Fabrication of flexible hybrid low molecular weight compound/polymer light emitting device by screen printing

Mariya P. Aleksandrova, Irena P. Nestorova

It is demonstrated successful fabrication of simple bicomponent single layer OLED produced by screen printing. The device exhibits high mechanical stability after 400 cycles of bending. Turn on voltage of 5 V and maximum brightness of 92 cd/m^2 is achieved at current flow 2.9 mA. Luminous efficiency is higher than the reported for similarly produced devices, reaching 3.94 lm/W and the power consumption is average 50 mW - very suitable for portable devices with battery power supply. Another advantage of the thick film technology is the higher thermal stability when operates at maximum possible voltage of 30 V for several tenth of hours. It is due to the more efficient heat dissipation from 2 μm thick organic coating in comparison with the thin ones (hundreds nanometers).

Изготвяне на гъвкава хибридна нискомолекулна/полимерна светоизлъчваща структура чрез ситопечат (Мария Александрова, Ирена Несторова). *Показано е успешното получаване на прост еднослоен двукомпонентен OLED (органичен дисплеен елемент) чрез ситопечат. Структурата проявява висока механична устойчивост след 400 цикъла на огъване. Напрежението на запалване на луминесценцията е 5 V, а максималната яркост е 92 cd/m^2 и е достигната при ток от 2.9 mA. Луминесцентната ефективност е подобрена спрямо докладвани в литературата стойности за подобен тип устройства и е 3.94 lm/W, а консумираната мощност е средно 50 mW, което прави структурата подходяща за приложение в мобилни устройства Друго предимство, произтичащо от прилагането на дебелослойна технология е по-добрата термична устойчивост при работа с максимално напрежение от 30 V в продължение на няколко часа. Това се дължи на по-ефективното топлинно разсейване от дебелия 2 μm органичен слой в сравнение със случая на тънък нанослой.*

Introduction

Despite of the significant improvement of the multilayer organic light emitting devices (OLEDs) [1], [2], single layer OLED should not be neglected, because of their simpler structure and easier fabrication process [3]. Low molecular weight compound (LMWC) OLEDs have been more developed in comparison with the high molecular weight compound (polymer) OLEDs. Both classes of materials are implemented in the electroluminescent “sandwich” type devices (the active layer is situated between two electrodes) as a thin 50-150 nm films. In order to increase the efficiency of the single layer OLED different approaches have been used as electrode’s surface treatment for roughness decrease [4], replacing of the transparent electrode material [5] or doping with different nanoparticles, blended to the main emissive material [6]. Recently, some papers regarding application of screen printing technique for organic electroluminescent layers [7], [8]. In [7] are reported 100 nm screen printed film with four component blend from polystyrene doped with NPB, Alq3 and rubrene. In [8] has been processed polystyrene, rubrene, α-NPD and DPVBi for white OLED produced by screen printed film. It is used substance Ir(ppy)3 to enhance device brightness to 470-750 cd/m^2, but the activation voltage hasn’t still been reduced and varied between 28-33 V. Earlier, Pardo et. al. have demonstrated screen printing of even less than 100 nm film as a new approach to fabricate OLEDs [9]. As can be seen, in the researches reported until now, screen printed films are thin. However, if the screen printed film is thick (which is actually the idea of this method), then the volume of the functional organic material would be higher and generated heat during operation would be better spread in the surrounding environment, instead to accumulate inside the structure and causes melting of the flexible substrate.

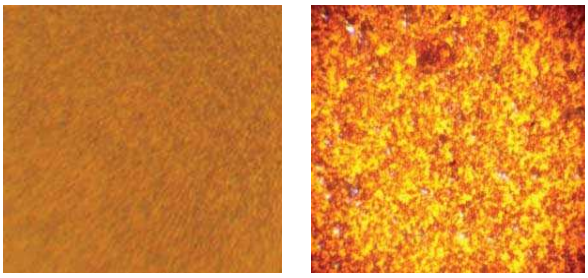
In our paper we present results from fabrication and testing of single layer hybrid flexible OLED, obtained by screen printing. The samples produced are characterized by high stability after hundreds of bending cycles, because of the binder presence as well as by high thermal stability due to the thick organic film, dissipated effective the heat generated during operation. There are no data about investigation of hybrid between LMWC and hole conductive host polymer, playing a role of binder in the same time. By our knowledge there are no reports in the literature about application of screen printing method for flexible OLED fabrication, as well as about using of such bi-component organic mixture for glass or flexible based device, independently on the deposition method.

Materials and methods

Polyethylentherephtalate (PET) foil with sizes 30x30 mm served as a flexible substrate. Indium tin oxide (ITO) electrode with thickness 180 nm, sheet resistance 22 ohms/square and transparency for the visible light 83%, was achieved by RF reactive sputtering followed by UV treatment [10]. Tris (8-hydroxyquinolinato) aluminium soluble derivative (Alq3-D) was used as yellow-green electroluminescent material. It is mixed with binding host polymer polyvinylcarbazole (PVK) having enhanced hole transporting properties. The weight ratio of LMWC and the polymer was Alq3-D:PVK=3:1, dissolved in 10 mg chloroform. Produced organic paste was deposited onto PET/ITO substrate by screen printing method. Produced film thickness (2 µm) was then dried in oven at 30 C˚ for 10 minutes to achieve homogenization of the coating and fully evaporation of the solvent. Finally, aluminum cathode film with thickness 200 nm was thermally evaporated through shadow mask, defining 4 separated emissive areas on common substrate. The average thickness of the screen printed layer was measured by KLA - Tencor Alphastep 500 Profilometer. Current – voltage characteristics were measured by ampermeter Keithley 6485. Luminance intensity versus supplying voltage characteristics were measured by luminancemeter Konika Minolta LS-110. Samples are put in special chamber with round opening for conduction of optical measurements eliminating some errors during brightness detection, that originate from the space dependence of the light intensity.

Results and discussion

In previous investigations [11] it was demonstrated that electroluminescent organic devices with films in micrometer thickness range can work stable at voltages 20-30V, providing high brightness of the generated emission with no substrate damages, caused by the heat. The reason is higher volume of organic material, dissipating much better the heat to the ambient through the upper metal electrode without thermal breakdown in comparison to thin films. The host polymer PVK, which also play a role of hole transporting material, added to the main material provides viscosity increase and enhances the adhesion of the electroluminescent layer to the flexible substrate. Although it is not shown on the figures, when the concentration of the binder increases, the current flow and the luminance decrease, which could be due to the quenching of the excited states from dominated host particles. The surface morphology of the screen printed hybrid LMWC/polymer coating was found to be strongly affected by the conditions such as stencil resolution, strength and angle of the squeegee moving across the screen stencil, forcing paste into the mesh openings and planarity of the covered surface. Microscopic view of the produced thick film's surface is shown on Fig. 1 at magnification 100. As can be seen in this case, after supplying of the screen printed organic crystal/polymeric coating on flexible PET/ITO substrate there are no pinholes formed in the film in comparison with the way they occur in polystyrene 100 nm film screen printed on glass/ITO [7].

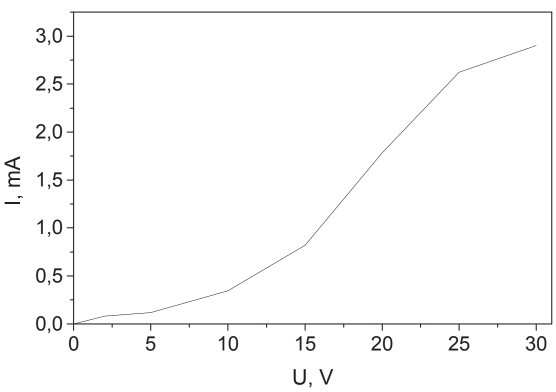


a) *b)*

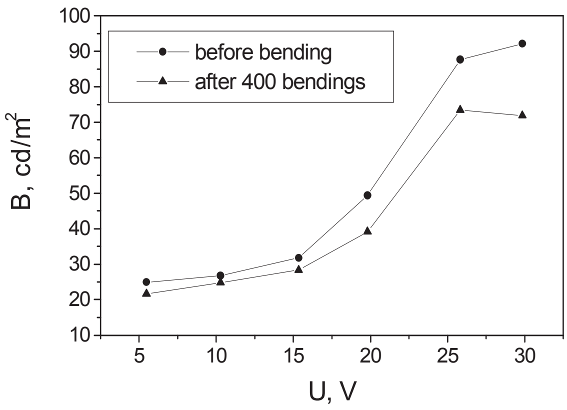
Fig. 1. Microscopic picture of the screen printed LMWC/polymer coating on ITO surface at magnification 100 a) treated with UV b) none treated with UV.

Although the surface energy of the substrate and interfacial forces, defined cohesion and wetting process are not quantitatively measured it is obvious that interfacial energy between this film and the substrate is high enough to prevent dewetting. This is due to the UV treatment of the ITO surface for enhancement of the film's polycrystallinity and to decrease its sheet resistance. More details about the UV treatment can be found elsewhere [10]. For comparison the same organic layer was screen printed onto none UV treated ITO surface and the result is shown on Fig. 1b. As can be seen the wetting conditions are not favorable, although the film is relatively dense. Pinholes exist, which can be noticed as tiny light dots. The layer is evidently irregular as can be observe from the color gradient. Although the device is single layer, due to the mixture with typical hole injecting and transporting material such as PVK, it was expected brightness comparable with bilayer thin film based OLEDs. The difference here is the greater stability of the structure against the dissipated heat at voltages higher than 10V as will be shown later. The device was fully turned on at 5 V (at this voltage, the brightness was measurable) and reached maximum brightness of 92.18 cd/m^2 at 30V. At voltages ~ 2 V leakage currents of ~81 μA occur, which may be ascribed to non uniformity of the organic layer, leading to non uniformity of the contacts with the electrodes and causing local distortions of the electrical field distribution between both contacts. This effect is unwanted and should be avoided. Current-voltage and brightness-voltage characteristics of the hybrid screen printed OLED are shown on Fig. 2a and Fig. 2b respectively.

When the current flows through the electrode-organic semiconductor junctions, it stimulates weak emission. It can not be detected correctly, because not entire area is homogeneously emissive, but only separated microgranules emit light. This was the reason for the abrupt beginning of the brightness-voltage curve after 5V, although there was a current flow different than zero before fully turning on. Even when the luminance intensity is high enough and can be easily measured we should mention that the emission from the screen printed hybrid OLED was not uniform but seems like scattered from tiny emissive dots all over device area. From this observation, we could conclude that the organic particles were not regularly dispersed in the organic paste mainly due to the lower dissolving ability of the LMWC.



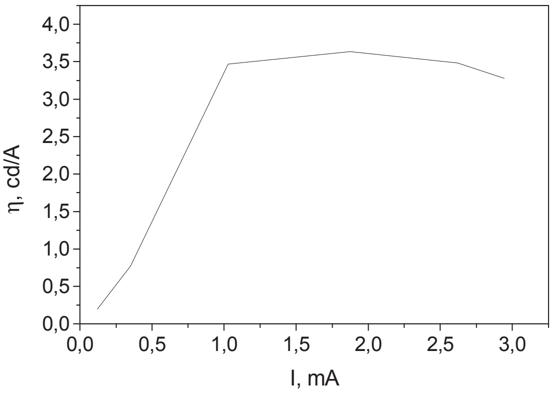
a)



b)

Fig. 2. a) Current-voltage characteristic of screen printed hybrid LMWC/polymer OLED; b) Brightness-voltage characteristic of screen printed hybrid LMWC/polymer OLED before and after 400 cycles of bending.

It can be seen from Fig. 2b that after 400 bendings and several tenths of hours work at maximal possible voltage, the brightness decreases only by 23%. For comparison, there are evidences in the literature for brightness decrease with 25 % in the first 50 h of operation or 50% from its initial value due to degradation mechanisms in OLED [12,13]. Measured results don't step back to the reported before for screen printed complex OLED device glass/ITO/PS: a-NPD:DPVBi: rubrene/Al with host polymer polystyrene [8]. The authors demonstrate that 90 cd/m2 can be achieved at 36 V (turn on voltage 10-15V) after optimization of the polystyrene concentration to 5%. The advantage of the proposed by us approach is competitive light intensity, achieved at 6 V lower voltage (which means improved efficiency) and involving less variety of materials for tuning of the electro-optical properties. This can be ascribed to the better charge transporting properties of the selected host polymer, ensuring suitable energy level alignment with the ITO electrode [14], as well as to the better distribution of the organic paste on the hydrophilic PET/ITO UV treated surface. Fig. 3a shows the luminance efficiencies at different currents and Fig. 3b shows photo of the produced and tested sample. The average efficiency was found to be 3.5 cd/A for brightness ranging from 50 to 90 cd/m^2, where the voltages were 20-25V. Power consumption in this range was extremely low – from 35.7mW to 73.4mW, which is great advantage for portable devices with battery power supply. Power efficiency for the maximum brightness was calculated to be 3.94lm/W.



a)

b)

Fig. 3. a) Luminance efficiency of screen printed hybrid LMWC/polymer OLED; b) Prepared OLED sample at initial stage of degradation after 400 cycles of bending.

Typical phenomena for OLED devices working in extreme conditions are the dark spots [15]. They can be observed here too, but after supplying of 400 bending cycles of the flexible structure with frequency 50 Hz and 30V (maximum luminance's point). The spots are clearly visible on Fig. 3b. They can be attributed to the fact that the hybridized particles in the screen printed OLED aggregated, because of the weak solubility of LMWC. Meanwhile, there are still no data about operation of OLED at such intensive mechanical and thermal influence. These results were achieved thankful to the strong adhesion of the organic coating on the PET/ITO substrate, ensuring high durability against mechanical treatment, as well as to the higher organic layer thickness, providing good thermal dissipation.

Conclusion

Single-layer bicomponent OLED was successfully fabricated by screen printing method and its performance was competitive to the reported multi-component blended OLEDs and thin film screen printed OLED. It was proved that suggested binder enhances stability of the entire device after bending due to good adhesion of the organic coating to the PET/ITO surface. Separately, UV treated ITO surface leads to avoiding of wetting problems and obtaining of pinholes free, uniform screen printed layers. At this stage of the research although the brightness is 92 cd/m^2, luminous efficiency is higher than the reported for similarly produced devices (3.94 lm/W) and power consumption is far below the typical values of hundreds mW (less than 100 mW). This is due to the decreased turn on voltage, caused by the suitable hybridization between LMWC and host polymer, as well as to the optimized deposition printing conditions. Our future work will be related to application of screen printing on patterned relief ITO surface and research of the uniformity of the organic layer near the patterned edges.

Acknowledgements

The work was financially supported by № 141ПР0005-03/2014 funded by Technical university of Sofia – research and development sector. Special thanks to Dr. Svetozar Andreev from Department of Microelectronics for the coating's thickness measurements.

REFERENCES

[1] Rostami, A., M. Noori, S. Matloub & H. Baghban. Light extraction efficiency enhancement in organic light emitting diodes based on optimized multilayer structures. Optik – Int. J. Light and Electron Optics, Volume 124, 2013, pages 3287-3291.

[2] Yang, S. H., D. W. Zhuang. Enhancement of efficiency of multilayer polymer light-emitting diodes by inserting blocking layers. J. Luminescence, Volume 131, 2011, pages 801-807.

[3] Feng, X. Fluorene derivatives for highly efficient non-doped single-layer blue organic light-emitting diodes. Organic Electronics, Volume 15, 2014, pages 57-64.

[4] Hong, J. W., D. H. Oh, C. H. Kim, G. Y. Kim, T. W. Kim. Efficiency enhancement of the organic light-emitting diodes by oxygen plasma treatment of the ITO substrate. J. Ceramic Processes Research, Volume 13, 2012, pages 193-197.

[5] Li, N., S. Oida, G. S. Tulevski, S. J. Han, J. B. Hannon, D. K. Sadana, T. C. Chen. Efficient and bright organic light-emitting diodes on single-layer graphene electrodes. Nature Communications, Volume 4, 2013, Article number: 2294.

[6] Gong, X., S. H. Lim, J. C. Ostrowski, D. Moses, C. J. Bardeen, G. C. Bazan. Phosphorescence from iridium complexes doped into polymer blends. J. Appl. Phys., Volume 95, 2004, p.948.

[7] Lee, D. H., J.S. Choi, H. Chae, C.-H. Chung, S.M. Cho. Screen-printed white OLED based on polystyrene as a

host polymer. Current Applied Physics, Volume 9, 2009, pages 161–164.

[8] Lee, D.H., J.S. Choi, H. Chae, C.H. Chung, S.M. Cho. Highly efficient phosphorescent polymer OLEDs fabricated by screen printing. Displays, Volume 29, 2008, pages 436–439.

[9] Lee, D. H., J. Choi, H. Chae, Ch. H. Chung, S. M. Cho. Single-layer organic-light-emitting devices fabricated by screen printing method. Korean Journal of Chemical Engineering, Volume 25, 2008, pages 176-180.

[10] Pardo, D. A., G. E. Jabbour, N. Peyghambarian. Application of screen printing in the fabrication of organic light-emitting devices. Advanced Materials, Volume 12, 2000, pages 1249–1252.

[11] Aleksandrova, M., I. Cholakova., G. Bodurov., G. Kolev., G. H. Dobrikov. Influence of UV treatment on the electro-optical properties of indium tin oxide films used in flexible displays. Journal of WASET, Volume 71, 2012, pages 1337 – 1340.

[12] Aleksandrova, M., G. Dobrikov, S. Andreev. Comparative study of thin and thick film technology for organic light emitting structures preparation. Int. J. Adv. Eng, Sc. Technol., Volume 1, 2011, pages 42-48.

[13] Burrows, P.E., S.R. Forrest; T.X. Zhou, L. Michalski. Operating lifetime of phosphorescent organic light emitting devices. Appl. Phys. Lett., Volume 76, 2000, pages 2493 – 2495.

[14] Aziz, H., Z. D. Popovic. Degradation phenomena in small-molecule organic light-emitting devices. Chem. Mater., Volume 16, 2004, pages 4522–4532.

[15] Wen, W., J. Yu, L. Li, T. Ma, X. Tang, Y. Jiang. Influence of PVK: NPB hole transporting layer on the characteristics of organic light-emitting devices. Optoelectr. Lett., Volume 4, 2008, pages 201-204.

[16] Kim, S. Y., K. Y. Kim, Y. H. Tak, J. Lee. Dark spot formation mechanism in organic light emitting diodes. Applied Physics Letter., Volume 89, 2006, Article number: 132108.

Assist. Prof. Dr. Mariya P. Aleksandrova *works currently in the Department of Microelectronics, Faculty of electronic engineering and technologies in Technical university of Sofia. She has defenced her PhD thesis in 2010 in the same department, presenting research in the field of technology for optimization of organic optoelectronic devices. Her scientific interests are related to the material science for microelectronics, thin film technologies, organic based microdevices, flexible microelectronics (flexible substrate based) and nanotechnologies. She has been awarded with several international prizes for her researches in the field of organic electroluminescent devices produced on solid and flexible substrates.*

tel.: 0887627183 e-mail: m_aleksandrova@tu-sofia.bg

Eng. Irena P. Nestorova *is future PhD student in the Department of Microelectronics, Faculty of electronic engineering and technologies in Technical university of Sofia, willing to make research in the field of organic electroluminescent materials. She has graduated her engineering degree in 2013 in the same department.*

tel.: +3592 965 30 85 e-mail: nestorova@gmail.com

Received on: 26.05.2014
