Preparation of Light-Emitting Diodes with Poly(p-Phenylene Vinylene)

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1. Introduction

Tang and VanSlyke first reported an organic double layer electroluminescent(EL) device in 1987[1].

On the other hand the Cambridge group has been interested in polymer semiconductor devices for molecular electronic devices [2] and finally fabricated the first polymer light-emitting diode(PLED) from poly(p-phenylene vinylene) in 1990.

In 1992, UNIAX corporation and Heeger group[3] fabricated flexible PLED, polyaniline(PANI)(+)/poly(2-methoxy,5-(2′-ethyl-hexoxy)-1,4-phenylene vinylene (MEH-PPV)/Ca(-). So they gave us the possibility of a "roll-up" TV.

Sweden researchers[4] made PLED with variable colours from polymer blends. They utilized phase separation of polymer blends with 3-substituted polythiophene. Their devices emit different colors when applied voltage changes.

The aim of this research is to find an easier way to the preparation of PLED from PPV.

2. Experimental

2.1. PPV preparation

We followed the general synthetic procedure of Gmeiner et al.[5] As it is seen in **Fig.1**, 0.75M α,α′-dichloro-*p*-xylene was reacted with 2.25M tetrahydrothiophene at 50℃ in a 20% water and 80% methanol solution for 20h. The 1,4-phenylenedimethylene-bis(tetramethylene sulfonium chloride) salt monomer was purified by precipitating the reaction mixture in cold acetone(0℃). The monomer was filtered and vacuum dried.

In a 1*l*, 3-necked flask, 16.0g(45.5mmol) of the bis-sulfonium salt are dissolved in a mixture of 80ml of water and 45ml of methanol. The mixture is purged with nitrogen for one hour, cooled to 0℃ and 91ml(45.5mmol) of NaOH(0.5M) are added at once with rapid stirring. After stirring for 1 hr at 0℃, the polymerization is quenched by adding 36ml of 0.5M HCl until pH 6-7 is reached. The neutralized solution is dialyzed against deionized water for several days in order to separate the polymer from monomer
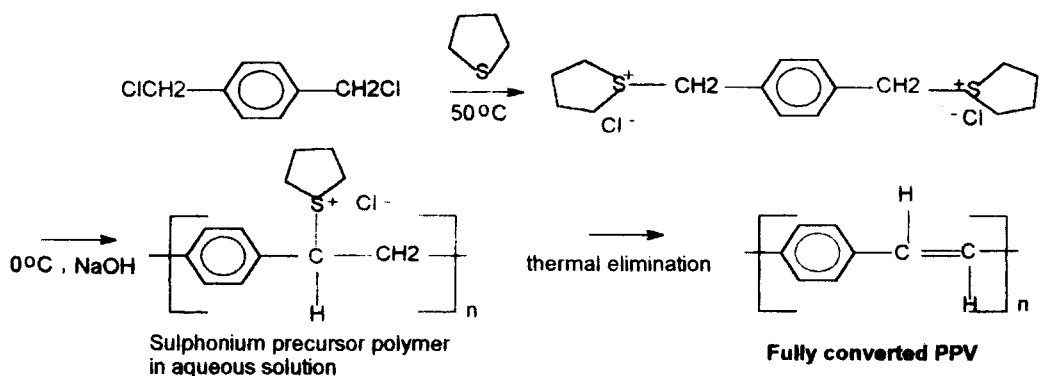
Fig.1. Synthetic route to Poly(*p*-phenylenevinylene).

residues. We use the dialysis tube of Speta/Por 3, lower-limit molecular weight cut-off 3500 Da.

2.2. Thermal elimination — TGA measurements

All the PPV polymer was obtained after the elimination reaction in the precursor film. To find the optimum condition for thermal elimination, we obtained TGA themograms and Infra-red spectra under various conditions.

2.3. Preparation of PPV LED

The precursor film was formed on the ITO glass by spin-coating with adjustment in both spin-speed and solution concentration. The concentration of precursor solution was about 1% and the thicknesses of coated film were measured by ellipsometry.
The precursor-coated ITO glass was then thermally converted at several tempeatures in vacuum and dry nitrogen stream (50 l/min) to convert the precursor polymers into PPV. Pure Al(99.9999%) electrodes were vacuum deposited on the PPV layer. The chamber was evacuated to 10^{-6} torr.

2.4. DC conductivity

DC conductivity of the PPV film was measured with the Keithley Electrometer (Model 617) in two-probe configuration. The conductivities of free-standing precusor of PPV films were measured co-planar geometry (mechanically pressed ITO contacts). External wires were fixed with to the electrodes with an alligator type connections.
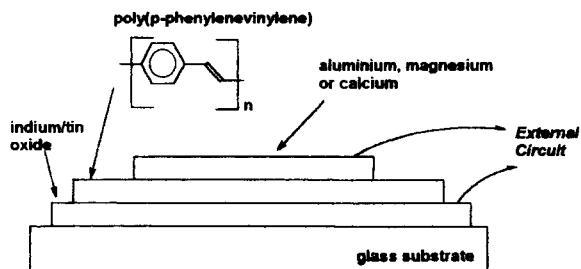
Single-layer polymer LED

Fig.2. Schematic sturcture of the PPV-based LEDs used in this study

3. Results and discussion

The thickness of spin coated film was agreed with the value of calculated and ellipsometry measurements. The density of PPV is reported to be 1.28g/cm^3 (Polyarylenevinylene films ; Tokio et al. 1990) and the wavelength of 6328 Å was used in Ellipsometry measurements.

spin rpm	Thickness(Å)			
	gravimetry	Ellipsometry		
		n	period	thickness
1000	2785	2.0092	1782.4	3870.7
1000	"	2.25	1782.4	2903.8
1000	"	2.7671	1215.8	2297.8
2000	2785	2.3159	1782.4	2259.5
3000	928	2.1791	1495	627.4
4000	928	2.2671	1609	517.3
5000	–	2.1817	1533.8	334.1

Table 1. Thickness of PPV film spin coated onto ITO substrate under various spin rpm.

The thinner film have more rapid elimination reaction than the thicker one, because of the slow heat conduction.

Thermal conversion to PPV is monitored by the disappearance of the absorption band at 3000 and 1450 cm^{-1}., which are aliphatic C-H absorptions.

From the onset of the $\pi - \pi^*$ absorption of PPV, the optical band gaps can be

determined, in this case 500nm or 2.48 eV.

We use the ITO layer as the hole injection layer and Al as electron injection layer. The devices emit yellow-greenlight from the turn-on voltage of 4 V. From 8V the device emitted bright stable light. At about 14 V the devices show sparks due to the short circuit and died away. In this case the devices were very hot.

The optimal thickness of polymer layer must be 0.2~0.3 μm.

We found that 1 minute are sufficient for the elimination of sulfonium salt at 230℃ in N_2 atmosphere. We could confirm this kind of behavior by t.g. anlaysis and IR spectrum, etc.. We also found that the post annealing of the device was effective in observing stable and large area bright light. Usually the annealing was conducted at 160 ℃ under nitrogen atmosphere for 2 hr after the Al electrode was vacuum evaporated.

4. Conclusions

The optimal method for fabricating PLED based on PPV was set up as follows:

To accomplish a more stable PLED, all the impurities except polymer must be removed from the precursor solution.(e.g., removing gel fraction of the polymer in the precursor solution.)

For 230℃ heat treatment for elimination of precursor film, heating time does not have to be longer than 1 min.

The post annealing at lower temperature is needed for stable observation of the emitting light.

The optimum thickness of the PPV layer was about 0.2~0.3 μm.

Acknowledgement

References

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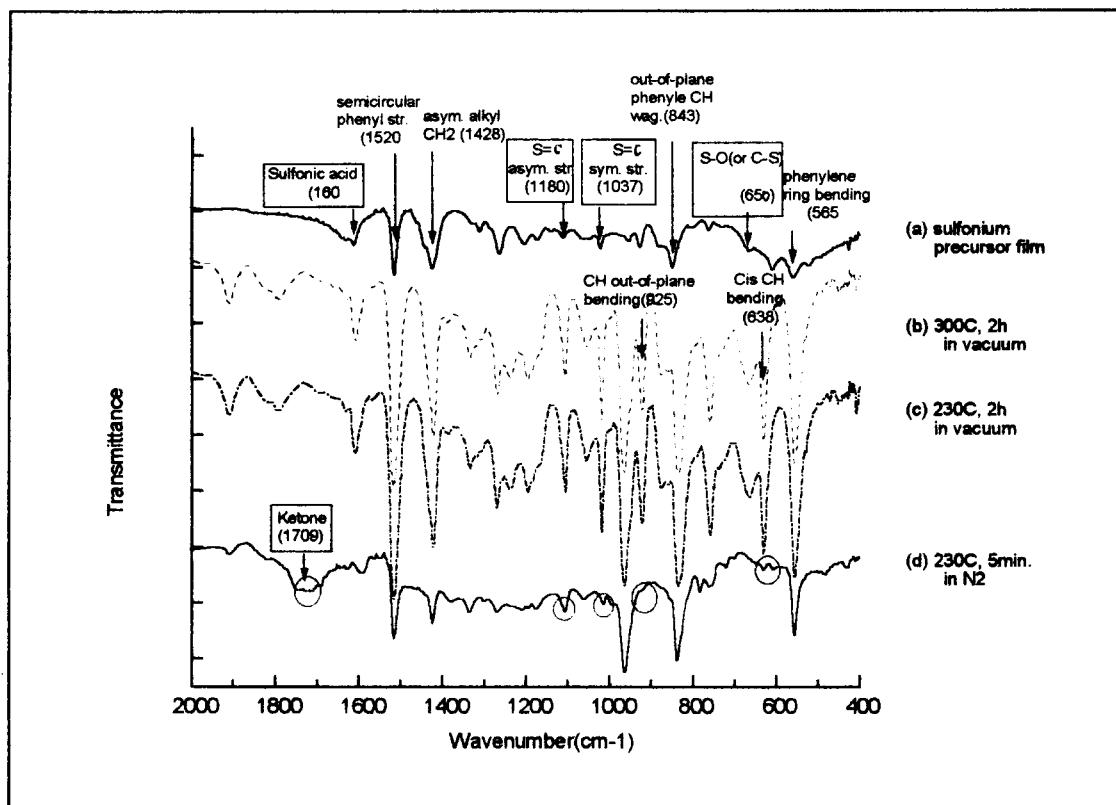5) J.Gmeiner, S.Karg, M.Meier, W.Riess, P.Strohriegl and M.Schwoerer, Acta Polymer, 44, 201(1993)

Fig. 3. Infra-red spectrum of PPV under various elimination conditions.
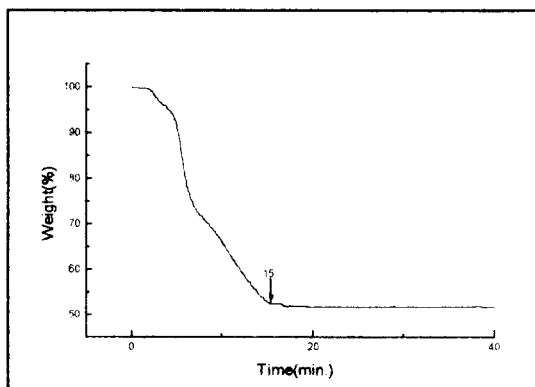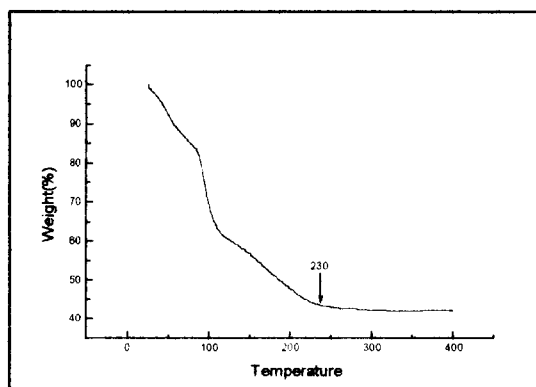

Fig. 4. TGA data of PPV with time.

Fig. 5. TGA data of PPV with temperature.