Ink-jet printing of doped polymers for organic light emitting devices

T. R. Hebner, C. C. Wu, D. Marcy, M. H. Lu, and J. C. Sturm Department of Electrical Engineering, Center for Photonic and Optoelectronic Materials (POEM), Princeton University, Princeton, New Jersey 08544

(Received 9 October 1997; accepted for publication 2 December 1997)

Ink-jet printing was used to directly deposit patterned luminescent doped-polymer films. The luminescence of polyvinylcarbazol (PVK) films, with dyes of coumarin 6 (C6), coumarin 47 (C47), and nile red was similar to that of films of the same composition deposited by spin coating. Light emitting diodes with low turn-on voltages were also fabricated in PVK doped with C6 deposited by ink-jet printing. © *1998 American Institute of Physics*. [S0003-6951(98)00905-X]

Recently, there has been increased interest in light emitting diodes made from organic polymers because of their potential low cost and potential applicability to color flat panel displays. The organic materials are typically deposited by spin coating (in the case of polymer materials),^{1,2} or by evaporation (in the case of small organic molecules).^{3,4} In either case, the single material covers the substrate so that only devices of a single color can generally be fabricated. The straightforward integration of multiple organic layers (for the fabrication of red, green, and blue emitters for color displays) would require the patterning of the individual organic layers. Because of their solubility in and sensitivity to aqueous solutions and many solvents, the such patterning of organic materials by conventional photoresist and wet processing techniques is difficult. Efforts to date to integrate organic light emitting diodes (OLED's) from materials which emit different colors on the same substrate have patterned them only indirectly (through the use of cathodes evaporated through shadow mask as dry-etch masks),⁵ or avoided the issue all together by putting the three devices on top of each other (relying on shadow masks to pattern the organics so that contacts to the multiple layers may be made).⁶ In this work we describe the direct deposition of patterned luminescent doped polymers by ink-jet printing, and the successful fabrication of OLEDs from ink-jetdeposited organic films.

The ink-jet printer used was a Cannon PJ-1080A Color Ink-Jet Printer with a resolution of 640 dots per line. This printer uses piezoelectric technology to squirt ink droplets from a nozzle with a 65 μ m opening. There are four ink cartridges and four nozzles enabling the printer to print four different colors simultaneously. As the printer head scans the page and the piezoelectric materials are pulsed, ink is squirted from the nozzles onto the page. The only modification to the ink-jet printer for printing OLEDs was to replace the ink cartridges with polymer solutions. Ink jet printing has previously been used to manufacture color filters for liquid crystal displays,^{7,8} but we are aware of no previous work on luminescent polymers.

The organic materials used were similar to those in our earlier work using doped polymer blends deposited by spin coating, in which OLEDs with over 1% external quantum efficiency and brightness of 4000 cd/m² were produced.⁹ The hole-transport polymer polyvinylcarbazol (PVK) and light emitting dyes coumarin 6 (C6), coumarin 47 (C47), and nile

red were dissolved into chloroform solution, which was then deposited by ink-jet printing, or spin coating for comparison. After deposition the chloroform evaporates leaving a dopedpolymer material. Typical concentrations of PVK dissolved in chloroform were 10 g/l, and dye dissolved in chloroform were 0.1 g/l, yielding on the order of 1% dye in the PVK. These concentrations are less than those used for spin coating, which were typically 15.4 g/l PVK in chloroform and 0.05 g/l dye in chloroform, yielding on the order of 0.3% dye in the PVK. In this initial ink-jet printing work, no electron transport agent was used. PVK, which had a high weightaverage molecular weight M_w of 1 100 000 g/mole reported by the supplier, was purchased from Aldrich Chemical Inc. and used as received. Green dye C6 and blue dye C47 were purchased from Lambda Physik Inc. Nile red was purchased from Aldrich. Chloroform solutions containing different amounts of PVK and luminescent materials were prepared



FIG. 1. (a) Optical micrograph of ink-jet printed dots from above. (b) Surface profile of a dot.

519

Downloaded 16 Nov 2001 to 128.112.49.151. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/aplo/aplcr.jsp

^{© 1998} American Institute of Physics



FIG. 2. Photograph of the ink-jet printed luminescent polymer letters of nile red doped PVK excited by an ultraviolet lamp. The letters were ink-jet printed using "bold" mode.

by stirring and were passed through 0.45 μ m filters. Ink-jet printed thin films were printed onto 175- μ m-thick flexible polyester coated with indium tin oxide (ITO). Before deposition, the ITO was treated with an oxygen plasma to modify its surface properties for OLEDs.¹⁰

Figure 1 shows an optical micrograph of a number of ink-jet printed dots and a surface profile of the shape of a typical dot. The thickness of the dots ranged from 400 to 700 Å and the dot widths ranged from 150 to 200 μ m. The larger diameter dots tended to be thicker, indicating thickness variation is due to the total amount of deposited solution. In the optical micrograph one can see some structure within the dot, which may be evidence of some mass transport due to segregation as the solvent evaporated.¹¹ To demonstrate the ability of the ink-jet printing technique to deposit patterns, PVK doped with C6 dye was deposited with an ink-jet printed test pattern. This substrate was then illuminated using ultraviolet excitation, and a photograph was taken of the red emission of the patterned polymer (Fig. 2) (A filter was used to cut out most of the 420 nm polyester/PVK luminescence.) During the experiment the ink-jet printer was operated in the "bold" mode, which causes the printer to print every dot twice, which is why the letters appear double.

Figure 3 shows the photoluminescence spectra of three individual ink-jet printed thin films and spin-coated films made from the same solution, each with a different dye. The spin-coated films were spun-on at a speed of 4000 rpm for 60 s. The photoluminescence was measured using a Perkin– Elmer LS50 luminescence spectrometer with an excitation λ of 380 nm for the C47 doped film and 440 and 520 nm for C6 and nile red doped films, respectively. No significant difference in shape or magnitude is seen between the films prepared by ink-jet printing versus spin coating. It should be

1.4



FIG. 4. Current vs voltage for devices fabricated with ink-jet printed and spin-coated films of PVK doped with C6.

noted that the peak of 420 nm in the C47 spectra is due to a combination of the polyester substrate and the PVK host, not the deposited film. The dye luminescence appears as a peak at 450 nm on the shoulder of the 420 nm peak.

It was difficult to fabricate devices directly on top of the polymer dots fabricated by ink-jet printing because of the difficulty in aligning a shadow mask for metal cathode formation directly over a polymer dot. Therefore to fabricate test devices the ink-jet printer was operated in a mode to create a continuous sheet of polymer rather than discrete dots. After ink-jet printing, the samples were loaded into a vacuum chamber with a base pressure of $< 10^{-7}$ Torr for the metallization step of device fabrication. Typically, at least \sim 90 min were allowed between loading of samples and metal evaporation, and no further heating of samples was done. Top metal cathodes were deposited through a shadow mask to form an array of 250-µm-diam devices on the polymer film. Metal alloys such as Mg:Ag (10:1) were deposited by coevaporation from two separate sources, followed by the deposition of Ag as a protective layer. The ITO on the polyester sheet served as the anode. The devices were then measured in air without any protective coating.

Figure 4 shows the I-V curves of typical devices made by this procedure and a control device fabricated on a film spin coated from the same polymer solution. The organic







Im doped with C47 (blue), C6 (green), and nile red. Downloaded 16 Nov 2001 to 128.112.49.151. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/aplo/aplcr.jsp

film thickness of the control device was about 50 nm. Current densities of $\sim mA/cm^2$ are achieved at a voltage of $\sim 7 \text{ V}$ for the control device, and $\sim 6-11 \text{ V}$ for the ink-jet printed devices. Almost all of these voltages are lower than the drive voltage of $\sim 10-11 \text{ V}$ seen in our earlier work on doped PVK devices without an electron transport agent, but in the earlier work the organic thickness was $\sim 100 \text{ nm.}^9$ Figure 5 shows the L-I characteristic of the two devices, which shows that the efficiency of the ink-jet printed device is about a factor of 2 less efficient than the spin coated device.

In summary, we have successfully directly deposited patterned luminescent doped polymers by ink-jet printing, and fabricated OLEDs from ink-jet deposited doped polymers. Future work is necessary to determine the ultimate resolution of the technique, and to improve the device efficiency by adding an electron transport material to the organic material.

This work was supported by NSF (ECS-9612281), DARPA, and the New Jersey Commission on Science and Technology.

- ¹J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. MacKay, R. H. Friend, P. L. Burn, and A. B. Holmes, Nature (London) **347**, 539 (1990).
- ²D. Braun and A. J. Heeger, Appl. Phys. Lett. 58, 1982 (1991).
- ³C. W. Tang and S. A. VanSlyke, Appl. Phys. Lett. **51**, 913 (1987).
- ⁴C. W. Tang, S. A. VanSlyke, and C. H. Chen, J. Appl. Phys. 65, 3610 (1989).
- ⁵C. C. Wu, J. C. Sturm, R. A. Register, and M. E. Thompson, Appl. Phys. Lett. **69**, 3117 (1996).
- ⁶P. E. Burrows, S. R. Forrest, S. P. Sibley, and M. E. Thompson, Appl. Phys. Lett. **69**, 2959 (1996).
- ⁷Y. Nonaka, N. Ishimaru, Y. Ikuta, A. Tashiro, T. Hasegawa, S. Kaneko, K. Kawakami, and M. Hirano, Conference Records of The International Display Research Conference, Society for Information Display, 1997, pp. 238–241.
- ⁸N. Ishimaru, Y. Nonaka, T. Hasegawa, A. Tashiro, Y. Ikuta, S. Kaneko, K. Kawakami, and M. Hirano, Conference Records of The International Display Research Conference, Society for International Display, 1997, pp. 69–72.
- ⁹C. C. Wu, J. C. Sturm, R. A. Register, J. Tian, L. Dana, and M. E. Thompson, IEEE Trans. Electron Devices 44, 1269 (1997).
- ¹⁰C. C. Wu, C. I. Wu, J. C. Sturm, and A. Kahn, Appl. Phys. Lett. **70**, 1384 (1997).
- ¹¹A. W. Adamson, *Physical Chemistry of Surfaces* (Wiley, New York, 1982), pp. 319–458.