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Citation: *Appl. Phys. Lett.* **93**, 163308 (2008); doi: 10.1063/1.2998599

View online: <http://dx.doi.org/10.1063/1.2998599>

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Stabilization of the work function of indium tin oxide using organic surface modifiers in organic light-emitting diodes

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(Received 8 August 2008; accepted 19 September 2008; published online 24 October 2008)

We herein report on the performance and improved stability of organic light-emitting diodes (OLEDs) in which the transparent indium tin oxide (ITO) electrode is modified using organic surface modifiers based on phosphonic acid anchoring groups. In contrast to air plasma treatment, a commonly used technique to increase the work function of ITO, treatment of the ITO surface with a partially fluorinated phosphonic acid results in a comparable change in work function but with a higher stability over time. The resultant lifetime of OLEDs also increased when this phosphonic acid modified ITO was used. © 2008 American Institute of Physics. [DOI: 10.1063/1.2998599]

During the past decades, organic electronic devices such as organic light-emitting diodes (OLEDs), organic field-effect transistors, and organic photovoltaic devices have received much attention due to their potential use in many applications.^{1–3} For efficient operation of an OLED, injection of charge carriers from electrodes into the organic layers needs to be optimized.^{4,5} Indium tin oxide (ITO) is widely used as a transparent anode. However, the work function of untreated ITO is generally in the range of 4.5–4.7 eV and does not provide for efficient hole injection into the highest occupied molecular orbital (HOMO) of common hole transport materials (HTMs) such as *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-1,1'-biphenyl-4,4'' diamine (α -NPD) (HOMO, 5.4 eV).^{6,7} In order to reduce the energy barrier height for injection between ITO and commonly used HTMs, different chemical and physical treatments have been proposed to increase the work function of ITO,^{8–10} including air or oxygen plasma treatment, UV ozone treatment, or the use of an intrinsically conducting polymer layer [e.g., poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS)].^{6,10,11} More recently, the use of organic surface modifiers based on silanes, as well as other organic molecules possessing anchoring groups such as COCl, SO₂Cl₂, etc., has been utilized to try to control and modulate the work function of ITO.^{12–14}

Here, we report on the modification of ITO using phosphonic acids with either alkyl or partially fluorinated alkyl chains and their role in changing the properties of ITO and characteristics in subsequent devices. The use of phosphonic acids was motivated by their superior bonding ability with hydroxyl terminated metal oxide materials like ITO.^{15,16} The effects of phosphonic acid modified ITO are also evaluated in OLEDs. High efficiency devices utilizing phosphonic acid modified ITO are demonstrated, and their performance is compared to that of reference devices in which the ITO work function was modified using air plasma treatment. Modification of the ITO with a partially fluorinated phosphonic acid is found to lead to devices with comparable efficiency but with improved lifetime that is attributed to a stabilization of the

change in work function of ITO over time compared to plasma-based treatments.

The chemical structures of octylphosphonic acid (OPA) and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctylphosphonic acid (FOPA) are shown in Table I. OPA and FOPA were synthesized as reported previously.¹⁷ ITO coated glass substrates (20 Ω/\square) (Colorado Concept Coatings, L.L.C.) were first cleaned in an ultrasonic bath using a dilute solution of Triton-X (Aldrich) in de-ionized (DI) water (20 min) followed by a final ultrasonication for 20 min in DI water. Further organic cleaning was done in the ultrasonic bath using acetone and ethanol for 20 min each. Cleaned ITO substrates were then dried in a vacuum drying oven at 70 °C under a pressure of 1×10^{-2} Torr for 1 h. The surface modification was performed by dipping the cleaned ITO substrates in a solution of the phosphonic acid (1 mM in CHCl₃:C₂H₅OH::2:1) for 1 h and 20 min, followed by annealing at 120 °C (1 h). Reference ITO samples were prepared by treating them with air plasma for 3 min. The work function of the modified and reference ITO samples was measured in air using a Kelvin probe (Besocke Delta Phi). To test the differently modified ITO in device geometry, electrophosphorescent OLED devices were fabricated with structure ITO/modifier/ α -NPD(40 nm)/coevaporated (6 wt %) fac-tris(2-phenylpyridinato-N,C^{2'} iridium in 4,4'-di(carbazol-9-yl)-biphenyl [CBP:Ir(ppy)₃](20 nm)/bathocuproine (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline BCP(40 nm)/LiF(2.5 nm)/Al (200 nm) using thermal evaporation [see Fig. 1(a) inset]. The devices were tested inside a glove box filled with N₂ having O₂ and H₂O level <20 and <1 ppm, respectively. For lifetime measurements the OLEDs were driven at a constant dc density, and the changes in luminance and voltage were monitored as a function of time.

The influence of the different surface treatments on the work function of ITO is shown in Table I. An untreated ITO sample showed an average work function of 4.6 eV. Upon air plasma treatment the work function is increased to a value of 5.4 eV. ITO modified with OPA did not exhibit any noticeable change in work function compared to the untreated ITO. In contrast, ITO modified with FOPA exhibited a work function of 5.3 eV, which is close to that of air plasma modified ITO. The large increase in the work function in FOPA modi-

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TABLE I. Work function measured by Kelvin probe and contact angle with water for differently modified ITO substrates averaged over three locations on the same substrate, and the EQE and luminous efficiency (cd/A) at 1000 cd/m² in phosphorescent OLED using surface modifiers.

Surface modifier	Work function (eV)	Contact angle	EQE % (cd/A)
Untreated	4.6 ± 0.02	36 ± 3°	6 (20)
Air plasma	5.4 ± 0.06	<10°	11 (37)
OPA	4.6 ± 0.03	104 ± 2°	6.6 (23)
FOPA	5.3 ± 0.04	108 ± 2°	11.2 (38)

fied ITO can be attributed to the surface dipole caused by the electronegative fluorine substituents pointing away from the surface. Another important aspect of surface modification is its impact on the surface energy of ITO. The measured contact angles with water for untreated, air plasma, OPA, and FOPA treated ITO were 36 ± 3°, <10°, 104 ± 2°, and 108 ± 2°, respectively (see Table I). The higher contact angles for phosphonic acid modified ITO indicate a more hydrophobic surface that is expected to be more compatible with generally more hydrophobic organic HTM in contrast to a hydrophilic air plasma surface.¹⁸

The current density–voltage (*J*-*V*) characteristics of the OLEDs fabricated on different modified ITO samples are shown in Fig. 1(a). An untreated ITO-based device shows leakage and exhibits poor diode characteristics. The leakage current in the device could be associated with the formation of pin holes in the organic layers due to the presence of dust particles or other surface contaminants on the ITO surface. In contrast, the device in which air plasma treatment was carried out before device fabrication shows an improved diode behavior with increased rectification. The improved charge injection in the air plasma-based device as compared to the untreated ITO device can be attributed to the higher work function of the ITO. When OPA was employed for surface

modification the subsequent devices were leakage free, but no improvement in current density was observed as the work function was not significantly altered. In contrast, devices utilizing ITO modified with FOPA show *J*-*V* curves similar to that of an air plasma treated ITO device, which is expected as both FOPA and air plasma treated ITO exhibit similar work functions (see Table I). Figure 1(b) shows the luminance (*L*) and external quantum efficiency (EQE) as a function of applied voltage for these devices. Both FOPA and air plasma modified anodes exhibit similar luminance, EQE, and turn on voltage. On the other hand, OPA modified and untreated anodes show higher turn on voltage and lower EQE. The EQE (η) at 1000 cd/m² for FOPA, air plasma, OPA, and untreated samples were 11.2%, 11%, 6.6%, and 6%, respectively. Hence, the efficiency achieved with FOPA is comparable to that of air plasma reference devices and comparable to state-of-the-art all evaporated OLEDs with similar materials.^{1,19}

In order to study the stability of the change in work function induced by the phosphonic acid surface modifiers, measurements were performed as a function of time in ambient for differently modified ITO electrodes as shown in Fig. 2. It can be seen that just after air plasma treatment, the work function is increased by 0.8 eV. The origin of the increase in work function by air plasma is not clear and has been the subject of several studies.^{8,10,20,21} As shown in Fig. 2, the change in work function is reversible and rapidly decreases when the samples are exposed to ambient conditions.

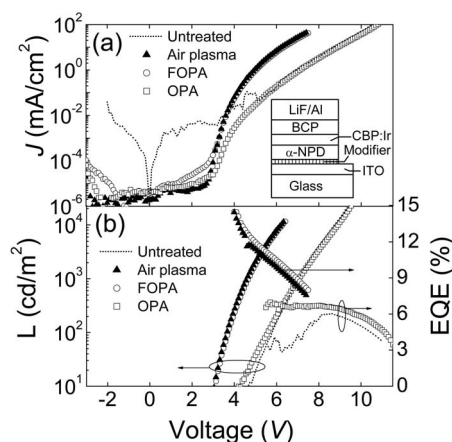


FIG. 1. (a) Comparison of current density–voltage (*J*-*V*) characteristics of untreated (dotted line), air plasma (filled triangles), FOPA (open circles), and OPA (open square) treated ITO devices. (b) Luminance (*L*) and EQE shown for the respective devices appearing in (a). The inset shows the structure of the phosphorescent OLED used in the study.

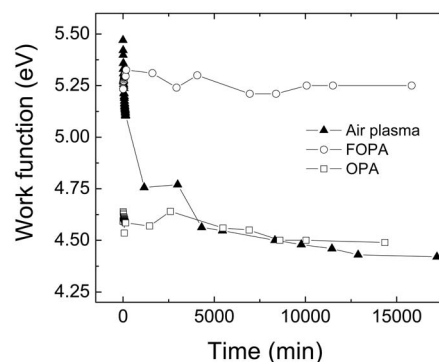


FIG. 2. Effect of ambient exposure on stability of work function over time in differently modified ITO substrates, air plasma (filled triangles), OPA (open square), and FOPA (open circles) treated ITO.

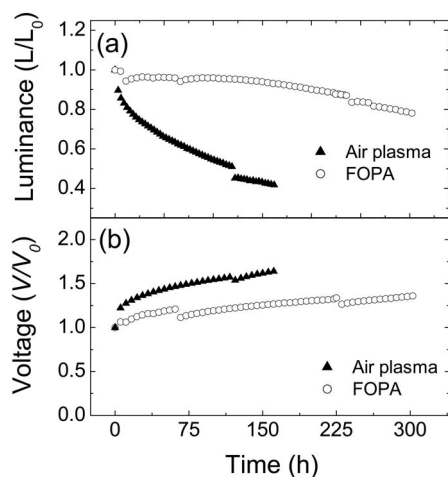


FIG. 3. Comparison of normalized (a) luminance and (b) voltage under constant current density (6 mA/cm^2) for air plasma (filled triangles) and FOPA (open circles) modified ITO-based device. Discontinuities in the luminance and voltage data correspond to points where operation was stopped and restarted in between measurements.

In contrast, the increase in work function induced by FOPA does not decrease even after 264 h. The variation in the work function for the FOPA modified ITO lies within $\pm 0.5\%$ of the initial value. Furthermore, the value of the work function could be maintained for over 70 days (not shown here) for FOPA modified samples. Hence, the work function increase due to a monolayer that is assigned to an effective dipole moment at the interface resulting from a chemical bonding between the ITO surface and the phosphonic acid-based molecules such as FOPA is very promising considering the stability of the ITO anodes over time.

This result motivated studies of the lifetime of electrophosphorescent OLEDs in which the ITO electrode was either modified with FOPA or air plasma treatment. The normalized luminance and voltage curves for fresh devices under prolonged operation at a constant current density of 6 mA/cm^2 are shown in Figs. 3(a) and 3(b). The initial luminance for air plasma and FOPA devices were 1059 and 1000 cd/m^2 , respectively. As shown in Fig. 3(a) luminance decays faster in a device with air plasma treated ITO in comparison to that of FOPA treated ITO. The device treated with air plasma yields a half-lifetime (time to reach half of the initial luminance) of 97 h. This value is comparable within a factor of 2 with the half-lifetime measured in devices comprising Ir(ppy)_3 as an emitter and BCP as a hole blocking layer.²² In contrast, a device based on FOPA modified ITO tested under similar conditions maintained 78% of the initial luminance even after 325 h [Fig. 3(a)] of operation, which gives an estimated half-lifetime of 616 h. The relative voltage increase [Fig. 3(b)] required to maintain the initial current density is also higher for air plasma treated OLEDs. This might suggest that the barrier for carrier injection is increased during device operation due to a reduction in the work function of ITO over time.

In conclusion, phosphonic acids were used to modify ITO, and ITO modified with FOPA in particular increased the work function by a value comparable to that induced by air plasma treatment. However, in contrast to air plasma the change in work function by modifying the surface with FOPA was found to be stable over time. The electrical and luminous performance of highly efficient electrophosphorescent OLEDs fabricated from FOPA modified ITO was found to be similar to that of reference devices treated with air plasma. However, stable phosphonic acid modification of the electrode was also found to enhance the operational lifetime of OLEDs.

This material is based on work supported in part by Solvay S. A., by the STC Program of the National Science Foundation under Agreement No. DMR-0120967, and by the Office of Naval Research.

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