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One-Step Electrodeposition of CZTS for Solar Cell Absorber Layer

Marta Farinella, Patrizia Livreri, Salvatore Piazza, Carmelo Sunseri and Rosalinda Inguanta

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Abstract

CZTS thin films were obtained by one-step electrochemical deposition from aqueous solution at room temperature. Films were deposited on two different substrates, ITO on PET, and electropolished Mo. Differently from previous studies focusing exclusively on the formation of kesterite ($\text{Cu}_2\text{ZnSnS}_4$), here, the synthesis of a phase with this exact composition was not considered as the unique objective. Really, starting from different baths, amorphous semiconducting layers containing copper–zinc–tin–sulphur with atomic fraction $\text{Cu}_{0.592}\text{Zn}_{0.124}\text{Sn}_{0.063}\text{S}_{0.221}$ and $\text{Cu}_{0.415}\text{Zn}_{0.061}\text{Sn}_{0.349}\text{S}_{0.175}$ were potentiostatically deposited. Due to the amorphous nature, it was not possible to detect if one or more phases were formed. By photoelectrochemical measurements, we evaluated optical gap values between 1.5 eV, similar to that assigned to kesterite, and 1.0 eV. Reproducibility and adhesion to the substrate were solved by changing S with Se. Preliminary results showed that an amorphous p-type layer, having atomic fraction $\text{Cu}_{0.434}\text{Zn}_{0.036}\text{Sn}_{0.138}\text{Se}_{0.392}$ and an optical gap of 1.33 eV, can be obtained by one-step electrochemical deposition.

Keywords: CZTS, electrodeposition, thin films, solar cells, photoelectrochemistry

1. Introduction

In the last years, the synthesis of copper, zinc, tin sulphide (CZTS) with kesterite structure and composition ($\text{Cu}_2\text{ZnSnS}_4$) has received great attention. The wide interest is due to its possible use as absorber layer in solar cells owing to several advantages. CZTS has a high absorption coefficient, of the order of 10^4 cm^{-1} [1], with a band gap between 1.45 and 1.6 eV [2] so that high conversion efficiencies are expected. In addition, CZTS contains only non-toxic and abundant

on the earth crust elements. The band gap of this material can be simply changed by controlling the composition of CZTS deposit as shown in Table 1 for e-beam-evaporated CZTS [3].

CZTS Composition				E_g (eV)
[Cu]	[Zn]	[Sn]	[S]	
1.76	1.33	0.9	4	1.47
1.76	1.29	0.94	4	1.47
1.67	1.41	0.92	4	1.48
1.59	1.57	0.84	4	1.48
1.62	1.52	0.86	4	1.49
1.75	1.21	1.03	4	1.62
1.78	1.21	1.01	4	1.63
1.79	1.18	1.03	4	1.63
1.77	1.29	0.94	4	1.64

Table 1. Chemical composition of e-beam-evaporated CZTS and relative energy-gap value

Commonly thinking that successful application of CZTS in the field of photovoltaics was due only to kesterite composition, prevailing attention has been devoted to thin film fabrication having this composition, and different routes were proposed, accordingly. Some of them are presented in Table 2.

Synthesis method	References
Sputtering by atomic beam	[2]
Sputtering by radio frequency magnetron	[4, 5]
Sulphurization of either electron-beam-evaporated or electrodeposited precursors	[6, 7]
Photochemical deposition	[8]
Spray pyrolysis	[9]
Pulsed laser deposition	[10, 11]
Sol–gel sulphurization	[12]
Chemical synthesis	[13, 14]
Review on non-vacuum processes to fabricate thin films of CZTS with kesterite structure and composition has been published	[15]

Table 2. Routes proposed for CZTS synthesis with kesterite composition

The state of the art in terms of application of CZTS as absorber layer is shown in Table 3 where the performances of solar cells with CZTS prepared by different methods are presented.

Synthesis method	Efficiency (%)	References
Spin coating	11.1	[15]
Co-evaporation	9.15	[15]
Sequential electrodeposition	7.3	[15]
One-step electrodeposition	3.4	[15]
Chemical vapour deposition	6	[15]
Sol-gel synthesis	5.1	[15]
Ionic layer adsorption and reaction (SILAR)	1.85	[15]
Spray pyrolysis	1.13	[12]
Blade coating	6.8	[1]
Co-sputtering	6.7	[1]
Sequential sputtering	4.6	[1]
Physical layer deposition	3.14	[1]
Sequential e-beam evaporation	1.7	[1]
Chemical bath deposition	0.16	[1]
Reactive co-sputtering	3.4	[1]
Stacked deposition (sputtering + evaporation)	6	[1]
Fast co-evaporation	4.1	[1]

Table 3. Performances of solar cells having CZTS absorber layer fabricated by different methods

The solar cells fabricated with all these methods have very different performance (see Table 3) because the composition of CZTS film was quite different and besides many secondary phases such as ZnS were present. In order to decrease these secondary phase, thermal treatment at different temperature either in inert or reactive atmosphere was performed. Thermal treatment was also conducted to control the crystallinity of the deposit, because some of above cited fabrication methods produce either amorphous or nanocrystalline CZTS film.

Among non-vacuum processes, electrochemistry can play a significant role, because electrochemical-based processes are easy to conduct, do not require sophisticated and expensive apparatus and usually can be easily scaled. In addition, precursors are cheap if aqueous electrolytes are employed.

Basically, two routes were proposed for electrochemical synthesis of CZTS thin films. One consists in the electrodeposition of the metallic precursors, followed by sulphurization either

in sulphur or H_2S atmosphere [16, 17]. An alternative route is one-step electrodeposition on different substrates, employing either ionic liquids [18] or aqueous electrolytes [19, 20]. In this last case, the true challenge is to be successful in levelling the reduction potential of the precursors, which have very different standard potentials. For this aim, electrolyte composition plays a fundamental role, because proper precursor concentration must be chosen together with addition of suitable complexing agents. Thus, parameters to be controlled for obtaining a desired composition are numerous. All previous investigations were oriented to synthesize CZTS with kesterite stoichiometry ($\text{Cu}_2\text{ZnSnS}_4$), owing to its good performance as light absorber for sun energy conversion. Whichever the procedure, this composition is highly difficult to achieve also at a lab scale; therefore, from an applicative point of view, it may be useless to try to obtain it. Even more so, other difficulties, limiting the scale-up of the process, exist. In order to give a real applicative perspective to this four-element material, which is one of the most reliable candidates to substitute Si in solar cells, the present study aimed to electrodeposit in one-step photoactive CZTS films with different atomic fraction was undertaken.

After a preliminary investigation on single-step electrodeposition of CZTS [21], a systematic investigation was undertaken to detect the fundamental parameters influencing composition of the deposited films. Here, we present the fundamental results of this study where different substrates and bath compositions were investigated. In particular, the study evidenced several difficulties in the one-step electrodeposition, in terms of reproducibility and also of adhesion of the deposited layer to the substrate.

The most significant finding of the present work consists in electrodepositing in a single step photoactive CZTS layers having good chemical and dimensional stability, so contradicting the usual opinion that it is mandatory to achieve the kesterite composition for fabricating CZTS-based solar cell. In order to find the best operative conditions leading to a deposit able to convert efficiently solar energy, the deposition process was investigated on different supports and at different pH and solution composition. The response under illumination was investigated by photoelectrochemical measurements.

2. Deposition of CZTS thin films

Indium–tin oxide film deposited on polyethylene terephthalate (ITO/PET $45 \Omega \cdot \text{cm}^{-1}$ from Aldrich) was used as flexible substrate. By SEM analysis, a thickness of 100 nm was evaluated for the ITO film, while PET was 100 μm thick. Since tin was present in CZTS and ITO, an energy dispersion spectroscopy (EDS) spectrum of the ITO/PET substrate was acquired immediately prior to depositing a new CZTS layer, in order to subtract the tin peak due to ITO/PET for avoiding errors in determining the composition of the deposited CZTS. X-Ray diffraction (XRD) analysis of ITO/PET was also conducted for detecting its typical diffraction peaks. In this case, knowledge of the XRD spectrum was useful to confirm the presence of a deposited layer. Really, XRD analysis conducted after deposition revealed only significant attenuation in the intensity of the ITO/PET substrate. This finding supports the conclusion that the

electrochemical deposited CZTS layer was amorphous. Before deposition, the substrate was ultrasonically degreased in acetone for 15 min, then washed with deionized water, DIW Millipore grade 18 mΩ cm (Younglin, Aqua Max Series Basic 360 and Ultra 370) and sonicated in isopropyl alcohol for further 15 min. After washing again with DIW, ITO/PET was dried under nitrogen flow and a deposition area of 3 cm² was delimited using an insulating lacquer (Lacomit, UK).

Mo sheet, 99.9999% pure and 100 μm thick (Alfa Aesar), was used. The electrode was embedded and insulated in order to expose only a limited surface to the solution. Before electrochemical deposition of CZTS, Mo surface was treated with emery papers up to 2000 grade and then was electropolished in order to remove oxide film and to obtain a defect-free smooth surface. The electropolishing was conducted for 10 min at a temperature less than −10°C, and at 20 V in an electrolyte containing 86% (w/w) ethanol and 14% (w/w) sulphuric acid [22, 23]. The features of Mo films are of fundamental importance because they can induce significant changes in the structural and electrical properties of CZTS-deposited films [23]. Currently, Mo films are obtained either by sputtering or by e-beam evaporation and their internal stresses are due to the deposition parameters [3]. In this work, we used Mo sheets that were previously electropolished in order to obtain a surface with a level of roughness as low as possible, taking into account that a value between 50 and 100 nm is acceptable [23]. The exact value of roughness was not accessible in the present work, but it can be inferred that a value close to the optimal one was achieved, taking into account that roughness between 50 and 130 nm was obtained by electropolishing after mechanical polishing with emery paper 500 grade. In the present work, the mechanical treatment was carried out with emery paper up to 2000 grade, thus the lowest level of roughness was obtained. From this point of view, the findings of the present work imply possible substitution of the vacuum-based techniques for fabricating Mo back contact of solar cells with a simple and very low-cost procedure.

For CZTS deposition on ITO/PET and molybdenum, a bath similar to that suggested by Pawar et al. was initially used [19]. In particular, SnSO₄ was replaced with SnCl₂ for solubility reasons; lactic acid was added as complexing agent in place of tri-sodium citrate and 10 M NaOH was used for adjusting pH at 5. Initially, the composition of the solution was as follows: 0.01 M CuSO₄, 0.01 M ZnSO₄, 0.02 M SnCl₂, 0.02 M Na₂S₂O₃ and 0.075 M C₃H₆O₃. Then, composition of the electrolyte was varied to explore its influence on deposited film composition. Finally, to improve chemical stability of the bath and therefore reproducibility of the deposit, we changed both complexing agent and pH regulator. In this latter case, electrolyte composition was as follows: 0.02 M CuSO₄, 0.01 M ZnSO₄, 0.02 M SnCl₂, 0.02 M Na₂S₂O₃, 0.2 M Na₃C₆H₅O₇ and 0.1 M C₄H₆O₆. Electrodeposition was carried out potentiostatically in a typical three-electrode cell, with a standard calomel electrode (SCE) as reference and a Pt gauze as counter electrode. Prior to deposition, the solution was de-aerated by bubbling ultra-pure nitrogen for 30 min, and an inert atmosphere was maintained during electrodeposition. A constant potential of −1.05 V (SCE) was applied using a PAR Potentiostat/Galvanostat (mod. PARSTAT 2273) connected to a PC and controlled through the POWERSUITE™ software. Duration of the electrodeposition was 45 min.

3. Physical–chemical characterization of CZTS thin films

X-Ray diffraction (ItalStructures, APD2000) allowed identification of the crystallographic structure of the deposit. The 2θ angle ranged from 10° to 100° with step of 0.04° using the copper $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). Since CZTS deposits were amorphous, only well-defined peaks due to ITO/PET were found in the case of deposition on such substrate. These peaks were identified by comparison with ICDD database [24], and were attributed to the substrate. Morphology was examined by scanning electron microscopy (SEM), using a FEI field-emission gun (FEG) environmental scanning electron microscope (model QUANTA 200). Chemical composition of the deposit was analysed by energy-dispersive spectroscopy (EDS). Raman spectra were obtained at room temperature using a Renishaw (inVia Raman Microscope) spectrometer equipped with a microprobe ($50\times$) and a CCD detector. The excitation was provided by the 633 nm line of a He:Ne laser with a spot size of $2 \mu\text{m}$ and calibrated by means of the Raman peak of a polycrystalline Si (520 cm^{-1}).

Photoelectrochemical behaviour of the films was investigated at room temperature in aerated $0.1 \text{ M Na}_2\text{SO}_4$ solution ($\text{pH}=5.6$), using a cell having flat quartz windows for allowing sample illumination. A Pt net served as the counter electrode, and the reference was a MSE electrode. Monochromatic irradiation was achieved using a UV–Vis Xenon lamp (Oriel) coupled to a UV–Vis monochromator (Baush & Lomb), mounted in an optical line equipped with quartz optics. For improving photocurrent resolution, a two-phase lock-in amplifier (EG&G, mod. 5206) was used in connection with a mechanical chopper (frequency: 10 Hz). Data were acquired by a desk computer through an analogic interface using a LABVIEW™ 7 software and processed according to home-written programs. Photocurrent spectra reported below were corrected for the photon emission at each wavelength of the lamp/monochromator system; the latter was detected using a calibrated thermopile (Newport). Details on experimental set-up for photoelectrochemical characterization can be found elsewhere [25–27].

All characterizations were performed before and after the thermal treatment that was carried out in a tube furnace (LTF 1200 Lenton) under flow of ultrapure N_2 for 1 h. Heating was performed at a rate of 5°C min^{-1} starting from room temperature to 450°C .

4. One-step electrodeposition of CZTS thin films

Initially, the fabrication of flexible cells was addressed; therefore, the study of the deposition of CZTS on ITO/PET was planned. This choice guaranteed the best compromise between cell flexibility and conversion efficiency higher than that of plastic semiconductors. The flexibility of the support is shown in Fig. 1, evidencing its adaptability to the different type of surfaces dedicated to support photovoltaic panels.

Layer deposited on ITO/PET, from solution containing lactic acid as stabilizer and with a pH adjusted to 5 (see Experimental section), had composition (at%): Cu = 59.2%, Zn = 12.4%, Sn = 6.3% and S = 22.1%. In comparison with kesterite stoichiometry ($\text{Cu}_{0.25}\text{Zn}_{0.125}\text{Sn}_{0.125}\text{S}_{0.5}$), usually

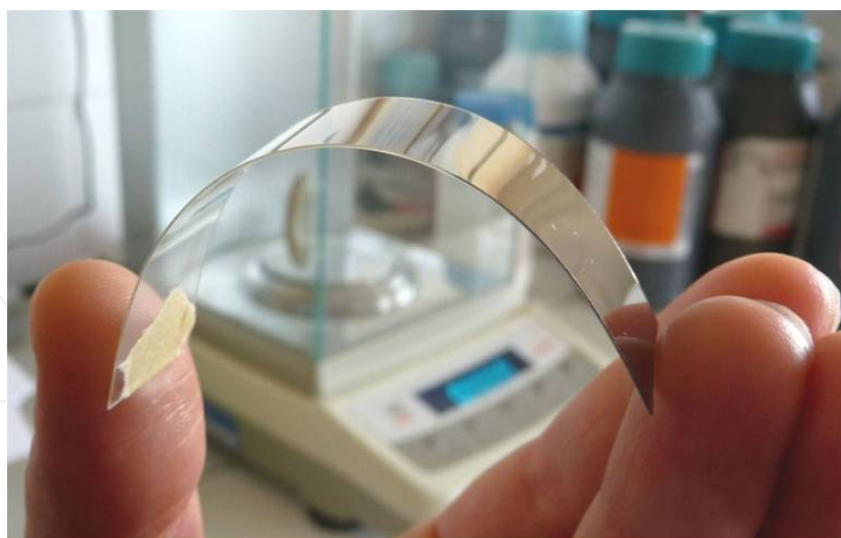
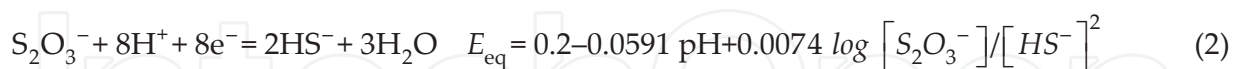


Figure 1. Flexible ITO/PET as substrate.

proposed in the literature as the best-performing light absorber layer, our film was richer of copper, and poorer of tin and sulphur. This comparison is formal because the as-deposited CZTS layers were amorphous; therefore, it was not possible to distinguish if the deposit was formed by one or more phases. This issue is not negligible because the electrochemical route can favour the deposition of different phases due to the different standard potentials for ions reduction. The overall reaction leading to CZTS can be written as [13]:



Considering possible reactions of the single species, we observe that thiosulphate ion, which is the sulphur source in the present study, can be reduced either to HS^- or directly to S^{2-} according to the following reactions [28]:



Despite HS^- is thermodynamically favoured as reduction product (reaction 2), the applied potential is cathodic enough to drive the direct formation of S^{2-} according to the reaction (3). Besides, at -1.05 V (SCE) , the simultaneous hydrogen evolution reaction causes a pH shift at the electrode/solution interface from 5 towards higher values with formation of HS^- , and S^{2-} which are stable at $\text{pH} \geq 7$ and 13.90, respectively [28]. Indeed, there is some experimental evidence that local pH assumes very high values [29, 30]; therefore, we can assume the prevalent presence of S^{2-} at the electrode interface, that is, the true sulphur source for the electrochemical synthesis of CZTS.

Other reactions to take into account concern the metallic ion reduction [28]:



Really, the standard potential of the Cu^{2+}/Cu couple could be depressed by the complexing action of lactic acid; therefore, it is likely that all metallic ions simultaneously combine with the just formed S^- ions with formation of copper–zinc–tin sulphide. This hypothesis is supported by the plot of Fig. 2 showing the composition of the deposit (expressed as atomic fraction) as function of the electrolyte composition.

It can be observed that the deposit is always richer in the most noble element (copper) and poorer in the less noble one (zinc), while tin shows an intermediate behaviour with a region, at low concentration of tin ion in solution, where the deposit contains less tin than solution, and a region where the deposit is richer. This finding evidences that copper ion results always the most ‘available’ ion to be transferred into the deposit, while zinc is always the less ‘available’. Since the ‘availability’, which depends on the activity of the ions in solutions, agrees with the standard potentials of the different couples, we cannot exclude the presence of either binary or ternary compounds in the deposit. In addition, a thermal treatment for crystallizing the as-deposited layer was excluded, due to the known difficulty of controlling sulphur content under heating, with possible modifications of deposit composition and structure [19, 31].

Owing to such difficulties, it was planned to investigate the response of the deposit under light, in order to check possible semiconducting behaviour of the films. The investigation was conducted by photoelectrochemical measurements on samples with the highest content of copper in order to discriminate between metallic and semiconducting behaviour in the most significant composition. Really, the deposit showed a semiconducting behaviour, as evidenced in Fig. 3 where two photocurrent action spectra, after correction for lamp emission, are shown. Spectra were measured at the open circuit potential (-0.36 V/MSE) and at -0.46 V (MSE) on a film about $2 \mu\text{m}$ thick, with a copper content (at%) of 59.2%. Film composition was evaluated from the EDS spectrum of Fig. 4 (peaks of C and O from PET while In, Sn and O from ITO). The optical gap of the deposit was evaluated by the extrapolation to zero photocurrent of the $(I_{\text{ph}} \cdot h\nu)^{0.5}$ vs. $h\nu$, assuming non-direct optical transitions (see inset of the figure). A value of about 1.5 eV was obtained, very close to 1.48 eV recently reported in [14] for CZTS thin films fabricated by chemical bath deposition having structure and composition of the kesterite. This result appears of some value for the engineering of CZTS, because it indicates that it is not mandatory to achieve a well-defined composition for getting the band gap value usually considered as optimum for this material. In addition, it suggests that in this case the measured optical gap gives a measure of the film mobility gap, according to the Tauc model [32].

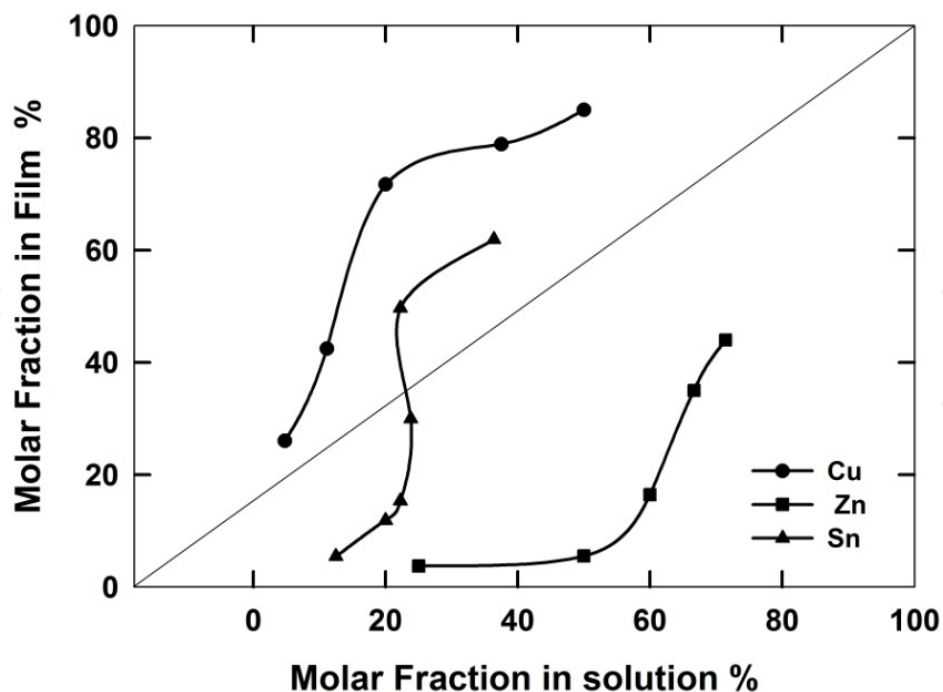


Figure 2. Molar fractions of metal ions into the film vs. the corresponding value in solution.

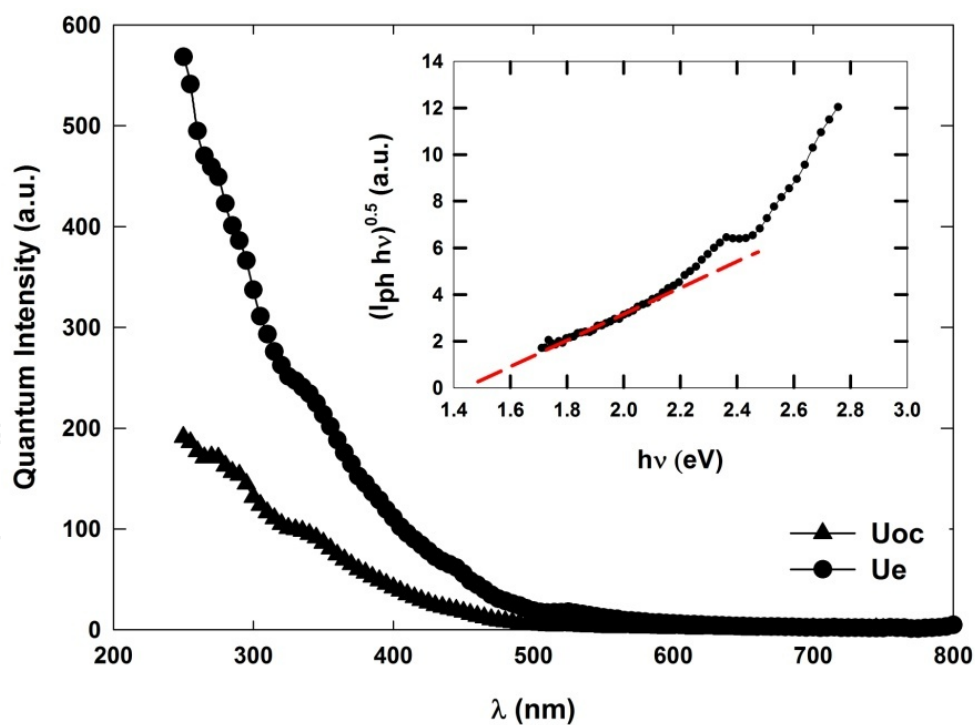


Figure 3. Photocurrent action spectra recorded for a Cu-rich film on ITO/PET (see text) at the open circuit potential (π) and under 0.1 V negative polarization with respect to U_{oc} ($\cdot$). Inset: determination of the optical gap according to non-direct transitions.

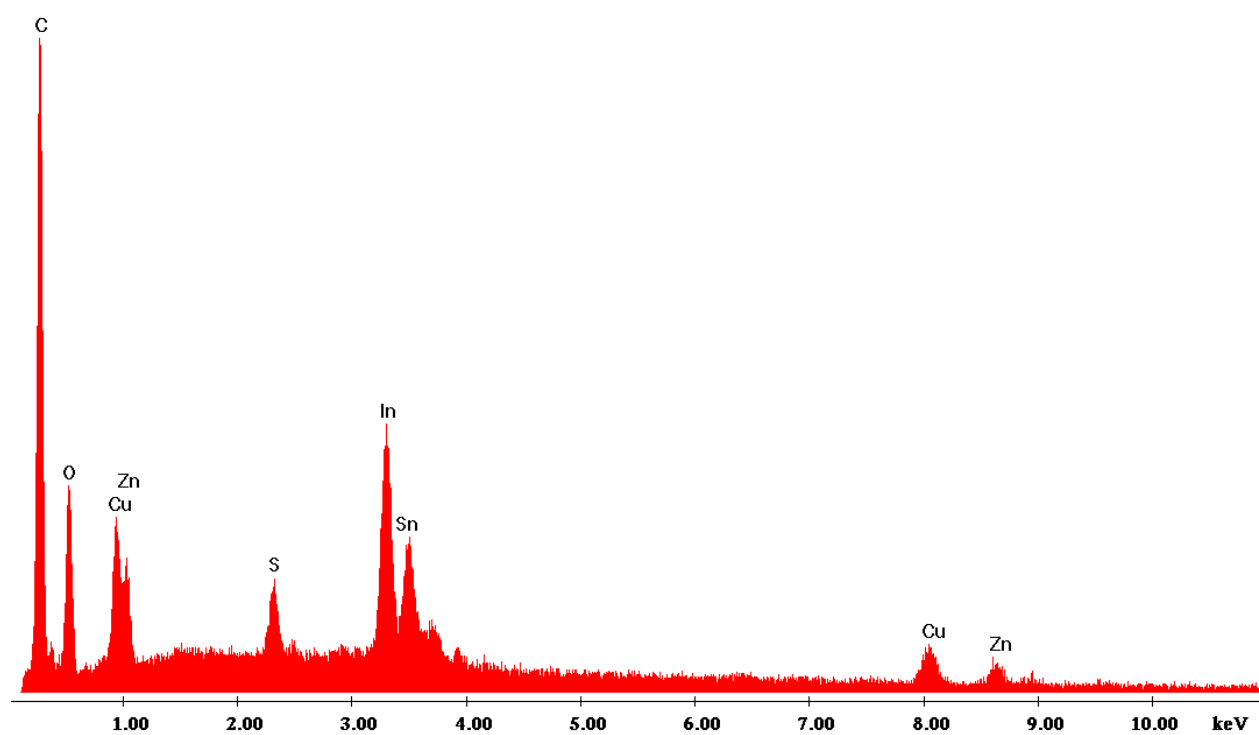


Figure 4. EDS spectrum of the Cu-rich film of Fig.3.

Morphology of this sample at different magnifications is shown in Fig. 5: a uniform deposit composed of micro-grains is evident at low magnification. The shape of these micro-grains and their aggregation to form the light-absorbing layer is shown in the picture at higher magnification.

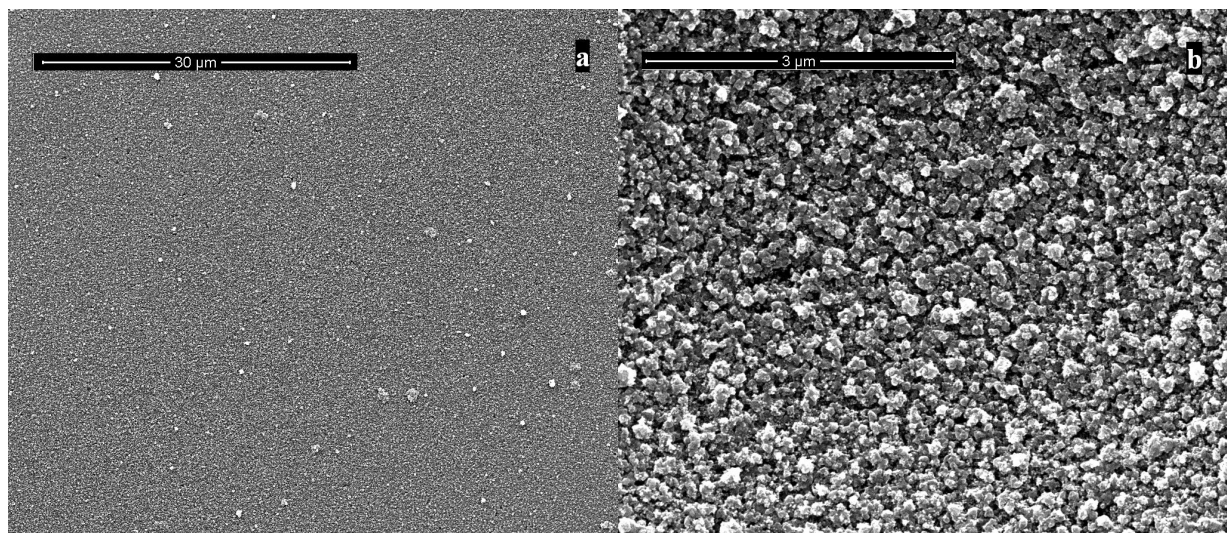


Figure 5. SEM images of a Cu-rich film on ITO/PET substrate at low (a) and higher (b) magnification.

The principal drawback encountered in the study of one-step electrochemical deposition of CZTS on ITO/PET was the scarce reproducibility of the results, probably due to the poor electrical conductivity of the substrate, and also to the overpotential of the possible reduction reactions. Therefore, ITO/PET substrate was substituted with molybdenum. Of course, the advantageous flexibility of the ITO/PET was lost; but, on the other hand, it was possible to scrutinize the possible causes of the poor reproducibility on ITO/PET, employing a metal forming an ohmic back contact with CZTS [33]. Also the one-step electrodeposition on molybdenum, in otherwise identical conditions, gave results poorly reproducible, although the quality of the film was satisfying in terms of uniformity. Under annealing at 450°C for 1 h, under argon flow, the layer was dimensionally stable without crack formation, so that at the end of the thermal treatment it was still uniform, and compact. In addition, no sulphur loss was detected during annealing, as confirmed by EDS analysis performed before and after thermal treatment.

Then, composition of the electrolyte was changed because the chemical instability of the original bath, revealed in some cases by loss of transparency, was considered a possible cause of the poor reproducibility. The most significant variations concerned the concentration of CuSO_4 , which was doubled from 0.01 to 0.02 M, the substitution of lactic acid with tri-sodium citrate and the use of tartaric acid as complexing agent, while pH was maintained in the interval 4.5–5. In practice, composition variation substantially improved the stability of the solution. The as electro-deposited layer was amorphous also in this case, with an atomic composition of Cu = 41.5%, Zn = 6.1%, Sn = 34.9% and S = 17.5% evaluated by EDS. In comparison with the previous deposit, this one was richer of tin, and poorer in the other elements. The change of composition reflected in a significant variation of the morphology. Fig. 6 shows a highly porous surface featured by uniformly distributed large clusters (Fig. 6a) formed by aggregation of rounded particles (Fig. 6b).

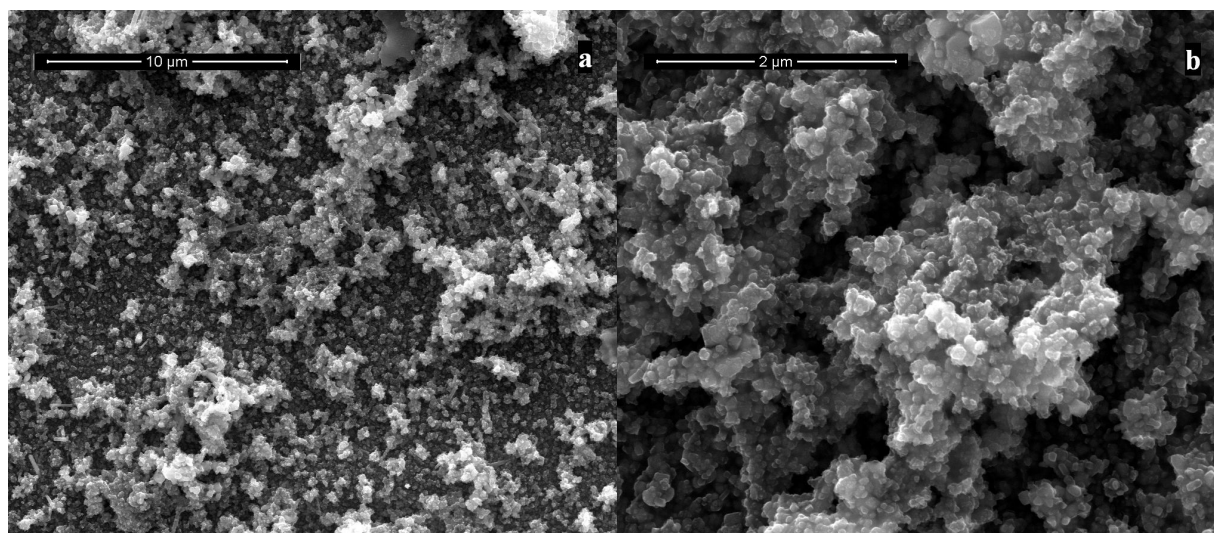


Figure 6. SEM images of a Cu-rich film on Mo substrate at low (a) and higher (b) magnification.

Raman spectroscopy did not reveal relevant peaks, while photoelectrochemical analysis gave the most significant results. The action spectra of Fig. 7, obtained at the open circuit potential of -0.43 and at -0.53 V/MSE, show a more intense photocurrent, likely due to the higher surface roughness.

Also in this case, the optical gap was derived assuming non-direct transitions (see inset of the figure), but the value (about 1.05 eV) was sensibly lower than the previous one. This finding confirms the tunability of the optical response of these films and it is explainable taking into account the very low Zn content of this sample; indeed band gap values ranging between 1.05 and 1.22 eV are reported for crystalline Cu–Sn sulphides [34]. Also other samples with a very low Zn content and various compositions show similar optical gap values. The photoelectrochemical investigation was completed with the response analysis of the deposit under intermittent light. Fig. 8 shows these responses at different wavelength and bias, evidencing the p-nature of the semiconductor, and the presence of significant spikes, likely due to a recombination of the photogenerated carriers. We mention that our films have truly a p-type semiconducting nature; in fact, photocurrent vs. applied potential curves at different wavelengths (not shown) display an increasing photocurrent when polarizing in the potential range negative with respect to the open circuit one, while no photoresponse was observed at more positive potentials.

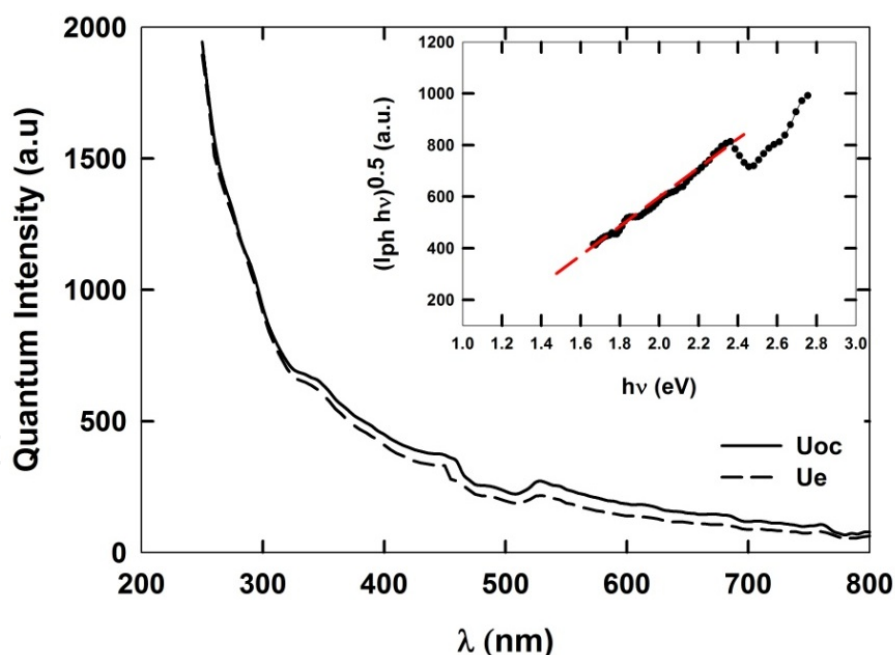


Figure 7. Photocurrent action spectra recorded for a Cu-rich film on Mo substrate (see text) at the open circuit potential (—) under 0.1 V negative polarization with respect to U_{oc} (---). Inset: determination of the optical gap according to non-direct transitions.

The principal drawback of this deposit was its poor adhesion to the substrate both molybdenum and ITO/PET. This finding is not a novelty, because it was recently evidenced by other authors [35, 36], who invoked the poor adhesion of the deposit to substrate to justify the scarce

composition reproducibility. Really, these are the same difficulties encountered in this study, even if it must be emphasized that, in our case, reproducibility improved with the change of bath composition, indicating that the main problem is the nature and concentration of the solution controlling the deposit composition. More likely, the amorphous nature of the deposit together with the nature of the compound plays a more fundamental role in determining adhesion. In fact, adhesion strength depends on the surface energy, which, in turn, is related to the wettability of the substrate [36]. In absence of any data, we initially attributed the poor adhesion to the chemical nature of the deposit.

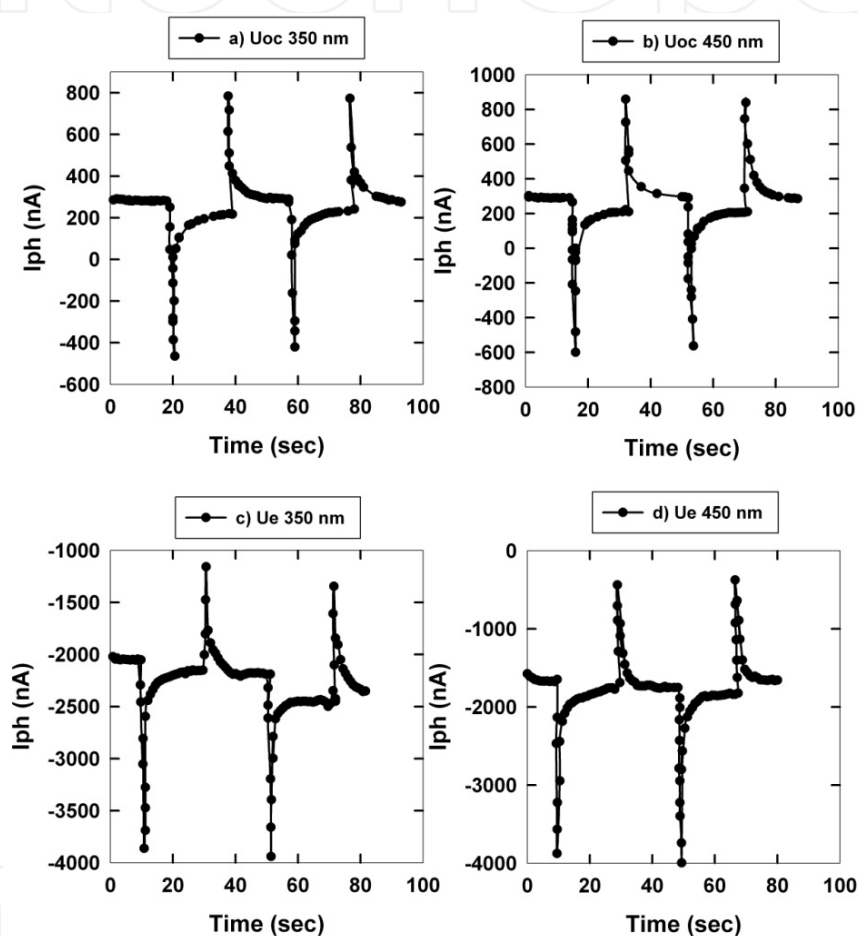


Figure 8. Total current under manually chopped illumination at different wavelength and bias for the film of Fig. 7.

Really, this approach was confirmed by further preliminary investigations showing that the adhesion improves by substituting sulphur with selenium. A p-type layer with Cu = 36.3%, Zn = 4.1%, Sn = 19.1% and Se = 40.5% was electro-deposited in one-step from a bath containing 0.005 M H_2SeO_3 (as selenium precursor), 0.5M $C_3H_6O_3$ (as complexing agent) and dilute NH_4OH , to regulate pH to 2.5. The most valuable finding is the optical gap value of about 1.3 eV. More work is in progress for improving further adhesion, and better characterizing the response of this compound under illumination, because it appears very attractive for application in solar cells.

5. Conclusions

A single-step fabrication of CZTS films by electrochemical deposition on different substrates was investigated. Since CZTS is a candidate to substitute Si in the solar cells, this study was aimed to scrutinize the possibility to obtain CZTS thin films with good photoactive properties in a direct and easily scalable way. At variance of previous studies focused on reaching the kesterite composition, considered as the best one for satisfying performances in solar cells, we devoted attention to the electro-deposition process, and to the consequent behaviour under illumination of the deposit. We found a satisfying response under illumination even with different film compositions, indicating that to achieve kesterite composition for getting a photoactive CZTS is not mandatory. Substrate and electrolyte composition were varied to improve the chemical composition reproducibility of the deposited layer, which always was amorphous. Using a bath at pH between 4 and 5, containing tri-sodium citrate, and tartaric acid, a p-type amorphous layer of composition Cu = 59.2%, Zn = 12.4%, Sn = 6.3% and S = 22.1% was obtained. It is noteworthy that this deposit showed a non-direct optical gap of about 1.5 eV, which is similar to that one of kesterite ($\text{Cu}_2\text{ZnSnS}_4$). On the contrary, films with very low Zn content display lower absorption edges, closer to 1 eV. In some cases, a poor adhesion of the deposit was observed. Further work is in progress for substituting sulphur with selenium. Very preliminary results are encouraging, because layers with Cu = 36.3%, Zn = 4.1%, Sn = 19.1% and Se = 40.5% composition and bandgap of about 1.3 eV were successfully deposited in one step.

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