All-Solution-Processed Micro/Nanowires with Electroplate Welding as Transparent Conducting Electrodes

Chaobin Yang, Juan M. Merlo, Luke A. D’Imperio, Aaron H. Rose, Yitzi M. Calm, Bing Han, Jinwei Gao, Guofu Zhou, Michael J. Burns, Krzysztof Kempa, and Michael J. Naughton*

An all-solution-processed transparent conductive electrode with sheet resistance one order of magnitude smaller than conventional nanowire-based transparent conductors has been developed. This is achieved by integrating all-solution produced microwires with a nanowire solution and electroplating and electrowelding. Advantages of the resulting transparent conductor are indium-free, vacuum-free, and lithographic-facility-free, and metallic-mask-free, with small domain size ($\approx 10 \mu m^2$), low sheet resistance ($R_s < 1 \Omega \square^{-1}$), high optical transmittance ($T > 80\%$), mechanical flexibility, and scalability, thus making it an excellent replacement for ITO.

Transparent conductive electrodes (TCEs), which combine high electrical conductivity with high optical transmittance, play an essential role in numerous modern devices, such as thin film solar cells, flat panel displays, touch screen displays, smart windows, energy harvesters, transparent memory, electromagnetic shielding, heaters, sensors, supercapacitors, and organic light-emitting diodes (OLEDs). Among all TCEs, the most successful one is tin-doped indium oxide (ITO). ITO has optical transmittance higher than 80% in the visible range and sheet resistance ($R_s < 1 \Omega \square^{-1}$), thus making it an excellent replacement for ITO.

There are several approaches in the literature for preparing continuous metallic networks that do not require such a welding step: (i) lithographically made patterns followed by vacuum-based metal deposition followed by solution-based metal deposition; and (iii) random self-cracking films as mask followed by vacuum-based metal deposition. It is necessary to mention, however, that self-cracking materials used at room temperature and pressure reported to date do not survive solution-based metal deposition. Suh et al. reported $Si_3N_4$ can crack with tensile stress in $Si_3N_4/Si$ systems but (low pressure and high temperature) chemical vapor deposition is used for $Si_3N_4$ deposition and TCEs made by this method must be transferred to flexible substrates, because Si is not transparent. To eliminate both costly lithographic facilities and costly vacuum-based metal deposition,

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some of the current authors previously reported a maskless photolithographic process called crackle photolithography (CPL)\cite{46,47} by replacing a conventional metallic mask with UV-stable self-cracking films. Random photoresist patterns produced by CPL survive solution-based metal deposition and CPL-based TCEs are fully solution-processed and do not require hard lithographic or mask writing facilities.\cite{47} Although continuous metal networks can achieve extremely low sheet resistance (\(<0.1\ \Omega \ \square^{-1}\)), lower than MNWs by electroplating\cite{47,48} the domain sizes in all the aforementioned continuous metallic network examples are limited by mask domain size or crackle size, and therefore are larger than for MNWs. For this reason, these metallic networks may be difficult to apply to display products, where there is a drive toward smaller pixel dimensions.

Here, we report the integration of Ag nanowires (AgNWs) with microscale continuous Ag networks made by CPL\cite{46,47} This combination maintains the qualities of both MNWs and continuous metallic networks, and results in scalable film structures that are flexible, indium-free, vacuum-free, lithographic-facility-free, and metallic-mask-free, with small domain size and high electrical conductivity. Here, silver is chosen because of its chemical stability and excellent conductivity. One can either spin coat Ag nanowires first (NF), then fabricate a microwire network, or reverse the process by fabricating a microwire network first (MF) and then depositing nanowires. One can also solder nanowires to microwires by electrowelding/plating to improve mechanical contact and further lower sheet resistance.

**Results and Discussion:** Figure 1 is a schematic of the two different approaches to obtain micro/nanowire TCEs. Panel 1 shows the NF process. A AgNW/isopropyl alcohol (IPA) solution is first spin coated onto a glass substrate and annealed in air at 200 °C. Annealing can provide better contact between AgNWs, and thus lower contact resistance.\cite{43} Next, microwires are produced via CPL (Figure 1(1b–1e)).\cite{46,47} Bis(trimethylsilyl) amine (HMDS) and Shipley S1805 photoresist are spin coated and soft baked to evaporate photoresist solvent. A self-cracking material solution (e.g., nail polish/water solution\cite{43,46,47}) is then spin coated which, upon drying in air at room temperature, self-cracks. TiO₂ nanoparticles,\cite{122} CA600 (an acrylic resin water-based dispersion),\cite{22} CYTOP\cite{23} and albumin\cite{48} are also known to crack spontaneously upon drying. To our knowledge, however, none of these self-cracking materials can survive conventional wet processes, so many previous works required vacuum-based metal deposition. Nail polish is particularly useful as a cracking template in CPL because it can block UV light, which makes it an appropriate photoresist mask and, therefore, CPL can avoid the fabrication of a conventional metal mask. After 2 s exposure to 405 nm UV light, only the photoresist not covered by the nail polish gets exposed. Exposed photoresist and nail polish mask will subsequently dissolve in the water-based photoresist developer MF319 and leave randomly cracked photoresist patterns over AgNW-coated glass (Figure 1(1c)). These photoresist patterns are transferred from nail polish; however, they will survive both acidic and alkaline solutions during conventional wet processes, and so can be used as masks for subsequent buffered oxide etch (BOE) and electroless Ag deposition processes. BOE will create \(~1\ \mu m\) deep channels. The purpose of BOE here is to activate the glass surface by creating silanol groups,\cite{49} thus increasing adhesion of electrolessly-deposited Ag. Using Tollen’s electroless reaction,\cite{50} about 100 nm thick Ag is deposited onto all surfaces. Using lift-off in acetone, the photoresist together with unwanted silver are removed, leaving the Ag microwire network. If desired, additional Ag can be electroplated to increase contact between micro/nanowires and as a result the sheet resistance of the whole sample can be further decreased.

Panel 2 in Figure 1 is the MF process. Microwires are made by the same CPL process above: spin coat and soft bake photoresist, spin coat nail polish which then cracks, UV expose and develop photoresist, BOE etch glass, electrolessly deposit Ag and lift off. Different from the NF process, one extra electroplating step can be done to increase the thickness of microwires before spin coating the nanowires. The electroplated Ag will fill the etched channels first without significantly increasing the microwires’ width, thus making the sheet resistance decrease faster than the transmittance decrease. After spin coating Ag nanowires, a second electroplating can also be done for micro/nanowire welding.

Figure 2(a) and (b) show optical images of TCEs on glass substrates made by the NF and MF methods. Corresponding SEM images by the two methods are shown in (c) and (d). One can clearly see nanowires cover the open space between the microwires in both methods. As a result, domain size drops significantly, to \(~10\ \mu m^2\) in micro/nanowires samples. In Figure 2f, a nanowire junction after electroplating (see Figure 1(1f)) is compared with junctions before electroplating...
Electroplating increases the width of the nanowires and makes two wires embedded into each other, rather than merely touching. This benefits the sheet resistance and only slightly decreases the transmittance. Figure 2g is a photograph of a 100 mm diameter glass substrate coated by micro/nanowires, placed in front of a building, demonstrating both the high transparency and the wafer-scalability of our process.

Electroplating is used in both the NF and MF methods for micro/nanowire welding (see Figure 1(1f and 2f)). Figure S1, Supporting Information demonstrates how the transmittance and sheet resistance of micro/nanowires change by varying electroplate welding time. Transmittance is measured at 550 nm and averaged over five different spots. Both transmittance and sheet resistance are scaled to the same sample before electroplate welding. Electroplate welding decreases transmittance and sheet resistance because micro/nanowire width increases. It is interesting to note that in the first 20 s, sheet resistance drops fastest. The reason is that nanowire junctions change from “touching” to “embedded” in this timeframe, as shown in Figure 2f. Because longer electroplating time can decrease transmittance and the decrease of sheet resistance saturates after 20 s, we chose 20 s for the electroplate welding time for both NF and MF micro/nanowires.

Particularly for the MF method, electroplating is used to increase Ag microwire thickness (Figure 1(2d)). Previous work has used electroplating to increase the conductivity of TCEs and has achieved good results,[48] but there remains one drawback: electroplated Ag grows in all directions, so the increasing widths of Ag metallic wires will decrease transmittance. The CPL process solves this problem by electroplating the silver within the etched channels, which largely constrain the microwire widths to the channel widths.[46,47] Thus, one can use relative longer electroplating time (e.g., 50 s) to increase the microwire thickness and reduce the sheet resistance by one order of magnitude without appreciably changing optical transmittance.

The domain size of the nail polish crack pattern can be controlled by spin speeds of the nail polish solution. In Figure S2, Supporting Information, we show optical microscope images of micro/nanowires made by the MF method using spin speeds from 2000 to 5000 rpm. The performance of samples made by all speeds is shown in Figure 3a, indicated by different colors. Each color has four points and from right to left they are: before the first electroplating (Figure 1(2c)); after the first electroplating (Figure 1(2d)); after spin coating
Ag nanowires (i.e., before the second electroplating, Figure 1(2e)); after the second electroplating (Figure 1(2f)). First, one can see lower nail polish spin speed yields larger domain sizes and lower microwire metal coverage, and thus higher transmittance, which is consistent with our previous CPL work.[47] Second, among all steps adding Ag to samples, the first electroplating, which the NF process does not have, decreases sheet resistance the most and this electroplating step turns out to be the reason that MF samples outperform NF samples.

A figure of merit (FoM) is often used to compare the performance of TCEs prepared by various methods. Haacke[51] proposed to use $\phi = T^{10}/R_s$, which puts heavy weight on transmittance $T$ and has units of $\Omega^{-1}$. Another popular one is the ratio of electrical conductance to optical conductance ($F_{TCE} = \sigma_{el}/\sigma_{opt}$) which can be written as $F_{TCE} = Z_0/[2R_s(T^{-1/2} - 1)]$, where $Z_0 = \sqrt{\mu_0}/\varepsilon \approx 377$ $\Omega$ is the impedance of free space, $R_s$ is sheet resistance and $T$ is transmittance at 550 nm.[30,41,52,53] We use both $\phi$ and $F_{TCE}$ here to compare our result in Figure 3b with various AgNWs from other work. Our NF results shown as red circles ($F_{TCE}$ up to 404, $\phi = 0.03$) are slightly better than almost all previous works, including those that deposit AgNWs by drop coating (crosses, $F_{TCE}$ = 211, $\phi = 0.02$)[19] and by Mayer rod coating (down triangles, $F_{TCE}$ = 100, $\phi = 0.0046$).[28] They are also superior to those that weld AgNWs by solution methods (mechanical pressing: up triangles, $F_{TCE}$ = 186, $\phi = 0.012$[27]; thermal heating: left triangles, $F_{TCE}$ = 223, $\phi = 0.02$[35]) and even lithography made nanogrids (right triangles, $F_{TCE}$ = 164, $\phi = 0.016$)[41]. The FoM of our MF samples (red squares, $F_{TCE}$ up to 2016, $\phi = 0.153$) is also higher than that of a micro/nanowires process made by photolithography (diamonds, $F_{TCE}$ = 579, $\phi = 0.026$).[54] For reference, commercial ITO (blue star) has an $F_{TCE}$ = 350 and $\phi = 0.03$.

Figure 3. TCEs made by MF and NF, and their performance. a) $T$ and $R_s$ of MF samples made by spin coating nail polish solution at speeds from 2000 to 5000 rpm. For each set of data, points from right to left represent performance before first electroplating (Figure 1(2c)), after first electroplating (Figure 1(2d)), after spin coating AgNWs (Figure 1(2e)) and after second electroplating (Figure 1(2f)). b) $T$ versus $R_s$ for TCEs made by the current NF (circles) and MF (squares) methods. Results from other silver nanowire approaches, as well as commercial ITO (star), are included for comparison.

Figure 4. Sheet resistance of MF sample measured while bending. a) $R_s$ over the first 1000 bending cycles, scaled to initial, unbent value. Each point is an average from 50 bending cycles divided by sheet resistance before bending. b) Scaled $R_s$ versus inverse radius of curvature for two bending cycles. Inset: Scaled $R_s$ during first six bending cycles.
Many applications of TCEs require mechanical flexibility. Our micro/nanowires can be transferred to flexible substrates, such as polyethylene terephthalate (PET). Figure 4 shows results from bending tests of the MF micro/nanowires on PET substrates. Figure 4a shows how sheet resistance changes in the first 1000 bending cycles. Each point in the figure is the average of the measured sheet resistance data over 50 cycles, scaled to the initial, unbent value $R_s$. After 1000 of these $\approx 90$ degree bends, the resistance was about 30% higher than the initial value, indicating some chronic changes to the network. Figure 4b shows how sheet resistance changes in each cycle, wherein the scaled $R_s$ increases by up to 300% at maximum bend but, at least for these first few bends (inset), largely recovers when unbent. We plot the data in Figure 4b against radius of curvature, indicating the ability of these flexible films to be bent to a few centimeters radius. The data in Figure 4 were measured by the 4-probe van der Pauw method.

In conclusion, we have demonstrated two variants of an all-solution method to produce Ag micro/nanowire films as transparent conductors. By integrating crinkle photolithography-based microwires with nanowires and electroplating welding, we obtain transparent conductors with $R_s < 1 \Omega \square^{-1}$, $T > 80\%$, and domain size $\approx 10 \mu m^2$. We also showed that samples can be transferred to flexible substrates, making a possible cost-effective candidate for flexible applications. Future effort will be devoted to more fully characterizing the details of the structural changes associated with flexing the films, toward minimizing such resistance changes.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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