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Journal of Luminescence 75 (1997) 361–365

JOURNAL OF
LUMINESCENCE

The effect of a metal electrode on PPV electroluminescence processes

Junbiao Peng^{a,*}, Byun-Yong Yu^b, Chong-Hong Pyun^b, Chang-Hong Kim^b, Jung-Il Jin^c

^a *The Laboratory of Excited State Processes, Chinese Academy of Sciences, 1 Yan An Street, Changchun, Jilin 130021, People's Republic of China*

^b *Solid State Chemistry Laboratory, Korea Institute of Science and Technology, P. O. Box 131, Dongdaemun, Seoul 130-650, South Korea*

^c *Department of Chemistry, Korea University, Seoul 136-701, South Korea*

Received 15 October 1996; received in revised form 19 May 1997; accepted 12 June 1997

Abstract

Two metal electrodes of aluminum (Al) and calcium (Ca), which have different work functions, were used to fabricate EL devices based on poly(p-phenylene vinylene) (PPV) with single-layer structure. A new experimental phenomenon is discovered. The electroluminescent (EL) spectra are different in EL devices with metal electrode of Al and Ca. The feature is expressed as a variation of the ratio of intensity from the peak at 550 nm to the peak at 510 nm. From this, we discussed the main type of carrier moving in PPV film with Al and Ca electrodes, respectively. By comparing the processes between EL and photoluminescence (PL), a reason for the difference in EL spectra with Al and Ca electrodes was analyzed.

Keywords: Electroluminescence; Photoluminescence; Metal electrode effect; Poly(p-phenylene vinylene) (PPV)

1. Introduction

Since Tang [1] and Adachi [2] reported high-performance organic thin film electroluminescence (OTFEL) devices, OTFEL is considered as a possibility for one of the excellent flat-plane display. Polymer is becoming a more and more important material for functional layers in EL devices due to its special stability towards heat and electricity. Conjugated polymers have non-localized state π electrons resulting in low drive voltage, high brightness and luminant efficiency. PPV is one of this kind of conjugated polymer.

PPV was synthesized first by Wessling [3] in 1968, and then Murase et al. [4] studied its conducting properties by doping. Until 1990 [5] PPV was discovered having excellent electroluminescent characteristics, subsequently polymer electroluminescence was studied.

Up till now, PPV and its family as EL materials were studied much [5–8]. In all the papers PPV is considered as a hole transport material. Under the influence of an applied electric field, holes as majority carriers migrate in PPV film. Because in PPV EL devices, the emissive region is opposed to the cathode interface, e.g., in the EL device with single-layer structure of ITO/PPV/Al (where ITO is $\text{In}_2\text{O}_3:\text{Sn}$ film as transparent electrode), the emissive region is near the interface of PPV/Al. So

* Corresponding author. Fax: 86-431-5955378; e-mail: pjbwl@public.cc.jl.cn.

to sandwich an electron-transport layer between PPV and a metal electrode can much improve EL brightness and efficiency [6]. Our previous work shows Al electrode can have influence on the EL spectrum in the interface of PPV/Al [9]. Now, by further research and experiments, we found that a metal electrode also can have influence on the main type of carrier which transports in PPV film. This result is very important for choosing an optimal EL structure.

2. Experimental

All the devices for a measurement have a single-layer structure of ITO/PPV/Al or Ca/Al which is a protection layer for Ca electrode against oxidation. ITO ($\text{In}_3\text{O}_2:\text{Sn}$ prepared by sputter on glass) with high work function of 4.6 eV is the transparent electrode. Before preparing the PPV film, an ITO substrate is cleaned thoroughly by the method of methanol and aston in ultrasonic, and then a PPV precursor methanol solution is spun-coated on cleaned ITO substrate.

A PPV precursor film is dried in an oven gradually and then put in a heating system with vacuum at pressure below 5×10^{-3} Torr, gradually heating it from room temperature to 360°C , keeping for 12 h at a constant temperature, and then naturally cooling it to room temperature. The PPV precursor can be converted to PPV fully. Al and Ca electrodes were evaporated in a vacuum at pressure below 5×10^{-6} Torr. The thickness of the metal electrode is about 1000 \AA . The typical emission area is about 8 mm^2 . The conversion route of PPV precursor to PPV is shown in Fig. 1. All the PPV

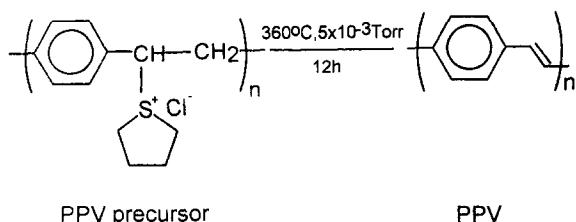


Fig. 1. PPV chemical structure and converted route from its precursor.

films used here are converted simultaneously. So it is reasonable that all the PPV films conversion conditions are same.

The PL spectra are measured in samples of ITO/PPV, ITO/PPV/Al and ITO/PPV/Ca/Al, respectively. The excitation wavelength is 350 nm. During measuring, the excitation beam through the ITO substrate excites PPV film with 45° angle between incident beam and sample surface and with vertical to viewing beam. For EL spectrum recording, the viewing direction is vertical to device surface. There is almost no fluorescence and absorption between 450 and 650 nm from ITO glass.

PL and EL spectra were recorded by a spectrofluorescence meter assembled by the laboratory of Korea Institute of Science and Technology. A thickness of PPV film was controlled by PPV precursor solution concentration and spin-coating rate and was measured using profile of Alpha-step 200 with resolution of 0.5 nm. All the measurements were performed in air at room temperature.

3. Results and discussion

Fig. 2 shows the PL and EL spectra from PPV film with Al electrode (for comparing conveniently, all the spectra are normalized at the peak of 510 nm). The PL spectrum in the sample of ITO/PPV is denoted to $P1$ which is same as that in Ref. [5], suggesting during the conversion long chains of PPV precursor are not oxidized, and converted to PPV fully. In the structure of ITO/PPV ($\sim 30 \text{ nm}$)/Al, an EL spectrum was measured (where the EL curve is denoted by $E1$), and the peak positions of $E1$ are almost same as those of $P1$, but the contour of $P1$ and $E1$ are much different. In $E1$, the ratio of the peak intensity of 550 nm (denoted by I_{E550}) to peak of 510 nm (denoted by I_{E510}) is much lower than that in $P1$, i.e. $I_{E550}/I_{E510} < I_{P550}/I_{P510}$. Therefore, the color in photoluminescence looks like yellowish-green, while the EL color is green. Besides, $E1$ contour is not changed much by a thickness of PPV film, see Fig. 2 (the thickness of PPV film for curve $E2$ is about 140 nm). What are the features that result in this kind of difference between $P1$ and $E1$ spectra?

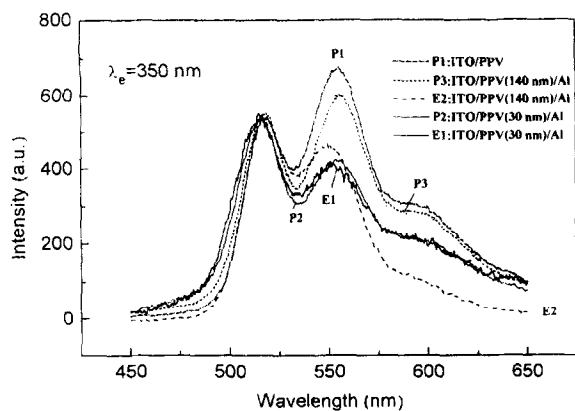


Fig. 2. The PL and EL spectra for PPV in the structure of ITO/PPV(30 and 140 nm)/Al and glass/PPV.

In general, some possible factors can (or may) influence the relative ratio of intensity among peaks in EL and PL spectra, such as optical interference in PPV film, self-absorption and reflection from Al and Ca electrodes. When measuring the PL and EL spectra for all the samples and devices used, changing the incident and viewing angles, the PL and EL spectra are not varied significantly, suggesting almost no interference phenomenon in the samples and devices. For PPV polymer, the absorption peak is at 430 nm [10], the emission peak at the shortest wavelength is at about 510 nm, so it is expected that a self-absorption effect is very weak. If there exists weak absorption, the intensity of the peak at 510 nm in an EL spectrum should be relatively lower, but higher. In addition, the reflection spectra were also measured from the samples of Ca and Al films on quartz substrate, no reflection peak is observed. Therefore, the possible factors of interface, self-absorption and metal electrode reflection are not the main reasons for the difference between *P1* and *E1*. It is considered that there is no essential difference between PL and EL processes which all are radiative transition of excitons formed by holes and electrons. Here the sole difference in the sample structures for *E1*, *E2* and *P1* is with or without Al electrode. So the thin PPV film with the structure of ITO/PPV(~ 30 nm)/Al was used to get a PL spectrum, of which curve is denoted as *P2* (see. Fig. 2). It is very clear that *P2* is closer to *E1*, suggesting the

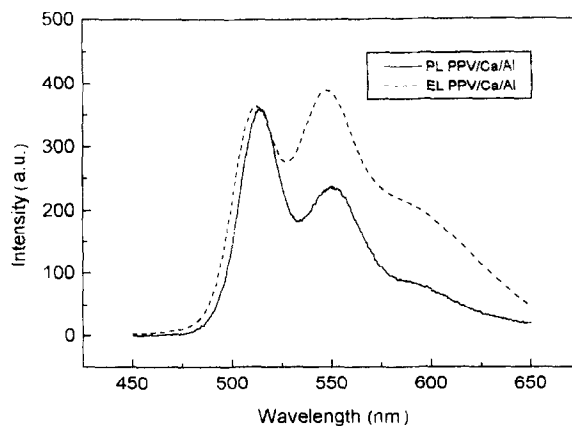


Fig. 3. The PL and EL spectra for PPV in the structure of ITO/PPV (30 nm)/Ca/Al.

difference between *P1* and *E1* is due to the influence of the Al electrode. For PL spectrum, the influence of the Al electrode is decreased as increasing the thickness of PPV film, such as curve *P3* (see. Fig. 2) measured in PPV film 140 nm thick. This may be explained as follows in PL processes, the exciton recombination region (where giving rise to PL and EL emission) fill the entire PPV film. The influence from Al electrode is just limited to near the interface of PPV/Al, while in EL processes, by increasing PPV film thick, the EL contour is not changed much (see. curve *E2* with 140 nm PPV thick in Fig. 2). From this, it can be deduced that exciton recombination region with Al electrode is close to the interface of PPV/Al. So under high electric field, holes injected from ITO electrode are transported passing the PPV film to the interface of PPV/Al, where holes form the excitons with electrons injected from the Al electrode, suggesting the main type of carrier is a hole but an electron.

Fig. 3 shows PL and EL spectra in the structure of ITO/PPV(~ 30 nm)/Ca/Al (for comparing conveniently, here just show the normalized spectra). It is evident that the peak positions of PL and EL spectra are almost the same, but the situation is just opposite to that with the structure of Al electrode. In the case of Ca electrode, the ratio of I_{E550}/I_{E510} is larger than that of I_{P550}/I_{P510} , and the contour of EL curve is close to the *P1* measured in the structure of ITO/PPV (see. Fig. 2). It suggests that Ca

electrode can also influence PL spectral band. The PL spectrum is influenced by the Ca electrode seriously. As with Al electrode, experiments show that the influence decreases with increasing PPV thickness. It suggests that the influence from the Ca electrode is also limited near the interface of PPV/Ca. However, the EL spectral band is almost not influenced by the Ca electrode, suggesting that the exciton recombination region in the EL processes with the Ca electrode is close to the interface of ITO/PPV, only far from the Ca electrode, the EL spectral band can avoid the influence of the Ca electrode. So, in the EL processes with Ca electrode, the main type of carrier in PPV film under high electric field is an electron but a hole.

We present some possible reasons for the luminescent spectra influenced by a metal electrode. First, during preparation of the Al or Ca electrode, using a method of heat evaporation in a high vacuum, the Al or Ca atoms from hot source may penetrate and diffuse into the PPV film causing rise of PPV polymer interchains and makes the spectra blue-shift. Second, it is possible that existing some chemical reaction between Al or Ca with PPV [11,12]. These factors all can reduce the valid conjugated length of PPV chains at the interface of PPV/Al or Ca, resulting in luminescent spectra similar to that in PPV copolymer [13].

Why is the main type of carrier in PPV film different in structure for various metal electrodes? Possibly the reason is the work function of the metal electrode. An electron electrode with high work function can produce high barrier at the interface of PPV/metal electrode. In addition, after spin coating, the PPV precursor film on ITO glass is of noncrystal structure. So a carrier injection from electrode and transportation in PPV film depend on high electric field ($\sim 10^6$ V/cm). Under high electric field, the main type of carrier depends on not only electrical properties of bulk material, but the injection efficiency from metal electrode to PPV film. The work function of Ca electrode (2.87 eV) is much lower than that of Al (4.28 eV). So the injection efficiency of electron from Ca electrode is higher than that from Al electrode, and it is possible that the injection effi-

ciency is also higher than that of hole injection from ITO into PPV.

4. Conclusions

Al and Ca electrodes can influence the PL and EL spectra of PPV polymer. This is due to different exciton recombination regions. When Al is the electrode, the region is near to the interface of PPV/Al. When Ca is the electrode, the region is moved to the interface of ITO/PPV. These are due to the different work function between Al and Ca resulting in different injection energy of electrons under high electric field. We can expect that inserting a hole transport layer between the interface of ITO/PPV can much improve EL efficiency in the structure of Ca as electrode. In the EL device with Al electrode, inserting an electron transport layer between the interface of PPV/Al can much improve the EL efficiency.

Acknowledgements

This work was supported by the Korea Center for International Science and Technology Cooperation, Science and Technology Policy Institute (STEPI).

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