ISFOE 14
7th International Symposium on Flexible Organic Electronics
7 - 10 July 2014, Thessaloniki, Greece   isfoe.physics.auth.gr
www.upt.ro
INCD EMC
www.incemc.ro

OPTIMIZATION OF THE ELECTRICAL AND MECHANICAL PROPERTIES OF TRANSPARENT ELECTRODES BASED ON SILVER NANOWIRES SUPPORTED ON POLYETHYLENE TEREPHTALATE

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

[1] University "Politehnica" of 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 recent years several reports demonstrated that random networks of AgNWs, due to their high dc conductivity and optical transmittance, are a promising replacement of ITO-based transparent conductive electrodes for flexible electronics [1-3]. The aim of this study was to improve the electrical and mechanical properties of thin films obtained from silver nanowires (AgNWs) deposited on a flexible support of polyethylene terephtalate (PET). First, AgNWs were obtained by the "polyol" liquid phase synthesis method in the presence of chloride ions. The as obtained AgNWs were characterized by scanning electron microscopy (SEM), UV-Vis spectroscopy, energy dispersive X-ray analysis and X-ray diffraction. After purification, the AgNWs were deposited on a flexible support of PET. To improve the adhesion of the AgNWs coating to the substrate, thin films of polymethyl methacrylate (PMMA) were interposed between the layer of AgNWs and the PET substrate, and thus flexible transparent conducting thin films were obtained. The as obtained AgNWs/PET and AgNWs/PMMA/PET structures were characterized by SEM, UV-Vis spectroscopy and the sheet resistance of the transparent conducting films was determined by the van der Pauw method. It was observed that further heat treatment of PET/PMMA/AgNWs at temperatures higher than the softening temperature of the PMMA improves conductivity and coating adhesion of AgNWs to the PET substrate.

Experimental

Synthesis of Ag nanowires

Silver nanowires (AgNWs) were synthesized through a modified polyol process, as described below [4, 5].
The precursor was injected at ambient temperature and the whole mixture was heated up to 160 °C. 0.3 mmol of $AgNO_3$ is dissolved in 5 mL of analytical grade ethylene glycol (EG) (solution 1). In solution 1, 0.5 mL NaCl ethanol solution is added dropwise under stirring in the dark.
By addition of the NaCl solution, the AgCl precipitation reaction takes place:

$AgNO_3 + NaCl \rightarrow AgCl_{(s)} + NaNO_3$ (1)

It is stirred for 5 minutes using a magnetic stirrer. 0.9 mmol 40,000 PVP is dissolved in 10 mL ethylene glycol (EG) (solution 2) and then the solution degassed by bubbling N_2. The AgCl suspension in EG is injected into the reactor at ambient temperature. The reaction mixture is heated at the same rate (4°C/min) up to 160°C under stirring at 200 rpm under nitrogen. After reaching the temperature of 160°C, the mixture is kept under stirring 1 hour. The cooling of the reaction mixture is made naturally by removing the reactor from the oil bath.
Purification of a AgNWs is made by extracting the original solvent used in the synthesis (EG) by centrifugation at a speed of 4000 rpm and re-dispersing the nanowires in ethanol 96%. After three cycles of washing and centrifugation and replacement of dispersant, the nanowires are redispersed in 5 mL ethanol.

Deposition of thin films based on AgNWs

For deposition of thin films based on AgNWs, transparent polyethylene terephtalate (PET) sheets are used as substrate, over which is deposited a thin layer of polymethylmethacrylate (PMMA) designed to increase the adhesion of silver nanowires on PET support.
Deposition of thin films involves the following steps (Fig. 1):
1. On the PET sheet a thin layer of PMMA using 5% PMMA solution in chloroform is deposited by doctor blade method. Drying is done at least 24 hours at room temperature in a dust-free environment.
2. The layers of AgNWs are deposited from a suspension of AgNWs in ethanol, also by means of doctor blade method. 2 to 6 layers of AgNWs are deposited sequentially with intermediate drying in an oven after each deposition for 15 minutes at 50°C and cooling to room temperature another 15 to 20 minutes.

Characterization

The obtained silver nanostructures were characterized by X-ray diffraction (X'Pert PRO MPD PANalytical diffractometer, CuKa 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). Sheet resistance of the transparent electrodes obtained by AgNWs deposited on PMMA/PET was determined by van der Pauw method using the experimental setup presented in Fig. 2. Electrical contacts were made on each corner of the sample by coating with electro-conductive paint based on silver (Bison). For each sample four consecutive measurements of the currents were conducted corresponding to four values of the voltage applied to the contact points A, B, C, D located in the corners of the samples. The configuration used to carry out the measurement is shown in Fig.3 [6]:
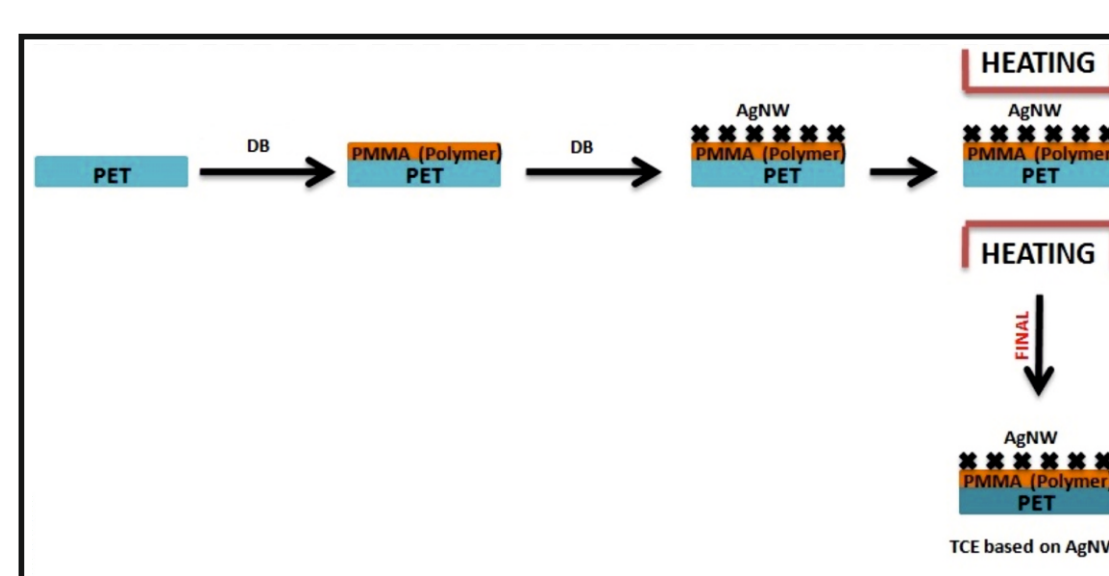

Fig. 1. AgNWs-based transparent electrodes manufacturing steps (DB = doctor blade).

Fig. 2. Experimental setup for the measurement of sheet resistance of AgNWs on PMMA/PET transparent conductig films

Practically, voltages V_{DC}, V_{AB}, V_{BC} şi V_{AD} were applied and currents I_{AB}, I_{DC}, I_{AD} and I_{BC} respectively were read. The electrical resistances were calculated using Ohm's Law:

$R_{AB,DC} = V_{DC} / I_{AB}$ (2)

$R_{DC,AB} = V_{AB} / I_{DC}$ (3)

$R_{BC,AD} = V_{AD} / I_{BC}$ (4)

$R_{AD,BC} = V_{BC} / I_{AD}$ (5)

Two partial sheet resistances were calculated according to the relations (6) and (7):

$$\rho_1 = \frac{\pi}{2\ln 2} f\left(\frac{R_{AB,DC}}{R_{BC,AD}}\right) \frac{R_{AB,DC} + R_{BC,AD}}{2}$$ (6)

$$\rho_2 = \frac{\pi}{2\ln 2} f\left(\frac{R_{DC,AB}}{R_{AD,BC}}\right) \frac{R_{DC,AB} + R_{AD,BC}}{2}$$ (7)

where $f(R_{AB,DC} / R_{BC,AD})$ and $f(R_{DC,AB} / R_{AD,BC})$ are correction factors. The final sheet resistance was calculated as the arithmetic mean of the two partial resistances.
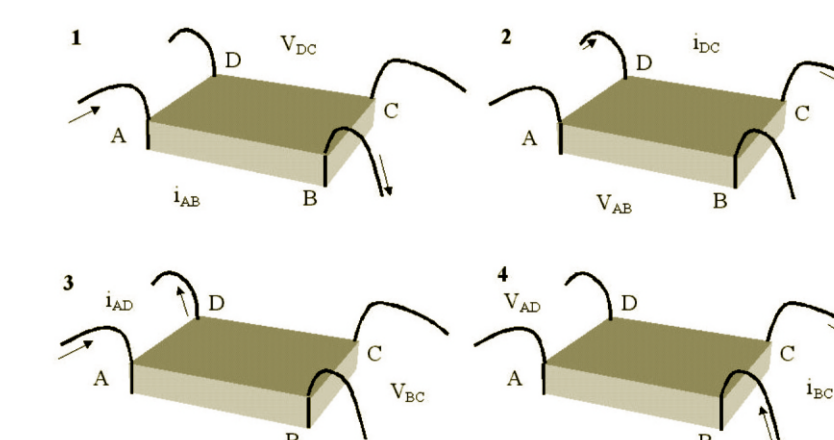

Fig. 3. Configuration of contacts in the van der Pauw method [6].

Results and Discussion

The XRD profiles of the synthesized AgNWs samples revealed the presence of cubic Ag grown preferentially along the (111) direction as the major phase along with some tetragonal Ag. The UV-Vis plasmon absorption spectra highlighted the presence of nanowires by a characteristic peak located at 378 nm. From the SEM image of AgNWs synthesized by injecting the precursors at 25°C (Fig. 4) it can be seen that their average diameter is about 50 nm.

SEM micrographs of the AgNWs on PMMA/PET films, obtained by depositing successive 2, 4, and 6 layers of silver nanowires are shown in Fig. 5 and their photographic images in Fig. 6.

The UV-Vis diffuse transmittance spectra for two (samples 2x$_i$), four (samples 4x$_i$) and six (samples 6x$_i$) layers of AgNWs deposited on PMMA/PET are presented in Fig. 7. One can observe that the diffuse transmittance at 530 nm of the PMMA/PET substrate is around 90%. Diffuse transmittance at 530 nm decreases with increasing number of layers deposited, reaching 75% for two layers, 65% for four layers and 58% for six layers of AgNWs deposited. The two minima in the diffuse transmission spectrum located at 352 nm and 378 nm correspond to the absorption peaks observed in the plasmon absorption spectra of the silver nanowires.

The results of electrical measurements made by the van der Pauw method are shown in Table 1. The samples obtained by application of two layers of nanowires were not appropriate for electrical measurements because not all corners of the samples were in electrical contact with the surface of the film. This is due to the inhomogeneity of the arrangement of nanowires on the surface of the substrate, also observed from the SEM images.
All thin layers obtained by applying four (4.x$_i$) and six layers (6.x$_i$) nanowires exhibited electrical conductivity, regardless of the points on the surface of the sample used to measure it.

Table 1. Results of electrical measurements made by the van der Pauw method

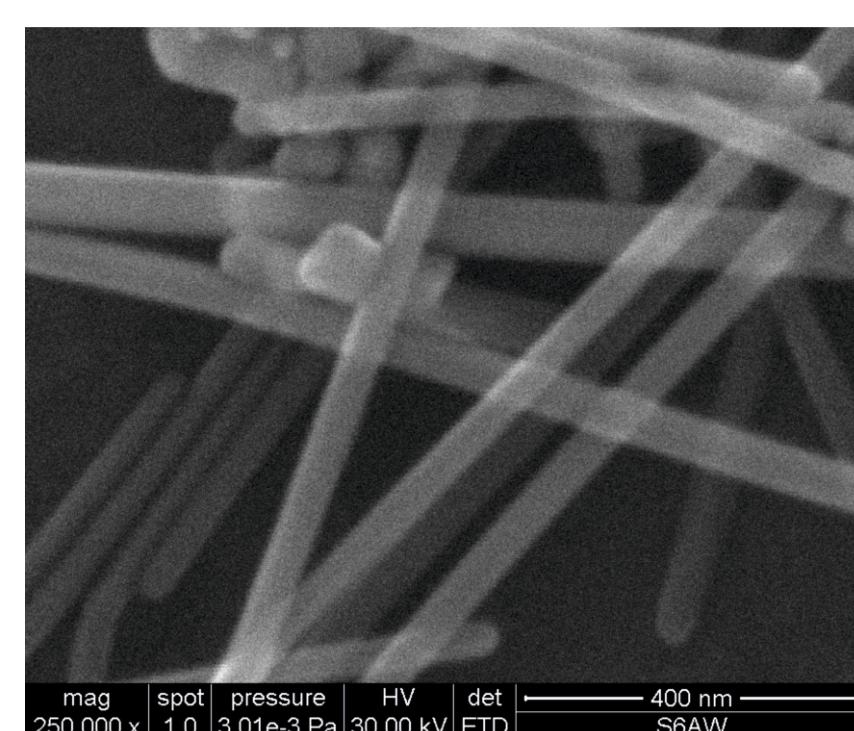| Sample no.	4.2	4.2a	4.2b	4.3	6.1	6.3
V_{DC} [V]	5,87	5,74	5,65	5,86	4,44	4,09
I_{AB} [mA]	1,43	2,13	2,49	0,74	1,02	3,27
$R_{AB,CD}$ [kΩ]	4,10	2,69	2,27	7,92	4,35	1,25
V_{AB} [V]	5,87	5,74	5,64	5,86	4,40	4,08
I_{DC} [mA]	1,49	2,15	2,45	0,76	1,05	3,17
$R_{DC,AB}$ [kΩ]	3,94	2,67	2,30	7,71	4,19	1,29
V_{BC} [V]	5,87	5,04	4,86	5,86	2,41	2,03
I_{AD} [mA]	3,5	3,72	3,61	2,92	3,33	3,45
$R_{AD,BC}$ [kΩ]	1,68	1,35	1,35	2,01	0,72	0,59
V_{AD} [V]	3,86	5,12	4,83	5,86	2,36	2,05
I_{BC} [mA]	3,56	3,86	3,85	2,96	3,60	3,70
$R_{BC,AD}$ [kΩ]	1,08	1,33	1,25	1,98	0,66	0,55
Sheet resistance kΩ/☐	5,55	4,35	3,94	9,60	4,40	1,97

Fig. 4. SEM image of AgNWs synthesized by injecting the precursors at 25°C.
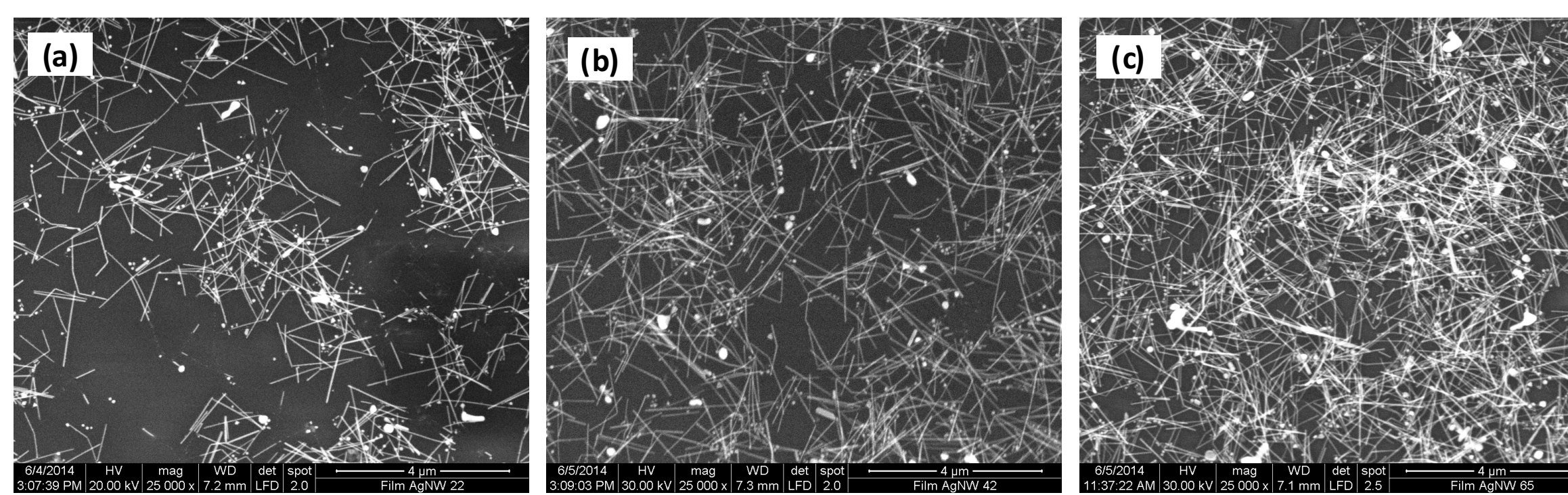

Fig. 5. SEM micrographs of AgNWs on PMMA/PET films for two layers (a); four layers (b) and six layers (c) of AgNWs.
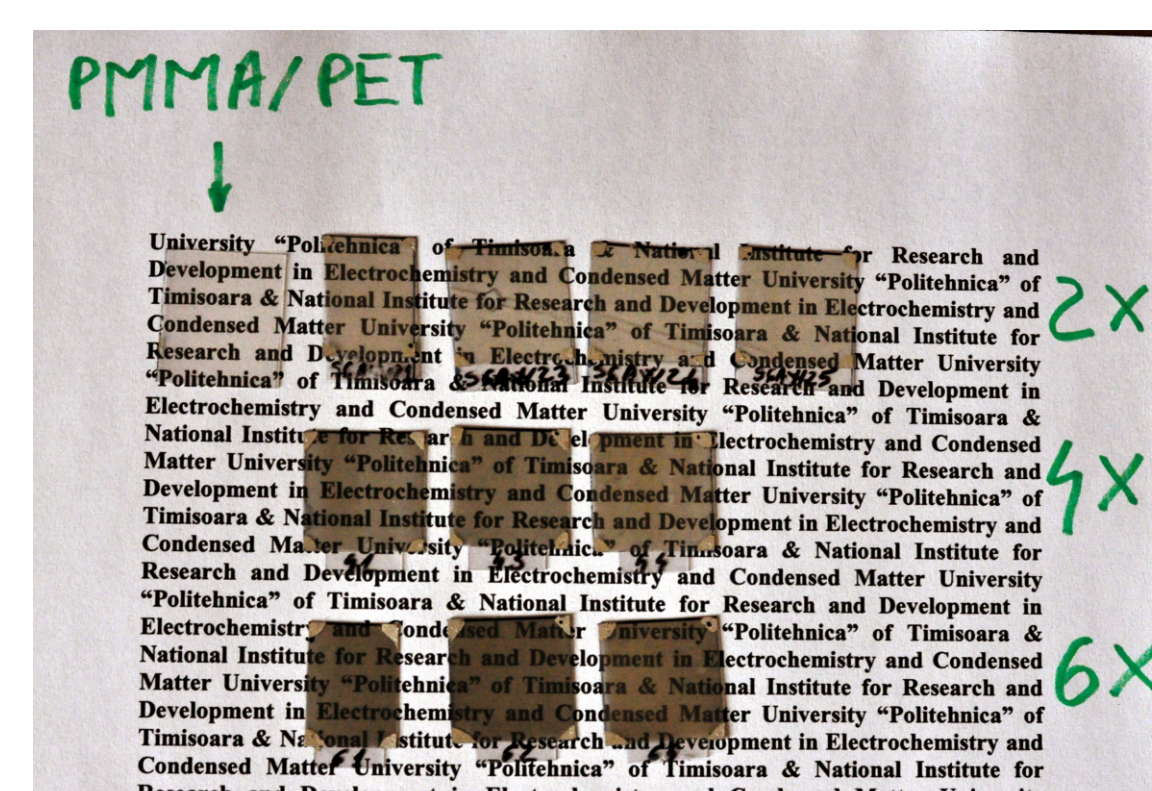

Fig. 6. Photographic images of transparent conductor thin films based on AgNWs obtained by deposition of 2, 4 and 6 layers of nanowires on PMMA/PET.
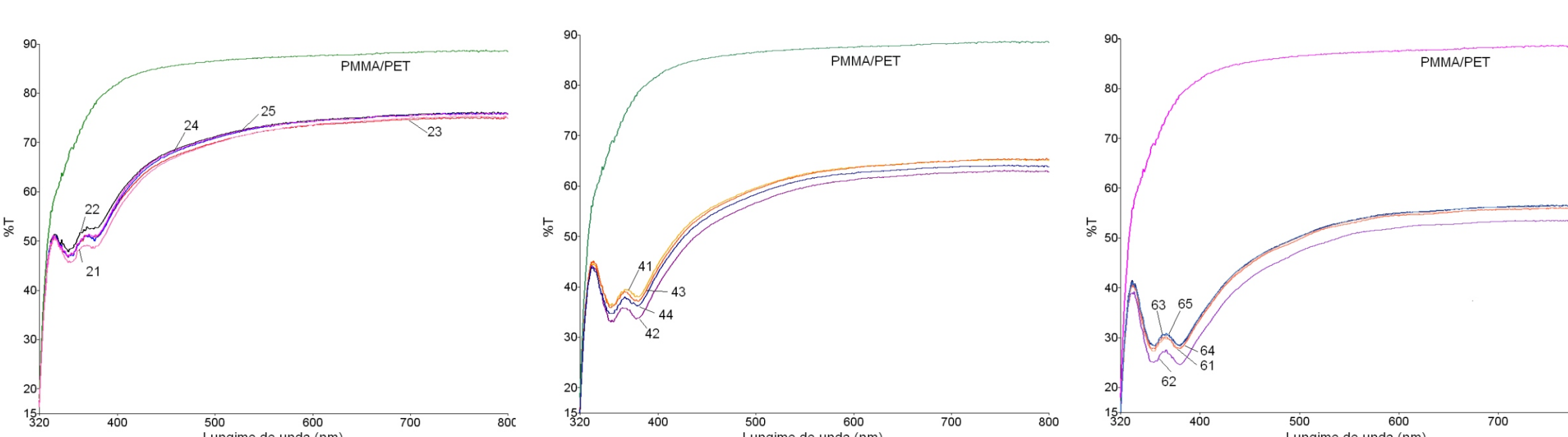

Fig. 7. UV-Vis diffuse transmittance spectra for two (samples 2x$_i$), four (samples 4x$_i$) respectively six (samples 6x$_i$) layers of AgNWs deposited on PMMA/PET.

Conclusions

- It can be noted that by depositing two successive layers of AgNWs the film is discontinuous and inhomogeneous, however for four and six layers of AgNWs a more homogeneous film is obtained, with an increased density of nanowires.
- Diffuse transmission spectra indicates that the diffuse transmittance at 530 nm decreases with increasing number of layers, reaching 75% for 2-layer, 65% for four layers and 58% for six layers of AgNWs deposited. The transparent electrodes obtained by depositing the same number of AgNWs layers present close transmittance values in the visible indicating good homogeneity of the distribution of wires on the surface.
- Electrical measurements indicate quite important variations of sheet resistance for the same type of samples, probably due to differences in the number of contact points between the nanowires. Sheet resistance can be improved by heating the film at 150°C for 40 minutes, which has the effect of improving the electric contact between the nanowires and a decrease of sheet resistance by about 30%.
- An optimal compromise between the electrical resistance and diffuse transmittance of AgNWs on PMMA/PET films obtained by the method described above is achieved for four layers of AgNWs deposited.

References

[1] Liangbing Hu, Han Sun Kim, Jung-Yong Lee, Peter Peumans and Yi Cui, Scalable Coating and Properties of Transparent, Flexible, Silver Nanowire Electrodes, ACS Nano, 2010, 4 (5), pp 2955–2963
[2] Sukanta De, Thomas M. Higgins, Philip E. Lyons, Evelyn M. Doherty, Peter N. Nirmalraj, Werner J. Blau, John J. Boland and Jonathan N. Coleman, Silver Nanowire Networks as Flexible, Transparent, Conducting Films: Extremely High DC to Optical Conductivity Ratios, ACS Nano, 2009, 3 (7), pp 1767–1774
[3] Cai-Hong Liu, Xun Yu, Silver nanowire-based transparent, flexible, and conductive thin film, Nanoscale Research Letters 2011, 6:75
[4] R. Banica, R. Baies, R. Bucur, C. Locovei, A. Kellenberger, T. Nyari, Study of liquid phase synthesis of silver nanowires for solar cell applications, 3rd European Energy Conference – E2C, October 27 – 30, 2013, Budapest, Hungary
[5] R. Banica, R. Baies, A. Kellenberger, D. Ursu, T. Nyari, Silver nanowires synthesis in the PVP-silver chloride system, International conference "ECOIMPULS 2013 – Environmental Research and Technology", November 07 – 08, 2013, Timisoara, Romania
[6] D. Daghero, Experimental study of non-conventional gap features in novel superconductors PhD Thesis, 2002.