

## DEVIATIONS FROM STOICHIOMETRY AND MOLECULARITY IN THE SOLAR CELL MATERIAL $\text{CuInS}_2$

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### Abstract

The chalcopyrite group of semiconductors is known to represent attractive materials for achieving more efficient and low-cost solar cells. From this group of materials the  $\text{CuInS}_2$  (CIS) is intensively investigated as p-type absorber layer in 3D solar cell concepts. An important issue in studies focusing on improvements of solar cell efficiencies is related to the defect chemistry of CIS.

Based on theoretical and experimental studies several aspects of the defect chemistry of  $\text{CuInS}_2$  are discussed. The anti-site point defects, which form the Cu-Au ordered structure are studied in samples of pure, Cu-rich, In-rich, and cation doped CIS. Cu-Au ordering was identified via Raman spectroscopy and XRD studies on pure and doped  $\text{CuInS}_2$  with a deviation from molecularity.

### Introduction

Sustainable energy sources that produce electrons, like solar cells, can be connected to the electrical energy infrastructure to directly reduce carbon dioxide emissions from fossil fuel combustion. The state-of-the-art solar cells are practically all silicon-based. The introduction of the dye-sensitized solar cell by Grätzel and co-workers [1,2] has stimulated investigations on novel nanostructured materials for three-dimensional (3D) solar cells. Dye-sensitized solar cells (DSSCs) of the Grätzel-type comprise anatase nano-sized  $\text{TiO}_2$  particles that are sintered together to form a 3D nanostructured network with a monolayer of visible-light absorbing dye molecules chemically bonded to the n-type  $\text{TiO}_2$  surface, which inject optically excited electrons into the conduction band of  $\text{TiO}_2$ . Regeneration of the oxidized dye molecule occurs via a redox electrolyte, comprising acetonitril with an iodide/iodine redox couple, which mediates the electron to the oxidized state of the dye molecule. Besides this dye-sensitized solar cell, all solid-state dye-sensitized solar cells [3],

Extremely-Thin-Absorber (ETA) solid-state solar cells [4], and three-dimensional (3D) nanostructured solar cells [5,6] have been and are being studied world wide. Alternative materials and these novel solar cell concepts are being studied in order to arrive at low-cost devices.

The pure and doped ternary chalcopyrite semiconductors, like  $\text{CuInS}_2$ ,  $\text{CuInSe}_2$ , and  $\text{CuGaSe}_2$ , are being studied as visible-light absorbing materials in, for example, the nano-structured ETA and 3D solar cells. As a solar cell material,  $\text{CuInS}_2$  (CIS) has already been studied in detail some decades ago [7,8] along with the defect chemistry of this material [8-11]. In general,

ternary materials may exhibit deviations from stoichiometry and deviations from molecularity, as has been discussed by Ueng and Hwang [9-11]. Recently, it has been recognized that, in particular anti-site disorder, which leads to Cu-Au ordering effects, has to be minimized for the optimization of 3D solar cells.

In this paper, we focus on novel 3D solar cells based on CIS and on the defect chemistry of CIS in relation to Cu-Au ordering effects.

### **Copper Indium Disulfide**

As a visible-light absorbing material  $\text{CuInS}_2$  (CIS) has been used in between transparent n- and p-type conducting material in the ETA-type solar cells, as well as in 3D nano-structured solar cells. As p-type conducting  $\text{CuInS}_2$  is a very efficient visible-light absorbing material, it has been studied in an all-solid-state 3D nanostructured composite solar cell, based on anatase  $\text{TiO}_2$  [4-6]. In the 3D architecture, CIS is indeed the visible-light absorbing p-type material, and it is deposited inside the pores of nanoporous  $\text{TiO}_2$ , comprising 50nm particles, by Atomic Layer Deposition (ALD) [5,6,12], a modified Chemical Vapour Deposition (CVD) technique. Due to its high absorption coefficient ( $10^5 \text{cm}^{-1}$  at  $\lambda=500 \text{nm}$ ) and its direct optical bandgap ( $E_g=1.55\text{eV}$ ), which is well matched to the solar spectrum, the choice of CIS requires additional buffer layers, because the valence band energies of CIS and  $\text{TiO}_2$  do not match well, while the conduction energy bands of  $\text{TiO}_2$  and CIS match reasonably well. For that reason, a buffer layer of  $\text{In}_2\text{S}_3$  with valence-band energy between that of  $\text{TiO}_2$  and CIS is applied. Because the copper and indium ions, depending on the composition of CIS, are mobile in CIS [6,10-12] the nano-porous  $\text{TiO}_2$  layer is protected with a few atom layers of inert  $\text{Al}_2\text{O}_3$  by ALD to prevent cation diffusion from CIS into the titanium dioxide layer during solar cell operation. To date, simple aerosol spray pyrolysis (ASP) techniques are being explored in order to further reduce the manufacturing costs of this type of solar cells [14,15].

### **ALD and ASP of Solar Cells with CIS**

In the nano-composite solar cells, a stable semiconductor with low solar light-to-electrical energy conversion efficiency, like titanium dioxide or zinc oxide, is combined with a visible-light absorbing p-type conducting material, here CIS as described above. ALD and ASP are being used to manufacture the 3D architecture.

Atomic Layer Deposition, which is also known as Atomic Layer Epitaxy (ALE) and Atomic Layer Chemical Vapour Deposition (AL-CVD), has been developed for the fabrication of polycrystalline luminescent  $\text{ZnS:Mn}$  and amorphous  $\text{Al}_2\text{O}_3$  films. Since the early 1990s, ALD has been introduced in the field of IC-technology. The decreasing dimensions of IC-devices call for well-defined extremely thin films, of the order of 1-20 nm in thickness [16-18]. A schematic presentation of the principle of ALD is given in Figure 1.

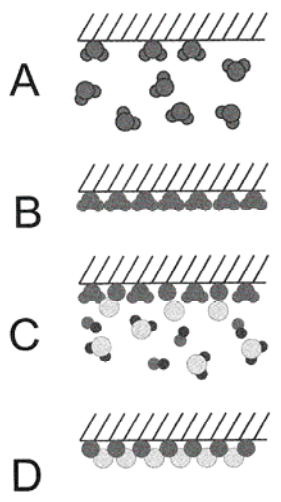


Figure 1. Principle of Atomic Layer Deposition

When a binary compound is deposited, the ALD process comprises four steps. First, an excess precursor A is introduced into the reactor chamber and one monolayer chemisorbs at the internal surface of the nano-porous substrate and the excess precursor A is removed subsequently by an inert gas purge. In contrast to CVD, ALD precursors have to chemisorb self-limiting at the surface of the substrate, in that adsorption stops if one monolayer has been adsorbed, hence the growth rate becomes independent of the pulse time of the precursor. In addition all the precursors need to be stable at the deposition temperature, preventing decomposition upon chemisorption, which usually results in the loss of self-limitation. Finally, the reaction rates should be very high, in order to avoid long saturation pulse times [16]. Details of the ALD process conditions have been reported [5,6,16].

In ASP an atomized solution of precursors is directed to a heated substrate. This technique is widely used in industrial large-area coating processes. Its introduction into the photovoltaic industry allows a revolutionary reduction of the process costs along with a significant reduction of the energy payback time as compared to multi-crystalline silicon solar cells. Details of the deposition conditions and the precursors have been reported [14,15].

Highly porous, nano-structured anatase  $\text{TiO}_2$  layers ( $2\mu\text{m}$ ) and obtained using a doctor blade process are used as a substrate for ALD and ASP of CIS. Figure 2 presents the schematics of a 3D nano-structured solar cell, obtained with ALD of CIS (a) [5,6] and one obtained with ASP (b) [14,15].

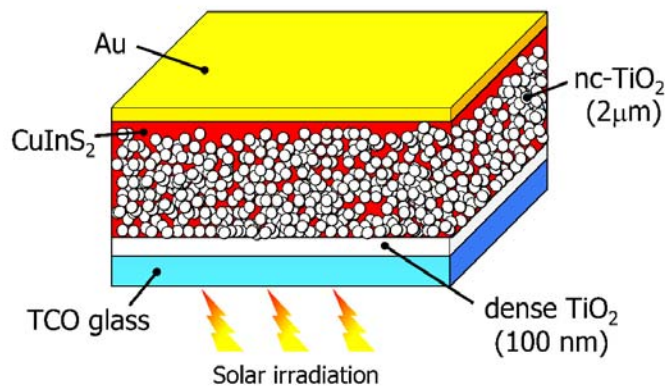


Figure 2-a. 3D nano-structured solar cell. CIS applied by ALD.

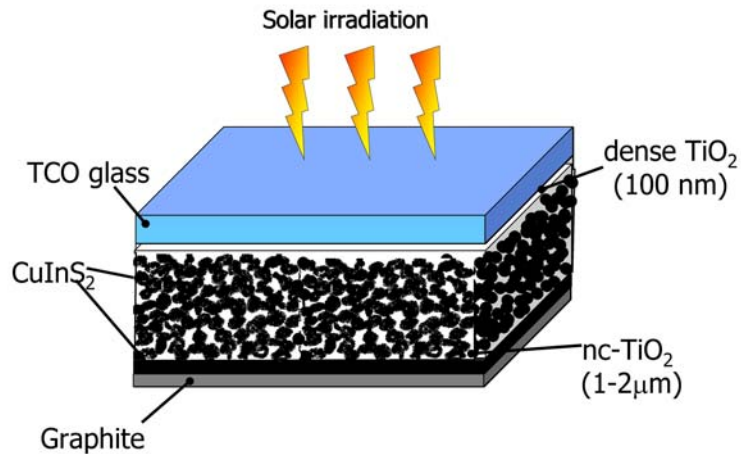


Figure 2-b. 3D nano-structured solar cell. CIS applied by ASP

The interpenetrating network of n-type and p-type semiconductors on a nano-meter scale guaranties that visible-light absorption takes place near the active interface between the p-type and the n-type materials. Accordingly, the minority-carrier diffusion length, i.e., electron holes in n-type and electrons in p-type semiconductors, is limited to only a few tens of nanometers. This provides a large tolerance to the presence of electron-hole recombination centres in the visible-light absorbing p-type semiconductor. Hence, an excited-state lifetime of less than a nanosecond is still sufficient for the efficient collection of the charge carriers at the electrodes. Accordingly, bulk recombination will be suppressed but, due to an increased interfacial contact area between the n-type and p-type components, interfacial recombination becomes more important. Smart engineering of the interface by a clever choice of materials and the use of buffer layers is required in order to deal with this important issue. In the case of CIS deposited by ASP, first an  $\text{In}_x(\text{OH})_y\text{S}_2$  thin film is deposited by ASP, and post annealing in air converts this layer into  $\text{In}_2\text{S}_3$  [14,15].

The infiltration of CIS into a nano-structured matrix has been studied using Rutherford Back-Scattering (RBS) and grazing-incidence X-ray diffraction (GI-XRD) [12]. In Figure 3, Scanning Electron Microscopy (SEM) (a) and Transmission Electron Microscopy (TEM) (b) images are shown for a 50 nm  $\text{TiO}_2$  matrix filled with CIS [6]. The lattices of the solar cell components have close contact on an atomic scale, which is a prerequisite for fast electron transfer across the interfaces.

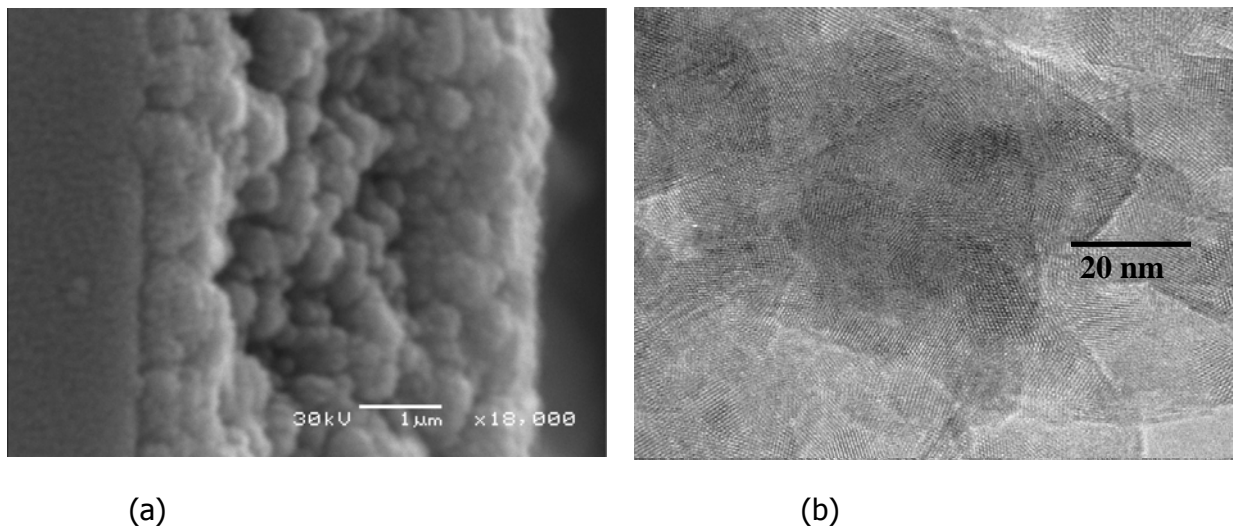


Figure 3. SEM (a) and TEM (b) images of a nano-composite solar cell. The nano-pores of the  $\text{TiO}_2$  are completely filled with CIS [6].

The I-V characteristics of these 3D nano-structured solar cells in the dark and under irradiation of a calibrated source (AM 1.5) are presented in Figure 4. The solar cell with ALD CIS (a) reveals a conversion efficiency of 4 % and the solar cell with ASP CIS (b) exhibits a conversion efficiency of 5.4%.

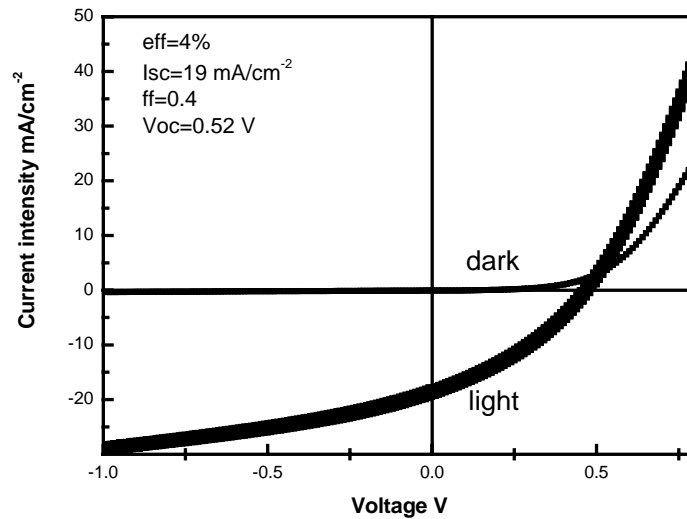


Figure 4-a. I-V characteristics of the 3D solar cell based on  $\text{TiO}_2 | \text{In}_2\text{S}_3 | \text{CuInS}_2$  nanocomposite obtained by atomic layer deposition

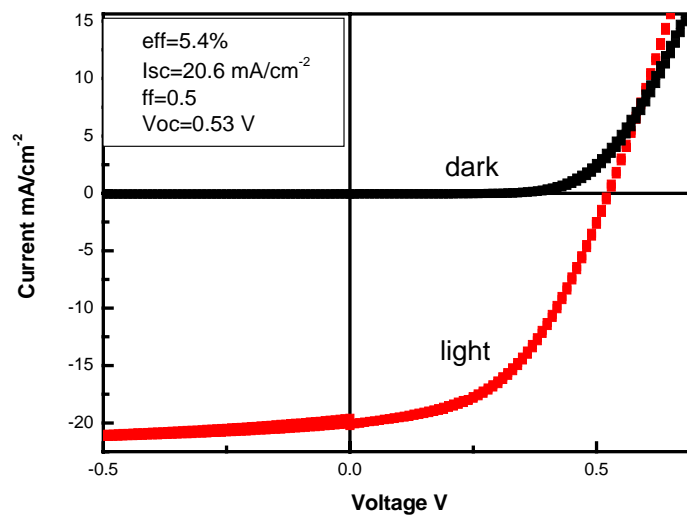


Figure 4-b. I-V characteristics of the 3D solar cell based on  $\text{TiO}_2 | \text{In}_2\text{S}_3 | \text{CuInS}_2$  nanocomposite obtained by spray pyrolysis

Figure 5 presents the energy diagram of the 3D nano-structured solar cell, including the buffer layers, i.e.,  $\text{TiO}_2/\text{Al}_2\text{O}_3/\text{In}_2\text{S}_3/\text{CIS}$ , and the current collectors.

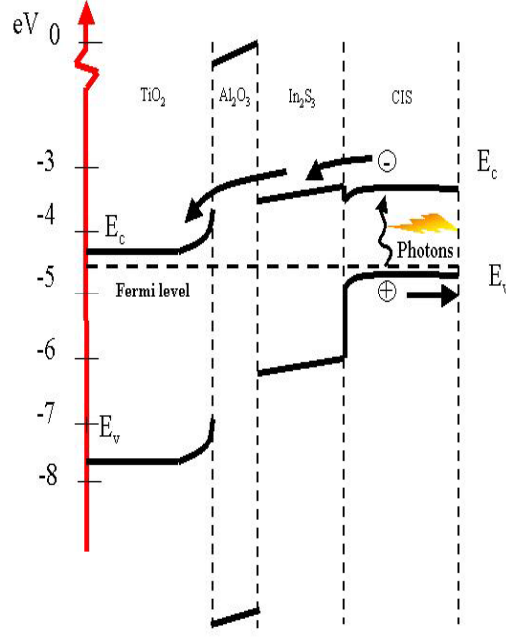


Figure 5. Band diagram of a 3D solar cell based on  $\text{CuInS}_2$  as light absorber

### The defect chemistry of CIS

Depending on the growth conditions, In-rich or Cu-rich can be obtained [19-21]. Nanu et al. [21] have studied Raman and Photoluminescence spectra of Cu-rich  $\text{CuInS}_2$  ( $\text{Cu}/\text{In} = 1.8$ ) obtained by sulfurization of Cu-In layers. These authors characterized the following donor-acceptor levels, i.e. sulfur vacancies ( $V_S^{\bullet\bullet}$ ), interstitial copper ions ( $\text{Cu}_i^{\bullet}$ ), indium ions occupying a copper site ( $\text{In}_{\text{Cu}}^{\bullet}$ ), and as acceptor copper ion vacancies ( $V_{\text{Cu}}^{\bullet}$ ), indium ion vacancies ( $V_{\text{In}}^{\bullet\bullet\bullet}$ ) and copper ions in indium sites. Here, the Kröger-Vink defect notation is used [22]. The question, therefore, arises according to which mechanism these point defects are generated in  $\text{CuInS}_2$ .

CIS, being a ternary compound, may exhibit deviations from molecularity, in addition to a deviation from stoichiometry. In the first case extrinsic ionic point defects are generated, while in the case of deviation from stoichiometry always a combination of ionic point defect and electronic defect occurs. Antisite defects are involved in the Cu-Au ordering, which adversely affect the response of a CIS-based solar cell.

For  $\text{CuInS}_2$  (CIS), the following defect equations can be written, using the Kröger-Vink notation.

**Schottky disorder** (formation of cation and anion vacancies)



**Frenkel disorder** (interstitial cation and cation vacancies)

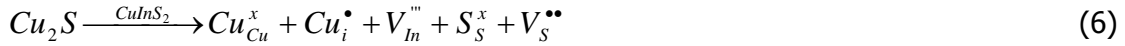


**Anti-Frenkel disorder** (interstitial anion and anion vacancy)



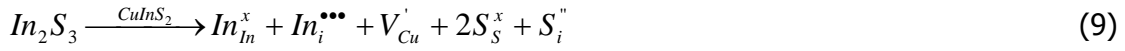
In  $\text{CuInS}_2$ , deviation from molecularity is due to excess of  $\text{Cu}_2\text{S}$  (Cu-rich material) or  $\text{In}_2\text{S}_3$  (In-rich material). In these cases, ionic defects characterize the material.

**$\text{Cu}_2\text{S}$  excess**



Equation (7) describes the formation of antisite defects in Cu-rich  $\text{CuInS}_2$ . Alvarcz-Garcia et al. [23] reported the role of anti-site defects in Cu-Au ordering.

**$\text{In}_2\text{S}_3$  excess**

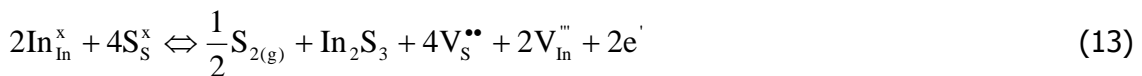
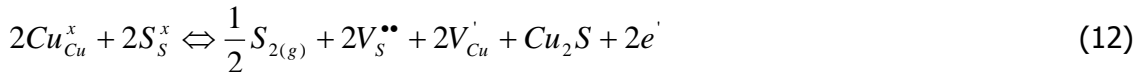


With regard to anti-site disorder, reaction (10) can be considered as well. In both cases (Cu-rich and In-rich material), the ionic defects govern the properties of the material.

The deviation from stoichiometry in  $\text{CuInS}_2$  is described for the sulfur excess or deficiency, explaining the mixed ionic and electronic conductivity of the material.



The sulfur incorporation in the material can be described also through the following equations:



Reactions (12) and (13) combine a deviation from molecularity with a deviation from stoichiometry.

The presence of Cu-Au ordering in CIS structure was demonstrated to be correlated to sulfur vacancies ( $V_S''$ ) [21]. The oxygen incorporation equation can be written in the following form,

explaining the passivation of sulfur vacancies and the influence on the p-type conductivity of the material:



In recent studies Vouwzee [24] has analysed structural properties of pure and doped CIS, and of CIS with deviations from molecularity. Using Raman Spectroscopy Cu-Au ordering was studied. XRD and Raman spectra revealed the chalcopyrite phase, CuInS<sub>2</sub>, for undoped stoichiometric CIS and for CIS doped with Ga, Sn, and Sb. For Cu-rich, Ga and Sn-doped Cu-rich compositions Raman spectra revealed the presence of Cu-Au ordering. Cu-Au ordering occurred in In-rich and Ga-doped In-rich compositions.

## Conclusions

The chalcopyrite I/III/VI semiconductors are ideal candidates as visible-light absorbers for the ETA solar cell and the 3D nano-structured solar cell. Here, CuInS<sub>2</sub> has been taken to review recent developments in 3D nano-structured solar cells. CIS has been deposited using ALD and ASP. It is clear that the conversion efficiency of a solar cell based on ASP-deposited CIS is improved compared to a solar cell based on ALD-deposited CIS. Copper-ion diffusion in CIS and valence band edge mismatch require buffer layers of Al<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>S<sub>3</sub>, respectively.

Being a ternary compound, CIS may exhibit both a deviation from stoichiometry and molecularity, which introduce extrinsic point defects, among which anti-site disorder. Anti-site disorder is involved in Cu-Au ordering, while passivation of sulfur vacancies by oxygen incorporation results in less ordering. It seems that here the role of dopants in relation to Cu-Au ordering is less important than deviations from molecularity. In general, the used dopant concentrations are relatively small compared to the deviations from molecularity [24]. The presented defect chemical reactions are currently being used in a detailed analysis of the electrical properties of undoped, doped, and CIS with deviations from stoichiometry and molecularity. In addition, these defect chemical reactions shall be used to construct three-dimensional Brouwer diagrams, i.e., defect concentrations as function of sulfur partial pressure, [In<sub>2</sub>S<sub>3</sub>], as well as sulfur partial pressure, [Cu<sub>2</sub>S], respectively.

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