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Cu-Sb Based Library for Solar Cell Absorber Material Identification

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Abstract

In this paper we report on the sulphurisation of a combinatorially graded co-sputtered Cu-Sb precursor thin film library, deposited on Mo/glass substrate. The library was sulphurised at 500 °C using a graphite susceptor in Ar atmosphere. Compositional data and X-ray diffraction (XRD) maps of the metallic precursor and sulphurised library were collected. Measurements were taken by line scans across the full specimen with a step size of a few mm. The composition of the metallic precursor ranged from Cu 34 to 88 at% and Sb 12 to 66 at%. The analysis of the XRD map combined with the compositional data showed a predominant formation of Cu_3SbS_3 in the monoclinic or cubic systems, depending on the compositions of the precursor.

Introduction

Currently, the most efficient thin-film solar cells are those based on $Cu(In,Ga)(Se,S)_2$ (CIGSS) absorber layers [1]. This technology is also showing one of the fastest growing capacities in commercial production with a total that is expected to exceed 2GWp by the end of 2011. However, when looking forward to 2050 and the predicted multi-TWp market deployment , this technology has a potential vulnerability due to the reliance on relatively scarce and expensive materials such as In and Ga [2]. It is therefore necessary to research alternative materials that are based on more abundant resources. The system Cu-Sb-S is emerging as a possible alternative for low cost absorber in thin film photovoltaics. Several compounds such as $CuSbS_2$ and Cu_3SbS_3 are thought of as possessing suitable photovoltaic properties [3]. Our previous work [4] on Cu_3SbS_3 and the results of other authors on $CuSbS_2$ [5, 6] confirmed that these new types of semiconductors are suitable for solar photovoltaic applications. The conventional evaluation of the growth of new materials can be very time consuming when specimens are grown individually. In order to investigate the broad range of compositions available in this new ternary system we have used the more time efficient combinatorial approach where compositional gradients are intentionally constructed across a single thin film specimen. These specimens are known as 'libraries' as they can be considered to contain a wide range of compositions and are used to search and optimise the material's composition.

Experimental

Cu-Sb metallic precursor films were co-deposited at room temperature by DC magnetron sputtering, from 3" diameter Cu and Sb elemental targets (5N purity). Molybdenum coated soda-lime glass (SLG) with dimensions 76 mm x 26 mm x 1 mm was used as substrate. The sputtering system was calibrated in order to achieve a uniform gradient of the two elements in terms of thickness in the order of 300nm.

The library was sulphurised evaporating a layer of elemental sulphur (99.99% Sigma Aldrich) of ~1.5 µm directly onto the precursor at a pressure of ~1×10^{-3} mbar. The thickness of sulphur was monitored using a quartz crystal microbalance. The library was then placed in a closed graphite box and heated in a tube furnace to a at a rate of 20 °C/min, under Ar at 1mbar. The sample was held at 500 °C for 30 min before being left to cool to room temperature (1 °C/min).
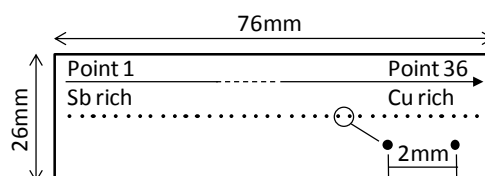

Figure 1 Diagram representing the analysed library. A total of 36 points were recorded along the middle line of the

sample. X-ray powder and atomic composition data were collected for an area approximately 0.5 mm^2.

The composition of the converted layers was characterised by dispersive X-ray microanalysis (Oxford Instruments and FEI Quanta 200 electron microscope). Structural properties were determined by X-ray diffraction (XRD) acquired on a Bruker D8 microdiffractometer with a Cu Kα source and GADDS area detector (spot size ~500 µm). The analysis points are shown in Figure 1.

Results and discussion

The phases identified by the XRD mapping of the sputtered Cu-Sb metallic precursor are reported in Table 1. The composition of the metallic precursor ranged from Cu 34 to 88 at% and Sb 12 to 66 at%. The compositional gradients across the substrate are showed in Figure 2 a). The precursor phases can be grouped in 4 different areas of the library defined in capital letters the bottom part of Figure 2 c). The area A (Sb rich part) consists of Sb phase with no crystalline Cu detected. Elemental Sb and Cu phases have been identified in the area B, with no binary compound detected. The Cu_2Sb phase characterises the area C containing a range of compositions around the Cu:Sb 2:1 stoichiometry. In the areas D and E where the library becomes increasingly Cu rich, the Cu_2Sb phase is still dominant together with an increasing presence of Sb and $Cu_{3.3}Sb$ as the Cu content in the film increases.

Table 2 shows the phases identified from the analysis of the XRD map of Figure 2 c) for the sulphurised library at 500 ºC. The five different areas described earlier for the precursor are also applied to the evolution of the phases of the Cu-Sb-S system. The area A (Sb rich region) is characterised by the presence the

Cu_3SbS_3 phase (monoclinic structure, see III Table 2) together with a strong Sb phase, which can be explained by the high content of Sb in this region which remains unreacted after sulphurisation. Area B still contains some Sb phase, however a gradual drop of the intensity of the Sb peak can be seen, according to the reduction in its concentration in both the precursor and the sulphurised film. For this region of the library the Cu_3SbS_3 phase changes from a monoclinic into a cubic structure (see II Table 2). It then changes back to the monoclinic form in the area C where the Cu content increases. In this region the Sb phase can still be observed.

Identified phases (PDF code)	System	Zone
Cu_2Sb (00-003-1023)	Tetragonal	C, E
Sb (01-071-1173)	Rhombo.	A,B, E
Cu (00-004-0836)	Cubic	B
$Cu_{3.3}Sb$ (00-012-0075)	Hexagonal	D, E

Table 1 Phases identified in the library before the sulphurisation process. The zones are defined in the caption of Figure 2 c).

The area D can be seen as a transition zone where the monoclinic Cu_3SbS_3 phase gently decreases and another type of cubic phase starts to grow (see IV, Table 2). This area is also characterised by the complete disappearance of the Sb phase. The last region of the library (area E) that corresponds to a very high Cu content, shows the clear predominance of the Cu_3SbS_3 phase with the cubic structure (see IV, Table 2) together with a weak presence of the monoclinic system. Also, a strong signal for the Cu_2S phase (see V, Table 2) can be seen, correlating to the Cu rich composition in this region of the library.
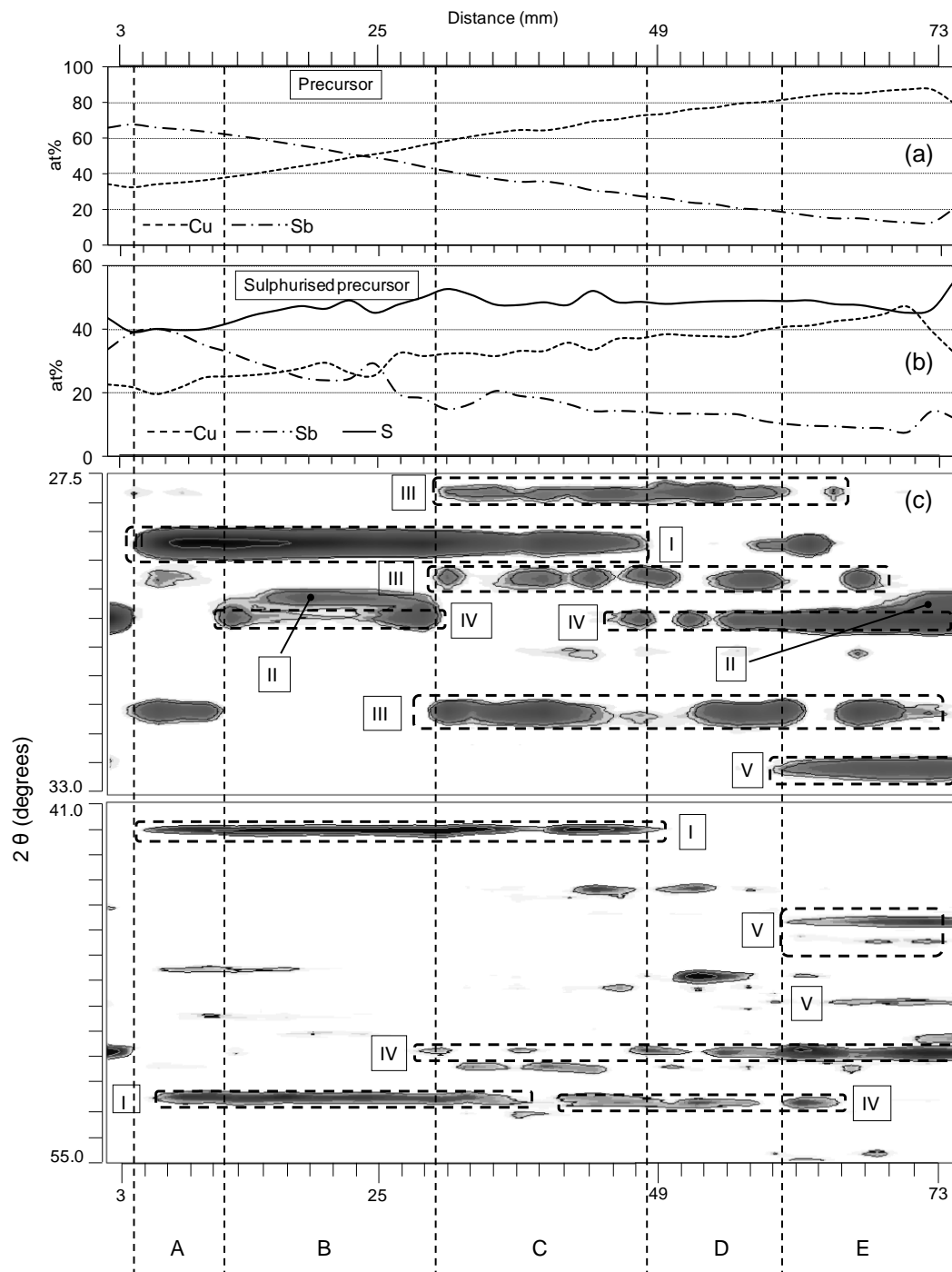
Figure 2 Compositional mapping of the metallic precursor (a) and sulphurised (b) library and XRD mapping of the sulphurised library (c). The x-axis, common for all the plots, gives the distance in mm from one edge of the library to another, as depicted in Figure 1. The two dimensional contour graph in c) represents the map of the powder diffraction spectra collected on 36 points alongside the sulphurised library, for two different ranges of 2θ degrees. The areas in the dotted line squares and the associated roman numbers on the edge indicate the identified phases (see Table 2) evolution along the library. Five compositional zones are also identified at the bottom of the diagram in capital letters, indicating the ranges of distance and atomic composition linked to specific phases as reported in the text.

Identified phases (PDF code)	System	Label
Sb (01-071-1173)	Rhombo.	I
Cu_3SbS_3 (00-031-0450)	Cubic	II
Cu_3SbS_3 (01-083-0563)	Monoclinic	III
Cu_3SbS_3 (01-075-1574)	Cubic	IV
Cu_2S (01-072-1071)		V

Table 2 Phases identified for the entire library after the sulphurisation process.

In other work by the authors [4], the formation of Cu_3SbS_3 phase (monoclinic structure, (see III Table 2) was identified using a single precursor composition within the same range as the area C. Also the Cu_2Sb phase for the single composition precursor was confirmed in the range C. Both the library and the single composition precursor were sulphurised under the same experimental conditions. This demonstrates that the combinatorial approach can be a rapid and effective system to explore a wide range of compositions with high throughput of structural and compositional information that can be applied to a single composition process.

Conclusions

Library of Cu-Sb metallic precursors with composition 0.5<Cu/Sb<7.3 were suplurised at 500°C. This wide range of composition allowed the exploration of phases across the full range of Cu/Sb ratios both prior and post sulphurisation. The precursor layers showed a range of Cu_xSb binary phases along with elemental Cu and Sb. After sulphurisation the dominant ternary compound was Cu_3SbS_3 recrystallizing in the monoclinic (complex) or cubic system. Surprisingly no other ternary phases were detected. The presence of pure metallic Sb is detected for composition up to Cu:Sb = 3:1 at which point the Sb is then incorporated into the Cu_3SbS_3 system.

Acknowledgments

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