Physical properties of silver nanowire networks

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ABSTRACT

Our work on the physical properties of silver nanowire (Ag NW) networks is presented in this contribution and shows that such emerging transparent conductive materials (TCM) exhibit very promising electro-optical properties. In particular the optical transmittance of Ag NW networks is still very high in the near infra-red region which is not the case for other TCM such as Indium Tin Oxide.

The present work demonstrates that high quality Ag NW networks can be obtained by using an optimal Ag NW density, together with a controlled annealing step. In-situ electrical measurements reveal the effects of thermal annealing on the electrical properties of Ag NW networks. This allowed us to determine the optimal thermal treatment and network density needed to obtain a high transparency along with a sufficient electrical conductivity.

This work sheds light on the physical mechanisms behind the change in electrical properties of the specimen during a thermal annealing step. It also leads to an improvement of the electrical properties by optimising the association of the Ag NW density together with the effects of a controlled thermal annealing.

In addition this investigation shows that the mechanical properties of such networks are compatible with applications requiring flexible substrate.

Keywords: transparent electrodes, metallic nanowires, electro-optical properties, sintering, flexible electronics.

1 INTRODUCTION

Transparent conductive materials (TCM) are commonly used in industry and the associated market has grown exponentially over the past decade due to the proliferation of large LCDs, thin film solar cells, OLEDS, or electronic devices with touch screens... Transparent and conductive thin films play a key role in the operation of such devices. For instance, in the case of thin film solar cells, the front electrode must be highly transparent to let the sun light pass but should also efficiently collect the charge carriers at the surface.

Doped metal oxides (known as Transparent Conductive Oxides) historically dominate the market as they were discovered in the mid 20th century and a lot of studies have been devoted to these materials [1]. In particular Indium Tin Oxide (ITO) has been extensively investigated and its electro-optical properties have already been optimized. However, such conducting oxide material suffers from three main drawbacks: cost, the method of deposition which currently uses vacuum techniques and brittleness. Therefore the development of other transparent conductive materials is necessary to overcome these issues. Several new materials have recently emerged, including graphene, metallic grids, carbon nanotubes and metallic nanowire networks [2].

Among them, metallic nanowire networks are attracting growing interest due to their potential use as transparent electrodes in optoelectronic devices such as solar cells or flat panel displays, as demonstrated by the pioneer work of Lee et al.[3]. Moreover, such networks are flexible and resistant to mechanical fatigue. This is of paramount importance for fabricating flexible electrodes for thin film solar cells, organic light emitting diodes or liquid crystal displays. In addition, metallic NW networks can be deposited using low cost deposition techniques such as spray coating while demonstrating very interesting electro-optical and mechanical properties.

2 ELECTRO-OPTICAL PROPERTIES

Silver nanowires (Ag NWs) synthesized by SeaShell Technology [4] were deposited by spin coating and spray deposition to fabricate random networks such as the one depicted in Figure 1. In terms of electro-optical properties an optimal nanowire density has to be considered [5]. The nanowire density must be high enough to allow percolation through the network, but sufficiently low to maintain a good transparency of the deposited network. This optimal density also depends on the NW geometry (namely the NW's aspect ratio). The effect of the density on the resistance change was explored by varying the concentration of material deposited. Then the density was measuredfrom SEM images via the software *Image J,* and related to the optical transmission and electrical resistance of the network.

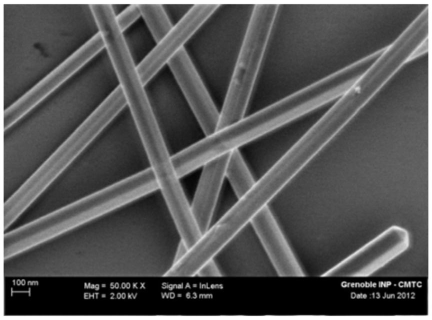

Figure 1: Scanning Electron image of a silver nanowire network deposited by spin coating.

Optimized Ag NW networks exhibit both low sheet resistance (a few Ω/sq) and high transmittance over a large range of wavelengths (≈ 90%, when the substrate contribution is subtracted) as shown in Figure 2. For the two specimen shown in Figure 2 the sheet resistances are 5 and 12 Ω/sq for Ag NW network and fluorine-doped Tin Oxide (FTO), respectively. This clearly shows that Ag NW networks exhibit excellent electro-optical properties when optimized. In addition, they have an advantage over FTO as they are also transparent in the near infra-red region: a property which can be useful for some solar cell applications. The optimization of the electro-optical properties, and in particular the electrical conductivity, can require for instance thermal annealing as discussed below.

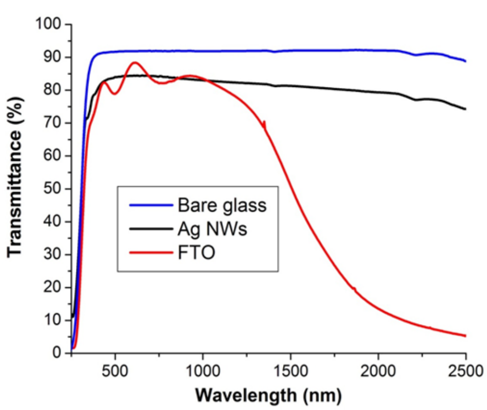

Figure 2: Total transmission spectra of a bare glass substrate (blue curve), an Ag NW network (black curve) as compared to a state of the art Fluorine doped Tin Oxide (FTO) sample (red curve) deposited by spray pyrolysis.

3 THERMAL ANNEALING EFFECTS

Thermal annealing can drastically improve the electrical contact between metallic nanowires, leading to an increase in electrical conductivity without significantly changing the optical properties of the network. However above a certain threshold temperature, morphological instabilities occur, canceling out the beneficial effects. The investigation of the physical mechanisms involved in thermal annealing of Ag NW networks is investigated.

In-situ measurement of the effects of annealing on the electrical resistance R versus temperature, R(T), was performed in air with a temperature ramp of 15 °C.min^{-1}. A typical example is shown in Figure 3. At temperature lower than 100°C a significant decrease of the resistance occurs and can be attributed to organic solvent residue desorption. The decrease of the resistance goes on and reaches a minimum value near 320 °C where local sintering between Ag NW can be clearly seen from SEM images, and seem to be optimized (at least for this given thermal ramp).

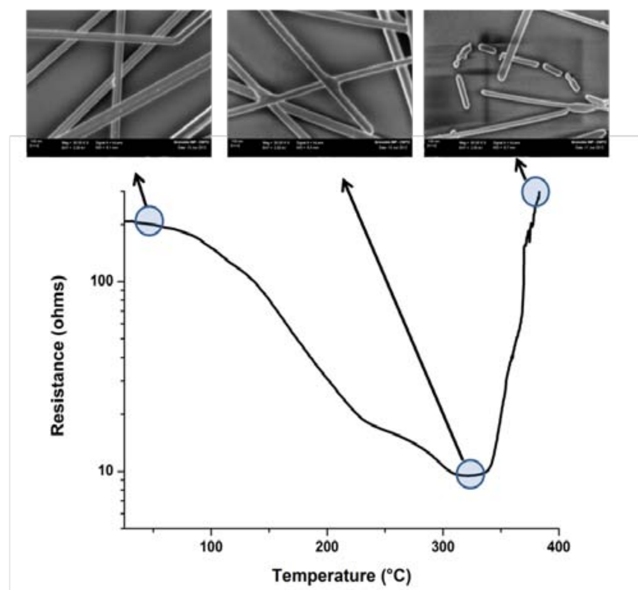

Figure 3: Dependence of the electrical resistance of a Ag nanowire network versus temperature during a thermal ramp of 15 °C/min. The different invoked mechanisms responsible for such a change from non-annealed nanowires (left insert) concern desorption of organic residues, local sintering at the junctions between nanowires (middle insert) and morphological instabilities of Ag nanowires (right insert).

This value of 320ºC to achieve the minimum resistance is observed when we perform a temperature ramp of 15 °C/min, which includes unwanted thermal effects such as thermal loading and thermal lag. We find a slightly different temperature when the ramp slope is changed for example. Higher temperature causes morphological instabilities and in particular Rayleigh instabilities [6] resulting in a sharp loss of electrical conductivity as the nanowires are starting to become morphologically unstable (above 350°C). The driving force of such instabilities is the reduction of surface energy, which tends to force a shape evolving towards sphereoidization. Regardless, let us note that the optical measurements do not show a large variation of transmittance up to the onset of Rayleigh instabilities.

We have investigated the influence of the Ag NW concentration in a constant volume of solution deposited by spin coating on the resistance changes versus temperature. Similar thermal behaviour was seen between the different samples but the resistance value clearly depends on the density (see Fig. 4). The minimum resistance value tends to increase as the density of the network decreases.

The nature of the glass substrate appears as well to play a role especially for the high temperature behaviour. This seems to imply that the Ag NW instability was triggered differently depending on the substrate nature. Currently this is not fully understood and further experiments will be performed to elucidate this point.

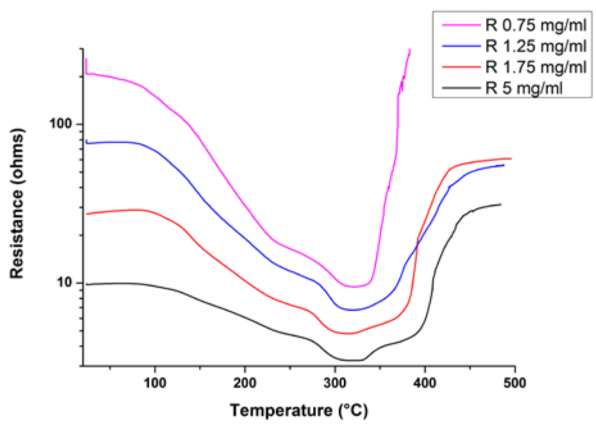

Figure 4: Effect of the temperature on the AgNW network resistance for samples deposited with various concentrations. The minimum value of resistance is always reached around 320°C (for this given ramp of 15°C/min), and becomes higher as the concentration decreases.

4 MECHANICAL PROPERTIES

When fabrication of Ag NW networks takes place on flexible substrates, their electro-optical properties are also associated with excellent mechanical properties especially with regards to fatigue. This is shown in Figure 5 which exhibits the influence of the number of bending cycles on the measured in-situ electrical resistance. While the commercial ITO resistance increases (note the log-scale of R) due to its brittleness, the Ag NW network shows very stable behaviour under bending tests (at a radius of curvature equal to 5 mm).

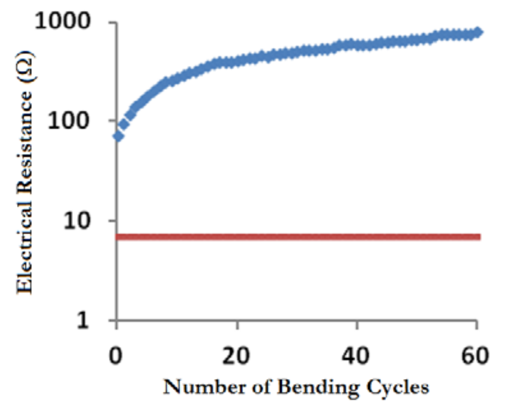

Figure 5: Comparison of the electrical resistance (in log scale) of a commercial ITO thin film (in blue) and Ag NW network (in red) under bending cycles.

In fact the bending induces micro cracks in the ITO films which then tend to propagate, causing a sharp increase of the electrical resistance. Under SEM observation it can be seen that these cracks occur at semi-regular intervals perpendicular to the axis of compression or tension of the sample (see Figure 6).

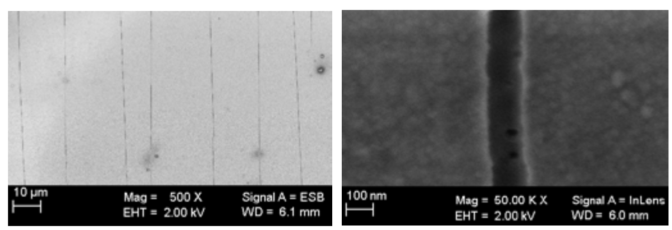

Figure 6: Cracks in ITO layers after undergoing several hundred bending cycles to a radius of curvature of 5mm. Left image shows that the cracks occur at a semi-regular interval of about 10 µm. Right image shows crack width to be 100 nm.

Although the cracks are small, they have a significant effect on the resistance of the film. Otherwise no change in the nanowire network morphology is observed. Obviously failure at low strains may not be significant for application in rigid devices but it constitutes a severe limitation for flexible device applications. Therefore AgNW networks appear to be one of the most promising transparent conducting material for these kinds of applications.

5 CONCLUSIONS AND PERSPECTIVES

We have demonstrated the fabrication of Ag NW networks with very good electro-optical properties (≈90% transparency and a sheet resistance of 5 Ω/sq). To reach such optimized properties, it is useful to measure in-situ the thermal annealing effects. This also allows the observation of the thermal stability of Ag NW networks.

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The mechanical properties of Ag NW networks were also investigated in-situ, demonstrating a stable electrical resistance under bending.

A natural consequence of the present study will be to combine our results for annealing experiments with in-situ thermal annealing SEM and TEM experiments to gain further insight into thermal instabilities and associated defects. We expect for instance, that the nanowire diameter could have an important influence on the thermal behaviour of the networks.

Future work will also concern the encapsulation of the metallic nanowires with transparent oxides such as ZnO or TiO_2. Works reported in the literature clearly show that this leads to an improvement of the nanowires thermal stability [7], [8]. With such embedding, one can expect as well to improve the oxidation stability of Ag NWs, with only a slight degradation of the optical transparency.

In terms of applications, the integration of Ag NWs as front electrodes in solar cells will be pursued. In addition to the high visible transparency and low sheet resistance, Ag NW networks can also demonstrate a diffuse light component (Haze coefficient) which increases their chances of supplanting standard TCOs as front electrodes in some solar cells.

Eventually, investigating other metallic nanowires could be also interesting. Indeed replacing silver by an alloy such as NiCu appears promising, due to the fact it has both a higher resistance against oxidation and a lower cost [9].

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