

Cu(InGa)Se₂ THIN-FILM SOLAR CELLS: COMPARATIVE LIFE-CYCLE ANALYSIS OF BUFFER LAYERS

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ABSTRACT: A motivation for replacing the current CdS buffer layer in CIGS PV is to avoid potential environmental- and human- health risks related to cadmium compounds. However, to gain a full perspective, such risks should be evaluated throughout the entire life cycle of the CdS, and also of alternative buffer layers. Based on data from the National Renewable Energy Laboratory and Global Solar Energy, we examined the life-cycle Cd emissions during materials production and the deposition processes for CdS and ZnS buffers. We found that the Cd emissions from the buffer layers are minimal compared to the upstream emissions from fossil-fuel-based electricity that the electricity generated from CIGS PV will replace. Accordingly, assuring a higher efficiency of CIGS PV is the best strategy to minimize Cd emissions to the environment. In addition, the production of ZnS (and InS) entails some Cd emissions as Cd is present in Zn ores. Based on the current efficiencies of alternative cell designs, CIGS/CdS will create a smaller amount of net Cd emissions than the CIGS/ZnS or CIGS/InS-based alternatives.

Keywords: Cu(InGa)Se₂, CdS, Environmental Effect

1 INTRODUCTION

Cu(InGa)Se₂-based thin-film solar cells have high conversion-efficiencies (the laboratory record in efficiency is 19.5%), long-term stability, and high radiation-resistance: accordingly, they are suitable for large-scale terrestrial applications [1]. One main thrust in the R&D of CIGS solar cells is to replace the cadmium sulfide (CdS) buffer layer between the CIGS and the transparent conducting oxide area with other material. The rationale underlying this effort is to lower occupational- and environmental-risks entailed in CdS deposition, and potentially to elevate conversion efficiency in the 350-550 nm spectral region [2]. Candidates for an alternative buffer layer include zinc sulfide (ZnS), indium sulfide (InS), and zinc selenium (ZnSe); another option is having a CIGS cell without a buffer layer. However, emissions of toxic substances, criteria pollutants, and greenhouse gases are generated throughout all stages of the entire life-cycle of a solar cell (i.e., material production, module manufacturing, installation, and recycling). Furthermore, cadmium is a by-product of zinc production, and may be emitted when fabricating zinc-based buffer compounds. Therefore, the impact of cadmium emissions on environmental- and human-health must be assessed throughout the entire life cycle of CdS and of alternative buffer layers.

In consultation with Global Solar Energy and National Renewable Energy Laboratory (NREL), we identified critical parameters for the life-cycle environmental impacts of CdS and ZnS buffer layers and examined their ranges and uncertainties within a life-cycle framework. The thickness of each buffer layer is assumed to be equal. The current conversion efficiency of the CIGS PV with CdS buffer layer is 10.5%. For each alternative, we compared emissions of heavy metals including Cd, criteria pollutants, and greenhouse-gases. Our focus is on an inventory analysis in which emissions are aggregated across stages and sources.

2 LIFE-CYCLE INVENTORY OF CdS BUFFER LAYERS

Life cycle assessment (LCA) compiles and evaluates the inputs, outputs, and the potential impacts of a product throughout its life cycle [3]. We applied the life-cycle inventory framework that involves collecting data, and quantifying material and energy to examine the emissions specifically during the stages of materials production and buffer formation for the CdS and ZnS layers. Hynes et al. (1994) estimated an energy requirement of 23 kWh/m² for a CdS window layer in a 200-nm thick CdTe module, based on chemical-bath deposition (CBD) [4]. They stated that 99% of this requirement is associated with the CBD operation and equipment manufacturing; negligible amounts of energy are embedded in the precursor materials for the buffer layers. Kato et al. (2001) obtained a value of 11-18 kWh/m² for a 50-70 nm CdS layer [5]. However, Global Solar Energy reports that the electricity use in their current operation is about 10 times lower than these older estimates. For cross-verification, we compiled the material balances of the CBD process and the integrated bath recycling processes from other published values [6-9].

Table 1: Materials (g) and energy (kWh) inputs required for the CBD of a 1 m² CdS and ZnS layer

<i>Inputs</i>	<i>Min</i>	<i>Max</i>
Sulfate*	0.61 (CdS)	2.1 (CdS)
	0.58 (ZnS)	2.0 (ZnS)
Thiourea, NH ₂ CSNH ₂	0.2	6.7
Ammonia, NH ₄ OH	1.3	13.2
Electricity	0.4	21 (CdS)
		42 (ZnS)

* Cadmium Sulfate, Cd(SO₄) or Zinc sulfate, Zn(SO₄)

Table 1 summarizes the ranges of materials and energy inputs for the CBD of 1 m² of CdS and ZnS layers assuming a thickness of 80 nm. We also considered that the material utilizations of the sulfur precursor (thiourea) and complexing agent (ammonia) are the same for both layers. The indirect emissions and energy used to produce these materials were taken from the Ecoinvent database [10].

The potential for impacting health should gaseous- and aqueous Cd emissions occur during the CBD process, along with concern about future regulatory restrictions on the amount of Cd inside solar cells are driving efforts to develop Cd-free buffer layers [2]. However, for a complete picture, we must take into account a holistic, life-cycle analysis of both direct and indirect emissions from all the stages of the life of a module. Synthesizing the precursors of CBD consumes energy and electricity that largely involves burning fossil fuel thereby releasing the cadmium inside the fuel. Using electric energy to heat up the chemical bath and to recycle the used bath is another source of indirect Cd emissions. We did not account in this study for consumables, such as acids and cleaning agents, which may be used in recycling and cleaning processes; however, their impacts are expected to be negligible.

Figure 1 presents the ranges of direct- and indirect- (upstream) Cd emissions associated with CBD. Indirect Cd releases to water linked to the electricity supply during the CBD were as important as those directly released during the process. No gaseous Cd emissions were detected from a U.S. commercial-scale CBD line [11]. However, indirect (upstream) gaseous Cd emissions are inevitable as the average US electricity grid relies heavily (>70%) on burning coal and natural gas [12]; our recent study underlined the importance of indirect emissions in power generation [13]. Accordingly, we demonstrated that replacing electricity from the average US grid mixture with electricity generated by CdTe solar cells would eliminate over 90% of the life-cycle gaseous Cd discharges (Figure 2). Similar results are expected from CIGS solar cells as they utilize a comparable amount of life-cycle energy as does CdTe [14].

To illustrate the significance of these indirect emissions, Figure 1 shows the amount of Cd emissions that would be abated by 1 m² of CIGS PV with an efficiency of 10.5% based on the US average insolation, 1,800 kWh/m²/yr, a 30-year lifetime, and a 80% performance ratio. Our analysis reveals that the total Cd emissions associated with a CdS buffer layer are several orders-of-magnitude lower than the reduction in Cd emissions achieved using CIGS/CdS PV.

The supply of Cd is largely governed by the volume of zinc- and lead-production since Cd is generated primarily as a byproduct of their smelting. Should the demand for Cd fall short of the supply, the surplus of Cd-containing residues from these smelters are disposed of, or treated and stored [15]. Disposing Cd-containing waste in landfills often entails risks of leaching and other undesirable processes. One of the most effective strategies to prevent the environmental release of Cd is to hermetically contain it inside products, such as Ni-Cd batteries and CdTe solar cells, so that it can be collected and recycled at the end of the product's lifespan. The Cd emissions during the life cycle of the latter, including

accidental emissions (e.g. fire) are well documented elsewhere [15].

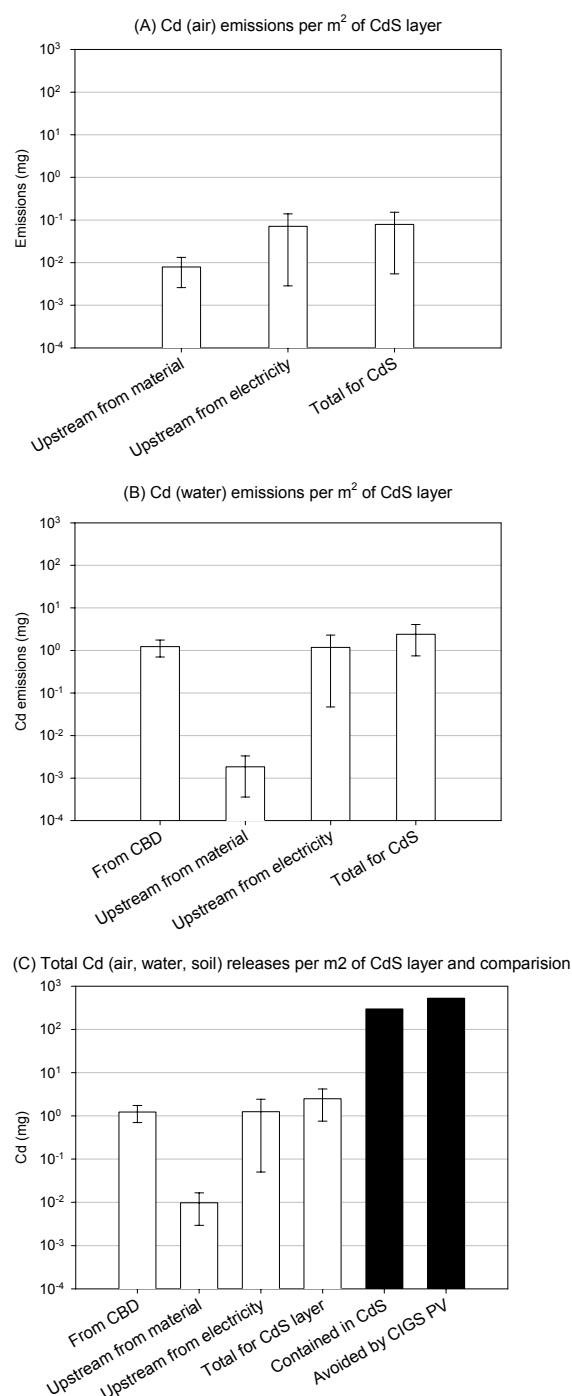


Figure 1: Cd emissions for the deposition of a 1 m² CdS buffer layer.

In Figure 1(C), we compare the total Cd content of the CdS buffer layer with the total Cd emissions generated in the life-cycle of this layer. The amount in the CdS layer is about 100 times greater than the total emissions from fabricating it (i.e., 1-4 mg vs. 300 mg per m² of module). If the Cd impurities in Zn smelters are not used, they are disposed as solid waste. Figure 1(C) also indicates that the amount of Cd abated by using

CIGS to generate electricity is more than the amount contained in the module (i.e., 520 mg per m² of module). These findings highlight the benefits of using a CdS buffer layer that generally are overlooked when the focus is on the product's embedded Cd; such advantages may be attained if the Cd in CdS layer is collected, disposed of, or recycled in ways that prevent its release or leaching.

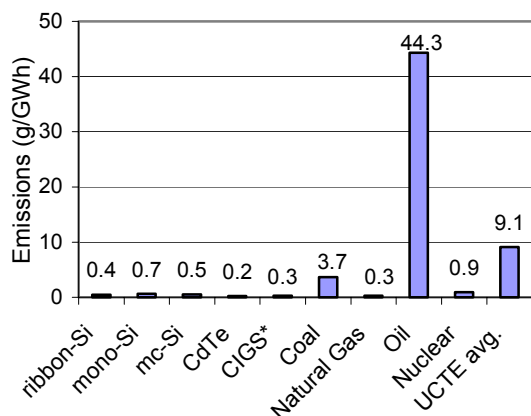


Figure 2. Life-cycle atmospheric Cd emissions for PV systems normalized for insolation of 1,800 kWh/m²/yr, performance ratio of 0.8, and lifetime of 30 yrs. Each PV system is assumed to include a ground-mount balance of system (BOS) [13]. *Estimated from primary energy [14].

3 COMPARISON WITH OTHER BUFFER LAYERS

There are no commercial production data for ZnS and InS buffer layers yet as they still are under development. Therefore, our references pertain to laboratory conditions. The zinc in the CBD of a ZnS buffer layer comes from zinc sulfate (ZnSO₄), the counterpart of cadmium sulfate (CdSO₄) in the CdS buffer layer (Table 1). Kinetic studies of the deposition of CdS and ZnS on CIGS, indicate that the growth rate of a ZnS buffer layer is half that of a CdS layer [16-18]. Specifically, the reported growth rate of CdS on CIGS in the laboratory ranges from 3.3 to 3.6 nm/min, while that of ZnS ranges from 0.04 to 1.7 nm/min. For the lower bound, we assume that the energy requirement is the same for the CBD of both layers. But, for the upper bound, we assumed that the energy requirement for CBD is proportional to its deposition time; hence, the CBD for the ZnS buffer layer would consume twice the amount of energy required for a CdS buffer layer (Table 1). Several additional steps are required to obtain a good-quality ZnS buffer layer. First, the CBD of ZnS entails agitating the bath solution to prevent precipitation, which degrades the quality of the device. In addition, after the CBD of the ZnS layer, the device often is annealed and lightly soaked to heighten its performance. Herein, we assumed that the environmental impacts are negligible, but this needs further investigation.

Figure 3 compares the life-cycle Cd emissions from a CdS and a ZnS buffer layer. The ranges from both largely overlap, although uncertainties are evident reflecting the current difficulties in measuring emissions.

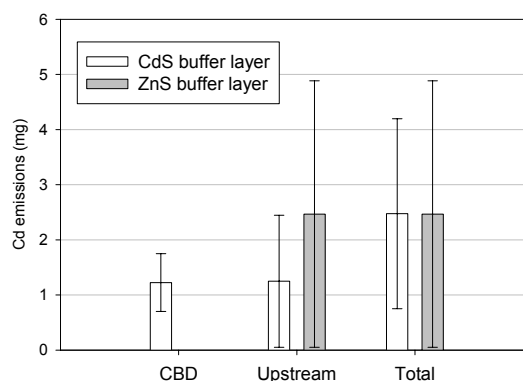


Figure 3: Comparison of total Cd emissions for deposition of 1 m² CdS and ZnS buffer layers during material production and CBD stages

As discussed earlier, electricity generated by CIGS PV may replace that generated by power plants burning fossil fuels, thereby preventing the Cd emissions from them. Estimating the amount of electricity generated during the lifetime of CIGS/CdS and CIGS/ZnS will allow us to measure the systems' preventative effects. We analyzed the systems' Cd-emission mitigation performance for a range of conversion efficiencies (Figure 4). The maximum amount of Cd emissions prevented will be the difference between the Cd emissions from average electricity grid mixture, and the minimum Cd emission estimated for each buffer layer, and vice versa. Presently, CIGS/ZnS PVs have lower efficiencies than CIGS/CdS PVs although the gaps are narrowing (Table 2). Data published in 2006 reveal that the highest efficiency of CIGS/CdS produced on a commercial scale by Würth Solar is 13.0%, slightly higher than 12.8% of CIGS/ZnS by Showa Shell.

Table 2: Conversion efficiencies of CIGS solar cells

Buffer	Method	Efficiency (%)	Size (cm ²)	Institute	Reference
CdS	CBD	19.5	0.41	ISE /NREL	[19]
ZnS	CBD	18.6	<1	NREL /AGU	[20]
In2S3	CBD	15.7	<1	IPE /ÅSC	[21]
In2S3	ALD	16.4	<1	ENSCP /ZSW	[22]
CdS	CBD	10.2*	8390	Global Solar Energy	[23]
CdS	CBD	13.0	6500	Würth Solar	[23]
ZnS	CBD	12.8	3600	Showa Shell	[23]
No buffer		15.7	<1		[24]
No buffer		16.2	<1		[25]

CBD: Chemical Bath Deposition; ALD: Atomic Layer Deposition; ISE: Institute for Solar Energy Systems; AGU: Aoyama Gakuin University; IPE: Institut für Physikalische Elektronik; ÅSC: Angstrom Solar Center; ENSCP: L'Ecole Nationale Supérieure de Chimie de

Paris; ZSW: Zentrum für Sonnenenergie - und Wasserstoff – Forschung.

*This is slightly lower than the latest 10.5% in 2007 [11].

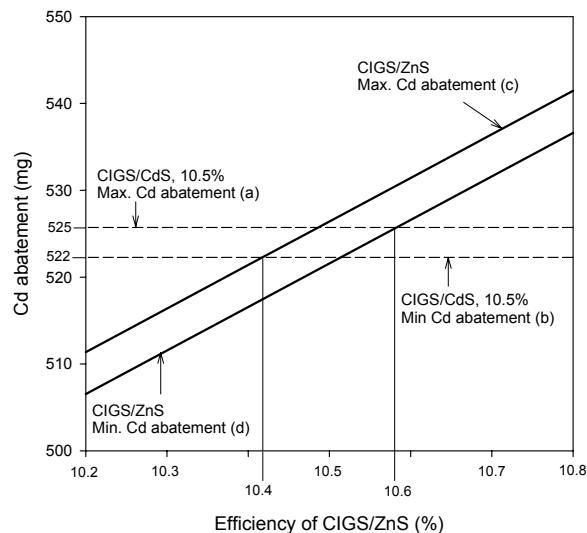


Figure 4: Comparison of abatements in total Cd emissions (air, water, and soil) during the lifetime of CIGS/CdS and CIGS/ZnS based on the US average insolation of 1,800 kWh/m²/yr, performance ratio of 0.8, and a lifetime of 30 years. The calculation of the amount of Cd emissions is based on the Cd emission factors of the US average grid mixture [26].

Figure 4 compares the amount of Cd abated (i.e., Cd emissions from average US grid minus Cd emissions from the life cycle of buffer layers). We assumed a fixed efficiency of 10.5% for the CIGS/CdS cell and we let the efficiency of CIGS/ZnS gradually increase as the technology probably will advance. We did not account for indirect (energy related) Cd emissions in the life cycle of CIGS since these do not change with different buffer alternatives. If the efficiency of CIGS/ZnS is less than 10.4%, then the CIGS/CdS will abate more Cd emissions (i.e., (a) and (b)) than CIGS/ZnS (i.e., (c) and (d)), while over 10.6%, the net Cd abatement of CIGS/ZnS will surpass that of CIGS/CdS. A definitive answer is unattainable for CIGS/ZnS efficiency between 10.4 and 10.6% due to uncertainty in the data (Table 1). This exercise verifies the large benefits of employing PV technology i.e., in preventing Cd emissions, and the relatively small risks associated with generating the buffer layer. A slight increase in conversion efficiency will be translated into a large net reduction in Cd emissions. This advantage becomes more apparent considering the Cd emissions from the average US grid are 0.12 mg per kWh (air, water, and solid) and that 1 m² of CIGS with 10.5% could replace 4,500 kWh of the average US grid electricity during its 30-year lifetime, while the life-cycle Cd emissions during production of the materials and the CdS buffer layer for the same area are only 0.17-0.92 mg. Accordingly, emphasis should be on improving the efficiency of PVs, i.e., generating more electricity and displacing more fossil fuel combustion,

rather than on the small amounts of Cd compounds encapsulated in the modules.

Our comparative analysis of Cd emissions may be applied to the InS buffer layer deposited by the CBD method. There is a dearth of information for such analyses of the Atomic Layer Deposition (ALD) method that is more widely used for InS. Nonetheless, it is unlikely that energy use and emissions during the ALD are substantially higher than those of the CBD.

4 CONCLUSIONS

Our analysis indicates that the indirect, upstream Cd emissions for CdS, ZnS, and, probably, InS buffer layers are comparable to, or greater than the direct Cd emissions associated with the CdS buffer layers. The sources of these indirect emissions include the synthesis of precursors for chemical bath deposition (CBD), electric energy to heat up the chemical bath and to recycle the used chemical bath, and the consumables, such as acids and cleaning agents. The ranges of Cd emissions from the life cycle of CdS and ZnS buffer layers largely overlap. The performance of a CdS buffer layer is equal or superior to that of other alternatives in abating emissions of Cd, along with discharges of criteria pollutants and greenhouse-gases from the average US grid mix that is dominated by fossil-fuel-based generation. Accordingly, from a life-cycle perspective, replacing the CdS buffer layer with ZnS or InS buffer layers does not reduce the risks of Cd emissions if, by doing so, it degrades the conversion efficiency of CIGS PV. Thus, using alternatives to CdS makes sense only if they increase the efficiency of conversion of photons to electricity in a PV system.

However, we did not discriminate between Cd emissions to employees versus public health effects, a choice that allowed us to aggregate the emissions across life-cycle stages and emissions sources (i.e., direct and indirect sources). Better understanding of the potential impact of Cd emissions to the public and workers along with that to the environment will provide a clearer comparison of risk from the buffer layers analyzed.

It has already been discussed in literature that containing Cd inside environmentally friendly products, such as double-glass CdTe PVs, will reduce further the risks of Cd emissions by isolating the Cd inevitable produced during Zn smelting. Using the CdS layer as a buffer for CIGS may offer the same benefits. The appraisal and discussion about buffer layers in this paper will add a new criterion of technology assessment, comprehensive environmental and human-health costs for selecting materials for the buffer layer.

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