Tuning the emission of Poly (9,9-dioctylflorenyl-2,7-diyl) using one dimensional photonic band gap

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Received: 06 April 2016, Revised: 08 August 2016 and Accepted: 20 December 2016

DOI: 10.5185/amp.2017/3012
www.vbripress.com/amp

Abstract

Here we present fabrication of one dimensional photonic band gap structure (1D-PBG) based on periodic layers of silver and magnesium fluoride (MgF_2) for tuning the emission of polyfluorene derivative, Poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO). Transmittance measurements were used to characterize the photonic band gap. 1D-PBG structure with varying thickness of silver was fabricated on the back side of PFO coated glass substrate. Photoluminescence studies confirmed that blue emission was enhanced while the secondary peaks were suppressed. Photoluminescence spectra shows that the blue to green peak intensity ratio was improved by 1.7 times approximately with PBG. These type of PBG structures can be used to enhance the color purity of PFO based blue organic light emitting diodes. Copyright © 2017 VBRI Press.

Keywords: One dimensional photonic band gap, polyfluorene, organic light emitting diode, colour purity, photoluminescence.

Introduction

Organic light emitting diodes (OLEDs) are attracting researchers as an effective candidate for display technology due to their properties like flexibility, light weight, wide viewing angle and self-emission etc. [**1**]. Emission of OLEDs can be tuned over the entire visible region by using different materials in emissive layer [**2-4**]. Red and green color OLEDs with good efficiency and color purity have already been reported but blue color is still facing the problems [**5,6**]. Blue color OLEDs are very important for display devices because they can be used to irradiate green and yellow phosphors for generating white light [**7-9**]. Blue color can also be used to make white light emitting diodes. Blue OLEDs based on polymer like polyfluorenes and small molecules like Bis[2-(4,6-difluorophenyl)pyridinato C2,N] (pico-linato)iridium (FIrpic) are previously described by different researchers [**10,11**]. Polymer based organic light emitting diodes (PLEDs) have attracted more attention due to their ease of fabrication. Thin film of polymers in PLEDs can be fabricated using spin coating which is suitable for making large area displays. Polyfluorenes are one of the most important class of polymers known for blue emission. The main problem with polyfluorene derivatives is that along with the blue emission at 440 nm they also give two undesirable green peaks in long wavelength region at 460 nm and 490 nm [**10**]. These two peaks in green region affect the color purity of polyfluorene based devices. Different reasons such as keto defects, excimer formation etc have been given by different researchers for origination of these two unwanted peaks [**11,14**]. A lot of work have been done to enhance the color purity of polyfluorenes based devices or polyfluorenes such as incorporation of nanostructures, charge transfer materials, end capping, block copolymerization and substitution etc. [**15-17**]. All these techniques involve typical chemical synthesis and high purity chemicals as finally modified material is to be used inside the device. Furthermore, modification in device structure and polymer affects the device stability to a great extent.

Metallo-dielectric, one dimensional photonic band gap (1D-PBG) crystals is another technique that can be designed to transmit a particular wavelength of light. Metallo-dielectric 1D-PBG is made up of alternate thin films of metallic and dielectric materials [**18**]. As a result of these periodic layers, only some of wavelengths are allowed to be transmitted and a range of wavelength is proscribed. These properties of partial transmittance shown by PBG crystal can be used to tune the color emission or to reduce the green emission from the polyfluorenes

based OLED which leads to enhanced color purity. Mark et. al. studied photonic band gap structure to tune the transmission of light over a range of frequencies [**19,20**].

Here we report 1D-PBG structure based on alternate thin layers of conducting silver (Ag) and dielectric magnesium fluoride (MgF_2) to enhance the color purity of polyfluorene derivatives. This is first time when the PBG structure was used for the selective emission of polyfluorenes. Effect of varying the thickness of silver was studied on the emission of polymer Poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO). Photoluminescence studies were done to study the effect of 1D-PBG on the color purity of PFO emission and results are reported.

Experimental

Materials

Poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO) with molecular weight Mw = 50,000~150,000 was purchased from Luminescence Technology Corp., Taiwan. Chloroform ($CHCl_3$) of HPLC grade (purity > 99.5%), solvent for polymer and Magnesium fluoride (MgF_2) of optical grade (purity > 99.99%) were purchased from Sigma Aldrich. All the chemicals were used without any further purification.

Fabrication of 1D-PBG

On pre-cleaned glass substrate alternate thin films of conducting metal Ag and dielectric materials MgF_2 were evaporated using thermal vapor deposition technique by maintaining the pressure at 10^{-5} mbar. Different samples of 1.5 periods of PGB were prepared with varying thickness of Ag between 90 to 190 Å. Configuration of PBG crystal was glass/Ag (x Å)/MgF_2(1400 Å)/Ag(x Å)/MgF_2 (700 Å), where x = 90 Å to 190 Å

On the backside of each sample prepared above, freshly prepared solution of PFO polymer in chloroform (2mg/ml) was spin coated using Apex digital spin coater and dried for 30 min at 100°C in vacuum oven. Transmittance spectra of each sample were recorded using UV-Visible spectrophotometer (Shimadzu, model 2600). Then photoluminescence spectra of polymer were studied using spectroflurometer (Shimadzu, model-RF-5301Pc). All measurements were done at room temperature in normal atmospheric conditions.

Results and discussion

Reflection of light waves from metal surface is well known which makes metals look shiny but before getting completely reflected, light wave travels up to a certain distance in metal. That distance up to which light wave can travel is known as skin depth (δ) of that metal and can be calculated according to the formula:

$$\delta = \frac{\lambda c}{4\pi\eta i}$$

Skin depth depends upon wavelength (λ) of incident light and extinction coefficient (η_i) of metal. Here c is speed of light (3×10^8 m/s). To inhibit the unwanted green peak at 460 nm, calculations for the skin depth of silver metal were made according to the above formula by taking the value of η_i =2.4680. It was found that light with wavelength (λ) 460nm can travel into the Ag metal upto 145 Å whereas light with λ= 440 nm can penetrate upto 150 Å.

Fig. 1 shows the schematic diagram of glass substrates coated with PBG structure on one side and polyfluorene on the other side. The thickness of Ag was varied from 90Å to190Å whereas thickness of MgF_2 was kept constant for all the samples. Thickness of MgF_2 was 1400Å thick for first layer and 700 Å for uppermost layer.

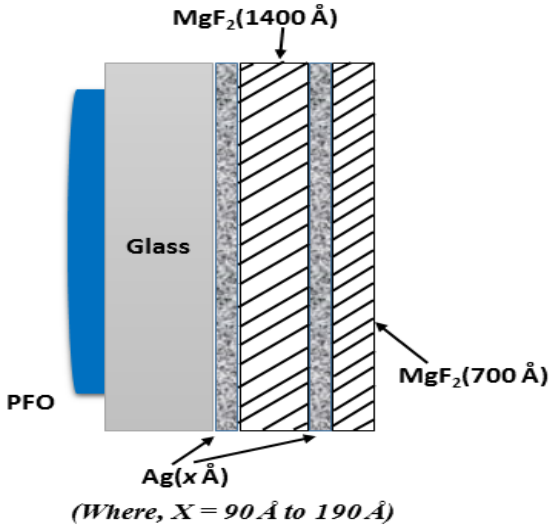

Fig. 1. Schematic diagram of PBG on one side of glass substrate and PFO on the other side.

Fig. 2 shows transmittance spectra of 1D-PBG samples deposited over cleaned glass substrates as explained in the experimental section. Spectrum 1 to 11 shows the transmittance of 1D-PBG with varying thickness of Ag from 90Å to 190Å.

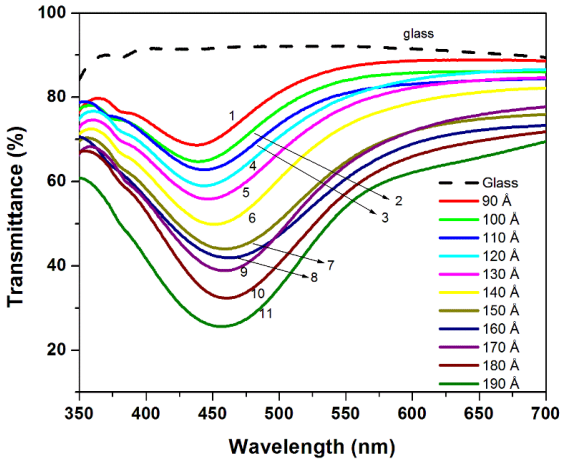

Fig. 2. Transmittance of plain glass (dotted line) and 1D-PBG coated glass with varying thickness of Ag (90 Å - 190 Å).

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The dotted line in **Fig. 2** is the reference spectrum from glass substrate. The transmittance from the reference substrate was 90% in visible region (400-700 nm). With PBG structure fabricated on the glass substrates, the transmittance was dependent on the thickness of the Ag layer in the visible region (400-700 nm). In addition, with increasing thickness of Ag layer, the transmission spectra were found to be red shifted. The wavelength for minimum transmittance (λ_{min}) for each spectra were recorded. This red shift for λ_{min} becomes saturated when thickness of Ag was increased beyond 150 Å. It was found that transmission @ λ_{min} decreased from 70% to 22% with increasing thickness of Ag layer from 90Å to 190Å which is obvious because transmittance is directly dependent on the thickness of the materials.

For silver layer of 90 Å and 150 Å, λ_{min} was found to be 438 nm and 455 nm, respectively. **Fig. 3** shows λ_{min} for each sample of PBG with different thicknesses of Ag layer.

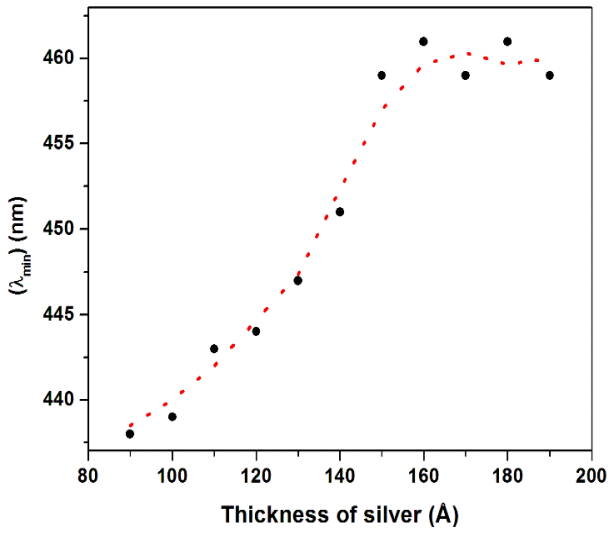

Fig. 3. λ_{min} (nm) versus thickness of Ag (90Å - 190Å).

The thickness of Ag in PBG were also investigated for color purity of PFO emission. Photoluminescence (PL) spectrum of PFO coated on the other side of glass substrate with 1D-PBG structure are shown in **Fig. 4(a)**. PL spectrum of pristine PFO deposited on plain glass substrate was also recorded as reference. PFO is known to have blue emission but the defects generated during the film formation process lead to the unwanted green peaks. PL of PFO polymer shows two emission peaks at 440 nm and 460 nm along with a shoulder at 490 nm. Peaks at 460 nm and 490 nm usually arise due to keto defect generated due to oxidation of aliphatic chains of PFO [**6**]. As a result of these two peaks overall color purity of the device get affected. When 1D-PBG structures were deposited on the backside of the glass substrates coated with PFO polymer thin films, PL spectra shows less intense green peak at 460 nm. This is due to the fact that PBG allows to pass emission peak at 440nm whereas act as barrier for the green peak at 460 nm. This effect increases as the thickness of Ag increases. With increasing thickness overall intensity of emission also get affected as shown in **Fig. 4(b)**. Small effect on the intensity of the peak at 490 nm can also be observed as the thickness of the Ag increases in PBG structure.

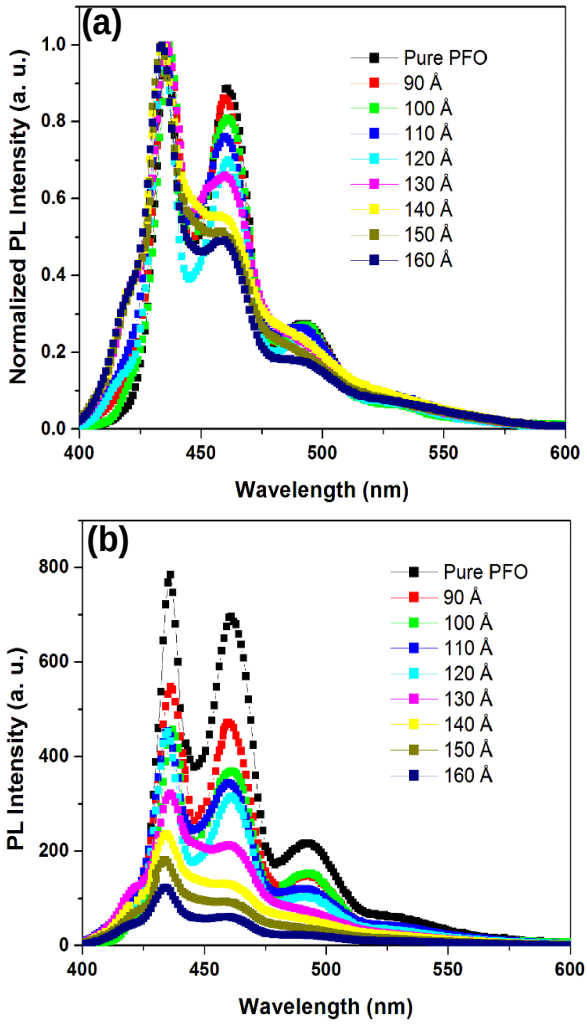

Fig. 4. (a) Normalized photoluminescence and (b) photoluminescence spectra of PFO coated over plain glass and 1D-PBG coated glass.

To study the effect of PBG on color purity of PFO, blue to green emission intensity ratio (I_{blue}/I_{green}) was calculated. **Fig. 5** shows the blue to green intensity ratio against thickness of Ag layer of 1D-PBG. Ratio of intensity of blue peak at 440 nm (I_{blue}) to green peak at 460 nm (I_{green}) was calculated and plotted against thickness of Ag in PBG. There is increase in value of I_{blue}/I_{green} as the thickness increases from 90 Å to 160 Å, as shown in **Fig. 5**. For PFO deposited on glass, the ratio I_{blue}/I_{green} was low (1.127) as compared to PBG sample with 160 Å thickness of Ag for which I_{blue}/I_{green} was 1.9729.

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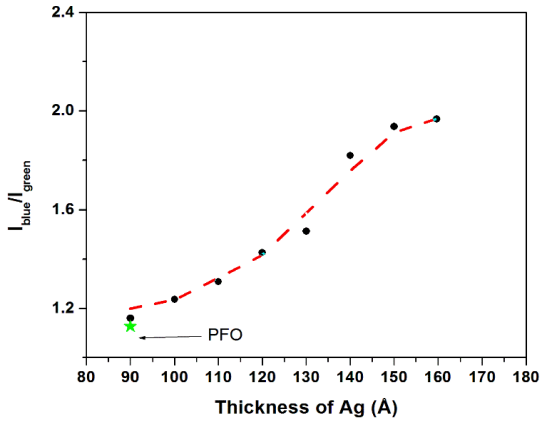

Fig. 5. Blue to green peak intensity ratio (I_{blue}/I_{green}) with varying thickness of Ag.

By using 1D-PBG emission properties of the PFO can be tuned without any alteration in device structure or the polymer which helps to enhance the color purity without adding any foreign material inside the device structure. Although emission intensity decreases with increasing thickness of Ag, **Fig. 5** shows that green peak is significantly suppressed by PBG based on periodic layers of Ag and MgF_2 and thus color purity enhanced.

Conclusion

1D-PBG based on alternate layers of conducting Ag and dielectric material magnesium fluoride was used to suppress the green peak in the emission spectrum of PFO. Effect of varying thickness of Ag layer in PBG was studied. PBG with 150 Å thick Ag was effective to obstruct the green peak at 460 nm. Also the blue to green intensity ratio was increased to 1.9729 for PBG with 160Å thick PBG as compared to 1.127 for PFO without PBG.

Acknowledgements

The authors are grateful to Dr Ashok K Chauhan, Founder President, Amity University Uttar Pradesh and Dr V K Jain, Distinguished Scientist and Professor, AIARS (M&D) Amity University,Uttar Pradesh, India for their continuous encouragements. The authors are grateful to the Department of Science and Technology for the financial assistance through (grant no. DST/TSG/PT/2011/192).

References

1. Held, G.; Introduction to Light Emitting Diode Technology and Applications; CRC Press, USA, **2008**.
2. Jou, J-H.; Shen, S-M.; Chen S-H.; Wu, M-H.; Wang, W-B.; Wang, H-C.; Lin, C-R.; Chou, Y-C.; Wu P-H.; Shyue, J-J.; *Appl. Phys. Lett.*, **2010**, *96*, 143306.
3. Jeon, W. S.; Park, T. J.; Kim, S. Y.; Pode, R.; Jang, J.; Kwon, J. H.; *Appl. Phys. Lett.*, **2010**, *93*, 063303.
4. Saxena, K.; Singh, G.; Thallapakac, B.; Mehta, D. S.; *J. Inf Disp,*, **2014**, *15*, 119.
5. C-H.; Tao, Y-T.; Chou, P-T.; Datta, S.; Liu, R-S.; *Adv. Mater*., **2003**, *15*, 884.
6. Kim, S-J.; Zhang, Y.; Zuniga, C.; Barlow, S.; Marder, S. R.; Kippelen B.; *Org. Electron.*, **2011**, *12*, 492.
7. Tsai, Y-S.; Hong, L-N.; Jaung F-S.; Chen, C-Y.; *J. Lumin.*, **2014**, *153*, 312.
8. Li, X-L.; Ouyang, X.; Chen, D.; Cai, X.; Liu, M.; Ge, Z.; Cao, Y.; Su, S-J.; *Nanotchnology*, **2016**, *27*, 12.
9. Zhang, Z.; Wang, W.; Dai, Y.; Liu, Y.; Wang L.; Ma D.; *Org. Electron*., **2009**, *10*, 491.
10. Duan, L.; Hou, L.; Lee, T-W.; Qiao, J.; Zhang, D.; Dong, G.; Wang, L.; Qiu, Y.; *J. of Mater. Chem*., **2010**, *20*, 6392.
11. Giovanella, U.; Botta, C.; Galeotti, F.; Vercelli, B.; Battiatoc, S.; Pasinia, M.; *J. Mater. Chem*., **2013**, *1*, 5322.
12. Zhao, W.; Cao, T.; White, J. M.; *Adv. Funct. Mater*., **2004**, *8*, 783.
13. List, E. J.W.; Gaala, M.; Guentnerc, R.; Freitasc, P. S.; Scherfc, U.; *Synth. Met*., **2003**, *139*, 759.
14. Luptona, J. M.; Craig, M. R.; Meijer, E. W.; *App. Phys. Lett*., **2002**, *80*, 4489.
15. Miteva, T.; Meisel, A.; Knoll, W.; Nothofer, H. G.; Scherf, U.; Müller, D. C.; Meerholz, K.; Yasuda, A.; Neher, D.; *Adv. Mater*. **2001**, *13*, 565.
16. Hung, M. C.; Liao, J. L.; Chen, S. A.; Chen, S. H.; Su, A. C.; *J. Am. Chem. Soc*., **2005**, *127*, 14576.
17. Li, J. Y.; Ziegler, A.; Wegner, G.; *Chem. Eur. J*., **2005**, *11*, 4450.
18. Lee, G. J.; Lee, Y. P.; Jung, S. G.; Jung, B. Y.; Hwangbo, C. K.; Kim S.; Park, I.; *J. Korean Chem. Soc*., **2007**, *51*, 431.
19. Scalora, M.; Bloemer, M. J.; Pethel, A. S.; Dowling, J. P.; Bowden, C. M.; Manka, A. S. *J. Appl. Phys*., 2015, *83*, 2377.
20. Bloemer, M. J. and Scalora M.; *Appl. Phys. Lett*. **1998**, *72*, 1676.

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