Secondary phase formation during monoclinic Cu_2SnS_3 growth for solar cell application

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ABSTRACT

Cu_2SnS_3 is investigated as a potential solar absorber material, which is known to exist in several polymorphs. In the present work, the transition to the most efficient monoclinic polymorph is investigated and an explanation is given why this one seems to be the best for solar cells. Cubic, mixed polymorphs and monoclinic polymorphs are synthesised with increasing temperature. Photoluminescence spectra of the mixed and cubic polymorphs show mainly defect emissions below the band-gap energy, while the monoclinic modification shows only one sharp peak, which is attributed to the conduction to valence band transition. The monoclinic polymorph also grows in combination with a secondary phase containing sodium, Na_xCuSnS_3, with x between 0.5 and 1. It exhibits a cubic (F43m) crystal structure like $CuSn_{3.75}S_8$ and a band-gap of around 1.6 eV. Devices with absorber layers of monoclinic Cu_2SnS_3, in which Na_xCuSnS_3 is either present or removed, gave similar power conversion efficiencies of above 1%.
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1. Introduction

The emerging p-type compound semiconductor Cu_2SnS_3, consisting of only earth abundant and non-toxic elements, attracts attention as an absorber layer for thin film solar cells. Cu_2SnS_3 exhibits a high optical absorption coefficient of greater than 10^4 cm^{-1} and a band-gap energy of between 0.9 and 1.4 eV [1–11]. The variation of the band gaps measured is due to the existence of different Cu_2SnS_3 polymorphs. There is neither a consensus on the synthesis temperature at which the polymorphs are formed nor their exact band-gap. Reported polymorphs of Cu_2SnS_3 include cubic, tetragonal, monoclinic, or triclinic. Between temperatures of 300 and 450 °C, a tetragonal crystal structure is observed [1–5], while above 400 °C the compound is present as cubic and/or monoclinic polymorph [1,5,7]. Between 400 and 550 °C there is a large variation in the measured band-gap energies, varying between 0.95 [8] to 1.11 [6] eV for the cubic/monoclinic structures. The reported data above 520 °C show more consensus, with the monoclinic structure measured to have a lower band gap at 0.93 eV and another optical transition at 1.0 eV [9–11]. This polymorph also shows the highest reported solar cell power conversion efficiency for a standard solar cells structure [11]. Like other chalcogenide based compound semiconductors the introduction of

sodium through NaF has led to even higher device efficiencies [10]. The aim of this manuscript is to investigate the transition to the pure monoclinic polymorph which is around 520 °C and why it seems to be the best material quality for solar cells. Additionally, an effect of Na is also presented.

In the present work, metallic precursors are annealed in a sulphur and tin sulphide environment at various temperatures just below 520 °C and at 520 °C degrees in order to investigate the monoclinic transition of Cu_2SnS_3. It is demonstrated that the monoclinic polymorph is grown from a cubic via a cubic/monoclinic mixture to the monoclinic polymorph at 520 °C. Photoluminescence measurements show that this polymorphic transition decreases the defects in the materials. Furthermore it is shown that the monoclinic polymorph grows with a new semiconductor compound containing sodium. The composition is preliminary determined to be Na_xCuSnS_3 and a band gap of 1.55 eV is derived. Additionally Raman spectra are recorded and an electron backscatter diffraction (EBSD) measurement is performed. To investigate the influence of this secondary phase on solar cell performance, monoclinic absorber layers with and without this secondary phase are made into devices.

2. Material and methods

Cu/Sn precursors are prepared by a wet-chemical method. Similar chemistry has been used to make highly efficient

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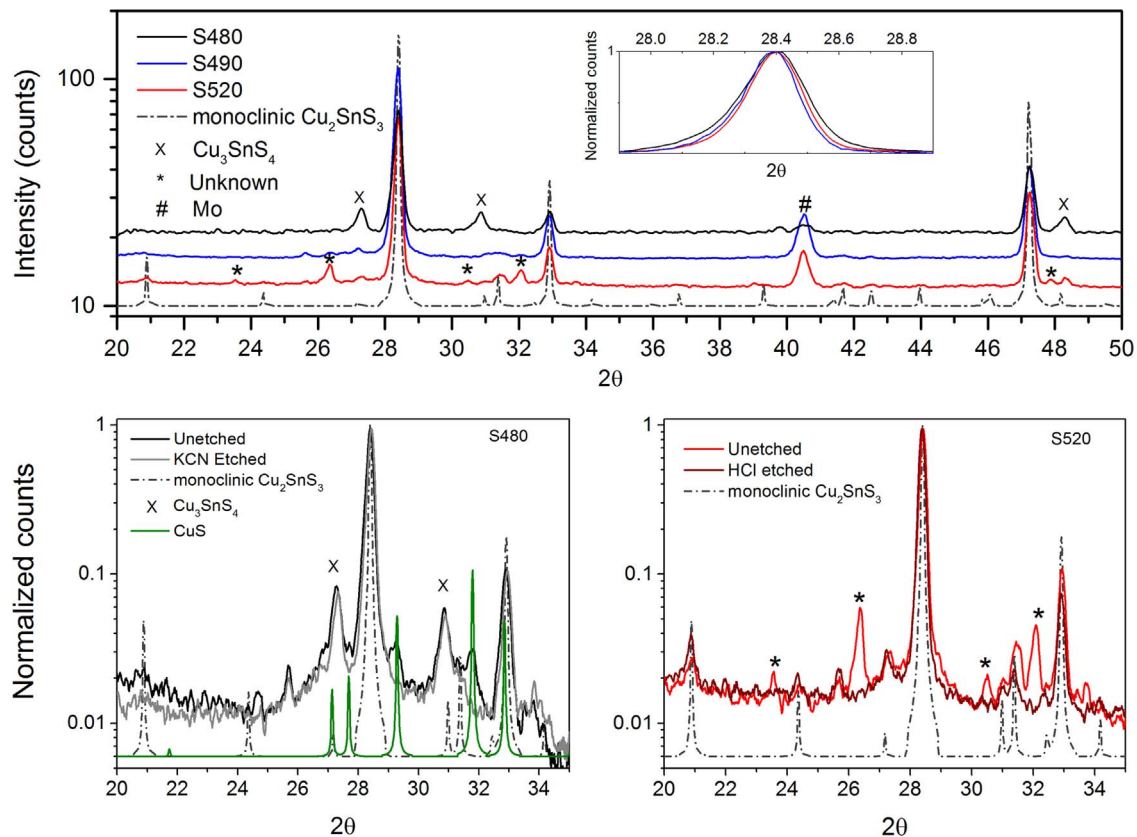 E-mail address: jessica.dewild@uni.lu (J. de Wild).

Fig. 1. GIXRD of S480, S490, and S520 samples. The main peak is at 28.4° consistent with Cu$_2$SnS$_3$ polymorphs. S480 has an additional Cu$_3$SnS$_4$ (X) [PDF 00-036-0217] and a CuS phase [PDF 00-006-0464] (KCN etch, left below). The monoclinic phase [PDF 04–010-5719] is pronounced at 520 °C with unidentified peaks (*) that can be removed by HCl etch (right below).

Cu(In,Ga)Se$_2$ containing solar cells [12] and it was subsequently adapted to the Cu$_2$ZnSnS$_4$ system [13]. The metals are introduced in tetramethylguanidine (TMG, 99%, Sigma Aldrich) as organic salts: tin methoxide (Sn(OCH$_3$)$_2$, Alfa Aesar) and copper formate (Cu(COOH)$_2$ prepared from copper nitrate (99.999%, Abcr) dissolved in formic acid (> 95%, Sigma Aldrich). Methanol (anhydrous, 99.9%, Abcr) is added to reduce the viscosity of the Cu/Sn solution and the salts are dissolved around 105 °C. The ink is then passing through a 200 nm diameter filter to reduce the amount of undissolved particles which cause pinholes in the precursor. The filtered ink is coated on soda lime glass, or molybdenum covered soda lime glass substrates by blade. The use of glass substrates allows the measurement of optical properties whereas the Mo is required for an electrical back contact. 'Reduction of the metals on the substrate happens with heating the substrate with the liquid on a hot plate up to 210 °C in 10 min in a nitrogen atmosphere and leave it for 5 min at 210 °C. During the increasing temperature the metals are reduced with the release of CO$_2$ and the other organic constituents, methanol and TMG, evaporated [12,13].' The metallic precursors are annealed in a closed box with sulfur (100 mg, 99.99995%. Alpha Aesar) and SnS (10 mg, 99.95%, Alpha Aesar) powders for 30 min. Prior to device preparation, the sample is etched for 30 s in aqueous (0.77 M) KCN solution and/or HCl (75 °C, 10 M) solution to remove possible secondary phases, then a CdS buffer layer is deposited by chemical bath deposition. Devices are finished with a sputtered i-ZnO/AZO layer and a Ni/Al front contact grid.

Cu$_2$SnS$_3$ absorber layers are characterized with grazing incidence-XRD (GI-XRD: $\Theta=0.5°$, Bruker D8, Cu K$_{\alpha(1+2)}$ X-ray source), Raman (Renishaw inVia Micro-Raman spectrometer with several excitation wavelengths at 633, 532 and 422 nm), diffuse and specular reflection and transmission (LAMBDA 950 UV/Vis/NIR spectrophotometer). Where applicable, powder cell was used to plot the reference diffraction spectra. Micrographs are recorded with a scanning electron microscope (Hitachi SEM (SU-70)) and Cu/Sn/S compositions are measured by EDX/WDX (Oxford instruments INCA X-MAX, 20 keV). One sample was analyzed by EBSD to determine the crystalline structure of the secondary phase using an Oxford Instruments NordlysNano EBSD detector, attached to a Zeiss Ultraplus scanning electron microscope, and the AZtec acquisition and evaluation software. Room temperature photoluminescence measurements were done in homebuilt set up (514 nm, 50 kW/cm^2). Finished devices are characterized by homebuilt current density-voltage (IV) and external quantum efficiency spectra (EQE) measurements.

3. Results and discussion

3.1. Cu$_2$SnS$_3$ formation

The metallic precursors are annealed in S and SnS vapor. SnS vapor is required to stop Sn losses from the front surface of the forming Cu$_2$SnS$_3$, via release of volatile SnS [14,15]. Fig. 1 top shows the GI-XRD of the absorber layers annealed at 480, 490 and 520 °C (referred to as S480, S490 and S520 respectively). All samples show peaks belonging to a Cu$_2$SnS$_3$ polymorph of which S520 shows clearly the monoclinic structure and an additional phase assigned with *. Above 520 °C no significant phase changes in the diffractogram are found, see S1. S480 and S490 show a mixture of Cu$_2$SnS$_3$ polymorphs; there are signatures of the monoclinic phase but not all of the minor peaks are visible. The inset in Fig. 1 top shows that the main peak is at 28.4° for all samples, with only a little broadening for S480, which could