

Interface Control between ITO and Hole-Transport Polymer by a Photoreactive Self-Assembled Monolayer

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1. Introduction

The junction between an organic layer and an inorganic electrode is one of the key elements to construct organic electronic devices. However, due to the fundamentally different physical and chemical properties, their interfaces involve various problems such as poor adhesion strength and charge injection barrier. The film growth morphology of the organic layer is also largely influenced by the characteristics of the electrode surface. It has been reported that these issues can be alleviated by use of self-assembled monolayer (SAM) on the inorganic surface. The role of SAM has been attributed to such effects as the improvement of wettability by the organic materials, modification of work function of the inorganic surface, etc.

On the other hand, the authors proposed to control the organic/inorganic interface by forming stable covalent bonds through a SAM that has a reactive terminal group [1]. Polymer thin films that are tethered to the inorganic surface can be prepared by vapor deposition of appropriate monomers on the surface of the SAM that works as the polymerization initiator [2]. A surface-tethered polymer film can also be obtained by spin-coating the polymer on a SAM that has a reactive terminal group. For example, poly(*N*-vinylcarbazole) was anchored on the surface of indium-tin oxide (ITO) that was modified with a SAM having benzophenone terminal (BP-SAM) using a photochemical reaction [3]. This paper describes the effect of using the BP-SAM between the ITO electrode and a hole-transport polymer, and the result was applied for the preparation of an organic light-emitting diode (OLED).

2. Experimental

Figure 1 shows the reaction scheme employed in this work. The photoreactive BP-SAM was prepared by immersing the ITO substrate into 5 mM toluene solution of 3-glycidoxypropyl trimethoxysilane for 12 h at room temperature and then into 0.02 M chloroform solution of amino benzophenone for 12 h at 40°C. On this surface, a copolymer of phenoxazine and dioctylfluorene (H5) was spin-coated to a thickness of 100 nm, and then irradiated with UV light from a high-pressure mercury lamp at a power of 5 mW/cm² for 1 h. The binding of H5 to ITO was confirmed by contact angle measurement and ellipsometry after removing the physisorbed molecules by sonicating in chloroform.

H5 is known to work as a hole-transport material [4]. Electrical characterization was performed by preparing hole-only devices (HODs) in the structure shown in Fig. 2 (a). OLEDs were also prepared in the structure of Fig. 2 (b) by vapor-depositing tris(8-hydroxyquinolato) aluminum (Alq₃) emissive layer and bathocuproin (BCP) electron transport layer on the surface of H5 layer prepared with and without the BP-SAM on the ITO surface. The UV irradiation was achieved in both cases after spin-coating the H5 layer.

3. Results and Discussion

Formation of Surface-Tethered H5 on ITO

After the process shown in Fig. 1, the physisorbed molecules were removed by washing in chloroform. The contact angle remained unchanged by washing only when

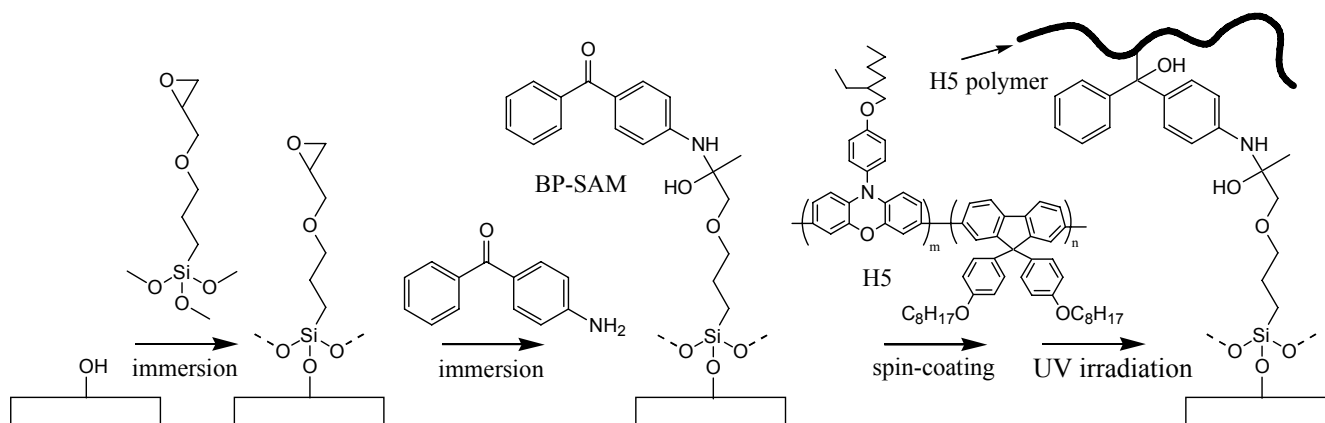


Fig. 1 Schematic route of preparing the BP-SAM of BP and binding H5 polymer on its surface.

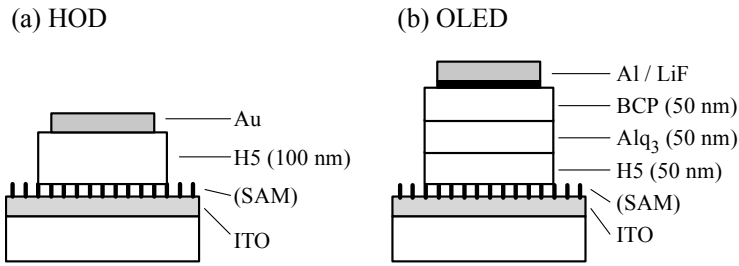


Fig. 2 The structures of HOD (a) and OLED (b) used for electrical characterization.

H5 was deposited on BP-SAM followed by the UV irradiation. Figure 3 shows the thickness of H5 that remained after washing. The surface-tethered layers of 1.7 to 6.1 nm-thick were obtained on the BP-SAM by increasing the UV irradiation time from 10 to 60 min, while little film remained without the BP-SAM.

Electrical Characterization

The current-voltage (I-V) characteristics of the HODs prepared with and without the BP-SAM are shown in Fig. 4. Although the BP-SAM does not have a conductive unit in its structure, higher current was observed by inserting the BP-SAM at the interface of ITO and H5. In addition, a leaky feature at a low operation voltage was suppressed by inserting the BP-SAM. It is expected that the BP-SAM can improve the physical contact at the interface, which resulted to enhance the current injection from ITO to H5.

Figure 5 shows the luminance-voltage characteristics of the OLEDs prepared with and without the BP-SAM. Due to the improved adhesion at the interface, the device having the BP-SAM showed higher luminance. However, it was also found that the UV irradiation process can damage the H5 layer spin-coated on the BP-SAM. This problem needs to be solved by resorting to an alternative activation process to generate the radicals of BP-SAM.

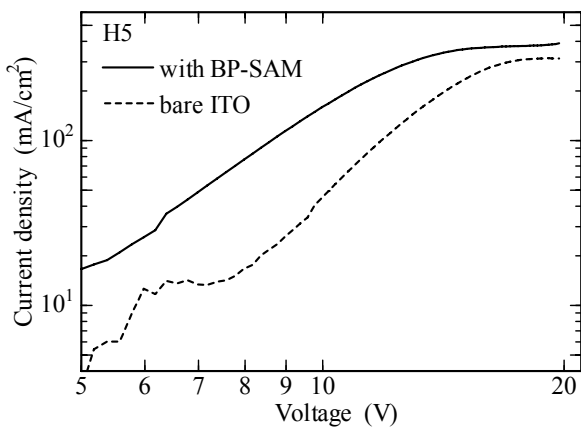


Fig. 4 I-V characteristics of the HODs prepared with and without the BP-SAM.

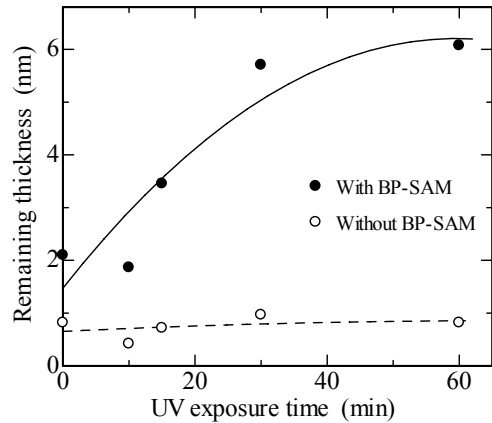


Fig. 3 Thickness of H5 that remained after washing by chloroform with and without the BP-SAM.

4. Conclusions

A polymer layer tethered to the ITO surface was obtained by introducing the BP-SAM at the interface. Chemical binding at the interface was achieved only when the BP-SAM and UV irradiation was combined. Although the BP-SAM does not have a conductive unit, hole injection and OLED performance were improved by introducing the BP-SAM, due probably to the formation of better contact at the film/substrate interface. It is expected that the BP-SAM can be applied in various occasions to improve the interface between inorganic surfaces and polymer layers required for device fabrication.

References

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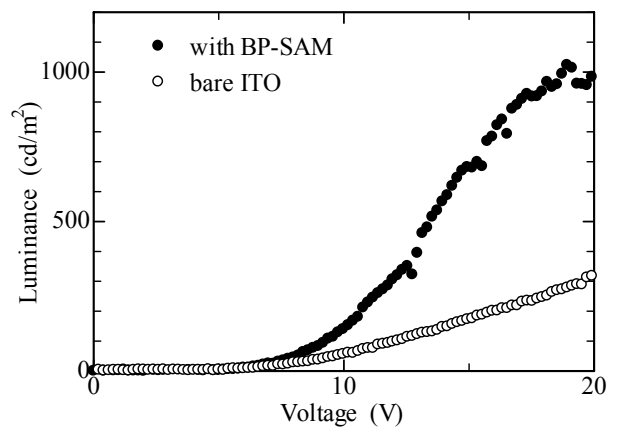


Fig. 5 Luminescence characteristics of the OLEDs prepared with and without the BP-SAM.