Thin Solid Films xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Influence of indium/gallium gradients on the Cu(In,Ga)Se_2 devices deposited by the co-evaporation without recrystallisation

Tomasz Drobiazg [a,b,*], Ludovic Arzel [b], Adem Dönmez [c], Paweł Zabierowski [a], Nicolas Barreau [b]

[a] Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warsaw, Poland
[b] Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS-UMR 6502, 2, rue de la Houssinière, BP 32229, F-44322 Nantes Cedex 3, France
[c] Faculty of Science, Department of Physics, Muğla Sıtkı Koçman University, 48000, Muğla, Turkey

ARTICLE INFO

Available online xxxx

Keywords:
Cu(In,Ga)Se_2
CIGSe
Recrystallisation
Indium gradient
Gallium gradient
Notch position
Secondary barriers
Electrical characterisation

ABSTRACT

In the laboratory scale, cells based on Cu(In,Ga)Se_2 grown by the 3-stage process reach the best performance because of high open-circuit voltage and short-circuit current (V_{OC}–J_{SC}) combination. One of the reasons for that could be the V-shaped gradient of Ga to In atomic ratio throughout the Cu(In,Ga)Se_2 layer, which results from large differences in the diffusion coefficients of In and Ga. The location of the lowest Ga-content in the Cu(In,Ga)Se_2 (i.e. Ga notch), also corresponds to the Cu-poor to Cu-rich transition during the 2nd stage. Since this transition is associated to a phenomenon of recrystallisation, the arising question is whether high V_{OC}–J_{SC} combination is effectively inherent to V-shaped gradient or to recrystallisation. In our work we attempt to eliminate the influence of recrystallisation to exclusively study the influence of Ga/In gradients. Our approach was to co-evaporate samples by the one-step process with different gradients by the continuous modification of In and Ga fluxes during the deposition and keeping constant that of Cu in a way that its ratio to group III elements was 0.9. With this method, we could obtain a set of Cu(In,Ga)Se_2 layers either free of gradient, with linear gradient (i.e. no notch) or V-shaped gradient with notch at a different distance from the Cu(In,Ga)Se_2 surface. We observe that depending on the presence of notch in conduction band or the position of notch it is possible to modify the impact of secondary barriers on current–voltage characteristics.

1. Introduction

High value of the short circuit current (J_{SC}) of solar cells based on Cu(In,Ga)Se_2 (CIGSe) deposited by the 3-stage process is attributed to the beneficial role of conduction band grading which serves as a chute for the charge carriers. Besides that, high open-circuit voltage (V_{OC}) is one of the characteristics of CIGSe devices which have experienced the recrystallisation phenomenon at the end of the second stage of the deposition. This transition improves the quality of the absorber layer, i.e. grains are much larger which results in the reduced area of the grain boundaries, they also become oriented along one of the favourable crystallographic directions, (112) or (220)/(204) depending on the sodium supply [1]. Since the shape of the indium and gallium distribution profile is strongly related to the transition from the Cu-poor to the Cu-rich conditions where the recrystallisation takes place [2] it is difficult to distinguish between the advantageous role of the band gap grading or the recrystallisation itself. In many scientific papers people are studying the impact of the band gap shape by means of computer simulations but so far not much effort has been done to study these effects in real samples which have the gradient but did not recrystallise [3,4]. From the point of view of electronic defects both the absolute position of the conduction band due to the indium and gallium ratio and the cleansing effect of the recrystallisation seem to be very important. Activation energies of defects depend on the position of conduction and valence bands and even a slight change in the values of energies can dramatically alter the charge density inside the device which in turn modifies the device electrical parameters, i.e. the metastable defects [5]. One can presume that one of the consequences of recrystallisation is the reduction of electronic defect density.

Our approach was to simplify the problem as much as possible. This is why we have decided to prepare our samples in the process where all of the elements are deposited at the same time to avoid any recrystallisation which in turn gives us an opportunity to precisely control the spatial composition of the absorber layer.

2. Experimental details

Analyzed solar cells have been prepared in the one-stage co-evaporation process from the elemental sources of copper, indium, gallium and selenium. We used soda–lime glass substrates covered with the 650 nm of molybdenum which serves as the back contact of the device. The p-side of the junction is the 1.8 μm thick CIGSe for samples H, M, L, NF and NC and 1.45 μm for GC. Names of samples stand for High, Medium and Low from high, medium and low Ga content, respectively and

---

[*] Corresponding author.
E-mail address: drobiazg@if.pw.edu.pl (T. Drobiazg).

http://dx.doi.org/10.1016/j.tsf.2014.09.069
0040-6090/© 2014 Elsevier B.V. All rights reserved.

Table 1
Summary of prepared samples. Sample names stand for: High, Medium, Low, Gradient Constant, Notch Far and Notch Close, respectively.

Sample	Desired E_G (eV)	Notch (if yes, distance from the surface)	Composition from EDX, x = [Ga] / ([In] + [Ga])	E_G from EQE (eV)
H	1.25	No	x = 0.45	1.26
M	1.16		x = 0.30	1.15
L	1.08		x = 0.15	1.07
GC	1.25 → 1.08		See Fig. 2	1.09
NF	1.25 → 1.08 → 1.16	350 nm		1.09
NC	1.25 → 1.08 → 1.16	170 nm		1.09

Notch Far, Notch Close and Gradient Constant depending on the position or presence of notch (Table 1). Different thickness of sample GC is to maintain the same slope of conduction band as in sample NF where it is decreasing (the conduction band) from Mo/CIGSe to CIGSe/CdS interface (see Fig. 1). The n-side has been completed by the chemical bath deposition of the 50 nm thick CdS layer and sputtered layer of highly resistive ZnO (50 nm) and Al doped ZnO (350 nm) acting as a window. We have prepared a set of six complete CIGSe devices. Three of them do not have any indium and gallium gradients and the only difference is the band gap value. Three remaining samples have artificially induced indium and gallium grading which is obtained by the modification of the rates of elements during the deposition process. Before the deposition the fluxes of the elements were carefully calibrated which allowed us to obtain the desired composition. Composition of the samples has been measured with the use of a scanning electron microscope (JEOL JSM 5800LV) combined with an electron dispersive X-ray spectroscopy (EDX) detector; the accelerating voltage has been set to 20 kV and the beam current to 0.3 nA. Samples H, M and L have been prepared in order to see what will be the impact of different values of band gap and no gradients on the solar cell performance under different measurement conditions (different light and bias conditions). Samples with gradients should inherit the combination of properties of samples without indium and gallium gradients as some specified points in the conduction band correspond to the same points in samples with flat band gap. For example band gap values in sample GC at Mo/CIGSe and CIGSe/CdS interface correspond to band gap in samples H and L, respectively thus the properties of the first interface should be similar in samples GC and H and properties of the latter interface should be the same in samples GC and L.

3. Results and discussion

Profiles of gallium over indium plus gallium are close to the desired ones (Fig. 2) for samples GC and NF. Since the notch for sample NC was assumed to be placed 170 nm from the surface (first 10% of the layer thickness) it is not visible in the EDX profile due to roughness of comparable amplitude (that was checked with the SEM). The value of x for the sample NF in the position of the notch is around 0.20 which is slightly overestimated. The measured value of the band gap is 1.09 eV thus this corresponds to the value of x of 0.15, exactly the desired value for this sample in the notch position.

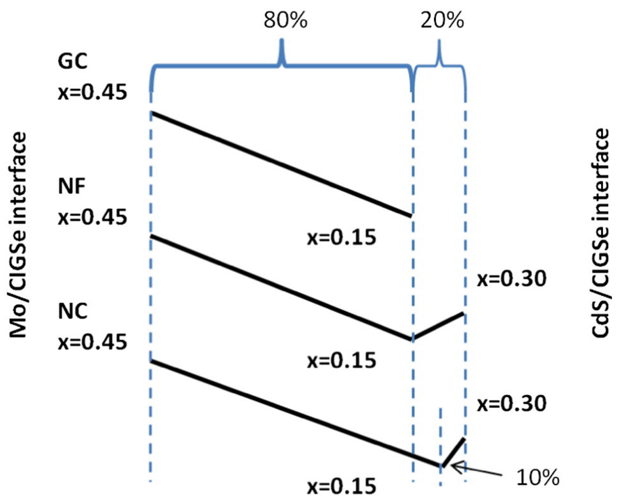

Fig. 1. Desired x = [Ga] / ([In] + [Ga]) ratios throughout the sample thickness.

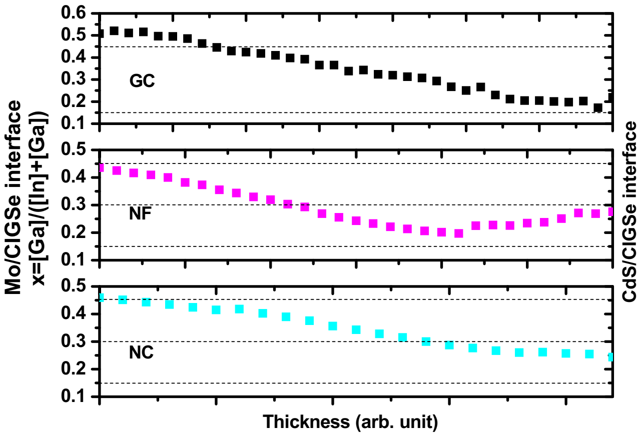

Fig. 2. EDX profiles of samples with indium and gallium gradients.

To obtain the solar cell parameters current–voltage (JV) measurements have been performed in standard test conditions (STC). More careful JV analysis comprises of measurements in white light in the relaxed and light soaking conditions. To measure in the relaxed state the sample has been kept for one night in darkness at room temperature. In the light soaking state the sample is illuminated with strong, white light from a halogen lamp for 30 min at room temperature and then cooled down to 100 K with light still illuminating the surface. Space charge widths and net acceptor concentrations have been obtained by means of capacitance–voltage measurements (CV).

Evolution of J_{SC} and V_{OC} for samples H, M and L is not very surprising (Fig. 3), only the fill factor of sample M stands out. Regardless of lower thickness sample GC (1.45 μm compared to 1.8 μm for the remaining five) does not exhibit any loss in the J_{SC}. It is either due to the lack of importance of the thickness change or artificially created band gap grading. Since the light absorption in CIGSe solar cells is very high the 350 nm difference in thickness is not enough to dramatically modify

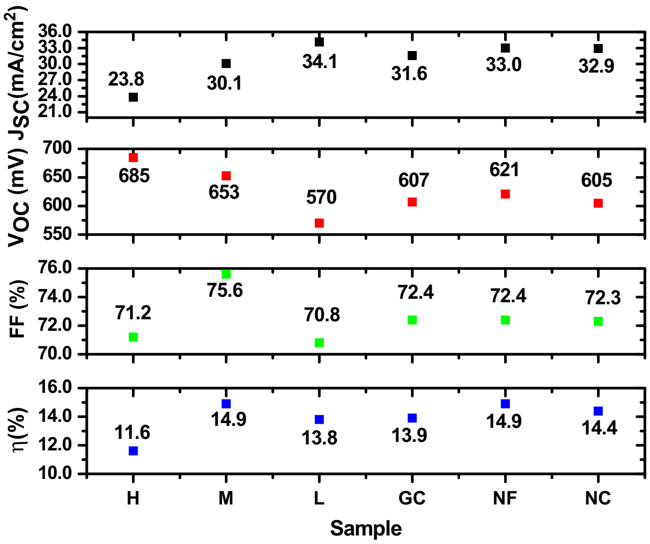

Fig. 3. Average STC electrical parameters. Each value is the average of 14 solar cells.

Please cite this article as: T. Drobiazg, et al., Influence of indium/gallium gradients on the Cu(In,Ga)Se_2 devices deposited by the co-evaporation without recrystallisation, Thin Solid Films (2014), http://dx.doi.org/10.1016/j.tsf.2014.09.069