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Gentle plasma process for embedded silver-nanowire flexible transparent electrodes on temperature-sensitive polymer substrates

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Abstract

The present study investigates processing routes to obtain highly conductive and transparent electrodes of silver nanowires (AgNWs) on flexible polyethylene terephthalate (PET) substrate. The AgNWs are embedded into a UV-curable polymer to reduce the electrode roughness and enhance its stability. For the purpose of device integration, the AgNWs must partially protrude from the polymer, which demands that their embedding is followed by a transfer step from a host substrate to the final substrate. Since the AgNWs require some sort of curing (thermal or plasma) to reduce the electrode sheet resistance, a thermally stable host substrate is generally used. This study shows that both thermally stable polyimide, as well as temperature-sensitive PET can be used as flexible host substrates, combined with a gentle, AgNW plasma curing. This is possible by adjusting the fabrication sequence to accommodate the plasma curing step, depending on the host substrate. As a result, embedded AgNW electrodes, transferred from polyimide-to-PET and from PET-to-PET are obtained, with optical transmittance of $\sim 80\%$ (including the substrate) and sheet resistance of $\sim 13 \Omega$ /sq., similar to electrodes transferred from glass-to-glass substrates. The embedded AgNW electrodes on PET show superior performance in bending tests, as compared to indium-tin-oxide electrodes. The introduced approach, involving low-cost flexible substrates, AgNW spray-coating and plasma curing, is compatible with high-throughput, roll-to-roll processing.

Keywords: transparent electrodes, silver nanowires, spray coating, plasma processing

Supplementary material for this article is available online.

(Some figures may appear in colour only in the online journal)

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1. Introduction

Modern optoelectronic semiconductor devices, such as organic light emitting diodes (OLEDs), thin film inorganic, organic and perovskite solar cells, liquid crystal-and touch screen displays, rely on transparent electrodes (TEs) to assure simultaneous light interaction with the active device layers



 $(\mathbf{\hat{h}})$

and efficient charge carrier extraction. The state-of-the-art TE is tin-doped indium oxide (ITO), which belongs to the class of transparent conductive oxides (TCOs), i.e. wide bandgap and highly-doped, n-type semiconductors. ITO has the lion's share (more than 95%) of the constantly growing TE market [1, 2]. The rest is shared among other TCOs, such as fluorine-doped tin oxide (FTO) and aluminum-doped zinc oxide (AZO), transparent organic conductors, such as poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), graphene and carbon nanotubes (CNTs), as well as metal composites/grids and metal nanowires [3].

Since the development of polyol synthesis for silver nanowires (AgNWs) in 2002 by Sun *et al* [4], intensive research on the use of AgNWs as TE has been carried out [5]. AgNW TEs typically achieve sheet resistance (R_s) of 10– 13 Ω /sq. at 76%–80% transmittance (T) [6] (for the purpose of comparison, the transmittance *including the substrate* is reported throughout the paper). Nevertheless, AgNW electrodes show some drawbacks, such as the need for post deposition treatments to minimize contact resistance [4], high roughness [6] and poor adherence to flexible substrates [7]. These issues are especially critical to overcome, as the most common flexible and transparent substrate is polyethylene terephthalate (PET), with a glass transition temperature of 70 °C [8], which prohibits heat-intensive processing.

Therefore, different approaches have been reported to address these issues for flexible substrates. Tokuno *et al* [9] showed that pressing AgNW films on PET with 25 MPa for 5 s yields electrodes with R_s of 13 Ω /sq. and a transmittance at 550 nm (T_{550}) of \sim 72% (assuming bare PET transmittance of \sim 90%). The root mean square roughness (RMS) was 18 nm. However, pressing negatively affects the transmittance of the NW film due to broadening of the NW diameter, as shown by Hu *et al* [10].

Another reported technique to minimize the contact resistance between the NWs without damaging the heat-sensitive PET substrate was the use of plasmonic flash light curing [11] In this case, an RMS roughness of 10.5 nm and a relatively high R_s of ~51 Ω /sq. was reported. Due to the low NW density the transmittance was rather high at $T_{550} \sim 85\%$. Such a high R_s value would be, however, unsuitable for certain applications like solar cells.

To address the issue of the heat sensitivity of PET, different NW transfer techniques have been also reported. In these techniques, the thermal processing of the AgNWs takes place on a thermally stable *host* substrate before the NWs are transferred to the *final* substrate.

Xie *et al* developed a process where AgNWs are deposited on mixed cellulose ester (MCE) substrates via vacuum filtration [12]. The AgNWs were dried for 30 min at 80 °C before the MCE/AgNW was mounted to the PET substrate and further processed in acetone vapor. Finally, the MCE was dissolved in acetone to obtain the PET/AgNW electrode. This yielded an electrode with $T_{550} \sim 73\%$ and R_s of 130 Ω /sq., which is again quite high. Another transfer approach used float transfer from Al-coated PET to various substrates [13]. The AgNWs were Meyer-rod-coated on the Al-coated PET and then treated for 1 h in plasma. The Al-coating was then etched for over 8 h in NaOH and the floating film was then transferred to the final substrate. The free-standing AgNW films yielded $T_{550} \sim 91\%$ and 13 Ω/sq .

The above processes are time-consuming and lack upscale potential. Another approach used anodized aluminum oxide (AAO) membranes and vacuum filtration to coat the membranes with AgNWs. The membranes withstood the heat treatment at 200 °C for 20 min, after which the AgNW films were transferred via a polydimethylsiloxane (PDMS) mold to a PET substrate [14, 15]. The process yielded electrodes with 10 Ω /sq. and $T_{550} \sim 76\%$.

Further techniques include not only transfer, but also embedding of AgNWs to smoothen the electrode surface and increase the adhesion on the substrate and the stability. Nam *et al* reported such a technique in 2014 [16]. A rigid substrate was coated with AgNWs and cured for 5 min at 100 °C. Then the UV-curable Polymer NOA63 (from Norland Products) was spin-coated over the AgNWs. The AgNWs/NOA63 layer was then peeled off the substrate. The embedded AgNW electrode showed $T_{550} \sim 82\%$, RMS roughness of 0.4 nm and R_s of 16 Ω/sq . In this case the used wires featured a large aspect ratio (average diameter of ~35 nm and an average length of ~25 μ m), which favors high performance without excessive post-deposition treatment.

Later, Li *et al* used this transfer technique with silicon as host substrate [17]. The AgNWs were spin-coated and cured in Ar plasma for 15 min. Afterwards, the conductive AgNW films were coated with NOA63 and peeled off the wafer. A $T_{550} \sim 79\%$ was obtained, with 1.58 nm RMS roughness and $R_{\rm s}$ of 7.2 Ω /sq.

Alternatively to NOA63, polyurethane (PU) was used in a peel off process from a PET host substrate [18]. The NWs on PET were treated with heat, NaCl and HCl. This yielded an electrode on PU substrate with $T_{550} \sim 85\%$, 6.7 nm RMS roughness and R_s of 15 Ω /sq. However, the PU curing time of 40 min hampers fast processing.

The most relevant, roll-to-roll process for embedding and transferring AgNW electrodes so far, was reported, by Jung *et al* [19]. Thermally stable polyimide (PI) was used as initial substrate for the NW deposition, followed by infrared flash light curing of the NWs. The NWs were simultaneously embedded in NOA63 and transferred to PET, similar to the works of Nam and Li. The roughness was 2.3 nm, while $T_{550} \sim 79\%$ and the $R_{\rm s}$ 8.3 Ω /sq. Again, high aspect ratio AgNWs were used with 27 μ m length and 32 nm diameter.

This work presents an embedding and transfer process for AgNWs, deposited by ultrasonic spray coating, from a flexible host substrate to PET final substrate. In a first variant, the AgNWs are sprayed on polyimide, cured in an ambient atmosphere plasma, embedded in a UV-curable resist and finally transferred to PET. In a second variant, the AgNWs are sprayed directly on PET. From there, they are firstly embedded and then transferred to the final PET foil before being plasma-cured. In this case, it is shown that the polymer matrix acts as a thermal buffer to enable the plasma curing of the AgNWs without damaging the PET substrate. Both variants were shown to lead to high performance TEs, with differences in the roughness and optical haze. Electrode performance is shown to be similar to the one achieved when using glass as final and host substrate. AgNWs on PET show superior performance in all bending tests as compared to ITO on PET.

2. Experimental techniques

AgNWs were purchased from Sigma Aldrich (product code: 739421). According to the manufacturer's specifications, the mean wire length and diameter are 10 μ m and 60 nm, respectively. AgNWs were delivered in an isopropyl alcohol (IPA) suspension with 0.5% solid content. For the depositions presented here, this suspension was further diluted to a ratio of 1:5 with IPA, resulting to a 0.1% AgNW solid content solution. The dilution of the suspension from its initial concentration was necessary to avoid deposition of AgNW agglomerates on the substrate, which were otherwise observed. During optimization, spray depositions took place using 1:1 up to 1:5 diluted suspensions, with the later being the best compromise, offering homogeneous, agglomerate-poor films at fast deposition time (as decreasing the suspension's solid content increases the spraying cycles needed to achieve the same substrate coverage with AgNWs).

1 mm-thick glass substrates from Thermo Scientific (Menzel Gläser, microscope slides, pre-cut to $25 \times 25 \text{ mm}^2$) were cleaned in a 2% Hellmanex III (Hellma Analytics)—ultrapure water solution in an ultrasonic bath for 15 min. The substrates where then rinsed with ultrapure water and sonicated first in acetone and then in isopropanol for 15 min. PET (Melinex[®] 504 with one pretreated side) and polyimide (Kapton[®] HN from DuPontTM) foils were cut to $25 \times 25 \text{ mm}^2$ pieces and cleaned with the same procedure as glass, excluding only the acetone sonication step. At the end of the cleaning procedure the substrates were dry-blown with compressed nitrogen.

AgNW suspension was sprayed with a Sonotek ExactaCoat coating unit, equipped with a Sonotek ultrasonic nozzle, operating at a frequency of 120 kHz. Optimum spraying conditions were obtained for a nozzle to substrate distance of 200 mm and shaping air pressure set to 9 bar. The flow rate of the suspension from the syringe to the nozzle was set to 0.4 ml min⁻¹ and the power of the nozzle ultrasonic transducer to 1.7 W. The number of scans of the nozzle above the substrate was 20.

The curing of the wires was done in a plasma tool (FEMTO DIENER PLASMA), with a stimulating plasma frequency of 2.45 GHz and maximum output power of 100 W. After the samples were put in the plasma chamber, the chamber was evacuated, until the pressure in the chamber reached 0.3 mbar. The residual gas in the chamber was ambient air. At this point the plasma was ignited with the plasma generator set to its maximum power output (100 W) and the timer to 1–3 min. After the process time elapsed, the plasma was automatically switched off, the chamber was vented, and the cured AgNW films were taken out of the chamber.

For the embedding of AgNWs, the UV-curable polymer OrmoComp[®] and its adhesion promoter OrmoPrime[®] 08 were

used (from micro resist technology GmbH). Details of the embedding and transfer process are described in a previous publication [20]. In short, the host substrate (HS), coated with AgNWs, was drop-coated with OrmoComp[®]. The final substrate (FS), coated with OrmoPrime[®] 08, was placed on the HS and the whole stack was then placed under UV light for 10 s, to cure the polymer. The UV lamp was a POLY-LUX 500 with a 315–400 nm wavelength emission. Finally, a mechanical lift-off was performed, transferring the embedded AgNWs from the HS to the FS, with the AgNWs being now on the top of the FS and partially protruding from the embedding polymer.

The plasma curing of the AgNWs can take place either on the HS, before the application of the polymer, or on the FS, after the transfer process has taken place, as schematically shown in figure 1.

The sample surfaces were characterized with atomic force microscopy (AFM) (Molecular Imaging, Pico Plus) in tapping mode, using SSS-NCHR tips from NanosensorsTM. Additionally, conductive contact mode measurements were carried out with contact mode tips from Nanoworld (CONT Tips), which were sputter-coated in-house with 5 nm Ti, followed by 20 nm Au. For these measurements, a bias was applied to the AFM tip while the sample was grounded. The maximum current that can be recorded is 10 nA.

Scanning electron microscopy (SEM) (Zeiss, SUPRA 40) was performed, using 5 kV acceleration voltage and an in-lens detector.

For optical transmittance and reflectance measurements a Bruker Vertex 70 Fourier transform (FT) spectrometer, equipped with an additional visible light source was used. For the wavelength range 330–550 nm a GaP-detector was used and for the range 550–1150 nm a Si detector. To measure total transmittance (specular- plus diffuse transmittance) a tefloncoated integration sphere from Bruker was used.

Sheet resistance of the samples was measured with a 4point, in-line probe (Nagy SD—600), as well as with a 4point, in-line probe connected to a semiconductor parameter analyzer (Agilent 4156 C).

Bending tests were performed with a MARK 10 ESM303 tension/compression force setup at a speed of 1 m min⁻¹. The bending radius was 4 mm for compressive and for tensile stress. The electrical resistance of the samples during the bending tests was measured from one edge to the opposite edge of the sample, along the stress direction. Silver paste, combined with Cu adhesive tape, were used as contacts. The resistance was measured at the relaxed state after a certain number of bending circles. Figure 2 shows a scheme of the sample geometry and setup for the bending tests.

AZO layers were sputtered (Leybold Univex 450 C tool) at DC (direct current) magnetron mode, from a 4-inch diameter ZnO target, doped with 2 wt.% Al₂O₃. The base pressure in the deposition chamber was $1.4-2.4 \times 10^{-5}$ Pa. The sputter deposition took place in pure Ar atmosphere, at 0.1 Pa and 60 W, resulting to a rate of 0.28 nm s⁻¹. The target-to-substrate distance was 100 mm and no heating was applied to the substrate.



Figure 1. Schematic representation of the spraying/plasma curing/embedding/transferring process, defined as *standard process* (SP), as well as the spraying/embedding/transferring/plasma curing process, defined as *inverse process* (IP).



Figure 2. Sample geometry and experimental setup used for the bending tests.

3. Results and discussion

As a starting point of the investigation, the spraying parameters for the AgNW suspension had to be optimized, so as to achieve the best trade-off between light transmittance and sheet resistance. The optimized spraying parameters are reported in the previous section. After the spraying of the AgNWs, the different curing, embedding and transferring processes took place. In-depth analysis of the influence of the different process steps on the properties of the AgNW electrodes was realized and is reported in the following sections.

3.1. Morphology of the AgNW electrodes on glass as host and final substrate

Figure 3 shows SEM images of the AgNW films obtained after different process steps, using glass both as host and final substrate. This case is denoted as glass-to-glass, or 'G2G'. In the *standard process* (SP) the AgNWs are sprayed (figure 3(a)) and then plasma-cured (figure 3(b)) on the HS. Then, they are embedded in the polymer on the HS and finally transferred to the FS (figure 3(c)). In the *inverse process* (IP), after the spraying of the AgNWs on the HS (figure 3(d)) and their embedding, their transfer to the FS takes place (figure 3(e)), followed by plasma curing (figure 3(f)). Corresponding higher magnification SEM images are provided in figure S1 (available online at stacks.iop.org/NANO/31/365303/mmedia).

The sprayed AgNWs form a homogeneous film. In the standard process, the curing process does not lead to significant morphological changes, apart from the location of the NW junctures, where a close contact is formed. A significant drop of the sheet resistance from $\sim 200 \text{ k}\Omega/\text{sq}$. for the assprayed films to $\sim 13 \Omega/\text{sq}$. is observed after plasma curing. The sheet resistance remains unchanged after the transfer process has taken place.

Both the standard and inverse processes give rise to the same sheet resistance for the final embedded NW electrode. However, plasma curing of the AgNWs after their embedding and transferring to the FS, has adverse effects that are visible in figure 3(f) and S1(f). The arrows in figure 3(f) mark holes in the OrmoComp[®] polymer, caused by etching in the O₂-containing plasma [21]. The induced porosity in the OrmoComp[®] layer increases the RMS roughness, but does not influence the total optical transmittance, as will be seen later. It is noted that, experiments realized with reduced plasma power, required extended plasma treatment duration to achieve the same AgNW film resistance, thus causing similar roughness features to the embedding polymer.

3.2. Morphology of the AgNW electrodes on flexible host and final substrates

The standard process is not applicable when PET is used as HS (for PET-to-PET or 'P2P' transfering). Indeed, the plasma curing of the AgNWs on PET leads to the damaging of the substrate due to the excessive thermal budget transferred to it. On the other hand, the inverse process can be applied: after



Figure 3. SEM images of the electrode surface after different process steps, for glass as host and final substrate: (a) as-sprayed AgNWs on the HS; (b) cured AgNWs on the HS; (c) embedded and cured AgNWs on the FS; (d) as-sprayed AgNWs on the HS; (e) embedded AgNWs on and the FS (f) cured and embedded AgNWs on the FS.

the AgNWs spraying (figure 4(a)), where a homogenous film is obtained, the NWs are transferred onto the FS (figure 4(b)) and then plasma-cured (figure 4(c)). The thermal budget due to the plasma curing can be evacuated to the OrmoComp[®] layer, thus invoking no damage to the PET substrate. Corresponding zoomed-in SEM images are provided in figures S2(a)–(c). The sheet resistance decreases from >200 kΩ/sq. for the assprayed films on PET to ~13 Ω/sq. for the embedded AgNWs on PET after plasma curing, i.e. the same value as the resistance achieved for the G2G case.

Alternatively, Kapton[®] (polyimide) as HS was also investigated, as it is a widely-used, temperature stable polymer. The Kapton-to-PET case is denoted as 'K2P'. It was anticipated that the standard process could be used for AgNW transferring from the polyimide to the PET substrate. Figures 4(d) and (e) show the sprayed AgNWs on the polyimide substrate before and after plasma curing, respectively. For the curing of the NWs on polyimide the curing time had to be decreased compared to what was used for glass. After 3 min curing time the wire junctures showed pronounced sinter necks and the wires were roughened and deformed as a result of increased temperature. Broken and/or melted pieces of wires were observed over the surface. Moreover, a good embedding and transfer process was inhibited as the wires adhered strongly to the polyimide substrate. For these reasons the curing time was reduced to 1 min, for which the wires showed no damage and the transferring process was not inhibited. The measured sheet resistance after 1 min curing time was $\sim 12 \Omega/sq$. Again, corresponding higher magnification SEM images for the K2P case are provided in figures S2(d)–(f).

The differences in the observed plasma curing effects on glass and polyimide are attributed to two reasons. First, on the different thermal conductivities of glass and polyimide (Kapton[®] HN), which are 0.96 and 0.12 W/(m·K), respectively [22, 23]. Due to the lower thermal conductivity of polyimide, heat cannot be easily evacuated, giving rise to more pronounced AgNW curing, thus inducing damage to the wires. Second, the roughness of polyimide is higher than the roughness of glass, reducing the contact area (*A*) between the AgNWs and the substrate. According to the 1D Fourier's



Figure 4. SEM images of the electrode surface after different process steps, on flexible substrates: (a) as-sprayed AgNWs on the HS (PET); (b) embedded AgNWs on the FS (PET); (c) embedded and plasma-cured AgNWs on the FS (PET); (d) as-sprayed AgNWs on the HS (Kapton); (e) plasma-cured AgNWs on the HS (Kapton); (f) plasma-cured and embedded AgNWs on the FS (PET).

law: $\frac{Q}{\Delta t} = -kA\frac{\Delta T}{\Delta x}$. With a smaller contact area, the heat Q transferred from the AgNWs to the substrate per time Δt decreases, making the AgNW curing more pronounced, as the temperature increase, ΔT , becomes larger (k the Boltzmann constant).

3.3. Topography comparison between electrodes processed on glass and flexible substrates

To quantify the topographic properties of the electrodes, AFM measurements were performed. Figures 5(a) and (b) show the embedded AgNW electrode fabricated by the standard and inverse process on glass, respectively. The RMS roughness is significantly larger for the IP sample, namely 28 nm compared to 5 nm for the SP. The reason is the occurrence of holes in the OrmoComp[®] caused by the plasma treatment. For the P2P inverse process (figure 5(e)) the occurrence of holes also gives rise to RMS roughness of 25 nm. Height profile data were taken from figures 5(b) and (e) (along the marked lines) to determine the depth of the holes. The profiles are

shown in figures 5(c) and (f). The hole depth is 100–120 nm. On the other hand, the AFM image for the K2P standard process shows no holes (figure 5(d)) and 18 nm RMS roughness. The roughness of the electrodes is largely determined by the background roughness of the host substrate. In the IP, the plasma-induced holes in the polymer have a significant additional contribution. For comparison, the roughness of bare glass is 1.5 nm, of Kapton 13.0 nm and of PET 15.0 nm. AFM images of the substrates are shown in figure S3.

3.4. Current mapping

Using contact-mode conducting AFM, it was verified that there is a direct electrical contact at the surface between the embedded AgNWs and the conducting AFM tip. Figure 6 shows the topographic AFM image (figure 6(a)) together with the current map image (figure 6(b)), acquired simultaneously for a G2G SP sample. A bias voltage of 1 V was applied to the tip. The saturation current from the amplifier is 10 nA. Most of the NWs appearing in the topographic



Figure 5. AFM images of the AgNW electrodes for: (a) G2G SP, (b) G2G IP, (c) height profile for the dashed line marked in (b), (d) K2P SP, (e) P2P IP, (f) height profile for the dashed line marked in (e).

image led to saturated current flow in the current-map image. The average distance between 2 neighbouring wires is less than 1 μ m. Figures S4(a) and (b) show larger magnification images. Corresponding cross section line profiles were extracted from the topographic and current map images (lines in figures S5(a) and (b)). In figure S5(c) these profiles are plotted. One can see that the topographic spikes corresponding to the AgNWs lead also to current spikes, where the current is saturated. No current is measured between the wires, on the OrmoComp[®] matrix.

3.5. Optical properties

Figure 7 shows the transmittance spectra of the different electrodes. Figure 7(a) shows spectra after each step of the G2G standard process. The total transmittance (specular and diffuse) of the as-sprayed AgNW film (black line) and of the plasma-cured (red line) are very similar. As the conductivity of the plasma-cured film goes up, the transmittance in the range from 450–650 nm decreases by approximately 1%. The embedding of the AgNW film leads to pronounced specular transmittance decrease at low wavelengths due to the polymer absorption (blue dashed line). In the range from 450–600 nm the transmittance decreases slightly compared to

the plasma-cured film (red line), while from 650–1100 nm the embedded film shows a higher transmittance. The total transmittance (blue solid line) is significantly higher than the specular one at low wavelengths, which shows that the haze ($H = 100 \times (T_{\text{diffuse}}/T_{\text{total}})$) has an important contribution (table 1).

Figure 7(b) shows the transmittance spectra for the G2G inverse process. The transmittance of the initial film is the same as in figure 7(a) (black line). The orange line represents the transmittance of the embedded (but not plasmacured) AgNW film. At low wavelengths, the same drop in transmittance as before is observed, due to the OrmoComp[®] absorption. The transmittance decrease in the 450-600 nm range, as well as the increase in the 650-1100 nm range, seem to be caused by the OrmoComp[®] layer, as well. After plasma curing, the embedded AgNW film shows a decrease in specular transmittance (blue dashed line) in the visible and infrared, caused by the effect of the plasma treatment on the polymer. The total transmittance, on the other hand, is comparable to the one obtained in figure 7(a), which shows the increased haze contribution for the inverse process (table 1).

Figures 7(c) and (d) show transmittance spectra for the P2P and K2P cases, respectively. The polyimide substrate lacks



Figure 6. Simultaneously acquired AFM images of the (a) topography and (b) current map of an embedded electrode (G2G SP). In the conducting areas the current is saturated.



Figure 7. Transmittance spectra measured for the (a) G2G SP, (b) G2G IP, (c) P2P IP, (d) K2P SP samples at different stages of their fabrication.

transparency, which is evident from the spectrum in figure 7(d) (red line). The total transmittance of the final films both in the P2P and K2P cases are similar to glass, while the haze is significantly higher for the P2P case than for the K2P due to the aforementioned roughening of the embedding polymer in the plasma.

Key performance figures for the electrodes are summarized in table 1. The Haacke's figure-of-merit [29], $\Phi = (T^{10}/R_S)$, for transparent electrodes is also included in the table, using either the average total transmittance T_{av} (yielding Φ_{av}) in the visible (400–700 nm) range or the total transmittance at 550 nm T_{550} (yielding Φ_{550}). H_{av} is the average haze value (400–700 nm), while R_S^{BE} and R_S^{AE} denote the series resistance before and after embedding, respectively.

3.6. Bending tests

To quantify the flexibility of the electrodes on PET, bending tests were performed. Figure 8 shows the results of the bending experiments. First, compressive bending was performed with a bending radius of 4 mm. When considering the simple approximation of a negligible film thickness versus the much greater substrate thickness d (OrmoComp[®] + PET), in this case 480 μ m, a nominal strain ε can be calculated by ε = d/(2r) [30]. The calculation yields 6% film strain ε . Compared to the commercial ITO on PET (60 Ω /sq. sheet resistance), the AgNW electrode presents much higher stability. After 5000 bending cycles, practically no change in the sheet resistance of the embedded electrode was observed, while the

Table 1. Summary of the properties of the developed electrodes on different substrates. The RMS column shows in parenthesis the RMS roughness of the HS (extracted from $12 \times 12 \mu m^2$ AFM images for the samples in this work). Also listed in the table are properties of electrodes from the literature, based on AgNWs, CNTs, graphene, PEDOT:PSS and combinations of these. The average transmittance, wherever not given in the source, is extracted from published spectra. The symbol '-' is used for values that are not given in the sources or are not relevant.

Samples (this work)	Embedded?	T _{av} (%)	T ₅₅₀ (%)	H _{av} (%)	$R_{\rm S}^{\rm BE}$ (Ω /sq.)	$R_{\rm S}^{\rm AE}$ (Ω /sq.)	RMS (nm)	$\Phi_{\rm av} \ (10^{-3}/\Omega)$	Φ_{550} (10 ⁻³ / Ω)
AgNWs (glass)	No	81.2	81.5	28.1	13.2	13.2	32.0 (1.5)	9.7	10.1
G2G SP	OrmoComp [®]	79.2	80.4	9.2	12.8	13.2	5.1 (1.5)	7.4	8.6
G2G IP	OrmoComp [®]	78.3	80.5	11.8	_	13.2	28.3 (1.5)	6.6	8.7
P2P IP	OrmoComp [®]	76.8	78.8	24.0		12.7	25.3 (15.0)	5.6	7.3
K2P SP	OrmoComp [®]	76.4	78.8	14.7	11.6	11.6	18.1 (13.0)	5.8	7.9
Samples (literature)									
AgNW (PI-to-PET) [19]	NOA63	74.7	79.2	_		8.3	2.3 (0.7)	6.5	11.7
CNT (on PET) [24]	No	74.2	82.7	_	150	_	8 (-)	0.34	1.0
Graphene [25] (Cu foil-to-PVC ^a)	EPDM ^b - PAni ^c	86.3	86.7		—	1700	20.1 (-)	0.14	0.14
PEDOT:PSS (on PES ^d) [26]	No	79.7	81.0	_	120		1.6 (-)	0.9	1.0
AgNWs in PEDOT:PSS (on PET) [27]	No	—	83.0		15		7.5 (-)	_	10.3
AgNWs with graphene [28] (free-standing)	PUA ^e	80.2	82.5	—	—	14	—	7.9	10.1

^aPolyvinyl chloride.

^bEthylene propylene diene monomer.

^cPolymerized polyaniline.

^dPoly(ether sulfone).

^ePolyurethane acrylate.



Figure 8. Relative resistance changes of ITO and embedded AgNW electrodes uppon compressive and tensile bending stress. R_0 is the initial electrode resistance (before the bending experiments) and R the actual resistance.

resistance of the ITO electrode increased 28 times after only 70 bending cycles. For the tensile bending test with 4 mm bending radius, the AgNW electrode showed a relative resistance increase of \sim 2 times after 5000 bending cycles, which is again drastically better than for ITO on PET, which shows catastrophic failure after few bending cycles. This resistance increase is related to the development of cracks in the polymer layer and the consequent detachment of the wires from

the embedding matrix. The effect of pressure on the AgNW electrodes (P2P) was also tested. For this, a cylinder of PDMS was casted and hardened. The cylinder was then rolled over the electrodes twice, with a force of 200 N. The experiment was repeated with forces of 300, 400 and 500 N. After each experiment, the sheet resistance was measured, and no changes were observed whatsoever.

3.7. Sputter coating of embedded AgNW films

For implementation in devices, the AgNW electrodes would have to be combined in most cases with a metal oxide interfacial layer, for example as an electron or hole transporting layer. Here, an AZO layer of 100 nm was sputtered on an embedded AgNW electrode produced through the P2P approach. Figure 9 shows the structural and optical properties of the AZO-coated AgNW electrode. The transmittance (figure 9(c)) is lower after the AZO coating (average visible transmittance drops from 76.8 to 66.2%). The haze is decreased after the AZO coating with respect to the uncoated electrode (from 24.0% to 18.7%). The decrease of the haze is attributed to the partial filling of the holes in the OrmoComp[®] layer (caused by the plasma) by the sputtered film. An AFM and SEM image of the coated electrode are shown in figures 13(a) and (b) respectively. The RMS roughness remains at the same level compared to the uncoated film but the depth of the holes is reduced, as shown in the depth profile (figure 9(a)). Also, the electrode sheet resistance is not changed after the AZO deposition.



Figure 9. (a) and (b) AFM and SEM images, respectively, of the embedded AgNW electrode (P2P IP), sputter-coated with 100 nm AZO. The inset of (a) shows the height profile of one of the holes in the polymer layer. (c) Transmittance spectra for the embedded AgNW electrode before and after coating with the AZO layer.

4. Conclusions

In conclusion, the paper presented processing routes for highperformance, embedded AgNW electrodes. These routes can be applied on glass and flexible substrates and are compatible with fast processing. Plasma curing was shown to be a gentle, but efficient and fast method to reduce the AgNW resistance to a regime relevant for electrode implementation in solar cells and optoelectronic devices. Most interestingly, it was possible to use plasma curing even in the case where the embedded wires resided on a temperature-sensitive PET substrate. This was due to the fact that the embedding UV-curable polymer acts as a thermal buffer, dissipating the generated heat, thus preventing substrate damage. As a result, embedded AgNW electrodes, transferred from polyimide-to-PET and from PETto-PET were obtained, with transparency of $\sim 80\%$ (including the substrate) and sheet resistance of \sim 13 Ω /sq., similar to electrodes transferred from glass-to-glass substrates. The roughness of the final electrode depends on the host substrate roughness and on the effect of the plasma on the embedding polymer. The induced roughness influences the optical properties by increasing light scattering. The embedded AgNW electrodes show dramatically better mechanical bending stability than ITO on PET and can be easily combined with metal oxide films for device implementation. The impact of the introduced processes concerns therefore applications where highthroughput production must be combined with sensitive, flexible substrates and ultra-thin device architectures, like OLEDs and organic- or perovskite-based photovoltaics.

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