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Plasma Polymerization for the Deposition of an Electroluminescent Polymer Layer

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Radio frequency plasma polymerization is introduced to fabricate an emissive polymer layer as an organic electroluminescence (EL) device. Utilizing this technique, a thin polymer film is deposited directly onto a substrate from a starting monomer, and the thin polymer film obtained was found to be uniform and smooth. By employing a cell of ITO(indium-tin oxide coated glass)/plasma polymerized naphthalene/Al configuration, a stable and uniform blue-green (centers at 485 nm) EL is observed over 6 V DC bias. The external quantum efficiency of this device is estimated to be about 0.01%, which is comparable with those of the single-layer polymer EL cells in which the emitting polymers are synthesized by chemical polymerization.

KEYWORDS: plasma polymerization, poly (naphthalene), poly (paraphenylene), photoluminescence, electroluminescence, blue-green light emission

Organic electroluminescence (EL) devices have made a substantial progress in the past few years.[1–8] The materials employed in the organic EL device consist of the low-molecular-weight materials such as metal complexes and dyes,[1–3] the high-molecular-weight materials such as the conjugated and non-conjugated polymers,[4–6] and their combination.[7,8] The EL polymers are usually superior to the low-molecular-weight materials which are used in this kind of devices in the thermal stability. The usual method for preparing a thin polymer film is spin or dip coating from a polymer solution. By the casting method it is difficult to avoid the defects such as pin-holes and impurity containment in the polymer thin film. Another problem that remains in fabricating a polymer thin film is that some EL polymers such as poly (paraphenylene vinylene) (PPV) and poly (paraphenylene) (PPP) are insoluble in the most of the solvents. In order to prepare the thin films of these polymers, a sophisticated procedure such as a synthesis of precursor polymer is required.[4,6]

Plasma polymerization is a technique by which a thin polymer layer can be directly deposited from a starting monomer.[9] The applications of plasma polymerization in surface modification, dielectric and waveguided film depositions have been developed.[10] Conducting polymers such as poly (thiophene) and its derivatives obtained by plasma polymerization have been reported.[11] This technique is also a practical way for preparing an emissive polymer layer as an organic EL device.[12] The thin film of plasma polymer is usually dense, uniform, and free of pin-hole, all of which are indispensable for fabricating a high-quality EL polymer film. Furthermore, plasma polymerization is compatible with the processing technology in microelectronics, *e.g.*, with the PCVD (plasma chemical vapor deposition) technique in the semiconductor industry; therefore plasma polymerization provides a possible way to fabricate an optoelectronic device with the combination of organic EL and inorganic microelectronics in application.

PPP attained by the conventional chemical polymerization is a well-studied EL polymer for blue-green light emission.[6] Utilizing plasma discharge to polymerize benzene has been reported,[13] however, the obtained polymer did not have the aromatic structure due to the destruction of benzene ring by the plasma glow in the polymerization process. In order to overcome this problem, we selected naphthalene as a starting monomer, by which we can avoid the destruction of the aromatic rings due to the bulky size of this monomer. Naphthalene has been found to be a suitable starting monomer to deposit an aromatic polymer, and the plasma polymerized naphthalene (PPN) shows a similar optical absorption, photoluminescence (PL) and EL spectra with those of PPP which has been synthesized by chemical polymerization.[6] By employing a single-layer structure, the EL efficiency of PPN is as high as those of the EL polymer such as PPV and PPP which are obtained by chemical polymerization.

The plasma polymerization apparatus shown in Fig. 1 is composed of three parts: a vacuum system, a plasma source, and a monomer delivery system, more details are reported in ref. 14. The polymerization process was as follows: before polymerization, a piece of pre-cleaned ITO (indium-tin oxide) coated glass substrate (sheet resistance: 30–40 Ω/square, size: 75 × 25 mm) was placed on a water cooled stand in the vacuum chamber, and then the surface of ITO substrate was cleaned and sensitized with a plasma of purified air for 5 minutes at about

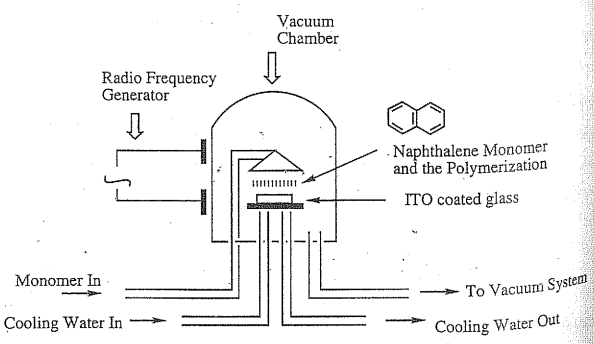

Fig. 1. Experimental apparatus of the plasma polymerization.

60 Pa pressure. The reason for using air plasma to treat the ITO surface is that it is known that oxygen ion in an air plasma can improve the hole injection efficiency for the ITO surface.[15] Next the naphthalene monomer was delivered in a flow rate of 20 cm^3/s to the reactor at about 1–10 Pa pressure. As the monomer molecules flew through the vacuum chamber, a radio frequency plasma discharge (100 W and 13.56 MHz coupled with coils of a 15 cm diameter) started, and it energized and dissociated the monomer molecules into neutral particles and reactant fragments in the forms of electrons, ions and free radicals. The recombination of these fragments deposited to form a plasma polymer layer; the deposition rate was about 5 Å/s, and the final thickness was about 1000 Å. Viewed by an optical microscope, the thin film shows uniform and smooth. The polymer layer adheres to the ITO coated glass substrate strongly, and can not be dissolved in the common organic solvents such as chloroform and benzene. Finally, an aluminum cathode (2000 Å) was vacuum deposited on the top of polymer layer at 1.5×10^{-3} Pa pressure. The luminescent area was 12 mm^2. The absorption, PL, and EL spectra of PPN thin films were recorded with a Hitachi F-4010 spectrophotometer. All the measurements were performed in air at room temperature.

The optical absorption spectrum of PPN is shown in Fig. 2(a), which consists of two obvious peaks at 325 nm and 265 nm. By analyzing the absorption spectrum of naphthalene monomer,[16] which demonstrates three sharp absorption peaks at 286, 275, and 265 nm respectively, the absorption of PPN from 400 to 300 nm peaking at 325 nm is attributed from the π-π^* interband transition of the polymer main chain and the absorption peak at 265 nm is from the phenyl ring. The absorption spectrum of PPN is similar to that of PPP obtained by the Ballard method, which has been used as a blue-green emitter for an EL device;[6] this suggests that PPN has the aromatic structure. The PL spectrum of PPN excited at 350 nm is depicted in Fig. 2(b). The emission spectrum shows a peak at 435 nm and a shoulder at 475 nm. The PL spectrum of PPN resembles that of PPP prepared by the Ballard method,[6,17] but it is not the case for PPP synthesized by the Kovacic method, *e.g.*, the PL peak of this kind of PPP is located at 660 nm excited at 337 nm.[18] This implies that PPN has a shorter conjugation length. The FWHM of the PL spectrum of PPN is 90 nm, which is narrower than that of plasma polymerized methyl methacrylate (PPMMA) which covers the whole visible range from 380 to 700 nm with a 200 nm FWHM.[19] It is well known that the plasma polymers such as PPN have branches and cross-links in the polymer chains because all the sites of the radicals are equivalent to react simultaneously in a starting monomer molecule.[9] The interchain interaction in the linear chain conjugated polymer has been known to influence both the charge transport property and PL efficiency.[20] To what extent that the branched chain and crosslink in the plasma polymers such as in PPN affects the PL efficiency and charge transport ability is not clear yet.

Under an ITO forward DC bias over 6 V, a stable and uniform blue-green EL emission was observed from the ITO/PPN/Al cell. The EL spectrum is shown in Fig. 2(c). The emission peak locates around 480 nm, which is red shifted from the PL peak. This shift may be due to the thin-film interference effect in the EL cell or the self absorption of the polymer layer, as discussed in the organic EL device.[1] The I-V and luminance-driving voltage (L-V) curves are shown in Fig. 3. The threshold voltage of EL is 6 V. The luminance of the present EL cell reaches 0.4 cd/m^2 at 10 V driving voltage (5 mA/cm^2), and 3 cd/m^2 at 15 V driving voltage (12 mA/cm^2). The EL efficiency (photons/electron) of PPN is estimated at 0.01–0.03% order with an Al cathode.[1] This value is nearly equal to that of PPV and PPP with a single-layer EL structure,[4,6] for instance, the EL quantum yield of a single-layer PPV EL cell is about 0.01% with a Mg cathode,[21] and that of PPP is 0.01–0.05% with an Al cathode.[6] This means that the EL performance of plasma polymer is not inferior to the EL polymers that are synthesized by the conventional chemical method. However, the EL brightness of the present PPN single-layer EL cell is not sufficient to be applied in real devices. Further work on the plasma polymers for the EL device application should include selections of suitable monomers to obtain green and red light emitting polymers; a fabrication of bilayer plasma polymer

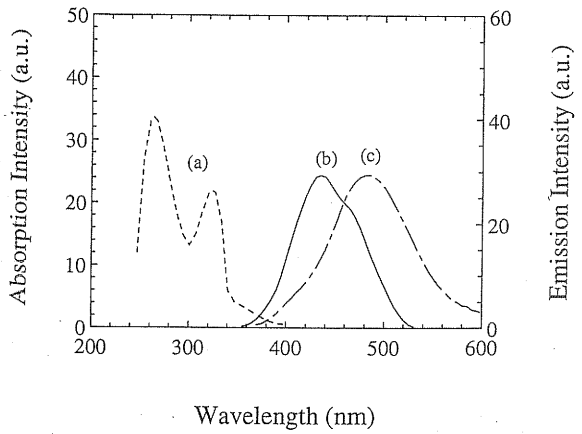

Fig. 2. UV/Visible absorption spectrum (a), photoluminescence spectrum (excited at 350 nm) (b) of plasma polymerized naphthalene, and the EL spectrum (c) of the ITO/plasma polymerized naphthalene/Al cell.

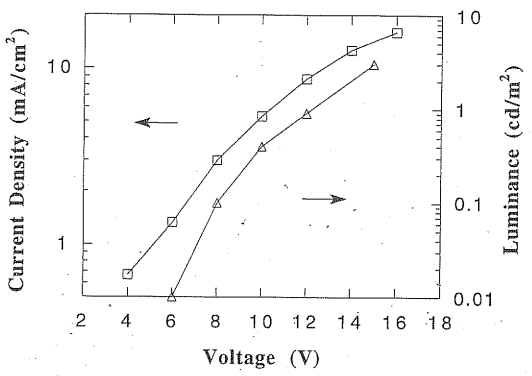

Fig. 3. I-V (square) and L-V (triangle) characteristics of the ITO/plasma polymerized naphthalene/Al cell.

EL cell in which each layer only transports monopolar carrier; an improvement of charge transport ability, *e.g.* by doping with electron acceptors and donors. Doping electron acceptors or donors in the conjugated polymers can increase their conductivity and this method is also possible for the plasma polymer,[11] although doping may quench the luminescence of these polymers.[20] In this case the doped plasma polymer can be employed as a charge transport or charge injection layer (as transparent electrode) for a bilayer EL device.

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