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Photolithographic Micropatterning of an Electroluminescent Polymer Using Photobase Generator

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Introduction

The potential for making flat-panel displays from organic molecules at low cost has driven much of the recent research in the area of organic light-emitting diodes (OLEDs).[1,2] In the case of low-molecular-weight organic molecules, various layers of vacuum-deposited organic thin films and differently evaporated masks are used for fabricating full-color displays based on OLEDs.[3,4] The conjugated polymers are processed from solution by coating techniques. These techniques have the advantage of being readily processable to form thin films of large area, morphologically stable over a wide temperature range, and relatively cheap to manufacture.[4] However, because of the restriction of micropatterning fabrication for the device configuration, polymer LEDs have been not yet commercialized in the area of full-color displays, where OLEDs based on low-molecular-weight organic molecules begin to be commercialized as adopted in mobile telephone display. The patterning methods of conjugated polymers are attracting increased interest from some researchers. There have been several challengeable attempts to overcome the above issue. Their approaches include microcontact printing,[5] screening printing,[6,7] inkjet printing,[8] the photolithographic method,[9−11] the selective photobleaching method,[12] and the laser-induced thermal image method.[13]

Recently, much attention has especially been focused on the techniques of photopatterning for conjugated polymer by introducing the chemical amplified photolithographic (CAP) method,[14] which is used in conventional manufacturing methods for the intergrated circuit (IC) chip. This technology uses the application of generating acid upon photolysis and solubility change between exposed area and unexposed area. Renak et al.[10] reported the patterning of poly(*p*-phenylenevinylene) (PPV) derivatives by using a photoacid generator (PAG) in elimination reaction upon the irradiation through a photomask. Also, Holdcroft et al.[9] showed the patterned photoimage using thiophene-based polymer containing an acid labile group by the chemical amplification method.

In the present work, we report a new photolithographic micropatterning method for conjugated polymer using halo-precursor conjugated polymer and photobase generator (PBG)[15,16] and its application for polymer LEDs. The methods of PPV synthesis were published abundantly in previous literature.[17−21] Especially, the Gilch route is a prevalent method using excess strong base because of simplicity without thermal elimination step and relatively rare side reactions. But if base less than one equivalent is used, an organic soluble halo-precursor polymer is obtained, and then it can be converted into the fully conjugated polymer by thermal elimination. *o*-Nitrobenzyl carbamate derivatives such as PBG are well-known to generate the base upon the photolysis reaction, which is photolytically converted of carbamate derivatives to amine upon irradiation with UV light below 400 nm. Consequently, the generated amine rendered the halo-precursor PPV to conjugated PPV by base-catalyzed dehydrohalogenation reaction (E2 elimination). The photochemical cleavage of these photosensitive protecting groups is illustrated in Scheme 1.

Experimental Section

Materials. Poly[{2-(dimethylphenylsilyl)-1,4-phenylene}(1-bromoethylene)]-*co*-{2-dimethylphenylsilyl}-1,4-phenylenevinylene]][22] and 2-nitrobenzyldiphenyl carbamate[18] were synthesized according to a literature method. PBG {[(2,6-dinitrobenzyl)oxy]carbonyl}diphenylamine was prepared according to a literature synthetic method.[10] As a developer, cyclohexanone was purchased from Aldrich Chemical without further purification.

UV and PL Measurement of Photopatternable Polymer. Precusor polymer in 2 wt % cyclohexnone solution was spin-coated onto quartz substrate and prebaked at 80 °C for 2 min. The film thickness was 100 nm found by a Tencor Alpha-Step 500 surface profiler. Exposure was carried out on a Hg arc lamp with I-line (365 nm) filter (ORIEL exposure) for 5 min at room temperature, and sequentially, irradiated quartz substrate was baked for 1 min at 100 °C; UV absorption and PL spectra were measured by ISSPC spectrometer and spectrofluorometer.

UV and PL Measurement of Thermally Eliminated Polymer. After making spin-coated substrate by the above-mentioned method, for the thermal conversion, precusor-coated polymer quartz substrate was baked to 250 °C in vacuo for 6 h. UV absorption and PL spectra of thermally converted polymer were measured by an ISSPC spectrometer and spectrofluorometer.

Fabrication and Characterization of Polymer LEDs. A glass substrate coated with transparent ITO was cleaned by successive ultrasonic treatment in isopropyl alcohol and acetone, then dried with nitrogen gas, and heated for further drying. A hole injection layer of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonic acid) (PSS) (PEDOT:PSS, Bayer CH8000) having a high sheet resistance (∼10 000 Ω/□) in order to prevent the direct recombination of holes and electrons between electrodes was prepared from water dispersion and baked at 100 °C in vacuo for 1 h with a thickness of 30 nm. Precursor polymer solution (2 wt % in cyclohexanone) was spin-coated onto PEDOT:PSS layer with thickness of 80 nm. Polymer film was exposed by using Hg arc lamp for 5 min at room temperature, and sequentially, irradiated quartz substrate was baked for 1 min at 100 °C. Ca/Al (100 nm/100 nm) cathodes were vacuum-deposited onto the polymer film at a pressure below 5×10^{-7} Torr, yielding an active area of 0.2 cm². EL spectra of the LED device were measured with a spectroradiometer (Minolta CS-1000). Voltage−current−luminescence ($V-I-L$) characteristics were recorded using a programmable current/voltage source (Keithly 238) and a luminance meter (PR650).

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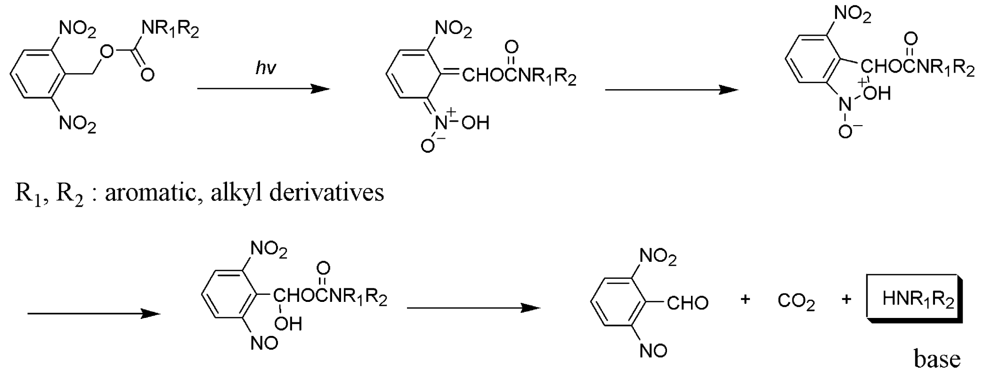
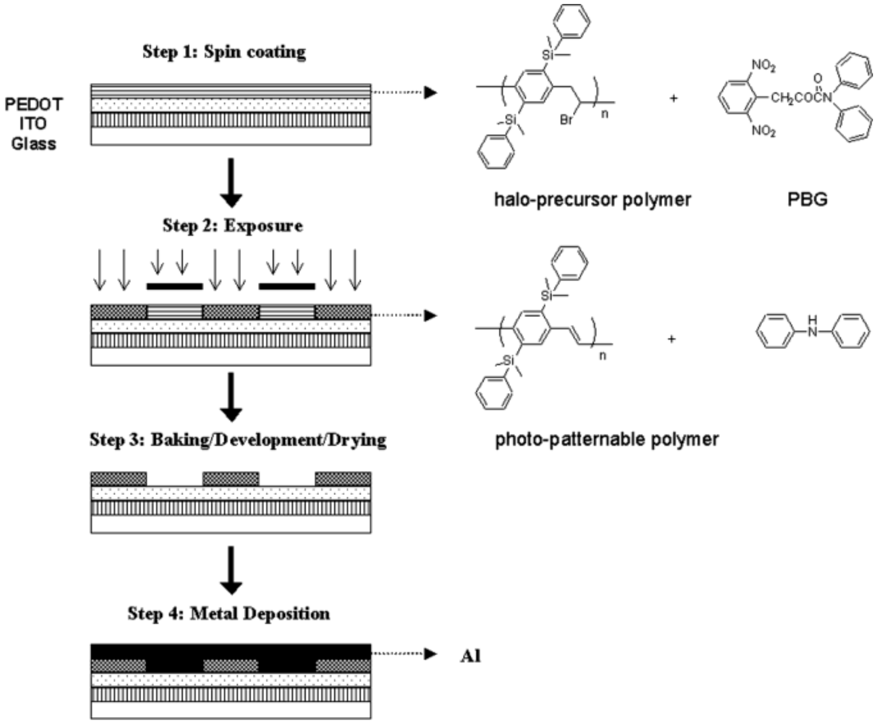
Scheme 1. Photolytical Reaction Mechanism of Photobase Generator (PBG)



Scheme 2. General Scheme for Steps Used in the Photolithographic Patterning of Halo-Precursor PPV and Chemical Conversion



Patterned EL Device Fabrication of Photopatternable Polymer. After cleaning the ITO-coated substrate, hole injection layer with a higher sheet resistance (∼10 000 Ω/□) of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonic acid) (PSS) (PEDOT:PSS) was spin-coated from water dispersion and baked at 100 °C in vacuo for 1 h.The precursor polymer and PBG (0.2 wt % in polymer) solution (2 wt % in cyclohexanone) was filtered through 0.2 μm membrane filter and spin-coated onto PEDOT:PSS layer. After prebaking at 90 °C for 90 s, the polymer film was exposed by using a Hg arc lamp for 5 min through the patterned Cr photomask at room temperature. Sequentially, the unexposed region was developed by cyclohexanone and dried in vacuo for 3 h. The patterned images were indentified by a scanning emission microscope (SEM). The deposition of Ca/Al cathodes was carried out by the same above-mentioned procedure. All the fabrication and measurements were done under ambient laboratory conditions.

Results and Discussion

This molecular structural change between precursor and eliminated polymer occurred the solubility change in organic solvent and is capable of fabricating the pattern by wet development. The halo-precursor conjugated polymer employed here was previously reported poly[{2-(dimethylphenylsilyl)-1,4-phenylene}(1-bromoethylene)]-*co*-{2-dimethylphenylsilyl}-1,4-phenylenevinylene]],[22] and well-known [{(2,6-dinitrobenzyl)oxy}-carbonyl]diphenylamine was used as PBG. Scheme 2 summarizes the procedure for patterning fabrication of halo-precursor polymer. As expected, the photolytically halogen-eliminated conjugated polymer, poly[{2,5-bis-(dimethylphenylsilyl)-1,4-phenylene}] (BDMPS−PPV), was insoluble in some organic solvents, such as cyclohexanone, and the unexposed region that remains, precursor polymer, is soluble and so easily developed by cyclohexanone. The use of PEDOT having high sheet resistance(∼10 000 Ω/□) can prevent to form ohmic contacts between the two electrodes in unexposed region. Therefore, the patterned emissive layer can be operated. In our devices, active areas are determined from patterned ITO and emissive layer through the photolithographic method, respectively. In Figure 1, the obtained polymer presented 10−30 μm negatively patterned lines and spaces, dotted pattern, and number-shaped pattern. This high resolution of conjugated polymer pattern is enough to directly achieve of color PLED subpixel in microdisplay, which desired sizes

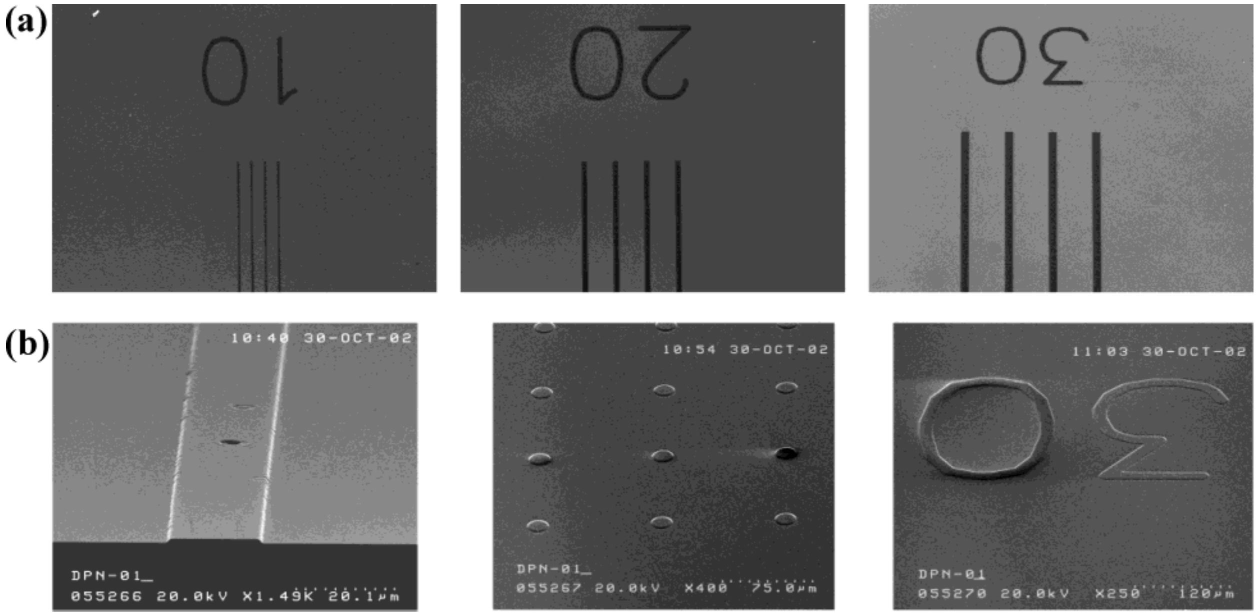


Figure 1. SEM images of photopatternable polymer: (a) 10−30 μm resolution line and space pattern; (b) isolated pattern, dotted pattern, and number shaped pattern.

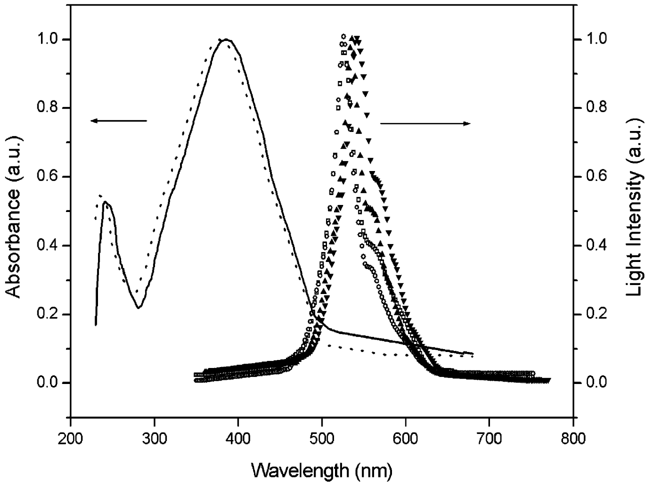


Figure 2. UV−vis absorption spectra of photopatternable polymer (solid line) and thermally eliminated polymer (dashed line) in thin film coated on a quartz plate. Photoluminescence spectra of photopatternable polymer (□) and thermally eliminated polymer (○) in thin film coated on a quartz plate: Electroluminescence spectra from ITO/PEDOT/photopatternable polymer/Ca/Al device (▲) and from ITO/PEDOT/thermally eliminated polymer/Ca/Al device (▼).

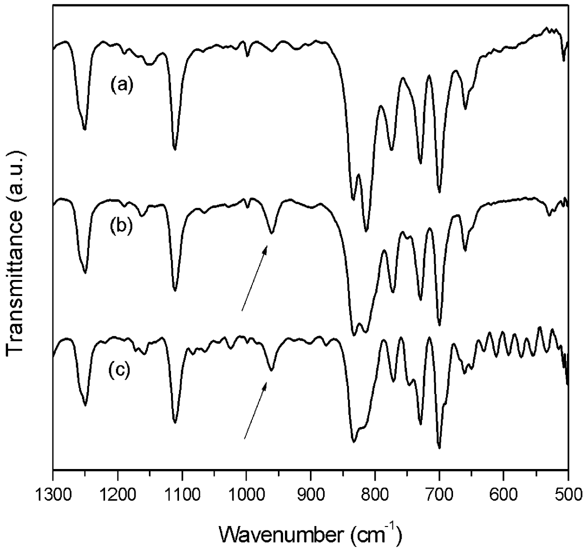


Figure 3. FT-IR spectra of (a) halo-precursor polymer, (b) thermally eliminated polymer, and (c) photopatternable polymer.

have to be in the 12−24 μm range. Currently, the way of producing color in OLED microdisplay is using color filter or color conversion materials on white LEDs deposited across the whole active area because of the resolution limit of shadow mask in the evaporator.[23] Our new method, which is enable to finely pattern the emitting layer, can offer an alternative to the design of microdisplay based on LED.

Figure 2 shows the UV−vis absorption spectra for thermally eliminated polymer and photopatternable polymer by PBG on quartz plate. It can be seen that these polymers showed similar absorption profile and absorption peak located around 380 nm due to the π−π* transition of the conjugated polymer backbone, which suggests the conversion into conjugation was fully achieved to the same extent. Also, the photoluminescence and electroluminescence spectra of each polymer exhibit the almost same peak position and well-resolved vibronic structures with similar photoluminescence quantum efficiency (Figure 2). These indicate that any side reactions do not happen, and the residue, diphenylamine, does not affect optical properties of the emitting polymer. Moreover, the conversion of the halo-precursor polymer to conjugated polymer by thermal elimination or photopatterning could be easily seen by infrared spectroscopy (Figure 3). The infrared spectra of thermally eliminated polymer and photopatternable polymer with PBG showed the strong absorption at 961 cm^{-1} in comparison to the halo-precursor polymer, which corresponds to the out-of-plane bending mode of *trans*-vinylene.[24,25] This proves that the vinylene double bond formation has been successful.

For the investigation of electrical properties, Figure 4 shows current density−luminance−voltage (J−V−L) characteristics of the ITO/PEDOT/polymer/Ca/Al. The current density increases in an exponential manner

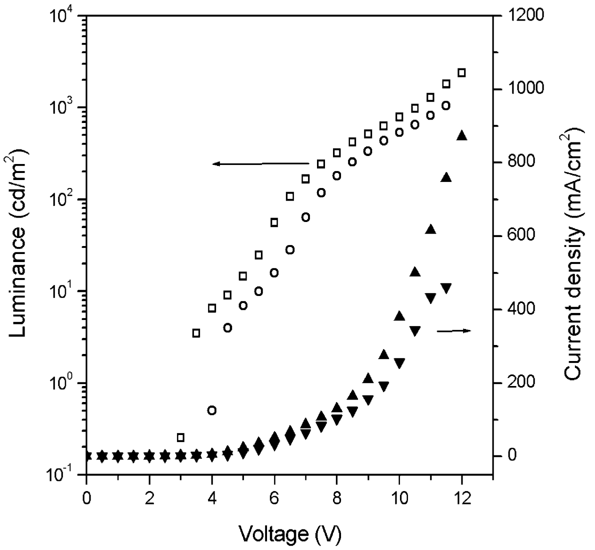


Figure 4. Current density (J) and luminance (L) vs voltage (V) for devices ITO/PEDOT/photopatternable polymer/Ca/Al ($J-V$: ▲; $L-V$: ▼) and ITO/PEDOT/thermally eliminated polymer/Ca/Al ($J-V$: □; $L-V$: ○).

with increasing forward bias, which is typical of diode characteristic. Surprisingly, the turn-on voltage (at 1 cd/m^2) of the photopatternable polymer is relatively lower (3.3 V) than thermally eliminated polymer (4.1 V) and also the maximum brightness of photopatternable polymer exhibited much higher values than that of thermally eliminated polymer. In our method, the enhanced EL characteristics after patterning is shown unlike to recently reported technique of patterning conjugated polymers using by cross-linking polymers, which devices after patterning showed higher operating voltage due to lower hole mobility than un-cross-linked layer[26] or lower efficiency due to the luminescence quenching by the remained photoinitiator.[27] From above results, we can guess that the produced diphenylamine upon the photolysis may play the role of hole-transporting material on the π-electron system as well as the base catalyst of dehydrohalogenation reaction. As previous reports about hole-transporting compounds,[28−30] such as arylamine, are well-known, the residual diphenylamine takes the improvement in hole-injecting and transporting ability within polymer, and thus the LED based on photopatternable polymer shows better performance than that based on thermally eliminated polymer. Figure 5 displays the patterned emission image of photopatternable polymer fabricated by the photolithographic method.[31]

Conclusions

We have patterned conjugated emissive polymer first using the photobase generator-based photolithographic method and have successfully fabricated LEDs composed of patterned emissive layer. Most importantly, the device with photopatternable polymer by PBG shows better EL performances (lower turn-on voltage, higher maximum brightness, and EL efficiency) in contrast to behavior of patterned LED through other photolithographic methods. The residual generated base may play the role of hole-transporting material, which influenced the enhanced electrical properties compared to thermally eliminated polymer. We expect that this method will have several benefits for fabricating the device; in particular, the halo-precursor vinyl polymer can be simply patterned by the above method. Therefore, this photolithogaphic method is a potentially useful new technique for PLED fabrication in the market from microdisplay to large flat-panel display.

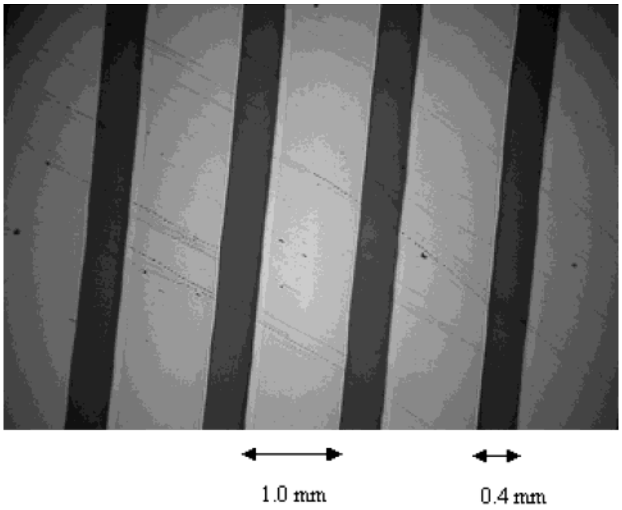


Figure 5. Photograph of patterned LEDs.

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(31) An enlarged photograph was taken through optical microscope (×1000) at low voltage because identification of patterned emitting profiles is impossible at real small size and at high voltage due to light diffusion.

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