MATERIALS SCIENCE

Fabrication and study of thin transparent conductive films prepared by Spin Coating from metal nano-wires

CIENCIA DE MATERIALES

Fabricación y estudio de películas delgadas conductoras y transparentes de nano-hilos metálicos preparadas por Spin Coating

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(Recibido: Noviembre 25 de 2015 – Aceptado: Marzo 30 de 2016)

Abstract

Transparent conductive thin films on glass substrates from metal nano-wires were produced by the spin coating method by varying the speed of rotation between 1000 and 9000 RPM. Morphological and structural properties of the deposited layers were studied by Scanning Electron Microscopy (SEM). The electrical and optical properties were studied as a function of layer thickness by the Van Der Paw method and transmittance measurements in the range between 350 and 800 nm. A correlation between the thickness of the deposited layers and their electrical and optical properties is obtained, showing less sheet resistance to larger thickness while its transmittance decreases. Samples with sheet resistance of about 20 Ω/sq and with average 77% light transmittance at 550 nm were obtained.

Keywords: *Metal nano-wire, spin-coating, thin films, transparent conductors.*

Resumen

Se fabricaron películas delgadas conductoras y transparentes sobre sustratos de vidrio a partir de nano-hilos metálicos por el método spin coating, variando la velocidad de rotación entre 1000 y 9000 revoluciones por minuto. De las capas depositadas se hizo un estudio de sus propiedades morfológicas y estructurales mediante microscopía electrónica de barrido (SEM). Las propiedades eléctricas y ópticas se estudiaron en función del espesor de las capas mediante el método de Van Der Paw y con medidas de transmitancia en el rango entre 350 y 800 nm. Se encuentra una correlación entre el espesor de las capas depositadas y sus propiedades eléctricas y ópticas, presentando menor resistencia de hoja a mayores espesores a la vez que su transmitancia disminuye. Se obtuvieron muestras con resistencia de hoja alrededor de 20 Ω/sq y transmitancia óptica promedio de 77% a 550 nm.

Palabras clave: *Conductores transparentes, nano- hilos metálicos, películas delgadas, spin coating*

1. Introduction

Modern opto-electrical and electrochemical devices demand a new material which on being synthesized in thin film shape, have a high charge carrier density in its conduction band and allow the passage of light in the visible spectrum, that means, a conductive and transparent material which can be used as a transparent electrode in such devices. Among those devices are LCDs, solar cells, touch screens, flexible panels, LEDs, OLEDs, etc. Currently, the Transparent Conductive Oxides (TCOs) are used as transparent and conductive films, but the most commonly used it is the Indium Tin Oxide (In_2O_3:Sn or ITO) because of its high transparency in the visible ($T \approx 85$ %) and low sheet resistance ($Rs < 100$ Ω/sq). The TCOs are transparent in the visible light region because their energy gap is higher than the energy of photons in the visible spectrum. For ITO, the gap is 3.8 eV (Pasquarelli et al., 2011).

Although the ITO has optimal properties, there are many drawbacks in its use for the current technology, so it is necessary to find a new alternative. Between the drawbacks, we find: the Indium is a scarce element which have been highly exploited; the industrial fabrication process of ITO thin films is so expensive and complex; the ITO has got ceramic properties, doing it useless for the flexible opto-electrical devices. Getting a new material that having the best physical properties become a big challenge. (Dinh et al., 2013; Larson et al., 1997; Chung et al., 2012; Tokuno et al., 2011).

The metal Nano Wires (Cu or Ag principally) have got high acceptance like an ITO substitute. They have been used in solar cells and LEDs, getting a performance as higher as ITO. (Dinh et al., 2013; Tokuno et al., 2011; Hosseinzadeh, 2013). The nanowires are nanostructures that resemble the wire shape with diameters of the order of dozens of nanometers and lengths of tens and hundreds of micrometers. The Silver conductivity (6.3 x 10^7 S/cm), the higher in all metals and the fact that there are simple processes to obtain the silver nanowires, have displaced the applications with copper nanowires that, in addition, in its fabrication process has harsh and costly techniques (Wang et al., 2011).

Even though the Silver nanowires (Ag NW) have optical and electrical properties as good as ITO, there have presented troubles in Ag NW thin films, like inhomogeneity, adherence lack and longevity of the material on the substrate, challenges that we have to try to make it a viable replacement of ITO. Establishing a good fabrication process of Ag NW thin films which we can control the deposit on the substrate and the physical conditions of the process, it is so important, because they are connected with the final properties of the product. For example, the film thickness, although we are not going to measure it directly, is of great relevance, the bigger will be, it will indicate considerable quantity of material layers, therefore a low film transmittance, because there are much material that is absorbing light, but, for this same reason, there will be more connections among the Ag NW, getting to improve the final film conductivity (less sheet resistance). Otherwise, will happen with lower thickness (Dinh et al., 2013; Larson et al., 1997; Tokuno et al., 2011; Hosseinzadeh, 2013).

The spin coating is characterized to be a simple and cheap technique (TechnischeFakultat Der Christian -Albrechts-UniversitatZu Kiel, Master's degree program in Materials Science and Engineering, 2002). This technique will be used to deposit the material in the Ag NW thin films fabrication process. The method comprises the application a small amount of liquid solution containing the film material to be deposited on a flat substrate that is going to rotate at high speed. The centripetal force is going to spread the liquid, coating and leaving a thin film of solution over the substrate surface. The thin film thickness, as all the other physical properties, will depend of the solution composition as well as of the parameters used in the thin film fabrication, like the solution viscosity, solvent evaporation rate, solution concentration, angular frequency and rotation time (Pasquarelli et al., 2011;

Wang et al., 2011; South Dakota State University, 2012). The final thin films are characterized and analyzed by three techniques: Scanning Electron Microscopy (SEM) to observe the films structure and morphology; the four point probe method, to determine the sheet resistance, and UV-VIS-NIR spectroscopy to study the optical properties by transmittance.

2. Methodology

The Ag NW solution used in the experimental process was acquired to Blue Nano Inc. In the specifications we find that the Ag NW average diameters and lengths are 35 nm and 10 μm respectively. The solvent is ethanol, with a standard concentration of 1.5 wt% and a density of 10 mg/ml. In the solution 95.5 % is Silver and the remaining are impurities (Blue Nano Inc, 2012).

For the layer's deposit, it was used glass substrates in a Spin Coater from Laurell Technologies Corporation. We deposited the solution perpendicularly with a dropper when the glass substrates achieved the desirable speed. The lack adherence of the material on the glass is one of the problems that we had. To improve the adherence, the glass has to stay as clean as possible, for this, the glasses were put to a cleaning protocol that involved degreaser soap, deionized water, acetone, isopropyl alcohol, nitrogen drying and plasma process, which we can obtain optimally clean surfaces.

We used square glasses of 15 x 15 mm as substrates made according to the Spin Coater. The quantity of material supplied per thin film was three drops, scattered over the glass by rotation for about 20s with room temperature. The speed range used in the films fabrication varied between 2000 and 9000 RPM. Just a solution fraction is vapored in the processes of rotation, centrifugation and coated over the substrate, therefore, the films fabricated are dried with a heating process on a hotplate at (100.0 ± 3.0) °C during 10 min.

The optical characterization of the films was made via the transmittance spectra, measured with a Cary 5000 spectrometer from Varian, in a spectral range of 300 to 800 nm (UV until Near Infra-Red). On the other hand, the electrical characterization was obtained through the sheet resistance by the four-point probe with the FPP 5000 equipment from Veeco, calibrated to measure from mΩ/sq to MΩ/sq.

The morphological and structural analysis of the thin film surfaces was made with the TESCAN VEGA3 SBU SEM equipment. The surface images obtained, have a range between a maximum orders of 500 μm until a minimum order of 1 μm. These images allow us to study morphology, homogeneity, orientation and Ag NW occupancy percentage. By last, it is important to clarify that the only initial condition we varied was the angular frequency of the substrates (that means we keep the solution quantity, rotation time, and temperature and drying time). It was studied the variation of transmittance, sheet resistance and material occupancy area as a function of the angular frequency.

3. Results

With the Spin Coating technique and the right substrates cleaning protocol it was possible the fabrication of Ag NW thin films.

Fig. 1 shows different images obtained by SEM, alternating the magnification orders (on the scales of 500 μm, 50 μm and 2 μm, respectively), for the same thin film fabricated at 4000 RPM. Fig1a shows a material scattering over the glass substrate that seems homogenous, except some impurities, but a deeper look reveals inhomogeneous dispersions. Fig. 1b clearly details material agglomerations on the substrate. These agglomerations may be due to the fact that the nanowires inside of solution were not enough homogeneously dissolved. By last, Fig. 1c illustrates that there is not any chosen orientation, establishing a metal and random nano-network. The electric current flow through the metal contacts on the network indicating that the greater the number of contacts, the greater the conductivity in the films (lower sheet resistance), making the occupation area of the material a relevant parameter, as it gives a quantification of the amount of material present in the abundant areas of the surface, as well as an idea of the number of contacts of the Ag NW. This fact affects the value of transmitted light because more material will cause increased scattering of the incident light. Later, we are going to do a measure of these phenomena (Seeing Fig. 2b). It is important to clarify that, images on Fig. 1 show a behavior continuously seen in all thin films fabricated, that means, an apparent homogeneity at scales of 500 µm that is lost when we appreciate material agglomerations showed at lower scales.

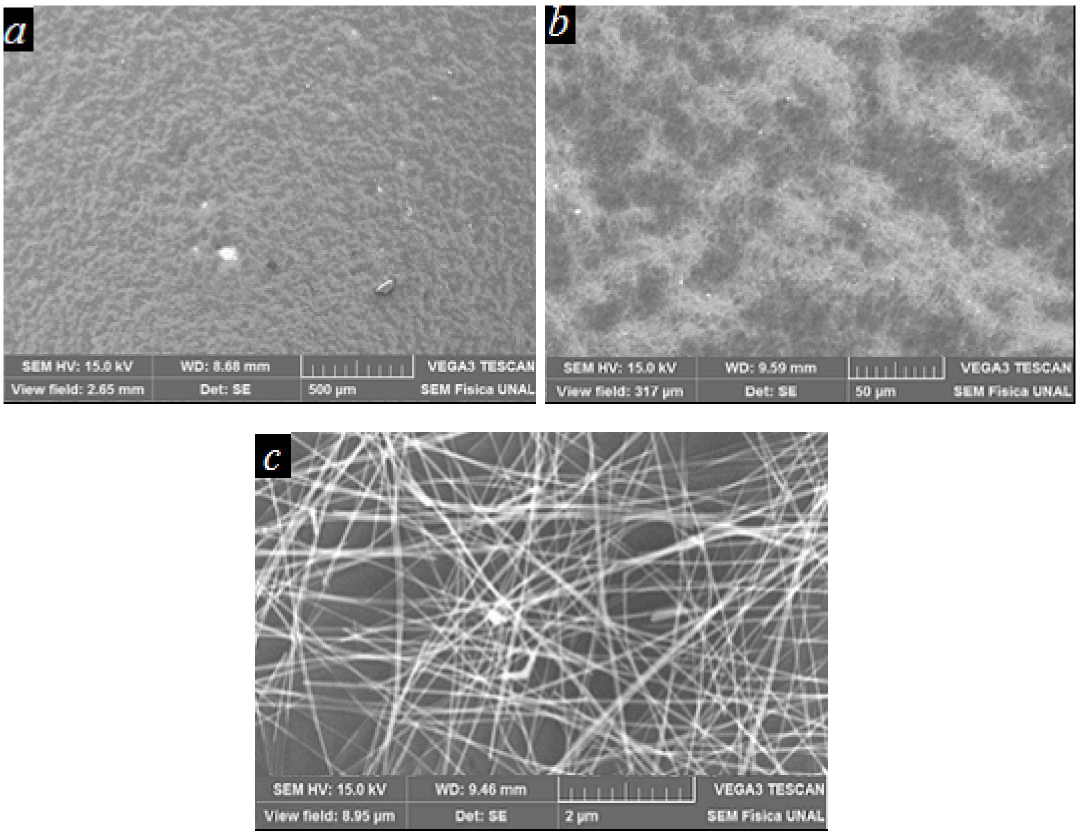


Figure 1. *SEM images of an Ag NW thin film fabricated at 4000 RPM. Scales used respectively: a: 500 µm, b: 50 µm and c: 2µm.*

These films are intended to be used as transparent electrodes in opto-electronic devices, so they must satisfy electrical and optical minimum conditions. This requirement sets two opposite sides between both physical properties. As we have explained, more transmittance implies lower electrical conductivity (or higher sheet resistance) and vice versa, so the goal is to get the best initial fabrication conditions which allows us find a good equilibrium point between the properties.

To probe this behavior, the measurement of sheet resistance and transmittance was made with films fabricated in an angular frequency range between 1000 and 5000 RPM. The average of sheet resistance for each measured frequency is shown in Fig 2a. This interval that we denominated "low frequencies", the sheet resistance in function of angular frequency, is approximately linear, as it can see. The values obtained on this frequency interval, represent an optimal electrical behavior for its use in transparent electrodes (the ITO sheet resistances are lower than 100 Ω/sq), fact that contrast with optical characterization results measured. The thin films transmittance spectra are shown in Fig. 2b, the higher transmittance percentages were 73.1 %, 72.8% and 72.0 % at 541nm by films produced to 4500, 5000 and 4000 RPM, respectively.

Although the 4500RPM film registers higher percentage than that of 5000 RPM, the difference is not significantly, this is due to the dispersion presented in the statistical analysis and that transmittance values have a lower growth rate as the angular velocity is increased. Despite these parameters do not have a linear relation, as illustrated in Fig. 2c., we got that relation between transmittance and sheet resistance is growing, ratifying descriptions about contradictions on these parameters. It is possible to conclude that the results as a whole, are below even the properties of ITO or other TCOs, and it is found that with the manufacturing technique, it is possible to obtain films on a wide range of speeds, with sheet resistance values (Rs < 30 Ω/sq) and optimal transmittances (around 72.5 %).

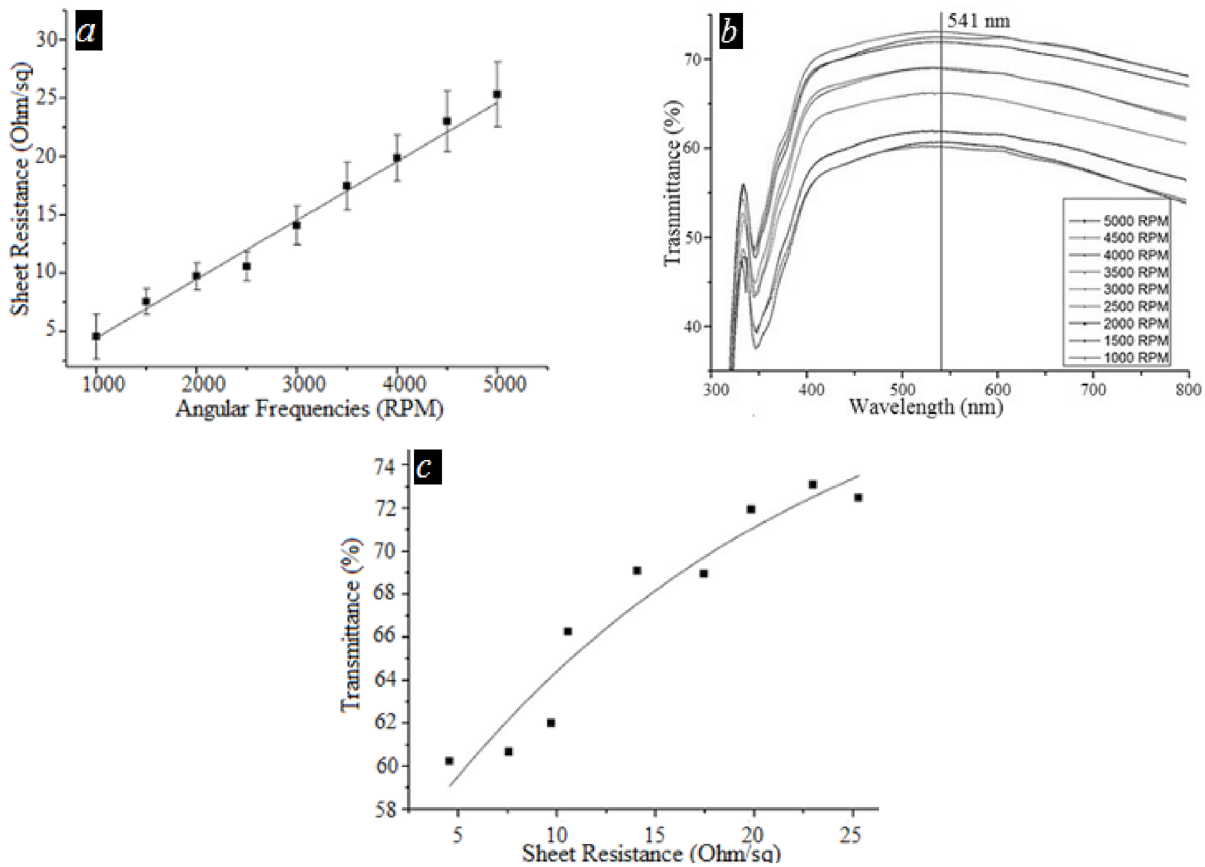


Figure 2. *a. Sheet resistance as a function of angular frequency. b. Transmittance spectra for films fabricated to [3000−5000] RPM interval. c. Transmittance as a function of sheet resistance at 541 nm wavelength.*

To improve the transmittance, we made thin films in a new frequencies interval, since 7000 to 9000 RPM. The physical properties obtained were promissory. Fig. 3a shows the average sheet resistances, where there are two main points to analyze. First of all, despite of high velocities, it still presents sheet resistances lower than 50 Ω/sq, which are still optimal values to apply the films like transparent electrodes; second, there is an unusual behavior in films fabricated at 8500 RPM, and it showed a sheet resistance considerably lower than other samples. That could be explained by the high homogeneity obtained to this sample, involving a material agglomerations decreasing on the surface and a further spread of this over the glass substrates. The optical spectra (Fig. 3b) illustrate the promissory results, as the main transmittance values are between 75-80% at 541 nm, as close as

ITO transmittance and higher than obtained with low frequencies.

The transmittance spectra obtained for low and high velocities (Fig. 2b and 3b respectively) suffer a strong decreasing at approximately 340 nm, the near ultraviolet. The energy for this wavelength is 3.6 eV. The decreasing is due to molecular electronic transitions of silica or silicon dioxide (SiO_2), main chemistry compound of glasses.

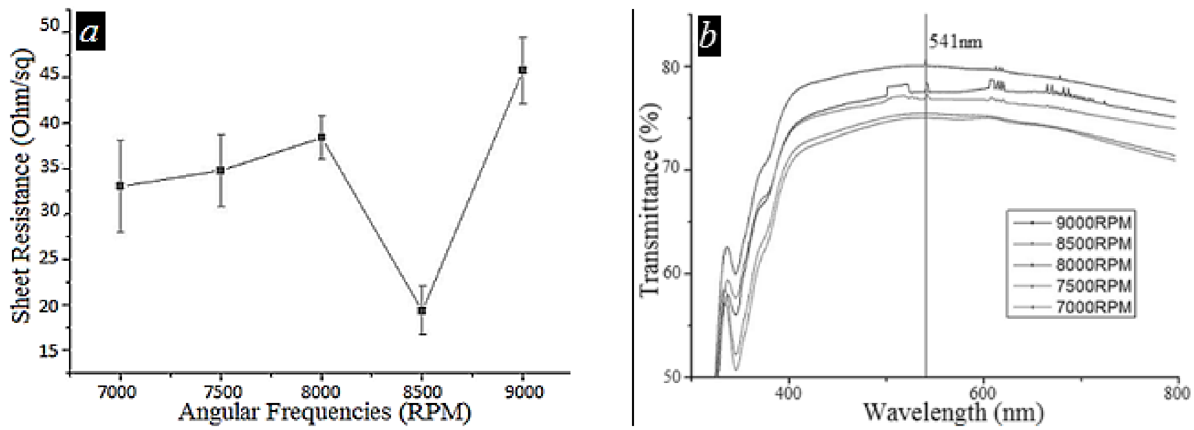
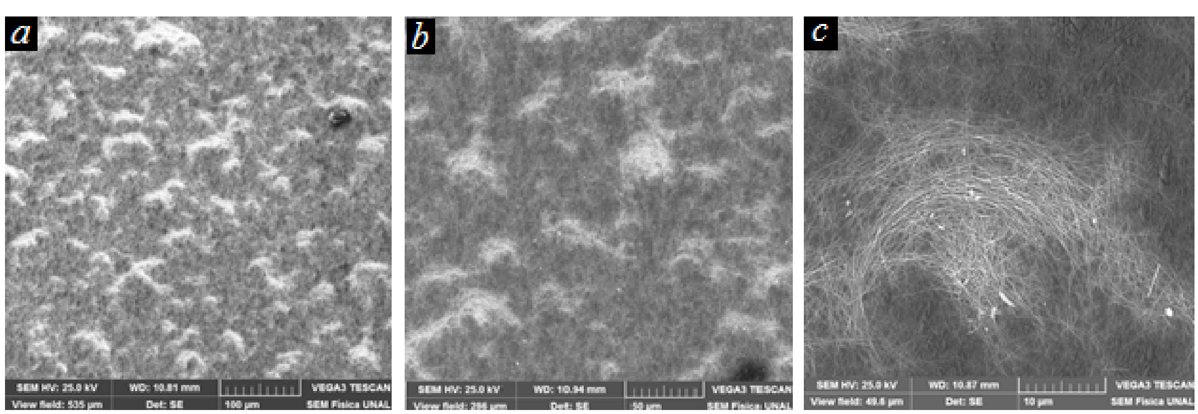


Figure 3. *(a): Sheet resistance as function of angular frequency to films fabricated at (7000 – 9000) RPM. (b): Transmittance spectra to films fabricated at high frequencies.*

The best results were found in two different films fabricated at 8000 and 8500 RPM, their average sheet resistance were: (38.4 ± 2.4) Ω/sq and (19.4 ± 2.7) Ω/sq, furthermore, each transmittance at 541 nm obtained was: 80.1 % and 77.1 % respectively. The first six SEM images (Fig. 4 a-f) correspond to the thin film fabricated at 8500 RPM in different scales (2 µm, 5 µm, 10 µm, 50 µm and 100 µm), other three images (Fig. 4 g-i) show the films fabricated at 8500, 4500 and 3500 RPM, respectively, with a 2 µm scale. The software alterations illustrated in white indicate the material map over substrate, obtaining, in this way, the occupied area values by the material on that observed region. The areas were 11352 µm² (13.9 %), 27245 µm² (33.4 %) and 35177 µm² (43.9 %) for each film fabricated at 8000, 4500 and 4000 RPM, respectively. Every percentage represents the agglomerations occupancy with respect to whole area. These measurements indicate that doubling the rotational speed from 4000 to 8000 RPM, the agglomerations are reduced almost three times, indicating that the way to solve the trouble of Ag NW agglomerations is increasing the angular frequency.



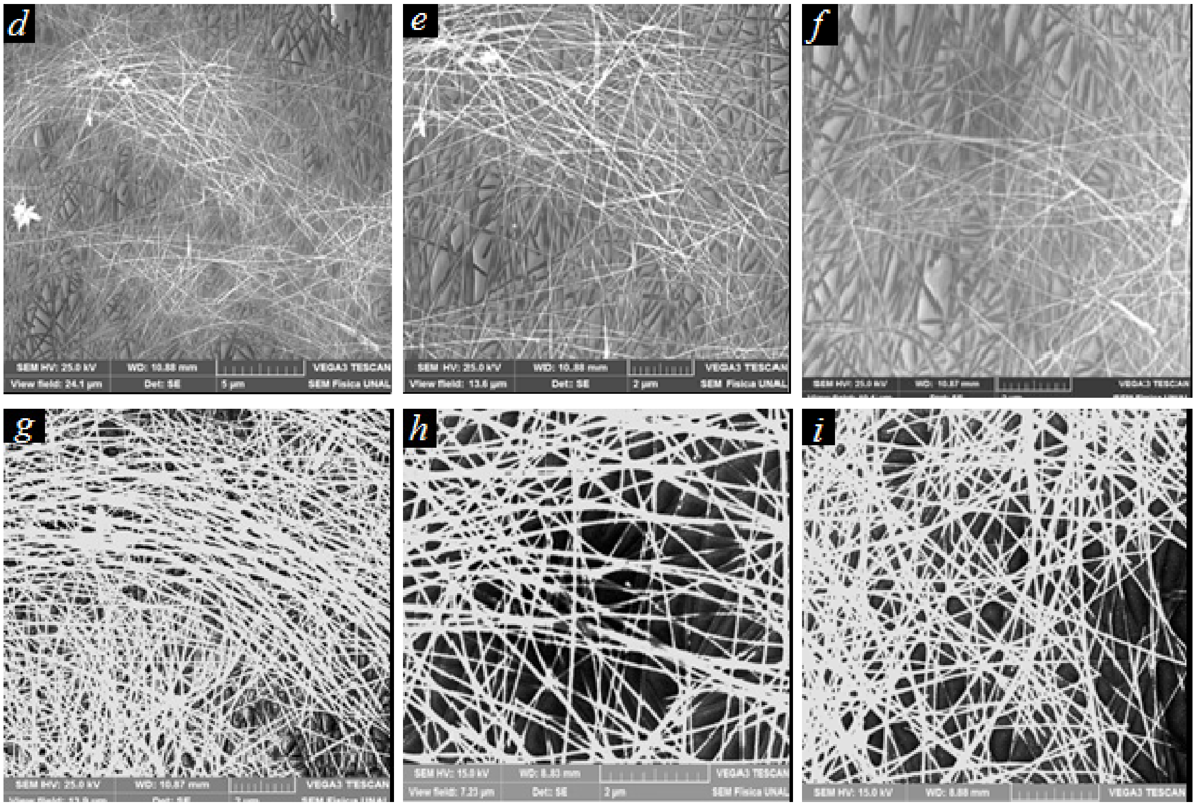


***Figure 4**. The first six images (from “a” to “f”) allow to see films fabricated at 8500 RPM in different scales. The other images (g, h and i) illustrate the map of Ag NW (Bright zones).*

By last, it is important clarify that optical, electrical and superficial properties measured over thin films fabricated with the Spin Coating method, are optimal to use them as transparent electrodes, besides, allow us to propose this material like a promissory material to replace the ITO and TCOs. Necessarily, we have to research deeply about some topics were not named, such as adherence, rugosity, thickness, solution homogeneity, etc., which should be studied and improved if we want to use the Ag NW thin films in opto-electronic devices.

4. Conclusions

We could demonstrate that the Spin Coating technique allow the Ag NW thin films fabrication between a large frequencies interval, obtaining optimal results in optical and electrical properties. This technique, can be impulse as a favorable, simple and cheap transparent electrodes fabrication method with our material.

It was possible to make films with sheet resistance lower than 50 Ω/sq and transmittance between 75 – 80% at 541 nm, minimum exigencies to replace the ITO by Ag NW films.

The material agglomeration was a problem found in films fabrication, made them inhomogeneous. One way found to solve this trouble, was increasing the angular frequencies. It was showed how these agglomerations are related with light absorbance. The 8500 RPM thin film fabricated showed the best physical results, as its sheet resistance was (19.4 ± 2.7) Ω/sq and transmittance 77.1 %.

The Optimal properties gotten, allow us to propose this material like a promissory material to replace the ITO and TCOs. There are still problems do not relate on this paper, such as adherence, rugosity, thickness, solution homogeneity, etc., which should be studied and improved, if we want to use the Ag NW thin films in opto-electronic devices on future.

5. Acknowledgments

The authors of the present publication are grateful to *Departamento Administrativo de Ciencia, Tecnología e Innovación*, COLCIENCIAS, for the support by funding the research Project code 1101-521-28577.

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