PREPARATION AND CHARACTERIZATION OF $CuInS_2$ THIN FILMS FOR LOW COST SOLAR CELLS

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Thin films of copper indium disulphide were grown on indium tin oxid (ITO) coated glass substrates using a two stage process: electrodeposition of Cu-In alloys and subsequent sulfurisation. The influence of sulfurisation temperature was investigated with X-ray diffraction, scanning electron microscopy and optical measurements. Single phase chalcopyrite $CuInS_2$ films were obtained after treatment of Cu-In alloys in 5 % H_2S/Ar at 500 °C for 10 min. Indeed, only peaks from $CuInS_2$ are present in the XRD pattern after KCN etching. SEM analyses have shown that the film consisted of homogeneous grains with sizes of about few hundreds of nm in good agreement with TEM investigations. The films were copper-rich as evidenced by EDS analysis. The band gap value deduced from the optical measurements is about 1.44 eV. This value is in good agreement with that measured on sulphurised Cu-In layers obtained by high vacuum process.

Keywords: solar energy, structural materials

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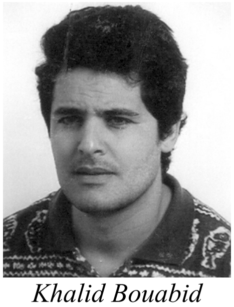

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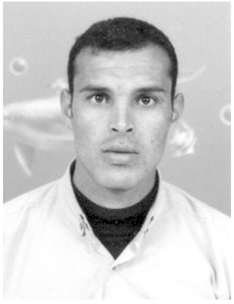

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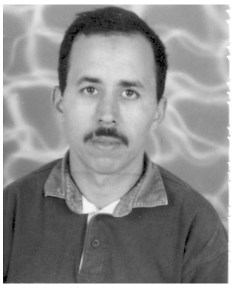

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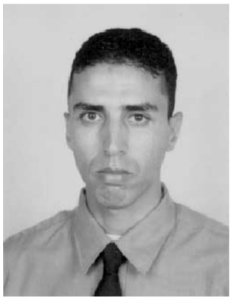

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Introduction

Because of the growing emissions of greenhouse gases like CO_2, due to the burning of fossil fuels, the average planet surface temperature is expected to rise drastically in the 21th century [1]. Such temperature increase (phenomenon known as global warming) will have a negative impact on our environment. Searching alternative sources of energy is then a vital issue for our planet. Solar energy is not only renewable and abundant but also environmentally friendly. Power obtained from solar energy finds more and more utilization worldwide. Among these alternatives, photovoltaic (PV), (direct conversion of sun energy into electricity) holds the best promise for the reduction of CO_2 emissions. Unfortunately, the price per kW for photovoltaic-electricity remains higher than its traditional energy counterpart because of the high cost of silicon single crystal based solar cells processing. Reducing the price of PV-electricity is then a major challenge for scientists and industrials. One approach to bring down the costs is the developpment of thin film solar cells. In this way, ternary chalcopyrite semiconductors, $CuInSe_2$ (CISe) and their alloys with gallium CIGSe are becoming among the leading candidates for high efficiency and low-cost terrestrial photovoltaic devices. Indeed, polycrystalline CISe and CIGSe based solar cells have achieved efficiencies of about 19 % on a laboratory scale [2-4] and around 14 % for modules [5]. However, selenium is harmful and should be avoided in mass production. Chalcogene elements such as sulphur is environmentally friendly and could be used instead of Se. $CuInS_2$ (CIS), is Se free compound and exhibits a direct band gap value of 1.5 eV suitable for efficient sun light conversion. Unfortunately, the best reported conversion efficiency for CIS based solar cells is 12.7 % [6, 7] less than those obtained with CISe based solar cells. In the present paper we report on some results concerned with $CuInS_2$ (CIS) thin films prepared by a simple, cost-effective non-vacuum process (electrodeposition).

Experimental methods

Electrochemical process was used to prepare CuIn thin films onto commercially available indium tin oxide (ITO) coated glass substrates. The substrates were thoroughly degreased with isopropanol, and cleaned ultrasonically in distilled water and finally dried under nitrogen. The deposition was carried out at room temperature using three electrodes potensiostat system with a saturated calomel electrode (SCE) as the reference electrode and platinum as the counter electrode. The concentration of precursors were chosen to be $CuSO_4$ $3{\cdot}10^{-3}$ M, $In_2(SO_4)_3$ $3{\cdot}10^{-3}$ M. The pH of the solution was adjusted to 2 using concentrated sulfuric acid. Citric acid (0.1 M) was used as a complexing agent and K_2SO_4 (0.1 M) was used as supporting electrolyte. The polarization curves were investigated at a sweep rate of 10 mV/s. All the films were grown at a potential of -0.6 V (vs. SCE). The obtained films were then sulfurised under a continuous flow of 5 % H_2S/Ar atmosphere at 300, 400 and 500 °C for 10 minutes. The optical properties were carried out with a spectrophotometer Cary 500 (Varian) and Shimadzu UV-3101 UV-Visible-IR spectrophotometer operating in the wavelength range 320 to 3200 nm.

The structural properties of all the obtained films were analyzed by X-Ray diffraction (XRD) using Philips PW 1840 diffractometer with CuK_α source (λ = 15418 Å). The morphology of the samples surface was investigated with the help of JEOL 5500 electronic microscope for scanning electronic microscopy (SEM) and transmission electron microscopy (TEM).

Results and discussion

Fig. 1 shows the SEM micrographs of the CuIn layer sulfurized at 500 °C under 5 % H_2S/Ar atmosphere during 10 min.

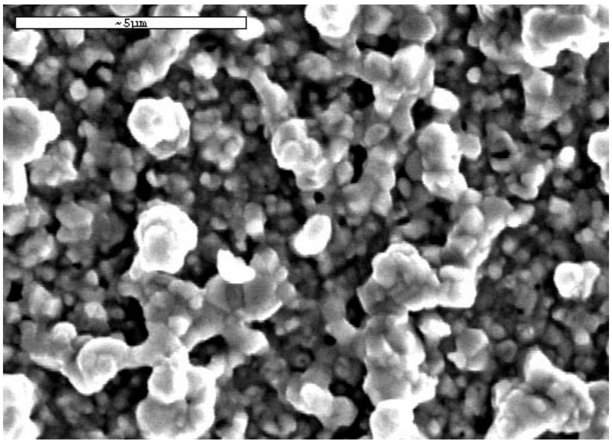

Fig. 1. *SEM micrograph of CuIn layer sulfurised at 500 °C under 5 % H_2S/Ar during 10 min*

This figure suggests a good morphological aspect of the CIS film. It shows a good and uniform coverage of the surface of the substrate. The film consists of grains with a size of about 1 µm. No pinholes are observed. However, one can notice the blurred structure of the film probably due to the presence of secondary phases like Cu_xS. These results are comparable to those reported on $CuInS_2$ thin films prepared by rf-sputtering in our previous work [8].

The XRD pattern corresponding to this sample is shown in Fig. 2:

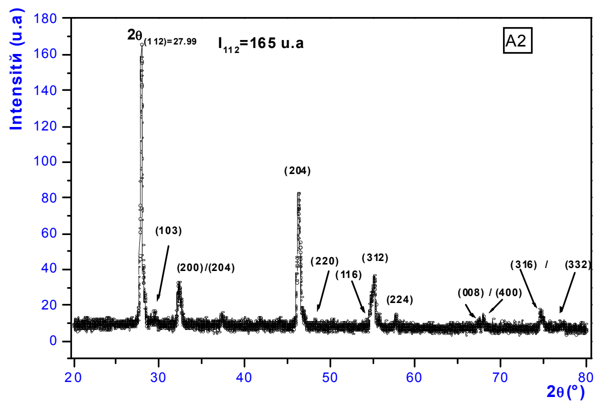

Fig. 2. *XRD pattern of CuIn layer sulfurised at 500 °C under 5 % H_2S/Ar during 10 min*

The sharpness of the peak at 2θ = 27.6° suggests a good cristallinity of the film. This observation is in good agreement with that reported by other authors [9].

EDS analyses performed on this sample have shown that our film is copper-rich. Atomic percentage of the elements are the next: Cu: 35.65 %, In: 17.24 %, S: 47.11 %. Fig. 3 shows the SEM micrograph of the sample of Fig. 1 after KCN etching.

This attack has removed the superficial layer and has lead the appearance of weak coverage of the substrate. The atomic percentage of the elements deduced from EDS analysis is the next: Cu: 28.05, In: 22.57, S: 49.38. The film is still copper rich, however, the atomic ratio Cu/In is 1.24 instead of 2 before KCN etching.

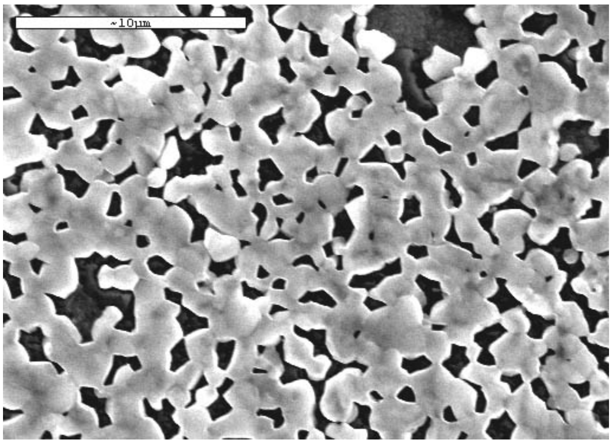

Fig. 3. *SEM micrograph of the sample of Fig. 1 after KCN etching during 3 min*

TEM image of the film of Fig. 3 is shown in Fig. 4. The film consists on grains of about few hundreds of nm, in good agreements with SEM observations.

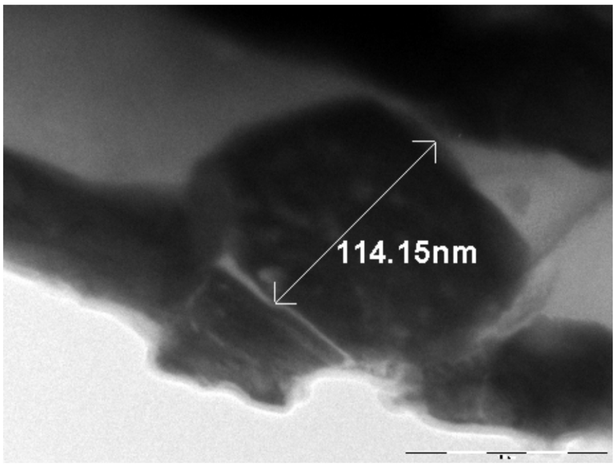

Fig. 4. *TEM image of the sample of Fig. 3*

Optical measurements have shown that our film is highly absorbing. Absorption values as high as 10^5 cm^{-1} were measured on our sample. The band gap value deduced from optical measurements is about 1.44 eV. This value is in good agreement with that measured on sulfurised Cu-In layers obtained by high vacuum process [8] and close to 1.5 eV suited for the photovoltaic conversion of solar energy.

Conclusion

Non-vacuum process was used to prepare good quality $CuInS_2$ thin films. The technique consists in the preparation of CuIn layers by electrodeposition and a subsequent sulfurisation in 5 % H_2S/Ar atmosphere. The obtained films were polycrystalline and copper rich. The grain size is about few hundreds nm. KCN etching procedure has lead to the formation of the well known chalcopyrite $CuInS_2$ single phase. The films are highly absorbing with an absorption coefficient close to 10^5 cm^{-1} and exhibit a band gap value close to 1.5 eV suitable for solar energy conversion.

Acknowledgements

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