

Synthesis and interfacial charge separation of the hetero-structured self-assembly of an α -terthiophene derivative covalently bonded on *p*-silicon

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Abstract

An inorganic/organic hetero-structured self-assembly (α -3TCp/*p*-Si) has been fabricated by covalently coupling (2, 2' : 5', 2''-terthiophene)-5-carboxylic acid (α -3T) on a *p*-type silicon wafer (111, *p*-Si) by means of a silane-based coupling agent (Cp). Its formation was proved by the changes in static contact angles and X-ray photoelectron spectra (XPS). Interfacial electron transfer of α -3TCp/*p*-Si was studied by surface photovoltage (SPV) spectroscopy. The results indicate that α -3TCp/*p*-Si possesses rather high SPV response intensity in comparison with that of an analogue self-assembly of α -3T/*p*-Si prepared through the LB technique, i.e. a direct adsorption method. This implies that high charge transfer effect can be generated at the interfaces of the organic layer α -3TCp and *p*-type silicon. The reason for that was explained through an energy band model. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Terthiophene derivative; *p*-Silicon; Hetero-structured materials; Self-assembling monolayer

1. Introduction

There is a continually growing interest in oligomers of polythiophenes due to their special optoelectronic sensitivity. The oligomers have found many applications in electronic devices as components, such as light emitting diodes and field-effect transistors, and various chemical sensors [1–3]. Properties of these devices appear to be comparable to those achieved by polythiophenes. However, attachment and organization of oligothiophenes onto a solid surface to form functional hetero-structured assemblies is a problem of its own, because of low molecular orientation and low adhesion. So far, none of chemical vapors deposition (CVD) method, Langmuir–Blodgett technique (LB), spin-coating method, and dip-coating technique, is capable of building such assemblies with good attachment to substrates. Molecular self-assembling provides us with a good chance to anchor oligothiophenes onto solid substrates. Specially, the preparation of chemisorbed monolayers, regarded as an extension of physisorbed ones [4], is beneficial to construction of ever

more complex molecular structures (i.e. superlattices and monolayers) and stable assemblies on the solid surfaces by the making of covalent bonds in a controlled and precise fashion. Some of the techniques, such as monolayer building methods, the assembling of organosulphur on metals as well as of alkyl and organosilicon derivatives on silicon, have been discussed elsewhere [5,6]. With respect to the construction of *p*(*n*)-hetero-structured semiconductor materials, monolayers of organosilicon derivatives on silicon surface are probably one of the most studied self-assembling monolayers to date [7–14], since versatile self-assemblies can be obtained by surface chemical reactions of the end-substituted alkyl derivatives of the organosilicons with functional compounds.

In this paper, we present a new organic/inorganic hetero-structured self-assembly (α -3TCp/*p*-Si) fabricated by assembling mono-carboxylized α -terthiophene (α -3T) onto a *p*-silicon wafer (*p*-Si) by means of alkylaminosilane (Cp). Measurements of surface photovoltage (SPV) spectra show that illuminating the self-assembly, its SPV response intensity at 390 nm is 460 times higher than that of an analogue self-assembly of α -3T monolayer on *p*-Si (α -3T/*p*-Si) formed by the LB technique. An energy band model has

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been built up to illustrate this photoinduced charge transfer. We anticipate that the self-assembly α -3TCp/*p*-Si might be used as materials in optoelectronic devices.

2. Experimental

2.1. Preparation of the self-assembly α -3TCp/*p*-Si

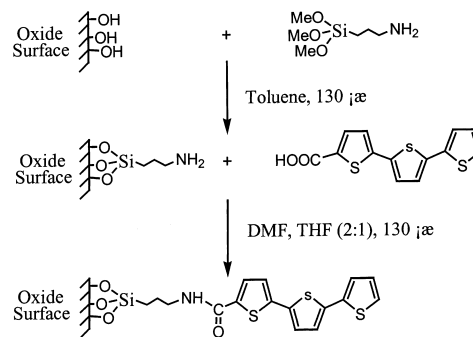
Chemicals and solvents were purchased from Aldrich and Tiantai Fine Chemical Industry. All solvents were dried and then distilled before use, unless specially mentioned. (2, 2': 5', 2''- Terthiophene)-5-carboxylic acid (α -3T) was synthesized according to a method reported in detail elsewhere [15]. *p*-Type silicon wafer (111, *p*-Si) from the Color Metal Institute of the Chinese Sciences Academy was pretreated according to an RCA method [16]. SiO₂ layer with OH groups was generated on the *p*-Si by an oxidation method with H₂SO₄/H₂O₂ [17,18].

A coupling layer (Cp) was formed by putting the pretreated *p*-Si in an anhydrous toluene solution containing 0.10 mol/l of 3-aminopropyltrimethoxysilane [(CH₃O)₃Si-(CH₂)₃NH₂] and refluxed at 130°C for 5 h, before it was transferred into neat toluene and cleaned by sonication four times for 2 min each. The Cp/*p*-Si formed was rinsed with acetone and then dried in air. A typical static contact angle θ_a (H₂O): *p*-Si, 41.8°; Cp/*p*-Si, 57.8°. Elements identified by X-ray photoelectron spectroscopy (XPS): C_{1s} = 284.6 eV, N_{1s} = 400.1 eV, O_{1s} = 532.6 eV, Si_{2p} = 103.2 eV.

It was found that α -3T was linked onto Cp/*p*-Si by refluxing Cp/*p*-Si in an anhydrous mixture solution of DMF/THF (volume ratio = 2 : 1) containing α -3T (0.69 mmol/l) for 3 days at 130°C. After cooling, the obtained self-assembly (α -3TCp/*p*-Si) was cleaned by sonication four times for 2 min. each in neat DMF/THF (2 : 1) and thoroughly rinsed with acetone and then dried in air. A typical static contact angle θ_a (H₂O) for α -3TCp/*p*-Si is 59.4°. Elements identified by XPS: C_{1s} = 284.6 eV, N_{1s} = 399.3 eV, O_{1s} = 532.6 eV, Si_{2p} = 102.6 eV, S_{2p} = 167.8 eV.

2.2. Measurements of cyclic voltammetry and surface photovoltage spectroscopy (SPS)

Cyclic voltammetric measurement was carried out on a model 79-1 voltammetric analyzer (Jinan Fourth Instrument Plant, China). Cyclic voltammetric curves were recorded on a model TYPE-3086 recorder (Yokogana Hokuskin Electric, Tokyo, Japan). A three-electrode cell consisting of a glass-carbon working electrode with a diameter of 3.0 mm, a platinum counter electrode with a large surface area, and a reference electrode, i.e., Ag⁺/Ag electrode (0.01 mol/l AgNO₃ in acetonitrile CH₃CN). LiClO₄ (0.1 mol/l) was used as the electrolyte. The potential of Ag⁺/Ag reference electrode vs. normal hydrogen electrode (NHE) was deter-



Scheme 1. Self-assembling process of α -3TCp/*p*-Si.

Table 1
X-ray photoelectron spectra (XPS)

XPS (eV)	O _{1s}	Si _{2p}	C _{1s}	N _{1s}	S _{2p}
<i>p</i> -Si	532.6	103.2			
Cp/ <i>p</i> -Si	532.6	103.2	284.6	400.1	
α -3TCp/ <i>p</i> -Si	532.6	103.3	284.6	400.1	167.8

mined where an acetonitrile solution of ferrocene as positioner was employed. The solution was deoxidized by high pure argon gas before measurement.

SPS was obtained through a surface photovoltaic spectrometer. A photovoltage cell, ITO/sample/ITO, was used, where two pieces of ITO glass were utilized as the top and bottom electrodes. We used a light source-monochromator-lock-in detection technique. The principle has been described in detail elsewhere [19–24].

3. Results and discussion

3.1. Self-assembling of α -3TCp/*p*-Si

A general procedure of assembling α -3T monolayer onto a *p*-Si wafer by means of alkylaminosilane coupling layer Cp is summarized in Scheme 1. It shows that the assembling process can be divided into two steps. First, Cp is bound to a silica layer with OH groups, which was obtained by oxidizing the *p*-Si with H₂SO₄/H₂O₂, via a methoxy replacement reaction to form the Cp/*p*-Si. The formed siloxane with amino group is capable of providing α -3T monolayer to be assembled with not only chemical and structural stability but also relatively structural regularity. Second, α -3T is anchored on the Cp/*p*-Si via an acylation reaction so that α -3TCp/*p*-Si assembly is constructed.

The formations of Cp and α -3TCp monolayer on the *p*-Si were firstly followed by measurements of XPS. Table 1 shows the differences between the states of the monolayer before and after joining α -3T to Cp/*p*-Si with reference to the pure *p*-Si wafer. It can be seen that, in the XPS of silica, there are two signals of element oxygen (O_{1s} = 532.6 eV) and silicon (Si_{2p} = 103.2 eV). After Cp coupling, two ad-

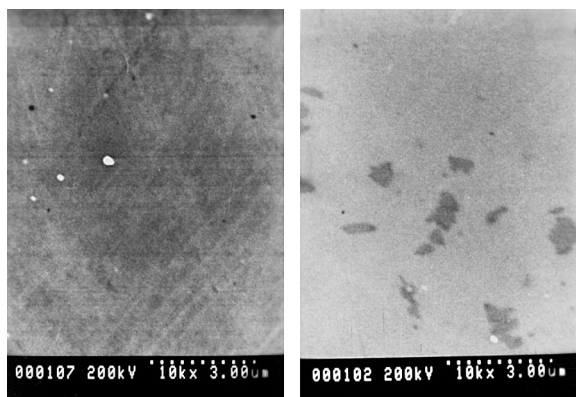


Fig. 1. SEM images (A: Cp/*p*-Si, B: α -3TCp/*p*-Si).

ditional peaks emerge at 284.6 and 400.1 eV. They are attributed to the incorporation of element carbon (C_{1s}) and nitrogen (N_{1s}). This demonstrated the success of bonding Cp onto the *p*-Si. Moreover, the emergence of signal of element sulphur ($S_{2p}=167.8$ eV) shows the formation of the self-assembly α -3TCp/*p*-Si.

Another evidence is the changes in static contact angles, θ_a (H_2O), after Cp and α -3TCp were coupled. It is found that the static contact angles increase with *p*-Si (41.8°), Cp/*p*-Si (57.8°), and α -3TCp/*p*-Si (59.4°) in turn. This can arise from the different hydrophobic ability of HO- groups on SiO_2 layer, $NH_2CH_2CH_2CH_2-$ of Cp, and $C_4H_3S(C_4H_2S)_2-$ of terthiophene.

A small difference in the contact angles between Cp/*p*-Si (57.8°) and α -3TCp/*p*-Si (59.4°) can be noticed, however. It is suggested that there is an assembling defect that was produced by jointing α -3T onto Cp/*p*-Si. SEM image of self-assembly α -3TCp/*p*-Si. (Fig. 1(B)) verifies this point. In the image, some black domains exist in the white substrate. Due to the difference of the height between α -3TCp and Cp on the *p*-Si, the black domains are regarded as Cp, and the white ones as α -3TCp, since no obvious defects were observed in the SEM image of Cp/*p*-Si (Fig. 1(A)). Therefore, it can be concluded that the assembling defect is brought about by the incomplete acylation of the end-substituted amino group of silane with α -3T.

3.2. Interfacial charge separation of the self-assembly α -3TCp/*p*-Si

On account of the different forbidden band gaps of α -3T and *p*-Si, a barrier forms between their interfaces. When illuminating the self-assembly α -3TCp/*p*-Si, the photogenerated electron-hole pairs are separated under the effect of the barrier and flow to individual opposite directions through Cp, so that a potential is produced. The phenomena of photovoltage polarity, i.e. interfacial charge separation, can be demonstrated by surface photovoltage spectra (SPS).

SPS of the pure α -3T (a) and bare *p*-Si (b), and the self-assembly α -3TCp/*p*-Si (c) are depicted in Fig. 2, and

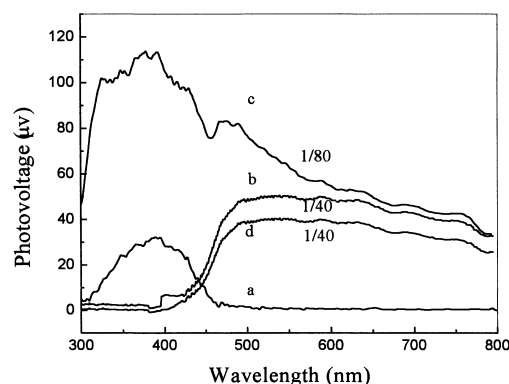
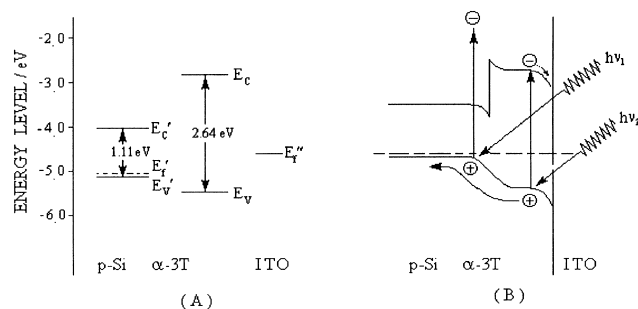


Fig. 2. Surface photovoltage spectra of (a) pure α -3T, (b) bare *p*-Si wafer, (c) α -3TCp/*p*-Si, and (d) α -3T/*p*-Si.



Scheme 2. (A) Energy level positions of *p*-Si, α -3T and ITO, (B) Energy band model for the self-assembly α -3TCp/*p*-Si.

the surface photovoltage (SPV) response intensity of *p*-Si and α -3TCp/*p*-Si is reduced forty- and eighty-folds of the original ones. In comparison, a self-assembly α -3T/*p*-Si (d) prepared by the LB technique (i.e. the physical adsorption method) is also given. It can be seen that SPS of α -3T/*p*-Si is basically identical with that of the *p*-Si. Their absorption bands emerge in the range of 800–450 nm. This implies that the interfacial charge separation generated in the self-assembly α -3T/*p*-Si can be ignored. It is surprising that the SPV response intensity of the self-assembly α -3TCp/*p*-Si is about 460-fold of that of α -3T/*p*-Si at 390 nm, and is similar to that of *p*-Si or α -3T/*p*-Si in the range of 800–450 nm.

In an effort to illustrate this electron transfer behaviour of α -3TCp/*p*-Si, an energy band mold was built-up on the basis of HOMO and LUMO and also Fermi levels of ITO glass [24–25], *p*-Si [26–29], and α -3TCp (Scheme 2(A)). Here, we assume that the pure α -3T and α -3TCp possess analogue energy levels and band bends. Thus, HOMO and LUMO and also the direction of band bend of α -3TCp can be replaced by α -3T and determined by means of the corresponding cyclic voltammetry (Fig. 3.) and electric-field-induced surface photovoltage spectra (Fig. 4. EFISPS), respectively.

In Fig. 3, a single peak, i.e. electrodynamic potential (E^{ox}) of α -3T vs. Ag^+/Ag electrode, occurs at +0.25 V. It is known that Ag^+/Ag reference electrode vs. normal hydrogen electrode (NHE), and 0 V of NHE vs. vacuum energy

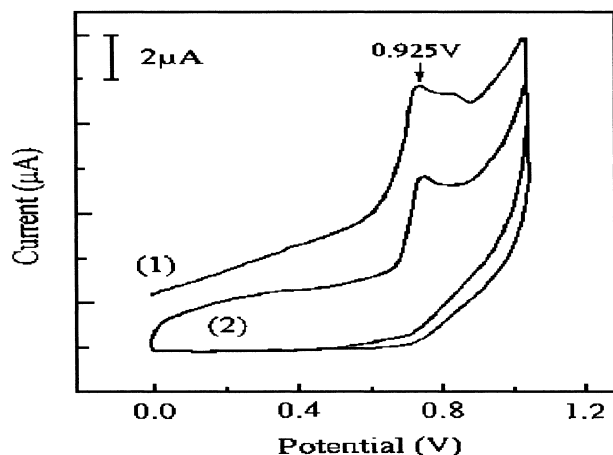


Fig. 3. Cyclic voltammetric current response vs. potential for α -3T (Scanning rate: 50 mV/s).

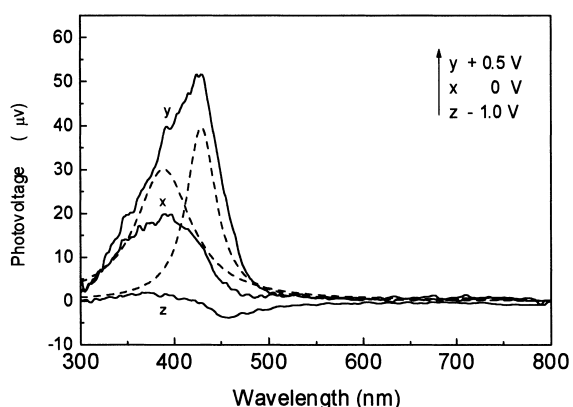


Fig. 4. Electric-field-induced surface photovoltage spectra (EFISPS) of α -3T: x, 0 V; y, +0.5 V; z, -1.0 V.

level (VEL) are +0.1125 V and -4.44 eV, respectively. Thus, HOMO energy level (Ev), i.e. E^{ox} vs. VEL, is -5.48 eV. Additionally, EFISPS (Fig. 4) shows that the SPV response intensity of α -3T increases as an external field of +0.5 V is applied, but it decreases as that of -1.0 V is applied. Based on the principle of surface photovoltage spectroscopy, it can be concluded that Fermi level (E_f) of α -3T should be lower than that of ITO glass and the band bend of α -3T on the illuminated interface between α -3TCp and ITO should be downward. LUMO energy level of α -3T (-2.84 eV) can be obtained by a simple additivity of HUMO (-5.48 eV) and band gap (2.64 eV) emerging at 470 nm in curve (x) of Fig. 4.

By using such a model, the enhancement of the SPV response intensity of α -3TCp/ p -Si can be explained as follows. When the self-assembly α -3TCp/ p -Si was irradiated with light of 800–450 nm, α -3TCp layer did not generate electron transition. But, monochromatic light is able to pass through the α -3TCp layer and illuminate the surface of p -Si wafer. Therefore, the electrons in the valence band (E_v') of p -Si were excited into the higher energetic level above conduction band (E_c'). Next, some of these electrons might pass through the hetero-structured interface into the conduction

band (E_c) of α -3TCp and then fly to the surface of ITO. Some electrons flew to the hetero-structured interface between p -Si and α -3TCp along the E_c' of p -Si. Other electrons recombine with the holes on the E_v' of p -Si. The holes were left in the E_v' of the p -Si. Consequently, some of the photogenerated electron-hole pairs were separated from each other, which resulted in the generation of the photovoltaic response signal of α -3TCp/ p -Si in the range of 800–450 nm.

When the self-assembly was irradiated with the light of 450–300 nm, the electrons in the valence band (E_v) of α -3TCp were excited to the E_c , and then flew into the surface of ITO. Simultaneously, the photogenerated holes were transferred into the body of the p -Si along band bend, whereas the electrons in the E_v' of the p -Si passed through the hetero-structure and flew into the E_v of α -3TCp. The relative movement of the electron-hole pairs supplied enough electrons into the valence band of α -3TCp and led to an obvious increase in the rate of electrons injecting from the valence band to the conduction band of α -3TCp. The photogenerated electrons getting to the surface of ITO glass were increased, too. Therefore, the SPV response intensity of self-assembly α -3TCp/ p -Si was increased close to 460 times in the region of 450–300 nm, compared with that of α -3T/ p -Si.

4. Conclusions

α -3T has been covalently assembled on the surface of a p -Si wafer with a silica layer by means of a coupling agent $[(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{NH}_2]$ to form a self-assembly α -3TCp/ p -Si. The assembling process was accomplished by a two-step method, namely methoxy replacement reaction of siloxane with OH groups on the silica layer as well as an acylation reaction of α -3T with the amino groups of the coupling agent. SPS shows that the SPV response intensity of α -3TCp/ p -Si is increased 460 times in comparison with the LB assembly α -3T/ p -Si at 390 nm. Based on the HOMO and LUMO and also Fermi levels of ITO glass, p -Si and α -3T, an energy band model for the self-assembly was set up. It is suggested that the enhancement of the SPV response intensity of the self-assembly is caused by the generation of interfacial charge transfer between the surfaces of the p -Si wafer and α -3TCp monolayer. The flow of the formed electrons and holes provides abundant electrons to the valence band of α -3TCp. Furthermore, much more electrons were excited to its conduction band, so that the extent of the interfacial charge separation is greatly increased.

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