Single-layer organic electroluminescent devices by vapor deposition polymerization

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A novel method is presented herein regarding the preparation of a single-layer organic electroluminescent (EL) polymer thin film device. The device was made by simultaneously co-depositing two polymer thin film forming monomers, a hole-transporting molecule triphenylidiamine derivative (TPD) and an EL active molecule 1,1,4,4-tetraphenyl-1,3-buta diene (TPB) on an indium-tin-oxide (ITO) glass substrate. The device structure was composed of the ITO glass, the TPD, and TPB co-doped polymer thin film, and a thermally evaporated aluminum electrode. Carrier injection from the two electrodes was significantly observed and the blue light in EL spectra, with an emission maximum at 435 nm, was triggered at a driving voltage of 17 V.

Organic electroluminescent (EL) devices become attractive for their potential applications in large-area, flat-panel, and high luminance full-color displays working at a low driving voltage.1–12 Tang and Van Slyke1 were the first to report a high performance EL device composed of vacuum sublimed double layer dye film. They had demonstrated a maximum EL intensity of more than 1000 cd/m² and an external quantum efficiency of 1% (photon/electron) at a driving voltage below 10 V. Since then, various multilayered structure devices, fluorescent dyes, and electrode materials have been studied to improve the efficiency and stability of the devices.3–6

In order to simplify fabrication process and enhance structural stability of the devices, several single-layer-type EL devices have been proposed.7–10 Conventionally, those dye-doped polymer thin films are prepared by the solvent-dependent method such as spin coating or casting. These methods are convenient but it is difficult to obtain a large-area thin and uniform pinhole-free film.11,12,13–15 In addition, the films formed by the above methods may be easily contaminated by various impurities in the solvents used or in the solutes applied. The impurities, as known, may markedly reduce the luminescence efficiency of the devices. It should be carefully minimized so that long lifetime and high performance can be achieved.11,12 An alternative to overcoming the aforementioned drawbacks is to use the vapor deposition polymerization (VDP) technique. This useful method was first demonstrated by Salem et al.16 and Iijima et al.17 The advantage of this dry process is that many fewer impurities can be expected and also the film thickness can easily be controlled.13,16,17

Hence, in this letter, we will present a new method for preparing such a single-layer EL polymer thin film. This has been done successfully by simultaneously co-depositing an EL active molecule, a hole-transporting material, and polymer matrix forming monomers on an indium-tin-oxide (ITO) glass substrate in a vacuum chamber. Experimental details and results are given below.

Figure 1 shows the configuration of the present EL device and the molecular structures of the materials used in this experiment. In the device, N, N'-diphenyl-N, N'-(3-methyl phenyl)-1, 1'-biphenyl-4, 4'-diamine (TPD) was used as a hole transport material. Blue emitting fluorescent dye, 1,1,4,4-tetraphenyl-1,3-butadiene (TPB) was also used as an emitting center. The substrate was a precleaned ITO (5 × 2.5 cm²) conductive glass with a sheet resistance of 80 Ω per square. The single-layer EL polymer thin film was prepared by simultaneously co-depositing the EL active molecule, the hole-transporting material, and two polymer thin film forming monomers on an ITO glass substrate. The polymer thin film forming monomers were pyromellitic dianhydride (PMDA) and 4,4'-diaminodiphenylene (ODA), which were used to form a polyamic acid (PAA) thin film.

FIG. 1. Configurations of the present EL device and the EL-active molecules used.
Due to the space limitation of the current system, only three sets of source boats were equipped. One was used for PMDA and ODA monomers, one for TPD, and the final one for the TPB. To achieve a high degree of polymerization, it is required to accurately control the stoichiometric ratio of the two monomers, PMDA and ODA. In this experiment, the best processing condition was obtained by separately determining the temperature-dependent deposition rates of the two monomers, TPB and TPD, using a quartz oscillation thickness monitor prior to the co-deposition process. In this study, the source boats were preheated to 10 °C below the desired starting deposition temperature before the beginning of the deposition process. Then, the shutter under the substrate was briskly opened as the co-deposition process was started.

Reasonably good single-layer EL thin film had been obtained by co-depositing PMDA (~0.1 g) and ODA (~0.06 g) monomers from 100 to 150 °C with a ramp rate of 6.7 °C/min, TPD molecule (~0.02 g) from 150 to 180 °C with a ramp rate of 5 °C/min, and TPB molecule (~0.05 g) from 100 to 160 °C with a ramp rate of 10 °C/min. The molar ratio of ODA to PMDA was 0.9 at the beginning of the deposition process, and 0.8 at the end. The average molar ratio of ODA to PMDA in the resultant thin films was estimated to be 0.85. The TPB and TPD molecules were observed to homogeneously disperse in the resultant PAA polymer film. The deposition process began in a vacuum of 5 × 10⁻⁵ Torr and the resultant co-deposition film was 5000 Å thick. Thermal curing of the as-deposited sample was carried out in vacuum after the deposition process. The specimens were elevated to 140 °C at a ramp rate of 2 °C/min and held for 30 min. The top electrode was an Al metal (~6000 Å) with a square area of 0.5 × 0.5 mm² by thermal evaporation in a vacuum of 4 × 10⁻⁶ Torr to form an Al/TPD and TPB co-doped polymer thin film/ITO glass sandwich device.

A Jasco FR-770 spectrometer was employed to obtain both the photoluminescence and electroluminescence spectra of the resultant device. The current–voltage (I–V) curve of the resultant device was measured using a programmable Keithley 237. The electroluminescence intensity of the device was recorded using a photodiode detector connected with a Newport (model 1815-C) power meter. All the measurements were carried out at ambient condition. The structure and composition of the resultant VDP thin films were characterized using Fourier transform infrared (FTIR) spectrometry. The FTIR spectra were obtained using a Bomem DA 3002 spectrometer with a resolution of 2 cm⁻¹.

Figure 2 shows the FTIR spectra of the films before and after curing. From the FTIR spectrometry, the as-deposited film exhibited an absorption peak at 1650 cm⁻¹, which corresponded to the characteristic absorption of the amide carbonyl group of PAA. This absorption confirms the formation of PAA structure, indicating that synthesis of the polyamic acid was not disturbed by the co-deposition of the TPD and TPB molecules. After curing at 140 °C for 30 min, imidization of the resultant VDP thin film was proven by the presence of the absorption peaks of the imide group at 725, 1380, 1720, and 1780 cm⁻¹. The peak of amide at 1650 cm⁻¹, however, did not diminish completely. This indicates that some of the PAA chains had not been converted into the polyimide (PI) counterpart.

Figure 3 shows the current–voltage and the electroluminescence (EL) intensity-voltage results of the resultant devices. The threshold voltage was observed to be 17 V in the devices. This corresponded to an electric strength of 3.4 × 10⁵ V cm⁻¹ for the film. When the applied voltage exceeded the threshold voltage, the EL intensity was propor-
tionally linear to the applied voltage. The EL intensity was observed as from 17 V and up. This corresponded to a current density of 4 mA/cm².

Figure 4 shows the PL spectra of the TPD doped and the TPB doped polymer thin films. The EL spectra of the TPD and TPB co-doped polymer thin film is also included in the figure for comparison. The TPD doped thin film exhibited a peak at 410 nm, whereas the TPB film peaked at 427 nm. However, the TPB and TPD co-doped polymer thin film exhibited only one peak at 435 nm, confirming the hole-transporting role of the TPD molecules. The electroluminescence characteristics can therefore be concluded here to be originated from the TPB molecule.

In conclusion, a novel method for preparing single-layer EL thin films was presented. This method, which was proven in this work to be feasible experimentally, was executed by simultaneously co-depositing an EL active dye, a hole-transporting molecule, and two polymide thin film forming monomers on an ITO glass substrate. The EL function was triggered at a voltage of 17 V. The peak emission wavelength was 435 nm, a blue visible light. The present method may hopefully be applied to many other fluorescent dye-doped polymer thin systems without going through the conventional synthesis and fabrication processes. However, long-term durability of the device is now under investigation.

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