Steps Towards Industrialization of Cu–III–VI₂ Thin-Film Solar Cells: Linking Materials/Device Designs to Process Design For Non-stoichiometric Photovoltaic Materials

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The concept of in-line sputtering and selenization become industrial standard for Cu–III–VI₂ solar cell fabrication, but still it’s very difficult to control and predict the optical and electrical parameters, which are closely related to the chemical composition distribution of the thin film. The present review article addresses onto the material design, device design and process design using parameters closely related to the chemical compositions. Its variation leads to change in the Poisson equation, current equation, and continuity equation governing the device design. To make the device design much realistic and meaningful, we need to build a model that relates the opto-electrical properties to the chemical composition. The material parameters as well as device structural parameters are loaded into the process simulation to give a complete set of process control parameters. The neutral defect concentrations of non-stoichiometric CuMSE₂ (M = In and Ga) have been calculated under the specific atomic chemical potential conditions using this methodology. The optical and electrical properties have also been investigated for the development of a full-function analytical solar cell simulator. The future prospects regarding the development of copper–indium–gallium–selenide thin film solar cells have also been discussed.

1. Introduction

During the past few decades, the photovoltaic (PV) market has grown at a remarkable rate, particularly in thin film solar cells (TFSCs) which are on their way to become one of the major sources of electricity production around the whole globe. It was predicted that the market share for Cu–III–VI₂ TFSCs will be 5% by year 2010 and 15–20% by year 2020. However, research and development of copper–indium–gallium–selenide TFSCs are still in a crucial phase due to fundamental obstacles—such as low production yields, non-reproducibility, and non-uniformity over large area—confronted during the industrialization and commercialization of CIGS thin film solar cells. Concerning such issues, we published our first research paper in year 2003.[3] After this, the concept of in-line sputtering and selenization has become the international standard globally. In the last decades, dozens of CIGS manufacturing units have been established worldwide, but claims of successful production are rare, due to difficulty in predicting and controlling the local chemical composition distribution of the film, despite the availability of commercial device simulation tools. Moreover, the production efficiency of large-area PV cells and panels varies in a wide range from 6% to 13%.

In 2003, we again published research[2] pointing out the problems encountered during the commercialization. Over the years, many experimental and theoretical research works published in many journals have focused on various subjects of problems and its solutions for CIGS TFSCs.[1–10]

In 2013, we published one more research article.[1] This article pointed out how the new concept of metal organic sputtering could be used for the fine tuning and tailoring of film compositions based on the programmed material and device design. The scheme of our intelligent material and device design, shown in Figure 1, described the detailed calculation of the neutral defect concentrations of non-stoichiometric CuInSe₂, CuGaSe₂ and ZnO under specific atomic chemical potential conditions (μ_st = 0, X = Cu, In/Ga, Zn).
These calculations are the main procedure of the intelligent design and key to the device and process design. The carrier concentration and the electrical properties of these materials with variable atomic constitutions are further calculated which demonstrate the main functions of the computer aided design (CAD) tool used.\(^{[2,12–14]}\)

In the present Review, we sum up these designs to get in-depth knowledge about the chemical compositional variation to obtain the complete set of process control parameters. These design tools will help moderately to overcome all the obstacles encountered during industrialization of CIGS thin film solar cells. The future aspects for industrialization of CIGS TFSCs are also discussed.

### 2. Brief Discussion of Intelligent Material Design

#### 2.1. Experimental Data

It's well known that Cu–III–VI\(_2\) typically have a wide phase stability region, which extends a few atomic percent of the chemical composition of the thin film, in contrast to III–V and II–VI compounds. The chemical composition for a near-stoichiometric CuInSe\(_2\) is shown in Figure 2. The variations in CuInSe\(_2\) film were detected using a transmission electron microscope (TEM) equipped with a field emission gun.\(^{[11]}\) A similar result had also been reported for CIGS thin film.\(^{[12]}\)

#### 2.2. Theoretical Data

In 2003, we published an example of the design tool using the concept of minimization of total free energy\(^{[2,13,14]}\) which includes the configurational entropy, defined as:

\[
G(T,\text{Crystal size}) = \Sigma n_i E_g - T S_{\text{config}},
\]

\[
S_{\text{config}} = k \ln \frac{N_{\text{total}}!}{n_i! N_i!}
\]

Where \(n_i\) is the number of the \(i\)th defect, \(E_g\) is the formation energy, \(T\) is the temperature, \(S_{\text{config}}\) is the configurational entropy, \(k\) is the Boltzmann constant, \(N_{\text{total}}\) is the total number of lattice sites, \(N_i\) is the total number of defect sites of the \(i\)th defect. We find the possible results for the co-existence of
donors and acceptors in CuMSe$_2$ (M = In, Ga), which includes either the new defects produced through interaction or donor–acceptor pair/cluster formation.

Table 2 shows the defect formation energies and the defect transition levels. We also find the possible phases of CuMSe$_2$ resulted due to the compensated donor–acceptor pairs in different Cu concentration, for example Cu$_{1.8}$M$_{3.8}$Se$_5$ phase is observed by 80% Cu$_{1.8}$M$_{3.8}$Se$_5$ and 20% CuMSe$_2$.\[^{[19]}\]

For solving the charge neutrality equation a few parameters are required, such as the carrier concentrations, ionized/neutral defect concentrations, and Fermi level at a certain temperature. Figure 3 shows the calculated carrier concentration and electrical conductivity of CuInSe$_2$ and CuGaSe$_2$ at 300 K. Note that in Figure 4, for the film composition from stoichiometry to Cu-poor, the conductivity will rise first and then fall down, the conductivity is even lower than that of the stoichiometry.

3. Brief Discussion of Device Design

For numerical analysis of CIGS solar cells, the device simulator SCADS 3.2\[^{[15]}\] has been widely used. In 2014, Naoki Ashida et al.\[^{[16]}\] simulated the 19% efficiency of a solar cell in which the 2 μm thick CIGS absorber layer was divided into two regions, such as low defect density layer (front side) and high defect density layer (back side). The thickness of low defect density layer resulted in 97% of cell efficiency on assuming a fixed bandgap of 1.2 eV and a carrier diffusion length of 0.72 μm.

We also developed an alternate full-function (indoor, outdoor, I–V, C–V) analytic solar cell simulator, in which the following (time-independent) device equations are considered.

a. The continuity equation

\[
0 = -\frac{1}{q} \frac{d}{dx} \left( \tau_p \frac{d \Delta p}{dx} \right) - G_p - R_p \tau_p \Delta p = \tau_p \tau_n \Delta p = p_n - p_{n0} \tag{2}
\]

b. Transport equations

\[
\tau_p = p \mu_p E - q D_p \frac{dp}{dx} \tag{4}
\]

\[
\tau_n = n \mu_n E + q D_n \frac{dn}{dx} \tag{5}
\]

All the boundary conditions (front contact, n-QNR/SCR interface, p-QNR/SCR interface, and back contact) are considered, where QNR stands for quasi neutral region and SCR stands for space charge region for a typical n-CdS/p-CIGS device structure. The example of our simulation results show that the higher efficiency cells are distributed along the line from Cu:Se = 0.3:0.5 to the stoichiometric point and the line from Cu:Se = 0.21:0.52 to the stoichiometric point. For comparison of the computed efficiencies with the NREL experimental data, the consistence are shown in Figure 5. The device structures of these cells are ZnO/CdS/CuInSe$_2$. The atomic compositions of the higher efficiency cells are concentrated near Cu:Se = 0.22:0.51 or along the line from Cu:Se = 0.22:0.51 to the stoichiometric point.

In the last decades, many studies on interface and surface compositional profile have dealt with the advanced characterizations for the high efficiency CIGS solar cells. A few examples are:

1. Conduction band profiles are changed by the three stage seleniumization.\[^{[17]}\]
Ordered defect compounds (ODC: CuInSe$_2$, CuIn$_3$Se$_5$, CuIn$_5$Se$_8$ etc.) obtained from CuInSe$_2$/CIGS solar cell studies revealed the depletion of Cu near the surface in X-ray photoelectron spectroscopy (XPS) investigations, ordered defect compound structured was predicted by theory as well experiments.$^{[18]}$

Low energy electron diffraction (LEED), angular-resolved ultraviolet photoelectron spectroscopy (ARUPS), and auger electron spectroscopy (AES) investigations show, in Figure 6, that the CuInSe$_2$ surface is stabilized by defect pairs (2V$_{cu}$ and In$_{cu}$) and band alignment gives hole barrier at the interface.$^{[19]}$

Secondary ion mass spectrometry (SIMS) depth profile of Cu, In, Ga, Se, Cd and Na revealed the CdS/CIGS/ZnO diffusion phenomena, as shown in Figure 7.$^{[20]}$

Defect in grains and grain boundaries.$^{[21]}$

The knowledge of electronic properties of the interfaces in semiconductor devices is critically dependent on the detailed atomic structure of the contact plane. Thus, the attempt to model the junction in chalcopyrite thin films by well-defined interface to classify the influence of grain boundaries, lateral inhomogeneity and chemical variations in compositions and their distributions across and aside the contact planes. All this information can be obtained utilizing modern analytic tools, like XPS, ultra-violet photoelectron spectroscopy (UPS), LEED, scanning tunneling microscopy (STM), and X-ray photoemission electron microscope (XPEEM). In situ band alignment, band broadening, chemical reacted interfaces, and crystalline structure with high resolution have been determined by experiments and incorporated with our material analysis for better accuracy and reproducibility obtained in the device design for the future industrial applications.

### Table 2. The defect formation energies and defect transition levels used in our calculations.$^{[19]}$

|          | E$_{tr}$ | E$_{D}$/E$_{A}$ | CuGaSe$_2$ | E$_{tr}$ | E$_{D}$/E$_{A}$ | ZnO | E$_{tr}$ | E$_{D}$/E$_{A}$ |
|----------|---------|----------------|-------------|---------|----------------|-----|---------|----------------|
| V$_{Cu}$ | 0.60    | E$_{v}$ + 0.03 | V$_{Cu}$    | 0.66    | E$_{v}$ + 0.01 | V$_{In}$ | 0.10    | E$_{v}$ – 0.5  |
| –1       | 0.63    | –              | –1          | 0.67    | –              | –1  | 0.10    | E$_{v}$ + 0.0  |
| V$_{In}$ | 3.04    | E$_{v}$ + 0.19 | V$_{Cu}$    | 0.32    | E$_{v}$ + 0.38 | V$_{In}$ | 0.10    | E$_{v}$ – 0.25 |
| –2       | 3.21    | E$_{v}$ + 0.41 | –1          | 3.02    | E$_{v}$ + 0.38 | +1  | 1.5     | E$_{v}$ – 2.4  |
| –3       | 3.62    | E$_{v}$ + 0.67 | –2          | 3.40    | E$_{v}$ + 0.66 | 0   | 2.4     | E$_{v}$ – 0.6  |
| $V_{Se}$ | 1.12    | E$_{v}$ – 0.1  | $V_{Se}$    | 1.01    | E$_{v}$ – 0.38 | Zn$_{In}$ | 0.23    | E$_{v}$ + 1.1  |
| +1       | –       | +1             | –           | +1      | 2.1             | E$_{v}$ + 0.8 |
| 0        | 3.00    | –              | 0.36        | 0.61    | 0.6             | E$_{v}$ + 0.95 |
| Cu$_{In}$| 1.0     | E$_{v}$ – 0.20 | Cu$_{In}$   | 0.91    | E$_{v}$ – 0.21 | O$_{In}$ | 0.97    | E$_{v}$ + 0.7  |
| 0        | 2.88    | –              | 0.38        | –1      | 10.4             | E$_{v}$ + 1.7 |
| C$_{Cu}$ | 1.54    | E$_{v}$ + 0.29 | C$_{Cu}$    | 1.41    | E$_{v}$ + 0.29 | Zn$_{Cu}$ | 0.4     | E$_{v}$ + 1.5  |
| –1       | 1.83    | E$_{v}$ + 0.38 | –1          | 1.70    | E$_{v}$ + 0.63 | +1  | 5.2     | E$_{v}$ + 1.1  |
| –2       | 2.41    | –              | 2.33        | 0.96    | E$_{v}$ + 1.3  |
| In$_{Cu}$| 1.85    | E$_{v}$ – 0.34 | In$_{Cu}$   | 2.04    | E$_{v}$ – 0.69 | 0   | 3.03    | E$_{v}$ – 0.49 |
| +1       | 2.55    | E$_{v}$ – 0.25 | +1          | 3.03    | E$_{v}$ – 0.49 |
| 0        | 3.34    | –              | 4.22        | –       |                |
| $V_{Se}$ + 2V$_{Cu}$ | 0.63 | – | $V_{Se}$ + 2V$_{Cu}$ | 3.65 | – |
| $V_{Se}$ + Cu$_{Cu}$ | 0.17 | – | $V_{Se}$ + Cu$_{Cu}$ | – | – |
| 2Cu$_{In}$ + Cu$_{In}$ | 0.31 | – | 2Cu$_{In}$ + Cu$_{Cu}$ | 3.20 | – |
| In$_{Cu}$ + 2V$_{Cu}$ | 0.33 | – | Ga$_{Cu}$ + 2V$_{Cu}$ | 0.74 | – |

2. Brief Discussion of Process Design

In previous sections, the two aspects including structure and composition greatly affect the opto-electrical properties of the polycrystalline semiconductors. In this section, we describe better understanding of the way to generate poly structure through careful observation of the particle transfer procedures during the manufacturing processes after knowing the final positions of the deposited atoms and the materials microstructures. On controlling and modifying the process, the composition as well structure can be tuned directly by varying the process parameters to acquire the desired opto-electrical properties.

The original Thornton’s zone model$^{[23]}$ describes the metallic grain structures according to the sputtering gas pressure and the substrate temperature. The magnetron sputtering process is most preferred for the industrial application since the
deposition rate is very high. Also, the energy dependent sputter yield is noted. Ellmer[24] further built a model to illustrate the inter-relationships between the process parameters (like substrate temperature and deposition rate) and the structural/opto-electrical properties. However, the pressure (particles momentum) effect is not considered in this model.

4.1. Berg's Model

This model is particularly used for the ZnO reactive sputtering. Basically, the surface coverage on the deposited film is not just the composition of the film, but the composition is not easy to control since the system is unstable and it requires the plasma diagnose sensor to undergo feedback control. The basic idea of Berg's model[25,26] where the changes of the number of absorbed oxygen atoms per unit area $N_x$ at the surfaces of the target is:

$$\frac{dN_x}{dt} = 2\alpha_x (1-\theta_x) - J_x S_x \theta_x$$  \hspace{1cm} (6)

at the substrate:

$$\frac{dN_x}{dt} = 2\alpha_x F(1-\theta_x) + \frac{J_x S_x \theta_x A_x}{A_c} (1-\theta_x) - \frac{J_x S_x \theta_x A_x}{A_c} \theta_x$$  \hspace{1cm} (7)

Where $\alpha_x$ are the sticking coefficients, $S_X$ are sputtering yields, and $\theta_x$ are the coverage. Figure 8 shows $\theta$ an example of the simulation result of the ZnO reactive sputtering system ($\theta_2$ always <1). We could also use Berg's model to predict the composition of the compound thin film, we can also predict
if the operating point is stable. Thus, we can study the time-
dependent behavior of the reactive sputtering system.

From Berg’s model, we can get expressions of \( \theta_1, \theta_2 \) and \( R \), the total sputtering rate (consumption of the target) in

\[
R = \frac{J}{e} \left[ S_0 \theta_1 + S_{in} (1 - \theta_1) \right]
\]

(8)

And we can generate some lines passing the origin of the Rplot, each line represents a specific \( \theta_2 \) value. However, our goal is to know if it is possible to control the composition by controlling \( \theta_2 \). Figure 9 shows a simulation result of the ZnO reactive sputtering system and we want to know if it is possible for \( \theta_2 \) to be larger than one.

4.2. CISe RTP—IEC’s Model

After we finish the CuInSe\(_2\) defect concentration calculations, we can apply the result to the model which was developed by IEC to predict the processing time under a certain process temperature.

For CuIn

\[
2\text{In} + \text{Se} \rightarrow \text{In}_2\text{Se} \ldots K_3 \quad (9)
\]

\[
\text{In}_2\text{Se} + \text{Se} \rightarrow 2\text{InSe} \ldots K_3 \quad (10)
\]

\[
2\text{CuIn} + 2\text{Se} \rightarrow \text{Cu}_3\text{Se} + \text{In}_2\text{Se} \ldots K_3 \quad (11)
\]

\[
2\text{InSe} + \text{Cu}_3\text{Se} + \text{Se} \rightarrow 2\text{CuInSe}_2 \ldots K_7 \quad (12)
\]

where \( K_i = K_{i0} \exp \left( -\frac{E_i}{RT} \right) \) and \( V = \sum n_{\text{unit cell}} \) is the film volume taken as a time-independent constant. \( n_i = [i] \times V \) are the mole numbers, \( n_{\text{unit cell}} \) is the number of pairs of the atoms in the unit cells. Figure 10 shows an example of the Se or H\(_2\)Se RTP of CuInSe\(_2\) films at 450 °C, \( \mu_{\text{Cu}} = 0, \mu_{\text{In}} = 0 \); the mole ratio of the constituent atoms (in the film) as functions of the processing time (film volume = \( (2.5 \text{ cm})^2 \times 2 \mu\text{m} \)). In our non-stoichiometric case, the initial mole concentrations of Cu and In taken from our
calculated data. Then, these were input to the Cu$_x$In$_y$ and In mole concentrations in order to solve the ordinary differential equation system.

Regarding building the non-stoichiometric structures, we build the X-ray diffraction (XRD) spectrum. The supercell values have been used to calculate the XRD spectrum of non-stoichiometric CuInSe$_2$ and CuGaSe$_2$. In our work, the method described by Attia et al. [28] has been incorporated and only modify the structural factor by summing over all the atoms in the supercell. The defect site in each defect cells has been chosen randomly. We observed the presence of extra small peaks in the XRD spectrum, as shown in Figure 11. [47]

Nomalous neutron diffraction scattering of synchrotron X-ray radiations gives more accurate data of composition distributions. [28] However, in situ XRD is the most convenient tool for monitoring the deviations from the stoichiometric compositions. A substantial increase in full wavelength half maximum (FWHM) indicates an incapability gap, in which the lattice constants depends on Ga/III and follow Vegrad’s law. [29–31] More work should be done to make it more feasible to be used for industrial use for future process monitoring and control.

5. Some Means to Improve Film Composition Control

During the fabrication of CIGS thin films, there will be chemical fluctuation-induced nano-domains. A novel metal-organic sputtering (MO-sputtering) technique was developed in our work, in which a metal-organic compound like TMGa (trimethylgallium) as the reactant was used during the reactive sputtering procedure. Figure 12 shows the change of Ga/(Ga + In) ratio as a function of TMGa flow rate and substrate temperature as well,[1] and the linear relationship of Ga/(Ga + In) with the TMGa flow rate adjust the deposit thin film composition is particularly interesting. Note also in Figure 13 and Figure 14 that the result from the micro-Raman spectroscopy, in which the Raman shift as a function of the film composition change of Cu/(Ga + In) is presented. It is clear that the micro-Raman shift is sensitive as the composition change of the CIGS thin films. To combine the use of MO-sputtering for the film growth and its feedback monitoring with the Raman shift, it might provide a means to better control the stoichiometry of thin film during the manufacturing steps.

From the Raman scans, we can observe that the Raman shift is sensitive to the composition change in the CIGS thin films. The continuous monitoring of CIGS thin films grown using MO-sputtering with Raman shift provides better control on the stoichiometry of thin film during the fabrication process. This allows them to achieve a fundamental improvement of the manufacturing technology.
Recent report by Rommel Noufi of NREL, USA addressed on science and technology of high efficiency CIGS thin film solar cells,[41,43–46] which include schematic profiles of “3-stage process for CIGS”, fundamental understanding of defects in the bulk and surface regions, studies on the device structure, properties of thin film layers, growth dynamics of the CIGS films; focusing on the restructured surface, development of grain and grain boundary structures model, etc. are dealt in-depth. Most studies are related to the film compositional profiles.

An alternate way is that once the film compositional profiles and their distributions are accurately determined from our theory and experimental analysis, that is the essential electrical and optical properties can be computed from our material design and device design, these data can be checked from reports in the literatures,[41] and they are meaningful device structural parameters to be loaded into the renowned device simulator SCADS 3.2[15] to get the photo conversion efficiencies, and a “big database” can thus be constructed, and they should help improve the production yields for cells and modules manufacturing.

Figure 11. Simulated XRD spectra of non-stoichiometric CuInSe$_2$, Cu:In:Se$_2$ = 0.21:0.26:0.53.[17]

Figure 12. Preliminary result on the metal organic sputtering of CIGS photovoltaic. a) Ga content as a function of TMGa flow rate. b) The content of Ga as a function of substrate temperature. c) Plain view SEM image of the deposited CIGS film. d) Cross-sectional SEM image of a CIGS photovoltaic. Reproduced with permission.[1] Copyright 2003, Elsevier.
6. Future Prospects

Moreover, the status reports on different stages of CIGS developments have been periodically published by NREL, USA and Fraunhofer ISE Germany. These reports assisted the promotion of technology development and industrialization of thin-film CIGS produces. Although, many challenges still lie ahead, including optimization and control on the CIGS absorber film stoichiometry, interface and film uniformity over large areas for the power module fabrication.

Nowadays, despite PV production of monocrystalline Si and multicrystalline Si dominating in the PV market, the importance of TFSCs will steadily rise in the coming decade; moreover, in recent time the CIGS already wins its own counter parts like CdTe and a-Si (Figure 15).[40,41]

As viewed from Figure 16, the recent report from NREL[41] the potential to utilize continuous technologies to close the gap between laboratory cells and modules are greatly needed, and this is the purpose to develop science and technology to indicate possibility to realize optimization and precise control of non-stoichiometric Cu–III–VI$_2$ compound in the future manufacturing.

7. Conclusions

Materials design, with change in chemical compositions, has been described, and some of the most important academic solar cell simulators have been compared. However, these simulators do not read a lot of files one by one and inevitably one analytic simulator is favored, especially for the non-stoichiometric PV materials, based on defect concentration of the CIGS alloy. This might be one of the first steps in developing comprehensive intelligent design (materials/devices/process) and much refined work must be undertaken to further fulfill the need of PV cells for large area non-stoichiometric materials for industrial applications. A fundamental improvement on the manufacturing technology and use of the concept of intelligent design are necessary to improve the process flow and performance of CIGS photovoltaics.

Figure 13. Room temperature Raman shift in CuIn$_{1-x}$Ga$_x$Se$_2$ thin films of thickness 600 nm deposited on glass substrate with change in Ga content, the Raman peak shifted from 173.8 cm$^{-1}$ to 184.6 cm$^{-1}$ in A$_1$ mode and $u$ is Se shift parameter. Reproduced with permission.[33,35]

Figure 14. Room temperature Raman shift in Cu(In$_{1-x}$Ga$_x$)Se$_2$ thin films, of thickness 600 nm on glass substrate, with change in Ga concentration.[14,33]

Figure 15. Thin-film technologies worldwide annual PV module production in MWp.[41]
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