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Preparation and optical absorption of electrodeposited or sputtered, dense or porous nanocrystalline $CuInS_2$ thin films

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Abstract

Copper indium disulphide thin films were obtained by one-step deposition with two different techniques. Films are synthesised by electrodeposition using a single electrolytic bath and by r.f. sputtering using a single target. Deposition rates were about 75 nm/min and 2.5–6.5 nm/min, respectively. Electrodeposited films have rough and porous surfaces, with no preferential orientation. Smooth or particle-covered surfaces were observed for sputtered films with a highly (112)-oriented chalcopyrite structure. Absorption coefficients calculated from transmittance spectra have high values in visible range. Electrodeposited samples present higher absorption coefficients on a larger wavelength range. A relationship between morphology and optical properties was found; absorption coefficients increase with porosity and roughness of the films. Band gap values of about 1.3 eV for electrodeposited and 1.5 eV for sputtered thin films were calculated. ***To cite this article: R. Cayzac et al., C. R. Chimie 11 (2008).***

Résumé

Des couches minces de disulfure de cuivre et d'indium ($CuInS_2$) ont été obtenues en une seule étape grâce à deux techniques de déposition. Les films ont été synthétisés, d'une part, par dépôt électrochimique en utilisant un bain électrolytique, d'autre part, par pulvérisation cathodique radiofréquence grâce à l'utilisation d'une cible unique de $CuInS_2$. Les vitesses de déposition sont, respectivement, de l'ordre de 75 nm/min et de 2,5–6,5 nm/min. Les films déposés par voie électrochimique sont caractérisés par une surface rugueuse et poreuse. Aucune orientation préférentielle n'est observée. En revanche, des surfaces lisses ou couvertes de particules ont été observées pour les films obtenus par pulvérisation cathodique avec une orientation préférentielle selon la direction (112). Les coefficients d'absorption calculés grâce aux spectres de transmission optique ont des valeurs élevées dans le visible. Les échantillons obtenus par déposition électrochimique présentent un coefficient d'absorption plus élevé dans un domaine de longueur d'onde plus étendu. Une relation entre morphologie et propriétés optiques a été mise en évidence ; le coefficient d'absorption augmente avec la porosité et la rugosité de la couche. Les valeurs de *band-gap* calculées sont de 1,3 eV pour les couches déposées électrochimiquement et de 1,5 eV pour les couches obtenues par pulvérisation. ***Pour citer cet article : R. Cayzac et al., C. R. Chimie 11 (2008).***

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1. Introduction

Multicrystalline silicon is today mainly used to build p–n homojunction solar cells with conversion efficiencies around 15%. Unfortunately, solar electricity is still too expensive [1] and two approaches are investigated to overcome this problem. First, solar cells using smaller quantities of new materials are developed, including heterojunctions between different nanocrystalline semiconductors. The chalcopyrite compound family $Cu(In,Ga)(Se,S)_2$ provides some of the most efficient thin film solar cells [2]. This is mainly due to the high light absorption coefficient of these compounds and a band gap value between 1 and 2.4 eV, which is suitable for photovoltaic application [3]. High efficiencies about 19% have been achieved in laboratory using chalcopyrite based solar cells [2]. The main problem is the use of a toxic selenium gas treatment. Many studies are presently focused on the use of sulfured compounds such as $CuInS_2$. Efficiency of 12.5% [4] has been obtained using $CuInS_2$ thin film based solar cells.

The second approach is focused on the deposition techniques of these materials. The up-scaling of vacuum-based technologies is believed to reduce manufacturing cost effectively. One of the most used vacuum deposition techniques for $CuInS_2$ synthesis is reactive sputtering [5]. Other works focused on ion plating or r.f. sputtering without H_2S processing [6–8] to obtain chalcopyrite semiconductors. For example, a two-phase sputtering target, composed of Cu_2S and In_2S_3, has been successfully used [6,7] to prepare $CuInS_2$ thin films. However, in all these cases, chalcopyrite phase is obtained by heating the substrates (400 °C).

An alternative is the use of low-cost thin film deposition techniques. These studies investigated principally chemical bath deposition [9], spray pyrolysis [10] and electrodeposition [11]. However, in precedent electrodeposition and spray pyrolysis techniques, a sulfuration step under H_2S gas or sulfur vapour is used in order to control the sulfur concentration in films, or toxic KCN is used to remove secondary copper-rich phase, particularly in spray pyrolysis. In order to avoid such treatment, chemical bath deposition [9] and one-step electrodeposition technique has been successfully used [12–14].

The aim of the present work is to develop direct and safe preparations of nanocrystalline $CuInS_2$ thin layers using one-step electrodeposition and one-step r.f. sputtering [15]. In the context of electrochemistry, sulfur is present in solution as sodium thiosulfate. Moreover, concentration of copper, indium and sulfur precursors was chosen in order to avoid the presence of secondary phases and therefore the use of KCN. For physical vapour deposition, a crystalline chalcopyrite $CuInS_2$ target prepared by solid reaction was used for the first time, making sulfuration treatment unnecessary.

The point of this study is to present the characteristics of $CuInS_2$ thin films obtained by both techniques, especially their optical properties. At this stage, it is important to note that a so-called *comparative study of sputtered and electrodeposited CI(S,Se)* has been recently published [16]. However, this paper compared $CuInS_2$ thin layers prepared by sputtering with $CuInSe_2$ thin layers synthesised by electrodeposition, considering microstructural and structural aspects. In our work, $CuInS_2$ films were prepared by one-step deposition techniques in order to obtain various structures and microstructures. Furthermore, the objective is to discuss the influence of structure and morphology on the optical absorption of $CuInS_2$ thin films in order to improve solar cells' properties in the future.

2. Experimental details

2.1. Sputtered films

A crystalline $CuInS_2$ target was prepared by mixing Cu_2S (Alfa Aesar, 99.5%) and In_2S_3 (Aldrich, 99.99%) powders. The resulting mixture was calcined at 950 °C for 2 h under vacuum. X-ray Diffraction (XRD) patterns, recorded with a Siemens D5000 Diffractometer using Cu Kα radiation ($\lambda = 0.154$ nm), showed that a crystalline $CuInS_2$ chalcopyrite phase was obtained with only 1% Cu_2S remaining in the mixture. The resulting powder was then cold pressed in a 4-cm-diameter dye. Energy dispersive X-ray spectroscopy confirmed chalcopyrite composition of the target.

Thin films were prepared by r.f. sputtering at 13.56 MHz frequency using argon plasma in a home-made deposition device. The distance between the target and the substrate was set at 3 cm. ITO glass (Sigma–Aldrich) was used as substrate, cleaned ultrasonically in organic solvents and rinsed in deionised water. The substrate temperature was kept near room temperature. Argon pressure, sputtering power and