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Interfacial chemistry control in thin film solar cells based on electrodeposited $CuIn(S,Se)_2$

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Abstract

In this work, we present a study on $CuIn(S,Se)_2$ absorbers prepared by electrodeposition followed by rapid thermal annealing promising to lower manufacturing cost. However the annealed material contains copper sulpho-selenide of $Cu(S_y,Se_{1-y})$ type which is harmful for the electrical properties of photovoltaic devices. These phases are removed by a cyanide etching. Because of an intrinsic variability of absorber fabrication process, the presented survey is based on statistic approach. We highlighted the influence of a cyanide treatment on surface and bulk compositions. The surface composition follows a distribution according to a $Cu(S,Se)$–$CuIn(S,Se)_2$ system and the bulk composition agrees with $Cu(S,Se)_2$–$CuIn_3(S,Se)_5$ system. Moreover, surface composition can be modified by adjusting the cyanide concentrations of etching solution without any changes in the bulk one. It ensues that Cu(S,Se) is not only present on the surface but also in the bulk of samples.

Keywords: $CuIn(S,Se)_2$; Solar cells; Etching; Surface and bulk composition

1. Introduction

Chalcopyrite compounds of the family $Cu(In,Ga)(S,Se)_2$ have led to the highest laboratory efficiencies for thin film solar cells (19.2%) [1] and their modules have been successfully produced on an industrial scale [2–4]. However, the market share of these devices is still very small (<1%) [5]. In order Cu $(In,Ga)(S,Se)_2$-based photovoltaic modules to become a market reality, low-cost production techniques are necessary. CuIn $(S_xSe_{1-x})_2$ ($x>0.9$) can be produce combining electrodeposition method with a post thermal annealing [6,7].

However, films of $CuIn(S_x,Se_{1-x})_2$ ($x>0.9$) tend to build phase segregation like CuS (mineral name: covellite). The formation of binary phases is extremely critical for solar cells because of their metallic conductivity [8]. These phases can be removed by NaCN etching or by an optimised electrochemical process [9].

The control of etching step and parameters optimisation require the understanding of etching mechanism. We have investigated the effect of cyanide etching on surface and bulk composition of $CuIn(S_x,Se_{1-x})_2$ samples.

2. Experimental

A Mo layer is sputter-deposited on soda lime glass substrates by Saint-Gobain. Precursor elements of copper, indium and selenium are first dissolved in an aqueous acidic bath, and then co-deposited at the glass/Mo electrode, according to the following cathodic reaction, exemplified for CuInSe2 [10]:

$$Cu^{2+} + In^{3+} + 2H_2SeO_3 + 13e^- + 8H^+ \rightarrow CuInSe_2 + 6H_2O$$

The deposited layer is nano-crystallized. Rapid thermal annealing is then performed under inert atmosphere, in presence of elemental sulphur, to provide the layer with semiconductor properties. Thereafter, we call 'as-grown the' samples after the annealing.

During annealing, the grain size increases and sulphurization occurred. After this step, ternary compounds such as copper sulpho-selenide remain and they prevent $CuIn(S,Se)_2$-based photovoltaic devices with having good electrical properties.

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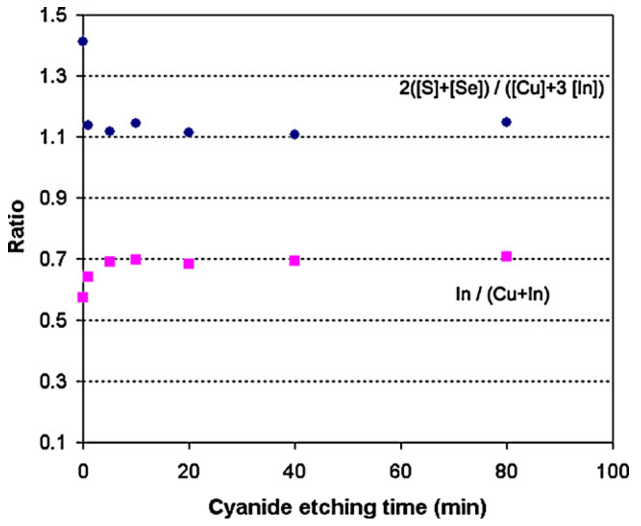

Fig. 1. Atomic surface compositions determined by XPS analysis for 0.1 M cyanide etched samples. Squares and circles represent respectively $\frac{[\mathrm{In}]}{[\mathrm{Cu}]+[\mathrm{In}]}$ and $\frac{2([\mathrm{S}]+[\mathrm{Se}])}{[\mathrm{Cu}]+3[\mathrm{In}]}$.

This phase is removed with a NaCN etching. The understanding of etching mechanism and optimisation of parameters require knowing of all experimental parameters influence.

This work deals with the influence of the cyanide concentration on surface and volume atomic compositions. The studied concentrations are in the 0.0001–1 M range and the samples were treated at 50 °C during 1 to 1000 min. The composition is essentially represented by the molecularity (i.e. $m=\frac{2([\mathrm{S}]+[\mathrm{Se}])}{[\mathrm{Cu}]+3[\mathrm{In}]}$) and the stoichiometry ratio (i.e. $s=\frac{[\mathrm{In}]}{[\mathrm{Cu}]+[\mathrm{In}]}$). Molecularity is the relationship between chalcogen species and metals. Coefficients 2 for sulphur and selenium and 3 for indium relate to the valence of the elements in material. The stoichiometry ratio represents the relationship between the metallic species.

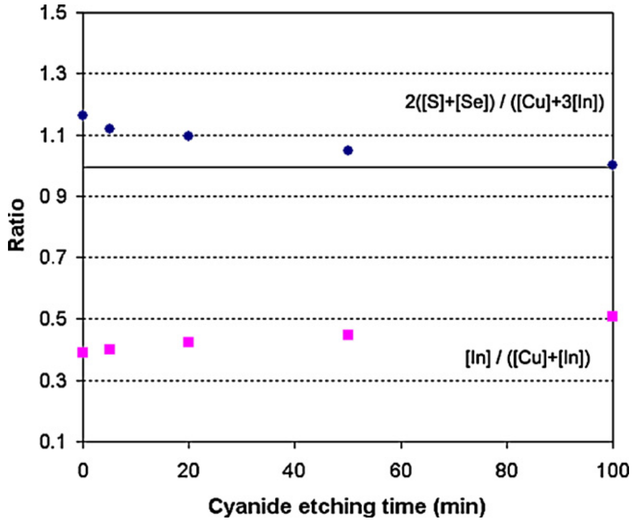

Fig. 2. Atomic bulk compositions determined by EPMA for 0.1 M cyanide etched samples. Squares and circles represent respectively $\frac{[\mathrm{In}]}{[\mathrm{Cu}]+[\mathrm{In}]}$ and $\frac{2([\mathrm{S}]+[\mathrm{Se}])}{[\mathrm{Cu}]+3[\mathrm{In}]}$.

Surface compositions are calculated from X-ray photoelectron spectra performed using a VG 220i XL system. X-ray photoelectron spectroscopy (XPS) conditions have been fixed to a constant analyse energy mode with 20 and 50 eV as pass energy, and monochromatic Al Kα X-ray excitation. Atomic composition was determined using Cu2p, In3d5/2, S2p and Se3d core level and the error is around 10%. Bulk composition is determined by using electron probe micro analysis (EPMA).

3. Results and discussion

3.1. Methodology

Our approach consists of plotting bulk and surface compositions for as-grown samples and comparing with those obtained after cyanide etching.

In a first step, results obtained with a 0.1 mol/l concentration are presented. The time range is 0 to 100 min.

Fig. 1 shows the evolution of atomic ratios of surface composition determined by XPS as a function of the etching time.

Surfaces of as-grown samples (time = 0 min) are indium rich in comparison of the amount of copper ($s>0.5$). However, the presence of copper sulphide was expected. To explain this indium rich composition we suppose the existence of copper vacancies at the surface of chalcopyrite material. During the cyanide etching, s increases because of Cu(S,Se) removing. Composition changes for etching time up to 5 min and no evolution can be noticed for longer time.

Moreover, surface molecularity of as-grown samples is about 1.4 which indicates S–Se rich surface. This ratio quickly decreases for cyanide etching time up to 5 min and becomes stable at a 1.1 for longer duration.

Bulk compositions of all the samples are represented on Fig. 2 by atomic ratio plotting. Because the spot size of XPS analysis is greater than EPMA one, more than 10 EPMA were performed for each sample and averaged. Contrary to surface,

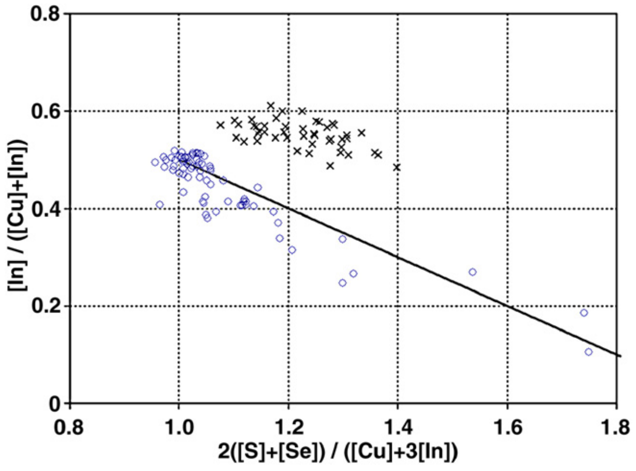

Fig. 3. Molecularity versus stoichiometry for surface (squares) and bulk (circles) atomic compositions of as-grown samples. The straight line determines the couples (0–0.5) to (2–0) i.e. $\mathrm{CuIn(S}_x\mathrm{,Se}_{1-x})_2$–$\mathrm{Cu(S}_y\mathrm{,Se}_{1-y})$.