .3 Schematic process of synthesis reactions of C_{60} derivatives.

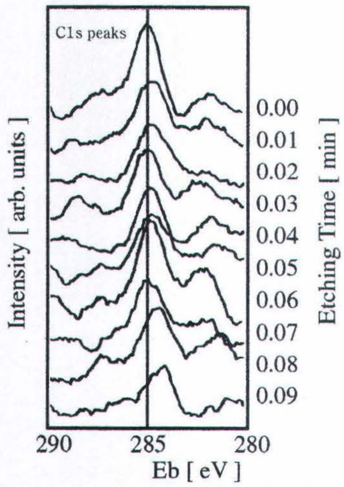
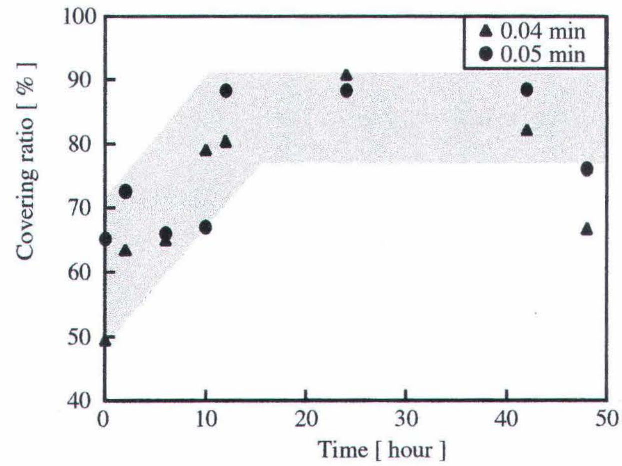
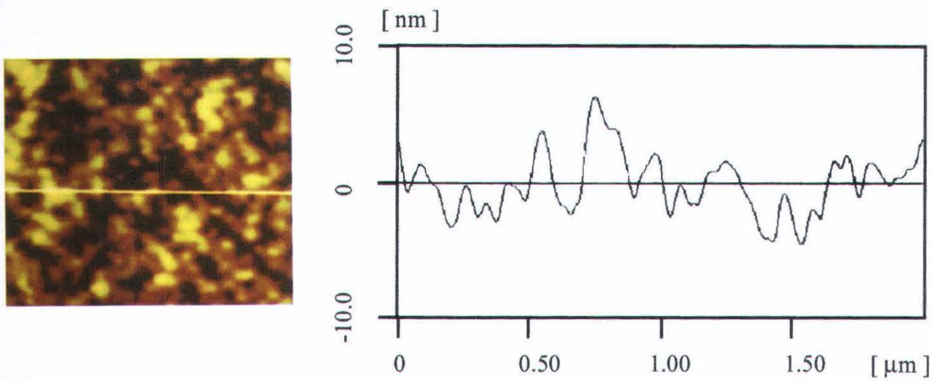


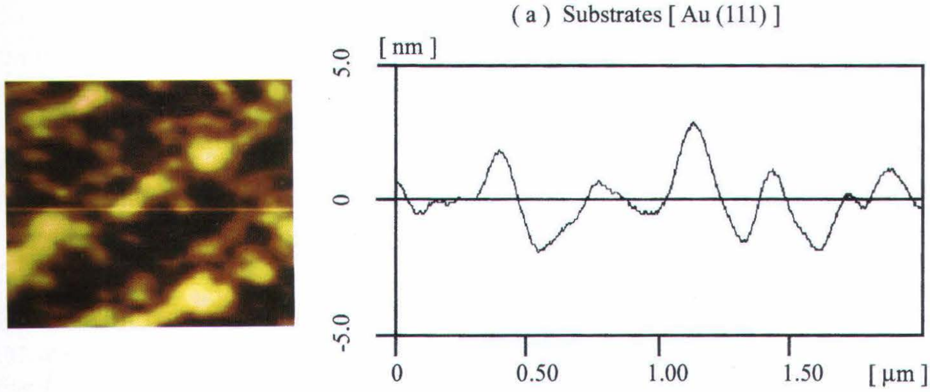
Fig .5 (a) Depth profile of XPS C_{1s} spectrum of the SAM soaked 42hr.



(b) Covering ratio of SAM denied as peak intensity of C_{60} of SAM to that of evaporated C_{60} thin film vs. soaking time. Date of etching time 0.04min ▲ ,and 0.05min ●.



(a) Substrates [Au (111)]



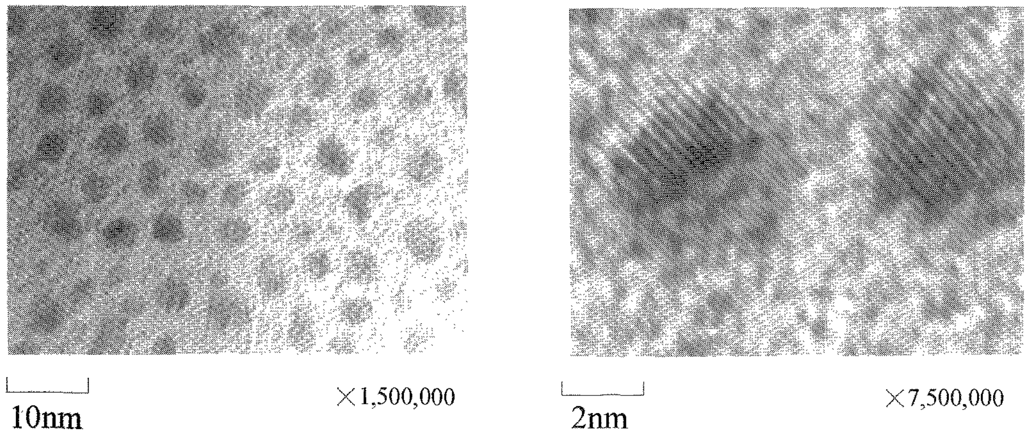
(b) Specimen film soaked for 15hr

Fig. 6 AFM images of surfaces and line profiles of undulation.

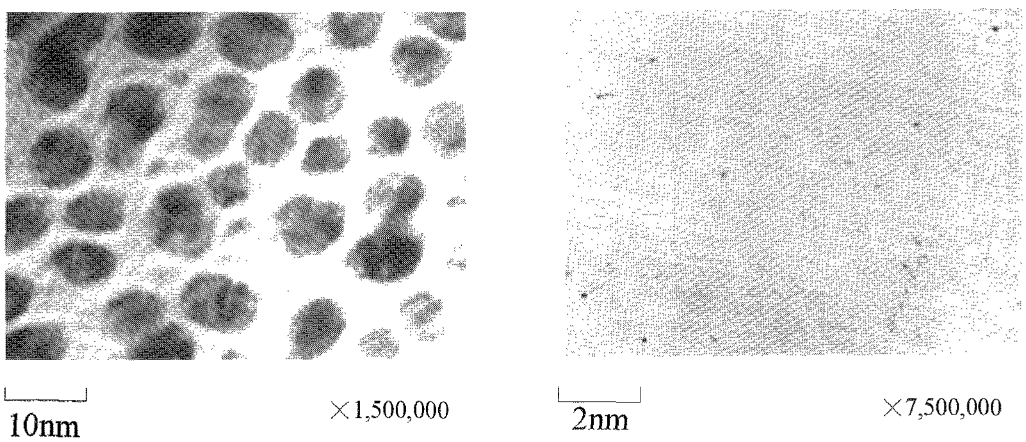
AFM observation. Since the full length of the C_{60} derivatives is a few nm, the surfaces also may become more smooth by derivatives adsorptions.

3.3 Observation of SAM on Au by TEM

As a substrate an ultrathin Au film was deposited by sputtering on collodion meshes for TEM observations. Figure 7 (a) shows TEM photographs of the SAM by soaking for 15hr. Islands of Au with the size of about 3nm were observed. It was noticed that interference fringes like a moire pattern appeared on some Au islands. The observed interval of fringes was about 0.25nm. When a lattice distance of C_{60} derivatives is almost integral multiples of that of Au, the interval of the moire fringes is



(a) Au islands coated by SAM soaked for 15hr.



(b) Au islands as a substrate.

Fig. 7 TEM photographs.

considered Au lattice distance, 0.25nm. For the comparison TEM photographs of non-soaked substrate are shown in Fig. 7 (b), only Au islands were observed without any interference fringes.

These results of TEM observations indicate that some kinds of ultrathin films exactly covered on Au substrates.

4. Conclusion

The SAM of C_{60} derivatives was prepared and its structures were studied. The covering ratio of C_{60} derivatives was evaluated from the C_{1s} XPS peak intensity and the ratio was saturated in the specimens soaked for about 15hr. The surface undulations of the AFM images were changed after the SAM process. Characteristic moire - image interference fringes were observed on Au islands after the formation of SAM. Conclusively obtained results suggest that the self-controlled adsorption , the SAM process was achieved on Au in benzene solution of C_{60} derivatives. We will continue to obtain molecular TEM images and also to measure electronic conductivity of the SAM.

Acknowledgments

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