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 terephthalate (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 polyethylene methylacrylate (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/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 FET/PIMMA/AgNWs at temperatures higher than the softening temperature of the PMMA improves conductivity and coating adhesion of AgNWs to the PET substrate.

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 100 °C. 1.1 mmol of AgNO₃ was dissolved in 5 mL of analytical grade ethylene glycol (EG) (solution 1), and 0.3 mmol NaOH ethanolic solution was added dropwise under stirring in the dark. By addition of the NaOH solution, the Ag precursor solution turns transparent. 

AgNWs deposition

It is stirred for 5 minutes using a magnetic stirrer. 6.6 mmol 40,000 PVP is dissolved in 10 mL of ethanol.

Deposition of thin films

2 to 6 layers of AgNWs are deposited sequentially with intermediate drying in an oven at 160°C, the mixture is kept under stirring 1 hour. The cooling of the reaction mixture is made in EG is injected into the reactor at ambient temperature. The reaction mixture is heated at the same rate (4°C/minute) up to 160°C under stirring at 200 rpm under nitrogen. After reaching the temperature of 160°C, the mixture is kept under stirring 5 hours. The cooling of the reaction mixture is made naturally by removing the reactor from the oil bath.

Characterization

The obtained silver nanostructures were characterized by X-ray diffraction (XRD) using a PANalytical X’Pert PRO diffractometer, CuKα radiation, -2θ step scanning, Bragg-Brentano geometry, Automatic Degenereous SMD, UV-Vis spectroscopy (Lambda 950 Perkin-Elmer spectrophotometer with integrating sphere), scanning electron microscopy (FEI Quanta 3D Ligero G2).

Sheet resistance of the transparent electrodes obtained by AgNWs deposited on PMMA/PET was determined by the 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 pastes based on silver ( Silvacon). For each sample, two partial sheet resistance measurements of the conductance 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.

Ref.: 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 transmittance spectra indicate that the diffuse transmittance at 550 nm of the PMMA/PET substrate is around 90%. Diffuse transmittance at 550 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 transmittance spectrum is determined by depositing the same number of AgNWs layers present clear transmittance values in good agreement with those found for AgNWs deposited on PET. The optical transmittance is affected by the distribution of nanowires on the surfaces.

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 films 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 50%.

An optical compression 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.

Results and Discussion

The XRD profiles of the synthesized AgNWs samples revealed the presence of cubic Ag grown preferentially along the (111) direction in the major phase along with some tetragonal Ag. The UV-Vis diffuse transmittance spectra show the presence of nanowires at 370 nm. From the SEM image of AgNWs synthesized by injecting the precursor at 25°C (Fig. 1) can be seen that the as-obtained nanowires exhibit an average diameter of about 50 nm.

SEM micrographs of the AgNWs deposited on PMMA/PET films, obtained by depositing successive 2, 6, and 10 layers of silver nanowires are shown in Fig. 4 and their photograph images in Fig. 5. The UV-Vis diffuse transmittance spectra for two samples (samples 2a, 4) and six samples (samples 6a) layers of AgNWs deposited on PMMA/PET are presented in Fig. 7. One can observe that the diffuse transmittance at 550 nm of the PMMA/PET substrate is around 95%. Diffuse transmittance at 550 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 transmittance spectrum located at 250 nm and 370 nm correspond to the absorption peaks observed in the plasma 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 measurement as a consequence not all of the nanowires were in electric 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 the layers obtained by applying four (4x) and six (6x) layers of nanowires exhibited electrical conductivity, regardless of the points on the surface of the sample used to measure it.

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 transmittance spectra indicate that the diffuse transmittance at 550 nm of the PMMA/PET substrate is around 95%. Diffuse transmittance at 550 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 transmittance spectrum is determined by depositing the same number of AgNWs layers present clear transmittance values in good agreement with those found for AgNWs deposited on PET. The optical transmittance is affected by the distribution of nanowires on the surfaces.
- 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 films 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 50%.
- An optical compression between the electrical resistance and diffuse transmittance of AgNWs deposited on PET film is observed and it is achieved for four layers of AgNWs deposited.

References