

Preparation of a Hole-Transport Layer Tethered to ITO Surface via a Self-Assembled Monolayer Having Reactive Terminal Group

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Abstract

Interface characteristics between a polymer and an indium-tin oxide (ITO) was controlled by forming covalent chemical bonds at the interface through self-assembled monolayers (SAMs) having reactive terminal groups. It was suggested that the hole injection from ITO to a hole-transport polymer can be improved by chemically tethering the interface.

1. Introduction

Notwithstanding the rapid development of organic semiconductors, these materials still suffer from thermal and interfacial instabilities because of the weak intermolecular forces inherent to organic materials. The thermal instability can be alleviated by using polymeric materials instead of small molecules. We have used a vapor-deposition polymerization method by evaporating small molecules to form stable polymer thin films on the substrate. This can be achieved by depositing vinyl or acryl derivatives of functional molecules under assistance of electron or UV irradiation. Thermal activation is also possible to initiate the polymerization of deposited monomers [1]. On the other hand, chemical bonding at the interface can be achieved by utilizing SAMs that have a reactive terminal group. It was found that an azo-terminated SAM is effective in initiating polymerization reaction, improving thermal stability, and enhancing charge injection at the interface [2].

This report investigates the effect of different SAMs for the formation of a hole-transporting layer (HTL) on the surface of an ITO electrode. SAMs having benzophenone, epoxide, and vinyl terminal groups were prepared on ITO surface, on which a divinyl derivative of an aromatic amine was deposited with a purpose to obtain a covalently tethered HTL layer.

2. Experimental Procedure

Figure 1 shows the chemical structures of the molecules used in this experiment. On the surface of ITO, SAMs having terminal groups of epoxide (GPS-SAM), benzophenone (BP-SAM) and vinyl groups (VTMS-SAM) were prepared. The GPS-SAM was formed by dipping the ITO substrate into a 5 mM toluene solution of 3-glycidoxypropyl trimethoxysilane. The BP-SAP was obtained by immersing the GPS-SAM into a 20 mM chloroform solution of amino benzophenone for 12 h at

40°C. The VTMS-SAM was obtained by immersing the ITO into 2 mM toluene solution of vinyltrimethoxysilane. Formation of SAMs was characterized by the contact angle measurement and ellipsometry.

On these surfaces, the HTLs were prepared by vapor-depositing *N,N'*-diphenyl-*N,N'*-bis (4-vinylphenyl) benzidine (DvTPD) to a thickness of 100 nm, and then thermally annealing at 100 to 200°C for 1 h in vacuum. For comparison, a HTL was also prepared by depositing DvTPD on a bare ITO surface. After the annealing, the films were sonicated in chloroform for 10 min to remove physisorbed molecules, and their surfaces were observed with an optical microscope. The film thickness remaining after the sonication was measured with a scanning probe microscope to confirm the formation of stable polymer thin films that are tethered to the ITO surface.

The electrical property of the ITO/SAM/DvTPD structure was investigated by measuring current-voltage (I-V) characteristic of a hole-only device (HOD) that was prepared by vapor-depositing a silver electrode on the surface of DvTPD layer. In this case, the 100-nm-thick DvTPD layer was used without sonicating in chloroform.

3. Results and Discussion

Formation of SAMs

The bare ITO substrate had a water contact angle of 30°. After forming the SAMs of GPS, BP and VTMS, the contact angle showed a substantial increase to 62°, 63°, and 63°, respectively. SPM observation did not reveal notable

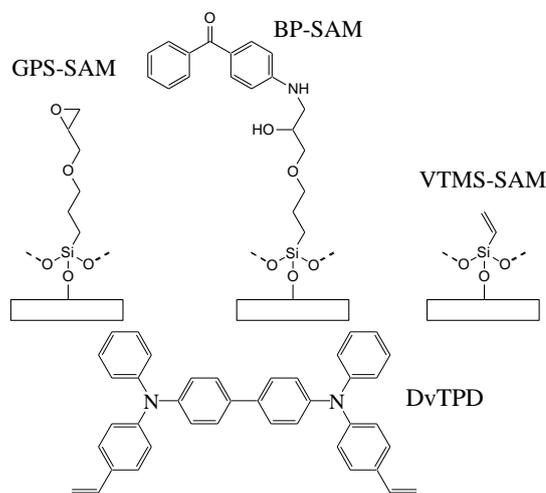


Fig. 1 Molecular structures of SAMs and deposition material.

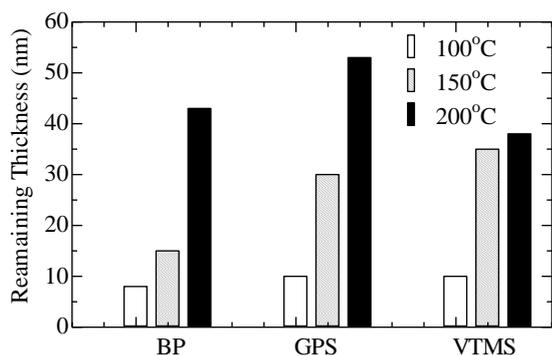


Fig. 2 Thicknesses of DvTPD films that remained after sonicating in chloroform.

structures on the SAM-modified surfaces. The arithmetic average surface roughness R_a of the ITO substrate was 1.2 nm, while those of GPS, BP, and VTMS SAMs were 0.7, 1.1 and 0.8 nm, respectively. The ellipsometric thickness of SAMs obtained by assuming optical constants of $n = 1.45$ and $k = 0$ were 0.50, 1.51, and 0.22 nm for the SAMs of GPS, BP, and VTMS, respectively. These results suggest the formation of uniform SAMs without serious aggregation.

Formation of DvTPD HTL

The monomer film of DvTPD readily dissolves in chloroform. The deposited film was polymerized by annealing at a temperature higher than 100°C. However, the film was easily delaminated from the bare ITO surface by applying ultrasonic agitation. On the other hand, the films prepared on the SAMs showed higher adhesion strength, and were not removed completely by sonicating in chloroform. Figure 2 shows the film thicknesses that remained after sonication of the films annealed at different temperatures on different SAMs. It was observed that 40 to 50-nm thick layers remain without delamination when the vapor-deposited DvTPD films were annealed at 200°C on the SAMs, suggesting covalent tethering of DvTPD polymer films via the SAMs.

Electrical Characterization

We have found that the BP-SAM can tether polymer films spin-coated on its surface, improving the hole

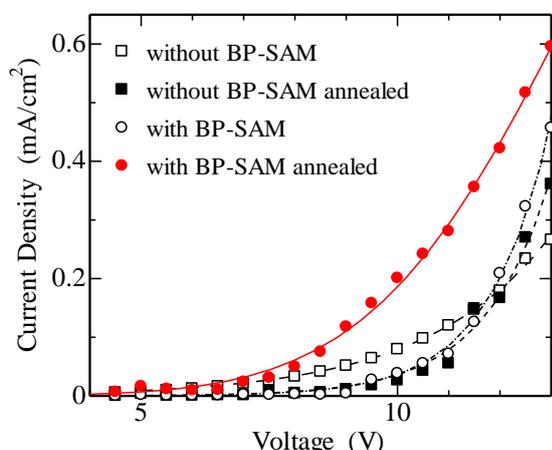


Fig. 3 I-V characteristics of HODs prepared with/without BP-SAM and with/without annealing.

injection from ITO to the polymer layer [3]. A similar improvement in the interfacial characteristics can be expected for the vapor-deposited and polymerized film on the surface of BP-SAM. Figure 3 shows the I-V characteristics of HODs prepared on ITO surfaces with/without BP-SAM and with/without annealing at 200°C. A substantial increase in the current was observed when the film was deposited on BP-SAM and then annealed to activate the chemical reaction.

Figure 4 shows the I-V characteristics of HODs prepared on bare ITO and the surfaces modified with different SAMs. The DvTPD layers were annealed at 200°C. All the HODs having SAMs drew current higher than that without SAM. Moreover, the leakage current in the backward direction was reduced by using the SAMs. Among the three SAMs shown in Fig. 1, the VTMS-SAM gave the highest current, probably due to the length of the SAM molecule is the shortest with VTMS.

4. Conclusions

A HTL tethered to the ITO surface was obtained by vapor-depositing DvTPD monomer on SAMs that have reactive terminals, followed by thermal annealing. The surface-tethered HTL showed strong adhesion to the ITO surface and were not removed by sonicating in a solvent. Moreover, the chemical tethering had a possibility of enhancing hole injection from ITO to the HTL. It was observed that a shorter SAM molecule is more effective from the standpoint of current injection. It can be concluded that the formation of stable covalent bonds can be an effective procedure in controlling the film/electrode interface of organic devices.

Acknowledgement

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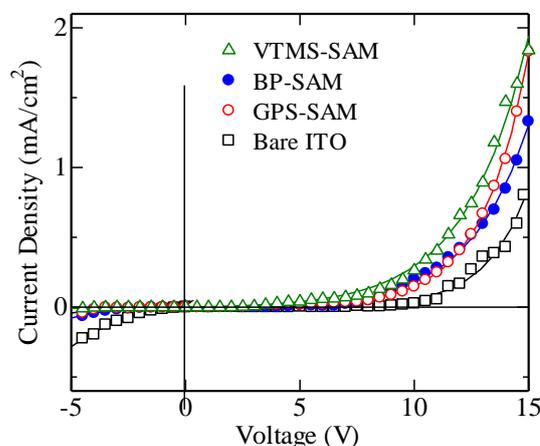


Fig. 4 I-V characteristics of HODs prepared with different SAMs.