Thin Film Solar Cells based on Earth Abundant and Non-toxic Materials: The cases of $Cu_2ZnSn(S,Se)_4$ and SnS

A.F. da Cunha[1], M.G. Sousa[1], P.A. Fernandes[1], J.P. Teixeira[1], J.P. Leitão[1]

$Cu_2ZnSn(S,Se)_4$ (CZTS) has been object of intense research worldwide for around half a decade with the main goal of replacing, the more mature, $CuIn_{1-x}Ga_x(Se_{1-y}S_y)_2$ (CIGS) as absorber layer in thin film solar cells. The advantage of this new compound is that it uses low cost and low toxicity elements. CZTS is a compound whose intrinsic point defects lead to p-type semiconductor behaviour. It presents a direct energy band gap of approximately 1.5 eV and as a result it shows a high absorption coefficient of 10^4 cm^{-1}. These properties confirmed CZTS as a good candidate for replacing CIGS. More recently, SnS has also started to emerge as an alternative to CIGS and CZTS. Even though it is an indirect band gap semiconductor it has an allowed direct transition at around 1.3 eV which leads to a high absorption coefficient around 10^4 cm^{-1} and it shows p-type conductivity derived from intrinsic defects, mostly Sn vacancies. Groups at Harvard University and MIT have recently demonstrated solar cells with 4.4% efficiency.

In our group, we are also working on the development of CZTS and SnS thin films and solar cells. We have established a growth method based on the annealing, in a rapid thermal processing furnace, of metallic and sulphide precursor stacks. The method is sketched in figure 1. We studied the influence of heating rate, maximum annealing temperature, time at maximum temperature and amount of evaporated sulphur on the properties of the films. The morphological, electrical and optical properties of the resulting layers are being optimized. These studies revealed that samples annealed at higher temperatures, shorter times and higher amount of evaporated sulphur exhibited larger grain sizes. We have, so far, produced, entirely in the University of Aveiro, functioning solar cells based on CZTS with 3.1% efficiency.

As for the work on SnS, we are working on development of a growth procedure to achieve single-phase SnS thin films. The bulk of the resulting films is formed predominantly by SnS but capped by a very thin layer of β-Sn. The results, so far, show that increasing the heating rate leads to the enhancement of the crystallinity of the SnS and decreasing the time at maximum temperature lowers the amount of the β-Sn phase detected on the film. The latter may result from the SnS decomposition at the surface. A summary of the growth method and main results is shown in figure 2.

In both cases, the growth methods under development are compatible with large-scale industrial production.

1 — Department of Physics & I3N, University of Aveiro

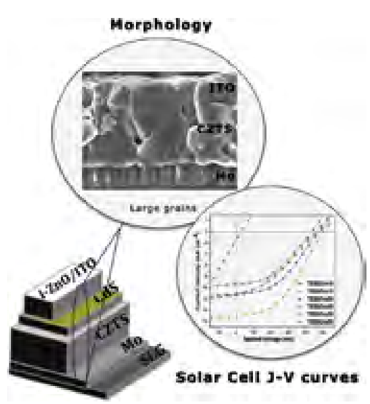

FIGURE 1
Cu_2ZnSnS_4 growth method and solar cell characterization results.

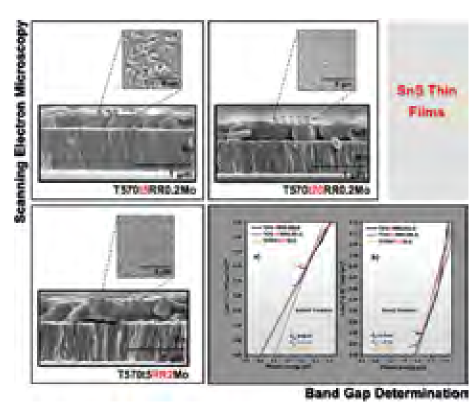

FIGURE 2
Some results representative of the SnS thin films optimization work.