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Highly conductive silver nanowire networks by organic matrix assisted low-temperature fusing

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ABSTRACT

In silver nanowire (AgNW) percolation network electrodes, the junction resistance at the wire-to-wire contact is crucial for the electrode performance. We introduce an organic sublayer between the substrate and the AgNW electrode to improve the sheet resistance and avoid the frequently applied high-temperature post-annealing process. Upon introduction of such a sublayer, a strong reduction of the sheet resistance (R_S) in the same order as it would be expected from a post-annealing process (e.g. 90 min@210 °C) is observed. This effect is investigated in-depth by using different sublayer material classes such as polyelectrolytes, tensides or differently charged polymers. Independent of charge and material class, especially those materials with hydrophobic and hydrophilic parts, dramatically reduce the sheet resistance. Consequently, hydrophobic interaction between substrate and nanowires and capillary forces during drying can be attributed as driving force. Using polyvinylpyrrolidone (PVP), also used as stabilizer for the AgNWs, leads to the largest reduction in sheet resistance of the investigated materials resulting in AgNW electrodes exhibiting $R_S = 10.8\ \Omega/\square$ at 80.4% transparency (including substrate) without additional post-annealing at high temperatures.

Finally, we demonstrate the application of the novel NW electrode to organic n-i-p type solar cells resulting in devices with higher power conversion efficiencies than reference AgNW electrodes without sublayer.

1. Introduction

Technological progress in highly efficient organic light emitting diodes (OLEDs) [1] and organic solar cells (OSCs) [2] has generated considerable interest in low-cost, high performance, transparent electrode technologies for flexible substrates, including temperature-sensible polymer webs for roll-to-roll manufacturing. These technologies include thin metal layers [3], carbon nanotubes (CNTs) [4,5], graphene sheets [6], highly conductive PEDOT:PSS [7,8] or percolative networks made of metallic nanowires [9–11]. Among those, silver nanowire based network electrodes (AgNWs) show the best properties. In comparison to ITO on glass, they show an equal opto-electrical performance on flexible substrates, e.g. on PET substrate with $R_S = 13\ \Omega/\square$ and $T_{550} = 93.5\%$ (without substrate) while being stable over more than 1000 bending cycles at a fixed radius of 1.5 mm [12].

The key difference to other electrode types is the percolative nature of the nanowire electrode, with the network parameters defining the electrode properties. Directly after the deposition of a nanowire layer, the sheet resistance (R_S) is usually very high. The crucial parameters influencing the

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sheet resistance are the junction resistance (R_J), the wire resistance (R_W) and the number of junctions per area. The R_S can be reduced by reducing the R_J, while the R_W and the number of junctions per area are kept constant, i.e. the transmission and the material stays constant. The stabilizing polymer shell of polyvinylpyrrolidone (PVP) around the AgNW hinders the direct contact at the junctions resulting in high R_J values [13]. Therefore a reduction of the wire-to-wire distance at the junction or local removal of the polymer shell causes a large improvement of the R_S of an AgNW electrode. The most frequently applied method, besides mechanical pressing [14], galvanic treatment [15] or light treatment [16] is thermal annealing of the network, improving the R_J and yielding good electrode performance. As the temperatures involved are greater than 180 °C, post-annealing is not well suited for plastic films.

Recently, Lee et al. reported on solvent washing of the as-synthesized nanowires which reduces the initial thickness of the insulating and wire-stabilizing PVP shell [13]. Another complimentary method to reduce the sheet resistance is demonstrated by Choi et al. where PEDOT:PSS, modified by dimethyl sulfoxide (DMSO) is coated on top of the nanowire electrode which lead to a reduced R_S due to the adhesive forces induced by the lateral shrinkage and the substantial reduction in the thickness of the PEDOT:PSS layer on the NW electrode [17].

Inspired by a paper from Magdassi et al. [18], we investigate an alternative way to achieve low temperature processed highly conductive AgNW electrodes, avoiding the necessity of mixing complicated AgNW inks or having to coat the acidic and hydrophilic PEDOT:PSS on the electrode.

Magdassi et al. report on sintering of silver nanoparticles (AgNPs) at room temperature [18]. With the help of the strongly positive charged polyelectrolyte poly(diallyldimethylammonium chloride) (PDAC), they are able to force AgNPs that carry a negative charge due to their stabilizing poly(acrylic acid) sodium salt (PAA) shell to coalescence at typical ambient temperatures. Combining this technique with inkjet printing, they were able to deposit patterned conductive metal-films at room temperature.

Here, we apply this method to PVP stabilized AgNW electrodes and investigate the various effects observed. We study the influence of different sublayers, composed of tensides, polymers, and polyelectrolytes, on the performance of AgNW electrodes deposited on top. The resulting electrode films are investigated concerning sheet resistance, appearance of the junctions, transmittance, figure of merit (FoM) and comparison to reference AgNW electrodes without any sublayer or to ITO. The systematic comparison of different sublayer materials leads to a deeper understanding of the basic mechanism.

2. Results and discussion – sublayer characterization and investigation of the fundamental process

To evaluate the ability of PDAC to act as a coalescence-inducing sublayer for NWs an AgNW electrode is deposited on a PDAC sublayer. As reference, glass substrates are coated with PDAC or AgNWs only. The corresponding results are illustrated in Fig. 1 and compared to ITO on glass.

Fig. 1A depicts the wavelength dependent transmittance of the pure glass substrate and glass substrates coated with AgNWs, AgNWs with a PDAC sublayer, ITO and PDAC. To evaluate the electrode performance of the respective thin-film, the R_S values, the transmittance at 550 nm (T_{550}), and the figure of merit (FoM) according to De et al. [19] of (1)–(3) are given in the legend of the plot. For an appropriate comparison to ITO, the FoM for bulk-like behavior is chosen, which is valid for high wire coverages only.

The T_{550} of the glass substrate is 92.6%. Coated with a thin layer of PDAC the sample exhibits a comparable T_{550} of 91.9% (most of the extra absorption of the PDAC layer can be attributed to optical thin-film effects). Since both glass and PDAC are insulating, no R_S is measured in these cases. The AgNW network shows a T_{550} of 82.7% and a sheet resistance of 1980 Ω/□ directly after deposition. Simultaneously, the same amount of AgNWs is coated on a second glass substrate, pre-coated with PDAC. Although no post-annealing was applied in both cases, the resulting electrode with the PDAC sublayer exhibits a remarkably low R_S of 11.6 Ω/□ at a corresponding transmission (T_{550}) of 81.7%. Consequently, the combination of a thin PDAC sublayer with an AgNW network leads to a sheet resistance reduction of two orders of magnitude from 1980 Ω/□ to 11.6 Ω. The effect on the sheet resistance is comparable to the effect of annealing the NW film [10].

Compared to our lab standard ITO films (26 Ω/□@82.0%), a lower R_S of 11.6 Ω/□ is achieved for the AgNWs by using this simple and low-energy method while the corresponding T_{550} values differ by 0.3% only. For an

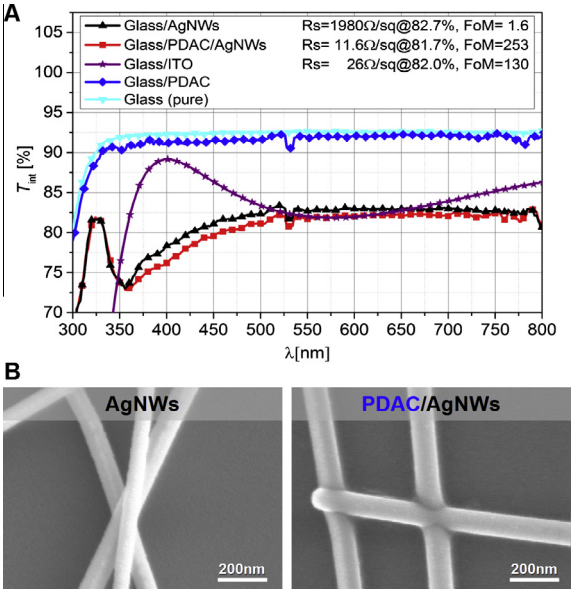

Fig. 1. (A) Wavelength dependent transmittance of glass substrates with the different coatings. Additionally, the corresponding values of R_S, T_{550} and FoM are given. (B) SEM images of selected AgNW junctions on glass in comparison to AgNWs with a PDAC sublayer, showing a different behavior at the junctions.

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