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# Analysis of the gallium gradient in $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ absorbers by X-ray diffraction

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## Abstract

In order to analyze why the CIGS ( $\text{CuInGaSe}_2$ ) - based solar cells efficiency decrease for wide band gap (high Ga content), we have performed a series of samples by PVD using the three stage process. The average compositions of our solar cells range from  $x=0$  to  $x=0.88$ , as measured by X-ray diffraction. An important feature of this process is to create a double Ga gradient into the absorber, which contributes to improve efficiencies, and this has a major impact on the determination of the sample composition from x-ray diffraction data. We have developed a model in order to assess this impact and question the validity of the compositions extracted from x-ray data. This model allows to get some information about gradient shapes. Using our model, we have obtained some insights on the evolution of the gallium gradient in samples with increasing Ga content, and we determine that this gradient is less pronounced when increasing the amount of gallium. It is a well known fact that this gradient assists the extraction of photocreated carriers, and the modifications of the gallium profile that we have determined may explain, for some part, the degradation of solar cells efficiency for high gallium compositions.

**Keywords:**  $\text{CuInGaSe}_2$ , x-ray diffraction, gallium gradient, wide bandgap, solar cells, CIGS

## 1. Introduction

CIGS ( $\text{CuInGaSe}_2$ ) is a promising material for renewable energy. Indeed, with a strong absorption coefficient and a direct bandgap, the integrality of solar radiation can be absorbed within only  $2\ \mu\text{m}$  of material thickness. Moreover, the band-gap tunability from 1.02 eV ( $x=0$ ) to 1.67 eV ( $x=1$ ) opens a wide range of opportunities to develop tandem solar cells. Efforts made since decades by research teams to increase efficiency have led to important progress. Recently, the record CIGS cells have reached a 23.35% efficiency (Solar Frontier company, 2019). Nonetheless, high efficiencies CIGS based solar cells are obtained for band gap of 1.2 eV ( $x=0.35$ ), while increasing the gallium content in the cells has, up to now, invariably and surprisingly been associated with a degradation of the performances. Despite an impressive number of investigations (see for example [1, 2] and references therein), the factors leading to this limitation of the efficiency are still a matter of debate. Among the steps which have led to high efficiency CIGS solar cells, the 3 stage growth process has been decisive [3]. Two main advantages arise from this process [4]. On the one hand, a recrystallisation occurs and consequently the grain sizes increase, leading to an overall reduced defect density [5]. On the other hand, the CIGS layer composition is not uniform, with a double Ga gradient formed along the growth axis (examples of experimental evidences of this gradient can be found, for example in [6, 7, 8]). This double Ga gradient has a positive effect on the short circuit current density, by absorbing photons with lower energy and also increasing the conversion efficiency for photons of higher energy as compared to a cell having the same composition but without Ga gradient. Simultaneously, a positive effect on the open circuit voltage is observed due to the creation of a quasi electrical field, which enhances the collection of minority carriers from quasineutral region and thus decreases recombinations [9, 10, 11, 12]. This gradient leads to a distribution of the lattice parameters, thus complicating the interpretation of x-ray diffraction patterns commonly used to determine the cell compositions. In this work, we develop a model which allows us to predict the shape of the x-ray diffraction line from the gallium gradient profile. This allows for a detailed analysis of the x-ray pattern versus composition, demonstrating that the sample average composition is often not corresponding to the

x-ray peak position. Moreover, although the gradient profile cannot be uniquely determined from our model, gradient shapes may be classified as compatible, or not, with the x-ray diffraction data obtained on the samples. Diffusion of group III elements in CIGS under different growth conditions have been studied in the past [13],[14] and is a determinant effect of the formation of the Ga gradient. We will show that our model enables us to get some interesting insights on the diffusion of group III elements in the layer

## 2. Experimental

In this study, we have grown a set of solar cells with different average gallium compositions ( $x$ ), ranging from  $x = 0$  to  $x = 0.87$ . Our solar cells have the following “classical” structure: SLG/Mo/CIGS/CdS/ZnO:i/ZnO:Al [15]. The experimental growth techniques are detailed in the supplementary information. Compositions of solar cells are adjusted by varying the ratio between Ga and In fluxes, but by keeping the total group III flux constant. This last disposition is taken in order to use a constant growth rate, to compare samples with similar thicknesses, as well as to not induce kinetic modifications in the growth mechanisms. In order to study the double Ga gradient using X-ray diffraction, we recorded the (112) CIGS diffraction peak, using a high resolution setup (see the Supplementary information). The determination of the composition must be handled with great care. In presence of a compositionnal gradient, all experiments to determine the composition will average a given depth of material. In this work, average composition is estimated using transmission and EQE optical experiments, which determine bandgap. Bandgap in turn is related to composition using a quadratic relationship, with a bowing parameter taken to be 0.24 [16]. Some samples have also been investigated using Energy dispersive X-ray spectroscopy (EDS). All these measures are used to cross check the average sample compositions deduced from our model.

## 3. Results and discussion

### 3.1. Electrical characteristics of our solar cells

The 0.25cm<sup>2</sup> solar cells were characterized at 25°C under AM1.5 illumination (100 mW/cm<sup>2</sup>). Electrical characteristics are gathered table 1.

$x$	Voc (mV)	Jsc (mA/cm <sup>2</sup> )	FF (%)	$\eta$ (%)
0	470	35.4	65.9	11.0
0.19	567	33.0	68.3	12.8
0.37	706	32.0	69.6	15.7
0.47	756	29.5	70.0	15.6
0.65	827	24.3	63.0	12.7
0.87	818	14.8	59.6	7.2

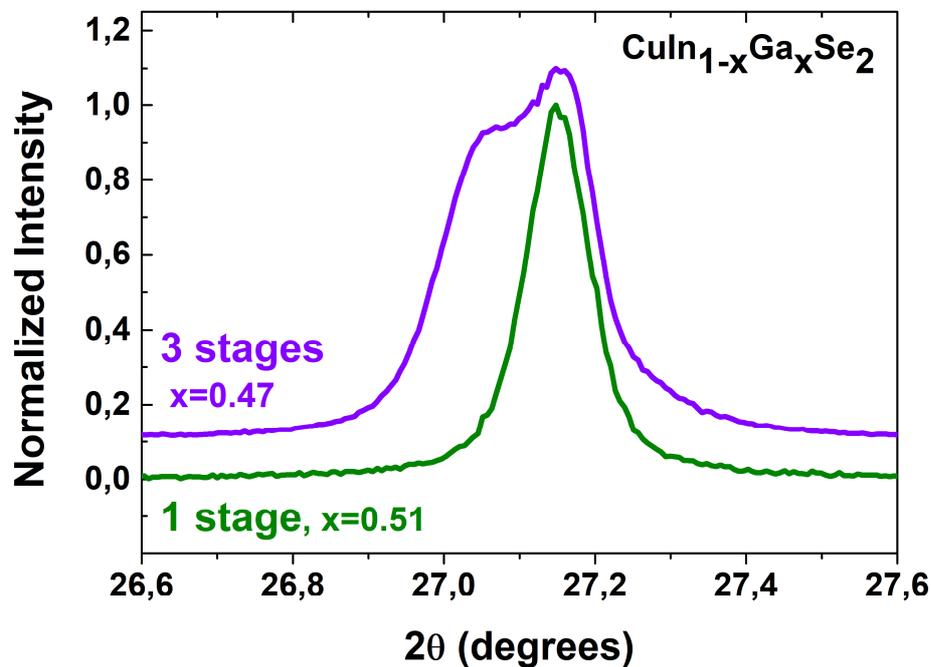
**Table 1:** Electrical characteristics of our solar cells

As table 1 shows, the decrease in efficiency for high band gap solar cells ( $x > 0.5$ ) is primarily due to a stagnation of the open circuit voltage and a drop of the fill factor. We should expect an increase of Voc, at more or less constant FF, with increasing Ga content, due to the increase of the absorber bandgap. Many

factors are likely to contribute to this limitation, including an increase of the recombination centers (crystalline defects, either point or extended ...), modification of the group III element gradient. This will be discussed in the next sections.

### 3.2. Experimental effect of the double Ga gradient on the x-ray diffraction peak

In order to analyze the effect of the double Ga gradient on the X-ray diffraction, a cell with composition,  $x = 0.51$  has been grown using the so-called 1-step process. In this process, all the elements are provided simultaneously, and no composition gradient is to be expected within the samples grown using this method. We have also prepared a sample with similar average composition, but using the 3-stage process. In this process, the elements (In, Ga, Se) and (Cu, Se) are introduced during different sequences, and intermixing and diffusion leads to the final result. A double gradient (decreasing from the sample surface, the increasing) is naturally formed under such dispositions. Figure 1 shows the x-ray diffraction patterns of both cells with and without Ga gradient.



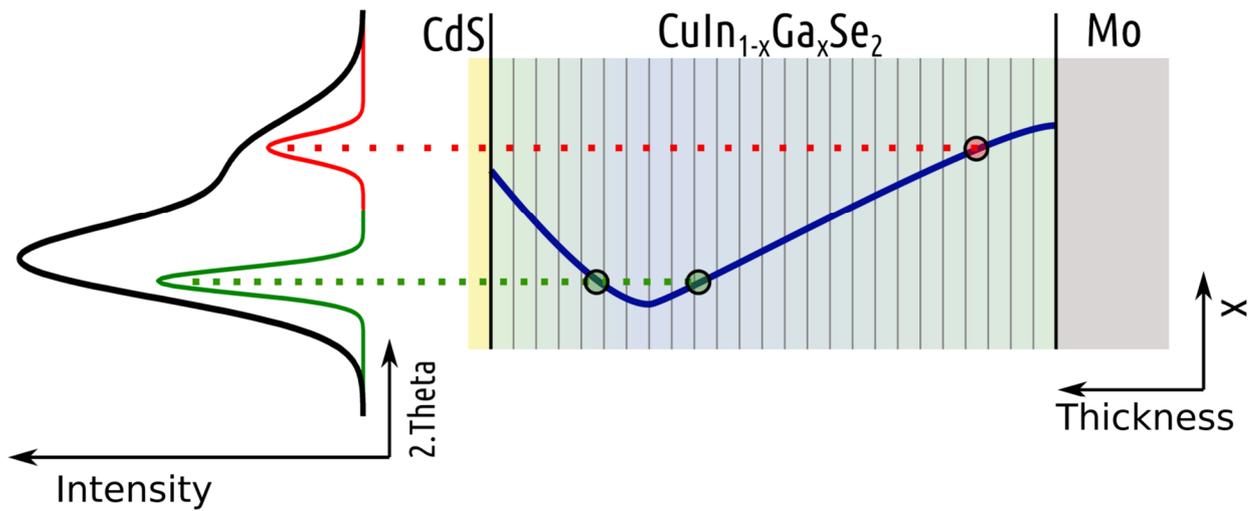
**Figure 1:** (112) x-ray diffraction peak of two CIGS solar cells produced with the so-called 1-step process (green) and the 3-stage process (violet). Both have comparable average Ga composition. The 3-stage process induces a double Ga gradient in the solar cell in opposition to the 1-step process.

As shown Fig 1. the double Ga gradient causes an enlargement and a structuration of the (112) X-ray diffraction peak. Usually, the “expected” average composition is obtained by using the position of the main diffraction peak. In figure 1, we have selected a sample which exhibit a clear structuration of the (112) peak, due to the gradient. However, in many cases the structuration is not as pronounced, and the inclination to interpret the peak maximum as corresponding to the average composition is even more natural. This method can be questioned, and we may also expect to extract additional information on the gradient from the experimental x-ray data : therefore we have proceeded to a modeling of the (112) x-ray diffraction peak in order to investigate these aspects. The presence of possible secondary phases, which could complicate the interpretation of our data has been checked on all samples : Prior to examining the (112) peak in details, a full scan over a large angular domain is performed, precisely to check all existing phases. No evidence of secondary gallium related phases could be detected in any of our samples.

### 3.3. Modelization and interpretation of (112) x-ray peak diffraction pattern

Figure 2. displays a schematic interpretation of the observed (112) peak, and provides the core elements

of our model.



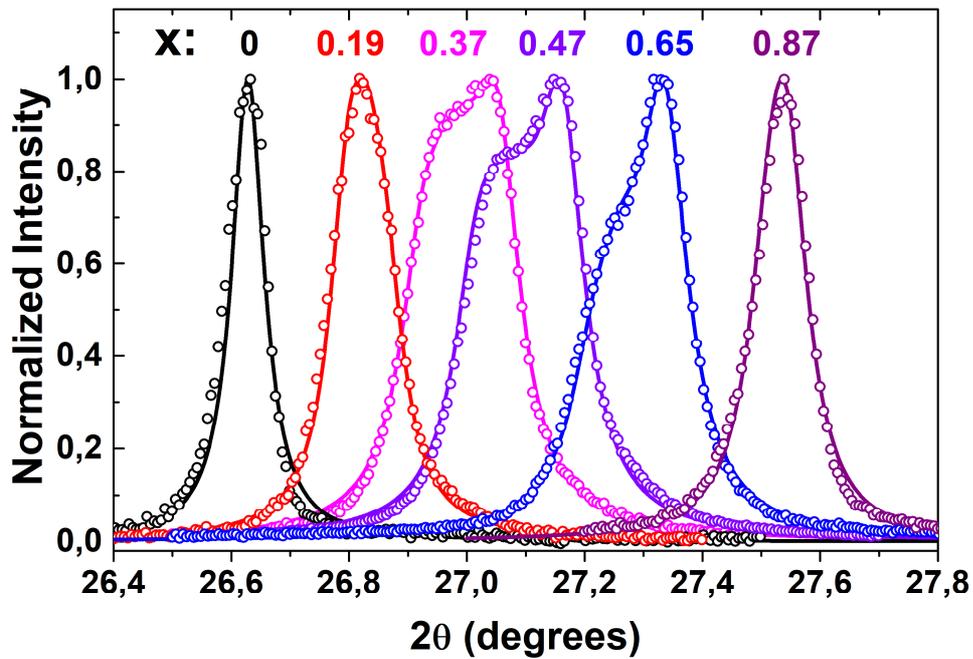
**Figure 2:** Schematic representation of modelization (112) peak diffraction

The thickness of the absorber layer is discretised into several sub-layers with an assigned, supposedly homogeneous, Ga composition. In this way, we may reproduce any profile for the double Ga gradient. According to the Bragg relation, sub-layers with different Ga ratio will have different lattice parameters and diffract at different angles. This is the root cause for the observed enlargement of X-ray diffraction peak. The signal at the lowest angle corresponding to the minimum Ga concentration, i.e. the notch composition, and the signal at highest angles corresponding to the maximum Ga concentrations, the compositions close to the interface between the absorber and back electrode.

We compute the overall diffraction intensity by summing the signals from each sublayer, where several factors have been taken into account. First, there is the multiplicity of sub-layers having the same composition. As Figure 2. shows, some sub-layers have the same composition and consequently have a multiple contribution. However, absorption plays a key role and intervenes differently for sublayers placed at different depths. Such an approach has already been presented in [17], but no mention is made the method used to sum up all contributions, which should include the effect of the broadening due to defect densities and experimental resolution. A more detailed approach is given in [7], where all intensity contributions are included in a histogram, which is weighted by absorption and by a gaussian distribution assuming a constant peak width. Here, we have reworked these ideas, in our model detailed in the supplementary material.

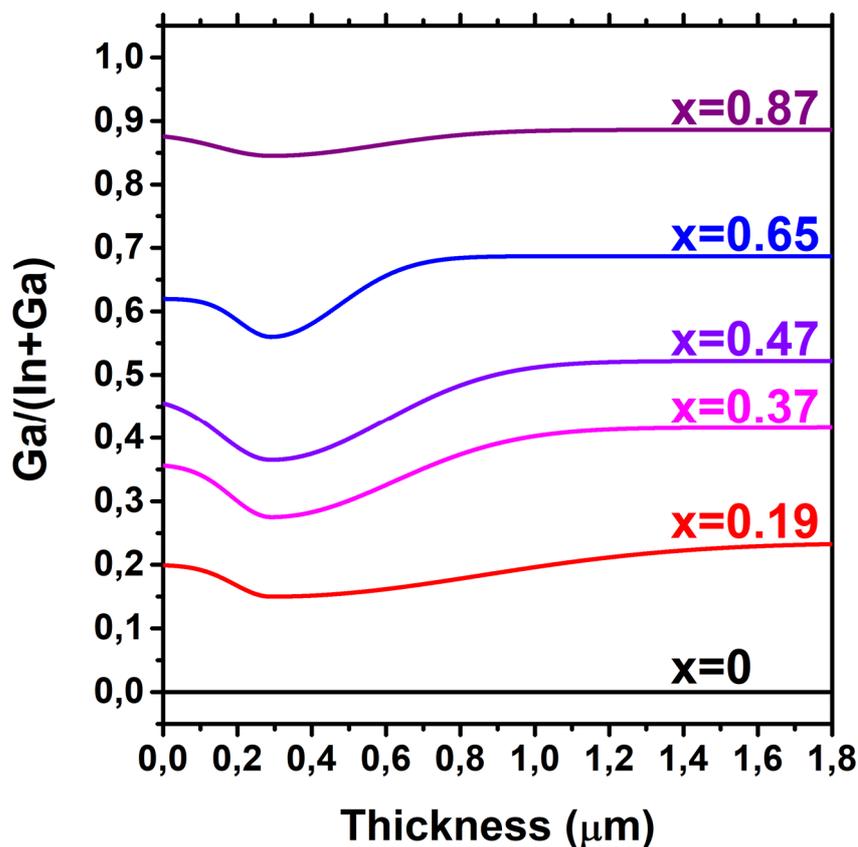
### 3.4. Fitting the experimental data

Figure 3. shows the (112) x-ray diffraction peaks obtained for the series of samples and the best fits obtained from our model.



**Figure 3:** Experimental x-ray data for (112) peaks (stars) and calculated data (solid lines). Lorentzian lineshapes were used in the abovementioned model to fit the data presented here.

From Figure 3. we observe that the structure of the x-ray diffraction peak is composed of two main contributions. One at low angle and another at higher angle. There is a clear trend with Ga concentration. By increasing the Ga content, the contribution at lower angles decreases while the other one increases. The patterns are clearly broadened for middle compositions, while extreme compositions are symmetric and thinner. The (112) x-ray diffraction peak of a CIS solar cell is also shown. In this ternary absorber, no gradient due to differential group III element diffusion can occur, since only In is present. This is confirmed by the narrow (112) diffraction peak observed. Figure 4. shows the compatible gradient shapes used in our modelization. It must be noted that the gradient shape cannot be “extracted” from our model. A shape has to be assumed and parametrized, and its validity has to be tested by computing the differences between calculated data and experimental points. However, we observed that the postulated gradient shapes are constrained within reasonably narrow sets that enable us to extract precious information on the evolution of the gradient profiles.



**Figure 4:** Compatible Ga gradient shapes used in our modelization to reproduce accurately the experimental (112) x-ray diffraction peaks shown in Figure 3.

From figure 4, it is clear that with high Ga content, the double Ga gradient becomes less pronounced and the composition from the Mo/CIGS interface is more uniform, on a increasing depth.

### 3.5. Discussion

By modeling the (112) x-ray diffraction peak, we have been able to analyze the shape of the double Ga gradient in our solar cells. Moreover, due to the large size of the x-ray spot (0.2 x 15 mm in our case), the measure gives an average value on its size, while roughness and spatially limited measure may sometimes cause artifacts with SIMS analysis. Our analysis also lead to an important conclusion, in terms of layers characterization : since the x-ray peak is distorted due to the Ga gradient, the location of its maximum cannot be interpreted as corresponding to the mean gallium composition in the layer. The resulting error may amount up to a 5% compositionnal difference between the position of the peak maximum and the mean composition calculated from the fitted composition profile. In our experiments, we have used a high resolution x-ray setup which allows a clear resolution of the peak structure, but in many laboratories, a simpler setup, providing CuK $\alpha$ 1 and CuK $\alpha$ 2 lines will hide this fact, by broadening the peaks. Our method thus provide a way to extract much more precise evaluations of the mean compositions of the samples.

Concerning the evolution of gradient shapes with Ga content, it can be analyzed in terms of a decrease in the interdiffusion of group III elements. The consequence is a reduction, with increasing Ga content, of the width of the zone where a pseudo-electric field, due to the composition gradient, exists. Since the double graded Ga profile engineering belongs to the efficiency optimisation technological means [9, 10, 11, 12], this will in turn negatively impact the carrier collection efficiency, and decrease the cells efficiency at high Ga content. However, the efficiency decrease at high Ga content cannot be only attributed to this Ga gradient reduction. The influence of deep Ga-related defects play also a dominant role [18, 19]. From the x-ray analysis, we have not found any evidence for a marked decrease of the crystalline quality of the material when the gallium content is increased (no need to attribute different

broadening parameters for different compositions - all layers could be fitted using a unique broadening parameter, for all depths).

The effect of the growth temperature is an important point : it clearly appears that the gradient width is reduced in samples with high Ga content. In order to efficiently collect photogenerated carriers, it is desirable to increase its width. The factors governing this width are the factors governing diffusion in solid phase, namely time spent at the elevated process temperature and interdiffusion coefficients. Both intervenes in a linear manner in the Fick equations ruling the diffusion phenomenon, but the interdiffusion coefficients are thermally activated, and thus increase exponentially with temperature. The simplest way to increase interdiffusion to obtain a proper gradient is then to increase the temperature in the second and third steps of the 3 stage process. Further improvements are also to be expected, in avoiding strong local compositionnal fluctuations, that may be present as demonstrated by thermodynamical modeling performed using density functionnal calculations by Ludwig and coworkers [20]. Finally, Contreras et al. have shown that by increasing the temperature, the efficiency of wide-gap solar cells is improved, owing to an increase of Voc[21] , which is compatible with our hypothesis.

#### 4. Conclusion

We have developed a model which allows us to reproduce with high accuracy the measured (112) x-ray diffraction peak in CIGS layers, within solar cells. It allows to build and test composition gradient profiles, and lead us determine i) the exact mean composition of our samples, which is often different than what can be deduced from the main x-ray peak position and ii) to obtain insights on the group-III elements interdiffusion. Our technique has the benefit of being non destructive, to probe a large area of the sample, and to be usable of full solar cells, with buffer and window layers deposited on top of the CIGS layer. From the resulting analysis of the elements interdiffusion, we observe that using an identical process temperature for sample grown with increasing Ga content, the region where a pseudo-electric field exists in CIGS is noticeably reduced for higher Ga contents, explaining, at least for a part, the reduction of the performances, due to decreased carrier collection. We propose that growth temperature has to be tuned for each gallium composition, increasing it with increasing gallium content.

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