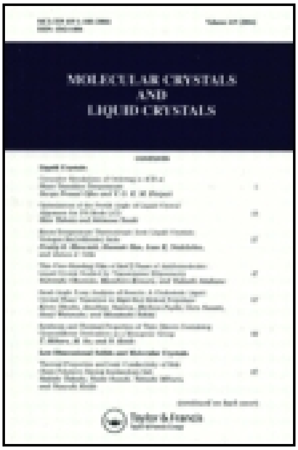

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# Built-in Voltage in $Alq_3$ Based Organic Light-Emitting Diodes Incorporating PEDOT:PSS and LiF Layer

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# Built-in Voltage in $Alq_3$ Based Organic Light-Emitting Diodes Incorporating PEDOT:PSS and LiF Layer

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*Built-in voltage was measured in $Alq_3$ based organic light-emitting diodes incorporating a PEDOT:PSS and LiF layer by using a modulated photocurrent technique at ambient conditions. A device was made with a structure of anode/$Alq_3$/cathode. Either an ITO or an ITO/PEDOT:PSS was used as an anode, and a LiF/Al was used as a cathode. The built-in voltage of the device is determined from a bias voltage-dependent photocurrent. The applied bias voltage when the magnitude of modulated photocurrent is zero corresponds to a built-in voltage. It was found that an incorporation of PEDOT:PSS layer between the ITO and $Alq_3$ increases a built-in voltage by about 0.4 V. This is consistent to a difference of a highest occupied energy states of ITO and PEDOT:PSS. This implies that a use of PEDOT:PSS layer in anode lowers a hole barrier height. With a use of bilayer cathode system LiF/Al, it was found that a built-in voltage increases as the LiF layer thickness increases in the thickness range of $0 \sim 1$ nm. It indicates that a very thin alkaline metal compound LiF lowers an electron barrier height. These results could be related to an improvement of device efficiency brought about by the insertion of PEDOT:PSS and LiF layer.*

**Keywords:** built-in voltage, modulated photocurrent, organic light-emitting diodes

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## 1. INTRODUCTION

There have been a great concern and lots of progress in organic light-emitting diodes since the first report by Tang and VanSlyke in 1987 [1]. The organic light-emitting diodes open a new research area such as flexible display, organic thin-film transistors, organic photovoltaic cells, organic detectors and etc. [2]. A basic feature of the device is a sandwich structure lying the organic layer in between the electrodes. Researches are mostly concerned on efficiency, lifetime, and operation voltage of the organic devices [3]. One of the well-known phenomena is that ITO/PEDOT:PSS combined anode has given a promising performance in device performance. lifetime, and an operating voltage. Here, PEDOT:PSS is a poly(3,4-ethylene dioxythiophene), PEDOT, doped with poly(styrene sufonate), PSS. By simply introducing a doped conductive and transparent polymer PEDOT:PSS in anode, hole injection and transport were highly improved.

Since the organic semiconductor is in general, an insulator, there occurs an electric field across the organic layer in the device even at zero bias voltage. This built-in electric field in the device is basically generated by an alignment of the Fermi level of the two electrodes. And a built-in voltage corresponds to a difference in the work functions of the anode and cathode. Study on the built-in voltage could contribute to an understanding of carrier transport and development of efficient organic light-emitting diodes, because it gives an information on work function of the electrodes and energy barrier height for charge injection at the electrodes.

Electroabsorption and modulated photocurrent spectroscopy are being commonly used in determining a built in voltage experimentally [4–6]. Brown *et al.*, reported that a built-in voltage increases by 0.5 V by inserting a PEDOT:PSS layer to the polymer device [4]. They employed an electroabsorption technique for a determination of the built-in voltage. And his group also reported a proper cathode structure in polymer device by measuring the built-in voltage [5].

In this paper, we discuss an implication of the built-in voltage obtained from the measurement of modulated photocurrent with a use of sing-layer sandwich structure of anode/$Alq_3$/cathode. Either an ITO or an ITO/PEDOT:PSS combination was used as an anode and a LiF/Al bilayer was used as a cathode.

## 2. EXPERIMENTAL

Figure 1 shows a device structure used in our study. Two types of device structure were made: One is ITO/$Alq_3$/LiF/Al and the other

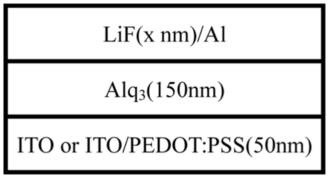



**FIGURE 1** Device structures of organic light-emitting diodes. One is ITO/$Alq_3$/LiF/Al and the other is ITO/PEDOT:PSS/$Alq_3$/LiF/Al. Thickness of LiF layer was varied from 0 to 1 nm.



is ITO/PEDOT:PSS/$Alq_3$/LiF/Al. Either an Indium-tin-oxide (ITO) or an ITO/PEDOT:PSS was used as an anode, and a LiF/Al was used as a cathode. The ITO substrate has a thickness of 180 nm and surface resistance of 10 Ω/sq, which was purchased from Asahi Co. After patterning the ITO strip line on 2 cm × 2 cm substrate, it was cleaned in chloroform ($CHCl_3$), ethyl alcohol ($C_2H_5OH$), and distilled water for 20 minutes each at 50°C in ultrasonic cleaning chamber. Cleaned ITO glass was dried with $N_2$ gas. The PEDOT:PSS solution (BAYTRON P) purchased from Bayer Werk Co was spin coated at 4000 rpm for one minute and dried at room temperature for a day. A measured thickness of PEDOT:PSS layer was about 50 nm. A 150 nm thick $Alq_3$ layer was formed by thermal evaporation at a pressure of $10^{-6}$ torr. And after 30 min, a LiF was thermally evaporated with a deposition rate of 0.5 Å/s successively. A thickness of LiF layer was made to be in the range of 0 to 1 nm. And then a 100 nm thick Al layer was thermally evaporated for electrode at a pressure of $10^{-6}$ torr.

Figure 2 shows a block diagram of an experimental setup for a measurement of modulated photocurrent spectroscopy. The organic light-emitting diode was connected in series with 5 kΩ external resistance, and these two were electrically connected to Keithley 236 source-measure unit for an application of bias voltage. The device was irradiated by the light from the 450 W Xenon light source (ORIEL Instruments 66021) chopped by rotating blade (Stanford Research SR540). Modulated frequency was set to 20 Hz. And the modulated photocurrent generated in the diode was measured as a function of the applied bias voltage using a dual phase lock-in amplifier (Stanford Research SR530) and an oscilloscope (Agilent 54610B). Phase-sensitive lock-in amplifier measures a magnitude and phase of photocurrent simultaneously.

## 3. RESULTS AND DISCUSSION

Figure 3 shows a typical behavior of magnitude and phase of modulated photocurrent as a function of the bias voltage measured by using

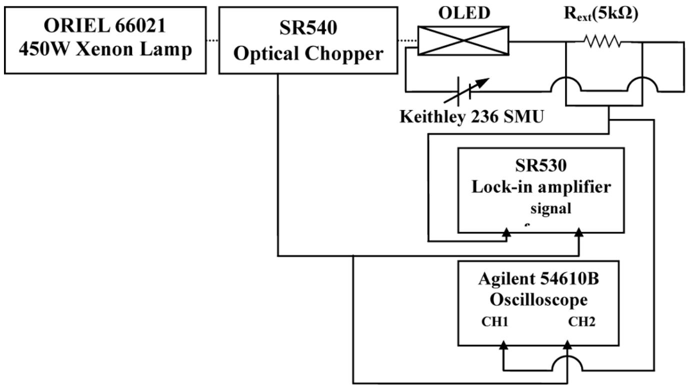
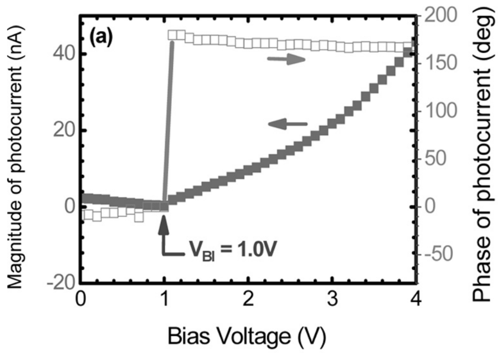



**FIGURE 2** Block diagram of experimental setup for a measurement of modulated photocurrent spectroscopy. The device is irradiated by the light from the Xenon light source chopped by rotating blade. And the modulated photocurrent is measured using phase-sensitive a lock-in amplifier and oscilloscope.

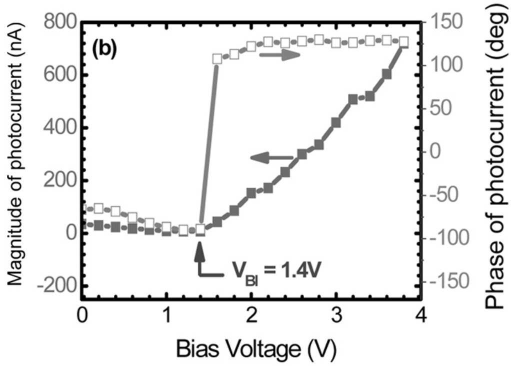


a phase-sensitive lock-in amplifier. The solid square(■) and the open square(□) in the figure represent a magnitude and phase of modulated current, respectively. Figure 3(a,b) are the results obtained from the ITO/$Alq_3$/Al device and ITO/PEDOT:PSS/$Alq_3$/AI device, respectively. This figure shows that as the bias voltage increases, the magnitude of photocurrent decreases up to certain voltage, and then increases again. In this case, the voltage when the magnitude of photocurrent is minimum corresponds to a built-in voltage. Around this voltage, the phase of photocurrent changes by about 180 degrees. In this way. we obtained the built-in voltage of 1.0 V in the device of ITO/$Alq_3$/Al, and 1.4 V in the device of ITO/PDOT:PSS/$Alq_3$/Al. From these results, we can see that the built-in voltage increases by 0.4 V when the PEDOT:PSS layer is inserted to the device. This increment of built-in voltage is consistent to a difference of highest occupied energy states of ITO and ITO/PEDOT:PSS. This implies that a use of PEDOT:PSS layer in anode reduces a barrier height for hole injection, which results in an improvement of efficiency of the device [7].

We can understand a mechanism of modulated photocurrent quantitatively as follows. When the $Alq_3$ molecules absorb the incident light, bound electrons are excited from the lower energy level to the higher one. Hence, there is a formation of excitons. The created excitons are tightly bound with a binding energy varying from 0.1 to 0.5 eV [5]. These excitons can dissociate into free electrons and holes under the influence of an electric field, the dissociated electrons and




(a)




(b)

**FIGURE 3** Magnitude and phase of modulated photocurrent as a function of bias voltage measured from the device of (a) ITO/$Alq_3$/Al and ITO/PEDOT:PSS/$Alq_3$/Al. The solid square(■) and the open square(□) represent a magnitude and a phase of photocurrent, respectively. Built-in voltage is the one when the magnitude of photocurrent is minimum.

holes drift through the organic layer due to an electric field across the organic layer. So that there is a photocurrent in the device. If we see Fig. 3, there is a non-zero photocurrent in the device even at zero applied bias voltage. It indicates that there is already a built-in electric field across the organic layer even at zero bias voltage. When the applied bias voltage compensates the built-in voltage, the free carriers do not drift in average because of flat-band formation across the organic layer. In this case, there is no net photocurrent flow. When the applied bias voltage is above the built-in voltage, there occurs an electric field across the organic layer in the opposite direction to the previous one. In this situation, a direction of photocurrent flow is

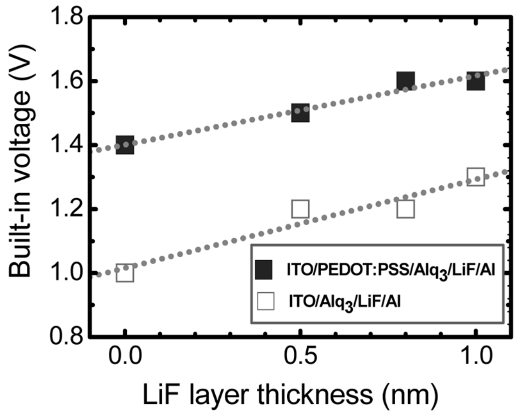



**FIGURE 4** Built-in voltage of ITO/$Alq_3$/LiF/Al(□) and ITO/PEDOT:PSS/$Alq_3$/LiF/Al (■) devices as a function of LiF layer thickness varying from 0 to 1 nm. There is an increase of built-in voltage as the LiF layer thickness increases.

opposite to the previous one. This causes a phase change of photocurrent by 180 degrees around the built-in voltage.

Figure 4 shows a built-in voltage of ITO/$Alq_3$/LiF/Al and ITO/PEDOT:PSS/$Alq_3$/LiF/Al device for several ultrathin LiF layer thickness varying from 0 to 1 nm. Since the general behavior of modulated photocurrent in these devices are similar to those of Fig. 3, we just plot the measured built-in voltages of these devices as a function of LiF layer thickness. The open square (□) and the solid square (■) in the figure represent the built-in voltage for ITO/$Alq_3$/LiF/Al device and ITO/PEDOT:PSS/$Alq_3$/LiF/Al device, respectively. In general, as can be seen in the figure, there is an increase of built-in voltage as the LiF layer thickness increases. We can also see that the built-in voltage in ITO/PEDOT:PSS/$Alq_3$/LiF/Al is higher than the one in ITO/$Alq_3$/LiF/Al by about 0.4 V in the thickness range of LiF layer that we have used. There are several explanations for this lowering of barrier height [7,8]. One of the possible mechanism is the following. A deposition of aluminum on the LiF layer generates free Li atom, and it acts as a dopant to $Alq_3$, so that it makes a good electron injecting contact to $Alq_3$. Experimentally, it is detected as a lowering of a barrier height, and hence there is a lowering of work function of cathode. Our result that a use of ultrathin LiF layer in cathode increases a built-in voltage indicates a lowering of work function of cathode, which is consistent to the other reported works performed by different technique [8].

The lowering of barrier height in anode and cathode may affect on the efficiency of the device. Thus, we have also studied current-luminescence-voltage characteristics of these devices to investigate the efficiency. Even though they are not shown in this paper, a use of PEDOT:PSS layer gives an improvement in external quantum efficiency by a factor of three, and the efficiency of the device with 0.8 nm thick LiF layer is about ten times higher than the one with Al-only device.

## 4. CONCLUSION

We have studied a built-in voltage of the $Alq_3$-based organic light-emitting diodes using a modulated photocurrent spectroscopy. It is found that an incorporation of PEDOT:PSS layer between the ITO and $Alq_3$ causes an increase in built-in voltage by about 0.4 V. This amount of increment of built-in voltage is consistent to the difference of highest occupied energy states of ITO and PEDOT:PSS. It indicates that a use of PEDO:LPSS layer in anode reduces a barrier height for hole injection. We have also found that an implement of ultrathin alkaline metal compound LiF layer in cathode functions as a lowering of the electron barrier height. As the LiF layer thickness increases, the built-in voltage increases as well in the thickness range of LiF below 1 nm. From the measurement of modulated photocurrent, we were able to determine the built-in voltage, which is useful in constructing an optimum device structure.

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