

Electrochemical and Auger Electron Spectroscopic Studies of Poly(p-phenylene vinylene) LB Film Based Electroluminescent Device

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INTRODUCTION

Electroluminescence (EL) of polymeric materials has attracted widespread attention since Burroughes et al.¹ demonstrated that the light-emitting diode based on a spin-cast film of poly(p-phenylene vinylene) (PPV) could be readily fabricated. Meanwhile, the advantages of polymers, such as good thermal stability and mechanical strength, over low molecular weight dyes and the potential applicability for polymers for use in the large area displays stimulated research on polymer LEDs.²⁻⁶

In the review of current research concerning PPV EL devices, a lot of efforts have been put into improving the EL efficiency. As an available approach, chemical modification of the polymer structure or structural modification of the device has been employed, and considerable progress has been made.⁴⁻⁶

In our previous papers,^{7,8} we reported the fabrication of PPV EL devices with only polymeric LB films, wherein a significant improvement of the EL efficiency was realized by incorporation of a hole transporting layer (HTL) - polyimide LB film between the ITO anode and light emitting layer - PPV LB film. In the current work, in order to explain the function of the HTL polyimide in our EL device, the oxidation potential as well as ionization potential of the polyimide and PPV LB film was compared. Furthermore, the interface between the evaporated Mg-Ag electrode and organic layer was investigated by auger electron spectroscopy (AES).

EXPERIMENTAL

The EL device, which consisted of a light emitting PPV and a hole transporting polyimide LB layers and which were sandwiched between a semi-transparent ITO anode and a Mg-Ag alloy cathode, was prepared following the method as reported in reference 7.

The cyclic voltammetry of PPV LB film and polyimide LB film deposited on ITO coated substrate was performed under inert conditions using a three-electrode cell. A Pt plate was used as the counter electrode and a Ag wire inserted in the supporting electrolyte containing 0.1 mol/l AgNO₃ was used as the reference electrode. The supporting electrolyte was prepared under N₂ atmosphere using acetonitrile as the solvent into which 0.1 mol/l Et₄NClO₄ was dissolved. The scan speed was 100 mV/s. The electrochemical cell was not calibrated.

The auger electron spectroscopy (AES) was measured with Ar⁺ ion sputtering with a take-off angle of 75°.

RESULTS AND DISCUSSION

Oxidation and ionization potential

The ITO electrode was used as the anode in the EL device and for electrochemical measurements the PPV and the polyimide LB films were deposited on the ITO coated substrate. Figure 1 shows the sequential cyclic voltammograms of PPV and polyimide LB films against a Ag/Ag⁺ reference electrode. For the polyimide LB film, little variation was seen when repeated cycling between the oxidized and neutral states.

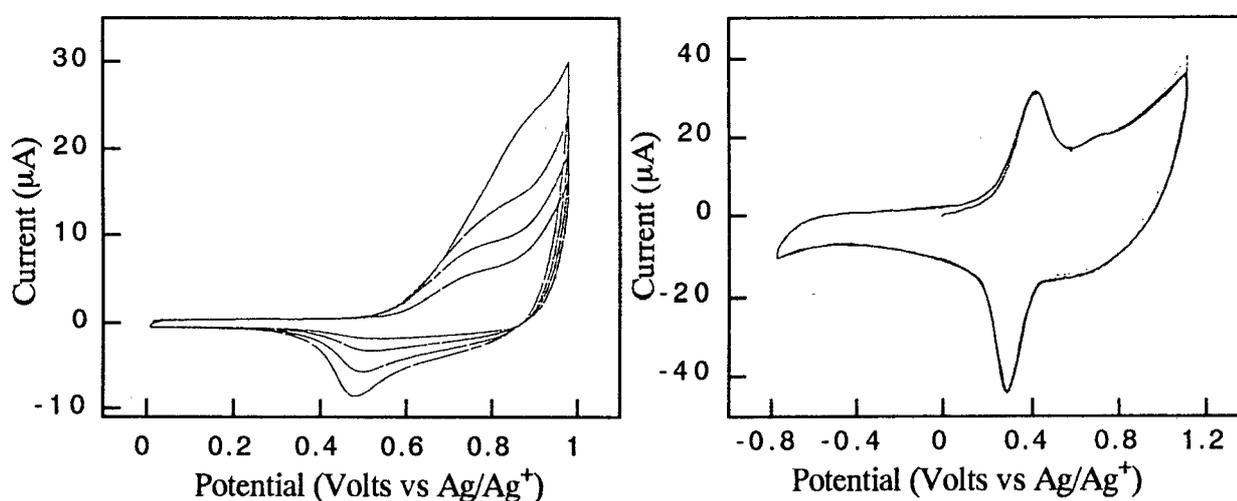


Fig. 1. Sequential cyclic voltammograms of LB films at a scan speed of 100 mV/s.
 a: PPV LB film deposited as 41 layers on an ITO coated substrate.
 b: HTL polyimide LB film deposited as 41 layers on an ITO coated substrate.

Table 1. Relative peak position of cyclic voltammogram and ionization potential (I_p) of the PPV and the polyimide LB films

LB film	Potential Vs Ag/Ag ⁺			I_p (eV)
	E_{ox} (V)	E_{red} (V)	$E_{1/2}$ (V)	
PPV	0.81	0.50	0.66	5.7
HTL	0.45	0.32	0.39	5.45

The relative peak position of cyclic voltammogram of the PPV and the polyimide LB films is listed in Table 1. It should be noted that the doping threshold potential for the polyimide LB film was located about 0.29 V lower than that of the PPV LB film. This may indicate that the HOMO of the polyimide LB film is at a higher energy state than that of the PPV LB film by

about 0.29 eV. Meanwhile, the oxidation potential vs Ag/Ag^+ were located at about 0.66 V and 0.39 V for the PPV and the polyimide LB film, respectively. The low oxidation potential of the polyimide LB film implied that the polyimide LB film is easier to donate an electron to the ITO electrode than the PPV LB film. On the other hand, it became clear that the hole injection from the ITO electrode to the polyimide LB film is more easily done than to the PPV LB film. A similar result can also be seen in the ionization potentials listed in Table 1. Since the work function of ITO is reported to be about 4.6 eV,⁹ the energy gap between the ITO and the polyimide LB film, as well as the PPV LB film, was about 0.85 eV and 1.1 eV, respectively. The difference of the ionization potential between the polyimide LB film and the PPV LB film was about 0.25 eV, which indicated that the electron is easily injected from the former one.

In conclusion, the improvement of EL efficiency by incorporation of the polyimide LB film resulted from the promotion of hole injection from the ITO electrode. For the polyimide used in our work, the ability to donate electrons is attributed to the triphenyl amine group incorporated into the polymer backbone. The triphenyl amine derivatives, for example, N, N'-diphenyl-N, N'-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) are well known as hole transporting material in sublimed organic dye EL devices.¹⁰ The idea of introducing a functional group into the polymer has proven to be a novel and acceptable idea in molecular design and device fabrication.

Auger electron spectroscopy

In our previous studies of PPV LB film based EL, it was obvious that the current density was very high when the vacuum evaporated Mg-Ag alloy was used as the cathode. Since the thickness of polymer LB film was in the range of about 10 nm, the higher current density may be considered to be a result of the leakage current. Therefore, it raised a suspicion that the LB film itself was defective with pin-holes or that the LB film was defective when the metal electrode was deposited. As an approach to understand this problem, in-depth analysis of the interface between the electrode and organic layer was carried out by auger electron spectroscopy (AES).

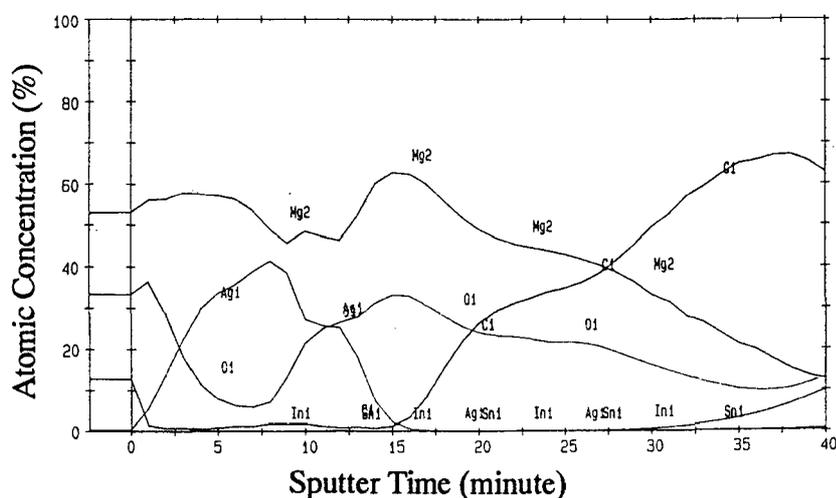


Fig. 2. AES profile of ITO/HTL(61L)/PPV(50L)/Mg-Ag EL device.

Using ion sputtering, information on the distribution of elements in the sample can be obtained by analyzing the dependence of line intensity on the sputtering time. Figure 2 shows the AES profile of the EL device, ITO/HTL(61L)/PPV(50L)/Mg-Ag. It is seen that in the outer-surface of the Mg-Ag alloy, the content of Ag is quite small and Mg may be oxidized, which is indicated by the high content of oxygen in the surface. The dependence of the content of Ag and carbon on the sputtering time revealed an interface between the metal and the organic layer for sputtering times of about 15 minutes. On the contrary, the content of Mg remained relatively high even in the organic layer. This indicated that Mg became incorporated into the organic layer after evaporation. Also the content of oxygen was higher in both layers, especially, in the organic layer it decreased in the same tendency as does Mg. This implied that Mg may exist in the form of magnesium oxide. The existence of Mg deep the organic layer may be the main reason for the leakage of current. However, it remained unclear as to why only Mg became incorporated into the organic layer, even though Mg and Ag was deposited at the same time but different deposition rates. A more detail investigation of LB film surface and the interface are under way.

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