Programmable organic light-emitting devices

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In this letter, we report a promising type of electrically programmable, i.e., reconfigurable, organic light-emitting devices (OLEDs) incorporating a thin carrier-blocking layer as the sacrificial fusing layer. In such devices, the carrier-blocking layer has a lower glass transition temperature than neighboring layers. By raising the internal temperature of the device above the transition temperature of the carrier-blocking layer with a large enough current, interdiffusion between organic layers could occur through such a layer. As a consequence, neighboring layers are fused and a new path for carrier transport is formed, bypassing the carrier-blocking property and altering the device characteristics. A device that emits blue light as fabricated but can be transformed into a green-emitting one is demonstrated. Such a type of device may be used for color pixels in OLED displays, user-programmable OLED applications, and nonvolatile memory devices. © 2001 American Institute of Physics. [DOI: 10.1063/1.1414305]

Organic light-emitting devices (OLEDs) based on either low-molecular-weight compounds or polymers have attracted worldwide interest due to their applications in efficient, low-voltage, large-area, and full-color displays.^{1,2} For most of the OLEDs reported to date, the device configurations, and consequently device characteristics, are determined on completion of fabrication, not reconfigurable afterward. Reconfigurable OLEDs, particularly electrically reconfigurable ones, may have some interesting applications due to their programmability. Devices that can be programmed to emit different colors may be used for color pixels in OLED displays. Thus, only one type of device needs to be fabricated and the definition of color pixels can be performed by applying electrical programming pulses, simplifying display manufacturing. Such devices also make possible OLED applications that allow users to program colors or patterns for their own purposes. Furthermore, with irreversible reconfiguration, such devices may be used as programmable and nonvolatile memory devices, utilizing shifts of emission wavelengths or electrical characteristics to represent stored states. The closest matches to electrically programmable OLEDs are those with bias- or polarity-controlled emission colors.^{3–6} These devices, however, in general suffer from insufficient color contrast, limited brightness in some color, or poor efficiency. Furthermore, none of these previous devices have memory. In this letter, we report a type of electrically reconfigurable OLEDs, whose device configurations and characteristics can be programmed electrically without necessarily losing efficiency or brightness. The transformation induced is irreversible and, therefore, nonvolatile.

The device structure and materials studied are shown

in Fig. 1. Bis-4,4'-[(diphenylmethylsilyl)vinyl]biphenyl (DPSVB) was synthesized from nickel-catalyzed silylolefination of the corresponding bisdithioacetal.^{7–9} DPSVB is able to form homogeneous films through vacuum evaporation and its thin film exhibits an absorption onset and fluorescence around 365 and 390 nm, respectively. The device on the glass substrate has the typical structure of multiple organic layers sandwiched between the bottom indium–tin–oxide (ITO) anode and the top Mg:Ag/Ag bilayer cathode. The stack of organic layers consists of a thin layer of conducting polymer polyethylene dioxythiophene/polystyrene sulphonate (PEDT/PSS, Bayer Corp.) as the hole-injection layer,¹⁰ α -naphthylphenylbiphenyl diamine (α -NPD) as the hole-transport layer, tris-(8-hydroxyquinoline) aluminum (Alq₃) as the electron-transport layer,^{1,8} and DPSVB inserted between α -NPD and Alq₃. The function of DPSVB will be described in the following paragraphs. All the compounds of low molecular weight were purified by sublimation before use in device fabrication. The PEDT/PSS layer was prepared by spin coating. α -NPD, DPSVB, and Alq₃ were deposited at a rate of 2–3 Å/s by thermal evaporation in a multiple-source vacuum chamber with a base pressure of $<10^{-6}$ Torr. The thicknesses of PEDT/PSS, α -NPD, DPSVB, and Alq₃ were ~ 300 , 600, 150, and 300 Å, respectively.

In the current–voltage–brightness (I – V – L) characteriza-

FIG. 1. Structures of the device and the compound.

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FIG. 2. (a) EL spectra, (b) I - V , and (c) L - V characteristics of a pristine device, an electrically transformed device, and a thermally transformed device. Transformation conditions: 500 mA/cm², 5 s, or annealing at 60 °C, 3 min.

tion of the devices by continuously scanning bias voltage (e.g., 0.5 V step, 1 s hold time), it was repeatedly observed that the device initially emitting blue light irreversible transformed into a green-emitting one if the driving current exceeded 200–250 mA/cm². Further characterization revealed that the device could be fully transformed into a green one with a high current pulse (e.g., 500 mA/cm², 5 s). The electroluminescence (EL) spectra taken under much shorter pulse driving (tens of ms) for the original blue device and the transformed green device exhibited hardly any bias dependence. The phenomena observed here are, therefore, different from previously reported OLEDs with bias-controlled colors.^{3–6} The spectral and representative I - V - L characteristics of devices, before and after such a transformation, are shown in Fig. 2. The EL spectra of the original blue device and the transformed green device are identified as emission characteristics of α -NPD and Alq₃, respectively. It indicates that the carrier recombination in the original device occurs within the α -NPD layer and that DPSVB actually functions as an effective hole-blocking and electron-transport layer. Nevertheless, stressing the device with a large enough current had caused some irreversible structural change, having the emission take place at Alq₃ instead. The original blue device has an external quantum efficiency of $\sim 0.9\%$ – 1.0%

FIG. 3. (Color) Photograph of a device under the heat-sink experiment.

photon/electron and can be scanned to a brightness up to ~ 1000 cd/m² before visible transformation takes place. The transformed green device, correspondingly, gives a quantum efficiency of 0.6%–0.7% and a brightness over 10,000 cd/m². Compared to the original blue device, the I - V - L characteristics of the transformed green device shift to lower voltages. The transformed device, therefore, is still a well-behaved and functional device. All the above characteristics make the present device an electrically programmable one, whose emission color and electrical characteristics can be programed through a high-current pulse after device fabrication.

The changes induced by the applied current may be due to some electrochemical mechanism¹¹ or due to some thermal effect caused by joule heat.¹² To determine which is the dominant mechanism, we performed a heat-sink experiment, in which a portion of the cathode area of a device was in contact with a heat sink to keep it cooler than the remaining area while a current (~ 200 mA/cm²) was applied. It was found that the transformation of the contacted area was much retarded in comparison with the noncontacted area, as shown in Fig. 3. Since the current was initially uniformly distributed, such a test clearly suggests that the transformation is mainly of thermal origin. The usually reported thermal effects on the organic layers in OLEDs have been the recrystallization¹³ or the interdiffusion between organic layers,^{14,15} both depending on the considered temperatures relative to the glass transition temperatures (T_g) of organic materials. T_g of α -NPD and Alq₃ are ~ 100 and ~ 170 °C, respectively.^{13,15} The differential scanning calorimetry (DSC) of DPSVB shows a distinct glass transition around 30 °C. Hence, it was suspected that the lower T_g of DPSVB is the origin of the structural change in the present device. For confirmation, we performed another set of thermal annealing experiments, in which the complete organic stack was annealed at various temperatures for 3 min prior to or after the cathode deposition. In both cases, annealing at 50–100 °C ($>T_g$ of DPSVB, but still $<T_g$ of α -NPD and Alq₃) had readily made the devices green-emitting ones without further electrical stressing. The green devices transformed through thermal annealing have similar characteristics as those transformed through electrical stressing, as also shown in Fig. 2. All the above evidence suggests that electrical stressing

FIG. 4. PL spectra of a pristine device, an electrically transformed device, and a thermally transformed device. Transformation conditions: 500 mA/cm², 5 s, or annealing at 60 °C, 3 min.

caused similar thermal effects on the DPSVB layer as direct thermal annealing.

From the optical microscopy, even though substantial morphological changes were observed in annealing (50–100 °C) a thin DPSVB layer (150 Å) individually deposited on a substrate, the stack of organic layers subject to either thermal annealing or electrical stressing, however, still exhibited a homogeneous appearance and emission from the transformed devices was uniform. It is, therefore, less likely that the transformation of device characteristics was due to dramatic morphological change, such as formation of dense pinholes in DPSVB. Instead, investigation of resonant energy transfer between chromophores in the pristine device and in annealed or stressed ones revealed interdiffusion of chromophores through the DPSVB layer. Figure 4 shows the photoluminescence (PL) spectra collected from the ITO/glass side for the organic stacks in a pristine device, an electrically transformed device (500 mA/cm², 5 s), and a thermally transformed device (60 °C, 3 min). An excitation at 365 nm was adopted here because at this wavelength the optical densities of both DPSVB (150 Å) and Alq₃ (300 Å) are much smaller than that of α -NPD (600 Å). The PL spectrum of the pristine device shows a dominant α -NPD emission, while those of both transformed devices exhibit substantial contribution from Alq₃, clearly indicating energy transfer from α -NPD to Alq₃ in both fully transformed devices. Further PL studies using the excitation at 310 nm (for maximizing absorption in DPSVB and minimizing absorption in α -NPD and Alq₃) showed the increase of energy transfer from DPSVB to α -NPD and Alq₃ with the degree of annealing or stressing even before the energy transfer from α -NPD to Alq₃ was observed with the 365 nm pumping. These PL results suggest the interdiffusion actually starts at both DPSVB/ α -NPD and DPSVB/Alq₃ interfaces and eventually leads to the substantial mixing of the initially separated α -NPD and Alq₃ layers in fully transformed devices. The mixing and bridging of α -NPD and Alq₃ through DPSVB then results in the formation of a new path for the carrier transport, bypassing the hole-blocking property of DPSVB and altering device characteristics. Such mixing and bridging may also explain the reduction of operation voltage in the transformed devices.

In the present device, owing to the rather low T_g of the hole-blocking DPSVB layer, the blue operation of the original configuration can maintain only up to 200–250 mA/cm² under scanning operation. Under dc operation, the transformation is much more retarded by reducing the current below 10 mA/cm², but is still slightly detectable. Eventually, to make practical programmable devices, it is necessary to raise the transition temperatures of all compounds involved to ensure stable operation within the nominal temperature range. Correspondingly, higher programming currents may be needed, which in turn may impose requirements on the strength of all interfaces in devices.¹⁶ Currently, further work is toward the extension of the device operation range and reliability.

In summary, we report a promising type of electrically programmable or reconfigurable OLEDs incorporating a thin carrier-blocking layer. The carrier-blocking layer has lower T_g than neighboring layers, so that by raising the internal temperature of the device above its T_g with a large enough current, interdiffusion could occur through such a layer. As a consequence, neighboring layers are fused, bypassing the carrier-blocking property and altering the device configuration and characteristics. The concept disclosed in this work may be further generalized to make an OLED structure containing more than one carrier-blocking layer with different T_g as sacrificial fusing layers, so that the device may be programmed more than once. Such programmable OLEDs may have some interesting applications.

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