

CuGaSe₂ BASED THIN FILM SOLAR CELLS FABRICATED BY RAPID THERMAL PROCESSING

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ABSTRACT: In a rapid thermal annealing process CuGaSe₂- absorber films are produced from a stacked elemental layer of the evaporated pure elements. Especially in processes, in which a material loss occurs, as in the case of the RTP process, composition control is of great importance. This work shows the possibilities of the X-ray fluorescence technique (XRF) in thin film analysis and emphasizes the advantages over the widespread electron probe microanalysis (EPMA). Besides the composition measurement it is possible to determine the total amount of material and the film thickness very accurately. Furthermore a real multi layer analysis allows for example to determine the CdS, ZnO and Mo thickness simultaneously with the absorber measurement. By the use of certain techniques information about a vertical composition gradient can also be gained.

Keywords: Thin Film - 1: Characterisation - 2: Polycrystalline - 3

1. INTRODUCTION

1.1 Production of CGS thin film solar cells

CuGaSe₂ (CGS) is of considerable interest for thin film solar cell application. Due to its wide bandgap of 1.68 eV, it could serve as the top absorber of a tandem-cell with an CuInSe₂ bottom cell. The method of CGS-film preparation used in this work consisted of depositing elemental layers of Cu, Ga, and Se on molybdenum coated soda lime glass, followed by an annealing step of the precursor in a commercial Rapid Thermal Processing (RTP) furnace. Thermal evaporation was utilized for element deposition. An annealing time of five minutes at 550 °C was found sufficient to transform the precursor to single phase (X-ray diffractometry) CGS-films[1].

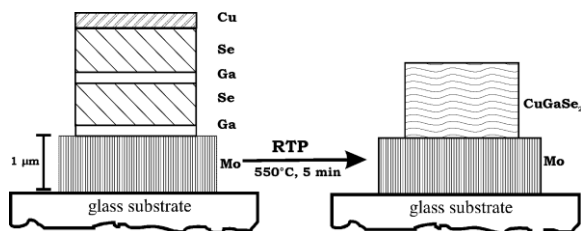


Fig 1: Transformation of the SEL- precursor to a CGS-absorber layer.

Molybdenum films with a thickness of 1 μm were deposited via radio frequency-sputtering onto 1 mm thick soda lime glass designed for use as microscopy slides. Physical vapor deposition was used to fabricate the elemental Cu/Ga/Se precursor. In a sequence of five evaporation steps two layers of gallium and selenium and one layer of copper were deposited. The precursors were enclosed in a graphite box, which was heated in the RTP-furnace by tungsten halogen lamps. A CdS buffer layer of 50 nm thickness was deposited on the CGS by a chemical bath procedure. 50 nm of intrinsic ZnO were sputtered on top of this layer. For current collection a 350 nm thick Al doped ZnO layer of low resistivity was deposited by means of RF-sputtering. The solar cells were completed by the evaporation of silver front contact fingers.

The CGS-films were analyzed by means of X-ray diffraction (XRD), photoluminescence and Hall- measurements. Scanning electron microscopy (SEM) was used to determine grain size and shape and the surface morphology on a microscopic scale. There are several publications which deal with the latter characterization methods[1,2]. A in this field quite unknown characterization technique, the X-ray fluorescence, shows a remarkable suitability for the analysis of CGS films, and thin film analysis in general. Because of these more recent results a major aim of this work is to introduce this technique and outline the new possibilities.

1.2 Composition measurements

An important topic in the characterization of thin film chalcopyrite solar cells are composition measurements. This is valid for laboratory work, to correlate stoichiometric variations with solar cell properties, as well as for the quality control in an industrial process. There are several more or less suitable methods of chemical analysis, but most of them have the disadvantage that the analyzed sample is being destroyed for the measurement or, in the case of thin film samples, has to be removed first from the substrate.

By far the most common used method for this class of samples is the electron probe micro analysis (EPMA), sometimes slightly incorrect called EDX or EDS. This method is nondestructive, fast and a lateral resolution can be obtained. A further reason why this method is so widespread, especially in scientific laboratories, is that it can easily be added to an electron microscope. In spite of these striking advantages sometimes the results are not very reproducible or show a considerable deviation from the expected values. A remarkable improvement in reproducibility and precision can be achieved by a quite similar technique, the X-ray fluorescence (XRF). But there are also further advantages. Simultaneous to the relative contents of the elements in a layer also the total mass per unit square (mg/cm²) of the analyzed elements is determined easily. This is especially of interest if a loss of material has to be determined, for example after an annealing step. All this is possible not only for single-

layers but also in real multi-layer structures. By using signals with lower energy, more surface sensitive measurements are possible.

There are several publications which report on thin film investigations with the EPMA [3,4] but most of the samples investigated in these publications have much smoother surfaces than polycrystalline thin films and/or are considerably thinner. All of these publications however show the complicated conditions that are caused by the strong interaction of the electrons with the sample material. Even if sophisticated calculations, like in commercially available software, are used to gain control of these difficulties there still exist problems which can not be considered sufficiently. The XRF shows by far more suitable properties for the thin film analysis because the excitation process is less complicated.

2. COMPARISON OF XRF AND EPMA

Both systems detect the characteristic X-rays that are sent out by an excited sample. For each element there are characteristic lines at specific energies by which the elements can be identified. Both systems can use the same detection techniques. One possibility is to measure the whole energy spectrum directly with an energy sensitive detector, an other possibility is to use a goniometer and an analyzing crystal with θ - 2θ coupling. By means of the Bragg equation $n\lambda = 2d \sin \theta$ the energy of a measured peak can be determined from the 2θ -position of the detector. The first technique is known as **energy dispersive spectrometry** (EDS or EDX) while the second, the **wavelength dispersive spectrometry**, is abbreviated as WDS or WDX.

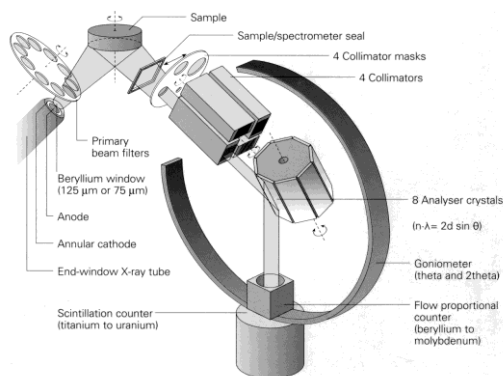


Fig.2: The SRS 3000 XRF-WDX used in this work schematically (Illustration by Bruker-AXS).

What makes the wavelength dispersive spectrometry outstanding is a considerably better energy resolution that leads to more detailed spectra than in the case of EDS, where for example lines with lower intensities can be covered by more pronounced signals. The EDS on the other hand has the advantage of recording the complete spectra at once which results in a shorter measuring time. The difference between XRF and EPMA is thus not the detection but only the excitation of the characteristic radiation.

For the quantitative analysis the intensity of a selected emission line has to be related to the concentration or mass fraction of this element in a sample. To achieve reasonable results the system has to be calibrated which is managed by the comparison with standards of known composition. Best results will in general be obtained if the standards and the unknown samples agree as much as possible.

Since the intensity of a particular spectral line is also strongly influenced by the absorption within the sample and the radiation of some elements can even excite the characteristic emission of others, these influences must be corrected by theoretical calculations. The more different the used standards, compared to the unknown sample are, the more important becomes the correct consideration of these latter effects, known as matrix effects.

To understand the reasons for the better suitability of the XRF for this class of samples one must throw a glance at the excitation process. In the case of the EPMA the characteristic radiation is excited by an incident electron beam. The electrons are decelerated in the sample material and, besides other effects, inner electron shells of target atoms become ionized; This causes the emission of the characteristic radiation as a countermove. One electron can cause several ionisation events and it will be strongly deflected or even backscattered while being slowed down in the sample. Monte Carlo simulations can visualize the electron diffusion (Fig.3)[5].

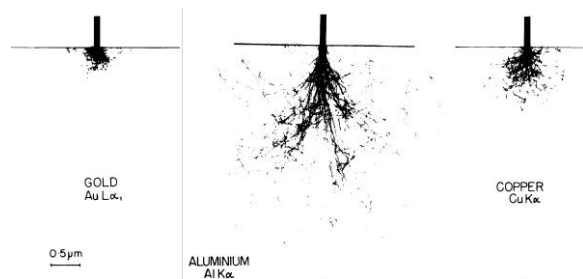


Fig.3: Monte Carlo simulations of the electron diffusion in different materials. The acceleration voltage is 20 kV [5].

The distribution of the primary X-ray generation depends mainly on the acceleration voltage, the material density, the scattering of the primary electrons, the variation of the ionisation cross section with the electron energy and some other effects. All these properties have to be taken into account for a quantitative analysis and result in more or less reliable numerical factors.

For thin film chalcopyrite solar cells and typical acceleration voltages the excited volume is of the same magnitude as a single grain of the absorber layer.

Even if all the effects which influence the excited volume, the radiation gain, the secondary and the matrix effects are calculated properly, there are still some disadvantageous material properties for a reproducible EPMA-analysis (Fig.4). Disadvantageous are all deviations from a flat, homogeneous and semi- infinite appearance. A special software may consider the cases "A" to "C" in figure 4 [5].

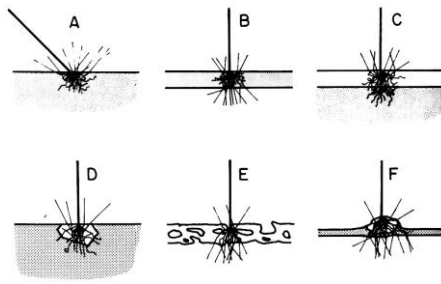


Fig.4: Unfavorable properties for EPMA analysis[5]:
 A) Changing angle of incidence (rough surface)
 B) Unsupported uniform film C) Supported film
 D) Embedded particle E) Film of irregular thickness
 F) Free particles

Chalcopyrite absorber films, and polycrystalline thin films in general, show nearly all of these unfavorable properties (See Fig.5).

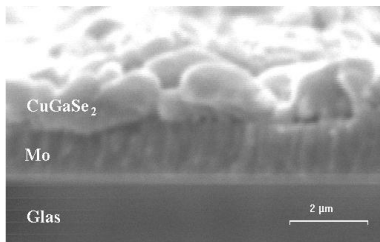


Fig.5: SEM picture of a CGS absorber layer produced by RTP-SEL, molybdenum back contact and glass substrate.

Besides these effects, which cause fluctuations in the output, there is a problem with the calibration standards which can lead to systematical errors. Normally the used standards are pure elements, either in the form of a "bulk" or as a thin film. Another possibility is to use similar thin film samples which are said to have a known composition. The use of pure element standards is a doubtful way, because the surface properties of the standards will be totally different from those of the unknown samples. The use of similar film standards will be a better choice, but will only lead to correct results as long as the unknown samples have a similar thickness, grain size, homogeneity and substrate material as the used standards. An additional problem is the check of the standard sample reliability.

While a EDS-system uses an e-beam, the XRF-technique uses X-ray radiation (primary radiation) to excite the characteristic radiation (fluorescence radiation), which leads to a clearly less complicated situation. Samples in the magnitude of chalcopyrite thin film absorbers (1 to 3 µm) are penetrated completely, their thickness is negligible compared to the penetration depth of X-rays. For this class of samples the excitation therefore does not show the complicated conditions as in the case of e-beam excitation.

The information depth is thus not determined by the excitation but only by the depth profile of the emitted radiation. In the case looked at here the information depth is also far larger than the film thickness. If a CGS sample would be a "bulk"- material 90% of the emitted radiation ($K\alpha$ - lines of the main elements) is emitted out of a depth

up to about 70 µm. The dependence of intensity (I) vs. film thickness (d) for those signals is

$$I/I_0 = 1 - \exp(-\mu \rho d).$$

(Fig.6)

I_0 is the intensity for a bulk sample, μ stands for the mass absorption coefficient and ρ is the material density. For thin films we are in a range which is practically linear.

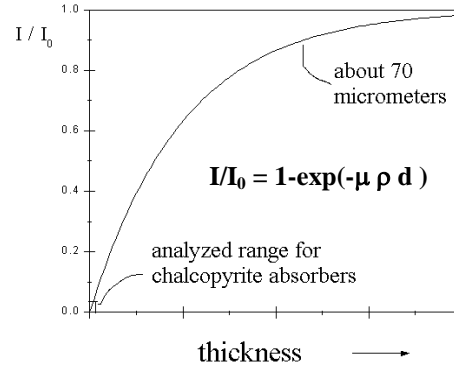


Fig.6: Magnitude of $K\alpha$ - intensity versus film thickness schematically for the main elements of a CGS thin film.

The latter properties of the XRF- technique allow several very interesting and advantageous applications for the thin film analysis. Because in the range of interest the intensity to thickness dependence is very pronounced, the XRF is a sensitive tool for thickness measurements. The actually determined quantity by the use of the XRF is not the thickness itself but the mass per square (mg/cm^2). Using the density the thickness is then calculated. If this step is omitted, which also avoids mistakes because the thin film density is normally not equal to the bulk density, the XRF thus measures the total amount of the elements. This is of particular interest, because the loss of material, for example after annealing steps, can be determined. In figure 7 the scans (intensity versus a selected 2θ range) of a CGS absorber layer before and after the RTP- step are shown.

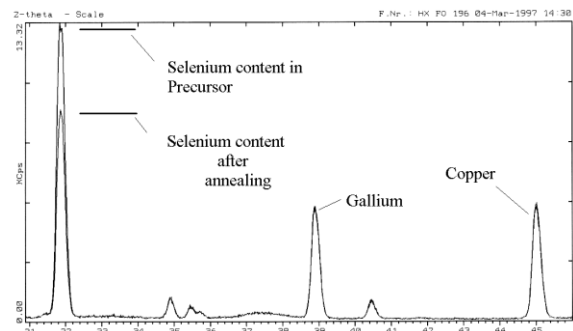


Fig.7: XRF-WDX scan of a CGS absorber layer before and after annealing. (Intensity versus 2θ - range).

It is clearly visible in figure 7 that the amount of copper and gallium remains unchanged, while there is a remarkable loss of selenium. By measuring at different spots on the sample it could for example also be seen that if the pressure in the annealing chamber is below an atmospheric, there is a very strong dependence between the chamber temperature and the selenium loss. Even the small

temperature gradient in the chamber causes very pronounced differences of the selenium content. The perfect correspondence of the signals in figure 7 outside the selenium peak can be taken as an example for the reproducibility of the XRF-WDX.

Since the information depth is so much larger than a typical layer thickness not only the absorber material but also the other layers of a thin film cell can be analyzed. In the case of typical chalcopyrite solar cells that means for example that the thickness of the very thin CdS buffer layer can be determined as well as those of the molybdenum and ZnO- layers. The thickness of a layer can be determined directly but also by the weakening of a signal sent out by an underlying material.

A further advantage of the relatively large information depth is that there are practically no grain size or surface effects, for this class of samples, which could influence the obtained results. Therefore also a lot more samples of known composition can be used as calibration standards, if only the different matrices are considered correctly. Suitable standards in the case of CGS thin films are for example GaAs- wafers, brass samples with known copper compositions or evaporated thin films of the pure elements, to mention only a few of the possibilities.

3. ANALYSIS OF DEPTH PROFILES

3.1 The etching method

There is a quite accurate method to measure a vertical composition gradient of the sample. If the sample is etched in bromium methanol step by step, and subsequently measured by XRF, a possible gradient can be determined from the signals of the remaining layer. The layers produced by SEL- RTP show practically no change in the Cu/Ga ratio but, because of the MoSe₂ formation, there is a steady growth of the selenium content with increasing depth. Films grown on a glass substrate without a molybdenum layer show good homogeneity over the whole thickness range. The SEL-RTP process is therefore suitable in principle to produce homogeneous CGS absorber layers. But it could also be shown that this process leads to a quite pronounced formation of MoSe₂ in the annealing step causing a high contact resistance. Tests with Tantalum as a back contact material showed promising properties. The resistance of TaSe₂ is lower and no negative influence to the film properties could be determined by XRD. The specific contact resistance for a Tantalum back contact is with a measured resistance of 0.02 Ω cm² about 30% lower than by the use of Molybdenum. Unfortunately up to now there are adhesion problems of the Ta- layer on the glass substrate.

3.2 L_α- lines analysis

There is also nondestructive way to gain information about a compositional depth profile. If instead the K_α- the L_α-lines with lower energy are used, the analysis becomes more surface sensitive. The information depth, again defined as in figure 6 as depth which leads to 90% of the intensity of a bulk sample, is then in the range of 1 μm for the CGS main elements. As the surface effects and homogeneity are playing a more important role here, the conditions are more complicated in this case. But because

the penetration depth of the primary radiation is still the same there is at least no depth profile in the excitation as in the case of the EPMA. Figure 8 for example shows a scan of the L_α- lines for 5 CGS- absorbers with different annealing times, starting with a precursor. It is clearly visible how the Gallium L_α- intensity is increasing with proceeding annealing time. This means that the Gallium content at the surface is increasing steadily (Gallium is not at the top of the precursor). A new program for a quantitative analysis with the L_α- lines is in preparation.

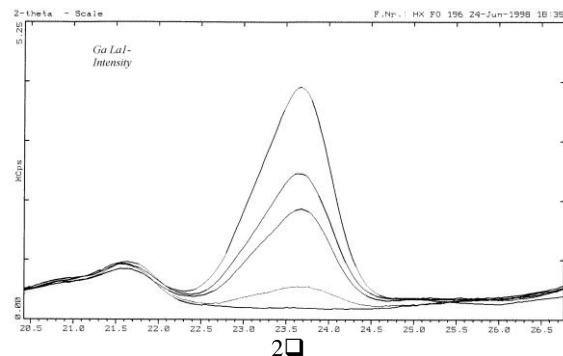


Fig.8: 5 CGS- absorbers with different annealing times, starting with a precursor. The shown signal (Ga-L_α) becomes stronger with increasing annealing time.

4. CONCLUSIONS

In a rapid thermal annealing process CuGaSe₂- absorber films are produced from a stacked elemental layer of the evaporated pure elements. A new tool for characterizing this class of samples and thin films in general is introduced, the X-ray fluorescence. Reasons for the superiority of the XRF over a quite similar and widespread technique, the EPMA, are shown. The very advantageous properties of the XRF allowed a gain of information which lead to further improvements in the material quality.

Our best cell obtained by SEL-RTP demonstrates an open circuit voltage of $V_{oc} = 604$ mV, a short-circuit current of $J_{sc} = 9.43$ mA/cm² and a fill factor of $FF = 56.8$ % resulting in a conversion efficiency of 3.80 % under 100 mW/cm², AM1.5 illumination.

5. REFERENCES

- [1] O.Schenker, J.H.Schön, F.Raiser, K.Friemelt, V.Alberts, E.Bucher, Proceedings 14th EC Photovoltaic Solar Energy Conference, Barcelona (1997)
- [2] J.H.Schön, O.Schenker, L.L.Kulyuk, K.Friemelt, E.Bucher, Solar Energy Materials and Solar Cells 51 (1998) 371
- [3] Bishop, H.E., Poole, J.Phys.D, Appl. Phys. 6, 1142 (1973)
- [4] Spencer, L.V., Phys.Rev.98, 1597 (1955)
- [5] Heinrich, K.F. Electron beam x-ray microanalysis, Van Nostrand Reinhold Company, New York, (1981)