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Compositional grading of CZTSSe alloy using exponential and uniform grading laws in SCAPS-ID simulation

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ABSTRACT

The SCAPS (Solar cell capacitance simulation) program were employed to analyze the compositional dependence of CZTSSe (Copper Zinc Tin Sulphur Selenium) absorber layers with Cadmium Sulphide (CdS) as buffer layer and Zinc Oxide (ZnO) as window layer for thin film solar cells applications. The primary motivation of this simulation work is to optimize the composition for Se/(S + Se) ratio, which would yield higher efficiency. The exponential and uniform grading law in SCAPS were set for the composition grading $y(x)$ over a layer, as well as to set the composition dependence $P(y)$ of a property. By varying the different compositions with exponential law and by using uniform law for the same composition, best efficiency of 14.97% were achieved for 0.4–0.1 composition of sulphur and selenium with Se/(S + Se) ratio of 0.80. Higher efficiency were obtained with higher Se content. The influences of the band gap of the CZTSSe alloys, which decreases linearly with an increase in its Se content, were further analyzed. The corresponding open circuit voltage, short circuit voltage, fill factor and efficiency of the simulated values on a photovoltaic cell with Mo back contact were studied in detail.

1. Introduction

The earth abundant and a low cost Kesterite $Cu_2ZnSn(Se,S)_4$ alloy is one of most sought out and promising semiconductor absorber layer for thin film photovoltaic cells and found to be a good competitor for CIGS based solar cells [1–9]. This Kesterite based devices utilizes abundant, nontoxic, rare-metal free absorber layer, and used as a substitute for CIGS absorber layer, thereby reducing energy losses and harvest more photons from the sun [1,10]. Copper-zinc-tin-sulphide (CZTSSe) solar cells have achieved a highest efficiency of 12.6% [11] which is directing towards low cost electricity generation. To fabricate a high-efficiency $Cu_2ZnSn(Se,S)_4$ solar cells, precise compositional accuracy is one of the acme issue that has to be studied detail oriented. CZTS is a quaternary semiconducting compound having a larger bandgap close to the optimal single–junction value of ~1.5 eV. CZTSSe has the same crystal structure, but varies with their bandgap energy, due to the influence in its composition, structural, electronic and the defect properties of the alloys [2,12–16]. The Kesterite based CZTSSe absorber layer materials of conventional thin film solar cells are directed to have optimised band gap energy (E_g) profile, which enhances photon absorption and carrier diffusion [2]. High current and voltage depends upon the trade-off between lower and the higher bandgap of the materials used. The CZTSSe based thin film solar cells involves a grading of the bandgap $E_g(x)$ by

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bringing in a spatial variation of the S and Se content within the CZTSSe layer. One of the major features of Kesterite semiconductor layer is the continuous tuning of the band-gap layer due to the isovalent exchange of groups (eg., Se–S) which improves the collector efficiency [17]. Thus, under illumination effects, the quasi Fermi level splits and absorbs the broad range of photons, which are responsible for higher open circuit voltage of the cell performance [1,18]. Individual elemental fluxes are the most important parameters that must be precisely controlled during the deposition process that affects compositional gradients due to different reaction kinetics. The open circuit voltage of the Kesterite based thin film devices can be further increased by the partial substitution of selenium with sulfur, which further widens the surface bandgap and the passivation of recombination centers within the space charge region. The main aim of using this compositional depth profile grading is to make out a well suited band gap profile in-order to increase the short circuit current, while maintaining the open circuit voltage. The Shockley–Queisser (SQ) limit, for a Kesterite based thin film solar cell is given by an efficiency of over 30% whereas practically it is limited to 12.6% [11,24,25]. So research has been focussed further, to enhance this practical efficiency limit. One of the major key factors that influence the efficiency of the photovoltaic cell performance is the depth profile of the bandgap energy. In CIGSe solar cells, the bandgap is tuneable in the range of 1 to 1.7 eV by tuning the Ga/(In + Ga) ratio. By increasing the Ga content there will no change in valence band maximum (E_v) and on the other hand the conduction band minimum (E_c) shifts towards the higher energy direction. This graded Ga in the absorber layer leads to the tuning of the bandgap [19–23]. High efficiency CIGSe solar cells were obtained using a three-stage evaporation process, in which the bandgap profile is controlled by the individual deposition parameters. Depending upon the single and the double band-gap depth profiles, there will be an improvement in the open circuit voltage (V_{oc}) and the short circuit current (J_{sc}) of CIGSe solar cells. For CZTSSe solar cells, the band-gap is tuneable from 1.0 eV of $Cu_2ZnSnSe_4$ (CZTSe) to 1.5 eV of Cu_2ZnSnS_4 (CZTS), whereas for CZTSSe solar cells the bandgap tuning is done by the Se/(S + Se) ratio [26]. This can be done in a very structured & systematic way by using a simulation tool for thin film photovoltaics.

In this work a SCAPS (Solar cell capacitance simulation) program developed by university of Gent, were used to assist the designing of the graded band-gaps of the modern CZTSSe solar cells. For grading in SCAPS environment the position dependent value of the materials parameters have to be taken into account. Grading in SCAPS environment involves modifying the semiconductor equation governing the problem. Exponential and uniform law in SCAPS simulation program were utilized for the analysis of graded CZTSSe absorber layer for thin film solar cells applications [27]. The bandgap tuning is one of the major key factors involved in the improvement of efficiency in thin film solar cell. So the main aim of this simulation is to optimize the composition for Se/(S + Se) ratio, inorder to obtain high efficiency thin film solar cells. SCAPS simulations were further utilized in-order to have a complete understanding of the grading and to obtain a champion efficiency by varying the sulphur and selenium composition.

2. Numerical simulation in SCAPS

SCAPS simulation model is based on solving the basic one dimensional semiconductor equation (Poisson equation and the electron- and hole-continuity equations) [28]. The equations are expressed in bulk form as follows, from Eqs. (1–5)

$$\frac{\partial}{\partial x}\left(\varepsilon_\circ \varepsilon_r \frac{\partial \Psi}{\partial x}\right) = q\left(p - n + N_D^+ - N_A^- + \frac{\rho_{def}}{q}\right) \tag{1}$$

$$-\frac{\partial J_n}{\partial x} - U_n + G = \frac{\partial n}{\partial t} \tag{2}$$

$$-\frac{\partial J_p}{\partial x} - U_p + G = \frac{\partial p}{\partial t} \tag{3}$$

The charge carrier denoted with drift and the diffusion is given as

$$J_n = -\frac{\mu_n n}{q}\,\frac{\partial E_{Fn}}{\partial x} \tag{4}$$

$$J_p = +\frac{\mu_p p}{q}\,\frac{\partial E_{Fp}}{\partial x} \tag{5}$$

Where, Ψ is the electrostatic potential, $\varepsilon_\circ$, ε_r the permittivity of vacuum and semiconductor, n and p the free carrier concentration, N_D^+ and N_A^- the density of ionized donors and acceptors, ρ_{def} the charge density of defects, G is the generation rate, J_n and J_p the electron hole current density. When grading is used in SCAPS environment extra driving terms such as the gradient of the electron affinity ∇_χ,, the gradient of the band gap ∇E_g and the gradients of the effective density of states in the conduction and valence bands: $\nabla(\log N_c)$ and $\nabla(\log N_v)$. The electron and hole continuity equations will be modified due to the presence of a mobility gradient $\nabla\mu_n$ or $\nabla\mu_p$, and the Poisson equation modified by a gradient $\nabla\varepsilon$ in dielectric constant. This will be further implemented in SCAPS [27,28].