DEVELOPMENT OF A NOVEL PRECURSOR FOR THE PREPARATION BY SELENIZATION OF HIGH EFFICIENCY $CuInGaSe_2$/CdS THIN FILM SOLAR CELLS

N. Romeo[1], A. Bosio[1], V. Canevari[2], R. Tedeschi[1], S. Sivelli[1], A. Romeo[3] and F.V. Kurdesau[4]
[1]Department of Physics, University of Parma, INFM, Italy
[2]Imem-CNR, Parma, Italy
[3]Scientific and Technological Department, University of Verona, Italy
[4]ETH Zürich Thin Films Group, Zürich, Switzerland
[1]Parco Area delle Scienze 7/a, 43100 Parma, Italy, Ph.+39 0521 905257,
Fax. +39 0521 905223, e-mail: romeo@fis.unipr.it
[2]Parco Area delle Scienze 37/a, 43100 Parma, Italy, Ph.+39 0521 269226,
Fax. +39 0521 269206, e-mail: canevari@fis.unipr.it
[3]Ca' Vignal 2, Strada delle Grazie, 37134 Verona, ph. +39 045 8027053,
e-mail: Alessandro.Romeo@univr.it
[4]Technoparkstrasse 1, Einstein Building, Zürich, Switzerland. Ph.+41 1 4451485,
Fax. +41 1 4451499, e-mail: kurdesau@phys.ethz.ch

ABSTRACT: A novel precursor suitable to prepare uniform $CuInGaSe_2$ thin films on an 1 $inch^2$ area has been developed. The precursor is obtained by depositing in sequence In_2Se_3, Cu and Ga on a Mo covered glass and by a subsequent annealing at 400°C in vacuum for 1-2 hours. By selenizing this precursor in a Se-flux in vacuum for half an hour at 500°C substrate temperature a uniform and well crystallized $CuInGaSe_2$ film is obtained. Solar cells prepared by depositing in sequence on top of the $CuInGaSe_2$ film 60 nm of CdS, 100 nm of pure ZnO and 2 μm of ZnO:Al exhibit a uniform efficiency of 14,5% over the 1 $inch^2$ area.
Keywords: $Cu(InGa)Se_2$, Thin Films, Selenization

1 INTRODUCTION

$CuInGaSe_2$ based solar cells exhibit the highest conversion efficiency for an all thin film solar cell.

A 19.2% efficiency has been obtained by Romero et al. [1] for an area smaller than 1 cm^2 with a three-steps coevaporation method [2]. However, this technique is hard to be used in an industrial scale, since the simultaneous evaporation from different sources gives non homogeneous films on large areas. A technique that is quite suitable for large scale application is the selenization of stacked elemental layers. This technique has been used by Shell Solar that has already fabricated 40 Wp modules with an efficiency around 12% [3].

Increasing further the module area seems to be a great challenge.

The most important step in the selenization method is the precursor preparation.

In the past we tried to make the precursor by depositing in sequence In, Cu, Ga in stoichiometric proportion, and mix them by making an annealing in vacuum at a substrate temperature of 400°C for half an hour [4]. Despite we were able to obtain 15% efficient cells on small area, the efficiency was not uniform on all the 1 $inch^2$ glass substrate.

We attributed this to the fact that the phase diagram of Cu-In-Ga contains a high amount of liquid that, due to the surface tension, tends to form drops and as consequence the stoichiometry is not uniform over the whole area. In this work, we report a new precursor, based on the mixing of In_2Se_3, Cu and Ga, that exhibits an optimum stoichiometry uniformity over all the 1 $inch^2$ glass substrate.

2 EXPERIMENTAL RESULTS

As a substrate a 1 $inch^2$, 4mm thick soda lime glass has been used. Mo, In_2Se_3, Cu and Ga were evaporated from a single rotatable crucible containing four sources by an electron gun in a chamber in which a vacuum of 10^{-7} mbar was routinely made, as shown in fig. 1.

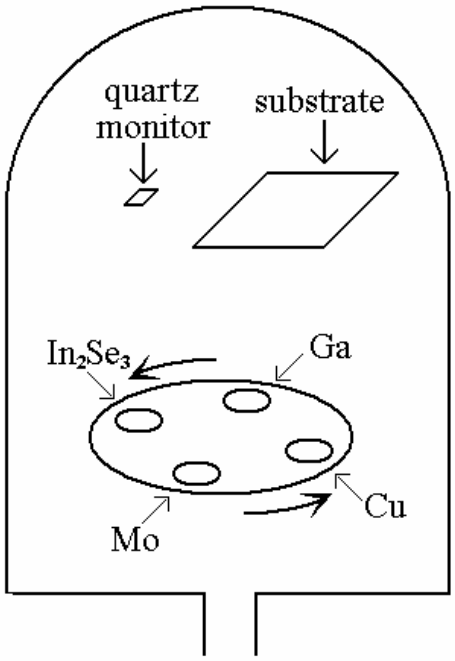

Figure 1: scheme of the electron beam deposition chamber.

First, a 1 μm thick Mo film was evaporated at a substrate temperature of 500°C onto the glass substrate. Then, the substrate temperature was lowered down at a value lower than 100°C and a 500 nm thick film of In_2Se_3 was deposited onto Mo. In sequence 100 nm of Cu and 50 nm of Ga were evaporated on top of the In_2Se_3 layer. The substrate temperature was increased at a value of 400°C at which an annealing of a few hours was done. This substrate temperature was chosen since it has been

found out that higher temperatures tend to separate Cu-rich phases from In-rich phases.

This precursor resulted to be very smooth and homogeneous on all the 1 inch^2 substrate. In fig. 2 an Atomic Force Microscopy (AFM) image, where the smoothness of the layers is put in evidence, is shown.

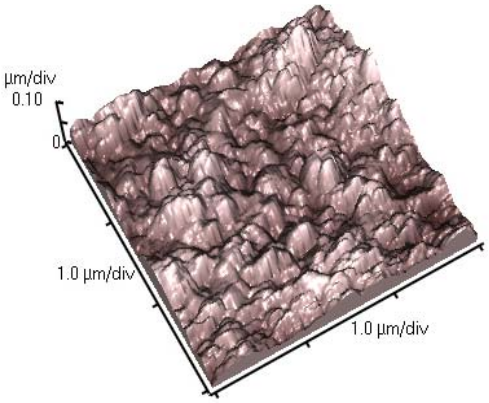

Figure 2: AFM image of the precursor. The average roughness is about 20 nm

In this first step the ratio Cu/(In+Ga) is about 0.85, while the ratio Cu/In is about 1.16 and the Ga content is about 26% in respect to In+Ga.

This precursor is then selenized in a vacuum chamber at a substrate temperature of 500°C by exposing it for half an hour to a Se vapour. An homogeneous and smooth film of Cu(InGa)Se_2 of about 0.9 µm is formed.

In order to make a Cu gradient and also to increase the thickness, a second step is done by depositing on top of this film 500 nm of In_2Se_3, 80 nm of Cu and 50 nm of Ga. Here the ratio Cu/In is decreased to 0.93.

The stacked layers are annealed for 1 h at 400°C substrate temperature and a second selenization is done at a substrate temperature of 500°C. Finally, in order to increase the Ga content close to the surface a third step is done by depositing in sequence 30 nm of Cu and 50 nm of Ga with a Cu/Ga ratio close to 1 and by making a third selenization.

The final thickness of the film is about 1.8 µm.

An AFM image of the finished film is shown in fig. 3.

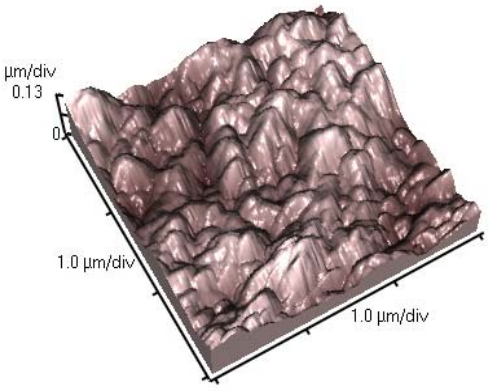

Figure 3: AFM image of the selenized precursor. The average roughness is about 50 nm.

The film is quite smooth and the grain size is on the order of 0.5 – 1 µm.

An X-ray analysis has shown that the material is principally oriented along the 112 direction and has a Ga content of 25-30%.

Solar cells were made by depositing in sequence 60 nm of CdS, 100 nm of pure ZnO and 2 µm of ZnO:Al on top of the above described $CuInGaSe_2$ film (see fig. 4).

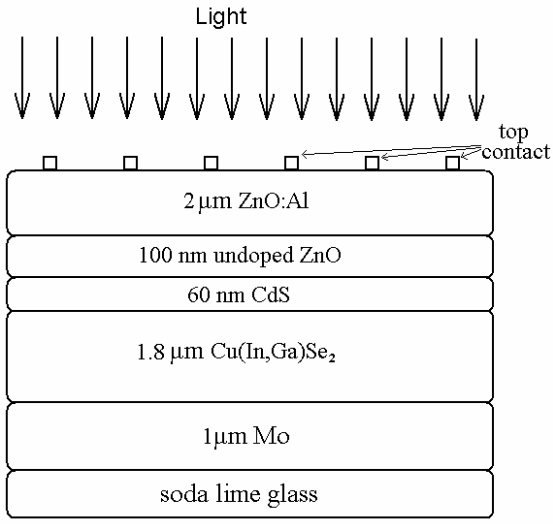

Figure 4: structure of the cell.

CdS was deposited both by RF sputtering at 200°C substrate temperature or by chemical bath deposition (CBD), while ZnO and ZnO:Al were deposited by RF sputtering at 100°C substrate temperature.

No significant difference concerning the cell performance has been found between cells made with CBD CdS deposition and cells made with CdS sputtering deposition.

The efficiency of the $CuInGaSe_2$/CdS solar cells was measured by using an Oriel solar simulator with an AM1.5, 100 mW/cm^2 solar light.

The best cell prepared by the process here described exhibits the following parameters:

Voc ≈ 610 mV,

Jsc ≈ 34 mA/cm^2

ff ≈ 0.7

η ≈ 14.5%

In any case one has to consider that the efficiency is uniform over all the 1 inch^2 area. This demonstrates that this process is suitable to be scaled up.

3 CONCLUSIONS

A new precursor, made by depositing in sequence In_2Se_3, Cu and Ga on top of a Mo covered 1 inch^2 soda lime glass, has been realized.

This precursor has the characteristics of being very smooth and uniform over all the 1 inch^2 area of the substrate and gives the possibility to make uniform $CuInGaSe_2$ films by selenization in a Se vapour.

Cells prepared with this precursor exhibit a uniform efficiency of 14,5% on the 1 inch^2 substrate area.

By changing the stoichiometry of the layers which compose the precursor, it is possible to further increase the cell efficiency.

Besides, this precursor could also be prepared by sputtering by simply using two targets, namely an In_2Se_3 target and a CuGa alloy target containing 25% of Ga, and by making an annealing at 400°C.

Sputtering, being a technique more scalable than electron beam gun, could give the possibility to produce this type of solar cells on an industrial scale.

REFERENCES

[1] M. J. Romero, K. Ramanathan, M. A. Contreras, M. M. M. Al-Jassim, J. Abushama and R. Noufi. Proc. of the NREL Photovoltaic Meeting, 2003.

[2] A. M. Gabor, J. R. Tuttle, M. Contreras, D. S. Albin, A. Franz, D. W. Miles, R. Noufi, Proc. of the 12th European Photovoltaic Solar Energy Conference (1994), p. 939.

[3] R.D. Wieting, Proc. of 29th IEEE Photovoltaic Specialists Conference (IEEE New York, 2002), p. 478.

[4] N. Romeo, A. Bosio, V. Canevari, R. Tedeschi, A. Romeo, V. Canevari, F. Fermi, Proc. Of the 14th European Photovoltaic Solar Energy Conference held in Barcelona, Spain (1997), p1224.