Regular Article

Impact of thermal stability of poly(3,4-ethylenedioxythiophene): poly(4-styrenesulfonate) used as buffer layer in organic solar cells

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Abstract. We compared the performances of polymer-based photovoltaic devices prepared from different formulations of poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS). The PEDOT:PSS buffer layer is incorporated between the indium tin oxide (ITO) electrode and the active layer, which is composed of a blend of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM). A highest efficiency of 3.86% (under AM1.5 solar illumination) was achieved for device prepared from a PEDOT:PSS trade-named high conductivity grade. However, annealing devices at a temperature over 120 °C results in decreased photovoltaic performance. This study shows that attention has to be paid to chemicals used to formulate high conductive PEDOT:PSS to become compatible with the production of solar cells involving thermal processing.

1 Introduction

Among the number of π-conjugated polymers, polythiophene derivatives remain one of the most important and widely studied materials. Polythiophenes have been extensively used in a variety of applications for electronic organic such as field-effect transistors [1], polymer light-emitting diodes [2] and organic photovoltaic cells [3,4]. Poly(3,4-ethylenedioxythiophene) (PEDOT) was patented at *Bayer AG* in the end of 1980s, and later developed by other groups [5,6]. Poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) (PEDOT:PSS) is the most important and successful conducting polymer in the field of organic electronics. PEDOT:PSS is commonly used in a wide range of electronic devices [6], including organic solar cells [7], organic light-emitting diodes [8,9], organic field-effect transistors [10] and sensors [11]. Polymeric conductors, used as electrode, are promising for the development of flexible devices [10,12,13]. Thin film of PEDOT:PSS can be conveniently created using wet processing methods, including spin coating, ink-jet printing, doctor blading and roll-to-roll printing [14–17]. These coating techniques can be performed under ambient conditions and scaled up to large areas with limited loss of materials.

Conventional structure of organic solar cells is typically composed of an active layer sandwiched between a transparent indium tin oxide electrode (ITO) and an electrode with a lower work function e.g., aluminum (Al). The aqueous dispersion of PEDOT:PSS forms a thin and uniform buffer layer between the ITO and photoactive layer. Indeed, the layer of PEDOT:PSS provides a well-defined work function which is higher than that of ITO [18,19], but still compatible with hole extraction from the polymer. PEDOT:PSS ensures the ohmic contact and enhances the collection of hole [7,20]. The higher work function of PEDOT:PSS regarding ITO may lead to an improved V_{oc} [21]. In addition, the layer of PEDOT:PSS flattens the spiky roughness of ITO surface, avoiding random short circuit and percolation paths between two electrodes [18,22]. It has also been reported that the interlayer of PEDOT:PSS prevents the diffusion of indium [23] as well as the migration of oxygen into the active layer [24]. The conductivity in the thin film of PEDOT:PSS is distinctly lower than that of ITO. Solar cells prepared with only PEDOT:PSS as electrode showed the significant drop in voltage, and thus a lower efficiency. Using thicker polymer films may reduce the resistance of electrode. However, the optical transmission is decreased since they are not intrinsically transparent materials. Up to date, most efficient organic solar cells are built up from substrates of ITO/PEDOT:PSS.

In this work, four different formulations of PEDOT:PSS were used to create buffer layer for fabricating polymer solar cells. The active layer is composed of a P3HT:PCBM blend, which has been extensively used in organic solar cells as active layer [25]. Indeed, P3HT exhibits a

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suitable solubility in standard organic solvents and chemical stability [26], a relatively low band gap (1.9–2 eV) [26,27] and high mobility of hole [1,28,29]. This polymer was blended with PCBM, which acts as an electron-acceptor material. This fullerene derivative has high solubility in common organic solvents [30]. The present work aims to show the influence of PEDOT:PSS formulations on the photovoltaic performance of solar cells. The different PEDOT:PSS solutions in this study used are PEDOT:PSS (high conductivity grade–Aldrich, HC), PEDOT:PSS (low conductivity grade–Aldrich, LC), PEDOT:PSS (conductivity grade–Aldrich, C), and PEDOT:PSS (Clevios).

2 General procedure of experiment

Polymeric solar cells were fabricated with the following structure: glass/ITO/PEDOT:PSS/P3HT:PCBM/Al. The glass/ITO substrates (15×15 mm^2) were successively cleaned in ultrasonic baths, including deionized water, acetone, ethanol and isopropanol. Substrates were then subjected to UV-ozone treatment for 15 min to remove residual contaminants and to render the ITO surface hydrophilic, facilitating therefore the deposition of the aqueous dispersion of PEDOT:PSS [19,31]. In addition, it has been reported that the UV-ozone treatment of ITO exhibits higher work function, with regard to non-treated ITO surfaces [19]. Four dispersions of PEDOT:PSS were investigated in this work. Properties of these as-received dispersions are given in Table 1. All solutions of PEDOT:PSS were filtered using a PTFE 0.45 μm filter, before their deposition by spin coating in air. The speed and the time of spinning were kept at 4000 rpm and 1 min, respectively. Samples were baked under vacuum at temperature of 110 °C for 30 min to remove residual water. The thickness of the resulting films is reported in Table 2. All further subsequent elaborations and characterizations of devices were carried out under inert atmosphere (N_2) inside glove box with residual O_2 and H_2O concentrations <0.1 ppm. P3HT (Mn = 56.875 kg/mol, Mw = 104.9 kg/mol, PDI = 1.84) (Plextronics) and

PCBM (Solaris Chem) were used as received. The P3HT:PCBM (1:1, in weight) solution in ortho-dichlorobenzene (total concentration of 20 mg/mL) were stirred at 50 °C overnight to ensure a good dissolution of the blend. The photoactive solution was then spin-casted at 1000 rpm for 90 s on the top of the PEDOT:PSS layers. The thickness of the resulting active layer is reported in Table 2. All samples were placed in Petri dish closed container for 2 h. This technique has been proven successful for producing highly ordered thin films of polymer by slow evaporation of solvent [3,32–34]. Devices prepared with ITO alone (without PEDOT:PSS layer) were also fabricated as reference cell. Finally, the aluminum top electrode of 100 nm was thermally deposited on the P3HT:PCBM layer under secondary vacuum (2×10^{-6} mbar). Despite improvements in morphology induced by solvent annealing alone, in some cases, additional thermal treatment appeared to be necessary to obtain higher efficiency [3,35–37]. In the present study, solar cells are therefore thermally annealed in the glove box at 150 °C for 20 min. A set of at least 16 devices prepared from each formulation of PEDOT:PSS has been characterized in order to take into account the experimental error. The power conversion efficiency (PCE) values were taken as the average from those sets of measurements. In order to measure the perpendicular conductivity of PEDOT:PSS, devices with diode structure (glass/ITO/PEDOT:PSS/Al) were fabricated with crossbar type electrodes. Before the deposition of aluminum, the ITO/PEDOT:PSS layers were baked under vacuum at temperature of 110 °C for 30 min. The intersection surface area between the aluminum and the ITO electrode is 10 mm^2. Current density-voltage (J-V) characteristics of devices were measured using a Keithley 2400 under AM1.5G solar simulator set at 100 mW/cm^2 with a calibrated *IL1400BL* thermopile.

3 Results and discussion

Photovoltaic performances of devices prepared from different PEDOT:PSS dispersions are shown in Figure 1.

Table 1. Properties data of as-received of different dispersions PEDOT:PSS.

Trade name	Sources	Abbreviation	Concentration (%)	Ratio PEDOT:PSS
Low conductivity grade	Aldrich	LC	2.8	0.14:2.6
Conductivity grade	Aldrich	C	1.4	0.5:0.8
High conductivity grade	Aldrich	HC	1.3–1.7	NI
Clevios P VPAl 4083	H. C. Starck	Clevios	2.6–3.2	1:6

Table 2. The thickness of PEDOT:PSS and of P3HT:PCBM active layer as well as the conductivity measured by using diode configuration glass/ITO/PEDOT:PSS/Al.

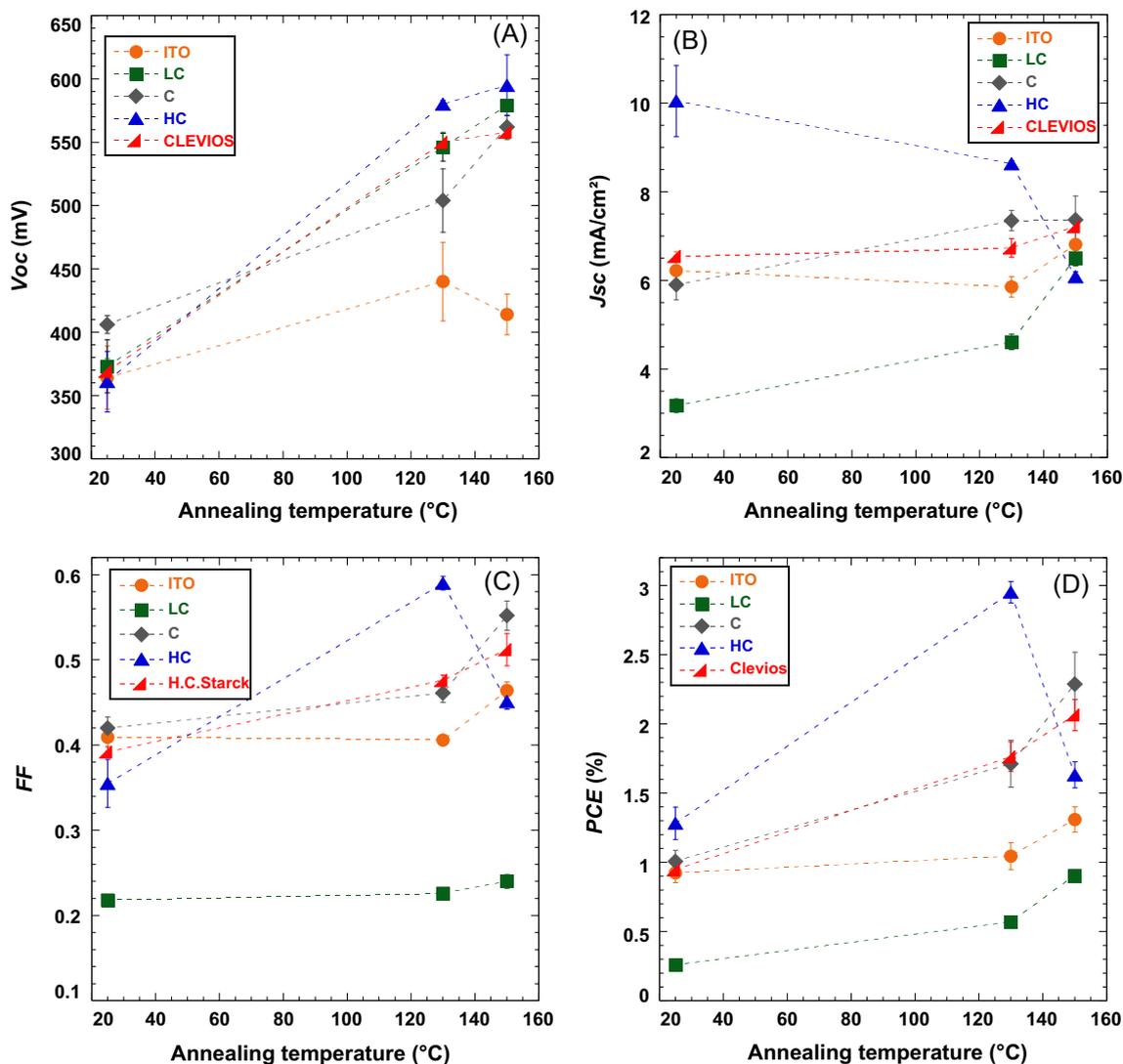| Electrode/buffer layer	ITO	ITO/LC	ITO/C	ITO/HC	ITO/CLEVIOS
$d_{\text{PEDOT:PSS}}$ (nm)		65 ± 3	59 ± 5	60 ± 2	31 ± 3
$d_{\text{PEDOT:PSS+P3HT:PCBM}}$ (nm)	76 ± 6	165 ± 3	141 ± 3	131 ± 5	121 ± 4
$d_{\text{P3HT:PCBM}}$ (nm)	~ 75	~ 100	~ 80	~ 70	~ 90
Measured conductivity (S m^{-1})		5×10^{-5}	10^{-3}	10^{-3}	3×10^{-4}

Fig. 1. Performance of glass/ITO/PEDOT:PSS/P3HT:PCBM/Al photocells prepared from different formulations of PEDOT:PSS under simulated solar light (AM1.5G @ 100 mW/cm^2) as a function of annealing temperature.

Devices without PEDOT:PSS were also examined. Non-annealed devices made from PEDOT:PSS with low conductivity grade (LC) show the lowest J_{sc}, FF and the resulting lowest efficiency. The performance of devices created with PEDOT:PSS (LC) is found to be lower than those prepared from ITO alone, presumably resulting from the lower perpendicular conductivity of PEDOT:PSS (LC) and from the slightly thicker active layer (Tabs. 1 and 2). The latter factor may favor the recombination of excitons. Solar cells prepared with PEDOT:PSS named conductivity grade (C) and Clevios give the comparable efficiencies. This presumably results from the balance between the conductivity in PEDOT:PSS, the thickness of the PEDOT:PSS films and the thickness of the active layers. The efficiency of solar cells fabricated from PEDOT:PSS (HC) was barely higher than those created from other dispersions of PEDOT:PSS, resulting from higher current density.

Thermal treatment has proven effective for achieving efficient solar cells [4,38–40]. In this study, all devices were annealed after the deposition of aluminum electrode. The beneficial effect of thermal annealing on performance of devices has been well documented in the literature [41]. Improved efficiency originates from increased light absorption, enhanced exciton dissociation and transport of charge, resulting from an effective morphology with productive phase separation within the active layer [4,41]. However, performance of devices appeared to be dropped when solar cells are subjected to treatment at temperature above the optimal temperature as well as prolonged thermal annealing. Overannealing induces the formation of large aggregates of PCBM in films. Temperature and duration of thermal annealing have been previously determined for the same P3HT and PCBM batch. Optimal conditions were found at 150 °C for 20 min [42], indicating that the active layer is not damaged under these
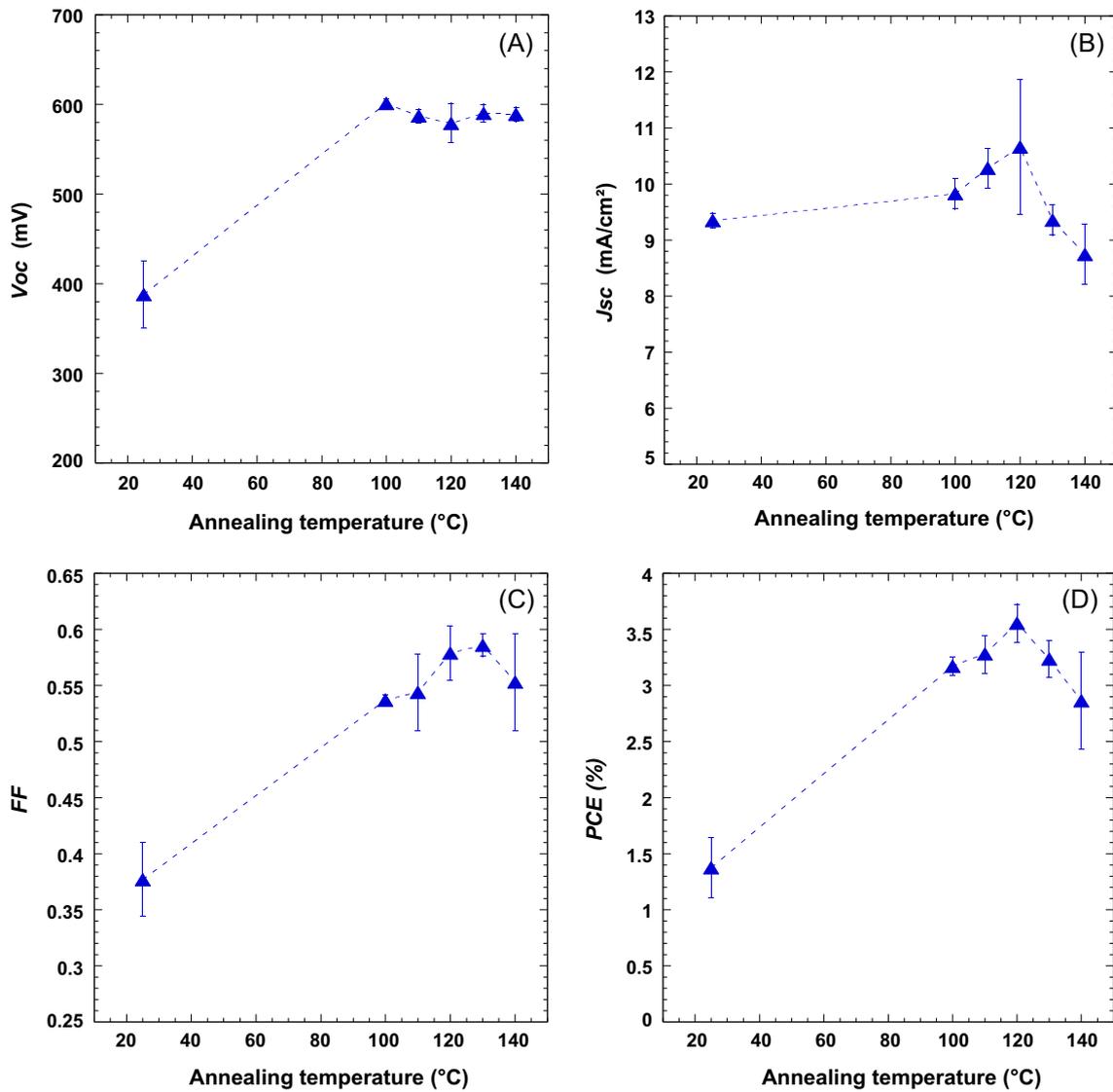
Fig. 2. Device performance of cells fabricated with PEDOT:PSS (HC), under illumination 100 mW/cm^2. The completed devices were annealed on a hot plate for 20 min.
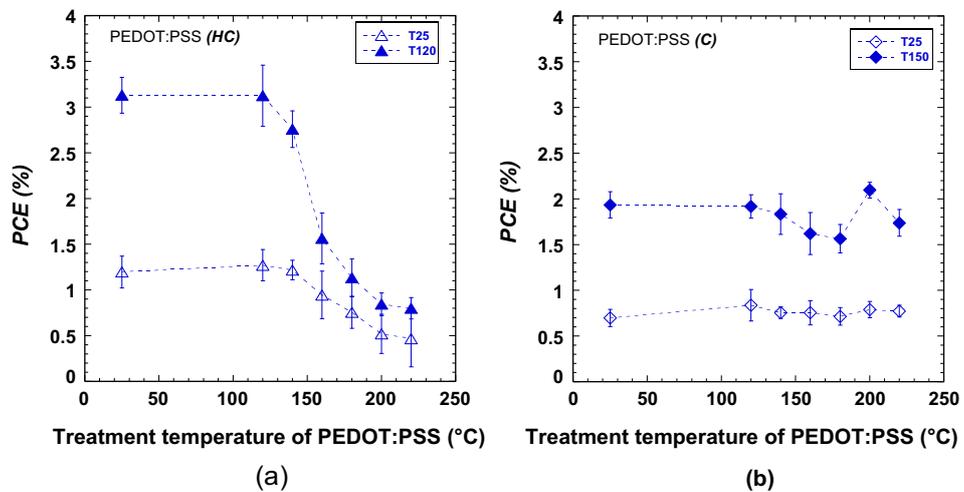

Fig. 3. Efficiency of solar cells as a function of temperature treatment of PEDOT:PSS.

conditions of treatment. Variations are thus mainly due to the PEDOT:PSS interlayer. In this study, annealing cells at 150 °C for 20 min significantly alters the efficiency of devices incorporating HC. As matter of fact, a thermal annealing is then applied at 130 °C. The duration for thermal treatment is kept at 20 min. At this temperature, devices incorporated HC show the highest efficiency. However, this annealing temperature of 130 °C is barely low, regarding those reported in the literature [25]. To better understand this phenomenon, attention has been turned to HC for the fabrication of organic solar cells. We measured the efficiency of cells which are treated at temperatures in the range 110–140 °C for 20 min. The photovoltaic performances of devices are summarized in Figure 2. The best performance is obtained for devices annealed at 120 °C. The device yields a J_{sc} of 10.7 mA/cm^2, a V_{oc} of 0.58 V, and a FF of 0.62, which translate to a power conversion efficiency of 3.86%. It should be noted that the obtained density current in the present study is high for solar cells prepared from the benchmark P3HT:PCBM blend. It could be due to the crossbar electrode configuration since the area of illumination is larger than the overlapped area of the crossbar electrodes because no mask has been used during the measurement. However, cells made without ITO have very poor power conversion efficiency if we keep the same PEDOT:PSS layer thickness because the conductivity of the layer remains too low. Finally, this short current density is in the range of what we can find in the literature for this couple of materials [25]. In addition, it is noteworthy that the optimal annealing temperature of HC PEDOT:PSS (i.e., 120 °C) is lower than those reported in the previous studies [25]. Actually, this temperature is related to the PEDOT:PSS formulation (HC) because it seems to degrade at higher temperature.

In order to examine the behavior of PEDOT:PSS against temperature of annealing, films of C and HC on ITO are baked in oven under vacuum at temperature of 110 °C for 10 min to remove residuals water. All films are then annealed on a hot plate in glove box for a range of temperatures from 120 °C to 240 °C for 20 min before the deposition of P3HT:PCBM active layer. After deposition of the active layer and electrodes, a thermal treatment of devices is performed at 120 °C for 20 min. The dependence of power conversion efficiency as a function of temperature of annealing is shown in Figure 3. The efficiency of devices assembled with C appears to be independent of the temperature of PEDOT:PSS treatment even up to 220 °C, indicating that film prepared from this PEDOT:PSS formulation is stable up to this high temperature. In contrast, devices incorporated HC give higher efficiency which is however strongly dependent on the treatment temperature of PEDOT:PSS. The efficiency is continuously dropped when the heating layer of PEDOT:PSS (HC) is at temperature above 120 °C. These observations confirm that using HC formulation for creating buffer layer leads to unstable thin films versus temperature. Thermogravimetric analysis (TGA) has been carried out but due to the presence of volatile compound, it has not been possible to extract reliable data.

4 Conclusion

In summary, we have evaluated the organic solar cells created from different formulations of PEDOT:PSS. Our results show the influence of PEDOT:PSS films on the performance of P3HT:PCBM-based solar cells. Efficiency as high as 3.86% using PEDOT:PSS trade-named high conductivity grade supplied by Aldrich. Thermal treatment allows the separation of phases within the active layers to be controlled by properly tuning the temperature and/or duration of annealing. A wide range of temperatures and times have been reported in the literature to build up efficient P3HT:PCBM-based solar cells; in addition, the optimal conditions of treatment differ from laboratory to laboratory. These discrepancies presumably result from variations in the properties of materials used, the compositions of blends and the solvents selected [47,48]. In this study, we demonstrated that annealing can affect the stability of the films prepared from some PEDOT:PSS formulations. Although high efficient solar cells can be achieved with the high conductivity grade PEDOT:PSS supplied by Aldrich, we showed that the PEDOT:PSS (HC) layer is not stable for temperature above 130 °C. This result shows that the thermal annealing under appropriate temperature and time should take into consideration the buffer layer as well as the intrinsic properties of active layer.

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