## Evaluation of CdS and Zn<sub>x</sub>Sn<sub>y</sub>O<sub>z</sub> buffer layers in CIGS solar cells

**J. P. Teixeira**<sup>1</sup>, P.M.P Salomé<sup>2</sup>, Jan Keller<sup>3</sup>, R-Ribeiro Andrade<sup>2,4</sup>, N. Nicoara<sup>2</sup>, D. G. Stroppa<sup>2</sup>, M. Edoff<sup>3</sup>, T. Törndahl<sup>3</sup>, S. Sadewasser<sup>2</sup>, J.P. Leitão<sup>1</sup>

 <sup>1</sup> I3N and Department of Physics, University of Aveiro, Aveiro, Portugal
 <sup>2</sup> International Iberian Nanotechnology Laboratory, 4715-330 Braga, Portugal
 <sup>3</sup> Ångström Laboratory, Solid State Electronics, Ångström Solar Center, Uppsala University, SE-751 21 Uppsala, Sweden

<sup>4</sup> Departamento de Física, Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, Caixa Postal 702, 30123-970 Belo Horizonte, MG, Brasil

## jenniferpassos@ua.pt

Thin film solar cells based on Cu(In,Ga)Se2 (CIGS) have recently achieved a power conversion efficiency of 21.7% [1], being this value comparable with the record of multicrystalline Si based solar cells [2]. The record cells are fabricated using a CdS buffer layer, however there are many advantages in replacing the CdS for other material. The ideal buffer layer should have the same electrical properties as CdS, but a higher bandgap energy, contain only non-toxic elements and allow the deposition by a vacuum compatible technique [3]. Buffer layers thinner than the current thickness of 70 nm of the CdS layer are also wanted since then, these layers would be effectively more transparent. In this work we focus on a 20-30 nm alternative buffer material  $Zn_xSn_yO_z$  (ZnSnO) and the comparison of its properties and electrical performance with traditional CdS.

The two buffer layers and resulting devices are analyzed using several techniques: glow discharge optical emission spectroscopy (GDOES), x-ray fluorescence (XRF), current-voltage (J-V) under illumination, Kelvin Probe Force Microscopy (KPFM), surface photovoltage (SPV), capacitance-voltage (C-V), transmission electron microscopy (TEM) and photoluminescence (PL). In this talk, we will focus on the electronic levels' structure in both samples as investigated by PL. Normalized spectra of CdS and ZnSnO samples measured at 10 K and with an excitation power of ~3.6 mW, are presented in Fig. 1. Both samples show a broad band emission centered at ~1.09 eV, being the one from the CdS sample slightly blueshifted with regards to the emission from the ZnSnO sample. Both emissions reveal some asymmetry, and higher on the CdS sample. Frequently this asymmetry is more pronounced as the compensation ratio increases [5-7]. Thus, the results showing a higher asymmetry suggest a higher density of ionized defects for the CdS sample, than for the ZnSnO sample. In order to fully understand the differences between the two emissions, we also performed excitation power dependence measurements. The results show a blueshift of 13.5 meV/decade and 10.5 meV/decade for the CdS and the ZnSnO samples, respectively (Fig. 2). Such high blueshift values are typical of highly doped and compensated semiconductors and can be explained by the electrostatic fluctuating potentials model [5, 8]. The higher blueshift as well as the higher asymmetry of the emission for the CdS sample, suggests a stronger influence of the fluctuating potentials in that sample as a consequence of a larger density of ionized defects for the CdS sample. The results from PL suggest a better surface passivation of defects at the interface CIGS/buffer in the ZnSnO sample in comparison with the CdS one. Such interpretation is also validated by the higher ideality factor and the higher saturation current  $(J_0)$  of the CdS device compared with the ZnSnO one. Additionally, TEM analysis showed for localized areas of the interface, a diffusion of Cd into the CIGS layer and an out-diffusion of Cu into the CdS layer, which contribute to a higher density of defects near the interface CIGS/CdS in comparison with the CIGS/ZnSnO interface.

We confirmed that the alternative buffer layers ZnSnO can provide devices with performances very close to CdS, 14.9% and 14.6%, respectively, and the general trend that Cd-free buffer layers usually provide solar cells with higher values of short circuit current ( $J_{sc}$ ) and with lower values of open circuit voltage( $V_{oc}$ ) and fill factor (FF). The overall PL results show a strong influence of fluctuating potentials in both samples, being higher for the CdS sample. The conjugation of the PL results with the other measurements, namely C-V, J-V, and TEM, suggest a better surface passivation of defects at the interface CIGS/ZnSnO in comparison with the CIGS/CdS one. This work shows that by replacing the CdS layer with the ZnSnO, we create an interface with better properties. However, there are limitations to the Voc and FF of the ZnSnO devices that need to be further investigated.

## References

[1] Manz AG press release, September 23, 2014.

[2] M. A. Green, K. Emery, Y. Hishikawa, W. Warta and E. D. Dunlop, Prog. Photovoltaics, 23 (2015) 1.
[3] N. Naghavi, D. Abou-Ras, N. Allsop, N. Barreau, S. Bücheler, A. Ennaoui, C.-H. Fischer, C. Guillen, D. Hariskos, J. Herrero, R. Klenk, K. Kushiya, D. Lincot, R. Menner, T. Nakada, C. Platzer-Björkman, S. Spiering, A.N. Tiwari and T. Törndahl, Progress in Photovoltaics: Research and Applications, 18 (2010) 411.

[4] J. Lindahl, U. Zimmermann, P. Szaniawski, T. Törndahl, A. Hultqvist, P. Salomé, C. Platzer-Björkman, and M. Edoff, IEEE JOURNAL OF PHOTOVOLTAICS, **3** (2013.) 3.

[5] P. W. Yu, Journal of Applied Physics, **48** (1977) 5043.

[6] P. W. Yu, Journal of Applied Physics, **47** (1976) 677.

[7] J. P. Teixeira, R. A. Sousa, M. G. Sousa, A. F. da Cunha, P. A. Fernandes, P. M. P. Salomé, J. P.

Leitão, Physical Review B, 90 (2014) 235202.

[8] J.P. Teixeira, R.A. Sousa, M.G.Sousa, A.F. da Cunha, P.A. Fernandes, P. M.P. Salomé, J.C. González, J.P. Leitão, Applied Physics Letters, **105**, (2014) 163901.

## Figures



Fig. 1 Normalized PL spectra of CdS and ZnSnO samples measured at 5 K and with an excitation power of ~3.6 mW.



Fig 2. Dependence on the excitation power of the peak energy of the broad and asymmetric bands for CdS and ZnSnO samples.