Evidence of band bending observed by electroabsorption studies in polymer light emitting device with ionomer/Al or LiF/Al cathode

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We report electroabsorption studies of indium–tin–oxide (ITO)/poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylenevinylene] insulating layer/Al light-emitting devices. An ionomer and LiF were used as the insulating layer. The internal electric field was nullified at the same bias voltage of 0.6 V for different cathodes of Al, ionomer/Al, and LiF/Al. The bias voltage is close to the work-function difference between ITO and Al. Average electric field in the emitting layer was increased by inserting the insulating layers. On the contrary, current density was increased significantly. These observations suggest band bending in the devices with ionomer/Al or LiF/Al cathode. © 2000 American Institute of Physics. [S0003-6951(00)01116-5]

Electroluminescence from organic and polymeric materials is under active research nowadays because of its application to displays. In the device, indium–tin–oxide (ITO) is usually used as a transparent anode for the hole injection and low work function metals like Ca, MgAg alloy, and AlLi alloy as a cathode. However, the low work function metals are susceptible to degradation upon exposure to air. It is therefore desirable to use less volatile metals like Al.

Recently, it has been shown that insertion of a thin insulating layer between an emitting layer and a cathode make it possible to use Al as the cathode without the reduction of device performance. Various materials such as SiO₂, poly(methylmethacrylate) (PMMA), LiF, Al₂O₃, a self-assembled layer, and an ionomer have been exploited as the insulating layers. Even for a wide range of the material characteristics, the device incorporating the insulating layers showed similar characteristics. They improve emission efficiency significantly, reduce the threshold or the operation voltage, and increase the maximum achievable luminance compared to the device without the insulating layer.

Various mechanisms have been proposed to explain the characteristics for different device systems. They include the lowering of the effective barrier height resulting from the large voltage drop across the insulating layer to help the tunneling of electrons, band bending, removal of exciton-quenching gap states formed at the organic/metal interface, appearance of dipoles at the interface to reduce the barrier height or bridging the Al electrode and the emitting layer by ions. However, similar characteristics of the devices incorporating the insulating layer indicate that there are common mechanisms applicable to them although other mechanism may play a role for a specific system.

In this report, we used electroabsorption technique (EA) to directly measure the electric field in the emitting layer of the ITO/poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEHPPV)/insulating layer/Al system. We used LiF and an ionomer of sodium sulfonated polystyrene (SSPS) as the insulating materials. EA signal showed that the average electric field in the emitting layer was reduced under the same external bias as the insulating layers were inserted. The direct-current (dc) bias to null the internal electric field is the same for the different insulating materials. Combined with current–voltage–luminance characteristics, the observations indicate that the band bending and the tunneling model can be applied to the systems.

We fabricated two types of devices, ITO/MEHPPV/SSPS/Al and ITO/MEHPPV/LiF/Al with various insulator thicknesses. ITO glass was obtained from Samsung Display Inc. and cleaned in an ultrasonic bath of isopropyl alcohol, aceton, and methanol, respectively, followed by drying in the vacuum oven at 100 °C. MEHPPV dissolved in dichloroethane was spin coated on the ITO. The thickness of the MEHPPV was about 100 nm. SSPS ionomer was prepared in ethylene dichloride using acetyl sulfonate as a sulfonation agent. The ion content was controlled at 6.7 mol %. Details of the ionomer synthesis are described elsewhere. The ionomer was coated upon MEHPPV with the thickness of 10–25 nm. LiF and Al were evaporated. The pressure during the deposition was about 10⁻⁶ Torr. The thickness of LiF was varied between 0.5 and 1.5 nm, and that of the Al layer was about 200 nm. The electroluminescence intensity was measured by a calibrated silicon photodiode.

The EA measurements were performed in the reflection geometry. Monochromatized light from a tungsten lamp was focused on the device. 500 Hz modulation signal from a function generator was applied to the sample as an alternating-current (ac) bias. A photomultiplier and a lockin amplifier were used to detect the modulated light. All the measurements were performed at room temperature in air.

Figures 1(a) and 1(b) shows the current density and luminescent intensity versus forward bias voltage in the ITO/MEHPPV/SSPS or LiF/Al devices. The devices with the ins-
Insulating layers were turned on at lower bias voltage compared to the corresponding MEHPPV single layer device. The turn on voltage was lowered significantly when a 12–15-nm-thick SSPS layer was inserted and the highest light output was obtained from the device with a 15-nm-thick SSPS layer. It is interesting to note that the current density in the device with a 12-nm-thick SSPS layer increased sharply at the lower voltage than in the device with a 15-nm-thick layer. In contrast, the devices were turned on at the nearly same voltage and the device with the 15-nm-thick SSPS layer exhibits a higher light output, resulting in a higher quantum efficiency. The insulating layers improved the device quantum efficiency by one order of magnitude with lower turn on voltage compared to the device without them. Further increment of the thickness of the SSPS layer reduced the current density and increased the turn on voltage. The trend was almost the same in the ITO/MEHPPV/LiF/Al devices. The current density and the luminescent intensity peaked at 0.5 nm and were decreased with further increment of the thickness. The characteristics of the devices with the thicker LiF layers are not included in the figures for clarity.

The absorption and the EA spectra are shown in Fig. 2. The onset of absorption is at 2.17 eV and its peak occurs at 2.47 eV. The EA responses measured at the peak wavelength of 576 nm are displayed as a function of the applied dc bias in Fig. 3 for the ITO/MEHPPV/Al, ITO/MEHPPV/SSPS/Al, and ITO/MEHPPV/LiF/Al devices. The signal was measured with an ac bias of 6 V and the dc bias was scanned from −4 to 4 V. The EA responses were the linear functions of the applied dc bias. The EA signals become zero at the applied bias of 0.6 eV for all the devices, which is close to the work function difference between the ITO and Al. Since the voltage nullifying the EA signal corresponds to the bias to cancel the internal electric field, the results indicate that the insertion of the SSPS or LiF insulating layers does not change the energy level alignment of the comprising electrodes and the emitting layer. The result is in contrast to the report of the highest occupied molecular orbital (HOMO) level shift in the Alq3 devices observed by X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) experiments.4 The reason of the difference is not clear yet.

The EA signal from ITO/MEHPPV/SSPS/Al at a certain bias voltage is smaller than that from ITO/MEHPPV/Al. As the insulating layer is getting thicker, the EA signal becomes smaller (low electric field). The results indicate that there is a significant potential drop through the ionomer or LiF layer. The potential drops are about 30% for 12-nm-thick SSPS layer and 70% for the 15- and 22-nm-thick layers, respectively. It is interesting to note that a lower average electric field in the MEHPPV layer of the ITO/MEHPPV/SSPS/Al device results in a higher current density than the ITO/
MEHPPV/Al device. Since the major component of the observed current is the hole current as proved by the previous works on the MEHPPV single layer and ITO/MEHPPV/SSPS/Al devices, the fact implies that the hole injection works on the MEHPPV single layer and ITO/MEHPPV/SSPS/Al devices.

The behavior can be understood by considering the band bending and tunneling model as schematically shown in Fig. 4. For the device with the 12-nm-thick SSPS layer, the electric field near the ITO electrode must be larger than the single layer device to have a larger current. The average electric field in the emitting layer, however, must be smaller as manifested by the low EA signal. These two requirements naturally lead to the band bending as schematically shown in Fig. 4(b). If a large electric field is applied to the ionomer, the rearrangement of the sodium ions toward the Al electrode and sulfonium ions toward the MEHPPV layer may take place. The pile-up of anions at the interface between the ionomer and the emitting layer may induce the band bending. With the insulating layer getting thicker, the average electric field becomes smaller due to the large potential drop caused by the insulating layer. As a result, the electric field near the anode will be reduced resulting in lower current. On the contrary, there is a possibility that the large potential drop improves the electron injection from the cathode. The situation is schematically shown in Fig. 4(c). This may be the case observed in the device having the 15-nm-thick ionomer layer.

In summary, we have studied the effect of the ionomer and LiF layer inserted in a polymer light emitting device on the electric field by electroabsorption measurement along with the $I-V-L$ characteristics. The internal electric field is nullified at the same bias voltage independent of the insulating materials and the thickness, and the current density is increased with the appearance of the insulating layers. On the contrary, the average electric field in the emitting layer is reduced by inserting the SSPS or LiF layers. The behavior can be understood by considering the band bending and tunneling model.

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