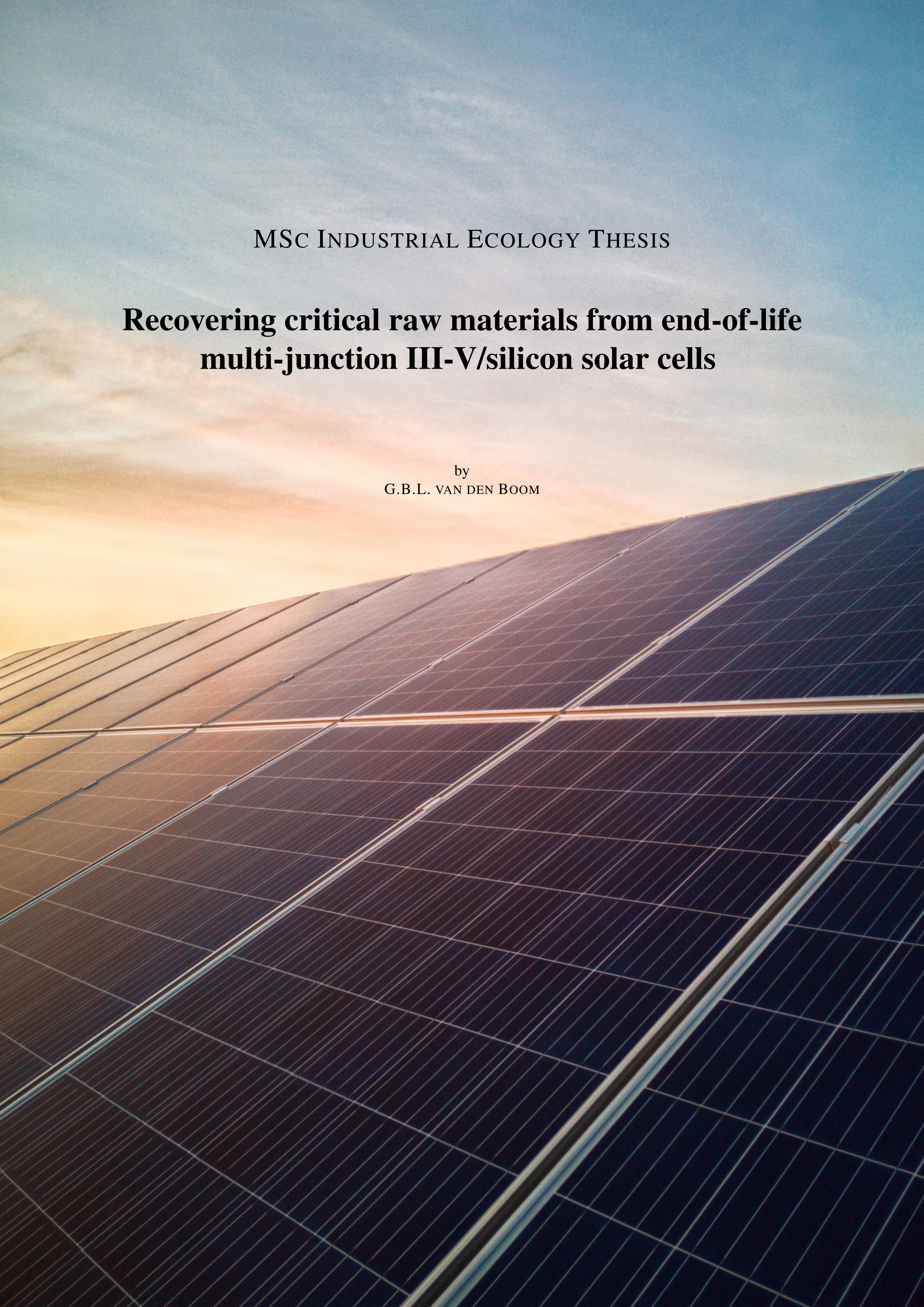

MSc Industrial Ecology Thesis

Recovering critical raw materials from end-of-life multi-junction III-V/silicon solar cells

by
G.B.L. van den Boom

MSc INDUSTRIAL ECOLOGY THESIS

Recovering critical raw materials from end-of-life multi-junction III-V/silicon solar cells

A criticality assessment of gallium, indium and silicon for large scale production of multi-junction III-V/silicon solar cells and an assessment of the environmental impacts and economic feasibility of recycling end-of-life multi-junction III-V/silicon solar panels

by

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Abstract

This thesis studies the criticality of gallium, indium and silicon for a 1GWp production of III-V/silicon solar cells and assesses the environmental impacts and economic costs & benefits of a recycling process for these solar cells. III-V/silicon is an emerging solar cell technology, that is expected to enter the market in between 2025 and 2035. It was found that gallium availability can become restrictive for large scale production of III-V/silicon cells, because the amount of high-purity gallium needed for an annual 1 GWp production of III-V/silicon cells (176.3 tons) is close to the entire 2019 world production of high-purity gallium (205 tons). It is therefore recommended to create additional high-purity refineries to refine low grade gallium to high-purity gallium. Moreover, in the long term, gallium can be recycled from end-of-life III-V/silicon cells. Various gallium recovery technologies from end-of-life products have been summed up from a literature review. One of them, an ethanol dilution process, is included in the flowchart of a recycling process for III-V/silicon solar panels. The environmental impacts of the recycling process are compared to the cradle-to-gate impacts of the production of the panels, by performing a life cycle assessment (LCA). The impact categories where the recycling process scores high are climate change, marine eutrophication, freshwater ecotoxicity, fossil resource depletion and ozone layer depletion. A suggestion to reduce the climate change impacts is to recycle the waste plastic that comes from the EoL panels, instead of incinerating this plastic. Finally a cost-benefit analysis (CBA) is performed. The CBA shows that recycling gallium, indium and silicon from 1GWp end-of-life III-V/silicon cells is likely to be profitable. With a product lifetime of 25 to 30 years, recycling is assumed to be profitable starting in the timeframe 2050-2065.

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List of Abbreviations

$(CH_2)_4(COOH)$	adipic acid
Al	aluminium
AlGaAs	aluminium gallium arsenide
AlInP	aluminium indium phosphate
ARC	anti-reflective coating
As	arsenic
c-Si	crystalline silicon
$Ca(OH)_2$	calcium hydroxide
CBA	cost-benefit analysis
CE	circular economy
CH_3CH_2OH	ethanol
CIGS	copper indium gallium selenide
CRMs	critical raw materials
EC	European Commission
EDTA	ethylenediaminetetraacetic acid
EoL	end-of-life
EQE	external quantum efficiency
EVA	ethylene-vinyl acetate
Ga	gallium
GaAs	gallium arsenide
GaAsP	gallium arsenide phosphide
GaN	gallium nitride
GaP	gallium phosphide
GaPN	gallium phosphide nitride
Ge	germanium
GWp	gigawatt-peak
H_2O_2	hydrogen peroxide
H_2SO_4	sulfuric acid
H_2SO_4	sulphuric acid
HCl	hydrogen chloride
HNO_3	nitric acid
ILCD	International Reference Life Cycle Data System
In	indium

InP	indium phosphide
K	Kelvin
kg	kilogram
LCA	life cycle assessment
LED	light emitting diodes
m^2	square meter
MJ	multi-junction
MOVPE	metalorganic vapour-phase epitaxy
N	nitrogen
NH_4Cl	ammonium chloride
P	phosphorus
PERC	Passivated Emitter and Rear Cells
PV	photovoltaic
SDGs	Sustainable Development Goals
SDR	social discount rate
Si	high purity silicon
TMGa	trimethylgallium
TMIn	trimethylindium
Å	angstrom

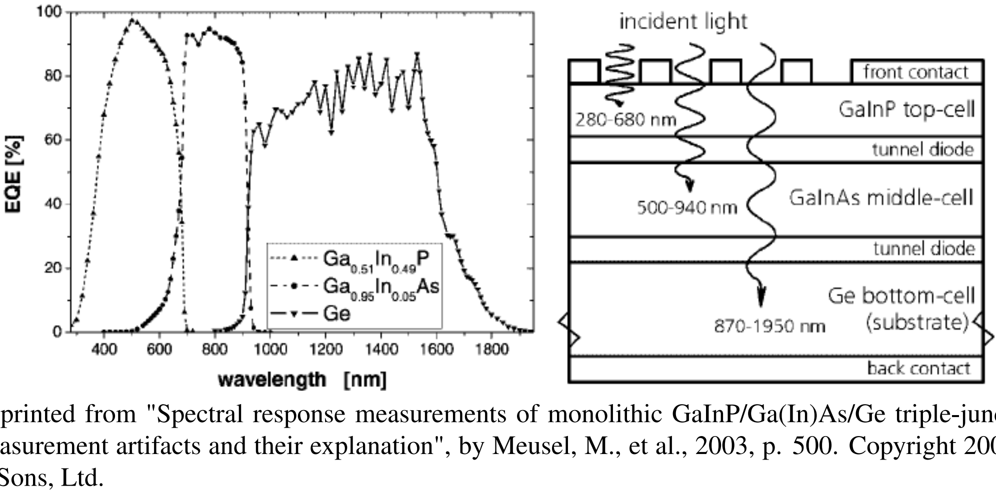
1 Introduction

1.1 General context

In today's society a lot of energy is used in the form of electricity, fuels and heat. Various sectors that use energy include agriculture, mining, manufacturing and heating, lighting and usage of appliances in buildings. Most of this energy is produced by burning crude oil, coal and natural gas. These three fossil fuels account for 81.3% of the world total primary energy supply in 2018 (32%, 27.1% and 22.2% respectively) (IEA, 2019). Burning these fossil fuels to produce energy has negative side effects. Fine dust particles ($PM_{2.5}$) and nitrogen oxides (NO_x) that are produced by fossil fuel combustion cause air pollution, which is a danger to human health (Farrow, Miller, & Myllyvirta, 2020). Furthermore, fossil fuel combustion produces greenhouse gases, such as carbon dioxide (CO_2) and methane (CH_4), which are stored in the Earth's atmosphere and oceans. These anthropogenic greenhouse gases contribute to observed climate changes, such as global warming and ocean acidification. These changes in climate have impacts on the natural habitats of many people, animals and plants (IPCC, 2014). Therefore, there is an increasing need to produce energy from sources that cause fewer air pollution and greenhouse gas emissions. Non-fossil sources that are currently commercially available include biomass-, nuclear-, hydro-, geothermal-, wind- and solar-energy.

This study focuses on so called III-V multi-junction (MJ) solar photovoltaic (PV) cells. Solar PV cells are a proven electricity producing technology and could play an increasingly important role in generating affordable and clean energy to meet the growing world energy demand (Pathak et al., 2019). There are various types of PV cells, with varying conversion efficiencies. The conversion efficiency being the portion of the energy in the sunlight that is converted to electricity. III-V MJ solar cells use crystalline semiconductor alloys from the III and V columns of the periodic table, or group 13 and group 15 respectively. Examples of elements from the III column are aluminium (Al), gallium (Ga) and indium (In), where as elements from the V column include nitrogen (N), phosphorus (P) and arsenic (As). These cells can be highly efficient. The best research cell efficiency of a III-V MJ cell is 47.1%, while the highest measured conversion efficiency for a crystalline silicon (c-Si) cell is 27.6% ("Best Research-Cell Efficiency Chart", n.d.). The high efficiency of III-V MJ cells is possible because each material junction is able to capture a different range of wavelengths of sunlight. Therefore, these cells are able to capture a greater total range of wavelengths than homojunction solar cells, such as conventional c-Si solar cells. The different ranges of wavelengths a III-V MJ cell can capture, can be read from an external quantum efficiency (EQE) diagram. The EQE of a solar cell equals the probability that a photon that hits the cell surface produces an electron in the external circuit of the cell (Markvart, & Castañer, 2018). An EQE diagram of a GaInP/Ga(In)As/Ge triple-junction solar cell, together with the general structure of this cell are shown in Figure 1.1.

Figure 1.1
An external quantum efficiency (EQE) diagram of a GaInP/Ga(In)As/Ge triple-junction solar cell (left) & the general structure of the cell (right)



Note. Reprinted from "Spectral response measurements of monolithic GaInP/Ga(In)As/Ge triple-junction solar cells: Measurement artifacts and their explanation", by Meusel, M., et al., 2003, p. 500. Copyright 2003 by John Wiley & Sons, Ltd.

Despite their high efficiency, III-V MJ solar cells also have disadvantages compared to other type of PV cells, such as c-Si and copper indium gallium selenide (CIGS); III-V MJ solar cells are more costly to produce and require rare elements, such as Ga and/or In. In the production process of a III-V MJ solar cell, a top cell that consists of III-V semiconductors is grown on top of a wafer, using metalorganic vapour-phase epitaxy (MOVPE) for which the material germanium (Ge) is most often used ("III-V PV Technology", n.d.). The Ge substrate is expensive compared to silicon (Si) (for c-Si) or glass (for CIGS) and is the main contributor to the production cost of III-V cells (Horowitz, Remo, Smith, & Ptak, 2018). Ge is used as wafer because the lattice constant of Ge, 5.658 angstrom (Å) at 300 Kelvin (K), matches the lattice constant of commonly used III-V alloy gallium arsenide (GaAs), 5.65325 Å at 300 K, very well ("Basic Parameters of Germanium", n.d.; "Basic Parameters of Gallium Arsenide", n.d.). The lattice constant of Si, 5.431 Å at 300 K, is significantly lower ("Basic Parameters of Silicon", n.d.) Although material quality is generally higher when materials with similar lattice constants are grown on top of each other and lower when the lattice constant mismatches, lattice mismatched growth is becoming more common in recent years (Dimroth, 2017). Despite the lattice mismatch, a high material quality can still be achieved. So called transition layers are applied, in which the lattice constant smoothly grades, while threading dislocation densities remain low (Dimroth, 2017). This makes it possible for Si wafers, which are much cheaper than Ge wafers, to be used as substrate. According to the U.S. Geological Survey, the average Ge metal price per kg in 2019, $1240, was more than five times higher than the average Si metal price per kg, $242.5 (U.S. Geological Survey, 2020b; U.S. Geological Survey, 2020c). Because of their high cost, III-V MJ solar cells are currently only applied in niche applications, such as space- and military-missions (Blanco et al., 2020). However, using Si as a substrate instead of Ge could make III-V solar cells cost competitive against other types of solar cells, especially in space-restricted areas.

1.1.1 Space-restricted markets

An example of a so called 'space-restricted' area is rooftop area in developed countries. Nowadays rooftops are used for various applications, such as green roofs, that offer various benefits compared to conventional roofs. Green roofs can act as a rainwater buffer, provide insulation, which contributes to energy saving, mitigate the urban heat island effect, provide a pleasant environment to work or live around and increase biodiversity (Getter & Rowe, 2006; Williams, Lundholm, & Maclvor, 2014). Another often encountered application for rooftops are leisure terraces. Because of the competition from e.g. green roofs and terraces, only a limited amount of space remains for PV installations. In the design of rooftops it could therefore be desirable to use III-V solar panels instead of c-Si solar panels.

Another example of a space-restricted area is commercial land in developed countries. Because the land value of commercial land in developed countries is high, it could be financially beneficial to only need two-thirds of the area, with 1.5 times as efficient PV panels, to produce the same amount of electricity. In places where the land value is low, on the other hand, it is harder for III-V/Si solar cells to compete with a larger area of c-Si cells, in terms of price per unit of electricity (C.F. Blanco Rocha, personal communication, May 30, 2020).

1.1.2 SiTaSol

In an ongoing project named SiTaSol, which has received funding from the European Union's Horizon 2020 research and innovation program, several research institutes are investigating whether it makes sense to produce Si based III-V (III-V/Si) tandem solar cells in large scale ("Project Description", n.d.). The main objective of SiTaSol is to make high-efficiency III-V/Si PV cells cost effective, in order to become a future alternative for c-Si cells, in space-restricted markets (C.F. Blanco Rocha, personal communication, February 13, 2020). However, not only the economical feasibility is being researched, but also the environmental impacts are considered. A cradle-to-gate life cycle assessment (LCA) of large scale production of III-V/Si solar cells (yearly production of 1 gigawatt-peak (GWp) suggests that these cells could be beneficial compared to c-Si when it comes to environmental performance (Blanco et al., 2020). The end-of-life (EoL) disposal was not included in the cradle-to-gate LCA, since potential recycling options for III-V/Si cells were not yet defined. This is where this research comes in. The schematic representation of a III-V/Si SiTaSol PV cell that is used in this study can be found in appendix A, figure A1. This cell design is taken from Blanco et al. (2020). However, Blanco et al. (2020) assumed the Si wafer thickness to be 270 micrometre, while for this study a Si wafer of 160 micrometre thick is assumed. These thinner Si wafers are more common nowadays (Woodhouse, Smith, Ramdas, & Margolis, 2019).

1.1.3 Raw material criticality and its parameters

III-V/Si cells contain Ga, In and Si, which have been labeled as critical raw materials (CRMs) by various studies (Schrijvers et al., 2020). Raw material criticality is a relatively new field of studies, which originates in military studies, but only gained significant attention from 2007, when China introduced export restrictions on rare earth elements (Schrijvers et al., 2020). This lead to the launch of the Raw Materials Initiative by the European Commission (EC) in 2008 (Morales, 2014). Ever since many studies were, and are still are, performed by various government bodies, research institutes and academics, that classify certain raw materials as 'critical'. One of the reasons behind a growing interest in material criticality is the rising demand for certain materials due to technological developments. Examples are the shift towards electric vehicles instead of internal combustion engine vehicles in the automotive industry, increased production of electronics and the shift towards solar panels and wind turbines instead of fossil fueled plants for electricity generation.

There are certain parameters that are usually part of a criticality assessment, which are the supply risk, or the likelihood that a supply disruption occurs and the vulnerability to supply disruptions (Frenzel, Kullik, Reuter, & Gutzmer, 2017).These two parameters are discussed further in the sections 1.1.3.1 and 1.1.3.2 respectively. The two main variables used in the criticality assessment methodology of the EC are similar: supply risk and the economic importance, where economic importance relates to the economic impact of a supply disruption. More specifically, the parameter of economic importance gives an insight on how important a material is, based on the value a material adds to the end-use applications and the corresponding manufacturing companies (Blengini et al., 2017). However, these are not the only two indicators used in criticality assessments. Therefore, section 1.1.3.3 elaborates on other parameters that are used in criticality assessment.

1.1.3.1 Supply risk

For certain raw materials, a huge share of the supply is coming from a single, or a few countries. According to the EU 2020 report on CRMs, 80% of Ga, 48% of In and 66% of Si supply comes from China ("European Commission, Study on the EU's list of Critical Raw Materials, Final Report", 2020). Moreover, the processing of these raw materials is done by few, large mining corporations with significant market pricing power. Reasons for supply disruptions could be e.g. export restrictions or workers striking in monopolistic supply countries. A taxation of certain raw materials can also cause a disruption in supply and rise in prices of certain materials (Glöser, Tercero Espinoza, Gandenberger, & Faulstich, 2015). The fourth list of CRMs for the EU was published in 2020 and includes three CRMs used in III-V/Si solar cells, namely Ga, In & Si. Both Ga and In are usually mined as a by-product of a so-called carrier element, because mining them individually is economically not feasible (Frenzel, Ketris, Seifert, & Gutzmer, 2016; Lokanc, Eggert, & Redlinger, 2015). Therefore, their supply cannot be increased independently. If the demand of these elements increases faster than the demand of their carrier element, these elements become scarce and market prices can skyrocket (Glöser et al., 2015).

1.1.3.2 Vulnerability to supply disruptions

An important factor is how substitutable a material is by another material, in terms of technical- and cost-performance ("Critical raw materials", n.d.). Graedel, Harper, Nassar & Reck (2015) estimated the overall substitute performance of Ga to be 38 on a scale from 0 (exemplary substitutes for major uses) to 100 (no substitutes currently available), where as the overall substitute performance of In scores 60 on the same scale. Their methodology was to look into the most used applications of the elements and to define the material that is the best substitute for every application, based on literature and interviews with material scientists and product designers. Furthermore, based on material science literature and expert opinion, every substitute material was given a rating: 'exemplary', 'good', 'adequate' or 'poor'. The respective values for these ratings are 12.5, 37.5, 62.5 and 87.5. The result for all 62 elements studied by Graedel et al. (2015) is presented in Table S1 of their work. The applications of Ga & In and their primary substitutes and substitute performances is shown in Table 1.1.

From Table 1.1 it can be seen that Graedel et al. (2015) defined indium phosphide (InP) to be the main alternative for Ga in solar cells and GaAs to be the main alternative for In in solar cells. A supply risk of both Ga and In would therefore be a serious problem for the production of III-V solar cells.

1.1.3.3 Environmental implications and other indicators in criticality assessments

Although in most studies criticality is indicated by the two indicators described in sections 1.1.3.1 and 1.1.3.2, several scientist have defined criticality differently. A well known method in the field of industrial ecology is the so called Yale methodology, which includes the additional dimension ’environmental implications’. This variable gives an indication on the damages a material causes to human health and ecosystems (Graedel et al., 2012). Although criticality assessments are usually only taking an economic perspective, considering the risk of a supply interruption and the consequences of such an interruption, the environmental perspective is important to consider as well. The environmental perspective is nowadays quite often included in academic research, but unfortunately it is still hardly used in politics (A.R. Balkenende, personal communication, August 18, 2020).

Table 1.1

Ga & In applications with primary substitutes and substitute performance according to Graedel et al. (2015)

Metal	Application	Application Details	Percentage into Application	Primary Substitute	Substitute Performance	Analysis Details
Ga	Integrated circuits	Used in integrated circuits	67% (global)	silicon	good	
	Optoelectronic devices	Includes laser diodes, light-emitting diodes, and **solar cells**	31% (global)	indium phosphide	good	
	Other	Includes research and development and specialty alloys	2% (global)	not applicable	not applicable	
In	Indium tin oxide thin-film coatings (mostly for liquid crystal displays)	Used in flat-panel devices and liquid crystal displays	84% (global)	aluminum-doped zinc oxide	adequate	Global values are for 2007
	Solders and alloys	Used in solders and alloys in aircraft and automotive applications, as well as in bearings, dies, seals, and sputtering targets	8% (global)	gallium	good	Global values are for 2007
	Electrical components and semiconductors	Used in computers, batteries, photodetectors, and **photovoltaic/solar cells**	2% (global)	gallium arsenide	good	Global values are for 2007
	Other	Includes research and compounds	6% (global)	not applicable	not applicable	Global values are for 2007

Note. Adapted from "On the materials basis of modern society", by Graedel, T., et al., 2015, *Proceedings of the National Academy of Sciences, 112*(20), Suppl. S1.

Schrijvers et al. (2020) performed a review of methods and data for determining raw material criticality, which includes 26 methodologies for material criticality determination. The ones using either additional or different indicators are discussed in appendix B.

1.1.4 Advantages and disadvantages of recycling

1.1.4.1 Advantages

Firstly, recycling, or secondary raw material production, causes a decline in the need to mine and process primary raw materials, which can cause energy savings and reduction in ecosystem disturbance (Norgate, & Haque, 2010). Whether energy is saved in the case of Ga, In & Si recycling is to be researched. Secondly, increasing the recycling rate of Ga, In & Si, increases the supply for these materials sustainably in the long term, which improves resilience of the supply chain and therefore lowers the criticality of these materials. Thirdly, recycling could arguably become economically preferable to mining in the long-term, because of economy of scale, new recycling techniques and scarcity. Fourthly, if materials are landfilled or incinerated, (toxic) materials are released into the environment (air, water & soil). Although this also can be the case in recycling, recycling is usually less polluting than landfilling or incineration. Lastly, recycling could create jobs and increase environmental awareness. Although recovering Ga, In and Si from EoL products is challenging, it is certainly not impossible. The environmental impacts and economic feasibility of potential recycling techniques for III-V/Si cells are to be researched.

1.1.4.2 Disadvantages

For various materials it is hard for the recycling industry to compete economically with mining. Considering for instance Ga, Licht, Peiró, & Villalba (2015, p.894) state that "recycling could be an option for countries with no primary Ga extraction, but is, by no means, comparable to the potential Ga supply that could result from improving mining efficiencies and manufacturing efficiencies". Secondly, exposure to metals, chemicals and dust, could have adverse health consequences for employees in the recycling industry. Lastly, a specific disadvantage for materials that are used in small amounts, such as the CRMs in III-V/Si solar cells, is that recycling often favors high volume bulk materials.

1.2 Research objectives

In accordance with the defined context, three research objectives are formulated. The first objective of this research is to discuss the limitations for large scale production of III-V/Si solar cells, that could be a consequence of criticality of Ga, In and Si. Secondly, several potential recycling processes are defined in a literature study and a process flowchart is created, with processes that could be suited for recycling EoL III-V/Si solar cells. Finally, the environmental performance of this recycling process and the economic feasibility of building and running a recycling supply chain are assessed.

1.3 Knowledge gap and problem statement

In this section, the knowledge gap and problem statement that this thesis addresses are defined. These lead to the research questions defined in section 1.4 and the sub-questions defined in section 2.3.1.

Knowledge gaps: III-V/Si PV technology is expected to enter the market in between 2025 and 2035 (Gervais, Shammugam, Friedrich & Schlegl, 2021). Research is needed to conclude weather the development of this emerging technology could be limited because of the criticality of the raw materials used in production of the cells. Although there is already a lot of knowledge being created on criticality of raw materials, a knowledge gap exists in how criticality of gallium, indium and silicon could limit or accelerate large scale production of III-V/Si solar cells. Furthermore, knowledge gaps exists on how these elements could be recycled from end-of-life III-V/Si solar cells and what would be the environmental- and economic-performances of such a recycling process.

Problem statement: Criticality of gallium, indium and silicon could be a limiting factor in large scaled production of III-V/Si solar cells. Little is known on recycling processes to recover gallium-, indium- and silicon from end-of-life III-V/Si solar cells, and the environmental performance and economic feasibility of such a process.

1.4 Main research questions

In accordance with the research objectives, knowledge gap and problem statement, the following main research questions are formulated:

1. *Could criticality of gallium, indium and silicon limit the development of III-V/silicon solar cells towards a yearly production of 1 gigawatt-peak?*

&

2. *What is a potential recycling process for III-V/silicon solar panels that recovers bulk elements (glass, aluminium and copper) as well as gallium, indium and silicon?*

&

3. *What are the environmental- and economic impacts of the recycling process for end-of-life III-V/silicon solar panels?*

2 Research perspective, approach & sub-questions

In this research various methods are used to answer the research questions. In this chapter, the taken research perspective, approach and methods are defined.

2.1 Industrial ecology perspective

Graedel & Allenby (2010, p.41) define industrial ecology as "the study of technological organisms, their use of resources, their potential environmental impacts, and the ways in which their interactions with the natural world could be restructured to enable global sustainability". The industrial ecology perspective that is used, lies in line with this definition. Systems thinking is used to perform a criticality assessment of the resources that are needed to produce III-V/Si solar cells. The performed environmental impact assessment and economic cost-benefit analysis (CBA) of recycling III-V/Si solar panels also requires systems thinking. These assessments respectively provide findings on whether gallium, indium and silicon are critical for a 1GWp production of III-V/Si solar cells, on what the environmental hot spots of the recycling process are and on whether the recycling process could be economically beneficial or not.

III-V/Si solar cells can contribute to decarbonize the global energy supply, which reduces the anthropogenic influence on global warming and therefore enables global sustainability. On the other hand, III-V/Si solar cells include raw materials that have been classified as critical by various studies. The assessments of recycling possibilities to recover Ga, In and Si from EoL III-V/Si photovoltaics could help improve recycling in the future and therefore reduce criticality of these materials. Recycling materials contributes to a circular economy (CE). Opposed to the currently dominant economic development scheme, the "take, make, dispose", or "linear" economic model, CE promotes a more environmentally friendly approach to resources. CE can help society to increase sustainability and welfare at low environmental cost. In order to implement CE successfully, industrial systems have to be changed on a system level. Increased recycling is an important part of this system change. CE helps to decouple economic growth from environmental impact due to natural resource consumption (Preston, 2012). To meet the United Nations Sustainable Development Goals (SDGs), moving towards a CE for metals is essential. III-V/Si solar cells and a responsible way of recycling them could contribute to SDGs 7 and 12, being "affordable and clean energy" and "responsible production and consumption". Only by complying with these SDGs, other SDGs on both economic development and the environment, can be complied with simultaneously (Van der Voet, n.d).

2.2 Systems description

Before looking into recycling processes, the raw material criticality of Ga, In & Si for mass production of III-V/Si solar cells is described. Knowing the aspects of criticality helps to understand the benefit, or even necessity, of increased recycling rates. The researched system for the criticality of Ga, In & Si is visualised in figure 2.1. The researched system for the recycling technologies to recover CRMs from EoL III-V/Si solar cells, with data inputs, methods and outputs, is visualised in figure 2.2.

Figure 2.1
Criticality determination system description

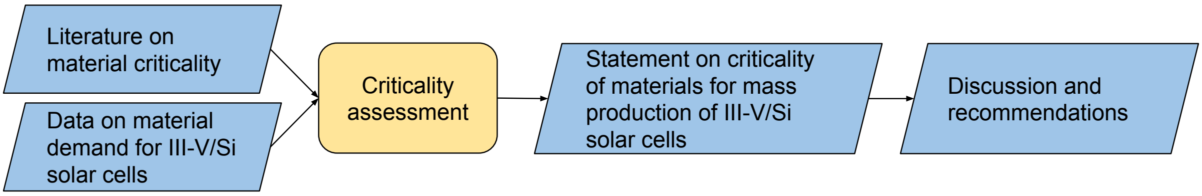
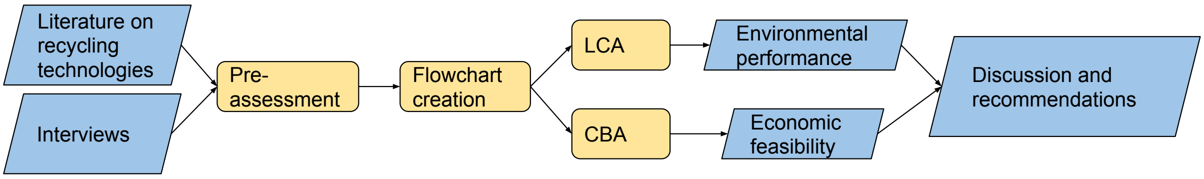


Figure 2.2
Recycling technologies system description



2.3 Design-oriented approach

In order to reach the research objective in a logically structured manner and break the main research question into sub-questions, a clear research approach is necessary. Because the knowledge gaps consider the design and analysis of a technical system, a design-oriented research approach is used in this research. Van Strien (1997) describes such an approach. A general outline of the approach is visualised in figure 2.3. The specific approach to study recycling technologies and their environmental- and economic-impacts, is visualised in figure 2.4. The circular shape of this figure indicates the iterative characteristic of the approach.

Figure 2.3
Design-oriented research approach. A variation on the regulative cycle, based on Van Strien (1997)

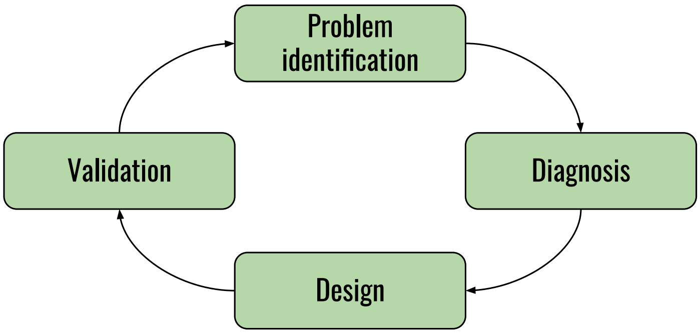
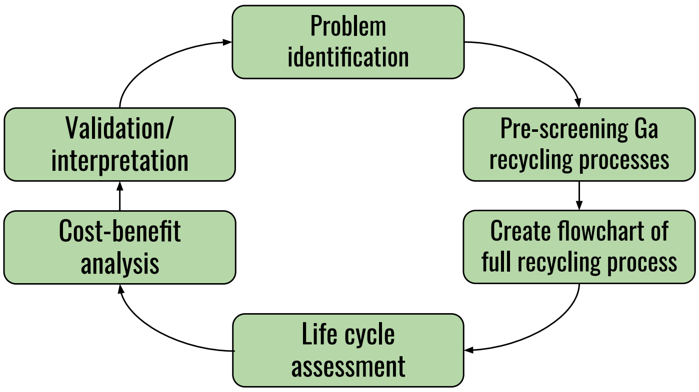


Figure 2.4
Research approach



2.3.1 Sub-research questions

In line with the taken perspective and approach, the main research questions are split into nine sub-questions. Research questions 1 & 2 relate to the first main research question. Research questions 3 & 4 relate to the second main research question. Research questions 5 to 9 relate to the third main research question.

Research question 1: *Could criticality of gallium, indium and silicon limit the development of III-V/silicon solar cells towards a yearly production of 1 gigawatt-peak?*

Research question 2: *How does end-of-life recycling of III-V/silicon solar cells affect criticality of gallium in the long term?*

Research question 3: *What are potential recycling processes to recover gallium from end-of-life III-V/silicon solar cells and which of these processes could be performing well environmentally?*

Research question 4: *What is a potential recycling process for III-V/silicon solar cells that recovers bulk elements (glass, aluminium and copper) as well as gallium, indium and silicon?*

Research question 5: *What are the estimated environmental impacts of the defined recycling process and how does this compare to the environmental impacts of the cradle-to-gate production of III-V/silicon solar panels?*

Research question 6: *What are the estimated economic impacts of the defined recycling process and how does this compare to the economic impacts of a recycling process that recovers only the bulk materials (glass, aluminium and copper)?*

Research question 7: *Are the environmental impact results consistent and complete?*

Research question 8: *What are the contributions of the various processes in the environmental and economic impacts?*

Research question 9: *How does a changing gallium price and the amount of gallium and indium recovered change the economic impacts results?*

3 Methods

3.1 Methods per research question

1. Could criticality of gallium, indium and silicon limit the development of III-V/silicon solar cells towards a yearly production of 1 gigawatt-peak?

To answer this research question, it is needed to study literature on criticality of Ga, In and Si in general first. To search for literature the databases ‘Scopus’ and ’Web of Science’ are used. The literature study was mainly performed in the months May and June 2020. The search string used in the search on raw material criticality in Scopus is "criticality AND "raw material*" OR metal* OR mineral* AND NOT quantum AND PUBYEAR > 2006". Similarly, the search string used in Web of Science is "TI=(criticality) AND TI=("raw material*" OR metal* OR mineral*) NOT TI=(quantum)" with a time span 2007-2020. Apart from using these keywords in Scopus and Web of Science, information on CRMs was also found in articles that were published on the website of the publication office of the European Union ("EU Publications", n.d.). Subsequently, criticality of Ga, In and Si for a 1 GWp production of III-V/Si solar cells is assessed by comparing the material availability of these elements to the demand for these elements for the production of III-V/Si solar cells. For Ga it should be noted that in the production of III-V/Si high purity (semiconductor-grade) Ga is needed. In this research, criticality is assessed using the Yale analytical framework as described by Graedel et al (2012). This methodology uses supply risk, vulnerability to supply disruptions and environmental implications as criticality dimensions. This methodology suits this research, since it considers both the economic- and the environmental-risks and consequences.

The material demands of Ga, In & Si for a 1GWp production are estimated from internal SiTaSol data. This data includes the amount of cells per GWp, the area of a cell (in m^2) and the amount of trimethylgallium (TMGa), trimethylindium (TMIn) and Si consumed per m^2. Using this data, the amount of Ga & In is estimated using their molecular weights in TMGa and TMIn. The material demands of Ga, In & Si for a 1GWp production, that are used in this research, can be found in appendix E.

2. How does end-of-life recycling of III-V/silicon solar cells affect criticality of gallium in the long term?

The influence of an increased EoL recycling of Ga on its criticality (as defined in research question 1) is assessed by applying the Yale methodology to two future scenarios; a scenario with EoL recycling and a scenario without EoL recycling.

3. What are potential recycling processes to recover gallium from end-of-life III-V/silicon solar cells and which of these processes could be performing well environmentally?

In order to find potential Ga recycling processes that may be applicable to the III-V/Si solar cells, the recycling processes of Ga in other production processes are studied from literature. The main focus lies on Ga, since the studied III-V/Si solar cell contains approximately 220 mg Ga and only 2,3 mg In (Blanco et al., 2020). Despite Ga being the main focus in the literature study, some studied recycling processes also recover In. Apart from studying academic literature, patents on Ga-recycling technologies from light emitting diodes (LEDs) and other integrated circuits using similar materials in a crystalline structure (e.g. circuits in laptops or photonic sensors) were looked into as well. The search string used in the search on Ga recycling methods in Scopus is "recycl* OR recover* AND gallium AND semiconductor* OR pv OR photovoltaic* OR integrated circuit* OR LED". Similarly, the search string used in Web of Science is "TI=(recycl* OR recover*) AND TI=(gallium) AND TI=(semiconductor* OR pv OR photovoltaic* OR "integrated circuit*" OR LED*)". After potential Ga recycling options are defined, a semi-quantitative assessment method is used to pre-assess these recycling processes. This pre-assessment method is explained in section 3.2. In addition to the literature review, three experts are asked for suggested recycling options in interviews. Firstly, prof. dr. ir. B.J. (Bart) Kooi from the ’Nanostructured Materials and Interfaces’ research group of the University of Groningen. Secondly, dr. Frank Dimroth, the SiTaSol project coordinator and head of the department III-V photovoltaics and concentrator technology at Fraunhofer Institute for Solar Energy Systems (ISE). And thirdly, prof. dr. A.R. (Ruud) Balkenende, professor at Delft University of Technology in circular product design and former scientist at Philips, where he performed research on photonic materials and devices. The Ga recycling process that scores highest in this pre-assessment, is included in the flowchart of the recycling process flowchart (figure 4.8).

4. What is a potential recycling process for III-V/silicon solar cells that recovers bulk elements (glass, aluminium and copper) as well as gallium, indium and silicon?

The literature study and the three interviews make it possible to create a recycling process flowchart with processes that recover glass, Al, Cu, Ga, In & Si from EoL III-V/Si solar cells. The processes are based on the c-Si PV waste recycling processes defined by Stolz et al. (2017) and Latunussa, Ardente, Blengini, & Mancini (2016). The Ga & In recycling process is based on the findings in research question 3. The environmental- & economic impacts of the created recycling process will be assessed in research question 5 & 6.

5. What are the estimated environmental impacts of the defined recycling process and how does this compare to the environmental impacts of the cradle-to-gate production of III-V/silicon solar panels?

After having picked the Ga recycling process step and subsequently having created the full recycling process in section 4.3, the impact analyses are performed in section 4.4. It should be noted that the technical processes that are needed to split various materials in the recycling process of III-V/Si MJ solar cells are uncertain and therefore assumptions are needed in the flowchart of the recycling process. Firstly, an environmental impact assessment is performed, in the form of an *ex ante* LCA, as described in section 3.3. A first approach was to compare the environmental impacts of recycled Ga to that of virgin Ga. However, because of allocation and subjective modeling choices, these results are however too uncertain to objectively argue whether the environmental implications of recycled Ga is bigger or smaller than that of virgin Ga. Therefore, a more robust approach is taken, comparing the environmental impacts of the full recycling process to the cradle-to-gate environmental impacts of the III-V/Si cell.

Firstly, the data for recycling of the bulk materials (glass, Al & Cu) is retrieved from Stolz et al. (2017). Secondly, the data on the recovery of Si is retrieved from Latunussa et al. (2016). Finally, data for the recovery of Ga & In comes from the recycling process that is picked in research question 3. These three data sources combined make it possible to perform a LCA on the studied system, the full recycling process. The impacts of this studied system will be compared to a reference system, being the cradle-to-gate impacts of III-V/Si panels without recycling, as defined in "D6.4 Ex-ante LCA of III-V/Si tandem solar modules" (SiTaSol, 2021).

6. What are the estimated economic impacts of the defined recycling process and how does this compare to the economic impacts of a recycling process that recovers only the bulk materials (glass, aluminium and copper)?

Next to the LCA, the economic costs and benefits of setting up and executing a recycling process is assessed by applying a CBA, which is explained in section 3.4. Two scenarios are considered. Firstly, a recycling process that recovers only the bulk materials (glass, Al & Cu). Secondly, a recycling process that also recovers Ga, In and Si from the EoL III-V/Si solar cells. Assumptions have to be made, since there are big uncertainties in how the technology and metal prices will develop in the future.

7. Are the environmental impact results consistent and complete?

The goal of the seventh research question is to provide a reflection on the LCA results. The consistency and completeness of the LCA will be checked.

8. What are the contributions of the various processes in the environmental and economic impacts?

A contribution analysis is performed to check the contribution of the different processes to the overall impacts. This helps to understand what processes contribute the most to the defined impact categories and the costs. These processes can be focused upon, when trying to reduce the environmental impacts or the economic cost.

9. How does a changing gallium price and the amount of gallium and indium recovered change the economic impacts results?

Finally, a sensitivity analysis is performed on the CBA results. A change in the price per kg Ga, changes the outcomes of the CBA, as well as a change in the amount of Ga and In recovered. The recoverable amount of Ga and In depend mainly on the design of the III-V/Si cells. The benefits and costs related to Ga and In are scaled linearly.

3.2 Recycling processes pre-assessment method

If assuming that all processes that are defined from the literature study could be effective for recycling Ga from III-V/Si PV cells, all of these recycling processes could be analysed in the LCA and CBA. Doing so however, is out of the scope of this research. Moreover, some processes could be preferable over others. Therefore, the defined recycling processes are pre-assessed, using the following method:

A semi-quantitative pre-assessment is made to determine which Ga recovery process could be preferred over the other processes. The first factor that is included is the estimation of the environmental performance of the processes, based on the type of treatments and process parameters. The environmental performance values are determined according to life-cycle impacts of chemicals used in the defined processes.

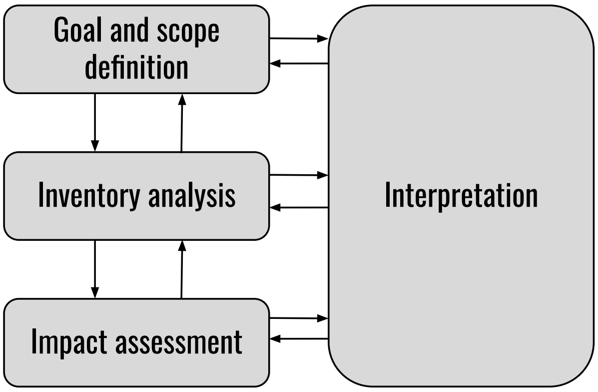
The ecoinvent 3.4 database is imported in OpenLCA 1.10.3 and product systems are created for the chemicals that are used in the recycling processes. A quick calculation is performed using the latest International Reference Life Cycle Data System (ILCD) method; the ILCD 2.0 2018 midpoint method. This environmental assessment of the chemicals that are used in the processes, gives a rough estimation of the environmental performance of these processes, which helps to make a choice on which process to analyse more in depth in research question 4 and beyond. Furthermore, the estimated data availability is included in the assessment. If all required data is estimated to be available, the data availability variable is given a value of 1. In case some data could not be acquired from ecoinvent 3.4 (e.g. because of usage of unusual chemicals), a score of .666 is assigned to the estimated data availability variable. If most process data may not be available at all (e.g. because data on involved chemicals is confidential), a value of .333 is assigned. Lastly, as third variable, the Ga recovery decimal is included. The following 'PAR'-formula is used to assign an overall score to each defined recycling, in which P is the estimated environmental performance variable, A is the estimated data availability variable and R is the Ga recovery decimal:

$$\text{Score} = P * A * R$$

3.3 Life cycle assessment (LCA)

The LCA method as described by the International Standards Organization (ISO) 14040 series is used. Hence, the LCA consists of a goal & scope definition, inventory analysis, impact assessment and interpretation, as shown in figure 3.1 (ISO 14040, 2006). Because the LCA assesses a new potential recycling technology, the type of LCA is *ex ante* (van der Giesen, Cucurachi, Guinée, Kramer & Tukker, 2020).

Figure 3.1
Life cycle assessment framework (ISO 14040, 2006)



3.4 Cost-benefit analysis (CBA)

The CBA is based on the ten step method described by Boardman, Greenberg, Vining, & Weimer (2018). The only difference with their method is the addition of a contribution analysis. Hence, the CBA consists of the following steps:

1. explaining the purpose
2. specifying the set of alternatives
3. deciding whose costs and benefits count (specify standing)
4. identifying and classifying the impact categories
5. predicting the impacts quantitatively
6. monetizing all impacts
7. discounting the costs and benefits to obtain present values
8. computing the net present value of each alternative
9. performing contribution analysis
10. performing sensitivity analysis
11. coming up with a recommendation

Because the performed CBA is conducted before the decision to implement the project is made, the type of CBA is *ex ante*. The data for material prices mainly comes from the ecoinvent v3.4 database. Cost estimates for other costs, such as personnel costs, machines, workstations and building depreciation and maintenance costs are taken from Bisselink & Steeghs (2016).

3.5 Data sources & limitations

The data that is used in this research was gathered from peer-reviewed scientific literature, from interviews with experts in the fields of material science and from ecoinvent v3.4. Limitations of the chosen research methods include the limited amount of expert interviews, a simplification of certain processes and a limited amount of environmental- and economic indicators that are taken into account. Moreover, the data on the input and output flows is estimated based on references that used data from different scales; laboratory-scale and pilot-scale. When setting up a recycling process at larger scale (industrial scale), the inputs, throughputs and outputs should be monitored and optimized.

4 Results

4.1 Results criticality (research question 1)

The general Ga-, In- and Si-criticality developments, based on Schrijvers et al. (2020), is discussed in section 4.1.1. The material criticality of those materials for a yearly III-V/Si solar cell production of 1 GWp is discussed in section 4.1.2.

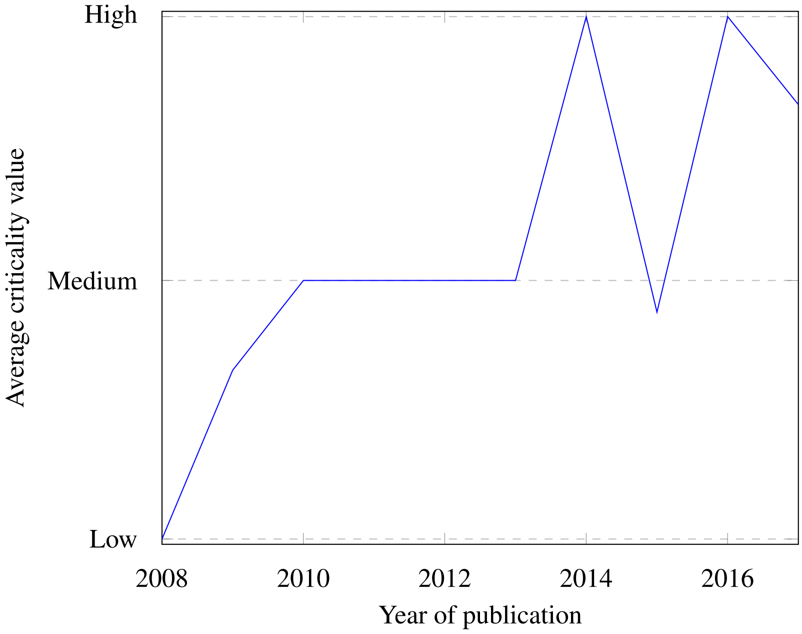
4.1.1 General gallium-, indium- and silicon-criticality development

4.1.1.1 Gallium criticality development

According to the review of Schrijvers et al. (2020), Ga criticality is high according to 14 studies, medium according to 3 studies, and low according to 10 studies. The paper by Graedel, Harper, Nassar, Nuss, & Reck (2015) does not provide a single judgement on criticality, but a score on the three defined indicators as follows: 'medium (supply risk) - low (vulnerability) - low (environmental implications)'. In Schrijvers et al. (2020) this is interpreted as an overall criticality of 'medium'. These numbers only seem semi-alarming, but it should be noted that the defined studies use different methodologies to assess criticality. Therefore, there is a strong indication the criticality of Ga is medium at least and over recent years mostly classified as high. As can be seen in figure 4.1, recent studies (2014-2017) mostly classify Ga criticality as high, while most older studies, around 2008-2009, classified Ga criticality as low. Supplementary data can be found in appendix C. In the EU 2020 report on CRMs Ga is considered a critical raw material ("European Commission, Study on the EU's list of Critical Raw Materials, Final Report", 2020).

Figure 4.1

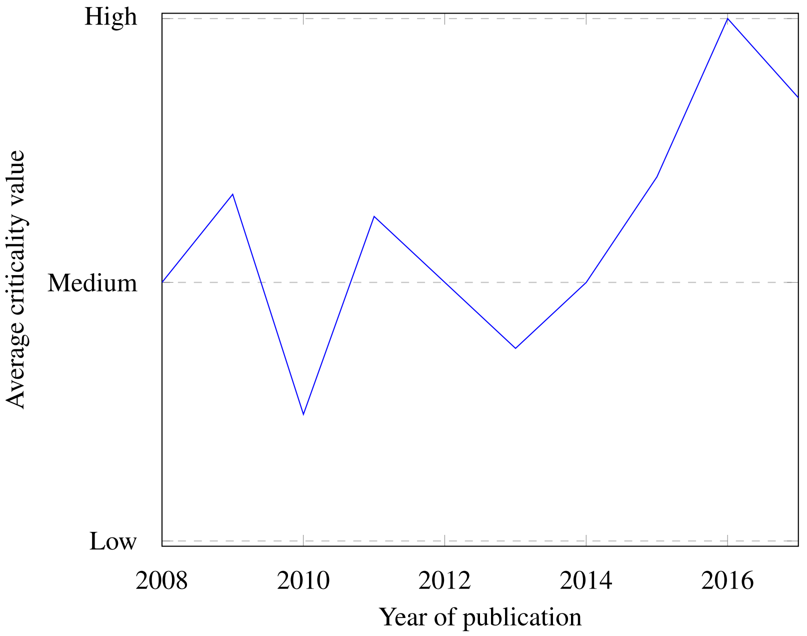
Gallium criticality over time - based on Schrijvers et al. (2020)



4.1.1.2 Indium criticality development

According to the review of Schrijvers et al. (2020), In criticality is high according to 15 studies, medium according to 7 studies and low according to 5 studies. Similar to the Ga criticality, In criticality is generally higher in recent studies. The average criticality value that has been given to In over the years is visualised in figure 4.2. Supplementary data can be found in appendix C. In the EU 2020 report on CRMs In is considered a critical raw material ("European Commission, Study on the EU's list of Critical Raw Materials, Final Report", 2020).

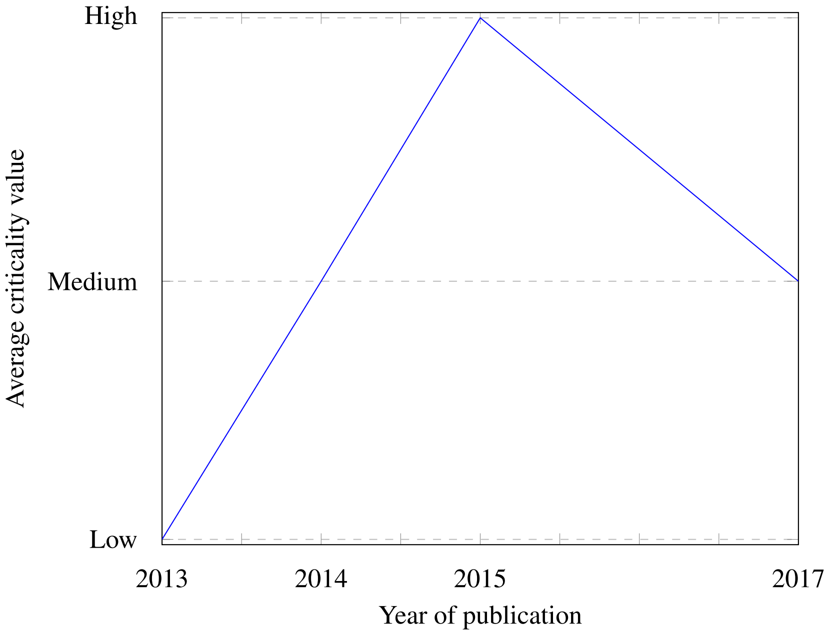
Figure 4.2
Indium criticality over time - based on Schrijvers et al. (2020)



4.1.1.3 Silicon criticality development

According to the review of Schrijvers et al. (2020), Si criticality is high according to 4 studies, medium according to 1 study and low according to 4 studies. Seven of the nine studies that look at Si criticality have been conducted in 2013 or later. The average criticality value that has been given to Si from 2013 to 2017 is visualised in figure 4.3. Supplementary data can be found in appendix C. In the EU 2020 report on CRMs Si is considered a critical raw material ("European Commission, Study on the EU's list of Critical Raw Materials, Final Report", 2020).

Figure 4.3
Silicon criticality over time - based on Schrijvers et al. (2020)



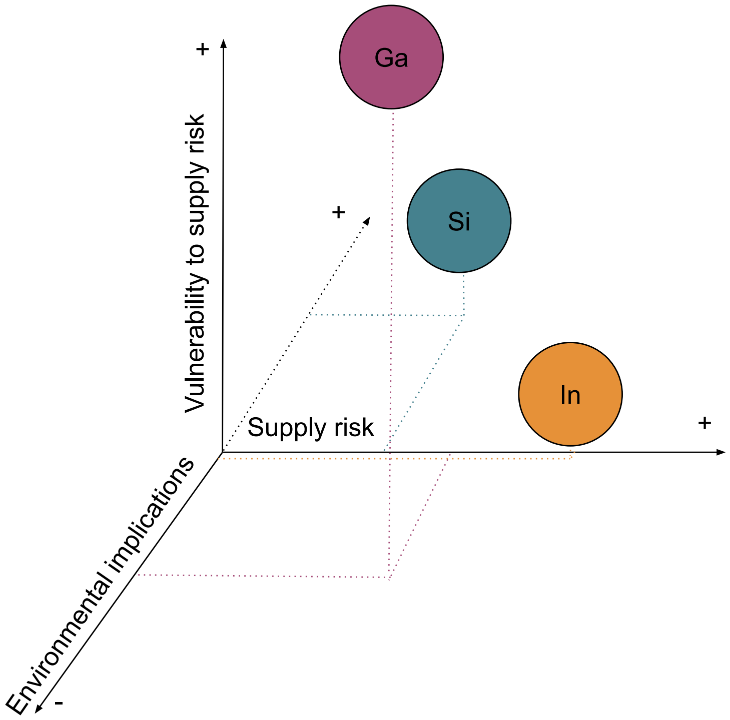
4.1.2 Gallium-, indium- and silicon-criticality for a yearly III-V/Si solar cell production of 1 gigawatt-peak

The criticality results are shown in table 4.1 and figure 4.4. The supply risk values are taken from "European Commission, Study on the EU's list of CRMs, Final Report" (2020). The EC labels the supply risk critical if it is above 1, on a scale from 0 (lowest) to 7 (highest). Furthermore, the vulnerability to a supply disruption of Ga is considered 'high', as Ga is essential for III-V/Si PV production. The vulnerability to a supply disruption of Si is assessed as 'low-medium'. Although Si is essential as well, in case of a supply disruption, producing III-V/Si PV cells could be more attractive than c-Si, since only two-thirds of the amount of Si is needed for the same amount of power produced. In case of a huge Si supply disruption, which is highly unlikely to happen, Si could temporarily be replaced by Ge or GaAs. The vulnerability to a supply disruption of In is assessed as 'low', because using In can be avoided by replacing the aluminium indium phosphate (AlInP) containing layer with a aluminium gallium arsenide (AlGaAs) layer (F. Dimroth, personal communication, July 08, 2020). As discussed in the subsections 4.1.2.1, 4.1.2.2 & 4.1.2.3, the demand for Ga increases when III-V/Si cells production increases, the demand for In is hardly effected and the demand for Si decreases, compared to a scenario in which the same amount of solar capacity is installed with c-Si PV cells. A rising demand for virgin materials causes a higher environmental burden (negative environmental implications). The lower demand for Si on the other hand, has positive environmental implications. Or in other words environmental burden is avoided.

Table 4.1
Criticality of gallium, indium and silicon for III-V/Si PV production

	Supply risk (EU 2020)	Vulnerability to supply disruption	Environmental implications
Ga	1.26	High	Negative
In	1.79	Low	Slightly negative
Si	1.18	Low - Medium	Positive

Figure 4.4
Yale analytical framework criticality space for gallium, indium and silicon used in III-V/Si solar cells



4.1.2.1 Gallium criticality for a yearly III-V/Si solar cell production of 1 gigawatt-peak

The Ga needed for production of III-V/Si solar cells increases the demand for Ga. For an annual production of 1 GWp, the amount of Ga needed is estimated to be 176.3 tons (appendix E). The Ga needed, needs to be semiconductor grade, in other words high-purity Ga. According to the EC, the processing of Ga is considered the critical stage, the extraction is not critical ("European Commission, Study on the EU's list of Critical Raw Materials, Final Report", 2020). Therefore, the high-purity refined Ga capacity is more relevant to this study than the overall Ga production. The 2019 world production of high-purity refined Ga was estimated to be 205 ton Ga, with a high-purity refinery capacity of 330 tons per year (U.S. Geological Survey, 2020a). So in 2019 there was an unused capacity of 125 tons per year. Thus, the 176.3 tons increase in demand that is caused by the 1 GWp production of III-V/Si solar cells seems to be problematic to obtain in the current market. Furthermore, as argued by Blanco et al. (2020), the amount of Ga needed required for a 1 GWp production of III-V/Si solar cells is significant enough to influence the criticality of Ga and market dynamics of high-purity refined Ga. To meet the increased demand, refineries that produce high-purity Ga from low-grade Ga should upscale their production and new refineries should be constructed. The latter needs serious investments, because other emerging technologies could increase the demand for high-purity Ga too.

4.1.2.2 Indium criticality for a yearly III-V/Si solar cell production of 1 gigawatt-peak

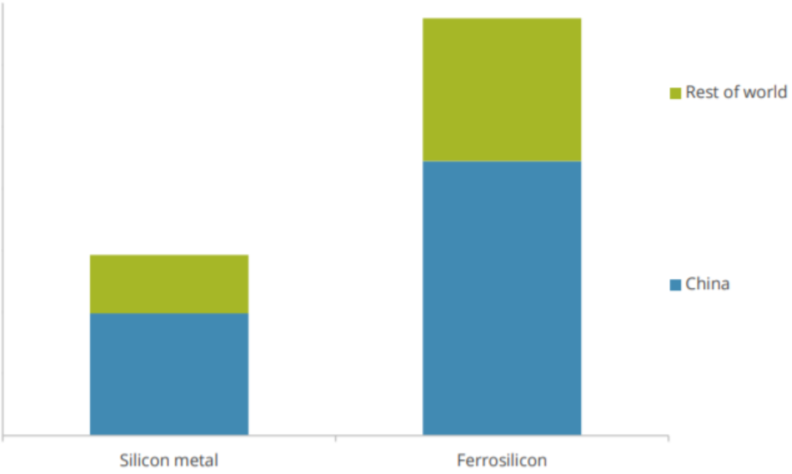
The In needed for production of III-V/Si solar cells increases the demand for In. For an annual production of 1 GWp, the amount of In needed is approximately 1.03 tons (appendix E). The 2016 world production of In was estimated to be 655 tons In (U.S. Geological Survey, 2017a). The 2016 production capacity of In was estimated to be 1400 tons per year (U.S. Geological Survey, 2017b). The 1.03 ton increase in demand that is caused by the 1 GWp production of III-V/Si solar cells equals around 0.15 % of the 2016 world production and 0.08 % of the 2016 world production capacity. Therefore, the increase in In demand caused by an annual 1 GWp production of III-V/Si solar cells is not significant enough to play a big role in the worldwide criticality of In.

4.1.2.3 Silicon criticality for a yearly III-V/Si solar cell production of 1 gigawatt-peak

The Si needed for production of III-V/Si solar cells doesn't necessarily increase the demand for Si, since III-V/Si solar cells are an alternative to c-Si solar cells. By 2050 III-V/Si cells could eventually reach an efficiency of 35-40%, and c-Si Passivated Emitter and Rear Cells (PERC) are expected to reach 24-25% efficiency (Gervais et al., 2021). Being able to produce around 1.5 times the amount of electricity compared to the same area of c-Si, III-V/Si solar cells could actually decrease the demand for Si. For an annual production of 1 GWp, the amount of Si needed is approximately 2070 tons (appendix E). The amount of Si needed for 1GWp c-Si is would be around 1.5 times higher, because of the 1.5 times lower efficiency. The 2019 world production of Si (all silicon) is estimated to be 7,000,000 ton per year (U.S. Geological Survey, 2020c). This includes not only high purity silicon, but ferrosilicon too. According to "Silicon and Ferrosilicon: Outlook to 2029, 17th edition" (2020), high purity silicon, which is referred to as *silicon metal*, makes up for approximately 30% of the total world production of silicon, which equals roughly 2,100,000 tons. The other 70% being ferrosilicon (see figure 4.5). The 2070 tons for an annual production of 1 GWp III-V/Si cells is therefore not significant enough to play a big role in the worldwide criticality of Si.

Figure 4.5

2019 silicon production



Note. Reprinted from "Silicon and Ferrosilicon: Outlook to 2029, 17th edition", 2020, retrieved from: https://roskill.com/market-report/silicon-ferrosilicon/
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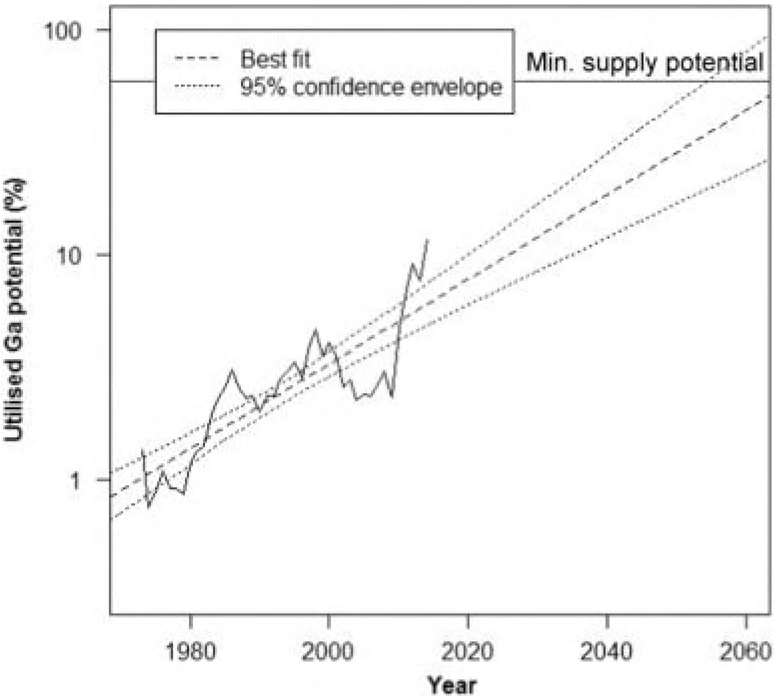
4.2 Results influence of end-of-life recycling on criticality (research question 2)

The EoL recycling rate of Ga, In and Si is lower than 1 percent ("European Commission, Study on the EU's list of Critical Raw Materials, Final Report", 2020). However, there is potential to increase the amount of Ga, In and Si that is recovered in EoL recycling. With the right technological improvements and economic incentives, the EoL recycling rate of Ga, In and Si could increase. As concluded in the results of research question 1 (section 4.1), the amount of Ga used for a 1GWp annual production of III-V/Si solar cells is significant enough to influence the criticality of Ga, whereas the amount of In & Si used are not significant enough to play a big role in the worldwide criticality of these elements. Therefore, research question 2 focuses on Ga.

Frenzel et al. (2016) estimated that with a continuous annual growth of 4.6%, primary Ga supply is unlikely to be a bottleneck until at least 2050 (see figure 4.6). However, after 2050 there could come a time in which primary Ga supply can not meet Ga demand. This is one of the reasons why recycling Ga from EoL products, such as III-V/Si PV panels, could become economically viable.

Figure 4.6
The past trend of primary gallium supply and the estimated future primary gallium supply based on this past trend (annual growth of 4.6%)

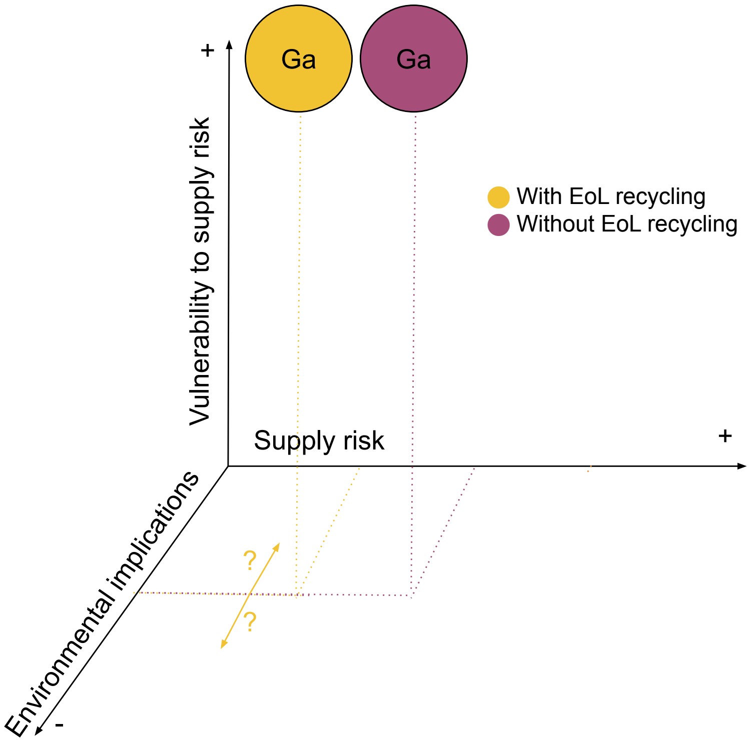


Note. Reprinted from "On the current and future availability of gallium" by Frenzel, M., et al., 2016, *Resources Policy, 47*, p.49.

Another argument for recycling Ga is that an increase in recycling, or secondary production, will reduce the dependency on the Ga producing countries and companies, that are the reason of supply risk. Therefore, increased recycling of Ga will decrease supply risk. However, the vulnerability in case of a supply risk, or economic importance of Ga, remains the same (see figure 4.7). Given that the EC assesses the supply risk for Ga critical (see section 4.1.2), recycling Ga from III-V/Si PV panels may be worth the investment.

The ecoinvent data for virgin Ga describes simultaneous extraction of Al and Ga from Bayer liquor and does not allocate any upstream burden to Ga (Tuchschmid, 2017). Because of this, there is no objective proof on whether the environmental implications of recycled Ga are bigger or smaller than those of virgin Ga. A further study on the environmental implications of virgin Ga compared to recycled Ga lies outside the scope of this study. Therefore, there are question marks displayed at the environmental implication dimension of figure 4.7.

Figure 4.7
Yale analytical framework criticality space for gallium used in III-V/Si solar cells, with & without end-of-life recycling



4.3 Results gallium recycling processes (research question 3)

4.3.1 Potential recycling processes to recover gallium from end-of-life III-V/Si solar cells from literature

Multiple researches with regard to recycling Ga from various waste materials are identified. Some of the techniques described in these researches also recover other materials, e.g. In. Technologies that are described peer-reviewed articles include hydrothermal treatment with hydrogen peroxide (H_2O_2), dilution in ethanol (CH_3CH_2OH), ionic liquid leaching + solvent stripping, pressurized leaching with hydrogen chloride (HCl), bio-leaching using *Acidithiobacillus ferrooxidans* bacteria, mechano-chemical- & thermal-treatment + HCl solubilisation, vacuum decomposition, pyrolysis + vacuum separation and high-temperature chlorination with ammonium chloride (NH_4Cl) (Zhan, Zhang, Ahmad, & Xu, 2020b; Zhan, Wang, Zhang & Xu, 2020a; Van den Bossche, Vereycken, Van der Hoogerstraete, Dehaen, & Binnemans, 2019; Chen, Hsu & Wang, 2018; Pourhossein & Mousavi, 2018; Nagy, Bokányi, Gombkötő, & Magyar, 2017; Zhang & Xu, 2016; Zhan, Xia, Ye, Xiang, & Xie, B., 2015; Gustafsson, Steenari, & Ekberg, 2015). Moreover, a relevant patent on recycling waste CIGS PV panels was identified, which uses leaching with sulphuric acid (H_2SO_4) & hydrogen peroxide (H_2O_2) + solvent extraction (Bisselink & Brouwer, 2018). An overview of all defined Ga recycling processes is given in table 4.2.

4.3.2 Expert opinions on potential recycling processes to recover gallium from end-of-life III-V/Si solar cells

The recycling process to recover Ga from III-V/Si solar cells will be similar to the processes used for other EoL electronic waste, existing of a combination of mechanical, thermal and chemical processing. However, what temperature and chemicals to use is heavily dependant on what semiconductor is in the EoL product. Therefore, a different solvent is needed to dissolve materials from the III-V/Si PV cells (e.g. gallium arsenide phosphide (GaAsP)) than to dissolve for instance gallium nitride (GaN) from LEDs (B.J. Kooi, personal communication, April 28, 2020).

In the recycling process the III-V top cell of the SiTaSol cell should first be separated from the Si bottom cell. This could be done by applying a chemical that is able to split these two parts, by being active on only the Si-GaPN bonds. Another possibility could be to adjust the SiTaSol solar cell design. An intermediate layer could be applied between the bottom cell and top cell, that could be dissolved by a specific chemical, that does not react with the other materials in the cell, so called *selective etching*. This design change would be part of a design for recycling approach (B.J. Kooi, personal communication, April 28, 2020).

According to F. Dimroth (personal communication, July 08, 2020), recycling is challenging, because lamination makes it hard to split the individual materials. Therefore, the only possible recycling technique would be to break apart everything and thereafter split the Ga from the Si. In this phase of the research, the assumption is that In recycling does not make sense, because In is only 25% of a 30 nanometer layer.

LEDs are similar in structure to III-V/Si cells, but LEDs are more difficult to recycle, because of their small size, GaN content and encapsulation of the III-V chip. The reason why LEDs might be recycled is usually not their Ga content, but their gold content (F. Dimroth, personal communication, July 08, 2020). The recycling process of other thin-film cells are probably comparable to a recycling process for the III-V/Si cell. To make the SiTaSol module more easily recyclable, the current design could be replaced with a glass-glass module. Such a module can be dismantled, making it easier to separate the cells from the plates compared to lamination. This is however currently economically unfavourable (F. Dimroth, personal communication, July 08, 2020).

A.R. Balkenende (personal communication, August 18, 2020) states that physically a LED is the exact opposite of a solar cell; a LED emits light and a solar cell absorbs light. Practically LEDs and III-V/Si solar cells are pretty different. Most LEDs are white LEDs, which usually contain GaN. The III-V/Si solar cells contain GaAs and/or gallium phosphide (GaP), which behave very differently on a chemical level. A couple of decades ago, GaN was only used and insulator, but nowadays it is also used as semiconductor. GaN is much harder to etch than GaAs and GaP, because GaN is a more stable material. More energy in the bond content, means more energy is required to break the bond. Therefore, recycling III-V/Si solar cells in an environmentally friendly way might be a little easier than recycling LEDs. Solar cells may also be easier to etch, if they have a large surface area; LEDs always have a small surface area (a few square millimeter). GaAs/GaP can be etched by strong oxidizers (e.g. nitric acid (HNO_3)), which does not attack the Si. An example of a chemical compound that etches Si is hydrofluoric acid. In higher pressure conditions, this will change. Plasma etching could be an option but would be too expensive for recycling.

Changing the design for the sake of better recyclability could cause more defects, which lowers the conversion efficiency of the cell. This has a bigger negative impact on the overall environmental performance than the possible increase in recycling. A design with adhesive bonds, with a transparent conductive coating layer, is more easily recyclable than a design in which III-V layers are grown directly on top of Si, because the transparent conductive coating layer could be etched away more easily. The top anti-reflective coating (ARC) may be very difficult to etch. Grinding may be required to facilitate access to the underlying layers. Moreover, the selectivity of an etching process is the main technical barrier for recycling III-V/Si cells. There is however quite a lot of well-known chemistry that can be used (A.R. Balkenende, personal communication, August 18, 2020).

Table 4.2
Overview of gallium recycling processes

Recovered material(s)	**Waste material**	**Type of treatment**	**Process(es) and optimal parameters**	**Max. recovery**	**Grade**	**Reference**
GaAs	Scrap integrated circuits	Chemical, thermal & vacuum	1. Hydrothermal treatment *1 L high pressure reactor* $T = 275^{\circ}C$, $t = 120$ *min*, $\omega = 300$ *rpm*, *solvent* = H_2O_2 *(5%) 300 mL*, *buffer* = *0.001 M* PO_4, *pH = 7.6* 2. Vacuum filtration 3. Grinding & screening	Ga: 99.9% As: 95.5%	GaAs: 96%	Zhan, Zhang, Ahmad, & Xu (2020b)
Ga, In, As, & Ag	Waste LEDs	Chemical & thermal	1. Dissolving in ethanol $p = 7.5$ *MPa*, $T = 250^{\circ}C$, $t = 90$ *min*, *solvent = 200 mL* CH_3CH_2OH 2. Water-ethanol degradation $T = 300^{\circ}C$, $t = 240$ *min*, *water:ethanol ratio = 60%:40%*	Ga: 93.1% In: 85.72% As: 93.79% Ag: 99.99%	Not specified	Zhan, Wang, Zhang, & Xu (2020a)
Ga, $In(OH)_3$ & As	EoL LEDs	Chemical	1. Grinding/milling 2. Mechnical/physical separation 3. Leaching in ionic liquid $[P_{44410}][Br_3]$ 4. Stripping As *solvent = 4M NaBr* *organic to aqueous volume ratio = 2* 5. Stripping Ga *solvent = MilliQ water* *organic to aqueous volume ratio = 1* 6. Stripping $In(OH)_3$ *solvent = 5 equivalents of NaOH* *organic to aqueous volume ratio = 0.5*	Ga: ∼96% In(OH)3: ∼99% As: ∼95%	Ga: ∼99%	Van den Bossche, Vereycken, Van der Hoogerstraete, Dehaen, & Binnemans (2019)
Ga, In, & Mo	Waste CIGS PV panels (<2 mm glass fraction)	Chemical & thermal	1. Leaching $T = 95^{\circ}C$, $t = 1440$ *min*, *solvent = 0.5 M* H_2SO_4 *+ 2%* H_2O_2 liquid-solid ratio = 1:1 2. Mo solvent extraction $t = 120$ *min*, *extractant = 20% LIX63 in Shellsol D70* *leach solution:extractant ratio = 1:4* 3. In solvent extraction $t = 120$ *min*, *extractant = 20% di-(2-ethylhexyl)* *phosphoric acid (DEHPA) in Shellsol D70* *leach solution:extractant ratio = 1:4* 4. Ga solvent extraction $t = 120$ *min*, *extractant = 0.3 M di-octyl phenyl acid* *phosphate (DOPAP) in Shellsol D70* *leach solution:extractant ratio = 1:4*	Ga: 41% In: 100% Mo: 93%	Ga: 91.8% In: 98.9% Mo: 98.4%	Bisselink & Brouwer (2018)
Ga	GaN waste from LEDs	Chemical & thermal	Pressurized leaching $p = 15$ *atm*, $T = 200^{\circ}C$, $t = 180$ *min*, *solvent = 0.25M HCl*, *liquid-solid ratio = 30 mL/g*	Ga: 98.46%	Not specified	Chen, Hsu, & Wang (2018)
Ga, Ni & Cu	LED waste	(Bio)-chemical	1. Shredding, ball milling & sieving 2. Culturing *A. ferrooxidans* $T = 29^{\circ}C$, $t = 30$ *days*, $\omega = 140$ *rpm* *9K medium containing 3g* $(NH_4)_2SO_4$, *0.5g* K_2HPO_4, *0.5g* $MgSO_4 * 7H_2O$, *0.1g KCl, 0.01g* $Ca(NO_3)_2$ *and* *44.22g* $FeSO_4 * 7H_2O$ *and* *1000 mL deionized (DI) water* pH adjusted to 2, using H_2SO_4 (98%) 3. Bio-leaching *liquid to solid ratio = 50 mL/g*	Ga: 60% Ni: 96% Cu: 84%	Not specified	Pourhossein, & Mousavi (2018)
Ga	EoL LEDs containing GaN	Mechano-chemical & thermal	1. Cutting 2. Electrostatic separation 3. Mechano-chemical treatment in stirred media mill $t = 120$ *min*, $d = 200$ *mm*, $U = 30$ *kV*, $\omega = 3600$ *rpm*, *salt* = Na_2CO_3 *1:1 w/w%* 4. Drying in furnace $T = 60^{\circ}C$, $t = 120$ *min* 5. Thermal treatment $T = 1200^{\circ}C$, $t = 240$ *min* 6. Solubilisation $T = 80^{\circ}C$, $t = 120$ *min*, *solvent = 4M HCl*, *liquid-solid ratio = 50 mL/g*	Ga: 99.52%	Not specified	Nagy, Bokányi, Gombkötő, & Magyar (2017)
Ga	Waste wafer chips from EoL GaAs solar cells	Thermal & vacuum	1. Grinding & screening 2. Vacuum decomposition $p = 1$ *Pa*, $T = \sim 950^{\circ}C$, $t = 40$ *min*	Ga: ∼80%	Not specified	Zhang, & Xu (2016)

Continued on next page

Table 4.2 - continued from previous page

Recovered material(s)	Waste material	Type of treatment	Process(es) and optimal parameters	Max. recovery	Grade	Reference
Ga & In	Waste LEDs	Thermal & vacuum	1. Pyrolysis $T = \sim 500^\circ C$ 2. Physical disaggregation, crushing screening & grinding 3. Vacuum metallurgy separation $p = 0.01\text{-}0.1\ Pa,\ T = \sim 1100^\circ C,\ t = 60\ min$	Ga: 93.48% In: 95.67%	Ga: 92.8%	Zhan, Xia, Ye, Xiang, & Xie, B. (2015)
Ga, In & Cu	CIGS solar cell waste materials	Chemical & thermal	High-temperature chlorination Ga recovery: $T = 260^\circ C,\ t = 360\ min$ 5 mol NH_4Cl per mol metal In recovery: $T = 340^\circ C,\ t = 360\ min$ 3.4 mol NH_4Cl per mol metal Cu recovery: $T = 560\ ^\circ C,\ t = 240\ min$	Ga: 97.2% In: 93.6%	Ga: 90.6% In: 97.7% Cu: 90.0%	Gustafsson, Steenari, & Ekberg (2015)

4.3.3 Choice of recycling process

As explained in section 3.2, 'PAR'-scores are used to compare the defined recycling processes. These scores are shown in table 4.3. The life cycle impacts assessment on which the P-values are based, are shown in appendix F. Based on these results, processes using mainly H_2SO_4 or CH_3CH_2OH are estimated to have a high estimated environmental performance, processes using mainly H_2O_2, HCl or HNO_3 are estimated to have medium environmental performance and processes using $(NH_4)_2SO_4$ or NH_4Cl are estimated to have low environmental performance.

Table 4.3
Pre-assessment of defined recycling processes

Reference	Chemical(s) used	Estimated environmental performance (P)	Estimated data availability (A)	Maximum gallium recovery (R)	Score
Zhan et al. (2020b)	H_2O_2	medium[1]	high[2]	.999	**.666**
Zhan et al. (2020a)	CH_3CH_2OH	high[3]	high	.931	**.931**
Van den Bossche et al. (2019)	$[P_{44410}][Br_3]$	unknown[4]	low[5]	.96	**NA**
Bisselink & Brouwer (2018)	H_2SO_4 & H_2O_2	high	low	.41	**.137**
Chen et al. (2018)	HCl	medium	high	.9846	**.65**
Pourhossein & Mousavi (2018)	$(NH_4)_2SO_4$ & $FeSO_4$	low[6]	medium[7]	.6	**.133**
Nagy et al. (2017)	Na_2CO_3 & HCl	medium	high	.9952	**.663**
Zhang & Xu (2016)	-	unknown	high	.8	**NA**
Zhan et al. (2015)	-	unknown	high	.9348	**NA**
Gustafsson et al. (2015)	NH_4Cl	low	high	.972	**.324**

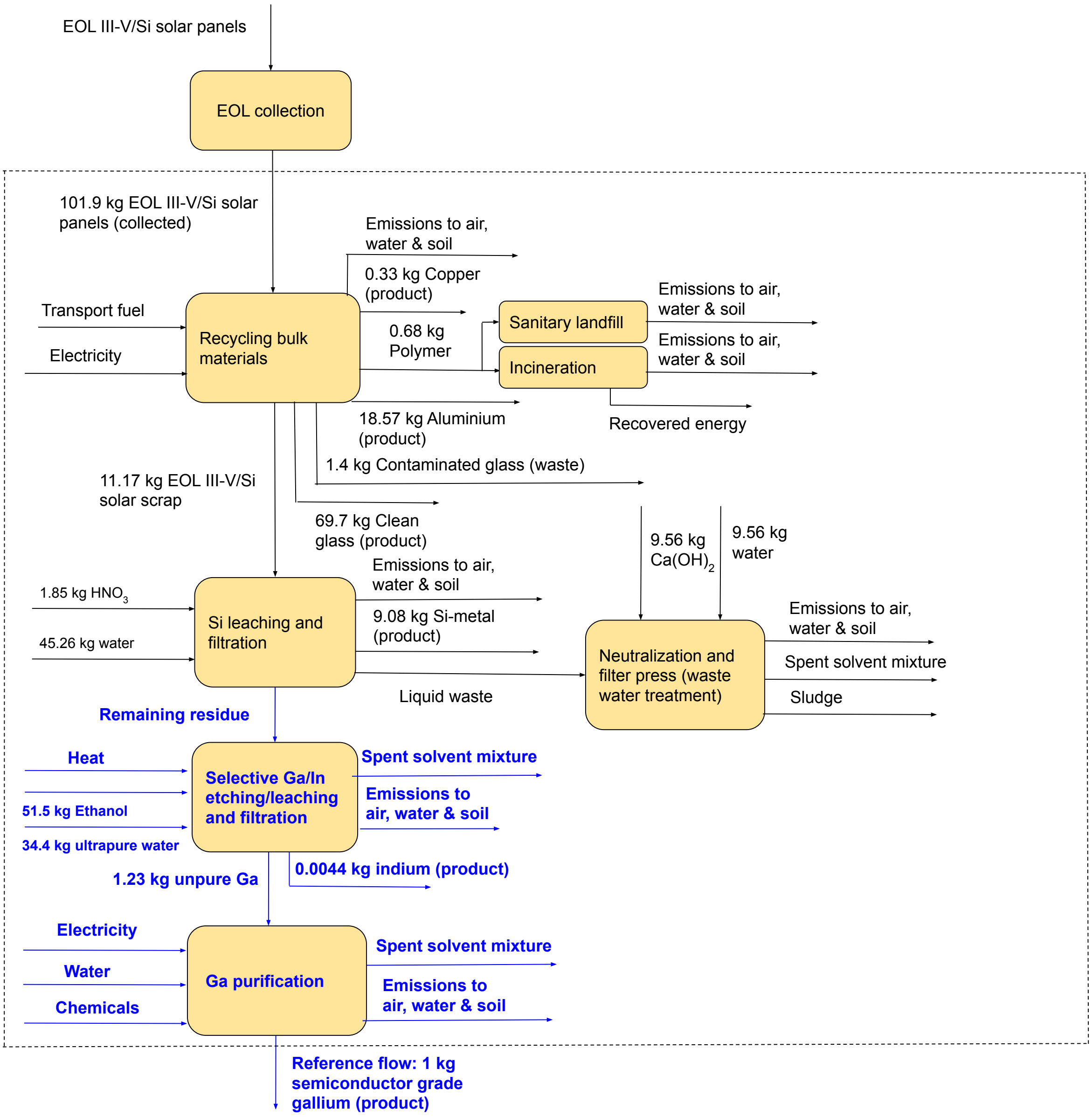
[1] chemical(s) involved in process are estimated to have medium environmental impacts (value = .666)
[2] all required data is estimated to be available (value = 1)
[3] chemical(s) involved in process are estimated to have low environmental impacts (value = 1)
[4] Unknown environmental performance, because of usage of unknown chemical (Bisselink & Brouwer, 2018) or vacuum separation technology (Zhang & Xu, 2016; Zhan et al, 2015) (value = NA)
[5] most process data may not be available at all (e.g. because data on involved chemicals is confidential) (value = .333)
[6] chemical(s) involved in process are estimated to have high environmental impacts (value = .333)
[7] some data could not be acquired from ecoinvent v3.4 (e.g. because of usage of unusual chemicals) (value = .666)

Of the ten defined processes, one process has a PAR-score greater than 0.9, which is the ethanol dilution recycling process defined by Zhan et al. (2020a). Therefore this recycling process will be included in the recycling process flowchart, of which the environmental- and economic performances are analysed in the impact assessments.

4.4 Results overall recycling process (research question 4)

Before Ga can be retrieved from the EoL III-V/Si solar panels, the panels have to be collected first. After collection these panels need to be transported to a recycling facility. The first step in the recycling process is to disassemble the junction box, cables, back sheet, aluminum frame and glass. Consequently, the ethylene-vinyl acetate (EVA) layer is removed. This can be done using organic solvents such as toluene ($C_6H_5CH_3$) or trichloroethylene (C_2HCl_3) (Azeumo et al., 2019; Latunussa et al., 2016). Other possibilities to remove the EVA are pyrolysis or cooling (Latunussa et al., 2016; Dassisti, Florio & Maddalena, 2020). Moreover, the solar cells are shredded to remove the III-V/Si lamination. After being shredded, the selective etching or leaching takes place. Finally, the Ga that remains after this process needs to be purified before it is ready to be sold at market prices. The full recycling process is shown in appendix G. This process is based on the c-Si PV waste recycling process defined by Latunussa et al. (2016) and sections 4.3.1, 4.3.2 and 4.3.3. The flows that are based on the c-Si recycling process defined by Latunussa et al. (2016) are shown in black, the flows and processes that are specific for III-V/Si PV are expressed in blue. The displayed amounts are scaled in such a way that the amount of semiconductor grade gallium (product) is equal to 1 kilogram (kg). The process flow chart used in the LCA, where the first four processes of the full recycling process are modelled in one process called *Recycling bulk materials*, is shown in figure 4.8.

Figure 4.8
Recycling process flowchart



4.5 Results environmental impact assessment (LCA) (research question 5)

4.5.1 Goal & scope definition

Goal definition

The goal of this LCA is to identify and quantify the life cycle environmental impacts of the defined recycling process for III-V/Si solar cells and compare these impacts to the cradle-to-gate life cycle environmental impacts of the III-V/Si solar cells. This can help to understand the relative environmental impacts of the recycling process, compared to the impacts of the production of III-V/Si PV panels.

Functional unit: : 1kWh of electricity generated from a slanted-roof PV installation under 1700 kWh/m^2 average annual irradiance conditions.

Studied system: III-V/Si PV panels with recycling.

Reference system: III-V/Si PV panels cradle-to-gate (without recycling), scenario F2v6 (fully optimized MOVPE growth) (SiTaSol, 2021).

Scope definition

Life-cycle-stages studied system: Raw material extraction, manufacturing and EoL processing stage.

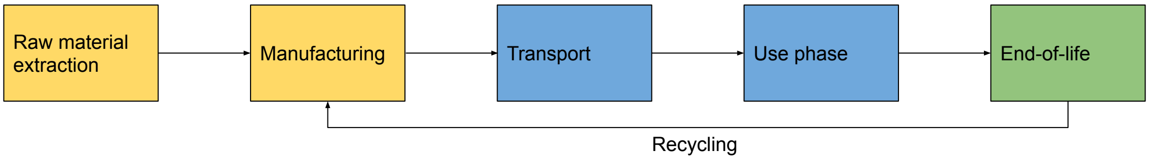
Life-cycle-stages reference system: cradle-to-gate: raw material extraction stage and manufacturing stage.

The life cycle stages are visualised in figure 4.9. With the life cycle stages that are included in both the studied system and the reference system in yellow, the life cycle stages that are excluded in blue and the life cycle stage that is included in the studied system, but not in the reference system, the EoL processing, in green. Only the impact difference between the studied system and the reference system, being the recycling process impacts, will be shown in the results and compared to the reference system impacts.

Environmental impact categories: ILCD 2.0 2018 midpoint categories (appendix H).

Figure 4.9

Life cycle stages



Geographical scope

Involved processes are taken from the ecoinvent v3.4 database. In the detailed process flowcharts (figure 4.10 and 4.11), the geographical boundary is indicated with e.g. 'GLO' for global, 'Europe without Switzerland', 'CH' for Switzerland and 'RoW' for rest of the world.

Temporal scope

The data used in this LCA comes from recent scientific literature, the ecoinvent v3.4 database and data from the SiTaSol consortium. The choice was made to use current state-of-the-art recycling processes. The consumed energy is also assumed to come from current energy sources, such as diesel for transportation and natural gas for heat. Although processes may in reality be different when the recycling process is assumed to take place, which is assumed to be somewhere in between 2050 and 2065 (when the first batch of III-V/Si panels are at their EoL). This assumption is based on a product life time of 25 to 30 years and III-V/Si entering the market in 2025 or 2035 (Gervais et al., 2021). It is not within the scope of this research to estimate what different process could be used in that timeframe. Since the recycling impacts are compared to the cradle-to-gate impacts, which are also based on state-of-the-art data, this modelling assumption is justified. In reality the cradle-to-gate data will also be different in the future.

Modelling approach
A cut-off approach is used. Economic allocation is used, which means that the environmental impacts are allocated based on the price of the co-products.

4.5.2 Inventory analysis

Flowchart of processes and system boundary
The process flowchart can be found in figure 4.8. From the process of EoL collection up until the process of cutting & sieving, the processes for c-Si and III-V/Si are the same. Only the selective Ga etching/leaching process and the Ga purification are unique to III-V/Si cells. Therefore, a more detailed process flowchart, including the background processes of these two processes, can be found in figure 4.10 and 4.11.

The only process where the facility construction is included is Ga purification, since for that process, facility construction data was available. Because data about the other infrastructure at the recycling plant and equipment needed are lacking, these elements are left out of the system boundary of this study. Cutting off these processes can be justified, because their relevance in the overall process is assumed to be minor compared to the consumed chemicals, heat and electricity.

The life cycle inventory results can be found in Appendix I.

Figure 4.10
Selective Ga etching/leaching process flowchart

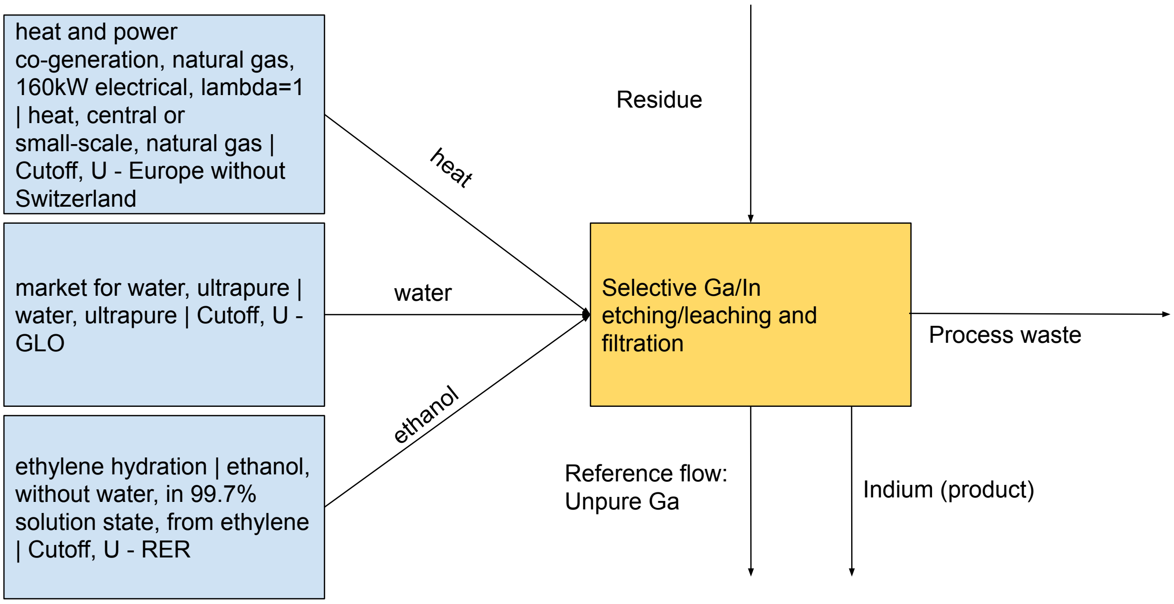
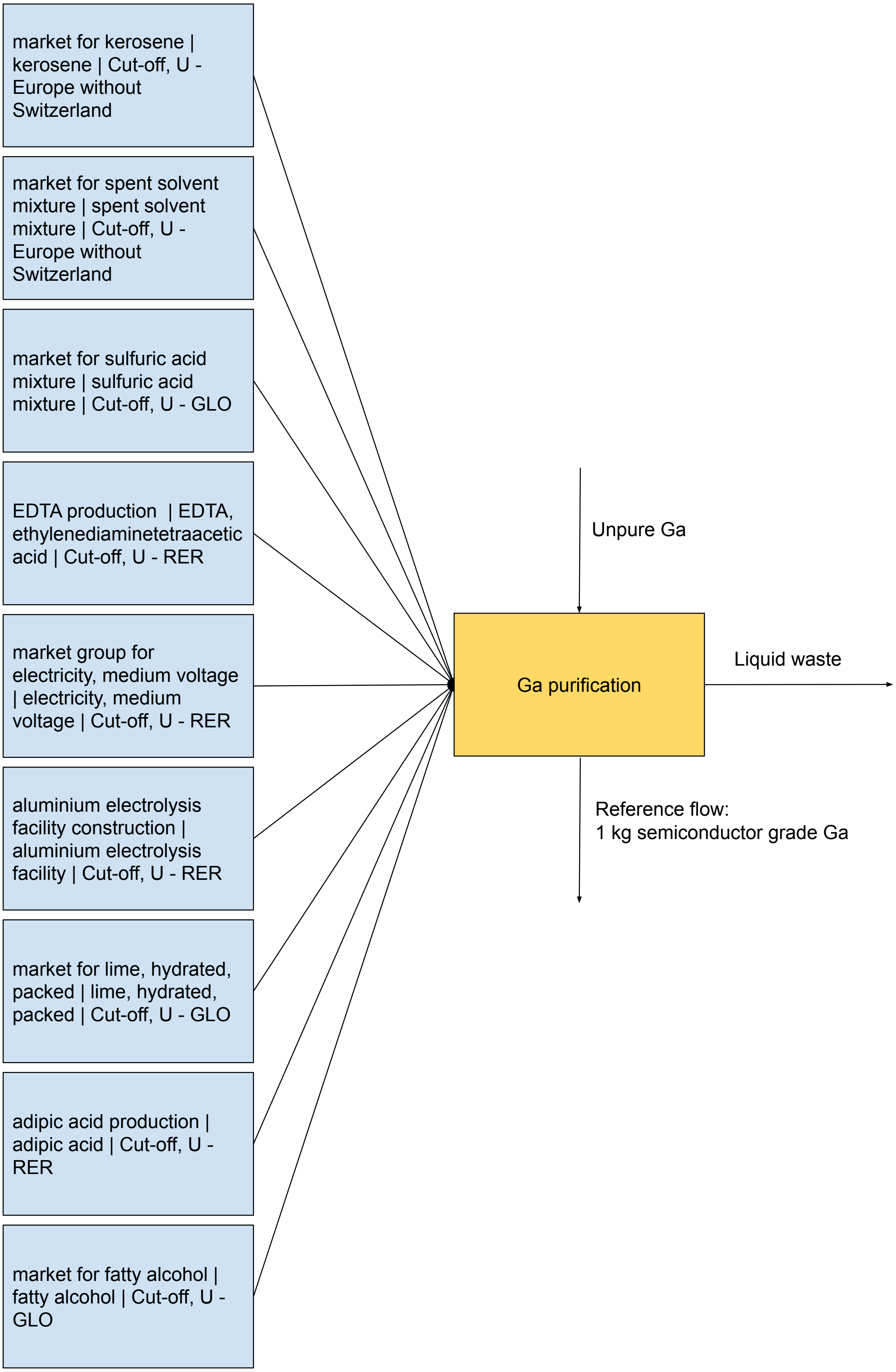


Figure 4.11
Ga purification process flowchart



4.5.3 Impact assessment

The results of the life cycle impact assessment can be found in table 4.4. The relative impacts of the recycling process, compared to the cradle-to-gate impacts of the raw material extraction and production phases, is plotted in figure 4.12. In every category the impact values of the recycling are lower than the cradle-to-gate values. The relative impacts of recycling versus cradle-to-gate range from 0.17% for mineral resource depletion to 21.65% for climate change. Other categories that score relatively high are marine eutrophication (15.37%), freshwater ecotoxicity (13.96%), fossil resource depletion (13.17%) and ozone layer depletion (13.13%). The full LCIA results can be found in appendix J.

4.5.4 Interpretation

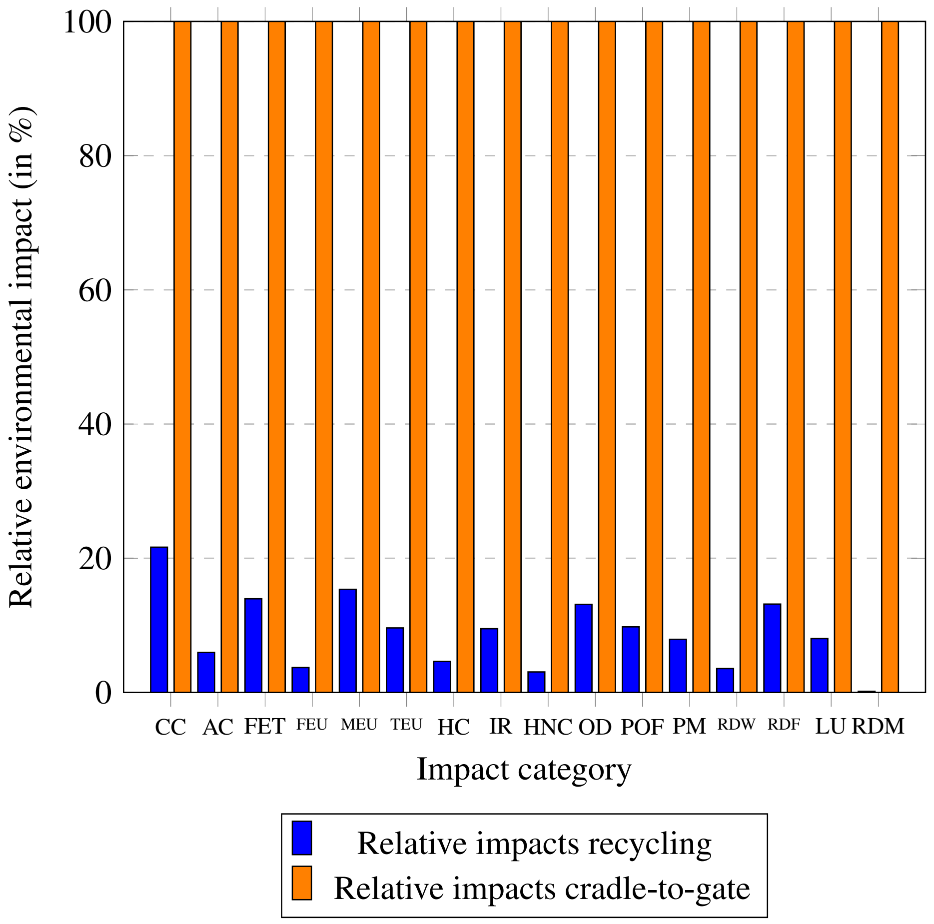
To find out what recycling processes contribute the most to every impact category, a contribution analysis is performed in section 4.7.1.3. Furthermore, a sensitivity analysis can be found in section 4.7.1.4. The results are discussed in section 5.1.

Table 4.4

Life cycle impact assessment results

Category	**Unit**	**Values recycling**	**Values cradle-to-gate**	**Ratio recycling /cradle-to-gate**	**As percentage**
Climate change | climate change total (CC)	kg CO2-Eq	6.26E-03	2.89E-02	0.02165	21.65%
Ecosystem quality | freshwater and terrestrial acidification (AC)	mol H+-Eq	1.37E-05	2.30E-04	0.0596	5.96%
Ecosystem quality | freshwater ecotoxicity (FET)	CTU	6.00E-03	4.30E-02	0.1396	13.96%
Ecosystem quality | freshwater eutrophication (FEU)	kg P-Eq	1.10E-06	2.96E-05	0.0371	3.71%
Ecosystem quality | marine eutrophication (MEU)	kg N-Eq	5.58E-06	3.63E-05	0.1537	15.37%
Ecosystem quality | terrestrial eutrophication (TEU)	mol N-Eq	3.58E-05	3.72E-04	0.0962	9.62%
Human health | carcinogenic effects (HC)	CTUh	4.44E-11	9.62E-10	0.0462	4.62%
Human health | ionising radiation (IR)	kg U235-Eq	3.31E-04	3.48E-03	0.0950	9.50%
Human health | non-carcinogenic effects (HNC)	CTUh	3.43E-10	1.12E-08	0.0306	3.06%
Human health | ozone layer depletion (OD)	kg CFC-11-Eq	4.15E-10	3.16E-09	0.1313	13.13%
Human health | photochemical ozone creation (POF)	kg NMVOC-Eq	1.04E-05	1.06E-04	0.0978	9.78%
Human health | respiratory effects, inorganics (PM)	disease incidence	1.34E-10	1.69E-09	0.0792	7.92%
Resources | dissipated water (RDW)	m3 water-Eq	1.21E-03	3.40E-02	0.0356	3.56%
Resources | fossils (RDF)	MJ	5.71E-02	4.34E-01	0.1317	13.17%
Resources | land use (LU)	points	2.14E-02	2.67E-01	0.0803	8.03%
Resources | minerals and metals (RDM)	kg Sb-Eq	9.32E-09	5.41E-06	0.0017	0.17%

Figure 4.12
Environmental impacts of the recycling process for III-V/Si PV panels relative to the cradle-to-gate impacts of these panels - ILCD 2.0 2018 impact categories



4.6 Results economic impact assessment (CBA) (research question 6)

4.6.1 Purpose

The purpose of a CBA is to determine whether the benefits of undertaking or implementing a policy or project outweigh the costs (Boardman et al., 2018). In this case the project is constructing a recycling facility for III-V/Si PV panels.

4.6.2 Set of alternatives

Two alternative recycling processes are considered. The first alternative being a recycling process that only recovers the bulk materials (glass, Al & Cu) from the III-V/Si PV panels. The second alternative being a recycling process that recovers the bulk materials as well as the CRMs (Si, Ga & In).

4.6.3 Standing

A global perspective is taken. The costs and benefits are calculated from different data sources. Where possible a European perspective is taken.

4.6.4 Impact categories (benefits & costs taken into account)

The following benefits are taken into account:

- Revenues recovered materials
    - Glass
    - Al
    - Cu
    - Si
    - Ga
    - In

The following costs are taken into account:

- Chemicals
    - HNO_3
    - Calcium hydroxide ($Ca(OH)_2$)
    - CH_3CH_2OH
    - Ethylenediaminetetraacetic acid (EDTA)
    - Kerosene
    - Fatty Alcohol
    - Adipic acid ($(CH_2)_4(COOH)$)
    - Sulfuric acid (H_2SO_4)
- Water
- Energy (heat & electricity)
- Hazardous waste disposal
- Non-hazardous waste disposal price
- Personnel
- Machines, workstations and building depreciation
- Maintenance
- Transport
- Unexpected costs

4.6.5 Impacts (benefits & costs quantified)

The yearly benefits & costs for recycling 1GWp III-V/Si PV panels can be found in table 4.5.

Table 4.5
Yearly benefits & costs for recycling 1GWp III-V/Si PV panels

Recovered materials	**Weight (tons)**	**Price (€/ton)**	**Revenues only bulk**	**Revenues bulk + Si, Ga & In**
Glass (clean)	19810	3160 (Kellenberger, 2017a)	€62,599,600	€62,599,600
Al	5351	806 (Bourgault, 2017a)	€4,312,906	€4,312,906
Cu	609	2840 (Parada Tur, 2017)	€1,729,560	€1,729,560
Si	1177	2320 (Bourgault, 2017b)	-	€2,730,640
Ga	120	300000 (Tuchschmid, 2017)	-	€36,000,000
In	0.9	855000 (Classen, 2017)	-	€769,500
Total benefits estimate			**€68,642,066**	**€108,136,206**
Used energy	**Amount (MJ)**	**Price (€/MJ)**		
Heat	179520	0.01 (Heck, 2017)	-	€1,795
	Amount (kWh)	**Price (€/kWh)**		
Electricity to recover bulk materials	3181330	0.1 (Treyer, 2017)	€318,133	€318,133
Electricity to recover Si, Ga & In	462264	0.1 (Treyer, 2017)	-	€46,226
Used chemicals	**Weight (tons)**	**Price (€/ton)**	**Costs only bulk**	**Costs bulk + Si, Ga, In**
Water (regular)	12499	4.6 (Jungbluth, 2017a)	-	€57,495
HNO_3	422	471 (Osses, 2017a)	-	€198,762
$Ca(OH)_2$	2570	110 (Kellenberger, 2017b)	-	€282,700
CH_3CH_2OH	11747	365 (Sutter, 2017a)	-	€4,287,655
Water (ultrapure)	7847	470 (Sutter, 2017b)	-	€3,688,090
EDTA	4998	1120 (Hischier, 2017a)	-	€5,597,760
Kerosene	296	297 (Jungbluth, 2017b)	-	€87,912
Fatty alcohol	30	2100 (Hischier, 2017b)	-	€63,000
$(CH_2)_4(COOH)_2$	19	1080 (Althaus, 2017)	-	€20,520
H_2SO_4	384	31 (Osses, 2017b)	-	€11,904
Transport costs	**Weight*distance (tons*km)**	**Price (€/(ton*km))**		
Transport	2577000 (bulk) 2801700 (bulk + Si, Ga, In)	0.03945 (Simons, 2017)	€101,663	€110,527
Other costs	**Weight (tons)**	**Price (€/ton)**		
Contaminated glass waste disposal	407	4.88 (Doka, 2017)	€1,986	€1,986
Liquid waste disposal	8903	4.88 (Doka, 2017)	-	€43,447
Hazardous waste disposal	1464	110[1]	-	€161,040
Personnel	25770 (bulk) 28017 (bulk + Si, Ga, In)	50[2](Bisselink & Steeghs, 2016)	€1,288,500	€1,400,850
Depreciation	25770 (bulk) 28017 (bulk + Si, Ga, In)	50[2] (Bisselink & Steeghs, 2016)	€1,288,500	€1,400,850
Maintenance	25770 (bulk) 28017 (bulk + Si, Ga, In)	40[2] (Bisselink & Steeghs, 2016)	€1,030,800	€1,120,680
Total costs estimate			**€4,029,582**	**€18,901,333**
Unexpected costs (10%)			€402,958	€1,890,133
Total costs estimate (Incl. unexpected costs)			**€4,432,540**	**€20,791,466**
Net benefits			**€64,209,526**	**€87,344,740**

[1] "How Much Does Hazardous Waste Disposal Cost in 2021?" (n.d.). Approximately 95 pound sterling/ton ≈ 110 euro/ton.

[2] The recycling facility for III-V/Si PV panels would process 1GWp of panels yearly, which are estimated to weight 28017 tons. With an assumed active time of 18-20 hours a day and 365 days a year, the recycling facility should be able to process 4 ton per hour. Bisselink & Steeghs (2016) estimate the personnel costs for a 2 ton/hour plant to be 25 euro/ton. Therefore the personnel costs are estimated to be 50 euro/ton. Similarly, the depreciation costs are estimated to be 50 euro/ton and the maintenance costs are estimated to be 40 euro/ton.

4.6.6 Net present values

Now that the yearly net benefits of both alternatives have been calculated, the next step is to calculate the net present value of the alternatives. To do so the following assumptions are made:

1. The construction of the recycling facility takes two years.
2. The construction of a recycling facility for the bulk materials costs 20 million euro.
3. The construction of a recycling facility for the bulk and CRMs costs 30 million euro.
4. The net benefits are constant over the years.
5. The social discount rate (SDR) is 4 percent.

Table 4.6
Yearly net benefits and net present values for the two alternative recycling processes - Recycling only the bulk materials (glass, Al & Cu) or recycling both these bulk materials and the CRMs (Si, Ga & In)

Year	**Only bulk**	**Bulk + Si, Ga & In**
0	€-10,000,000	€-15,000,000
1	€-10,000,000	€-15,000,000
2	€64,209,526	€87,344,740
3	€64,209,526	€87,344,740
4	€64,209,526	€87,344,740
5	€64,209,526	€87,344,740
6	€64,209,526	€87,344,740
7	€64,209,526	€87,344,740
8	€64,209,526	€87,344,740
9	€64,209,526	€87,344,740
10	€64,209,526	€87,344,740
11	€64,209,526	€87,344,740
NPV (SDR 4%)	**€500,746,513**	**€651,819,950**

4.6.7 Interpretation

Interpretation of the CBA, in the form of contribution- & sensitivity analyses, can be found in section 4.7.2. The results are discussed in section 5.1.

4.7 LCA consistency and completeness (research question 7)

4.7.1 LCA consistency check

Both the studied system and the reference system were modeled using OpenLCA 1.10.3. For both the studied system and the reference system processes imported from the ecoinvent 3.4 database were used. The first part of the recycling system is based on the panel recycling process that recovers the bulk materials: glass, Al & Cu (Stolz et al., 2020). The second part, Si leaching and filtration, is based on Latunussa et al. (2016). The third part, Ga & In leaching and filtration is modelled using data from Zhan et al. (2020a). The final part, Ga purification, is modelled using data from Tuchschmid (2017). When studying the impact results, it should be kept in mind that the different parts of the recycling system are based on different references and in reality the recycling flowchart may contain different processes.

4.7.2 LCA completeness check

Data on most of the infrastructure at the recycling plant and the needed equipment is lacking. The only process where the facility construction is included is Ga purification, since for that process, facility construction data is available. The other infrastructure at the recycling plant and equipment needed are left out of the system boundary of this study. Although these elements are assumed to have a minor impact compared to the rest of the modelled processes, adding processes for the infrastructure and equipment would increase the overall impact score of the recycling process. Furthermore, the inputs for selective Ga/In etching/leaching and filtration are scaled linearly from the amounts described by Zhan et al. (2020). It should be noted that in reality, industrial bulk recycling may be more effective than the lab scale recycling described by Zhan et al. (2020). This may decrease the overall impact score of the recycling process.

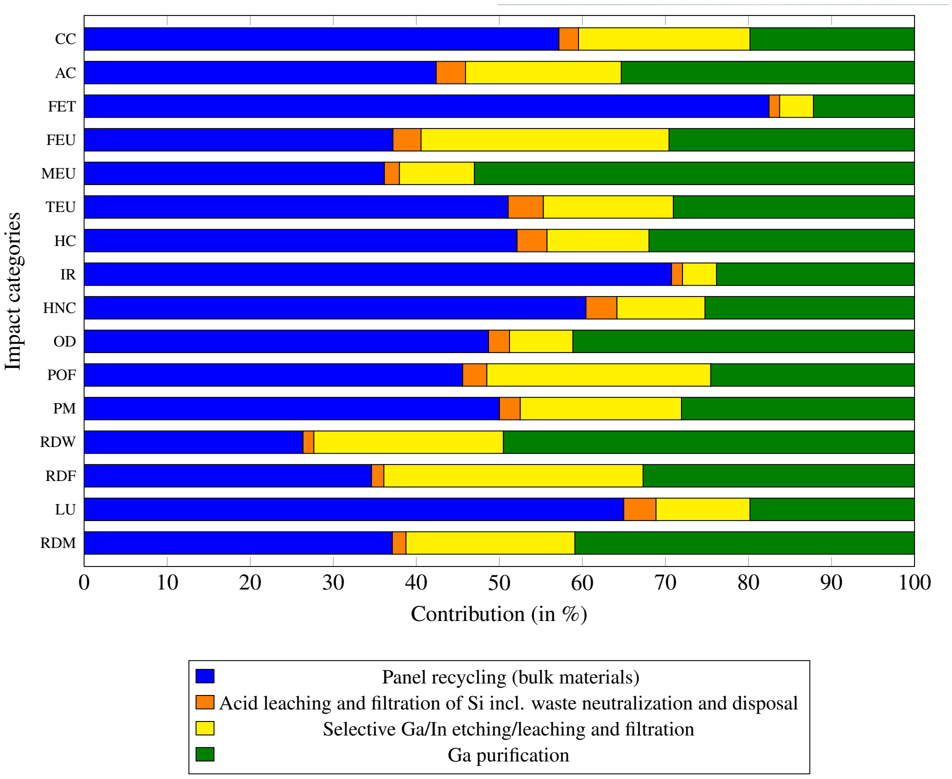
4.8 LCA and CBA contribution analyses (research question 8)

4.8.1 LCA contribution analysis

In this contribution analysis, the contribution of the various parts of the defined recycling process for III-V/Si PV panels are visualised (figure 4.13). This analysis makes it possible to understand which process steps have the highest impacts in each impact category. In most impact categories the bulk material recycling process is the main contributor, followed by Ga purification and Ga/In etching/leaching and filtration. When focusing upon the five highest scoring impacts categories defined in section 4.5.3, for climate change the main contributing process is the bulk material recycling with more than 57% of the total impacts. For marine eutrophication the main contributing process is Ga purification with 53%. For freshwater ecotoxicity, the main contributing process is the bulk material recycling with more than 82%. For fossil resource depletion, bulk material recycling, Ga/In etching/leaching and filtration and Ga purification all contribute a significant amount (approximately 35%, 31% and 33% respectively). Finally, in the category ozone layer depletion, bulk material recycling contributes approximately 49% and Ga purification approximately 41%.

Figure 4.13

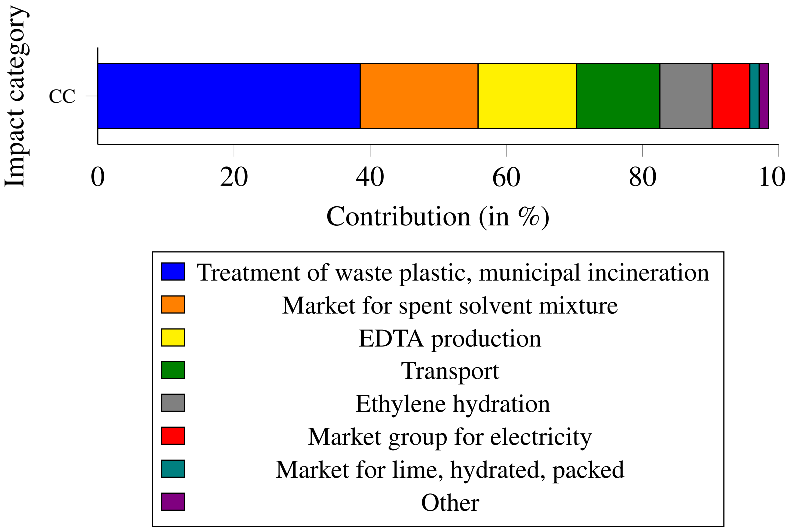
Environmental impacts contributions of the main processes in the recycling process for III-V/Si PV panels



4.8.2 Climate change contribution analysis

For the category climate change, the highest scoring impact category, a more detailed contribution analysis is performed. The relative impacts of the involved background processes were analysed and are shown in figure 4.14. This makes it possible to define so called hot spot processes, which can be focused upon when trying to reduce the environmental impacts of the recycling process. The municipal incineration of waste plastic contributes 38.58% to the total amount of kg CO_2 equivalent emitted. The market for spent solvent mixture contributes 17.3%, EDTA production 14.48%, transport 12.22%, ethylene hydration (to produce ethanol) 7.68%, electricity 5.53%, the market for hydrated, packed lime ($Ca(OH)_2$) 1.38% and all other processes account for the remaining 2.87%.

Figure 4.14
Contribution analysis of climate change impacts of the recycling process for III-V/Si PV panels



4.8.3 CBA contribution analysis

The revenue contributions of the recovered materials in case of recycling only the bulk materials and in case of recycling the bulk materials and CRMs are shown in figure 4.15 and 4.16 respectively. The cost contribution in case of recycling the bulk materials and CRMs is shown in figure 4.17.

Figure 4.15
Revenue contribution for only bulk recycling

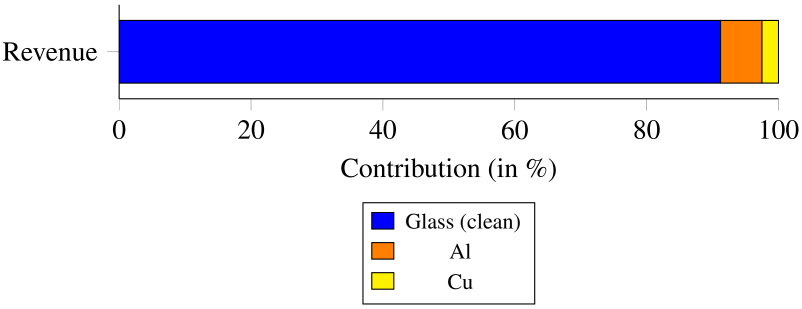


Figure 4.16
Revenue contribution for bulk + Si, Ga & In recycling

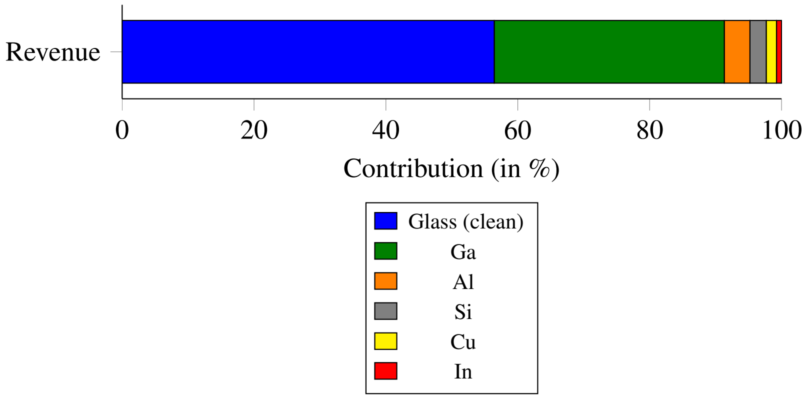
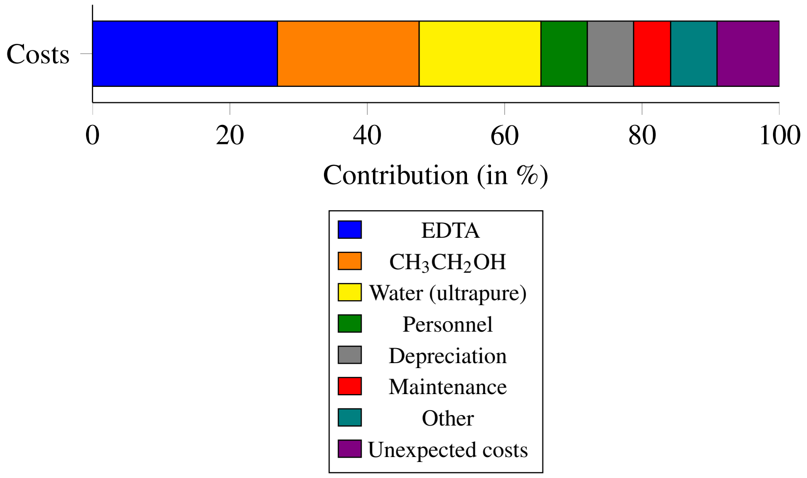


Figure 4.17
Cost contribution for bulk + Si, Ga & In recycling



4.9 CBA sensitivity analysis (research question 9)

The price of Ga tends to fluctuate significantly over the years. According to the EC, the Ga price fluctuated between $ 318 and $ 688 between 2011 and 2018 (Appendix K, figure K1) ("European Commission, Study on the EU's list of Critical Raw Materials, Critical Raw Materials Factsheets (Final)", 2020). For this sensitivity analysis, Ga prices of 200, 300, 400, 500 and 600 euro per kg are considered. How these price affect the net present value of the recycling process is visualised in figure 4.18.

The results of the CBA also heavily depend on the amount of Ga & In recovered. In the CBA, the amount of Ga and In recovered, 120 tons and 0.9 ton respectively, is based on the III-V/Si cell design shown in figure A1 (appendix A) and the recovery efficiencies from Zhan et al. (2020a). However, Gervais et al. (2021) assume various different amounts of Ga and In embodied in III-V/Si cells. The amount of Ga/In that could be recovered from the III-V/Si cells in their scenarios range from 35.4/12.9 tons Ga/In per GWp to 19.8/7.7 tons Ga/In per GWp. The Ga & In recovery efficiencies are included. How these amounts of Ga and In affect the net present value of the recycling process is visualised in figure 4.19. The data on which this figure is based can be found in appendix L.

Figure 4.18

Sensitivity analysis - net present value of bulk + Si, Ga & In alternative with various Ga prices

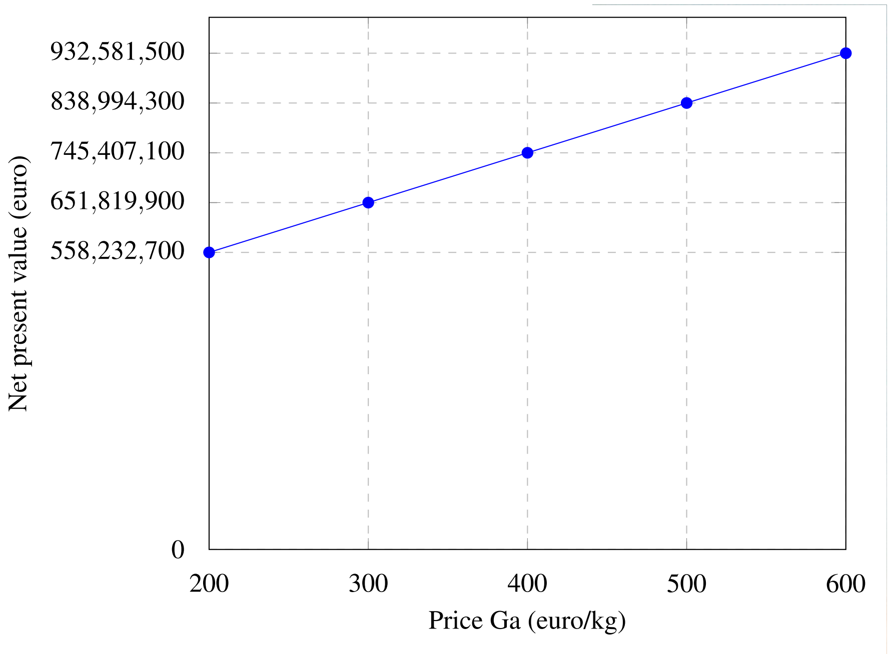
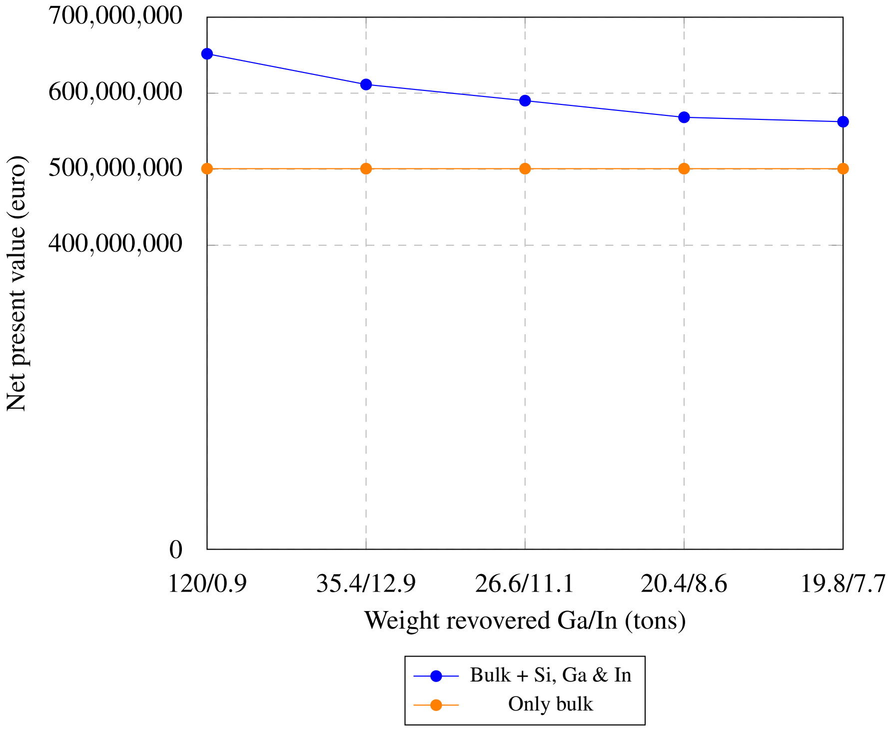


Figure 4.19

Sensitivity analysis - net present value of bulk + Si, Ga & In alternative with various amounts of Ga & In recovered, based on Gervais et al. (2021)



5 Discussion & conclusion

5.1 Discussion

This study has examined the criticality of Ga, In and Si for a 1 GWp production of III-V/Si PV cells as well as the environmental impacts and economic feasibility of recycling III-V/Si PV panels. For the criticality assessment, the Yale analytical framework was used. For the environmental impact estimation of the recycling process, an ex-ante LCA was performed. And finally, for the economic feasibility of recycling, a ex-ante CBA was performed.

Looking at the criticality graphs of Ga, In & Si (figures 4.1, 4.2 & 4.3), there is generally an upward trend in the criticality of these materials. For the production of III-V/Si PV cells, Ga is the most critical of these CRMs (see table 4.1 and figure 4.4). The rise in Ga demand, due to large scale production of III-V/Si solar cells, could increase the environmental implications of Ga production. For III-V/Si PV, Ga is also the most vulnerable to a supply disruption. With a shortage in Ga, production of III-V/Si PV is likely to be halted. The EC estimates the supply risk for In to be the highest of the three studied CRMs, but for the case of III-V/Si solar, In is still less critical than Ga, because the III-V layer that contains In can be replaced with a AlGaAs layer (F. Dimroth, personal communication, July 08, 2020). When it comes to Si criticality, III-V/Si PV cells are a preferable alternative to c-Si cells, because III-V/Si PV has a lower Si demand per kWh.

A 1GWp production of III-V/Si PV cells is estimated to require 176.3 tons of high-purity Ga, while the 2019 world production of high-purity Ga was a merely 205 tons (U.S. Geological Survey, 2020a). Moreover, the U.S. Geological Survey (2020a) states that the refinery capacity to purify Ga into high-purity Ga was 330 tons. Therefore, the criticality of high-purity Ga can become restrictive for large scale production of III-V/Si PV cells. To prevent this, additional high-purity refineries to refine low grade Ga to semiconductor grade Ga are needed. The amounts of In and Si used for the III-V/Si SiTaSol PV cells are not a limiting factor for the development towards large scaled production.

Recycling Ga from EoL III-V/Si PV cells reduces its criticality, because it lowers the supply risk. Therefore, recycling possibilities were studied. The best scoring Ga recycling process was included in the recycling process flowchart. Recovering Ga from III-V/Si panels is technically possible. The main challenge in recycling is delamination of the various layers. The selectivity of an etching process is the main technical barrier in this (A.R. Balkenende, personal communication, August 18, 2020). Scientific literature and patents describe many techniques that could be used for recycling Ga from LEDs and CIGS panels. Mechanical-, chemical-, thermal- and vacuum-techniques, or a combination of these methods. Recovering Ga from III-V/Si PV cells is possible using similar methods. Although many techniques can be used, this study is limited to one. The most suited recycling process was chosen by using an semi-quantitative assessment method that considered the estimated environmental performance, data availability and maximum Ga recovery. The Ga recycling method that scored highest, the ethanol dilution process defined by Zhan et al. (2020a), was included in the recycling process flowchart. Apart from Ga, the bulk materials glass, Al & Cu, and the other CRMs In & Si can be recovered using the depicted recycling processes. Heat & electricity are used to recover the bulk materials. HNO_3 and filtration is used to recover Si. Ethanol dilution can be used to recover Ga & In. Finally, the Ga is purified using a combination of chemicals and electricity, as defined by Tuchschmid (2017).

The environmental impacts of the recycling process for III-V/Si PV panels were compared to the environmental impacts of cradle-to-gate production of these panels. The highest scoring impact category for recycling, relative to the cradle-to-gate production, was found to be climate change, followed by marine eutrophication, freshwater ecotoxicity, fossil resource depletion and ozone layer depletion. When optimizing the recycling process, these environmental impacts should therefore be focused upon.

For the climate change impact category, a more detailed contribution analysis was performed. It was found that municipal incineration of waste plastic contributes a stunning 38.58% to the total amount of kg CO_2 equivalent emitted. One suggestion to lower the climate change impacts of the III-V/Si PV panel recycling process is therefore to put effort in recycling the plastic waste as much as possible, instead of incinerating it.

The economic feasibility of recycling the CRMs was studied by performing a CBA. It was found that with the current cell design (see appendix A) and Ga prices, recovering Ga in recycling is economically feasibility. With the assumptions that were made, it is estimated that recycling the bulk materials (glass, Al & Cu) from 1GWp of III-V/Si PV panels can turn a profit of approximately 500.7 million euros in 10 years. Recovering Ga, In & Si as well could raise this profit to approximately 651.8 million euros.

Gervais et al. (2021) assume various different amounts of Ga and In embodied in III-V/Si cells. With a lower amount of Ga in III-V/Si PV cells recycling the CRMs could become less profitable. An increased module efficiency and increased TMGa production efficiency, could lower the Ga demand to 29 tons per GWp and the amount of retrievable Ga to 19.8 tons. Assuming the amount bulk materials (glass, Al & Cu) remains the same, the recycling of bulk materials would in the case still make a profit of approximately 500.7 million euros in 10 years. Recovering Ga, In & Si too would have a net profit of approximately 562.5 million euro (see figure 4.19). Although it is not expected from these results, there could be a case in which recovering Ga, In & Si would have a net financial loss. In this case the EC could consider subsidising this recycling process, since it is beneficial to lower the supply risk of these elements and therefore lower their criticality.

After an expected lifetime of 25 to 30 years, the III-V/Si PV panels will be dismantled. This is when bulk recycling can start. In the meantime technological advances can be made in recycling. Moreover, the economic market could change into an economic system that not only values internal costs, but also includes external costs (from pollution). This could raise the chances of the recycling of the CRMs further.

It has to be kept in mind that for recycling to happen, sufficiently large batches of III-V/Si panels should be collected. This is because recycling is only done in bulk. Collection at EoL should be centralized to make sure to obtain enough panels to make recycling an option (A.R. Balkenende, personal communication, August 18, 2020).

Where most data sources on Ga recovery that were used in this research are from lab scale processes. Project 'RECLAIM' (2013-2016) demonstrated that recovering Ga & In from CIGS PV panels is possible on pilot scale, in at the company Coolrec in Tisselt, Belgium ("RECLAIM", n.d.). Ir. Toon Ansems from the Dutch organization of applied scientific research TNO, has mentioned that the RECLAIM consortium is currently working on a follow-up of the project (A.M.M. Ansems, personal communication, May 07, 2020). The data and results of this follow-up project are confidential. One European (Slovakian) company was found that already commercially recycles Ga from Ga containing waste ("CMK, recycling", 2021). It is however unclear if any of this recycling is from EoL products.

Some elements that have been touched upon by this research, require further research. Firstly, the environmental impact of requiring virgin Ga can be more thoroughly investigated and compared with the environmental impact of recycled Ga. Secondly, the ethanol dilution recycling process could be tested on III-V/Si cells. The Ga and In recovery efficiency should be checked and if possible be further optimized.

The results of this research have contributed to the understanding of the criticality of the materials involved in III-V/Si solar cells: Ga, In & Si. In order to upscale this type of solar technology, developers should firstly focus upon the criticality of Ga. In the long term recycling the CRMs from the III-V/Si solar cells, is expected to be economically feasible and environmentally desirable. However, this conclusion is based on certain assumptions which could change in the future. It should be kept in mind that the performed research was performed with data which may not depict the eventual reality. III-V/Si solar is an emerging technology and there is research still to be performed considering this solar technology and the economic- and environmental considerations involved. The results of this thesis show that, although Ga is critical, with the right incentives, III-V/Si could develop towards a 1GWp production and further. Moreover, recycling Ga, In & Si is technically possible and expected to be profitable.

5.2 Conclusions

This research has answered three main research questions. The first main research question being:

1. Could criticality of gallium, indium and silicon limit the development of III-V/silicon solar cells towards a yearly production of 1 gigawatt-peak?

It was found that gallium criticality can limit the development of III-V/silicon solar cells towards a yearly production of 1 gigawatt-peak. As described in section 4.1.2.1, the amount of high-purity Ga needed for a yearly production of 1 gigawatt-peak is estimated to be 176.3 tons. This is a significantly high amount, considering the 2019 world production of high-purity Ga was 205 tons. To meet the increased demand, refineries that produce high-purity Ga should upscale their production and new refineries should be constructed.

The amount of In used in III-V/Si cells is estimated to be 1.03 tons, which is low relatively to the amount of Ga. As described in section 4.1.2.2, In criticality therefore does not seem a limiting factor for upscaled III-V/Si PV cell production.

Si criticality does not limit the development of III-V/silicon solar cells towards a yearly production of 1 GWp. The opposite holds, because because III-V/Si has a lower per GWp Si consumption compared with c-Si.

The second main research question of this study is:

2. What is a potential recycling process for III-V/silicon solar panels that recovers bulk elements (glass, aluminium and copper) as well as gallium, indium and silicon?

The potential recycling process for III-V/Si solar panels can be found in figure 4.8 and appendix G.

The third and final main research question of this study was:

3. What are the environmental- and economic impacts of the recycling process for end-of-life III-V/silicon solar panels?

The results of the LCA have shown that the recycling process for EoL III-V/Si solar panels has significant environmental impacts when compared to the cradle-to-gate production, especially in the categories climate change, marine eutrophication, freshwater ecotoxicity, fossil resource depletion and ozone layer depletion. Further research into reducing the environmental impacts of recycling EoL III-V/Si is therefore recommended to focus on these impact categories. Considering the economic impacts, the results of the CBA show that recovering Ga, In & Si from 1GWp EoL III-V/Si solar panels can be profitable. The sensitivity analysis has shown that the profitability of recycling the CRMs depends on the cell design.

Concluding, this study has contributed to the understanding of why Ga can be a limiting factor in the estimated upcoming growth of III-V/Si PV cells. It has also contributed to the understanding that In is far less problematic and rising Si criticality may be beneficial for the development of III-V/Si solar panels, because III-V/Si has a lower per GWp Si consumption compared with c-Si. Moreover, a deeper understanding on how to recycle CRMs from EoL III-V/Si PV cells has been achieved. The recycling process flowchart from this study can be of use for further research in the area of III-V/Si PV recycling. Finally, the environmental- and economic-performances of the recycling process are mapped. These performances can be improved, by further optimizing the recycling process.

References

Althaus, H.-J. (2017). adipic acid, RER, Allocation, cut-off by classification, ecoinvent database version 3.4.

Azeumo, M. F., Germana, C., Ippolito, N. M., Franco, M., Luigi, P., & Settimio, S. (2019). Photovoltaic module recycling, a physical and a chemical recovery process. *Solar Energy Materials and Solar Cells, 193*, 314–319. https://doi.org/10.1016/j.solmat.2019.01.035

Bach, V., Finogenova, N., Berger, M., Winter, L., & Finkbeiner, M. (2017). Enhancing the assessment of critical resource use at the country level with the SCARCE method – Case study of Germany. *Resources Policy, 53*, 283–299. https://doi.org/10.1016/j.resourpol.2017.07.003

Basic Parameters of Gallium Arsenide (GaAs). (n.d.). Retrieved 7 April 2020, from http://www.ioffe.ru/SVA/NSM/Semicond/GaAs/basic.html

Basic Parameters of Germanium (Ge). (n.d.). Retrieved 7 April 2020, from http://www.ioffe.ru/SVA/NSM/Semicond/Ge/basic.html

Basic Parameters of Silicon (Si). (n.d.). Retrieved 15 July 2020, from http://www.ioffe.ru/SVA/NSM/Semicond/Si/basic.html

Best Research-Cell Efficiency Chart. (n.d.). Retrieved 27 May 2020, from https://www.nrel.gov/pv/cell-efficiency.html

BGS (2015). Risk List 2015 - An Update to the Supply Risk Index for Elements or Element Groups That are of Economic Value. British Geological Survey.

Bisselink, R. J. M., & Brouwer, J. G. H. (2018). Combined Metal Recovery. https://patentscope.wipo.int/search/en/detail.jsf?docId=WO2018164578

Bisselink, R., & Steeghs, W. (2016, June 20). Recovery of Gallium and Indium from Liquid Crystal Displays and CIGS Photovoltaic modules [Powerpoint Slides]. Retrieved 30 December 2020, from http://www.4980.timewarp.at/sat/reclaim/Reclaim%20Pr%C3%A4sentationen%20HP/Pr%C3%A4sentationen%20Mechelen%20June%202016/RECLAIM%20Suez%20Water%20June%202016.pdf

Blanco, C. F., Cucurachi, S., Dimroth, F., Guinée, J. B., Peijnenburg, W. J. G. M., & Vijver, M. G. (2020). Environmental impacts of III–V/silicon photovoltaics: Life cycle assessment and guidance for sustainable manufacturing. *Energy & Environmental Science 13*(11), 4280–4290. https://doi.org/10.1039/D0EE01039A

Blengini, G.A., Blagoeva, D., Dewulf, J., Torres de Matos, C., Nita, V., Vidal-Legaz, B., Latunussa, C.E.L., Kayam, Y., Talens Peirò, L., Baranzelli, C., Manfredi, S., Mancini, L., Nuss, P., Marmier, A., Alves-Dias, P., Pavel, C., Tzimas, E., Mathieux, F., Pennington, D. & Ciupagea, C. (2017). *Assessment of the Methodology for Establishing the EU List of Critical Raw Materials - Annexes*, Publications Office of the European Union, Luxemburg, 2017, 978-92-79-70213-6, https://doi.org/10.2760/875135, JRC107008

Boardman, A. E., Greenberg, D. H., Vining, A. R., & Weimer, D. L. (2018). Cost-Benefit Analysis: Concepts and Practice. Cambridge University Press.

Bourgault, G. (2017a). aluminium scrap, post-consumer, prepared for melting, GLO, Allocation, cut-off by classification, ecoinvent database version 3.4.

Bourgault, G. (2017b). silicon, metallurgical grade, GLO, Allocation, cut-off by classification, ecoinvent database version 3.4.

Buchert, M., Schüler, D., & Bleher, D. (2009). Critical metals for sustainable technologies and their recycling potential. *UNEP*

Calvo, G., Valero, A., & Valero, A. (2018). Thermodynamic Approach to Evaluate the Criticality of Raw Materials and Its Application through a Material Flow Analysis in Europe. *Journal of Industrial Ecology, 22*(4), 839–852.
https://doi.org/10.1111/jiec.12624

Chen, W.-S., Hsu, L.-L., & Wang, L.-P. (2018). Recycling the GaN Waste from LED Industry by Pressurized Leaching Method. *Metals, 8*(10), 861.
https://doi.org/10.3390/met8100861

Chen, W.-T., Tsai, L.-C., Tsai, F.-C., & Shu, C.-M. (2012). Recovery of Gallium and Arsenic from Gallium Arsenide Waste in the Electronics Industry. *CLEAN – Soil, Air, Water, 40*(5), 531–537.
https://doi.org/10.1002/clen.201100216

Choudhury, S. A., Fairooz, F., Rifat, R. A., & Chowdhury, M. H. (2019). Chapter 13 — Metal nanostructures for solar cells. In S. Thomas, E. H. M. Sakho, N. Kalarikkal, S. O. Oluwafemi, & J. Wu (Eds.), Nanomaterials for Solar Cell Applications (pp. 447–511). Elsevier.
https://doi.org/10.1016/B978-0-12-813337-8.00013-8

Classen, M. (2017). indium, RER, Allocation, cut-off by classification, ecoinvent database version 3.4.

CMK, recycling. (2021). Retrieved 22 March 2021, from
http://cmk.sk/services/recycling/

Critical raw materials. (n.d). Retrieved 11 February 2020, from:
https://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical_en

Dassisti, M., Florio, G., & Maddalena, F. (2020). Cryogenic delamination: Mathematical modeling and analysis of an innovative recycling process for photovoltaic crystalline modules. *Journal of Remanufacturing, 10*(1), 43–56.
https://doi.org/10.1007/s13243-019-00073-8

Dimroth, F. (2017). III-V Solar Cells – Materials, Multi-Junction Cells – Cell Design and Performance. In *Photovoltaic Solar Energy* (pp. 371–382). John Wiley & Sons, Ltd.
https://doi.org/10.1002/9781118927496.ch34

Doka, G. (2017). treatment of inert waste, inert material landfill, RoW, Allocation, cut-off by classification, ecoinvent database version 3.4.

EU Publications — Publications Office of the EU. (n.d.). Retrieved 14 April 2020, from
https://op.europa.eu/en/web/general-publications/publications

European Commission, Study on the EU's list of Critical Raw Materials, Critical Raw Materials Factsheets (Final) (2020). Retrieved 08 December 2020, from
https://rmis.jrc.ec.europa.eu/uploads/CRM_2020_Factsheets_critical_Final.pdf

European Commission, Study on the EU's list of Critical Raw Materials, Final Report (2020). Retrieved 08 September 2020, from
https://rmis.jrc.ec.europa.eu/uploads/CRM_2020_Report_Final.pdf

Farrow, A., Miller, K.A. & Myllyvirta, L. (2020). Toxic air: The price of fossil fuels. Seoul: Greenpeace Southeast Asia. 44 pp. February 2020.

Feifel, M., Rachow, T., Benick, J., Ohlmann, J., Janz, S., Hermle, M., Dimroth, F., & Lackner, D. (2016). Gallium Phosphide Window Layer for Silicon Solar Cells. *IEEE Journal of Photovoltaics, 6*(1), 384–390.
https://doi.org/10.1109/JPHOTOV.2015.2478062

Frenzel, M., Ketris, M. P., Seifert, T., & Gutzmer, J. (2016). On the current and future availability of gallium. *Resources Policy, 47*, 38–50.
https://doi.org/10.1016/j.resourpol.2015.11.005

Frenzel, M., Kullik, J., Reuter, M. A., & Gutzmer, J. (2017). Raw material ‘criticality’—Sense or nonsense? *Journal of Physics D: Applied Physics, 50*(12), 123002.
https://doi.org/10.1088/1361-6463/aa5b64

Geissdoerfer, M., Savaget, P., Bocken, N. M. P., & Hultink, E. J. (2017). The Circular Economy – A new sustainability paradigm? *Journal of Cleaner Production, 143*, 757–768.
https://doi.org/10.1016/j.jclepro.2016.12.048

Gervais, E., Shammugam, S., Friedrich, L., & Schlegl, T. (2021). Raw material needs for the large-scale deployment of photovoltaics – Effects of innovation-driven roadmaps on material constraints until 2050. *Renewable and Sustainable Energy Reviews, 137*, 110589.
https://doi.org/10.1016/j.rser.2020.110589

Getter, K. L., & Rowe, D. B. (2006). The Role of Extensive Green Roofs in Sustainable Development. *HortScience, 41*(5), 1276–1285.
https://doi.org/10.21273/hortsci.41.5.1276

Ghisellini, P., Cialani, C., & Ulgiati, S. (2016). A review on circular economy: The expected transition to a balanced interplay of environmental and economic systems. *Journal of Cleaner Production, 114*, 11–32.
https://doi.org/10.1016/j.jclepro.2015.09.007

Glöser, S., Tercero Espinoza, L., Gandenberger, C., & Faulstich, M. (2015). Raw material criticality in the context of classical risk assessment. *Resources Policy, 44*, 35–46.
https://doi.org/10.1016/j.resourpol.2014.12.003

Graedel, T. E., & Allenby, B. R. (2010). *Industrial Ecology and Sustainable Engineering*. Prentice Hall.

Graedel, T. E., Barr, R., Chandler, C., Chase, T., Choi, J., Christoffersen, L., Friedlander, E., Henly, C., Jun, C., Nassar, N. T., Schechner, D., Warren, S., Yang, M., & Zhu, C. (2012). Methodology of Metal Criticality Determination. *Environmental Science & Technology, 46*(2), 1063–1070.
https://doi.org/10.1021/es203534z

Graedel, T. E., Harper, E. M., Nassar, N. T., Nuss, P., & Reck, B. K. (2015). Criticality of metals and metalloids. *Proceedings of the National Academy of Sciences, 112*(14), 4257–4262.
https://doi.org/10.1073/pnas.1500415112

Graedel, T. E., Harper, E. M., Nassar, N. T., & Reck, B. K. (2015). On the materials basis of modern society. *Proceedings of the National Academy of Sciences, 112*(20), 6295–6300.
https://doi.org/10.1073/pnas.1312752110

Gustafsson, A. M. K., Steenari, B.-M., & Ekberg, C. (2015). Recycling of CIGS Solar Cell Waste Materials: Separation of Copper, Indium, and Gallium by High-Temperature Chlorination Reaction with Ammonium Chloride. *Separation Science and Technology, 50*(15), 2415–2425.
https://doi.org/10.1080/01496395.2015.1053569

Hatayama, H., & Tahara, K. (2015). Criticality Assessment of Metals for Japan’s Resource Strategy. *Materials Transactions, 56*(2), 229–235.
https://doi.org/10.2320/matertrans.M2014380

Heck, T. (2017). heat, central or small-scale, natural gas, Europe without Switzerland, Allocation, cut-off by classification, ecoinvent database version 3.4.

Hischier, R. (2017a). EDTA, ethylenediaminetetraacetic acid, RER, Allocation, cut-off by classification, ecoinvent database version 3.4.

Hischier, R. (2017b). fatty alcohol, RER, Allocation, cut-off by classification, ecoinvent database version 3.4.

Horowitz, K. A., Remo, T. W., Smith, B., & Ptak, A. J. (2018). A Techno-Economic Analysis and Cost Reduction Roadmap for III-V Solar Cells (NREL/TP–6A20-72103, 1484349; p. NREL/TP–6A20-72103, 1484349).
https://doi.org/10.2172/1484349

How Much Does Hazardous Waste Disposal Cost in 2021? (n.d.). Checkatrade. Retrieved 16 June 2021, from
https://www.checkatrade.com/blog/cost-guides/hazardous-waste-disposal-cost/

IEA. (2019). Key World Energy Statistics 2019. IEA.
https://webstore.iea.org/download/direct/2831

III-V PV Technology | 5.1 III-V PV Technology | ET3034TUx Courseware | edX. (n.d.). Retrieved 15 July 2020, from
https://courses.edx.org/courses/DelftX/ET3034TUx/2013_Fall/courseware/

IPCC, 2014: Summary for policymakers. In: *Climate Change 2014: Impacts, Adaptation, and Vulnerability. Part A: Global and Sectoral Aspects. Contribution of Working Group II to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* [Field, C.B., V.R. Barros, D.J. Dokken, K.J. Mach, M.D. Mastrandrea, T.E. Bilir, M. Chatterjee, K.L. Ebi, Y.O. Estrada, R.C. Genova, B. Girma, E.S. Kissel, A.N. Levy, S. MacCracken, P.R. Mastrandrea, and L.L.White (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, pp. 1-32.

IRP (2020). Mineral Resource Governance in the 21st Century: Gearing extractive industries towards sustainable development. Ayuk, E. T., Pedro, A. M., Ekins, P., Gatune, J., Milligan, B., Oberle B., Christmann, P., Ali, S., Kumar, S. V, Bringezu, S., Acquatella, J., Bernaudat, L., Bodouroglou, C., Brooks, S., Buergi Bonanomi, E., Clement, J., Collins, N., Davis, K., Davy, A., Dawkins, K., Dom, A., Eslamishoar, F., Franks, D., Hamor, T., Jensen, D., Lahiri-Dutt, K., Mancini, L., Nuss, P., Petersen, I., Sanders, A. R. D. A Report by the International Resource Panel. United Nations Environment Programme, Nairobi, Kenya.

ISO 14040 (2006). Environmental management - Life-cycle assessment - Principles and framework, International Organization for Standardization, Geneva, 2006.

Jungbluth, N. (2017a). water, completely softened, from decarbonized water, at user, RER, Allocation, cut-off by classification, ecoinvent database version 3.4.

Jungbluth, N. (2017b). kerosene, Europe without Switzerland, Allocation, cut-off by classification, ecoinvent database version 3.4.

Kellenberger, D. (2017a). flat glass, uncoated, RER, Allocation, cut-off by classification, ecoinvent database version 3.4.

Kellenberger, D. (2017b). lime, hydraded, packed, RoW, Allocation, cut-off by classification, ecoinvent database version 3.4.

Latunussa, C. E. L., Ardente, F., Blengini, G. A., & Mancini, L. (2016). Life Cycle Assessment of an innovative recycling process for crystalline silicon photovoltaic panels. *Solar Energy Materials and Solar Cells, 156*, 101–111.
https://doi.org/10.1016/j.solmat.2016.03.020

Licht, C., Peiró, L. T., & Villalba, G. (2015). Global Substance Flow Analysis of Gallium, Germanium, and Indium: Quantification of Extraction, Uses, and Dissipative Losses within their Anthropogenic Cycles. *Journal of Industrial Ecology, 19*(5), 890–903.
https://doi.org/10.1111/jiec.12287

Lokanc, M., Eggert, R., & Redlinger, M. (2015). The Availability of Indium: The Present, Medium Term, and Long Term. United States.
https://doi.org/10.2172/1327212.

Markvart, T., & Castañer, L. (2018). Chapter I-1-A - Principles of Solar Cell Operation. In S. A. Kalogirou (Ed.), *McEvoy's Handbook of Photovoltaics (Third Edition)* (pp. 3–28). Academic Press.
https://doi.org/10.1016/B978-0-12-809921-6.00001-X

McCullough, E., & Nassar, N. T. (2017). Assessment of critical minerals: Updated application of an early-warning screening methodology. *Mineral Economics, 30*(3), 257–272.
https://doi.org/10.1007/s13563-017-0119-6

Meusel, M., Baur, C., Létay, G., Bett, A. W., Warta, W., & Fernandez, E. (2003). Spectral response measurements of monolithic GaInP/Ga(In)As/Ge triple-junction solar cells: Measurement artifacts and their explanation. *Progress in Photovoltaics: Research and Applications, 11*(8), 499–514.
https://doi.org/10.1002/pip.514

Morales, A. (2014, October 6). What makes a Material Critical?
http://www.criticalrawmaterials.eu/wp-content/uploads/CRM_InnoNet-Grenoble.-AMoralespdf.pdf

Morley, N., & Eatherley, D. (2008). *Material security: Ensuring resource availability for the UK economy*. C-Tech Innovation Ltd.

Nagy, S., Bokányi, L., Gombkötő, I., & Magyar, T. (2017). Recycling of Gallium from End-of-Life Light Emitting Diodes *Archives of Metallurgy and Materials, 62*(2), 1161-1166.
https://doi.org/10.1515/amm-2017-0170

Norgate, T., & Haque, N. (2010). Energy and greenhouse gas impacts of mining and mineral processing operations. *Journal of Cleaner Production, 18*(3), 266–274.
https://doi.org/10.1016/j.jclepro.2009.09.020

Osses, M. (2017a). nitric acid, without water, in 50% solution state, RER, Allocation, cut-off by classification, ecoinvent database version 3.4.

Osses, M. (2017b). sulfuric acid, RER, Allocation, cut-off by classification, ecoinvent database version 3.4.

Parada Tur, S. (2017). copper scrap, sorted, pressed, GLO, Allocation, cut-off by classification, ecoinvent database version 3.4.

Pathak, A. K., Chopra, K., Singh, H. M., Tyagi, V. V., Kothari, R., Anand, S., & Pandey, A. K. (2019). Role of Solar Energy Applications for Environmental Sustainability. In R. C. Sobti, N. K. Arora, & R. Kothari (Eds.), Environmental Biotechnology: For Sustainable Future (pp. 341–374). Springer.
https://doi.org/10.1007/978-981-10-7284-0_14

Pourhossein, F., & Mousavi, S. M. (2018). Enhancement of copper, nickel, and gallium recovery from LED waste by adaptation of Acidithiobacillus ferrooxidans. *Waste Management, 79*, 98–108.
https://doi.org/10.1016/j.wasman.2018.07.010

Preston, F. (2012). A Global Redesign? Shaping the Circular Economy. Briefing Paper. Retrieved 5 October 2020 from
https://www.chathamhouse.org/publications/papers/view/182376/bp0312_preston.pdf

Project Description | Sitasol. (n.d.). Retrieved 19 February 2020, from
https://sitasol.com/projectdescription/

RECLAIM. (n.d.). Retrieved September 29, 2020, from
http://www.re-claim.eu/

Schrijvers, D., Hool, A., Blengini, G. A., Chen, W.-Q., Dewulf, J., Eggert, R., van Ellen, L., Gauss, R., Goddin, J., Habib, K., Hagelüken, C., Hirohata, A., Hofmann-Amtenbrink, M., Kosmol, J., Le Gleuher, M., Grohol, M., Ku, A., Lee, M.-H., Liu, G., … Wäger, P. A. (2020). A review of methods and data to determine raw material criticality. *Resources, Conservation and Recycling, 155*, 104617.
https://doi.org/10.1016/j.resconrec.2019.104617

Silicon and Ferrosilicon: Outlook to 2029, 17th edition (2020). Retrieved 13 January 2021, from
https://roskill.com/market-report/silicon-ferrosilicon/

Simons, A. (2017). transport, freight, lorry 7.5-16 metric ton, EURO5, RER, Allocation, cut-off by classification, ecoinvent database version 3.4.

SiTaSol. (2021). *D6.4 Ex-ante LCA of III-V/Si tandem solar modules*. Confidential document.

Smets, A. H. M., Jager, K., Isabella, O., Van Swaaij, R. A. C. M. M., & Zeman, M. (2016). Solar Energy: The Physics and Engineering of Photovoltaic Conversion, Technologies and Systems. UIT Cambridge Ltd.

Stolz, P., Frischknecht, R., Wambach, K., Sinha, P., & Heath, G. (2017). Life Cycle Assessment of Current Photovoltaic Module Recycling, IEA PVPS Task 12, International Energy Agency Power Systems Programme, Report IEA-PVPS T12- 13:2018.

Sutter, J. (2017a). ethanol, without water, in 99.7% solution state, from ethylene, RER, Allocation, cut-off by classification, ecoinvent database version 3.4.

Sutter, J. (2017b). water, ultrapure, RoW, Allocation, cut-off by classification, ecoinvent database version 3.4.

Treyer K. (2017). electricity, medium voltage, DE, Allocation, cut-off by classification, ecoinvent database version 3.4.

Tuchschmid, M. (2017). gallium, semiconductor-grade, GLO, Allocation, cut-off by classification, ecoinvent database version 3.4.

U.S. Geological Survey. (2017a). Mineral commodity summaries 2017: U.S. Geological Survey, 202 p.
https://doi.org/10.3133/70180197

U.S. Geological Survey. (2017b). Minerals Yearbook 2017 INDIUM [ADVANCE RELEASE]. Retrieved 02 December 2020, from
https://prd-wret.s3.us-west-2.amazonaws.com/assets/palladium/production/atoms/files/myb1-2017-indiu.pdf

U.S. Geological Survey. (2020a). Gallium Data Sheet. Retrieved 15 July 2020, from
https://pubs.usgs.gov/periodicals/mcs2020/mcs2020-gallium.pdf

U.S. Geological Survey. (2020b). Germanium Data Sheet. Retrieved 15 July 2020, from
https://pubs.usgs.gov/periodicals/mcs2020/mcs2020-germanium.pdf

U.S. Geological Survey. (2020c). Silicon Data Sheet. Retrieved 15 July 2020, from
https://pubs.usgs.gov/periodicals/mcs2020/mcs2020-silicon.pdf

Van den Bossche, A., Vereycken, W., Van der Hoogerstraete, T., Dehaen, W., & Binnemans, K. (2019). Recovery of Gallium, Indium, and Arsenic from Semiconductors Using Tribromide Ionic Liquids. *ACS Sustainable Chemistry & Engineering, 7*(17), 14451–14459.
https://doi.org/10.1021/acssuschemeng.9b01724

Van der Giesen, C., Cucurachi, S., Guinée, J., Kramer, G. J., & Tukker, A. (2020). A critical view on the current application of LCA for new technologies and recommendations for improved practice. *Journal of Cleaner Production, 259*, 120904.
https://doi.org/10.1016/j.jclepro.2020.120904

Woodhouse, M., Smith, B., Ramdas, A., & Margolis., R. (2019). Crystalline Silicon Photovoltaic Module Manufacturing Costs and Sustainable Pricing: 1H 2018 Benchmark and Cost Reduction Roadmap. Golden, CO: National Renewable Energy Laboratory. Retrieved 22 March 2021, from
https://www.nrel.gov/docs/fy19osti/72134.pdf

Zhan, L., Wang, Z., Zhang, Y., & Xu, Z. (2020a). Recycling of metals (Ga, In, As and Ag) from waste light-emitting diodes in sub/supercritical ethanol. *Resources, Conservation and Recycling, 155*, 104695.
https://doi.org/10.1016/j.resconrec.2020.104695

Zhan, L., Xia, F., Ye, Q., Xiang, X., & Xie, B. (2015). Novel recycle technology for recovering rare metals (Ga, In) from waste light-emitting diodes. *Journal of Hazardous Materials, 299*, 388–394.
https://doi.org/10.1016/j.jhazmat.2015.06.029

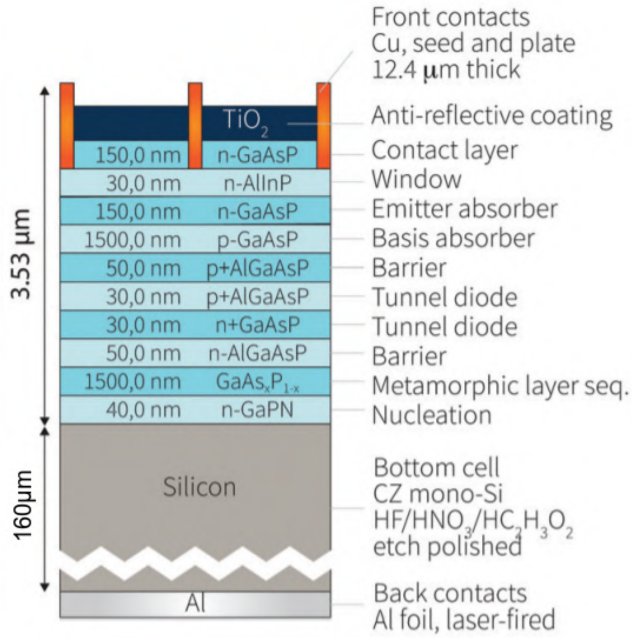
Zhan, L., Zhang, Y., Ahmad, Z., & Xu, Z. (2020b). Novel Recycle Technology for Recovering Gallium Arsenide from Scraped Integrated Circuits. *ACS Sustainable Chemistry & Engineering, 8*(7), 2874–2882. `https://doi.org/10.1021/acssuschemeng.9b07006`

Zhang, L., & Xu, Z. (2016). Separating and Recycling Plastic, Glass, and Gallium from Waste Solar Cell Modules by Nitrogen Pyrolysis and Vacuum Decomposition. *Environmental Science & Technology, 50*(17), 9242–9250. `https://doi.org/10.1021/acs.est.6b01253`

Appendix A - III-V/Si (SiTaSol) PV cell

Figure A1

Schematic representation of a III-V/Si (SiTaSol) PV cell



Note. Adapted from "Environmental impacts of III–V/silicon photovoltaics: life cycle assessment and guidance for sustainable manufacturing", by Blanco, C.F., et al., 2020, *Energy & Environmental Science 13*(11), p. 4282.

Appendix B - Additional criticality assessment indicators

The US National Science and Technology Council uses two additional indicators next to supply risk, namely ’production growth’ and ’market dynamics’. These respectively indicate whether there is shrinkage, constant growth or accelerating growth in a materials production and the price fluctuations over a chosen range of years (McCullough & Nassar, 2017). Furthermore, the Japanese New Energy and Industrial Technology Development Organization assess criticality based on supply risk, price risk, demand risk, recycling restriction and potential risk. The last being related to the possibility of restriction on the usage of a material (Hatayama & Tahara, 2015). Calvo, Valero, & Valero (2018) propose a variable called ’thermodynamic rarity’ to be added to criticality assessments. This indicator incorporates both the amount of exergy needed to produce the assessed raw material from current mines, as well as the exergy needed to produce the raw material in case all elements are dispersed throughout the Earth’s crust (a scenario named ’Thanatia’). Therefore, thermodynamic rarity is dependent on the average grade of the assessed material in the Earth’s crust, the average grade of the assessed material in the ore it is currently mined from (e.g. bauxite in case of gallium and zinc in case of indium) and on the processes and technologies that are used to obtain the material (Calvo et al., 2018). Bach, Finogenova, Berger, Winter, & Finkbeiner (2017) use the so called SCARCE method, which uses an ’availability’ dimension, which is related to, among other indicators, supply risks and demand growth. Apart from assessing criticality, which is part of the economic sustainability dimension (related to economic profit), Bach et al. (2017) also assess the societal acceptance, which relates to the social and environmental sustainability dimensions of resource use. The indicators for this are ’compliance with social standards’ and ’compliance with environmental standards’, which are measured by e.g. human rights abuse and contributions to climate change respectively (Bach et al., 2017). Morley & Eatherley (2008) use, next to a supply risk indicator, an indicator called material risk, which includes both vulnerability to supply risk and environmental impacts related to the studied materials. Finally, Buchert, Schüler, & Bleher (2009) defined demand growth, supply risks and recycling restrictions as the three indicators for critical raw materials.

Appendix C - Gallium, indium & silicon criticality data

Table C1

Gallium, indium & silicon criticality data based on Schrijvers et al. (2020)

Research method	Criticality and corresponding criticality value	Gallium	Indium	Silicon
Oakdene Hollins 2008	Criticality ($\geq$ 20 critical, $<$ 20 not critical)	16	16	15
	Corresponding criticality value[1]	0	0	0
NRC, US (2008)	Criticality	Not critical	Critical	NA
	Corresponding criticality value	0	1	NA
NEDO (2009)	Criticality	Not critical	Critical	NA
	Corresponding criticality value	0	1	NA
Oko-institut (2009)	Criticality	Short-term critical	Short-term critical	NA
	Corresponding criticality value	1	1	NA
Angerer (2009)	Criticality	Not critical	Not critical	NA
	Corresponding criticality value	0	0	NA
US DOE 2010	Short term (0-5 years)	Not critical	Critical	NA
	Medium term (5-15 years)	Not critical	Near critical	NA
	Corresponding criticality value	0	0.5	NA
US DOE 2011	Short term (0-5 years)	Not critical	Near critical	NA
	Medium term (5-15 years)	Not critical	Not critical	NA
	Corresponding criticality value	0	0	NA
Thomason (2010)	Criticality	Shortfall	-	Shortfall
	Corresponding criticality value	1	0	1
Moss 2011	Criticality	High	High	NA
	Corresponding criticality value	1	1	NA
Moss 2013	Criticality	High	Medium-to-high	NA
	Corresponding criticality value	1	0.75	NA
EU 2011	Criticality	Critical	Critical	NA
	Corresponding criticality value	1	1	NA
EU 2014	Criticality	Critical	Critical	Critical
	Corresponding criticality value	1	1	1
EU 2017	Criticality	Critical	Critical	Critical
	Corresponding criticality value	1	1	1

Continued on next page

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[1] if ‘low’ or ‘not critical’ the assigned value is 0, if ‘medium’ 0.5, if ‘high’ or ‘critical’ the value is 1; correspondingly the value for e.g. ’medium-to-high’ is 0.75 and for ’medium-low-low’ (0.5+0+0)/3 = 0.16667

Table C1 - continued from previous page

Research method	Criticality and corresponding criticality value	Gallium	Indium	Silicon
BGS2011	Criticality	Low	Medium	NA
	Corresponding criticality value	0	0.5	NA
BGS2012	Criticality	Medium	Medium	NA
	Corresponding criticality value	0.5	0.5	NA
BGS2015	Criticality	High	High	NA
	Corresponding criticality value	1	1	NA
Yale, US (global) (2015)	Supply risk	Medium	High	NA
	Vulnerability to supply disruption	Low	Medium	NA
	Environmental implications	Low	Low	NA
	Corresponding criticality value	0.16667	0.5	NA
Yale, US (national economy) (2015)	Supply risk	Medium	High	NA
	Vulnerability to supply disruption	Low	Medium	NA
	Environmental implications	Low	Low	NA
	Corresponding criticality value	0.16667	0.5	NA
OECD 2015	Criticality	High	High	High
	Corresponding criticality value	1	1	1
KIRAM/ KITECH (2014)	Criticality	High	NA	Medium
	Corresponding criticality value	1	NA	0.5
iCIRCE (Zaragoza University) (2017)	Criticality	Critical	Critical	NA
	Corresponding criticality value	1	1	NA
BRGM (2015)	Criticality	Low	Medium	NA
	Corresponding criticality value	0	0.5	NA
NSTC, US (2013 & 2014)	Criticality 2013	Not critical	Not critical	Not critical
	Corresponding criticality value	0	0	0
	Criticality 2014	Critical	Not critical	Not critical
	Corresponding criticality value	1	0	0
Augsburg 2016	Criticality	High	High	NA
	Corresponding criticality value	1	1	NA
Werner (2017)	Criticality	NA	High	NA
	Corresponding criticality value	NA	1	NA
SCARCE (2017)	Level of criticality (On scale of 1 to 5)	3	2	1
	Corresponding criticality value	0.5	0.25	0

Note. Adapted from "A review of methods and data to determine raw material criticality", by Schrijvers, D., et al., 2020, *Resources, Conservation and Recycling, 155,*104617, Appendix A. Retrieved from `https://ars.els-cdn.com/content/image/1-s2.0-S0921344919305233-mmc2.xlsx`

Table C2

Summary of criticality values, as used in figures 4.1, 4.2 & 4.3

	Year	Gallium	Indium	Silicon
Average criticality values per year of publication	2008	0	0.5	0
	2009	0.33333	0.66667	NA
	2010	0.5	0.25	1
	2011	0.5	0.625	NA
	2012	0.5	0.5	NA
	2013	0.5	0.375	0
	2014	1	0.5	0.5
	2015	0.46667	0.7	1
	2016	1	1	NA
	2017	0.83333	0.8125	0.5

Appendix D - Interview questions

Prof. dr. ir. B.J. (Bart) Kooi (University of Groningen)

Similarity of SiTaSol cell to LEDs and CIGS PV cells

1. What kind of processing steps are needed to recover Ga from III-V/Si solar cells?
2. To what extent are recycling methods that are designed for LEDs extrapolatable to III-V/Si solar cells?

Dr. Frank Dimroth (Fraunhofer Institute for Solar Energy Systems)

Similarity of SiTaSol cell to LEDs and CIGS PV cells

1. How similar is the material structure of the III-V top cell of a SiTaSol cell to LEDs? And to CIGS PV cells?
2. Do you think recycling technologies that are designed to recover Ga/In from end-of-life LEDs/CIGS cells could be effective for recovering Ga/In from end-of-life SiTaSol cells?

How to split the III-V layers from the silicon in recycling

3. Is it possible to include a thin sacrificial layer in the current (concept A) design, which can be selectively dissolved (epitaxial lift-off), splitting the top (III-V) cell from the bottom (Si) cell in recycling?
4. Could another thin film release method (e.g. sonic wafering or controlled spalling technology) be used to split the top (III-V) cell from the bottom (Si) cell in recycling?

Technical-, environmental- and economic performance

5. What could be technical- or economic barriers to recover Ga/In from end-of-life SiTaSol cells?
6. Do you think a certain type of Ga-recovery treatment (chemical, thermal and/or vacuum processes) is economically and environmentally preferable for end-of-life SiTaSol cells?

Prof. dr. A.R. (Ruud) Balkenende (Delft University of Technology)

Similarity of III-V/Si solar cells to LEDs

1. To which extent is the material structure of a III-V/Si solar cell similar to the material structure of a LED?
2. Do you think recycling technologies that are designed to recover Ga (gallium) from end-of-life LEDs could be effective for recovering Ga from end-of-life III-V/Si cells cells?

Splitting the III-V layers from the silicon in recycling

3. What method(s) do you think could be effective for splitting the top (III-V) cell from the bottom (Si) cell in recycling?
4. What would you change in the current cell design to make it more easily recyclable (design for recycling (DfR) approach)?

Technical-, environmental- and economic performance

5. What could be technical- and/or economic barriers to recover Ga/In from end-of-life III-V/Si solar cells?
6. Which Ga-recovery treatment (chemical, thermal and/or vacuum processes shown in the table on the next pages) could in your opinion be economically and environmentally preferable to the other treatments?

Comments/recommendations

7. Do you have any other comments and/or recommendations?

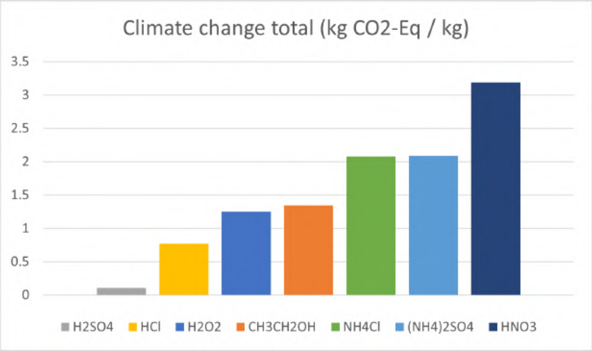
Appendix E - Critical raw materials needed for 1 gigawatt-peak production

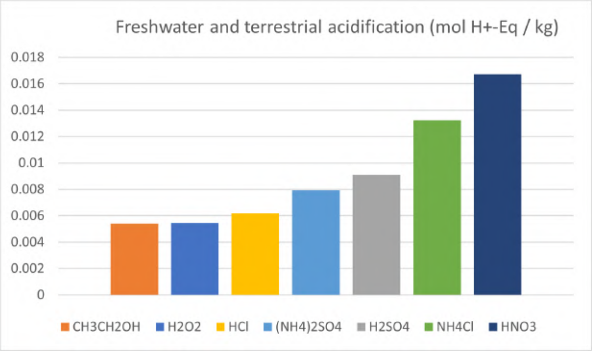
Table E1

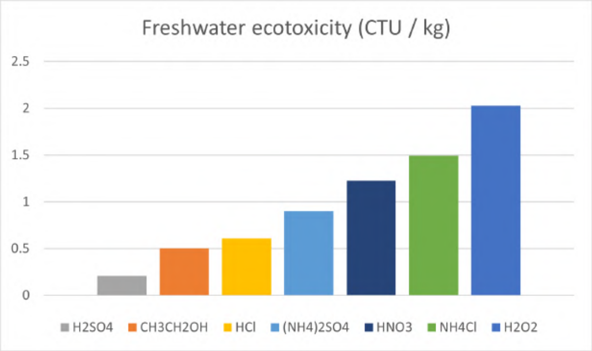
Critical raw materials needed for 1 gigawatt-peak production

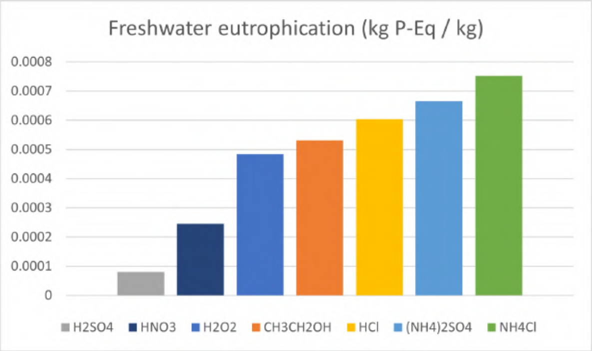
Round wafer (III-V) diameter	0.1	m			
Round wafer (III-V) area	0.00785	m2			
Square wafer (Si) area	0.02443	m2			
# cells	1.29E+08	/GWp			
Total area	3.16E+06	m2/GWp			
	g per 31 x 4" wafer	g per 1 x 244cm2 wafer	g / m2	To cell (%)	To waste/ recycling (%)
TMGa	21.77		89.41427384	90%	10%
TMIn	0.11099		0.455860829	95%	5%
Si		16	655.0	57%	43%
			g/GWp		
		TMGa	2.83E+08		
		TMIn	1.44E+06		
		Si	2.07E+09		
			ton/GWp	In cells	Scrap
		TMGa	282.5258896	254.2733006	28.25258896
		TMIn	1.44040186	1.368381767	0.072020093
		Si	2069.755413	1177.173391	892.582022
		Ga	176.2961551	158.6665396	17.62961551
		In	1.03415453	0.982446803	0.051707726

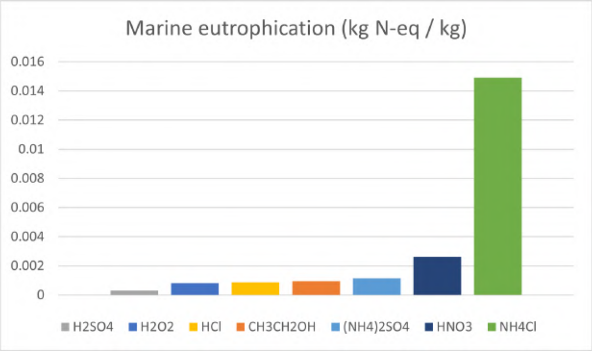
Appendix F - Life cycle impacts chemicals

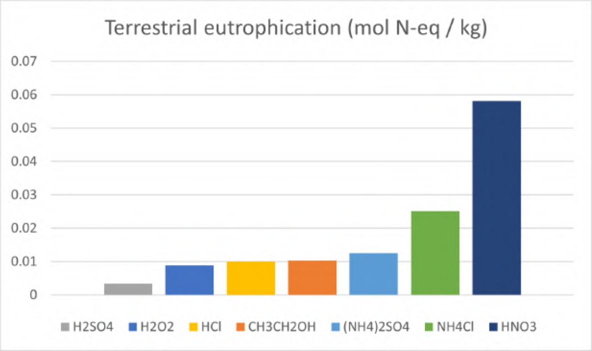


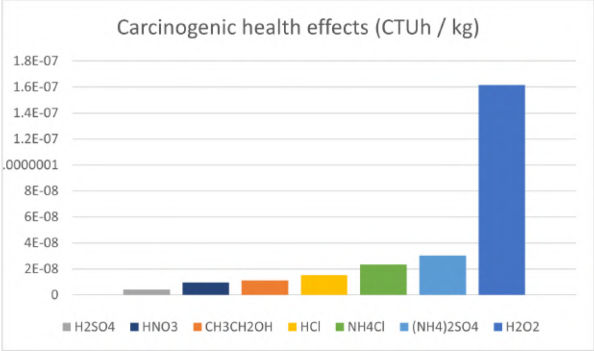


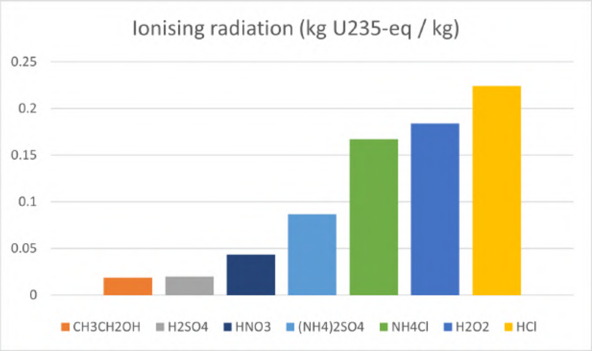


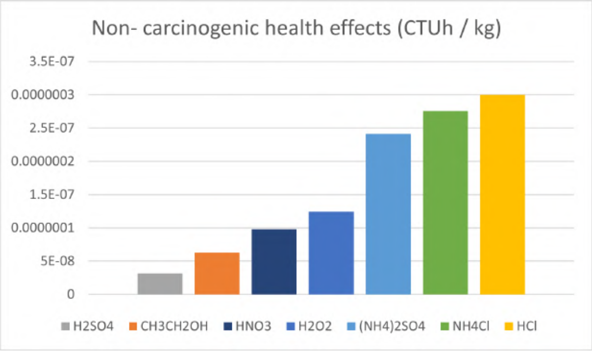


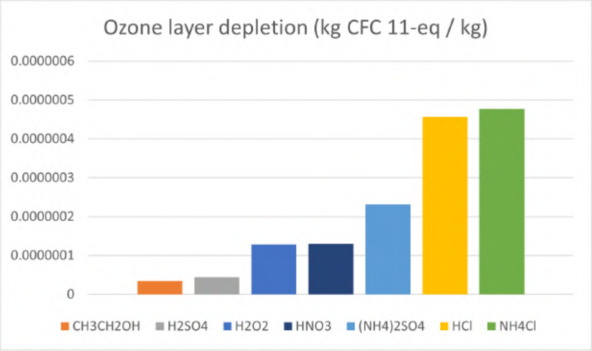


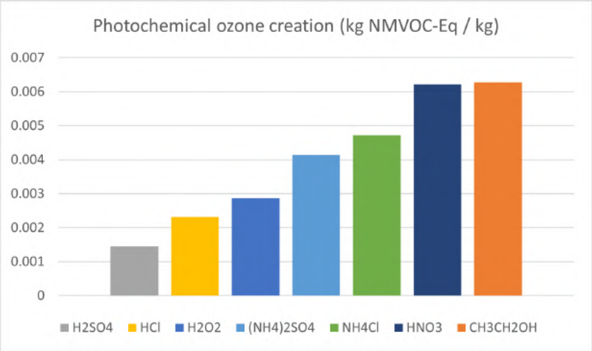


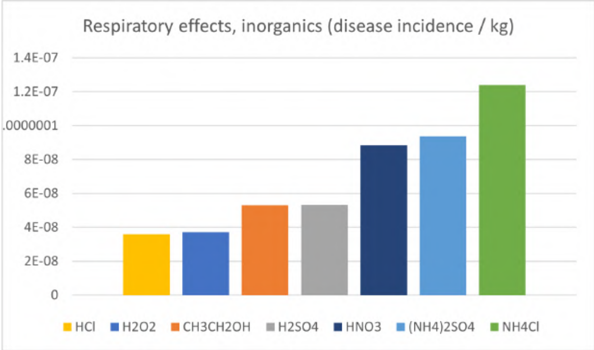


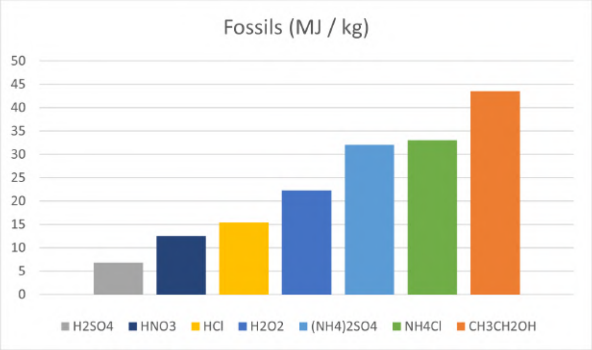


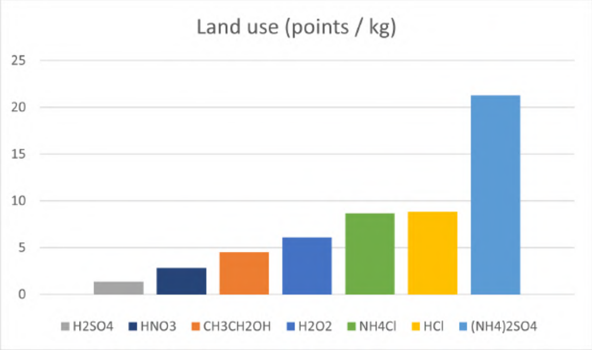





Photochemical ozone creation (kg NMVOC-Eq / kg)
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
H2SO4
HCl
H2O2
(NH4)2SO4
NH4Cl
HNO3
CH3CH2OH


Respiratory effects, inorganics (disease incidence / kg)
1.4E-07
1.2E-07
.0000001
8E-08
6E-08
4E-08
2E-08
0
HCl
H2O2
CH3CH2OH
H2SO4
HNO3
(NH4)2SO4
NH4Cl


Fossils (MJ / kg)
50
45
40
35
30
25
20
15
10
5
0
H2SO4
HNO3
HCl
H2O2
(NH4)2SO4
NH4Cl
CH3CH2OH


Land use (points / kg)
25
20
15
10
5
0
H2SO4
HNO3
CH3CH2OH
H2O2
NH4Cl
HCl
(NH4)2SO4

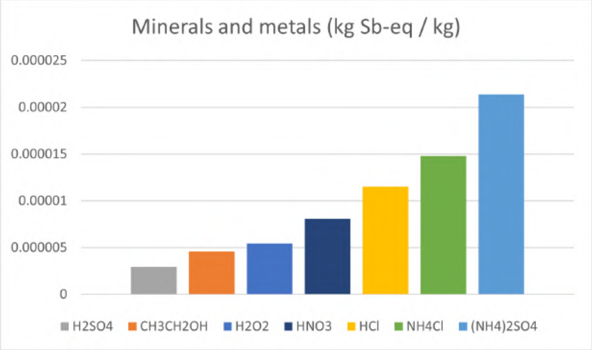

Minerals and metals (kg Sb-eq / kg)
0.000025
0.00002
0.000015
0.00001
0.000005
0
H2SO4
CH3CH2OH
H2O2
HNO3
HCl
NH4Cl
(NH4)2SO4

Table F1

Life cycle impact assessment results of chemicals that could be effective in recycling Ga

Ecoinvent v3.4 name	Hydrogen peroxide, without water, in 50% solution state	Ethanol, without water, in 99.7% solution state, from ethylene	Sulfuric acid	Hydrochloric acid, without water, in 30% solution state	
Corresponding chemical formula	H2O2	CH3CH2OH	H2SO4	HCl	
Location	RER	GLO	RER	RER	
Unit	kilogram	kilogram	kilogram	kilogram	**Unit**
Climate change | climate change total	1.249673209	1.343243513	0.108597335	0.772672247	**kg CO2-Eq**
Ecosystem quality | freshwater and terrestrial acidification	0.00545103	0.005410575	0.009111706	0.006192128	**mol H+-Eq**
Ecosystem quality | freshwater ecotoxicity	2.030025836	0.501354732	0.208199258	0.609570002	**CTU**
Ecosystem quality | freshwater eutrophication	0.000484659	0.000531154	8.07756E-05	0.000604106	**kg P-Eq**
Ecosystem quality | marine eutrophication	0.000818339	0.00095147	0.000305922	0.000877691	**kg N-Eq**
Ecosystem quality | terrestrial eutrophication	0.008893544	0.010289268	0.003320166	0.010018305	**mol N-Eq**
Human health | carcinogenic effects	1.61559E-07	1.11554E-08	4.29904E-09	1.52676E-08	**CTUh**
Human health | ionising radiation	0.184014844	0.018829517	0.019818112	0.224028411	**kg U235-Eq**
Human health | non-carcinogenic effects	1.24392E-07	6.29904E-08	3.14395E-08	2.9981E-07	**CTUh**
Human health | ozone layer depletion	1.27817E-07	3.37016E-08	4.37592E-08	4.56512E-07	**kg CFC-11-Eq**
Human health | photochemical ozone creation	0.002869414	0.006278009	0.00145038	0.002321282	**kg NMVOC-Eq**
Human health | respiratory effects, inorganics	3.71378E-08	5.30074E-08	5.32936E-08	3.59391E-08	**disease incidence**
Resources | dissipated water	0	0	0	0	**m3 water-Eq**
Resources | fossils	22.26975686	43.51380585	6.767180808	15.43983905	**MJ**
Resources | land use	6.092823178	4.536077176	1.352843104	8.847176489	**points**
Resources | minerals and metals	5.43201E-06	4.59897E-06	2.92735E-06	1.15212E-05	**kg Sb-Eq**

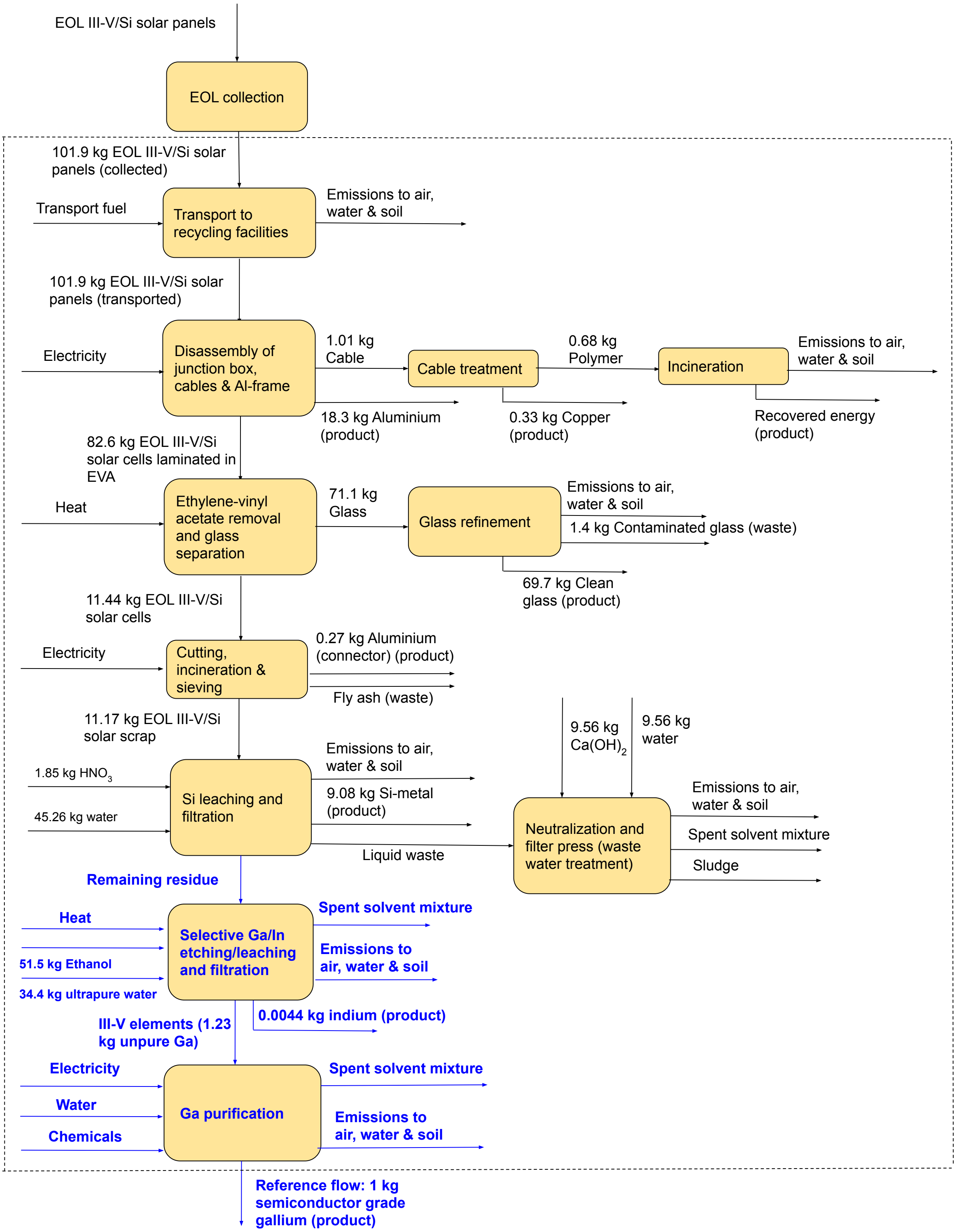
Table F1

Life cycle impact assessment results of chemicals that could be effective in recycling Ga

Ecoinvent v3.4 name	Ammonium sulphate, as N	Ammonium chloride	nitric acid, without water, in 50% solution state	
Corresponding chemical formula	(NH4)2SO4	NH4Cl	HNO3	
Location	RER	GLO	RER	
Unit	kilogram	kilogram	kilogram	**Unit**
Climate change | climate change total	2.085504423	2.077179839	3.189524576	**kg CO2-Eq**
Ecosystem quality | freshwater and terrestrial acidification	0.00793801	0.013252548	0.016732988	**mol H+-Eq**
Ecosystem quality | freshwater ecotoxicity	0.902956784	1.494923641	1.226526571	**CTU**
Ecosystem quality | freshwater eutrophication	0.000664893	0.000753238	0.000245608	**kg P-Eq**
Ecosystem quality | marine eutrophication	0.001144715	0.01490393	0.002623682	**kg N-Eq**
Ecosystem quality | terrestrial eutrophication	0.012542932	0.02514462	0.058077028	**mol N-Eq**
Human health | carcinogenic effects	3.02394E-08	2.3439E-08	9.44966E-09	**CTUh**
Human health | ionising radiation	0.086636643	0.167142293	0.043249298	**kg U235-Eq**
Human health | non-carcinogenic effects	2.41082E-07	2.75651E-07	9.7885E-08	**CTUh**
Human health | ozone layer depletion	2.31154E-07	4.77318E-07	1.30192E-07	**kg CFC-11-Eq**
Human health | photochemical ozone creation	0.004138052	0.004723434	0.006213642	**kg NMVOC-Eq**
Human health | respiratory effects, inorganics	9.36302E-08	1.23937E-07	8.83331E-08	**disease incidence**
Resources | dissipated water	0	0	0	**m3 water-Eq**
Resources | fossils	32.07411182	33.01780322	12.52034822	**MJ**
Resources | land use	21.29445233	8.65690133	2.833207107	**points**
Resources | minerals and metals	2.13692E-05	1.47785E-05	8.08861E-06	**kg Sb-Eq**

Appendix G - Recycling process flowchart

Figure G1
Recycling process flowchart



Appendix H - ILCD 2.0 2018 midpoint categories and their abbreviations

- Climate change | climate change total (CC)
- Ecosystem quality | freshwater and terrestrial acidification (AC)
- Ecosystem quality | freshwater ecotoxicity (FET)
- Ecosystem quality | freshwater eutrophication (FEU)
- Ecosystem quality | marine eutrophication (MEU)
- Ecosystem quality | terrestrial eutrophication (TEU)
- Human health | carcinogenic effects (HC)
- Human health | ionising radiation (IR)
- Human health | non-carcinogenic effects (HNC)
- Human health | ozone layer depletion (OD)
- Human health | photochemical ozone creation (POF)
- Human health | respiratory effects, inorganics (PM)
- Resources | dissipated water (RDW)
- Resources | fossils (RDF)
- Resources | land use (LU)
- Resources | minerals and metals (RDF)

Appendix I - Life cycle inventory results

Life cycle inventory results (Excel sheet)

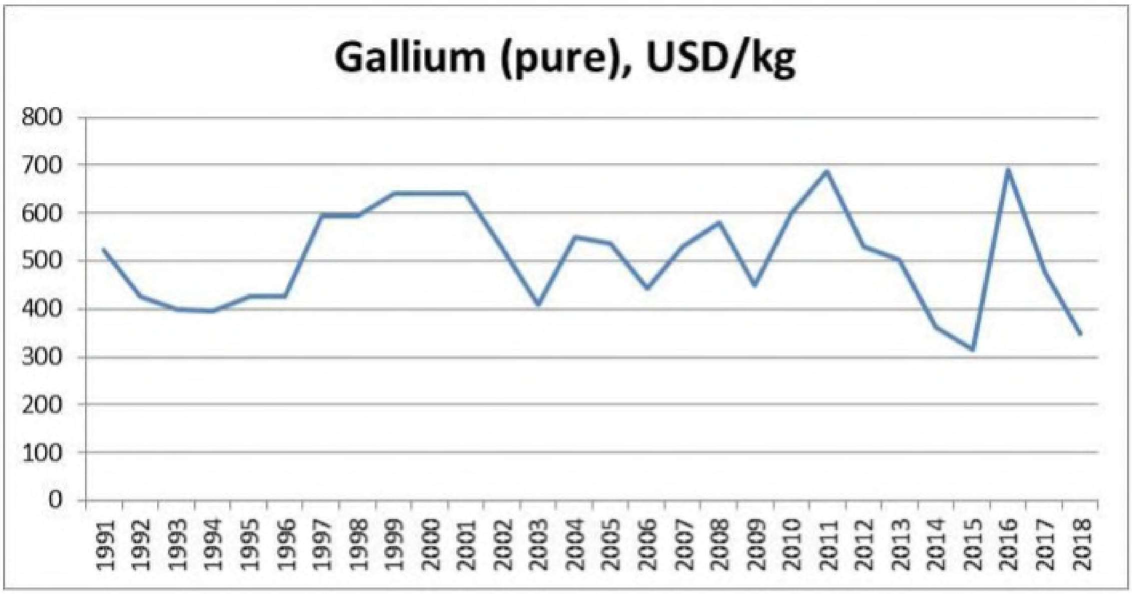
Appendix J - LCA results

LCA recycling product system (Excel sheet)

Appendix K - Price trend gallium

Figure K1

High purity gallium price trend 1991 - 2018, data from U.S. Geological Survey



Note. Reprinted from "European Commission, Study on the EU's list of Critical Raw Materials, Critical Raw Materials Factsheets (Final)", p. 224.

Appendix L - CBA sensitivity analysis data

Table L1

Yearly benefits & costs for recycling 1GWp III-V/Si PV panels, 35.4 tons Ga & 12.9 tons In recovered

Recovered materials	**Weight (tons)**	**Price (€/ton)**	**Revenues only bulk**	**Revenues bulk + Si, Ga & In**
Glass (clean)	19810	3160 (Kellenberger, 2017a)	€62,599,600	€62,599,600
Al	5351	806 (Bourgault, 2017a)	€4,312,906	€4,312,906
Cu	609	2840 (Parada Tur, 2017)	€1,729,560	€1,729,560
Si	1177	2320 (Bourgault, 2017b)	-	€2,730,640
Ga	35.4	300000 (Tuchschmid, 2017)	-	€10,620,000
In	12.9	855000 (Classen, 2017)	-	€11,029,500
Total benefits estimate			**€68,642,066**	**€93,022,206**
Used energy	**Amount (MJ)**	**Price (€/MJ)**		
Heat	71719	0.01 (Heck, 2017)	-	€717
	Amount (kWh)	**Price (€/kWh)**		
Electricity to recover bulk materials	3181330	0.1 (Treyer, 2017)	€318,133	€318,133
Electricity to recover Si, Ga & In	184676	0.1 (Treyer, 2017)	-	€18,468
Used chemicals	**Weight (tons)**	**Price (€/ton)**	**Costs only bulk**	**Costs bulk + Si, Ga, In**
Water (regular)	12499	4.6 (Jungbluth, 2017a)	-	€57,495
HNO_3	422	471 (Osses, 2017a)	-	€198,762
$Ca(OH)_2$	2570	110 (Kellenberger, 2017b)	-	€282,700
CH_3CH_2OH	4693	365 (Sutter, 2017a)	-	€1,712,945
Water (ultrapure)	3135	470 (Sutter, 2017b)	-	€1,473,450
EDTA	1474	1120 (Hischier, 2017a)	-	€1,650,880
Kerosene	87	297 (Jungbluth, 2017b)	-	€25,839
Fatty alcohol	9	2100 (Hischier, 2017b)	-	€18,900
$(CH_2)_4(COOH)_2$	6	1080 (Althaus, 2017)	-	€6,480
H_2SO_4	113	31 (Osses, 2017b)	-	€3,503
Transport costs	**Weight*distance (tons*km)**	**Price (€/(ton*km))**		
Transport	2577000 (bulk) 2699500 (bulk + Si, Ga, In)	0.03945 (Simons, 2017)	€101,663	€106,495
Other costs	**Weight (tons)**	**Price (€/ton)**		
Contaminated glass waste disposal	407	4.88 (Doka, 2017)	€1,986	€1,986
Liquid waste disposal	8903	4.88 (Doka, 2017)	-	€43,447
Hazardous waste disposal	1464	110[1]	-	€161,040
Personnel	25770 (bulk) 26995 (bulk + Si, Ga, In)	50[2](Bisselink & Steeghs, 2016)	€1,288,500	€1,349,750
Depreciation	25770 (bulk) 26995 (bulk + Si, Ga, In)	50[2] (Bisselink & Steeghs, 2016)	€1,288,500	€1,349,750
Maintenance	25770 (bulk) 26995 (bulk + Si, Ga, In)	40[2] (Bisselink & Steeghs, 2016)	€1,030,800	€1,079,800
Total costs estimate			**€4,029,582**	**€9,860,540**
Unexpected costs (10%)			€402,958	€986,054
Total costs estimate (Incl. unexpected costs)			**€4,432,540**	**€10,846,594**
Net benefits			**€64,209,526**	**€82,175,612**

[1] "How Much Does Hazardous Waste Disposal Cost in 2021?" (n.d.). Approximately 95 pound sterling/ton ≈ 110 euro/ton.

[2] The recycling facility for III-V/Si PV panels would process 1GWp of panels yearly, which are estimated to weight 28017 tons. With an assumed active time of 18-20 hours a day and 365 days a year, the recycling facility should be able to process 4 ton per hour. Bisselink & Steeghs (2016) estimate the personnel costs for a 2 ton/hour plant to be 25 euro/ton. Therefore the personnel costs are estimated to be 50 euro/ton. Similarly, the depreciation costs are estimated to be 50 euro/ton and the maintenance costs are estimated to be 40 euro/ton.

For Ga/In recoveries of respectively 26.6/11.1, 20.4/8.6 & 19.8/7.7 similar calculations were performed.

Table L2

Yearly net benefits and net present values for the two alternative recycling processes - Recycling only the bulk materials (glass, Al & Cu) or recycling both these bulk materials and the CRMs (Si, Ga & In), 35.4 tons Ga & 12.9 tons In recovered

Year	**Only bulk**	**Bulk + Si, Ga & In**
0	€-10,000,000	€-15,000,000
1	€-10,000,000	€-15,000,000
2	€64,209,526	€82,175,612
3	€64,209,526	€82,175,612
4	€64,209,526	€82,175,612
5	€64,209,526	€82,175,612
6	€64,209,526	€82,175,612
7	€64,209,526	€82,175,612
8	€64,209,526	€82,175,612
9	€64,209,526	€82,175,612
10	€64,209,526	€82,175,612
11	€64,209,526	€82,175,612
NPV (SDR 4%)	**€500,746,513**	**€611,459,447**