

Kelvin probe study of energy level bending at interface of solution-processed alkyl-substituted phthalocyanine thin film and n-Si substrate

Ryo Ishiura¹, Akihiko Fujii¹, Makoto Arita², Koichi Sudoh³ and Masanori Ozaki¹

¹ Graduate School of Engineering, Osaka Univ.

2-1 Yamada-oka, Suita, Osaka 565-0871, Japan

² Faculty of Engineering, Kyushu Univ.

744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan

³ The Institute of Scientific and Industrial Research, Osaka Univ.

8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

E-mail: afujii@opal.eei.eng.osaka-u.ac.jp

Abstract

Surface potential of solution-processed thin films of 1,4,8,11,15,18,22,25-octahexylphthalocyanine (C6PcH₂) on n-Si substrate were studied by using scanning probe microscope, and the interface properties of organic/inorganic semiconductors were discussed. The molecular step and terrace structure due to the stacking columns of C6PcH₂ was observed on the top surface of the solution-processed C6PcH₂ thin film. Though the difference of the Fermi levels between C6PcH₂ and n-type silicon must be about 0.4 eV, it was found that the surface potential changed depending on the distance from the interface. The changes of the surface potential with a linear and non-linear relations were discussed by taking the vacuum level shift and impurity carriers into consideration.

1. Introduction

Organic semiconductors are expected to be applied to lightweight and flexible electronic devices by using solution processes on plastic substrates [1]. In device applications, such as organic transistors and organic light-emitting diodes, carrier injection from the electrode is indispensable for the normal operation, therefore, it is significant to clarify the fundamental properties of the organic semiconductor/electrode interface [2]. Though the interface properties of vacuum-evaporated organic semiconductor thin film/electrode was reported [3], those of solution-processed organic semiconductor thin film with electrode still remain to be clarified.

C6PcH₂ is an organic semiconductor material exhibiting liquid crystallinity and solubility in organic solvents. C6PcH₂ molecules form a columnar structure in a self-organizing manner, and exhibit high carrier mobility in the column axis direction [4]. In addition, C6PcH₂ single-crystalline thin film fabrication on a substrate by solution process is possible, and the electronic device application was reported [5]. The electrical contact at the interface of C6PcH₂ thin film fabricated by solution process and the electrode in the electronic device should be important for understanding the device performance.

In this study, we investigated the surface potential of solution-processed C6PcH₂ thin film on phosphorus-doped n-type silicon (n-Si) substrate instead of an electrode by using Kelvin probe force microscope (KFM), and the surface

potential change depending on the distance from the interface of C6PcH₂/n-Si was discussed.

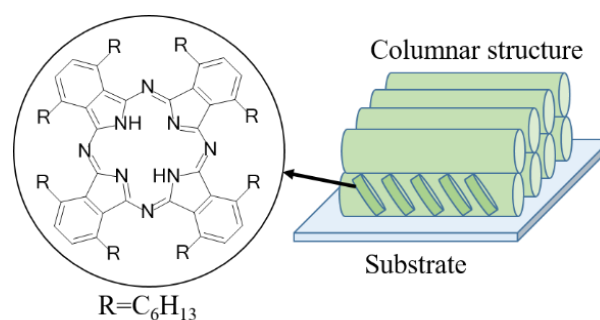


Fig. 1 Molecular structure of C6PcH₂ and schematic drawing of molecular orientation on the substrate.

2. Experimental

Figure 1 shows the molecular structure of C6PcH₂, and the schematic drawing of molecular orientation on a substrate. C6PcH₂, which was synthesized and purified as reported [1], was used in this study. An n-Si substrate (Silicon Technology Co., Ltd.) was prepared by removing a thermal oxide layer of about 300 nm in thickness by treating 55% hydrogen fluoride for 1 minute and then washing with distilled water for 10 seconds three times.

C6PcH₂ solutions were prepared at the concentrations of 40 mg/L and 10 g/L using chloroform as a solvent. Then, the C6PcH₂ solution was cast on the n-Si substrate and spontaneously dried to be the C6PcH₂ thin film. In the case of the thin film made by the C6PcH₂ solution of 10 g/L, a part of C6PcH₂ thin films was removed to expose the surface of the n-Si substrate by wiping with a cotton swab soaked in chloroform.

The surfaces of the n-Si substrate and the C6PcH₂ thin film were observed by the KFM mode of the scanning probe microscope (SPM) (SHIMADZU SPM-9700) to obtain the surface shape and surface potential images. A platinum/iridium coated cantilever (POINTPROBE EFM-20, Nano World) was used for the KFM observation. The scanning range of SPM was 5 μm × 5 μm, and the scanning rate was 0.1 Hz. All processes were performed at room temperature in air.

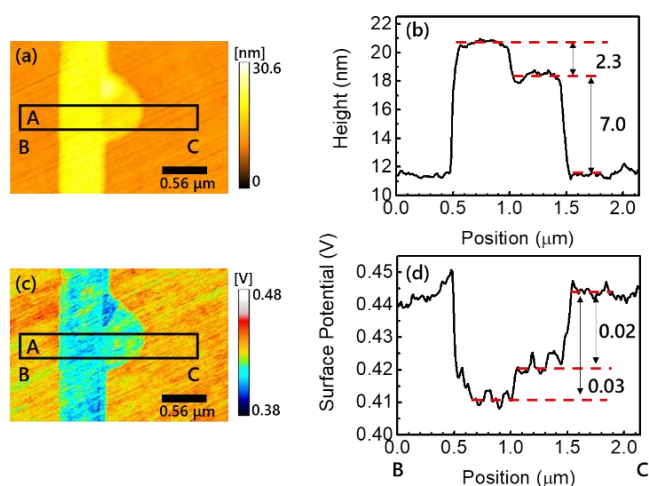


Fig. 2 (a) Atomic force microscopy image (AFM) of the C6PcH₂ thin film, (b) average of line profile of height between B and C in area A, (c) KFM image of the C6PcH₂ thin film, (d) average of line profile of surface potential between B and C in area A.

3. Results and discussion

Figure 2 (a) shows a typical AFM image of the surface of the C6PcH₂ thin film fabricated with the solution of 40 mg/L. Figure 2 (b) shows the average height of the line profile between B and C in the area A in Fig. 2 (a). The rod-shaped microcrystal with the clear terrace and step structure could be found on the n-Si substrate. The minimum step height was estimated to be 2.3 nm. The C6PcH₂ molecule is known to be disk-shaped, and the diameter of the molecular disk is approximately 2.0 nm [6]. The terrace and step structure indicates to be a part of C6PcH₂ single crystal as reported previously [7].

Figure 2 (c) shows the KFM image of the C6PcH₂ thin film. It is noted that the surface potential changed depending on the film thickness of C6PcH₂. Figure 2 (d) shows the average line profile of the surface potential between B and C in the area A in Fig. 2 (c). Although the energy gap between the Fermi levels of C6PcH₂ and n-Si should be approximately 0.4 eV, merely the slight potential difference existed near the interface of the C6PcH₂ and n-Si.

Setting the surface potential of the n-Si substrate as zero, the film thickness dependence of the surface potential of the C6PcH₂ thin film is shown in Fig. 3. As the film thickness increased, the surface potential gap with the n-Si substrate surface markedly increased and became larger than 0.4 V. This potential gap should originate from the difference of Fermi levels between C6PcH₂ and n-Si. Furthermore, the surface potential of the C6PcH₂ thin film exhibited a linear change within about 20 nm in thickness, while a non-linear relationship was exhibited for the thicker film than about 20 nm. The explanations could be given using the vacuum level shift due to the arrangement of interface dipoles [3,8], and band bending due to impurity carriers, such as oxygen [9], respectively.

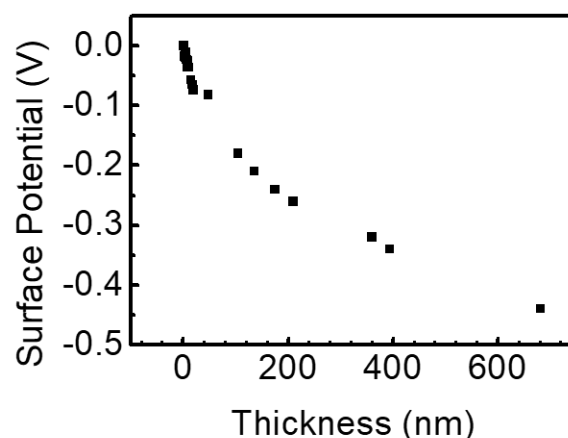


Fig. 3 Film thickness dependence of the surface potential of the C6PcH₂ thin film on the n-Si substrate.

4. Conclusions

The C6PcH₂ thin film prepared by solution process on an n-Si substrate was observed by using KFM, and the n-Si/C6PcH₂ interface properties were discussed. The surface potential gap between the C6PcH₂ thin film and the n-Si substrate increased as the film thickness increased, and became larger than 0.4 V. The linear and non-linear relationships were interpreted by the vacuum level shift and band bending, respectively.

Acknowledgements

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