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# Synthesis of in-gap band CuGaS<sub>2</sub>:Cr absorbers and numerical assessment of their performance in solar cells

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## ABSTRACT

CuGaS<sub>2</sub> thin films were obtained by sulfurization of CuGaSe<sub>2</sub>. CuGaSe<sub>2</sub> thin films were first electrodeposited from aqueous solutions containing CuCl<sub>2</sub>, GaCl<sub>3</sub>, and H<sub>2</sub>SeO<sub>3</sub> and subsequently annealed at 400 °C for 10 min in forming gas atmosphere and in the presence of molecular sulfur. This sulfurization process resulted in the complete conversion of CuGaSe<sub>2</sub> into CuGaS<sub>2</sub>. The formation of CuGaS<sub>2</sub> was proven by X-Ray diffraction and optical spectroscopy. Diffraction peaks of CuGaS<sub>2</sub> shifted to higher angles than those observed for CuGaSe<sub>2</sub> films, and the optical band gap shifted to blue rising from 1.66 eV for CuGaSe<sub>2</sub> to 2.2 eV for CuGaS<sub>2</sub>. When Cr ions were added to the initial electrolyte, the final CuGaS<sub>2</sub> films exhibited a broad in-gap absorption band centred at 1.63 eV that can be attributed to Cr atoms at the Ga sites. The performance of solar cells based on CuGaS<sub>2</sub>:Cr absorbers containing an in-gap absorption band was then estimated by numerical simulation using Solar Cell Capacitance Simulator Software. Both quantum efficiency and short circuit current of simulated Mo/CuGaS<sub>2</sub>:Cr/CdS/ZnO solar cells rose proportionally to the amount of Cr present in the CuGaS<sub>2</sub>:Cr absorbers. As a result, the photo conversion efficiency of the simulated devices changed from 14.7% for CuGaS<sub>2</sub> to 34% for CuGaS<sub>2</sub>:Cr absorbers. Nevertheless, when neutral defects related to Cr-doping were introduced in the absorber layer, the positive effect of the enhancement of photon harvesting due to IGB was compensated by a decline in the carrier collection and the overall efficiency of the device diminished considerably.

## 1. Introduction

CIGS chalcopyrite semiconductors are among the most promising materials to be used in high-performance photovoltaic devices due to their direct bandgap, which can be tuned between 1.1 for CuInSe<sub>2</sub> and 2.2 eV for CuGaS<sub>2</sub>. Also, their cost-effectiveness and easy processing are well known. Recently, CIGS thin-film photovoltaic devices reached a record solar efficiency of 22.3% [1]. Among thin film technologies, CIGS solar cells have achieved highest conversion efficiencies at laboratory scale [2,3]. Efforts to seek an economical and scalable method for the production of stoichiometric CIGS thin-films have been made to allow the commercialization of these devices. Among several techniques, electrodeposition has demonstrated to produce CIGS devices with high efficiency [4]. Currently efforts are being made with regard to theoretical studies and also to improve inexpensive deposition strategies for the chalcopyrite absorber layer [5].

The band gap energy of semiconductor materials plays a key role in the performance of photovoltaic devices [6]. According to the Shockley–Queisser limit, the optimal band gap energy of a single band gap PV device was calculated to be about 1.4 eV [7]. Therefore, it would be

unreasonable to use CuGaS<sub>2</sub> thin film as absorber in photovoltaic devices based on one junction due to their high band gap which is about 2.2 eV. However, this energy matches the optimal band gap to host an in-gap band (IGB) (also known as intermediate band) intended to absorb photons with energies lower than the gap. In the proposed IGB material, electrons can follow two ways to be promoted from the valence band to the conduction band: a) absorbing a photon with a higher energy than the band gap, and b) through the absorption of two photons with energy below the bandgap. The absorption of one photon promotes one electron from the valence band to the partially filled IGB and then the electron is transferred from this IGB to the conduction band after the absorption of a second photon, allowing a more efficient use of the solar spectrum in photovoltaic devices. This type of solar cell would be able to utilize the solar spectrum more efficiently, resulting in a theoretical efficiency limit of 63.2% [8], which is significantly higher than the 40.7% limit of conventional single band-gap photovoltaic cells [7]. Such devices would possess higher open circuit voltages and increased short circuit currents due to the higher band gap energy of the absorbing material and the greater absorption coming from sub-band gap photons, resulting in an increase of the overall efficiency [9].

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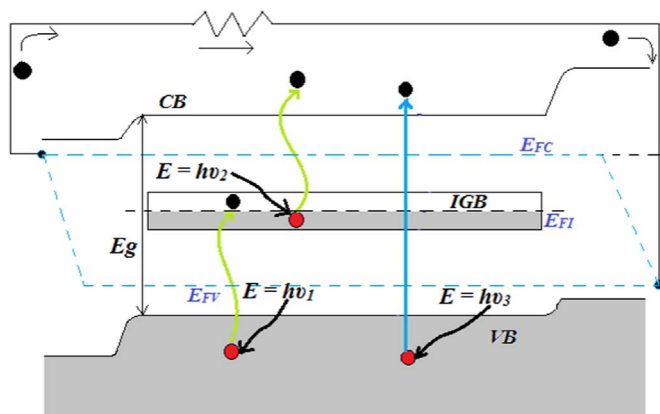


Fig. 1. The electronic structure and design of an IGB solar cell.

The in-gap absorption band concept is based on an adjustment of the electronic structure of a semiconductor, by introducing a partially filled absorption band inside the gap, as presented in the Fig. 1. This IGB divides the band gap into smaller energy units, sub-band gaps. The IGB then acts as a stepping stone for low-energy photons and allows the promotion of electrons from the Valence Band to the Conduction Band using two photons with energies below the band gap.

The semi-filled IGB will function as an electron receiver as well as an electron supplier. The electronic structure of an IGB photovoltaic device will in other words allow absorption of three photons at the same time. The multi-absorption creates higher density of electron-hole pairs available for increasing the electric current without lowering the open voltage of the cell. As a result, the efficiency of the cell rises due to the enlarged energy output per unit of incoming radiation.

High expectations have been placed in this theoretically model of wide-spectrum absorption of chalcopyrite by introducing various dopants (Ti, V, Cr, Ni, etc.) [10]. The partially-filled IGB can provide empty states to receive the electrons pumped by photon  $h\nu_1$  and further pump the electrons from there by photon  $h\nu_2$ . The solar response is significantly extended to lower energy photons, especially in the near-infrared region. As a consequence, the multi-photon absorption of two sub-band gaps (EV and EC) improves the photocurrent operationally without photo-voltage degradation.

According to the literature [11], chrome substituting Ga in  $\text{CuGaS}_2$  chalcopyrite lattices would generate an IGB separated from both valence and the conduction bands. When the transition metal (Cr) IGB introduced into the  $\text{CuGaS}_2$  lattice, it produces a partially filled band separated from both conduction and the valence bands that allows promoting an electron-hole pair through a two photons absorption process with sub-band gap energies. Therefore, the use of an IGB absorber would allow harvesting higher amounts of solar photons.

The main determination of the present work is to dope  $\text{CuGaS}_2$  thin films with the transition-metal Cr to create a suitable IGB absorber [12]. Herein, we report the synthesis and optical characterization of  $\text{CuGaS}_2$  and  $\text{CuGaS}_2\text{:Cr}$  thin films containing an IGB associated to Cr.  $\text{CuGaS}_2$  thin films were produced by sulfurization of previously electrodeposited  $\text{CuGaSe}_2$  films. The replacement of Se by S was completely carried out after sulfurization. Optical analysis showed that the band gap shifted from 1.66 for  $\text{CuGaSe}_2$  to 2.20 eV for  $\text{CuGaS}_2$ , with the sulfurization, the position of X-Ray diffractogram peaks also shifted from 27 to 29 degrees. The effectiveness of Cr-doping was inferred from the presence of Cr in  $\text{CuGaS}_2$  layers detected by microanalysis and the optical detection of an in-gap absorption band. Furthermore, the behaviour of photovoltaic devices based on  $\text{CuGaS}_2$  absorbers, with and without an IGB was calculated by specific Solar Cell Capacitance Simulation (SCAPS) software [13].

## 2. Experimental

$\text{CuGaSe}_2$  layers were electrodeposited from an electrolyte solution containing  $2 \text{ mMol L}^{-1} \text{ CuCl}_2$ ,  $4 \text{ mmol L}^{-1} \text{ H}_2\text{SeO}_3$ ,  $10 \text{ mmol L}^{-1} \text{ GaCl}_3$ ,  $50 \text{ mmol L}^{-1} \text{ KSCN}$ ,  $100 \text{ mmol L}^{-1} \text{ NH}_4\text{Cl}$  and  $300 \text{ mmol L}^{-1} \text{ LiCl}$ . The precursor solution pH was adjusted between 2.3 and 2.4 by adding hydrochloric acid (HCl) and potassium hydroxide (KOH). For better stability of the deposition bath solution, LiCl was used as a supporting electrolyte, also improving the quality of the deposited layers.

Electrodeposition was performed on a standard 3-electrode electrochemical cell. The  $\text{CuGaSe}_2$  thin films were deposited onto a  $1 \mu\text{m}$  thick Mo-coated soda lime glass substrate acting as a working electrode, a platinum wire was used as counter electrode and Ag/AgCl as a reference electrode.

For doping purposes,  $\text{Cr}^{3+}$  ions were added to the electrolyte described above.  $150 \text{ mMol L}^{-1}$  of Cr ( $\text{CrO}_4$ )<sub>3</sub> was dissolved in 40 mL of the electrolyte aqueous solution. The pH of the final solution was adjusted between 2.3 and 2.4 using concentrated HCl. Electrodeposition produced Cr-doped  $\text{CuGaSe}_2$  films and these films, which were subsequently sulfurized following the sulfurization procedure described below.

$\text{CuGaS}_2$  layers were obtained after subsequent sulfurization of previously electrodeposited  $\text{CuGaSe}_2$  layers. A complete replacement of the selenium by sulfur, transforming the precursor  $\text{CuGaSe}_2$  wurtzite film into a  $\text{CuGaS}_2$  chalcopyrite film took place in a quartz tube kept inside a cylindrical oven at a  $400^\circ\text{C}$  temperature for 10 min in a forming gas atmosphere.

The crystal structure of  $\text{CuGaSe}_2$  and  $\text{CuGaS}_2$  thin films were investigated by X-Ray Diffraction (XRD) with a Rigaku Ultima IV diffractometer in the Bragg-Brentano configuration using  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54060 \text{ \AA}$ ). The chemical composition was analysed by means of Energy Dispersive Spectroscopy (EDS) with a FESEM Zeiss model Ultra55.

Numerical simulations were performed using SCAPS, which is a one dimensional computer software to simulate electrical characteristics of thin film heterojunction solar cells. SCAPS was developed for CIGS and CdTe thin film solar cells but it has been applied to other thin film materials [14].  $\text{CuGaS}_2\text{:Cr}$  absorber layers with different Cr contents were used in the simulation. Besides, the effect of neutral defects related to Cr-doping on the performance of solar cells was also studied and discussed.

## 3. Results and discussion

Fig. 2 shows the XRD patterns of  $\text{CuGaSe}_2$  and  $\text{CuGaS}_2$  thin films at their different preparation stages: (a) electrodeposited  $\text{CuGaSe}_2$  thin films and (b) sulfurized  $\text{CuGaSe}_2$  thin films annealed for 10 min at  $450^\circ\text{C}$ . The diffractogram obtained for  $\text{CuGaSe}_2$  thin films matches the tetragonal crystal system JCPDS No. 075-0104 pattern well. The major peaks were located at  $27.9^\circ$ ,  $45.7^\circ/46.2^\circ$  and  $54.3^\circ/55.2^\circ$  corresponding to (1 1 2), (2 2 0)/(2 0 4) and (3 1 2)/(1 1 2) diffraction planes, respectively.

The sulfurization process of the electrodeposited  $\text{CuGaSe}_2$  films took place after a short annealing time in the presence of molecular sulfur, resulting in the formation of the  $\text{CuGaS}_2$  chalcopyrite phase as revealed by the XRD pattern of sulfurized films [Fig. 2(b)]. The XRD peaks shifted to higher angles with the sulfurization process. The main XRD peak corresponding to (1 1 2) diffraction peaks shifted from  $27.9$  to  $29.0$  degrees. Furthermore, the peaks corresponding to (2 2 0) and (2 0 4) and (3 1 2) and (1 1 6) diffraction planes observed for annealed  $\text{CuGaSe}_2$  films also shifted to higher angles for sulfurized films. These XRD peaks match the JCPDS No. 75-0103 pattern corresponding to  $\text{CuGaS}_2$  films. This diffraction pattern confirms the replacement of Se atoms by S atoms after sulfurization, and consequently,  $\text{CuGaSe}_2$  thin films were transformed into  $\text{CuGaS}_2$  [15–17].

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