P-52: The Investigation of Photolithographic Patterning Method for Polymer Light Emitting Diodes

Mi Kyung Kim[1], Jeong-Ik Lee[1], Duck Il Kim[1], JiYoung, Oh[1], Chi Sun Hwang[1], Sang-He Ko Park[1], Yong Suk Yang[1], Hye Yong Chu[1]
[1]Electronics and Telecommunications Research Institute, Daejeon, 305-350, Korea

Suk-Kyung Kim[2], Do-Hoon Hwang [2]
[2]Kumoh National Univ. of Tech., Gumi, Gyungbuk, 730-701, Korea

Hyung-Jong Lee[3]
[3]Zen Photonics Co., Daejeon 305-380, Korea

92kangkang@etri.re.kr
Tel: +82-42-860-5094
Fax: +82-42-860-5202

Abstract

We have investigated the photolithographic patterning method of light emitting polymer film for polymer light emitting diodes (PLEDs). Blue light emitting polymers based on polyfluorene, which can be cured photochemically to yield an insoluble form, have been synthesized using Ni(0) mediated Yamamoto polymerization. The relationship between patterning property and several variables such as the intensity of the exposed UV light, the concentrations of additives, has been studied by using optical microscope analysis, UV/visible spectroscopy, and photoluminescence. We have successfully fabricated PLEDs composed of the patterned emissive layer and their electroluminescence property has been also investigated. In this presentation, the detailed photolithographic patterning method and its application for polymer light emitting display will be discussed.

1. Objectives and Background

In recent years, organic light-emitting diode (OLED) have been of great interest for applications as high-quality self-emission displays for portable devices such as mobile telephone display. Multi-color OLEDs have been successfully fabricated by vacuum-deposition of small electroluminescent molecules, but solution processing of conjugated polymers (electro-luminescent polymers) would result in a cheaper and simpler manufacturing process. However, polymer LEDs have been not yet commercialized in the area of multi-color displays due to the restriction of high-resolution patterning techniques. The patterning method of conjugated polymers attracting increased interest from some researchers. Their approaches include microcontact printing, screen printing, ink jetting, the photolithographic method, the laser-induced thermal image method and so on. Recently, much attention has especially been focused on the techniques of photopatterning for conjugated polymer by introducing the chemical amplified photolithographic method. This technology uses the application of generating acid upon photolysis and solubility change between exposed area and unexposed area.

In this paper, we have investigated the photolithographic patterning method of polymer LED by solution process using blue light emitting polymers with photoresist properties, that is, soluble polymers, which can be cured photochemically to yield an insoluble form. The detailed results on the relationship between patterning property and several variables such as the intensity of the exposed UV light, the concentrations of additives, will be discussed.

2. Results

We synthesized spirobifluorene polymer containing photocrosslinkable functional group (PM) via Ni(0) mediated Yamamoto polymerization. The structure of the polymer is shown in figure 1. The synthesized polymer was confirmed with proton Nuclear Magnetic Resonance (^{1}H NMR) and Fourier

Transform Infrared Spectroscopy (FTIR) spectroscopic analysis.

The synthesized polymer dissolved in *p*-xylene and then mixed 2% photoacid generator (PAG) and 30% crosslinking promoter. The solution was spin-coated onto the glass substrate doped PEDOT:PSS layer for the photopatterning experimental. The thickness of the coated polymer film is about 1000A. The polymer film was exposed by using Hg arc lamp for about 30s through the shadow mask in inert gas atmosphere. Afterward, to further advance the crosslinking process in the growing network, the films were annealed at 95℃ for 2min. Sequentially, the unexposed region was developed by THF and the exposed region polymer networks were found to be insoluble in any common solvent. The result was confirmed with microscope analysis and the photoluminescence image of patterned film (figure 2).

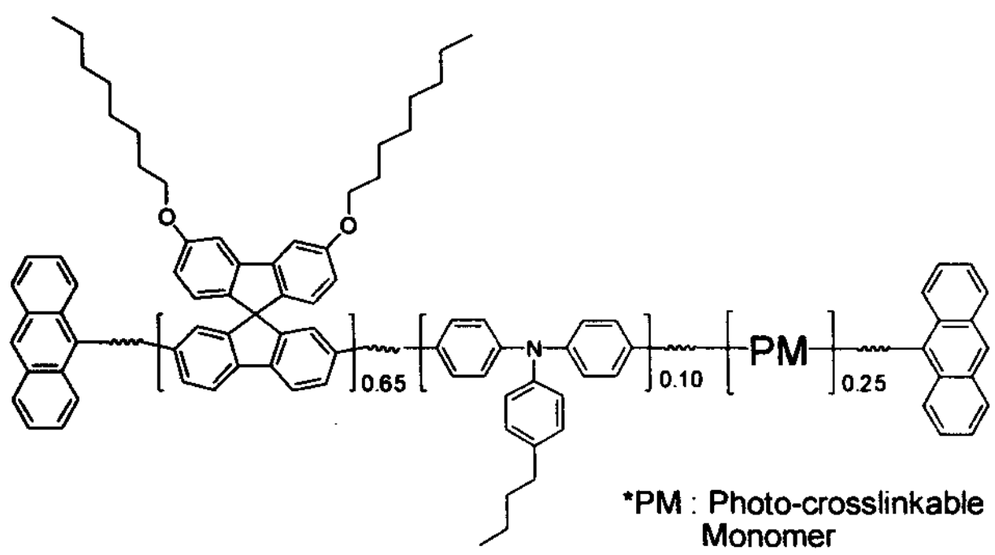


Figure 1. The structure of the polymer containing photo-crosslinkable functional group.

Figure 2 shows photographs of photo-patterning polymer after patterning process on glass substrate after patterning process optimization. For the investigation of electrical properties, Figure 3 (a) shows electrolumine- scence spectra from ITO/PEDOT/polymer/LiF/Al devices (**P1** and **P2** are pure polymer and the mixture of polymer and 30% crosslinking promoter, without patterning process, respectively. **P3** is the mixture of polymer, 30% crosslinking promoter and 2% PAG after patterning process). The electroluminescent spectrum of **P2** resulted in red shift compared to **P1** which might be due to polymer/crosslinking promoter mixture's phase separation effect. In the case of **P3,** it resulted in blue shift compared to **P1** which might be due to the

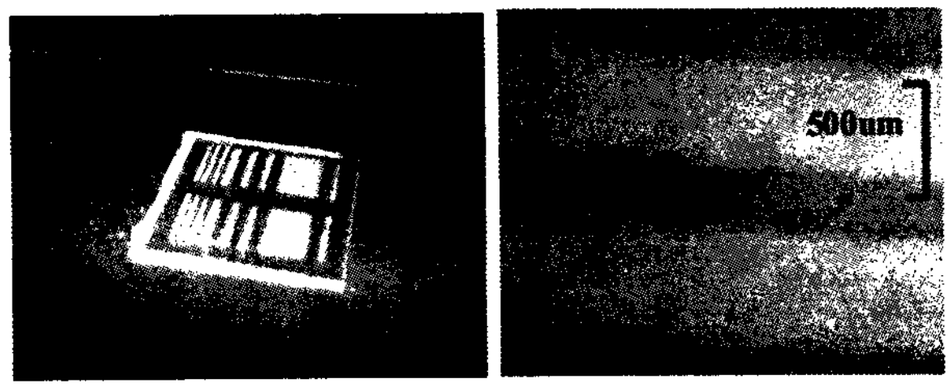
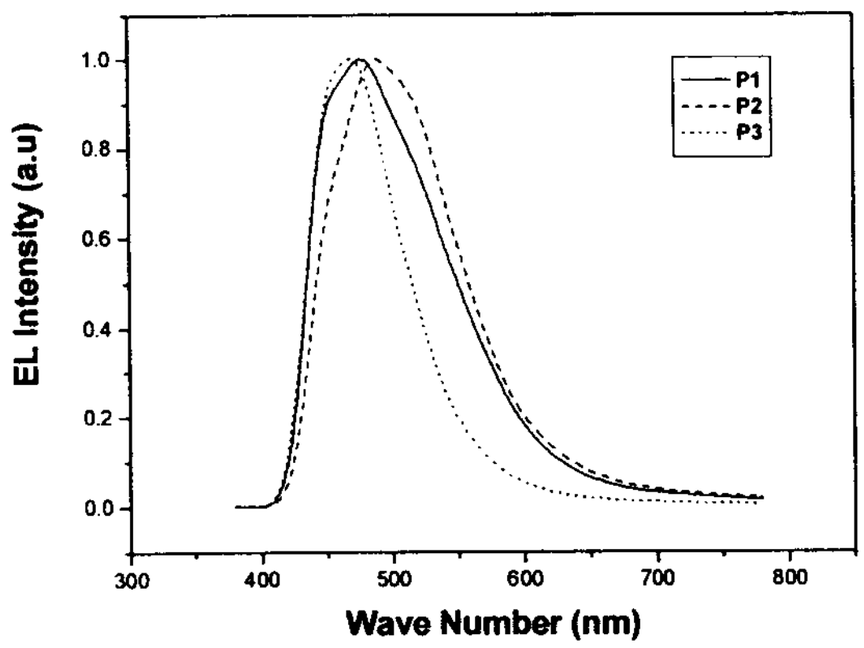
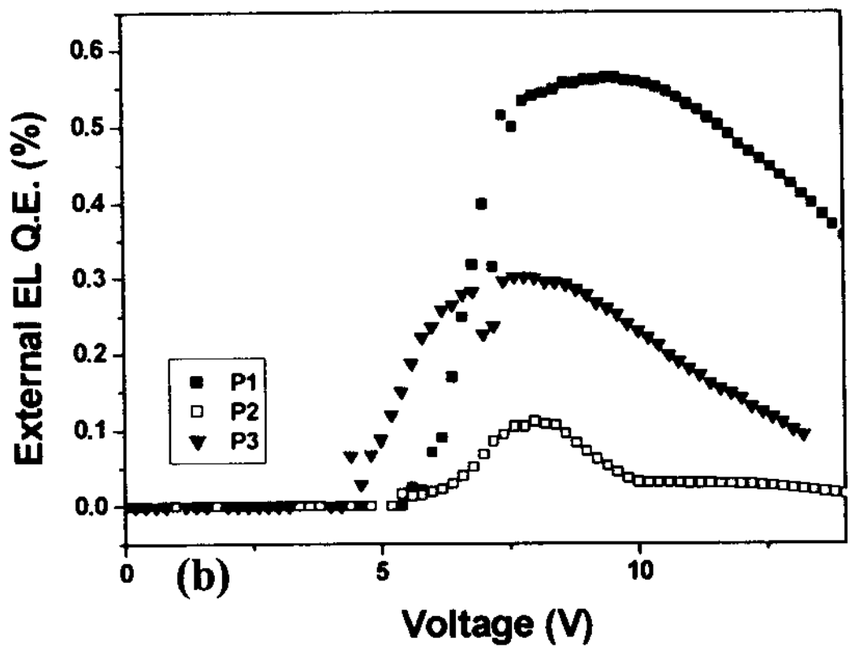


Figure 2. Photographs of the polymer thin film after the photolithography process on glass substrate.



(a)



(b)

morphology transformation of polymer side chain and the decreased thickness of the polymer film after process.

Figure 3 (b) shows the external quantum efficiency (Q.E.) curves of the devices. The maximum Q. E. (%) of **P1** was 0.6%, but that of **P2** containing 30% crosslinking promoter was 0.1%. The introduction of the crosslinking promoter led to poor device property in our results, which weight be related to some phase separation between the polymer and crosslinking promoter. As for **P3**, it was better device performance than **P2**, which might be explained by the decrease of the polymer thickness after the patterning process. In our experiment (not shown here), maximum device performance was obtained with the polymer film thinner than **P2**.

In this study, we have investigated the photolithographic patterning method of polymer LED by solution process using blue light emitting polymers with photoresist properties. Afterward, we will also discuss the optical properties of the polymer after patterning, such as UV, photoluminescence and electroluminescence according as difference of the concentration of crosslinking promoter and PAG in detail.

3. Summary

We have patterned conjugated emissive polymer using the photoacid generator-based photolithographic method and have successfully fabricated PLEDs composed of patterned emissive layer. The result was confirmed with microscope analysis and the photoluminescence image of patterned film (Figure 2). Also, according as difference of the concentration of crosslinking promoter the optical properties of the polymer before or after patterning will be discussed in detail.

4. Acknowledgements

The Korea Ministry of Information and Communications financially supported this work.

5. References

[1] R.H. Friend et al, Nature, 397 121 (1999).

[2] A. Kraft, A. C. Grimsdale & A. B. Holmes, Angew. Chem. Int. Edn 37 402 (1998).

[3] A. Kumar, G. M. Whiteside, Appl. Phys. Lett. 63, 2002 (1993).

[4] D. A. Pardo, G. E. Jabbour & N. Peyghambarian, Adv. Mater. 12, 1249 (2000).

[5] J. Bharathan, Y. Yang, Appl. Phys. Lett. 72, 2660 (1998).

[6] J. Yu, M. Abley, C. Yang, S. Holdcroft, Chem. Commun. 1503 (1998).

[7] M. L. Renak, G. C. Bazan, D. Roitman, Adv. Mater. 9, 392 (1997).

[8] P. F. Tian, P. E. Burrows, S. R. Forrest, Appl. Phys. Lett. 71, 3197 (1997).

[9] T. L. Seong, et al. SID Digest Tech. Pap. 33, 784 (2002).

[10] H. Ito, C. G. Wilson, J. M. Frechet, M. J. Farrall, E. Eichler, Macromolecules 16, 150 (1983).