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Performance characteristics by inserting MoO_3 layer into organic light-emitting diodes

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In this study, we investigated the performance characteristics optimized by molybdenum trioxide (MoO_3) used as a buffer layer between an anode and a hole transport layer. MoO_3, which acts as a carrier ladder, allows for easy hole injection. The small difference between the highest occupied molecular orbital (HOMO) level of N,N'-Bis (3-methylphenyl)-N,N'-diphenylbenzidine (TPD) and the conduction band of MoO_3 leads to an easy carrier transfer effect. It was found that when the thickness of MoO_3 as a buffer layer was 15 nm, the current density was improved by about 3 times and the luminance by about 3.87 times at a voltage of 7 V, compared to those of a basic device without a buffer layer. The 60% lifetime of the device was improved by a factor of 3.17 and 1.55 at the MoO_3 layer thickness of 5 nm and 15 nm, respectively, compared to that of the basic device. It was found that when the thickness of MoO_3 is more than 15 nm, the thickness of MoO_3 acts as a resistance component, thus reducing the current density and luminance characteristics. The electrical and optical characteristics of the device were determined by varying the thickness of the hole-transport layer TPD to be 25, 35, and 55 nm with the fixed layer thickness of MoO_3 to 15 nm which showed a high current density and luminance. The current density, luminance, and lifetime of the organic light-emitting diodes were improved by about 2.6 times, 3 times, and 5.5 times, respectively, at the TPD layer thickness of 25 nm and the MoO_3 layer thickness of 15 nm.

Key words: Organic Light-Emitting Diodes, Buffer layer, Molybdenum trioxide.

Introduction

Organic light-emitting diode (OLED) is a self-light emitting device composed of a multilayer organic material placed between metal electrodes. In the organic light-emitting diode, when a voltage is applied between the two electrodes, injected charge carriers recombine and form electron-hole pairs in an emissive layer, which emit light by having transition to the ground state. Since the organic light-emitting diode is a self-light emitting device, it does not require backlight unlike liquid-crystal displays. Also, it makes possible to realize thinner, lighter and more various types of displays. Further, it provides a wide-view angle and a fast response time and, is resistant to vibration and physical impact. The main research subjects in organic light-emitting diodes are the efficiency and lifetime, which are related to device structure, energy level, injection barrier, deterioration phenomenon, and etc. In 1963, Pope et al. at New York University demonstrated electroluminescence resulting from DC upon application of several hundred volts to an anthracene single crystal and a crystal doped with tetracence using a silver electrode with a small area [1]. In 1970, Dresner et al. succeeded in injecting a current density of 50 mA/cm^2 into an anthracene single crystal by using a thin film of SiO_2 [2]. In 1987, Tang and VanSlyke of Kodak reported the high quantum efficiency, luminous efficiency, and luminance at low driving voltage of an organic thin film of two-layer structure, and thereafter, organic light-emitting diodes began to be studied in earnest [3]. Tang and VanSlyke achieved the luminance of 1000 cd/m^2 at 10 V by using an anode ITO and a cathode Mg:Ag in the structure of an alumiquinolinol complex and an aromatic amine, where the electronic properties of those two are different [3]. Transition metal oxides have a high work function and a high transmittance, and are known as materials for the electrode or charge generation and recombination. Among the transition metal oxides with these advantages, MoO_3 has advantages such as good electrical properties and low light absorption in the visible region. Tokito et al. demonstrated that hole injection is improved by the use of vanadium and molybdenum oxide as an intermediate layer between the anode and an organic material in the OLED [4]. Since then, many researchers have conducted a number of studies to improve the OLED performance [5-10]. In this study, we investigated a role of holes in organic light-emitting diodes in terms of electrical and optical

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properties, by using MoO_3 as a buffer layer between an anode and a hole-transport layer.

Experimental Procedure

The indium-tin-oxide (ITO) used in this study was obtained by patterning a product of Samsung Corning. Wet-etching was carried out using aqua regia vapor to construct a stripe pattern of the ITO. The aqua regia used for wet etching, which is a yellowish liquid, is made by mixing hydrochloric acid (HCl, M.W. = 36.46) and nitric acid (HNO3, M.W. = 63.02) at a volume ratio of 3 : 1. After the etching, the ITO glass substrate is cleaned sufficiently with running water so that the aqua regia residues do not remain on the ITO glass substrate. And then, the resistance of the patterned ITO is measured with a multimeter to check the etched state. The resistance of the patterned ITO is about 30 Ω. Fig. 1(a) shows the schematic shape of the patterned ITO electrode.

The following wet chemical cleaning process is conducted on the etched ITO to remove the oil, ion, metal, and contaminants on the coated surface: Firstly, a jig including the ITO glass substrate is immersed in a SC-1 (Standard Cleaning 1) solution obtained by mixing ammonia (NH4OH), hydrogen peroxide (H2O2), and distilled water (H2O) at a ratio of 1 : 1 : 5 and ultrasonic cleaning is performed at 50°C for 20 minutes. In the SC-1 aqueous solution, etching by ammonia and oxidation by hydrogen peroxide are repeated, and thereby particles on the surface of the ITO are effectively removed. Secondly, ultrasonic cleaning is performed at the same temperature and time interval as SC-1, using acetone (99.5%), ethyl alcohol (94.5%), and distilled water. The washed ITO is dried using nitrogen (N_2) gas and dried on a hot plate at a temperature of 90 ºC for 30 minutes to remove the remaining water.

In this experiment, the organic light-emitting diode was fabricated using a vacuum thermal deposition method and the pressure during the vacuum deposition was 1×10^{-5} Torr. The structure of the device used in this experiment is ITO (180 nm)/MoO_3 (x nm)/TPD (40 nm)/Alq3 (60 nm)/Al (100 nm) as shown in Fig. 1(b). Organic materials and MoO_3 were deposited at a rate of about 0.5 ~ 1 Å/s and aluminum at a rate of about 5.0 ~ 7.0 Å/s. The current density-voltage characteristics, external-quantum efficiency, and lifetime of the device were measured by using a Keithley 236 (source-measure unit) and a Keithley 617 (electrometer).

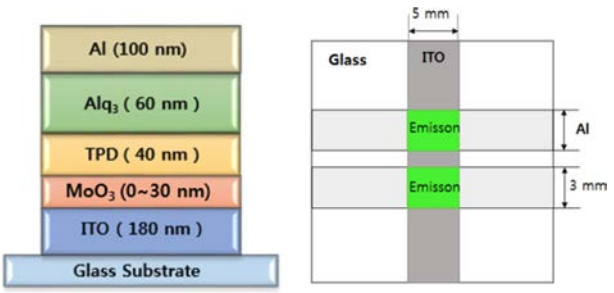

Fig. 1. Schematic structure of the organic light-emitting diode and the patterned ITO anode used in our study.

Results and Discussion

The deposition of MoO_3 on the ITO glass substrate was identified by a contact method and a non-contact method. First, in the contact method used for measuring the thickness of the thin film, the difference in height between the substrate and the deposited thin film was measured with Alpha-Step (α-step 200). An accurate measurement is possible only when there is a boundary between the two layers with different heights. MoO_3 was deposited to a thickness that the Alpha-Step can recognize, using a thermal-deposition apparatus. Scan on the film was performed in the Alpha-Step for 8 seconds with a covered range of 40 μm.

Fig. 2 shows the measured thickness of MoO_3 layer with Alpha-Step. The thickness of MoO_3 layer deposited on the ITO substrate was about 20 nm. It is believed that a gradual change of the thickness at the interface results from the shadow effect of the deposition mask.

In the non-contact method, the change in MoO_3 thickness depending on the wavelength was determined based on UV-vis absorbance. The results are shown in Fig. 3. As seen in the figure, no distinctive absorption peak was observed in the visible region higher than about 400 nm. In addition, it was found that the absorption intensity increases slightly as the thickness of MoO_3 increases.

The electrical and optical properties depending on the thickness of the hole-injection layer of MoO_3 are shown in Fig. 4. Fig. 4(a) shows the current density-voltage characteristics. As the thickness of MoO_3 layer increases from 0 to 15 nm, the current density and

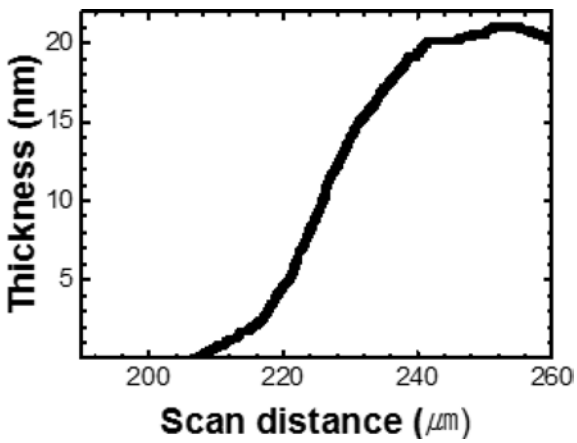

Fig. 2. Thickness of MoO_3 film measured with Alpha-Step.

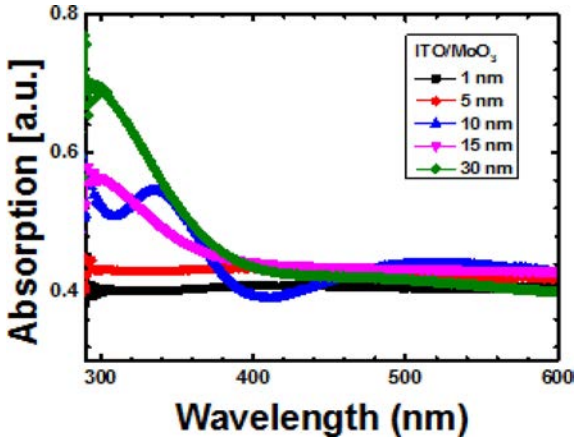

Fig. 3. UV-vis. absorption spectra of MoO_3 film for several thicknesses.

luminance are improved. The work functions of ITO and ITO/MoO_3 were measured to be 4.7 eV and 5.3 eV, respectively [11-12]. The work function of TPD was measured to be 5.4 eV [13-14]. Our results show that the introduction of MoO_3 layer allows for easy hole injection because it acts as a carrier ladder with almost no hole injection barrier. Given that the hole injection barrier between the ITO substrate and the TPD is 0.7 eV, it can be understood that the hole injection therebetween is not smooth. The difference between the HOMO level of TPD and the conduction band of MoO_3 is 0.96 eV, which means that the carrier transport is easy. The current density at 7 V in the device with 15 nm of MoO_3 layer is about three times higher than the one in the device without a buffer layer. Therefore, the introduction of MoO_3 in the OLED as a buffer layer decreases the driving voltage. It can be understood that the driving voltage increases when the thickness of MoO_3 layer is more than 20 nm. It was found that the current density of the device decreases as the MoO_3 layer is thicker than 15 nm. The conduction current density J is calculated as $J = qn\mu$ V/d. Here, q is the charge, n is the charge-carrier density, μ is the mobility, V is the applied voltage, and d is the thickness of the organic material [15]. It is believed that the change of the current density and luminance of the device depending on the thickness of MoO_3 layer seems to be due to the following reasons: Thin MoO_3 layer thickness has good hole-injection and hole-transport properties due to the carrier ladder and the carrier transport effect, respectively. However, MoO_3 layer thickness higher than 15 nm in the device serves as a resistance component according to the conduction current density formula. Fig. 4(b) represents luminance-voltage characteristics of the devices, which shows a similar tendency as those of Fig. 4(a). Fig. 4(c) shows the elapsed time-dependent normalized luminance of the OLEDs with the MoO_3 layer thickness varying from 0 to 30 nm at room temperature and a constant current density of 10 mA/cm^2. Here, the initial luminance of the

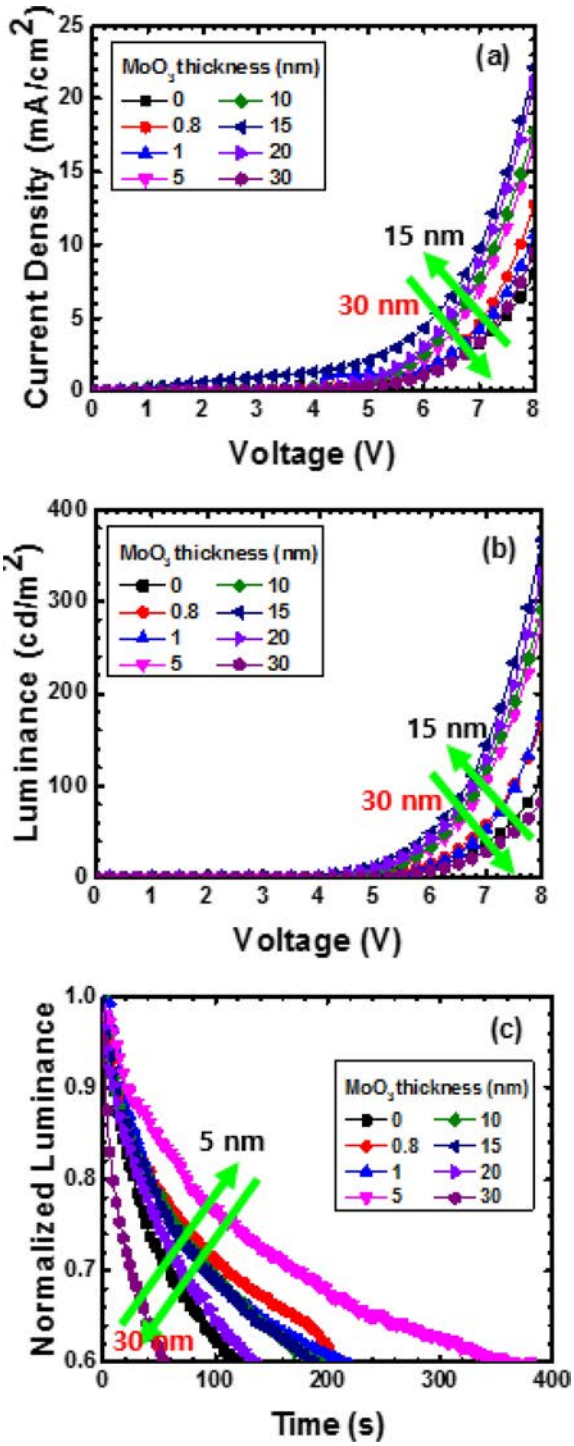

Fig. 4. (a) Current density-voltage characteristics, (b) luminance-voltage characteristics, and (c) normalized luminance over elapsed time for the several thickness of the MoO_3 layer.

device was about 200 cd/m^2. A constant current was applied to the devices at intervals of 3 seconds, and the luminance was measured over time. The luminance of the OLED without MoO_3 sharply decreased, whereas, when the buffer layer of MoO_3 was inserted between an anode (ITO) and a hole-transport layer (TPD), the initial degradation was suppressed. It was observed that the

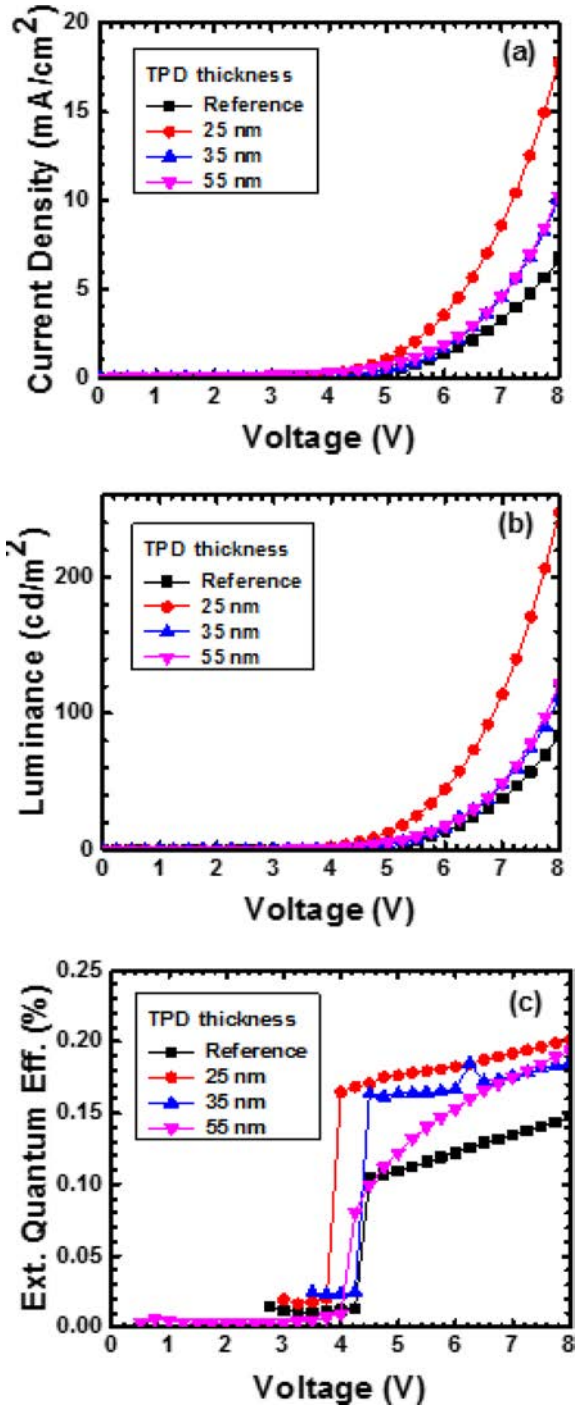

Fig. 5. (a) Current density-voltage characteristics, (b) luminance-voltage characteristics, and (c) external quantum efficiency-voltage characteristics of the OLEDs for the several thicknesses of TPD layer.

device with 5 nm of MoO_3 layer is stable more than three times compared to that of the OLED without MoO_3 layer. Even though the current density and the luminance are higher in the device with 15 nm of MoO_3 layer, the lifetime is longer in the device with 5 nm of MoO_3 layer, which is thought to be due to the higher external-quantum efficiency and lower resistance. Next, we studied the electrical and optical properties of

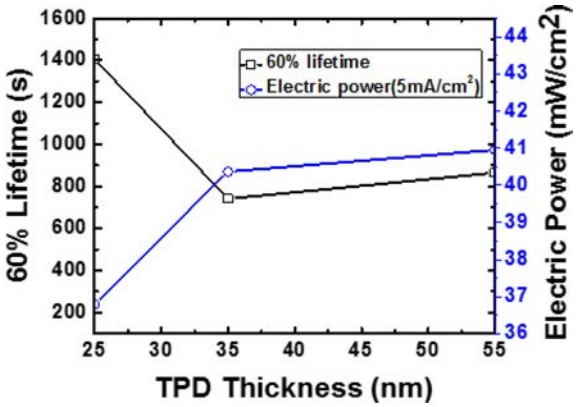

Fig. 6. 60% lifetime and power consumption of the OLEDs at a current density 5 mA/cm^2 as a function of layer thickness of TPD with a layer thickness of MoO_3 fixed at 15 nm.

the devices in which a transition-metal oxide MoO_3 is used as a buffer layer.

Since the hole-transit path becomes longer in these devices due to the insertion of MoO_3 layer compared to the one of the device without the buffer layer, we investigated the optimum efficiency and lifetime of the device by adjusting the thickness of the hole-transport layer of TPD. A structure of the reference device was ITO/TPD (40 nm)/Alq3 (60 nm)/Al (100 nm) and that of the device with the TPD thickness adjusted was ITO/MoO_3 (15 nm)/TPD (25, 35, 55 nm)/Alq3 (60 nm)/Al (100 nm). The devices were fabricated by changing the thickness of TPD layer with the thickness of MoO_3 layer fixed at 15 nm, and the characteristics of each device were analyzed. Figs. 5(a-c) show the voltage-dependent current density, luminance, and external-quantum efficiency of the OLEDs, respectively. It was observed that the current density and the luminance of the OLEDs were 8.60 mA/cm^2 and 114 cd/m^2, 4.50 mA/cm^2 and 47.6 cd/m^2, and 4.58 mA/cm^2 and 49.1 cd/m^2 for the thicknesses of TPD layer of 25 nm, 35 nm, and 55 nm, respectively. By varying the thickness of TPD layer, higher current and luminance were achieved compared to those of the reference device. Higher current density and luminance were achieved in the OLED with the thickness of TPD layer of 25 nm. Fig. 5(c) shows the external-quantum efficiency of the OLEDs, in which the external-quantum efficiency of the reference device at 7 V is 0.14%. And the external-quantum efficiency of the OLEDs is 0.19%, 0.18%, and 0.18% when the thickness of the hole-injection layer of TPD is 25 nm, 35 nm, and 55 nm, respectively. In the device for a thickness of MoO_3 buffer layer to be 15 nm and that of TPD hole-transport layer to be 35 or 55 nm, the current density, the luminance, and the external-quantum efficiency at 7 V are improved by about a factor of 1.3, 1.2, and 1.3, respectively, compared to those of the reference one. However, in the device with a 25 nm-thick of TPD layer, the current density, the luminance, and the external-quantum

efficiency at 7 V are improved by about a factor of 2.6, 3.0, and 1.4, respectively, compared to those of the reference one.

Fig. 6 shows the 60% lifetime and the power consumption of the OLEDs at a current density of 5 mA/cm^2 as a function of layer thickness of TPD. The thickness of the MoO_3 layer in the buffer layer was fixed at 15 nm, and the luminance of the device was measured over elapsed time. The lifetime of the reference device was measured to be 257 s, and that of the device was measured to be 1405 s, 740 s, 864 s for the devices with a layer thickness of TPD to be 25 nm, 35 nm, and 55 nm, respectively. While reference device exhibited the shortest 60% lifetime and the highest power consumption among the measured devices, the device with 15 nm of the buffer layer MoO_3 and 25 nm of TPD exhibited the longest 60% lifetime and the lowest power consumption. From the TPD layer thickness adjusted OLEDs, it was found that when the thickness of MoO_3 in the buffer layer is 15 nm and that of the hole-transport layer TPD is 25 nm, the higher current density, luminance, and external-quantum efficiency and the longest lifetime are achieved.

Conclusions

In this study, the electrical and optical properties of organic light-emitting diodes were analyzed using MoO_3 as a buffer layer thereof. The devices were fabricated by varying the thickness of the MoO_3 buffer layer from 0 to 30 nm, and the current density, luminance, external-quantum efficiency depending on the voltage and the lifetime were measured. In the OLED for the thickness of MoO_3 layer to be 15 nm, the current density, the luminance, and 60% lifetime at 7 V are improved by a factor of about 3.0, 3.9, and 1.6, respectively, compared to those of the reference device without a buffer layer. The introduction of MoO_3 as a buffer layer led to excellent electro-optic properties due to its carrier ladder role and carrier transport effect. However, when the thickness of MoO_3 is more than 15 nm, the resistance component seems to be predominant. The electrical and optical characteristics and the lifetime were measured by varying the thickness of the hole-transport layer TPD to 25, 35, and 55 nm, with the thickness of MoO_3 layer fixed at 15 nm achieving a high current density and luminance. The current density, luminance and lifetime of the organic light-emitting diodes were improved by a factor of about 2.6, 3, and 5.5, respectively, when the thickness of TPD layer was 25 nm. The optimized OLED structure is expected to exert a favorable influence on the field of display applications.

Acknowledgments

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References

1. M. Pope, H. Kallmann, P. Magnante, J. Chem. Phys. 38 (1963) 2042-2043.
2. J. Dresner, A.M. Goodman, Proceedings of the IEEE 58 (1970) 1868-1869.
3. C.W. Tang, S.A. Vanslyke, Appl. Phys. Lett. 51 (1987) 913-915.
4. S. Tokito, K. Noda, Y. Taga, J. Appl. Phys. D. 29 (1996) 2750-2753.
5. T. Mori, S. Nishino, T. Nishikawa, S. Ogawa, Jpn. J. Appl. Phys. 47 (20080 455-458.
6. T. Mori, S. Nishino, T. Nishikawa, S. Ogawa, Org. Electron 9 (2008) 63-69.
7. T. Mori, T. Morimoto, T. Nishikawa, Appl. Phys. Expr. 4 (2011) 111601-1-3.
8. D.H. Hwang, O.T. Kwon, W.J. Lee, J.W. Hong, T.W. Kim, Phys. Stauts Solidi A211 (2014) 1773-1777.
9. S.G. Park, T. Mori, H. Wang, Opt. Commun. 333 (2014) 129-132.
10. S.G. Park, T. Mori, ECS J. Solid State Sci. Technol. 6 (2017) R53-R55.
11. P.R. Huang, Y. He, C. Cao, Z.H. Lu, NPG Asia Materials 5 (2013) e57-e63.
12. K.S. Yook, J.Y. Lee, Synth. Met. 159 (2009) 69-71.
13. T.B. Song, N. Li, Electronics 3 (2014) 190-204.
14. Y. Yi, S.W. Cho, S.J. Kang, Appl. Phys. Lett. 97 (2010) 016101-1-2.
15. D.K. Cheng, Field and Wave Electromagnetics, Addison-Wesley, 2nd edition (1991) p.203.