



# Material alternative to ITO for transparent conductive electrode in flexible display and photovoltaic devices



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## ABSTRACT

The mechanical stability of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) films spin coated onto a UV treated PET substrate was investigated. It was found that the UV exposure modifies the PET surface and improves the wetting conditions for PEDOT:PSS films deposition. The adhesion strength of PEDOT:PSS to UV treated PET surface was found to be 50 N/cm<sup>2</sup> versus 19 N/cm<sup>2</sup> to the untreated one. Furthermore, the resistance change of PEDOT:PSS on UV treated PET at 20,000 cycles of bending was measured to be only 3.8%. In contrast, the same polymeric films on untreated PET exhibit 8.7% resistance change and the conventional indium tin oxide (ITO) electrode 23.5%, which demonstrates the superior flexibility of the UV PET/PEDOT:PSS electrodes. The transparency of the produced coatings is 81%. Single layer organic light-emitting device with MEH-PPV electroluminescent polymer was successfully fabricated on UV PET/PEDOT:PSS. The electrical measurements indicate the possibility of using UV PET/PEDOT:PSS as a transparent electrode system, replacing ITO in the flexible optoelectronic devices.

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## 1. Introduction

Recently, the flexible displays and solar cells have attracted much attention due to their light weight, thinness and portability [1]. Most of the optoelectronic applications consist of thin films deposited on plastic substrates of polyethylene terephthalate (PET). Crucial for the efficiency of such devices is the front panel transparent electrode. Typically, metal oxides such as indium-tin-oxide (ITO) are used as transparent electrodes [2,3]. However, ITO is found to be brittle and when it is deposited on flexible substrates cracks are revealed at multiple cycles of bending and device's reliability decreases [4,5]. Higher cost of indium and its limited supply are also obstacles for the mass production. In contrast to ITO, the conductive polymer poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) is found as a perspective for electrode films in the flexible optoelectronic devices due to its superior mechanical properties (higher elasticity, coefficient of thermal expansion closer to that of the substrate), as well as cheaper and easier processing [6]. However, PEDOT:PSS is not equivalent to ITO in terms of conductivity and patterning ability. Some of the approaches for PEDOT:PSS conductivity improvement are treatment with solvents [7], annealing [8] or doping

with metal nanoparticles [9,10]. UV ozone treatment is widely applied for PEDOT:PSS work function increase, but such films exhibit a two-order of magnitude higher resistivity in comparison to untreated ones [11]. Additionally, the low free surface energy of the flexible substrates such as PET, polyethylene sulfonate (PES) or polyethylene naphthalate (PEN) leads to poor adhesion of the PEDOT:PSS coatings and therefore additional surface modification is needed, such as plasma treatment and wet processes [12]. Such methods, however, change not only the wettability but also alternate the chemical composition in the polymer surface, increase the surface roughness and may induce thermal stress in the plastic substrate. To avoid these drawbacks we suggest pre-deposition UV treatment of PET. By our knowledge there are no reports in the literature, concerning PEDOT:PSS films deposition on UV treated PET for the improvement of the films conductivity, adhesion and durability at bending, aiming at the effective replacement of the conventional indium-tin oxide as an electrode coating for displays and solar cells.

## 2. Materials and methods

For PET surface modification, a mercury lamp with a power of 200 W and a wavelength of 365 nm was used. To avoid changes of the samples' properties due to possible temperature changes,

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an IR filter was mounted for heating component rejection. The UV light exposure time was 4 min. The PEDOT:PSS solution was purchased from Sigma Aldrich. Films with thickness of 35 nm were deposited on UV treated and untreated PET substrates by spin coating at 2000 rpm. The films were dried at 60 °C for 20 min. Film thickness was measured by KLA Tencor Alpha-Step Surface Profiler.

For comparison of the properties of UV/PET-PEDOT:PSS electrodes with those of the conventional ones, ITO films with same thickness were RF sputtered on PET from a target, consisting of  $\text{In}_2\text{O}_3$  and  $\text{SnO}_2$  in a weight proportion of 95:5 mol%. The sputtering conditions were as follows: sputtering power was 60 W (target voltage of 500 V and plasma current of 120 mA), the oxygen partial pressure was set to  $2 \times 10^{-4}$  Torr and a total pressure (reactive and sputtering argon gas) of  $2.5 \times 10^{-2}$  Torr was maintained in the chamber. Four pieces of PET with size  $2.5 \times 2.5$  cm were put in the vacuum chamber for ITO deposition in same time. Similarly, 8 PET samples (4 UV treated and 4 untreated) with the same size were covered with PEDOT:PSS film. Finally, to demonstrate the UV treated PET/PEDOT:PSS electrode efficiency, a simple single layer organic light emitting device (OLED) was prepared by spin coating of a 150 nm thin electroluminescent film of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) on the PEDOT:PSS. Aluminum top contacts were deposited by vacuum thermal evaporation via shadow mask, defining 3 cathodes per each sample. In this way 12 OLEDs with ITO anodes and 24 OLEDs with PEDOT:PSS anodes (12 UV treated and 12 untreated) were fabricated and the measured results were averaged. Optimization of the emissive recombination is out of the aim in this work, as the main indication for working sample is the current, flowing through the interfaces.

The mechanical stability in term of bendability and adhesion strength of the UV treated and non-treated PET with deposited PEDOT:PSS films were estimated by lab-made electromechanical setup for tension test (Fig. 1). The strain applied to the substrate is related to the force intensity generated by the electromechanical system. The force is alternative and its frequency can be varied. For these experiments a force with an intensity of 25 N from peak to peak and constant frequency of 50 Hz was supplied to the sample. The total number of bends was chosen by setting different time durations of the cyclic force.

A four point probe FPP5000 resistance measurement system was used to measure the change in the sheet resistance of the films after different numbers of mechanical loading cycles. The transparency of the films for the visible light was measured using a UV-VIS Specord spectrograph. Optical microscopy was used to observe cracks revealed in the films after bending at magnification of 500. In order to determine the PET surface state and composition

before and after UV treatment X-ray photoelectron spectroscopy (XPS) was conducted using a ESCALAB Mk II (VG Scientific) spectrometer with aluminum radiation ( $h\nu = 1486.6$  eV). X-ray diffraction spectra are collected on Bruker D8 Advance diffractometer using  $\text{CuK}$  radiation and SolX detector. Current–voltage characteristics of the OLED samples were measured by ampere meter Keithley 6485. All measurements were conducted at room temperature.

### 3. Results and discussion

Fig. 2 shows the O 1s XPS spectra of UV treated and untreated PET substrates. It was found that UV exposure influences the carboxyl bonds strength and modifies the surface oxygen functional groups. This can be concluded from the 532 and 534 eV peaks intensity change in the XPS spectrum after exposure. Before the UV treatment both peaks had almost equal intensity and the XPS signal was symmetrical related to the binding energy of 533 eV. After the UV treatment, the peak ascribed to O1s increased with 10% in comparison to the untreated PET samples and it can be observed an asymmetry in the binding energy peaks in the range 530–534 eV. This is ascribed to incorporation of oxygen groups on the PET surface and results in free energy increasing, affecting the surface wettability. In the literature there is description of the typical for untreated PET peaks situated in the range 531–534 eV, corresponding respectively to  $\text{O}=\text{C}$  and  $\text{O}-\text{C}$  bonding [13]. After UV treatment increases of the single ethers and carboxyl bonding are observed (Fig. 2). This indicates that polar constituents were formed on the PET treated surface, which confirms the suggestion that UV exposure is the reason for the hydrophilic behavior of PET regarding PEDOT:PSS water solution [14]. Although the contact angle between the PEDOT:PSS solution droplets and the PET surface was not measured, its reduction was clearly observed after UV treatment. The droplets were spread due to the attraction from polar components (oxygen functional groups) attached to the polymer surface. Higher wettability resulted in better distribution of the polymeric film. We have observed that the PET surfaces treated by UV allow the droplets of PEDOT:PSS solution to be spread more uniformly during the spin coating, which was ascribed to the change of the surface chemistry and increased polar component, decreasing the contact angle.

Furthermore, the exited non bonded oxygen atoms on the PET surface possess energy close to the energy of the oxygen atoms in the bonds with sulfur atoms in the PSS chain [15] which exceeds the energies of the  $\text{PSS}-\text{H}^+$  and  $\text{C}-\text{O}-\text{C}$  bonds in the PEDOT backbone [16]. This is an indication for their oxidation from the oxygen atoms of the PET surface and bonding with the surface

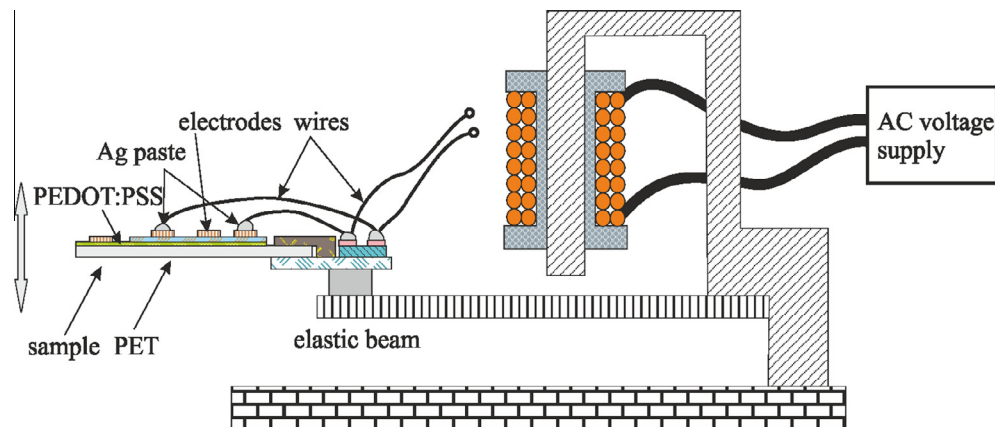


Fig. 1. Experimental setup for dynamic mechanical loading applied on the flexible substrates coated by transparent conductive films.

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