Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Efficiency Improvement of OLED by Aquaregia and RCA Treatment of ITO Substrate

Gyu-Chae Choi [a], Dong-Eun Kim [a], Jun-Woo Park [a], Byoung-Sang Kim [a] & Young-Soo Kwon [a]

[a] Department of Electrical Engineering & NTRC, Dong-A University, Busan, Korea

Version of record first published: 25 Jun 2009

Mol. Cryst. Liq. Cryst., Vol. 504, pp. 35–43, 2009

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400902939041

Efficiency Improvement of OLED by Aquaregia and RCA Treatment of ITO Substrate

Gyu-Chae Choi, Dong-Eun Kim, Jun-Woo Park, Byoung-Sang Kim, and Young-Soo Kwon
Department of Electrical Engineering & NTRC, Dong-A University, Busan, Korea

Indium tin oxide (ITO) is widely used as the anode material in organic light-emitting diodes (OLEDs) because of its good electrical transport, optical transparency, high work function, and efficient hole-injection properties. Surface treatments have an effect on ITO parameters such as the work function, surface roughness, carrier concentration, mobility, and surface sheet resistance, so that with appropriate surface treatment significant improvement in the OLED performance can be achieved. In this work, we investigated the effect of aquaregia (HNO_3, HCl, distilled-water = 1:3:20) and RCA (company name, NH_4OH, H_2O_2 distilled-water = 1:4:20) cleaning treatments of this interface on OLED performance. The layers used in the OLED were ITO/NPB/Alq_3/LiF/Al. The characteristics of the OLED's current density-voltage-luminance, and efficiency were measured. We found that the aquaregia and RCA treatments enhanced the performance of the OLED. For the ITO treatments, the maximum luminance and efficiency were increased by a factor of ~2 relative to the untreated device. Subsequent enhancement of performance of the diodes was obtained with treated ITO substrates, proving the effectiveness of the treatments. The mechanism of ITO treatment was investigated by analyzing the contact angle of water droplets on the surface.

Keywords: Aquaregia; contact angle; ITO; OLED; RCA; surface energy

1. INTRODUCTION

In recent years, the technology of organic light-emitting diodes (OLEDs) has advanced considerably [1]. OLEDs are attractive because

This study was supported by research funds from Dong-A University.
Address correspondence to Young-Soo Kwon, Department of Electrical Engineering & NTRC, Dong-A University, 840, Hadan2-Dong, Saha-Gu, Busan 604-714, Korea. E-mail: yskwon@dau.ac.kr

of their potential application in displays and, their low operating voltage, low power consumption, low cost, self-emission, and capacity for multicolor emission via the selection of emissive materials [2]. The interface between the electrode and the organic layer in the OLED affects the charge injection process and influences the OLED's electrical and luminance properties. It has been found that the properties of indium tin oxide (ITO) used as an anode in OLED can affect the performance of the devices by its morphology as well as its electronic properties [3]. Indium-thin-oxide (ITO) is frequently used as an electrode in flat-panel displays, and OLEDs due to its high electrical conductivity and optical transparency in the visible-spectral. In particular, the morphology and the oxygen defects on the ITO surface are known to be important factors in determining the charge injection at the interface [4]. The effect of various surface treatments (plasma, chemical, ultraviolet (UV) ozone, etc.) on the ITO properties and the OLED performance were have been extensively studied [5]. Kim *et al*. performed comprehensive studies on acid treatments and combined oxygen plasma and aquaregia-RCA treatments in different orders. They found that devices with oxygen plasma treatment had the lowest turn-on voltage. However, oxygen-plasma treatment followed by aquaregia-RCA treatment resulted in OLEDs with the highest luminous efficiency [6–7]. Thus far, surface treatments were have been found to affect the parameters of ITO, such as its work function, surface carbon removal, and carrier concentration. Hence, with appropriate surface treatment, significant improvements in OLED performance could be achieved [8].

In this work, we report the effects of aquaregia and RCA treatments on the performance of OLEDs. We measured the ITO surface energy and investigated the current density-voltage-luminance and efficiency characteristics for a range of treatment times of 1 min, 5 min, 10 min, and 15 min.

2. EXPERIMENTAL

In this work, the devices were fabricated on ITO-patterned glass substrates. The substrates used for the experiments were 100 nm thick ITO-coated glass wafers with a sheet resistance of $10\,\Omega/\square$. The samples were first cleaned by sonication in (1) Trichloroethylene for 10 min, (2) acetone for 10 min, (3) Isopropyl alcohol for 10 min, and (4) distilled water for 10 min, followed by nitrogen gas blow-drying. In this study, we investigated the effects of aquaregia and RCA treatment time on OLED performance.

The two treatment methods are described as follows:

(1) RCA treatment: The RCA solution was prepared by adding NH_4OH, H_2O_2 and distilled water in a ratio of 1:4:20 by volume. The substrates were first immersed in the RCA solution held at 60°C for different amounts of time, i.e., 1 min, 5 min, 10 min, 15 min, and then rinsed twice in distilled water. Isopropyl alcohol was used to displace the water, and the substrates were then dried in a nitrogen gas flow [9].

(2) Aquaregia treatment: A dilute aquaregia solution was made of HNO_3, HCl and distilled water in a ratio of 1:3:20 by volume. The substrates were immersed into the aquaregia bath under sonication, at room temperature for times ranging from 1 min to 15 min. The ITO substrates were then rinsed in distilled water and finally dried in a nitrogen gas flow [9].

The different layers used fabricating the OLED were ITO/NPB/Alq_3/LiF/Al. We used fixed the thicknesses of the NPB and the Alq_3 layers to 40 nm and 60 nm, respectively. We used (Alq_3) as a light emitting and electron-transport layer. In particular, we used the Tris-(8-hydroxyquinoline) aluminum as the (Alq_3), which is a well known material frequently used as the green-light emitter and electron-transport material OLEDs. The hole-transport layer used in the multilayer device was N,*N*′-bis(1-naphthyl)-N,N′-diphenyl-1,1′-bipenyl-4,4,-diamine (NPB). The characteristics of the current density-voltage-luminance, and efficiency, were measured with ITO substrates that were both treated, and untreated with the aquaregia and RCA solutions. The organic materials were successively evaporated on top of the ITO substrate at 5×10^{-6} torr and a deposition rate of about 0.1 nm/s. The emission areas for all devices were $3 \times 3\,mm^2$. The chemical composition and surface morphology of the ITO surface was measured using a video contact-angle system. With this system, measured advancing and receding contact-angles of two different liquids, i.e., water and methylene iodide, on differently-treated ITO surfaces. The contact-angle hysteresis and the surface energy of the treated ITO were obtained. The current density-voltage-luminance characteristics and CIE coordinates were measured with an IVL 300 series (JBS). All of the measurements were performed at room temperature under ambient conditions.

3. RESULTS AND DISCUSSION

The effects of aquaregia and RCA treatment on the ITO substrates of the OLED can be clearly seen in Figures 1–4. The aquaregia and RCA treated device had lower turn on voltages with increasing treatment time.

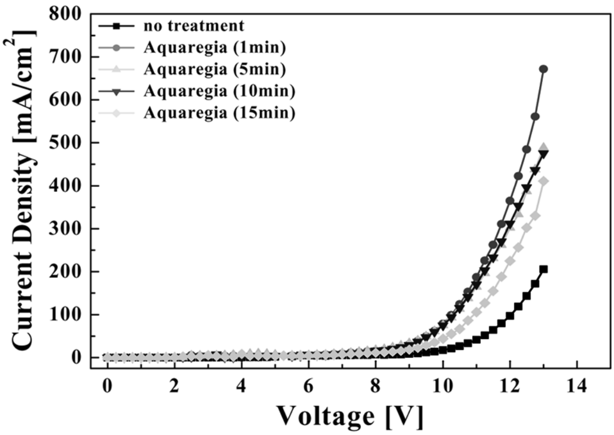

FIGURE 1 Current density and voltage characteristics of the device.

Figures 1 and 2 show the voltage-current density-luminance characteristics of the aquaregia (1, 5, 10, and 15 min)-treated and -untreated devices. Figure 1 shows the current density and voltage characteristics of the 1 min treated device. The current density dramatically increased with increasing applied voltage, as shown in Figure 1. Green-light emission occurred when the voltage was increased above 5.8 V. When comparing the aquaregia-treated anodes, we noticed an increase in current and luminance with increasing treatment time. The highest efficiency was achieved for devices treated for 1 min.

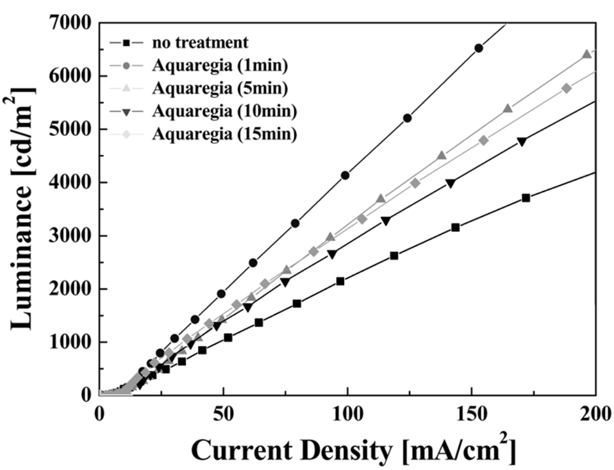

FIGURE 2 Luminance and current density characteristics of the device.

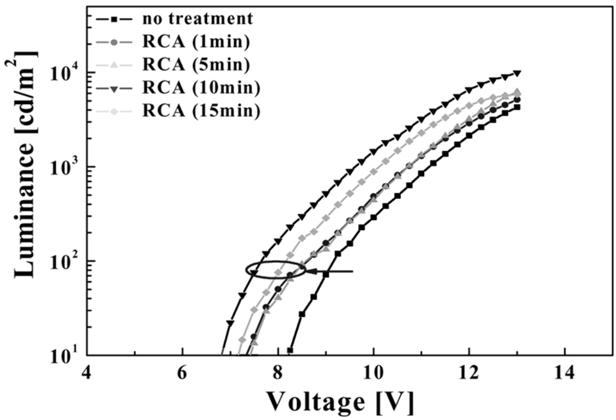

FIGURE 3 Luminance and voltage characteristics of the device.

Figure 2 shows that the maximum luminance of the aquaregia (1 min)-treated ITO was 4170 cd/m^2, and that of the untreated ITO was 2100 cd/m^2. For the aquaregia (1 min)-treated device, the maximum luminance and efficiency were increased by a factor of $\sim$2 compared to the untreated device. This may be attributed to the shift in the HOMO level, as reducing the barrier height will enhance hole injection from the ITO.

Figures 3 and 4 show the voltage-current density-luminance characteristics of the RCA (1, 5, 10, and 15 min)-treated and -untreated devices. In Figure 3, we see that the luminance dramatically increased

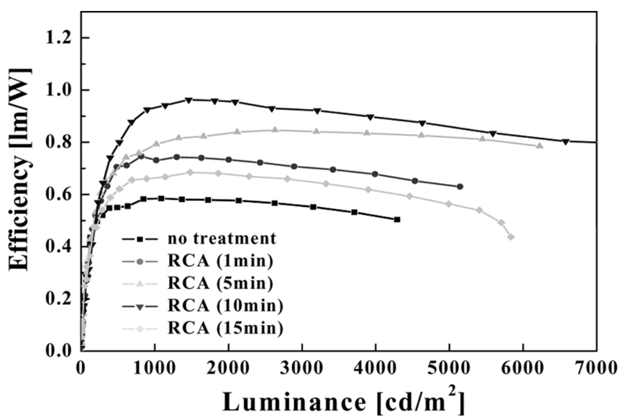

FIGURE 4 Efficiency and luminance characteristics of the device.

TABLE 1 Chemical Composition of ITO Aquaregia Treatment

Treatment method	Turn-on voltage [V]	Luminance at $100\,mA/cm^2$ $[cd/m^2]$	Luminance efficiency at $100\,mA/cm^2$ [lm/W]
No treatment	8.25	2100	0.86
Aquaregia (1 min)	5.83	4170	1.29
RCA (10 min)	6.79	3100	0.96

with increasing applied voltage. In Figure 4, the maximum luminance at $100\,mA/cm^2$ of the RCA-treated (10 min) ITO was $3100\,cd/m^2$, and that of the untreated ITO about $2100\,cd/m^2$. This result shows that the RCA treatment resulted in an increase in the maximum luminance of the OLEDs.

Table 1 shows an OLED fabricated from surface-treated ITO films to determine the impact on device performance: (a) untreated of ITO, (b) RCA-treated (10 min) of ITO, (c) aquaregia-treated (1 min) of ITO.

Figures 5 and 6 show contact angle images of the ITO surface. Figure 5 shows results for distilled-water, and methylene iodide images on RCA-treated surfaces, while Figure 6 shows the corresponding results for aquaregia-treated surfaces. The types of Van der Waals interactions contribute to the surface energy. In particular, the polar component of the surface energy results from two different intermolecular forces due to permanent and induced dipoles and hydrogen bonding, while the dispersion (nonpolar) component of the surface energy is due to instantaneous dipole moments.

We calculated surface energy from Ref. [10]. Two methods were employed to calculate the surface energies the ITO from contact-angle

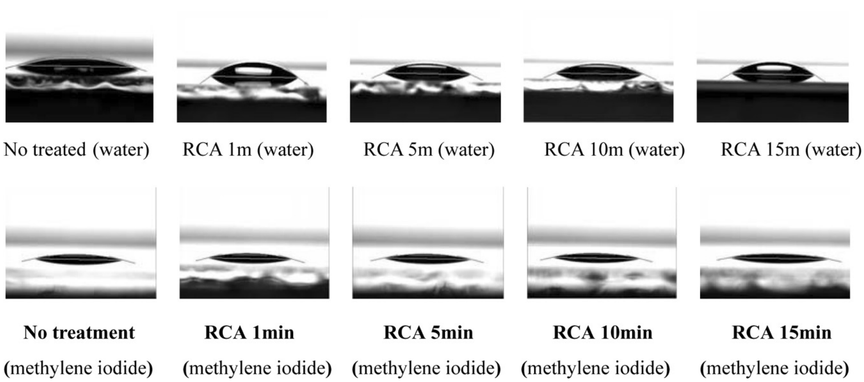

FIGURE 5 Distilled-water and contact angle images on ITO.

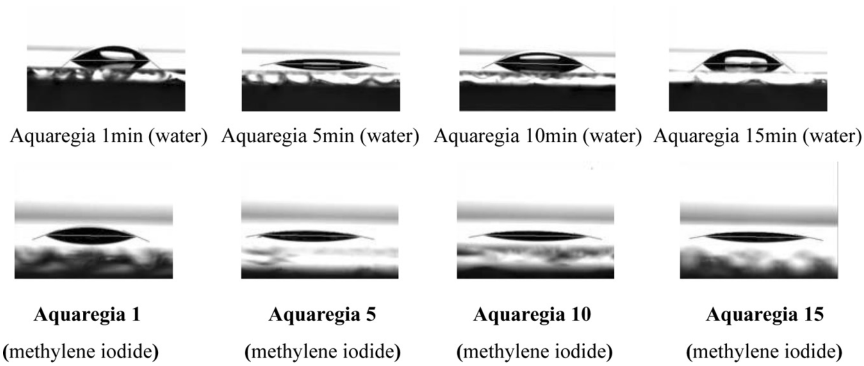

FIGURE 6 Distilled-water and methylene iodide image on ITO RCA treatment.

data. The first, as described by Esumi *et al.*, uses Kaelble's equation for the work of adhesion (W_a) between a liquid and a solid

$$W_a = \gamma_l(1 + \cos\theta) = 2\left[(\gamma_s^d \gamma_l^d)^{1/2} + (\gamma_s^p \gamma_l^p)^{1/2}\right] \tag{1}$$

where γ_l is the surface tension of the liquid; θ is the liquid-solid–air contact angle; γ_l^d is the dispersion component of γ_l, and γ_l^p is the polar component of γ_l; γ_s is the total surface free energy of the solid; and γ_s^d and γ_s^p are the dispersion and polar components of the solids, respectively [10]. The contact angles for two liquids, for which the dispersion and polar components of the surface tension are known, allowed for the solution of the two resulting simultaneous equations to, determine the dispersion and polar components of the solid.

The second method used was based on Neumann's equation of state:

$$\cos\theta = -1 + 2\sqrt{\frac{\gamma_s}{\gamma_l}}\, e^{-\beta(\gamma_l - \gamma_s)^2} \quad \text{where } \beta = 0.0001247 \tag{2}$$

The two liquids selected were water and methylene iodide (CH_2I_2) [11].

Table 2 shows the contact angles of water and methylene iodide on ITO, and Table 3 shows the calculated surface energy. From this calculation, the surface energy of the untreated device was 13.98 mJ/m^2. On the other hand, the maximum surface energy of treated device was 14.3 mJ/m^2.

TABLE 2 Contact Angles of Water and Methylene Iodide on ITO

	Contact angle, θ	
RCA, Aquaregia treatment time	Distilled-water	Methylene iodide
No treatment	15.68	14.05
Aquargia (1 min)	40.17	21.7
Aquargia (5 min)	12.59	12.33
Aquargia (10 min)	28.89	11.28
Aquargia (15 min)	32.01	11.29
RCA (1 min)	38.15	15.86
RCA (5 min)	25.8	14.2
RCA (10 min)	24.59	14.06
RCA (15 min)	32.01	11.5

The hole transport from the ITO can be explained by Fowler-Nordheim tunneling phenomenon [12].

$$\begin{aligned} J &\propto F^2 \exp(-\kappa/F) \\ \kappa &= 8\pi(2m^*)^{1/2}\Phi^{3/2}/3\,qh \end{aligned} \tag{3}$$

where F is the electric field, $2m^*$ is the effective mass of the charge carrier, h is the Planck constant, and Φ is the barrier height.

The results show that the component of surface energy due to dispersive forces did not change with surface treatment and treatment time. On the other hand, the component of the surface energy due to polar forces increased significantly with both RCA and aquqregia treatments.

TABLE 3 Calcuated Surface Energies of ITO Using Kaelble's Equation

	Surface energy (ERGS/cm^2)		
RCA, Aquaregia treatment time	γ_s^d	γ_s^p	γ
No treatment	5.83	8.15	13.98
Aquargia (1 min)	5.91	8.1	14.01
Aquargia (5 min)	5.84	8.17	14.02
Aquargia (10 min)	5.99	8.19	14.18
Aquargia (15 min)	6.1	8.19	14.3
RCA (1 min)	6	8.1	14.1
RCA (5 min)	5.91	8.14	14.06
RCA (10 min)	5.99	8.19	14.18
RCA (15 min)	6.1	8.19	14.29

Therefore, the RCA-Aquaregia treatment increased of the surface energy of ITO substrates for a better adhesion of the organic film, and reduced the interfacial energy between the organic film and the ITO substrate.

4. CONCLUSION

In this paper, the effects of several ITO surface treatments on the performance of OLEDs were investigated. We reported the effects of aquaregia and RCA treatments on ITO. It was shown that devices treated with both Aquaregia and RCA had improved performance relative to those that were not treated. The aquaregia (1 min), and RCA (10 min) treatment was the most successful in improving the surface characteristics, as evidenced by the extent of increased surface energy. We speculate that increasing the surface energy of the bottom electrode improved adhesion at the ITO/organic interface. As a result, we achieved better electronic contact between the two materials with a concomitant improvement of charge-carrier injection through the interface, and therefore better OLED performance.

REFERENCES

[1] Tang, C. W., VanSlyke, S. A., & Chen, C. H. (1989). *Appl. Phys. Lett.*, *85*, 9.
[2] Kim, W. J., Park, Y. H., Cho, K. S., & Hong, J. W. (2008). *Trans. EEM.*, *9*, 3.
[3] Ishii, M., Mori, T., Fujikawa, H., & Taga, Y. (2000). *J. Lumin.*, 87–89, 1165.
[4] Lee, H. K., Seo, J. H., Kim, Y. K., Koo, J. R., Lee, K. H., & Yoon, S. S. (2006). *J. Korean Phys Soc.*, *49*, 1052.
[5] Lee, J. J. & Choi, E. S. (2008). *KIEE J. Electr. Eng. Technol.*, *3*, 276.
[6] Kim, J. S., Granstom, M., Friend, R. H., Johanson, N., Salaneck, W. R., & Cacialli, F. (1998). *J. Appl. Phys.*, *84*, 6859.
[7] Kim, J. S., Cacialli, F., Cola, A., Gigli, G., & Cinolani, R. (2000). *Synth. Met.*, 111–112, 363.
[8] Kim, B. S., Kim, D. E., Jang, Y. K., Lee, N. S., Kwon, O. K., & Kwon, Y. S. (2006). *J. Korean. Phy. Soc.*, *50*, 1858.
[9] Besbes, S., Ben Ouada, H., Davenas, J., Ponsonnet, L., Jaffrezic, N., Alcouffe, P. (2006). *Mater. Sci. Eng. C.*, *26*, 505–510.
[10] Takashi, K., Hiroshi, U., Takashi, N., Mitsuru, W., Kimihiro, M., Hiroyoshi, N. (2008). *Thin Solid Films*, *517*, 1340.
[11] Sun, C. C., Lee, S. C., Dai, S. B., Tien, S. L., Chang, C. C., & Fu, Y. S. (2007). *Appl. Surf. Sci.*, *253*, 4094.
[12] Parker, I. D. (1994) *J. Appl. Phys.*, *75*, 1656.