

Effect of SAM Modification on ITO Surface for UV-Assisted Vapor Deposition of Carbazole Thin Films

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1. Introduction

Organic electronic devices are frequently constructed on transparent electrodes such as indium-tin oxide (ITO), but the interface between the organic layers and the substrates accompany such problems as wettability of organic material over the inorganic surface, adhesion strength, reaction at the interface, carrier injection barrier, etc. In order to overcome these difficulties, thin interfacial layers, called as buffer layer or charge injection layer, have been introduced at the interface. However, there has not been much concern about controlling the chemical bonds at the film/substrate interface. The authors have proposed a surface-initiated deposition polymerization technique, in which the monomers were deposited on the substrate surface modified with a self assembled monolayer (SAM) of a polymerization initiating reagent [1]. This method was found to be effective in improving the charge injection from the substrate [2] as well as thermal stability of the organic layer [3]. This report compares the film growth morphology of carbazole polymer thin films in connection with the SAM modification and ultraviolet (UV) irradiation in the process of film deposition on ITO surface.

2. Experiments

The reaction scheme of the surface-initiated deposition of carbazole is shown in Fig. 1. The ITO substrate was cleaned with organic solvents and immersed in methanol solution of (3-aminopropyl)triethoxysilane to form a SAM layer having amino end group. The substrate was dipped successively into solutions containing succinic anhydride, pentafluorophenol, and then VAZO56 (DuPont) to form a SAM layer having the azo end group as the polymerization initiator [4]. The substrate was rinsed with methanol, dried, and brought into a vacuum chamber for the vapor deposition of 2-(9H-carbazol-9-yl)ethyl acrylate (CEA). CEA was evaporated from a Knudsen-type cell at a temperature of 70°C for 10 min to grow thin films of about 100 nm thick at room temperature. During the deposition, the substrate was irradiated with UV light of 5 mW/cm² guided from a high pressure mercury lamp. Films were grown under conditions with or without the SAM layer and with or without the UV irradiation. The film morphology was examined with a scanning probe microscope. The films were also dissolved in tetrahydrofuran (THF) to

analyze the molecular weight by gel permeation chromatography (GPC). For comparison a film was grown on an ITO surface that was treated with UV-ozone cleaner (Filgen UV253) for 15 min to reduce its contact angle.

3. Results and Discussions

Film growth on bare ITO

Figure 2 shows the AFM images of the films deposited on bare ITO surface without (a) and with (b) UV irradiation. The UV irradiation during vapor deposition did not give an appreciable difference in accumulated film thickness. The simply evaporated film (a) showed crystal-like domain structure. The UV irradiation influenced the growth morphology, and the film consisted of smaller and rounded domains. The averaged surface roughness R_a was 92.4 and 50.7 nm for Fig. 2 (a) and (b), respectively, for the film thickness of about 100 nm. It indicates that the films grew in island structure without achieving a dense coverage. GPC analysis showed that the simply evaporated film totally consists of monomers, while the film prepared with UV irradiation contains 23% of polymer composition with number-average molecular weight of 10⁶. It is considered that the rounded grain shape reflects the presence of polymer component, which condenses to form amorphous solid. These results show that the bare ITO surface is not appropriate to grow uniform thin films of carbazole even with the UV-assisted vapor deposition.

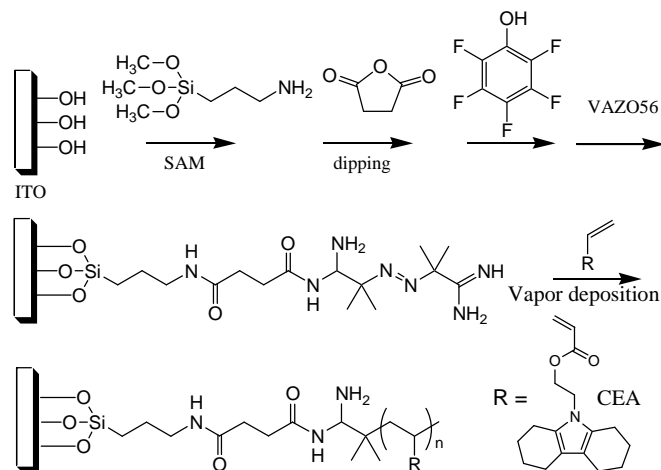


Fig. 1 Reaction scheme of film formation in this study.

Film growth on SAM surface

On the other hand, film morphology was drastically influenced by forming the SAM layer on the ITO surface. Figure 3 shows the AFM images of the films deposited on the SAM-modified ITO surface without (a) and with (b) the UV irradiation. Without the UV irradiation (a), the film accumulated in crystal-like domains. However, the grain size was much larger than the case deposited on bare ITO. It is noteworthy that the film deposited with UV irradiation on the SAM surface (b) grew in smooth and uniform morphology, having R_a of 5.7 nm. This film dissolved in THF only in part, while the film deposited on bare ITO (Fig. 2b) completely dissolved in THF. GPC analysis of the soluble portion gave a polymer fraction of 19% with molecular weight of 7×10^5 . The insoluble portion is considered to represent the polymer molecules that are chemically bound to the ITO surface through the SAM layer as depicted in Fig. 1. Although the polymerization is not complete, and not all polymers are bound to the substrate surface, the UV-assisted deposition on the initiator SAM is an effective method for preparing uniform polymer thin films of carbazole.

Film growth on UV-Ozone treated ITO

It is frequently observed that organic molecules deposited on inorganic substrates, whether by wet coating or by vapor deposition, do not wet the surface very well. It might be interpreted that the smooth film morphology observed on the SAM surface comes from the difference in wettability of bare and SAM-modified ITO surfaces. With a purpose to investigate the influence of wettability, CEA was deposited on an ITO surface that had been treated with UV-ozone cleaner, which is known to increase the number density of hydrophilic groups such as -OH on the surface. The water contact angle of bare, SAM-modified, and UV-ozone treated ITO were 50, 23, and 15 degrees, respectively, and the surface energy was 53, 77, and 83 mJ/m^2 , respectively. Therefore, the UV-ozone treatment was found to be more effective in improving the wettability of ITO surface than the SAM modification. Figure 4 shows the surface morphology of a CEA film by UV-assisted deposition on the UV-ozone treated ITO. In spite of the higher wettability of the UV-ozone treated surface, the film morphology was similar to the case deposited without SAM, forming loosely packed rounded islands. GPC analyses also showed a result similar to the case deposited on the bare ITO. This result indicates that the smooth morphology as shown in Fig. 3(b) can be achieved by controlling the chemical bonds at the interface rather than physical surface energy.

3. Conclusions

Carbazole polymer thin films were prepared by UV-assisted vapor deposition on ITO surfaces modified with SAM of polymerization initiator. It was found that the UV assisted deposition can initiate the polymerization of CEA molecules even on bare ITO surface. However, the film grew in island structure on bare ITO. Uniform

and smooth film was obtained only when UV-assisted deposition was achieved on the SAM layer. Comparison with the growth on UV-ozone treated ITO surface revealed that the effect of SAM is not simply modifying the surface energy to improve the wettability. It is considered that the formation of chemical bonds at the interface plays an important role for uniform film growth as well as for enhancing polymerization. It is concluded that the UV-assisted vapor deposition polymerization combined with the SAM of polymerization initiator can be an attractive method for growing organic layer on inorganic surfaces.

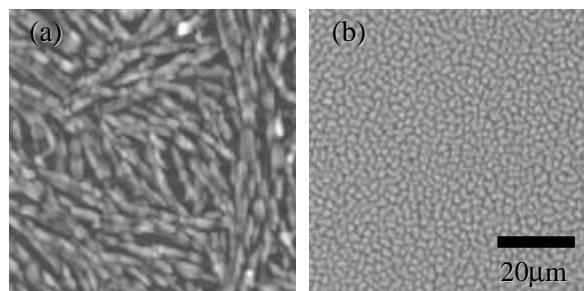


Fig. 2 Surface morphology of CEA films deposited on bare ITO surface without (a) and with UV irradiation.

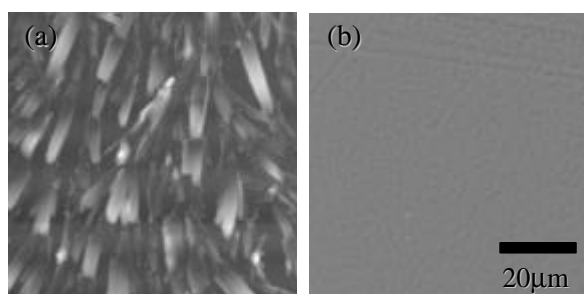


Fig. 3 Surface morphology of CEA films deposited on SAM surface without (a) and with UV irradiation.

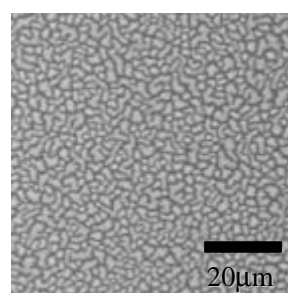


Fig. 4 Surface morphology of CEA film by UV-assisted deposition on UV-ozone treated ITO.

References

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