Application of Mixed Polymer Langmuir–Blodgett Films with Poly(3-hexylthiophene) to a Hole-injection Layer for Organic EL Devices

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Performance of the mixed poly(3-hexylthiophene) (PHT) Langmuir–Blodgett (LB) films on hole-injection for organic electroluminescent (EL) devices was investigated. Onset voltage of EL devices using PHT LB films decreased with increasing number of layers because of reduction of energy barrier of hole injection from indium-tin-oxide (ITO) anode to PHT films. Current efficiency was improved at the monolayer PHT LB film EL devices.

Organic electroluminescent (EL) devices[1] have been greatly investigated for the application to flat panel displays. Since organic materials for EL devices are basically insulating one, high operating voltage is needed to inject hole and electron from the indium-tin-oxide (ITO) anode and the metal cathode to the organic films, to transport them in the film along the electric field and to make recombination between hole and electron for emission. In particular, there is the energy barrier for the hole- and electron-injection processes at the interface of the ITO anode and the metal cathode because the work function of the ITO anode and the metal cathode is different from HOMO and LUMO energy levels of the organic EL materials, respectively. Moreover, the work function of the ITO anode is often influenced by surface treatment. So far, several hole-injection materials, such as cupper phthalocyanine,[2] aromatic amine derivatives,[3,4] polyaniline,[5] and poly(3,4-ethylenedioxythiophene) doped with polystyrene sulfonic acid (PEDOT/PSS)[6] are reported to improve operation-driven voltage and quantum efficiency. However, the film is prepared mainly by vacuum thermal vapor deposition, spin-coating or inkjet printing method. So, the resulting film would be thick and not uniform at a molecular level as a hole-injection layer. The matching of the energy potential between the work function of the ITO anode and HOMO energy level of the hole-injection materials is needed, whereas the thickness of the hole-injection layer would not be needed as an ideal hole-injection layer. To reduce the film thickness of the hole-injection layer, modification of ITO surface by self-assembled monolayers (SAMs) using alkylsilane and silylaromatic amine derivatives is reported.[7] Meanwhile, we have succeeded in preparing poly(3-hexylthiophene) (PHT) ultrathin film by mixed Langmuir–Blodegett (LB) technique using poly(*N*-dodecylacrylamide) (pDDA).[8] LB films can control film thickness at a molecular level. PHT is well known as a conductive hole-carrier materials with application to organic field effect transistors.[9] Furthermore, PHT was reported to be emitting materials of polymer EL devices.[10] In this report, we demonstrate whether mixed PHT LB film functions as a hole-injection layer of EL devices.

Monolayer behaviors of pure PHT and the mixtures of PHT with pDDA are investigated on a water surface. Surface pressure–area isotherm of pure PHT shows that the surface pressure does not raise, indicating that pure PHT does not form a stable monolayer at the air/water interface by itself and forms aggregates on a water surface. Meanwhile, the surface pressure–area isotherms of mixtures of PHT with pDDA in different mole fraction of PHT show that the collapse pressure and the limiting surface area increase with mole fraction of pDDA in the mixtures. This supposed that the mixtures would form a monolayer on a water surface. In the following, the mixed PHT monolayer at 0.67 mole fraction of PHT in the mixture was transferred to the ITO anode at deposition pressure of 25 mN/m.

In order to study hole-injection ability of mixed PHT LB films, the conventional construction of EL devices is used except the introduction of the mixed PHT LB films. The EL device was fabricated by LB deposition of mixed PHT monolayer as a hole-injection layer on ITO anodes at first, following the vacuum vapor deposition of *N*,*N*′-diphenyl-*N*,*N*′-di(*m*-toyl)benzidine (TPD) as a hole-transporting layer, tris(8-quinolinolato)-aluminum(III) (alq3) as an emitting and electron-transporting layer, calcium as a cathode and aluminum as a protecting metal, successively. The film thickness of TPD, alq3, Ca, and Al is fixed at 100 nm, respectively, to compare with each EL devices. The hole-injection ability of the mixed PHT LB films is investigated as a function of number of layers. The film thickness of the mixed PHT LB films per monolayer is estimated to be 1.8 nm from XRD.

Figure 1 shows the difference in luminescence between the presence and the absence of the mixed PHT LB films in the EL

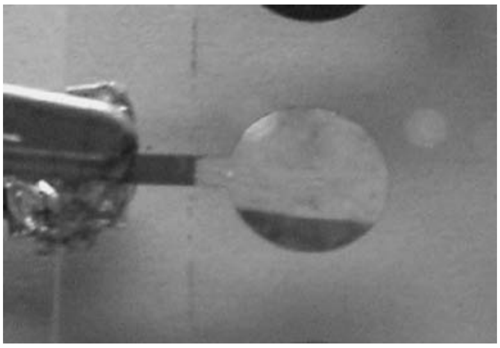

Figure 1. Photograph for the EL device applied at the voltage of 14 V. The upper green part is observed at the EL device in the presence of monolayer PHT LB film and the lower dark part is in the absence.

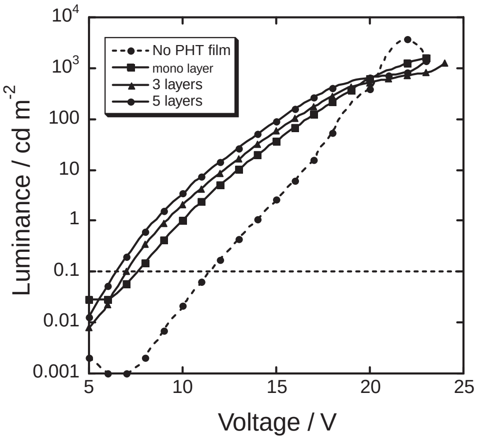

Figure 2. Semilogarithm plots for luminance vs voltage in the EL devices with the mixed PHT LB film in different number of layers.

devices. The upper green emission part was observed at the EL device with monolayer mixed PHT LB film and the lower no emission part was obtained without mixed PHT LB film at the same EL device at the same applied voltage of 14 V. It indicates that the mixed PHT LB film behaves as a hole-injection layer.

Semilogarithmic plots for luminance vs voltage at EL devices with the mixed PHT LB films with different number of layers are shown in Figure 2. The luminance of these EL devices increases with voltage. The luminance of the EL devices with mixed PHT LB films is much higher compared with no PHT film. Onset voltage, which is defined as the voltage obtained at the luminance of 0.1 cd/m^2, is 11 V at the no PHT film EL device. The onset voltage decreases with increasing number of layers and becomes almost constant value of 7 V. This means that the hole-injection energy barrier reduces to 4 V with mixed PHT LB films. Breakdown voltage, which is defined as the voltage before the EL devices are broken down by the high electric field or the heat damage produced by current, is 22 V at the EL device with no PHT LB film. The breakdown voltage at the EL devices with mixed PHT LB films is higher than that with no PHT film. The EL devices with pure pDDA LB films as a hole-injection layer were also investigated as a control experiment. Onset voltage increases with number of layers relative to that of the EL device without pDDA LB films (not shown in Figure 2). This shows that pDDA LB films behave as an insulator. Therefore, we found that the mixed PHT LB films can function as a hole-injection layer of EL devices.

Current efficiency is shown as a function of number of layers in Figure 3. The efficiency data at no PHT EL device are scattered. The current efficiency at monolayer PHT LB film EL device shows that the maximum value is about 1.5 cd/A and this value is higher than that of no PHT EL device at the same voltage. Moreover, the efficiency curve at the monolayer PHT LB film EL device is shifted to lower voltage compared with that of no PHT EL device. However, the increase in number of layers makes efficiency worse.

At the no PHT EL device, hole-injection energy barrier from ITO to TPD is estimated to be 0.7 eV according to the work function of the ITO anode (4.8 eV)[11] and the HOMO energy level of TPD (5.5 eV).[12] Meanwhile, it is down to 0.3 eV at the presence of PHT LB film because of the HOMO energy level of PHT (5.2 eV).[13] So, this lower energy barrier makes the onset voltage reduce. And also, current efficiency was improved at the monolayer PHT LB film because the carrier injection would be balanced. However, the efficiency decreased at more than three-layer PHT LB films, probably, owing to filter effect that is PHT absorption around 550 nm.

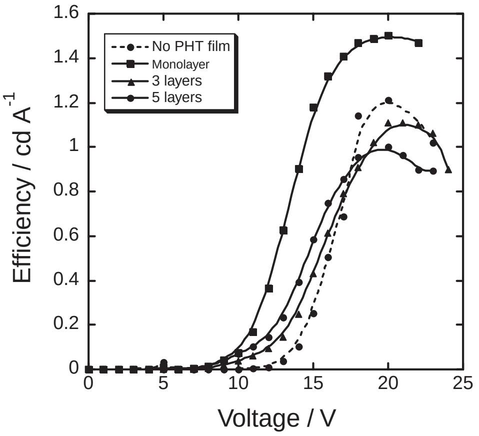

Figure 3. Plots for current efficiency vs voltage in the EL devices with the mixed PHT LB films in different number of layers.

In summary, we demonstrated that the mixed PHT LB films could function as a hole-injection layer for EL devices. Onset voltage of EL devices using PHT LB films decreased with increasing number of layers. The current efficiency was improved at the monolayer PHT LB film EL devices.

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