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Electrical and optical properties of transparent flexible electrodes: Effects of UV ozone and oxygen plasma treatments

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ABSTRACT

"Flextrodes" are flexible transparent electrodes consisting of ZnO(100 nm)/PEDOT:PSS/silver grid/polyethylene terephthalate (PET) fabricated using a roll-to-roll process. Flextrodes provide a zinc oxide surface on a high-conductivity electrode while maintaining reasonable transparency and good flexibility. They are optimized for use as cathodes (i.e. low work functions) in inverted organic solar cells (OSCs). As-received Flextrode samples have a surface contamination layer that insulates. Prior to use in OSCs, this contamination layer needs to be removed. We tested two surface cleaning methods, i.e., UV-ozone and oxygen plasma, with various treatment times. After cleaning samples were characterized in terms of water contact angle, UV–visible transmittance, and 4-point probe conductivity, using conductive atomic force microscopy, and X-ray/ultraviolet photoelectron spectroscopy. Based on these measurements, we identified optimal conditions and were able to recover work functions of 3.4–3.6 eV without damaging the Flextrodes.

1. Introduction

Transparent flexible electrodes are crucial for developing low-cost organic electronics such as organic solar cells (OSCs), because of their compatibility with roll-to-roll processing [1–9]. Several materials have been reported as potential candidates to provide an active surface, including conductive polymers like poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) [1], polyaniline doped with camphor-sulfonic acid [2], graphene [3,4], reduced graphene oxide [5], carbon nanosheets [6], carbon nanotubes [7], and silver grids [8,9]. Using such materials materials, flexible OSCs have been developed [10–12]. In order to satisfy all of the mechanical, electrical, chemical, and optical requirements, (e.g. flexibility, conductivity, gas-barrier, transparency, low work functions, etc.) multi-layer electrodes on flexible substrates are being used more frequently.

Flextrodes are made with ZnO/PEDOT:PSS/silver-grid on polyethylene terephthalate (PET) or on a barrier foil. Further details can be found in Ref. [13]. In brief, the first layer is a flexographic, printed, hexagonal grid that employs a water-based, silver-nanoparticle ink to improve conductivity. The second layer is a rotary-screen printed PEDOT:PSS layer that serves as a uniform conductive layer. The last layer is slot-die-coated zinc oxide, which acts as an electron extraction layer to lower Flextrode work functions. We investigated Flextrodes for use in large-area, inverted OSCs with demonstrated power conversion efficiency up to 1.8% [13,14]. Using these electrodes, a large scale organic photovoltaic based solar park (hundreds of square meters) is already functioning [13,15]. Its characteristics include transmittance of 60% across the UV–vis spectrum, sheet resistance of 10.4 Ω/□, roughness of 6.7 nm [13], and air stability [16,17]. There are a few other reports regarding Flextrodes, e.g. a study of the switching mechanism on the PEDOT:PSS layer of Flextrode–OSC [18] and a scanning electron microscopy investigation of Ag grids [19].

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However, the top ZnO layer of Flextrodes has not been fully studied yet. Surface science studies, including work functions, chemical states, and morphology are needed. The purpose of this study was to investigate these properties so that energy diagrams and working mechanisms could be defined for OSCs based on Flextrode substrates. Additionally, as-received Flextrodes were observed to have an insulating layer at the surface. Such a layer can be a serious problem for an OSC device because it impedes measurement and evaluation of intrinsic properties of the ZnO layer. In addition to surface science analysis, we evaluate sources of the insulating layer, and demonstrate that common cleaning methods, i.e. UV-ozone and oxygen plasma treatment, can remove insulating contaminants.

Here, we present surface science studies on surface-cleaned Flextrodes and demonstrate work function recovery after cleaning. To characterize Flextrodes, we examined the water contact angle, UV–vis transmittance, and conductivity, employing conductive atomic force microscopy (c-AFM), X-ray photoelectron spectroscopy (XPS), and ultraviolet photoemission spectroscopy (UPS). We compared the effectiveness of two widely used surface treatments, UV-ozone and oxygen plasma treatment. In addition, intrinsic properties of the ZnO layer of Flextrodes were determined. We discuss the existence and removal of carbon contamination on Flextrode surfaces, as well as its origin and effects on electrode physical properties. This study provides guidance for improving the roll-to-roll process of the ZnO layer coating and device fabrication using Flextrodes.

2. Materials and methods

Flextrodes on PET were received from DTU Energy Conversion and were kept in a dry-N_2 storage box prior to use to minimize exposure to ambient conditions. UV-ozone treated samples were prepared by applying 10, 20, or 60 min of UV-ozone exposure (Jelight Company Inc., UV-ozone42A-100). Oxygen plasma treated samples were prepared by applying 10 s, 1 min, or 10 min of plasma exposure (SPI, Plasma Prep III, 50 W, ca. 100 mTorr). Water contact angle, UV–vis transmittance, and 4-point probe resistances were measured with a DSA25 drop shape analysis system (KRUSS), an Evolution 600 spectrophotometer (Thermo Scientific), and a Pro4-440N 4-point resistivity system (Lucus Signatone), respectively. Topographic and current images of all samples were acquired with atomic force microscopy (ASYLUM Research MFP 3D) in contact mode. The tips of the cantilevers used for this work is Pt-coated silicon (Budget Sensors ContE-G). For high-resolution X-ray photoelectron spectroscopy (HRXPS) measurements, we used monochromated Al Kα ($h\nu$ = 1486.6 eV) and a multi-channel plate detector with a 180° hemispherical, 165 mm mean radius analyzer in an AXIS Ultra DLD (Kratos Surface Analysis). In the case of ultra-violet photoelectron spectroscopy (UPS), we used the He I line (21.2 eV) from a discharge lamp and an EA125 energy analyzer with single channeltron (Focus and Omicron Nanotechnology). Energy resolution was 0.5 eV for HRXPS and 0.15 eV for UPS, respectively. A Fermi edge of gold deposited on a highly n-doped Si substrate (0.011–0.015 Ω cm) was used to determine E_F position and instrumental resolution. Chemical states of all samples were obtained with Zn 2p, C 1s and O 1s core-level spectra. Binding energies were calibrated with reference to the Au 4$f_{7/2}$ level (84.0 eV) [20].

3. Results and discussion

A schematic of Flextrode structure is shown in Fig. 1a. We used Flextrode thickness values from Ref. [10]. The top ZnO layer is approximately 100 nm thick. The second layer is PEDOT:PSS. A hexagonal silver grid with cross sectional dimensions of 160 μm W by much less than 750 nm H [16] are under the PEDOT:PSS layer on the PET substrate.

After the cleaning processes, we checked sample appearance (Fig. 1b and c), transmittance, and four-point probe resistance of the samples. We observed no visible change in any sample, except the one with the longest plasma treatment (10 min). After 10 min plasma treatment, the Flextrode (Sample 8) was bent by heat and we observed a dramatic decrease in conductivity and transmittance (Table 1). After 2 min plasma treatment, the Flextrode (Sample 7) also showed a decrease in conductivity and transmittance; conductivity varied across the sample surface (Table 1). Except for these two plasma treated samples, the transmittance of all other samples at 500 nm was consistently around 64% (Table 1; Supplementary Fig. S1) and sheet resistances of Flextrodes were below 10 Ω/□. Macroscale conductivity is largely due to the PEDOT:PSS layer and the silver grid. These values are similar to those previously reported [13]. Transmittance spectra and resistance data indicate that proper cleaning methods do not negatively impact optical or electrical properties.

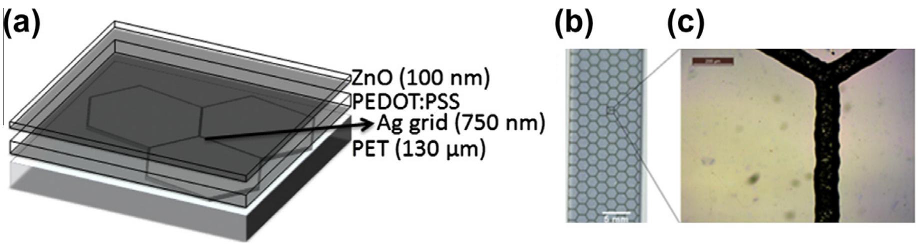

Fig. 1. (a) Schematic of sample geometry (not to scale) [10]. The electrode surface is a ZnO nanoparticle layer of approximately 100 nm. The second layer is PEDOT:PSS. The 160 μm width hexagonal silver grids were under the PEDOT:PSS layer on the PET substrate. The grid peak height is up to 750 nm. (b) Photo of the as-received sample. (c) Optical microscopic image of silver lines on an as-received Flextrode.