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CuInS₂ thin films grown sequentially from binary sulfides as compared to layers evaporated directly from the elements

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Abstract

CuInS₂ thin films have been obtained by rapid thermal annealing at 350 °C of binary sulfide precursors evaporated at a substrate temperature lower than 200 °C. The structure, morphology, and chemical and optical properties of these samples have been analysed and compared to CuInS₂ layers prepared directly by evaporation from the elements onto 350 °C heated substrates.

X-ray diffraction and x-ray photoelectron spectroscopy measurements showed similar structure and chemical characteristics for the CuInS₂ samples prepared by sequential and direct routes. Some differences in the optical absorption can be related to morphological variations observed by atomic force microscopy.

1. Introduction

In the last few years, polycrystalline CuInS₂ thin films have become a suitable alternative as photovoltaic absorbers for highly efficient and low-cost solar cells [1]. Main efforts have been focused on the development of preparation procedures that give high-quality material in a controlled and low-cost mode. The most extended is the sequential process consisting of the evaporation or sputtering of the metallic precursors at substrate temperature below 200 °C, and the subsequent sulfurization by heating above 350 °C in H₂S or sulfur atmosphere [1–4]. Usually, Cu is introduced in excess in the metallic precursors, because of its beneficial effect upon the grain growth of the chalcogenide film [5]. However, after the sulfurization process, the segregated Cu–S phase has to be removed by KCN treatment because of its detrimental effect on the photovoltaic performance. The use of binary sulfides instead of metallic precursors has been proven beneficial to improve the adhesion to the substrate and also to avoid formation of In-rich hillocks on the sulfurized film surface [6, 7]. Besides, intents are being performed to approach the Cu/In ratio to the unity, in order to minimize secondary phases segregation and to avoid KCN treatment [7, 8].

Several studies on CuInS₂ synthesis from the metallic precursors indicate that the sulfurization reaction is a three-step process including the intermediate formation of various intermetallics and sulfur-rich binary compounds

such as CuS and In₂S₃ which further react to form CuInS₂ [2, 3]. According to this reaction mechanism, and for avoiding intermetallics formation, we have chosen a two-step process based on the binary sulfides deposition by sequential evaporation onto conventional soda lime glasses. At a substrate temperature $T_s = 150$ °C a CuS/In₂S₃ bilayer system is formed, which reacts to CuInS₂ by a short increase to $T_s = 350$ °C. The structure, morphology, chemical and optical properties of the two-step grown samples have been analysed and compared to layers prepared in a one-step process by Cu, In and S coevaporation at $T_s = 350$ °C. From the experimental point of view, the first process has the advantage of a smaller global power consumption. In all cases, the Cu/In ratio has been approached to the unity, in order to obtain single phase ternary compounds. A similar low-temperature route to CuInSe₂ formation has been demonstrated using rapid thermal annealing on the stacked precursor structure CuSe/In₂Se₃, where the binary layers were deposited at low temperature using a plasma migration-enhanced epitaxy reactor [9]. In this study, analogous two-step route and one-step coevaporation are developed and compared for CuInS₂ formation.

2. Experimental details

Conventional 3 mm thick soda lime glasses were degreased in a dilute detergent solution, rinsed in deionized water, and blown

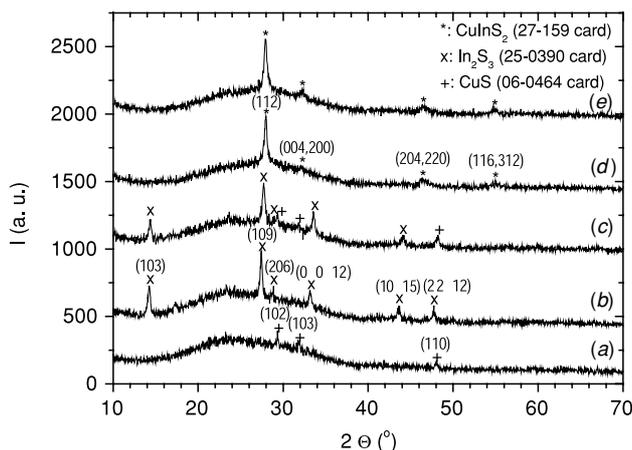


Figure 1. XRD diagrams corresponding to (a) the copper sulfide precursor layer, (b) the indium sulfide precursor layer, (c) stacked precursor layers as-grown at 150 °C, (d) stacked precursors after heating at 350 °C and (e) the copper indium sulfide layer directly grown at 350 °C.

dry in N₂ gas. Such cleaned glass substrates were introduced in an evaporation chamber, and heated to 150 °C after the base pressure achieved 10⁻⁷ mbar range. Then, copper sulfide and indium sulfide layers with a controlled thickness to give Cu/In = 1 atomic ratio were sequentially evaporated from the corresponding elemental sources, at a deposition rate that was adjusted between 5 and 7.5 Å s⁻¹. After the evaporation process, the substrate temperature was increased to 350 °C during 5 min to produce the reaction between the stacked compounds to obtain ternary CuInS₂ formation. Alternatively, and with a comparative purpose, CuInS₂ thin films were also obtained under analogous experimental conditions by coevaporation from the three elemental sources, maintaining the substrate temperature at 350 °C during all the preparation process.

The structure of the samples has been analysed by x-ray diffraction (XRD) by using the nickel-filtered Kα1 emission line of copper (λ = 1.5405 Å), in a Philips X'pert instrument. Optical measurements of the layers have been carried out with unpolarized light in the wavelength range from 300 to 1500 nm, with a double beam spectrophotometer Perkin-Elmer Lambda 9 including an integrating sphere to measure reflection as well as transmission. Film thickness was determined by profilometry. The sample topography was measured with an atomic force microscope (AFM) Topometrix TMX2000 on 3 × 3 μm² areas under ambient conditions. Surface composition of the layers was analysed by x-ray photoelectron spectroscopy (XPS) in a Perkin-Elmer PHI 5400 instrument. Composition-depth profiling was performed by sequential XPS surface analysis and Ar⁺ ion sputter etching.

3. Results and discussion

The crystalline structure of the individual and the stacked precursor layers, as-grown at 150 °C onto glass substrates, has been identified as hexagonal CuS [10] and tetragonal In₂S₃ [11] from the x-ray diffraction patterns shown in figure 1. From this figure, it can also be observed that after heating

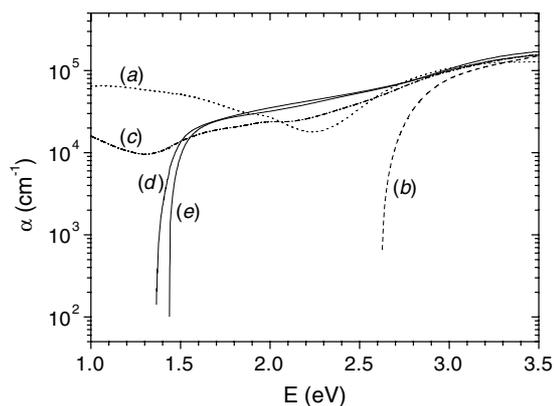


Figure 2. Optical absorption coefficient for (a) the copper sulfide precursor layer, (b) the indium sulfide precursor layer, (c) stacked precursor layers as-grown at 150 °C, (d) stacked precursors after heating at 350 °C and (e) the copper indium sulfide layer directly grown at 350 °C.

the stacked precursors at 350 °C, tetragonal CuInS₂ [12] has been obtained with the same structural characteristics that are obtained by direct coevaporation. The corresponding optical absorption coefficients (α) are shown in figure 2, as calculated from the reflectance (R) and transmittance (T) data according to the formula [13]

$$\alpha = -1/t \ln\left\{\left[\frac{(1-R)^4}{4T^2R^2} + 1/R^2\right]^{1/2} - (1-R)^2/2TR^2\right\} \quad (1)$$

being the film thickness value (t) determined by profilometry between 120 and 300 nm. For the CuS precursor layer an optical absorption edge minimum is found around 2.2 eV, while a high-absorption coefficient remains at lower energies. This is commonly observed for CuS films [14, 15], for which the near-infrared absorption is attributed to semi-metallic behaviour (free carrier absorption). The optical characteristic of the In₂S₃ precursor layer in figure 2 corresponds to a band gap value above 2.6 eV, which is typical for polycrystalline In₂S₃ thin films with small grain size [16, 17]. For the CuS/In₂S₃ stacked layers, optical absorption is not exactly the sum of the already analysed individual samples because a displacement of the absorption minimum towards a lower energy is detected. This is consistent with some reaction between the precursors during the growth at 150 °C to give CuInS₂ formation, although the structural data and the high absorption remaining in the near-infrared region indicate that such reaction between the precursors should take place to a low extent. By increasing the substrate temperature to 350 °C, the reaction to give CuInS₂ is completed, as evidenced by the lack of detection of binaries, and figure 2 shows the analogous optical characteristics for the annealed binary precursors and the ternary film directly grown. The direct band gap energy for the CuInS₂ layers prepared in the two different ways has been determined by linear fit of the α² versus photon energy plots, as is represented in figure 3. The fit results in a band gap energy E_g = 1.43 eV for the film grown from the binary sulfide precursors, slightly lower than E_g = 1.47 eV determined for the sample directly synthesized from the elements. For CuInS₂ single crystals E_g = 1.53 eV is reported [18]; however, lower energy is

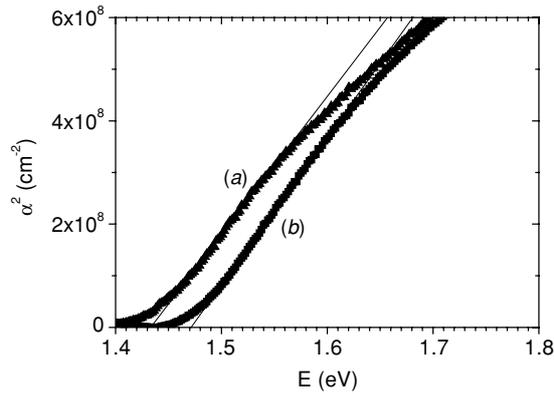


Figure 3. Band gap energy determination for the CuInS₂ thin films grown in two different ways: (a) sequentially from the binary sulfide precursors and (b) directly from the elements.

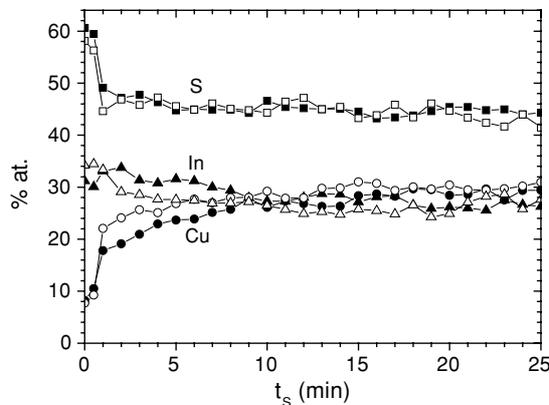


Figure 4. XPS composition depth profile for the CuInS₂ films grown in two different ways: sequentially from the binary sulfide precursors (hollow symbols) and directly from the elements (solid symbols).

usually found for polycrystalline CuInS₂ thin films, for which certain dispersion with values between 1.34 and 1.48 eV can be found [2, 19–21] depending on the layer preparation conditions. Lower band gap values are often related to higher optical absorption coefficient [19, 20].

The atomic composition, determined from the peak areas of the Cu 2p, In 3d and S 2p XPS signals, for the CuInS₂ films grown in the sequential and the direct modes is represented in figure 4 as a function of the sputtering time. These data show an indium and sulfur-rich surface composition, which becomes near stoichiometric with some sulfur deficiency in the bulk, as observed for similar CuInS₂ layers [21, 22]. The cation ratio in the most superficial region has a value $\text{In}/(\text{Cu} + \text{In}) = 0.75\text{--}0.80$ that changes to $\text{In}/(\text{Cu} + \text{In}) = 0.45\text{--}0.50$ in the bulk. This is in agreement with the data obtained by other authors [22] who indicated the possible existence of a CuIn₃S₅ phase in the near-surface region of CuInS₂ thin films with stoichiometric and In-rich bulk composition. Figure 5 illustrates the XPS near valence band spectra for the samples, after subtraction of the background. A small displacement of the valence band spectra towards lower energies has been detected in the CuInS₂ film obtained from the binary sulfide precursors as compared

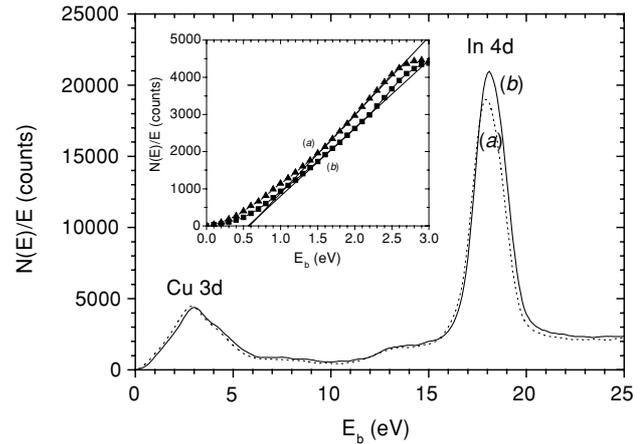


Figure 5. Valence band edge for the CuInS₂ films grown in two different ways: (a) sequentially from the binary sulfide precursors and (b) directly from the elements. Valence band maximum determination is included in the inset.

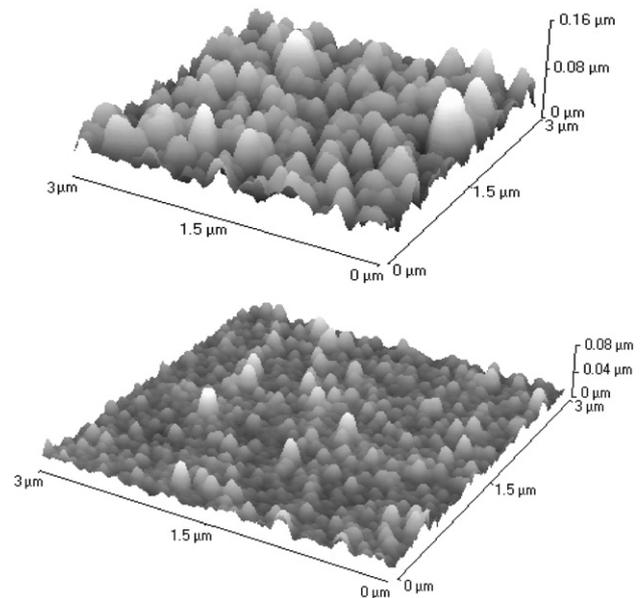


Figure 6. AFM images corresponding to the CuInS₂ thin films grown in different ways: sequentially from the binary sulfide precursors (up), and directly from the elements (down).

to the layer directly grown. For both samples, the difference between the valence band maximum E_v and the Fermi level E_F has been determined by linear extrapolation of the leading edge of the valence band spectra, as is represented in the figure inset. This gives an energy difference of 0.58 eV for the CuInS₂ film prepared sequentially and 0.56 eV for the directly grown, which can be considered the same value within the 0.01 eV accuracy estimated for the calculation [23]. Taking into account the band gap energy values obtained for the layers, the Fermi level is only slightly below the middle of the gap, as corresponds to samples with almost ideal composition [23, 24].

The sample topography is illustrated in figure 6 which shows AFM images of the CuInS₂ layers obtained by the

two different preparation routes. Both kinds of films are homogeneous, constituted of densely packed grains. The mean grain size (S) and the root-mean-square (RMS) surface roughness are higher for the CuInS₂ sample prepared from the binary sulfide precursors ($S = 250$ nm, RMS = 24 nm) as compared to that directly synthesized from the elements ($S = 150$ nm, RMS = 13 nm). It is known [25, 26] that the Cu/In ratio has a strong effect on the film surface morphology and the grain size. Usually, smooth layers are obtained for Cu/In near the unity, whereas grain size and roughness increase when the Cu/In ratio augments. This is attributed to the presence of copper sulfide phase that acts as a recrystallization agent for CuInS₂. The samples prepared sequentially from the CuS/In₂S₃ bilayer precursors can take advantage of the presence of the copper sulfide at the initial reaction stage to promote the CuInS₂ crystalline growth. Rougher surfaces constituted by larger grains can advance optical scattering making to increase the absorption coefficient, as already observed for CuInS₂ samples with a same atomic composition but different average grain sizes [19].

4. Conclusions

A low-temperature route to CuInS₂ formation has been demonstrated using rapid thermal annealing on the stacked precursor bilayer CuS/In₂S₃ evaporated at 150 °C substrate temperature. The sequentially prepared CuInS₂ layers can take advantage of the copper sulfide agent which promotes the ternary crystalline growth, and showed rougher surfaces constituted by larger grains than analogous CuInS₂ samples evaporated directly from the elements. This results in a slightly higher absorption coefficient and lower band gap energy for the sequentially deposited films. The Fermi level has been found only a little below the middle of the gap, as corresponds to almost ideal composition, for these CuInS₂ samples prepared by the sequential and direct methods.

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