Formation of CuSbS$_2$ and CuSbSe$_2$ thin films via chalcogenization of Sb-Cu metal precursors

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Abstract

Due to the availability and low cost of the elements, the ternary Cu-Sb-S and Cu-Sb-Se semiconductor systems are being studied as sustainable alternative absorber materials to replace CuIn(Ga)(S,Se)$_2$ in thin film photovoltaic applications.

Simple evaporation of the metal precursors followed by annealing in a chalcogen environment has been employed in order to test the feasibility of converting stacked metallic layers into the desired compounds. Other samples have been produced from aqueous solutions by electrochemical methods that may be suitable for scale-up.

It was found that the minimum temperature required for the complete conversion of the precursors into the ternary chalcogen is 350 °C, while binary phase separation occurs at lower temperatures.

The new materials have been characterized by structural, electrical and photoelectrochemical techniques in order to establish their potential as absorber layer materials for photovoltaic applications. The photoactive films consisting of CuSbS$_2$ and CuSbSe$_2$ exhibit band-gap energies of ~1.5eV and ~1.2 eV respectively, fulfilling the Shockley-Queisser requirements for the efficient harvesting of the solar spectrum.

1. Introduction

Among the class of compounds known as *sulphosalts*, with general formula A$_x$B$_y$C$_z$ (with A, B = metals and C= S, Se, Te), those that exist in the ternary systems Cu-Sb-S and Cu-Sb-Se are being considered as potential low cost sustainable absorber materials for inorganic thin film solar cells. CuSbS$_2$ and CuSbSe$_2$ [1-2], which have been only partially explored, appear to be direct band-gap semiconductors [3], which is essential for application in the field of thin film photovoltaics. The band-gap energy of CuSbS$_2$ is reported to be between 1.38 eV [4] and 1.5 eV [1], which is close to the optimum value required for terrestrial solar energy conversion (1.4 eV) [5-6]. A lower band-gap energy is expected for the isostructural CuSbSe$_2$, since S is substituted by Se. Zhou et al. [4] reported a band gap energy value of 1.05 eV for CuSbSe$_2$ crystals obtained from a solvothermal route; however, to the best of our knowledge, no measurement of the band-gap energy for thin films of CuSbSe$_2$ has been reported in the literature. Soliman et al. [2] studied the temperature dependence of the electrical conductivity for thin films of both CuSbS$_2$ and CuSbSe$_2$, but the temperature range (80-500 K) was too low to allow conclusions to be drawn regarding the band-gap energies.

Thin films of CuSbS$_2$ have been deposited using a range of different techniques such as spray pyrolysis [7], direct evaporation [2, 8], and chemical bath deposition followed by annealing treatment [1].

The general two-stage approach described by Basol et al. [9] for the production of polycrystalline thin films of semiconductor compounds by sequential deposition of stacked precursors layers, followed by heat treatment involving the introduction of additional volatile elements such as the chalcogen, has been successfully employed since the end of the 1970's [10]. The advantage of this approach is that it can be easily extended to scalable techniques such as electrodeposition. Promising results were obtained by Chu et al. [11] on conventional compounds such as CuInSe$_2$, and more recently on the newer and more sustainable Cu$_2$ZnSnS$_4$ by Araki et al. [12] and Scragg et al. [13].

So far, the formation of CuSb(S,Se)$_2$ through a simple two step process involving the heat treatment of a stacked Sb/Cu metallic precursor in the presence of the chalcogen vapour has not been reported. This could be an important study, as its application would be relevant to any electroplating/annealing route. In fact, although the work of Rodríguez-Lazcano et al. [1, 14] demonstrated that it is possible to obtain CuSbS$_2$ by heat treating chemically-deposited Sb$_2$S$_3$-CuS layers, the process of reaction/diffusion of the chalcogen from the vapour phase into a layered metallic precursor is evidently more complex than a plain diffusion couple [15]. Since heat treatment of a stacked metallic precursor by conventional means might lead to films of composition different from the one desired due to the formation of stable secondary phases, a different approach was investigated in

the present work. Our approach involves deposition of a mixed metallic alloy of the precursors, as this should allow a simpler reaction/diffusion mechanism, leading to formation of the desired stoichiometry in conventional (i.e. more readily scalable) annealing processes. This kind of approach was applied by Hodes et al. [16] who electrodeposited a Cu-In alloy and subsequently chalcogenized it via heating in $H_2S(e)$ to produce thin $CuInS_2$ and $CuInSe_2$. Here we discuss the formation of $CuSbS_2$ obtained by heat treatment in sulfur environment of an electrodeposited Cu-Sb alloy of the right stoichiometric ratio. An attempt of forming $CuSbSe_2$ in a similar fashion is also reported.

2. Experimental details

2.1 Sb/Cu evaporation and chalcogenization

Sequential evaporation of metallic Sb and Cu layers in a stacked configuration was carried out onto TEC-8 substrates (transparent electrically conductive SnO_2-coated glass by LOF) in order to obtain precursors with a relative Cu:Sb thickness ratio compatible with the stoichiometries of the final materials under investigation (i.e. Cu:Sb = 1). The thickness of the precursors was such that after complete conversion the chalcogenide layer was at least 2 μm thick.
The stacked metals were then annealed in a wire-wound quartz tubular furnace (Thermo Scientific) in the presence of chalcogen excess (0.1g) within graphite boxes at temperatures of 200, 250, 300, 350 and 400 °C with a heating rate of 10 °Cmin^{-1} and a dwell at the maximum temperature of 30 min; the samples were then allowed to cool down naturally to room temperature. The treatments were performed under a 10 mlmin^{-1} flux of nitrogen at the atmospheric pressure.
Together with the stacked precursors, the same treatments were also adopted for evaporated films of plain Cu and Sb on soda lime glass, in order to better understand the effect of the Sb/Cu interface in the formation of the desired compounds.

2.2 Sb-Cu alloy electrodeposition and chalcogenization

The deposition of a Sb-Cu alloy with suitable elemental ratio was performed by electrochemical means from a 3 M NaOH solution containing 0.2 M D-sorbitol as a complexing agent and $CuSO_4$ 0.15 M and $SbCl_3$ 0.10 M as metal precursor salts.
The electrolytic cell was in the typical three electrode configuration, the substrate held at the working electrode (W.E.) being Mo coated soda lime glass, the reference electrode (R.E.) being Hg/HgO/NaOH 1 M and the counter electrode (C.E.) being a Pt foil.
The alloy precursor was electrodeposited potentiostatically at -1.20 V vs R.E. in the stirred electrolytic solution until the electrical charge reached 0.471 C, which is the amount required for a 2 μm thick film of $CuSbS_2$ to be obtained after complete sulfurization of the Sb-Cu alloy deposited onto 0.25 cm^2 substrates (i.e. 5 electrons per $CuSbS_2$ formula unit), assuming a 100% electroplating efficiency. Appropriate electrochemical conditions for the 1:1 Cu:Sb alloy formation were obtained by systematically studying the effect of consecutive Cu^{2+} or Sb^{3+} salt additions on the composition of the electroplated films. The chalcogenization procedure followed with the alloy precursors was the same as for the evaporated Sb/Cu stacked precursors.

2.3 Film characterization

A Panalytical X'pert X-ray powder diffractometer was employed to characterize the samples from a structural point of view. This study was performed on the sulfurized samples only.
Morphological analyses were performed with a Jeol 6480LV SEM, and an INCA x-act EDS microprobe connected to the latter was employed to estimate the Cu:Sb ratio of the metallic precursors and annealed films after calibration with a Cu-Sb standard of known composition (accelerating voltage 20kV).
An electrolyte contact was used to assess the photoactivity of the samples. The electrolyte contained 0.2 M Eu^{3+} which acts as a scavenger of photogenerated electrons. A standard three electrodes cell was employed to carry out the photoelectrochemical characterizations with Ag/AgCl reference and a Pt wire counter electrodes, as described by Scragg et al. [17]. Photovoltammograms and chronoamperometric measurements were carried out under the pulsed illumination of a white LED while the potential was applied and the current recorded by a μ Autolab type III potentiostat. The

External Quantum Efficiency (EQE) spectra were acquired by illuminating the samples with monochromatic light of variable wavelength optically chopped at 27 Hz. The photocurrent was measured with a lock-in amplifier (Stanford Research Systems). The system was calibrated using a standardized silicon photodiode.

3. Results and discussion

3.1 Structural characterization

The evaporated samples annealed between 200 and 300 °C had a similar visual appearance, the stacked Sb/Cu samples being dark blue, shiny and adherent, the Cu samples being blue-green in colour and not adherent, the Sb samples being shiny grey and adherent. Annealing temperatures of 350 and 400 °C gave adherent grey Sb/Cu samples, while for the plain Sb samples it was possible to observe losses possibly incurred due to thermal means.

Conventional powder diffraction (XRD) analyses were performed on each heat treated sample of plain Sb, plain Cu and stacked Sb/Cu, in order to observe the effect of the sulfurization treatment on the interdiffusion of Cu and Sb in the range 200-400 °C (Fig. 1).
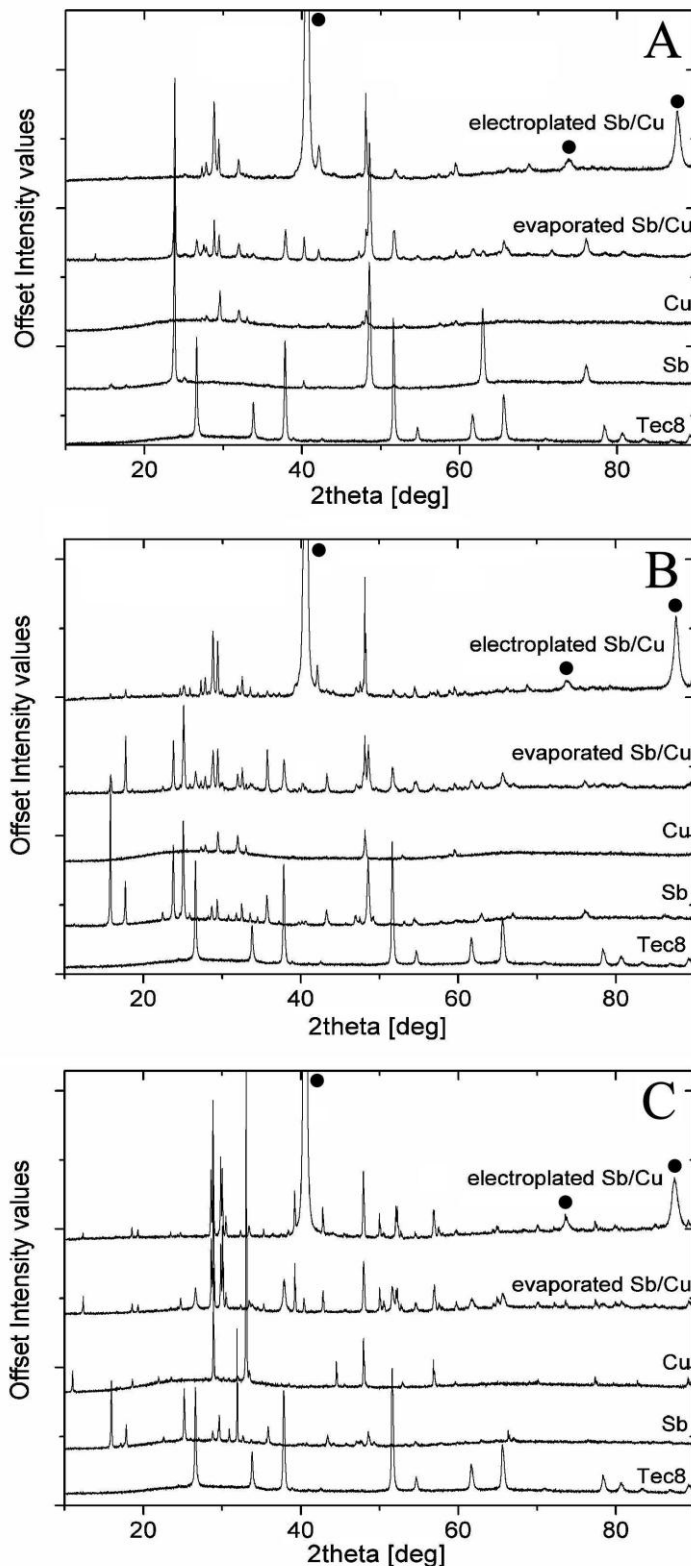
Fig. 1 XRD of evaporated Sb, Cu, Sb/Cu stacked and electroplated Sb-Cu alloy films sulfurized at 200 (A), 300 (B) and 400 °C (C). (The XRD of the TEC8 FTO substrate is also reported; ● labels refer to the Mo substrate).

From the analysis and comparison of the X-ray diffractograms it is clear that the Cu can be fully converted to its sulfide CuS at the annealing temperature of 200 °C, as its diffraction pattern peaks are consistent with hexagonal CuS (*Covellite*). The Cu samples treated at temperatures of 350 °C or higher show the emergence of a few other peaks, revealing some thermally induced modification.

The Sb sample treated at 200 °C does not show the presence of the corresponding sulfide peaks within the detection limit of the instrument (~5 %) and it is similar to the as evaporated Sb possessing highly (*00l*) preferred orientation. This sample also produced diffraction maxima possessing a systematic peak shift towards higher 2θ relative to the literature pattern of Sb indicating the presence of uniform strain, which causes the unit cell to be compressed along [*00l*]. This lattice distortion becomes less significant at higher temperatures as the lattice relaxes and leads to a pattern which is close to the standard powder pattern for Sb at the thermal treatment of 300 °C. Therefore the Sb is apparently more difficult to convert to its sulphide than the Cu, the conversion to Sb_2S_3 is incomplete below 350 °C, leaving mixtures of the two phases. However the diffraction peaks of the sulfide phase are a good match to orthorhombic Sb_2S_3 (*Stibnite*).

The series of X-ray patterns for the Sb/Cu stacked samples reveal that the system follows a sequential reaction/diffusion mechanism. Between 200 and 300 °C the diffractogram is the superimposition of the elemental Sb and Cu patterns (reaction step). However at 350 °C and 400 °C interdiffusion of the elements occurs leading to the formation of the ternary phase. The stacked precursor appears to be fully converted into the desired stoichiometry, the patterns matching those for orthorhombic $CuSbS_2$ (*Chalcostibite*). This trend appears to be consistent with the visual appearance of the samples, with a sharp variation from the bluish films annealed up to 300 °C and those annealed at 350 and 400 °C.

The visual appearance of the samples obtained by sulfurization of the electrodeposited films is similar to that of the evaporated/sulfurized ones, with bluish films obtained up to 300 °C and light grey films obtained at 350 and 400 °C. The diffractograms of the electroplated/sulfurized samples are also analogous to those of the evaporated/sulfurized, although the peaks due to the antimony start to appear at 300 °C and there are few small peaks that might be due to the precursor alloy. Further studies are needed in order to identify those peaks.

The comparison of the phase composition among the films treated between 200 and 400 °C is summarized in Table 1 together with the relative PDF card numbers.

	Evaporated Cu	Evaporated Sb	Evaporated Sb/Cu	Electroplated Sb-Cu
200 °C	CuS, PDF № 65-3561	Sb, PDF № 35-732	CuS, PDF № 65-3561 Sb, PDF № 35-732	CuS, PDF № 65-3561
250 °C	CuS, PDF № 65-3561	Sb, PDF № 35-732 Sb_2S_3, PDF № 42-1393	CuS, PDF № 65-3561 Sb, PDF № 35-732	CuS, PDF № 65-3561
300 °C	CuS, PDF № 65-3561	Sb, PDF № 35-732 Sb_2S_3, PDF № 42-1393	CuS, PDF № 65-3561 Sb, PDF № 35-732 Sb_2S_3, PDF № 42-1393	CuS, PDF № 65-3561 Sb, PDF № 35-732 Sb_2S_3, PDF № 42-1393
350 °C	CuS, PDF № 75-2236 (unindexed peaks at 2θ= 28.9° and 33.1°)	Sb_2S_3, PDF № 42-1393	$CuSbS_2$, PDF № 65-2416	$CuSbS_2$, PDF № 65-2416
400 °C	CuS, PDF № 75-2236 (unindexed peaks at 2θ= 28.9° and 33.1°)	Sb_2S_3, PDF № 42-1393	$CuSbS_2$, PDF № 65-2416	$CuSbS_2$, PDF № 65-2416

Table 1 Phase composition of evaporated Sb, Cu, Sb/Cu stacked and electroplated Sb-Cu alloy films after sulfurization treatments at 200, 250, 300, 350 and 400 °C.

3.2 Morphological and compositional characterization

Both the electroplated Sb-Cu precursors and the samples annealed up to 300 °C and 400 °C were analysed morphologically and compositionally using an SEM/EDS facility before and after KCN etching; the pictures are shown in Fig. 2.
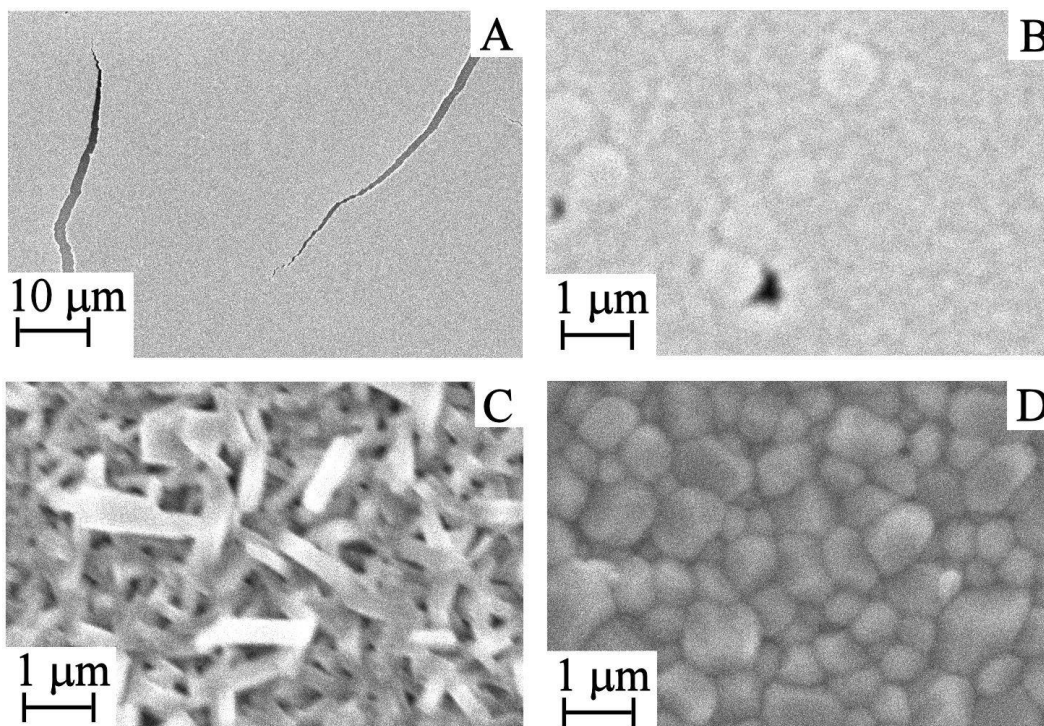
Fig. 2 Secondary electron images of the electrodeposited Sb-Cu alloy precursor untreated (A, B) and after sulfurization at 300 (C) and 400 °C (D).

The electroplated precursors show a fairly homogeneous and compact film, which looks suitable for a subsequent conversion to the corresponding chalcogenide, although some cracks and pin holes can be observed suggesting that the morphology can be slightly improved.

The samples treated below 350 °C show a characteristic surface covered thoroughly by idiomorphic crystals that the EDS microprobe identified with the stoichiometry CuS. The samples annealed at 350 and 400 °C show a nice and compact film, with grain size of the order of 1 μm, that the X-ray characterization showed to be $CuSbS_2$.

EDS microanalysis showed that the metallic precursors had a Cu:Sb atomic ratio of 1.3, which is slightly too high for the subsequent compound stoichiometry. Due to the characteristic morphology of the films annealed up to 300 °C, the EDS microprobe did not detect any Sb, as the electron beam was physically hindered by the voluminous CuS crystals present on top of the surface. Furthermore, the Cu:Sb ratio was found to increase up to 2.6 after the annealing treatments at 400 °C, suggesting that part of the Sb might got lost due to thermal means. However, the Cu:Sb ratio decreased substantially to 0.96 after the samples were etched in the KCN solution.

3.3 Photoelectrochemical characterization

The samples obtained by annealing both evaporated and electroplated metallic precursors were characterised photoelectrochemically in order to test their photoactivity. A white LED was flashed onto the samples as described in 2.3 and the current response recorded as a function of the applied potential. Chalcogenized samples annealed up to 300 °C did not show any photoresponse, those annealed at 350 °C and 400 °C were slightly photoactive, being *p*-type in character, as shown by the negative photocurrent response.

The photoactive samples were then etched in a 5 % weight KCN aqueous solution and this largely increased the magnitude of the photocurrent. Chronoamperometric analyses under pulsed white light were then performed at the potential of -0.5 V vs Ag/AgCl on samples etched for increasing time periods; the results are shown in Fig. 3.
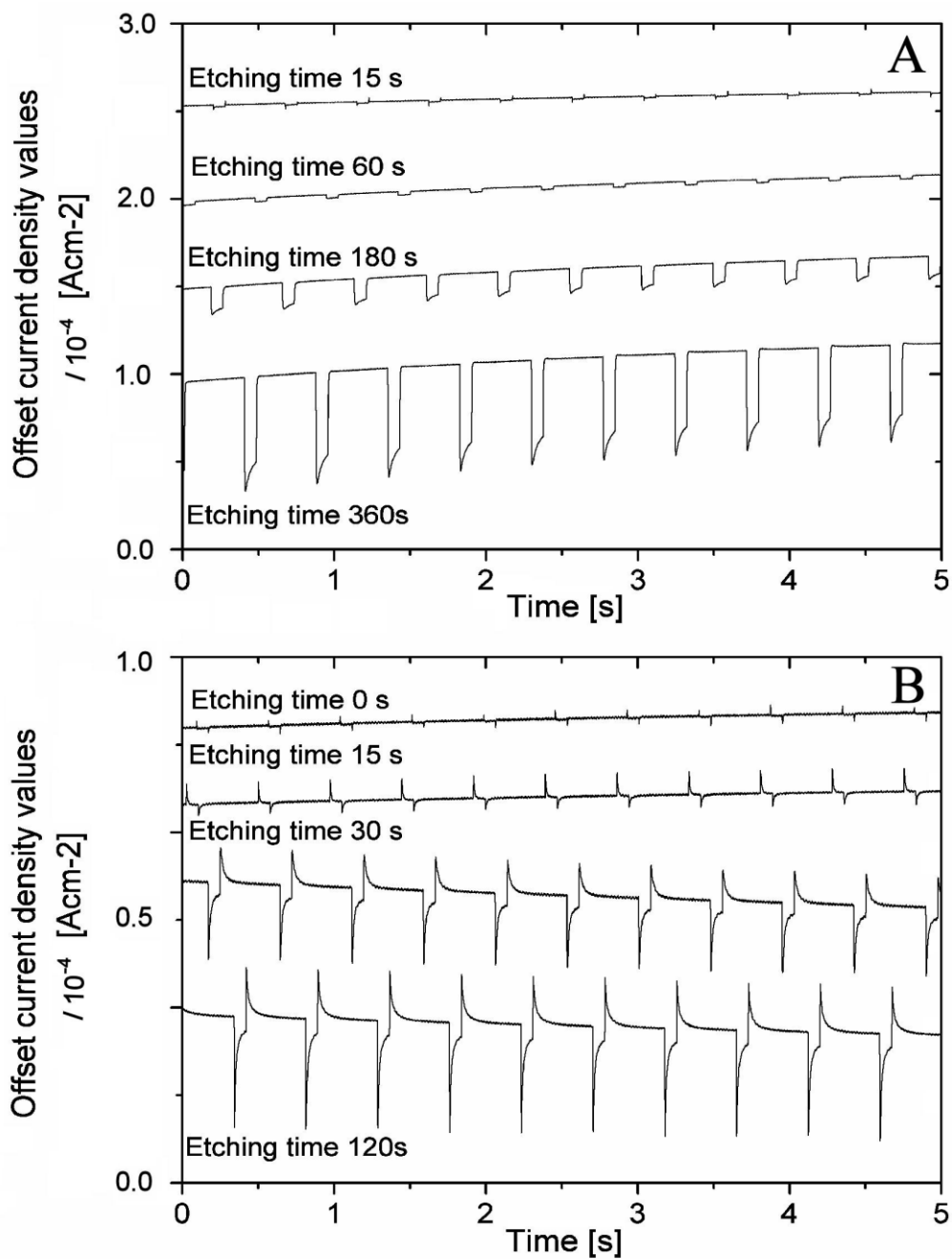
Fig. 3 Chronoamperometric tests in a 0.2 M Eu3+ solution at -0.5 V vs Ag/AgCl after KCN etch of increasing time periods under pulsed illumination with a white LED of electroplated samples after (A) sulphurization and (B) selenization at 400 °C. The negative sign of the photocurrent shows that the samples are *p*-type in character.

When the photoactive samples were left in the KCN solution for 60 seconds or more, the magnitude of the photoresponse was high enough for the EQE spectra to be acquired. Fig. 4 shows the EQE of the evaporated/annealed and of the electroplated/annealed samples.
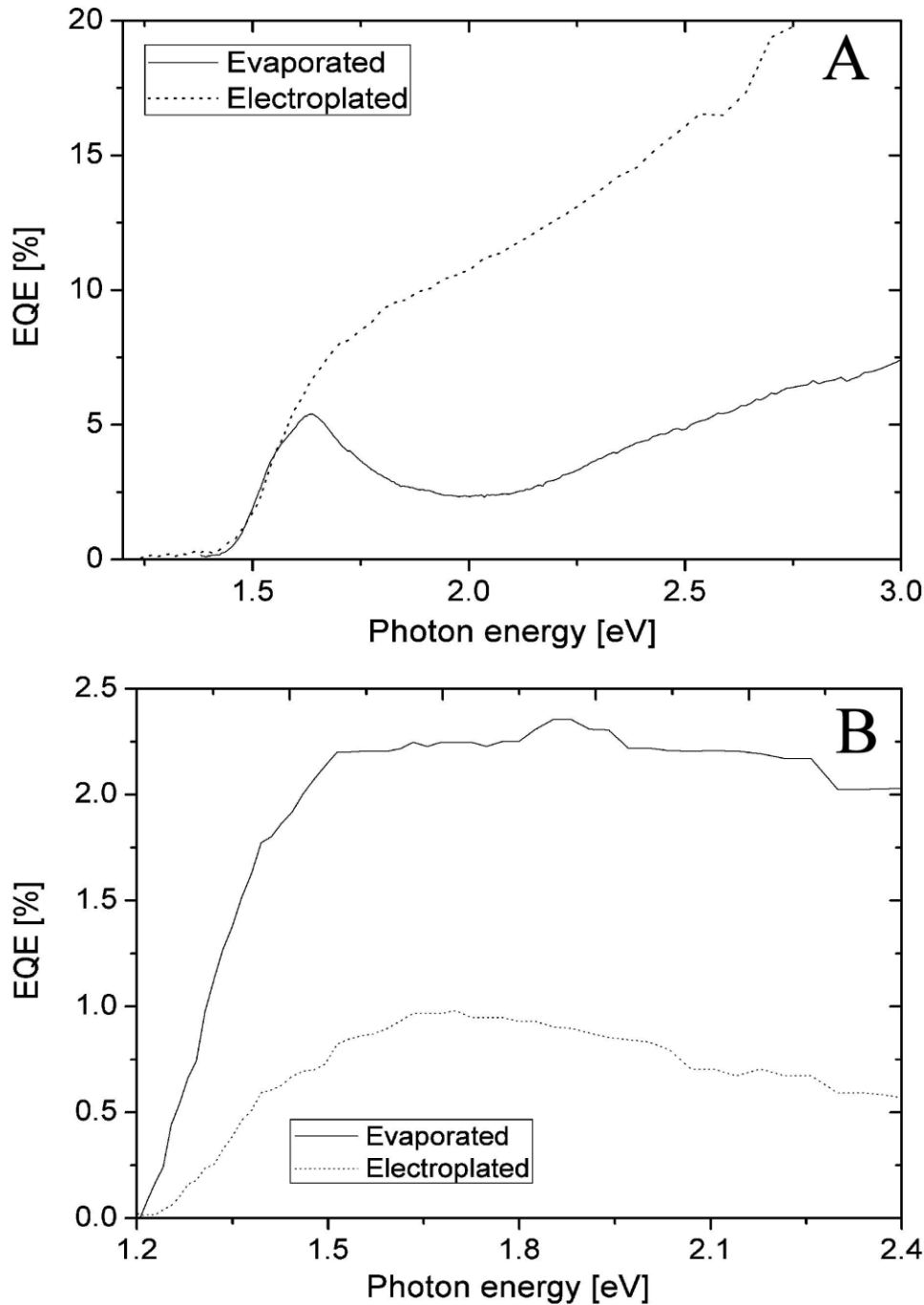
Fig. 4 EQE spectra of the evaporated Sb/Cu stacked and of the electroplated Sb-Cu alloy precursors sulfurized (the electroplated/annealed sample was analysed after 360 s of KCN etching) (A), and selenized (B) at 400 °C. The spectra were acquired in a 0.2 M Eu3+ solution with the samples held at -0.5 V vs Ag/AgCl.

The EQE of the films is low, reaching maxima of just ~8 % and ~20 % at 3 eV for the evaporated and for the electroplated sulfurized samples respectively. The unusual shape of the evaporated/annealed spectrum, with the presence of a maximum at the photon energy of ~1.65 eV could be explained with either the presence of a phase at the surface of the film absorbing the incident light with energy higher than ~1.65 eV, or to an effect due to photoconductivity. The former case would be consistent with the presence of $Cu_{31}S_{16}$ (*Djurleite*) as it was also reported by Bryant et al. [18], or Sb_2S_3 (*Stibnite*) on the surface of the evaporated/annealed film, both materials having a band-gap energy of ~1.8 eV [19].
The EQE of the selenized sample is very low, with maxima of just 2.5 %, consistent with the high rate of recombination seen in the photocurrent transients.

The plots generated to estimate the direct band-gap energy values for both the evaporated and electroplated samples annealed at 400 °C show the presence of edges in the region around 1.5 eV for the sulfurized samples and in the region around 1.2 eV for the selenized ones.

These results are in good consistency with Rodríguez-Lazcano et al. [1] who reported a band-gap energy for the $CuSbS_2$ film of 1.52 eV.

Fig. 5 Plot of $[h\upsilon \cdot ln(1-EQE)]^2$ generated to estimate the band-gap energies for stacked evaporated Sb/Cu and alloy electroplated Sb-Cu precursors sulfurized (A) and selenized (B) at 400 °C. Sharp edges in the range 1.47-1.53 eV are observed for the sulfurized samples, while broad edges in the range 1.2-1.3 eV are seen for the selenized ones.

3.4 Discussion

The morphological/compositional results together with the crystallographic analyses, suggest the following interpretation of the reaction sequence. As noted with the XRD, 350 °C is the minimum temperature required for the Sb to be thoroughly sulfurized to Sb_2S_3, while the Cu can be fully converted to CuS at 200 °C. Consequently most of the Cu contained in the Sb-Cu electroplated alloy precursor reacts selectively with sulphur at temperatures ranging between 200 and 300 °C, leading to the "bloom" of abundant CuS crystals on top of the former precursor surface. Therefore, as these temperatures are too low for the Sb to completely react with sulfur, the formation of the ternary phase by interdiffusion of the elements is prevented.

As observed for both the Sb/Cu evaporated stacked and the Sb-Cu electroplated alloy precursors, the minimum sulfurization temperature required for them to be converted to $CuSbS_2$ is 350 °C, which is also the minimum temperature that lead to the formation of photoactive films in both cases. This is consistent with what it was found by Rodríguez-Lazcano et al. [1] on the heat treatment of chemically bath deposited Sb_2S_3-CuS thin films.

The nice and compact morphology of the films annealed at 350 and 400 °C might suggest that the same were obtained by conversion of the Sb-Cu alloy directly to the ternary compound $CuSbS_2$ (plus excess CuS or with a broad compositional range), without the need to pass through the separation of the binary phases. After the sulfurization treatments at 350 and 400 °C the EDS analysis of the films revealed a Cu:Sb ratio approaching 2.6; however it must be highlighted that the penetration depth of the electron beam was lower than the thickness of the absorber layer, as no signal from the Mo substrate was detected. Therefore the EDS analyses could be affected by the presence of a concentration gradient through the absorber film. Nevertheless, it is not possible to exclude that Sb incurred losses due to thermal means, as the reported literature on the vapour pressure of Sb_2S_3 is rather contradictory (see Matei et al. [20]). In fact, although from what reported by Piacente et al. [21] this phenomenon might seem unlikely ($P_{Sb2S3}^{400\,°C} \sim 5 \cdot 10^{-13}$ Pa), Yang et al. [22] demonstrated the chemical vapour transport of Sb_2S_3 in the presence of sulfur excess at 500 °C under a flux of 10 mlmin^{-1} of Ar, suggesting that something similar might have happened in the present case. A compositional depth profile would help explaining the mechanism, as clearly a Cu richer layer would be present at the top of the films treated at 350 and 400 °C if binary phase separation occurred.

In any case, the magnitude of photoresponse was possibly restricted by the presence of Cu rich phases since, in analogy to what is commonly done with the CIGS(Se) as reported by Kessler et al. [23], the samples showed increased performance after being chemically etched with a CN$^-$ solution. However it was found that the treatment, which was performed for a time period of up to 6 minutes, affected the morphology of the sample, possibly limiting the beneficial effect of removing the CuS.

The selenization of the Sb-Cu electroplated alloy precursor was also performed at 400 °C, leading to the formation of a *p*-type semiconductor material.

4. Conclusions and future work

The formation of $CuSbS_2$ through annealing stacked evaporated Sb/Cu precursors in sulfur environment was investigated in the range 200-400 °C. The minimum temperature required to obtain the desired ternary phase was found to be 350 °C. Such films were found to be *p*-type semiconductors with band-gap energy suitable for the application in solar energy conversion (~1.5 eV).

The EQE of the sulfurized samples is still too low for the application in photovoltaic devices, however it is possible that Sb richer precursors may lead to stoichiometry closer to the one desired (without the need for KCN etching), and to films with enhanced performance.

It was demonstrated that films of good morphology were obtained by employing homogeneous Sb-Cu electroplated alloys as precursors for subsequent chalcogenization treatments. It is thought that the introduction of the chalcogen into a homogeneous phase rather than a stacked precursor should involve a simpler diffusion mechanism, which in the specific case it might occur, at the right temperature, without the "bloom" of segregated secondary phases.

In order to prove such a mechanism, further studies will be conducted with the aid of a rapid thermal processing furnace, with which the effect of the annealing ramp periods can be minimized. This will also be done on the electroplated precursor, in order to establish whether or not the metastable Sb-Cu alloy incurs phase separation prior to react with the chalcogen.

Provided that the films sulfurized at 400 °C might be Cu rich at the surface, the compositional analysis performed with the EDS microprobe revealed a Cu:Sb ratio of ~2.6. However, neither CuS nor Cu_3SbS_3 phases was detected via XRD; furthermore, the presence of $CuSbS_2$ with a broad solubility range should be discarded, as it would be in disagreement with what reported by Sugaki et al. [24] on the equilibrium Cu_2S-Sb_2S_3 phase diagram. All this leave uncertainties on the location of the Cu excess and further studies are required in order to elucidate this aspect. However, selective Cu leaching was achieved via the KCN etching, and the etched samples had a Cu:Sb ratio of ~0.96, close to the stoichiometric $CuSbS_2$.

Preliminary studies on the selenization of the Sb-Cu precursors gave photoactive films that are also *p*-type in character; although their photon to current efficiency was very low, their band-gap energy can be estimated as ~ 1.2 eV.

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