

X-RAY FLUORESCENCE INVESTIGATION OF THE MATERIAL LOSS FROM CHALCOPYRITE ABSORBERS PREPARED BY TWO STEP PROCESSES

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ABSTRACT: An often mentioned key problem of so called two step processes is an apparent metal loss during high temperature selenization steps. In this work precursor films of copper and indium and/or gallium were selenized by different techniques (Rapid Thermal Processing, Selenium Vapor, at varying temperatures). The samples were analyzed by X-ray fluorescence (XRF) before and after selenization.

Especially for thin film analysis the possibilities of the XRF go beyond composition measurements. The relevant XRF property for this work is the possibility to determine the total material amount of the chalcopyrite elements on a selected layer area. Possible material losses in the selenization step and the amount of selenium incorporation can be determined by directly comparing the measured fluorescence intensities which also excludes errors due to calibration.

The often reported loss of indium and/or gallium due to selenization at elevated temperatures could not be confirmed by XRF measurements, as the amount of the metals remained constant at typical process temperatures. Instead a segregation of the metals was observed in our experiments at those conditions. The apparent material loss could be explained in terms of a measurement artifact of the widely used electron probe micro analysis (EPMA or EDX) due to the metal segregation.

Keywords: Material Loss - 1: CuInSe₂ - 2: Spectroscopy - 3

1. INTRODUCTION

The loss of indium and gallium during so called two step processes is often reported as a key problem of these techniques in regard of application for chalcopyrite thin film absorbers [1,2,3]. In these processes the formation of the desired chalcopyrite material takes place in a separate thermal treatment step from starting precursor layers of elements and/or binary compounds. In contrast to co-evaporation several crystallographic phases are formed and converted before finally the desired chalcopyrite material is obtained. It is generally accepted that also volatile In₂Se and Ga₂Se phases are formed which are said to evaporate from the sample, resulting in compositional shifts or leaving behind a copper rich surface layer.

In this work the X-ray fluorescence (XRF) is applied to investigate suchlike effects. The X-ray fluorescence (not to be mixed up with the electron probe microanalysis, mostly abbreviated as EDS, EDX or EPMA) is able to measure the total amount of the respective elements in typical chalcopyrite absorber films. Therefore this technique is the ideal tool for this purpose.

The motivation for this work arose from the XRF results of the CuGaSe₂ absorbers, produced by our standard process (elemental layer stack, treated for 6 min by rapid thermal processing at 550°C, Ar-atmosphere, atmospheric pressure). When comparing the results from precursor and processed absorber we could never find neither any shift in the copper to gallium ratio nor any hint for a gallium loss. As this could be a property which is related to the conditions of this certain process, different heat treatments, of gallium as well as of indium containing precursors, were investigated. This was also done at considerably higher temperatures than normally applied for absorber layer synthesis.

2. EXPERIMENTAL

2.1 Comparison of the elemental material amounts

The X-ray fluorescence, a technique quite similar to the EPMA, was found to be excellently suited for chalcopyrite thin film analysis. A detailed discussion of the XRF application to chalcopyrite thin films and solar cells can be found elsewhere [4]. Here only a brief description can be given to explain the major properties of this technique which, for thin film analysis, go beyond composition measurements.

The XRF uses emitted characteristic X-ray intensities of the elements to determine the sample composition. Therefore the technique is in principle quite similar to the widely used electron probe micro analysis, but there is a decisive difference. Instead of using an electron beam to excite the characteristic radiation, like in the case of the EPMA, the XRF uses primary X-rays. The by far higher penetration ability of the X-rays leads to some striking advantages of the XRF for chalcopyrite thin film analysis. There is a homogeneous excitation of the elements throughout the whole layer thickness and the primary X-rays also allow the excitation of the K $\alpha_{1,2}$ lines for all of the chalcopyrite elements. Both properties lead to better reproducibility and lower influence of matrix effects. One further XRF property will however be emphasized in this work. The K $\alpha_{1,2}$ line intensities are proportional to the total mass per square of the respective elements in typical chalcopyrite thin film absorbers.

In order to show how the results in this study were obtained a typical example for a comparative K $\alpha_{1,2}$ measurement is shown in figure 1. Two scans of the same sample before and after treatment are depicted. The 2 θ -

plots were recorded by a wavelength dispersive (WDX) X-ray fluorescence spectrometer (SRS 3000; Bruker-AXS, Rh-anode, 60kV, 8mm diameter analyzed sample area). One measurement was made on a selenium containing stacked elemental layer precursor (glass/Ga/Se/Cu/Ga/Se), while the other was carried out on the same sample after a rapid thermal processing (RTP) step. This annealing step transforms the elemental multi layer into a polycrystalline CGS film. Only the $K\alpha_{1,2}$ peaks of the main elements are marked in this 2θ -sector for simplicity. It has to be mentioned that this restricted range does not give the total information but is only a small part of the whole spectrum.

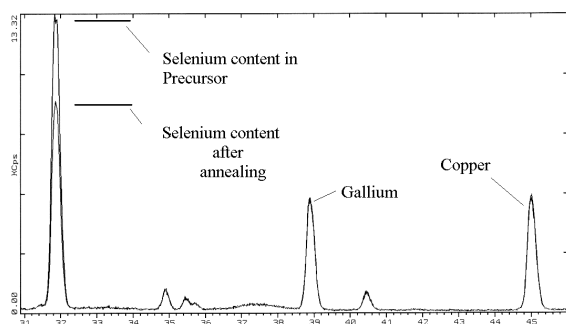


Figure 1: XRF-WDX scan of a CuGaSe_2 absorber layer, showing the $K\alpha_{1,2}$ range of interest, before and after annealing (Intensity vs. 2θ -range).

First of all the correspondence over a vast part of the 2θ -range, excluding the selenium peak, is noticeable. The correspondence can be taken as an example for the reproducibility of the XRF measurement and the small influence of the sample appearance (matrix effects) for chalcopyrite thin films, but it does even have an additional meaning. Since the measured intensities in the XRF thin film analysis are proportional to the mass per square, the total amount of the elements in the samples can be compared directly. It is clearly visible in Fig. 1 that the amount of copper and gallium stays unchanged, while there is a considerable loss of selenium noticeable after the annealing step. Thus the proportionality easily allows to determine possible material losses. According to the best of our knowledge the XRF is the only measurement technique which reveals this possibility.

2.2 The samples

Because also considerably higher temperatures than normally used for the absorber synthesis were applied, quartz glass had to be chosen as substrate material. Thermally evaporated elemental stacks of glass/Ga/Se/Cu/Ga/Se and glass/In/Se/Cu/In/Se were used to obtain films of about one micron thickness when reacted. The precursors had an intentional selenium excess of approximately 40 percent, compared to desired chalcopyrite structure. This selenium excess was necessary because there is always a selenium loss due to the heat treatment. All samples were slightly copper poor. The evaporated precursors were fragmented in several pieces and subsequently analyzed before and after thermal treatment. For the sake of comparability always an indium and gallium containing sample were processed simultaneously.

2.3 Applied processes:

Three different processes were systematically investigated at temperatures up to 900°C .

- I. Heat treatment in argon-flow for one hour at atmospheric pressure.

Carried out in a quartz glass tube at constant Ar-flow. The flow of Argon could support a possible loss of volatile indium or gallium selenides.

- II. Rapid thermal processing for six minutes in argon at atmospheric pressure.

This fast process may reveal differences to the ones of longer processing time. The process chamber is evacuated and filled with a certain amount of argon prior to the heating. Since the process chamber is closed, argon and selenium vapor surround the sample during the process. Because in the used furnace no excess pressure is allowed, the pressure in the processing chamber is always slightly lower than the atmospheric. A typical ramp time to 550°C is about one minute.

- III. Heating in an evacuated tube for one hour with additional selenium pellets.

The selenium loss in vacuum at higher temperatures rapidly leads to samples totally depleted of this element. Because in this case no chalcopyrite structure would have been present, additional selenium was placed close to the samples in order to reduce the loss.

3. RESULTS AND DISCUSSION

3.1 The figures

Aim of this work is to investigate possible material losses by means of the proportional dependency of intensity to material amount in XRF thin film analysis. Comparing the measured intensities directly, instead of using for example calculated atomic percents, excludes errors due to calibration. The results were obtained in a way similar to the example depicted in figure 1. A direct comparison of the measured fluorescence intensities, corresponding to the particular peak heights in figure 1, could be misleading. Due to the evaporation there are slight fluctuations in film thickness and composition from sample to sample. To get results that are not influenced by these unavoidable differences, each sample was measured prior to and after thermal treatment. By dividing each particular $K\alpha_{1,2}$ intensity after the treatment by the intensity before, a possible material loss can easily be seen. In figures 2.(a) to 2.(f) the corresponding unit is referred to as normalized intensity. If one keeps in mind that the intensities are proportional to the respective element amount, a value smaller than one means that there is a material loss due to the treatment.

3.2 Loss of selenium

If one takes a look at the figures 2.(a) to 2.(f) the most conspicuous property is the selenium loss occurring for all of the processes. Even if the indium and gallium loss is the major interest of this work the loss of selenium is also of considerable interest for chalcopyrite film production and

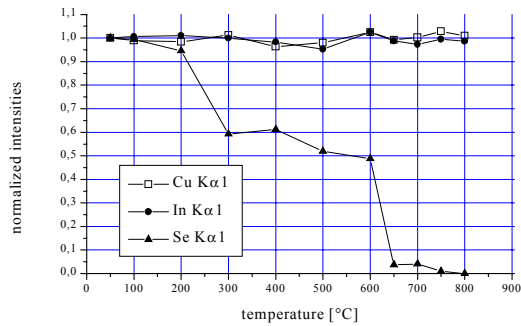


Figure 2.(a): Glass/In/Se/Cu/In/Se layers annealed for one hour in argon flow at atmospheric pressure.

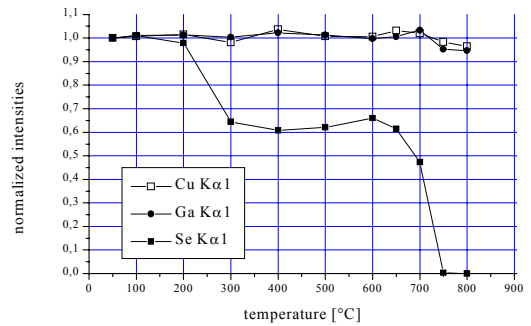


Figure 2.(b): Glass/Ga/Se/Cu/Ga/Se layers annealed for one hour in argon flow at atmospheric pressure.

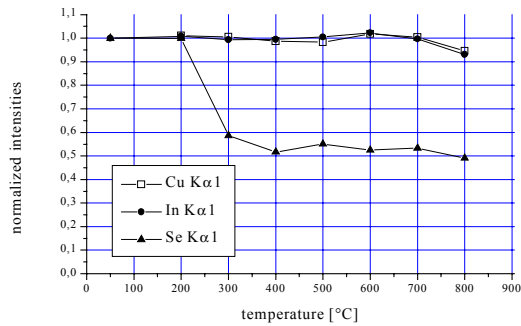


Figure 2.(c): Glass/In/Se/Cu/In/Se layers annealed for six minutes in a RTP furnace.

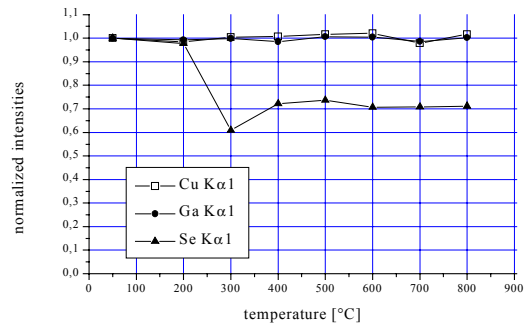


Figure 2.(d): Glass/Ga/Se/Cu/Ga/Se layers annealed for six minutes in a RTP furnace.

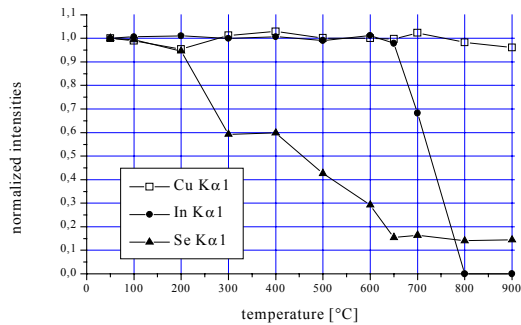


Figure 2.(e): Glass/In/Se/Cu/In/Se layers annealed for one hour in an evacuated tube with additional selenium.

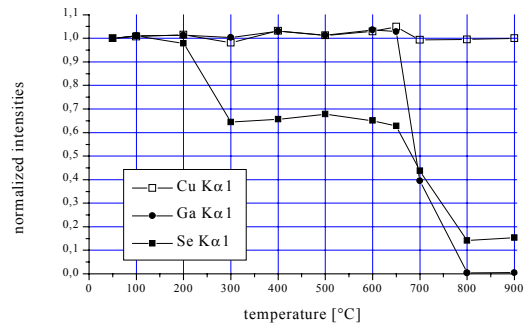


Figure 2.(f): Glass/Ga/Se/Cu/Ga/Se layers annealed for one hour in an evacuated tube with additional selenium.

will be discussed in the following. It has to be pointed out again that the precursors had an intentional selenium excess.

A moderate loss of selenium between 100 and 200°C can already be observed for the longer processes, while for the RTP process there is only a negligible shift. In the temperature range from 200 to 300°C there is a noticeable

correspondence for all of the graphs. In all cases the selenium amount after treatment was roughly about 60 percent of the precursor value. Expressed in atomic percent for all investigated processes a value close to, but slightly below (47 to 49 atomic percent), the desired 50 percent was observed.

In the temperature range between 300 and 600°C, the range in which the chalcopyrite formation takes place, there is a distinctive difference for the gallium and indium containing samples. For the glass/Ga/Se/Cu/Ga/Se layers the selenium incorporation has a minimum at about 300°C and is slightly increasing towards higher temperatures. For the indium containing structures no such increase is visible.

In this case the one hour lasting processes show a plateau between 300 and 400 °C and then a constant decrease, the RTP treated samples an approximately constant selenium incorporation. There are also differences in regard of reaching the minimum selenium amount for the glass/In/Se/Cu/In/Se and the glass/Ga/Se/Cu/Ga/Se layers. For the one hour lasting treatments the minimum values for the indium containing samples are already reached at 650°C, whereas the gallium containing ones reach that point at an about 100°C higher temperature. The RTP treated samples show in both cases the same, approximately constant, selenium level up to 800°C.

Summarizing one can emphasize the difference between the fast and the slow processes and the different behavior of the indium and gallium containing samples. For the temperature region where the chalcopyrite formation takes place the selenium incorporation, at least for the studied conditions, seems to be more effective for the gallium containing layers. This may indicate that for the growth of CuInSe₂ a maintaining selenium supply is of greater importance than for CuGaSe₂.

3.3 Loss of indium and gallium

The most remarkable result of this study is the behavior of gallium and indium. From what is often reported in literature a loss of these elements, due to volatile indium- or gallium selenides, should be expected.

For the processes at atmospheric pressure, depicted in figures 2.(a) to 2.(d), the result can be easily summarized. In these cases no loss at all of neither indium nor gallium can be observed. Up to 700°C the normalized fluorescence intensities stay close to 1 for all of these processes. In the high temperature range, between 700 and 800°C, figures 2.(b) and 2.(c) seem to indicate a small metal loss. At these temperatures however the sample morphology significantly worsened, leaving behind cracks and small amounts of material peeled off. Taking into account the relatively large analyzed sample area and the proportional behavior of the signal, the peeled off material must result in a lower measured intensity. This assumption is further backed by the observation that in these cases the copper and indium (gallium) intensities decrease simultaneously.

A very pronounced indium and gallium loss can however be seen for the samples which were heat treated for one hour in the evacuated ampoule. In both cases, shown in figures 2.(e) and 2.(f), the loss starts in the same temperature range, above 650°C. At 700°C both elements are still present in the sample, while at 800°C indium and gallium have totally vanished. The copper amount remains unchanged up to 900°C. Because of the selenium vapor, due to the additional selenium pellets in the closed tube, this element also remained present in the samples up to this temperature, in the form of Cu₂Se.

The interesting result in this case is the temperature range in which the loss happens. Between 550 and 600°C is the maximum temperature at which the usually used soda lime glass can be applied. In this temperature range we found again no evidence for any loss of neither indium nor gallium. The loss of these elements could only be observed above 650°C, which is about 100°C more than typically applied in chalcopyrite absorber synthesis.

3.4 Possible explanation for the often reported In/Ga loss

Because of the particularity of the investigated processes we can not state in general that there is never a loss of gallium or indium in two step processes at typical conditions. There are too many parameters which will differ in other types of processes, especially selenium partial pressures, different kinds of precursors, compositions, etc. But we can try to give an explanation what could be a reason for the reported loss of these elements.

Firstly, it has to be mentioned that the absence of these losses was always observed by us when using the XRF technique. Also for samples which were processed differently than the ones which were systematically investigated in this work. (For example H₂Se/Ar annealed metallic precursors [5]).

Secondly, we obtained the same compositional shifts like other groups when using the commonly applied measurement technique, the electron probe micro analysis.

Thirdly, we found evidence that there is an elemental segregation in two step processed chalcopyrite absorbers. Especially if the precursors consist of elemental layers and not binary selenides, a segregation of gallium and indium towards the back contact could be observed [5,6].

If one presumes that such a segregation is a common property of these processes, the discrepancy between XRF and EPMA (EDX, EDS) results can be easily explained, together with the often reported material loss.

In the case of the EPMA the detected characteristic radiation is excited by an impacting electron beam. This electron beam excites the radiation mostly in the upper half of typical chalcopyrite absorber films of about two microns thickness [4,7]. If there actually is a inhomogeneous elemental depth distribution, the measured composition will therefore deviate from the average value and will often erroneously be taken as the result for the whole layer. In case of an indium/gallium segregation to the back contact an above average copper rich volume will be excited, leading to the interpretation of an apparent indium or gallium loss.

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