Formation of Cu$_3$BiS$_3$ thin films via sulfurization of Bi-Cu metal precursors

D. Colombara$^a$, L. M. Peter$^a$, K. Hutchings$^b$, K. D. Rogers$^b$, S. Schäfer$^c$, J. T. R. Dufton$^a$ and M. S. Islam$^a$

$^a$Department of Chemistry, University of Bath, Bath BA27AY, UK
$^b$Centre for Materials Science and Engineering, Cranfield University, Shrivenham, SN68LA, UK
$^c$Enthone GmbH Elisabeth-Selbert-Strasse 4, Langenfeld 40764, Germany

Abstract

Thin films of Cu$_3$BiS$_3$ have been produced by conversion of stacked and co-electroplated Bi-Cu metal precursors in the presence of elemental sulfur vapour. The roles of sulfurization temperature and heating rate in achieving single-phase good quality layers have been explored. The potential loss of Bi during the treatments has been investigated, and no appreciable compositional difference was found between films sulfurized at 550 °C for up to 16 hours. The structural, morphological and photoelectrochemical properties of the layers were investigated in order to evaluate the potentials of the compound for application in thin film photovoltaics.

Keywords:

Wittichenite, Availability, Electrodeposition, Sulfurization, RTP, Photoelectrochemistry, Solar cell.

1. Introduction

The search for earth-abundant non-toxic materials for large scale deployment of photovoltaics is becoming increasingly important. Current technologies using rare elements such as indium and gallium are unlikely to be able to satisfy the rapidly growing demand for thin film solar cells. The United States Geological Survey assessed the 2010 annual world mine production of Bi as 7600 t with estimated world reserves of 320000 t. These figures can be compared with the annual world production (only by refinery) of 574 t for In with no established estimation for its world reserves [1]. During 2010, the price for Bi was below 20 U.S. $ kg$\(^{-1}\), while In had an average price over 500 U.S. $ kg$\(^{-1}\). Owing to its low toxicity as well as relatively low cost, Bi has been considered in the framework of the COST Action 531 as a potential candidate for the development of lead-free soldering alloys [2-5], and some of its compounds are employed in a range of pharmaceutical and cosmetic products.

The potential application of the sulfosalt Cu$_3$BiS$_3$ as a $p$-type absorber film in photovoltaics was first considered by Nair et al. [6]. This compound, which occurs naturally as the mineral Wittichenite, crystallises in an orthorhombic unit cell ($a = 7.723$ Å, $b = 10.395$ Å, $c = 6.715$ Å) [7] containing 4 formula units. Its low temperature polymorph belongs to the space group $P2_12_12_1$, so that its structure differs from that of the cubic and tetragonal semiconductors derived from the Si crystal structure, which form the basis of current solar cell technology. The coordination of
the Cu atoms is nearly trigonal planar (Fig. 1), while the Bi atoms show a particularly
unusual trigonal pyramidal geometry with the three nearest sulfur atoms (Fig. 2). The
structure is comprised of infinite chains of edge-sharing distorted square pyramidal
BiS₃ units aligned along the a axis, separated by the CuS₃ units (Fig. 3).

Makovicky et al. [8] have found that Cu₂BiS₃ undergoes a series of phase
transitions, starting from 118.5°C, that involve reorganization of the Cu distribution
with their conversion from a stationary to a mobile state, turning the compound into a
solid electrolyte at relatively low temperatures. The recent results of Mesa et al. [9]
show that the optical and electrical properties of Cu₂BiS₃, including a direct forbidden
band gap of 1.4 eV [10], confirm its potential for application as a solar absorber in
single heterojunction thin film solar cells.

Thin films of crystallographically pure Cu₂BiS₃ have been synthesized by
annealing diffusion couples of chemical bath deposited Bi₂S₃ and CuS layers [6] as
well as chemical bath deposited CuS and thermally evaporated Bi layers [11].
However, it is unclear from these reports whether such methods lead to films with
suitable morphology for the application in solar cells (Scanning Electron Microscopy
-SEM- images were not published). By contrast, a one-step reactive sputter deposition
route developed by Gerein et al. [10] produces phase pure Cu₂BiS₃ films with optical,
electrical and morphological properties that are ideal for incorporation into devices. A
combinatorial strategy for rapid device screening was reported to be in progress [12,
13], but no results have yet been published. Previous work by the same group [14] on
a two-step synthesis process using metal and metal sulfide precursors demonstrated
complete conversion into the phase pure ternary chalcogenide under H₂S, but the
morphology of the films was found to be unsuitable for use in photovoltaics. Best
results were achieved with co-sputtered precursors at processing temperatures as low
as 270 °C, but with very long heating times (> 16 h). According to this report, the
useful range of processing conditions for the formation of the ternary chalcogenide is
limited by the volatility of Bi above 300 °C, since treatments at higher temperatures
resulted in Bi depletion [14].
Co-electrodeposition of metal precursors followed by conversion into the
chalcogenide has proved to give promising results on laboratory scale Cu₂ZnSnS₄
(CZTS) -based devices [15]. The method has potential for fabrication of large area
uniform films with low cost capital equipment. The present study sets out to
investigate the conversion of electroplated layered Cu/Bi/Cu precursors and
homogenous Cu-Bi deposits of appropriate overall composition into Cu₂BiS₃ films
with a continuous morphology. Sulfur incorporation was achieved by the action of the
chalcogen vapour on the metal precursors. Following the approach taken previously in
a study of the CuSb(S,Se)₂ system, the conversion of the single elements to binary
sulfides was investigated as well as the subsequent reaction to form the ternary
chalcogenide[16].

2. Experimental

2.1 Precursor preparation and sulfurization

Sequential electrodeposition of Cu/Bi/Cu layers with the desired elemental ratio was
conducted by Enthone GmbH R&D laboratories using commercially available
electroplating solutions (Cupralyte 1525 and adapted Stannostar® SnBi). The substrate
was Mo-coated soda lime glass. The same substrates were also used for co-
electrodeposition of Cu and Bi from a solution containing 0.030 M CuSO₄, 0.010 M
Bi(NO₃)₃, 2 M NaOH, 0.1 M D-sorbitol. The electrolytic cell used was a standard
three electrode configuration. A 4 cm² substrate masked with polyimide tape was
connected to a rotating disc working electrode placed opposite to a large Pt foil
counter electrode. A saturated calomel reference electrode was used, and all potentials
are given vs. SCE. A µ Autolab type III potentiostat was used to carry out
potentiostatic plating at -0.80 V with a rotation speed of 300 rpm. The charge cut-off
was set as 2.1 C cm⁻² in order to attain precursors that can be converted – after
complete sulfurization – into 2 µm thick films of Cu₄BiS₃ (i.e. 9 electrons per Cu₄BiS₃
formula unit, assuming a 100% electroplating efficiency). Films of metallic Bi were
vacuum-evaporated onto soda lime glass substrates, and a thickness of ~ 0.5 µm was
ensured by loading a calibrated amount of elemental Bi into the tungsten boat of the
evaporator.

The metal precursor samples were placed in a graphite box with an excess of
sulfur (0.05 g) and annealed in an AS-Micro Rapid Thermal Processor (RTP)
(AnnealSys). The treatments were performed in the range 270 to 550 °C with dwell
periods in the range 5 - 960 minutes and heating rates between 5 and 600 °C min⁻¹. A
static background pressure of 7 × 10⁻⁴ Pa of nitrogen was maintained during annealing
in the RTP furnace. The dependence of the sulfur partial pressure as a function of the
nitrogen background pressure within our RTP system has been modelled by Scragg
[17]. From such modelling it can be estimated that the initial partial pressure of sulfur
vapour inside the graphite susceptor is ~ 5 × 10⁻⁴ Pa. By consideration of the total
volume of the chamber and of the sulfur load, this pressure is expected to decrease to
~ 2.3 × 10⁻⁵ Pa when sulfur vapour diffusion inside the chamber is complete, with no
expected sulfur condensation.

2.2 Film characterization

A Panalytical X'pert X-ray powder diffractometer (XRD) was employed for structural
characterization of the samples. Morphological and compositional analyses were
performed with a Jeol 6480LV SEM connected to an INCA x-act Energy Dispersive
Spectroscopy (EDS) microprobe. The Cu:Bi ratios of the metallic precursors and
sulfurized films were estimated after acquisition of the X-Ray spectra obtained with
an accelerating voltage of 20 kV. The M₆ line of Bi and L₆ line of Mo are just 0.13
keV apart, but the resolution of the microprobe is enough for the two contributions to
be discerned quite well with the software deconvolutions. Localised EDS analyses
averaged over several points across the films were found to be reasonably consistent
with those obtained by Flame Atomisation Atomic Spectroscopy (AAnalyst 100 –
Perkin Elmer) on samples dissolved in concentrated HNO₃: HCl 1:1 solution (± 2% at.
for Bi). The EDS method was mainly employed for practical reasons. However, since
the energy difference between the M₆ line of Mo and the K₆ line of S is too small
(0.015 keV), it was not possible to discriminate the contributions of these two
elements, unless the line scan was performed in the cross section and the signals
compared to the micrograph (section 3.2 for details). EDS profiles of the cross
sections were performed on the samples previously embedded in carbon-loaded resin
with a Bühler moulding unit and polished up to a 0.1 µm alumina finish with a
universal polishing machine.

To assess the photoactivity of the samples, an electrolyte contact was used
containing 0.2 M Eu³⁺ to act as an electron (minority carrier) scavenger. A standard
three electrodes cell was employed to carry out the photoelectrochemical
ccharacterizations with Ag/AgCl reference and a Pt wire counter electrodes, as
described by Scragg et al. [18]. Photovoltammograms and chronoamperometric
measurements were carried out under pulsed illumination provided by a white Light
Emitting Diode (LED), while the potential was applied and the current recorded by a
µ Autolab type III potentiostat.

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 calibrated silicon photodiode traceable to National
Bureau of Standards standards.

3. Results and discussion

3.1 Structural characterization

The Cu/Bi/Cu precursor shows the presence of elemental Cu and Bi only, with the
XRD spectrum matching the powder patterns of the elements. XRD patterns of the as-
deposited and annealed (without sulfur) co-electroplated (Cu$_3$Bi) films at 250 and 500
°C for 5 minutes are shown in Fig. 4.

The as-deposited co-electroplated (Cu$_3$Bi) precursor shows an XRD spectrum typical
of an amorphous material; very broad peaks are seen at ~ 18, 27, 31, 44 and 59 ° (Fig.
4a), among which only those at 27 and 44 ° are centred in correspondence to Bi and
Cu diffractions, while the others do not match the elements’ patterns. They might
arise from low-range ordered domains [19], whose size and quantity are such that
only broad and low diffraction peaks are detectable. On a larger scale the Cu and Bi
atoms within the film are likely to be randomly distributed.

Annealing at 250 °C for 5 minutes causes the elements in the co-deposit to
separate, forming Bi and Cu aggregates which give XRD patterns that match
reasonably well with the corresponding powder patterns (Fig. 4b). Annealing at 500
°C for 5 minutes causes the Bi and Cu aggregates to enlarge, as can be seen from the
sharper XRD peaks (Fig. 4c). The Bi aggregates exhibit strong (104) texturing that
may arise from directional crystallisation of Bi caused by the strong cooling rate
employed.

In order to relate the formation of the ternary chalcogenide to initial
conversion of the precursor metals into the corresponding binary sulfides, ex-situ
XRD analyses were performed on a series of bismuth samples sulfurized for 5
minutes at different temperatures between 350 and 550 °C. Films of copper were not
studied since it is known from previous work [16] that Cu can be fully converted to
CuS in the presence of elemental sulfur vapour even at temperatures as low as 200 °C,
with its diffraction pattern peaks being consistent with hexagonal CuS (Covellite).
The evaporated Bi samples showed a gradual greyscale variation from dark to light as
the temperature of the sulfurization treatment was increased. The corresponding series
of XRD patterns is depicted in Fig. 5.
The evaporated film of Bi exhibits (00l) preferred orientation (Fig. 5a). This is similar to what it was found for the Sb case [16]. Sulfurization for 5 minutes up to 350 °C causes the Bi to react partially with sulfur, leading to a mixture of unreacted Bi and Bi$_2$S$_3$. It can be observed from Fig. 5b that the remaining Bi shows a strong (012) preferred orientation as opposed to (001) for the as-deposited Bi, suggesting that the element has undergone melting and subsequent directional crystallisation. It is interesting to note the effect possibly due to the different substrate (bare glass or Mo coated glass) on the directionality of Bi crystallisation, (cf. Fig. 4).

The sulfurization treatments result in a bismuth sulfide with an XRD spectrum matching that of orthorhombic Bi$_2$S$_3$ (Bismuthinite), apart from a systematic peak shift towards lower diffraction angles indicative of the presence of expansion strains affecting its lattice. This strain does not seem to be appreciably relieved even if the film is sulfurized up to 550 °C in the time frame of 5 minutes. Since liquid Bi is denser than the solid, it is probable that Bi$_2$S$_3$ formed on the surface of liquid Bi is subject to expansion strains when the substrate of unreacted Bi expands during solidification. Within the 5 minutes period investigated, complete conversion of Bi to Bi$_2$S$_3$ occurs at the temperature of 400 °C (Fig. 5c), when the strong peak at 20 = 26.9° corresponding to the (012) planes of rhombohedral Bi is no longer detectable.

Fig. 6 shows the series of XRD patterns of the sulfurized ternary compound precursors. The standard powder patterns of CuS (Covellite), Bi$_2$S$_3$ (Bismuthinite) and Cu$_3$BiS$_3$ (Wittichenite) are also shown. The structural analysis reveals that sulfurization below 400 °C leads only to the binary sulfides, leaving traces of unreacted Bi. For sulfurization at 450 °C, some of the peaks related to the ternary chalcogenide start to appear, but the sample still shows the coexistence of the binary sulfides. At 500 °C, the conversion of the precursors to Cu$_3$BiS$_3$ is complete and the treatment at 550 °C does not seem to alter appreciably the structural properties attained at 500 °C.

The series of XRD patterns for the stacked Cu/Bi/Cu and co-electrodeposited (Cu$_3$Bi) samples reveal very little dependence of the final phase composition of the resulting film on the starting precursor configuration. Regardless of whether the layered or homogenous deposits are used as precursor films, the formation of the binary sulfides is observed to occur prior to the development of the ternary compound.

In terms of phase evolution versus temperature, it is important to note that our results are strikingly dissimilar to those reported by Gerein et al. [14]. In our case, ternary chalcogenide was not formed at 270 °C, even with sulfurization periods lasting up to 16 hours. By contrast, 5 minute treatments at temperatures above 450 °C resulted in the formation of Cu$_3$BiS$_3$ films, without any loss of Bi. Indeed, no appreciable Bi depletion could be detected even when the treatment at 550 °C was extended to 16 hours; the resulting films were still Cu$_3$BiS$_3$ with unaltered lattice parameters.

Gerein’s sulfurization treatment consisted in the use of ~7×10$^5$ Pa of hydrogen sulfide, while elemental sulfur vapour was employed here, with an initial partial pressure that can be estimated as ~5×10$^4$ Pa at 270 °C. These different sulfurization conditions might be responsible for the observed discrepancies between our work and Gerein’s.

3.2 Morphological and compositional characterization
As can be seen in Fig. 7, (Cu$_3$Bi) precursor layers with a thickness up to 2 μm could be easily deposited, with grains of roughly the same size and a reasonably uniform Cu:Bi molar ratio distribution approaching 3:1. From the charge cut-off and the thickness of the co-deposited films, it was inferred that the co-deposited films are around 60% less dense than bulk Cu and Bi, suggesting the presence of porosity at a nanoscale level, that is not detectable with the SEM. However, the films look very uniform and therefore they were thought suitable for subsequent sulfurization treatments.

After sulfurization, the co-electroplated (Cu$_3$Bi) films and the Cu/Bi/Cu stacked films had the same colour. Both series of specimens were dark blue after annealing up to 450 °C, dark grey after 500 °C and light grey after 550 °C. However, the films obtained by sulfurization of (Cu$_3$Bi) precursors suffered from poor uniformity if the heating rate employed was higher than 5 °C min$^{-1}$.

The SEM analysis of the stacked Cu/Bi/Cu precursors sulfurized at 350 °C for 5 minutes with a heating rate of 600 °C min$^{-1}$ shows a surface comprised entirely of crystals with euhedral features identified by the EDS microprobe as CuS (Fig. 8a). The same precursor sulfurized at 500 °C for 5 minutes shows a rough surface with crystallites that appear to be poorly attached to a more compact under layer (Fig. 8b).

Invariably, for sulfurizing temperatures higher than ~270 °C and for heating rates exceeding 5 °C min$^{-1}$, the (Cu$_3$Bi) samples exhibited poor morphology and delamination (Fig. 8c). Localised EDS analysis shows the presence of Cu, Bi and S in the remaining parts of the film, while just Mo is detected on a large fraction of the sample area. On the other hand, heating rates of 5 °C min$^{-1}$ or less resulted in Cu$_3$BiS$_3$ films with improved adhesion and morphology (Fig. 8d-e). This can be explained by the fact that the sulfur uptake is likely to occur before the melting point of Bi is reached, when this is wholly converted to Bi$_2$S$_3$ that melts at much higher temperature (775 °C [20]). With dwell periods of 30 minutes and maximum temperature of 500 °C the film shows well-defined grains with average size of ~1 μm. The cross section micrograph (Fig. 8e) shows a film thickness of ~1.8 μm, revealing a volume expansion from the precursor of ~13%, caused by conversion to the chalcogenide. A volume expansion of ~94% is predicted based on the density difference between the bulk metals and the ternary chalcogenide. We believe that this discrepancy arises from the low density of the amorphous (Cu$_3$Bi) deposit employed as the precursor (which was found to be about 60% less dense than the bulk metals, Fig. 7). The compositional profile of the cross section reveals a quite even lateral distribution of the elements Cu, Bi and S; EDS localised analyses averaged over several points throughout the film show that it is slightly Cu deficient, its Cu:Bi ratio being 2.6±0.2, as for the precursor.

3.3 Photoelectrochemical characterization

The samples obtained by sulfurization of the two metal precursor configurations of at 500 °C for 30 minutes were characterised photoelectrochemically in order to ascertain their minority carrier type. For this purpose, the samples were immersed in a 0.2 M
aqueous solution of Eu(NO₃)₃ and illuminated with a pulsed white LED while running
a cyclic voltammogram, as described in 2.2. A cathodic photocurrent response was
observed that corresponds to the reduction of Eu⁺⁺⁺ at the surface of the working
electrode, showing that the samples are p-type.

Etching with a 5% wt. KCN solution improved the photoactive properties of
the films obtained by sulfurization of the stacked precursors. However, in contrast to
the behaviour seen with CuSbS₂ [16], etching periods longer than 60 seconds resulted
in the sudden and complete suppression of photoactivity. The samples obtained by
sulfurization of the (Cu₃Bi) precursors were photoactive “as-grown”, but etching with
a more dilute solution (0.5% wt. KCN) even for shorter periods (5 seconds)
suppressed their photosresponse. More work is needed in order to understand the KCN
etching process and its influence on surface composition and photosresponse.

External Quantum Efficiency (EQE) spectra of the Cu₃BiS₃ films are
illustrated in Fig. 9.

Although the photoelectrochemical properties of the films are rather poor, with
external quantum efficiencies below 12%, the band-gap energy of the compound can
be estimated as ~1.3 - 1.4 eV, which is consistent with the values reported in the
literature [9, 10]. It can be noticed that the onset of the EQE spectra of the samples
obtained by sulfurization of the (Cu₃Bi) precursor (Fig. 9a-b) is sharper than the one
of the Cu/Bi/Cu precursor (Fig. 9c). The latter was measured after 60 seconds etching,
as this was required to enhance the signal. The shape of the EQE spectra of the
sulfurized (Cu₃Bi) films is similar, although the data corresponding to the sample
heated with a rate of 600 °C min⁻¹ has been multiplied by a factor of 5 for sake of
comparison (note the higher signal to noise ratio). This difference in the magnitude is
attributed to the poor morphology of the (Cu₃Bi) films sulfurized with higher heating
rate, as apparent from Fig.9c.

An order of magnitude estimate for the naturally occurring acceptor density of
the Cu₃BiS₃ films obtained by sulfurization of the (Cu₃Bi) precursors was obtained by
analysing the dependence of EQE - measured near the onset region of absorption
(photon energy 1.7 eV).- on applied potential. The EQE, Φ, of a semiconductor
photoelectrode is described by the reduced Gärnter equation as follows [18]:

\[ \Phi = 1 - \exp(-\alpha W) \]

where \( \alpha \) is the optical absorption coefficient of the material and \( W \) is the width of the
space charge region. Eq. (1) is valid when the electron diffusion length, \( L_p \), is
negligibly small (i.e. \( \alpha L_p \ll 1 \)).
The width of the space charge region at the semiconductor-electrolyte interface is
given by:

\[ W = [2eE_0(E_{FB} - E)/(eN_a)]^{1/2} \]

where \( E \) is the applied potential, \( E_{FB} \) is the flat-band potential (i.e. the potential at
which the semiconductor energy bands are not bent), \( \varepsilon \) is the relative permittivity of
the material, \( \varepsilon_0 \) is the vacuum permittivity, \( e \) is the elementary charge and \( N_a \) is the
acceptor density for p-type semiconductors).

By combining Eqns. (1) and (2) it follows that:
(3) \[ (\ln(1-\Phi))^2 = 2\alpha^2 \varepsilon e \varepsilon_d (E_{FB}-E)/(eN_0) \]

Fig. 10 shows a plot of \((\ln(1-\Phi))^2\) versus \(E\) for a typical Cu_{3}BiS_{3} film. The linear section in the onset region has a gradient equal to \(2\alpha^2 \varepsilon e \varepsilon_d/(eN_0)\), from which \(N_0\) can be extracted.

Taking the value of \(\alpha\) (at 1.7 eV) reported by Gerein et al. [10] \((-6 \times 10^4 \text{ cm}^{-1}\)), and a value of \(\varepsilon\) typical of an inorganic sulfide like CuInS_{2} (10) [21], gives an acceptor density of \(\sim 3 \times 10^{17} \text{ cm}^{-3}\). This is about one order of magnitude higher than that reported by Mesa et al. [22] for Cu_{3}BiS_{3} films obtained by co-evaporation of the elements. It is known that typical carrier concentrations of device quality chalcogenides such as CuIn(Ga)(S,Se)_{2} [23] lie in the region of \(10^{16} \text{ cm}^{-3}\), but substantially higher values are generally reported for the newer Cu_{2}ZnSn(S,Se)_{2} absorber [24]. Further studies are required in order to estimate the electron mobility and diffusion length of the material which are key factors for its potential application in thin-film photovoltaic devices.

4. Conclusions and future work

From the series of ex-situ XRD patterns it seems that the configuration of the Bi-Cu metal precursors employed, stacked or co-deposited, does not influence the qualitative phase evolution during sulfurization. From comparison of the XRD patterns corresponding to the series of sulfurized Bi and Bi-Cu films, it appears that the formation of Bi_{2}S_{3} is not the limiting factor for the growth of the ternary chalcogenide. The critical stage appears to be the reaction between the binary sulfides, although further studies are required to investigate this aspect.

For treatments lasting 5 minutes, the minimum temperature required for the formation of phase dominant Cu_{3}BiS_{3} films was found to be 450 °C. The partial pressure of S_{2} (g) employed herein can be estimated as \(\sim 5 \times 10^4 \text{ Pa}\) at 270 °C during the first stages of the sulfurization (slowly decreasing to a minimum of \(\sim 2.3 \times 10^3 \text{ Pa}\) owing to S_{2} (g) diffusion out of the graphite susceptor), as opposed to a pressure of only \(\sim 7 \times 10^4 \text{ Pa}\) of H_{2}S employed by Gerein et al [14]. The different sulfurization conditions employed might account for the higher temperature required for the ternary chalcogenide to form in the present work. Further studies are required in order to clarify the different behaviour of the reacting atmosphere.

Reasonably homogenous and compact Cu_{3}BiS_{3} films were obtained by sulfurization of the co-deposited (Cu_{3}Bi) precursors at 500 °C for 30 minutes provided that the heating rate was restricted to 5 °C min^{-1}. Higher heating rates resulted in poor morphology with peeling of the film from the Mo substrate. No appreciable Bi depletion was detected in the converted compound even at 550 °C in the time frame up to 16 hours, the resulting films being Cu_{3}BiS_{3} with unaltered composition and lattice parameters. It seems clear that the partial pressure of S_{2} (g) employed during the treatments (\(\sim 2.3 \times 10^3 \text{ Pa}\)), is sufficient to overcome the potential Bi losses at elevated temperatures via the Le Chatelier effect on the decomposition equilibria of Cu_{3}BiS_{3}. A detailed thermochemical investigation of such aspects would be required for the definition of the temperature and S_{2} (g) pressure annealing boundaries. Part of these aspects are addressed in a more recent work [25].
The acceptor density of the deposited Cu$_3$BiS$_3$ was found to be $\sim 3 \cdot 10^{17}$ cm$^{-3}$ and the band-gap energy was estimated as $\sim 1.3 - 1.4$ eV with the best films showing a maximum EQE of about 10% only. However, investigation of the effects of S$_2$(g) partial pressure on the morphological and photoelectrochemical properties of the films might let some room for improvement. Furthermore, if the homogeneity range of the Cu$_3$BiS$_3$ phase allows some mutual solubility [9], the effect of the Cu:Bi molar ratio could also be considered as a parameter for the optimisation of the film properties. In this context, an approach consisting on the sulfurization of Bi-Cu 1D libraries centred on the 1:3 stoichiometry would be beneficial for the rapid screening of the photoelectrochemical properties.

The results from the present study are promising, but clearly further work would be required to increase the EQE to a level where the construction of solar cells becomes feasible and worthwhile.

Acknowledgements

We are grateful to J. M. Mitchels, A. Løken and Charles Cummings c/o University of Bath for assistance with SEM analyses, preliminary work [26] and fruitful discussions. The Mo coated SLG substrates were kindly provided by Stefan Schäfer (Enthone). The visualizations of the crystalline structure were created with the aid of VESTA software [27]. Funding was provided by the EPSRC Supergen PV-21 consortium.

References

List of figures and captions

**Fig 1** (Colour online) Trigonal planar CuS$_3$ unit showing the coordination of Cu atoms in the structure of Cu$_3$BiS$_3$ and the distances between Cu (red) and S (yellow) atoms.

**Fig 2** (Colour online) Distorted square pyramidal BiS$_5$ unit showing the coordination of Bi atoms in the structure of Cu$_3$BiS$_3$ and the distances between Bi (grey) and S (yellow) atoms.
**Fig 3** (Colour online) Unit cell of Cu$_3$BiS$_3$ showing trigonal planar CuS3 (red) and distorted square pyramidal BiS5 units (grey) and S atoms (yellow).

**Fig 4** XRD patterns of the Cu$_3$Bi electroplated precursors as-deposited (a) and after thermal treatment at 250 (b) and 500 °C (c) for 5 minutes. Standard powder patterns for Bi PDF no 44-1246 (black) and Cu PDF no 70-3038 (red) are included (● labels refer to the Mo substrate).
**Fig. 5** Series of XRD patterns of the evaporated Bi films as deposited (a) and after sulfurization at 350°C (b), 400°C (c) and 450°C (d) for 5 minutes with fast heating rate (600 °C·min⁻¹). Standard powder patterns for Bi PDF no 44-1246 (black) and Bi₂S₃ PDF no 6-333 (red) are included. The substrate employed is soda-lime glass.
**Fig. 6** Series of XRD patterns of typical Cu/Bi/Cu stacked (A) and Cu$_3$Bi (B) precursors after sulfurization at temperatures between 350 and 550 °C for 5 minutes (heating rate: 600 °C·min$^{-1}$). Standard powder patterns of the relevant phases: CuS PDF no 65-3561 (red), Bi$_2$S$_3$ PDF no 6-333 (grey) and Cu$_3$BiS$_3$ PDF no 9-488 (black) (● labels refer to the Mo substrate).
Fig. 7 SEM cross section (a) and top view (b) of an as deposited (Cu$_3$Bi) precursor. The inset shows the EDS compositional profile corresponding to Cu (red), Bi (black) and Mo (dashed), performed on the same sample embedded in carbon loaded resin.
**Fig. 8** SEM top views of typical Cu/Bi/Cu stacked precursor sulfurized at 350 °C (a) and 500 °C (b) for 5 minutes with heating rate of 600 °C min⁻¹. Morphology of (Cu₃Bi) precursors after sulfurization at 350 °C for 5 minutes with heating rate of 600 °C min⁻¹ (c) and at 500 °C for 30 minutes at 5 °C min⁻¹ (d, e). Inset (e): EDS compositional profile corresponding to Cu (red), Bi (black), Mo and S (dashed).
Fig. 9 EQE spectra of Cu₃BiS₃ films obtained by sulfurization of the Bi-Cu metal precursors at 500 °C for 30 minutes. Cu₃Bi precursor with heating rate of 600 °C min⁻¹ (x5) (a) and 5 °C min⁻¹ (b); Cu/Bi/Cu precursor with 60 seconds etching in KCN 5% wt. (c). Acquisition conditions: 0.2 M Eu³⁺ solution, -0.5 V vs. Ag/AgCl, chopping frequency 27 Hz.
Fig. 10 Plot of $[\ln(1-\Phi)]^2$ vs applied potential of a typical Cu$_3$BiS$_3$ film obtained by sulfurization of a Cu$_3$Bi precursor at 500 °C for 30 minutes. Acquisition conditions: 0.2 M Eu$^{3+}$ solution, 1.7 eV, chopping frequency 27 Hz.