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MANUFACTURE OF ULTRATHIN TRANSPARENT ELECTRODES BASED ON SILVER NANOWIRES WITH APPLICATIONS TO THREE-DIMENSIONAL SOLAR CELLS

R. Banica[1,2]*, C. Sarvas[1], S. F. Rus[2], D. Ursu[1,2], S. Novaconi[2], A. Kellenberger[1], T. Nyari[1,2]

[1] University Politehnica Timisoara, Piata Victoriei 2, 300006 Timisoara, Romania
[2] Renewable Energies Laboratory – Photovoltaics, National Institute for Research and Development in Electrochemistry and Condensed Matter, Str. Dr. A. Păunescu Podeanu 144, 300569 Timisoara, Romania
*E-mail: radu.banica@yahoo.com

Summary

In this paper a simple method of manufacturing ultrathin and transparent electrodes based on metal nanowires is presented. In the first stage, silver nanowires (AgNWs) were obtained by the "polyol" method. After their purification, a thin film of silver nanowires was deposited by tape casting method on aluminum foil previously coated with a thin film (<10 microns) of polymethyl methacrylate (PMMA). To improve adhesion of Ag nanowires to the polymer layer, the AgNWs/PMMA/Al structure was subjected to heat treatment at 170°C in air. The aluminum foil was used both as mechanical support to prevent bending of the polymer during heat treatment and to obtain a homogeneous temperature distribution on the surface of the polymeric substrate. After heat treatment, the aluminium substrate was selectively dissolved and gave an ultrathin and transparent film of AgNWs/PMMA. The morphology of the electrically conductive transparent and flexible film was studied by scanning electron microscopy, its transmittance was determined by UV-Vis spectroscopy and the sheet resistance was measured by the van der Pauw method. These ultrathin and ultra-flexible films based on silver nanowires supported on transparent thermoplastic substrate can be used to manufacture solid three-dimensional solar cells at micrometer scale.

Experimental

Synthesis of Ag nanowires

Silver nanowires (AgNWs) were synthesized through a modified polyol process [1-3]. The purification process of AgNWs and redispersing in ethanol method is also described in detail in [1].

Deposition of thin films based on AgNWs

In the paper [1] is presented the manufacture in two stages of AgNWs/PMMA/PET-type transparent and electrically conductive electrodes, where PET is polyethylene terephthalate. In this paper, a method of manufacturing ultrathin transferable films of AgNWs/PMMA is presented. The film transfer to a support that provides mechanical strength is necessary due to the high fragility of AgNWs/PMMA films. To demonstrate the transferability of AgNWs/PMMA films, commercial transparent adhesive tape (ADT) was used as support material.

The process of manufacturing AgNWs/PMMA-type transferable transparent and electrically conductive electrodes (Fig. 1) is based on six main stages:

1. Deposition of a thin film of PMMA on commercial aluminum foil with a thickness of 9 microns.
2. Deposition of a layer of silver nanowires on the surface of PMMA film.
3. Heat treatment at 170°C in air for 10 minutes to create chemical bonds between the PMMA and AgNWs film.
4. Selective dissolution of the aluminum support in a 2M NaOH aqueous solution and stretching the film on the water surface.
5. The transfer of the AgNWs/PMMA film from the water surface on a smooth glass surface.
6. The transfer of the AgNWs/PMMA film from the glass surface onto the ADT.

Other films were obtained eliminating steps no. 3 and 4, the steps that remained were the same.

Name of samples and the method of manufacture

Samples P1 and P2 are obtained without using the heat treatment at 170°C and without selective dissolution of the aluminum substrate. These samples were not subjected to mechanical stress.
Sample P3 was obtained by heat treatment at 170°C, followed by selective dissolution process of aluminum and transfer in two stages on ADT. This sample was not subjected to mechanical stress.
P2.1 – This sample was obtained as samples P1 and P2, but using a larger number of AgNWs layers. This sample was subjected to mechanical stress (repeated bending).
P3.1 – This sample was obtained similarly to P3. This sample was subjected to mechanical stress (repeated bending).

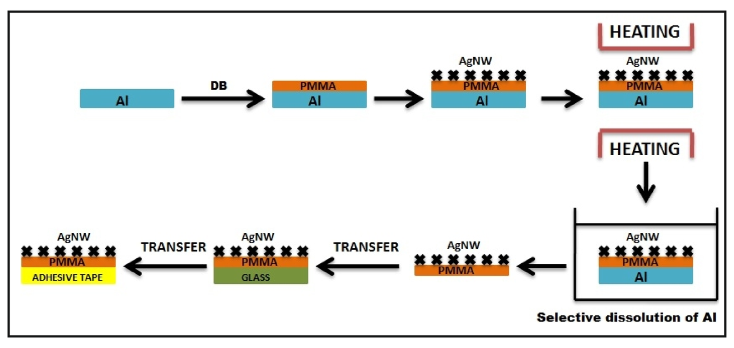

Fig. 1. Transferable AgNWs-based transparent electrodes manufacturing steps (DB – doctor blade).

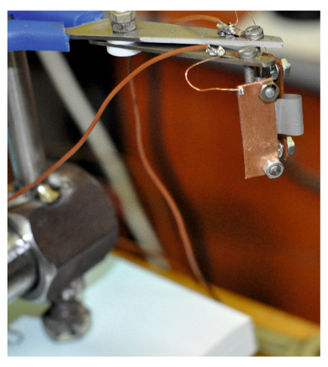

Fig.2. Photo showing sample 2.1 during the bending process.

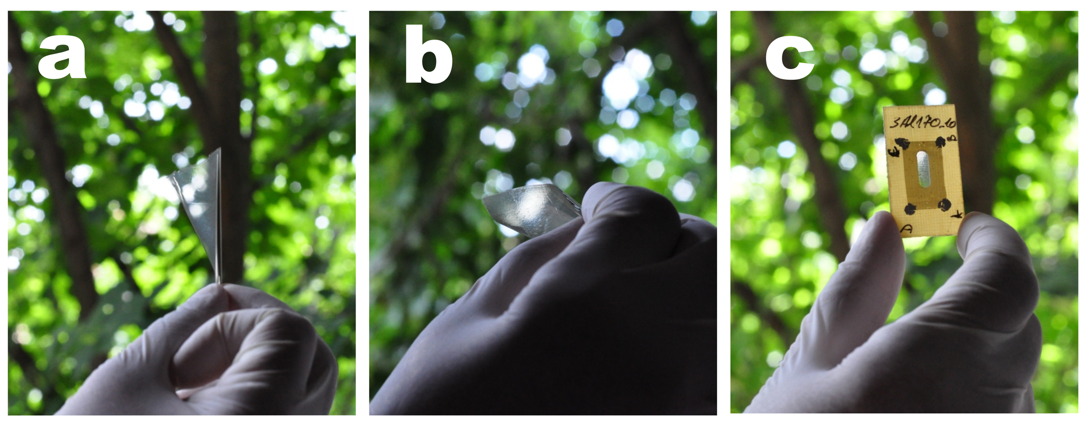

Fig. 3. Photos of AgNWs/PMMA electrodes: before supporting (a), supported on ADT (b) and prepared for electrical and optical measurements (c).

Characterization

The obtained silver nanostructures were characterized by X-ray diffraction (X'Pert PRO MPD PANalytical diffractometer, CuKα radiation, λ=1.54184 Å, Bragg-Bretano geometry, Automatic Divergence Slit), UV-Vis spectroscopy (Lambda 950 Perkin-Elmer spectrometer with integrating sphere), scanning electron microscopy (FEI Inspect S / QUANTA FEG 250).
Sheet resistance of the transparent electrodes obtained from AgNWs deposited on PMMA/ADT was determined by van der Pauw method using the experimental setup presented in [1].

After fabrication, the AgNWs/PMMA/ADT-type electrodes were characterized as follows. The morphology of the electrically conductive transparent and flexible film was studied by scanning electron microscopy, its transmittance was determined by UV-Vis spectroscopy and the sheet resistance was measured by the van der Pauw method.
Repeated bending strength was assessed by measuring the electrical resistance of the film during the bending process. Figure 2 presents the experimental setup that allowed the repeated bending of the electrodes to a radius of 2 mm with an oscillation frequency of 0.33 Hz.

In Figure 3 are shown photographs of transparent and electrically conductive electrodes based on silver nanowires unsupported on ADT (3a), supported on ADT (3b) and supported on ADT and prepared for sheet resistance measurements (by deposition of electrical contacts at the corners) and for optical transmittance measurements (3c).

After subjecting the samples to mechanical stress, they were studied by optical microscopy to determine the cause of electrical sheet resistance diminishing.

Results and Discussion

The synthesized AgNWs samples were characterized by XRD. From the diffractogram (Fig. 4) it can be observed that the major phase is the cubic Ag grown preferentially along the (111) direction. Also, some tetragonal Ag is present. The UV-Vis plasmon absorption spectra highlighted the presence of Ag nanowires by a characteristic peak located at 378 nm (Fig 5).

Diffuse transmittance spectra for the electrodes (Fig. 6 and 7) highlight two minima, at the wavelengths 382 nm and 357 nm, corresponding to absorption maxima of the absorbance spectrum of the suspension of nanowires (see Fig. 5) of the plasmon absorption of AgNWs and macrocrystalline Ag, respectively.

Electron microscopy (Fig. 8) does not highlight welding phenomena of silver nanowires after heat treatment but polyvinylpyrrolidone desorption can take place. Due to the three-dimensional nature of AgNWs film, it is likely that only part of the silver nanowires are fixed during thermal treatment on the polymer layer. Using simultaneously pressing and heating may be a better method of increasing the adhesion of nanowires on the substrate.

The method for the electrical sheet resistance measurements is extensively described in [1, 4]. Sheet resistance values determined for the samples P1 and P2 are 1.7 and 1.2 kΩ / sq, respectively. Determination of sample P3 sheet resistance could not be done accurately as partial surface resistance value ρ2 is about 42% lower than ρ1 resistance. The average value of sheet resistance for that sample is only 92 Ω/ sq.

The determined values for resistances and transmittances prove that by the method described it is possible to obtain AgNWs/PMMA-type electrodes that can be used in manufacturing three-dimensional solar cells. These electrodes require however significant improvements of diffuse transmittance.

From Fig. 9 it can be observed that the sample obtained without using the heat treatment (P2.1) shows a constant value of the electrical resistance of the layer of nanowires along a number of 1190 bendings. During mechanical stress, in the electrode obtained by heat treatment (170°C for 10 minutes) and selective dissolution of aluminum, cracks are formed perpendicular to the bending arms plane. These cracks lead to a sharp rise of electrical resistance after 370 and 1192 bendings respectively from 9.3 Ω to 11.8 Ω during the four bending in the first round, then from 11.9 Ω to 13.3 Ω in the other 24 in the second bending stage. After the appearance of these cracks, the electric resistance is slowly-growing, probably due to the last cracks extension to the edge of the electrode. So the increase of the film's electrical resistance is due to the sudden shrinkage of the electronic conductor section by AgNWs film breaking.

Optical microscopy images (Fig. 10) fully supports this hypothesis. Moreover, it is observed that the central crack, which is the cause of the electrical resistance growth, is parallel to the direction of pull of the aluminum substrate during its rolling process of fabrication. Thus PMMA film thickness along the section perpendicular to the rolling direction of the aluminum substrate is not constant, but follows the aluminum substrate profile. This is well demonstrated in Figure 10a which shows a AgNWs/PMMA film exfoliated from the aluminum support. This is the cause of directional cracking of the AgNWs/PMMA electrode subjected to repeated bending.

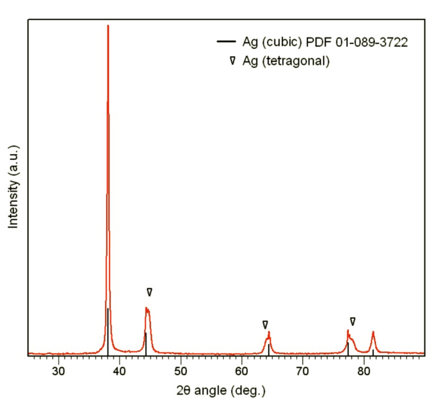

Fig. 4. XRD profile of silver nanowires.

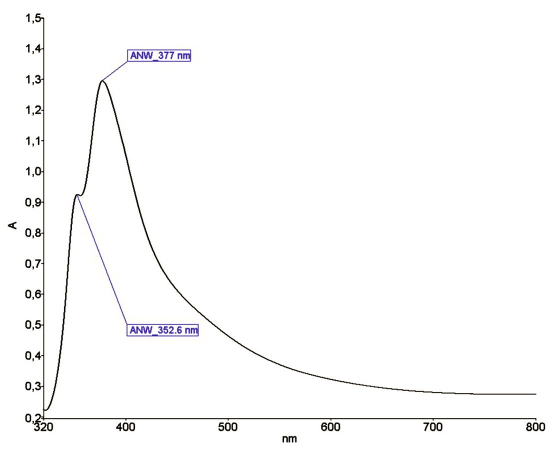

Fig. 5. UV-Vis absorption spectrum of silver nanowires.

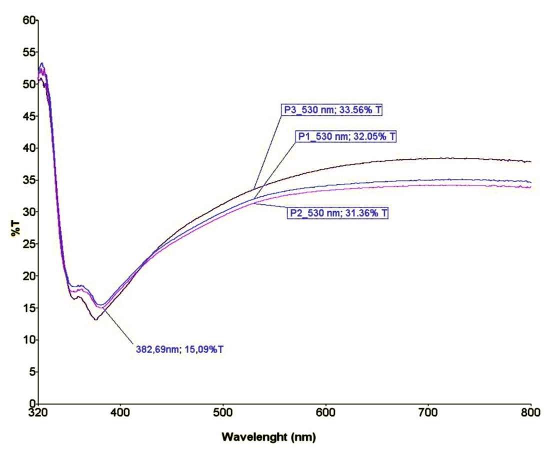

Fig. 6. Diffuse transmittance spectra of AgNWs/PMMA/ADT electrodes not subjected to mechanical stress (P1, P2, P3).

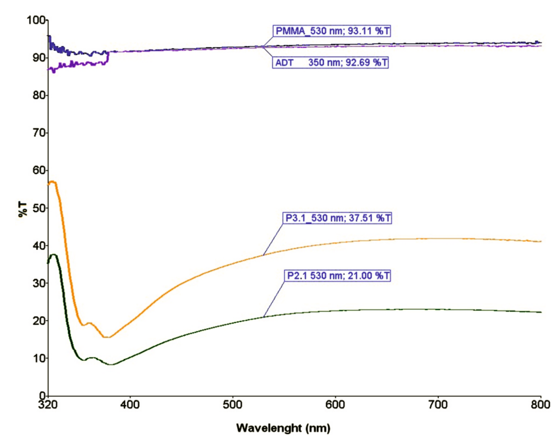

Fig.7. Diffuse transmittance spectra of AgNWs/PMMA/ADT electrodes subjected to mechanical stress (P2.1, P3.1), of PMMA film and tape (ADT).

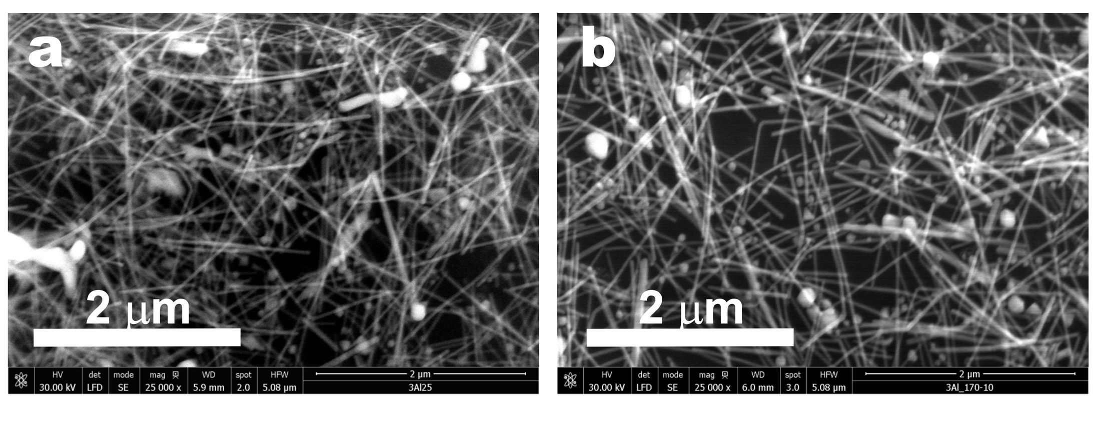

Fig. 8. SEM images of the electroconductive electrodes obtained without heat treatment (a) and with heat treatment at 170°C for 10 minutes (b).

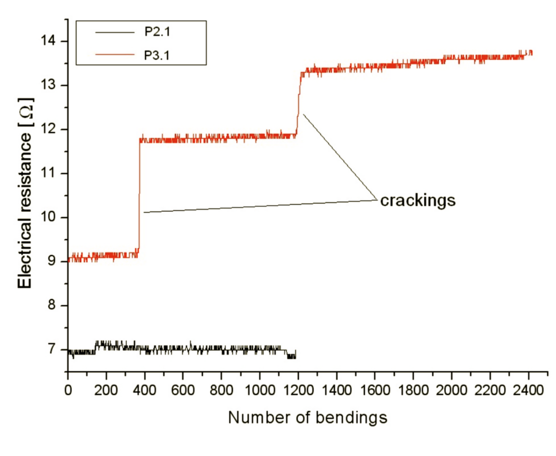

Fig. 9. Variation of electrical resistance of P2.1 and P3.1 samples with the number of bends.

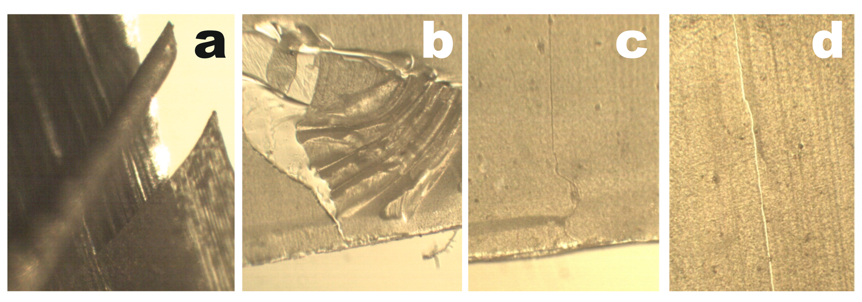

Fig. 10. Optical microscopy images of the AgNWs/PMMA/Al sample (a) and of P3.1 sample after 2,400 bendings (b, c, d). In Figure 10b, peeling layer process of AgNWs was not due to bending, but due to surface damage during handling.

Conclusions

- It was developed a new inexpensive method for manufacturing AgNWs/PMMA-type thin and transferable electrodes.
- The AgNWs/PMMA-type electrodes were obtained by 4 and 6 distinct stages: with and without heat treatment of the AgNWs/PMMA/Al film and with and without selective dissolution of Al substrate.
- The AgNWs/PMMA electrodes were transferred onto a transparent adhesive tape to improve the mechanical properties.
- The electrodes were subjected to mechanical deformation by repeated bending with simultaneous measurement of the electrical resistance. Differences between their electrical behavior depending on method of manufacture have been found.
- The sheet resistance and diffuse transmittance values determined prove that by the method described it is possible to obtain AgNWs/PMMA-type electrodes that can be used in manufacturing three-dimensional solar cells. To improve the optical and electrical properties of these electrodes it is necessary to optimize the method of manufacture.

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