

PERFORMANCE ENHANCEMENT OF ORGANIC LIGHT-EMITTING DIODES USING ELECTRON-INJECTION MATERIALS OF METAL CARBONATES

Jong-Yeol Shin^{*} — Tae Wan Kim^{**} — Gwi-Yeol Kim^{***}
Su-Min Lee^{***} — Bhanu Shrestha^{***} — Jin-Woong Hong^{***}

Performance of organic light-emitting diodes was investigated depending on the electron-injection materials of metal carbonates (Li_2CO_3 and Cs_2CO_3); and number of layers. In order to improve the device efficiency, two types of devices were manufactured by using the hole-injection material (Teflon-amorphous fluoropolymer –AF) and electron-injection materials; one is a two-layer reference device (ITO/Teflon-AF/Alq₃/Al) and the other is a three-layer device (ITO/Teflon-AF/Alq₃/metal carbonate/Al). From the results of the efficiency for the devices with hole-injection layer and electron-injection layer, it was found that the electron-injection layer affects the electrical properties of the device more than the hole-injection layer. The external-quantum efficiency for the three-layer device with Li_2CO_3 and Cs_2CO_3 layer is improved by approximately six and eight times, respectively, compared with that of the two-layer reference device. It is thought that a use of electron-injection layer increases recombination rate of charge carriers by the active injection of electrons and the blocking of holes.

Key words: organic light-emitting diodes, electron-injection materials, metal carbonates, Li_2CO_3 , Cs_2CO_3

1 INTRODUCTION

As the information and communication technologies develop, future electronic system is required such as lightness, low-power consumption, ease of handling, and *etc* [1, 2]. New and creative methods which could be applied to the future electronic systems are being developed [3, 4]. And, as the society becomes more informative rapidly, the importance of the display is growing and a trend is switched to a flat-panel display [5, 6]. Because of low-driving voltage, organic light-emitting diodes (OLEDs) have advantages such as various application area, low-power consumption, low cost, self-light emission, full color, *etc* [7, 8]. In order to satisfy the demand of stable operating parameters, high brightness, and high efficiency of the OLEDs, research on the carrier injection, transport, mechanism of the light emission, cathode material, roughness of indium-tin-oxide (ITO) surface, interface between the electrode and the organic thin film, buffer layer, and efficient emissive materials are being actively carried out [9, 10].

Continuous study of the OLEDs application has been done since the late 1980s, and they have been commercialized [11, 12]. The OLEDs are being competitively developed globally for large displays [13, 14]. The large organic light-emitting display is rapidly developing, and it will be soon a current display around us [15, 16].

In this paper, in order to improve the efficiency of the OLEDs, their performance was investigated by studying the electrical properties depending on electron-injection

materials. Two types of devices were manufactured and properties of the devices were compared. The reference device consisting of two-layer (ITO/Teflon-AF/Alq₃/Al), and a three-layer (ITO/Teflon-AF/Alq₃/metal carbonate/Al) device inserting the metal carbonate material below the cathode. Teflon-AF was used as a hole-injection material. Two metal carbonates (Cs_2CO_3 and Li_2CO_3) were used, and the influence of metal carbonates on the properties of OLEDs was investigated.

2 EXPERIMENT

ITO substrate with a surface resistivity of approximately $8\ \Omega/\square$ was used as an anode. It was patterned by etching process done directly in our laboratory. ITO was etched using a vapor composed of mixed HCl and HNO₃ with a volume ratio of 3 : 1. The distance between the ITO glass and the solution was set to be approximately 20 mm and the etching time was 20 min. After confirming a proper etching, it was then washed in flowing water. Removing the water out of the substrate by blowing with nitrogen gas, the glass was cut into 20 mm × 20 mm segments and then placed into a square glass chamber for washing [17]. Figure 1 shows a shape of patterned ITO anode and a glass size.

Aluminum (Al) was used as a cathode, which was purchased from Aldrich Company. The cathode was deposited at a rate of 0.5 ~ 1.0 Å/s to an initial thickness of 10 nm by using a tungsten boat at a pressure of

^{*} Department of Car Mechatronics, Sahmyook University, Seoul 139-742, Korea, ^{**} Department of Physics, Hongik University, Seoul 121-791, Korea, ^{***} Department of Electrical Engineering, Kwangwoon University, Seoul 139-701, Korea, ealab@kw.ac.kr

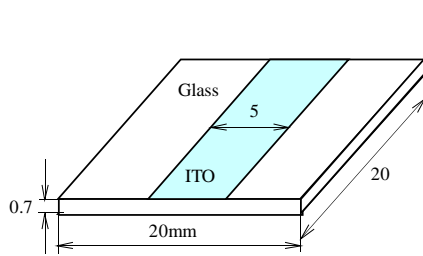


Fig. 1. Patterned shape of ITO substrate

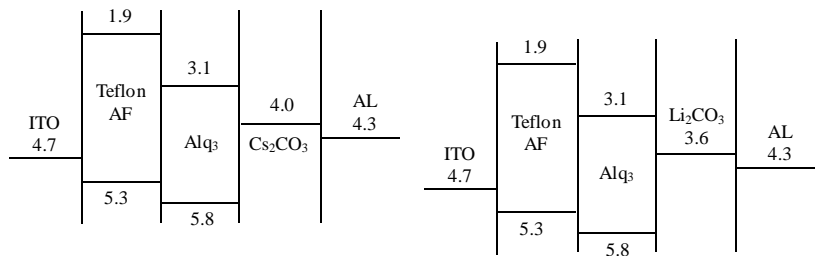


Fig. 2. Energy-level diagram for three-layer OLED device

Table 1. Electrical properties of OLEDs due to the electron-injection layer and hole-injection layer

Classification		L_{\max} (cd/m ²)	$V_{L\max}$ (V)	η_{EQ} (%)
2 Layer	HIL Tefflon AF	195	11	0.02
	EIL Cs ₂ CO ₃	570	9.5	0.07
	EIL Li ₂ CO ₃	602	12.25	0.07
3 Layer	EIL Li ₂ CO ₃ HIL: 15 400	10.25	0.14	
	EIL Cs ₂ CO ₃ Tefflon AF 9 800	12.50	0.19	

$V_{L\max}$ is the voltage at the maximum luminance L_{\max} and η_{EQ} represents the external-quantum efficiency.

5×10^{-6} Torr and deposited at a rate of 5 \AA/s to a thickness of 20 nm, and then deposited quickly continuously to a thickness of 100 nm at a rate of 15 \AA/s . Active area of 15 mm^2 was produced by using a shadow mask [18].

Figure 2 shows an energy-level diagram for the three-layer device used in our experiment. It is known that the deposited metal carbonates, Cs_2CO_3 and Li_2CO_3 , are semiconductors rather than metal. Thus, an injection of electrons from Al cathode to the conduction band of this electron-injection layer becomes easier. This behavior may contribute to the electrical conduction, and results in the improvement of electrical and optical properties of the OLEDs.

Current density–voltage–luminance (J-V-L) characteristics of the OLEDs were measured with a use of Keithley 6517 electrometer and Keithley 2000 multimeter. Programmable DC power supply of Vupower Company and the Lab-view software to control the apparatus to measure the voltage, current, luminance, luminous efficiency, and external-quantum efficiency were used. In order to measure the efficiency of the device, silicon photodetector was placed at the front of the device and photocurrent was measured as a function of the applied voltage with Keithley 2000 multimeter.

Since the photocurrent is the one flowing through the device by the illumination of light, it is proportional to the number of photons, and the current flowing through the device is proportional to the number of electrons. Thus, the luminous efficiency and the external-quantum efficiency of the device can be obtained by using the photocurrent and conduction current. The luminous efficiency is a useful parameter for display applications,

being given by $\eta = \pi L_0 / JV$, where L_0 is the emission luminance that is measured normal to the emitting surface. J is the current density, and V is the applied voltage. Since the external-quantum efficiency is a ratio of extracted photons out of the device to the injected charge carriers, it is calculated using the L_0 and J [19]. All the experiments were carried out at room temperature, and the applied voltage was increased with a step of 0.25 V/1,000 ms and delay time of 100 ms [17, 20].

3 RESULTS AND DISCUSSION

3.1 Two-layer reference device

Figure 3 shows the current density–voltage–luminance (J-V-L) characteristics, luminous efficiency, and external-quantum efficiency for the two-layer reference device (ITO/Tefflon-AF/Alq₃/Al). It shows that the current density is proportional to $V^{1.6}$ below the electric field of $2 \times 10^7 \text{ V/m}$ (2 V). However, the current density increases very rapidly above the electric field of $3 \times 10^7 \text{ V/m}$ (3 V). We can see that there is a negative-resistance region between the electric field of $4.5 \times 10^7 \text{ V/m}$ (4.5 V) and $6 \times 10^7 \text{ V/m}$ (6 V). The light emission starts from the beginning of negative-resistance region and the luminance becomes more active near the end of negative-resistance region. Thus, it is thought that the negative-resistance region is related to the light-emitting properties. Even though the two-layer reference device clearly shows the negative-resistance region, it gives a low luminance of 195 cd/m^2 , possibly due to the lack supply of electrons and holes. However, there is an improvement of luminance by 25 % compared to that of one-layer OLEDs with the 100 nm thick Alq₃ layer. It is thought that this improvement of the device performance comes from an increase of recombination of electrons and holes due to a contribution of hole injection and the blocking of electrons by the hole-injection layer. The obtained maximum luminous efficiency and the external-quantum efficiency for the two-layer reference device are 2.5 lm/W and 0.023% , respectively.

Figure 4 shows the electrical properties of the two-layer device (ITO/Alq₃/Cs₂CO₃ or Li₂CO₃/Al), where the electron-injection material of metal carbonate (Cs₂CO₃ or Li₂CO₃) is inserted. In Fig. 4(a), the current density is proportional to $V^{1.6}$ below 3 V, and there is a negative-resistance region below the applied voltage of 5 V. As the negative-resistance characteristics is more clear, the

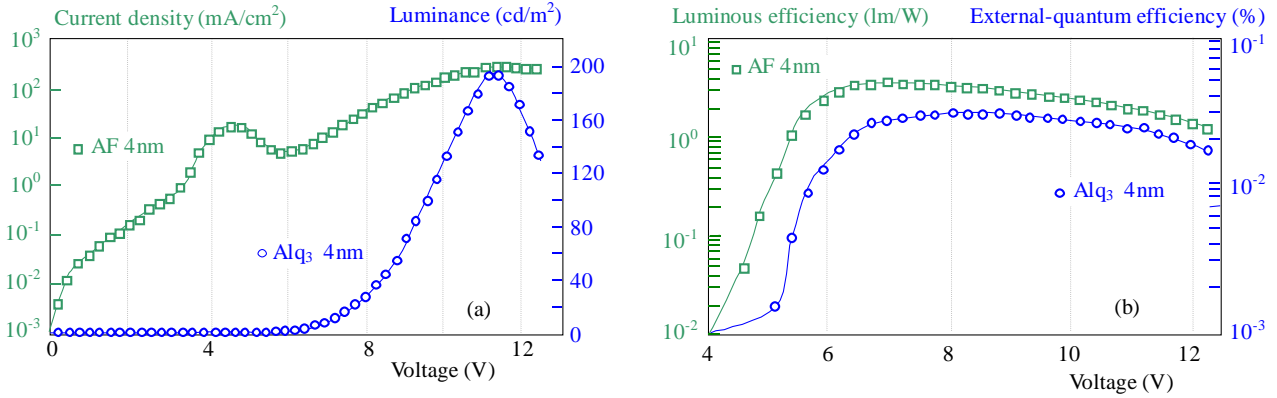


Fig. 3. (a) — Current density-voltage-luminance and (b) — luminous efficiency-voltage-external-quantum efficiency characteristics for the two-layer device (ITO/Teflon-AF/Alq₃/Al)

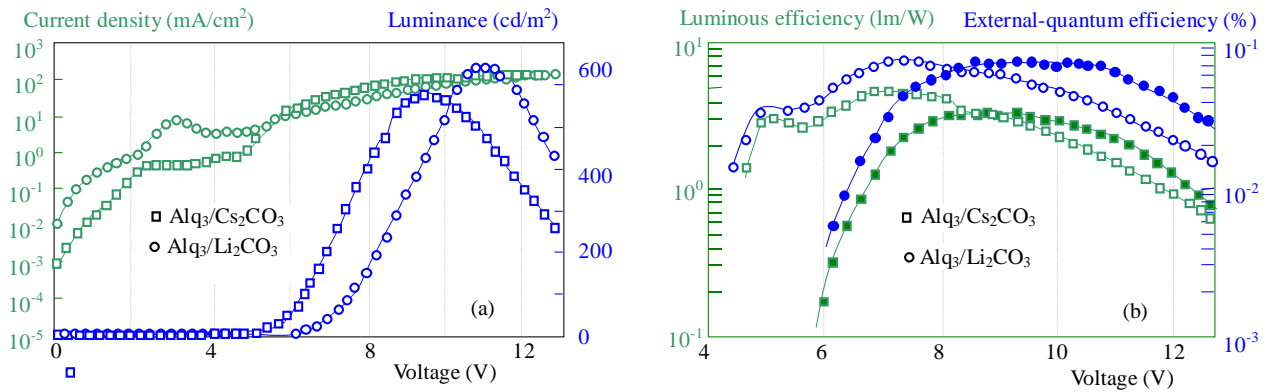


Fig. 4. (a) — Current density-voltage-luminance and (b) — luminous efficiency-voltage-external-quantum efficiency characteristics for the two-layer device (ITO/Alq₃/Cs₂CO₃ or Li₂CO₃/Al)

luminance is more outstanding. Figure 4(a) shows that the luminance of the device with Li₂CO₃ is higher than that of the device with Cs₂CO₃ layer at the same voltage above 10 V. However, the luminous efficiency and the external-quantum efficiency are close to each other for those two devices. Furthermore, it was found that the voltage-dependent luminance and the external-quantum efficiency for the two-layer device with electron-injection layer (Cs₂CO₃ and Li₂CO₃) are approximately two times higher than those of the two-layer device with Teflon-AF. It is thought that this is due to a contribution of easy injection of charge carrier.

3.2 Three-layer device

Figure 5 shows the current density-voltage-luminance characteristics for the three-layer device (ITO/Teflon-AF/Alq₃/Cs₂CO₃ or Li₂CO₃/Al) inserted metal carbonate layer, which acts as an electron-injection layer. It shows that the current density is proportional to $V^{1.6}$ below the electric field of 2×10^7 V/m (2 V), with a slight rapid increase in the region below the electrical field of 3×10^7 V/m (3 V). And there is a negative-resistance region between the electric field of 3.25×10^7 V/m (3.25 V) and 4.5×10^7 V/m (4.5 V), and light emission starts from the beginning of negative-resistance region and the luminance becomes more active near the end of negative resis-

tance region. Negative-resistance characteristics is more clear in the device with Li₂CO₃ layer at low voltage, and high luminance of about 15400 cd/m² was obtained at an electric field of 10.25×10^7 V/m (10.25 V). This luminance is 77 times higher than that of the two-layer reference device. This improvement is due to an increase of recombination of electrons and holes caused by a contribution of electron injection and blocking of holes when the electron-injection layer of Li₂CO₃ is introduced. It was found that the external-quantum efficiency for the three-layer device with Li₂CO₃ layer is 0.14 %, which is improved approximately by a factor of six compared to that of the two-layer reference device. Even though this value of external-quantum efficiency is much lower than that of the other well-prepared fluorescent OLEDs with different materials and structure, which is about 4 %, our aim is to show the effect of carbonate layer. Negative-resistance characteristics is clear at low voltage in the three-layer device with Cs₂CO₃ layer, and the maximum luminance L_{\max} of 9800 cd/m² was obtained at an electric field of 12.5×10^7 V/m (12.5 V). This is an increase of luminance by a factor of fifty compared to that of the reference device. And it was found that the external-quantum efficiency for the three-layer device with Cs₂CO₃ layer is 0.19 %, which is improved approximately by a factor of eight compared to that of the two-

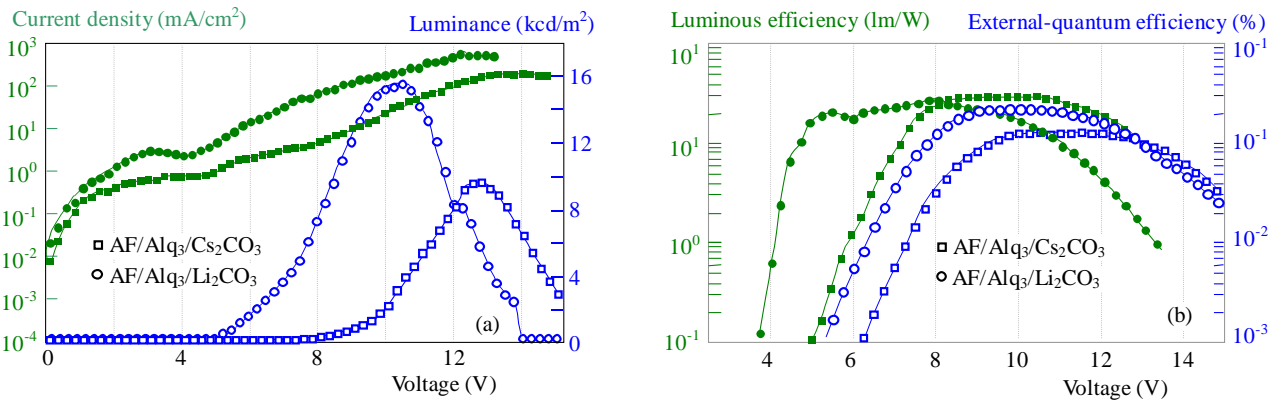


Fig. 5. (a) — Current density-voltage-luminance and (b) — luminous efficiency-voltage-external-quantum efficiency characteristics for the three-layer device (ITO/Teflon-AF/Alq₃/Cs₂CO₃ or Li₂CO₃/Al)

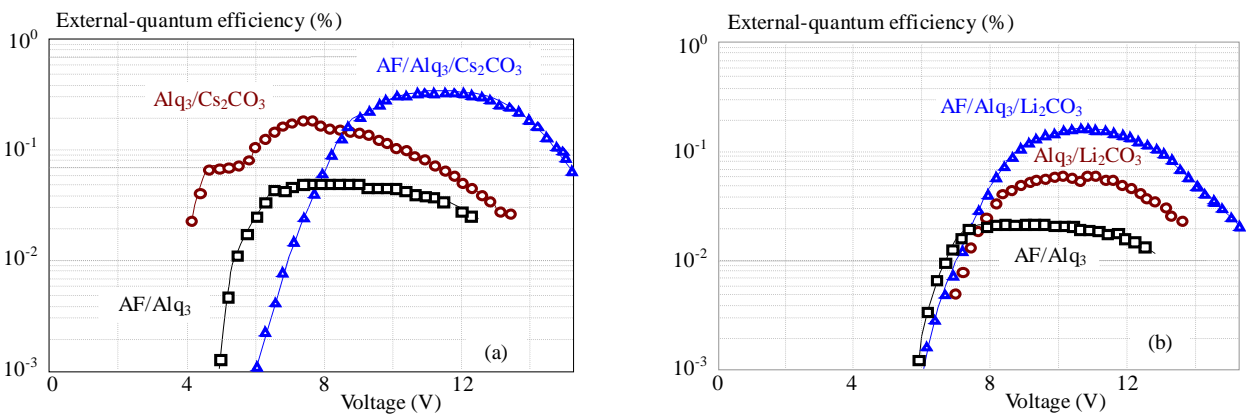


Fig. 6. External-quantum efficiency of the devices representing the effect of (a) — Cs₂CO₃ and (b) — Li₂CO₃ layer

layer reference device, and is also higher than that of the device with Li₂CO₃. The maximum luminance L_{\max} of the device with Li₂CO₃ layer is much higher than that of the device with Cs₂CO₃ layer. It is thought that this improvement is due to an easy transport of electrons and blocking of electrons by the Teflon-AF hole-injection layer as shown in the energy-level diagram of Fig. 2. These results are summarized in Table 1.

Figure 6 shows the external-quantum efficiencies of the devices representing the effect of Cs₂CO₃ and Li₂CO₃ layer. Figures 6(a) and 6(b) are the efficiencies for the devices with Cs₂CO₃ and Li₂CO₃ layer, respectively. It can be seen that there is a vivid improvement of the efficiency of the devices with an insertion of carbonate layer.

4 CONCLUSION

We have investigated the performance of the three-layer device (ITO/Teflon-AF/Alq₃/metal carbonate/Al) by introducing the electron-injection layer of metal carbonates to the two-layer reference device (ITO/Teflon-AF/Alq₃/Al). The two-layer reference device showed the negative-resistance characteristics, and a low luminance of about 195 cd/m² was obtained. However,

this luminance is 25 % higher than that of the one-layer (ITO/Alq₃/Al) device. And it was found that the external-quantum efficiency of the two-layer device with electron-injection layer (Cs₂CO₃ and Li₂CO₃) is approximately two times higher than that of the two-layer device with hole-injection layer (Teflon-AF). Thus, the electron-injection layer affects more on the electrical and optical properties of the OLEDs than the hole-injection layer. The luminance for the three-layer devices with Li₂CO₃ and Cs₂CO₃ layer is approximately eighty and fifty times higher than that of the two-layer reference device, respectively, which may be due to the increased recombination rate of electrons and holes by the active injection of electrons and the blocking of holes. And the external-quantum efficiencies for the three-layer devices with Li₂CO₃ and Cs₂CO₃ layer are improved by approximately six and eight times, respectively, compared to that of the two-layer device.

Acknowledgements

The present Research has been conducted by the Research Grant of Kwangwoon University in 2014.

REFERENCES

- [1] TOKITO, S.—NODA, K.—TAGA, Y.: High Performance Organic Electroluminescent Diodes with Microcavities, *Electro. Lett.* **32** (1996), 691–692.
- [2] TANG, C. W.—VANSLYKE, S. A.: Electroluminescence of Doped Organic Thin Films, *Appl. Phys. Lett.* **48** (1989), 3610–3616.
- [3] LEE, S. T.—GAO, Z. Q.—HUNG, L. S.: Metal Diffusion from Electrodes in Organic Light-Emitting Diodes, *Applied Physics Letters* **75** No. 10 (1999), 1404–1407.
- [4] HUNG, L. S.—TANG, C. W.—MASON, M. G.: Enhanced Electron Injection in Organic Electroluminescence Devices using an Al/LiF Electrode, *Applied Physics Letters* **70** No. 2 (1997), 152–154.
- [5] DIOUF, B.—WOO, S. J.—RAMCHANDRA, P.—JANG, H. K.: Efficiency Control in Iridium Complex-Based Phosphorescent Light-Emitting Diodes, *Adv. in Mat. Sci. and Eng.* (2012), 1–14.
- [6] GANZORIG, C.—FUJIHARA, M.: Improved Drive Voltages of Organic Electroluminescent Devices with an Efficient p-Type Aromatic Diamine Hole-Injection Layer, *Appl. Phys. Lett.* **77** (2000), 4211–4213.
- [7] TOKUHISA, H.—ERA, M.—TSUTSUI, T.—SAITO, S.: Electron Drift Mobility of Oxadiazole Derivatives Doped in Polycarbonate, *Appl. Phys. Lett.* **66** (1995), 3433–3435.
- [8] KWAK, J. H.—CHAE, J. W.—SON, S. H.—JUNG, B. J.: Highly Efficient Blue Fluorescent Organic Light-Emitting Diodes by Engineering Hole-Transporting/Exciton-Blocking Layer, *ECS Solid State Letts* **4** (2015), R5 to R9.
- [9] WANG, J. F.—JABBOUR, G. E.—MASH, E. A.—ANDERSON, J.—ZHANG, Y.—LEE, P. A.—ARMSTRONG, N. R.—PEYGHAMBARIAN, N.—KIPPELEN, B.: Oxadiazole Metal Complex for Organic Light-Emitting Diodes, *Adv. Mat.* **11** (1999), 1200–1209.
- [10] VAN SLYKE, S. A.—CHEN, C. H.—TANG, C. W.: Organic Electroluminescent Devices with Improved Stability, *Appl. Phys. Lett.* **69** (1996), 2160–2162.
- [11] LEE, J. H.—WU, M. H.—SHIAU, C. C.: Oxadiazole Derivatives Used as the Host of the Metal Doped Electron Transport Layer Material, *SPIE Proc., Taiwan Display Conferences*, 2004.
- [12] ZHENG, Z. B.—DING, X. M.—LEE, S. T.—W. A.: Enhanced Brightness and Efficiency in Organic Electroluminescent Devices using SiO₂ Buffer Layers, *Appl. Phys. Lett.* **74** (1999), 2227–2229.
- [13] LEE, H. K.—SEO, J. H.—KIM, J. H.—KOO, J. R.—LEE, K. H.—YOON, S. S.—KIM, Y. K.: Investigation of Blue Organic Light-Emitting Diodes (OLEDs) with Various Hosts, *J. of the Korean Phys. Societ.* **49** (2006), 1052–1056.
- [14] BRUTTING, W.—BERIEB, S.—MUCKL, A. G.: Device Physics of Organic Light-Emitting Diodes based on Molecular Materials, *Org. Electro.* **2** (2010), 1–36.
- [15] MEERHEIM, R.—WALZER, K.—PFEIFFE, M.—LEO, K.: Ultrastable and Efficient Red Organic Light Emitting Diodes with Doped Transport Layers, *Appl. Phys. Lett.* **89** (2006), 1111–1114.
- [16] BLOCHWITZ, J.—FRITZ, T.—PFEIFFER, M.—LEO, K.—ALLOWAY, D. M.—LEE, P. A.—ARMSTRONG, N. R.: Interface Electronic Structure of Organic Semiconductors with Controlled Doping Levels, *Org. Electro.* **2** (2001), 97–104.
- [17] HONG, J. W.—OH, D. H.—KIM, C. H.—KIM, G. Y.—KIM, T. W.: Efficiency Enhancement of the Organic Light-Emitting Diodes by Oxygen Plasma Treatment of the ITO Substrate, *J. of Ceram. Process. Resear.* **13** (2012), 193–197.
- [18] HONG, J. W.—KIM, C. H.—HAN, H. S.—KANG, Y. G.—LEE, J. Y.—KIM, T. W.: Dependence of the Efficiency Improvement of Organic Light-Emitting Diodes on the Thickness of the Cs₂CO₃ Electron-Injection Layer, *J. of the Kor. Phys. Societ.* **60** (2012), 1611–1615.
- [19] GU, G.—FOREST, S. R.: Design of Flat-Panel Displays based on Organic Light-Emitting Devices, *IEEE J. of Selected Topics in Quant. Electro.* **4** (1998), 83–99.
- [20] HONG, J. W.—OH, D. H.—SHIM, S. M.—LEE, Y. S.—KANG, Y. G.—SHIN, J. Y.: Effects Of Plasma Surface Treatment on the Electrical Properties of the ITO Substrate, *J. of the Kor. Phys. Societ.* **60** (2012), 1576–1581.

Received 15 January 2016

Jong-Yeol Shin was born in 1956 in south Korea. He received the PhD of electrical engineering at Kwangwoon University in Seoul in 2003. He is majoring electrical insulation materials and has been a professor in the department of car-mechatronics at Sahm Yook University since 1997. His research concerns mainly the organic materials.

Tae Wan Kim was born in 1958, in Seoul, Korea. He received PhD degree in 1990 in Physics from UCLA. He is interested in physical properties of organic conductors, especially conduction mechanism of organic light-emitting diodes (OLEDs). He has been a professor at Hongik University in the department of physics from 1991. He was a visiting researcher at University of Arizona, Tucson in 1999.

Gwi-Yeol Kim was born in 1959 in Korea. He received the PhD in 1989 in electrical engineering from Kwangwoon University in Seoul Korea, his major of fuel cell system and new energy system, organic and electrical insulation materials. He has been a director of energy technology research institute of NEOEN from 2011. He worked as a senior researcher at the KERI in 1989. He was a visiting researcher at Tohoku University and Kyushu University in 1994 and 1999, respectively. He was an assistant professor with the KOREATECH, Ulsan University, Hanyang University in 2000 and 2007, 2009 respectively.

Su-Min Lee was born in 1989 in Korea. He received the BS in 2015 in electrical engineering from Kwangwoon University in Seoul Korea, he was major of programing, embedded system and web hacking. He has been a Master course at Kwangwoon University in the department of electrical engineering from 2015 and his research nterests are organic light-emitting diodes. He has been research assistant at Applied Research Center for Electro-Fusion Technology from July 2015.

Bhanu Shrestha was born in Nepal in 1966. He received the BSc, MSc and PhD degree Kwangwoon University, Korea in 1998, 2004 and 2008, respectively. He was an adjunct professor from 2008 to 2011 in RFIC center at Kwangwoon University and He was an assistant professor from 2011 to 2015 at the same university in the department of Electronic Engineering (Kwangwoon Institute for Advanced Study). He is also an author of the book, 'Practical Design of MMIC VCOs'. He is currently an associate professor in the same university. His interests include RFIC/MMIC/ design and fabrication, OLED, computer networks.

Jin-Woong Hong was born in 1955 in Korea. He received the PhD in 1987 in electrical engineering from Kwangwoon University in Seoul Korea, his major of electrical insulation materials and organic light-emitting diodes. He has been a professor at Kwangwoon University in the Department of Electrical Engineering from 1989. He was a visiting researcher at Nagoya University and Kyushu Institute of Technology during in 1992 and 2000, respectively.