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Mixed dimensions silver nanowires for solution processed, flexible, transparent and conducting electrodes with improved optical and physical properties

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Abstract. In this work, we present an alternative method for the spray coating of silver nanowires contact electrodes by employing a mixture of short and long nanowires. Mixed silver nanowires are found to give improve optical properties with 2-5% higher transparency for the same sheet resistance of 25 Ωsq⁻¹, when compared to silver nanowires prepared with a single geometry nanowire. The figure of merit (FoM) for the 25 Ωsq⁻¹ sheet resistance electrode was found to be highest for the mixed composition AgNWs-M1 (mixture of AgNWs-30L and AgNWs-60S) based electrodes. Furthermore, the average root mean square surface roughness (Rq) parameter by white light interferometry (WLI) are found to be lower for the mixed composition silver nanowires electrodes (Rq = 3-4 nm) when compare to the individual parent fixed dimension type silver nanowire electrodes (Rq = 6-8 nm).

Keywords: silver nanowires, transparent conducting electrodes, surface roughness

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1 Introduction

Transparent conducting electrodes (TCEs) are an essential component of many electronic devices such as organic photovoltaic (OPV), electronic displays, wearable devices, transparent heaters and touch screens.¹-³ Indium tin oxide (ITO) based TCEs are most widely used by industry and have dominated the field of photo electronic applications for the last several decades. However, due to potential future increase in ITO cost and owing to the poor stability upon bending, a search for
new materials to replace ITO is a hot current research topic for both the academic and industrial communities. The potential replacements for ITO includes conducting polymer,4 graphene,5 carbon nanotubes,6-10 copper nanowires11,12 and silver nanowires (AgNWs).2,13-15 Among these materials, AgNW based TCEs have emerged as the lead alternative because of properties such as high transparency and low sheet resistance ($R_{\text{sh}}$) close to or even better than those with ITO2,14 An advantage of silver nanowires is the simple method of their synthesis with tailor made dimensions especially by the polyol process.16,17 Moreover, AgNW based TCEs can be made highly flexible, relatively less expensive and are compatible with a roll-to-roll manufacturing process.18 The general requirements for transparent conducting electrodes consists of low $R_{\text{sh}}$, typically less than 100 $\Omega$ sq$^{-1}$ whilst maintaining high transparency (above 90% in the visible region of the spectrum).19,20 The requirement also varies with the type of application, for instance, solar cell application required optimum optical haze whereas for display application, a low haze factor is important. Optical/electrical properties of silver nanowires based transparent electrodes depends on a number of factors including types of AgNWs,14 deposition process3 and post treatment of samples such as mechanical pressing21,22 fast sintering23 and thermal annealing24. Typical dimensions of silver nanowires are of mean diameter ($d_{\text{mean}}$) of 30-200 nm and mean length ($l_{\text{mean}}$) of 20-400 $\mu$m. There are a number of studies in the literature of the physical properties of transparent electrodes prepared by utilizing particular types of silver nanowires, for examples, silver nanowires with dimensions of nanowires of either thinner or thicker mean diameter14 and/or shorter or longer mean length.26 Currently, the best performance was obtained by Preston et al, who reported 13 $\Omega$ sq$^{-1}$ with 91% transparency in the visible region using post-processing5. The best performance achieved without post-processing was achieved by Andrés et al who used spray coating of ultra-long nanowires to achieve 13 $\Omega$ sq$^{-1}$ having 91%.14 Despite this impressive
performance, the RMS roughness, $R_Q$, of the samples was measured at 14nm and maximum peak to valley, $P_V$ (nm) was measured at 90nm, which is typical for AgNW films.

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http://pubs.rsc.org/en/content/articlelanding/2014/tc/c3tc31726a#!divAbstract

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In this work, we focus our attention on the physical properties of electrodes prepared by using a mixed composition of two different geometries of silver nanowires. The mixed silver nanowires were used as a precursor dispersion in the solvent (ethanol) for coating flexible transparent substrates by employing the simple and cost effective air spray coating technique.

Three types of silver nanowires were used for the study namely thin-short nanowire; AgNWs-60S ($d_{\text{mean}} = 60 \text{ nm, } l_{\text{mean}} = 20-30 \mu \text{m}$), thin-long nanowire; AgNWs-30L ($d_{\text{mean}} = 30 \text{ nm, } l_{\text{mean}} = 100-200 \mu \text{m}$) and thick-long nanowires; AgNWs-100L ($d_{\text{mean}} = 100 \text{ nm, } l_{\text{mean}} = 100-200 \mu \text{m}$). The shorter nanowires are advantageous for achieving high conducting networks at low concentration and the longer nanowires provide higher conductivity performance. The combined advantages of short and long nanowire were exploited by coating them together. Two mixed silver nanowires composition were prepared, one consisted of the type: thin-short nanowires (AgNWs-60S) with thin-long nanowires (AgNWs-30L), denoted as ‘AgNWs-M1’, and another one consist of the type: thin-short nanowires (AgNWs-60S) with thick-long nanowires (AgNWs-100L), denoted as AgNWs-M2. The results show a moderate improvement in the electrical/optical performance and in the surface roughness.
2 Experimental

2.1 Materials

Silver nanowires of the type AgNWs-60S, AgNWs-30L and AgNWs-100L (silver purity 99.5%, concentration 20 mg/mL in ethanol) were purchased from ACS materials. All materials were diluted with ethanol to the concentration of 0.5 mg/mL prior to spray coating. Flexible transparent substrates of planarised polyethylene-napthalate (PEN) with thickness 125 µm were used for this work. PEN was spin coated with poly methyl methacrylate (PMMA) (molecular weight 495K, 8% solution in anisole) purchased from Microchem. For this work, a PMMA buffer layer was employed to reduce the surface roughness of the substrates. HPLC grade isopropyl alcohol (IPA), ethanol (EtOH) and acetone were purchased from Sigma-Aldrich and used as such.

2.2 AgNW film preparation

Mixed composite silver nanowires AgNWs-M1 dispersion was prepared by mixing AgNW-60S and AgNWs-30L as supplied in 1:1 volume by volume (V/V) ratios and then diluted with ethanol to 0.5 mg/mL final concentration. After some initial tests, the ratio of 1:1 was found to be the optimum, so all benchmarking of performances were done at this ratio. Similarly, AgNWs-M2 was prepared with AgNWs-60S and AgNWs-100L. Silver nanowires dispersions in ethanol of each type (0.5 mg/mL) were sonicated for 5 minutes to minimized aggregates before air spray coating. Ultrasonication and was used prior to spray coating to ensure that the AgNWs were dispersed in the suspension prior to spray coating. A short duration was used (<5 minutes) at low power in order to ensure no breakage of AgNWs. For air spray coating, a back pressure of air kept at 1 bar using a piston type oil-less airbrush compressor was used for uniform gas/liquid flow rate (0.2 ml/min) at the nozzle. The spray nozzle diameter was 0.5 mm and the fluid cup capacity was
7 cm$^3$ with the air compressor. Substrates PEN of area 15 mm $\times$ 18 mm were thoroughly cleaned with DI water, acetone and IPA followed by drying with a jet flow of nitrogen. PMMA was spin coated on cleaned PEN substrates at 2500 rpm for 20 seconds followed by annealed at 100 °C for one minute. The substrates were placed on the substrate heater at 60 °C and the silver nanowires dispersion was air sprayed onto the heated substrates to evaporate the EtOH. The deposition time for preparing electrodes with $R_{sh} \approx 25$ Ω sq$^{-1}$ was found to be approximately 5 mins ±30 seconds. However, using mixed geometry electrodes, the deposition time was approximately 50% lower. This represents a significant advantage for future scale up of the technology.

### 2.3 Physical properties characterization

Transmittance spectra of silver nanowire-polymer composite electrode were recorded in the region 350 nm to 1000 nm with PEN as reference using HR4000CG-UV-NIR high resolution spectrometer (Ocean optics, Inc. USA). Sheet resistance ($R_{sh}$) was measured by four probe setup (A & M. FELL Ltd., England). Surface roughness was estimated by white light interferometer measurement (WLI) using Micro XAM surface mapping microscope (KLA tensor, USA). Scanning electron microscopes (SEM) images were obtained using a Leo 1455VP SEM operating at 30 kV with 10 pA beam current at typical magnifications of x10,000.

### 3 Results and Discussion

**Fig.1a** depicts a schematic diagram for the preparation of the silver nanowires-polymer composite TCEs technique developed in this work. PMMA was spin coated on PEN followed by annealing at 100 °C for 1 min to give about 10 μm thick planarization layer. After cooling, the substrate was
placed on hot plate at 60 °C onto which silver nanowire dispersion was spray coated to produce the TCE.

![Diagram](image)

**Fig. 1** a) Schematic diagram of spray coat technique for a silver nanowires-polymer composite electrode preparation b) Image of spray coated silver nanowire on PMMA coated PEN substrate based TCE develop in this work.

For illustration, a sample silver nanowire TCE prepared is showed in **fig. 1b**, displaying the conducting surface area of 12 mm x 15 mm on the substrate.

SEM images of the conducting surface of silver nanowires electrodes prepared from fixed dimension type silver nanowires AgNWs-30L and AgNWs-60S is shown in **fig. 2a** and **fig. 2b** while a mixed composition type AgNWs-M2 is shown in **fig. 2c**. The inter mixing of short-thin nanowires AgNWs-60S with long-thick nanowires AgNWs-100L can be clearly seen from **fig. 2c**, which provides more even surface coverage and as a result of fewer aggregations at nanowire junctions.
3.1 Optical properties

The transmittance spectra of TCE prepared by the different type silver nanowires dispersion with a similar $R_{sh}$ of 25±1 Ω sq$^{-1}$ are represented in fig. 3. This value of $R_{sh}$ was chosen as it represents a sizeable improvement over ITO on a flexible substrate and is comparable to the value of ITO often used on glass substrates. It has been reported in the literature that for a given $R_{sh}$, longer silver nanowires have greater transmittance than shorter nanowires and also, to some extent, thicker nanowires greater than thinner ones.\textsuperscript{14, 26, 28} It can be seen from fig. 3 that longer silver nanowires electrodes (AgNWs-100L, AgNWs-30L) shows 5-10% transmittance improvement in the visible region of spectrum compare to the shorter nanowires AgNWs-60S. In addition, the thin-long nanowires (AgWS-30L) electrode was found to show higher transmittance than the thick-long nanowires (AgNWs-100L) electrode with same $R_{sh}$ of 25 Ω sq$^{-1}$ (Fig. 3). The mixed composition silver nanowires AgNWs-M1 electrode shows similar overall transmittance values to the longer nanowire component AgNWs-30L, but with moderate improvement in the region 400 nm to 550 nm of visible spectrum. This could be a significant result for academics and industrialists working with blue OLEDs, who wish to maximize the light output in this region. Likewise, the AgNWs-M2 electrode displayed better transmittance compared to its parent silver nanowires
Due to the reduced aggregation and better percolation of the mixed AgNW films, the transparency is greater for the same sheet resistance. Due to the reduced aggregation and better percolation, the overall silver content of the film is lower. For the samples shown in table 2, the silver content is calculated at 2 mg/cm² for mixed, which compares to 3 mg/cm² four long AgNWs and for 4 mg/cm² short AgNWs.

Table 2. Silver content for mixed (AgNWs-M1), long (AgNWs-30L) and short (AgNWs-60S) electrodes.

Commented [L1]: Estimate to 1 or 2 decimal points
To quantify the optical and electrical properties a figure of merit (FoM) is commonly defined by the community given in equation (2), where $R_{sh}$ is the sheet resistance and $T$ is the transmittance.\(^2\)

$$FoM = \frac{188.5}{R_{sh}(\sqrt{T} - 1)}$$

One of the highest FoM value reported in literature is 338 for silver nanowires electrodes with a $R_{sh}$ of 20 $\Omega$ sq\(^{-1}\) electrodes and transparency at 550 nm of 94.7\%, prepared by spray deposition of silver nanowires.\(^1\) By comparison, for commercial ITO films on PET used in our laboratory, the FoM is around 58 ($R_{sh} = 60$ $\Omega$ sq\(^{-1}\), transparency = 90\%, source Sigma Aldrich, UK).

<table>
<thead>
<tr>
<th>Type</th>
<th>$R_{d}$ ((\Omega$ sq(^{-1})) (Best)</th>
<th>$R_{d}$ ((\Omega$ sq(^{-1})) (Average)</th>
<th>$R_{m}$ ((\Omega$ sq(^{-1})) (Best)</th>
<th>$R_{m}$ ((\Omega$ sq(^{-1})) (STDV)</th>
<th>$T$ (%) (Best)</th>
<th>$T$ (%) (Average)</th>
<th>$T$ (%) (STDV)</th>
<th>FoM (Best)</th>
<th>FoM (Average)</th>
<th>Haze (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgNWs-M1</td>
<td>25.7</td>
<td>25.9</td>
<td>0.2</td>
<td>90.2</td>
<td>89.8</td>
<td>0.5</td>
<td>138.6</td>
<td>131.6</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>AgNWs-M2</td>
<td>25.1</td>
<td>25.4</td>
<td>0.4</td>
<td>87.1</td>
<td>86.4</td>
<td>0.9</td>
<td>105.0</td>
<td>97.8</td>
<td>0.9</td>
<td></td>
</tr>
</tbody>
</table>

Commented [L2]: Can you add 2 decimal points
Table 3. Average (from 5), best and standard deviation of sheet resistance and transmittance of
(AgNWs-M2), short (AgNWs-60S) and long (AgNWs-30L) electrodes

<table>
<thead>
<tr>
<th></th>
<th>Sheet resistance (Ω sq⁻¹)</th>
<th>Transmittance (%T)</th>
<th>FoM</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgNWs-60S</td>
<td>25.6</td>
<td>26.0</td>
<td>0.8</td>
</tr>
<tr>
<td>AgNWs-30L</td>
<td>25.3</td>
<td>25.8</td>
<td>0.7</td>
</tr>
<tr>
<td>AgNWs-100L</td>
<td>25.2</td>
<td>25.4</td>
<td>0.3</td>
</tr>
</tbody>
</table>

The FoM values calculated for various silver nanowires electrodes of 25 Ω sq⁻¹ Rₚ with transmittance (%T) at 550 nm is plotted in fig. 4. Among the different silver nanowire type electrodes studied, the mixed composition silver nanowires electrodes AgNWs-M1 (FoM = 138.6, Fig. 4) has the highest FoM value while lowest for short-thin nanowires AgNWs-60S (FoM = 85.1, Fig. 4). Mixed composition silver nanowires electrodes (AgNWs-M1, AgNWs-M2) optical performance in terms of FoM is found higher compare to the parent silver nanowires electrodes (AgNWs-30L, AgNWs-60S, AgNWs-100L) Rₚ of 25 Ω sq⁻¹. In table 3, the best and average performances of the three most promising combinations are shown i.e. (AgNWs-M2), short (AgNWs-60S) and long (AgNWs-30L). When considering the FoM, the mixed AgNW films show around 10-15% improvement over the best obtained results from an AgNW film prepared from a single nanowire geometry (AgNWs-30L). In addition, the mixed AgNW film shows 30-40% improvement over AgNW films prepared with short nanowires. The results support the conclusion that short nanowires do not provide good percolating networks and therefore exhibit poorer performance than longer nanowires. However, they could still have industrial applications, should they be used in combination with longer nanowires.
Fig. 4 Best and average figure of merit (FoM) of silver nanowires electrodes with sheet resistance of 25 Ωsq⁻¹.

3.2 Roughness

The surface roughness of the conductive surface of the AgNW electrodes was examined by white light interferometry (WLI). Fig. 5 shows the topological images of AgNWs-30L, AgNWs-60S and AgNWs-M2 electrodes, respectively. The surface roughness is an important factor for optimum performance of thin-film electronic devices such as OLEDs and OPVs. These devices tend to have thin interlayers and active layers and high surface roughness can lead to electrical shorts between the anode and cathode. One disadvantage of metallic nanowire electrodes has been the high surface roughness, which is primarily due to junctions formed where two or more nanowires are stacked on top of one another, creating large local height spikes. As a result of the local height spikes, the peak-to-valley (PV) values can reach up to three times the value of the diameter of the
nanowires.\textsuperscript{22,30,31} This effect is more pronounced when metallic nanowires are deposited on rigid surfaces such as glass, for instance, peak-to-valley value above 500 nm as determined by atomic force microscopic (AFM) measurements.\textsuperscript{30} In order to reduce the surface roughness of silver nanowires electrode several approaches has been reported including mechanical pressing\textsuperscript{22,32-34} and peel off using cross linked polymers.\textsuperscript{25-27}.

Table 4 shows the surface roughness of various types of nanowires electrodes, (AgNW-30L, AgNW-60S, AgNWs-100L, AgNWs-M1, AgNWs-M2) by WLI measurement over large area of 278 µm x 207 µm. In this work, the surface roughness was calculated from an average of five different samples and the average root mean square roughness ($R_q$) and maximum peak-to-valley (P-V) roughness was calculated.

For all samples, the highest average P-V roughness was obtained for the short nanowires (PV = 87.2nm), although the surface roughness is overall much lower than other reports. The low peak-to-valley roughness was attributed to the PMMA layer, which possibly facilitate the embedding of nanowires, thereby smoothening the surface.
The root mean square roughness ($R_q$) for the mixed composition silver nanowires electrodes (AgNWs-M1, AgNWs-M2) are found in the range 3-4 nm while for the fixed dimension type nanowires electrodes (AgNWs-30L, AgNWs-60S, AgNW-100L) the values are in the range 6-8 nm. This indicates that the mixed composition silver nanowires electrodes possess a somewhat smoother surface compared to the fixed dimension type silver nanowires electrodes, attributed due to a more evenly distributed surface coverage (see figure 2). For illustration, topological images of a short, a long and a mixed composition type nanowires electrodes are shown in fig. 5. It can be seen by visual inspection of fig.5 that AgNWs-M2 ($R_q = 3.7$ nm, PV = 79.6 nm), based electrodes topological image is smoother compare to AgNWs-30L ($R_q = 5.5$ nm, PV = 77.3 nm) and AgNW-60S ($R_q = 7.9$ nm, PV = 81.7 nm) electrodes. The high surface roughness of AgNWs is a result of
multiple AgNWs overlapping upon one another, or by aggregation of multiple nanowires. The procedure developed in this paper involves depositing the long AgNWs initially. A low volume of material is used during this deposition, so the long AgNWs are dispersed quite evenly across a sample and the amount of overlap is relatively low. Long AgNWs tend to form more aggregates during the spray coating deposition, so by minimising the volume deposited, the concentration of aggregates are reduced, thus reducing the overall surface roughness. Subsequently the short AgNWs are deposited. Short AgNWs do not tend to form large aggregates. Therefore, these act as an ‘in-fill’ into the long AgNW mesh, providing the percolation and ensuring no major aggregation points are formed.

Table 4. Surface roughness parameters of mixed (AgNWs-M2), short (AgNWs-60S) and long (AgNWs-30L) electrodes

<table>
<thead>
<tr>
<th>Type</th>
<th>Rq (nm) average</th>
<th>Rq (nm) STDV</th>
<th>Pv (nm) average</th>
<th>Pv (nm) STDV</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgNWs-M1</td>
<td>3.2</td>
<td>0.2</td>
<td>75.2</td>
<td>2.1</td>
</tr>
<tr>
<td>AgNWs-M2</td>
<td>4.1</td>
<td>0.4</td>
<td>80.9</td>
<td>2.9</td>
</tr>
<tr>
<td>AgNWs-60S</td>
<td>8.5</td>
<td>1.2</td>
<td>87.2</td>
<td>3.9</td>
</tr>
<tr>
<td>AgNWs-30L</td>
<td>6.2</td>
<td>0.6</td>
<td>85.9</td>
<td>3.8</td>
</tr>
</tbody>
</table>
4. Conclusions

We have demonstrated an alternative approach for spray coating AgNW electrodes onto flexible substrates by employing AgNW with mixed geometries. The advantage of mixed composition silver nanowires, comprising of short nanowires length ($l_{\text{mean}} = 25 \, \mu\text{m}$) with long nanowire ($l_{\text{mean}} = 150 \, \mu\text{m}$), include shorter spray coat deposition time, better electrical/optical properties (as evidenced by the FoM values) and lower surface roughness electrodes. We believe that the simple technique demonstrated in this work will be effective in saving time and cost for large-scale production of silver nanowires based transparent conducting electrodes and helpful for further development of metallic nanowires based electrodes in general. One combination which has not been investigated in this paper is the combination of AgNWs60S, AgNWs30L and AgNWs100L. This could provide an alternative strategy for improving the performance further. However, the preparation time will increase by ~60%, due to the application of an additional long AgNW layer, which is unlikely to be suitable for large-scale production of AgNW films.
Acknowledgments

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