The effect of transition metals coated by the laser ablation technique on the photoluminescence of MEH-PPV(poly(2-methoxy,5-(2'-ethyl-hexyloxy)-p-phenylenevinylene))

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Abstract

Using transition metals including Ni, Fe and Cu as dopants and MEH-PPV (poly(2-methoxy,5-(2'-ethyl-hexyloxy)-p-phenylenevinylene)) as the organic material we studied the PL intensity of the doped polymer. It has been found that PL intensities decreased by laser ablation of metals in all cases except in the case of Fe when the laser ablation process was carried out for 30 s. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Conjugated polymer electroluminescence devices (CPELD) have received a rapidly expanding attention over the last decade after discovery of poly(p-phenylene vinylene) (PPV) [1–3]. The first CPELD device was consisted of a PPV sandwiched between a metal electrode coated with an indium thin oxide (ITO) layer and a sole metal layer [4]. Since then there have been continuous improvements on the CPELD materials resulting in excellent physical properties such that full color displays (including three main blue, red and green colors) are now available [5–8]. It has been found that adding a side group such as MEH(2-methoxy-5-(2'-ethylhexyloxy) to PPV could result in even better performances for CPELD [1].

The nature of the anode and cathode electrodes is as important as the organic material with respect to a successful display device. Under application of a dc bias, electrons are injected from a low work function cathode and holes are injected from a high work function anode into the organic polymeric material, where they meet and emit photons. Therefore, the lower or higher work functions of selected cathodes and anodes could affect the extent of the produced luminescent excitation [9,10]. In 1996 Sheats et al. [9] reported that the use of Al, Ca, Mg and Ag as electrode materials can affect not only the light output but also the lifetime of the display devices.

Besides organic material and the electrodes, temperature plays an important role in the performance of CPELD. Sheats et al. [9] also pointed out that increasing the temperature from 30 to 60°C reduced the lifetime of a MEH-PPV display device by a factor of 20.

Another crucially important parameter that has received enormous attentions from scientists in the area of organic display devices (ODD) is the polymer/electrode interface. An alternative to improve interface properties is the use of a metal doped electron injecting layer. Kido and Matsumoto demonstrated that using this method could result in lowering the driving voltage [11,12].

Considering all of the above-mentioned parameters in development of a CPELD, we, now, report on a new study on the effect of metal (as dopant) on photoluminescence properties of MEH-PPV. In this study we have selected a series of transition metals (Cu, Ni, and Fe) incorporated to the organic polymer via laser ablation.

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2. Experimental

The synthesis of poly(2-methoxy-5-(2'-ethyl-hexyloxy)-p-phenylenevinylene) was carried out based on the previously published work [13] as shown in Fig. 1. The polymerization was followed by the metal doping process using the laser ablation technique. The MEH-PPV film (with approximately 1000 thickness) was prepared on the glass employing the spin coating method. Various transition metals were incorporated to the polymer by laser ablation for several duration of time (30, 120 and 240 s). In the laser ablation process, the metal target was mounted 2 cm away from the substrate (glass coated with polymer) and a focused Nd:YAG laser beam (266 nm, 40 mJ/pulse, 10 Hz) impinged the rotating metal target in an inert atmosphere (using He at 200 mTorr).

To study the structure of polymer/metal interface, depth profiles of the doped samples were examined by the X-ray photoemission spectroscopy (XPS). Thickness of samples were measured by Alpha-Step 500 (Tencor Instruments). After preparation of the doped MEH-PPV photoluminescence (PL) measurements were carried out using the configuration shown in Fig. 2. Ar$^+$ ion laser light was used for excitation at 488 nm. All experiments were carried out at room temperature. Metal targets (Ni, Fe and Cu) were provided by Nilaco Co.

3. Results and discussion

As explained in the Section 2, Ni, Fe and Cu were incorporated to the polymer film via laser ablation technique. Using this technique different amount of metals were deposited on/into the polymer by increasing the time (from 30 s up to 4 min) consumed during the laser ablation. This process was followed by PL intensity measurements. The PL spectra for the Ni, Fe and Cu incorporated in MEH-PPVs are presented in Figs. 3–5, respectively.

As can be seen from Fig. 3, although the increase of the ablation time caused noticeable changes in the line shape and peak position of the PL spectra, there have been dramatic changes in the PL intensity when Ni was used as dopant. The undoped polymer lost almost half of its PL intensity after 30 s incorporation of Ni by the laser ablation method. The PL intensity continued to decrease as the laser ablation time increased.

Interestingly, this is not the case with Fe (Fig. 4) since improvements in PL intensity have been observed after 30 s of the laser doping. Such improvement in the PL intensity could be more appreciated by disclosing the transmittance information (Fig. 6). As can be seen from the figure there is
no difference in transmission at 488 nm which corresponds to the excitation energy of the PL measurements. The transmittance usually decreases with metal doping and also with increasing the thickness of the metal thickness. However, we obtained an optimum time for the laser doping of Fe (30 s) such that PL intensity improvement was achieved with similar transmission. As explained above in most cases in the field of semiconductors including organic materials the PL intensity decreases by doping [14] because of the defect creation that is induced by the doping process. Hence, similar to Ni, PL intensity reduction was experienced for Fe (as shown in Fig. 4) as the time of laser ablation increased to 120 and 240 s.

This theory can be supported by examination of the X-ray photoemission spectroscopy (XPS) result (Fig. 7). The XPS of the interface between Fe and MEH-PPV has shown that the transition metal has first been chemically incorporated into the polymer chains (sputter time 5–10 min in Fig. 7) and then physically covered the thin polymer/metal interface. This result rejects any possibility of the involvement of Fe deep into the bulk polymer. From our observations and with respect to the sputter time shown in Fig. 7, the metallic/polymeric interface region is between 5 and 15 min, and the polymer/glass interface region was seen between 35 and 40 min. By increasing the time of laser ablation, no change of the polymer/metal structure was observed while we increased the thickness of the metallic layer resulting in less PL intensity.

Using Cu as dopant (Fig. 5) resulted in a very linear change in the PL intensity of MEH-PPV. In this linear profile the PL intensity decreased by increasing the time of laser incorporation of the metal. It should be noted that although the changes in the height of the peaks are different for Ni, Fe and Cu cases (Figs. 3–5, respectively) the position of the peaks are similar in all cases. Therefore, irrespective to the type of the transition metal used in this study the MEH-PPV samples could show the same color with different PL intensities.

4. Conclusion

In conclusion, based on experimental evidence from XPS and PL profiles we found that the incorporation of transition metals (Ni, Fe and Cu) decreased the PL intensity of MEH-PPV. Nevertheless, if an optimum amount of Fe is incorporated to the polymer (using the laser ablation for 30 s) a higher PL intensity could be achieved. As the thickness of the metal layer increased the PL intensity decreased in all cases studied in this research. The PL intensity was drastically decreased when Ni and Cu were used.

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