Increased work function in PEDOT:PSS film under ultraviolet irradiation*

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(Received 22 July 2013; revised manuscript received 29 October 2013; published online 12 February 2014)

An increase of work function (0.3 eV) is achieved by irradiating poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) film in vacuum with 254-nm ultraviolet (UV) light. The mechanism for such an improvement is investigated by photoelectron yield spectroscopy, X-ray photo electron energy spectrum, and field emission technique. Surface oxidation and composition change are found as the reasons for work function increase. The UV-treated PEDOT:PSS film is used as the hole injection layer in a hole-only device. Hole injection is improved by UV-treated PEDOT:PSS film without baring the enlargement of film resistance. Our result demonstrates that UV treatment is more suitable for modifying the injection barrier than UV ozone exposure.

Keywords: poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) film, work function, ultraviolet, hole injection layer

PACS: 85.30.Hi, 81.65.Cf **DOI:** 10.1088/1674-1056/23/3/038504

1. Introduction

Poly(3,4-ethylenedioxythiophene) (PEDOT) is an insoluble conjugated polymer with high electrical conductivity and good transparency. Aqueous PEDOT:PSS solution is formed with the help of poly(styrene sulfonate) (PSS) as a charge balancing dopant, providing an easy way to use PEDOT via a low-cost technique. Stable PEDOT:PSS film can be fabricated by spin coating or a printing process with commercial PEDOT:PSS solution, and works as a hole transport layer or anode in organic devices.[1,2] It is well known that the work function of hole transport layers or anode materials has a significant influence on the hole injection/extraction barrier. Therefore, modification of work function of PEDOT:PSS film is needed in order to achieve ideal transport or block characteristics in organic devices.

The work function of PEDOT:PSS film has been tuned by different preparation methods, such as an annealing environment or PSS/PEDOT ratio in solution/film. The *in situ* photoelectron spectroscopy revealed that annealing in high vacuum (1×10^{-10} mbar) increases the work function of PEDOT:PSS significantly.[3] However, such an improvement of work function is unstable when this sample is brought under air exposure, indicting a limitation of this treatment. The PSS/PEDOT ratio at the film surface was found to be a determinative factor for the work function of as-prepared PEDOT:PSS film formed by solution technique. A thin PSS-rich layer (3.5 nm in thickness) always appears at the surface of PEDOT:PSS film due to a vertical phase separation during the period of film formation.[4] Because the work function of PSS is higher than that of PEDOT, PEDOT:PSS film shows a little higher work function than that of pure PEDOT. Further improvement of work function was achieved by increasing the PSS content at the film surface with PSS-enriched PEDOT:PSS solution.[5] A small reduction of work function (0.1–0.3 eV) was obtained by removing such a thin PSS-rich layer via addition of high bolting temperature solvent or polar solvent.[6,7] Ultraviolet (UV) treatment is another way to enhance the work function of PEDOT:PSS film. A slight enhancement of work function in PEDOT:PSS film after 365-nm UV treatment was observed by Lin *et al*., and a change of PEDOT structure was the reason for the increase of work function.[8] A larger increase of 0.2–0.4 eV was measured after several minutes of UV ozone treatment.[9] The improvement of work function seems to obey a simple time-dependent law in this case. This phenomenon is reasonable because the work function enhances with the amount of oxidized bonds at the surface, which was produced monotonously with the treatment time of UV ozone. However, a shortcoming of this method is the enlargement of the film resistance after treatment.[9] There still remains a challenge to improve the work function of PEDOT:PSS film while keeping its high conductance.

Sophisticated methods for measuring the work function of PEDOT:PSS film include ultraviolet photoemission spectroscopy (UPS, in high vacuum),[3,10] Kelvin probe (KB, in air),[2,6,7] and photoelectron yield spectroscopy (PYS, in air).[5,9] Different from above techniques, we introduce an alternative way to detect the change of work function *in situ* without surface oxidation or contamination in this work. PEDOT:PSS is often regarded as a metal in organic electronics.[1]

*Project supported by the National Natural Science Foundation of China (Grant Nos. 61076057, 61376059, 61171023, and 91221202,) and the National Basic Research Program of China (Grant Nos. 2012CB932701 and 2011CB933001).

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This fact means that we may use some investigation methods for metal to measure the work function change in PEDOT:PSS film. Field emission measurement is a well-developed technique to study the work function of metal and the reliability of the analysis model, the Fowlar–Nordheim theory, has been proved numerous times several decades ago. In this paper, we study the change of work function in PEDOT:PSS film under 254-nm UV irradiation by two complementary techniques: *ex situ* PYS and *in situ* field emission. A large increase of work function (0.3 eV) is achieved by irradiating PEDOT:PSS film in vacuum. Then these results are used to adjust the barrier height in a hole-only device. Our experiment demonstrates that 254-nm UV treatment is more suitable to modify the injection barrier than UV ozone exposure.

2. Fowlar–Nordheim theory

The well-known Fowlar–Nordheim theory describes the field emission from metal tip surface,[11] which is usually expressed as

$$J = 1.54 \times 10^{-6} \frac{F^2}{\phi} \exp\left(-6.83 \times 10^7 \frac{\phi^{3/2}}{F}\right), \tag{1}$$

where J is the emission current density, F is the field at the tip surface, and ϕ is the work function of the metal. The field in this equation can be calculated by $F = \beta V$, where β is the local field conversion factor, and V is the voltage applied on the field emission tip. It should be noted that the local field conversion factor β used here is different from the field enhancement factor β in some other papers. The difference between these two β can be found in Ref. [12]. Defining A as the emitting area of the tip and taking the logarithm of Eq. (1), we obtain

$$\ln\left(\frac{I}{V^2}\right) = -13.38 + \ln A + \ln\left(\frac{\beta^2}{\phi}\right) - 6.83 \times 10^7 \frac{\phi^{3/2}}{\beta} \frac{1}{V}. \tag{2}$$

According to Eq. (2), a linear relationship will be found in $\ln(I/V^2) \sim 1/V$ plot when field emission happens, and such a linear behavior is often used to analyze the tip's work function. A better approximation for the slope of the plot, which considers the effect of the imaging force, gives

$$S = -6.83 \times 10^7 \frac{\phi^{3/2}}{\beta} s(y), \tag{3}$$

where $s(y)$ is a slowly varying function with the value ranging from 1 to 0.833, and 0.917 can be used as the value in first order approximation.[11] Because only one value (slope) can be obtained from the F–N plot and there are two undetermined factors (ϕ and β) in Eq. (2), it is impossible to determine the value of work function via field emission technique definitely. Nonetheless, detecting work function change by field emission technique has been proved as an effective method for analyzing the absorption at the metal surface several decades ago.[11] This method requires the value of β not to change, which can be achieved by maintaining the shape of the tip and the distance between tip and the anode. This assumption is true since no variation of shape and distance occurs under the treatment of UV irradiation.

3. Experimental details

Commercial PEDOT:PSS solution (Clevios P VP AI 4083) was used in this work. PEDOT:PSS films were deposited on UV ozone-cleaned ITO glasses by spin coating and then baked at 160 °C in air for 20 min. Then the samples were fixed on a copper sample holder in the chamber of field emission microscope for UV irradiation through a quartz window (wave length 254 nm, SunMonde, 8 W). The base pressure for thin film experiment was about 10^{-4} Pa. The work function of PEDOT:PSS film was measured by photoelectron yield spectroscopy (Riken Keiki, AC-2). The chemical bonding states at the film surface were evaluated with X-ray photo electron energy spectrum (XPS, Kratos Axis Ultra). Hole-only devices were fabricated to examine the barrier height change due to UV-treated PEDOT:PSS film. A layer of N,N′-diphenyl-N,N′-bis-(1-naphthyl)-1-1′-biphenyl-4,4′-diamine (α-NPD, Luminescence Technology) was deposited on PEDOT:PSS film by thermal evaporation and then square gold electrode (2×2 mm^2) was deposited to complete the device. I–V measurements were performed with a digital source meter (Keithley 2602).

For field emission measurement, a tungsten tip was fabricated with a thin tungsten wire (diameter 0.1 mm) by normal etching method in NaOH solution. The deposition of PEDOT:PSS film on tip was realized by dipping the W tip into a droplet of PEDOT:PSS and then dried in air for several times. Scanning electron microscope (SEM) observation proved that a smooth thin film was formed on the tip surface. We call such a tip as PEDOT:PSS-W tip. This PEDOT:PSS-W tip was put into the field emission microscope for work function measurement before/after UV illumination. The base pressure of field emission microscope was about 2×10^{-7} Pa. During the heating process for degassing the system, the heating temperature was always lower than 200 °C to avoid decomposing PEDOT and PSS.

4. Results and discussion

4.1. Work function change measured by PYS

For PEDOT:PSS film, work function improvement after UV ozone exposure was well studied and an oxygen induced

dipole at the decomposed film surface was proposed as the reason for the higher work function.[9] The work function of PEDOT:PSS can also be increased by forming a thick PSS layer on the top of as-prepared PEDOT:PSS film. One shortcoming of these methods is a enlargement of device series resistance. By separating UV decomposition and oxidization, we increase the work function of PEDOT:PSS film without damaging its high conductance. This result is proved by current-voltage and PYS measurement. *I–V* measurement shows a better conductance after UV illumination, which will be published elsewhere.

In photoelectron yield spectroscopy technique, a linear dependence between square root of photoelectron yield and the photon energy above the threshold is simulated to calculate the work function in metal. While for destination of the highest occupied molecular orbital (HOMO) in semiconductor, the relation between a cubic root of photoelectron yield and the photon energy above the threshold is used instead. Generally, PEDOT:PSS is regarded as a metal in organic devices and work function measurement.[9] It is known that the work function of PEDOT:PSS is sensitive to the preparing condition. We find that there is a variation of 0.1–0.2 eV in different as-prepared PEDOT:PSS samples. This value is comparable to measured work function of PEDOT:PSS (4.9–5.2 eV, Clevios P VP AI 4083).[6,7,13] Two sets of samples were measured in order to determine the effect of illumination time on work function: 0, 3, 5 min (short time) and 0, 10, 20 h (long time). The data of PYS are shown in Fig. 1. The values are 4.96, 5.08, 5.19 eV for 0, 3, 5 minute samples (Fig. 1(a)), and 5.17, 5.48, 5.41 eV for 0, 10, 20 hour samples (Fig. 1(b)), respectively. A universal increase of work function was observed from all samples in our experiments, which can be basically explained by an oxidation effect at the surface during ambient PYS measurement. The environment for PEDOT:PSS film changes from vacuum (pure and weak decomposition) to air (pure and weak oxidation) in PYS measurement. Decomposition effect of 254-nm UV light on chemical bonds has been studied for a long time.[14] The dangling state due to the cleavage of α-hydrogen bond in PSS may keep a long time in vacuum,[15] and then these broken bonds are sufficiently reactive for oxidation under ambient atmosphere, resulting in a more negatively charged surface and a positive space-charge layer beneath the surface.[11] The highest work function detected after 10 hours of UV irradiation indicates that the density of broken bonds reaches saturation at the surface. Although the above oxidation effect is easy to understand, the time dependence of work function enhancement is not usual in our experiment. The power of UV light used here is much smaller than that used in UV Ozone. However, only 5 minutes of UV irradiation produces an obvious increase of 0.23 eV, which is close to the result of UV ozone treatment.[9] This fact gives a strong hint that the mechanism for work function improvement in our experiment cannot be described by a simple time dependent model. PEDOT structure change can be excluded because no position shift and shape change are observed from Raman spectra in our experiments.[8]

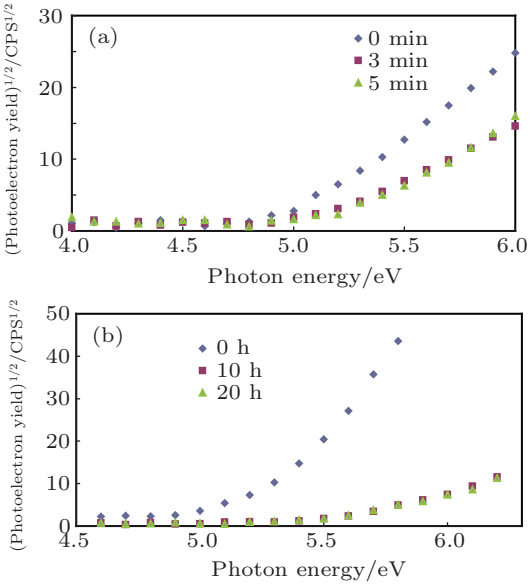


Fig. 1. (color online) Photoelectron yield spectra of PEDOT:PSS films: (a) untreated (diamond), after 3 min (square), and after 5 min (triangle) of irradiation; (b) untreated (diamond), after 10 h (square), and after 20 h (triangle) of irradiation.

In general, the work function of as-prepared PEDOT:PSS film is highly related with the PSS content at the surface. In order to verify the surface composition before and after UV treatment, XPS analysis was used to determine PSS content. The peaks around 168 and 164 nm in XPS spectrum correspond to the sulfur atoms in PSS and PEDOT (S 2p peaks), respectively. The ratio of PSS peak area to PEDOT peak area in XPS plot can be used to evaluate the content at the film surface within several nanometers.[6] A series of PEDOT:PSS film after 3 min, 5 min, 10 h, and 20 h of UV treatment are analyzed by XPS and the S 2p spectra are shown in Fig. 2. The ratios of S peak area (PSS to PEDOT) are calculated with the data in Fig. 2. The values are 5.05, 6.58, 6.23, and 5.28 for no treatment, 3 min, 5 min, and 10 h of UV treatment samples, respectively. These values reveal two phenomena in present experiments: (i) the ratio of PSS/PEDOT increases significantly at the surface after a short time of UV irradiation; (ii) this ratio decreases as the illumination time prolongs. For the first phenomenon, we think that the detrimental effect on PEDOT by UV treatment induces such a ratio increase. We know that the detrimental effect of 254-nm UV on PSS is stronger than that of PEDOT. Nonetheless, both PSS and PEDOT can be decomposed simultaneously if the light intensity is high enough, as in the case of UV Ozone treatment. It is well known that the PEDOT content at the outmost surface (thin exposing layer in the top PSS-rich layer) is quite low because PEDOT's surface

potential is larger than that of PSS.[4] Therefore, if the outmost surface (where the light intensity is strongest) is decomposed indiscriminately by UV irradiation, even a small decomposition of PEDOT (reduction of absolute amount) may increase the PSS/PEDOT ratio (increase of relative ratio) evidently. In other words, at the very start of illumination, decomposition occurs without selectivity at the outmost surface. This assumption is coincident with the XPS result (Fig. 2), in which the intensity of both PEDOT and PSS peak decrease after a short time UV treatment. The explanation for the second phenomenon is simple: longer UV irradiation breaks more bonds in PSS during the following period.

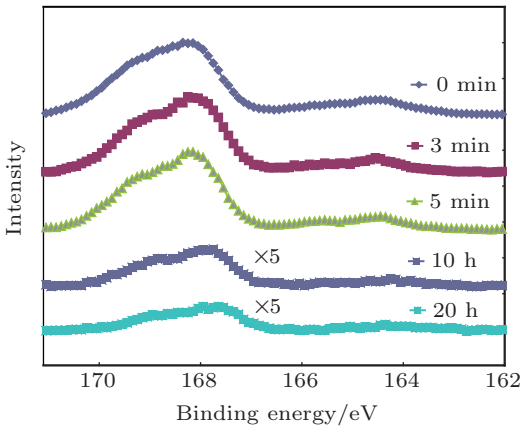


Fig. 2. (color online) S 2p core spectra of PEDOT:PSS films: untreated, after 3 min, 5 min, 10 h, and 20 h of irradiation. The intensity values of 10-h and 20-h samples are magnified with a factor of 5 in order to show the peak.

A remaining question for UV treatment is a small decrease of work function after 20 h of irradiation (from 5.48 eV for 10-h sample to 5.41 eV for 20-h sample). This reduction of work function may come from the accumulating effect of the cleavage of sulfonic acid group by UV irradiation. Hong *et al.* reported that the work function of PSS wrapped carbon nanotubes droped 0.3 eV after strong UV illumination in vacuum because of the cleavage of the sulfonic acid groups.[13] In XPS spectrum of a sample after 20 h of UV treatment (Fig. 2), the intensity of S 2p peak for PSS is rather weak, revealing that most sulfonic acid groups have been removed from PSS at the film surface. We think that this effect is much weaker than the influence of oxidation. Only in long-time irradiating samples, reduction of work function due to cleavage of sulfonic acid groups may be observed.

In summary, two mechanisms work for the improvement of work function after UV illumination: increasing PSS/PEDOT ratio and the oxidized surface. The first mechanism shows apparent effect after short time of UV illumination in vacuum and the second one plays a key role in air.

4.2. Work function change measured by field emission

From above discussion, we may draw a conclusion that an improvement of work function will happen after a short period of UV irradiation even without oxidation. We choose field emission technique to conduct such a measurement. We find that a stable field emission is easier to obtain from PEDOT:PSS-W tip than from normal W tip. No additional heating is applied on the PEDOT:PSS-W tip. Therefore, work function change due to remaining water in PEDOT:PSS is eliminated. No movement is taken on the PEDOT:PSS-W tip during all the time in one experiment.

We measure the field emission property from untreated PEDOT:PSS-W tip in the dark firstly. The fitting line for F–N plot is shown in Fig. 3. The value of slope of the fitting line is calculated and listed in Table 1. Then we irradiate the PEDOT:PSS-W tip for 5 min. Corresponding fitting line and the value of slope are shown in Fig. 3 and listed in Table 1, respectively. It is clear that the slope value increases a lot after 5 min of UV irradiation. Using 4.96 eV as the work function of untreated PEDOT:PSS film, which is measured by PYS, the work function of PEDOT:PSS film is calculated to be 5.37 eV. This result convinces the above conclusion that the improvement of work function after short time of irradiation is mainly caused by the increase of PSS/PEDOT ratio because no oxidation occurs in field emission experiment. A problem for field emission measurement is the accuracy of this technique. After the same treatment (5 min of UV irradiation), the work function measured by field emission method is higher than that measured by PYS (5.19 eV). The reason for this difference is not clear. One possible reason may be the variation of work function in different PEDOT:PSS samples. We note that the improvement of work function after UV illumination has nothing to do with the residual water in PEDOT:PSS.

Table 1. Slope of F–N line and calculated work function. PYS measured work function is also listed for comparison.

Treating time	Slope (absolute value)	Work function/eV	PYS work function/eV
No treatment	27993	4.96	4.96
5 min	30445	5.37	5.19

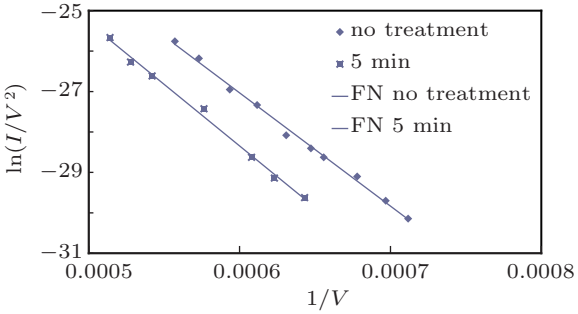


Fig. 3. (color online) FN fitting lines of PEDOT:PSS without treatment and after 5 min of UV illumination.

4.3. Performance of UV-treated PEDOT:PSS film in organic device

Although UV ozone exposure of PEDOT:PSS has been used to improve device performance in some

experiments,[16,17] a confusing question for the actual effect of this treatment is under debate. α-NPD is a common hole transport material. *I–V* measurements showed that the hole injection from PEDOT:PSS after UV ozone treatment to α-NPD was depressed,[16] conflicting with the anticipation of smaller injection barrier due to the improvement of work function of PEDOT:PSS. Helander *et al*. found that the increase of work function in UV ozone treated PEDOT:PSS film was caused by a metastable interfacial dipole layer, but this dipole also created a higher injection barrier.[18] Schematic energy diagram of UV ozone treated PEDOT:PSS/α-NPD is shown in Fig. 4(b). The energy diagram of untreated PEDOT:PSS/α-NPD is shown in Fig. 4(a) for comparison. This result shows that UV ozone exposure is not a suitable method to tune the barrier height when contacting organic semiconductor in real device.

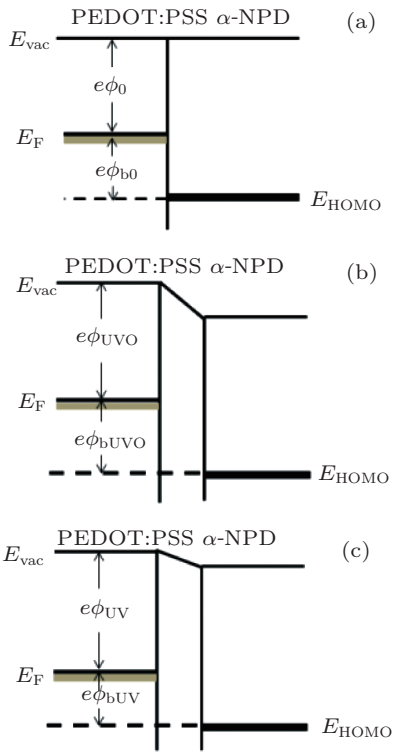


Fig. 4. (color online) Schematic energy diagram of α-NPD and (a) untreated PEDOT:PSS, (b) UV ozone treated PEDOT:PSS, and (c) UV-treated PEDOT:PSS. Vacuum energy alignment is assumed for untreated PEDOT:PSS/α-NPD interface. Both $e\phi_{UVO}$ and $e\phi_{UV}$ are larger than $e\phi_0$, $e\phi_{bUVO}$ is larger than $e\phi_{b0}$, and $e\phi_{bUV}$ is less than $e\phi_{b0}$.

We fabricated hole-only devices to testify the effect of UV treatment. The device structure is schematically drawn in the inset of Fig. 5. PEDOT:PSS layers treated after 0, 10, and 22 h of UV irradiation were used in these devices. In order to preclude the possible build-in potential generated by organic-electrode contact,[19] we deposited a thick layer (500 nm) of α-NPD on PEDOT:PSS layer to construct a hole-only device. Figure 5 shows the measured *I–V* curves of three devices. It is clear that there are two regions in the plots: space charge limited region (>1 V) and injection limited region (<1 V). The well overlap of three curves in space charge limited region reveals that PEDOT:PSS layer treated by different conditions does not influence the charge transport under larger bias voltage in these devices, which is different from the results of UV ozone treatment.[16,18]

A distinct impression from *I–V* curves in injection limited region is that a larger work function of PEDOT:PSS corresponds to a larger current in device, indicating that the injection barrier is reduced by UV illuminated PEDOT:PSS. However, more attention should be paid to the surface state of PEDOT:PSS, which enhances the height of injection barrier in device employing UV ozone treated PEDOT:PSS.[16,18] Hole injection from PEDOT:PSS to α-NPD layer may be modeled with a thermally activated mechanism and the detailed analysis of *I–V* characteristic is described according to this model in Ref. [20]. The dependence of current density on the barrier height in the injection limited region is described by $J \propto \exp(-e\phi_b/k_BT)$, where $e\phi_b$ is the barrier height, e is the electron charge, k_B is the Boltzmann constant, and T is the temperature.[20] We estimate the effect of UV treatment on device performance by this method. A reduction of barrier height ($\Delta e\phi_b$) is calculated with the data in Fig. 5 and the values are 0.11 and 0.07 eV for 10 and 22 hour sample, respectively. These values are smaller than the improvement of work function (ΔE_F), 0.31 and 0.24 eV for 10 and 22 hour sample, respectively. This difference reveals that, with UV-treated PEDOT:PSS as a hole injection layer, the height of injection barrier is not only controlled by the work function difference, but also by the surface state of PEDOT:PSS. A dipole should exist between UV-treated PEDOT:PSS and α-NPD ($\Delta E_F - \Delta e\phi_b$, 0.20 and 0.17 eV for 10 and 22 hour sample, respectively), and this dipole counteracts part effect of the improvement of work function of UV-irradiated PEDOT:PSS film. Schematic energy diagram of UV treated PEDOT:PSS/α-NPD is shown in Fig. 4(c).

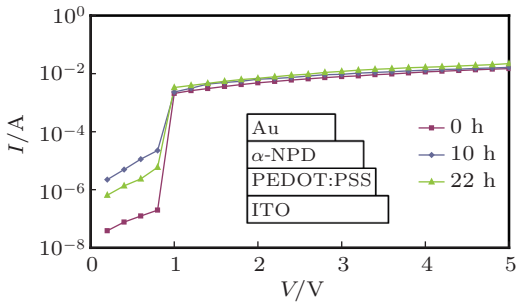


Fig. 5. (color online) *I–V* curves of hole-only devices. Inset: device structure.

A different behavior between UV-treated and UV ozone treated PEDOT:PSS film was observed with the same device structure. By separating UV decomposition and oxidation, a

lower injection barrier is achieved in a hole-only device, revealing the advantage of UV irradiation over UV ozone exposure. Other than oxidation effect, enhancing PSS/PEDOT ratio is determined as the other independent mechanism for work function improvement under UV irradiation. We suggest that this content variation causes the reduction of barrier height, which is not influenced by the interfacial dipole. We believe that our result provides a better way to control the interface between PEDOT:PSS and organic semiconductor.

5. Conclusions

The effect of 254-nm UV irradiation on work function of PEDOT:PSS film was investigated in this work. PYS and field emission were used to study the change of work function in air and in vacuum, respectively. The improvement of work function was observed in UV-treated PEDOT:PSS film. Increased PSS/PEDOT ratio and oxidized surface were determined as the reasons. With UV-treated PEDOT:PSS as a hole injection layer, the height of hole injection barrier was modified effectively. Our result shows that the increase of work function in PEDOT:PSS film can be achieved without baring the enlargement of film resistance.

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