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Efficient flexible organic photovoltaics using silver nanowires and polymer based transparent electrodes

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ABSTRACT

Planarization and filling voids between wires are key issues when using nanowire electrodes in flexible solar cells such as organic photovoltaics (OPV). For this purpose, we use poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT: PSS) which leads to an electrically well connected silver nanowire (AgNW) network. Furthermore, the use of water based PEDOT: PSS leads to humidity assisted AgNW fusing, resulting in a maximum processing temperature of only 120 °C. OPV cells using this AgNW/PEDOT: PSS transparent electrodes exhibit power conversion efficiencies up to 7.15%. Moreover, OPV devices on PET substrates with an alumina encapsulation and barrier adhesive show excellent mechanical flexibility.

1. Introduction

Small molecule organic photovoltaics (OPV) are prospective candidates for future renewable energy production because of their potential scalability, low cost, and flexibility. For establishing flexible organic devices, a highly transparent, conductive and flexible electrode is required, replacing indium tin oxide (ITO) which is brittle and requires high temperature processes. Many alternative materials such as conductive polymers [1–3], graphene [4], carbon nanotubes [5–7], thin metal [8–10] and metal nanowires [11–13] have been studied. Among these, metal nanowires, especially silver nanowire (AgNW) networks, show outstanding flexibility, conductivity, and transparency [14,15]. However, AgNW network electrodes have a few structural innate problems. First, after deposition of the AgNW network, there is a poor electrical contact between wires, resulting in a low conductivity. Secondly, overlapping wires cause roughness, often resulting in electrical shorting of devices deposited on top of these electrodes. To create a smooth and well connected network, post-treatment techniques such as mechanical pressure [16], plasmonic welding [17,18], thermal treatment [12], and humidity assisted low temperature treatments [19] have been applied. Thirdly, open spaces between wires can be in the range of square micrometers. Charge carriers photogenerated in the absorber layer within such a void might not be able to reach the highly conductive network and get lost due to recombination. To overcome this, the nanowire network [20] can be coated by a solution–processed hole transport layer, planarizing the nanowire network. Both low conductive PEDOT: PSS [21] and high conductive PEDOT: PSS [12] have been deposited on AgNW electrodes to form conductive bridges between open spaces and to smoothen the sharp points of the network. The required annealing temperature of 180 °C is incompatible with low-cost flexible PET substrates. A low temperature process (60 °C) employing two-step spray-coated silver nanowires and PEDOT: PSS has been reported [22]. However, this process results in shunts in the organic photovoltaic device and a low (25%) fill factors. Moreover, residual water in the PEDOT: PSS could still be present due to the low annealing temperature (60 °C), affecting the device stability.

In this work, Spray-coated AgNW electrodes with thin PEDOT: PSS are prepared on glass and PET substrates and maximum 120 °C process is done during preparation (PET is stable at 120 °C but over

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140 °C it shrinks). A sheet resistance (R_S) of 30 Ω/□ and a total transmittance of 86% are achieved for both NW35 and NW90. This performance is comparable to a NW90 electrode with 85% total transmittance and R_s of 28.6 Ω/□ [19] and significantly better than that of a 120 nm PEDOT: PSS electrode, which has an Rs of 100 Ω/□, insufficient for large size devices. OPV devices were deposited on these electrodes with glass and PET substrates. The power conversion efficiency of OPV devices on glass with AgNW and ITO are 7.15% and 7.92%, respectively. Moreover, flexible devices on a PET substrate achieve a PCE of 6.91%.

2. Results and discussion

AgNW electrodes combined with PEDOT: PSS (total transmittance: 86%, R_S: 30 Ω/□) are prepared, using less Ag than for neat AgNW electrodes [19] (total transmittance: 85%, R_S: 28.6 Ω/□) by reducing the number of AgNW sprayed in our setup. For making AgNW/PEDOT: PSS electrode, AgNW networks on substrates with 90% transmittance are prepared; for these layers, the Rs is too high to be measured in our setup. However, by subsequently spin-coating 40 nm of PEDOT: PSS (600 Ω/□) and an annealing at 120 °C for 15 min, the R_S decreases to less than 30 Ω/□, with the total transmittance decreasing to 86%. To check whether the electrical enhancement primarily comes from the conductivity of PEDOT: PSS or the formation of AgNW networks by annealing, R_S is measured after 5 min, which is too short for forming the network between wires. In this case, R_S is higher than 500 Ω/□ as shown in Fig. 1. This result indicates the conductivity of the AgNW electrode is mainly improved by electrical connections between AgNWs and only slightly improved by the conductivity of PEDOT: PSS.

AFM images in Fig. 2(a) and (c) show the morphology of the AgNW network with and without the additional PEDOT: PSS layer after 15 min annealing on a 120 °C hotplate. Although three nanowires overlap in Fig. 2(c), the highest point is 142 nm which is less than the sum of three nanowires of 90 nm diameter. Without the use of PEDOT: PSS, the overall roughness is significantly larger (Fig. 2(a)). This shows that PEDOT: PSS helps fusing the nanowires. AgNW electrodes with and without PEDOT: PSS on glass with one corner contacted by silver paste are measured by Conductive AFM (c-AFM). The resulting current maps with the applied bias voltage

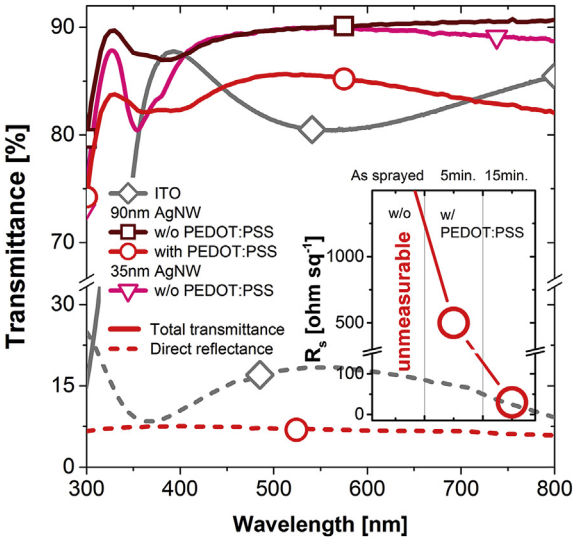

Fig. 1. Total transmittance and direct reflectance of silver nanowires network with and without PEDOT: PSS. The inset shows sheet resistance before PEDOT: PSS coating and after PEDOT: PSS depending on the annealing time.

of 1 V are shown in the inset of Fig. 2(b), No current could be detected by c-AFM for nanowires without PEDOT: PSS (Fig. 2(b)). On the other hand, a uniformly distributed current is measured for the AgNW network embedded in PEDOT: PSS. The AgNW shape still appears in the c-AFM image, as marked with arrows in Fig. 2(d). Lower conductivity spots are observed on the left side of wires, which is an artifact of the direction of measurement. Scanning electron microscopy (SEM) is used to compare the topography of the electrodes. AgNW annealed at 120 °C without PEDOT: PSS do not show a fused, interconnecting network of wires. Moreover, the surfactant polyvinylpyrrolidone (PVP), used as stabilizer for silver nanowires synthesis, is still observed around the AgNW (Fig. 3(a) and (b)). After coverage of the AgNW by PEDOT: PSS deposition, it is impossible to observe whether PVP is still present. However, we expect that the water-soluble PVP has been partly washed off, improving the connection between the wires. Fig. 3(c) and (d) show that the network is smoothened upon PEDOT: PSS deposition. These results indicate that PEDOT: PSS deposition helps connecting the AgNW network by filling the voids between the AgNWs, by fusing the junctions, and softening the rough and sharp spots. The possible reasons why AgNWs are fusing at relatively low temperature are (i) a softening of the wet PVP shell, which allows an elastic alignment of the NWs and thereby enhancing electrical contact between wires as mentioned by Weiβ et al. [19]. (ii) A removal of PVP from the AgNWs during PEDOT: PSS processing might open free paths for a surface diffusion of silver atoms and the formation of joints between wires as explained by Zhu et al. [23].

The electrode performance of the AgNW network is evaluated in OPV devices using a DCV5T-Me:C_{60} bulk heterojunction absorber layer. The photovoltaic device is deposited on top of AgNW electrodes with and without PEDOT: PSS on both a glass and PET substrates. A reference device containing an ITO electrode was fabricated in parallel. The AgNW electrode without PEDOT: PSS yields short-circuited devices for both NW35 and NW90. However, when using a PEDOT: PSS smoothed AgNW electrode, the shunt resistance (24.8 kΩ for NW30, 25.5 kΩ for NW90) is comparable to that of a device on ITO (26.4 kΩ) as shown in Table 1. As shown in Fig. 4 and 7.15% of power conversion efficiency (PCE) with a short-circuit current density (J_{sc}) of 12.34 mA/cm^2, open circuit voltage (V_{oc}) of 0.955 V, and a fill factor (FF) of 60.67% are achieved by the device using a NW90 electrode with PEDOT: PSS. Even if this value is not as high as OPV using ITO electrode (7.92%), it is the best performance published up to now using small molecule OPV on AgNW electrode, to best of our knowledge. The reason why OPVs using ITO electrodes still show higher performance than OPVs using AgNW electrodes is that the direct reflectance of AgNW electrode is lower than that of ITO as shown in Fig. 1 and the low direct reflection does not support a microcavity effect [24] as discussed in a previous study [25].

The NW35 electrode with PEDOT: PSS is also tested in OPV devices. With 30 Ω/□, the electrical performance of NW35 and NW90 electrodes is very similar. However, J_{sc} shows 11.57 mA/cm^2 which is 7% less as compared to NW90. As shown in Fig. 1, NW35 electrodes exhibit a stronger plasmonic dip around a wavelength of 350 nm and lower transmittance from 600 nm to 800 nm as compared to NW90 explaining the reduced J_{sc}.

Using PET as substrate, we further demonstrate a fully flexible, encapsulated OPV device. The device is protected by a flexible 20 nm AlO_x (Water vapor transmission rate of 2×10^{-5} g/m^2 day) thin-film encapsulation [26]. A maximum PCE of 6.91% is achieved; the degradation of OPVs with this encapsulation has been investigated by Bormann et al. [27]. For checking the electrical stability of AgNW/PEDOT: PSS as electrode for flexible devices, a bending test is performed in ambient condition. The performance of devices is stable over 20 cycles of bending with 3 mm radius as shown in