THE DEPOSITION OF CuInSe₂ LAYER ON GLASS SUBSTRATE BY SILAR METHOD

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The copper indium selenide (CuInSe₂) layer was successfully deposited on glass substrate via the successive ionic adsorption and reaction (SILAR) method. The layer has been deposited in three steps and then was annealed for 12 hours under nitrogen atmosphere at 100°C. Diseleniumtetraphionate (H₂Se₂S₂O₆) acid solution was used as the selenization precursor. The solid intermediates obtained at different steps of layer deposition process was investigated in detail by X-ray diffraction analysis (XRD) and X-ray photoelectron spectroscopy (XPS) in order to understand the reaction pathway. XRD and XPS data showed that the annealing process for successful layer of copper indium selenide formation is necessary and the layer deposition phases sequence was Se → CuₓSe → mixture of phases → CuInSe₂. Based on experiment results, the possible reactions that take place during the process of layer formation have been proposed.

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1. Introduction

Solar cells are one of the most prominent and promising energy technology today. It is not only sustainable, but also, renewable, clean, completely noise free, scalable, minimal amount of maintenance is required and it produces zero emissions.

CuInSe₂ is one of many potentially efficient materials for solar cell applications. Among these, it exhibits great optical absorption coefficient (>10⁵ cm⁻¹) [1, 2], low direct band gap (1.04 eV) [2] and high thermal resilience [3]. Also, these optical properties do not get worse under highly intense irradiation [4]. Today, CuInSe₂ layers can reach 20.5% efficiency, while in solar cell 18.7% [5].

CuInSe₂ layers can be obtained using chemical or physical deposition. These methods include chemical vapor deposition [6], spin-coating [7,8], electrochemical deposition [2,3,9], chemical bath deposition (CBD) [10]. Physical deposition methods include sputtering [11], molecular beam epitaxy [12], electron beam evaporation [13,14], printing [15,16] and others. These methods, on the other hand, offers better quality layers, while often requiring high cost low-pressure, high-temperature equipment and it does not offer good scalability for large area coating. Physical deposition techniques often require annealing in H₂Se atmosphere, which results in reagent wastage, even lower cost efficiency and toxic work environment [9]. In regards to electrochemical deposition, it is rather difficult to co-deposit three elements (Cu, In, Se) simultaneously with widely spread redox potentials. Often, unwanted non stoichiometric Cuₓ₂–xSe phase is formed that degrades layer’s properties. Another downside for electrochemical deposition is the formation of non-conductive hydroxides on cathode. Various organic solvents can be added to avoid this, neglecting health hazard free environment. Sol-gel method is not a subject to this [9]. Thus, chemical deposition methods could be most convenient way to deposit CuInSe₂, by avoiding hazardous selenization process. SILAR method is presently attracting considerable attention, as it does not require sophisticated instrumentation like vacuum system and other expensive equipment.

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Simple equipment like hot plate with magnetic stirrer is needed. The starting chemicals are commonly available and cheap. By using this method homogeneous layers are formed and it is easy scalability for large surface area coatings. However, it usually requires annealing to obtain crystalline CuInSe2 layer [1].

The present work brings a complete study on the deposition of CuInSe2 and In2Se3 layer using SILAR method in a three steps process and annealing in nitrogen atmosphere. To understand the reaction pathway of CuInSe2 layer its composition was investigated through X-ray diffraction and X-ray photoelectron spectroscopy measurements.

2. Experimental

2.1. CuInSe2 layer deposition

The glass substrates where used 20 mm × 20 mm × 1 mm with a matte finish on a single side. All substrates were washed with liquid soap and distilled water and dried. Then they were cleaned in ultrasonically in acetone bath for 10 min at 40 °C. The CuInSe2 layer was deposited in three steps plus annealing. First, selenium layer was formed by submerging glass substrate into 0.4 M H2SeO3 and 1 M KHSO3 1:1 mixture at 60 °C for three hours. Then the sample was rinsed with distilled water and was placed for 10 min in solution of 0.4 M CuSO4 with addition of 1% hydroquinone at 60 °C. It is a mixture of univalent and divalent copper salts consisting of 0.34 M Cu(II) and 0.06 M Cu(I) salt. Next, it rinsed with distilled water and was submerged in 0.1 M InCl3 solution for 10 min at 40 °C. Lastly, the sample was dried over CaCl2 for 24 h and was annealed 12 h in inert nitrogen atmosphere at 100 °C.

Potassium hydrosulphite (KHSO3) (≥98.0% from Sigma–Aldrich), selenous acid (H2SeO3) (99.999% trace metals basis from Aldrich), crystalline copper sulphate pentahydrate (CuSO4·5H2O) (crystals and lumps, 99.999% trace metals basis, from Sigma–Aldrich), and hydroquinone (C6H4(OH)2) (flakes, ≥99% Reagent Plus® from Sigma–Aldrich) and indium (III) chloride (InCl3) (reagent grade, 98%, powder from Sigma–Aldrich) for experiments were used.

2.2. XRD characterization

X-ray diffraction analysis of the layers deposited on glass substrate surface after each step was performed using a D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) operating at the tube voltage of 40 kV and tube current of 40 mA. Diffraction patterns were recorded in a Bragg-Brentano geometry using a fast counting 1-dimensional detector Bruker Lynx Eye based on silicon strip technology. The X-ray beam was filtered with Ni 0.02 mm filter to suppress Cu-Kα radiation and specimens were scanned over the range 2θ = 3–70° at a scanning speed of 6° 1/min using a coupled two theta/theta scan type. Diffractometer is supplied together with software package DIFFRAC.SUITE™. X-ray diffractograms of deposited layers were processed using the software packages Search Match, ConvX, Xfit and Microsoft Office Excel.

2.3. XPS characterization

XPS measurements was carried out to obtain information about the elemental chemical states and surface composition of the layers deposited on glass substrate surface on the upgraded Vacuum Generator (VG) ESCALAB MKII spectrometer fitted with a new XR4 twin anode. The non-monochromatised MgKα X-ray source was operated at hv = 1253.6 eV with 300 W power (20mA/15kV) and the pressure in the analysis chamber was lower than 5×10−7 Pa during spectral acquisition. The spectra were acquired with an electron analyser pass energy of 20eV for narrow scans and resolution of 0.05 eV and with a pass energy of 100 eV for survey spectra. All spectra were recorded at a 90° take-off angle and calibrated from the hydrocarbon contamination using the C 1s peak at 284.6 eV. The spectra calibration, processing and fitting routines were done using Avantage software (5.918) provided by Thermo VG Scientific. Core level peaks of Se3d, Cu2p, In3d, O1s, Cl2p and C1s were analysed using a nonlinear Shirley-type background and the calculation of the elemental composition was performed on the basis of Scafoil’s relative sensitivity factors. The layer surface was sputtered by Ar+ ions having the energy of 2 keV and duration of 15 s.
3. Results and discussion

3.1. The formation mechanism of In$_2$Se$_3$ and CuInSe$_2$ layer on glass substrate

The glass substrates with a matte finish on a single side for formation the In$_2$Se$_3$ and CuInSe$_2$ layer on its surface were used. A three-step mechanism of this layer can be proposed. In the first step selenium layer was formed by submerging glass substrate into mixture solutions of H$_2$SeO$_3$ and KHSO$_3$. The components of mixture react with each other and the acid of diselenium tetrathionate in solution according to reaction is formed[17]:

$$2H_2SeO_3 + 5KHSO_3 \rightarrow 2H_2Se_2S_2O_6 + 3K_2SO_4 + KHSO_4 + 3H_2O$$ (1)

H$_2$Se$_2$S$_2$O$_6$ then decomposes and releases elemental selenium, which is deposited on glass substrate [18]:

$$Se_2S_2O_6^{2-} \rightarrow Se + SeS_2O_6^{2-}$$ (2)

During next step the glass substrates with selenium layer was placed to solution of CuSO$_4$ with hydroquinone. The elemental selenium on glass substrate is reacted with Cu(I) ions and Cu$_x$Se layer formation proceeds according to reaction:

$$Se + 2xCu^+ \rightarrow Cu_xSe + xCu^{2+}$$ (3)

In the next step the glass substrates with the layer of copper selenide was treated with solution of InCl$_3$. Possible formation reactions of In$_2$Se$_3$ layer are:

$$3CuSe + 2In^{3+} \rightarrow In_2Se_3 + 3Cu^{2+}$$ (4)

$$3Cu_2Se + 2In^{3+} \rightarrow In_2Se_3 + 6Cu^+$$ (5)

$$2Cu_2Se + In^{3+} \rightarrow CuInSe_2 + 3Cu^+$$ (6)

An exchange of ions is possible because the solubility product for In$_2$Se$_3$ is $5.6 \times 10^{-92}$, whereas for CuSe and Cu$_2$Se the solubility products are $1.4 \times 10^{-36}$ and $1.1 \times 10^{-51}$, respectively [19]. Lastly, the samples where annealed in inert (nitrogen) atmosphere at 100 °C. Possible solid-state reactions are these:

$$2CuSe + In_2Se_3 \rightarrow 2CuInSe_2 + Se$$ (7)

$$Cu_2Se + In_2Se_3 \rightarrow CuInSe_2$$ (8)

Formation of CuInSe$_2$ layer on glass substrate during the reactions (1) through (8) result in change of the glass substrate colour from transparent through red to dark grey, as shown in Fig. 1.

Fig. 1. Schematics of CuInSe$_2$ layer on glass substrate synthesis procedure
Nevertheless, to make sure that the layer of CuInSe$_2$ on glass substrate was formed this layer requires further investigation. To understand the reaction pathway of CuInSe$_2$ on glass substrate by SILAR method, the solid intermediates obtained at different stages of synthesis process were investigated in detail by XRD and XPS methods.

### 3.2. XRD analysis

The Fig. 2 shows XRD patterns of solid intermediates and CuInSe$_2$ layers on the glass substrate obtained on different steps of their formation process. It can be seen that there are clear characteristic peaks of the layers on all four patterns. When the glass substrate was submerged into a mixture of solutions H$_2$SeO$_3$ and KHSO$_3$ at 60 °C for three hours (pattern (a)), only one peak (+) at 2θ = 23.5° phase of monoclinic selenium (JCPDS: 24-714) appears (Table 1). Only single selenium peak indicates that majority of selenium is in amorphous phase, which is red color. It is known, that amorphous selenium is more active than black crystalline selenium[20]. That is why amorphous selenium should react more actively with copper ions.

![XRD patterns](image)

**Fig. 2.** XRD patterns of solid intermediates and CuInSe$_2$ layers on the glass substrate obtained on different steps of their formation process: (a) the deposition layer of selenium; (b) the formation layer of Cu$_x$Se; (c) the formation layer of CuInSe$_2$; (d) the annealing layer of CuInSe$_2$. Peaks were identified and assigned as follows: (+) – Se (24-714) monoclinic selenium; (*) – Se (73-465) hexagonal selenium; (◊) – Cu$_{0.87}$Se (83-1814) hexagonal klockmanite; (▲) – In$_{1.7}$Se$_{2.3}$ (20-492) cubic indium selenide; (○) – In$_2$Se$_3$ (17-356) indium selenide; (●) – CuInSe$_2$ (23-207) cubic copper indium selenide.

This pattern confirms the (1) and (2) equations of reactions which take place during first step when layer of selenium on the glass substrate was formed. When the glass substrate with layer of selenium was submerging into solution of CuSO$_4$ with hydroquinone, the peak corresponding to phase of monoclinic selenium on pattern (b) disappears, but the four peaks (◊) at 2θ = 26.6, 28.1, 31.1 and 50.0° of copper selenide phase – hexagonal klockmanite Cu$_{0.87}$Se (JCPDS: 83-1814) appear (Table 1). The disappearance phase of monoclinic selenium and the appearance phase of copper selenide indicated that the reaction of the formation of Cu$_x$Se which was described in equation of (3) has taken place. When the glass substrate with layer of copper selenide was submerging into solution of InCl$_3$, one peak (●) at 2θ = 46.0° phase of cubic indium selenide In$_2$Se$_3$ (JCPDS: 20-492) appears (pattern (c)) (Table 1). It indicates the formation of new phase of indium selenide according equations (4) and (5). Therefore, the intensively and clear characteristic peaks of the Cu$_{0.87}$Se in the XRD pattern (c) showed that the layer formed after third step consists of only Cu$_{0.87}$Se phase and a little amount of In$_2$Se$_3$ phase. Looking at our results, we see, that annealing is needed to obtain CuInSe$_2$ phase. Finally, sample was annealed 12 h in the inert (nitrogen) atmosphere at 100 °C. Then on the XRD pattern (d) in Fig. 2 of annealed layer can be seen noticeable big changes. The intensities of four diffraction peaks of hexagonal klockmanite Cu$_{0.87}$Se markedly decrease and the diffraction peak of cubic indium selenide disappears. It should be noted that two intensive diffraction peaks (∗) at 2θ = 23.5, 29.7° and two
weak diffraction peaks at 56.3 and 61.7° of new phase of hexagonal selenium (JCPDS: 73-465) can be clearly observed. Meanwhile, comparing with two weak diffraction peaks (▲) at 43.6 and 51.8° of phase of cubic copper indium selenide (JCPDS: 23-207) and three diffraction peaks (○) at 28.6, 41.3 and 45.3° of new phase of indium selenide (JCPDS: 17-356). These detected results definitively can be illustrated by solid-state reactions which were described in equations (7) and (8), when phases of hexagonal selenium (JCPDS: 73-465) and copper indium selenide (JCPDS: 23-207) were formed. In addition, as a result of these reactions, the amount of phase of copper selenide CuS\textsubscript{0.87}Se (JCPDS: 83-1814) decreases significantly and phase of indium selenide In\textsubscript{2}Se\textsubscript{3} (JCPDS: 20-492) disappears completely.

This confirms the mentioned above variation intensities of diffraction peaks attributed to the following phases in the XRD pattern (d). It is possible that selenium and cation of univalent copper had formed during reactions (5), (6) and (7) react with each other and according to equation (3) and copper selenide is formed. Then copper selenide react with cations of In\textsuperscript{3+} according to equations (4) and (5) and the phase of indium selenide (JCPDS: 17-356) formed.

Table 1. XRD 2θ peaks and their assignment of CuInSe\textsubscript{2} layer on glass substrate formed by SILAR method.

<table>
<thead>
<tr>
<th>Stage of layer formation</th>
<th>Symbol in Fig. 1 – crystallographic phase (JCPDS file number): peak positions 2θ, degrees</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1</td>
<td>(+) – Se (24-714): 23.52</td>
</tr>
<tr>
<td>Step 2</td>
<td>(◊) – CuS\textsubscript{0.87}Se (83-1814): 26.62, 28.11, 31.08, 50.00</td>
</tr>
<tr>
<td>Step 3</td>
<td>(○) – CuS\textsubscript{0.87}Se (83-1814): 26.62, 28.11, 31.08, 50.00</td>
</tr>
<tr>
<td></td>
<td>(▲) – In\textsubscript{2}Se\textsubscript{3} (20-492): 46.05</td>
</tr>
<tr>
<td>After annealing</td>
<td>(*) – Se (73-465): 23.52, 29.70, 56.25, 61.67</td>
</tr>
<tr>
<td></td>
<td>(▲) – CuInSe\textsubscript{2} (23-207): 43.61, 51.78</td>
</tr>
<tr>
<td></td>
<td>(○) – In\textsubscript{2}Se\textsubscript{3} (17-356): 28.57, 41.32, 45.30</td>
</tr>
<tr>
<td></td>
<td>(○) – CuS\textsubscript{0.87}Se (83-1814): 26.62, 28.11, 31.08, 50.00</td>
</tr>
</tbody>
</table>

3.3. XPS analysis

In order to get more information about the formation of CuInSe\textsubscript{2} layer on the glass substrate it was analyzed by X-ray photoelectron spectroscopy (XPS). The surface of layer obtained, when the glass substrate was submerged into mixture of solutions H\textsubscript{2}SeO\textsubscript{3} and KHSO\textsubscript{4} (first step), and the surface of CuInSe\textsubscript{2} layer and it deeper areas after etching (up to 20 μm) were studied. The signal of a freshly prepared selenium layer shown in Fig 3 Se3d region, curve (c) exhibits a signal at 55.70 eV which corresponds to the selenium in elemental state (Se\textsuperscript{0})[21]. The high resolution XPS spectra of CuInSe\textsubscript{2} layer in Cu2p, In3d and Se3d regions are also shown in Fig. 3 curves (a). For surface layer of CuInSe\textsubscript{2}, the binding energy (BE) of Cu2p\textsubscript{3/2} and Cu2p\textsubscript{1/2} is 932.33 eV and 952.58 eV respectively, which is consistent with BE values of CuInSe\textsubscript{2}[22] and CuS or Cu\textsubscript{2}O[23,24]. The BE value of 55.18 eV for the Se3d\textsubscript{5/2} level is assigned to the CuInSe\textsubscript{2}[22] and elemental Se [25]. The predominant features of InCl\textsubscript{3} exhibiting BE of 445.91 eV and 454.03 eV for the In3d\textsubscript{3/2} and In3d\textsubscript{5/2} levels[26,27].

The high resolution XPS spectra of the etched layer of CuInSe\textsubscript{2} in Cu2p, In3d and Se3d regions are shown in Fig. 3 curves (b). The BE of XPS peaks corresponding to levels Cu2p and Se3d (Cu2p\textsubscript{3/2} at 932.33 eV, Cu2p\textsubscript{1/2} at 952.58 eV and Se3d\textsubscript{5/2} at 55.18 eV) are not changed and indicates that compound composition remain unchanged deeper that 20 μm from surface.

However, the both peaks of BE of In3d\textsubscript{3/2} and In3d\textsubscript{5/2} for etched layer shifted to direction of lower BE than that of non-etched surface of layer. The BE of In3d\textsubscript{3/2} is 445.10 eV respectively, which is consistent with BE values of In\textsubscript{2}Se\textsubscript{3}[28].

The lower intensity peaks can be observed Cu2p and Se3d in XPS spectra of non-etched surface, while higher intensity of same spectra can be clearly observed on etched surface (Fig 3). On contrary, In3d in XPS spectra peaks are slightly more intense of non-etched surface as opposed to etched one. This is suggesting that concentration of Se and Cu is lowering CuInSe\textsubscript{2} layer surface.
as one of those elements in deeper layer of surface. In the meantime, the concentration of In is higher on the layer surface.

Fig. 2. High-resolution XPS spectra in Se3d5/2, Cu2p3/2 and In3d5/2 regions for Se and CuInSe$_2$ layers prepared by SILAR method (a) as deposited layer, (b) annealed layer and (c) selenium layer.

Table 2. Atomic content of elements on the surface of CuInSe$_2$ layer evaluated from XPS and atomic ratios of Cu/In and Se/(Cu+In)

<table>
<thead>
<tr>
<th>Elements and atomic ratios</th>
<th>Atomic content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Not etched</td>
</tr>
<tr>
<td>Cu</td>
<td>4.02</td>
</tr>
<tr>
<td>In</td>
<td>7.11</td>
</tr>
<tr>
<td>Se</td>
<td>9.77</td>
</tr>
<tr>
<td>O</td>
<td>10.94</td>
</tr>
<tr>
<td>Cl</td>
<td>13.44</td>
</tr>
<tr>
<td>C</td>
<td>54.71</td>
</tr>
<tr>
<td>Cu/In</td>
<td>0.57</td>
</tr>
<tr>
<td>Se/(Cu+In)</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Some impurity elements such as O, Cl and C were also detected by XPS (Fig. 3, XPS). Among these elements, O is due to exposure to the atmosphere, and Cl is residual element from the precursor solution, C 1s of adventitious carbon is used as reference.

Composition analysis of CuInSe$_2$ layer surface before and after etching is shown in Table 3. It is found out that in the surface of the CuInSe$_2$ layer, the atomic ratio of Cu/In is about 0.57 which is lower than the atomic ratio of Se/(Cu+In). After the layer etching, the Cu/In ratio increased to 1.91 and became higher than Se/(Cu+In) ratio although this ratio increased too from
Based on the XPS results, it can be concluded that in the valence of Cu, In and Se in surface layer of and its depth up to 20 μm were in form CuInSe$_2$, In$_2$Se$_3$ and InCl$_3$ were Cu$^{1+}$, In$^{3+}$ and Se$^{2-}$, respectively.

From the analysis of XRD and XPS, we try to understand the reaction pathway of CuInSe$_2$ layer deposited on SILAR method. It can be seen, that firstly, selenium layer was deposited that consists, mostly of red, amorphous selenium that has charge of Se$^2$. Next, layer was treated with solution, containing Cu$^+$ ions, thus obtaining Cu$_{0.87}$Se phase. When this layer was exposed to solution containing In$^{3+}$ ions, the XRD analysis had shown that compounds of Cu$_{0.85}$Se and In$_2$Se$_3$ in the layer of CuInSe$_2$ coexist. However, XPS analysis shows both CuInSe$_2$, In$_2$Se$_3$ and elemental Se are present in CuInSe$_2$ layer. Copper selenide was not found due to (4), (5) and (6) reactions, because it remained deeper inside layer than 20 μm XPS etching. Formed CuInSe$_2$ and Se must be amorphous, because there were no XRD signals observed from freshly prepared layer. However, it is very likely that after annealing amorphous CuInSe$_2$ and Se phase changes to crystalline cubic CuInSe$_2$ and hexagonal Se, both are found using XRD analysis. Also, solid phase reactions (7) and (8) can take place and form same of on reaction (6). It can be seen, that order of CuInSe$_2$ layer formation does influence deposited layer composition. In order to obtain homogeneous, crystalline CuInSe$_2$ layer, it is necessary to anneal it in inert (nitrogen) atmosphere.

4. Conclusions

CuInSe$_2$ layer on glass substrate was prepared in three steps by SILAR method and the composition of layer after each step has been studied. In addition, the effect of post-annealing treatment on the composition of this layer was studied. According to XRD analysis the formation sequence and the composition of CuInSe$_2$ layer was Se (24-714) (Step 1) → Cu$_{0.87}$Se (83-1814) (Step 2) → Cu$_{0.87}$Se (83-1814), In$_2$Se$_3$ (20-492) (Step 3) → CuInSe$_2$ (23-207), In$_2$Se$_3$ (17-356), Cu$_{0.87}$Se (83-1814), Se (73-465) (After annealing). Quantification of XPS peaks of Se3d, Cu2p and In3d confirms that after the third step formed phases of CuInSe$_2$ and Se, which must be amorphous, because no XRD signals from this layer were observed. It is necessary to anneal in nitrogen atmosphere, in order to form CuInSe$_2$ layer having a phase of crystalline CuInSe$_2$. The atomic ratios of Cu/In and Se/(Cu+In) on surface of CuInSe$_2$ layer are 0.57 and 0.88 and they increasing with depth of layer (20 μm) from its surface accordingly up to 1.91 and 1.14. Based on experiment results, the possible reaction pathway of the layer of CuInSe$_2$ on glass substrates synthesis procedure by SILAR method was proposed.

References