Synthesis and surface properties of polyamide–CuₓSe composite thin films

Remigijus Ivanauskas, Jonas Baltrusaitis

Abstract

A study of copper selenide (Cu₃Se) thin film deposition on PA 6 polymer surface via adsorption/diffusion method and the resulting surface properties is presented. A two stage process used to deposit these thin films involves (a) selenization in 0.1 M K₂Se₂O₆ at pH 2.15 and 60 °C followed by (b) treatment with 0.34 M Cu(II) and 0.06 M Cu(I) salt solution at 80 °C. Resulting chemical and physical properties of Cu₃Se films were investigated using XRD, XPS, SEM and sheet resistivity measurements. XRD data showed a complex mixture of Cu₃Se phases with peaks due to the elemental Se present at longer exposures. Thin film bulk elemental composition varied with the exposure time whereas XPS analysis showed surface to be slightly copper enriched. Additionally, mostly Cu₃–Se bonds were observed on the surface with minor oxidation products. SEM cross sectional analysis showed distinct Cu₃Se film formation on PA 6 surface with thickness of ~1–5 μm. Finally, it was found that sheet resistance of 150 ± 10 Ω/□ was achieved after 120 min of selenization for all samples and remained constant after longer exposures.

1. Introduction

For several decades, new composite materials with varying combinations of physical and chemical properties are rapidly gaining importance in various fields of modern technology. Polymers modified by thin films of binary copper selenides on their surface are of considerable interest in the fields of selective coating for solar energy harvesting [1,2], optoelectronic devices [3], optical filters [4] and electrical and electronics devices [5] due to the unique copper selenide conductive properties [6]. Surface properties of the resulting thin films, both physical and chemical alike, would determine the usability of the composite materials for any practical device. Of particular importance for solar energy harvesting or optoelectronics is the ability to obtain copper selenide films of controlled stoichiometry and crystalline phase, which in turn will possess very different optical properties, such as bandgap.

A number of various preparation techniques such as selenisation [7], chemical bath deposition [8–11], vacuum evaporation [12], flash evaporation [13], metal organic chemical vapor deposition method (MOCVD) using organometallic precursors [14] and solid state reactions [15] have been reported in formation of copper selenide thin films. As an emerging alternative method, adsorption–diffusion can be viewed as a simple and promising candidate in obtaining these binary copper selenide thin films on polymers. This method does not require high temperatures while resulting in an excellent adhesion between Cu₃Se thin film and the polymer due to the partial film incorporation. The deposition process also does not require an ultrahigh vacuum since it proceeds in aqueous solution. Polyamide (PA) as a semi-hydrophilic polymer is capable of adsorbing ions from aqueous solution of various electrolytes [16]. This fact enabled incorporation of anions from aqueous solutions of the simplest selenopolythionate homologue – selenotrithionate (SeS₂O₆²⁻) – into the PA surface as thin films [17]. After treating polythionic ion containing polymer films with Cu(II/I) salt aqueous solutions, Cu₃Se (where x stands for varying ratio of Cu to Se in the films obtained) thin films can be obtained of varying electrical conductivity depending on the experimental conditions [18].

In this work, copper selenide thin films with varying ratio of copper to selenium were deposited onto polyamide substrates using adsorption/diffusion method. Physical and electrical properties of the resulting composite material surfaces were analyzed using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM) and reported with emphasis in obtaining a temporal distribution of surface chemical and crystallographic information.
2. Experimental

2.1. Cu6Se film deposition

Films of polyamide 6 (further PA 6) [specification TY 6-05-1775-76, grade PK-4] 15 mm × 70 mm, 70 μm in thickness were used as substrates. PA 6 film is almost non-porous due to the pore size being much less than 1.5 nm [19] as measured using a β-method and Quantasorb [Japan]. Before the selenization, the samples of polyamide were boiled in distilled water for 120 min to remove the remainder of the monomer and dried using the filter paper followed by desiccation with CaCl2 for 24 h. The samples of polyamide film were then selenized in 0.1 M K2Se2O6 at pH 2.15 adjusted using 0.1 M HCl at 60 °C. The longest duration of PA 6 selenization was 270 min. The salt of potassium selenonitrathioate, K2Se2O6, was prepared according to procedures reported previously [20].

To form Cu6Se thin films, selenized samples of PA 6 were treated from 3 to 20 min with a Cu(II/I) salt solution at 80 °C. Cu(II/I) salt solution was prepared using a crystalline CuSO4·5H2O and a reducing agent hydroquinone. It is a mixture of univalent and divalent copper salts consisting of 0.34 M Cu(II) and 0.06 M Cu(I) salt. After treatment in Cu(II/I) solution samples were rinsed with distilled water, dried over CaCl2 for 24 h followed by a mild heating at 50 °C for 120 min and analyzed physicochemically.

2.2. XRD characterization

X-ray diffraction analysis Cu6Se thin films deposited on PA 6 surface was performed using a DRON-6 diffractometer equipped with a special device for beam limitation at low and medium diffraction angles using graphite-monochromatized Cu-Kα radiation source (λ = 1.54178 Å) operating at 30 kV and a current of 30 mA. The XRD patterns were recorded with a step size of 0.05° from 2θ = 25 to 70°. X-ray diffractograms of modified PA 6 films were processed using the software packages Search Match, ConvX, Xfit and Microsoft Office Excel.

2.3. SEM characterization

SEM imaging was performed using Hitachi S-3400 scanning electron microscope operating in variable pressure mode, Uncoated or otherwise modified as-synthesized samples were imaged under residual pressure of 30 Pa, sufficient to avoid imaging artifacts, e.g. sample charging, commonly resulting during the high energy electron beam analysis. Energy dispersive spectroscopy was performed using a Bruker XFlash SDD detector. Standard-less ZAF method was used to quantify elements detected with EDS. Sample crosssection was prepared by cutting PA 6 with a sharp razor blade and mounted for imaging using a carbon tape.

2.4. XPS characterization

Surface elemental analysis of the PA-Cu6Se was performed using a custom-designed Kratos Atlas Ultra X-ray photoelectron spectroscopy system [21]. The surface analysis chamber is equipped with aluminum Kα X-ray gun and 500 mm Rowland circle silicon single crystal monochromator. The X-ray gun was operated using a 15 mA emission current at an accelerating voltage of 15 kV. Low-energy electrons were used for charge compensation to neutralize the sample. High-resolution spectra were acquired in the region of interest using the following experimental parameters: 20–40 eV energy window; pass energy of 20 eV; step size of 0.1 eV, and dwell time of 1000 ms. One sweep was used to acquire a survey spectrum of all binding regions. The absolute energy scale was calibrated to the Cu 2p3/2 peak binding energy of 932.6 eV using an etched copper plate. All spectra were calibrated using the adventitious C1s peak at 285.0 eV. A Shirley-type background was subtracted from each spectrum to account for inelastically scattered electrons that contribute to the broad background. CasaXPS software was used to process the XPS data [22]. Transmission corrected relative sensitivity factor (RSF) values from the Kratos library were used for elemental quantification. An error of ±0.2 eV is reported for all peak binding energies.

2.5. Other methods

The conductivity at constant current of Cu6Se thin films was measured using an E7-8 numerical measuring instrument equipped with custom designed electrodes and presented here as sheet resistance, Ω/□.

The total amount of selenium and copper on PA 6 was determined using a Perkin-Elmer 503 atomic absorption spectrometer (λ1 = 196 nm and λ2 = 325 nm).

2.6. Results and discussion

2.6.1. Cu6Se thin film formation mechanisms, bulk chemical composition and the resulting sheet resistance

A series of Cu6Se thin films were deposited on PA 6 using the adsorption/diffusion method by changing either the selenization or copper deposition time while keeping the other parameters constant. These are presented in Table 1. A two-step mechanism of Cu6Se thin film formation on PA 6 can be proposed. In the first step Se2O3O2− ions adsorb and diffuse into the PA 6 polymer. For the first 1.5 h both adsorption and diffusion of Se2O3O2− ions proceeds while afterwards chemical reactions of Se2O3O2− anions takes place both in solution and on the polymer according to reactions (1) and (2):

\[
\text{Se}_2\text{O}_3\text{O}_2^- + \text{H}_2\text{O} \rightarrow \text{Se}_2\text{O}_3^{2-} + 2\text{H}^+ + \text{SO}_4^{2-}
\]  

(1)

\[
\text{Se}_2\text{O}_3\text{O}_2^- + \text{SeO}_3^{2-} \rightarrow \text{Se}_2\text{O}_6^{2-} + \text{SO}_4^{2-}
\]  

(2)

Divalent selenium containing compounds remain adsorbed on the polymer while hexavalent sulfur compounds dissolve back into solution. In the second step selenized polymer is reacted with a mixed Cu(I/II) ion solution and Cu6Se thin film formation proceeds via both Cu+ and Cu2+ ion reactions with the adsorbed Se2O3O2−, Se2O3O2− and SeO3O2− ions according to reactions (3)–(8):

\[
\text{Se}_2\text{O}_3\text{O}_2^- + 2\text{Cu}^+ + 2\text{H}_2\text{O} \rightarrow \text{Cu}_2\text{Se} + 2\text{H}_2\text{SO}_4
\]  

(3)

\[
\text{Se}_2\text{O}_3\text{O}_2^- + 2\text{Cu}^+ + 2\text{H}_2\text{O} \rightarrow \text{Cu}_2\text{Se} + \text{Se} + 2\text{H}_2\text{SO}_4
\]  

(4)
Table 2
Molar concentrations of copper and selenium in Cu-Se thin films on PA 6 and their corresponding measured sheet resistance.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molar concentration of Se, mg/g</th>
<th>Molar concentration of Cu, mg/g</th>
<th>Molar ratio of Cu/Se</th>
<th>Sheet resistance (Ω/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA-Cu-Se-1</td>
<td>0.174</td>
<td>0.202</td>
<td>1.166</td>
<td>2000 ± 200</td>
</tr>
<tr>
<td>PA-Cu-Se-2</td>
<td>0.223</td>
<td>0.261</td>
<td>1.171</td>
<td>410 ± 20</td>
</tr>
<tr>
<td>PA-Cu-Se-4</td>
<td>0.282</td>
<td>0.335</td>
<td>1.187</td>
<td>150 ± 10</td>
</tr>
<tr>
<td>PA-Cu-Se-6</td>
<td>0.367</td>
<td>0.335</td>
<td>1.014</td>
<td>150 ± 10</td>
</tr>
<tr>
<td>PA-Cu-Se-8</td>
<td>0.367</td>
<td>0.294</td>
<td>0.801</td>
<td>150 ± 10</td>
</tr>
<tr>
<td>PA-Cu-Se-10</td>
<td>0.282</td>
<td>0.140</td>
<td>0.496</td>
<td>400 ± 20</td>
</tr>
<tr>
<td>PA-Cu-Se-11</td>
<td>0.282</td>
<td>0.239</td>
<td>0.847</td>
<td>210 ± 20</td>
</tr>
<tr>
<td>PA-Cu-Se-4</td>
<td>0.282</td>
<td>0.335</td>
<td>1.187</td>
<td>150 ± 10</td>
</tr>
<tr>
<td>PA-Cu-Se-12</td>
<td>0.282</td>
<td>0.353</td>
<td>1.248</td>
<td>150 ± 10</td>
</tr>
<tr>
<td>PA-Cu-Se-13</td>
<td>0.282</td>
<td>0.379</td>
<td>1.343</td>
<td>150 ± 10</td>
</tr>
</tbody>
</table>

*PA 6 was first treated with 0.1 M solution of K₂Se₂O₆ at 60 °C followed by 10 min in 0.34 M Cu(II) and 0.06 M Cu(II) solution mixture at 80 °C.

SeSO₃²⁻ + 2Cu⁺ + H₂O → Cu₂Se + H₂SO₄

SeSO₃²⁻ + Cu₂⁺ + H₂O → CuSe + H₂SO₄

Se₂SO₄⁻ + Cu₂⁺ + 2H₂O → CuSe + Se + 2H₂SO₄

Se₂O₂Se⁻ + Cu₂⁺ + 2H₂O → CuSe + 2H₂SO₄

Formation of Cu₄Se thin films during the reactions (3) through (8) results in the change of PA 6 color from transparent to dark brown with the concomitant increase in electrical conductivity. Bulk chemical analysis performed on a selected samples using atomic absorption spectroscopy is shown in Table 2 together with the corresponding measured sheet resistance. It can be seen that molar Se concentration in PA 6 sample bulk increases from 0.202 to 0.295 with the increase in the seleniumization exposure time while molar Cu/Se ratio decreases from 1.166 to 0.801. The opposite effect can be seen for Cu₄Se thin films formed at constant seleniumization time of 120 min with varying copper deposition time. Here Cu molar concentration as well as Cu/Se molar ratio increases with Cu(II)/I solution exposure time from 0.140 to 0.379 and from 0.496 to 1.343, respectively.

When PA 6 is seleniumized for more than 180 min, bulk molar Cu concentration as well as molar Cu/Se ratio starts decreasing. This is due to the decomposition of the adsorbed/diffused SeSO₃²⁻ ions to form elemental Se via reaction (9):

SeSO₃²⁻ + 2H⁺ → Se + H₂O + SO₂

Due to these decomposition reactions there is a decrease in the amount of divalent Se in thin films formed on PA 6 thus decreasing the amount of Cu₄Se formed during the treatment with Cu(II)/I solution since elemental Se is unreactive toward copper ion solution. When copper exposure time is increased with a constant seleniumization time of 120 min, bulk molar Cu concentration, as well as molar Cu/Se ratio monotonically increase from 0.140 to 0.379 and from 0.496 to 1.343, respectively (Table 2). This is due to the increased interaction time between the adsorbed-diffused Se and Cu(II)/I ions allowing for reactions (2) through (8) to form more of the Cu₄Se thin film.

Sheet resistance of the PA 6 samples with Cu₄Se adsorbed/diffused was measured and the data are shown in Table 2. It decreases within each sample treatment method, e.g. both with increasing seleniumization time as well as increasing Cu (II)/I solution exposure time. This phenomenon is particularly emphasized during the seleniumization process due to the increased number of divalent Se molecules adsorbing/diffusing into the polymer and becoming available to form Cu₄Se during the second thin film formation step. This increases molar Cu concentration concomitantly with the decrease in the sheet resistance. Specifically, when molar Cu concentration increased from 0.202 to 0.335 mg/g, a corresponding Cu₄Se sheet resistance decreased from ~2000 to 150 Ω/cm for samples PA-Cu-Se-1 and PA-Cu-Se-6, respectively. Sheet resistance reaches a plateau already after 120 min seleniumization and remains constant afterwards, even though molar Cu/Se ratio slightly decreases due to the decomposition of adsorbed/diffused SeSO₃²⁻ ions.

The second step of Cu₄Se film formation, seleniumized PA 6 sample exposure to Cu(II)/I solution, has smaller effect on the measured sheet resistance. Increasing Cu ion exposure from 3 to 20 min leads to the decrease of the sheet resistance from ~400 to 150 Ω/cm for samples PA-Cu-Se-10 and PA-Cu-Se-13, respectively, while the corresponding molar Cu concentration is monotonically increasing due to the longer reaction time. It has been shown previously that sheet resistance of Cu₄S reduces by one million times when value of x is reduced from 2 to 1 [23,24]. Metal selenides have physical properties close to those of sulphides. Thus, one would expect that the sheet resistance of Cu₄Se would reduce in a similar fashion when value of x is reduced from 2 to 1. In this work, however, when molar Cu/Se ratio changes from 1.343 to 0.801 (samples PA-Cu-Se-4, PA-Cu-Se-6, PA-Cu-Se-8, PA-Cu-Se-12 and PA-Cu-Se-13) the corresponding sheet resistance does not change and remains constant at 150 ± 10 Ω/cm. This can be explained by the fact that molar Cu/Se ratio is estimated by measuring total Cu and Se amount absorbed/diffused into the PA 6 film. However, from reactions 4, 7, 9, 10 it can be seen that some Se amount will not form compound with Cu and remain in its elemental, neutral state. This would be especially true for Cu₄Se thin films formed during the longer exposures. Thus formation of the elemental Se is critical in obtaining desired sheet resistance of these films and needs to be investigated using XRD analysis.

2.6.2. Cu₄Se thin film XRD characterization

Structural characterization of these Cu₄Se thin films was performed using XRD; complex diffraction patterns were obtained due to the polycrystalline nature of the resulting Cu₄Se thin films concomitant with a simultaneous existence of many copper selenide phases of varying chemical composition and high crystallinity degree of the PA 6 itself. The intensity of PA 6 XRD peak maximum at 20° ± 25° exceeded intensity of the copper selenide films several times. Therefore, only the spectral region of 20° ≥ 25° was interpreted in detail using a combination of available literature data [25–30] and JCPDS reference patterns. X-ray diffraction analysis presented in Figs. 1 and 2 with the corresponding peak values tabulated and assigned in Table 3 revealed the existence of multiple crystalline phases, presence of which was dependent on the deposition conditions. Selected XRD spectra of Cu₄Se thin films on PA 6 with the increasing seleniumization time are shown in Fig. 1 whereas those for varying exposure time to Cu(II)/I at constant time of 120 min seleniumation are shown in Fig. 2. It can be seen that with increasing seleniumization time there is an increase in the number of Cu₄Se phases formed, as well as their concentration. Namely, sample PA-Cu₄Se-1 selenized for 30 min and shown in
Fig. 1a contains two crystalline phases of copper selenide, monoclinc copper selenide Cu2Se (27-1131) (7 peaks in XRD pattern) as well as hexagonal knockmate Cu4.87Se (83-1814) (3 peaks in XRD pattern) (Fig. 1a). A predominant crystalline phase here is a relatively low conductivity Cu2Se (27-1131), conductivity of which also has been shown to depend on the thickness of the film [31], with the lowest molar amounts of both Cu and Se resulting in the largest sheet resistance among all samples (2000 ± 200 Ω/□). While some reported Cu2Se electrical measurements show metallic conduction [32], that can be attributed to a non-perfect structure with Cu deficiencies [33]. In PA-CuSe-2 (Fig. 1b) Cu2Se (27-1131) phase is still present but no more predominant. Peaks in XRD pattern due to three new crystalline phases can be seen and were assigned to the cubic krutite CuSe2 (26-1115), tetragonal umanite Cu3Se2

Fig. 1. X-ray diffraction patterns of (a) PA-Cu2Se-1, (b) PA-Cu2Se-2, (c) PA-Cu2Se-4, (d) PA-Cu2Se-6 and (e) PA-Cu2Se-8. Peaks were identified and assigned as follows: (●) – Cu2Se (27-1131) monoclinc copper selenide; (○) – Cu4.87Se (83-1814) hexagonal knockmate; (◇) – Cu0.87Se (26-556) hexagonal copper selenide; (▼) – CuSe (26-1115) cubic krutite; (♦) – Cu2Se (47-1745) tetragonal umanite; (▲) – CuSe2 (26-556) orthorhombic copper selenide; (▲) – CuSe2 (26-556) orthorhombic copper selenide; (◇) – Cu5Se4 (21-1016) predominant crystalline CuSe phase. PA 6 was selenized in 0.1 M K2SeS2O6 solution at 60 °C with increasing exposure time followed by 10 min exposure to 0.34 M Cu(II) and 0.06 M Cu(I) solution mixture at 80 °C.

Fig. 2. X-ray diffraction patterns of (a) PA-Cu2Se-10, (b) PA-Cu2Se-11, (c) PA-Cu2Se-4, (d) PA-Cu2Se-12 and (e) PA-Cu2Se-13. Peaks were identified and assigned as follows: (○) – Cu0.87Se (83-1814) hexagonal knockmate; (◇) – Cu2Se (21-1016) orthorhombic athabascaite; (▼) – Cu2Se (47-1745) tetragonal umanite; (▲) – CuSe (26-556) hexagonal copper selenide; (♦) – CuSe (26-1115) hexagonal copper selenide; (▲) – CuSe (26-556) orthorhombic copper selenide; (◇) – Cu2Se (26-556) orthorhombic copper selenide; (◇) – Cu5Se4 (21-1016) predominant crystalline CuSe phase. PA 6 was selenized for 120 min in 0.1 M K2SeS2O6 solution at 60 °C followed by increasing exposure time in 0.34 M Cu(II) and 0.06 M Cu(I) solution mixture.

Table 3

<table>
<thead>
<tr>
<th>XRD pattern sample name</th>
<th>Symbol in Fig. 1 – crystallographic phase (JCPDS file number): peak positions 2θ, degrees</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA-Cu2Se-1</td>
<td>(●) – Cu2Se (27-1131): 32.2, 37.0, 38.7, 41.3, 50.0, 51.8, 54.4.</td>
</tr>
<tr>
<td>PA-Cu2Se-2</td>
<td>(●) – Cu2Se (27-1131): 35.9, 38.7, 40.4, 41.3, 46.6, 49.0, 50.9, 55.9.</td>
</tr>
<tr>
<td>PA-Cu2Se-4</td>
<td>(●) – Cu2Se (26-556): 31.2, 35.7, 59.5, 61.5.</td>
</tr>
<tr>
<td>PA-Cu2Se-6</td>
<td>(●) – Cu2Se (26-556): 31.6, 36.5.</td>
</tr>
<tr>
<td>PA-Cu2Se-8</td>
<td>(●) – Cu2Se (26-556): 31.6, 36.5.</td>
</tr>
<tr>
<td>PA-Cu2Se-10</td>
<td>(●) – Cu2Se (26-556): 31.5, 33.3, 34.3, 38.7, 40.6, 46.8, 51.8.</td>
</tr>
<tr>
<td>PA-Cu2Se-11</td>
<td>(●) – Cu2Se (26-556): 31.6, 36.5.</td>
</tr>
<tr>
<td>PA-Cu2Se-12</td>
<td>(●) – Cu2Se (26-556): 31.6, 36.5.</td>
</tr>
<tr>
<td>PA-Cu2Se-13</td>
<td>(●) – Cu2Se (26-556): 31.6, 36.5.</td>
</tr>
</tbody>
</table>

While some reported Cu2Se electrical measurements show metallic conduction [32], that can be attributed to a non-perfect structure with Cu deficiencies [33]. In PA-Cu2Se-2 (Fig. 1b) Cu2Se (27-1131) phase is still present but no more predominant. Peaks in XRD pattern due to three new crystalline phases can be seen and were assigned to the cubic krutite CuSe2 (26-1115), tetragonal umanite Cu3Se2

Fig. 3. SEM backscattered electron images of (a) PA-Cu$_x$Se-1, (b) PA-Cu$_x$Se-4, (c) PA-Cu$_x$Se-8, (d) PA-Cu$_x$Se-10, (e) PA-Cu$_x$Se-12, (f) PA-Cu$_x$Se-13 sample crossections. Bright stripe on the right edge of the sample correspond to the high atomic number Cu$_x$Se thin film. Scale bar is 30 μm. In (g) a representative EDS spectra of two spots on PA-Cu$_x$Se-13 sample are shown to confirm Cu$_x$Se thin film formation.

(47-1745) and orthorhombic athabascaite Cu$_5$Se$_4$ (21-1016). The corresponding sheet resistance decreases five times from ~2000 to ~410 Ω/□. When further increasing selenization time, increase in the number of XRD peaks can be observed which can be assigned to a new monoclinic Se (75-1162) phase formation. This supports the assumption above that new, possibly elemental Se phase, is formed in increased selenization time, as inferred from bulk elemental composition and measured sheet resistance data shown in Table 2.

Elemental Se can form via decomposition of adsorbed/diffused SeSO$_3^{2-}$ and Se$_2$S$_2$O$_6^{2-}$ ions according to reaction (9). In addition, it can form during the second stage of Cu$_x$Se thin film formation process via Se$_2$S$_2$O$_6^{2-}$ ion reaction with Cu(II/I) ions. Elemental Se cannot conduct electrical current; however, measured sheet resistance of longer exposure Cu$_x$Se thin films is the smallest (Table 2). This is due to the formation of other, highly conductive copper selenide phases due to the deficit of the electrons with respect
to the closed shell configuration [34], such as hexagonal copper selenide CuSe (26-556) and CuSe (27–185), while low conductivity monoclinic copper selenite Cu₂Se₂ (27–1131) phase does not form.

Resulting crystalline phase formation upon changing the Cu(II)/I exposure time while keeping the selenization time constant at 120 min was explored with the corresponding XR patterns shown in Fig. 2. Selenized sample was reacted in Cu(II)/I solution at 3, 5, 10, 15, 20 min with 10 min sample also shown in Fig. 1 but added to Fig. 2 due to the completeness. It can be seen that all samples in Fig. 2 contain monoclinic Se (75-1162) and hexagonal CuSe (27–185) crystalline phases. The most intense peaks of elemental Se are in Fig. 2d and e corresponding to the samples PA-CuSe-12 and PA-CuSe-13 and 15 and 20 min Cu(II)/I exposure time. The increase in elemental Se concentration can be explained by reaction (8) where longer exposure result in Se₂S₄O₂⁻ ion reaction with Cu(I). It also can be seen that with the increase in Cu(II)/I exposure time, more compounds are formed with x value in Cu₅Sₓ approaching 1. This would result in a decreasing sheet resistance. Specifically, in the 3 min Cu(II)/I exposure sample, Cu₃Se₂ is predominantly due to the orthorhombic athenasgite Cu₂Se₂ (83–1814) with the corresponding sheet resistance of 400 ± 20 Ω/□. With 5 min Cu(II)/I exposure (Fig. 2b) the peaks due to the orthorhombic athenasgite Cu₂Se₂ (47–1745) decrease with the concomitant increase in two new crystalline phases due to hexagonal klockmite Cu₄Se₉ (83–1814) and orthorhombic athenasgite Cu₂Se₄ (21–1016) with predominant phase due to hexagonal copper selenide (27–185). Sheet resistance of the sample decreases to 210 ± 20 Ω/□. When exposure to Cu(II)/I is increased to 10 min, low conductivity [8] Cu₂Se₂ (47–1745) phase is being substituted by more conductive hexagonal copper selenide Cu₅S₄ (26-556) and orthorhombic Cu₂Se₂ (19-400) and hexagonal Cu₅S₄ (26-556) become predominant. That affects the measured sheet resistance which decreases to 150 ± 10 Ω/□ and does not change with the longer exposures to Cu(II)/I. From XRD data shown in Fig. 2d and e (15 and 20 min Cu(II)/I exposure) can be seen that Cu₅S₄ thin film phase composition remains essentially the same. Cu₂Se (26-556) and Cu₅S₄ (19-400) become absent with the increase in monoclinic selenium, which results in constant measured sheet resistivity of 150 ± 10 Ω/□.

2.6.3. SEM/EDS and XPS analysis of Cu₅Se thin films

Since Cu₅Se film formation described here is governed by the adsorption/diffusion processes, thin Cu₅Se films are formed on PA 6 surface morphology and surface elemental composition of which can be assessed using electron and light microscope and spectroscopy techniques. Backscattered electron images of representative (a) PA-Cu₅Se-1, (b) PA-Cu₅Se-4, (c) PA-Cu₅Se-8, (d) PA-Cu₅Se-10, (e) PA-Cu₅Se-12, (f) PA-Cu₅Se-13 sample crossections are shown in Fig. 3. Due to the high atomic number of Cu₅Se, resulting image formed using backscattered electrons is much brighter for the thin films than for PA 6 itself. To confirm the presence of stratified films elemental analysis using EDS was performed in a spot mode on the electron rich film and deeper layers of the polymer. These spectra are showed in Fig. 3g. There are peaks due to the Cu and Se originating from the Cu₅Se film but not in the deeper layers of the PA 6 thus confirming formation of well-defined thin films. From the crosssectional SEM images Cu₅Se thin film thickness was calculated and presented in Table 4. It can be seen that thinner (~1.5 μm) films are formed after 30 min selenization, while thicker (up to

Table 4

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample thickness, μm</th>
<th>Cu, %</th>
<th>Se, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA-Cu₅Se-1</td>
<td>1.5 ± 0.5</td>
<td>53.2</td>
<td>46.8</td>
</tr>
<tr>
<td>PA-Cu₅Se-2</td>
<td>2.6 ± 1.7</td>
<td>51.9</td>
<td>48.1</td>
</tr>
<tr>
<td>PA-Cu₅Se-3</td>
<td>2.3 ± 1.3</td>
<td>57.0</td>
<td>43.0</td>
</tr>
<tr>
<td>PA-Cu₅Se-4</td>
<td>3.5 ± 0.8</td>
<td>59.9</td>
<td>40.1</td>
</tr>
<tr>
<td>PA-Cu₅Se-5</td>
<td>2.7 ± 0.3</td>
<td>53.5</td>
<td>46.5</td>
</tr>
<tr>
<td>PA-Cu₅Se-6</td>
<td>3.8 ± 0.7</td>
<td>52.5</td>
<td>47.5</td>
</tr>
<tr>
<td>PA-Cu₅Se-7</td>
<td>3.0 ± 1.1</td>
<td>55.0</td>
<td>45.0</td>
</tr>
<tr>
<td>PA-Cu₅Se-8</td>
<td>2.7 ± 1.2</td>
<td>56.9</td>
<td>43.1</td>
</tr>
<tr>
<td>PA-Cu₅Se-9</td>
<td>3.3 ± 1.1</td>
<td>62.5</td>
<td>37.5</td>
</tr>
<tr>
<td>PA-Cu₅Se-10</td>
<td>2.9 ± 1.2</td>
<td>55.1</td>
<td>44.9</td>
</tr>
<tr>
<td>PA-Cu₅Se-11</td>
<td>4.8 ± 1.4</td>
<td>59.3</td>
<td>40.7</td>
</tr>
<tr>
<td>PA-Cu₅Se-12</td>
<td>3.4 ± 0.8</td>
<td>66.6</td>
<td>33.4</td>
</tr>
<tr>
<td>PA-Cu₅Se-13</td>
<td>5.2 ± 2.1</td>
<td>66.4</td>
<td>33.6</td>
</tr>
</tbody>
</table>

* Measured using SEM.

Cu and Se atomic concentrations for PA-Cu₅Se sample surfaces obtained from XPS analysis.
~3.5 μm) films were observed for the exposures up to 270 min showing very little change in thickness after the initial exposure. More distinct changes in Cu₃Se film thickness were observed for films formed via 120 min selenization and varying exposure time to Cu(II/I) shown in Fig. 3d. Their thickness increased from ~3 to ~5 μm as a function of exposure time. However, relatively large error associated with these measurements prevents from drawing more conclusions about film thickness change with an increase in selenization or copper Cu(II/I) exposure and possibly point to the diffusion as a limiting factor in Cu₃Se thin film formation.

While bulk analysis was performed with both atomic absorption and SEM/EDS, XPS was used in this work to perform surface (~3 nm) chemical composition of Cu₃Se films formed, as well as to investigate their speciation. Elemental composition was calculated using high resolution XPS spectra and is presented in Table 4. It can be seen that with varying selenization time sample surface is close to 1:1 Cu/Se ratio but in all cases slightly Cu rich. When varying Cu(II/I) exposure time, a trend became apparent with increased Cu concentration on the surface, close to that of Cu₃Se in PA-Cu₃Se-13, which can be due to the saturation of the surface layers with copper ions. These data is also in agreement with that shown in Table 2 where bulk Cu/Se ratio, determined with atomic absorption spectroscopy, increases with Cu(II/I) exposure time. This surface Cu saturation could also be related to the decrease in measured sheet resistance.

High resolution Cu 2p and Se 3d spectra of PA-Cu₃Se-1, PA-Cu₃Se-4, PA-Cu₃Se-8, PA-Cu₃Se-10 and PA-Cu₃Se-13 samples are shown in Fig. 4. Only corresponding Cu 2p₃/₂ peaks are identified in Cu₂p spectra. The main peak at 932.4 eV is due to CuSe [35] which also has similar binding energies to several other copper selenides, broadly defined as CuₓSe [36]. Peak due to the Cu⁺ (as in Cu₂O) and metallic Cu were also reported to be close to 932.2 eV [37] making it difficult to distinguish the exact speciation. Cu²⁺ was reported at 933.5 eV with typical satellites at higher binding energies (941.2 and 942.9 eV) [38]. Peak at 934.2 eV was previously assigned to Cu⁺ shake up satellite [36]. This peak, together with the 944.0 eV peak, shows slight oxidation of the surface via Cu-O bond formation under atmospheric conditions. Se 3d region showed the same peak structure for all the samples analyzed with Se 3d₅/₂ peak at 541.1 eV. This is typical to metal bonded Se [39] but lower in binding energy than in elemental Se at 55.5 eV [40]. Differently from XRD data no elemental Se was detected on any sample surface due to its possible oxidation under atmospheric conditions.

3. Conclusions

Cu₃Se thin films were deposited on PA 6 surface and their morphological, chemical and conductive properties were determined. A complex speciation was inferred from XRD data that changed with the exposure time from lower conductivity copper selenides to higher. In addition, elemental monoclinic Se was detected at longer exposures thus affecting film growth and conductive properties. Well defined ~1–5 μm films were observed in crosssectional SEM images with XPS surface elemental analysis showing primarily CuSe composition, albeit with slightly increased Cu content. Sheet resistance of 150 ± 10 Ω/square was measured at longer exposure time and remained constant after 120 min of selenization due to the conductive copper selenide phase formation.

Acknowledgment

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References