E-MRS Spring meeting 2009, Symposium B

Effect of the growth temperature on chemical composition of spray-deposited CuInS₂ thin films

A. Katerski, M. Danilson, A. Mere, M. Krunks*

Department of Materials Science, Tallinn University of Technology, Ehitajate tee 5, EE-19086 Tallinn, Estonia

Abstract

CuInS₂ films were deposited by spray pyrolysis method at 250 °C and 350 °C using aqueous solutions of CuCl₂, InCl₃, and SC(NH₂)₂ at molar ratio of precursors Cu:In:S=1:1:3 in spray solution. Films were characterized by X-ray diffraction (XRD), Raman and X-ray photoelectron spectroscopy (XPS) techniques. According to XPS, the films grown at 350 °C have Cu²⁺ containing pieces on the surface, the film composition in bulk region is not homogeneous and contains metal bonded oxygen in amount of 5-8 at.%. Deposition at 250 °C reduces the content of oxygen down to ~ 1 at. %, the films are low-crystalline with uniform distribution of the elements throughout the film and contain some excess of sulfur compared to stoichiometric CuInS₂.

© 2009 Published by Elsevier B.V.

Keywords: CuInS₂; Spray Pyrolysis; Thin Films; X-ray photoelectron spectroscopy; X-ray diffraction

Introduction

CuInS₂ (CIS) with chalcopyrite structure has been successfully used as a light absorber material in different types of solar cells. Optimum band gap of 1.5 eV, high absorption coefficient (more than 10⁴ cm⁻¹) and chemical stability make this material important for photovoltaic applications. Thin film solar cells with CIS absorber made by rapid thermal processing and reactive magnetron sputtering techniques exhibit conversion efficiencies of 11.4 % [1, 2]. For economical reasons, it will be useful to prepare thin films using a low-cost deposition technique. One of such methods is spray pyrolysis technique, which allows obtain large-area films at extremely low cost [3, 4]. Extremely thin absorber layer (ETA) cells with sprayed CIS absorber show conversion efficiencies ~ 7 % [5] and ~ 4 % [6], made on TiO₂ or ZnO nanostructures, respectively. The control of the film surface and bulk composition is extremely important to optimize the film preparation conditions to obtain the absorber material with properties suitable for efficient photovoltaic structures. X-ray photoelectron spectroscopy (XPS) employing argon ion sputtering is a technique to obtain this information. In the literature, there are few investigations on chemical composition of sprayed CIS films by XPS [7-9]. CIS films obtained by spray of Cu-rich solution resulted in the films with In-rich surface [7, 9] and contain In₂O₃ as a secondary phase [8, 9] which one is segregated at the grain boundaries [8]. The aim of the present study is to show the effect of the CIS deposition temperature on the properties of the thin films when spraying aqueous solutions with equimolar concentrations of indium and copper.

* Corresponding author. Tel.: +372 620-33-63; fax: +372 620-20-20.
E-mail address: malle@staff.ttu.ee.
chlorides. The films are characterized by XRD, Raman and XPS techniques. The effect of deposition temperature on the structure and elemental composition of spray-deposited CIS films is discussed.

Experimental

CuInS₂ films were deposited by spray of an aqueous solution containing CuCl₂, InCl₃ and SC(NH₂)₂ at precursors molar ratio of Cu:In:S=1:1:3 onto the preheated glass substrates. The films were deposited at growth temperatures of 250 or 350 °C whereat other deposition parameters such as spray solution volume of 50 ml, solution concentration ([Cu²⁺] = 2 mmol/l) and feeding rate were kept constant for all samples.

The crystal structure of the sprayed films was characterized by XRD patterns recorded on a Rigaku Ultima IV diffractometer. Micro-Raman scattering measurements were performed at room temperature with the excitation wavelength of 532 nm and output power of 2 mW on Horiba Jobin Yvon Model HR 800 spectrometer. X-ray photoelectron spectroscopic (XPS) measurements were performed using a Kratos AXIS Ultra DLD X-ray Photoelectron Spectrometer in conjunction with a 165 mm hemispherical electron energy analyser and delay-line detector. Analysis was carried out with monochromatic Al Kα X-rays (1486.6 eV) operating at 15 kV and 225 W. All XPS spectra were recorded using an aperture slot of 300 x 700 microns and pass energy of 20 eV. Binding energy values for CuInS₂ were calculated on the basis of the C1s peak at 285.0 eV. The atomic concentrations were determined from Cu2p₃/₂, In3d₅/₂, O1s, S2p, Cl2p and Si2p core level peak areas and sensitivity factors provided by the Vision 2.2.6 analysis software. To obtain information of the film bulk composition, minibeam I ion (Ar⁺) source (4 kV, 20 mA, 5×10⁻⁸ Torr, 60 s per cycle) has been used for the depth profiling.

Results and discussion

Figure 1 presents the XRD and Raman spectra of the films deposited at 250 and 350 °C. According to XRD (Fig. 1a), the film grown at 250 °C has poor crystallinity, the main diffraction peaks are belonging to the CuInS₂ phase (PDF card No. 00-027-0159). An additional diffraction peak at 2θ=26.4° (marked by ‘x’ in Fig. 1a) is recorded and could belong to InₓSₙ or CuIn₅S₈ phases [11]. Deposition at 350 °C leads to narrowing of the diffraction peaks indicating an increase in crystallite size. The crystallite size of 8 and 20 nm have been calculated from the XRD patterns of sprayed films deposited at 250 and 350 °C, respectively. The film grown at 350 °C show an additional diffraction peak at 2θ=30.5° belonging to the (222) diffraction peak of In₂O₃ phase (PDF card No. 00-006-0416). These results are in good correspondence with the earlier results on spray-deposited CIS films [3, 10, 11]. Fig. 1b shows the Raman spectra of as-deposited CIS films grown at 250 and 350 °C. It can be seen that the most intensive Raman band consists of two bands, A₁ band of chalcopyrite (CH) ordered compound at 294 cm⁻¹ and A₁* band of Cu–Au (CA) ordered phase at 305 cm⁻¹ [11]. Although the crystallinity of the films was strongly affected by the deposition temperature (Fig.1a), the short-range ordering of sprayed CuInS₂ films is similar and almost independent of the deposition temperature in the temperature region of 250-350 °C (Fig 1b).
According to XPS spectra of CIS films prepared by spray of aqueous solutions with molar ratio of precursors Cu:In:S=1:1.3 at 250 and 350 °C, the binding energies (BE) of Cu2p3/2, In3d5/2 and S2p core levels are placed at 932.5 eV, 445.0 eV and 162.0 eV, respectively. The binding energies recorded correspond to that of copper, indium and sulfur in spray deposited CIS films [7, 9]. The O1s core level peaks at BE of 532.0 and 530.0 eV, characteristic of oxygen in adsorbed (OH) groups and oxygen bonded to metal (Me-O) [12], respectively, were present in the XPS spectra recorded from the film surface. Also weak response from Cl2p at BE=198.7 eV has been detected in XPS spectra due to contamination originated from the metal chloride precursors. Content of chlorine impurity was about 1.0-1.5 at. % in the film deposited at 250 °C, its content drops below 1 at. % when the film was prepared at higher temperature.

Figure 2 presents XPS spectra of Cu2p3/2, O1s and S2p core levels of CIS film deposited at 350 °C after different Ar+ ion etching cycles. Number of the Ar+ sputtering cycles is given in the graphs: the upper spectrum is recorded from the non-cleaned surface, by increasing the number of etching cycles the signal is recorded from the film bulk region down to the substrate. Due to similarity of In3d binding energies in CulnS2 and in possible secondary phases such as In2O3, In2S3 etc., the chemical shift of In3d core level peak was not observed. Independent of the deposition temperature and profiling depth, the BE of In3d5/2 is located at 445.0 eV. This is a reason do not present In3d spectra in Figure 2. The second Cu2p3/2 core level peak at 935.0 eV and shake-up satellites in the BE region of 940-944 eV, both characteristic of Cu2+ state [13], are recorded from the non-cleaned surface (Fig.2). Also the second peak of S2p core level at BE=168.9 eV, corresponding to sulfur in sulfates, was detected on the surface (Fig. 2). These extra peaks were not detected after Ar+ sputtering. The intensity of O1s core level peak at BE= 532.0 eV (Me-O) is decreasing from the film surface to bulk. It can be observed that the Me-O peak intensity increases before the signal at BE=533.6 eV, characteristic of oxygen in silicates (in glass) [12], becomes apparent.

In the case of CIS films deposited at 250 °C, the secondary peaks of Cu2p3/2 and S2p core levels with BE of 935.0 eV and 168.9 eV, respectively, were not detected on the film surface (XPS spectra of the films deposited at 250 °C are not presented). The O1s peak at BE=532.0 eV was present in the spectrum recorded from non-cleaned surface and refers to the surface contamination from ambient. The intensity of O1s line at BE=530.0 eV was low on the surface and in the film bulk. The positions as well as the intensities of Cu2p3/2, In3d5/2 and S2p core level peaks were constant throughout the film.

The atomic concentrations of the elements vs. the number of Ar+ ion sputtering cycles of the films deposited at different temperatures are presented in Figure 3. Figure 3a shows the results of the depth profiling analysis of CIS film deposited at 350 °C. It can be seen that the distribution of the elements in the film is not constant and the film thickness could be divided into three regions. Non-uniform distribution of In and Cu is characteristic for the first (surface) region, where at Cu/In is much lower than 1. In the second region, the composition is still In-rich, but concentrations of In, Cu and O are almost constant and concentration of sulfur starts to decrease. In the third
region, the concentration of sulfur is decreasing from about of 44 to 30 at. % and is accompanied by an increase in amount of oxygen (Me-O). The presence of In$_2$O$_3$ phase was confirmed by XRD (Fig. 1a). The XPS depth profiling shows that In$_2$O$_3$ phase is present throughout the film thickness. Even more, the amount of oxygen (Me-O) is increasing (and sulfur concentration is decreasing) before the signal from glass substrate (Si) becomes apparent at about 15 Ar$^+$ sputtering cycles (Fig. 3a). It refers that In$_2$O$_3$ phase is easily formed in an initial stage of the film growth at this deposition temperature.

Concentration depth profiling of CIS film deposited at 250 ºC (Fig. 3b) shows homogeneous distribution of elements such as Cu, In and S throughout the film. Content of oxygen (Me-O) in the film is about 1 at. %. Concentration of sulfur is above 50 at. % and refers to a sulfur-rich film compared to the stoichiometric CuInS$_2$. Obviously, secondary phases such as In$_x$S$_y$ or CuIn$_x$S$_8$ could be present in the film deposited at 250 ºC. This assumption is supported by the XRD pattern of the film (Fig. 1) and is concorrent with literature data on CIS films deposited at low temperatures [8].

Conclusions

Spray pyrolysis deposition of aqueous solutions containing CuCl$_2$ and InCl$_3$ in equimolar concentrations and thiourea (Cu:In:S=1:1:3) at temperatures close to 350 ºC results in polycrystalline CuInS$_2$ films with the crystallite size of 20 nm. The films grown at 250 ºC have the crystallite size in the order of 8 nm. According to Raman spectroscopy studies both the chalcopyrite and Cu-Au ordered CuInS$_2$ phases are present, and the short-range ordering is almost independent of the growth temperature. According to XPS of the film deposited at 350 ºC, the Cu$^{2+}$ containing pieces are present on the surface of the film, the film elemental composition in the bulk region is not homogeneous, content of oxygen (oxygen bonded to metal) is 5-8 at.%. Oxygen is present in the form of In$_2$O$_3$ as also confirmed by XRD.

In this study we showed that CuInS$_2$ films with low amount of oxygen (1 at.% or less) and uniform distribution of the copper, indium and sulfur throughout the film can be produced by chemical spray pyrolysis technique in open air using the deposition temperature close to 250 ºC. These films are slightly sulfur-rich which refers that a sulfur-containing secondary phase could be present as well.

Acknowledgements

The study is financially supported by the Estonian Ministry of Education and Research (target financing project SF0140092s08) and the Estonian Science Foundation (grant ETF6954). M. Danilson likes to thank World Federation of Scientists for support.
References


