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Silver nanowire networks: Physical properties and potential integration in solar cells

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ABSTRACT

With the growing interest in flexible electronics and the increased utilization of Indium Tin Oxide electrodes for display and photovoltaic applications the need for new materials is emerging.

In this work we present the electro-optical properties of Ag nanowire networks as an alternative transparent conductive material. A comparison of different film deposition techniques is made and indicates that the properties of the network are independent of the fabrication method. Analysis of the electrical behavior as a function of nanowire density is made and compared with theoretical results as well as Monte Carlo simulations.

Thermal annealing is shown to reduce the sheet resistance from 1000 Ω/sq to 8 Ω/sq; this reduction is achieved by local sintering of the nanowire junctions.

Experimental optimization of Ag nanowire electrodes was undertaken and a peak in the electro-optical properties is observed at approximately 100 mg/m². Finally a discussion of the potential integration of Ag nanowire networks into solar cells is undertaken; we observe that these electrodes show promise as an emerging transparent conductive material, especially for flexible applications.

1. Introduction

Thin films which exhibit at the same time high electrical conductivity and optical transparency are crucial for many modern electronic devices such as e-papers, organic light-emitting diodes (OLEDs), liquid-crystal displays (LCDs), and solar cells. Many articles in the literature currently highlight the growing need to identify and develop new methods and materials for fabrication of transparent conductive materials. There are many reasons for this need and they have been discussed in depth by Kumar and Zhou [1] and Ellmer [2].

In the case of solar cells, the transparent electrode usually works as the anode for extracting separated charge carriers from the absorbing area. While transparent conductive oxides (TCOs) are usually well adapted for solar cells, they suffer from significant limitations such as costly fabrication process, scarcity (especially concerning Indium based TCOs like Indium Tin Oxide (ITO)) and brittleness. Hence a variety of other materials have been intensively investigated recently.

Kumar and Zhou highlight three main emerging materials that may provide a useful replacement for transparent conductive oxides (TCOs): graphene, carbon nanotubes and metallic nanowire networks. Ag NWs already exhibit very good physical properties, but still some issues inhibit the large-scale application of Ag NW electrode as for instance the need of a heating step or the low adhesion of the network onto the substrate. Clearly a better understanding of fundamental properties of Ag NW networks is needed as well through investigations of the effects of several parameters such as Ag NW morphology, or the influences of the experimental conditions and post-deposition treatments (thermal annealing, mechanical pressure, embedding, etc.). While the electro-optical properties are of prime importance, other properties are also crucial: electro-mechanical properties (often investigated under bending fatigue), stability (either thermal or chemical), and diffuse component of the transmitted light (haze factor). This emerging material has been studied only recently and deserves thorough investigations to better its physical properties and facilitate its integration into devices. Alongside all the physical properties, cost will be very important and Ag NW networks can exhibit advantages due to the small required quantity of silver and low-cost deposition techniques.

This article focuses on the physical properties of metallic nanowire networks, specifically silver, and whether this material will provide the necessary balance to meet the needs of photovoltaic

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applications. In order to obtain a metallic nanowire based transparent electrode which can be efficiently incorporated into a solar cell one can play with several parameters such as the chemical composition and morphology of the metallic nanowires (NWs), the density of the NW network and the use of post-processing such as mechanical pressing [3,4], chemical treatments [5] and thermal annealing [3,6]. We report here the influence of the density and annealing on the physical properties of Ag NW networks pertinent to their potential integration into a solar cell.

2. Experimental section

Ag NWs dispersed in isopropyl alcohol were acquired from Seashell Technology [7]. The average dimensions of the nanowires were 0.105 μm for the diameter and 37.5 μm for the length resulting in an aspect ratio of about 360. Films of different densities were fabricated from suspensions of different concentrations. Random Ag NW networks were generated by different techniques, including spin-coating, drop casting, rod coating and spray injection (as described in Ref. [8]) on low alkaline earth boro-aluminosilicate glass (Corning C1737-S111).

Field-emission scanning electron microscopy (FESEM) imaging was recorded with a FEI Quanta 250 to investigate the network morphology.

In-situ thermal annealing under atmosphere combined with real time electrical resistance acquisition using the two-point probe method and with a constant voltage of 1 V was performed to gain insight into the thermal behavior of the Ag NW networks. Silver paint strips acted as electrical contacts and the total sample size was $12.5 \times 12.5\ \mathrm{mm}^2$. Thus, the resistance values reported in this study represent an average over the surface previously mentioned.

The optical transmittance was recorded by using a Lambda 950 Perkin-Elmer spectrophotometer. No substrate subtractions were performed on any of the film reported in this study. In addition, optical transmission values are quoted at $\lambda = 550$ nm. The haze factor, quantifying the amount of light scattering, was calculated from the total (T(total)) and direct (T(direct)) transmittances as (T(total) − T(direct))/T(total).

Four point probe measurements were performed using a Keithley 2400 sourcemeter with a Lucas Labs Pro4-440N probe station.

3. Results and discussions

3.1. Electro-optical properties

Of the properties that are desirable for transparent conductive materials (TCMs) the obvious selection criteria are the transmission of light and the electrical resistance. Considering this, it is appropriate to make an initial comparison of Ag NW networks electro-optical properties with those of TCOs. All electro-optical properties that are discussed are measured on Ag NW networks after a thermal annealing step which was found to significantly decrease the resistance without having an impact on their transmittance. The changes of resistance are due to several factors that will not be discussed in depth here but in majority they are caused by local sintering at the junctions between the nanowires (as shown in Fig. 1). The local sintering occurs as a result of atomic migration to reduce the surface energy at points of high curvature. Fig. 1 exhibits scanning electron microscopy observation of two different junctions between two nanowires before and after annealing for 2 h at 200 °C in air. Although this is not the same junction before and after annealing these images represent typical morphologies. Local sintering at the junction is present after annealing, which leads to a decrease of sheet electrical resistance from 1000 Ω/sq to 8 Ω/sq.

The reduction of resistance via thermal annealing allows the production of highly conductive layers. Modifying the annealing profile enables networks with $R_S < 20\ \Omega$/sq to be created within 2 min at 250 °C or if there is a temperature restriction the same can be achieved with longer annealing at lower temperatures. At 200 °C the network resistance continues to drop for 2 h though the majority of the change occurs in the first 5 min.

The resistance and transmittance of Ag NW networks are dependent on the wire length and diameter as well as the density of the network [9]. The nanowire diameter plays a key role in the scattering properties of the network as highlighted by Preston et al. [10]. It is common to plot the transmittance as a function of sheet resistance [11]. Fig. 2 shows that the general behavior of transmittance is somewhat independent of deposition method.

A comparison of Ag NW networks, silver flakes, carbon nanotubes and graphene was also made by De et al. [11]. Their results concern NW networks created by vacuum filtration of a colloidal solution of Ag NW onto a membrane to form the network, which is then transferred to a PET substrate. The experimental results of the current contribution are presented in Fig. 2 for Ag NW networks generated by the various techniques mentioned in the legend of the figure. Comparison of these results with those of De et al. [11] suggests that there is only a slight dependence of electro-optical properties of Ag NW networks on the deposition method used. The majority of the behavior is dominated by the geometry of the wires. In strong agreement with the work of De et al. [11], the data fits well in both regimes: the percolation regime for sparse networks and the bulk regime for dense networks. As discussed below an optimal density has to be considered to reach a tradeoff in order to get high optical transmittance T and low sheet resistance R_S. Generally speaking a good quality transparent electrode for solar applications corresponds roughly to $T \approx 90\%$

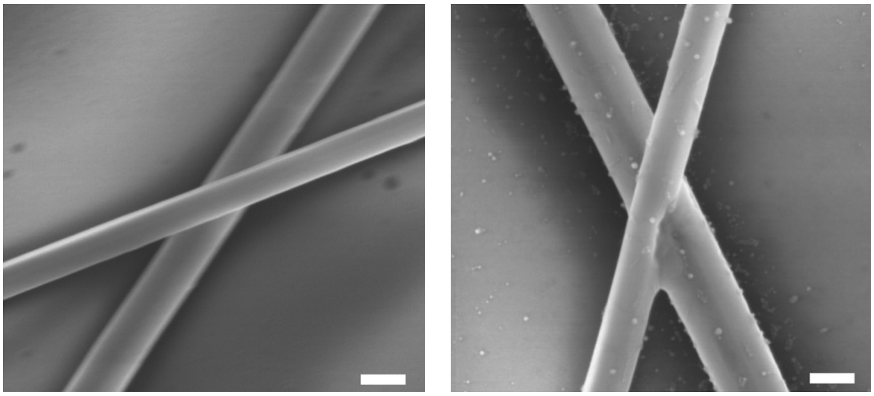

Fig. 1. SEM images of Ag NW junctions before (left) and after (right) annealing; the sheet resistance of this network reduced from 1000 Ω/sq to 8 Ω/sq. Scale bars indicate 100 nm.