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Interface Control by Surface-Initiated Deposition Polymerization and its Application to Organic Light Emitting Devices

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1. Introduction

Organic light emitting diodes (OLEDs) are expected to be potential candidate for the next-generation flat panel displays. For such an application, the thermal stability of the organic layers is one of the major issues in determining the device durability. In addition, the organic layer needs to have stable adhesion to the substrate in order to avoid delamination, especially for fabricating flexible devices. The interface of film and substrate also holds a key in controlling the charge injection from the electrode. The authors propose to solve these problems by using the surface-initiated deposition technique. The surface initiated deposition polymerization is a technique to deposit polymerizable monomers on the surface of a self-assembled monolayer (SAM) that bares a polymerization initiator as the end group [1]. This technique has been applied for preparing a polypeptide [2] and a vinyl polymer having carbazole unit [3]. The objective of this paper is to form vinyl polymer thin films having hole transport units on indium-tin-oxide (ITO) surface by the surface-initiated deposition polymerization. The OLED characteristics were compared for the hole transport layer (HTL) deposition with and without the SAM layer.

2. Experiments

Figure 1 shows the reaction scheme of surface-initiated deposition polymerization. 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 the solutions containing succinic anhydride, pentafluorophenol, and then VAZO56 (DuPont) to form a SAM layer having the azo end group as the polymerization initiator. The substrate was rinsed with methanol, dried, and brought into the vacuum chamber for OLED fabrication in the structure shown in Fig. 3. The hole transport layer was prepared by electron-assisted deposition [4] of 3-(N-carbazolyl)propyl acrylate (CPA) or vinyl derivative of tetraphenyldiaminobiphenyl (vTPD) shown in Fig. 2. The substrate was moved to another chamber where tris(8-hydroxyquinolato)aluminum (Alq_3) fluorescent layer, LiF electron injection layer and Al cathode were deposited by conventional evaporation. The device characteristics were measured without encapsulation.

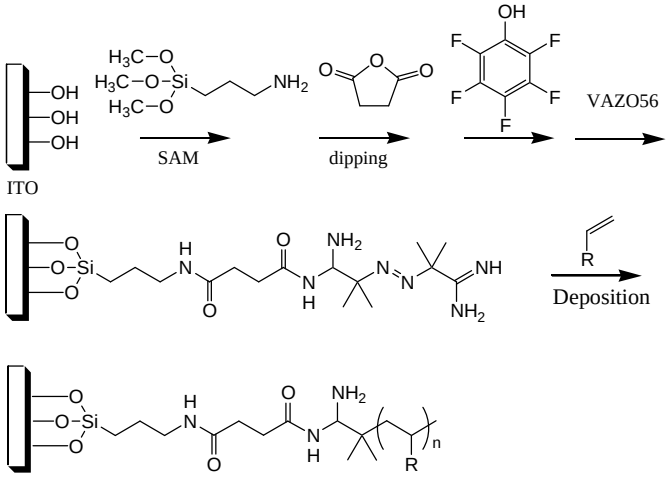

Fig. 1 Reaction route of surface-initiated deposition polymerization.

3. Results and Discussions

In the previous study of surface-initiated polymerization of CPA on Au surface, the initiator SAM

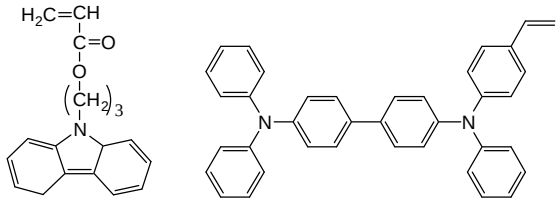

Fig. 2 Monomers for deposition polymerization of HTL.

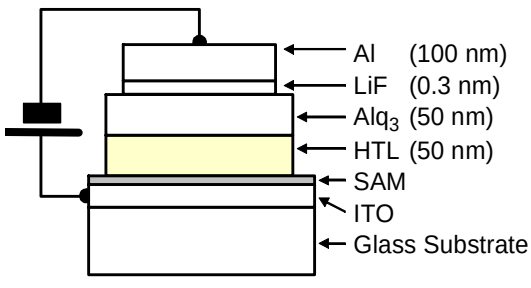

Fig. 3 OLED device structure.

was activated by UV irradiation. On the ITO surface, however, the number density of SAM molecules appeared to be much smaller than the case where thiole molecules were chemisorbed on Au surface. As a consequence, the UV irradiation was not very effective for enhancing the polymerization. On the other hand, electron-assisted deposition successfully formed polymer thin film of CPA. It is expected that the electron irradiation is effective in continually supplying radicals during the film accumulation, as well as in activating the azo unit of SAM. Although the number density of SAM molecules is smaller on ITO surface compared to Au surface, the SAM molecules can act as anchoring points to enhance the adhesion and to stabilize the deposited film. Optical microscope observation showed that the CPA film deposited on the SAM layer has much higher surface smoothness compared to the one on bare ITO. Moreover, the CPA films by the conventional evaporation underwent severe crystallization in the as deposited state regardless of the presence of SAM layer, and were not appropriate for device fabrication.

Figure 4 shows the voltage-luminance characteristics of the OLEDs having the HTL of CPA deposited with and without the SAM layer. It can be seen that the use of SAM layer substantially decreases the driving voltage required for the same luminance. After the devices were damaged by increasing the driving voltage up to breakdown, the device surface on the cathode was observed by optical microscope. It was found that the device prepared without the SAM layer was damaged over all the surface of cathode, while the one with SAM layer was damaged only on several spots, mostly leaving the smooth cathode surface.

Figure 5 shows a similar result of OLEDs having the HTL of vTPD deposited with and without the SAM layer. The TPD is known to have higher hole mobility than the carbazole unit, and the overall performance was superior than the devices of CPA HTL. Moreover, the device performance such as the luminance and the threshold voltage was considerably improved by use of the SAM layer. The microscope observation after the device breakdown showed that the vTPD device without SAM layer was damaged by delamination of electrode in large area, while the one with the SAM layer was damaged in limited numbers of spots. These results indicate that the use of SAM layer is effective in improving the device durability, as well as in enhancing the carrier injection.

3. Conclusions

Surface-initiated deposition polymerization was achieved by depositing vinyl monomers on SAM layers that have azo initiator as the end group. Although the density of silane SAM molecules were smaller on ITO surface compared to the case of thiole on gold, the polymerization was initiated effectively by electron-assisted deposition. OLEDs were prepared by depositing vinyl derivatives of carbazole or TPD hole transport materials followed by conventional evaporation of emission layer and cathode. It was found that the SAM layer was effective in improving the device durability as well as the luminescence characteristics. The surface-initiated deposition polymerization can be a promising technique for preparing organic thin film devices.

References

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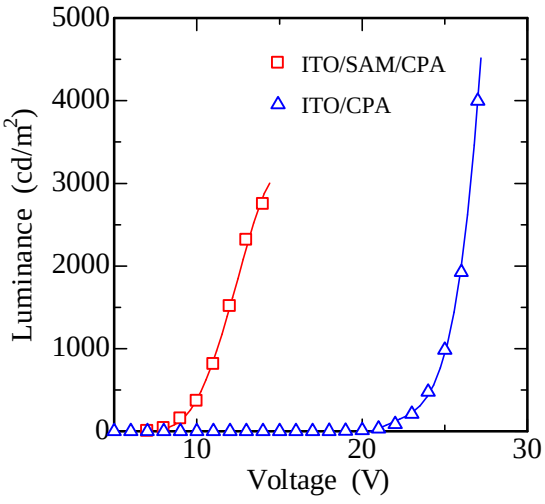

Fig. 4 Voltage-luminance characteristics of OLEDs using CPA for HTL with and without SAM layer.

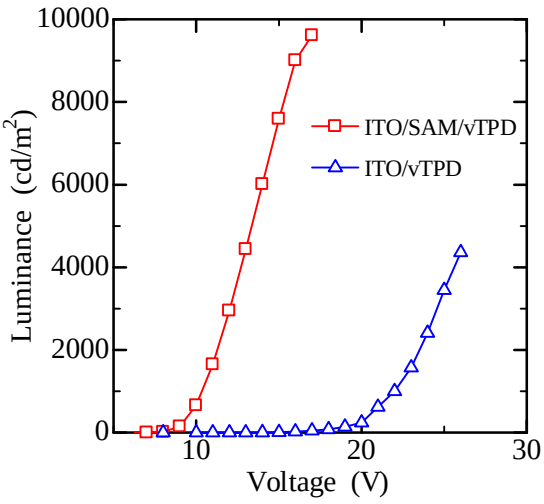

Fig. 5 Voltage-luminance characteristics of OLEDs using vTPD for HTL with and without SAM layer.