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Synthesis and Characterization of Amorphous Selenium, Cadmium and Silver Selenide Thin Films on Polyamide-6

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Abstract: Increasing photon absorption by capturing light is an important way to increase the efficiency of photovoltaic devices. In this regard, the small optical band gap (E_g) and high absorption coefficient of Se-containing thin nanofilms make them ideal for next generation photovoltaic devices based on selenides. Amorphous selenium was introduced into polyamide-6 (PA 6) via a chemical synthesis in a bath and the influence of the products of its reaction with Cd²⁺ and Ag⁺ ions on the film phase composition, topographic and optical properties were evaluated. AFM data have revealed that the surface roughness of the a-Se/PA 6 composite noticeably increases compared to that of unreacted PA 6. However, at later stages of film deposition, the roughness decreases, and the thin film becomes smoother and uniform. The incorporation of solid inorganic nanoparticles into flexible polyamide network causes chain stretching, which has been confirmed by ATR-FTIR spectroscopy data. The data of X-ray diffraction analysis, depending on the stage of synthesis, showed the crystalline composition of the film with peaks of Se₈, CdSe, Ag₂Se and Ag, which may explain the observed optical properties. The optical properties of the composites indicate a shift in the band gap from 4.46 eV for PA 6 to 2.23-1.64 eV upon the stepwise deposition of amorphous Se, CdSe and $Ag_2Se. E_g$ is conveniently located in the visible region of solar energy, making the obtained nanofilms ideal for solar energy harvesting.

Keywords: polyamide-6; selenium; cadmium; silver; selenides; nanofilms; optical properties; light-absorbing materials

1. Introduction

Nanoscale-sized inorganic materials within the polymers are interesting in optoelectronics as light-emitting devices [1] or photovoltaics [2], separation-catalysis [3] and bioelectronics [4]. The semiconductor nanoparticles embedded in the polymer film are easy to process [5]. These composites are usually made by mixing inorganic and organic components, and the obtained structure possesses physical and chemical properties that are not present in the individual components [1].

Selenium and selenium-containing materials have become the subject of many scientific studies due to their exceptional physical-chemical properties and photoelectric characteristics [6–8]. As an important inorganic material, selenium has also received a lot of attention due to its good semiconductor properties. For an a-Se film, the value of the band gap is 2.0–2.3 eV [9,10]. Due to their high photoconductivity, various selenides are some of the key materials widely used in optoelectronic devices such as photocopiers, light emitting diodes, xerography and solar cells [8,11–13].

Doping with impurity atoms is an effective strategy for optimising the properties required for the development of semiconductor technologies. Newly developed aliovalent doping provides extra electrons (n-type doping) or extra holes (p-type doping) to redefine their doping type for electronic requirements. For CdSe, the most studied nanocrystalline system, it has been proven that additional carriers from heterovalent dopants such as Ag,



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Cu and In [14,15] can enhance the electronic conductivity in films when they are excited by external energy. Incorporating aliovalent metal cations into binary semiconductors, such as CdSe, change the optoelectronic properties of the newly formed base material, providing greater performance in a number of applications, including solar cells, batteries and LEDs [16–18].

Polyamides are widely used as technical polymers with applications ranging from synthetic fibres to industrial and structural ones. Typically, optoelectronic devices use a combination of highly conductive semiconductor components due to their electrical pumping capability and the strong interaction of light and matter of the organic component [19]. The efficient inorganic materials used include cadmium selenide (CdSe) [11] and silver selenide (Ag₂Se) [12,13]. CdSe and Ag₂Se are direct band gap semiconducting materials with corresponding band gaps of 1.9 eV [20] and 1.8 eV [21], respectively.

Due to the high reduction potential of Se(IV)/Se(0), various reagents for the reduction of selenium (IV) compounds in several types of aqueous solutions have been evaluated. N₂H₄ [6,22], (NH₂)₂CS [23], metallic Fe or Zn [24–27], CuCl [28], TiCl₃ [29], SnCl₂ [30], Na₂S₂O₄ [31], *D*-fructose [32] and ascorbic acid [33] have been proposed as quantitative reducing agents for Se(IV) in acidic solutions. In industrial applications, SO₂ is the preferred reagent for the reduction of Se(IV) to its elemental state. According to the literature data [10,28], when working with hot (>80 °C) and relatively concentrated solutions of H₂SO₄ or HCl (pH < 1), the complete reduction of selenium occurs very quickly. However, high toxicity (hydrazine and thiourea), low efficiency (zinc, *D*-fructose, ascorbic acid) and high cost (CuCl, TiCl₃, Na₂S₂O₄ and SnCl₂) limit the applicability of these reagents. Sodium sulphite (Na₂SO₃) is a much better candidate as a strong reducing agent owing to its fast reaction rate, low cost and relatively low toxicity.

Solution-based chemical methods provide an excellent way to produce nano selenium and nano selenides. Each synthesis method has its advantages in obtaining the appropriate structures and properties for each system, and hence the right combinations of processing along with suitable systems must be found to achieve the desired goal.

This work is aimed at studying the change in the properties of polyamide-6 upon the stepwise introduction of amorphous Se, Cd^{2+} and Ag^+ ions and understanding the factors that determine the properties of these light-absorbing materials. These composites were prepared on the PA 6 using various chemical synthesis methods as follows: Se was deposited via chemical bath deposition (CBD), Cd^{2+} and Ag^+ selenides were synthesized via the successive ionic layer adsorption and reaction (SILAR) method and mixed Ag^+-Cd^{2+} selenide composites were obtained using cation exchange (CE). For a deeper understanding of the relationship between the composition and consumer properties of polyamide-6-based selenium nanocomposites, most attention was paid to the evaluation of the microstructure, topography and physicochemical properties.

2. Materials and Methods

Semicrystalline flexible TECAMID[®]6 (polyamide-6, PA 6) produced by Ensinger GmbH (Nufringen, Germany) was used as a thermoplastic matrix. Nominal characteristics provided by the manufacturer were: opaque PA 6 film, 0.5 mm thick, density 1.13 g/cm³, moisture absorption 3% and water absorption to equilibrium 9.5%. Experiments were performed on 2×6 cm² film samples. Prior to the experiments, PA 6 film samples were washed with NaHCO₃ and heated in distilled water for 2 h at 100 °C to remove surface contamination. The criterion for the quality treatment of the PA 6 substrate surface was its uniform wetting with distilled water. After treatment, the substrates were stored in a desiccator.

Selenious acid (H₂SeO₃, 99.0%), sodium sulphite heptahydrate (Na₂SO₃·7H₂O, 99.0%), sulphuric acid (H₂SO₄, 96%), cadmium nitrate tetrahydrate (Cd(NO₃)₂·4H₂O, 99.997% trace metals basis) and silver nitrate (AgNO₃, 99.0%) were purchased from Sigma-Aldrich Chemie GmbH (Munich, Germany) and used as received. All solutions were prepared using distilled water.

The first step involved the synthesis of Se via the CBD process. For Se deposition/insertion, the cleaned PA 6 film cuts were vertically immersed into a beaker with 0.1 M H₂SeO₃ and 0.15 M Na₂SO₃ solutions and exposed in a thermostatic vessel for 24 h at 20 ± 1 °C. The concentrations of the H₂SeO₃ and Na₂SO₃ solutions (pH 2 with the addition of H_2SO_4), the deposition temperature and exposure time were chosen to give excellent composites in terms of continuity, smoothness and adhesion to the substrate. The solution was clear at first, became slightly turbid after two hours and turned into a light red liquid after a few hours. The Se precipitate was very fine, but it aggregated into large clusters within ~24 h. This proposed mechanism for the formation of Se films is based on nucleation and the Ostwald ripening process [34]. The process is simple, controllable and reproducible. After the deposition/insertion of Se, the upper layer (Figure 1) was removed from the PA 6 surface with filter paper and samples were thoroughly washed with distilled water and stored in a desiccator between the individual processing steps. Then, obtained composites (referred to in the text as a-Se/PA 6) were used as the initial composite for the stepwise insertion of Cd²⁺ and Ag⁺ ions. For this, half of the a-Se/PA6 composites were treated for 3 h with 0.1 M Cd(NO₃)₂ solution (pH 5.4) at 80 \pm 1 °C. The second half of a-Se/PA6 composites were treated for 2 h with 0.1 M AgNO₃ solution (pH 6.35) at 20 ± 1 °C. The obtained composites were labelled as Cd-Se/PA 6 and Ag-Se/PA 6, respectively. Then, one part of the Cd-Se/PA 6 composites were treated for 10 min with 0.05 M AgNO₃ solution (pH 6.45, 20 \pm 1 °C) and washed well, as described above. After immersion into AgNO₃ solution, the resulting composites (throughout the text labelled as Ag-Cd-Se/PA 6) were uniformly black and highly reflective with good adhesion. In all cases, the samples were treated in a thermostated vessel. During the deposition process, the beaker was kept undisturbed. All deposited films were evaluated for adhesion by subjecting them to a steady stream of distilled water. After each deposition step, the samples were washed first with hot and then cold distilled water, dried at ambient temperature and stored in a desiccator until analysis. Figure 1 shows a schematic outline of the approach and optical micrograph images of the PA 6 and obtained composites.



Figure 1. Optical micrograph images of the PA 6 and obtained composites showing the principal route of combined CBD, SILAR and CE methods for the Se, CdSe and Ag₂Se deposition on PA 6. Magnification $\times 100$.

Solution pH was measured using a pH-meter WTW330 (WTW GmbH, Weilheim, Germany). Optical microscopy images were obtained using an Olympus CX31 optical microscope and a C-5050 camera (Tokyo, Japan).

The structure of the composites was analysed using X-ray diffraction method (XRD) on a Bruker D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany). The diffractometer was supplied together with the software package DIFFRAC.SUITE. (Diffract. EVA. v. 4.5, Bruker AXS, Karlsruhe, Germany). The XRD patterns were produced with CuK α ($\lambda = 0.154178$ nm) radiation in the 2 θ scanning mode. The XRD data were analysed by observing characteristic peaks in the X-ray diffraction patterns using software package Crystallographica Search Match v.2.1 and the PDF-2 2022 and PDF-4/Minerals 2022 database. Crystallite size (D_c) values were calculated from XRD patterns based on the Bragg and Scherrer equation [35]:

$$D_c = \frac{K\lambda}{\beta(2\theta)cos\theta} \tag{1}$$

where *K* is the constant with a normal value of 0.89, λ is the wavelength of CuK α radiation, $\beta(2\theta)$ is the full width at the half-maximum and θ is the Bragg angle. The dislocation density (δ) was evaluated by using the equation [36]:

$$\delta = \frac{1}{D_c^2} (\mathbf{m}^{-2}).$$
 (2)

The strain values (ε) were calculated from the following relation:

$$\varepsilon = \frac{\beta cos\theta}{4}.$$
(3)

Surface topography imaging was conducted using atomic force microscopy (AFM) using a NanoWizard[®]3 NanoScience microscope (JPK Instruments, Bruker Nano GmbH, Berlin, Germany). Obtained data were analysed using JPKSPM Data Processing software (Version spm-4.3.13). The AFM images (scanning area $5 \times 5 \ \mu\text{m}^2$) were collected using an AppNano production pyramidal-shaped i-type silicon cantilever (0.01–0.025 ohm/cm, spring constant of 2 N/m) working in contact mode.

Ultraviolet–visible (UV–Vis) absorption spectra (200 to 1100 nm) were recorded on a Spectronic^R GenesysTM 8 UV–Vis spectrophotometer (Spectronic instruments, Runcorn, UK) with compensation for PA6 absorption. The energy optical band gaps (E_g) were determined by applying the absorption spectrum fitting (ASF) method [37]. The fundamental absorption edge (λ_g) can be found using the following plot:

$$\left(\frac{A}{\lambda}\right)^{1/m} = f\frac{1}{\lambda},\tag{4}$$

where *A* is the absorption, λ is the wavelength, and *m* is the index that takes values 0.5, 1.5, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions, respectively. The extrapolation of the straight-line portion to cut the energy axis gives λ_g . Then, employing the obtained value of λ_g the E_g can be directly calculated from the following relationship [37]:

$$E_g = \frac{1239.83}{\lambda_g}.$$
(5)

The Urbach energy (E_U) is related to the absorption coefficient through the following exponential equation [38]:

$$\alpha = \alpha_0 \cdot e^{n\nu/E_U}, \tag{6}$$

where α_0 is a constant. In ASF procedure, Equation (6) can be written as: $A = D \cdot e^{h\nu/E_U\lambda}$, where *D* is ($\alpha_0 d/2.303$) [38]. Therefore, the values of E_U in eV, were calculated using the

slope determined from the linear part of the plot of between $\ln(A)$ versus $1/\lambda$ according to the following relationship [38]:

$$E_U = 1239.83/\text{slope.}$$
 (7)

The steepness parameter σ is related to E_U the via following equation:

$$\sigma = \frac{k \cdot T}{E_U},\tag{8}$$

where *k* is the Boltzmann constant and *T* is the absolute temperature assumed to be 298 K. The following equation is applied for calculating the interaction strength of electron–phonon (E_{e-p}) [39]:

$$E_{e-p} = \frac{2}{3\sigma}.$$
(9)

The optical electronegativity χ is related to E_g through following equation:

$$\chi = 0.2688 \cdot E_g. \tag{10}$$

The changes in the chemical structure and the binding configuration of the samples were analysed using attenuated total reflectance (ATR) Fourier transform infrared spectroscopy (FTIR). The ATR-FTIR spectra were recorded on a Perkin Elmer FT-IR Spectrum GX system (Perkin Elmer, Waltham, MA, USA) within the wavenumber range 4000–600 cm⁻¹. Spectra were recorded by averaging 64 scans with a wavenumber resolution of 1 cm⁻¹ at room temperature.

3. Results and Discussions

Adsorption membranes are some of the best ways to obtain semiconductor composites from aqueous solutions. According to the BET method (abbreviated from the Brunauer– Emmett–Teller theory), the determined pore size of less than 2 nm [40] indicates that the PA 6 film is microporous. Therefore, it can adsorb Se micro-particles and Cd²⁺ and Ag⁺ cations followed by their diffusion into the polymer. In most cases, adsorption matrixes are charged. Ions and the surface of the polymer attract each other due to opposite charges.

3.1. XRD Analysis

To determine the structural properties of the PA 6 and the obtained composites, XRD patterns were analysed. The XRD pattern of PA 6 sample heated in distilled water is shown in Figure 2, the XRD pattern of the a-Se upper layer scrub is shown in Figure 3, while the XDR pattern of the obtained composites is shown in Figure 4.



Figure 2. XRD pattern of the PA 6 sample heated in distilled water.



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Figure 3. (a) Optical micrograph of the red upper a-Se layer on a PA 6 (\times 100 magnification); (b) XRD pattern of the a-Se upper layer scrub. The red line is the experimental pattern, and the black pillars label the peaks from crystalline Se.



Figure 4. XRD diffractograms of (**a**) heated PA 6 and obtained composites: (**b**) a-Se/PA 6, (**c**) Cd-Se/PA 6, (**d**) Ag-Se/PA 6, (**e**) Ag-Cd-Se/PA 6. PA 6 peaks are not shown.

PA 6 crystallizes into stable α - and γ -, as well as unstable β -forms [41]. XRD studies of the PA 6 sample revealed the presence of main peaks at 2θ 9.52°, 20.26°, 23.56° and 28.64°. Two peaks at $2\theta = 20.26^{\circ}$ and 23.56° were assigned to the (200) reflection and (002)/(202) reflections of the α crystalline form of PA 6 [41]. XRD observations in [42] provided new information for the secondarily quenched PA 6. The diffraction patterns exhibit three sharp unknown diffraction peaks at $2\theta = 9.4^{\circ}$, 18.95° and 28.5°, which are derived from a new long-range order structure. The locations of these peaks do not correspond with a series of calculated 2θ values for the α -, γ -, β - and pleated α - form crystals of PA 6 [42]. It is likely that the diffraction peaks at $2\theta = 9.52^{\circ}$ and 28.64° also indicate the formation of such an ordered structure after heating the PA 6 samples in distilled water and cooling. Otherwise, the small diffraction peak at $2\theta = 9.52^{\circ}$ could be attributed to the (020) reflection of the γ crystalline form [41], while the sharp peak at 28.64° could be caused by impurities or instrumental mistakes.

Mixing H₂SeO₃ and Na₂SO₃ or sulphur dioxide solutions leads to the release of Se according to the following reaction [28]:

$$H_2SeO_{3(aq)} + 2Na_2SO_{3(aq)} \rightarrow Se_{(s)} + 2Na_2SO_{4(aq)} + H_2O_{(l)}.$$
 (11)

A red film was observed on PA 6 (Figure 3). The precipitate, characterised via XRD analysis (Figures 3 and 4), was identified as red amorphous selenium (a-Se).

Because the intensities of the diffraction peaks of PA 6 are very high and overlap with the main peaks of the materials inserted/deposited on the polymer, the XRD patterns of the obtained composites were given in the 2θ assortment of $30-65^{\circ}$. As can be seen from Figure 4b, in the a-Se/PA 6 composite, Se formed as a result of reaction (11) is in the amorphous form, i.e., not detected via XRD analysis.

The obtained positions of the diffraction peaks at $2\theta 42.74^{\circ}$, 43.46° , 48.68° and 51.09° in the Cd-Se/PA 6 composite (Figure 4c) were compared with standard values and mainly indexed as CdSe (PDF No. 77-2307). The peaks at $2\theta 32.66^{\circ}$, 33.49° , 37.64° , 38.46° , 45.16° , 52.66° , 53.77° , 54.83° and 59.73° are indexed as Se₈ (a cyclic molecule with a ring of eight Se atoms, PDF No. 71-528) with hexagonal and monoclinic unit cells, respectively (Figure 4c, Cd-Se/PA 6 composite). It was found that CdSe has a polycrystalline nature with a predominant (110) orientation plane. These experimental results agree well with the literature data. It is well known [43] that in the case of hexagonal lattices, the strongest chemical bonds are formed by atoms located in a semi-crystalline configuration on crystallographic planes (110) or (101).

Based on the analysis of the XRD results, it can be concluded that the immersion of the a-Se/PA 6 nanocomposite into Cd(NO₃)₂ solution at 80 ± 1 °C contributes to the gradual crystallisation of red a-Se into grey crystalline selenium (cr-Se), which is very reactive and reacts with various metal cations [44,45]. The solubility of a-Se ($2.2 \times 10^{-8} \text{ mol/dm}^3$ [46]) was approximately one order of magnitude higher than the solubility of cr-Se ($1.5 \times 10^{-9} \text{ mol/dm}^3$ [46]). The formation of CdSe can be described using the following reaction [47]:

$$3Se_{(s)} + 3Cd^{2+}_{(aq)} + 3H_2O_{(l)} \rightarrow 2CdSe_{(s)} + CdSeO_{3(s)} + 6H^+_{(aq)}.$$
 (12)

The formation of the Cd-Se/PA 6 composite leads to a colour change from red to brown (Figure 1).

The XRD diffractogram of Ag-Se/PA 6 nanocomposite (Figure 4d) shows diffraction peaks corresponding to the orthorhombic phase of Ag₂Se naumannite (PDF No. 01-071-2410) with two sharp lines of approximately the same intensity along the (112) and (121) planes, respectively. As can be seen, the dominant peak (121) of the orthorhombic system represents the preferred orientation along this plane. The identified peak positions correspond with those indicated in the literature for Ag₂Se nanowires [48] and nanoparticles [49]. The reaction involved in this process can be summarised as the following reaction equation [50,51]:

$$3Se_{(s)} + 6Ag^{+}_{(aq)} + 3H_2O_{(l)} \rightarrow 2Ag_2Se_{(s)} + Ag_2SeO_{3(s)} + 6H^{+}_{(aq)}.$$
 (13)

The formation of Ag_2Se leads to a colour change from red to black. Along the Ag_2Se phase, a minor amount of monoclinic Se_8 (PDF No. 71-528) at 2θ 32.66° may remain unreacted in the deposited film phase. Ag-Se/PA 6 composite XRD analysis showed that not only Ag_2Se but also the metallic Ag phase (PDF No. 04-003-1472) was identified in the diffractogram. As discussed in [52], excess Ag can be introduced in several ways: in the form of adsorbed metal chains, in the form of point defects or in the form of three-dimensional nano- or micro-inhomogeneities. Typically, the metallic structure of Ag is depicted by a sharp XRD peak at 2θ 38.12°, corresponding to the preferred (111) texture. Metallic Ag is the most probable impurity in chemically deposited Ag_2Se layers [48], as shown in the reaction equation as follows:

$$Se_{(s)} + 4AgNO_{3(aq)} + 3H_2O_{(l)} \rightarrow 4Ag_{(s)} + H_2SeO_{3(aq)} + 4HNO_{3(aq)}.$$
 (14)

The XRD pattern of the Ag-Cd-Se/PA 6 composite (Figure 4e) shows the multiphase crystalline composition of the film. Compared to the XRD pattern of the Cd-Se/PA 6 composite, Se₈ and CdSe phases are retained. However, after the treatment of the Cd-Se/PA 6 composite in AgNO₃ solution, not only did selenium react with Ag⁺ ions but CdSe was also partially converted into orthorhombic Ag₂Se. The XRD peak at 48.71°, corresponding to hexagonal CdSe, is the only one that did not shift. The remaining peaks disappeared, and a new peak appeared at 35.94°. Two peaks also appeared at 38.29° and 43.50°, corresponding to the metallic Ag phase. Figure 4e also shows that the intensity of the Se₈ peaks of the Ag-Cd-Se/PA 6 composite compared to those of the Cd-Se/PA 6 composite (Figure 4c) increases with the appearance of a new phase, which additionally indicates an increase in crystallinity. The broadening of the diffraction peaks is associated primarily with the finite sizes of the crystallites. The formation of Ag₂Se in the Cd-Se/PA 6 composite leads to a colour change from brown to black.

The structural parameters of PA 6 and the prepared composites calculated from XRD data are listed in Table 1.

Sample	Phase	$2 heta$, $^{\circ}$	D_c , nm	$\delta imes 10^{15}$, m $^{-2}$	$arepsilon imes 10^{-3}$
PA 6	PA6	23.5	16	3.70	2.11
a Sa /PA 6	PA6	23.7	17	3.33	2.00
a-3e/TA 0	a-Se	-	-	-	-
	$\begin{array}{ccc} PA6 & 23.5 \\ Se_8 & 33.5 \\ CdSe & 42.7 \\ PA6 & 23.6 \\ Se_9 & 31.8 \\ \end{array}$	17	3.38	2.01	
Cd-Se/PA 6	Se ₈	33.5	33	0.89	1.04
	CdSe	42.7	40	0.63	0.87
Ag-Se/PA 6	PA6	23.6	17	3.56	2.06
	Se ₈	31.8	31	0.91	1.07
	Ag ₂ Se	33.8	34	0.85	0.98
	Āg	43.4	34	0.89	1.02
Ag-Cd-Se/PA 6	PA6	23.7	17	3.58	2.08
	Se ₈	31.8	30	1.10	1.15
	CdSe	48.7	37	0.74	0.94
	Ag ₂ Se	33.6	35	0.84	1.00
	Ăg	43.5	34	0.88	1.03

Table 1. Structural parameters (phase, angle (2θ), crystallite size (D_c), dislocation density (δ), strain values (ε)) of PA 6 and prepared composites calculated from XRD data.

Since the other phases were not found in Cd-Se/PA 6, Ag-Se/PA 6 and Ag-Cd-Se/PA 6 nanocomposites, it could be assumed that SeO₃²⁻, SO₃²⁻ and SO₄²⁻ ions diffused from the a-Se/PA 6 reacted with the Cd²⁺ and Ag⁺ ions to form these compounds in the solution near the sample area. In another case, the by-products of Equations (12) and (13), due to the sufficiently high solubility (Table 2, CdSeO₃ ($K_{SP} = 5.0 \times 10^{-9} \text{ (mol/dm}^3)^2$) and Ag₂SeO₃ ($K_{SP} = 1.35 \times 10^{-16} \text{ (mol/dm}^3)^3$), were removed from the surface of the samples by rinsing the as-synthesized composites with excess hot water.

Table 2. Standard Gibbs free energy (G) (298.15 K, 1 bar) [53], bond dissociation energies (BDE) [54], solubility product constants (K_{SP}) [46] and the calculated solubility (S) of CdSe and Ag₂Se phases.

Phase or Ion	G, kJ/mol	BDE, kJ/mol	K_{SP} , (mol/dm ³) ⁿ *	S, mol/dm ³
a-Se	6.00 ± 2.2	-	-	$2.2 imes10^{-8}$
cr-Se	0.00	332.6 (Se-Se)	-	$1.5 imes10^{-9}$
Ag^+	77.11	-	-	-
Cd ²⁺	-77.16	-	-	-
CdSe	-141.60	127.6 ± 25.1	$1.0 imes10^{-33}$	$3.16 imes10^{-17}$
Ag ₂ Se	-46.90	210.0 ± 14.6	$3.1 imes 10^{-65}$	$3.14 imes 10^{-22}$

* n = 2 for CdSe, n = 3 for Ag₂Se.

A theoretical framework provides a general background to support our investigation. The sequence of phase formation in multicomponent systems depends on the structure of the starting material (SM). It is common knowledge that the exchange of cations can be achieved through simple mutual diffusion with other cations [55]. In addition, considering phase formation, the driving force of the solid-state interaction is also determined by the change in the Gibbs free energy, since the system always tends to the lowest possible free energy state [53]. The stoichiometric reactions at an interface between the Cd-Se/PA 6 and Ag⁺ salt aqueous solution can be written as follows:

$$CdSe_{(s)} + 2Ag^{+}_{(aq)} \rightarrow Ag_2Se_{(s)} + Cd^{2+}_{(aq)}, \Delta G^{\circ}_{reac,298} = -144.6 \text{kJ/mol.}$$
 (15)

The negative values of $\Delta G^{\circ}_{reac,298}$ indicate that thermodynamic conditions are provided for the proceeding of this reaction. The feasibilities of possible CE reactions were studied via thermodynamic deduction based on the thermodynamic law. CE reactions are based on significant difference in solubility product (K_{SP}) between the SM and the final product (FP). For insoluble materials, the relationship between the Gibbs free energy (ΔG) and the solubility product is expressed according to Equation (16):

$$\Delta G = RT \times ln \frac{l_{CP}}{K_{SP}},\tag{16}$$

where *R* is the universal gas constant (8.319 J/mol·K), *T* is the temperature (K), K_{SP} is the solubility product of the SM (in our case CdSe) and I_{CP} is the product of the concentration of FP ions (in our case Ag₂Se). I_{CP} can be calculated according to Equation (17):

$$I_{CP} = C_{Ag^+}^2 \times C_{Se^{2-\prime}}$$
(17)

where C_{Ag^+} and $C_{Se^{2-}}$ are the concentration of ions (mol/dm³). In this way, the transition reaction from a material with a higher K_{SP} (CdSe) to a material with a lower one (Ag₂Se) can proceed spontaneously. However, it is not easy to judge whether the CE reaction can proceed or not since this process is very complex and is associated with many factors, such as a barrier to the activation energy of the phase transition, change in surface free energy, temperature, the active concentrations of ions in the solution, etc. [56]. Therefore, a more correct criterion should be the difference in solubility (S) of the SM and the FP (see Table 2).

However, it should be emphasised that in the case of the solid-phase interaction in multicomponent systems, phase formation at the precursor/solution interface is a dynamic

non-equilibrium process that requires the careful consideration of the mechanistic pathways along which they proceed [57]. Apparently, the determining criterion for the possibility of a thermodynamic reaction in hybrid materials is the solubility of CdSe in the starting Cd-Se/PA6 material. The higher solubility of CdSe (Table 2) favours the transformation into Ag₂Se. When Cd-Se/PA 6 is immersed in AgNO₃ solution, Ag⁺ reacts with Se^{2-} ions formed from the ionisation of dissolved CdSe, leading to the formation of Ag_2Se particles, which results in the reduction of Cd^{2+} ions in the solution. Before explaining the formation of the Ag₂Se phase, it is necessary to discuss the active species that might be involved in the reaction path. Based on the discussion presented above, we assumed that the formation of Ag_2Se phases in the Cd-Se/PA 6 composite could be explained through complex mechanism reactions: Ag⁺ ions were attracted to the surfaces of metal chalcogenides particles due to the large specific area and then adsorbed Ag⁺ replaced Cd²⁺ ions from the CdSe lattice and formed Ag_2Se . In parallel, some Ag^+ ions featuring relatively high ion diffusivity [58,59] propagated into the interior of the polymer and reacted with cr-Se to form Ag_2Se according to the reaction (13). The obtained composites (denoted in the text as a-Se/PA 6, Cd-Se/PA 6, Ag-Se/PA 6 and Ag-Cd-Se/PA 6) were homogeneous with good adhesion.

3.2. AFM Analysis

Surface roughness is an important indicator of the quantitative characteristics of the sample surface. Uniform numerical parameters are useful for classifying surfaces from the same type of materials produced by the same method [60]. On a selected small scan area of $5 \,\mu\text{m} \times 5 \,\mu\text{m}$, 2D height data (Figure 5A) and 3D topographic (Figure 5B) AFM images of the respective PA 6 and a-Se/PA 6, Cd-Se/PA 6, Ag-Se/PA 6 and Ag-Cd-Se/PA 6 composites are shown. In particular, 3D images can better visualize the spatial characteristics of PA 6 and obtained composites. Since the composites did not have a pronounced texture but were characterized via complex relief topography, the roughness parameters were calculated from profilograms obtained for different surface areas (Figure 5C). The length of the scan areas was approximately 4.5– $6.5 \,\mu\text{m}$. The corresponding measured topographic parameters are collected in Table 3. Z is the maximum height of the surface. Surface roughness (R_a) is defined as the average value of the surface height relative to the central plane, and root mean square (RMS) is defined as the standard deviation of the surface height within a given area. Peak to valley roughness profile within the overall measuring distance [61].

Surface roughness is a component of surface texture and plays a significant role in determining how an object will interact with its environment since surface irregularities can act as nucleation centres for film growth [62]. Therefore, the surface texture of the substrate is very essential for obtaining a high-quality coating. Figure 5B shows an irregular and rough texture of PA 6 with a deep valley. At the initial stage of the a-Se film growth process, the particles may form islands, caused by the high diffusivity of adsorbed particles on a larger substrate. Additionally, the mobility and diffusion of the SO_3^{2-} and SeO_3^{2-} ions into the sub-surface space of PA 6 may enhance or inhibit the grain growth and affect the surface topography and roughness of the deposited films. The surface roughness is high. From the roughness values presented in Table 3, it can be seen that all measured parameters of the surface roughness of the a-Se/PA 6 composite increased noticeably compared to the analogous parameters of unreacted PA 6. However, at later stages of film deposition, the roughness decreased, since, apparently, the growth of CdSe and Ag₂Se occurred between the islands of the a-Se layer. These islands merged, and the thin film became smoother and uniform. Average roughness (R_a) and root mean square (RMS) correlate well between the obtained nanocomposites, as can be seen from Table 3, and are significantly reduced compared to the a-Se/PA 6 composite. An analysis of the surface topography has shown that the resulting Cd-Se/PA 6, Ag-Se/PA 6 and Ag-Cd-Se/PA 6 nanocomposites are relatively smooth with a R_a value of 7.93–9.82 nm and an RMS value of 10.17–12.17 nm. In addition, Rt varies from 41.32 to 61.81 nm.



Figure 5. Sequential 2D height data (**A**), 3D AFM topographic images (**B**) and the height profile (of the blue line in (**A**)) (**C**) of PA 6 and the obtained nanocomposites.

Table 3. Surface topographical parameters R_a, RMS and R_t obtained via AFM analysis.

Composite	R _a (nm)	RMS (nm)	R _t (nm)
PA 6	10.78	13.73	73.82
a-Se/PA 6	27.61	35.66	145.30
Cd-Se/PA 6	9.82	12.17	61.81
Ag-Se/PA 6	7.93	10.17	41.32
Ag-Cd-Se/PA 6	8.36	11.55	43.10

The non-Gaussian roughness profile distribution R_{sk} is sensitive to occasional deep valleys or high peaks, as it measures the symmetry of the profile distribution arond its midline (Figure 5C). According to the literature [63], a symmetrical distribution is reflected in

zero skewness, dominant profiles at peaks above a flatter average reflect positive skewness and negative skewness refers to profiles predominant in deep valleys. For the PA 6 film sample, in the height distribution, surface peaks dominate over valleys with a skewness value R_{sk} equal to 6.24. For the a-Se/PA 6 composite, R_{sk} is -0.014, and for the Cd-Se/PA 6 composite, R_{sk} is -0.0098, i.e., an almost symmetrical distribution. For the Ag-Se/PA 6 and Ag-Cd-Se/PA 6 composites, R_{sk} is 3.82 and 5.42, respectively, i.e., the surface peaks again dominate over the valleys. Film roughness has a sensitive effect on various physical properties, including optical ones.

3.3. ATR-FTIR Analysis

The FTIR study allows us to discover the conformational structural changes of the polymer chain, as well as the complexation and interaction between the polymeric matrices and inorganic nanoparticles. The ATR-FTIR spectra of the PA 6 and obtained nanocomposites within a wave number range from 650 to 1650 cm⁻¹ are displayed in Figure 6. PA 6 consists of (CH₂)₅ segments separated by a parallel or antiparallel arrangement of secondary amide groups [64]. The bands related to NH–CO fragments are mainly affected by the mutual arrangement of H–bonds, while the vibrations from CH₂ groups reflect the effect of the chain conformation [65]. In the PA 6 spectrum, the absorption bands at 834 cm⁻¹, 929 cm⁻¹, 960 cm⁻¹, 1031 cm⁻¹ and 1200 cm⁻¹ (Table 4) confirm predominantly the α -crystalline phase. The spectral features at 1476 cm⁻¹ and 1417 cm⁻¹ represent CH₂ scissoring vibrations next to –NH and >C=O groups, respectively. The band at 1463 cm⁻¹ corresponds to scissoring vibrations of CH₂. Two typical absorption bands at 1633 and 1535 cm⁻¹ represents the amide I and amide II group, respectively.



Figure 6. (a) FTIR spectra in the region of $1650-650 \text{ cm}^{-1}$ of the PA 6 matrix and the obtained nanocomposites; (b) schematic diagram of the internal amide network in the PA 6 and possible network in the obtained composites.

Band Location, cm ⁻¹					A	
PA6	a-Se/PA6	Cd-Se/PA6	Ag-Se/PA6	Ag-Cd-Se/PA6	- Assignment	
687	687	687	687	687	C–C bending	
730	730	729	730	729	CH ₂ waging	
834	835	833	833	833	CO-NH in plane	
-	-	877	877	876	CdSe or/and Ag_2Se	
929	929	930	930	930	CO-NH in plane	
960	959	961	960	960	CO–NH in plane (α crystalline)	
-	974	976	975	975		
1023	1023	1025	1024	1024	trans C–C backbone conformation	
1031	1031	1031	1032	1031	CO–NH in plane (α crystalline)	
1124	1112	1112	1108	1094	C–C stretching (sym)	
1169	1165	1166	1166	1165	N–C–O groups/CH ₂ twisting	
1200	1200	1200	1200	1201	C–CH bending (sym)	
1200	1200	1200	1200	1201	CH_2 twisting	
1238	1238	1236	1237	1235		
1264	1264	1261	1263	1263	C–N stretching (amide III)	
1365	1371	1376	1377	1377	CH_2 twisting	
-	1390	1392	1392	1391	C–C stretching (sym)	
1417	1417	1417	1416	1415	CH_2 scissoring next to >C=O group	
1463	1459	1460	1459	1459	CH ₂ scissoring	
1476	1475	1476	1475	1475	CH ₂ scissoring next to N–H group	
					C–N stretching and N–H bending	
1535	1534	1536	1536	1535	of hydrogen-bonded	
					N–H groups (amide II)	
1633	1633	1633	1633	1632	C=O stretching (amide I)	

Table 4. Band location and assignments of PA 6 and obtained nanocomposites spectra over wavenumber $1650-650 \text{ cm}^{-1}$.

The FTIR vibration bands of Se₈ rings are reported at 487.9 cm⁻¹ and 737.7 cm⁻¹ [66]. These peaks are absent in the FTIR spectrum of a-Se/PA 6, which confirms the XRD data that the inserted selenium is amorphous. The incorporation of solid inorganic nanoparticles into a flexible polyamide network causes chain stretching [65,67]. It can be seen that most of the characteristic vibration bands of PA 6 in the wavenumber region from 650 to 1650 cm⁻¹ are retained in the FTIR spectrum of a-Se/PA 6; however, the intensity of the peaks changes: some of them become more intense and some of them expand. It can be concluded that as a-Se nanoparticles are introduced between the polymer chains and stretched, the position and intensity of the peaks change. Thus, the peak of neat PA 6 at 1124 cm⁻¹ in a-Se/PA 6 spectrum shifts to 1112 cm⁻¹, and two new small peaks are recorded at 974 cm⁻¹ and 1390 cm⁻¹. C–C symmetry vibration causes IR absorption at the 1390 cm⁻¹ [68].

As reported in [20,69], the vibrational mode of CdSe is between 400 and 700 cm^{-1} . The IR absorption spectrum of selenium-rich CdSe nanocrystals shows a peak at 800 cm⁻¹ [70]. The infrared spectra for Ag₂Se nanoparticles of various sizes (from 5 nm to 28 nm) display a strong absorbing peak in the mid-IR range from 2100 cm^{-1} to 650 cm^{-1} . [71]. Thus, it is possible to avoid the problem of overlapping characteristic peaks of metal selenides and PA 6. The IR spectra of the Cd-Se/PA 6, Ag-Se/PA 6 and Ag-Cd-Se/PA 6 composites are very similar to the spectrum of a-Se/PA 6 but show an even greater shift of the peak at 1112 cm^{-1} to lower frequencies (Table 4) and the presence of another new peak at 877 cm^{-1} . In analogy with data [65], those weak vibrations can be attributed to the CdSe or Ag₂Se compounds. Another dimension of the functionality and complexity of inorganic-organic materials is introduced if the selenides are combined with each other. For example, the negative energies of chemical bond formation of CdSe and Ag₂Se promote the creation of Ag-Cd-Se interfacial bonds, which lead to non-selective nucleation in Ag₂Se/CdSe hetero-nanostructures [72]. Thus, the peak at 1108 cm⁻¹ in the IR spectrum of the Ag-Se/PA 6 composite shifts to 1094 cm^{-1} in comparison with the IR spectrum of the Ag-Cd-Se/PA 6 composite.

The shift and broadening of the C–C stretching vibration peaks, accompanied by the appearance of new small peaks of low intensity, allowed us to conclude that intermediate structures inside the polyamide chains were formed. The peak at 1124 cm^{-1} , arising from the all-trans C–C stretching vibrations, loses its spectral position. In addition, the peak was broadened, and its intensity noticeably increases in all spectra of the obtained composites (Figure 6).

3.4. UV–Vis Analysis

The experimental absorption spectra are presented in Figure 7.



Figure 7. (a) Absorption spectra of PA 6 and (b) obtained composites.

The absorption spectrum of PA 6 (Figure 7a) displays one absorption peak at around 225 nm. The colour of the obtained a-Se/PA 6 nanocomposite is red, suggesting a change in optical properties. As reported in [73,74], Se nanoparticles spectra, depending on their size, have a number of absorption peaks in the UV–visible region from 250 to 700 nm. In the UV–Vis absorption spectrum of the a-Se/PA 6 nanocomposite, a peak appeared at 475 nm (Figure 7b).

In the UV–Vis spectrum of the Cd-Se/PA 6 nanocomposite, a peak appeared at 535 nm. According to the literature data, CdSe quantum dots have a wide absorption band in the spectral range of 410–545 nm [75], and the absorption maximum of CdSe nanocrystals, depending on the particle size, is in the range from 492 to 578 nm [76]. Therefore, the peak at 535 nm can be attributed to CdSe.

In the Ag-Se/PA 6 UV–Vis spectrum, a peak appeared at 475 nm. Ag₂Se nanoparticles absorb in a wide spectral region from 300 to 600 nm [21], while two sharp peaks are observed in the spectrum of quantum dots at 440 and 607 nm, respectively [77]. Monodisperse silver nanoparticles, depending on the size, shape, and distribution in nanostructures, have two absorption bands: one broad peak in the range of 420–430 nm and a shoulder at 580–590 nm [78]. Therefore, a broad peak from 380 to 590 nm with a maximum at 475 nm can be attributed to the Ag₂Se phase with a small amount of Ag nanoparticles.

In the UV–Vis spectrum of the Ag-Cd-Se/PA 6 nanocomposite, the peak appeared at 555 nm. According to the literature data [79–81], the introduction of Ag⁺ ions into CdSe nanocrystals via the CE reaction does not lead to noticeable changes in the absorption spectra of CdSe in the UV–visible region. In contrast, other authors have suggested that the formation of the CdSe-Ag₂Se core–shell leads to the complete disappearance of the CdSe absorption peak in the UV–Vis spectra [82]. Thus, it can be stated that the absorption spectrum of the Ag-Cd-Se/PA 6 composite is a superposition of the individual absorption spectra of the CdSe, Ag₂Se and Ag phases. Its absorption edge was shifted to the longer wavelength region, and its absorption increases in the range of 375–555 nm compared to the region (375–535 nm) of Cd-Se/PA 6 and Ag-Se/PA 6 composites. This red shift of the λ_g may be related to the common complex alignment of the valence and conduction bands,

as well as to the presence of multiple defects and vacancies. The determination of the phase composition of the obtained composites according to the data of optical studies is in good agreement with the XRD data.

The experimental UV–Vis spectra correspond better to the rectilinear section on the graphs $A^2 \cdot \lambda^{-2} = (\lambda^{-1})$ (Figure 8), which confirm the direct transitions of the obtained nanocomposites.



Figure 8. Dependence $A^2 \cdot \lambda^{-2}$ on λ^{-1} for the PA 6 and obtained nanocomposites.

All the calculated optical parameters are provided in Table 5 for comparison.

Composite	λ_g , nm	Eg, eV	E_{U} , eV	σ	E _{e-p} , eV	χ
PA 6	278	$4.46 {\pm}~0.02$	1.31	0.020	33.33	1.20
a-Se/PA 6	556	$2.23 {\pm}~0.02$	0.95	0.027	24.69	0.60
Cd-Se/PA 6	605	$2.05{\pm}~0.02$	0.39	0.066	10.10	0.55
Ag-Se/PA 6	625	1.98 ± 0.02	0.55	0.047	14.18	0.53
Ag-Cd-Se/PA 6	756	$1.64{\pm}~0.02$	0.69	0.037	18.02	0.44
PA 6 a-Se/PA 6 Cd-Se/PA 6 Ag-Se/PA 6 Ag-Cd-Se/PA 6	278 556 605 625 756	$\begin{array}{c} 4.46 \pm 0.02 \\ 2.23 \pm 0.02 \\ 2.05 \pm 0.02 \\ 1.98 \pm 0.02 \\ 1.64 \pm 0.02 \end{array}$	1.31 0.95 0.39 0.55 0.69	0.020 0.027 0.066 0.047 0.037	33.33 24.69 10.10 14.18 18.02	1.20 0.60 0.55 0.53 0.44

Table 5. The optical parameters of PA 6 and studied nanocomposites.

The decrease in E_g of each subsequent nanocomposite compared to PA 6 is due to a change in the optical properties. E_g of nanocomposites can be affected by many factors, such as composition, particle size and distribution, shape, agglomeration/aggregation state, solubility, surface morphology/topography, structure crystallinity and many different structural defects or deformations [83,84]. The wavelength at which the signal becomes saturated is interpreted as being the value of the absorption edge or the E_g of the semiconductor. For a-Se/PA 6 composite E_g is 2.23 ± 0.02 eV. E_g measured for bulk a-Se is 1.99 ± 0.02 eV [85]. The introduction of Cd²⁺ ions occurred at 80 °C, and amorphous Se crystallized under heat treatment. E_g measured for cr-Se is 1.85–1.92 eV [85]. An increase in the crystallinity of the obtained composites (Figure 4) and the carrier concentration was accompanied by a decrease in E_g from 2.05 ± 0.02 eV for the Cd-Se/PA 6 composite and to 1.64 ± 0.02 eV for the Ag-Cd-Se/PA 6 composite (Table 5). The obtained values correspond with the literature data: CdSe and Ag₂Se have a band gap of 1.9 eV [20] and 1.8 eV [21], respectively.

One of the sources of unfavourable recombination is the sub-band absorption tail, which was characterized by the Urbach energy. Absorption tails are defined as densities of states that extend from the bands into the band gap of the photoactive layer. Tail states inside the band gap act as traps and recombination centres and trap charge carriers. The E_{U} is influenced by thermal and structural disturbances in semiconductor materials [86–88]. In this work, we analysed structure-dependent E_{U} . The Urbach energy plots were constructed and are shown in Figure 9, and the calculated values are given in Table 5. E_U reflects the density of states in the band tails and, hence, the local microstructural disorder [89]. As can be seen from the values presented in Table 5, the E_U of PA 6 is 1.31 eV and is higher than those of the obtained nanocomposites. The relatively high value of E_U indicates a greater tendency for the transformation of weak structural bonds into defects [90]. The a-Se/PA 6 nanocomposite (amorphous phase) is more structurally disordered. With the stepwise incorporation of Cd^{2+} and Ag^{+} ions, E_{II} decreased. That may be due to an increase in the structural ordering of nanocomposites, which has been confirmed by an increase in crystallinity detected via XRD analysis. In addition, it was previously reported [91] that thicker selenide films have less structural randomness, since with an increase in the thickness and density of the layers, structural defects are minimized and subsequently the E_{II} is also minimized.

The σ characterizes the broadening of the optical absorption edge arising from the electron-phonon interactions [39,92]. The steepness parameter of PA 6 is lower than that of the obtained nanocomposites at the same temperature (Table 5). The lower differences in electronegativity decrease the orbital overlap and the band gap.

An optical study of the formed coatings of Se, silver and cadmium selenides has revealed a decrease in the band gap in the range of 2.23–1.64 eV compared to the pristine PA 6 polymer (4.46 eV). It can be assumed that composites with such variations in E_g with the desired composition, crystallinity and surface topography can be considered potential candidates for new light and flexible solar cell technologies for sustainable energy harvesting. From a coating standpoint, such composites often contribute to significant cost savings by using inexpensive substrates while maintaining the properties of the coating material.



Figure 9. Urbach plots for PA 6 and obtained nanocomposites.

4. Conclusions

To sum up, the amorphous Se films conjugated with PA 6 were successfully obtained by exposing the PA 6 sample to an acidified aqueous solution of H_2SeO_3 and Na_2SO_3 . The surface topography of the a-Se/PA 6 consists of granular amorphous Se nanoparticles. This texture ensures the optimal deposition of the next phase. The use of prepared a-Se/PA 6 composites opens the way for the stepwise deposition of CdSe and Ag₂Se films using chemical methods. The positions of the diffraction peaks in the Cd-Se/PA 6 composite were mainly indexed as hexagonal CdSe and monoclinic Se_8 . XRD analysis has clearly shown that the Cd-Se/PA 6 and Ag-Se/PA 6 films are polycrystalline and exhibit a phase transformation from a-Se to a Se₈ monoclinic structure. The XRD pattern of the Ag-Cd-Se/PA 6 composite obtained via the CE method showed a complex crystalline composition of the film with peaks of monoclinic Se₈, hexagonal CdSe, orthorhombic Ag₂Se and metallic Ag. As indicated by the AFM results, the surface roughness of the a-Se/PA 6 composite noticeably increased compared to unreacted PA 6. However, at later stages of film deposition, the roughness decreased, and the thin film became smoother and uniform. ATR-FTIR spectroscopy data have revealed the formation of intermediate structures within PA 6. The resulting composites differed in colour, which affected their optical properties. The optical spectra show that the nanostructured films have a high absorption coefficient in the visible region. The studied composites are direct band gap semiconductors, which exhibit a redshift of the band gap from 4.46 eV for PA 6 to 2.23–1.64 eV upon the stepwise deposition of CdSe and Ag₂Se films due to a change in chemical composition and could be promising candidates for use in implantable micro-devices, as well as for solar electronics. Studies on E_U and σ describe the broadening of solar absorption edges around optical band gaps, which correlates with the polycrystalline composition and heterogeneous surface topography.

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