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# Non-stoichiometry effect and disorder in $Cu_2ZnSnS_4$ thin films obtained by flash evaporation: Raman scattering investigation

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## Abstract

The cation disorder in $Cu_2ZnSnS_4$ thin films grown by flash evaporation of ZnS, CuS and SnS binary compounds has been studied by Raman spectroscopy. Process parameters such as the substrate temperature during the evaporation and the Ar pressure in the post-thermal treatment determined the samples' composition and Raman spectra. As a measure of cation disorder, the half-width and relative intensity of the Raman band peaking at 331–332 $cm^{-1}$ is analysed. Comparison of the spectra for different samples of known composition showed that the relative intensity of the 331 $cm^{-1}$ defect peak correlates with the previously reported theoretical prediction about enhancement of antisite defect formation in $Cu_2ZnSnS_4$ under "Cu-poor, Zn-rich" conditions. For "Cu-rich, Zn-poor" films, further experimental confirmation was obtained of the previously detected effect of the enhancement of cation disorder under intense optical excitation.

*Keywords:* $Cu_2ZnSnS_4$; Solar cells; Cation disorder; Non-stoichiometry; Raman scattering

## 1. Introduction

Recently $Cu_2ZnSnS_4$ (CZTS) and similar quaternary chalcogenides have received considerable attention as potential materials for new-generation thin-film solar cells. The reasons for their appeal are their suitable direct band gap energy of about 1.5 eV, large optical absorption coefficient of $10^4$–$10^5$ $cm^{-1}$, and the fact that all constituents of CZTS are abundant in the Earth's crust, non-expensive and non-toxic. During last decade the efficiency of CZTSSe-based solar cells has been improved significantly and has reached 11.1% [1–3].

The efficiency of CZTS in photovoltaics is determined principally by the structural features of this material. This compound can be formed in two crystallographic structures: kesterite (KS) (space group $I\bar{4}$) and stannite (ST) (space group $I\bar{4}2m$) [2]. The kesterite structure possesses lower formation energy. However, s the binding energy difference between KS and ST is small (3 meV/atom according to calculations) [2,3], the object of the numerous experimental works published to date has been to determine the real structure of the samples obtained by different methods. It has been shown experimentally that CZTS usually crystallizes in the kesterite structure, but the problem is that the latter may contain a very high concentration of intrinsic defects related to non-stoichiometry in the cation sublattice [4]. The similarity of the properties of Cu and Zn atoms reduces significantly the ability of traditional X-ray diffraction to investigate this problem. In particular, a reliable identification of antisite-defects such as $Cu_{Zn}$ and $Zn_{Cu}$, which essentially define the electrical characteristics

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of the samples, requires more expensive techniques such neutron scattering and synchrotron radiation [5–9]. The dominance of different sorts of intrinsic defects in CZTS prepared by different methods is not only an interesting fundamental problem, but also a crucial issue for practical applications. It is known that the defects formed in CZTS under Cu-poor and Zn-rich growth conditions should be beneficial for solar cell performance [1].

The problem of non-stoichiometry in crystalline CZTS samples obtained by the Bridgman method and solid-state reaction of pure elements has been studied by means of Raman spectroscopy in our previous reports [10–12]. This issue was also discussed for CZTS films grown by pneumatic spray pyrolysis in Ref. [13]. Disordering of the cation sublattice for non-stoichiometry (Cu-poor, Zn-rich)-type CZTS material is accompanied by the appearance of a new Raman band at about 331 $cm^{-1}$. This band has properties of A-mode and is observed either simultaneously with or instead of the A-mode of the "normal" (i.e. ordered) kesterite, peaking at 338 $cm^{-1}$ [10–12]. The structure with a significant concentration of Cu–Zn antisite defects is called disordered kesterite [8,9] and is characterized by a change in the symmetry of the crystal lattice from $I\bar{4}$ to $I\bar{4}2m$ (the latter being the same as in stannite).

In this paper, we investigate the structure of CZTS thin films, obtained by flash evaporation, by Raman spectroscopy. A relationship between the spectral Raman features and growth conditions of CZTS films and their composition is established.

## 2. Experimental details

CZTS thin films were deposited by flash evaporation of ZnS, CuS and SnS binary compounds in powder form onto molybdenum-coated glass substrates at nominal substrate temperatures, $T_{sub}$, of 100 or 350 °C. The CuS and SnS powders used were synthesized in an evacuated quartz ampoule from the pure elemental constituents, while commercially available ZnS was used. A preferential re-evaporation of Zn has been observed during the flash evaporation process independent of the evaporation source used; this is related to the high partial vapor pressure of Zn [14]. Therefore, a precursor with excess ZnS was used in our deposition procedure. Table 1 summarizes the growth conditions and final chemical composition of the as-evaporated thin films. As shown in Table 1, the precursor with a ZnS excess >15% is necessary to achieve an atomic ratio of $[Zn]/[Sn] > 1$ which has been previously shown to be necessary for high-efficiency CZTS-based solar cells [1]. The composition was measured by energy dispersive X-ray spectroscopy (EDX) using an INCAx-sight spectrometer (Oxford Instruments) attached to a Hitachi S-3000 N scanning electron microscope. EDX measurements were carried out at 20 kV operating voltage and included Cu *K*, Zn *K*, Sn *L* and S *K* lines. It can be seen from Table 1 that the thin-film composition depends on the crucible temperature during evaporation, $T_{crucible}$. Lower crucible temperatures lead to higher Cu concentrations (samples F19 and F20). A substoichiometric CuS content was used for deposition of samples F26 and F27. The lower CuS content is important when the evaporation is carried out at higher substrate temperature because of an enhanced Cu incorporation at increasing $T_{sub}$. The first experiment was carried out at $T_{sub} = 100$ °C (sample F26) and no significant change in the Cu concentration was observed. In spite of the CuS content being 10% less than required for a stoichiometric compound, the resulting $[Cu]/([Zn] + [Sn])$ atomic ratio is still very high for the sample F27 grown at a substrate temperature of 350 °C.

The evaporated samples were annealed in Ar atmosphere (P = 100 or 1000 Pa) in a partially closed graphite container placed inside a quartz tube furnace. 20 mg of elemental sulfur was placed into the graphite box prior to heating. Variations of annealing temperature as well as of annealing times at maximum temperature were investigated in order to obtain a single-phase CZTS thin-film material (see Table 2). Heating rates from 10 to 21 °C $min^{-1}$ were used for the thermal treatments, and the samples were cooled down naturally. The importance of the Ar pressure is demonstrated by the different compositions obtained after applying thermal treatments 1 and 2.

Micro-Raman spectroscopy study was performed in backscattering configuration with a T64000 Horiba-Jobin-Ivon spectrometer using the 514.5 nm excitation wavelength of an $Ar^+$-ion laser. Laser radiation with power $I_o < 1$ mW was focused with a 50 × objective to a spot ~1 μm in size on the sample. Due to non-uniformity of

Table 1
Nominal conditions of the flash evaporation processes and composition of the as-evaporated thin films measured by EDX.

| Sample | Nominal conditions | | | | EDX composition | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $T_{cruc}$, °C | $T_{substr}$, °C | ZnS excess, % | CuS defect, % | Cu, % | Sn, % | Zn, % | S, % | [Cu]/([Zn]+[Sn]) | [Zn]/[Sn] | [S]/[M] |
| F19 | 1075 | 100 | 20 | – | 25.29 | 9.31 | 14.99 | 50.40 | 1.04 | 1.62 | 1.02 |
| F20 | 1100 | 100 | 20 | – | 22.26 | 11.63 | 13.96 | 52.15 | 0.87 | 1.20 | 1.09 |
| F24 | 1100 | 100 | 15 | – | 23.08 | 13.21 | 11.86 | 51.85 | 0.92 | 0.90 | 1.08 |
| F22 | 1100 | 100 | 10 | – | 22.55 | 14.65 | 11.45 | 51.36 | 0.87 | 0.78 | 1.06 |
| F26 | 1100 | 100 | 15 | 5 | 23.66 | 13.78 | 13.26 | 49.30 | 0.88 | 0.96 | 0.97 |
| F27 | 1100 | 350 | 20 | 10 | 27.22 | 12.56 | 9.35 | 50.87 | 1.24 | 0.75 | 1.04 |

M = metals = Cu + Zn + Sn.