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Deposition and characterization of silver sulfide layers on the polypropylene film surface

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Thin films of Ag_2S were deposited at room temperature on non-oriented isotactic polypropylene substrates immersed in a bath mixture containing aqueous solutions of silver nitrate, $AgNO_3$, for silver ion source, sodium thiosulfate, $Na_2S_2O_3$, for sulfide ion source and as a complexing agent, and nitric acid, HNO_3, for pH adjustment. Film samples were characterised by X-ray photoelectron spectroscopy (XPS) and chemical analysis. XPS analysis confirmed that a layer of Ag_2S was formed on the surface of the polypropylene film. The films were studied for their electrical conductivity and the results showed that the measured electrical sheet resistance depended on Ag : S ratio. A non-destructive millimeter wave analysis showed that distribution of Ag_2S particles according to resistivity distribution on the PP samples area is homogenous.

Key words: silver sulfide layer, chemical bath deposition, polypropylene, XPS

INTRODUCTION

In the recent years, metal chalcogenide semiconducting thin films on polymeric and other surfaces have been extensively studied due to their technological importance. Sulfides of many metals have low electrical resistivity [1] and can be used as electroconducting layers. Silver sulfide, Ag_2S, is an important chalcogenide compound which has been investigated for its numerous applications. Silver sulfide (Ag_2S) belongs to I–VI compound semiconductor materials with monoclinic crystal structure. Semiconductive silver sulfide films have attracted considerable attention because of being potential prospective optoelectronic and thermoelectric materials, such as photovoltaic cells, photoconductors, IR detectors, superionic conductors and ion selective electrodes [2–7]. In many cases, the quality of the fabricated material depends on spatial distribution of electrical or dielectric parameters in the whole area of the sample. This is especially important for large area semiconductor and dielectric substrates used in electronics and optoelectronics. A relatively short wavelength of the millimeter wave provides the possibility to utilize them for non-destructive homogeneity characterization of materials [8].

Ag_2S layers with different morphologies have been prepared via various methods, such as flash evaporation [9], radio frequency sputtering [10], thermal evaporation [11], hot pressing [12] and solution growth [13, 14], etc. All these techniques have advantages and disadvantages, depending on the type of application intended for the films. The conductivity of Ag_2S is strongly dependent on the stoichiometry. Hence, to study the conductance and switching properties of Ag_2S thin films we need a sample preparation technique, which is reproducible and results in thin films with the desired stoichiometry. Compared with the methods reported before, the chemical bath deposition technique is more convenient,

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facile, with low cost and low temperature atmospheric processing and environment-friendly because Ag_2S sediments from the reaction bath can be dissolved in nitric acid and obtained solution re-use [15].

In this study, an Ag_2S thin film on the hydrophobic polymeric material – polypropylene (PP) was synthesized using a chemical bath deposition (CBD) method. The technology is based on slow controlled precipitation of the desired compound from its ions in the reaction bath solution. A complexing agent is usually employed to control the reaction in a suitable medium as indicated by the pH to obtain crystal growth.

The surface morphology of Ag_2S layers on PP was characterized in the previous work [16].

In the field of surface chemistry X-ray photoelectron spectroscopy (XPS) gives extremely useful characteristics for studying the nature of surface films and their substrate. In this work, the chemical analysis and the XPS methods were used to determine the composition of the silver sulfide layers.

The aim of the present work was to form and determine the influence of immersion time of the polypropylene film in acidified aqueous solutions of silver nitrate and excess of sodium thiosulfate on the composition, electrical characteristics and homogeneity of deposited Ag_2S layers on PP.

EXPERIMENTAL

15 × 70 mm size samples of a non-oriented isotactic polypropylene (PP) film of 150 μm thicknesses (Proline X998, KWH Plast, Finland) were used for the experiments.

Distilled water, and analytically pure H_2SO_4, H_3PO_4, CrO_3, $Na_2S_2O_3 \cdot 5H_2O$, $AgNO_3$, reagents were used to prepare reaction solutions.

Before Ag_2S formation process, the surface of the PP samples was treated for 25 min at 90 °C with oxidizing solution (H_2SO_4/H_3PO_4 (1 : 1) saturated with CrO_3) in order to facilitate its adhesion properties.

The formation of Ag_2S layers on the oxidized PP was carried out in a thermostated glass reactor at constant temperature. A polypropylene substrate was dipped vertically into the reaction bath. Oxidized PP films were immersed for 40 min in aqueous $Na_2S_2O_3$ (0.2 mol/dm^3) and acidified aqueous $AgNO_3$ (0.08 mol/dm^3) solutions at 20 °C with pH 2.3. Solutions pH was measured by using a pH-meter WTW330, with a combinative glass and Ag/AgCl electrode and a temperature meter WTW SenTix 41 (Germany). Then obtained samples were removed from the reaction solution, rinsed with distilled water and dried at room temperature. The Ag_2S/PP samples were subjected for repetitive immersions in order to increase Ag_2S amount. After that the Ag_2S/PP samples were repeatedly immersed in the freshly prepared reaction solution. The immersion procedure was repeated for 5 times.

Before the chemical analysis, samples of PP strips plated with Ag_2S films have been mineralized. Samples were treated under heating with 6 mol/dm^3 nitric acid to oxidize sulfur compounds to sulfates. Heating with concentrated hydrochloric acid removed the excess of nitric acid. The resulting solution was poured into a 25 cm^3 flask and made up to the mark with distilled water. Then 5 cm^3 of this solution were taken for the sulfur concentration determination and the remaining part was used to determine the silver concentration.

The sulfur concentration in the silver sulfide layer was determined turbidimetrically [17]. Sulfate ions in the range from 1 mg/dm^3 to 15 mg/dm^3 may be readily determined by utilising the reaction with barium chloride in a solution slightly acidified with hydrochloric acid to give barium sulfate. A glycerolethanol solution helped to stabilise the turbidity of the barium sulfate suspension. The measurement of the intensity of the transmitted light as a function of the concentration of the suspension of $BaSO_4$ was carried out with a GENESYS 20 spectrophotometer (Thermo Spectronic, UK), at a wavelength λ = 400 nm. The standard deviation of the method with the photometric procedure in the range of concentrations from 5 mg SO_4^{2-} dm^3 to 10 mg SO_4^{2-} dm^3 was ± 8%.

The silver concentration was determined with an atomic Perkin-Elmer absorptionmeter 503 (λ = 328 nm). The sensitivity of the method is 0.06 μg/cm^3 for 1% Ag absorption.

The content of silver and sulfur was expressed as μmol/cm^2.

XPS measurements were performed with a Vacuum Generator (VG) ESCALAB MKII spectrometer. The non-monochromatic Al Kα X-ray radiation (hv = 1 486.6 eV) was used for excitation. The Al twin anode was powered at 14 kV and 20 mA. The photoelectron takeoff angle with respect to the sample surface normal was 90°, and XP spectra of Ag $3d_{5/2}$, S $2p_{3/2}$ and O 1s were taken at a constant analyzer energy mode (at 20 eV pass energy). The base pressure in the working chamber was kept bellow 5×10^{-7} Pa. The spectrometer was calibrated relative to Ag $3d_{5/2}$ at 368.0 ± 0.1 eV and Au $4f_{7/2}$ at 83.8 ± 0.1 eV. The quantitative elemental analysis was done by estimating peak areas and taking into account empirical sensitivity factors for each element [18]. A standard program was used for data processing (XPS spectra were treated by a Shirley-type background subtraction and fitted with mixed Gaussian-Lorentzian functions). Binding energies were referenced to C 1s (284.5 eV) on unsputtered surfaces. All samples were scanned as received – without an ion beam surface cleaning procedure. Assignation of the signals to specific structures or the given oxidation state of elements analysed was done by comparison with data reported by NIST standard Reference Database 20, Version 3.5 [19] and to literature references.

The electrical sheet resistance of Ag_2S layers was measured using a 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.

For the measurement of millimeter waves in the sample and transmitted (reflected) wave amplitude and phase at different points of the sample a millimeter wave bridge consisting of a reference signal and measuring signal channels was used. The tested sample is placed between special waveguide probes that provide both local excitation and reception of the low power millimeter wave signals. The sample can be moved relative to the exciting and receiving probes by scanning mechanism. Changes of the electric or dielectric parameters in the sample area cause changes in the amplitude and phase of the transmitted (reflected) signal. By probing the sample at different points with the millimeter wave beam, information about the homogeneity of the sample can be obtained. All measurement processes are computer controlled and the measurement results are compiled in the computer [8].

RESULTS AND DISCUSSION

Chemical analysis

As mentioned above, the method of preparation influences the composition and properties of sulfide layers. Therefore, the initial stage of the work was aimed to establish the chemical composition of the deposited silver sulfide.

The chemical composition of the silver sulfide layer obtained for different oxidized PP film immersion time in the acidified aqueous 0.08 mol/dm^3 $AgNO_3$ and 0.20 mol/dm^3 $Na_2S_2O_3$ solutions at 20 °C is presented in Fig. 1. As established, with increasing immersion time of the oxidized PP samples in the precursor solution, the concentration of silver (Fig. 1, curve 1) and sulfur (Fig. 1, curve 2) in the deposited layers increased.

Knowing the amounts of silver and sulfur, Ag and S molar ratios in the silver sulfide layers on PP were calculated. The results are presented in Table. It was shown that the composition of the obtained silver sulfide layers depended on the immersion time in the precursor solution and varied from $Ag_{1.4}S$ to Ag_2S.

XPS analysis

Ag_2S films deposited on the PP surface were examined by XPS measurements. The core levels S 2p, Ag $3d_{5/2}$ and O 1s spectra were measured. During formation of the Ag_2S layer on the

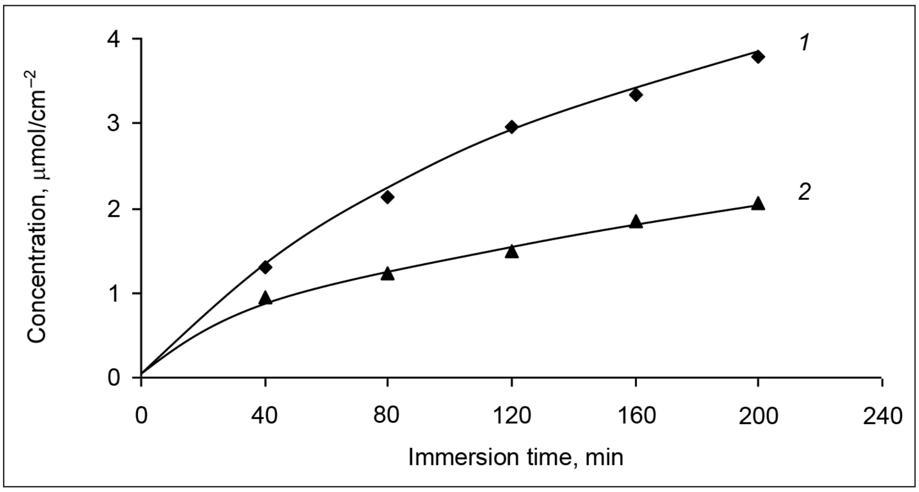

Fig. 1. Dependence of silver and sulfur concentrations in the deposited silver sulfide layers on the polypropylene immersion time in the acidified aqueous 0.08 mol/dm^3 $AgNO_3$ and 0.20 mol/dm^3 $Na_2S_2O_3$ solutions at 20 °C. The concentration, μmol/cm^2: *1* – Ag, *2* – S

Table. **XPS data on Ag_2S layers formed on oxidized PP surface**

Immersion time, min	Element	Content, at. %	Binding energy, eV	Possible composition	Ag:S		Sheet resistance, MΩ/cm^2
					XPS analysis	Chemical analysis	
40	Ag	33.33	368.5	Ag_2S	1.73	1.40	39.0
	S	22.23	160.8; 163.0; 168.8	Ag_2S; -S-S-; S(VI)-O			
	O	44.44	531.0; 532.1; 533.3	Ag-O; Ag_2SO_4; *$O_{2(ads.)}$			
120	Ag	50.70	368.2	Ag_2S	2.16	2.00	8.42
	S	24.67	161.0; 163.3; 168.4	Ag_2S; -S-S-; S(VI)-O			
	O	24.63	531.2; 532.0; 533.4	Ag-O; Ag_2SO_4; *$O_{2(ads.)}$			
200	Ag	40.68	368.0	Ag_2S	1.998	1.83	2.74
	S	22.18	160.8; 163.0; 168.8	Ag_2S; -S-S-; S(VI)-O			
	O	37.17	530.8; 531.9; 533.3	Ag-O; Ag_2SO_4; *$O_{2(ads.)}$			

* $O_{2(ads.)}$ – adsorbed oxygen.

surface of polypropylene, all processes proceed in an open medium; therefore, it is not possible to avoid ambient effects. Since the surface of this layer is active, it adsorbs oxygen, water, and other contaminants [20]. The layer of sulfide on the surface of the polymer is distributed in the form of islands [16] enabling an easy contact of the atmospheric oxygen with silver and sulfur ions. Therefore the surface of the Ag_2S layer can differ from the macrostructure and chemical composition of the entire layer. It is necessary to emphasize that the XPS method investigates very thin (up to few nm) surface layers.

The analysis of experimental XPS data shows (Figs. 2–4, Table) that the composition of Ag_2S layers formed at different

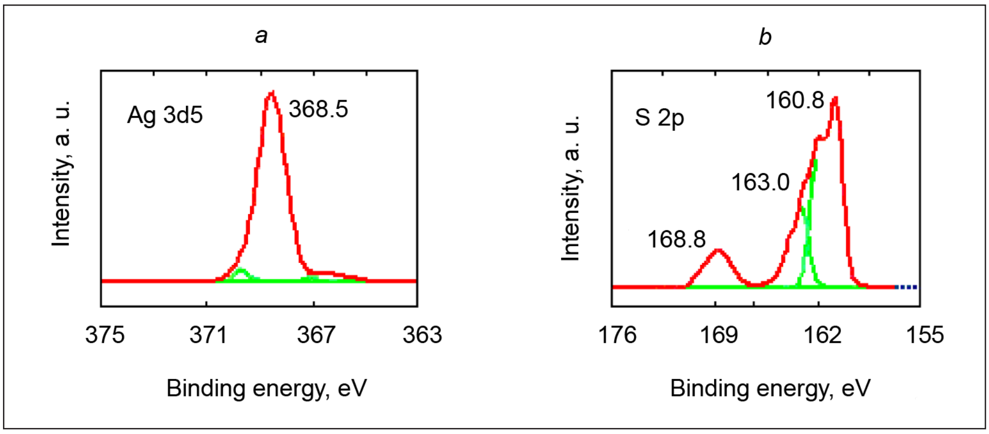

Fig. 2. Silver Ag 3d5 (*a*) and sulfur S 2p (*b*) XPS spectra of PP immersed for 1 time 40 min in the acidified aqueous 0.08 mol/dm^3 $AgNO_3$ and 0.20 mol/dm^3 $Na_2S_2O_3$ solutions at 20 °C

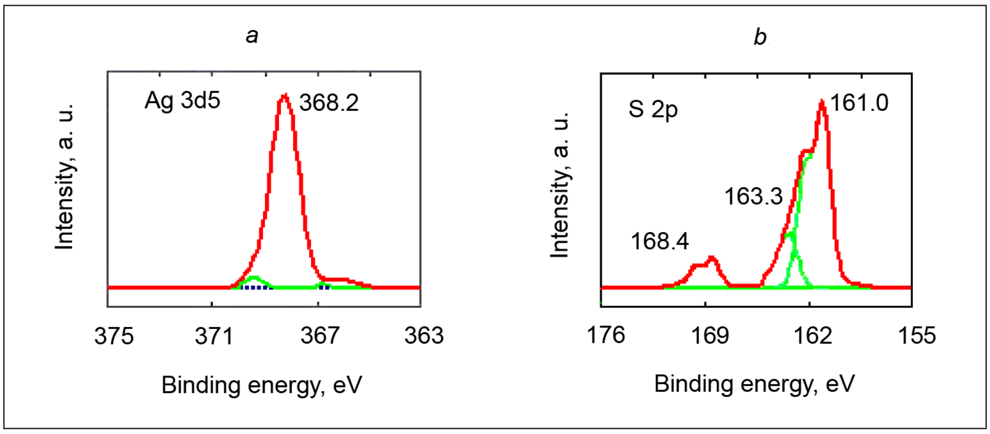

Fig. 3. Silver Ag 3d5 (*a*) and sulfur S 2p (*b*) XPS spectra of PP immersed for 3 times 120 min (3 × 40 min) in the acidified aqueous 0.08 mol/dm^3 $AgNO_3$ and 0.20 mol/dm^3 $Na_2S_2O_3$ solutions at 20 °C

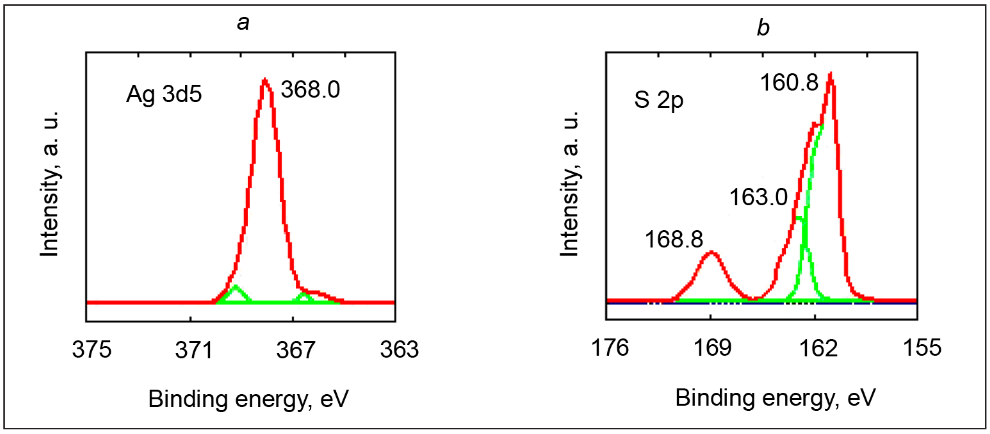

Fig. 4. Silver Ag 3d5 (*a*) and sulfur S 2p (*b*) XPS spectra of PP immersed for 5 times 200 min (5 × 40 min) in the acidified aqueous 0.08 mol/dm^3 $AgNO_3$ and 0.20 mol/dm^3 $Na_2S_2O_3$ solutions at 20 °C

immersion time is rather similar. They consist of silver, sulfur and oxygen in various combinations.

The S $2p_{3/2}$ spectra for film samples show three peaks at about 160.8, 163.0 and 168.8 eV. According to the NIST XPS database [19], the S $2p_{3/2}$ peak at 160.8 eV is assigned to the Ag–S–Ag bonding of Ag_2S and the S $2p_{3/2}$ peak at 163.0 eV is assigned to the –S–S– bonding. This peak probably resulted from the chemisorbed sulfide nanoparticles on Ag_2S rather than the incorporation of elemental sulfur since the S $2p_{3/2}$ peak occurs above 164.0 eV [21]. A spectral line at higher energies of about 168 eV originates from the oxidized sulfur [22]. For all samples the higher energy S $2p_{3/2}$ peak position at 168.8 eV well coincides with the known Ag_2SO_4 position (168.6 eV) [19]; therefore we assign this peak to the sulfur(VI) bond to oxygen.

According to literature data, the Ag $3d_{5/2}$ core level located at 368.3 eV corresponds to the binding energy of metallic silver [23] while the line at lower energies of 367.8 eV indicates the presence of Ag^+ [24, 25]. The peaks of Ag $3d_{5/2}$ at 368 eV and S $2p_{3/2}$ at 161.2 eV are the characteristic binding energies for Ag_2S [26] whereas the Ag $3d_{5/2}$ line for Ag bounded to sulfur has been reported at 368.9 eV [27]. The Ag $3d_{5/2}$ component with the binding energy of 367.9 eV was reported for Ag_2O [28], while for AgO it shifted by 0.5 eV to the value of 367.4 eV [29]. Summarising the analysis data of the experimental Ag $3d_{5/2}$ peak detected in the range between 383.5 to 368.0 eV (Table), it is difficult to distinguish between the Ag–O–Ag and Ag–S–Ag bond positions. However, concerning the S $2p_{3/2}$ core levels (Table) it can be noted that the majority of sulfur is in the S^{2-} state, confirming that the obtained layers are indeed Ag_2S.

The XPS spectrum for O 1s can be deconvoluted into free different contributions with binding energies at around 531.0, 532.0 and 533.3 eV. The peak at around 533.3 eV on the high binding energy side of the O 1s region was ascribed to the atmospheric oxygen adsorbed on the layer surface. The peak with the binding energy of 529.5 eV was reported for Ag_2O [28]. Two peaks at 528.7 and 531.0 eV are observed in the O 1s spectrum of AgO [30]. The presence of the component at 531.0 eV in all studied O 1s spectra confirms that the silver sulfide surface layer is oxidized.

Electrical sheet resistance measurements

The use of silver nitrate and excess of sodium thiosulfate precursors enables the formation of an electrically semiconductive layer of silver sulfides on the surface of PP. The sheet resistance of formed silver sulfide layers on the polypropylene was measured at room temperature. The dependence of the electrical sheet resistance of PP/Ag_2S layers as a function of the polypropylene immersion time in the precursor solution is displayed in Fig. 5. As expected, increasing immersion time leads to the increase of the the surface conductivity from 39 MΩ/cm² to 2.74 MΩ/cm². This value exhibits a minimum at the immersion time of 240 min (Fig. 5). In addition, no changes in the measured conductivity were observed by changing the position (direction) of the probes on the film samples.

The variation of the conductivity of Ag_2S layers on the PP surface shows an evident increase with increasing silver sulfide concentration in the formed layers. The formed layers may be considered more conductive. The sheet resistance value can be easily controlled by choosing the immersion time in the precursor solution.

Non-destructive homogeneity characterization

By probing the PP/Ag_2S sample at different points with the millimeter wave beam, information about the homogeneity of the sample was obtained (Fig. 6). It is seen that the PP/Ag_2S sample immersed for 5 times 200 min (5 × 40 min) in the acidified aqueous 0.08 mol/dm³ $AgNO_3$ and 0.20 mol/dm³

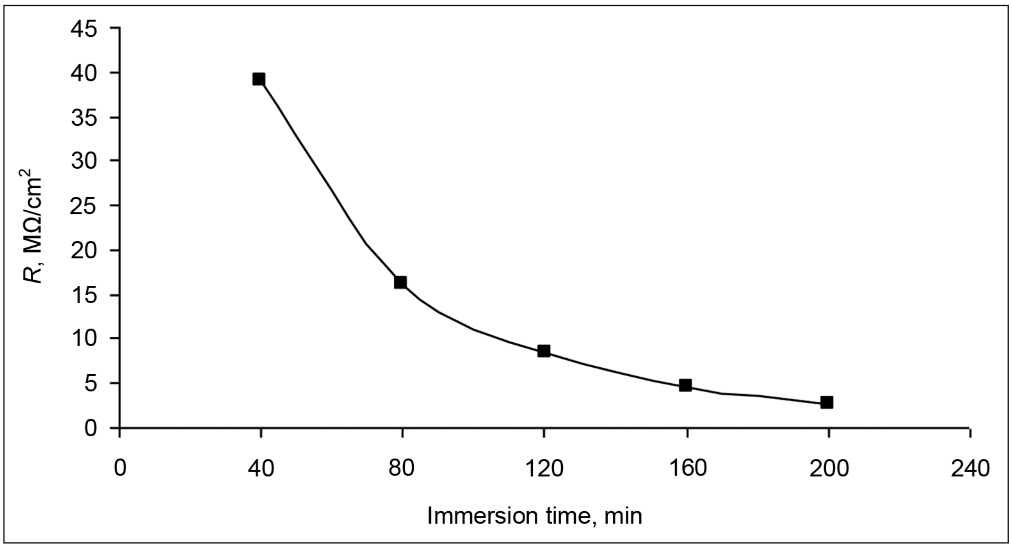

Fig. 5. Electrical sheet resistance of the PP surface covered with Ag_2S as a function of the immersion time in the acidified aqueous 0.08 mol/dm³ $AgNO_3$ and 0.2 mol/dm³ $Na_2S_2O_3$ solutions at 20 °C

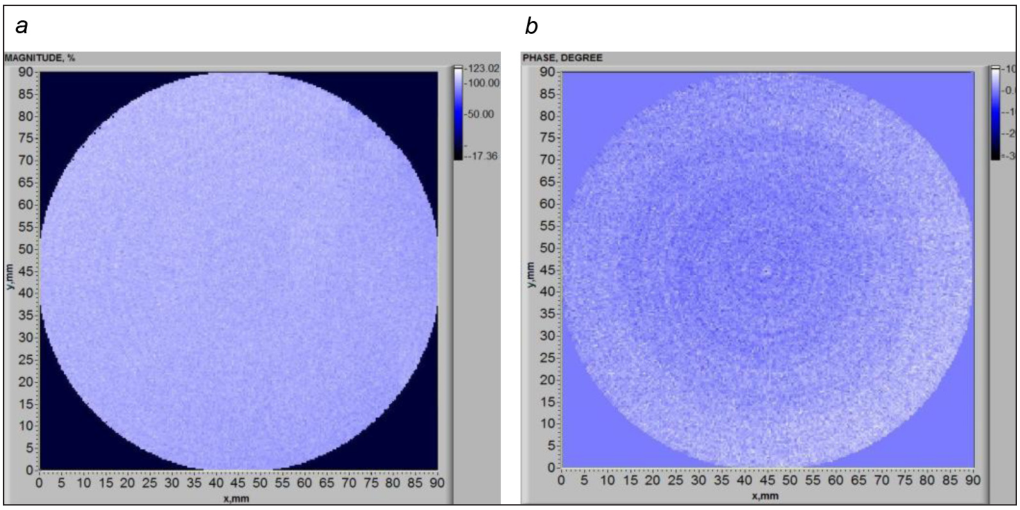

Fig. 6. Transmitted wave amplitude (*a*) and phase (*b*) homogeneity images for the PP/Ag_2S sample. PP immersed for 5 times 200 min (5 × 40 min) in the acidified aqueous 0.08 mol/dm^3 $AgNO_3$ and 0.20 mol/dm^3 $Na_2S_2O_3$ solutions at 20 °C. The thickness of the sample is 0.15 mm. The scanning area is 90 mm. The wave frequency is 118 GHz

$Na_2S_2O_3$ solutions at 20 °C is quite homogeneous according to resistivity distribution on the samples area.

CONCLUSIONS

1. Chemical and X-ray photoelectron spectroscopy analyses confirmed a formation of silver sulfide on the polypropylene surface.

2. The chemical composition of the obtained silver sulfide layers depended on the immersion time in the precursor solution and varied from $Ag_{1.4}S$ to Ag_2S.

3. By X-ray photoelectron spectroscopy various silver, sulfur and oxygen compounds (Ag_2S, Ag_2O, Ag_2SO_4, and adsorbed O_2) on the surface of polypropylene samples modified with silver sulfide were identified. The atomic percentage of the elements has shown that silver sulfide takes the major part in the layer.

4. The silver : sulfur ratio increases with increasing the immersion time in the precursor solution; this is in agreement with the results of samples' sheet resistance measurements since samples with a higher value of this ratio were more conductive. The value of electrical sheet resistance of silver sulfide layers on PP varies from 39 MΩ/cm^2 to 3.5 MΩ/cm^2.

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SIDABRO SULFIDO SLUOKSNIŲ POLIPROPENO PLĖVELĖS PAVIRŠIUJE NUSODINIMAS IR TYRIMAS

Santrauka

Ploni Ag_2S sluoksniai polipropeno (PP) plėvelių matricoje suformuoti cheminio nusodinimo metodu naudojant kambario temperatūros azoto rūgštimi parūgštintus sidabro nitrato ir natrio tiosulfato, kuris yra ne tik sulfido jonų šaltinis, bet ir kompleksadaris, vandeninius tirpalus. Cheminė analizė parodė, kad Ag : S molinis santykis kinta nuo 1,4 iki 2. Didėjant Ag : S santykiui paviršiaus elektrinė varža mažėja. Fazinė PP plėvelių, modifikuotų sidabro sulfido sluoksniu, sudėtis tirta rentgeno fotoelektroninės spektroskopijos metodu. Nustatyta, kad bandinių paviršiuje yra įvairių sidabro, sieros ir deguonies junginių – Ag_2S, Ag_2O, Ag_2SO_4 bei adsorbuoto O_2, tačiau sidabro sulfidas sudaro didžiausią sluoksnių dalį. Sidabro sulfido sluoksnių vienalytiškumas elektrinio laidžio pasiskirstymo juose atžvilgiu ištirtas skenuojančiu milimetrinių bangų mikroskopu.