

The influence of the deposition time on morphological and optical properties of Cu_xS films deposited on polypropylene substrate

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Copper sulfide (Cu_xS) films deposited on polypropylene substrate were obtained by chemical bath deposition (CBD) method. The influence of the deposition time on the morphology of Cu_xS films was studied by means of scanning electron microscopy. We have found that the average particles dimension increased from 37 to 49 nm with the increase of deposition time from 20 to 30 minutes. The study of optical properties of the copper sulfide films was carried out based on optical transmission spectra recorded in the 400 – 1000 nm wavelength range. The optical constants, such as refractive index, extinction coefficient and dielectric constant as well as electrical and optical conductivity of Cu_xS films were calculated. The obtained values are in accordance with the ones reported in the literature. We have shown that both, morphological and optical properties of Cu_xS films are strongly affected by the deposition time.

Keywords: Cu_xS ; polypropylene; CBD; surface morphology

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1. Introduction

The use of polymers as a substrate for thin-film semiconductors presents special interest for researchers [1–5]. Different polymers such as PES (Polyethersulfone) [3], HDPE (High Density Polyethylene) [6], ABS (Acrylonitrile-Butadiene-Styrene copolymer) [7], PE (Polyethylene) [8] and PP (Polypropylene) [1] were used as substrates for the Cu_xS film deposition. The copper sulfides obtained on polymer substrates have important applications in advanced technology field. Among the most important one, we can mention the antireflection coatings [9], solar control glass coatings [3, 9], solar cells [10, 11] and sensors [12–14]. The deposition of copper sulfide layers on a polymer substrate can be achieved by various methods. Chemical Bath Deposition (CBD) is easy to apply and ef-

fective from an economic viewpoint. The layer of copper sulfide is formed on a surface of polymeric material through adhesion of Cu_xS particles formed in the chemical bath. In order to improve the adherence of copper sulfide to the substrate, different treatments of the polymeric substrates can be done, thus favoring the formation of nucleation centers. Recently, R. Elaborate et al. reported the obtaining of Cu_xS layers on a polypropylene substrate applying the sulfurization method (using molten sulfur), followed by treatment with aqueous Cu (I/II) salt solution [1].

This study aimed at the obtaining and characterization of copper sulfide films on a polypropylene substrate. According to our knowledge, the synthesis of copper sulfide films on polypropylene substrates by CBD method has not been reported yet.

The influence of deposition time on optical and morphological properties of the Cu_xS films was studied.

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2. Experimental

Polypropylene (PP) was used as a substrate for the deposition of copper sulfide films by CBD.

In order to ensure a good adhesion of copper sulfide at the substrate surface, before performing the deposition of Cu_xS films, the polypropylene substrate was washed with water and detergent, and then treated with concentrated nitric acid (HNO_3) for 30 minutes.

The solution of the chemical bath used for the copper sulfide films deposition on the PP substrate was formed from: 1 ml $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (copper sulfate pentahydrate) 0.65 M, 0.7 g TEA (triethanolamine), 1 ml TU (thiourea) 0.65 M, 1.25 ml NH_3 (25 %) and 21 ml H_2O . The deposition process was conducted at 60 °C for about 20 minutes (sample Cu2) and 30 minutes (sample Cu5), respectively. The substrate was immersed in the solution immediately after reagents mixing.

Optical properties of Cu_xS films deposited on the polypropylene substrate were analyzed using a Lambda 35 (Perkin Elmer) spectrophotometer. The transmission spectra of the samples were recorded in the wavelength range of 400 – 1000 nm, using a clean substrate as a reference.

BX FT-IR spectrophotometer (Perkin Elmer) was used for IR spectra recording. The morphology of the films has been investigated using a field emission scanning electron microscope (FE-SEM) – Raith e-Line with in-lens electron detection capabilities. In order to avoid electrostatic charging of the insulator (PP) substrate, we used low accelerating voltages and a relatively low beam current.

3. Results and discussion

3.1. Optical properties of $\text{PP/Cu}_x\text{S}$ films

The influence of deposition time on the optical properties of Cu_xS films grown on the polymeric substrate was studied on the base of transmission measurements. Fig. 1 presents the transmission spectra of copper sulfide films obtained after 20 minute (Cu2), and 30 minute (Cu5) treatments. A shifting of the transmission peak to smaller wavelengths from the visible domain (734 nm) to NIR domain (831 nm) is observed for the sample

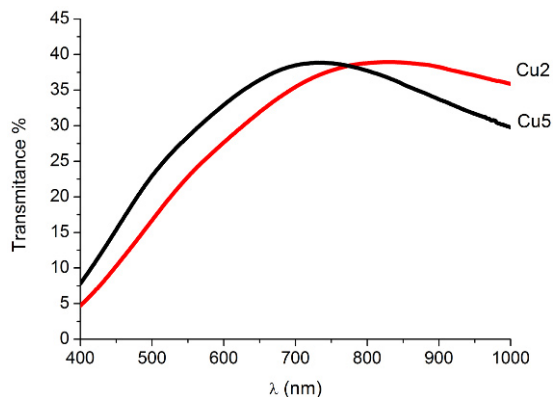


Fig. 1. Transmission spectra of $\text{PP/Cu}_x\text{S}$ thin films (Cu2, Cu5).

Cu5, when the deposition time was increased from 20 to 30 minutes.

The energy band gap of $\text{PP/Cu}_x\text{S}$ films obtained at different deposition times was determined using Tauc's law [9, 15, 16]:

$$\alpha \cdot h \cdot \nu = A \cdot (h \cdot \nu - E_g)^b \quad (1)$$

where α is the absorption coefficient, $h\nu$ is the incident photon energy, A is a constant, E_g is the gap energy between the conduction and the valence band of the film and b is equal to 1/2, 2, 3/2 or 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect electronic transitions, respectively.

The allowed direct energy band gap values were estimated by extrapolation of the linear portion of $(\alpha h\nu)^2$ versus $(h\nu)$ plot (Fig. 2). It can be seen that the band gap value is around 2.50 eV for sample Cu2 and 2.43 for sample Cu5. When the grains grow, the stoichiometry may change, and the grains of different diameters and hence different stoichiometry may show slightly different band gaps.

The values of energy band gap for the $\text{PP/Cu}_x\text{S}$ films obtained by CBD are consistent with the data reported in literature [9, 10, 16, 17].

Extinction coefficient (k) has been determined based on the relation [19]:

$$k = \frac{\alpha \cdot \lambda}{4 \cdot \pi} \quad (2)$$

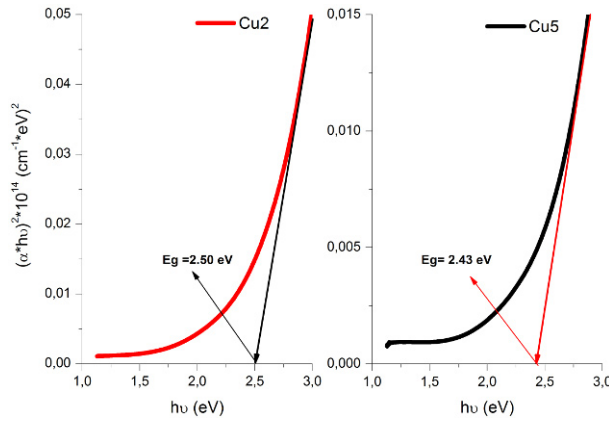


Fig. 2. Graphical determination of the energy band gap of Cu_xS in the form of thin films on PP (samples Cu2, Cu5).

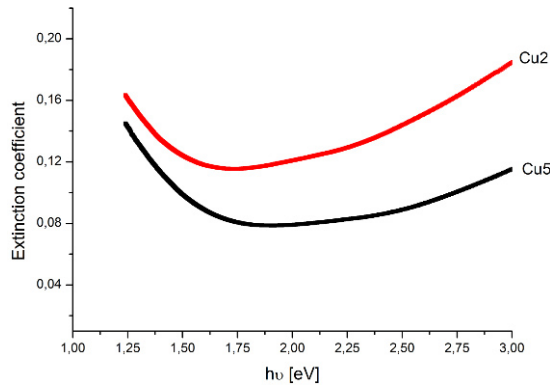


Fig. 3. Variation of the extinction coefficient (k) vs. photon energy for PP/ Cu_xS .

As it can be seen in Fig. 3, the values of k decrease with the increasing of energy, reaching a minimum at around 1.74 eV and then begin to increase. The maximum value of extinction coefficient for sample Cu2, $k = 0.19$ was reached at photon energy of 3 eV and $k = 0.12$ for sample Cu5 at the same value of incident photon energy. The increasing of the deposition time resulted in decreasing of the extinction coefficient due to the increase of the crystallites size [19, 21].

The refractive index (n) of Cu_xS was calculated based on the values of reflectance (R) and k , with the formula [18, 20]:

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad (3)$$

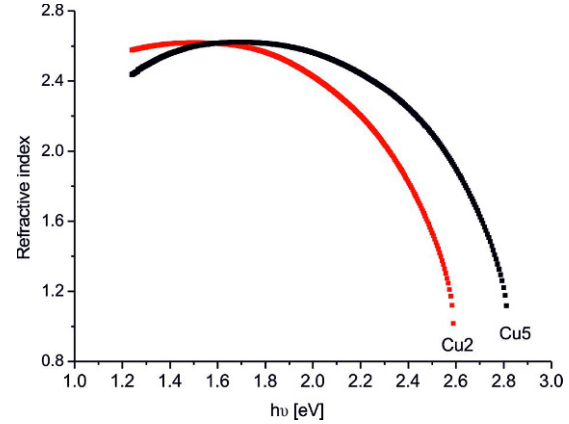


Fig. 4. Variation of the refractive index (n) vs. photon energy for PP/ Cu_xS .

where R is the reflectance, calculated on the base of the energy conservation law [9, 19]:

$$A + T + R = 1 \quad (4)$$

The variation of refractive index (n) vs. photon energy is presented in Fig. 4. We can observe that both the films (Cu2 and Cu5) have maximum of refractive index of 2.62 for photon energy around 1.6 eV. In the case of sample Cu2, the refractive index decreases at photon energy exceeding 1.7 eV, while for sample Cu5, the value of refractive index begins to decrease at higher energy (1.8 eV). The value of refractive index of the copper sulfide films grown on the PP substrate is greater than 1.9, which makes them a promising material to be used as solar cells and anti-dazzling coatings [9].

The relations (3) and (4) were used for the calculation of the real (ϵ_r) and imaginary (ϵ_i) part of dielectric constants [9, 18]:

$$\epsilon_r = n^2 - k^2 \quad (5)$$

$$\epsilon_i = 2 \cdot n \cdot k \quad (6)$$

where n and k are the refractive index and the extinction coefficient, respectively [9].

Fig. 5 and Fig. 6 show the representation of real (ϵ_r) and imaginary (ϵ_i) part of dielectric constant vs. photon energy. One can see that both samples (Cu2 and Cu5) show a decrease in the real part of the dielectric constant for energy higher

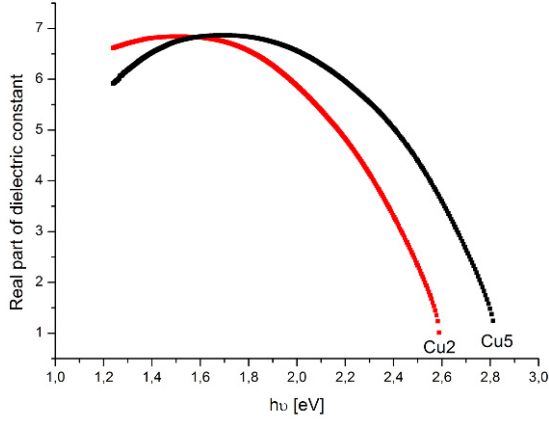


Fig. 5. Real part of dielectric constant ϵ_r as a function of $h\nu$ for PP/ Cu_xS .

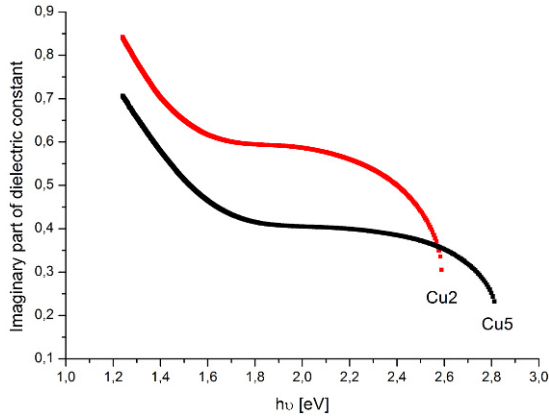


Fig. 6. Imaginary part of dielectric constant ϵ_i as a function of $h\nu$ for PP/ Cu_xS .

than 1.8 eV, in the VIS region (see Fig. 5) and the value of ϵ_r is higher for sample Cu5, deposited for 30 minutes, in comparison with that of sample Cu2 (20 minutes of deposition). Low values of the ϵ_r were reported by T.J. Alwan and M.A. Jabbar from some CuAlS_2 films obtained at different annealing temperatures [22].

A decrease in the imaginary part of the dielectric constant (ϵ_i) can be observed in the case of both samples (Cu2 and Cu5) when the energy increases. Sample Cu5 shows smaller values of the imaginary part of the dielectric constant.

The optical conductivity (σ_o) was calculated applying the following relation [19]:

$$\sigma_o = \frac{\alpha \cdot n \cdot c}{4 \cdot \pi} \quad [\text{s}^{-1}] \quad (7)$$

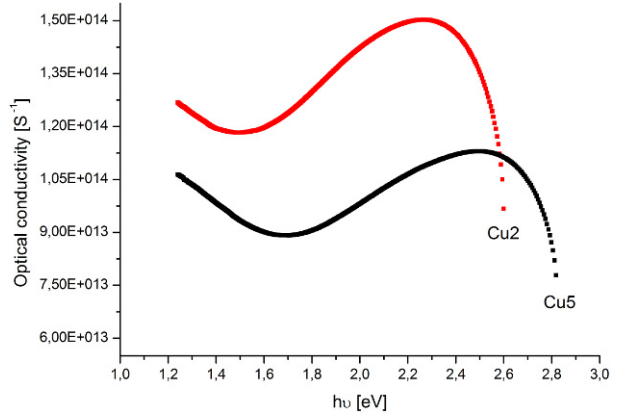


Fig. 7. Optical conductivity σ_o as a function of $h\nu$ for PP/ Cu_xS films.

where α is the absorption coefficient, n is the refractive index and c is the velocity of light ($c = 3 \cdot 10^8 \text{ m} \cdot \text{s}^{-1}$). Electrical conductivity (σ_e) was calculated applying the relation used by Nair et al. [3]:

$$\sigma_e = \frac{(16 \cdot 10^4 \cdot \pi \cdot c \cdot \epsilon_o)}{[(100 - R\%)^2 \cdot \lambda]} \quad [\Omega^{-1} \cdot \text{cm}^{-1}] \quad (8)$$

where c is the velocity of light, ϵ_o is the permittivity of free space ($\epsilon_o = 8.85418782 \cdot 10^{-12} \text{ m}^{-3} \text{kg}^{-1} \text{s}^4 \text{A}^2$), α is the absorption coefficient, n is the refractive index and R is the reflectance [9].

The obtained values of optical conductivity (σ_o) reach the value of about $1.5 \cdot 10^{14} \text{ s}^{-1}$ for the sample Cu2 and $1.1 \cdot 10^{14} \text{ s}^{-1}$ for the sample Cu5 (Fig. 7). The increase of deposition time resulted in a decrease of optical conductivity and a blue shift of σ_o maximum (from 2.27 to 2.5 eV). As Pathan et al. mentioned, the high values of the optical conductivity of copper sulfide films are due to their high optical absorbance [23].

According to Dimitriu and Vornicu [24], the value of electrical conductivity for the semiconductor material ranged between $10^{-8} - 10^4 [\Omega^{-1} \text{m}^{-1}]$. The electrical conductivity σ_e of the copper sulfide films deposited on polymeric substrates by CBD method shows an increase in the maximum values, from $3.218 \cdot 10^3$ to $3.558 \cdot 10^3 [\Omega^{-1} \text{cm}^{-1}]$, with increasing of the deposition time (Fig. 8). A blue shift of electrical conductivity maxima occurred due to

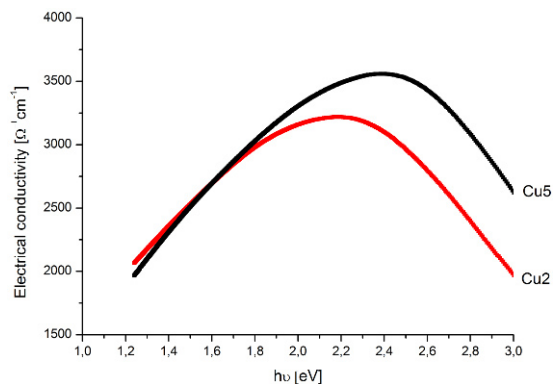


Fig. 8. Electrical conductivity σ_e as a function of $h\nu$ for PP/Cu_xS films.

increasing the deposition time. Nair *et al.* obtained PES–CuS films with an electrical conductivity between 10^3 and 10^4 [$\Omega^{-1}\text{cm}^{-1}$] [3].

3.2. FT-IR analysis of PP/Cu_xS films

The properties of PP/Cu_xS films are strongly affected by the treatment of PP substrate. An appropriate treatment should improve the adhesion of Cu_xS film to the PP substrate surface. Etching of polypropylene substrate is considered as an important step for obtaining good adhesion of PP/Cu_xS films. We have carried out the PP etching by immersion of polypropylene in concentrated nitric acid (HNO₃).

To elucidate possible formation of new functional groups as a result of the PP treatment, we measured the FT-IR absorption spectra of the samples etched in concentrated nitric acid for 30, 60, 90, 120, 150, 180 minutes and 3 days. No additional peaks appeared in the FT-IR absorption spectra due to new functional groups (Fig. 9).

The copper sulfide is known as a material which does not have absorption bands in the infrared domain. Based on the absorption spectra in infrared region, the presence of water, unreacted precursors or impurities in the Cu_xS films can be identified (Fig. 10).

Comparing the IR absorption spectra of PP and PP/Cu_xS, a decrease of the absorption peaks intensity for the Cu2 and Cu5 films can be observed. The Cu_xS film formed on PP surface caused a decrease in the intensity of the absorption peaks of PP, while

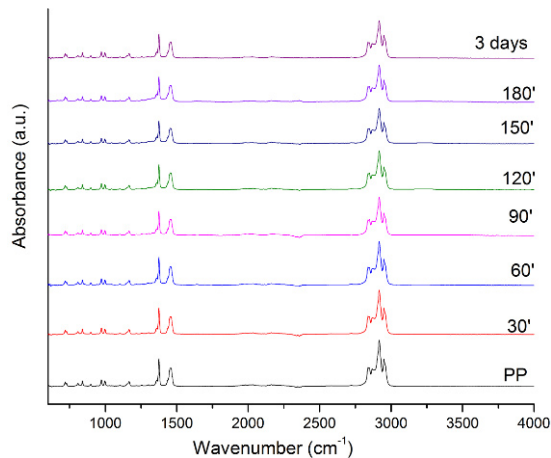


Fig. 9. ATR-FT-IR absorption spectra for PP substrates treated with concentrate HNO₃.

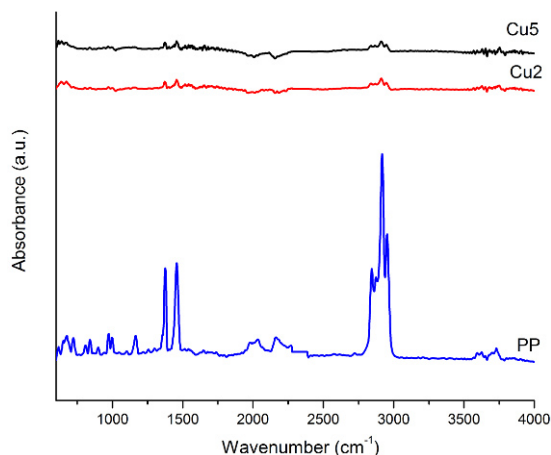


Fig. 10. FT-IR absorption spectra of the PP/Cu_xS films obtained in 20 minute (Cu2) and 30 minute (Cu5) deposition time.

the increased deposition time resulted in a further decrease in the intensity of absorption maxima of PP due to the reflecting properties of copper sulfide.

3.3. Morphological characterization of PP/Cu_xS films

The morphology of copper sulfide films deposited on the PP substrate for different deposition times is presented in Fig. 11.

It can be noticed that the Cu_xS films formed on the PP substrate are continuous for both samples. The average size of the grains formed on the PP

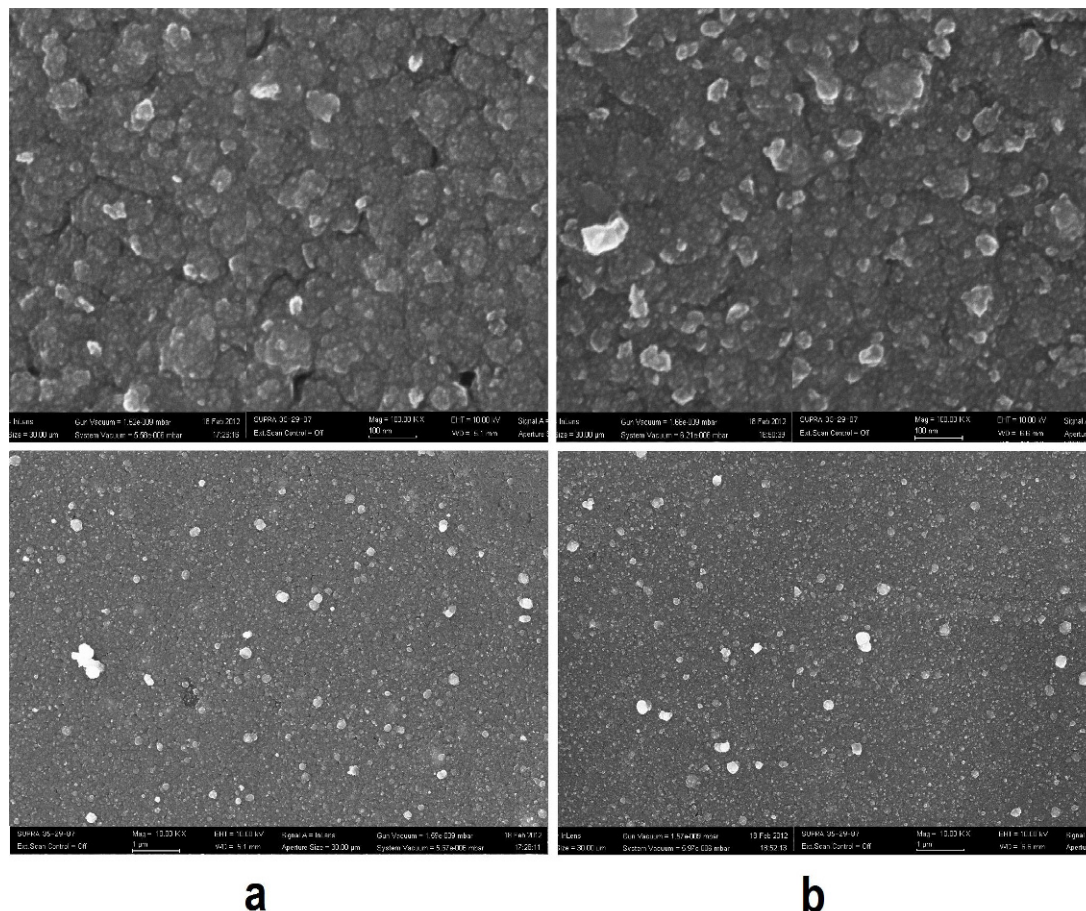


Fig. 11. SEM images of PP/ Cu_xS films: Cu2 (a) and Cu5 (b).

surface is about 37 nm and 49 nm for the samples obtained during 20 min and 30 min deposition, respectively. A. A. Sagade et al., using SGT method (a solution growth technique), obtained Cu_xS films on the glass substrate with the particles dimension around 60 nm (CuS), 90 nm ($\text{Cu}_{1.4}\text{S}$) and nano-discs with an average diameter of 120 nm [12]. Also, Anuar Kassim et al. reported the Cu_xS films on glass substrates, with the particle size between 25 μm and 30 μm , obtained by CBD method [25].

4. Conclusions

The PP/ Cu_xS films were obtained by CBD method. The polypropylene substrate was treated with concentrated nitric acid, which ensured the formation of adherent Cu_xS layers. Through characterization of the optical properties of

PP/ Cu_xS films we determined the values of energy band gap (E_g) (2.50 eV for sample Cu2 and 2.43 eV for sample Cu5), extinction coefficient (k), refractive index (n), real (ϵ_r) and imaginary (ϵ_i) part of dielectric constant, optical (σ_o) and electrical (σ_e) conductivity. The obtained values are in good agreement with the values for Cu_xS semiconductor bulk material. Performing the FT-IR analysis we revealed that after the treatment of PP substrate with concentrated nitric acid no new functional groups were formed. Based on the SEM images, the formation of continuous films was revealed for samples Cu2 and Cu5. The average size of the grain increased with the increase of the deposition time.

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