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Sn-deficiency in the electrodeposited ternary Cu$_x$Sn$_y$S$_z$ thin films by ECALE

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ABSTRACT

Ternary Cu$_x$Sn$_y$S$_z$ thin films with different Cu/Sn atomic ratios and thicknesses have been electrochemically deposited on the (111) face of a silver single crystal. The surface morphology and chemical composition of these chalcogenides, which have attracted considerable worldwide interest as low cost high conversion efficiency photovoltaic devices, have been characterized by means of SEM, parallel angle resolved (PAR-XPS) and TOF-SIMS depth profiling in order to gain insight into the morphology and element distribution within the layer and their effect on the band gap.

This study constitutes the first in-depth chemical study on Cu$_x$Sn$_y$S$_z$ thin films, providing evidence of notable discrepancies between the expected and real composition, especially regarding the Cu/Sn ratio. The samples were found to be chemically homogeneous through the whole deposit even though strongly tin depleted regardless their thickness or deposition sequence. Finally, the literature band gap data were discussed on the basis of these findings.

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1. Introduction

The progress in thin film solar cell technology represents one of the main technological breakthroughs for the development of a planet-scale economy based on renewable energy and the replacement of fossil fuels as supply of primary energy. Nevertheless, for such thin film solar cell technology to become viable, the development of low-cost deposition methods is essential. In fact, not only do we need materials with high energy-conversion properties, but it is also vital that large amounts of these materials are available to allow the mass production of cheap and efficient devices. The energetic and environmental costs of these devices must be considered in terms of their whole life-cycle. Hence, the device production, as well as their end-of-life issues, as recycling/disposal methodologies, must be rigorously taken into account. In the light of these considerations, devices based upon rare (indium, gallium, germanium, tellurium) or toxic (selenium, cadmium) elements must be avoided in all layers of new thin film solar devices [1–3].

The industrial interest is therefore moving towards the realization of cost-effective thin film solar cells based on relatively common, inexpensive and non-toxic elements. In this context, ternary (kuramite, Cu$_3$SnS$_4$) and quaternary (stannite, Cu$_2$FeSnS$_4$, and kesterite, Cu$_2$ZnSnS$_4$ or CZTS) chalcogenides are attracting increasing interest from researchers worldwide, due to their good performance based on relatively simple chemistry and the absence of significant economic or environmental concerns related to their production, use and disposal [4–6]. Multinary chalcogenides are usually synthesized by using high temperature and/or vacuum techniques. To further improve the competitiveness of these materials, viable routes that avoid the need of expensive high vacuum techniques, without loosing conversion efficiency, are being actively investigated [7,8].

Although, to date, there have been only a few reports regarding the preparation of CZTS solar cells entirely via non-vacuum

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techniques [8–10], the use of facile and scalable techniques is a mandatory step to further improve the competitiveness of thin film modules for photovoltaic applications [10–12]. Among the non-vacuum techniques, electrodeposition [13–15] and, especially, ECALE (Electrochemical Atomic Layer Epitaxy) represent the most promising alternative routes to deposit ternary chalcogenides [16]. The formation of a monolayer of the compound by ECALE consists of the alternating underpotential deposition of the metallic element and the underpotential deposition of the non-metallic element. The redox potential, pH and reactants can be adjusted to optimize the deposition process. In this perspective, the ECALE technique is a valid approach for the attainment of II–VI [17–20], III–V [21–23] compounds, as well as ternary and quaternary semiconductors on conductive substrates [24,25].

Clearly, the characteristics of the deposits change as a function of the deposition conditions, the number of cycles and the chemical composition. Since these differences can affect the optoelectronic properties, an in-depth knowledge of the physicochemical and morphological characteristics is mandatory for the optimization of these materials and their development for the mass production of photovoltaic devices.

In this study, we provide a detailed morphological and chemical description of ECALE-deposited $Cu_xSn_yS_z$ thin films characterized by different thicknesses and nominal Cu/Sn ratio highlighting, for the first time, considerable differences between the nominal and real composition of the compounds.

2. Materials and experimental setup

2.1. Sample preparation

The ternary compounds were prepared alternating the underpotential deposition of sulfur with that of copper and tin on Ag (111) [26]. A sketch depicting the underpotential deposition of ternary sulfides is illustrated in Fig. 1.

In principle, the stoichiometry of the electrodeposited ternary sulfide can be tuned using different deposition sequences, i.e. combining different numbers of ECALE cycles of each binary compound. In the same way, the thickness of the deposit can be controlled as a function of the number of cycles used, making this electrochemical approach very versatile. In this study, following the procedure previously described [26], two sets of $Cu_xSn_yS_z$ thin films were prepared and investigated; a thinner deposit, 10 cycles (S/Sn/S/Cu; 20 sulfur atomic layers) with a Cu/Sn=1 nominal ratio named sample #1 and a thicker one, twenty cycles (S/Sn/S/Cu/S/ Sn; 60 sulfur atomic layers) with double the amount of tin, Cu/ Sn=0.5 nominal ratio named sample #2. Table 1 resumes the details of both samples.

2.2. Characterization methods

Sample morphology and uniformity were determined by a Scanning Electron Microscope (SEM; Hitachi S-2300) operating at 20 kV.
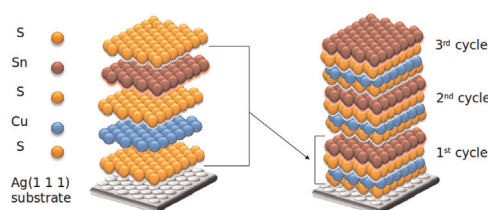

Fig. 1. Schematic representation of ternary compound thin film growth by means of alternating electrodeposition of S, Cu and Sn layers.

Table 1
Type of Ag/S/((Cu/S)k(Sn/S)j)n samples prepared.

Sample	Expected Cu/Sn ratio	Number of deposition cycles (n)	Number of sulfur layers
Sample #1 ($k=1$; $j=1$)	1	10	20
Sample #2 ($k=1$; $j=2$)	0.5	20	60

Near-surface chemical composition was obtained by means of X-ray Photoelectron Spectroscopy (XPS) measurements performed in an ultra-high vacuum system. Conventional XPS analyzes were performed using a VSW HAC 5000 hemispherical electron energy analyzer and a non-monochromatized Mg-Kα X-ray source (1253.6 eV). The source power was 100 W (10 kV × 10 mA) and the spectra were acquired in the constant analyzer energy mode (CAE) at pass energy E_{pas}=44 eV. The overall energy resolution was 1.2 eV, as full-width at half-maximum (FWHM), for the Ag $3d_{5/2}$ line of a pure silver reference. The recorded spectra were fitted using CasaXPS software employing Gauss–Lorentz curves after subtraction of a Shirley-type background.

The samples were introduced in the UHV system via a loadlock under an inert gas (N_2) flux, in order to minimize the exposure to air contaminants, and kept in the introduction chamber for at least 12 h before the measurements. Ion sputtering was performed using an argon beam (chamber pressure 10^{-7} mbar) at 2 kV and 20 mA current.

Parallel angle resolved XPS (PAR-XPS) analyzes were carried out using a Thermo Fisher Scientific Theta Probe Spectrometer equipped with a monochromatic AlKα source (beam spot diameter 300 μm) operating in CAE mode. Samples were not sputtered before analysis. Survey and high-resolution spectra (C1s, O1s, Ag3d, Cu2p, Sn3d, S2p, Cl2p, Na1s, Ag $M_{4,5}N_{45}N_{45}$, Cu $L_3M_{45}M_{45}$) were acquired at E_{pas} of 150 and 100 eV, respectively, and with a step size of 1.0 and 0.1 eV, respectively. Binding Energy (BE) scale was calibrated taking as reference the position of aliphatic C1s component (adventitious carbon) at 284.8 ± 0.1 eV. Curve-fit and element quantification were performed processing high-resolution XP spectra by Thermo Avantage software (v. 4.75, © 1999–2010).

Six emission angles (θ, angle measured with respect to the sample surface normal) were selected between 28° ("bulk" angle) and 78° ("surface" angle) with a 10° step, to collect angle resolved XP spectra. The overall acquisition time was kept well below 1 h per sampled point, as a good compromise between acceptable signal-to-noise ratio and prevention from X-ray artefacts. At least three sampling points were averaged to evaluate the surface chemical composition. No changes in the lineshape were observed within the analysis run time, as assessed by repetitive spectra acquisitions at regular intervals during the experiment.

TOF-SIMS depth profiling was achieved measuring positive secondary ion spectra in the mass range of 0.5–400 m/z using an upgraded VG Ionex IX23LS TOF-SIMS [27,28]. A focused liquid–metal Ga$^+$ gun MIG 300PB in the pulsed mode (6 kHz/40 ns) was employed as a source of probing ions. A beam current in the continuous mode at 14 keV of the primary energy was 15–20 nA. During analysis the Ga$^+$ beam was scanned over an area of 220 μm × 140 μm (10 kHz, 128 × 128 pixels). Data acquisition time was 60 s; the sample potential was +5 kV (the impact energy of the analysis ions was 9 keV).

Sputter depth profiling was carried out in the dual beam mode using a duoplasmatron DP50B as a sputter ion source of O_2^+ ions with 8 keV bombarding energy (samples were grounded during the sputtering cycle). The sample current was ca. 100–120 nA, raster size ca. 1 mm^2 (10 kHz, 128 × 128 pixels), and the time of