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Self-assembled microarray of organic light-emitting diodes using a self-assembled monolayer by microcontact printing

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A self-assembled microarray (SAMA) of organic light-emitting diodes (OLEDs) has been fabricated using self-assembled monolayers (SAMs) by microcontact printing (μCP). The hydrophobic methyl-terminated SAMs modify the surface properties of the substrates to become hydrophobic, i.e., with low surface energy. Thus, the hydrophobic SAMs pattern, by the μCP, can be applied to form SAMAs on the patterned SAMs since the difference of the local surface energy modifies the patterns on the substrates. In this study, octadecyltrichlorosilane based hydrophobic methyl-terminated SAMs have been used and the fabricated OLEDs, with the SAMAs show local light emissions on the micron scale with efficient performances. © *2009 American Institute of Physics*. [doi:10.1063/1.3222977]

Organic light-emitting diodes (OLEDs) have been receiving much attention for their application in the next generation of display systems, especially in small display devices such as mobile electronics and flexible displays, because of their advantages of self-emission, low power consumption, high contrast ratios, high speed operation, and overall flexibility.[1,2] Recently, there has been a great demand to develop efficient and simple micro- and nanofabrication techniques for flexible substrates and various imprinting methods, such as nanoimprint lithography and ultraviolet imprinting, have become good candidates to directly replicate the desired patterns from stamps to the substrates.[3,4] However, both these processes are limited in their ability to control the residual layers. To define micro- and nanopatterns without residual layers, microcontact printing (μCP) has been widely studied for realizing the next generation of printing techniques since it is suitable for producing flexible substrates, is easy to process, has high-resolution capabilities, involves a low cost process, and has high throughput potential.[5]

Recently, Mathijssen *et al.*[6] have reported that by patterning self-assembled monolayers (SAMs) of thiolated molecules with opposing dipole moments on a gold anode, the local emissions can be controlled with a micron resolution. It has been suggested that local light emissions can be enhanced or suppressed by changing the work function on a local scale. The SAMs affect the devices at low voltages, but at high voltages, above 12 V, the laminated devices show almost the same level of optical output and electroluminescence (EL) efficiencies, irrespective of the existence of the SAMs.[7] In this paper, OLEDs have been fabricated with self-assembled microarrays (SAMAs) which allow local emitting of the devices at any voltages for high resolution displays. We present a method to locally modify the surface energy of indium tin oxide (ITO) anode electrodes by μCP using the hydrophobic methyl-terminated SAMs. This process is a very simple and inexpensive method to form the SAMAs.

In order to fabricate the stamps, poly(dimethylsiloxane) (PDMS) (Sylgard 184, Dow Corning Co.) has been poured on a master, which is positively micropatterned by conventional photolithography on a silicon wafer substrate. The PDMS is then cured in an oven at 70 °C for over 2 h. The stamp patterns consist of repeating squares or circles, ranging in size from 5 to 150 μm and a few drops of a 1 mM octadecyltrichlorosilane (OTS) solution in anhydrous hexane are applied to the surface of the PDMS stamps.[8,9] Subsequently, the stamps are spin dried at 3000 rpm for 30 s. ITO coated glass is sonicated in acetone, methanol and de-ionized water; and then cleaned in an oxygen plasma. Figure 1(a) shows a schematic illustration of the hot μCP (HμCP) process. The inked stamp is then brought into contact with the cleaned ITO glass substrate, and a light pressure applied at 80 °C by HμCP, which facilitates spontaneous Si–O bond formation and forms highly localized and dense SAMs forming $RSiCl_3$.[10,11] After the stamping procedure, the samples are rinsed in an ultrasonic bath with isopropanol, and dried with nitrogen gas to remove the physisorbed molecules, except for chemisorbed molecules on the ITO glass. As the SAMAs are fabricated, a polar resin (MR I-7030, Microresist Technology Co.) is spin-coated on the patterned SAMs, on the ITO glass substrate, at 3000 rpm for 30 s. The OTS SAMs, which form nanoscopic film regions terminated by methyl functionalities, are densely packed with interchain spacings that are largely determined by van der Waals forces. Thus, the patterned OTS SAMs are characterized by their hydrophobic surfaces, whereas the unpatterned ITO surfaces are characterized by hydrophilic surfaces. The change of the surface properties forms the SAMAs spontaneously depending on the surface energies. The OLEDs with the SAMAs on the ITO anode are fabricated by thermal evaporation of 40 nm n,n'-bis(naphtha-1-yl)-n,n'-bis(phenyl)-benzidine and 20 nm 4,4′,4″-tris(carbazol-9-yl)triphenylamine as the hole transporting layers; a 25 nm 4,4′-bis(carbazol-9-yl)biphenyl doped tris(2-phenylpyridine)iridium(III) (8%) is used as the emitting layer; a 15 nm 2,9-dimethyl-4,7-diphenyl-1,10-

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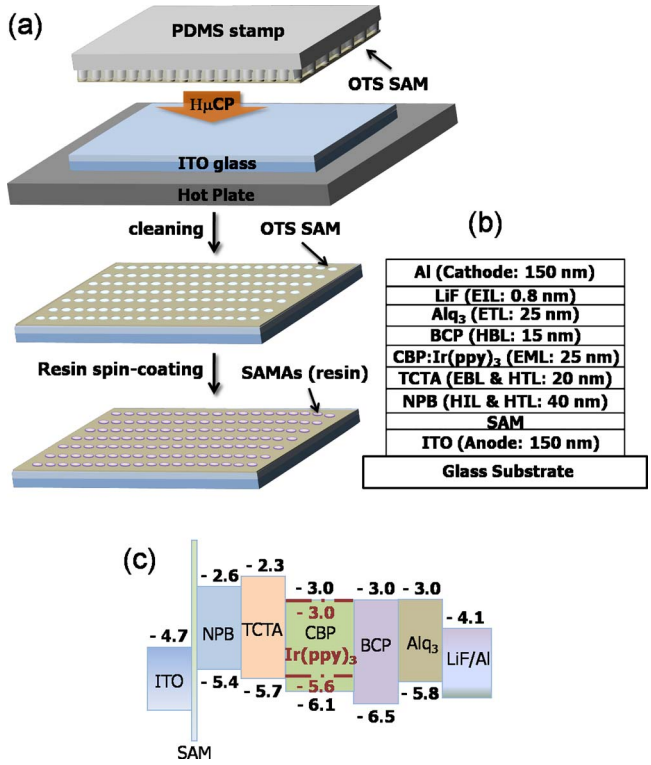

FIG. 1. (Color online) Schematic illustration of (a) the HμCP process, (b) the structure, and (c) the energy band diagram of the OLEDs. (The energy levels of LUMO and HOMO are taken from literature.)

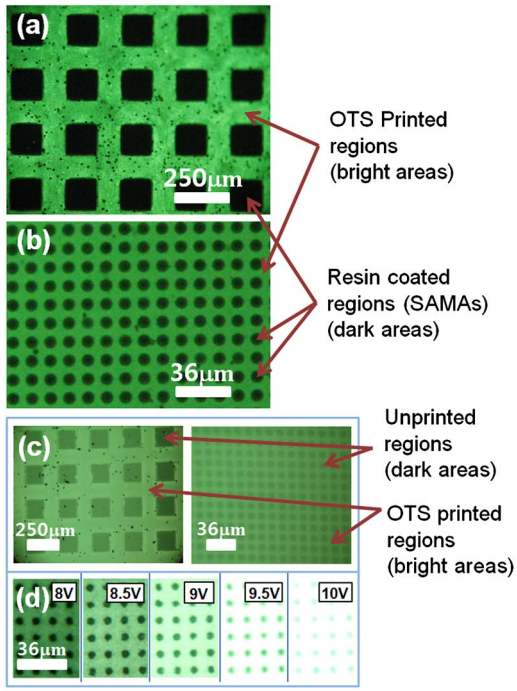

FIG. 2. (Color online) Optical microscopy images of emitting OLEDs using a printed SAM. (a) with 150 μm SAMA, (b) with 8 μm SAMA, (c) without SAMA and (d) with 5 μm SAMA biased from 8 to 10 V.

phenanhroline is used as the hole blocking layer (HBL); a 25 nm tris(8-hydroxy-quinolinato) aluminum is used as the electron transfer layer; and a 0.8 nm lithium fluoride and 100 nm aluminum is used as the cathode layer, consecutively [Fig. 1(b)]. In addition, we have compared four kinds of devices: a bare device, a SAM fully printed device, a SAM printed with 150 μm spacing device, and a SAM printed with 8 μm spacing device in order to define the effects of EL efficiency depending on the pattern sizes without SAMAs. The current-voltage characteristics have been measured using a Keithley 237 High-Voltage Source-Measure Unit (Keithley Instruments, Inc.), and the EL efficiency has been measured using a PR-670 SpectraScan Spectroradiometer (Photo Research, Inc.) in a dark box.

Figure 2 shows the light-emission images of the OLEDs with the SAMAs, driven at 7 V, observed under an optical microscope and pictured by a CCD camera in an air atmosphere. The light intensities are almost homogeneous over all the images, except for the presence of dark spots since they have been observed without any encapsulation.[12,13] In Fig. 2(a), the dark squares of size 150 μm are spin-coated with the polar resin on the hydrophilic surface of the ITO anode, and the emitting region is printed with the OTS SAMs. In Fig. 2(b), the dark circles of size 8 μm are well formed as the SAMAs in the same way. The contrast of light intensities between those on the SAMAs and those on the SAMs are obvious in comparison to those seen in Fig. 2(c) without the SAMAs. In addition, the light-emission images of the OLEDs are taken under various applied voltages from 8 to 10 V at the same exposure time in Fig. 2(d).

Highly efficient OLEDs have been fabricated with a HBL to clearly visualize the effect of the SAMs to the exclusion of any effects in degradation on the cathode side. Figure 3 shows the current density versus the voltage plot and the EL efficiency. As a reference device, the OLEDs without the SAMAs have been fabricated with the same organic layers and metal layers under the same conditions. Figure 3(a) shows that there is a subtle enhanced performance, rather than degradation, caused by the OTS SAMs between the bare device and the SAM printed devices. The SAMs act as a thin insulation layer that holes and electrons could tunnel through the devices.[7] Therefore, the *J-V* curves of the bare device and SAM fully printed device are quite close to each other. However, the SAM printed with 150 and 8 μm spacing devices have the patterns which plays in hole injection would result in increased current density since the island patterns lead to the change of electrical characteristics.[7] In addition, the SAM printed with 150 μm and 8 μm spacing devices have similar fill factor, 0.64 and 0.65, respectively. Therefore, the *J-V* curves of the set of devices are quite similar. As shown in Fig. 3(b), the effect of the OTS SAMs is not the dominant factor of the EL efficiency on the fabricated highly efficient OLEDs.

Nevertheless, the OTS SAMs are effective in the SAM patterned OLEDs without SAMAs. There is a contrast of the light intensities between the printed and the unprinted areas, as shown in Fig. 2(c) where the OTS SAMs printed areas are observed to have higher light intensities than in the unprinted areas. Therefore, the SAMs layer affects the injection energy barrier in the OLEDs since the work function of the ITO anode is changed by the dipole moment of various SAMs, which have been reported in previous studies.[14,15] Furthermore, the SAMs effects at low voltages have been observed, but at high voltages, above 12 V, the boundaries between printed and unprinted SAMs are ambiguous, i.e., the devices show almost the same level of optical output and device efficiency irrespective of the existence of the SAMs. Thus, the local light emission of the devices can be manipulated

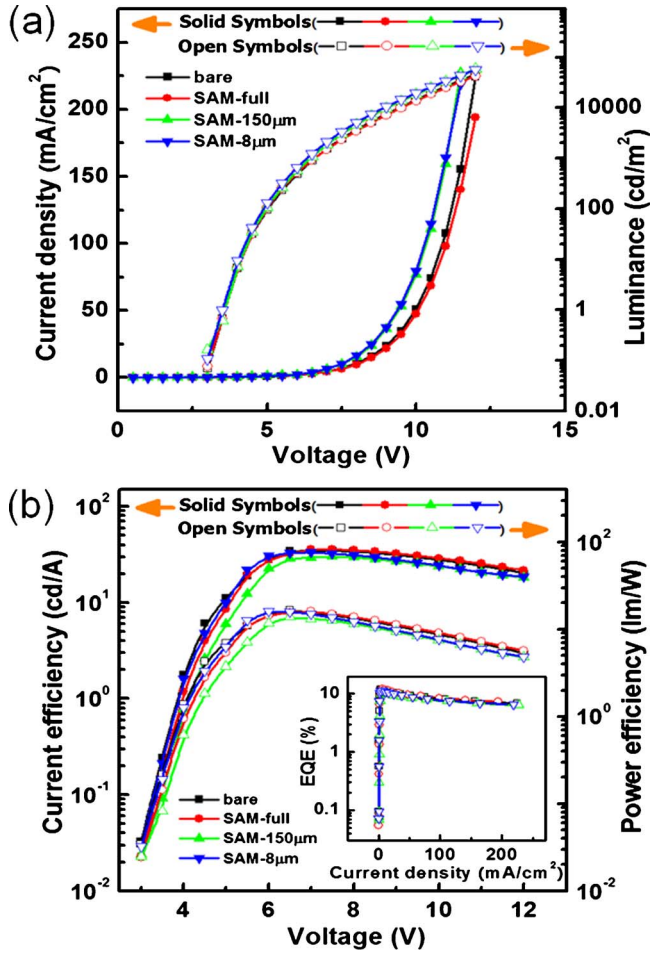

FIG. 3. (Color online) (a) The current density and the luminance characteristics as a function of the applied voltage. (b) The current efficiency and power efficiency characteristics as a function of the applied voltage. Inset: the external quantum efficiency (EQE) characteristics as a function of the current density of the OLEDs.

using an insulator as a separator at high luminance. Finally, the SAMAs can be fabricated on the SAMs patterned by the HμCP.

The macroscopic stamping, with the PDMS stamps by μCP can obtain microscopic patterns of the SAMs on the ITO anode of the OLEDs. In this way, the surface properties of the ITO anode can be manipulated, which are able to form the SAMAs on the patterned SAMs spontaneously. It has been demonstrated that local light-emission OLEDs can be fabricated on the micrometer scale, based on low cost and simple processes. In addition, the PDMS stamps are suitable for managing the patterning process on uneven surface substrates, as well as on three-dimensional or flexible substrates, and they are also good repeatable processes since they are elastic and durable. Moreover, the PDMS stamps are able to be applied to the roll-to-roll process, which would allow the printing of large OLEDs sheets on conventional printing presses, for use in coating on plastic substrates. Consequently, the μCP does not need expensive vacuum equipment, high temperature processes, or UV exposure for the patterning. Therefore, μCP is considered a very simple and inexpensive process as a candidate for the next generation of patterning processes.

In conclusion, OLEDs have been demonstrated with self-assembled microarrays, using SAMs, by (HμCP). The hydrophobic methyl-terminated OTS SAMs have been used in order to manipulate the surface properties locally on the ITO glass substrate. Thus, SAMAs have been formed on patterned SAMs. After fabrication of the OLEDs, two lateral length scales of the local light emissions have been found to be well formed and without any deterioration. As a result, the pattering technique of the self-assembled microarray has been developed, using SAM patterning by μCPs, which allows for the replacement of the photolithography to define the pixel area for future display devices.

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