

# IN SITU RESISTIVITY MEASUREMENTS OF $\text{CuGaSe}_2$ ABSORBERS PREPARED BY RAPID THERMAL PROCESSING

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**ABSTRACT:** Stacked elemental layers of selenium, copper and gallium are transformed by rapid thermal annealing to  $\text{CuGaSe}_2$  films. Four point in situ resistivity measurements during the RTP step are performed to get some insight into the reaction kinetics.

The obtained resistance curves show the metal-semiconductor transition and the typical behavior of these respective types of material. XRD measurements which indicate that chalcopyrite formation occurs via copper selenides could be related to the in situ resistivity measurements. One can also conclude from these measurements that after a process time of about five minutes the formation is in general complete from an electric point of view since no further changes in resistivity occur (at a constant high temperature).

Some peculiarities in the curves were observed especially after the cooling phase: When cooled down to room temperature the samples show long time relaxation effects with decreasing resistivity. This process can be accelerated by exposure of the films to ambient air (humidity). This resistivity relaxation can be reversed by heating the samples at 200 °C in argon atmosphere.

Keywords:  $\text{CuGaSe}_2$  - 1: Rapid Thermal Processing - 2: Experimental Methods - 3

## 1. INTRODUCTION

With a bandgap of 1.68 eV  $\text{CuGaSe}_2$  is an interesting material for the top cell in a tandem structure, as well as for the absorber in a single junction solar cell. Efficiencies of close to 10% have been demonstrated for cells that use  $\text{CuGaSe}_2$  as absorber material [1,2].

The stacked elemental layer Rapid Thermal Processing (RTP) technique we made use of in this work has the advantage of being a sequential process that is controllable, fast and scaleable to industrial size.

An in situ measurement of an electrical property can be valuable since phase formation in this non equilibrium process is not well understood. Chalcopyrite formation via copper selenide phases is likely but ex situ X-ray diffraction spectroscopy alone cannot prove that these phases are present during the RTP process rather than appear while the samples cool down. In situ resistivity measurements during the RTP step can give some insight into the reaction kinetics and also help to optimize the process parameters with regard to solar cell performance.

## 2. EXPERIMENTAL

Stacked elemental layers of copper gallium and selenium produced by thermal evaporation were transformed by an RTP process to  $\text{CuGaSe}_2$  absorber films. The thickness of the elemental layers in the precursors were chosen so that the resulting  $\text{CuGaSe}_2$  films were about one micron thick. Additional elemental selenium was offered in the RTP furnace. The samples were placed in an graphite box which excluded undesired photoconductivity effects during resistivity measurements. The RTP process consisted of a fast temperature ramp, followed by a plateau of six minutes at 555 °C. The reaction took place under 1 atmosphere of argon. Details can be found elsewhere [3].

For electrical measurements during the RTP step a setup as shown schematically in Figure 1 was chosen. A

patterned molybdenum back contact was sputtered onto soda lime glass substrates. We used a Keithley 2400 source meter connected to a computer system to record the resistivity data once every 1.5 seconds. The four point method was selected in order to avoid errors arising from the (changing) contact resistance between the contact fingers and the molybdenum back contacts.

It was found necessary to reverse the direction of the applied current between subsequent measured data points. In cases when this was not done the mobile copper ions migrated to one of the molybdenum back contacts leaving behind an area with properties not comparable to a typical layer and thus yielding unusable resistivity readings.

The gas system of the RTP furnace permitted to study the effects of controlled exposure of the  $\text{CuGaSe}_2$  layers to different atmospheres ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{H}_2$ , Ar) after the synthesis. This could be done without having to expose the samples first to ambient air or to discontinue the electrical measurements.

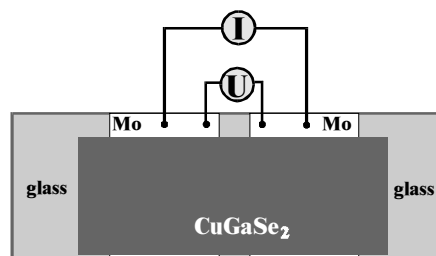


Figure 1: Setup for in situ resistivity measurements.

### 3. RESULTS AND DISCUSSION

#### 3.1 CuGaSe<sub>2</sub> Synthesis

The resistivity curves obtained during the RTP step (Fig. 2) can be related to crystallographic phases found by X-ray diffraction techniques in the films after the annealing step is interrupted at different times (Fig. 3). One has to keep in mind though, that the cooling process is relatively slow and therefore further reactions might take place during that time, i.e. that the XRD spectra do not necessarily reflect the state of the films at the time of stopping the heat process. The in situ resistivity curves on the other hand provide information that is unambiguously linked to a specific time in chalcopyrite formation.

The reading of the resistivity can be regarded as dominated by the phase in the film with the highest conductivity as long as this phase constitutes a non negligible connected portion of the total layer.

The precursors consist mainly of the metallic elemental layers and some amount of copper selenides hence the low resistivity at room temperature (section (a) in Fig. 2 and Fig. 3)

While the temperature is ramped (b) the resistivity increases first as is to be expected for metals. But as can be seen from the XRD peaks, the chalcopyrite phase already starts forming at this stage which leads of course to another change in resistivity. In the depicted case of a slightly gallium rich film (Cu/Ga = 0.96) it is a reduction.

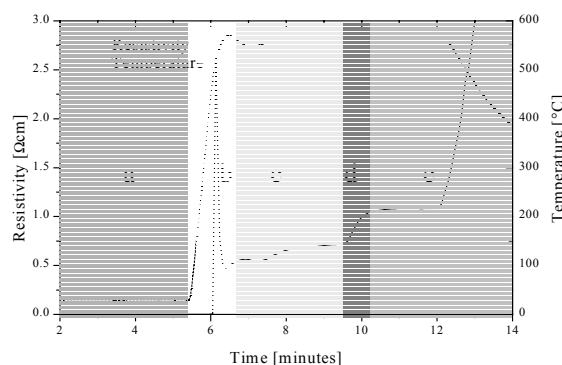
During the next three minutes (c) the resistivity increases slowly. We ascribe this to the main channel for the current in this period, the copper selenides, which are gradually transformed to the chalcopyrite phase with a higher electrical resistivity. The duration of this period is related to the copper to gallium ration of the layer. The higher the gallium excess the shorter this period and vice versa.

Stage (d) in which a quite abrupt increase in resistivity occurs at a fixed temperature can be accounted for by the vanishing copper selenide phases in favor of the CuGaSe<sub>2</sub>

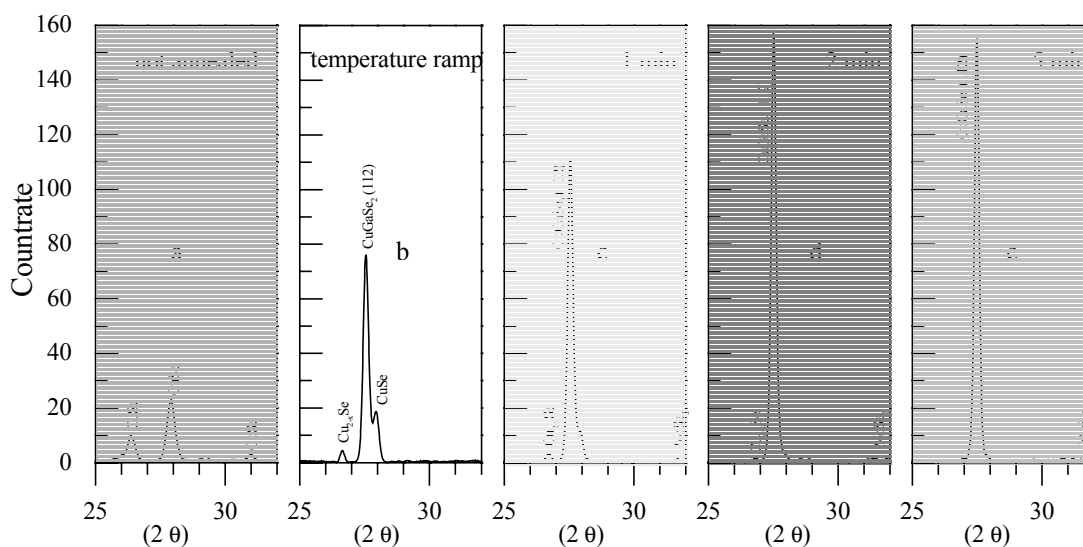
formation. For copper rich and even for stoichiometric layers this resistivity increase can not be detected. This confirms our interpretation of the observed course of the resistivity curve and additionally indicates the presence of copper selenide phases in that type of films even if they are too minute to be detected in the XRD measurements.

Over the last time period (e) shown in Figure 2 the resistivity is stable at 555 °C and only increases upon cooling to show that indeed a semiconductor formed. This means that after a temperature plateau of five minutes at 555 °C the formation of the absorber is finished from an electrical point of view as well as from a crystallographic point of view. Longer heating leads only to the formation of the unwanted MoSe<sub>2</sub> phase.

For a similar type of two stage process Zweigart et al. [4] found CuGaSe<sub>2</sub> formation times of about 45 minutes by also using an in situ resistivity technique. The main difference is that the selenisation in their case was performed in a high vacuum system where selenium incorporation needs longer for completion.



**Figure 2:** Temperature and resistivity during chalcopyrite synthesis in the RTP furnace.



**Figure 3:** Sections of XRD spectra of samples annealed for different times in the RTP furnace.

### 3.2 Post Absorber Formation Effects

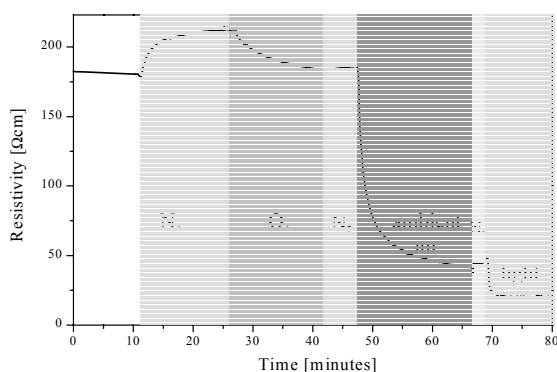
While the CuGaSe<sub>2</sub> films cool down from 555 °C to room temperature within half an hour, the resistivity increases from about 1 Ωcm to 800 Ωcm. After the cool down period though, a slow relaxation can be observed even if the layers are left in the closed RTP furnace and nitrogen atmosphere. For the film shown in Fig. 5 the resistivity decreases to about 250 Ωcm after 25.5 hours. Experiments in which the reaction chamber of the RTP furnace was purged with different gases (room temperature) after such a time span can hint to the source for the effect.

Nitrogen leads to a fast but limited reversal of the effect, oxygen to an acceleration but also only over a limited span (Fig. 4). Argon and hydrogen lead to the same effect as nitrogen.

A fast and dramatic large decrease in resistivity is caused by exposure of the sample to ambient air. This effect is by at least a factor of five larger than those induced by oxygen, nitrogen, argon, hydrogen or light exposure and takes place in the time scale of minutes. The resistivity drops to 20 Ωcm. Also it cannot be reversed by an exposure to other gases (N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, Ar) at room temperature.

Since H<sub>2</sub>O is the only species present in ambient air besides oxygen that is chemically not inert we are led to believe that the humidity in the atmosphere together with the oxygen cause the observed behavior. The long time relaxation in the closed reaction chamber mentioned earlier is possibly due to a slight leak the reactor so air from the lab can slowly trickle in.

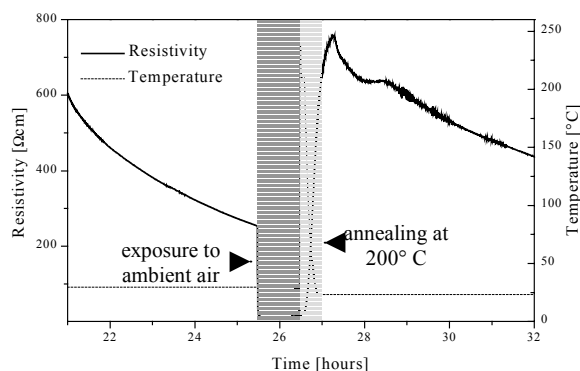
Nadenau et al. [2] report a considerable decrease in cell performance if the CuGaSe<sub>2</sub> layers (in that case fabricated by coevaporation) were exposed to air prior to the deposition of the CdS buffer layer. It seems likely that the resistivity relaxation observed here is related to that effect.



**Figure 4:** Resistivity of sample influenced by exposure to different atmospheres at room temperature.

Models were suggested by Cahen et al. [5] that explained effects observed when chalcogenide based solar cells and absorbers were annealed in air or oxygen. The core statement was that compensating selenium vacancies (donors) at the grain surfaces are passivated by oxygen atoms leading to a net increase of acceptor densities. This could also explain the resistivity relaxation effect observed by us, with the noticeable difference that we have room

temperature effects where the oxidation seems to be assisted by the moisture in the ambient air.



**Figure 5:** Reversibility of air exposure induced resistivity relaxation by annealing the CuGaSe<sub>2</sub> samples in Ar atmosphere at 200 °C for six minutes.

We found that the original high resistivity of the films directly after chalcopyrite formation and cooling could be restored with a heat treatment at 200 °C for six minutes in argon atmosphere (Fig. 5). After this the same type of resistivity relaxation took place as after the synthesis of the chalcopyrite. The observed behavior was reproduced for several air exposure/annealing cycles showing the reversibility of the effect.

## 4. CONCLUSIONS

Different phases of chalcopyrite formation can be distinguished with in situ resistivity curves. Especially the vanishing of the highly conductive copper selenides.

Ambient air exposure at room temperature affects the resistivity of CuGaSe<sub>2</sub> films a lot more than pure oxygen/nitrogen or light exposure. A decrease of the resistivity up to one order of magnitude has been observed.

The resistivity relaxation can be reversed by annealing the samples at 200 °C in argon atmosphere.

Further investigations using the promising in situ resistivity method correlated to different other experimental methods and ultimately to solar cell parameters could prove useful in explaining some effects not yet understood.

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