

Photovoltaic structures formed by thermal annealing of electrodeposited CuInSe₂ in H₂S

Julia Kois^{*}, Sergei Bereznev, Enn Mellikov, and Andres Öpik

Department of Material Science, Tallinn Technical University, Ehitajate tee 5, 19086 Tallinn, Estonia

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Abstract. Thin polycrystalline CuInSe₂ films were electrodeposited onto ITO/In(O,S) and ITO covered glasses from aqueous solutions with various ratios of elements. The obtained structures were annealed at 450 °C in H₂S. Current-voltage and impedance measurements were carried out for the produced heterostructures. The electronic quality of CuInSe₂ was found to have improved after thermal and chemical treatment.

Key words: photovoltaic structure, electrodeposition, thermal treatment, chemical treatment.

INTRODUCTION

The chalcopyrite I-III-IV₂ semiconductors are now established as effective absorbers in thin film photovoltaic cells. The materials CuInSe₂ (CIS), Cu(InGa)Se₂ (CIGS), and CuIn(SSe)₂ (CISSe) have been the most extensively developed because they allow tailoring of the energy band gap and other material properties to enhance device performance [1–3]. The feasibility of alloying CIS with either Ga or S has enabled the production of quaternary CIGS or CISSe with band gap (E_g) varying from 1.04 to 1.68 eV [4]. Thin film solar cells have been produced using these materials with a record efficiency of 18.8% [5].

As noted, CIS thin films have been deposited using various techniques such as elemental and binary compounds co-evaporation [5, 6], sputtering [7], pulsed laser deposition [8], and electrodeposition [3, 9–11]. Thin film photovoltaic devices with CIS electrodeposited films have reached the efficiency of 7.9% [12].

^{*} Corresponding author, julia@staff.ttu.ee

We studied electrodeposition of CIS and used it to produce thin film photovoltaic structures. The developed method is simple, the properties of CIS films could be easily controlled, and good quality films could be produced with a relatively large depositing area.

EXPERIMENTAL

Preparation of substrates

Two types of substrates were used for electrodeposition of CIS: (1) ITO-coated glasses cleaned in concentrated H_2SO_4 at $90^\circ C$ during 5 s, and (2) ITO/In(O,S) structures fabricated by annealing ITO glasses in the atmosphere of H_2S at $450^\circ C$ for about 15 min.

Electrodeposition of CIS

The constituents of the electrolyte used for electrodeposition were aqueous solutions of 3 mM $CuSO_4$, 7 mM $In_2(SO_4)_3$, and 11 mM SeO_2 . The pH in electrochemical bath was adjusted to 1.5 with H_2SO_4 .

The CIS thin films were prepared on the above-mentioned ITO and ITO/In(O,S)-conductive substrates by the one-step electrodeposition method [11] at a potential of -900 mV vs. Ag/3M AgCl electrode using potentiostat Wenking LT 87. The synthesis was performed in a standard three-electrode cell. A platinum plate was used as the counter electrode. The investigated films were deposited with excess of In and Se and with different Cu/In mixing ratios (Table 1).

Table 1. Performance of the In(O,S)/CISSe cells produced at various post-fabricating treatments

Electrolyte $Cu^{2+}/In^{3+}/Se^{4+}$, mM	First annealing in H_2S			Etching in 5% KCN			Additional annealing in H_2		
	J_{sc} , mA/cm ²	V_{oc} , mV	FF , %	J_{sc} , mA/cm ²	V_{oc} , mV	FF , %	J_{sc} , mA/cm ²	V_{oc} , mV	FF , %
2/7/11	-1.0	297	25.2	-2.7	271	24.1	-2.0	289	27.2
3/7/11	-3.7	269	27.8	-5.7	301	28.1	-10.0	332	32.2
4/7/11	-2.0	50.6	24.4	-2.0	368	23.8	-2.0	125	25.5
5/7/11	-1.0	373	24.7	-2.0	284.8	20.1	-2.0	358.2	23.0

J_{sc} – short-circuit current density; V_{oc} – open-current voltage; FF – fill factor

Device fabrication

After the deposition of CIS films, samples were heat treated in quartz tubes in the atmosphere of floating H_2S and/or H_2 at the temperature of $450^\circ C$ for about 30 min [1]. The thickness of annealed films was determined microscopically and was on average 1 μm . The morphology of the as-electrodeposited and annealed

CIS thin films were studied by a scanning electron microscope (SEM). Phase composition of the formed CIS films was characterized by X-ray diffraction (XRD) analysis using a diffractometer Bruker AXSD5005. Finally, back electrical contact to CISSe films was formed using conductive graphite paste. Dark and illuminated current–voltage (J – V) characteristics were measured using a KEITHLEY 2400 SourceMeter.

RESULTS AND DISCUSSION

Figure 1 shows the SEM images of thin films electrodeposited onto ITO covered substrates. Changes in the topography of annealed films compared with as-electrodeposited films were observed in these experiments. The surface of the as-deposited films contains cauliflower type features of various size (up to $1.2\ \mu\text{m}$). CIS films annealed at 450°C in H_2S for 30 min exhibit a smoother surface and more uniform grain size with sporadic impurities of about $1\ \mu\text{m}$. The cracks in annealed films may be caused by thermal stresses between the ITO substrate and the CIS film.

Figure 2 shows the XRD pictures of the electrodeposited and treated CIS thin films. The figure indicates that the electrodeposited film contains In_2Se_3 (JSPDS 40-1407). The film annealed in H_2S during 30 min and etched in 5% KCN for about 1 min contains CuInSe_2 (JSPDS 40-1480) and In_2S_3 (JSPDS 25-0390) that have very similar diffraction peaks to In_2Se_3 .

Optical transmission data (Fig. 3) were used to determine the adsorption coefficient and band gap values (Fig. 4) for CIS by the method described in [13]. The band gaps for as-deposited and annealed in hydrogen films are 1.23 and 1.24 eV, respectively. The wider value of E_g of prepared films in comparison

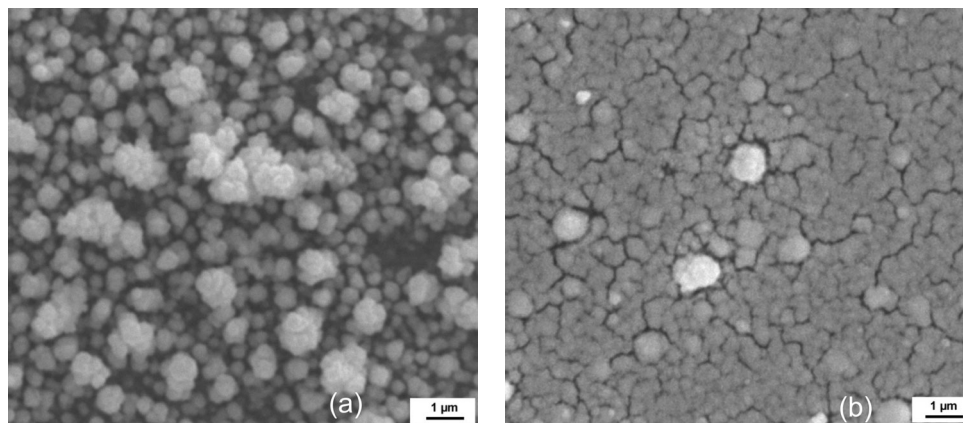


Fig. 1. Scanning electron micrographs of CIS thin films: (a) as-electrodeposited, (b) annealed at 450°C in H_2S for 30 min.

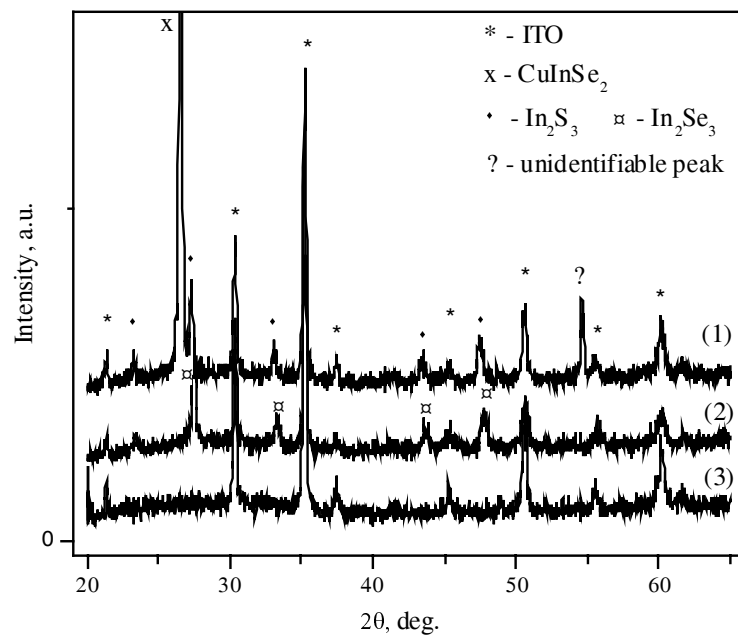


Fig. 2. The XRD picture of: (1) annealed in H_2S and etched in 5% KCN, (2) as-deposited CIS thin films, (3) ITO substrates.

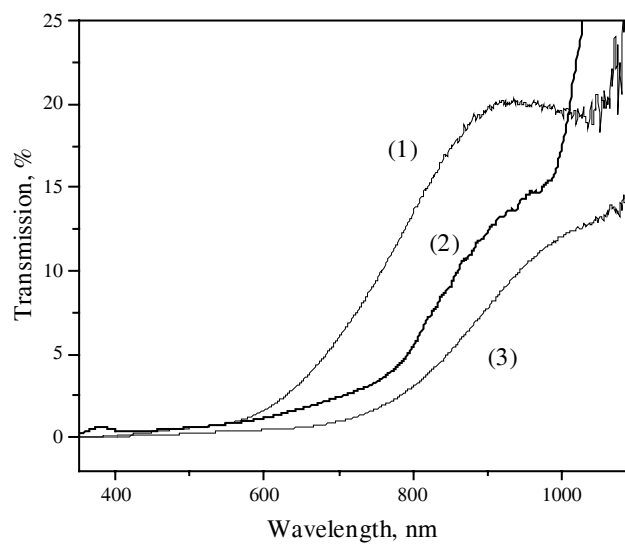


Fig. 3. The transmission spectra for CIS thin films: (1) deposited onto $\text{In}(\text{O,S})$ and annealed in H_2 for about 30 min, (2) deposited onto ITO and annealed in H_2S for about 30 min, (3) as-deposited.

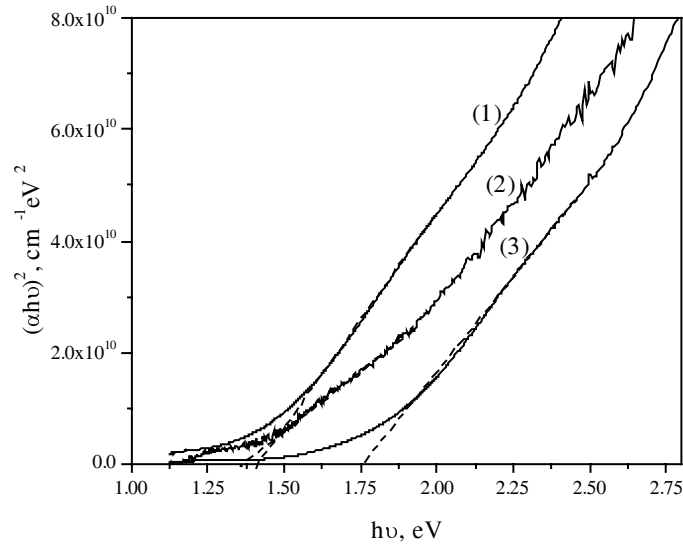


Fig. 4. The plot of $(\alpha h\nu)^2$ against the photon energy $h\nu$ for the CIS thin films. (1) deposited onto In(O,S) and annealed in H_2 for about 30 min, (2) as-deposited, (3) deposited onto ITO and annealed in H_2S for about 30 min.

with E_g for CIS (1.04 eV) can be explained with the enlargement of the band gap of Cu-poor chalcogenides [14]. The CISSe thin film treated in the atmosphere of H_2S at $450^\circ C$ during 30 min has a band gap of about 1.75 eV.

The formation of In(O,S) nano-size films accompanies the formation of $CuIn(S_xSe_{1-x})_2$ during the annealing of electrodeposited CIS in the atmosphere of H_2S . Sulphur diffuses through thin films of CIS and reacts with the surface of ITO-conductive substrates to indiumtinoxysulphide In(O,S). As a result, the as-deposited barrier-free ITO/CIS structure is transferred to ITO/In(O,S)/CISSe – a photovoltaic heterostructure.

The photovoltaic $J-V$ measurements were made on the formed ITO/In(O,S)/CISSe structures and after additional treatments of the structures (Table 1). Figure 5 presents $J-V$ curves of two photovoltaic structures – ITO/In(O,S)/CIS/graphite contact and ITO/In(O,S)/CISSe/graphite contact formed by two different methods: CIS film deposited onto In(O,S) substrates and annealed in the atmosphere of hydrogen (a), and CIS film deposited onto ITO substrates and annealed in H_2S (b).

In(O,S) thin film could be considered a buffer layer between n -ITO and CISSe in the PV structure of ITO/In(O,S)/CIS/graphite and ITO/In(O,S)/CISSe/graphite. The structures on the basis of thick (thickness $> 1.5 \mu m$) CISSe films on ITO annealed in H_2S demonstrate ohmic behaviour because the interdiffusion of sulphur through thick films of CIS in the annealing process was deficient for forming In(O,S) onto the surface of ITO. Similarly, the ITO/CIS structure shows ohmic resistance after annealing in hydrogen.

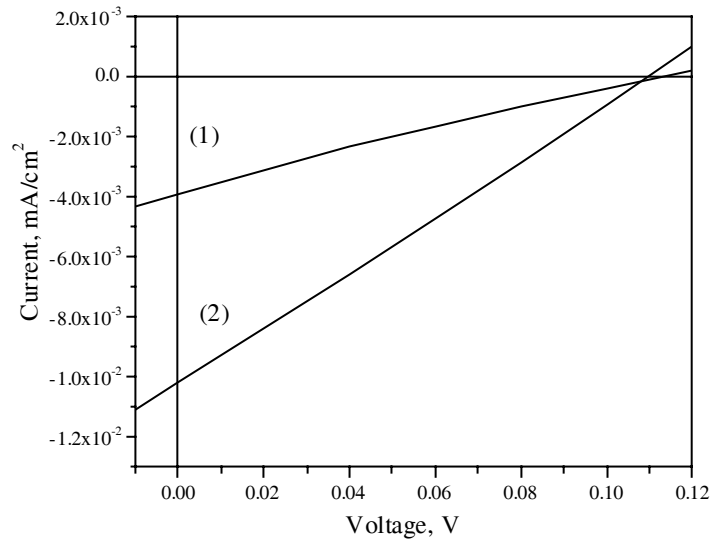


Fig. 5. Photovoltaic J - V characteristics for the structures ITO/In(O,S)/CIS annealed in H_2 (1) and ITO/CIS annealed in H_2S (2). Active area of the structures is 1 mm^2 .

The improvement of J - V characteristics of the structure ITO/In(O,S)/CISSe after additional treatments is shown in Fig. 6. Chemical etching in 5% KCN and 0.5% KOH has removed the contaminating high resistance phases (S, Se, In_2S_3)

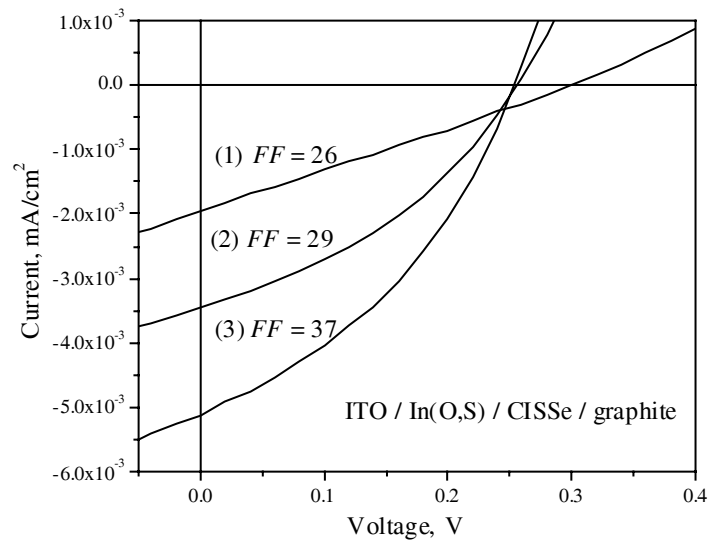


Fig. 6. Dark and photo J - V characteristics for the photovoltaic device: (1) annealed on H_2S at 450°C 30 min, (2) annealed on H_2S and chemically etched in 5% KCN and 0.5% KOH, (3) annealed on H_2S , chemically etched, and additionally annealed in the H_2 atmosphere at 450°C for 2 h. Active area of structures 1 mm^2 . FF – fill factor.

from the surface of the annealed films. As result, the short-circuit current density (J_{sc}) increased. After secondary annealing in the atmosphere of H_2 , the crystallinity was improved, open-current voltage (V_{oc}) deteriorated slightly, and the fill factor (FF) increased.

CONCLUSIONS

The photovoltaic structures ITO/In(O,S)/CISSe/graphite and ITO/In(O,S)/CIS/graphite were studied. The buffer In(O,S) film was obtained by sulphurization of electrodeposited CIS films at 450°C in the atmosphere of flowing H_2S . The electrical quality of the structure was improved by additional chemical and thermal treatments. We achieved J_{sc} 10 mA/cm^2 and V_{oc} 332 mV for the structure ITO/In(O,S)/CISSe/graphite with an active area of 1 mm^2 .

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Päikeseelemendid H₂S atmosfääris kuumutamise modifitseeritud elektrokeemiliselt sadestatud CuInSe₂ kilede baasil

Julia Kois, Sergei Bereznev, Enn Mellikov ja Andres Öpik

On uuritud struktuuride ITO/In(O,S)/CISSe/grafiit ja ITO/In(O,S)/CIS/grafiit elektrokeemilisel sadestamisel saadud päikeseelementide elektriliste parameetrite sõltuvust valmistamise preparatiivsetest tingimustest. In(O,S) puhverkiht loodi elektrokeemiliselt sadestatud CuInSe₂ õhukeste kilede sulfureerimisel temperatuuril 450°C H₂S voolus. Struktuuride elektrilisi parameetreid optimeeriti erinevatel termilistel ja keemilistel töötlustel. 1 mm² pindalaga struktuuri ITO/In(O,S)/CISSe/grafiit parameetriteks olid J_{sc} 10 mA ja V_{oc} 332 mV.