

Interface Control between an Electrode and a Hole-Transport Polymer via Self-Assembled Monolayers

Sotaro Ono¹, Satoshi Usui², Kuniaki Tanaka¹ and Hiroaki Usui¹

¹ Tokyo University of Agriculture and Technology
2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan
Phone: +81-42-388-7055 E-mail: h_usui@cc.tuat.ac.jp

² Niigata University
Ikarashi 2-no-cho, Nishi-ku, Niigata 950-2181, Japan

Abstract

ITO surface was modified with self-assembled monolayers (SAMs) having various terminal groups including methyl, vinyl, benzophenone, and azo groups. A hole transport layer of fluorene-phenoxazine copolymer was spin-coated on its surface and then irradiated with UV light to induce photochemical reaction at the interface. It was observed that the SAMs having benzophenone and azo terminal groups have an ability to tether the spin-coated polymer by the UV irradiation. The photochemical tethering was effective in increasing the current flow of hole-only devices prepared with the SAM. It is considered that the covalent tethering can be an effective strategy to improve the interfacial characteristics between the ITO electrode and the hole-transport layer.

1. Introduction

Interface between an inorganic electrode and an organic layer plays important roles in determining characteristics of organic devices. However, the interface between inorganic and organic materials accompanies several problems due to inconsistency in physical and chemical characteristics between these materials. It is reported that some kinds of self-assembled monolayers (SAMs) can alleviate the problems at the organic/inorganic interface by modifying the surface energy of inorganic substrates or by forming dipole layers to shift the apparent work function of the electrode.

On the other hand, there is a possibility to improve the interfacial problems by covalently tethering the interface via a SAM [1]. The covalent bonds are effective not only for improving the adhesion strength of film to the substrate but also for stabilizing the film morphology or improving charge injection at the interface. The covalent tethering has been

achieved by vapor-depositing monomers on a SAM having a function of polymerization initiator [2], or by spin-coating a polymer on a SAM having an ability of photochemical reaction [3]. This paper reports the effect of covalently tethering a spin-coated polymer to an indium-tin oxide (ITO) electrode on the electric characteristics of hole-only devices (HODs).

2. Experimental Procedure

Figure 1 shows structural formula of SAMs investigated in this work. SAMs of triethoxymethylsilane (MTES) and trimethoxyvinylsilane (VTMS) were prepared by immersing the ITO substrates in their 5 mM toluene solutions at room temperature for 12 h. V-BP and V-VAZO SAMs, having reactive terminal groups of benzophenone and azo, were prepared by oxidizing the VTMS SAM and then reacting with 4-aminobenzophenone and 2,2'-azobis(2-amidinopropane), respectively [4].

100-nm-thick thin films of fluorene-phenoxazine copolymer (H5, Fig. 2) were deposited either on a bare ITO or on the SAM-modified ITO by spin-coating. With a purpose to explore the possibility of photochemical tethering, the films were irradiated with UV light from a high-pressure mercury lamp at a power of 45 mW/cm² for 24 h through a photomask. The irradiated films were ultrasonically treated in acetone and in chloroform successively, and the films remaining on the surface were observed by an optical microscope.

For electrical characterization, HODs were prepared in a structure shown in Fig. 2. 100-nm-thick H5 layers were spin-coated on ITO substrates with or without the SAMs, and then irradiated with UV light of 0.6 mW/cm² for 15 min. Silver cathodes of 150-nm thick were deposited on the H5 layers and their current-voltage (J-V) characteristics were measured in air without encapsulation.

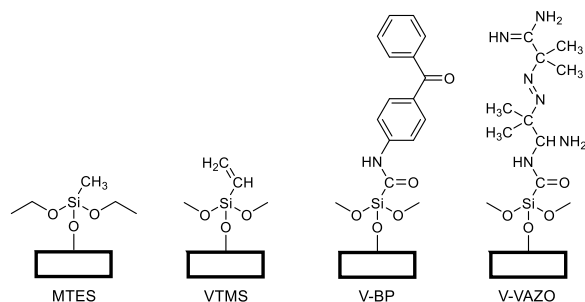


Fig. 1 Structures of SAMs.

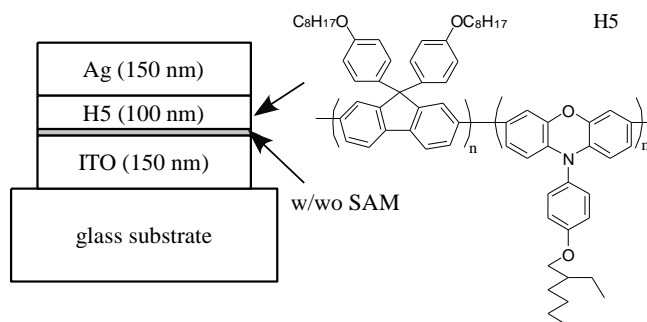


Fig. 2 Structures of H5 polymer and the HOD.

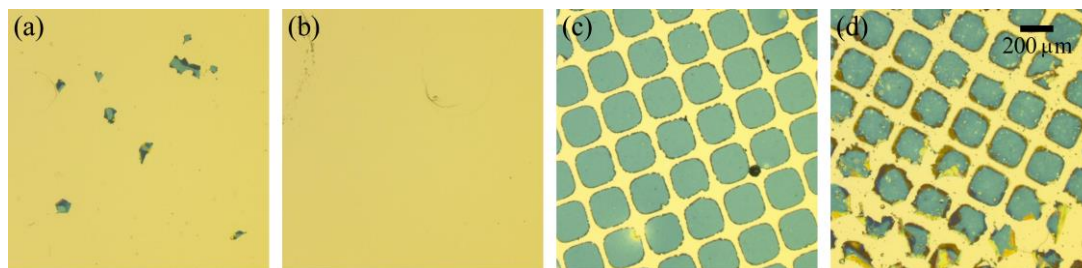


Fig. 3 Optical micrographs of H5 layers after sonicating in organic solvents. The films were deposited on ITO modified with SAMs of MTES (a), VTMS (b), V-BP (c), and V-VAZO (d).

3. Results and Discussion

Tethering via SAM

Bare ITO surface had a water contact angle of 35° , whereas water contact angles of the SAM-modified surfaces were 92° for MTES, 84° for VTMS, 76° for V-BP and 69° for V-VAZO. Films of 1 to 1.6-nm in thickness (assuming refractive index to be 1.4) were detected by ellipsometry on the surface of the SAM-modified ITO. H5 layers were deposited on these surfaces and sonicated in the organic solvents after the UV exposure through a photomask. Figure 3 shows optical micrographs of the H5 layers that remained after the sonication. The films on MTES and VTMS, as well as that on a bare ITO (not shown here), were mostly delaminated by the sonication, while those on V-BP and V-VAZO SAMs developed negative patterns of the photomask, suggesting that the parts irradiated with UV are stably bound to the ITO surface. These results indicate that the SAMs having reactive terminal groups, such as benzophenone and azo units, are capable of covalently tethering the interface between ITO and a polymer layer.

Electrical Characteristics

Figure 4 shows J-V characteristics of HODs prepared on ITO with different SAMs. The characteristics were compared for devices with and without the UV irradiation after spin-coating the H5 layer. The result of a HOD on a bare ITO is also shown in Fig. 4(a). The HOD prepared with non-reactive SAMs of MTES and VTMS showed almost the same characteristics with that prepared on a bare ITO, and their characteristics were not influence by the UV irradiation. On the other hand, the HODs prepared on the reactive SAMs of V-BP and V-VAZO showed substantial increase of current by the UV irradiation.

Quantum chemical calculations using a density functional theory (DFT) showed that the SAM molecules of MTES,

VTMS and V-BP have dipole moments directing to substrate normal with the negative poles facing the film surface. On the other hand, the dipole moment of V-VAZO molecule directed to an in-plane direction of the surface. Moreover, V-BP and V-VAZO molecules are much longer than MTES and VTMS molecules. All these factors can influence the J-V characteristics. However, notable increase in current was observed only by using the reactive SAM with the UV irradiation. This result suggests that the photochemical tethering at the interface via the reactive SAM can be an important factor in improving the charge injection at the interface.

4. Conclusions

SAMs having reactive terminal groups, such as benzophenone and azo units, can photochemically tether polymer thin films spin-coated on their surface. The covalent tethering at the interface is promising not only for improving adhesion strength of the films, but also for enhancing charge injection at the ITO/polymer interface.

Acknowledgements

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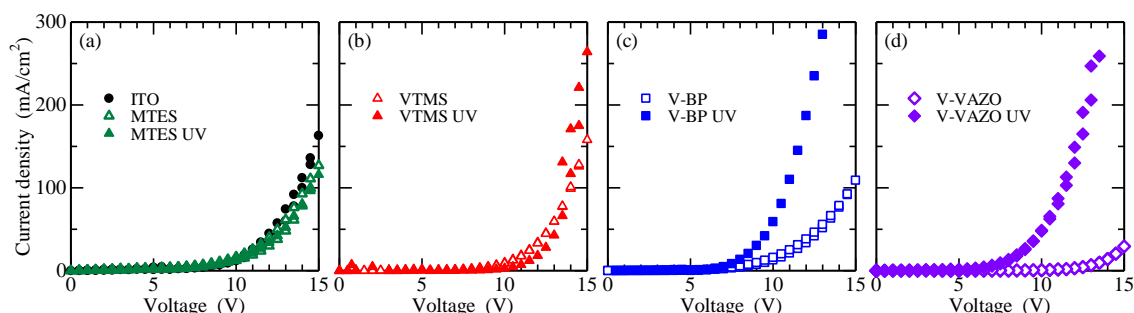


Fig. 4 J-V characteristics of HODs prepared without SAM (a), and with SAMs of MTES (a), VTMS (b), V-BP (c), and V-VAZO (d). The devices with SAMs were prepared with/without UV irradiation after spin-coating H5.