High conductive and scalable Ag nanowires flexible transparent electrode by nanowelding with physical methods

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Abstract. Transparent electrodes (TEs) are very important for electronic devices. At present, ITO is gaining the largest market share but will be reduced. Ag nanowires (AgNWs) TEs is acknowledged as one of the most potential alternative to ITO. However, AgNWs TEs still have electrical problems because of the low contact between the AgNWs. In this paper, we report three physics methods to increase the conductivity of AgNWs TEs by nanowelding the contact of nanowires. For heat-resistant materials, 200 °C heat-nanowelding can help to reduce the sheet resistance by 96.7%. For pressure resistant materials, 20 MPa pressure-nanowelding can help to increase the conductivity by 98.7%. And the transmittance (>90%) remains constant during the above process. Yet, both of these methods cannot improve the adhesion between nanowires and the substrates. Luckily, tight adhesion can be obtained by overcoating a PEDOT: PSS layer on AgNWs film which can reduce the sheet resistance by 87.8%. This means that things are usually not perfect, and they have their own advantages and lay the foundation for the popularization and application of AgNWs TEs. In a word, these three nano-welding methods are all suit for manufacture on a large scale for high conductive AgNWs TEs.

1. Introduction
By 2019, transparent electrode (TE) market will reach $4.6 billion. That’s because TEs are the essential components to a wide variety of electronic devices, such as transparent heaters, liquid crystal displays, organic light emitting diodes (OLEDs), touch screens, organic photovoltaics (OPVs), microchips, and smart windows.1-4 And Indium tin oxide (ITO) is the most wildly used TE that account for 93 % of the market.5 However, there are many problems which limit its further development. Due to the vapor-phase coating processes, the cost of ITO (10 Ω/sq.) is $ 26 m−2 which is correspondingly high.6 And we can see yellow for low-sheet resistance (< 60 Ω/sq.) ITO. In addition, the cost of indium is $ 600 kg−1 which is a little high because of the low abundance (0.05 ppm).7 What’s more, ITO would not work on flexible devices in principle. For these reasons, the search for alternatives to ITO is motivated. Professional assessment that China will become the largest winner of transparent electrodes. That’s because Chinese government controls the supply chain of indium/ITO, on the other hand, China will be the main consumer of TEs. Obviously, the ultimate market opportunity for alternative TEs is in fully flexible devices.

So far, the alternatives include Transparent Conduct oxides (TCOs), conducting polymers, carbon nanotube (CNT), graphene, and metal nanowires.8-11 It seems that the closer approach to ITO, the more likely to be recognized as a substitute. Unfortunately, all TCOs failed when encountering a
flexible device. At present the commonly used conducting polymers including Poly (3, 4-ethylenedioxythiophene) poly (styrenesulfonate) (PEDOT: PSS) and similar polythiophenes which performance is not really good (90 % 100 Ω/sq.). Conducting polymers have been widely used for anti-electrostatic layers, and PEDOT: PSS has been used as an alternatives in commercial products. For years, CNTs has received a high degree of attention. In many ways, the performance of CNT is not as good as ITO, and it needs to be improved. Due to the large contact resistance ($R_c$) of CNTs, the sheet resistance ($R_{sh}$) is 400 Ω/sq. at 90 % transmittance. But if exfoliated/doped with chlorosulfonic superacid, the $R_{sh}$ will be 60 Ω/sq. at 90.9 % transmittance which is still not good enough. Now, graphene is getting the most attention and considered to be the ultimate win because of its potential low cost. Graphene based on chemical vapor deposition (CVD) process has excellent performance but is not practical for production. And the graphene based on solution-phase coating is relatively poor performance (80 % 3 kΩ/sq.). There is still a long way before graphene really replaces ITO. The performance of metal grids fabricated by the nanopatterned method is better than ITO (90 % 0.8 kΩ/sq.). But nanopatterned method will lead to additional cost and lower yields. Fortunately, metal nanowires can meet the conditions of alternatives. At present, metal nanowires include gold (Au), copper (Cu), and silver (Ag) nanowires. As we all know Au is too expensive and Cu is 6 % less conductive than silver. Furthermore, Cu is oxidized quickly than Ag at ambient conditions. The performance of Ag nanowires (AgNWs) TE is even better than ITO (95 % 20 kΩ/sq.). In a word, AgNWs TE is acknowledged as the proverbial "low-hanging fruit" for potential alternative to ITO.

However, AgNWs TEs still have electrical problems because of the low contact between the AgNWs. As the experimental results, $R_c$ is the main source of $R_{sh}$. There are many methods to reduce $R_c$, such as laser nano-welding, graphene coating, chemical annealing, plasmonic welding, deposition of Au, TiO$_2$ or ZnO particles. Lee et al. have demonstrated that chemical annealing can be applied to the roll-to-roll production.

In this work, we report three physics methods to increase the conductivity of AgNWs TEs by nanowelding the contact of nanowires for high conductive AgNWs TEs. First of all, heat-nanowelding is a simple and effective way to reduce the film resistance. For heat-resistant materials, 200 °C heat-nanowelding can help to reduce the sheet resistance by 96.7% while the transmittance increases slightly to 92%. Secondly, pressure-nanowelding is an extremely effective way to even form the perfect contact at the junction. For pressure resistant materials, 20MPa pressure-nanowelding can help to increase the conductivity by 98.7%. And the transmittance remains 93% which is good enough for most of the devices. Yet, both of these methods cannot improve the adhesion between nanowires and the substrates. Luckily, tight adhesion can be obtained by overcoating a PEDOT: PSS layer on AgNWs film which can reduce the sheet resistance by 87.8%. Unsatisfactorily, PEDOT-nanowelding will cause a 10% reduction in transmittance. In a word, things are usually not perfect. This means that things are usually not perfect, and they have their own advantages and lay the foundation for the popularization and application of AgNWs TEs. In a word, these three nano-welding methods are all suit for manufacture on a large scale for high conductive AgNWs TEs.

2. Experiments

2.1. Formation of transparent and conductive film using colloid of Ag nanowires

Colloid of Ag nanowires was first prepared by dispersing the purified Ag nanowires into isopropanol solution with a concentration of 10 mg/mL. After ultrasonication for 2 min, the colloid was ready for film formation by spin-coating or doctor-blading. Substrates of sodium-line glass (SLG) or flexible poly (ethylene terephthalate) (PET) were then cleaned by sequential ultrasonication in acetone, ethanol and deionized water for 30 min, respectively. After cleaning, substrates were submitted to O$_2$ plasma treating to make the surface hydrophilic. Colloid was immediately spun or rolled on treated substrates to form a thin film. After drying, the film was heated in air at 150-200°C for 20 min and cooled naturally. To enhance the contact at the junction, pressure of 20 MPa was applied on Ag film between underlying PET substrate and a clean but hydrophobic PET. Tight adhesion of Ag nanowires on
underlying substrate was realized by overcoating a PEDOT layer on Ag film. Overcoating was realized by spinning or rolling isopropanol solution of PEDOT (PEDOT:isopropanol = 1:4 in volume) on Ag film and drying in air at 120°C for 5 min.

2.2. Characterizations
Optical reflection and transmission spectra were obtained on a UV-vis-NIR spectrometer (Shimadzu SolidSpec-3700) using an integral sphere detector. The sheet resistance values were measured by a four-point probe technique.

3. Results and discussions

3.1. Conductivity

![Figure 2. Conductivity of initial AgNWs TEs and AgNWs TEs by nanowelding with physical method.](image)

In fact, the conductivity of AgNWs TE is not always very well when they formed by doctor-blading. And the poor conductivity is due to poor contact between silver nanowires which forming a large contact resistance. The best way to solve this problem is the nanowelding between the nanowires. Inventive methods have been tried, such as PEDOT-nanowelding, heating-nanowelding or pressing-nanowelding. Figure 2a shows the conductivity of initial AgNWs TEs and AgNWs TEs by nanowelding with physical method. First of all, heat-nanowelding is a simple and effective way to reduce the film resistance. For heat-resistant materials, 200 °C heat-nanowelding can help to reduce
the sheet resistance from 700 down to 23 Ω/sq and decreased by 96.7%. Secondly, pressure-nanowelding is another extremely effective way to even form the perfect contact at the junction. For pressure resistant materials, 20MPa pressure-nanowelding can help to increase the conductivity from 1490 to 20 Ω/sq, an increase of 98.7%. Thirdly, overcoating a PEDOT: PSS layer on AgNWs film which can reduce the sheet resistance by 87.8%. Unsatisfactorily, PEDOT-nanowelding will cause a 10% reduction in transmittance. From the perspective of improved conductivity, the pressure method is more advantageous than the other two methods.

3.2. Morphology

Figure 3. SEM image of the junction of AgNWs. (a) PEDOT: PSS coating; (b) heating; (c) pressing.

Figure 3 is the SEM image of the junction of AgNWs progressed by three method: PEDOT: PSS coating, heating, and pressing. We can see that there is a common characteristic of the above three methods that they all assisted joining at the nanowire junctions. That is the real reason why they reduce the sheet resistance. As seen in Figure 3a, the nanowires are welded together under the action of PEDOT: PSS and there is a layer of organic matter on the contact. So we can speculate that the principle of PEDOT-nanowelding is that electronically transmitted via PEDOT: PSS material. As seen in Figure 3b, the nanowires are slightly welded together under the effect of heat-welding. This means that nanowires at the intersection of nanowires have a small amount of melting and welding together. By heat-welding the nanowires, electrons will be transported within the nanowire. As seen in Figure 3c, under the action of pressure, the nanowires form a perfect combination, even as there is just only one nanowire. As we all know, the pressure can make the metal to achieve perfect welding. So the transmission of electrons is certainly carried out within the nanowires. Contact the conductivity of the electrode, we know that the closer the nanowires are, the better the conductivity of the electrodes. And the transmission of electrons within the nanowires is better than the transmission of external matter.

3.3. Optical properties

In addition to conductivity, the transparency of the transparent electrode is also a very important parameter. Figure 4 is the optical properties of AgNWs TEs. We can see that, PEDOT: PSS layer coverage will reduce the transmittance by 10%, while the other two methods are maintained at about 92% transmittance, almost no impact. This is because PEDOT this dark blue semiconductor material that will enhance the absorption and scattering of light. Heat welding and pressure welding are only slightly changed the contact of the nanowires without other materials. It is not difficult to understand that the above two modes do not cause significant changes in transmittance. Taking into account the change in the optical transmittance, heating and pressing may be better than coating a PEDOT: PSS layer.
3.4. Adhesion with the substrate
In order to investigate the adhesion strength of the transparent electrode, a 90° peeling test was conducted. A 12-mm-wide piece of 3M scotch tape was attached to an electrode sample and then pulled off the tape. After coating a PEDOT: PSS layer, it was clearly shown that the adhesion between the substrate and the thin film was significantly increased as shown in Figure 5. While pristine AgNWs network film could be easily removed from the substrate during the 3M tape testing (Figure 5a), after the PEDOT: PSS treatment, the AgNW/PEDOT: PSS hybrid film showed very strong adhesion to the substrate while maintaining its original conductivity even after tape testing (Figure 5b). This strong and stable substrate adhesion might come from the film uniformity after the filling the gap between nanowires network with conducting polymer. Unfortunately, the film of the other two methods did not successfully pass the tape pasting test. This is due to the slightness van der Waals force of the nanowires with the substrate. From the perspective of improved adhesion with the substrate, the PEDOT-welding method is more advantageous than the other two methods.

Figure 5. Adhesion force test (3M tape test) of AgNWs electrodes of a) pristine AgNWs network before nanosoldering and b) AgNW/PEDOT:PSS hybrid film after nanosoldering.

4. Conclusions
In conclusion, we report three physics methods to increase the conductivity of AgNWs TEs by nanowelding the contact of nanowires: heating-nanowelding, pressure-nanowelding, and PEDOT-nanowelding. There is a common characteristic of the above three methods that they all assisted joining at the nanowire junctions. That is the real reason why they reduce the sheet resistance. From the perspective of improved conductivity, the pressure method is more advantageous than the other two methods. 20MPa pressure-nanowelding can help to increase the conductivity from 1490 to 20 Ω/sq., an increase of 98.7% while other two methods providing 87.8% and 96.7% growth. Contact the
the morphology of the junction of the junction, we know that the closer the nanowires are, the better the conductivity of the electrodes. And the transmission of electrons within the nanowires is better than the transmission of external matter. Taking into account the change in the optical transmittance, PEDOT: PSS layer coverage will reduce the transmittance by 10%, while the other two methods are maintained at about 92% transmittance, almost no impact. Therefore, taking into account the transmittance, heating and pressing may be better than coating a PEDOT: PSS layer. However, from the perspective of improved adhesion with the substrate, the PEDOT-welding method is more advantageous than the other two methods. This is due to the slightness van der Waals force of the nanowires with the substrate that the film of the other two methods did not successfully pass the tape pasting test. This means that things are usually not perfect, and they have their own advantages and lay the foundation for the popularization and application of AgNWs TEs. In a word, these three nanowelding methods are all suit for manufacture on a large scale for high conductive AgNWs TEs.

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