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Organized Assembling and Characterization of Monolayer Film Based on α -Terthiophene

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A self-assembled monolayer has been fabricated by assembling (2, 2'; 5', 2"-terthiophene)-5-carboxylic acid (TTPCA) on a n-Si wafer (111). The formation of the self-assembled film (TTPCp/n-Si) was characterized by advancing contact angle, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The film possesses a higher SPV response.

Keywords: α -Terthiophene; n-Si wafer; Cp; self-assembled film

INTRODUCTION

Parent thiophene oligomers H-Tn-H ($T=C_4H_2S$, $2 < n < 12$) and their derivatives have attracted more and more scientist's attention^[1-2], because they have better processing ability than polythiophenes. Especially in the field of electronic, they have been extensively investigated as building blocks for the development of novel materials like light-emitting-diode, various sensors, and coatings of electric prints. However, the performances of their

memory and storage have been a little reported. Lately, we constructed a new assembling system in which mono-carboxylized oligothiophene was linked to n-silicon wafer through alkoxyl silane. It is suggested that the monolayer film with organized structure might have high data storage ability. Here, we mainly present the assembling and the characterization of the film.

EXPERIMENTAL

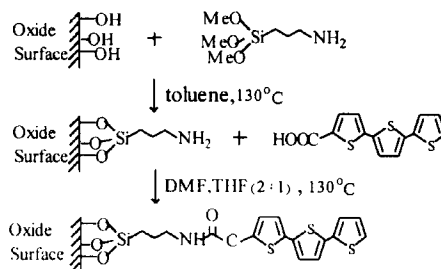
Chemicals and solvents were purchased from Aldrich Chemical Co. and Tiantai Fine Chemical Industry Co. All solvents were dried and then distilled before used, unless otherwise noted.

For assembling, TTPCA was firstly synthesized upon the method reported elsewhere^[3-4]. A silicon wafer was cleaned and treated according to the classical method to get an oxide layer^[5]. Then, the silicon wafer was put in dried toluene containing 0.1M 3-aminopropyltrimethoxysilane to reflux for 5 h at 130°C to form a coupling layer (Cp). Cp/n-Si formed was deal with sonication in neat toluene, rinsed with acetone and dried in air. At last, a monolayer of TTPCA was covalently attached to the Cp coupling layer by refluxing with 0.69 mM TTPCA in dried DMF and THF (v:v = 2:1) for 3 days at 130°C. After cooled, the obtained self-assembled film (TTPCp/n-Si) was cleaned by sonication in neat DMF/THF (2:1) and was thoroughly rinsed with acetone and then dried in air.

RESULTS AND DISCUSSION

The formation of self-assembled monolayer is summarized in Scheme 1.

Scheme 1



The formation of Cp layer on the n-Si and TTPCp monolayer can be characterized by the change in advancing contact angle $\theta_a(\text{H}_2\text{O})$. It is found that the $\theta_a(\text{H}_2\text{O})$ increased with n-Si (30.6°), Cp/n-Si (47.5°), and TTPCp/n-Si (49.3°) in turn. This is attributed to different hydrophobic ability of HO-groups on SiO_2 layer, $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{-}$ of Cp, and $\text{C}_4\text{H}_3\text{S}(\text{C}_4\text{H}_2\text{S})_2\text{-}$ of terthiophene. XPS can also give a difference between before and after joining TTPCA to Cp/n-Si. Elements identified by XPS are C(1s), N(1s), O(1s), Si(2p) for Cp/n-Si and C(1s), N(1s), O(1s), Si(2p), S(2p) for TTPCp/n-Si, here a signal of element sulphur (S_{2p}) emerges in XPS of TTPCp/n-Si which doesn't show up in that of Cp/n-Si. An AFM was employed to investigate the surface morphology of oxide layer (Fig. 1), Cp layer (Fig. 2) and TTPCp film (Fig. 3) on the silicon substrate. The results reveal that the Cp layer and TTPCp film have two-dimensional order in micron grade area. These differences indicate that the TTPCA was joining to the n-Si wafer, too. The results of SPV (Fig. 4) reveal that SPV response of TTPCp/n-Si is similar to that of TTPCA in the scanning range of $450 \sim 300 \text{ nm}$, but, the response intensity at 390 nm is greatly raised to about 600 folds compared to that of TTPCA. The increase of SPV response is another proof that the TTPCA was joining to the n-Si wafer.

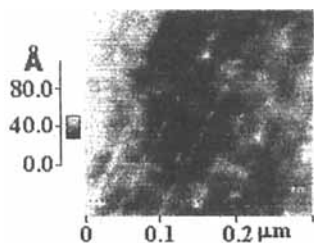


FIGURE 1. AFM image of n-Si wafer.

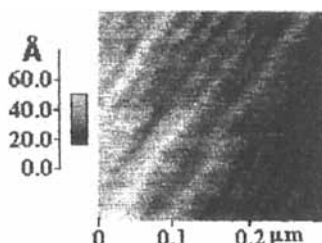


FIGURE 2. AFM image of Cp/n-Si.

See Color Plate II at the back of this issue. See Color Plate III at the back of this issue.

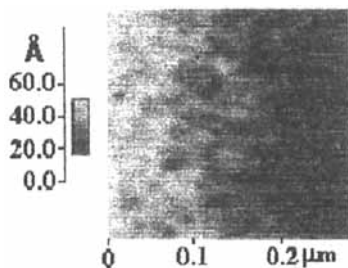


FIGURE 3. AFM image of self-assembled film TTPCp/n-Si.

See Color Plate IV at the back of this issue.

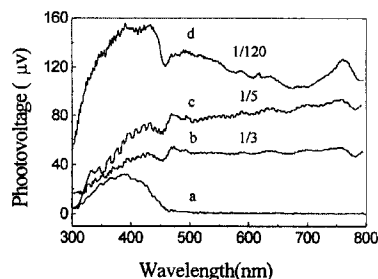


FIGURE 4. SPS of (a) TTPCA, (b) Cp/n-Si, (c) n-Si wafer, (d) TTPCp/n-Si.

Acknowledgements

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