



# Preparation of surface-tethered polymer layer on inorganic substrates by photoreactive self-assembled monolayer



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## ABSTRACT

A self-assembled monolayer (SAM) that has benzophenone (BP) terminal group was prepared on Si and indium-tin oxide (ITO) substrates, on which poly(9-vinyl carbazol) (PVK) was spin-coated and then irradiated with ultraviolet (UV) light. Upon UV irradiation, the BP unit reacted with the PVK backbone, yielding a crosslinked PVK layer that was covalently tethered to the substrate surface. Using this procedure, a patterned thin film of PVK was obtained by irradiating UV light through a photomask and then rinsing in chloroform. When polystyrene (PSt) was spin-coated on the BP-SAM, only a thin interfacial layer was tethered by UV irradiation because PSt does not crosslink upon UV irradiation. The BP-SAM improved the adhesion strength between the PVK layer and ITO substrate without reducing the carrier injection from ITO to PVK. The photoreactive BP-SAM appeared to be an effective method to improve the interface between an inorganic electrode and a polymer layer deposited on its surface.

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## 1. Introduction

For most of the organic devices, organic/inorganic junctions are essential as electrical interfaces to outer circuits. However, the structure of organic/inorganic junction is not well controlled due to the totally different nature of these materials. In most cases, the interface is constructed by weak interaction such as van der Waals force without forming stable chemical bonds. It causes not only poor adhesion strength, but also imperfect electrical contact at the interface. One method of controlling the organic/inorganic interface is to use a self-assembled monolayer (SAM) as an interfacial buffer between the organic layer and the inorganic substrate [1,2]. It is reported that film morphology of organic layers on inorganic substrates can be improved by forming SAMs on their surface [3,4]. SAMs are also known to be effective in enhancing charge injection from the inorganic electrodes to organic layers [5,6]. The role of SAMs is attributed to modification of physicochemical characteristics of the inorganic substrates such as surface free energy and work function. On the other hand, it would be significant to form stable covalent bonds at the organic/inorganic interface through a SAM.

The authors have shown that polymer thin films can be prepared by vapor-depositing monomer molecules on the surface of a SAM that has polymerization initiating group [7,8]. For example, a SAM that has azo terminal group generates radicals upon UV irradiation, and induces growth of a polymer thin film that is chemically tethered

to the substrate surface via the SAM. It was found that device characteristics of an organic light-emitting diode can be substantially improved by tethering the hole-transporting layer to the indium-tin oxide (ITO) electrode using this method [9]. The authors also investigated tethering of a spin-coated polymer layer on an ITO substrate by using a SAM that has a photoreactive terminal group, specifically benzophenone (BP) unit [10]. The BP unit is a distinctive photolinker having the features of good thermal stability, weak sensitivity to ambient light, chemical inertness in the absence of light, and nonspecific reactivity toward any C–H bonds [11,12].

In this work, a SAM having BP terminal group (BP-SAM) was prepared on Si and ITO surfaces, on which a polymer layer of poly(9-vinylcarbazole) (PVK) was deposited by spin-coating and then irradiated with UV light to initiate the reaction between the BP-SAM and PVK. This method was applied for photopatterning PVK thin films. For comparison, a polystyrene (PSt) layer was also tethered to Si substrate in the same procedure. In addition, the effect of the BP-SAM on the electrical characteristics was investigated by constructing a hole-only device (HOD) of PVK.

## 2. Experimental procedure

### 2.1. Sample preparation and photopatterning

Fig. 1 shows the scheme of tethering PVK on an oxide surface via the BP-SAM. A Si substrate having a native oxide was cleaned with a detergent, rinsed with pure water, and then sonicated in isopropanol,

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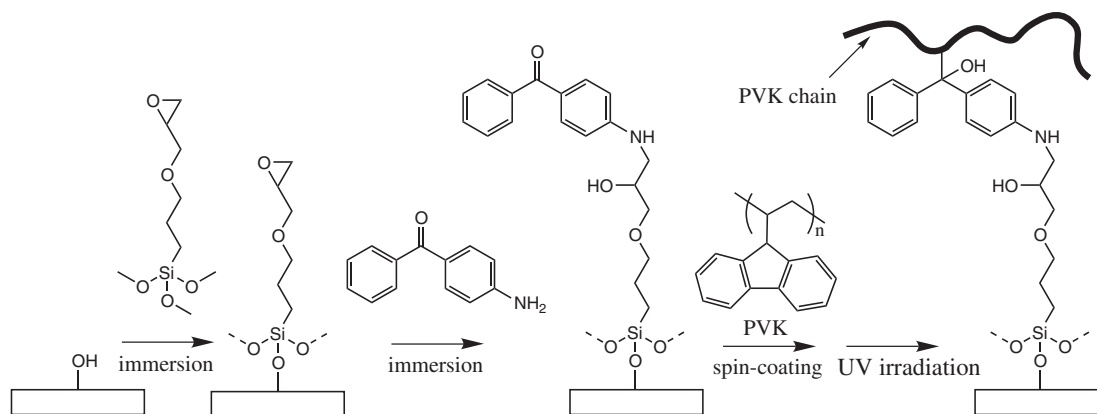


Fig. 1. The reaction scheme of forming BP-SAM followed by tethering of PVK on its surface.

hexane, and toluene, successively, followed by UV-ozone cleaning. The cleaned substrate was immersed in a toluene solution of 5 mM (3-glycidoxypropyl) trimethoxysilane (GPS) for 12 h at room temperature to form a SAM of GPS. After rinsing the surface with toluene, the substrate was immersed into chloroform solution of 20 mM 4-aminobenzophenone ( $\text{NH}_2\text{-BP}$ ) for 12 h at 40 °C. The solvent was dried by using zeolite, and GPS was used after filtering through a membrane filter of 0.45  $\mu\text{m}$  pore. The reactions were achieved in a sealed vessel purged with nitrogen flow. The amino group of  $\text{NH}_2\text{-BP}$  reacts with the epoxide terminal of the GPS-SAM to yield a SAM having BP terminal group.

On the surface of BP-SAM, a 100-nm thick PVK (Tokyo Chemical Industry Co.) was spin-coated from its 1 wt.% chloroform solution. After drying at room temperature, the film was exposed to UV light of 5  $\text{mW}/\text{cm}^2$  for 30 min using a high-pressure mercury lamp. The UV irradiation generates BP radicals, which react with the C–H bonds of the spin-coated polymer. In order to remove the physisorbed molecules, the film was rinsed in chloroform. For comparison, tethering of PSt was also investigated on the SAM-modified Si substrate. PSt (Sigma-Aldrich Co.) was spin-coated to a thickness of 100 nm by using 10  $\text{mg}/\text{mL}$  toluene solution, irradiated with UV light, and then rinsed with toluene.

It is considered that the tethering via BP-SAM can be achieved in a desired area by selectively irradiating UV light. With a purpose to apply this method for patterning the PVK thin film, the UV irradiation was achieved through a photomask of a 100-mesh grid. The photopatterning of PVK was tried both on Si and ITO substrates.

## 2.2. Characterization

The surface morphology of Si substrate was observed by using a scanning probe microscope (SPM, Keyence VN-8010, dynamic force mode) before and after forming the BP-SAM. After the polymer coating, UV irradiation, and rinsing in the solvents (chloroform for PVK and toluene for PSt), the surface was analyzed by water contact angle measurement (First Ten Ångström FTA 188) and by ellipsometry (JASCO M-150) to confirm the presence of spin-coated polymers that stayed without dissolving into the solvents. The ellipsometric thickness was obtained by fixing the refractive index to 1.4 and extinction coefficient to 0.0 for all the organic layers. The chemical binding of the film was analyzed by infrared (IR) spectroscopy using the attenuated total reflection method (Digilab FTS 7000). The pattern formation by selective UV irradiation was confirmed by optical microscope observation (Keyence VHX-500). The results were compared for films prepared on bare and SAM-modified substrates both with and without the UV irradiation after the spin-coating.

As for the electrical characterization, HODs were prepared to measure current–voltage (I–V) characteristics. A 100-nm thick PVK film

was spin-coated on an ITO substrate with and without the BP-SAM, and was irradiated with UV light as mentioned above. On this surface, a 100-nm thick gold electrode was vapor-deposited. In this case, the UV-irradiated PVK layer was used without rinsing in chloroform. The active area of the HODs was  $3 \times 3 \text{ mm}^2$ . The I–V characteristic was measured in air without encapsulation.

## 3. Results and discussion

### 3.1. Tethering of PVK thin films

Our previous report characterized each step in Fig. 1 by X-ray photoelectron spectroscopy (XPS), ellipsometry and water contact angle measurement [10]. The result of XPS analysis was consistent with the scheme shown in Fig. 1. Fig. 2 shows SPM images of (a) bare Si substrate and (b) the substrate after forming the BP-SAM. The surface of BP-SAM showed fine granular structure having an arithmetic-average surface roughness  $R_a$  of 1.5 nm. The BP-SAM may not be a completely uniform monolayer. However, our previous results of SAM formation on Si, ITO and tungsten oxide surfaces showed similar results [10].

Fig. 3 shows the IR spectra of the PVK films that remained on the Si substrate after rinsing in chloroform for different UV exposure times. The major bands around 1200, 1300 and  $1450 \text{ cm}^{-1}$  are attributed to the carbazole ring of PVK [13], while the broad absorption around  $3340 \text{ cm}^{-1}$  can be attributed to the stretching vibration of the O–H group that was generated by the reaction of BP unit with a C–H bond of the PVK backbone. This O–H band increased its intensity with increasing UV exposure time, suggesting that the photochemical reaction of BP-SAM and PVK layer proceeded as shown in Fig. 1.

Table 1 summarizes the water contact angle and the thickness of PVK layers that remained on the Si substrate after rinsing in chloroform for the cases with/without the BP-SAM and with/without the UV irradiation. Without the UV irradiation, most of the PVK films (initial thickness 100 nm) were removed by chloroform, while the UV-irradiated films partly remained without dissolving in chloroform. It is known that the UV irradiation induces crosslinking of PVK molecules [14,15], which explains the reason why considerable thickness of the UV-irradiated films remained without dissolving. In addition, the largest thickness remained when the PVK was deposited on the surface of BP-SAM.

### 3.2. Photopatterning of PVK thin films

Although the thickness of PVK that remained after rinsing was mainly determined by the UV irradiation, there was a marked difference in adhesion strength of the films depending on the presence of BP-SAM. After irradiating UV light through a photomask, the film

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