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### Authors

Eisenberg, Daniel A  
Yu, Mengjing  
Lam, Carl W  
[et al.](#)

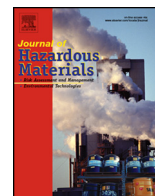
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## Comparative alternative materials assessment to screen toxicity hazards in the life cycle of CIGS thin film photovoltaics



Daniel A. Eisenberg<sup>a</sup>, Mengjing Yu<sup>a</sup>, Carl W. Lam<sup>a</sup>, Oladele A. Ogunseitan<sup>b</sup>, Julie M. Schoenung<sup>a,\*</sup>

<sup>a</sup> University of California, Davis, 1 Shields Avenue, Davis, CA 95616, USA

<sup>b</sup> University of California, Irvine, Irvine, CA 92697, USA

### HIGHLIGHTS

- Comparative alternatives assessment of thin film manufacturing technologies.
- Development of chemical alternatives assessment in a life cycle context.
- Screening of manufacturing and solar cell hazardous substances simultaneously.

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### ABSTRACT

Copper–indium–gallium–selenium–sulfide (CIGS) thin film photovoltaics are increasingly penetrating the market supply for consumer solar panels. Although CIGS is attractive for producing less greenhouse gas emissions than fossil-fuel based energy sources, CIGS manufacturing processes and solar cell devices use hazardous materials that should be carefully considered in evaluating and comparing net environmental benefits of energy products. Through this research, we present a case study on the toxicity hazards associated with alternative materials selection for CIGS manufacturing. We applied two numeric models, The Green Screen for Safer Chemicals<sup>TM</sup> and the Toxic Potential Indicator. To improve the sensitivity of the model outputs, we developed a novel, life cycle thinking based hazard assessment method that facilitates the projection of hazards throughout material life cycles. Our results show that the least hazardous CIGS solar cell device and manufacturing protocol consist of a titanium substrate, molybdenum metal back electrode, CuInS<sub>2</sub> p-type absorber deposited by spray pyrolysis, ZnS buffer deposited by spray ion layer gas reduction, ZnO:Ga transparent conducting oxide (TCO) deposited by sputtering, and the encapsulant polydimethylsiloxane.

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## 1. Introduction

Policy makers and manufacturers advocate photovoltaic (solar) panels as a sustainable alternative to fossil fuel-based energy sources [1]. Energy conversion efficiencies for copper–indium–gallium–selenium–sulfide (CIGS) solar cells (found within solar panels) of greater than 19% have already been achieved, making CIGS a feasible solar material for future industrial competition with the incumbent mono- and polycrystalline silicon-based solar cell technologies [2,3]. CIGS solar cells are comprised of nanometer to micrometer thick layers of materials deposited during manufacture. Each layer provides a specific function, where their combination creates a semiconductor that

converts light to energy. The relative thickness and material content of each layer varies among manufacturers. Six different layers are used in CIGS solar cells, as illustrated in [Table 1](#): substrate, metal back electrode, p-type absorber, buffer, transparent conducting oxide (TCO) (also referred to in the literature as an n-type window), and encapsulant [4]. The layered nature of CIGS solar cells allows for significant variation in material composition and manufacturing processing between solar cells. This, compounded with the search for new materials and processes that improve CIGS solar cell efficiency, mechanical properties, economic viability, and sustainability [3], creates a wide diversity of CIGS manufacturing processing and solar cell material composition options.

The recent European Union directive on the Restriction on the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (RoHS) [5], and the impending Safer Consumer Products Law in the State of California are examples of legislative initiatives that motivate for the removal of toxic substances from fabricated

\* Corresponding author. Tel.: +1 530 752 5840; fax: +1 530 752 9554.

E-mail address: [jmschoenung@ucdavis.edu](mailto:jmschoenung@ucdavis.edu) (J.M. Schoenung).

**Table 1**  
Material compositions of selected commercial CIGS solar cells from Niki et al. [4].

CIGS solar cells	Type 1	Type 2	Type 3	Type 4	Type 5	Type 6
TCO	ZnO:Al	ZnO:Al	ZnO:B	ZnO:Al	ZnO:Al	ZnO:Al
Buffer	CdS	CdS	Zn(S,OH) <sub>x</sub>	CdS	CdS	InS
P-type absorber	Cu(In,Ga)Se <sub>2</sub>	Cu(In,Ga)(S,Se) <sub>2</sub>	Cu(In,Ga)(S,Se) <sub>2</sub>	Cu(In,Ga)Se <sub>2</sub>	CuInS <sub>2</sub>	Cu(In,Ga)Se <sub>2</sub>
Metal back electrode	Mo	Barrier Mo	Barrier Mo	Barrier Mo	Mo	Mo
Substrate	SLG	SLG	SLG	Stainless steel foil	SLG	SLG

Notes: TCO, transparent conducting oxide; SLG, soda-lime glass.  
Cells with multiple entries are comprised of more than one material.

products [6]. Both pieces of legislation focus on the substances in products and neglect the potential toxic effects of the process chemicals used in their manufacture. This creates a situation that may increase the overall use of toxic substances, because the material composition of a product is the artifact of transformative chemical reactions – the use of toxic substances in manufacturing does not necessarily create a toxic product and vice versa. For CIGS solar cells, various toxic substances can be identified in both manufacturing process chemicals and in the resulting solar cells. For example, known toxic substances SeO<sub>2</sub>, H<sub>2</sub>S, and CdCl<sub>2</sub> are used in manufacturing while different toxic substances, such as CdS, are found within CIGS solar cells [7,8]. Because manufacturing process chemicals and solar cell material compositions are inherently linked, it is necessary to evaluate them concurrently in order to identify a less toxic process/product combination. At present, a wide variety of manufacturing process methods and CIGS solar cell material compositions are in development at the laboratory stage. The purpose of this work is to provide systematic and transparent classification of the lower hazard process/product combinations before extensive commercialization of laboratory scale technologies takes place.

For the purpose of this work, hazard is defined as the potential to cause damage, harm or an adverse effect to humans or the environment [9]. Chemicals exhibit select hazard traits that range from cancer causation to aquatic toxicity to flammability, as generally categorized into human health, environmental and physical hazards. For example, cadmium, beryllium, arsenic and vinyl chloride are known to cause cancer in humans [10]. In this context, these substances are considered to be hazardous to humans. The hazard evaluations herein do not consider fate, transport or exposure, but rather they focus solely on the human health, environmental and physical hazard traits of the substances evaluated. Furthermore, the evaluations do not account for material formulations or material quantity, in an effort to be conservative and to avoid the debate over the validity of hazard dilution [11].

The combined evaluation of the hazards associated with the substances used in manufacturing processes and the materials in the CIGS solar cells themselves into a single assessment requires life cycle thinking, but provides different guidance than a life cycle assessment (LCA). LCA is an assessment designed to quantify and combine the environmental impacts of material extraction, processing, use, and end-of-life stages of a product, process, or technology [12]. The focus of this work is to screen hazardous substances associated with the process chemicals in manufacturing and with the materials embodied in a CIGS solar cell, which correspond to hazardous impacts during the manufacture and end-of-life CIGS solar cell life cycle, respectively. Hazard is not of concern during the use stage if we assume the CIGS solar cell materials do not degrade during their lifetime. By considering the hazards of manufacture and end-of-life together, a certain degree of life-cycle thinking is applied, but this approach is not LCA for several reasons. Foremost, LCA assesses the entire product life cycle, where this assessment only considers the impacts associated with

manufacture and end-of-life. In addition, LCA assesses a greater range of environmental impacts, such as global warming potential and land use. Although more impacts are considered, their classification requires the quantity of substances used at each life cycle stage, which is not available for many novel CIGS manufacturing processes or solar cells material compositions [13]. Furthermore, LCA does not consider important toxicity information for selecting low-hazard process/product combinations, such as government regulations and banned substance laws [14]. Thus, LCA is not used in this study.

Instead of LCA, we use chemical alternatives assessments (CAA) of manufacturing process chemicals and solar cell material compositions to create a focused assessment of human and environmental toxicity and hazard [15]. This hazard based CAA requires the application of scoring and screening tools that facilitate hazard comparison [15]. Hazard scoring or screening tools are methods that provide guidance for substance selection via the combination of regulatory and industry accepted hazard classification metrics and properties into scores. Each tool assesses individual chemicals and materials, and their scores can be combined to represent the hazard associated with a device or process that consists of multiple substances. The final score provides a normalized baseline for judging the relative hazard between a material and its alternatives. Such tools use a comprehensive ranking system that streamlines the comparison of materials with unrelated hazard characteristics (e.g., when comparing a compound with potential impact on aquatic life to one that is flammable). Hazard assessment tools are adaptable to make hazard comparisons for entire manufacturing processes or for products. Therefore, through a detailed case study approach, they can provide decision support for selecting the preferred manufacturing processes and solar cell material composition using hazard as a basis.

Combining both manufacturing processes and solar cell material composition CAAs requires the use of a novel life cycle thinking methodology. CAA is designed to identify the least hazardous manufacturing process and CIGS solar cell material compositions separately. However, we wish to identify the least hazardous combination of manufacturing process substances and solar cell materials composition. Such a connection creates a hypothetical CIGS solar cell with reduced hazard in both life cycle stages. Lavoie et al. [15] suggest using life cycle thinking with a CAA, but the authors do not present explicit methodologies for accomplishing this goal. To do this, we implement what we call life cycle hazard projection (LCHP).

LCHP consists initially of making a CAA at a single life cycle stage, and then utilizes the assessment to guide choices for the other stages. For example, after the hazard assessment of CIGS manufacturing processes, the combination of all essential, lowest-hazard processes can be used to make a specific CIGS solar cell. Because it may not exist, we refer to the theoretical solar cell as having a projected material composition. This theoretical solar cell can then be assessed in a separate CAA to determine its potential hazards based on its projected composition. This links both life cycle stages

**Table 2**  
Substrate materials [4,24].

Industrial Rigid ceramics	Soda lime glass Zirconium dioxide
Metal foils	Molybdenum Copper Aluminum Iron/nickel alloy Titanium
Flexible polymers	Polyimide

Notes: This is the full list of substrate materials included in this study.

together and offers benefits similar to other life cycle methodologies by accounting for the extended impacts of manufacturing decisions [16]. A projection can be made to other life cycle stages as well, such as assessing the hazards associated with projected material extraction or use scenarios. Although such an expanded scope is beyond that of the current study, if these data are available, an entire life cycle thinking assessment can be created by combining CAAs of projections at each life cycle stage.

In this case study, we conduct two hazard-based CAAs to analyze: (1) the manufacturing process chemicals used in a variety of industrial and lab-scale manufacturing techniques for CIGS solar cells, and (2) the CIGS solar cell material compositions for solar cells found within various solar panels. Two hazard assessment tools are used to score and rank materials in this study: *The Green Screen for Safer Chemicals*<sup>TM</sup> (GS) and the *Toxic Potential Indicator* (TPI) developed by Clean Production Action (CPA) and Fraunhofer IZM, respectively [17–19]. After completing both CAAs, we use the LCHP methodology to establish a combined, low-hazard option for both manufacturing process chemicals and solar cell material composition simultaneously. Through this approach, this case study develops a life cycle thinking based methodology for reducing the use of hazardous substances in CIGS manufacturing and in CIGS solar cells.

## 2. Methods

### 2.1. Processing methods and solar cell materials

In Tables 2–4, we present a summary of the specific processes and materials examined in this study. Processing options exist for manufacturing the substrate, p-type absorber, buffer, TCO, and encapsulant layers. The metal back electrode is not listed in these tables because only one material option was analyzed, molybdenum. This list does not give a complete picture, as many processes have multiple input chemical options. For instance, hydrazine based liquid coating process can include ethylenediamine, dimethyl sulfoxide and ethanolamine, or neither of them. The complete list of options is provided in the supplementary material. The combination of material layers creates the final CIGS solar cell. A list of select CIGS solar cells available commercially in year

**Table 3**  
Encapsulants [23,27].

Abbr.	Status	Encapsulant
EVA	Industrial	Ethylene vinyl acetate
EEA	Emerging	Ethylene ethyl acrylate
EMA	Emerging	Ethylene methacrylic acid
EBA	Emerging	Ethylene butyl acrylate
EAA	Emerging	Ethylene acrylic acid
EAA-BA	Emerging	Ethylene acrylic acid-butyl acrylate
PDMS	Emerging	Polydimethylsiloxane
TP	Emerging	Thermoplastic polyurethane

Notes: This is the full list of encapsulants included in this study.

2010, with their corresponding layer compositions, is reproduced from Ref. [4] in Table 1.

An important characteristic for each processing method and material considered is whether it is an emerging technology or industrially used. Many emerging processing and material options offer benefits ranging from new functionality to higher throughput production. Although details on each layer within the CIGS solar cell cannot be provided in this work due to space limitations, the reader is referred to [4,20–27] for background on processes and materials and [4,23,24] for background on material choices and solar cell functionality. In Tables 2–4 the emerging and industrial status of the material or processes is labeled to simplify this comparison.

CIGS solar panels also use busbars and metal back contact barriers to harvest the energy from the solar cell. These are added after the adhesion of the TCO and before encapsulation through laser or direct machine contact patterning techniques [4]. Metal barriers placed on the metal back electrode provide added electrical insulation or prevent material diffusion. These components are neglected in the current study, so that the focus can be directly on the CIGS solar cells.

### 2.2. Hazard assessment tools

The Green Screen for Safer Chemicals<sup>TM</sup> version 1.0 (GS) considers 17 chemical hazard traits based on criteria designated by the United Nations' Globally Harmonized System of Classification and Labeling of Chemicals [28] and the U.S. Environmental Protection Agency's Design for the Environment program [29]. The 17 traits are grouped into five *hazard groups*: priority health effects (PE), human health (HH), environmental fate (EF), ecological (Eco), and physical (Phy), where the hazard of each specific trait is integrated into an overall hazard rating in each group. We collected data for the 17 hazard traits, and assigned to each a *hazard threshold* of low, medium, high, or very high, as defined within the GS methodology. After establishing hazard thresholds, we applied iterative GS decision logic to the hazard groups, and a *hazard benchmark* is established. The GS benchmarks are 1–4, representing progressively safer alternative chemicals.

The iterative decision logic uses a relative prioritization for each group to distinguish which hazard traits pose higher adverse impacts on human health and/or environmental quality [17]. The current decision logic causes the PE and EF groups to have a more pronounced effect on the final benchmark score. For example, ethyl acrylate and ethylenediamine both have “high” thresholds for certain hazard groups. Ethylenediamine receives a lower benchmark score than ethylene acrylate because its “high” threshold is in the HH group whereas ethylene acrylate's “high” threshold resides in the PE group. Additional information about GS and a sample assessment of cadmium sulfide are provided in the supplementary material.

We modified GS in our application to the CIGS case study by omitting the EF group from the final hazard comparisons. Some organic compounds cause increasingly greater health and environmental impacts after prolonged incubation in the environment. Therefore, the EF group can have a significant effect on GS benchmarks. Because this study focuses primarily on metal and inorganic materials with indefinite or uncertain environmental fates, if included, the EF hazard group may inaccurately lower the benchmark of almost every substance considered. We also note tiered levels of accuracy of a GS assessment, with the highest tier requiring independent expert validation. This study did not include external validation. To represent this, the GS results presented in this study are referred to as GS-based.

The Fraunhofer Institute in Germany developed the Toxic Potential Indicator model (TPI), which is more quantitative than GS. TPI includes three *hazard groups*: human health (HH), water

**Table 4**

P-Type absorber, buffer, and transparent conducting oxide (TCO) manufacturing processing methods [4,20–22,24–26].

P-Type absorber	Buffer	TCO
<b>Industrial methods:</b> (2)	<ul style="list-style-type: none"> <li>• Coevaporation</li> <li>• Selenization/sulfurization</li> </ul>	<ul style="list-style-type: none"> <li>• CdS bath</li> <li>• Showa Shell process: Zn(O,S,OH)<sub>x</sub></li> </ul>
<b>Emg. methods:</b>	<ul style="list-style-type: none"> <li>• Liquid coating of Cu(In,Ga)Se<sub>2</sub></li> <li>• Liquid coating of CuInS<sub>2</sub></li> </ul>	<ul style="list-style-type: none"> <li>• ZnO:Al</li> <li>• ZnO:B</li> <li>• ZnO:Ga</li> </ul>
<b>Ink printing or solution processing:</b> (11)	<ul style="list-style-type: none"> <li>• Hydrazine based liquid coating (3)</li> <li>• Spray pyrolysis (5)</li> <li>• Spin coating</li> </ul>	<ul style="list-style-type: none"> <li>• NREL process: ZnS</li> <li>• (Cd,Zn)S bath</li> <li>• Zn(S,OH) bath</li> <li>• Zn(Se,OH) bath</li> <li>• In<sub>x</sub>(OH,S)<sub>y</sub> bath</li> </ul>
<b>Emg. methods: Electrodeposition by Kapmann method:</b> (14)	<ul style="list-style-type: none"> <li>• Basic method (2)</li> <li>• With citric acid (2)</li> <li>• With ammonia (2)</li> <li>• With thiocyanate (2)</li> <li>• With ethanalamine (2)</li> <li>• With ethylenediamine (2)</li> <li>• With EDTA (2)</li> </ul>	<ul style="list-style-type: none"> <li>• ZnS</li> <li>• In<sub>2</sub>Se<sub>3</sub></li> <li>• Al<sub>2</sub>O<sub>3</sub></li> </ul>
<b>Emg. methods: Chemical Vapor Deposition (CVD):</b> (1)	<ul style="list-style-type: none"> <li>• Atmospheric pressure metal organic chemical vapor deposition</li> </ul>	<ul style="list-style-type: none"> <li>• CdS</li> <li>• ZnS</li> </ul>

Notes: The number after each bold process method is the number of related processes assessed in this study. The number to the right of a process name is the number of different processes assessed which use the same name if more than one.

Emg., emerging; EDTA, ethylenediamine tetracetic acid; CBD, chemical bath deposition; ALD, atomic layer deposition; ILGAR, ion layer gas reduction.

**Table 5**

Abridged results for CIGS manufacturing processes—chemical alternatives assessment.

P-Type absorber		GS-based benchmark frequency				TPI score frequency			
Type of processing	Deposition method	4	3	2	1	Low	Mid	High	Very high
<b>Industrial process</b>	<b>Coevaporation</b>	0	1	4	0	1	1	2	1
Ink printing	Hydrazine based coating	0	2	1	1	1	0	3	1
Industrial process	Sulfurization/selenization	1	1	4	1	1	1	3	1
Chemical vapor deposition	AP-MOCVD	0	0	6	1	3	0	2	1
Electrodeposition	Kapmann method	1	1	4	2	2	0	5	1
<b>Ink printing</b>	<b>Spray pyrolysis of CuInS<sub>2</sub></b>	0	0	2	1	0	0	3	0

Buffer layer		GS-based benchmark frequency				TPI score frequency			
Type of processing	Material deposited	4	3	2	1	Low	Mid	High	Very high
<b>Spray-ILGAR</b>	<b>ZnS</b>	0	1	1	0	1	1	0	0
NREL – CBD	ZnS	1	0	4	0	2	1	1	0
ALD	Zn(O,S)	0	0	1	1	0	1	1	0
CBD	In(OH,S) <sub>y</sub>	0	0	1	1	0	0	1	1
ALD	In <sub>2</sub> Se <sub>3</sub>	0	0	1	1	0	0	1	1
Industrial: Showa shell	Zn(O,S,OH) <sub>x</sub>	0	0	2	1	0	1	2	0

TCO		GS-based benchmark frequency				TPI score frequency			
Type of processing	Material deposited	4	3	2	1	low	mid	high	very high
<b>Sputtering</b>	<b>ZnO:Ga</b>	0	1	1	0	0	1	1	0
Sputtering	ZnO:Al	1	1	1	0	1	1	1	0
Sputtering	ZnO:B	1	0	2	0	1	1	1	0
Sputtering/spray-ILGAR	ZnO	0	0	1	2	0	2	0	1

Encapsulant		GS-based benchmark frequency				TPI score frequency			
Type of processing	Chemicals Used	4	3	2	1	low	mid	high	very high
<b>Chemical processing</b>	<b>PDMS</b>	0	0	1	0	0	1	0	0
Chemical processing	EMA	0	0	2	0	1	0	1	0
Chemical processing	EBA	0	0	2	0	1	0	1	0
Chemical processing	EVA	0	0	2	0	0	1	1	0
Chemical processing	TP	0	0	0	1	0	0	0	1

Notes: This is a subset of all materials analyzed. The full list is available in the supplementary material.

Bold indicates a process with the lowest overall hazard scores in GS-based and TPI results.

Acronyms: TCO, transparent conductive oxide; AP-MOCVD, atmospheric pressure metal organic chemical vapor deposition; CBD, chemical bath deposition; ALD, atomic layer deposition.



(representing environmental) (W-E), and other hazards (OH); which are represented by the following *hazard metrics*: European Permissible Exposure Limits (MAK) and European Carcinogenicity Classification Values, German Water Hazard Classification (WGK), and European Risk Phrases (R-Phrases), respectively. Data on these hazard metrics are widely available in the regulated European Material Safety Data Sheets (EU-MSDSs). Within the three hazard groups there is a relative prioritization of hazard metrics similar to GS, where certain metrics yield higher TPI values. The three hazard group scores are weighted equally, combined, and scaled into a 0–100 value (0 = no hazard, 100 = very hazardous) [18,19]. For example, ethylene has very high HH impacts but minimal W-E and OH impacts, with resultant TPI = 35. In comparison, gallium has very high W-E impacts and minimal HH and OH impacts, with resultant TPI = 34. Score interpretation can be made on either absolute or subjective bases depending on the necessity of precision. As the scores for ethylene and gallium are very similar, they can be described as exhibiting similar relative hazards. However, because these hazards derive from different hazard groups, it is legitimate to argue that ethylene is more hazardous than gallium using this model. Additional information about TPI and a sample assessment of cadmium sulfide is provided in the supplementary material.

### 2.3. Chemical alternatives assessment methods

To implement both the manufacturing processes chemical and solar cell material composition CAAs, the following databases and sources are used, [30–37] and [30,32–34,38], for GS and TPI, respectively.

GS uses fewer benchmark values (i.e., four) than TPI (i.e., 0–100), therefore we *post-processed* TPI scores into four hazard ranges to parallel the four GS benchmarks. The ranges used for this case study are:  $0 \leq \text{TPI} < 10$ ,  $10 \leq \text{TPI} < 33.3$ ,  $33.3 \leq \text{TPI} < 66.6$ , and  $66.6 \leq \text{TPI} \leq 100$ , which correspond to GS benchmarks 4, 3, 2, and 1, respectively. For simplicity, these four TPI hazard ranges are renamed to low, medium, high and very high hazard, respectively.

Based on these ranges, it was possible to implement equivalent *frequency aggregation* methods for both assessment tools for the hazards of mixtures, processes, and products. We combined results by hazard score *frequency*: the result for a mixture, process, or product is the aggregate of its constituent GS benchmarks and TPI ranges. Combining aggregate values produced a *hazard profile* instead of a single score. For example, GS and TPI results for ethylene acrylic acid derive from the GS-based benchmarks and TPI scores for ethylene (GS-based benchmark 1 (BM1), TPI range: high) and for acrylic acid (GS-Based benchmark 2 (BM2), TPI range: medium). Thus, ethylene acrylic acid is reported with the following hazard profile: GS-based: 1 – BM1, 1 – BM2 (i.e., consisting of one substance rated as BM1 and one substance rated as BM2); and TPI: 1 – high, 1 – medium (i.e., consisting of one substance rated as high and one substance rated as medium).

Two separate CAA assessments were conducted: (1) assessment of process chemicals used in a variety of industrial and lab-scale manufacturing techniques for CIGS solar cells, and (2) assessment of the CIGS solar cell material compositions found in solar panels. Overall, we investigated 8 substrate materials, the metallic back electrode, 28 p-type absorber processes, 12 buffer processes, 4 TCO processes, 8 encapsulation processes, and 6 commercial CIGS solar cell material compositions. Combined, these represented 109 substances that we assessed using GS and TPI (see supplementary materials). Substance-based hazard results from the manufacturing process-chemical assessment were aggregated for each corresponding manufacturing process. Results from the solar cell material composition assessment were aggregated for each corresponding CIGS solar cell. In the process-chemical CAA, *post-processing* and *frequency-based aggregation* were utilized on

a layer-by-layer basis to combine hazard assessment tool results. The substrate and metal back electrode layers, each consisting of a single input material, represented pure substances, and did not require post-processing or frequency-based aggregation methods. The p-type absorber, buffer, TCO, and encapsulant layers used processes with multiple chemical inputs. Therefore, we used the post-processing and frequency-based aggregation methods. For the solar cell material composition CAA, we combined the materials for each CIGS solar cell into a single hazard profile using the post-processing and frequency-based aggregation methods.

Where post-processing of data was required, a hazard screening approach was used to rank hazard profiles. The highest (i.e., least desirable) hazard scores possible are a GS BM1 and the TPI range “very high”. When comparing two hazard profiles, a profile with a frequency >0 – BM1 (or 1 – very high) represents a higher hazard than a hazard profile with 0 – BM1.

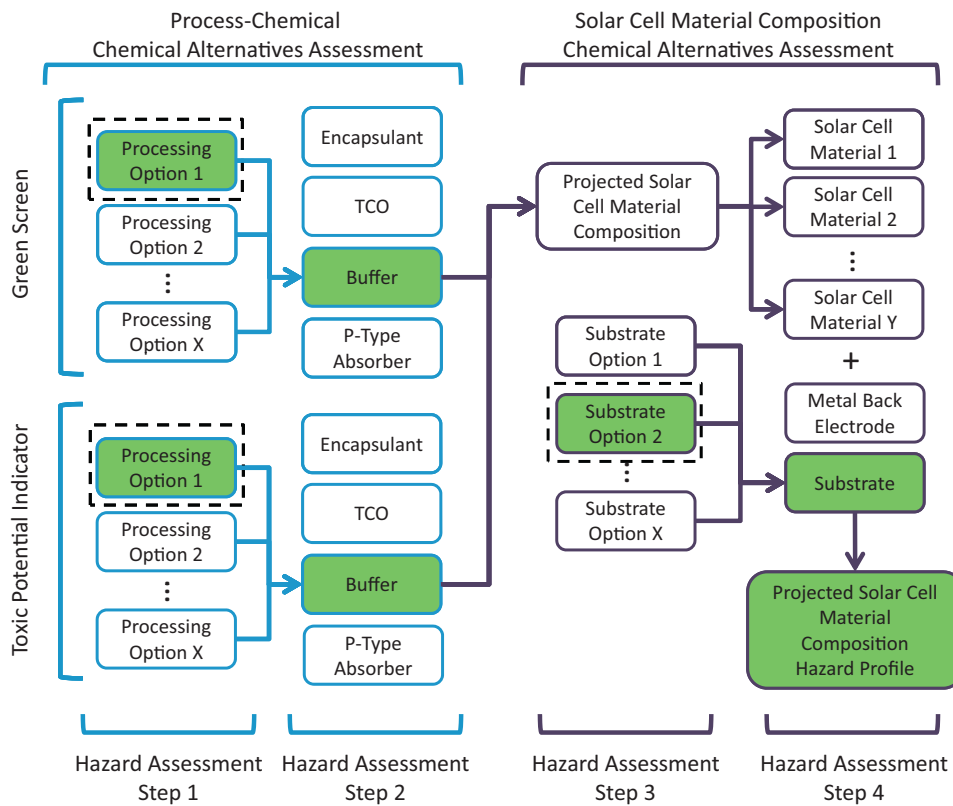
Complete hazard profiles were not available in the literature for some of the substances of interest to complete the assessments. For example, toxicological data on endocrine disruption potential for the majority of substances is not available. However, such data gaps do not generally influence the overall results because single hazard attributes dominate categorical hazard designations. In the few cases where too much data were missing, we employed surrogate substances as representative placeholders. We followed the methodology for surrogates found in the CHEMS-1 hazard assessment protocol [39]: representative surrogates chosen for these substances are their metal salts with the metal ion in an equivalent electronic state. The substances in this study that required surrogates were indium-, gallium-, and selenium-based inorganic chemicals used in manufacturing processes. Although, from the perspective of functionality, these substances constitute three of the most important materials in the p-type absorber layer, the use of surrogates did not change the overall conclusions of this study, as described in Section 4.

### 2.4. Hazard projection

We implemented a limited LCHP (process-chemical to solar cell material composition projection) to link both assessments together (Fig. 1). This assessment is referred to as limited to indicate that it does not assess hazard of every stage in a CIGS solar panel life cycle. We started by assuming that the lowest-hazard manufacturing process for each layer, as determined in the process-chemical CAA, correspond to the deposition of specific solar cell layer materials. These material layers are combined with low-hazard substrates and metal back electrodes to form two theoretical CIGS solar cell material compositions projected into the solar cell material composition CAA. The theoretical solar cells are not engineered or tested, and must be considered hypothetical for the purposes of this study. Each theoretical CIGS solar cell material composition was assessed using GS and TPI and compared to the commercial CIGS compositions presented earlier in Table 1. To facilitate comparison with commercial devices, the encapsulant layer was ignored for this projection because the identity of encapsulants used for commercial devices is unknown.

## 3. Results

The results of the process-chemical CAA (Table 5) highlight the lowest-hazard processing options for the p-type absorber, buffer, TCO, and encapsulant layers. Because these four layers require data post-processing and frequency aggregation methods, the results represent hazard profiles. In Table 5, both GS-Based benchmarks and TPI scores range from lowest to highest hazard, left to right. The results presented for the p-type absorber and buffer layers



**Fig. 1.** Sequence of steps taken to create the limited life cycle hazard projection between process-chemical and solar cell material composition CAAs: From left to right, Step 1, all process-chemical options for the buffer layer are assessed with Green Screen and Toxic Potential Indicator hazard assessment tools. Both tools determine the same processing option to be lowest in hazard. Step 2, low-hazard buffer layer made by processing option 1 is transferred to the projected CIGS solar cell material composition. This step is repeated to combine all low-hazard CIGS solar cell layer options together. Step 3, Green Screen and Toxic Potential Indicator are used to assess material options for the substrate CIGS solar cell layer. Step 4, projected CIGS solar cell material composition constituents are assessed and combined with low-hazard substrate and metal back electrode to create the complete low-hazard, projected solar cell material composition hazard profile. The projected solar cell composition material hazard profile is compared against commercial solar cell material composition hazard profiles to determine its relative hazard.

are a subset representing the lower-hazard deposition processing options for each processing method. This provides a comparison between processing methods in addition to determining the lowest-hazard deposition processes overall. For the TCO layer, four deposition processes were assessed. For the encapsulant layer, again only a subset of the results is presented in Table 5. These include ethylene based methods; the industry standard method: EVA; and emerging encapsulation methods: polydimethylsiloxane (PDMS) and thermoplastic polyurethane. The full list of hazard profiles for all p-type absorbers, buffer layers, and encapsulants is available in the supplementary material. Overall, the lowest-hazard processes determined by this study for manufacturing the p-type absorber, buffer, TCO, and encapsulant layers are coevaporation and spray pyrolysis, spray-ILGAR, sputtering, and chemical curing of PDMS, respectively.

The results of the solar cell material composition CAA are shown in Tables 6 and 7. Table 6 presents the lowest and highest hazard material options for the substrate and metal back electrode layers. Because no post processing of data is required for these layers, we report the GS and TPI scores. The results for the three lowest hazard substrate layers are: zirconium dioxide, titanium, and soda-lime glass (represented by amorphous silica); the highest-hazard substrate material is: polyimide. The only metal back electrode material assessed is molybdenum. The full list of substrate material results can be found in the supplementary material.

Table 7 presents the results for solar cell material compositions found in CIGS solar panels. These results required post-processing and frequency-aggregation methods for each CIGS solar cell material composition; therefore, Table 7 presents GS and TPI hazard

**Table 6**  
Abridged substrate/back electrode assessment results.

Material	GS-based benchmark	TPI score
<b>Titanium</b>		2.2
Zirconium dioxide	3	3.2
<b>Molybdenum</b>	2	1
Polyimide	1	92.8

Notes: This is a subset of all materials analyzed. Full list available in the supplementary material.

Bold indicates a material with the lowest overall hazard score in GS-based and TPI results.

Molybdenum is both a substrate material and metal back electrode material.

profiles for each solar cell material composition. Type 3 is the solar panel with the lowest-hazard CIGS solar cell material composition.

Also in Table 7 are two theoretical CIGS solar cell compositions as determined by the limited LCHP of process-chemical CAA results to the solar cell material composition CAA. Each of these theoretical CIGS solar cells consists of the same lowest-hazard substrate, metal back electrode, buffer, and top conducting oxide: titanium, molybdenum, ZnS, and ZnO:Ga, respectively, because they represent the lowest hazard options when combining the process-chemicals and solar cell material composition CAAs, as determined by both GS and TPI. For the p-type absorber processing options, however, the GS and TPI results from the process-chemical CAA do not agree. This yields two theoretical CIGS solar cell material compositions: the first one uses coevaporation to deposit CIGS as the p-type absorber; the second uses spray pyrolysis deposition to deposit CuInS<sub>2</sub> as the p-type absorber. Projecting these into the solar cell materials

**Table 7**  
Results for CIGS solar cell material composition chemical alternatives assessment.

Limited hazard projection solar cell compositions	GS-based benchmark frequency				TPI score frequency			
	4	3	2	1	Low	Mid	High	Very high
<b>Theoretical solar cell – CIS<sub>2</sub></b>	1	3	4	0	5	1	2	0
Theoretical solar cell – CIGS	1	3	4	0	4	2	2	0
Commercial solar cells [4]	GS-based benchmark frequency				TPI score frequency			
	4	3	2	1	Low	Mid	High	Very high
<b>Type 3</b>	0	5	6	0	6	2	3	0
Type 4	0	3	4	1	3	2	2	1
Type 5	0	3	5	1	5	2	1	1
Type 6	0	4	5	1	5	2	3	0
Type 1	0	4	5	1	5	2	2	1
Type 2	0	4	6	1	6	2	2	1

Notes: Bold indicates a solar cell with the lowest overall hazard scores in GS-based and TPI results.

composition CAA yields a lower overall hazard profile for the second theoretical CIGS solar cell. Therefore, by combining the results from both CAAs, the lowest-hazard CIGS manufacturing process uses spray pyrolysis to deposit a CuInS<sub>2</sub> p-type absorber. This theoretical CIGS solar cell also has a lower overall hazard than the lowest-hazard solar cell material composition found in the Type 3 CIGS solar panel.

## 4. Discussion

### 4.1. CIGS manufacturing hazards

The results presented above provide information on strategies to develop a “lowest-hazard” CIGS solar cell via the application of GS and TPI hazard assessment tools. To conduct this study, various changes needed to be made to each tool, and surrogates needed to be used. In this respect, these results are not definitive of the hazards associated with each CIGS manufacturing process or solar cell material composition. Nonetheless, by assessing these substances within the context of these two tools, specific materials that contribute most to the toxicity hazards can be pinpointed. Therefore, the results presented offer a basis for hazard screening of CIGS process-chemicals and solar cell material compositions.

Based on the results presented in Tables 5 and 6, high-hazard materials and manufacturing options occur throughout CIGS layers, and provide opportunities for substituting safer alternatives. For example, in the substrate layer, soda lime glass is a rigid material that does not offer the flexibility and applications possible with toxic polyimide (polyimide: GS-Based BM1, TPI: 92.8) [24]. Where solar cell flexibility is essential, the use of such a hazardous material may be warranted. However, titanium metal sheets can be made into flexible solar panels and offer a significantly lower hazard option (GS-Based BM3, TPI: 2.2) [4].

This assessment exercise also provides information on emerging processing and deposition technologies. For the p-type absorber, one of the two lowest-hazard processes is commercial, co-evaporation, and the other process is emerging, spray pyrolysis. This demonstrates that both commercial and emerging processes will play a role in low-hazard CIGS manufacturing. Conversely, certain emerging processes for processing the p-type absorber prove to be much higher in hazard. All electrodeposition p-type absorber manufacturing processes have a higher hazard profile than both commercial deposition options.

Variations in the hazards of emerging technologies exist in the encapsulant layer as well. The lowest-hazard encapsulant was found to be the emerging PDMS, versus the industry standard EVA. Inversely, the emerging technology with thermoplastic

polyurethane has a higher hazard profile than ethylene vinyl acetate.

For the buffer layer, the commercial chemical bath deposition of CdS is very high hazard compared to all indium and zinc based deposition processes. Although indium and zinc offer lower hazard options, this assessment further indicated that spray-ILGAR of ZnS is lowest overall. Although the lowest hazard deposition process produces a zinc buffer, certain zinc deposition processes, such as the Showa Shell process, can exhibit higher hazard profiles than low-hazard indium choices. Therefore zinc-based deposition should be preferred, but must be characterized to ensure it is indeed low hazard.

### 4.2. Hazard projection

Both theoretical solar cells projected by the process-chemical CAA results are the lowest-hazard solar cell compositions in the CIGS solar cell material composition CAA. While each CAA was successful at determining low-hazard options, by linking the two through a limited LCHP, it was possible to minimize the potential hazards of two life cycle stages. The discrepancy where the GS and TPI indicated different lowest-hazard processing methods for the p-type absorber demonstrates that using multiple hazard assessment tools can create conflicting results within a CAA. Such discrepancies occur because the fundamental bases for the two assessment tools are not identical. Furthermore, since the p-type absorber layer of a CIGS device is the largest and most important for the solar cell, this inconsistency weakens the CAA results. The hazard projection offset this weakness, as the projection presented herein established the solar cell that uses CuInS<sub>2</sub> as lower in hazard.

### 4.3. Sources of uncertainty and error

The two principal sources of error in our results stem from the post-processing and frequency-based aggregation methods and the use of surrogates in the final assessment. Since GS only has four benchmarks, it is most effective for screening out the highest-hazard substances amongst a list of alternatives. The TPI offers a higher resolution scoring method, which can serve a different purpose than hazard screening. For example, one alternative post-processing method is to sum chemical scores of mixtures into a single value [19]. For this case study, however, it was desirable to have the robustness of two sets of assessment scores as the basis for the hazard screening, therefore it was necessary to post-process the TPI results in such a way that comparisons to the GS results could indeed be made. A strong consistency between the two sets of results was observed even after frequency-based aggregation, highlighting the value and effectiveness of the approach.



In addition, although it is preferred to not use surrogates, the results from this case study demonstrate that the use of surrogates throughout the assessment does not change the overall conclusions. For the solar cell material composition CAA, no surrogates were required. All surrogates used are for manufacturing process chemicals implying that they only impact process-chemical hazard profiles. A surrogate could only make a hazard profile appear more hazardous by increasing the final value of the profile scores using the frequency-based aggregation method. Therefore, instead of disregarding the potential hazard of an unassessable substance, a more cautious approach is used that stipulates increased hazard. It is noted, however, that this cautious approach can skew the results by concealing lowest-hazard options.

## 5. Conclusions

In this work, we present a hazard assessment of CIGS manufacturing process chemicals and solar cell material compositions found within solar panels. We utilize two hazard assessment tools, GS and TPI, to create both processes-chemical and solar cell material composition CAAs. The CAAs are combined through a limited LCHP of the manufacturing and end-of-life life cycle stages. This combined assessment provides a basis for minimizing the hazard in both CAAs by hazard screening. The results indicate which emerging CIGS technologies are lowest in hazard using the GS and TPI tools. Furthermore, the case study presents benefits of using hazard assessment tools with a life cycle thinking based methodology to guide green engineering. Specific findings suggest that the least hazardous CIGS solar cell device and manufacturing protocol consist of a titanium substrate, molybdenum metal back electrode,  $\text{CuInS}_2$  p-type absorber deposited by spray pyrolysis, ZnS buffer deposited by spray ion layer gas reduction, ZnO:Ga transparent conducting oxide (TCO) deposited by sputtering, and the encapsulant polydimethylsiloxane.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2013.06.007>.

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