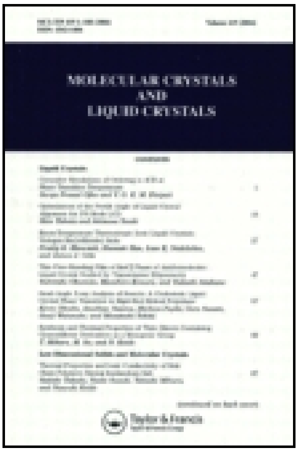

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Preparation of Poly(9-Vinylcarbazole) Thin Films Chemically Tethered to ITO Surface via Self-Assembled Monolayer Having Benzophenone Terminal Group

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Preparation of Poly(9-Vinylcarbazole) Thin Films Chemically Tethered to ITO Surface via Self-Assembled Monolayer Having Benzophenone Terminal Group

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With a goal of controlling the interface interaction between the indium-tin oxide (ITO) substrate and a polymer thin film, a self-assembled monolayer (SAM) bearing benzophenone terminal group was formed on the ITO substrate. The SAM formation was achieved by dipping the ITO substrate into solutions of 3-glycidoxypropyl trimethoxysilane and 4-aminobenzophenone, successively. A thin film of poly(9-vinylcarbazole) (PVK) was spin-coated on this surface and exposed to UV light to induce a photochemical reaction between the benzophenone terminal group of the SAM and the PVK. Surface characterization after removing the physisorbed PVK by an organic solvent revealed that PVK films prepared by this method are covalently bound to the ITO surface. The same process was achieved also on Si and WO_x surfaces.

Keywords Benzophenone; interface control; ITO; poly(vinylcarbazole); self-assembled monolayer

Introduction

Organic electronic devices, including organic light emitting diodes (OLEDs), organic photovoltaic cells, and organic thin film transistors (OTFTs), have attained rapid progress in recent years. These devices generally consist of organic thin films deposited on inorganic electrodes such as indium-thin oxide (ITO) and oxide gate insulators. These junctions can be constructed simply by depositing the organic materials on the inorganic surface using various film formation techniques, such as the vapor deposition and the wet coating processes. However, owing to the large differences in chemical and physical properties between the inorganic and organic materials, their interfaces encounter various problems, such as poor growth morphology of the deposited films, insufficient adhesion strength, electronic traps and charge injection barrier [1,2]. In the development of OLEDs, especially, the interface

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between the organic layer and the inorganic electrode is regarded to be an important factor for improving the device performance [3–10].

As a convenient measure to the problems arising from the interface, various kinds of buffer layers have been introduced on the surface of the electrode. The self-assembled monolayer (SAM) is one of the promising candidates as the interfacial buffer layer [11,12]. It is reported that the interfacial dipole layer formed by the SAM reduces the charge injection barrier height [13–15]. The SAM can also modify the surface free energy of the electrode to improve the wettability of organic materials on its surface, leading to the formation of uniform organic layers [16–18].

On the other hand, the authors have proposed to solve the problem of organic/inorganic interface by using the surface-initiated vapor deposition polymerization. This method forms a polymer thin film by evaporating monomer molecules on the surface of a SAM that has polymerization initiating group [20,21]. Upon UV irradiation, this SAM generates radicals and induces growth of a polymer thin film that is chemically bound to the substrate surface via the SAM [22,23]. The SAM plays an important role not only to initiate the polymerization but also to anchor the polymer film by stable covalent bonds to the substrate surface. As a consequence, the surface-initiated deposition polymerization was effective in improving the charge injection and luminescence characteristics of the OLED [24].

The background stated above leads us to an idea that a SAM that has a photoreactive terminal group can be effective in stabilizing the interface between an inorganic substrate and a polymer thin film deposited on its surface by a wet-coating process. It is reported that the benzophenone (BP) unit attached on a substrate is capable of tethering various molecules on its surface upon UV irradiation [25,26]. 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 unspecific reactivity toward any C-H bonds even in the presence of solvent water and bulk nucleophiles. This paper proposes to use a SAM that has BP terminal group as a surface modification and anchoring buffer layer between the ITO substrate and poly(9-vinylcarbazole) (PVK) thin films spin-coated on its surface. The formation of BP-SAM was achieved by two-step dipping process into solutions of a silane coupling reagent and a BP derivative. A PVK layer was prepared by spin-coating on this surface, and various characterizations were made at each step during the SAM formation and PVK deposition to confirm the successful formation of the SAM and anchoring of the PVK layer.

Experiment

Figure 1 shows the schematic route of the reaction scheme involved in the process proposed in this work. The process mainly consists of the SAM formation, spin-coating PVK layer followed by UV irradiation, and removal of physisorbed PVK. Both ITO and Si were used as the substrate. The ITO substrate was scrabbled in a detergent, rinsed in pure water, and then sonicated in isopropanol, hexane, and toluene for 10 min, respectively. After drying by nitrogen blow, the substrate was cleaned in a UV-ozone cleaner. The Si substrate was sonicated in a detergent for 15 min, and then in pure water, acetone, and pure water again for 5 min, respectively. The substrate was then immersed in a mixture of 70% sulfuric acid and 30% hydrogen peroxide for 30 min. After rinsing and sonicating in pure water for 10 min, the substrate was dried by nitrogen blow.

The SAM formation was achieved in two steps. The substrate was first immersed into a toluene solution of 5 mM 3-glycidoxypropyl trimethoxysilane (GPS) for 12 h at room temperature. After rinsing with the solvent, the substrate was immersed into 20 mM chloroform solution of 4-aminobenzophenone (NH_2-BP) for 12 h at 40°C. The immersion processes were achieved in nitrogen atmosphere. After forming the SAM layer, the PVK

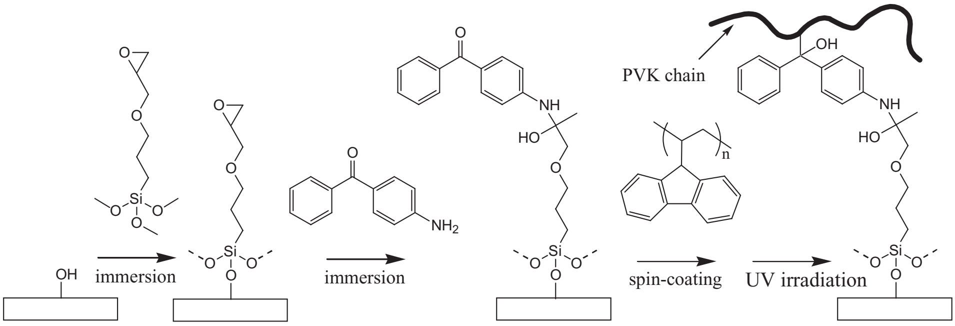

Figure 1. The reaction route of the process proposed in this work. The SAM having BP terminal group was prepared by dipping the ITO substrate into solutions of GPS and NH_2-BP, successively. After spin-coating PVK on this surface, the film was fixed by UV irradiation and then washed in chloroform to remove physisorbed PVK.

layer was deposited on its surface by spin-coating 1 wt% chloroform solution of PVK, and then irradiated with UV light of 5 mW/cm^2 for 1 h in air using a high-pressure mercury lamp. The UV irradiation generates BP radicals that react with the C-H bonds of the PVK backbone. The UV irradiation also enhances crosslinking between the carbazole units to form a network polymer of PVK. The film was immersed in chloroform for 24 h and then sonicated in chloroform for 5 min to remove the physisorbed PVK.

Each step of the process of the SAM formation and the PVK deposition was characterized by X-ray photoelectron spectroscopy (XPS), optical thickness measurement by ellipsometry, water contact angle measurement, and atomic force microscopy (AFM). The optical thickness was calculated by fixing the refractive indices of the organic layers to be 1.43 for GPS, 1.45 for NH_2-BP and 1.68 for PVK, and does not necessarily correspond to the physical thickness. The infrared (IR) measurement by the attenuated total reflection (ATR) was achieved to confirm the final attachment of PVK layer. The chemical analyses by XPS and IR spectroscopy were achieved for the films on the ITO substrates, while the physical analyses of contact angle measurement and ellipsometry were achieved for the films on the Si substrates. The AFM observations were made on both substrates. The experiment was also achieved on the surface of WO_x. The WO_x layer was prepared by resistive vapor deposition of WO_3 on an ITO substrate to a thickness of 10 nm.

Results and Discussion

XPS and IR Measurements

The reaction shown in Fig. 1 was verified by XPS analysis at each step in the process. Figure 2 shows C1s, O1s and Si2p spectra obtained by the XPS analysis on the ITO substrate after immersing it in the GPS solution followed by thorough rinsing with the solvent. The clear observation of carbon and silicon elements supports the existence of GPS molecules bound to the substrate surface.

The epoxide terminal group of GPS easily undergoes ring-opening reaction due to its highly strained structure. It is expected that a SAM having BP terminal group can be produced by immersing the SAM of GPS into the solution of NH_2-BP. Figure 3 shows the C1s, O1s, and N1s XPS spectra obtained at this stage. The observation of weak signal of N

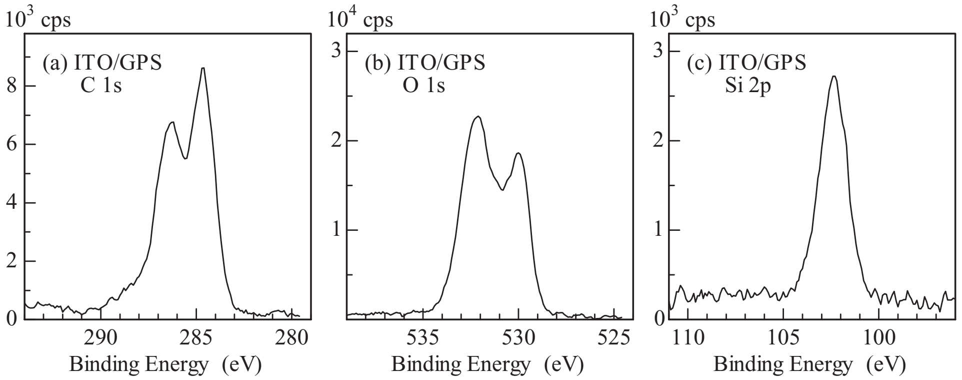

Figure 2. C1s, O1s, and Si2p XPS spectra of ITO substrate after immersing into GPS.

atoms suggests that NH_2-BP molecules have attached to the SAM of GPS. It is considered that the SAM having BP terminal group was prepared by the two-step immersion into GPS and NH_2-BP as mentioned above. Such a SAM is expected to have the capability of binding thin polymeric layers on UV irradiation even at room temperature.[22] As the final step, the SAM was coated with a 100-nm thick PVK by spin-coating, exposed to the UV light, and then washed with chloroform to remove the physisorbed component. Figure 4 shows the C1s, O1s, and N1s XPS spectra of the resulting specimen. Compared to the spectra shown in Fig. 3, C1s and N1s signals were markedly enhanced while the signal of O1s was suppressed substantially. This result strongly suggests that chemically bound PVK molecules exist on the surface of the BP-SAM.

Figure 5 shows the IR spectrum measured by the ATR method on the surface after removing the physisorbed PVK. Although the signal intensity was insufficient for detailed analysis, the major bands around 1200, 1300 and 1450 cm^{-1} are attributed to come from the PVK layer remaining on the surface. The broad absorption around 3300 cm^{-1} is considered to represent the stretching vibration of the OH group that is produced when the BP units reacted with the C-H bonds of the PVK main chain. The results of chemical analyses by XPS and IR are consistent with the scheme shown in Fig. 1, in correspondence with our

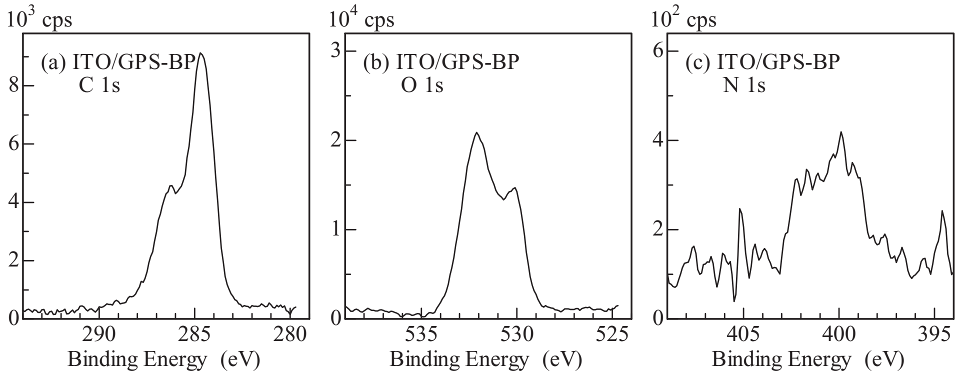

Figure 3. C1s, O1s, and N1s XPS spectra after immersing the SAM of GPS into NH_2-BP.

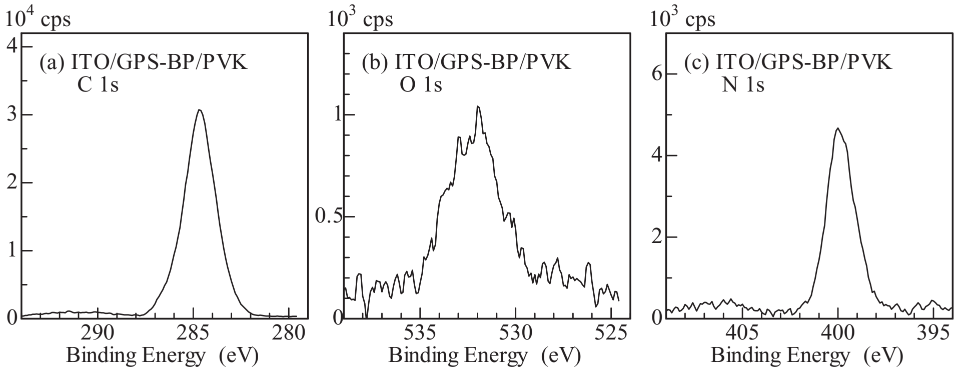

Figure 4. C1s, O1s, and N1s XPS spectra after spin-coating followed by washing the PVK layer on the SAM of GPS/NH_2-BP.

idea that the spin-coated PVK film can be chemically bound to the substrate surface through the SAM that has BP terminal group.

Ellipsometry and Contact Angle Measurement

As the physical analyses of the process, ellipsometry and water contact angle measurements were achieved on Si substrates. Table 1 summarizes the optical thicknesses and the water contact angles of the films at the steps of after immersing into GPS, immersing into NH_2-BP, spin-coating PVK, and washing with chloroform with or without the UV irradiation after the spin-coating. It should be noted that the optical thickness was calculated by fixing the refractive indices, and can be used only for relative comparison. By the two-step immersion into GPS and NH_2-BP, respectively, a steady increase of the optical thickness was observed, suggesting the successive growth of the SAM layer. After spin-coating the PVK layer of 100-nm thick, a distinct difference in the water contact angle was observed compared to that of the BP-SAM. A part of the specimen was irradiated with UV for 1 h after spin-coating PVK. After washing the specimen with chloroform, there were remarkable differences in film thickness and water contact angle between the films with and without the UV irradiation

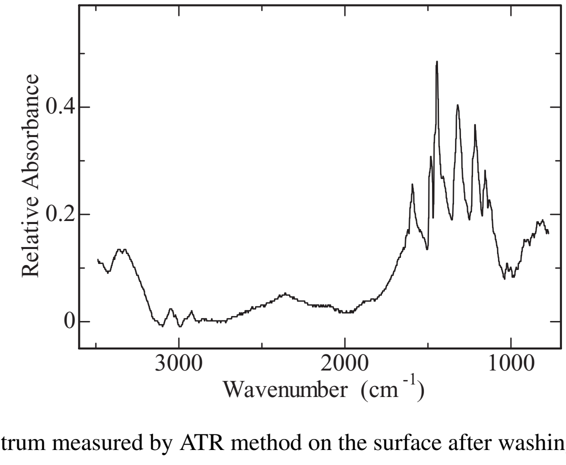

Figure 5. IR spectrum measured by ATR method on the surface after washing physisorbed PVK.

Table 1. Optical thickness and water contact angle of the films on Si substrates at each step in the process shown in Fig. 1.

Step	GPS immersion	NH_2-BP immersion	PVK spin-coating	UV irradiation	washing by chloroform
Thickness (nm)	2.8	4.5	100	1 h	98
				No	5.1
Contact angle (deg.)	63	66	85	1 h	85
				No	64

process. When the specimen was irradiated with UV, both the optical thickness and the water contact angle remained almost the same before and after the washing process. On the other hand, without the UV irradiation, both the optical thickness and the water contact angle returned to the values almost the same with those of the BP-SAM, suggesting the removal of PVK by washing with chloroform. These results strongly support our scheme that the SAM having BP terminal group can anchor the PVK layer upon UV irradiation.

The scheme shown in Fig. 1 suggests that only a monolayer that comes in contact with the BP-SAM can be tethered at the interface. On the contrary, our experimental result showed that almost the whole PVK layer remained undissolved by the washing process when the UV irradiation was achieved after the spin-coating. It is considered that the PVK layer was crosslinked by the UV irradiation, resulting in a stable insoluble bulk layer anchored to the substrate at the interface [27]. Our preliminary experiment that used polystyrene (PS) instead of PVK showed that only a thin interfacial layer can be tethered when the polymer material is not corosslinkable.

AFM Observation

The surface morphology was observed by AFM at the stages of (a) after immersing in GPS, (b) after immersing in NH_2-BP, and (c) after washing the UV-irradiated PVK layer with chloroform. Figure 6 shows the set of AFM images observed on Si substrate. Ultrafine granular morphology was observed after immersing in GPS (a) and NH_2-BP (b), giving the arithmetic average surface roughness R_a of 0.14 nm and 0.15 nm, respectively. This result suggests the formation of uniform SAMs of GPS and NH_2-BP/GSP by the dipping

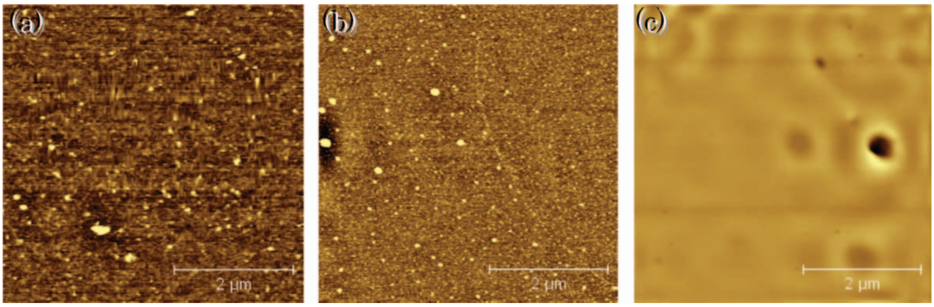

Figure 6. AFM images on Si substrate (a) after immersing in GPS, (b) after immersing in NH_2-BP, and after washing the PVK layer irradiated with UV.

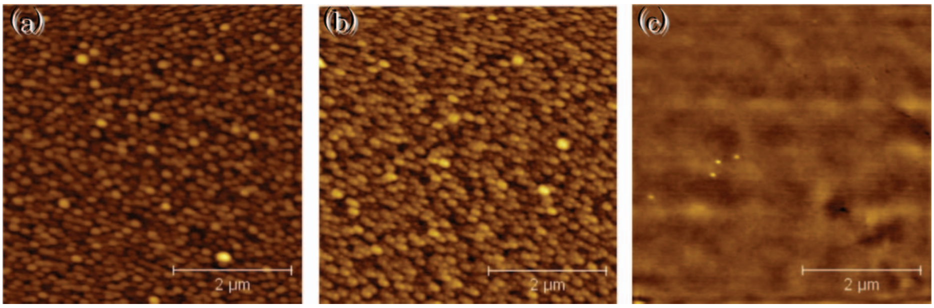

Figure 7. AFM images on ITO substrate (a) after immersing in GPS, (b) after immersing in NH_2-BP, and after washing the PVK layer irradiated with UV.

processes. The hillock-like island structure represents the polymeric or aggregated structure of the silane reagent. Such structure should be suppressed by carefully controlling the humidity and filtering the solution during the dipping process. On the other hand, the surface after washing the UV-irradiated PVK layer gave a feature largely different from the SAMs. Its R_a was 0.65 nm, which is substantially larger than those of the SAMs, but the surface showed a gentle curvature as a consequence of uniform coverage by the polymer thin film.

A similar tendency was also observed on the ITO substrate as shown in Fig. 7. In this case, the ITO itself had considerable surface roughness, and R_a was 2.19, 1.62 and 0.18 nm on GPS-SAM, NH_2-BP/GSP SAM, and after washing the UV-irradiated PVK, respectively. It reflects the planarization of the surface by accumulating the organic layers. Nevertheless, there was a distinctive difference in the surface morphology between the SAMs and the tethered PVK layer.

It is considered that the process proposed in this work can be achieved on the surface of various oxides that react with the silane coupling reagent. For example, the authors have shown that vapor-deposited WO_x film combined with a SAM layer on its surface can be an efficient buffer layer on ITO electrode [19]. In connection with this result, the process proposed in this work was adopted on the surface of a WO_x film vapor-deposited on an ITO substrate. The GPS SAM, NH_2-BP/GSP SAM, and the surface after washing the UV-irradiated PVK were observed by AFM as shown in Fig. 8. In this case also, the same features were observed as on the Si and ITO surfaces, suggesting successful binding

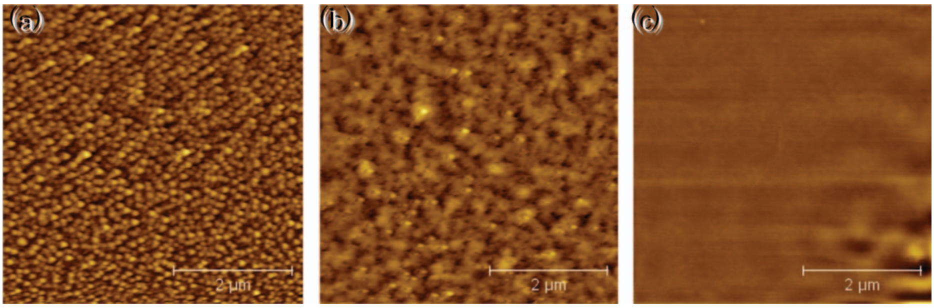

Figure 8. AFM images on WO_x surface (a) after immersing in GPS, (b) after immersing in NH_2-BP, and after washing the PVK layer irradiated with UV.

of PVK on the surface of WO_x. All the results shown in Figs. 6 to 8 indicate the versatility of the process proposed in this work.

Conclusions

A SAM that has BP terminal group was prepared on oxide substrates by the two-step dipping processes. This SAM provides a facile room temperature photochemical process through which the polymer molecules can be covalently bonded to the substrate surface. When a PVK layer was spin-coated on the BP-SAM followed by UV irradiation, the bulk of the film was stabilized by crosslinking in addition to the anchoring via the BP-SAM. For those polymers that do not crosslink, such as PS, only the interfacial region of the polymer film will be tethered to the surface. This process can be achieved on various kinds of oxide surface, including Si, ITO and WO_x that were already confirmed in this work. Moreover, the BP unit is reported to react with variety of C-H bonds. It is expected that the use of BP-SAM is effective in improving the characteristics of polymer/electrode interfaces that are indispensable for polymer electronic devices. Our experiments also suggested the possibility of using this process for patterning the polymer thin films, which will be reported in our future work.

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