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Flexible transparent conductors based on metal nanowire networks

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Few conductors are transparent and flexible. Metals have the best electrical conductivity, but they are opaque and stiff in bulk form. However, metals can be transparent and flexible when they are very thin or properly arranged on the nanoscale. This review focuses on the flexible transparent conductors based on percolating networks of metal. Specifically, we discuss the fabrication, the means to improve the electrical conductivity, the large stretchability and its mechanism, and the applications of these metal networks. We also suggest some criteria for evaluating flexible transparent conductors and propose some new research directions in this emerging field.

Introduction

Flexible transparent electrodes (FTEs) are crucial for flexible photoelectronics including flexible organic light-emitting diodes (OLEDs), flexible solar cells, touch screens, wearable devices, and electronic skins [1–6]. Conductors are typically neither transparent nor flexible, while transparent materials are often not conducting. Transparent conducting oxides (TCO) such as indium tin oxide (ITO) are very transparent due to the wide band gap, and are also conducting because of the donor level close to the conduction band [7]. ITO films have dominated the field of photoelectronics for several decades. However, TCO materials are brittle and they often break or form cracks at small strains [8], such that they cannot be used in flexible photoelectronics where folding, stretching, twisting, or serious bending is required. Percolating networks of carbon nanotubes (CNTs) were studied for using as FTEs several years ago [9–12]. However, CNT percolating networks do not possess a low sheet resistance (R_{sh}) and a high transmittance (T) simultaneously. For example, the spray-coated CNT films exhibited a R_{sh} of 328 Ω/□ at a T of 79% [2]. And to achieve a R_{sh} of less than 10 Ω/□, the CNT films require a thickness of more than 100 nm for which the transparency is quite limited [13]. A ratio of direct current conductivity to optical conductivity, σ_{dc}/σ_{op}, is often used as a figure of merit to evaluate the properties of a transparent electrode. Higher σ_{dc}/σ_{op} indicates combined higher transmittance T and lower sheet resistance R_{sh}. The relationship among T, R_{sh}, and σ_{dc}/σ_{op} is [10,14,15]

$$T = \left(1 + \frac{Z_0}{2R_{sh}}\frac{\sigma_{op}}{\sigma_{dc}}\right)^{-2} \quad (1)$$

where Z_0 is 377 Ω, the impedance of free space. However, the direct relationship among σ_{dc}/σ_{op}, T and R_{sh} seems not straightforward. Therefore to evaluate the properties of a transparent electrode, it is much simple by just comparing the transmittance and sheet resistance with commercial ITO films, which exhibit either R_{sh} = ~10 Ω/□ @ T = 80%, or R_{sh} = ~100 Ω/□ @ T = 90% in visible range [16,17]. Any transparent conductors with properties comparable or better than that of ITO are potentially useful in industry. CNT films are not comparable to ITO films due to the high nanotube–nanotube junction resistance, as well as the fact that part of the CNTs is semiconducting.

Metals have the best electrical conductivity and can be easily welded together on the nanoscale to eliminate the junction resistance and thus metal nanowire (NW) networks have been used to replace CNT networks. This review summarizes the fabrication, properties including flexibility and its mechanism, and applications of FTEs made of metal NWs. We discuss NW networks made by two routes: bottom up method, solution process to assemble the nanowires into a network, for which a post treatment is often required to weld the contacting nanowires; and top-down method, deposition of a metal film onto a template or a mask to form a fully interconnected network without any wire–wire junction resistance. Such

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1369-7021/ http://dx.doi.org/10.1016/j.mattod.2014.08.018

interconnects can be regarded as perforated metal films which exhibit better electrical conductivity and flexibility. In addition, we point out in this review that properties including haze, surface roughness, strain fatigue, adhesion, and stability of an FTE are also important depending on the application, and suggest new criteria considering these properties to properly evaluate FTEs.

Solution processed metal nanowires for FTEs

Percolating Ag NW networks

The first random metal NW network was made of solution processed Ag NWs to replace nanoimprinted metal grid and CNT films as the transparent electrodes [16,18,19]. Figure 1a–c illustrates the Ag NW suspension, scanning electron microscopy image of a Ag NW network, and optical image of a Ag NW network on flexible polyethylene terephthalate (PET) substrate. The Ag nanowires were synthesized by the reduction of Ag nitrate in the presence of poly(vinyl pyrrolidone) (PVP) in ethylene glycol [20]. A suspension of the Ag NWs was drop-casted to the substrate. After drying, a random percolating network of Ag NWs was formed. Such a network often has a large sheet resistance (R_{sh} = ~1 kΩ/□) as a result of the large wire–wire junction resistance and a comparable transmittance to that of ITO films [16]. The junction resistance can be as large as 1 GΩ due to a thin PVP layer coating on the surface of Ag nanowires (Fig. 2a) [21], and eliminating this resistance is an effective way to improve the electrical conductivity of the metal NW network FTEs (Fig. 2b–h). The PVP layer can be removed by annealing (typically at 200°C for 20 min), leading to direct contact and welding of NWs (Fig. 2b) [16]. However, for FTEs, the substrates are typically polymers which cannot survive under high temperature annealing. To solve this problem, several other methods avoiding high temperature were developed. The Cui group electrochemically coated a thin Au film (Fig. 2h) on the Ag nanowire networks, reducing the junction resistance from ~1 GΩ to ~450 Ω and R_{sh} to less than 100 Ω/□ [21]. Gannet et al. used laser illumination to cause local temperature rising around the junctions, resulting in plasmonic welding (Fig. 2g) which effectively increase the electrical conductivity by three orders of magnitude [22]. Because this process is self-limited, the welding effect is local and does not cause any damage to the other part of the nanowires or significant change of transmittance. The plasmonic-welded Ag NW networks could withstand folding, bending, and even crumpling without significant increase in resistance [22]. Tukono et al. developed a welding process by cold pressing at 25 MPa for 5 s. The Ag nanowires were well joined, and unlike the methods above, all the nanowires including the joints were in the same plane, such that the surface roughness of the FTEs is much smaller (Fig. 2d). Ag nanowire networks made with this process achieved a R_{sh} of 8.6 Ω/□ at a transmittance of 80%. The sheet resistance of the regular post-annealed Ag NW electrodes increased by more than six-fold after only 100 bending cycles with a curvature radius of 5 mm. By contrast, the sheet resistance of mechanically pressed Ag NW electrodes maintained its low sheet resistance, with a small increase of less than 19% even after 1000 cycles of bending due to the strong welding between NWs [23]. Lee et al. showed that R_{sh} of a Ag nanowire network could be significantly reduced by solvent washing (for removing the PVP) of the Ag nanowires followed by a spray process (Fig. 2f) instead of applying drops, without any post-treatments. Such Ag NW networks exhibited a R_{sh} of 18.9 Ω/□ at a T of 94% which is better than the results with post-annealing, together with a lower strain fatigue [24].

It is worth pointing out that the data in different references mentioned above may not be compared because the data are affected by the nanowire length and diameter, which were different in different reports. To this point, Lee et al. developed a multicycle growing method to produce 'very-long Ag nanowires' with an average length of ~100 μm, much longer than the Ag nanowires made by one-time growth (<20 μm). With a sheet resistance of 9 Ω/□, the network exhibited a transmittance of 89%, superior to that of the counterpart using common shorter nanowires (69%) [25]. Electrodes with longer nanowires exhibited excellent flexibility: no increase of resistance was seen after 10,000 cycles of bending at a bending radius of 2 mm [25].

Some recent theoretical and experimental results show that for stick networks, the sheet resistance decreases with increase of length to diameter ratio (L/D), or fraction of long sticks, or area fraction (AF) of the metal, or the decrease of junction resistance [15,26–28]. For stick networks with fixed L/D and junction resistance, increasing AF (above the percolation threshold) will lead to increasing of electrical conduction and decreasing of optical transmittance. With larger L/D or smaller junction resistance, we can decrease AF to some extent and hence increase the transmittance.

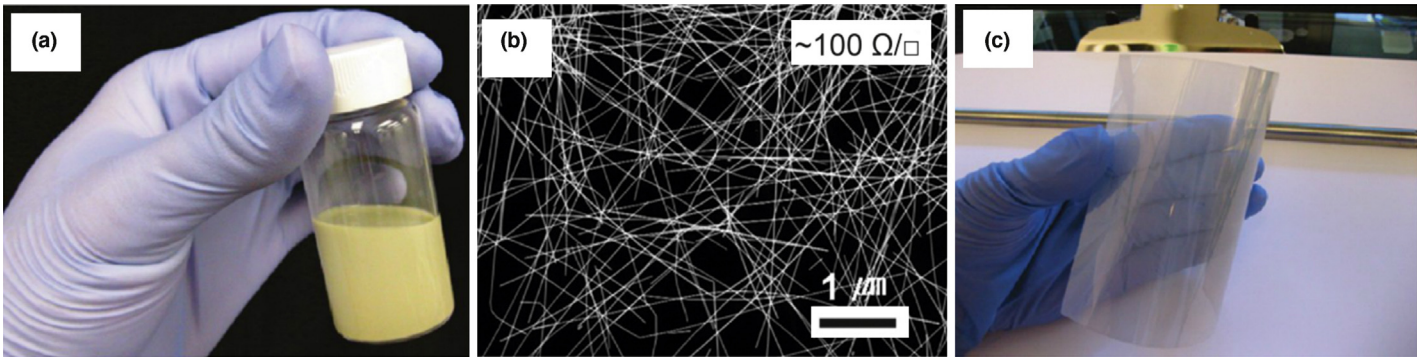

FIGURE 1

Solution processed Ag NW networks for FTEs. (a) Ag nanowire suspension. (b) Scanning electron microscopy (SEM) image of a Ag NW network. (c) Optical image of a Ag NW network on flexible polyethylene terephthalate (PET) substrate. Figures reprinted with permission from Ref [21]. Copyright American Chemical Society 2010.