Room-temperature ultraviolet emission from an organic light-emitting diode

C. F. Qiu, L. D. Wang, H. Y. Chen, M. Wong, and H. S. Kwok
Center for Display Research, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, China

(Received 8 January 2001; accepted for publication 25 July 2001)

Ultraviolet emission was obtained from *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-(1,1′-biphenyl)-4,4′-diamine. Gallium nitride was used as a hole-blocking layer to contain the holes. A peak emission wavelength of 400 nm was measured. The external quantum efficiency is about 0.35%.
 [DOI: 10.1063/1.1407300]

The organic light-emitting diode (OLED) offers many advantages in display applications. Light conversion efficiencies approaching 40 lm/W have been reported.[1] For full-color displays, several approaches have been proposed and demonstrated.[2] One of the approaches makes use of a deep-blue OLED and converting the blue light to either red or green light with phosphors or ''color converters.'' If the OLED can emit in the ultraviolet (UV), light conversion efficiencies to the visible, in principle, can be higher.

An UV-emitting OLED has been reported for the case of polymers.[3,4] Yuan *et al.* reported 410 nm emission from the silicon chain of a polymer.[3] External efficiency of 0.1% was obtained. For the case of a small-molecule OLED, there has been no report of pure UV emission so far, though there are some reports of blue emission near the UV region.[5] Kajima, Asai, and Tamura made use of a hole-blocking layer to obtain emission from 4,4′-bis[N-(1-naphthl)-N-phenyl-amino]biphenyl (α-NPD). However, that emission is very broadband and is mostly in the visible. In this letter, we wish to report an OLED from a similar molecule, *N*, *N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-(1,1′-biphenyl)-4,4′-diamine (TPD). In the present case, we were able to obtain pure emission from TPD in the 400 nm region.

The structure of the OLED studied is

ITO/CuPc/$(\text{TPD/GaN})_n$/TPD/Ag.

It consists of a multilayer structure of TPD and GaN sandwiched between the Ag and ITO electrodes. The CuPc layer is an anode buffer layer used to facilitate hole injection and does not contribute to the emission process. The layer that is in contact with Ag is always TPD, which functions as a cathode buffer layer. The number of TPD/GaN composite layers has been varied from 1 to 5. It was found that the best results were obtained with $n=2$. The thickness of the TPD layer, as well as the GaN layer, were also varied systematically to optimize the emission. The optimal thicknesses of the various layers are: TPD (2 nm), GaN (1.2 nm), and CuPc (1 nm). The samples were prepared in the usual manner in an evaporator, with the GaN also thermally evaporated using a GaN target.

The current–voltage characteristic of the $n=2$ device is shown in Fig. 1. The turn-on voltage of about 10 V is typical of a small-molecule OLED. The emission spectra of the UV OLED at 10 and 12 V bias are shown in Fig. 2. The normalized spectra at these bias voltages are exactly the same. It can be seen that the emission peak is at 400 nm, with another smaller peak at 420 nm. The peak wavelength corresponds well to the 3.08 eV separation of the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) levels in TPD. This electroluminescence spectrum is also very similar to the photoluminescence spectrum of pure TPD.[6] Thus, it is inferred that the observed emission is due solely to TPD. It is seen in Fig. 2 that most of the emission is well within the UV region, with some light emitted at the blue green as well. Hence, the emission appears to be blue to the eye.

The spectra and luminance of the light emission from this device were measured using a PRA650 spectrophotometer. The applied voltage and current were measured using a Fluke45 multimeter. At 12 V, the measured luminance is about 60 lm. But, it should be noted that the silicon diode used in the measurement is sensitive to only 380 nm. The ocular sensitivity of the human eye is also very low at the ultraviolet wavelength. Thus, the normally used luminous efficiencies in terms of Cd/A or lm/W are not good measures of UV OLED. A better measure of the efficiency is the photon quantum efficiency. At 10 V, the effective external quantum efficiency was 0.35%, estimated using the current and the photon flux provided by the multimeter and the spectrophotometer, respectively. This number compares quite favorably with those obtained with polymer OLEDs.[4]

It is important to understand why emission can be obtained from TPD and the role played by the GaN layers. From the discussions in Kajima, Asai, and Tamura,[5] it is known that a hole-blocking layer is needed in order for the holes to be confined in the hole transport layer (HTL). In our

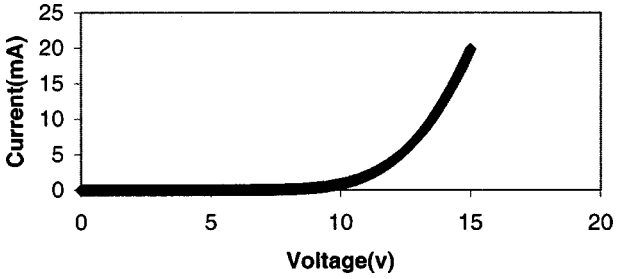

FIG. 1. $I-V$ characteristics of the UV OLED.

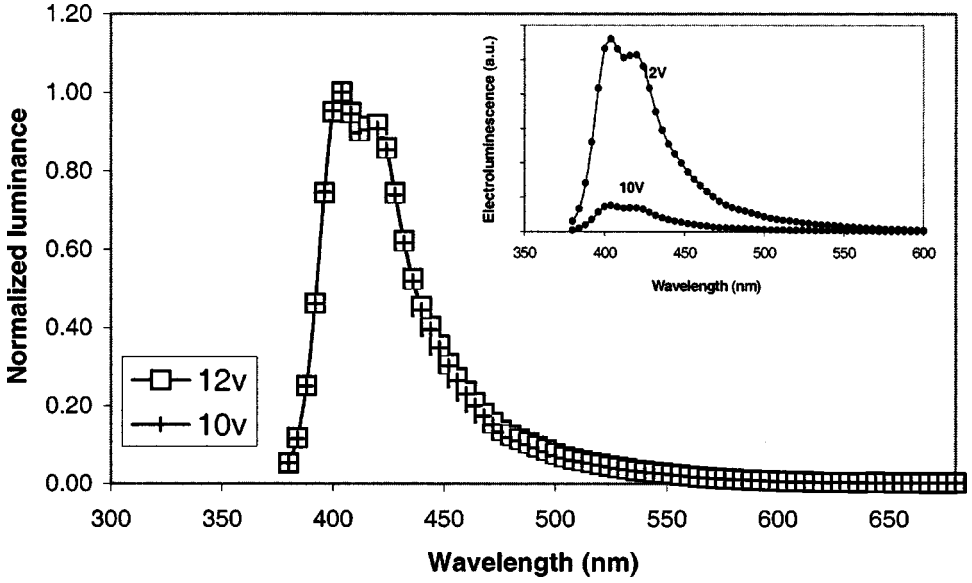

FIG. 2. Emission spectrum of the UV OLED at a bias of 12 V.

device, electrons are directly injected from the cathode into a TPD buffer layer, rather than into a conventional electron transport material. It is believed that GaN acts as a hole-blocking layer similar to 2,9-dimethyl-4,7-diphenyl-1,10-phenyanthroline (bathocuproine).[5] The conduction and valence bands of GaN have been measured to be at -2.5 and -5.9 eV below the vacuum level.[7] The LUMO and HOMO levels of TPD are at -2.29 and -5.37 eV, respectively. Hence, it is seen that GaN is both a hole and an electron barrier for TPD, confining electrons on the anode side and holes on the cathode side of the middle TPD layer of the $n=2$ device [Fig. 3(a)].

We have measured systematically devices with $n=0,1,..5$. It was found that because of the lack of electron blocking, the emission is very weak for the $n=1$ [ITO/CuPc/(TPD/GaN)/TPD/Ag] device [Fig. 3(b)], with a maximum luminance of only about 6 Cd/m^2. Similarly, for the $n=0$ [ITO/CuPc/TPD/Ag] device, there was some visible emission but it was too weak to be measurable with the spectrophotometer. The lifetime of the device was also extremely low. The device decayed away in a matter of seconds. For $n=3$ or higher, the threshold of current injection became very high. Over 20 V was needed to obtain light emission. Hence, it is concluded that the number of layers of GaN/TPD is optimal at $n=2$.

In the $n=2$ device, it is believed that most of the light emission comes from the middle TPD layer. The TPD on the Ag cathode side should emit rather weakly since there are few holes in that layer. Experimentally, it was found that if the GaN is in direct contact with the cathode, no emission could be obtained. It is probably because of the difference in electron injection for the Schottky junctions Ag/TPD and Ag/GaN. Since GaN has a larger band gap than TPD, the Ag/TPD junction should provide better electron injection than the Ag/GaN junction, as observed experimentally. In order to improve this UV OLED, other materials in contact with the cathode (Ag) can be used to increase the electron injection efficiency. Tris-(8-hydroxyquinoline) aluminum (Alq) is such a material, but it has been observed to contribute to undesirable light emission at longer wavelengths.

In conclusion, we have obtained emission from TPD in the UV. Reasonably efficient electroluminescence was measured. The emission efficiency can be improved by (1) replacing GaN by some material that will block the holes but not the electrons, (2) replacing the TPD layer by some material with better electron injection and transport efficiencies when in contact with the cathode.

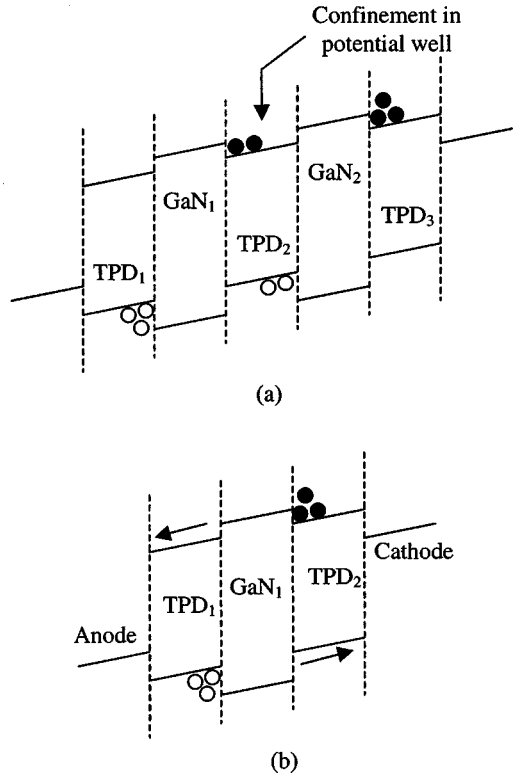

FIG. 3. Schematic energy diagrams for (a) an $n=2$ device showing the exciton confining potential well and (b) an $n=1$ device showing the lack of electron confinement.

This research was supported by the Hong Kong Research Grants Council under Contract No. HKUST6051/00E.

[1] P. E. Burrows, G. Gu, V. Bulovic, Z. Shen, S. R. Forrest, and M. Thompson, IEEE Trans. Electron Devices **44**, 1188 (1997).
[2] C. W. Tang, D. J. Williams, and J. C. Chang, U.S. Patent No. 5,294, 870 (1994).
[3] C. H. Yuan, S. Hoshina, S. Toyoda, H. Suzuki, M. Fujiki, and N. Matsumoto, Appl. Phys. Lett. **71**, 3326 (1997).
[4] Y. T. Tao, E. Balasubramaniam, A. Danel, and P. Tomasik, Appl. Phys. Lett. **77**, 933 (2000).
[5] Y. Kajima, N. Asai, and S. Tamura, Jpn. J. Appl. Phys., Part 1 **38**, 5274 (1999).
[6] L. D. Wang, C. F. Qiu, and H. S. Kwok, International Display Research Conference, Palm Beach, FL (2000), p. 43 (unpublished).
[7] R. J. Nemanich, P. K. Baumann, M. C. Benjamin, O. H. Nam, A. T. Sowers, B. L. Ward, H. Ade, and R. F. Davis, Appl. Surf. Sci. **130**, 694 (1998).