

## Investigation of Optical and Electrical Properties of Silver Sulfide Films Deposited on Polyamide Substrates

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A low cost chemical bath deposition (CBD) technique has been used for the preparation of Ag<sub>2</sub>S thin films on polyamide 6 (PA) substrates. Optical and electrical properties of these films were investigated. Optical micrographs have shown that the surface morphology depends on the number of immersions, becoming more continuous and homogeneous. The UV/Vis absorption spectra show that peak observed at 240 nm is assigned to sulfide functional group and less intense shallower band observed at 350 nm is attributed to silver. Analysis of IR spectrum shows that a new material (silver sulfide) is formed or bonded on the surface of PA after modification in acidic aqueous AgNO<sub>3</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O solution. The value of sheet resistance of silver sulfide layers varies from 39 MΩ/cm<sup>2</sup> to 1.26 MΩ/cm<sup>2</sup>. The sheet resistance depends on the concentration of silver nitrate solution and number of samples immersions in precursor solutions.

*Keywords:* polyamide, silver sulfide layers, CBD, composition, conductivity.

### 1. INTRODUCTION

Composite materials consisting of polymers covered by thin layers of inorganic compounds possess characteristic optical and semiconducting properties. The research of these modified polymers has attracted a considerable attention due to their potential application in different electronic components and devices like solar selective coatings, photoconductive and photovoltaic cells, IR detectors [1–2].

Polyamide (PA) is one of the most widely used polymers in polymer industry. Thus, the modification of PA surface can improve its mechanical adhesion and provide new ways of great application.

The semiconductor silver sulfide thin films have a number of applications in various devices, such as solar cells, photoconductors, IR detectors, where adhesion, optical and semiconductor properties are needed [1–10]. Also its layer on polyamide surface improves this polymer mechanical adhesion and thus, these PA matrices can be used for metallic covering.

Many methods can be used in the modification process of polymer surface. In this work we report the preparation of silver sulfide layers on PA films by the chemical bath deposition method using silver nitrate (AgNO<sub>3</sub>) and sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O) solutions. This method was chosen because of its simple technique, low cost and low temperature atmospheric processing.

The aim of present work was to form and characterize optical and electrical properties of silver sulfide layers on the surface of the hydrophilic polymeric material – polyamide 6 film (PA/Ag<sub>2</sub>S) by the means of optical microscopy, UV/Vis spectroscopy, (a good light transmission in visible region is one of the most important characteristic properties), FTIR and determine the

influence of immersions' number in aqueous solutions of AgNO<sub>3</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O on electrical resistance.

### 2. EXPERIMENTAL DETAILS

70 μm thick polyamide PA 6 tapes (specification TY 6-05-1775-76, grade PK-4, Russia) were used for the experiments. The porosity was measured by the BET method [11] using a Quantasorb sorption system (USA). The pores of PA 6 are much less than 1.5 nm. Film density was checked by the flotation method. It was found, that the density of PA is equal to 1.13 g·cm<sup>-3</sup> [12].

Prior to the experiments, samples of the PA 6 film 15 mm × 70 mm in size, were boiled in distilled water for two hours to remove the remainder of the monomer, and then dried with filter paper and in desiccators over CaCl<sub>2</sub> for 24 hours.

Distilled water, chemically and analytically pure reagents were used to produce solutions. Samples of PA were treated with aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O (0.2 mol/dm<sup>3</sup>) and AgNO<sub>3</sub> (0.06–0.08 mol/dm<sup>3</sup>) solutions at 20 °C with pH 2 (by adding nitric acid).

Solutions pH was measured using a pH-meter WTW330, with combinative glass and Ag/AgCl electrode and temperature meter WTW SenTix 41 (Germany).

After treatment, PA samples were rinsed with distilled water, dried over anhydrous CaCl<sub>2</sub> and used in further experiments.

Optical microscopy of PA samples modified by silver sulfides was carried out by an optical microscope Olympus CX31 (Olympus, Philippines) and photo camera Olympus C-5050 (Olympus, Japan), magnification ×400.

The UV/Vis spectra (from 190 nm to 790 nm) were recorded on a Spectronic Genesys 8 UV/Visible spectrophotometer with compensation of PA 6 absorption.

The changes on the surface structure were analyzed by IR. IR spectra were recorded with a Perkin Elmer FTIR Spectrum GX spectrophotometer (USA) by averaging 64

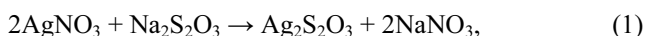
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scans with  $0.3 \text{ cm}^{-1}$  resolution at room temperature for each sample, the range  $4000 \text{ cm}^{-1} - 400 \text{ cm}^{-1}$ .

The resistance of  $\text{Ag}_2\text{S}$  layers was measured using MS8205F (Mastech, China) direct current numerical measuring device with special electrodes. The electrodes were produced from two nickel-plated copper plates. The plates were fixed with 1 cm spacing and the dielectric material was placed between them. The concept of sheet resistance is used to characterize thin deposited layers.

### 3. RESULTS AND DISCUSSION

In order to obtain the silver sulfide layers on PA film it was necessary to find the optimal conditions of the chemical bath deposition process. The silver sulfide was incorporated as follows: the films were immersed in aqueous solution of  $(0.06 - 0.08) \text{ mol/dm}^3$  silver nitrate ( $\text{AgNO}_3$ )/ $0.2 \text{ mol/dm}^3$  and sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) with pH adjusted to 2 by using nitric acid ( $\text{HNO}_3$ ) for 40 min at  $20^\circ\text{C}$  temperature. In the solution these reactions take place:

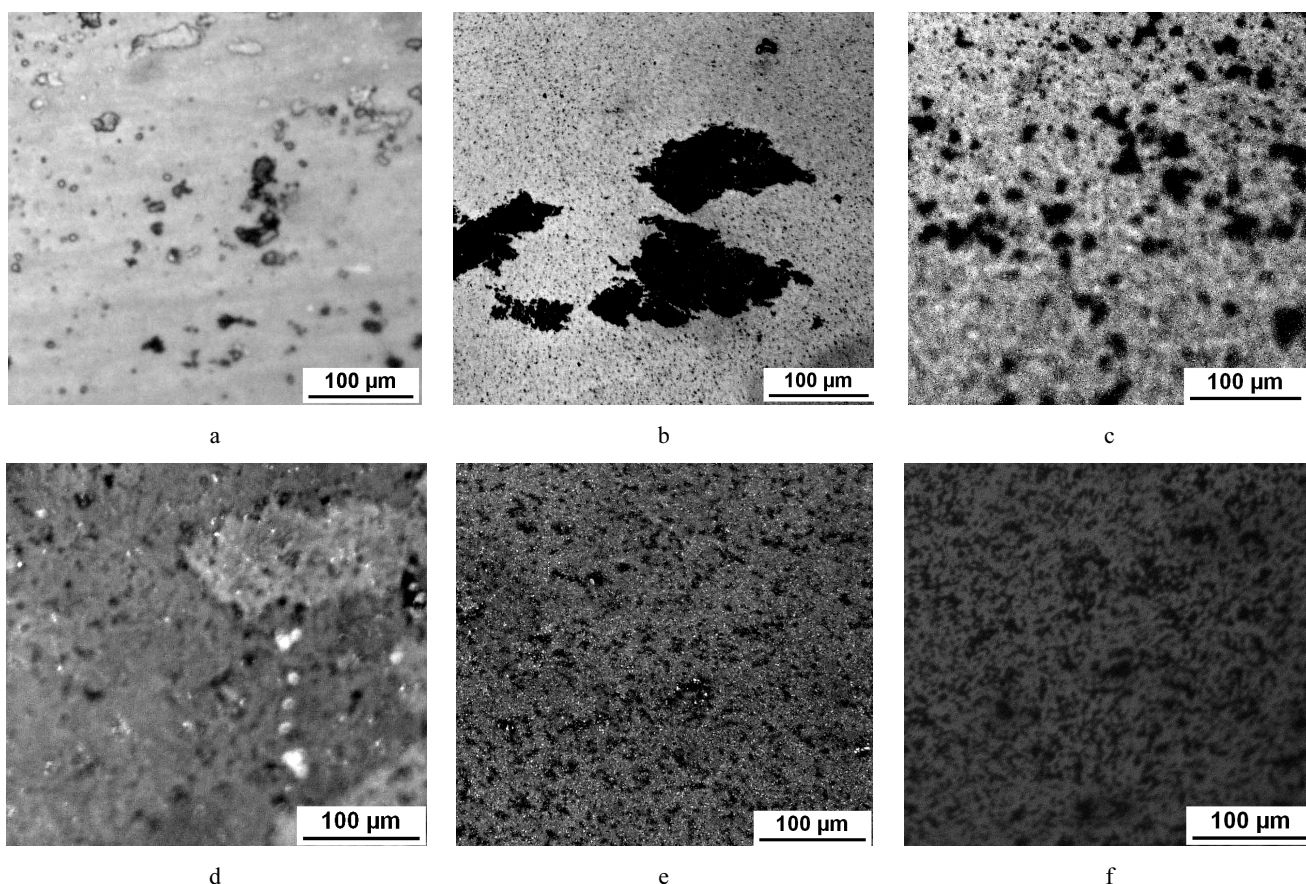


$\text{Ag}_2\text{S}_2\text{O}_3$  is an insoluble precipitate formed when a sodium thiosulfate reacts with silver nitrate. Silver thiosulfate in aqueous solution forms silver sulfide (final product of hydrolysis reaction) and sulfuric acid. Silver sulfide is one of the most insoluble salts known.

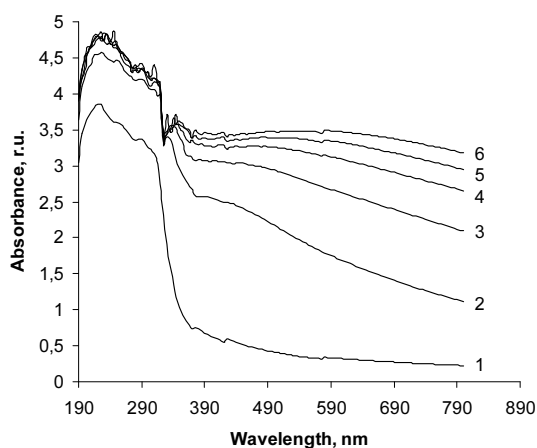
Procedure was repeated for 6 times. The  $\text{Ag}_2\text{S}$  films were obtained through reaction of silver sulfide on surface of polyamide.

The changes on the surface structure were monitored by optical microscopy. The optical micrographs of the PA/ $\text{Ag}_2\text{S}$  films with successive immersions in the precursor solution are shown in Figure 1. PA surface morphology changed and some irregularities appear after first treating immersions (Fig. 1, images a). The step 1 shows the nucleation process; on step 2 begins the growing of the nucleus; in step 3 the grown nucleus spread towards all directions; in step 4 begins the formation of new agglomerates over the first formed layer and in step 5 these latter particles spread over all directions, occupying the uncovered surface and/or the previous layer. After six immersion silver sulfide layer became more compact because formed  $\text{Ag}_2\text{S}$  layer was thicker (Fig. 1, images f). Color intensity of the PA samples with silver sulfide layers increased with increasing number of immersions and homogenous coating was formed on the surface of PA.

The changes of acidic aqueous precursor solutions of  $\text{AgNO}_3/\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , and the nature of particles formed in these solutions depending on reaction time were studied and characterized by means of UV/Vis absorption spectroscopy. These optical properties were investigated at  $20^\circ\text{C}$  temperature and normal atmospheric pressure. The UV/Vis absorption spectra of precursor solution depending on different reaction time are presented

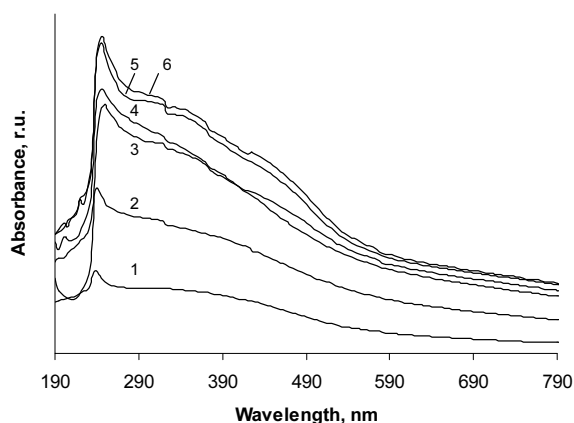


**Fig. 1.** Micrographs of PA samples (magnification  $\times 400$ ) immersed in acidic aqueous  $\text{AgNO}_3/\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  solutions for different time: a – 40 min, b – 80 min, c – 120 min, d – 160 min, e – 200 min, f – 240 min



**Fig. 2.** UV/Vis absorption spectra of acidic aqueous  $\text{AgNO}_3/\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  solutions depending on reaction time: 1 – (0–3) min, 2 – (4–6) min, 3 – (7–9) min, 4 – (10–12) min, 5 – (13–16) min, 6 – (17–20) min

in Figure 2. Three absorption peaks are observed in these spectra: after 0–3 minutes from reactions start (Fig. 2, curve 1) we can observe a strong absorption maximum at 225 nm, weakly defined shoulder at 260 nm and less intense peak at 295 nm. According to the data of lower polythionates  $-\text{S}_n-(\text{SO}_3)_2-$  [13] UV absorption spectra studying the absorption peaks of polythionate ions are most intensive at 256 nm ( $\log E = 3.15$ ) and 295 nm ( $\log E = 2.45$ ;  $E$  – molar extinction coefficient). In the anions of sodium thiosulfate  $-\text{S}-\text{SO}_3-$  sulfur atoms are  $-2$  and  $+6$  oxidation states. In addition, the UV absorption spectra of precursor  $\text{Na}_2\text{S}_2\text{O}_3$  are very closely identical. Absorption peak observed at 225 nm is assigned to  $-\text{SH}$  functional group (in this case  $\text{H}^+$  is replaced with  $\text{Ag}^+$  ion). A weakly defined shoulder at 260 nm and a less intense peak at 295 nm can be attributed to  $-\text{S}-\text{SO}_3-$  functional groups.



**Fig. 3.** UV/Vis absorption spectra of PA/ $\text{Ag}_2\text{S}$  layers depending on samples exposure time (min) in acidic aqueous  $\text{AgNO}_3/\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  solutions: 1 – 40, 2 – 80, 3 – 120, 4 – 160, 5 – 200, 6 – 240. The concentration of silver nitrates solution  $0.08 \text{ mol/dm}^3$

With increasing reaction time the peaks become more intense, significantly increased (Fig. 2, curve 2) and a new slight shoulder peak appears at 335 nm–340 nm. This absorption peak can be attributed and characterized by silver sulfide. In addition, the UV/Vis absorption spectra

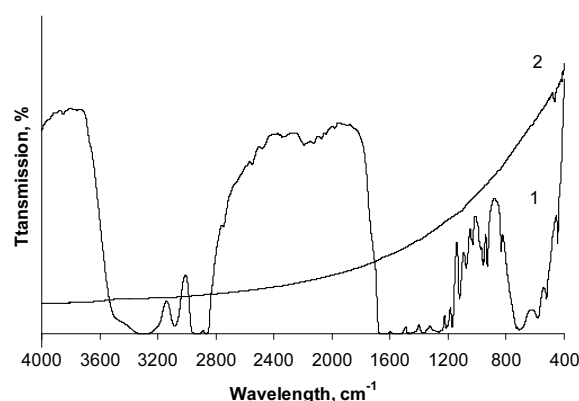
after 10 minutes from reaction start (Fig. 2, curves 4–6) are very closely identical. When silver reacts in an acidic aqueous medium with sodium thiosulfate the bands at 225 nm and 295 nm split into some less intense peaks, which locate in (225–245) nm and (280–320) nm ranges. After 12 minutes a slight shoulder peak at (335–340) nm eases up to 355 nm and a new band emerge at 585 nm. Prolongation of reaction time until 20 min in precursor solution resulted in increasing number of existing peaks. These UV/Vis spectra have the same feature according to the basis of the work data [14].

Thus, in the first reaction steps giving silver thiosulfate which further reacts to water, producing silver sulfide as the final product.

Seeking to investigate the changes on the surface structure of PA and PA samples, coated with a layer of silver sulfide, UV/Vis and FTIR spectra were recorded.

The UV/Vis absorption spectra of PA/ $\text{Ag}_2\text{S}$  samples immersed different time in precursor solution are presented in Fig. 3, where the spectrum of PA substrate is subtracted. Two absorption peaks are observed in these spectra: at 240 nm as a peak, and as a less intense and shallower band at  $\lambda = 350$  nm. Absorption peaks observed at 240 nm is assigned to sulfide functional group. A less intense shallower band at 350 nm is attributed to silver [15].

Thus, the UV/Vis absorption spectra confirm that the silver sulfide is deposited on PA 6 films. The intensity of absorption maxima in the spectra increases with increasing immersions time of polymer treatment in precursor solution.



**Fig. 4.** FTIR spectra of polyamide (1) and  $\text{Ag}_2\text{S}$  layers (2) formed after 6 immersions in acidic aqueous  $\text{AgNO}_3/\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  solutions. The concentration of silver nitrates solution  $0.08 \text{ mol/dm}^3$

Figure 4 shows a recorded FTIR spectra from  $4000 \text{ cm}^{-1}$  to  $400 \text{ cm}^{-1}$  range of virgin polyamide 6 film and polyamide 6 samples, coated with layers of silver sulphide ( $\text{Ag}_2\text{S}$ ) after 6 immersions in acidic aqueous  $\text{AgNO}_3/\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  solutions. The IR spectra of PA surface before and after modification processes show that, a new material formed or bonded on the surface of PA after modification.

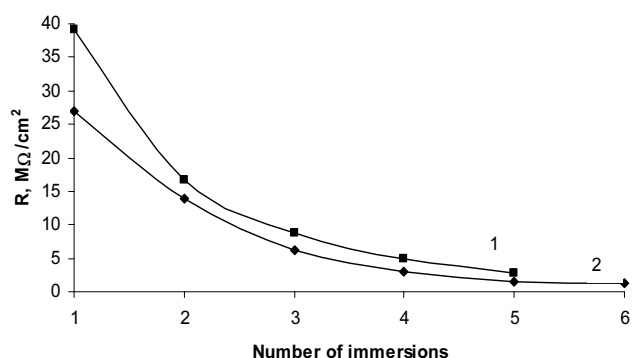
Absorption peaks were characterized following this literature: polyamide [12–16], silver sulfide [17–18]. It is reported that polyamide 6 has the structure  $-\text{[NH}-(\text{CH}_2)_5-\text{CO}]_n-$ , the infrared spectrum of PA results from the group frequencies of the C–H, C=O and

the N–H groups. On inspection of the higher wavenumber end of the spectrum, bands are observed at  $2867\text{ cm}^{-1}$  and  $2937\text{ cm}^{-1}$ , due to aliphatic symmetric and asymmetric C–H stretching, respectively. There is also a band at  $3300\text{ cm}^{-1}$  due to N–H stretching vibrations, while a strong band at  $1640\text{ cm}^{-1}$  is indicative of C=O. Hydrogen bonding plays a fundamental role in the structural and physical properties of polyamide 6 and is the most significant type of intermolecular interaction that influences the infrared spectrum of this polymer.

In the IR spectrum of  $\text{Ag}_2\text{S}$  layers formed after six immersions in precursor solution (Fig. 4, curve 2) a new absorption peak appears at  $467\text{ cm}^{-1}$ . Without it, it is still characterized by moderate-intensity peaks at  $318\text{ cm}^{-1}$  and  $122\text{ cm}^{-1}$  [18]. In recorded spectrum they are outside of the written wave frequency range.

PA films are treated in  $\text{AgNO}_3$  and  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  solutions, which contains silver ions and sodium thiosulfate sulfur (sulfide ion precursors). These ions react with each other and the resulting silver sulfide is deposited on the polymer. Thus, it's produced electrically semiconductive silver sulfide layer and the electrical resistance of the surface can be measured.

The dependence of the sheet resistance of PA/ $\text{Ag}_2\text{S}$  layers, obtained with different initial concentrations of  $\text{AgNO}_3$  solution, as a function of the number of immersions is displayed in Fig. 5.



**Fig. 5.** Sheet resistance of the PA surface covered with  $\text{Ag}_2\text{S}$  layers as a function of the number of immersions in acidic aqueous  $\text{AgNO}_3/\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  solution. The concentration of silver nitrates solution,  $\text{mol}/\text{dm}^3$ : 1 – 0.06, 2 – 0.08

A tendency of sheet resistance decrease with increasing the concentration of  $\text{AgNO}_3$  precursor solution was observed. Also PA/ $\text{Ag}_2\text{S}$  layers obtained by reaction with  $0.08\text{ mol}/\text{dm}^3$  solution (Fig. 5, curve 2), resistance is lower compared with values obtained when the reaction was taken place in  $0.06\text{ mol}/\text{dm}^3$   $\text{AgNO}_3$  solution (Fig. 5, curve 1).

The sheet resistance of silver sulfide layers formed over a wide concentration range ( $0.06\text{--}0.08\text{ mol}/\text{dm}^3$ ) of silver precursor solution was measured at room temperature. The use of silver nitrate and sodium thiosulfate precursors enables the formation on the surface of PA electrically conductive layer of silver sulfides with sheet resistance in the range of  $39\text{ M}\Omega/\text{cm}^2$  to  $1.26\text{ M}\Omega/\text{cm}^2$  depending on the concentration of initial silver precursor solution. This value exhibits a minimum at the number of immersions of 5 and 6 (Fig. 5).

The variation of the conductivity of  $\text{Ag}_2\text{S}$  layers on PA surface shows an evident of increasing silver sulfide concentration in formed layers. The formed layers may be considered more conductive. The resistance value can be easily controlled by choosing the concentration of the precursor solution and the number of immersions.

As expected, increasing number of immersions increases the surface conductivity. Concerning also the optical microscopy, UV/Vis and FTIR analysis, this fact is not assigned to a higher conductivity of the  $\text{Ag}_2\text{S}$  deposit according to the number of immersions, but suggests a more homogeneous one, with interconnected  $\text{Ag}_2\text{S}$  particles which provide the current flow between the probes of measurement. In addition, no changes in the measured conductivity were observed by changing the position (direction) of the probes on the film samples.

#### 4. CONCLUSIONS

1. The  $\text{Ag}_2\text{S}$  films can be obtained through reaction of silver sulfide on surface of polyamide 6.
2. Optical micrographs have shown that the surface morphology of  $\text{Ag}_2\text{S}$  films depends on the number of immersions, becoming more continuous and homogeneous. Moreover, as the number of immersion proceeds, a more uniform deposit is formed, interconnecting the isolated particles created in previous immersions.
3. Absorption peaks observed at  $240\text{ nm}$  is assigned to sulfide functional group. A less intense shallower band is observed at  $350\text{ nm}$  and can be attributed to silver ion. This fact was also suggested by the electrical conductivity measurements, which indicated also a formation of a crystalline phase of  $\text{Ag}_2\text{S}$ .
4. Analysis of IR spectrum shows that all absorption peaks intensity decreases with increasing number of PA immersions into  $\text{AgNO}_3/\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  solution.
5. IR spectra of modified PA showed that the new material  $\text{Ag}_2\text{S}$  was chemically bonded with PA functional groups after immersions in precursor solutions. The peak in the IR spectra of the  $\text{Ag}_2\text{S}$  into a polyamide was found at  $467\text{ cm}^{-1}$ , and assigned to the  $\nu(\text{Ag-S})$ .
6. The sheet resistance of the samples, formed using  $0.06\text{ M}\text{--}0.08\text{ M}$  solutions of silver nitrate and  $0.2\text{ M}$  sodium thiosulfate varies from  $39\text{ M}\Omega/\text{cm}^2$  to  $1.26\text{ M}\Omega/\text{cm}^2$ . The sheet resistance depends on the concentration of silver nitrate solution and number of samples immersions in precursor solutions.

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