Technical Digest of the International PVSEC-14, Bangkok, Thailand, 2004

Properties of CIGS solar cells developed with evaporated II-VI buffer layers

A. Romeo, R. Gysel, S. Buzzi, D. Abou-Ras, D. L. Bätzner, D. Rudmann, H. Zogg, A. N. Tiwari*

Thin Film Physics Group, Laboratory for Solid State Physics, ETH Zürich, Technoparkstrasse 1, 8005 Zurich, Switzerland, Tel: +41-1-4451474, Fax: +41-1-4451499

E-mail: tiwari@phys.ethz.ch

* also at CREST (Centre for Renewable Energy Systems and Technology),

Department of Electronic and Electrical Engineering, Loughborough University, Leicestershire, LE11

3TU, UK.

ABSTRACT

The CIGS layers were grown with a vacuum evaporation method. The CdS was deposited by a high vacuum evaporation (HVE) method at different substrate temperatures and post deposition treatments were applied. Properties of different CdS layers are characterized and the analyses of the current-voltage and spectral response measurements have been performed to identify the differences of CBD and PVD processes.

ZnS and ZnSe buffer layers were applied as an alternative to CdS. Layers of different thickness were grown by e-beam (EB) and thermal evaporation (VE) at different substrate temperatures (RT to 400 °C).

A post-deposition annealing was applied in order to control the diffusion of Zn into the CIGS. Upon light soaking, increase in Voc and FF are measured.

1. Introduction

High efficiency CIGS solar cells have been obtained with chemical bath deposited (CBD) buffer layers [1-2]. However, for an in-line production of modules vacuum deposition processes (PVD) are preferred for compatibility reasons and high throughput. Moreover, high band-gap alternative buffer layers are needed to reduce the optical absorption losses in low spectral wavelength range.

We present a comparison of the CIGS based solar cells made with CBD, PVD-CdS and PVD-Zn-based buffer layers.

2. CdS as buffer layer

CdS has been deposited by high vacuum evaporation (HVE) at a substrate temperature of 50 °C, with different thicknesses of 80, 150 and 300 nm, measured by a guartz crystal.

The CIGS layers were not given any chemical or thermal surface cleaning treatment prior to the deposition of HVE-CdS.

ZnO-i and ZnO:Al are subsequently deposited by RF sputtering and a Ni/Al grid is provided for contacting. Reference cells by chemical bath deposition have been prepared for comparison.

The cell performance was strongly dependent on the thickness of the CdS. 80 nm have shown to be not

sufficient for a complete coverage giving place to micro-shunts which reduced the current. Current was much higher with 150 nm but the intrinsic ZnO layer was necessary to have a high efficiency. Cells made with CdS of 300 nm have shown lower current density in case intrinsic ZnO was applied. Cells with thick PVD-CdS without intrinsic ZnO performed a high current density and high efficiency (see table 1).

Table1. Comparison of CIGS cells with different thickness of CdS and different front contacting

i:ZnO	Yes	Yes	Yes	No
CdS thickn.(nm)	80	150	300	300
Voc (mV)	570	527	589	583
$Jsc (mA/cm^2)$	23	28.3	28	28
f.f.	63	69	59	70

In any case CIGS with PVD-CdS showed efficiencies of 10 to 13% while the reference cells with CBD-CdS had efficiencies of around 14% (see figure 1).

Light soaking of the cells with PVD-CdS provided only a small improve.



Figure 1. I-V measurements of CIGS cells with PVD and CBD-CdS.

3. Alternative buffer layers

ZnS and ZnSe were applied as alternative buffer layers to CdS. Two different deposition system were used, e-beam gun and vacuum evaporation.

Buffer layers by e-beam evaporation

Zn-based layers were deposited with temperatures from 100 to 200 $^{\circ}$ C in vacuum (10⁻⁶ mbar).

Buffer layers (measured with a quartz crystal) were from 20 to 200 nm thick.

Mo/CIGS stacks were annealed in vacuum prior to deposition. Moreover to control and enhance a slight diffusion of Zn a post deposition annealing treatment was also applied.

As shown in figure 2, the initial efficiency of a CIGS cell with ZnS by electron gun is relatively poor. Nevertheless post-deposition annealing in vacuum increases the current density. 3 to 5 hours light soaking reduces the series resistance and improves considerably the cell performance



Figure 2. I-V measurements of CIGS cells with electron gun deposited ZnS buffer layers, a) as-deposited, b) after annealing in vacuum and c) after annealing and 3 hours light soaking.

Buffer layers by vacuum evaporation

For comparison and to have a better control of the source temperature vacuum evaporation of Zn based buffer layers has been also applied.

ZnS and ZnSe have been deposited in a vacuum chamber (10^{-6} vacuum range) at temperatures of 50 to 150 °C, source temperature of 700 to 900 °C.

As shown in figure 3, coverage on CIGS grains of a 50 nm evaporated buffer layer is conformal; it is known that CBD deposition method avoids micro pin-holes which for PVD can show up with thin layers.

Comparison of X-ray measurements of ZnSe layers deposited by CBD and PVD, show that in the first case there is an evident presence of oxygen while in the second only ZnSe is observed.



Figure 3. Surface coverage of 50 nm-thick PVD-Zn based buffer layer (in this case ZnSe) on CIGS.

XPS spectra of CIGS/ZnSe stacks show a clear diffusion of Zn into the absorber as expected from the previous experiments.

Cells made with this system show a similar behavior as the ones made with e-beam deposition. A post-

deposition annealing was necessary to get high efficiency cells. Moreover, light soaking seems to increase dramatically the performance of the solar cells; as shown in figure 4, where a 5.4% (AM 1.5) efficiency cell jumps up to 9.1% after 5 hours of light soaking.



Figure 4. I-V measurement of a CIGS/ZnS cell before (a) and after annealing and light soaking (b).

C-V and temperature dependent I-V have shown that a high number of defects are present in the interface region between CIGS and ZnS-ZnSe layers. XPS mapping has shown an oxidized layer of CIGS in case the buffer layer is deposited by PVD, while by CBD this is not seen. We believe that this high amount of defects are given by the absence of a intermediate cleaning-etching step before the buffer layer deposition (that in case of CBD is given by the bath itself) which reduces the oxidized surface of the CIGS layer. Cells made with in situ PVD-deposited CdS (in the same CIGS deposition chamber) have shown a better performance than ex-situ samples.

4. Conclusions

Solar cells prepared with 80 nm thick HVE-CdS yielded an efficiency of up to 12 % (without any surface treatment of the CIGS layers), while reference cells with CBD-CdS had 14 % efficiency. SEM images showed conformal coverage of ZnSe on CIGS and XPS showed an intermixing of the two layers. Post deposition annealing in air and a subsequent light-soaking showed to be crucial for high efficiencies, as the efficiency increased from 5.8% to 9.1 % for the cells with ZnS buffer layer.

ACKNOWLEDGEMENTS

Kerstin Gebhardt (Institut für Physikalische Elektronik (IPE)), Gorg Voorwinden and Dimitrios Hariskos (Zentrum für Sonnenergie und Wasserstoff (ZSW)) are thankfully acknowledged for the CIGS absorbers. This work was performed within the PROCIS project of the European JOULE program and supported by the Swiss Office of Education and Science.

REFERENCES

 Kannan Ramanathan, Miguel A. Contreras, Craig L. Perkins, Sally Asher, Falah S. Hasoon, James Keane, David Young, Manuel Romero, Wyatt Metzger, Rommel Noufi, James Ward and Anna Duda. "Properties of 19.2% Efficiency ZnO/CdS/CuInGaSe₂ Thin-film Solar Cells", Prog. Photovolt: Res. Appl. 2003; 11:225-230

 Tokio NAKADA and Masayuki MIZUTANI "18% Efficiency Cd-Free Cu(In, Ga)Se₂ Thin-Film Solar Cells Fabricated Using Chemical Bath Deposition (CBD)-ZnS Buffer Layers", Jpn. J. Appl. Phys. Vol.41, pp. L165-L167, Part 2, No.2B Feb 2002.