



LIFE CYCLE ASSESSMENT OF INTERFACE PASSIVATION PROCESSES IN THIN FILM SOLAR CELLS

PEDRO FILIPE RIBEIRO BERTOLUCI

TESE DE MESTRADO APRESENTADA
À FACULDADE DE ENGENHARIA DA UNIVERSIDADE DO PORTO
EM MEA-MESTRADO EM ENGENHARIA DO AMBIENTE

LIFE CYCLE ASSESSMENT OF INTERFACE PASSIVATION PROCESSES IN THIN FILM SOLAR CELLS

PRESENTED BY

PEDRO FILIPE RIBEIRO BERTOLUCI

Dissertation presented to obtain the degree of

MASTER'S IN ENVIRONMENTAL ENGINEERING

Supervisor at INL: Doctor António Vilanova

Supervisor at FEUP: Doctor Paula Dias

DEVELOPED WITHIN THE COURSE OF DISSERTATION

held in

Nanofabrication for Optoelectronic Applications (NOA) group -
International Iberian Nanotechnology Laboratory (INL) in collaboration
with the Laboratory for Process Engineering, Environment,
Biotechnology and Energy

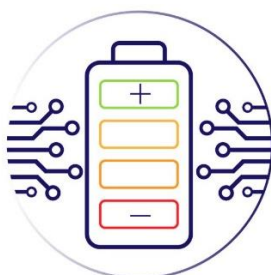
This dissertation his thesis received financial and technical support from: i) Base Funding - UIDB/00511/2020 of the Laboratory for Process Engineering, Environment, Biotechnology and Energy - LEPABE - funded by national funds through the FCT/MCTES (PIDDAC); ii) Projects SunFlow POCI-01-0145-FEDER-030510 and HopeH2 POCI-01-0145-FEDER-030760, both funded by FEDER funds through COMPETE2020 - POCI and by national funds (PIDDAC) through FCT/MCTES; iii) project Baterias 2030, with the reference POCI-01-0247-FEDER-046109, co-funded by Operational Programme for Competitiveness and Internationalisation (COMPETE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF); and iv) the Development of novel Ultrathin solar cell architectures for low-light, low-cost and flexible opto-electronic devices project (028075) co-funded by FCT and the ERDF through COMPETE2020.



REPÚBLICA
PORTUGUESA



UNIÃO EUROPEIA
Fundo Europeu de
Desenvolvimento Regional



BATERIAS
2030

Acknowledgements

Throughout this thesis, I have received a tremendous amount of help from many people.

Firstly I would like to give my warmest thanks to my supervisors at INL and FEUP, Doctor António Vilanova and Doctor Paula Dias, respectively, their expertise and scientific knowledge were of the utmost value as well as their treatment regarding my opinions and always ready to support my decisions and advise at the best of their abilities. Their motivation, encouragement, and teaching allowed me to bring this work to a higher level.

To the NOA group, where LCA was not a discipline of great focus, a gigantic thank you for the way you all welcomed me and made me feel included over these short four months I have spent with you, something I will truly never forget. Special mention to Tomás Lopes for the patience he had with me, the countless hours spent teaching me about the procedures in the cleanroom, which were incredibly valuable to ensure that this LCA study was the most complete it could be; also to Xavier Pinheiro and João Barbosa, a big thank you for the hours spent solving some problems that appeared during this thesis. Last, but not least, to Pedro Salomé for allowing me to have this incredible opportunity to work in such a prestigious institution as INL and to Jennifer Teixeira for the introduction to the CIGS topic and the work that is developed at NOA.

Special mention to my long-lasting friends, Daniel Carneiro, Mariana Barbosa, Tiago Barbosa, and Tiago Rodrigues, for the motivation, ideas, friendship, brotherhood, and support in my most desperate times. From the bottom of my heart, thank you.

To my parents Amélia and José, none of this could have been possible without you, from the very first day I was born you both fought tooth and nail so that I would never miss a thing, you gave me all conditions I could have asked for to become the very best person I can be. My brother Tiago, what more can I say than thank you for caring for me and making sure I was always well.

To Ana Amaral, one of the best people university has given me, my appreciation for what you have done for me knows no limits. Your kindness, and friendship I will always take very close to my heart. To Ana Soares, Beatriz Gomes, Beatriz Ribeiro, and Gabriela Santos thank you for your friendship, for all the laughs and memories we created together.

To my partner, Leonor Ribeiro de Almeida, without your motivation and support, I would not have made it this far, I hope to be able to keep discovering new and exciting things alongside you. Thank you for your friendship, patience and, most importantly, your love.

ABSTRACT

The increasing demand for energy over the last decades is one of the hardest battles of mankind, mainly due to the continuous dependence on fossil fuels for energy production, leading to severe social, health, economic and environmental consequences. Photovoltaic (PV) solar cells are a promising route to decarbonize the energy sector. Although the PV market is dominated by silicon-based solar cells, thin film cells have been on the headlines due to the remarkable increase in efficiency they have experienced and due to their flexibility, lightness, and low amount of required materials to be produced. Interface passivation processes are an efficient route to further optimize the performance of these cells. Still, it is important to understand if the environmental impact added by this production process outweighs the green benefits of the increase in efficiency. Life cycle assessment (LCA) is one of the most powerful tools to answer this question.

This study aimed at assessing the environmental impact of the interface passivation process performed by the NOA group at INL, in thin film Cu(In,Ga)Se₂ (CIGS) solar cells. The process was observed first-hand with visits to the clean room, allowing to make a complete inventory of inputs, outputs, and electricity consumption. The environmental impact was then quantified considering fourteen 5 x 5 cm² glass substrates as functional unit. SimaPro software, complemented with the ecoinvent database, the CML-IA methodology and the EU 25 normalization factors, were used to perform the calculations. It was concluded that the Si oxide etch is the most impactful subprocess, mainly due to the need of repeating this step, since the equipment of the clean room is optimized for Si wafers with a diameter of 20 cm and not for small square samples. The environmental impact was mainly attributed to the significant use of C₄F₈ gas, which has a high effect on human toxicity, ozone layer depletion, freshwater aquatic ecotoxicity, and marine aquatic ecotoxicity. Optimizing this subprocess for fourteen glass substrates, *i.e.* performing it once, would result in a 37.44 % decrease in the overall environmental impact.

To have a holistic view of the obtained results, the environmental impact of the passivation process was recalculated for different world leading PV producers. By varying the origin of the energy mix, it was concluded that a higher environmental impact would be achieved in Asian countries (China, South Korea, and Malaysia). Finally, it was concluded that four months are necessary to neutralize the environmental impact brought by the NOA passivation process, considering an efficiency increase of *ca.* 1.33% for passivated CIGS solar cells.

KEYWORDS: Life Cycle Assessment, CIGS Solar Cells, Interface Passivation Processes, Environmental Engineering, Photovoltaic Cells, Solar Energy, Energy Decarbonization.

RESUMO

A crescente procura de energia nas últimas décadas é uma das batalhas mais duras da humanidade, principalmente devido à contínua dependência dos combustíveis fósseis para a produção de energia, trazendo graves consequências a nível da saúde, social, económico e ambiental. As células solares fotovoltaicas (PV) são uma via promissora para descarbonizar o sector energético. Embora o mercado seja dominado por células solares de silício, as células de filme fino têm estado em foco devido ao aumento da sua eficiência e devido à sua flexibilidade, leveza e baixa quantidade de materiais necessários para a sua produção. Os processos de passivação de interface são uma via eficaz para otimizar ainda mais o desempenho destas células. Ainda assim, é importante compreender se o impacto ambiental acrescentado por este processo de produção compensa em termos ambientais, relativamente ao aumento da eficiência. A avaliação do ciclo de vida (ACV) é uma das ferramentas mais poderosas para responder a esta pergunta.

Este estudo tem como objetivo avaliar o impacto ambiental do processo de passivação de interface em células solares CIGS de filme fino, realizado pelo grupo NOA no INL. O processo foi observado em primeira mão com visitas à sala limpa, permitindo fazer um inventário completo de entradas, saídas, e consumo de eletricidade. O impacto ambiental foi então quantificado considerando catorze substratos de vidro de 5 x 5 cm² como unidade funcional. O software SimaPro, complementado com a base de dados ecoinvent, a metodologia CML-IA e os fatores de normalização da UE 25, foram utilizados para efetuar os cálculos. Concluiu-se que o ataque químico com óxido de silício é o subprocesso mais impactante, uma vez que o equipamento da sala limpa é otimizado para waffers de silício com um diâmetro de 20 cm e não para amostras quadradas de áreas reduzidas. O impacto ambiental foi principalmente atribuído à utilização significativa do gás C₄F₈, que tem um efeito elevado na toxicidade humana, na destruição da camada de ozono, na ecotoxicidade aquática de água doce, e na ecotoxicidade aquática marinha. Caso este subprocesso seja executado uma única vez, poderia alcançar-se uma diminuição de 37,44 % do impacte ambiental global.

Para se ter uma visão holística dos resultados obtidos, o impacto ambiental do processo de passivação foi recalculado para os líderes mundiais de produção de painéis PV. Variando a origem da mistura energética, concluiu-se que o impacto ambiental mais elevado seria nos países asiáticos (China, Coreia do Sul e Malásia). Finalmente, foi possível concluir que são necessários quatro meses para neutralizar o impacto ambiental trazido pelo processo de passivação do NOA, considerando um aumento de eficiência de cerca de 1,33%.

PALAVRAS-CHAVE: Avaliação do Ciclo de Vida, Células Solares CIGS, Processos de Passivação de Interface, Engenharia Ambiental, Células Fotovoltaicas, Energia Solar, Descarbonização de Energia

I declare, under oath, that this work is original and that all non-original contributions were properly referenced with identifying the source.

.

A handwritten signature in blue ink that reads "Pedro Bertolucci". The signature is written in a cursive, flowing style.

Pedro Filipe Ribeiro Bertoluci

Porto, 22 de Fevereiro de 2022

LIST OF CONTENTS

1	INTRODUCTION.....	1
1.1	<i>BACKGROUND AND MOTIVATION.....</i>	<i>1</i>
1.2	<i>OBJECTIVES OF THIS WORK AND PROJECT PRESENTATION.....</i>	<i>6</i>
1.3	<i>INL - NOA and FEUP - LEPABE</i>	<i>6</i>
1.4	<i>MAIN CONTRIBUTIONS OF THIS WORK.....</i>	<i>7</i>
1.5	<i>OUTLINE OF THIS WORK</i>	<i>7</i>
2	CONTEXT AND STATE OF THE ART	9
2.1	<i>WORKING PRINCIPLES OF PHOTOVOLTAIC CELLS</i>	<i>9</i>
2.1.1	<i>SILICON BASED SOLAR CELLS</i>	<i>11</i>
2.1.2	<i>THIN FILM SOLAR CELLS.....</i>	<i>12</i>
2.2.	<i>THE FUNDAMENTALS OF LIFE CYCLE ASSESSMENT.....</i>	<i>14</i>
2.2.1.	<i>GOAL AND SCOPE DEFINITION.....</i>	<i>15</i>
2.2.2.	<i>INVENTORY ANALYSIS.....</i>	<i>16</i>
2.2.3.	<i>IMPACT ASSESSMENT</i>	<i>17</i>
2.2.4.	<i>INTERPRETATION</i>	<i>18</i>
2.2.5.	<i>STRENGTHS AND LIMITATIONS.....</i>	<i>19</i>
3	TECHNICAL PROCEDURES AND MATERIALS	20
3.1	<i>GOAL AND SCOPE OF THIS STUDY</i>	<i>20</i>
3.1.1	<i>FUNCTIONAL UNIT</i>	<i>25</i>
4	RESULTS AND DISCUSSION.....	32
4.1	<i>ENVIRONMENTAL IMPACT OF THE NOA PASSIVATION PROCESS</i>	<i>32</i>
4.2	<i>HOLISTIC ANALYSIS TO THE NOA'S PASSIVATION PROCESS.....</i>	<i>38</i>
4.3	<i>ASSESSMENT OF THE ENVIRONMENTAL PERFORMANCE OF PASSIVATED CIGS SOLAR CELLS</i>	<i>42</i>
5	CONCLUSIONS	44

6	CLOSING REMARKS AND SUGESTIONS FOR FUTURE WORK.....	46
7	REFERENCES.....	49
	ANNEX A - OVERVIEW OF THE INVENTORY OF THE PASSIVATION PROCESS	52
	ANNEX B - INTERIM STEPS OF SIMAPRO	53
	ANNEX C - CHARACTERIZED VALUES OF THE NOA SUBPROCESSES REGARDING THE STUDIED ENVIRONMENTAL CATEGORIES.....	55
	ANNEX D - SUBSTANCES WITH THE HIGHEST CONTRIBUTION FOR EACH ENVIRONMENTAL CATEGORY	56
	ANNEX E - RELATIVE CONTRIBUTION OF EACH SUBPROCESS OF THE NOA PASSIVATION PROCESS FOR DIFFERENT ENVIRONMENTAL IMPACT CATEGORIES	61
	ANNEX F - ENERGY MIX FOR PORTUGAL, CHINA, USA, MALAYSIA, AND SOUTH KOREA.	66
	ANNEX G - RELATIVE CONTRIBUTION OF THE PASSIVATION SUBPROCESSES TO THE TOTAL NORMALIZED IMPACT CALCULATED FOR THE WORLD LEADING COUNTRIES IN PV SOLAR PANELS MANUFACTURING	67
	ANNEX H - NORMALIZED ENVIRONMENTAL IMPACT VALUES FOR THE ENVIRONMENTAL IMPACT CATEGORIES UNDER STUDY.....	70

LIST OF FIGURES

<i>Figure 1 - Global temperature differences for 2021 compared to the 1951-1980 timeframe. (extracted from [5])</i>	<i>1</i>
<i>Figure 2 - Highest contributors of GHG emissions by sector and the corresponding subsectors for the energy case. (adapted from [6])</i>	<i>2</i>
<i>Figure 3 - Installed capacity of renewable sources and their share between 2015 and 2020(adapted from [14])......</i>	<i>4</i>
<i>Figure 4 - Working principles and components of a general PV solar cell (adapted from ref [24]).....</i>	<i>10</i>
<i>Figure 5 - Siemens Process used for production of Polysilicon (adapted from ref [31]). ..</i>	<i>11</i>
<i>Figure 6 - Typical structure of a CIGS solar cell, comprising six different layers: a substrate black metal electrode (usually soda lime glass - SLG) covered with Mo, a p-type absorber (CIGS) film, a buffer thin layer based on CdS, and a transparent conducting oxide (adapted from the NOA group database).</i>	<i>13</i>
<i>Figure 7 - Representation of the fabrication process of a passivated CIGS solar cell. [47]</i>	<i>14</i>
<i>Figure 8 - Framework of the ISO 14040 standard.</i>	<i>15</i>
<i>Figure 9 - Main steps of the clean room procedure developed by the NOA group at INL for the passivation layers on CIGS solar cells, schematized in a black box arrangement.....</i>	<i>21</i>
<i>Figure 10 - SLG substrates after the passivation process.</i>	<i>21</i>
<i>Figure 11 - HMDS Prime Oven used at INL.....</i>	<i>22</i>
<i>Figure 12 - Obducat equipment used during the NIL subprocess.....</i>	<i>23</i>
<i>Figure 13 - NOA associated rolling the IPS stamp onto the SLG substrates.....</i>	<i>23</i>
<i>Figure 14 - SPTS Pegasus machine used for the removal of the residual layer.....</i>	<i>24</i>
<i>Figure 15 - Quanta FEI electron microscope.</i>	<i>24</i>
<i>Figure 16 - Cleanroom garments used by the NOA associates.....</i>	<i>28</i>
<i>Figure 17 - Impact of each phase from the passivation process from all the studied environmental impact categories.</i>	<i>33</i>
<i>Figure 18 - Environmental impact of each subprocess involved in the passivation of CIGS solar cells.....</i>	<i>35</i>
<i>Figure 19 - Environmental impact associated with all subprocesses, considering that the Si oxide etch is performed only once.</i>	<i>36</i>
<i>Figure 20 - Categories with the most environmental impact associated.</i>	<i>37</i>
<i>Figure 21 - Impact on the Ozone Layer Depletion of the NOA process in the world's leading PV solar cells producers.....</i>	<i>38</i>
<i>Figure 22 - Impact on the Fresh Water Aquatic Ecotoxicity of the NOA process in the world leading PV solar cells producers.....</i>	<i>39</i>

<i>Figure 23 - Impact in the Abiotic Depletion - Fossil Fuels of the NOA process in the world's leading PV solar cells producers.....</i>	<i>40</i>
<i>Figure 24 - Impact on Acidification of the NOA process in the world's leading PV solar cells producers.</i>	<i>40</i>
<i>Figure 25 - Impact in Eutrophication of the NOA process in the world's leading PV solar cells producers.</i>	<i>40</i>
<i>Figure 26 - Total Normalized Impact of the NOA passivation process, assuming that it would be carried out in the world's leading countries of PV cells manufacturing.</i>	<i>41</i>

LIST OF TABLES

<i>Table 1 - Experimental conditions of the NIL process.</i>	<i>22</i>
<i>Table 2 - Material Inputs of the 14 subprocesses in the NOA process.</i>	<i>25</i>
<i>Table 3 - Energy Consumption of the 14 subprocesses in the NOA process.</i>	<i>26</i>
<i>Table 4 - Outputs of the 14 subprocesses in the NOA process.</i>	<i>26</i>
<i>Table 5 - Normalization Factors used during the Normalization phase.</i>	<i>29</i>
<i>Table 6 - Normalization calculations of Stamford et 2019.</i>	<i>30</i>
<i>Table 7 - Total Normalized Impact of the production of 1kWh.</i>	<i>31</i>
<i>Table 8 - Studied Environmental Categories and their respective units of measurement.</i>	<i>32</i>
<i>Table 9 - Environmental payback time of standard CIGS solar cells and passivated CIGS solar cells using the NOA process, expressed in the necessary years to neutralize the environmental impact of the manufacturing process relative to the avoided environmental impact of energy production in world leading countries of installed PV capacity per capita.</i>	<i>41</i>

NOMENCLATURE

VARIABLES

Variables	Definition	Unit
CF	Characterization Factor	kg
E	Pollutant/Substance Emission	kg
N	Normalization Factor	Dimensionless
PI	Potential Impact	kg

SUBSCRIPTS

Subscripts	Definition
eq	Equivalent
I	Environmental Impact Category
x	Pollutant/Substance

ABBREVIATION

Abbreviation	Definition
AC	Alternate Current
a-Si	Amorphous Silicon
CIGS	Cadmium Indium Gallium Selenide
CML-IA	Institute of Environmental Sciences - Impact Assessment
CRMs	Critical Raw Materials
c-Si	Crystalline Silicon
CVD	Chemical bath deposition
DC	Direct Current
EPD	Environmental Product Declaration
eV	Electron Volt
FCT	Foundation for Science and Technology
GHG	Green House Gases

GHS	Global Harmonized System
HMDS	Hexamethyldisilazane
INL	International Iberian Nanotechnology Laboratory
i-ZnO	Intrinsic Zinc Oxide Layer
LCA	Life Cycle Assessment
LEPABE	Laboratory for Process Engineering, Environment, Biotechnology and Energy
MG	Metallurgical Grade
NIL	Nanoimprint Litography
NGO	Non-Governmental Organization
NOA	Nanofabrication for Optoelectronic Applications
ODP	Ozone Layer Depletion
PECVD	Plasma Enhanced Chemical Vapor Deposition
PFA	Per- and polyfluoroalkyl substances
PV	Photovoltaic
SLG	Soda-Lime Glass
STC	Silicon Tetrachlorosilane
STU	Simultaneous Thermal and UV
TCO	Transparent Conducting Oxide
TCS	Trichlorosilane
Traci	Tool for Reduction and Assessment of Chemicals and Other Environmental Impacts

1 INTRODUCTION

1.1 BACKGROUND AND MOTIVATION

Energy is a cornerstone of the global economy and modern lifestyle. Due to the world population increase and industrialization, global energy demand is estimated to increase by 4.6% in 2021, surpassing pre-Covid-19 levels. [1] Fossil fuels (coal, oil, and natural gas) have been powering economies for the last 150 years, serving as the main energy source for all kind of human activities, from transportation, agriculture, industry, to land use. With a current supply of > 80% of the world's primary energy consumption, the demand for all fossil fuels is set to continuously grow. [2]

The use of fossil fuels has a direct consequence on greenhouse gases (GHG) emissions, which include mainly carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and the so-called fluorinated gases (hydrofluorocarbons and perfluorocarbons) and sulphur hexafluoride (SF_6). [3] The GHG emissions act as a barrier that absorbs infrared radiation while stopping it from going into outer space. [4] The outcome is the temperature increase at the surface of the planet and in the atmosphere, which promotes so-called global warming. [2] Taking the late 19th century, *i.e.* from 1850 to 1900, as a benchmark for the pre-industrial times, the Earth's global average surface temperature has risen *ca.* 1.2 °C; 2016 and 2020 were the two warmest years since the 1880s. [5] According to the Berkeley Earth global temperature report from 2021, it is possible to see the global temperature changes from the 1951-1980 period until 2021 - Figure 1.

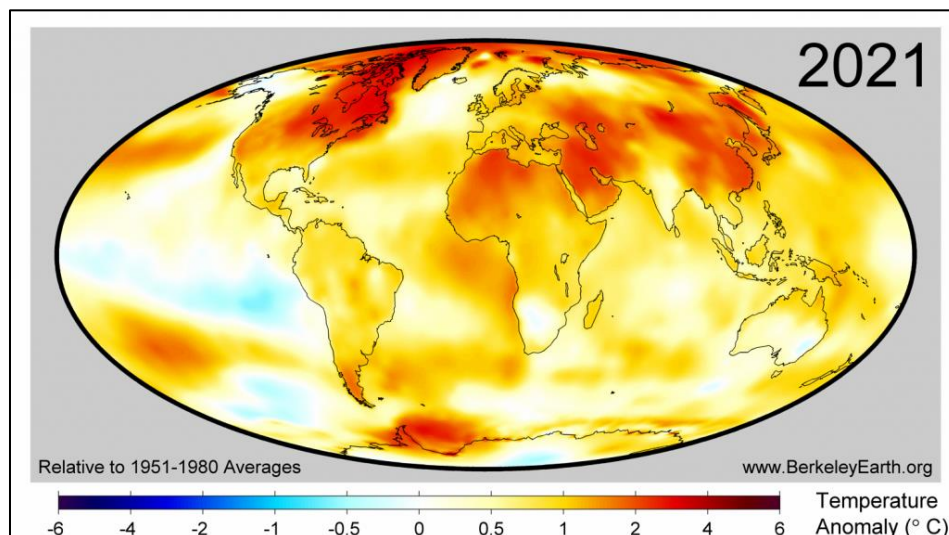


Figure 1 - Global temperature differences for 2021 compared to the 1951-1980 timeframe. (extracted from [5])

Usually, the global average increase in temperature is given by the combined increase on land and surface of the ocean. However, the ocean surface tends to absorb more heat than land, due to the specific heat capacity of water. This effect is also noticeable in Figure 1, as the temperature increase on land in 2021 was *ca.* 1.32 °C, whereas on the ocean surface was *ca.* 0.59 °C. Moreover, the northern hemisphere has experienced a higher increase in temperature, which has led to severe climate impacts, such as glaciers melting. [6] According to the Climate Analysis Indicators Tool (World Resources Institute), the majority of GHG sources come from the energy sector - Figure 2. [7]

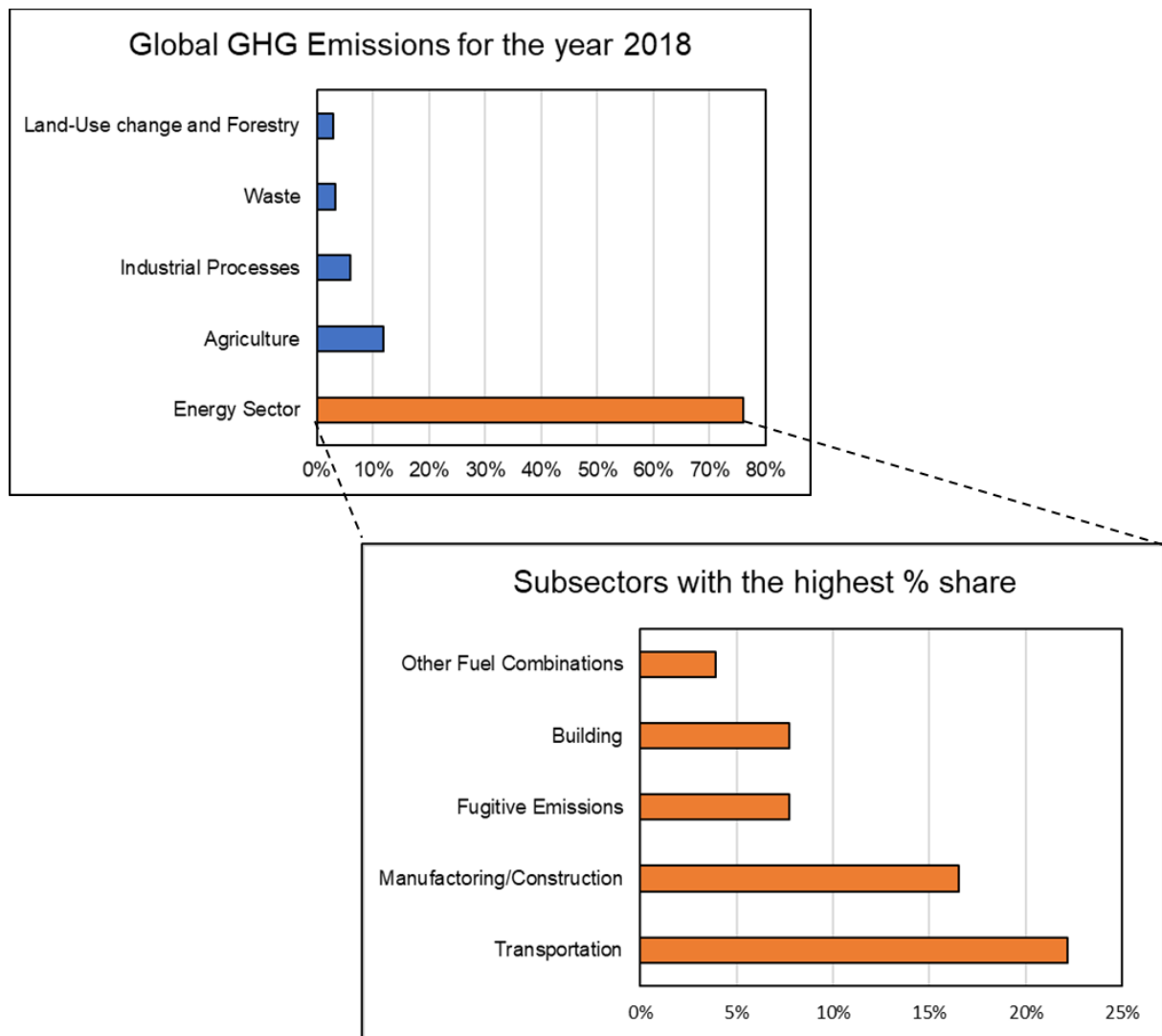


Figure 2 - Highest contributors of GHG emissions by sector and the corresponding subsectors for the energy case. (adapted from [6])

Within the energy sector, electricity and heat are the major contributors to GHG emissions, accounting for 42 %, whereas transportation accounts for 22 %, followed by manufacturing, and construction, accounting for *ca.* 17 %, other fuel combustion for *ca.* 8 %, and finally fugitive emissions for *ca.* 4 % - Figure 2. Since the energy sector is the largest

contributor to GHG emissions, energy decarbonization is the most important challenge that humanity faces nowadays, e.g. by reducing the amount of fossil fuels used for electricity supply and heat generation, while encouraging the use of public transportation and increasing the share of renewable sources.[6] Therefore, to develop a long-term and sustainable energy economy and face the consequences of climate change, governmental institutions have created multiple frameworks, such as:

- i. The European Green Deal [8]: aims at EU's climate, energy, transport and taxation policies for reducing net greenhouse gas emissions by at least 55 % by 2030, compared to 1990 levels.
- ii. Paris Agreement - United Nations Framework Convention on Climate Change [9]: seeking to avoid dangerous climate change by limiting global warming to at least 2 °C, pursuing efforts to limit it to 1.5 °C, while supporting countries in their battle against the impacts of climate change.
- iii. Green Paper: A 2030 climate and energy framework [10]: integrating a variety of different policy objectives, such as reducing GHG emissions, securing energy supply, and supporting growth, competitiveness and jobs, through high technology, cost-effective and resource-efficient approaches.
- iv. A policy framework for climate and energy in the period from 2020 to 2030.[11]

Renewable energy sources are the best alternative for the world's current dependence on fossil fuels, also giving a substantial contribution to energy decarbonization. Demand for renewables grew by 3 % in 2020 and is set to increase across all key sectors (power, heating, industry, and transport) in 2021; the share of renewables in electricity generation is projected to increase to ca. 30 %.[12] Solar energy is the most abundant renewable energy source on Earth, striking the planet with 120 PW of radiation at any time. Therefore, harvesting even a small fraction (< 0.1 %) of this clean renewable energy source would be enough to supply the world's energy needs. As an example, only 0.16 % of the Earth's surface area needs to be covered with 10 % efficient solar photovoltaic (PV) cells to fulfil the current humankind energy consumption of ca. 2.00×10^{10} kW.[13] Solar electricity production rose to a record of 1.30×10^{15} kJ in 2020, or almost 20 %, with its capacity expanding by 1.27×10^8 kW.[14] According to the International Renewable Energy Agency, from 2015 to 2020 the installed capacity of solar PV rose from 11.30 % to 24.30 % - Figure 3.[15]

The most promising and commercially available solar technologies are: i) solar PV panels, which are used for sunlight harvesting and conversion into electricity; ii) solar-thermal panels or solar collectors, where a fluid (usually water) flows through the panels and gets heated by absorbed solar energy, allowing to simultaneously store solar energy; and iii) concentrated solar power systems, which use mirrors or lenses to collect and concentrate solar radiation and convert it into heat. When concentrated light is converted to heat (solar

thermal energy), a heat engine (typically a steam turbine) linked to an electrical power generator or a thermochemical reaction generates electricity. [16, 17]

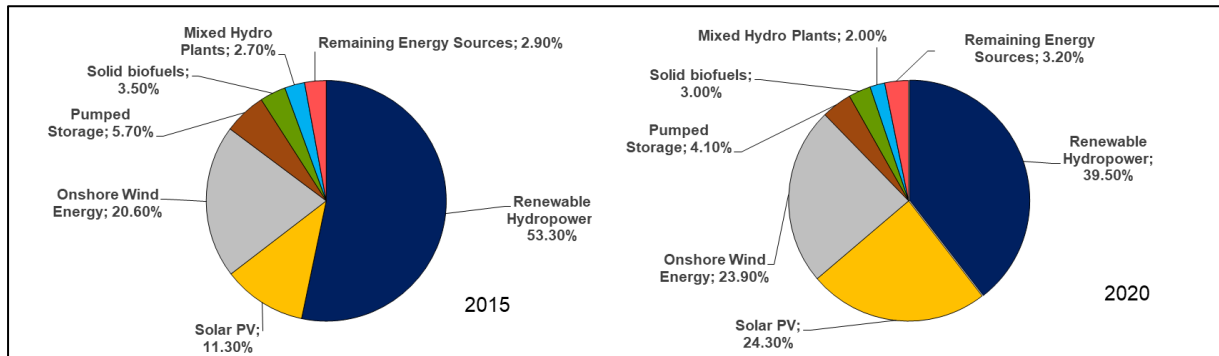


Figure 3 - Installed capacity of renewable sources and their share in 2015 and 2020. (adapted from [14]).

In terms of current market representativeness, PV panels can be divided into two categories: i) silicon-based technologies, the most well-known and leader in sales, with a 90 % representation on the market, and ii) thin film technologies, accounting for the remaining 10 %. [18] Silicon-based PVs present laboratory energy conversion efficiencies of over 25 % for single-crystal cells and over 20 % for multi-crystalline cells, whereas the industrial modules achieve efficiencies ranging from 18 % to 22 % under standard testing conditions. [19] Thin film solar cells based on $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) are among the most efficient polycrystalline solar cells with a world record of light to power conversion efficiency value of 23.35 %, surpassing CdTe thin film and even polycrystalline silicon solar cells. [20] Moreover, thin film solar cells have also become very attractive due to their high optical absorption coefficient, tuneable bandgap, fairly benign grain boundaries as well as low thicknesses of used materials, shorter payback period, monolithic integration, low-temperature and scalable fabrication procedures, and transparency. [21]

For pursuing a prominent position in the PV industry, the developments in the CIGS technology aim at: i) decreasing the CIGS thickness to the sub-micrometre range, with the light to power conversion efficiency reaching values as high as 15.20 % for a 490 nm thick CIGS device and 17.50 % for a 900 nm thick CIGS device; and ii) reducing the low interface recombination with a rear interface passivation strategy. [22] The CIGS thickness reduction from the standard 2 μm to the ultrathin range will allow for a reduction in production costs by increasing machine throughput. Moreover, the thickness reduction is in line with the recommendations from a recently conducted life cycle assessment study of CIGS PV installations that encourages a continuous reduction in the usage of the rare metals, allowing for lower production costs and lower environmental impact. [23] Concerning the interface passivation, this study is of the utmost importance to design a new generation of CIGS device architectures that permit achieving even higher levels of electrical performance.

Despite the recent advancements in PV solar cells and especially on the CIGS technology, not everything is positive like in many other technologies. For PV-power plants, land use can be a problem, especially when these facilities are located close to sensitive ecosystems, natural parks, or biodiversity endangered zones. Also, the application of a PV system in arable areas can raise social disagreements and indignation.[24] Other significant environmental impacts can arise from the fabrication stage, like the depletion of natural resources, and intensive energy use. Indeed, large amounts of bulk materials are needed, with thin film cells requiring less primary energy per generated Watt than the silicon-based ones. Finally, the use of toxic materials, such as cadmium, can significantly hinder the image of PV cells as an environmentally-friendly product.[24] To decrease the environmental impact associated with these cells, it is vital to determine what phase of the product life cycle is the most environmentally critical, from raw materials extraction, passing by the production and manufacturing phases, going through a period of use and closing with end-of-life activities. After knowing what phase possesses the greatest environmental impact, an assessment must be made to understand where that impact comes from. For example, if electricity is the main cause of impact, then the focus should be on reducing its consumption, or, if a certain material is the main source of impact, other substances that can be used as a replacement should be pursued, without affecting the overall quality and performance of the product.

One of the best ways to assess the environmental impact of a given technology, and also to conclude its environmental performance relative to its efficiency, is through the use of Life Cycle Assessment (LCA) tools. In short, an LCA is an instrument that can be used to evaluate the environmental impact of a product, process, or service throughout its life cycle, based on an intensive and extensive inventory of the energy and material flows involved in the processes under study.[25] LCA studies are also a very valuable tool for the early stage of the products' life cycle since redesigning a product or a process usually comes at a lower cost compared to the later stages of the life cycle.[26] This thesis aims to provide a detailed LCA for a specific process of interface passivation of CIGS and support the materials choice and environmental guidelines for future industrialization. In this work, the LCA study was performed for the NOA's interface passivation procedure. It should be emphasized that each deposition step comprises a high level of complexity and that there are quite a few LCA studies on CIGS solar cells, especially those focusing on the passivation processes. Therefore, the available data are very scarce as well as finding its flaws and learning how to improve them has been revealed to be a hard job. In this scenario, the present work represents a demanding challenge for a future environmental engineer, which should be routinely tasked with determining design options that offer the minimum environmental impact during the

stages of a given project. LCA is a uniquely valuable tool for assessing and documenting the evidence used in decision-making processes.

1.2 OBJECTIVES OF THIS WORK AND PROJECT PRESENTATION

The main objective of this dissertation is to evaluate the environmental impact of the interface passivation processes of thin film solar cells, namely of CIGS (Copper Indium Gallium and Selenide) solar cells, carried out at the International Iberian Nanotechnology Laboratory (INL). This work also aimed at identifying which are the sub-processes that have the highest environmental impact on the resulting solar cells, and at proposing mitigation and prevention options that can be implemented to reduce the environmental impact, not only at INL but globally. From a personal point of view, having the ability to apply years of environmental engineering knowledge to a specific scenario, while also being able to understand how thin film solar cells work in such a prestigious institution as INL, is an amazing experience, especially given the scarcity of LCA research on CIGS solar cells.

1.3 INL - NOA and FEUP - LEPABE

The International Iberian Nanotechnology Laboratory (INL) was founded by the combined efforts of the Portuguese and Spanish governments under an international legal framework to conduct research work and apply nanotechnology for the benefit of society, in an interdisciplinary environment. The Nanofabrication for Optoelectronic Applications - NOA - group is one of the multiple research groups at INL, having the objective of developing nanotechnology-based novel optoelectronic devices with industrial relevance and high innovation potential, always having the environmental, economic, and social impacts in mind. NOA's nanofabrication cornerstone relies on INL's cutting edge and semi-industrial cleanroom facilities and on the vast international experience of the group members in semiconductor materials, where advanced characterization capacities are the backbone. The conjugation of these competencies is the steppingstones that assure strong collaborations with international industrial and academic partners for developing novel technologies, prototyping, validating fabrication processes, products, among others, resulting in a great connection with industrial partners that seek a high innovation potential.

This work was also performed in collaboration with the Laboratory for Process Engineering, Environment, Biotechnology and Energy (LEPABE). LEPABE, as an interdisciplinary group, is today the largest research unit operating within the Faculty of Engineering of the University of Porto (FEUP) in the fields of Chemical, Environmental and Biological Engineering. LEPABE is classified as "Excellent" by the various international evaluation panels appointed by the Science and Technology Foundation (FCT). "From Science

to Innovation” is the LEPABE’s slogan that has been enforced by the combination of basic science with applied engineering and innovation investing in scientific research and technological development, as well as in advanced training, technology transfer and stimulating the establishment of new technology-based companies. LEPABE’s scientific architecture comprises three main areas: 1) Environment and Health; 2) Energy, Processes and Products; 3) Biotechnology and Interfaces. The present work aims at the area (2) led by Professor Adélio Mendes, who directs research laboratories at the Chemical Engineering Department of FEUP and Science and Technology Park of the University of Porto (UPTEC).

1.4 MAIN CONTRIBUTIONS OF THIS WORK

This work corresponds to the first LCA entirely performed by the NOA group. Despite the knowledge acquired in LCA studies and on data interpretation, the main contribution was the ability to optimize the passivation processes of CIGS that occurs in the cleanroom at INL and to achieve a more sustainable practice. Moreover, it aimed at understanding the impact of the passivation processes of CIGS on their performance and how to make these processes more environmentally friendly. Since the equipment available at INL are prepared to develop pre-industrial approaches, this LCA serves as the basis for large-area devices, giving a perspective of how close this technology is to becoming commercially viable.

1.5 OUTLINE OF THIS WORK

Chapter 1 - Introduction

A brief introduction to the global energetic scenario is made with the corresponding integration in the context of the energy production challenges for the upcoming years and environmental concerns. Decarbonization of energy supply routes plays a very central role in future energy policies, making it a major concern for an environmental engineer. The importance of renewable energy sources, in particular, solar energy is highlighted, with a focus on electricity generation using thin film PV panels. The objectives and contributions of this work are presented, the laboratory and the group where this dissertation was developed were introduced as well as the motivation behind this thesis and its relationship with environmental engineering.

Chapter 2 - Context and State of the Art

Important aspects of PV cells, both silicon-based and thin film technologies, their working principles and materials are explained; thin film solar cells are explained more in detail since they are the subject of the LCA. An overview concerning the materials used and their environmental constraints, such as toxicity and scarcity, is outlined. A brief description of the technological evolution that has been implemented to obtain efficient thin film cells is

reported. Finally, it is explained how life cycle assessments work, and why they are important in the PV market and critical for achieving a more sustainable future. A brief overview of the history of LCAs and the increase in their demand is also outlined.

Chapter 3 - Materials and Methods

The LCA methodology, including the goal and scope definition, inventory analysis, activity data collection and processing, modelling and calculation and the results' analysis are explained in detail. All the processes used for the passivation of thin film solar cells are described in this chapter. Finally, the calculation methodology and the used database are explained.

Chapter 4 - Results and Discussion

The main results obtained in this study are presented and discussed. In short, the environmental impact of each sub-process involved in the passivation of thin film solar cells is presented, followed by a recalculation of the environmental impact to allow for a comparison between the world leaders in PV solar cells manufacturers and PV solar capacity per capita. Finally, this chapter comprises a holistic overview, aiming at determining the “necessary time of green PV production” that passivated and non-passivated CIGS cells need to compensate for their environmental impact.

Chapter 5 - Conclusions

This chapter summarizes the main conclusions of the work developed during this dissertation and compares them with the proposed objectives.

Chapter 6 - Limitations and Future Work

In this final chapter, a wide reflection on the work developed is made, including the main limitations and adversities encountered during this period. It also comprises some suggestions for future work regarding the passivation process developed by NOA.

2 CONTEXT AND STATE OF THE ART

2.1 WORKING PRINCIPLES OF PHOTOVOLTAIC CELLS

A photovoltaic (PV) cell, usually referred to as a solar cell, converts sunlight into electrical energy. Solar radiation is composed of photons, which contain a diverse amount of energy corresponding to the distinct wavelengths that compose the solar spectrum. [27] PV solar cells are composed of semiconductor materials that rely on the photoelectric effect of semiconductor materials; these materials are doped to form a p-n structure as an internal electric field. The p-type (positive) semiconductor tends to accept electrons, being holes the majority charge carriers, while the n-type (negative) semiconductor accepts holes, having electrons as the main charge carrier. The advantage of a semiconductor is the spontaneous production of an electric field capable of separating the electron-hole pairs when solar photons with energy higher than the semiconductor's bandgap energy are absorbed. The excited electrons then get sufficient energy to migrate from the valence band to the conduction band and move to the positive electrode. The holes move randomly to the negative electrode. If electrical contacts are attached to the positive and negative (load) electrodes, forming an electrical circuit, the electrons can be captured in the form of an electric current, generating electricity. [28] The electricity can then be transported to an inverter, which transforms direct current (DC) into alternate current (AC), which can be used to power countless utilities and/or buildings. [29]

Figure 4 shows a schematic of the working principles of a PV solar cell, describing its components. A PV cell can be considered the starting point of a solar system; a single unit normally produces only 1 - 2 W, which is only capable of feeding small electronics, such as calculators and watches. [27] Several cells can be connected, forming a module, which can differ in size and the amount of produced electricity, depending on their intrinsic properties. [27] These modules are designed for electricity production, so, the generated current depends heavily on the amount of sunlight they receive.

In 1961, William Shockley and Hans-Joachim Queisser, calculated for the first time the Shockley-Queisser limit, which represents the maximum theoretical efficiency of a solar cell using a single p-n junction, where the only loss comes from radiative recombination. The maximum calculated efficiency was *ca.* 30% using a semiconductor material with a bandgap energy of 1.1 electron-volts (eV), is assumed as the target limit for solar energy production from PV cells. [30] When multijunction cells are used, each one can be tuned to a particular frequency on the solar spectrum, also having in mind that a particular cell is illuminated not only by sunlight but also by the electroluminescence of other cells.

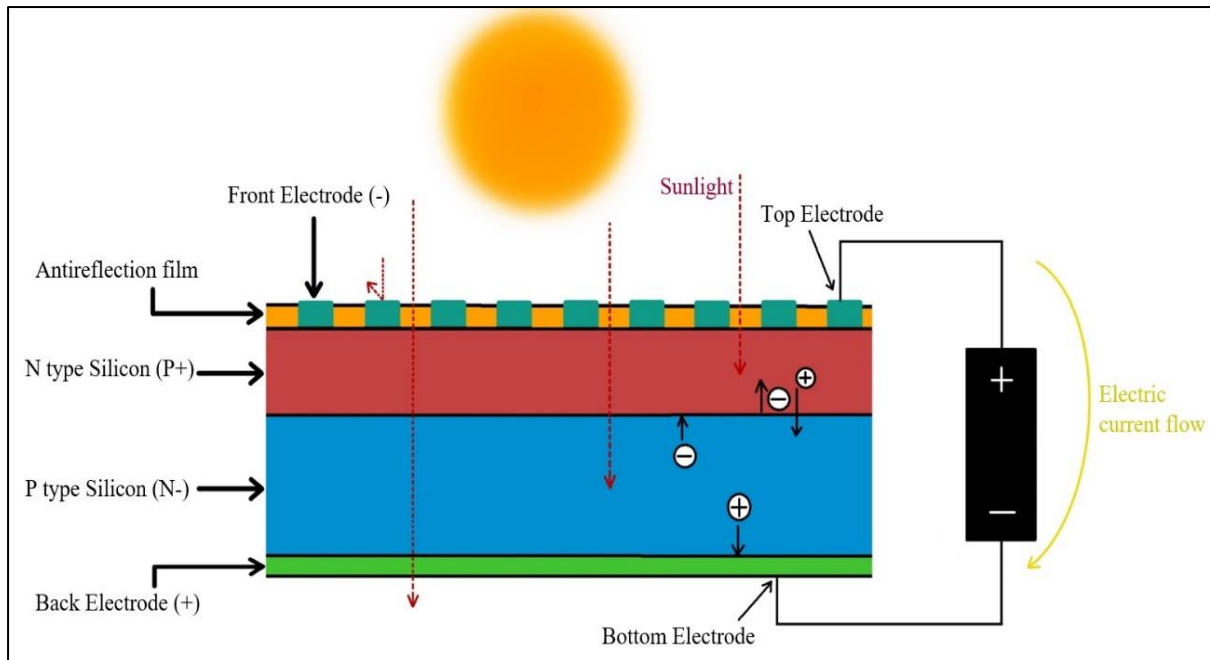


Figure 4 - Working principles and components of a general PV solar cell. (adapted from ref [24]).

The production of PV panels is on a downward trend in price, due to the relatively low maintenance and operating prices and the fact that they are relatively easy to assemble, making them much more desirable in the market for households. Most of the substrates used in the PV industry are Si-based (single crystal, multicrystalline, amorphous), with an amount of Si of *ca.* 90 %. However, with the market for PV solar cells growing and the demand for Si rising, the availability, cost and quality of Si is a major challenge.[31] To achieve ultrapure Si, most manufacturers use the Siemens process, shown in Figure 5.[32] The currently dominant technology entails producing tri-chlorosilane (TCS) from metallurgical grade (MG) Si, which later leads to the form of Si polycrystalline. Si is produced with major contamination of carbon, alkali-earth and transition metals; even with 98 % purity, it still goes through several distillation and condensation steps, and its decomposition in a thermal chemical vapour deposition (CVD) reactor, commonly referred to as the "Siemens reactor". This technique is responsible for *ca.* 90 % of the world's installed polysilicon capacity and production that creates a large number of by-products, mostly silicon tetrachloride (STC) and other chlorosilanes, which must be recycled in a closed-loop system.[32, 33]

Silicon has been part of PV cells from the very beginning, namely at Bell laboratories in 1954, where the first Si solar cell was created to be used in space vehicles as a form of power supply. From 1950 to 1980, Si solar cells were heavily studied and a desire to use this technology was truly alive. However, from 1980 to 2000, a more dormant period was observed due to economic factors related to oil reserves. From 2000 onwards, the relationship between environmental challenges and the role of energy production from

renewable sources changed this trend. China was one of the most committed counties, where government subsidies and low-cost labour allowed increasing the solar PV installed capacity from 1.9×10^4 kW in 2002 to 2.53×10^8 kW in 2020; this growth keeps on going. [34]

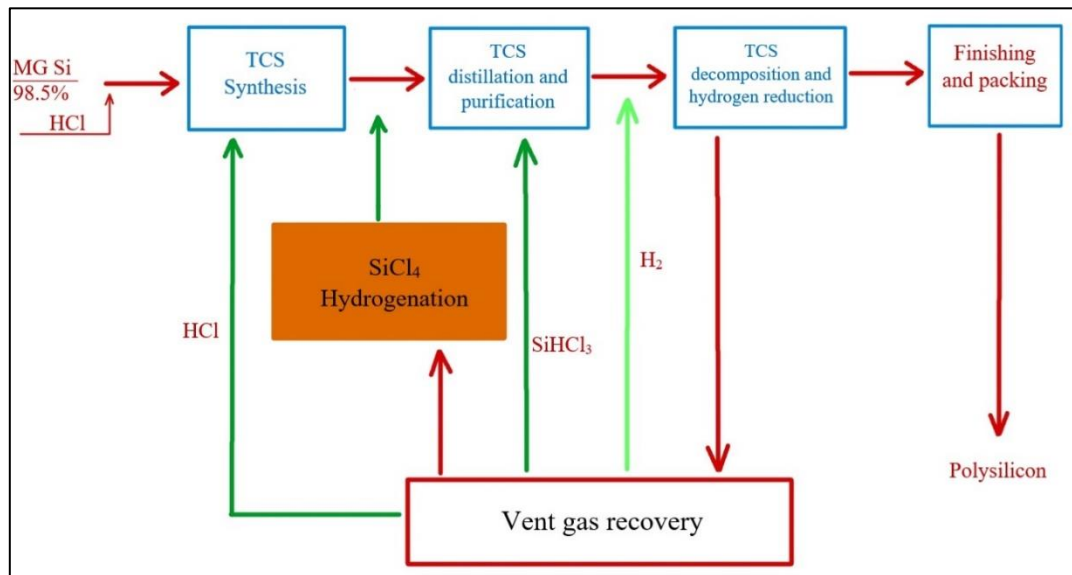


Figure 5 - Siemens Process used for production of Polysilicon (adapted from ref [31]).

2.1.1 SILICON BASED SOLAR CELLS

Most of today's solar cells are made from silicon (Si), accounting for 90 % of the current market. [18] Since Si is a nontoxic material with a huge abundance and a bandgap of 1.1 eV, suitable for achieving high efficiencies, it has been used since the foundation of PV devices and electronics in 1941, when the first PV device was developed. [35] Silicon-based solar cells can be divided in two main groups, monocrystalline and polycrystalline.

Monocrystalline-based modules are assembled using solar cells composed of single-crystal Si (in short, mono c-Si) and they are obtained by cutting Si cylindrical bars, in the shape of thin pellets with a thickness of *ca.* 300 μ m. These cells tend to have a homogenous appearance, usually a dark tint. Their singular composition enables electrons to move more freely than in a multi-crystal configuration. Therefore, the efficiency of mono c-Si cells is *ca.* 15%, higher than their polycrystalline counterparts, but their production costs are higher. [36, 37]

Polycrystalline-based solar modules use a high purity, polycrystalline form of Si, based on multiple small crystals. However, these modules have a lower price, since the manufacturing process is much simpler. [36, 37] These Si wafers are usually made by wire sawing block-cast Si ingots into a thin slice of wafer, with a thickness of *ca.* 180-350 μ m. [38] These cells usually have a bluish type of colour. [37] Overall, monocrystalline modules are more efficient and more resistance to higher temperatures, with a minimum of a 25-year life span, but they are also more expensive. [37]

2.1.2 THIN FILM SOLAR CELLS

Despite the current market dominance of Si-based solar cells, thin film-based solar cells have been at the centre of the most recent expansion of the PV market. This type of cells presents some unique advantages, such as sizeable suitability for low-light conditions, better heat tolerance, possibility to be deposited in different substrates, allowing it to be incorporated in transparent or semi-transparent products but also on flexible materials. There are three main types of thin film cells: cadmium-telluride (CdTe), amorphous silicon (a-Si), and copper indium gallium selenide (Cu(In,Ga)Se_2 - CIGS).

CdTe cells are synthesized from polycrystalline substances onto a glass substrate. The advantages of these cells are their small bandgap of 1.5 eV, high optical absorption coefficient, high stability and a record laboratory efficiency of 22.1 %.[39] a-Si solar cells are manufactured at low processing temperatures, which allows using of low-cost polymers and other flexible substrates, presenting laboratory efficiencies of 10 %.[40]

CIGS has a chemical formula of $\text{CuIn}_{(1-x)}\text{Ga}_x\text{Se}_2$, where the x value can vary from 0 for the pure copper indium selenide (CIS) to 1 for the pure copper gallium selenide; therefore, the bandgap energy can vary from *ca.* 1.0 eV for CIS to *ca.* 1.7 eV for Ga-based ones.[41] The composition of one of the first CIGS cells was based on copper, indium and selenide (CuInSe_2) covered with a thick layer of cadmium sulphide (CdS), *i.e.*, a $\text{CuInSe}_2/\text{CdS}$ thin film structure. This type of cells was fabricated by evaporating CuInSe_2 powder in the presence of excess Se vapour, showing efficiencies of *ca.* 5 %; the use of a co-evaporation technique doubles the efficiency.[42] Since then, a variety of breakthroughs have been demonstrated for increasing the efficiency of CIGS, namely through the inclusion of gallium (Ga) or sodium (Na) dopants, the reduction of the thickness of the CdS window layer and the deposition of intrinsic and doped zinc oxide (ZnO) layers.[43] The optical bandgap can be controlled by adjusting the Ga/In ratio to fit the solar spectrum, and a single-phase CIGS absorber can be manufactured more simply than a single-phase CIS absorber, which are two advantages of CIGS-based solar cells over CIS-based solar cells.[43] Moreover, some studies report CIGS solar cells having already achieved laboratory efficiencies of 23.35 %, which are currently the highest performing multicrystalline solar cells available.[22] Large progress has been made in recent years to achieve its maximum theoretical efficiency of *ca.* 30 %.[27]

The CIGS thin film solar cells can be deposited onto different substrates, such as soda lime glass (SLG), metal, or a polyamide film, to form the back surface contact; SLG is the most common, due to the presence of sodium, which increases the open-circuit voltage of these solar cells.[27, 44] A molybdenum (Mo) layer is normally deposited by sputtering if the substrate is composed of a non-conductive material, acting as a conductive layer, but it can also act as a reflective layer to decrease the amount of unabsorbed light. Following the Mo

deposition, a p-type absorber CIGS layer is grown, covered with an n-type thin buffer layer of CdS deposited via chemical bath deposition (CVD). The buffer layer is then passivated with a very thin intrinsic ZnO (i-ZnO) layer, followed by a thick coating of aluminium (Al) doped ZnO layer (ZnO:Al); i-ZnO protects the CdS against the damaging conditions of the deposition of ZnO:Al, commonly deposited by DC sputtering. [45] The front part of the cell needs to be transparent to allow the sunlight to reach the photoabsorber material; semiconductors like tin oxide (SnO_2) and ZnO are used to collect and transport electrons to the outside part of the cell while absorbing a very small fraction of sunlight. [46] Figure 6 shows a schematic of a typical structure of a CIGS solar cell.

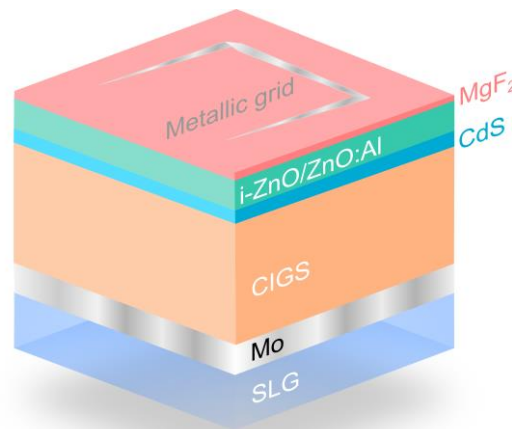


Figure 6 - Typical structure of a CIGS solar cell, comprising six different layers: a substrate black metal electrode (usually soda lime glass - SLG) covered with Mo, a p-type absorber (CIGS) film, a buffer thin layer based on CdS, and a transparent conducting oxide. (adapted from the NOA group database).

The composition of CIGS solar cells influences the way they are fabricated, allowing the search for new materials and processes that can improve their efficiency and stability, while reducing their cost and enhancing their environmental performance. [47] For further developments, the CIGS technology has to start incorporating different solar cell architectures and strategies that allow for very low interface recombination. It was demonstrated by the NOA group at INL that the rear interface can be effectively passivated by an aluminium oxide (Al_2O_3) nanopatterned layer (with 18 nm), forming a point contact structure. [48] Such passivation layer can lead to three advantageous effects: i) chemical passivation; ii) field-effect passivation; iii) increased reflection at the rear contact; while maintaining good electrical contact and devices with high values of fill factor. The use of passivation layers has emerged as a promising treatment for improving cell performance; especially at INL, the introduction of an optimized nanopatterned Al_2O_3 layer on a 350 nm CIGS layer allowed to achieve power conversion efficiency values up to 13.2 %, a 1.3 % improvement over the conventional substrate. [48, 49] Figure 7 shows the fabrication process of the passivated solar cells.

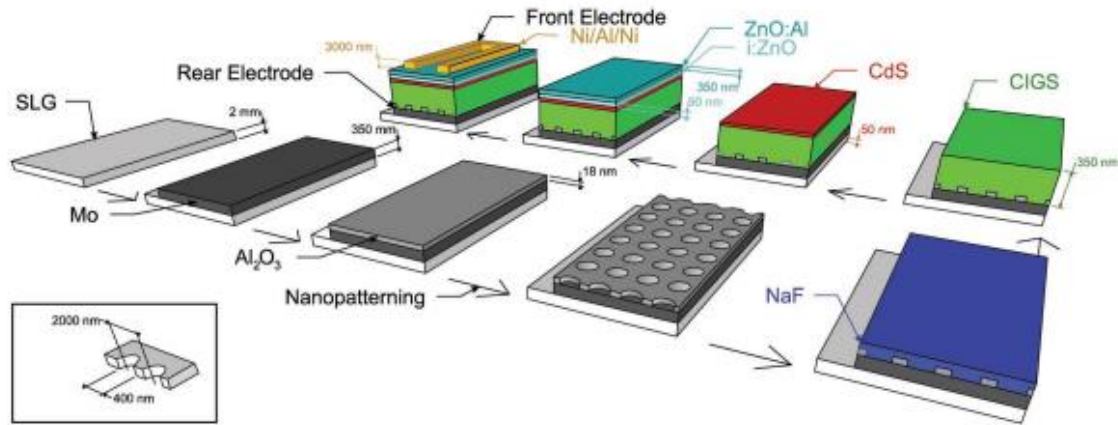


Figure 7 - Representation of the fabrication process of a passivated CIGS solar cell. (extracted from [47])

The biggest driving force for the investment in CIGS cells over recent years relies on their versatility and low-cost production, being highly flexible while presenting high efficiency, scalability, durability under extreme conditions as well as low maintenance, operating prices, no noise production, relatively easy to assemble and a downward trend in price.[23] However, CIGS cells also comprise some critical drawbacks. To start, some materials included in their elementary composition, like In and Ga are listed as Critical Raw Materials (CRMs). However, these metals are not mined directly, being by-products of Zn, Lead (Pb) and Al, mining these metals can lead to soil, air, water contamination and physical disturbances to the landscape. Undoubtedly, the extraction of these materials results in significant environmental impacts, with studies mentioning important contributions to ecotoxicity, human health, eutrophication, and ozone depletion. [18] In this context, a life cycle assessment (LCA) appears as an adequate and useful tool to improve the fabrication processes of CIGS cells and decrease their associated environmental impacts. Herein, LCA was applied to the passivation process of CIGS, which is the only manufacturing process under development at INL.

2.2. THE FUNDAMENTALS OF LIFE CYCLE ASSESSMENT

The first ISO (International Organization for Standardization) standard to regulate the LCA application was published in 1997 - the 14040 ISO standard. According to ISO 14040, an LCA is the compilation and evaluation of the inputs, outputs and potential environmental impacts of a product system throughout its life cycle, from the extraction of raw materials to waste removal. [50] An LCA can be applied during the development and improvement of a product, strategic planning, public policy making and marketing. This ISO standard allows distinguishing methodological frameworks of LCA according to its different applications, and it has a distinct and widely accepted framework, divided into

four main categories: i) goal and scope definition; ii) inventory analysis; iii) impact assessment; and iv) interpretation.[51] Two important frameworks were created: i) the ISO 14040 (Figure 8), which provides the principles and framework of the standard; and ii) the ISO 14044, which provides an outline of the requirements and guidelines. ISO 14040 was written with a managerial audience in mind, while ISO 14044 was written for practitioners.[52-54]

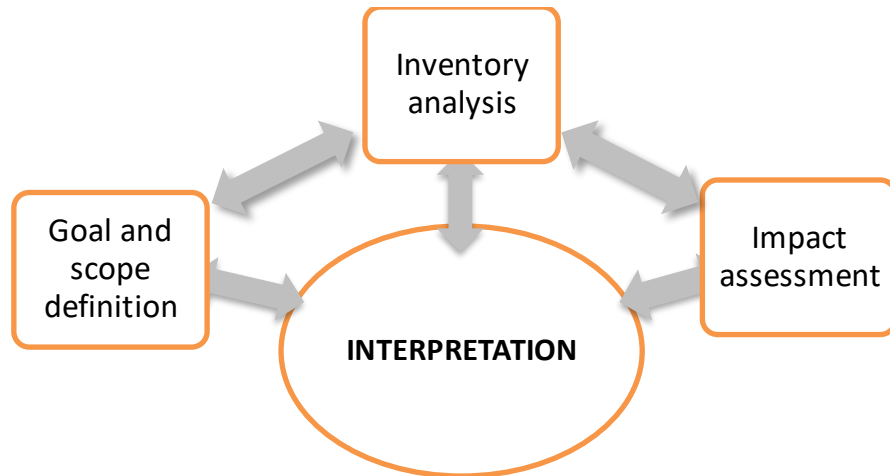


Figure 8 - Framework of the ISO 14040 standard.

An LCA study can be implemented following different approaches, mostly related to the system boundaries. If the boundaries encompass all steps from the extraction of raw materials to the disposal processes, a Cradle-to-Grave is adopted.[50, 55] A Cradle-to-Gate approach can be used if the focus of the study includes the processes from the extraction of the raw materials up to the factory gate. Finally, a Gate-to-Gate approach focuses only on one defined point (which can be a process or a phase) of the life cycle.[56] Independently from the adopted approach, and according to the ISO 14040 and ISO 14044, an LCA should be carried out following these four interconnected phases, as depicted in Figure 8.

2.2.1. GOAL AND SCOPE DEFINITION

The goal and scope definition is the first step of an LCA study, which is divided into two sub-steps. First, during the goal definition, the purpose of the study must be defined and two main questions must be answered: i) what are the intended applications of the results; and ii) what are the main reasons behind the LCA study.[56] This phase must be defined very cautiously because it will influence all the next phases, such as the selection of the system boundaries, the source of inventory data and the interpretation of results. The targeted audience must be considered during this stage, moulding the study to whom the results are intended to be communicated, including consumers, consumer organisations,

companies, non-governmental organizations (NGO), *etc.* The targeted audience influences how much detail the study should delve into, considering the technical level of the reporting. Second, the scope definition acts as a solid reference for how the subsequent LCA stages (Inventory analysis, Impact assessment, and Interpretation, including uncertainty and sensitivity analysis) should be carried out, as well as how the LCA should be presented. The scope definition's overarching goal is to assure and record the consistency of methodologies, assumptions, and data, as well as to improve the study's repeatability. One of the main objectives of the scoping phase is to ensure all inputs, outputs and energy sources refer to a single functional unit, this way calculations will always refer to the main focus of the study. Moreover, to compare LCA results within the same industry it is much easier to compare when referring to the same unit studied, *e.g.* kg of product, area of a product, kWh of energy produced. In LCA studies for the solar cells, it is often used impact by kWh of energy produced by the solar cell, or by m² of the active area of the cell. Finally, the system boundaries establish which processes must be included in the study. All limitations and suppositions must be recorded carefully since they might cause misinterpretation of results. [51, 53, 54]

2.2.2. INVENTORY ANALYSIS

The inventory analysis is usually the most extensive part of an LCA study, as it involves detailing all the flows and amounts of energy and materials, as well as soil, water, and air emissions. According to ISO 14044, a hierarchy of solutions is presented for the inventory analysis, as follows: i) avoid allocation by sub-division (a method that attempts to separate the product from the co-product, during the production phase); ii) avoid allocation through system expansion (a method that attempts to turn the production of the co-product independent); iii) allocation based in physical relationships (a method that intends to divide the inputs and outputs and allocate them based on existing physical relationships); and iv) allocation based in other relationships (a method that intends to divide the inputs and outputs and allocate them based on existing non-physical relationships). [51], [53] In the LCA under study, an avoid allocation by sub-division was used to separate the passivation process at NOA from the other processes of the production of CIGS solar cells, namely before and after the deposition of the passivation layers.

During data collection, certain LCA databases and literature sources can be used to fill in the gaps in the inventory. However, it is important to note that when secondary sources are used, the data could not be as accurate as those collected from primary sources. Even after documenting all differences between both, primary and secondary data must have temporal, geographical, and technological representativeness. A particularly tricky data collection field is the technosphere, also known as the human-made world. [57] In the life cycle

inventory (LCI) human-made products are very complicated to describe in terms of how much inputs are used, so, secondary sources are usually adopted.[58]

2.2.3. IMPACT ASSESSMENT

Unlike the previously mentioned phases, the impact assessment is mostly automated, usually via software. Still, the practitioner must know the LCA fundamentals, the relevant indicators and their meaning to fully understand the results calculated by the software. [51] Among the LCA research field, there are two software more widely used: Gabi and SimaPro.

GaBi software is a solution to evaluate product sustainability, using an LCA engine to support business applications, such as Life Cycle Assessment Design for Environment (developing products that meet environmental regulations), Eco-efficiency (reducing material, energy and resource use), Eco-design (developing products with smaller environmental footprints such as fewer GHG emissions, reduced water consumption and waste), and Efficient value chains (enhancing efficiency of value chains, e.g. research and development, design, production, suppliers, distribution). This software also allows presenting alternative options for manufacturing, distribution and recyclability. [59]

SimaPro is a source of science-based information, providing full transparency and avoiding black-box processes, being considered a professional tool that collects, analyses, and monitors the sustainability performance of a company, products, and services. This software can be used for a variety of applications, such as reports of sustainability, carbon and water foot printing, product design, generating environmental product declarations and determining key performance indicators, while also allowing the practitioner to make conscious decisions throughout the analysis, to ensure accurate results. [60]

According to ISO 14040 and 14044 there are some mandatory steps during the impact assessment, namely: i) the selection of impact categories, category indicators and characterisation models; ii) classification, assigning LCI results to the chosen impact categories based on their known environmental effects, using LCI databases or LCA software; and iii) characterization, quantitatively transforming LCI results within each impact category via characterization factors into impact category indicators. During the latter, it is recommended to convert all flows into common units for comparison.

Characterisation allows for environmental models to estimate the ability of each of the allocated elementary flows to influence the category's indicator, called environmental impact. These impact ratings are then characterised and expressed in a standard metric for the impact category, allowing all contributions to be combined into a single score that represents the entire influence of the product system on that category. The described impact profile of the product system is made up of a set of aggregated indicator scores for the several effect categories (each stated in its own metric). Some methodologies that

englobe characterisation factors are: i) CML-IA (Institute of Environmental Sciences - Impact Assessment), developed by the University of Leiden; [61] ii) Traci (Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts) developed by the US Environmental Protection Agency; [62] iii) ReCiPe LCA methodology, created by RIVM, CML, PRé Consultants, Radboud University and CE Delft. [63] Some non-mandatory steps include normalization (expressing the impact results relatively to those of a reference system), weighting (prioritising or assigning weights to each impact category) and grouping (aggregating several impact indicator results into a group). [51],[53],[54] Normalization expresses each of the characterised scores for the different impact categories relative to a common set of reference impacts - one reference impact per impact category - being used to inform about the relative magnitude of each of the characterised scores for the different impact categories. Some normalization factors have been proposed at different levels, *e.g.* Sleeswijk *et al.* (2008) for Europe and globally, Laurent *et al.* (2013) for the global scale, and Sala *et al.* (2015) for Europe, specifically for the EU27. [64-66] Grouping enables comparison across impact categories by ordering them according to perceived severity, or by weighing them, using factors that offer a quantitative statement of how severe each effect category is in relation to the others. When the results of the LCA are used in decision support alongside other condensed information, like the economic costs of the alternatives, quantitative weighting allows for the aggregation of all the weighted impact scores into one overall environmental impact score for the product system. [51]

2.2.4. INTERPRETATION

Interpretation is the final phase of an LCA study, is considered a technique to identify, quantify, check, and evaluate information from the results of the aforementioned phases, with the suppositions and limitations always being considered. In this phase, three main points must be addressed: i) the identification of significant issues based on the results of the LCI and impact assessment; ii) evaluation of the study considering completeness, sensitivity, and consistency checks; and iii) conclusions, limitations, and recommendations. [49, 50]

This phase is critical to determine the level of confidence in the results as well as in the entire LCA. It is not as easy as *e.g.* saying choice A is better than B, because A has a lower ecotoxicity impact. Understanding how accurate the results are, as well as ensuring that the goal that was defined at the beginning of the study was met, is crucial in this phase. Interpretation should be done through the identification of all data that impacts each category and evaluating the sensitivity of these data, while allowing to understand how the LCA study was conducted, also giving recommendations and conclusions. [51]

2.2.5. STRENGTHS AND LIMITATIONS

The main advantage of an LCA study, is the possibility of having a life cycle perspective in an easily understandable way, including hundreds of processes, used resources and emissions taking place at different locations and different timelines. Although it is useful to understand the entire life cycle of a product, good or service, sometimes it can be too extensive; this means that simplification and generalisation may be required in the modelling of the system, and the actual environmental impacts might not be truly exact. If it is complicated to map resources and emissions, both from a timeline and a geographical perspective, it might be more accurate to state that LCA calculates potential impacts, instead of real impacts. Another strong point of an LCA is its unbiased opinion. This means that certain single events, like oil spills, industrial accidents, fires and other types of disasters, are not assumed.[56] However, it is important to remind that certain resources may lack important information; e.g., nuclear energy is associated with a low environmental impact, since nuclear accidents are extraordinarily rare, however, when they happen, they are tremendously malign. LCA is not an all-type answer tool, although it is capable of answering key questions, like: i) is a product environmentally friendly?; ii) is this method of transportation environmentally safe?; and iii) what type of waste disposal is more environmentally friendly?. On the other side, this type of studies cannot answer questions that possess a social theme, such as if taxes should be increased to reduce pollution.[56] Overall, LCA encompasses a broad range of environmental problems that can be properly prioritized and tackled, namely global warming, usage of freshwater, land occupation and transformation, aquatic eutrophication and ecotoxicity, toxic impacts on human health, depletion of non-renewable resources, eco-toxic effects from various sources, like metals and synthetic organic chemicals, among others. [51]

3 TECHNICAL PROCEDURES AND MATERIALS

The main methodology used for the LCA of the passivation process of CIGS at NOA was the ISO 14040 and 14044 guidelines. The SimaPro software was used for most environmental impact calculations, with the CML-IA baseline methodology and the EU 25 references for normalization. All the data assumptions and sources adopted in the present work are referred to in detail. This chapter aims at describing the first three categories of the LCA: i) goal and scope of the study; ii) inventory data and assumptions; and iii) methodology and calculations.

3.1 GOAL AND SCOPE OF THIS STUDY

The main objective of this thesis was to understand the environmental impacts associated with the CIGS passivation process done by the NOA group at INL for increasing the efficiency of the CIGS solar cells, *i.e.*, to understand if the gains in efficiency compensate relatively for the additional environmental impact. The identification of the most critical subprocesses of the passivation process from an environmental point of view is also an important task, as well as the suggestion of improvement strategies.

At INL, the passivation process of CIGS solar cells is conducted on soda lime glass (SLG) and silicon-based substrates. However, due to time constraints related to the work plan of this thesis, it was only possible to study the passivation processes on CIGS solar cells produced on SLG substrates, which are the most commonly used. The complementary production processes of CIGS solar cells occur at Uppsala University, in Sweden. After the fabrication is completed, the complete cells are shipped back to INL for further characterization. NOA gives a big focus on the passivation processes, as a clever strategy to enhance the performance of CIGS solar cells. Figure 9 summarizes the passivation process carried out by the NOA research team; Teflon Si + SiO₂, NIL IPS and Teflon IPS subprocesses, which will be explained later, are distinguished from the remaining steps due to their flexibility to be performed at any moment (but they must be always done before the NIL subprocess).

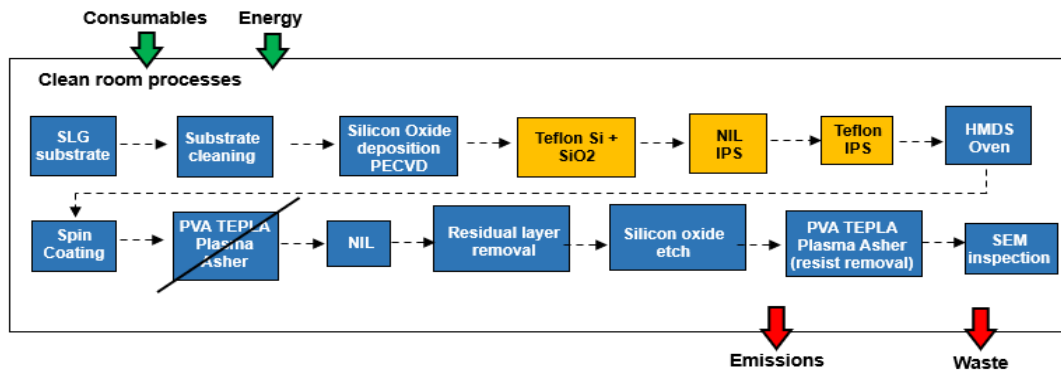


Figure 9 - Main steps of the clean room procedure developed by the NOA group at INL for the passivation layers on CIGS solar cells, schematized in a black box arrangement.

The first experimental process involved in the passivation of CIGS solar cells at NOA is substrate cleaning. SLG substrates with an area of $5 \times 5 \text{ cm}^2$ and a thickness of 3 mm (Figure 10), covered with a Mo layer deposited at Uppsala University, are sonicated in the following stepwise process: i) 25 ml of acetone for 10 min; ii) 25 ml of isopropyl alcohol for 10 min, and iii) 25 ml of deionized water for 5 min. This process is done for a batch of fourteen substrates with the aforementioned quantities; therefore, all inputs, outputs and electricity consumption are presented afterwards considering that a single batch comprises fourteen SLG substrates, being considered the functional unit of the study. Then, silicon di-oxide (SiO_2) is deposited onto the Mo layer by plasma-enhanced chemical vapour deposition (SPTS's Delta™ PECVD), at 0.119 kPa, 300 °C, during 45 to 50 s. The SiO_2 deposition occurs at a rate of 47.07 nm/min, with 1420 sccm of nitrous oxide (N_2O), 10 sccm of silane (SiH_4) and 392 sccm of nitrogen (N_2). To allow for better coverage and adhesion between layers, a thermal treatment is performed in an HMDS (Hexamethyldisilazane, an adhesion promotor) Prime oven (Figure 11) for dehydrating the wafers, under vacuum conditions at 150 °C over 25 to 30 min.[67]

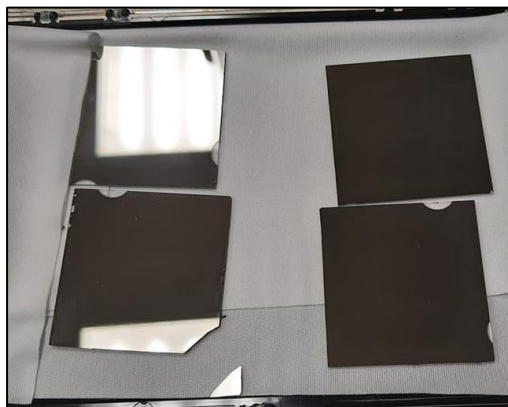


Figure 10 - SLG substrates after the passivation process.



Figure 11 - HMDS Prime Oven used at INL.

If the results do not agree with standard metrics, either the resist is in bad condition or it was not applied correctly. Therefore, when this situation occurs and has to be resolved, a plasma etching process is performed to allow removing the resist and reapply it. This process is conducted using 600 sccm of oxygen (O_2) and 50 sccm argon (Ar) for 8 min; however, due to available time constraints, this step was not taken into consideration. For the Nanoimprint lithography (NIL) patterned substrate, the lithography process started by spin coating a Simultaneous Thermal and UV (STU®) resist (TU7-120, Obducat) with a thickness of 150 nm (Figure 12). Before the imprint, the point contact pattern is transferred from a 150 mm nickel stamp to an Intermediate Polymer Stamp (IPS®) by UV-NIL. IPS® is used to prolong the lifetime of the first stamp and allows working at room temperature and moderate pressure. Using an Obducat Eitre 8 system, this process takes 7 min and 45 s. Then, the IPS is rolled on the SLG substrate to transfer the pattern to the samples (Figure 13). The imprint conditions are presented in Table 1.

Table 1 - Experimental conditions of the NIL process.

Order of Steps	Temperature (°C)	Pressure (kPa)	Time under use (s)	Ultraviolet light
First	22	0	10	OFF
Second	65	1500	100	OFF
Third	65	1500	180	ON

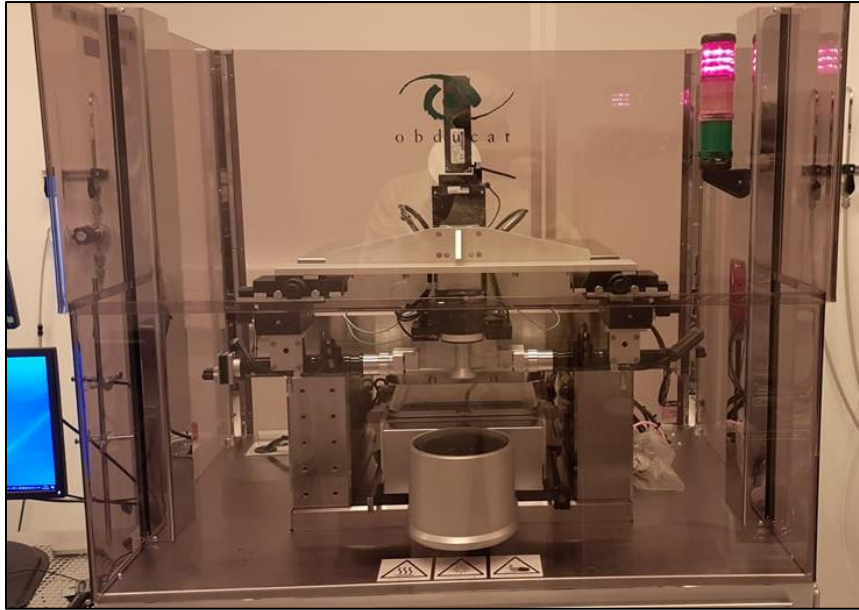


Figure 12 - Obducat equipment used during the NIL subprocess.

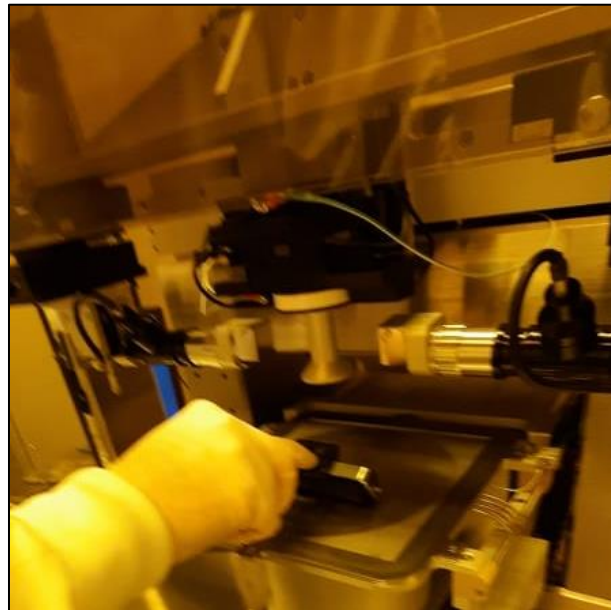


Figure 13 - NOA associated rolling the IPS stamp onto the SLG substrates.

Next, the residual layer is removed through bombing with O_2 in an STPS Pegasus system (Figure 14), with a 115 sccm flow and 13.56 MHz for 30 to 45 s. Then, the SiO_2 layer is removed by fluorinated chemistry using 50 sccm of C_4F_8 at, 200 sccm of He and 30 sccm of H_2 , for 22 s. Afterwards, the resist is removed with a Plasma Asher System operated with 600 sccm of O_2 and 50 sccm of Ar, for 8 min. Finally, an inspection is performed with a scanning electron microscope (Figure 15).



Figure 14 - SPTS Pegasus machine used for the removal of the residual layer.



Figure 15 - Quanta FEI electron microscope.

This LCA study focuses only on this fabrication step, leaving the others that take place before and after the passivation unaddressed, including raw materials extraction and preparation, transportation between partners, assembly and use of the cells and end-of-life. Overall, the energy required to operate the equipment needed to perform the passivation, regular lighting and maintenance and the input materials and emissions involved in the CIGS cells' passivation were considered. As an example, the gloves, masks, and suits for the cleanroom are important consumables included in the study, not being directly related to the passivation process itself, but necessary to conduct the experimental activities. Therefore, the main purpose of this LCA study is to quantify the environmental impact associated with the passivation process developed by the NOA group and investigate if the resulting improvements in the performance of the cell compensate for it. This study should also allow identifying which are the fabrication steps that contribute more to the global environmental impact and identify opportunities to improve it, both in terms of environmental and economic metrics.

3.1.1 FUNCTIONAL UNIT

Solar panels are used to generate electricity, which is widely quantified in kWh. However, since this LCA study focuses only on one process of the production stage, the efficiency of the cell, which translates into the generated electricity, cannot be considered as the baseline of the study. Therefore, the environmental impacts must relate to the production process itself, and not related to the final device, which involves many other fabrication steps. Hence, the functional unit was defined as 14 substrates of $5 \times 5 \text{ cm}^2$, being normalized into 1 square meter when necessary.

3.2 INVENTORY DATA COLLECTION AND ASSUMPTIONS

All of the processes involved in the CIGS solar cells passivation were divided into 14 subprocesses, for which, the individual material and energy flows were obtained. To ensure that this data was the most correct possible, several cleanroom visits were done alongside the NOA associates that are responsible for performing these processes. LCI data were obtained from both primary and secondary data sources, being the primary data source from the NOA associates and the equipment manufacturers, and secondary sources being the literature and LCA software databases, *i.e.* SimaPro. Tables 2, 3 and 4 showcases the inputs, outputs, and electricity consumption, respectively, that were taken into consideration during the entire process that occurs at INL.

Table 2 - Material inputs of the 14 subprocesses of the NOA process.

Inputs			
Subprocess	Material	Value	Unit
Substrate and Mo	SLG substrate	0.27	kg
	Molybdenum	1.26×10^{-4}	kg
Cleanroom Consumables	Gloves	8.00×10^{-3}	kg
	Shoe and head cover	9.00×10^{-3}	kg
	H ₂ O	0.85	l
Substrate Cleaning	Acetone	7.85×10^{-2}	kg
	Isopropyl Alcohol	7.86×10^{-2}	kg
	H ₂ O	0.10	l
PECVD	SiO ₂	5.74×10^{-4}	kg
	N ₂ O	1.42×10^{-2}	kg
	SiH ₄	7.28×10^{-5}	kg
	N ₂	2.72×10^{-6}	kg
Teflon Deposition (Si + SiO ₂)	C ₄ F ₈	5.49×10^{-2}	kg
	Kapton Tape	20	cm/sample
NIL IPS	Compressed Air	0.32	kg
	H ₂ O (cooling water)	1	l
Teflon Deposition IPS	C ₄ F ₈	5.49×10^{-2}	kg
HMDS OVEN	HMDS	5.39×10^{-5}	kg
SPIN COATING	RESIST	9.94×10^{-4}	kg
NIL	Compressed air	1.47	kg
	H ₂ O (cooling water)	1	l
Removing Residual Layer	O ₂	7.19×10^{-4}	kg
	C ₄ F ₈	0.21	kg
Silicon Oxide Etch	He	9.17×10^{-5}	kg
	H ₂	6.92×10^{-6}	kg
PVA Tepla Plasma Asher	O ₂	2.06×10^{-2}	kg
	Ar	1.99×10^{-3}	kg
SEM	----	----	----

Table 3 - Energy consumption of the 14 subprocesses of the NOA process.

Electricity		
Subprocess	Value	Unit
Substrate and Mo	-----	----
Cleanroom Procedures	7.63×10^{-3}	kWh
	1.27	
Substrate Cleaning	-----	----
PECVD	1.62	kWh
Teflon Deposition (Si + SiO ₂)	7.69×10^{-2}	kWh
NIL IPS	1.42	kWh
Teflon IPS	7.69×10^{-2}	kWh
HMDS OVEN	0.49	kWh
Spin Coating	1.31	kWh
NIL	6.61	kWh
Removing Residual Layer	2.02	kWh
Si Oxide Etch	2.14×10^{-2}	kWh
PVA Tepla Plasma Asher	1.38	kWh
SEM	----	----

Table 4 - Outputs of the 14 subprocesses of the NOA process.

Outputs			
Subprocess	Materials	Value	Unit
Substrate and Mo	----	----	----
Cleanroom Procedures	Detergent	1.80×10^{-6}	kg
	Acetone	0.079	kg
Substrate Cleaning	Isopropyl Alcohol	0.079	kg
	H ₂ O	0.10	l
PECVD	----	----	----
Teflon Deposition (Si + SiO ₂)	----	----	----
NIL IPS	H ₂ O (cooling water)	1	l
Teflon IPS	----	----	----
HMDS OVEN	----	----	----
Spin Coating	----	----	----
NIL	----	----	----
Removing Residual Layer	RESIST	3.18×10^{-4}	kg
	RESIST	2.91×10^{-4}	kg
Si Oxide Etch	SiO ₂	8.47×10^{-4}	kg
PVA Tepla Plasma Asher	RESIST	3.88×10^{-4}	kg
SEM	----	----	----

Substrate and Mo refer to the SLG substrate covered with a Mo layer that arrives at the INL facilities, from Uppsala University. Cleanroom consumables refer to every disposable item and procedure done before entering the cleanroom; the composition of each item and their weight were used from several online sources. Before entering the cleanroom the INL associates must go through a process, where air is pressurized and used to disinfect the person in question; for this thesis, it was assumed that the entire process was done by only one associate. The cleaning process of the cleanroom garments (Figure 16) was also taken into consideration. For that, the average electrical and water consumption were obtained for a 15 kg washing machine (typical industrial machine), with the average amount of detergent required to wash the volume of a cleanroom garment with the average measurements of a human.



Figure 16 - Cleanroom garments used by the NOA associates.

During the substrate cleaning, materials are not reused. The machines in the clean room at INL are not tailor made for SLG substrates; as so, it is required to use a silicon wafer as baseline, forcing the placement of the SLG substrates on top of it. The IPS phase (Teflon Si + SiO₂, NIL IPS and Teflon IPS), the HMDS OVEN phase and the SEM analysis are done only once, while the PVA Tepla Plasma Asher is done three times, NIL is done four times, Removal of Residual Layer and Si Oxide Etch are done seven times, and the Spin Coating need to be done fourteen times. The entire process of inventory gathering was done in Microsoft Excel and the associated table is available in Annex A.

3.3 CALCULATION METHODOLOGY

After the inventory was concluded and reviewed with the NOA associates, the SimaPro software was used to obtain the results regarding the environmental impact of each phase and the process in general. The CML-IA methodology was selected within SimaPro, developed by the Institute of Environmental Sciences at Leiden University, being widely used in LCA studies due to its reliability. Within this method, the ecoinvent database was used for the calculations. This database is used by many LCA studies and has been constantly updated through the years to better serve the practitioners of environmental assessments, LCA and Environmental Product Declarations (EDP). After inserting the inventory data in SimaPro, the

software proceeded with the calculations (some key steps are presented in Annex B). Firstly, the calculation of the impact potential was made (characterization phase) using equation 1,

$$PI_i = \sum_{x=1}^Y (E_{x,i} \times CF_{x,i}) \quad (1)$$

where PI refers to the potential environmental impact, E_x refers to the pollutant/substance emission, x refers to the pollutant/substance and CF refers to the characterization factor, being i the environmental impact category for which this calculation is being done.

Afterwards, normalization was made, referring to the calculation of the indicators of the environmental impact categories concerning a referential (country, region or worldwide), using equation 2,

$$N_i = \left(\frac{PI_i}{NF_i} \right) \quad (2)$$

where NF refers to the normalization factor and N refers to the normalized environmental impact for a certain environmental category.

The normalization factors used for each category of environmental impact are presented in Table 5. It is important to note these categories are the ones analysed using the CML-IA baseline methodology, and the EU 25 Normalization factors were chosen to complement the CML-IA methodology. The environmental impact categories analysed in this thesis were Abiotic Depletion - Fossil Fuels, Abiotic Depletion, Acidification, Eutrophication, Fresh Water Aquatic Ecotoxicity, Global Warming, Human Toxicity, Marine Aquatic Ecotoxicity, Ozone Layer Depletion, Photochemical Oxidation and Terrestrial Ecotoxicity.

Table 5 - Normalization factors used during the normalization phase.

Impact Category	Unit	Normalization Factor
Abiotic Depletion	kg Sb eq	3.15×10^{13}
Abiotic Depletion-Fossil Fuels	MJ	8.48×10^7
Acidification	kg SO ₂ eq	2.82×10^{10}
Eutrophication	kg PO ₄ --- eq	1.32×10^{10}
Fresh Water Aquatic Ecotoxicity	kg 1,4-DB eq	5.18×10^{11}
Global Warming	kg CO ₂ eq	5.03×10^{12}
Human Toxicity	kg 1,4-DB eq	7.75×10^{12}
Marine Aquatic Ecotoxicity	kg 1,4-DB eq	1.17×10^{14}
Ozone Layer Depletion	kg CFC-11 eq	8.93×10^7
Photochemical Oxidation	kg C ₂ H ₄ eq	8.48×10^9
Terrestrial Ecotoxicity	kg 1,4-DB eq	4.85×10^{10}

All the calculations were made for the NOA passivation process, which was carried out at INL located in Portugal; therefore, the Portuguese energy grid mix was considered for

calculations involving power consumption. However, to have a better understanding of how the environmental impact would change if this passivation process would be carried out in the world leading producers of PV cells, the same calculations were remade for China, USA, Malaysia, and South Korea.[68] Following a similar approach, to better assess if the passivation process is beneficial in environmental terms, the extra environmental impact imposed by the passivation process was compared against the gains in green energy production arising from the increase in efficiency. For that, a comparative analysis was made for the world leaders in solar PV installed capacity per capita, *i.e.* Australia, Germany, Japan, and the Netherlands assuming that a hypothetical CIGS solar field would have more probability to be installed in one of these countries.[69] For these calculations, the environmental impact of the production of 1 kWh of energy was calculated using the SimaPro software. After that, to be able to assess the separate contribution of the passivation process, it was necessary to determine the environmental impact of standard CIGS solar cells, in this case, using data available in the literature [23] - Table 6. Considering the environmental impact calculated by Stamford *et al.* as baseline for non-passivated CIGS solar cells, the normalized environmental impact of passivated cells was estimated by adding the environmental impact of the NOA passivation process to that reported elsewhere.[23]

Table 6 - Normalization calculations of the environmental impact of standard non-passivated CIGS solar cells based on Stamford *et al.* 2019.[23]

Impact Category	Unit	Value	Normalization Factor	Normalized Value
Abiotic Depletion-Fossil Fuels	MJ	0.20	8.48×10^7	2.34×10^{-9}
Eutrophication	kg PO ₄ eq	7.62×10^{-5}	1.32×10^{10}	5.78×10^{-15}
Fresh Water Aquatic Ecotoxicity	kg 1,4-DB eq	7.58×10^{-4}	5.18×10^{11}	1.46×10^{-15}
Global Warming	kg CO ₂ eq	1.46×10^{-2}	5.03×10^{12}	2.91×10^{-15}
Human Toxicity	kg 1,4-DB eq	1.12×10^{-3}	7.75×10^{12}	9.60×10^{-18}
Marine Aquatic Ecotoxicity	kg 1,4-DB eq	1.48×10^{-1}	1.17×10^{14}	1.91×10^{-14}
Ozone Layer Depletion	kg CFC-11 eq	6.85×10^{-9}	8.93×10^7	7.76×10^{-17}
Photochemical Oxidation	kg C ₂ H ₄ eq	2.93×10^{-1}	8.48×10^9	6.04×10^{-12}
Total Normalized Value				2.34×10^{-9}

To answer the question mentioned before, it was needed to plot the normalized impacts in terms of energy production and manufacturing as function of time (equation 3),

$$I_{total} = (I_{CIGSu} - I_{1kWh}) \times \eta_{CIGS \text{ solar cell}} \times t + I_{Manufacturing \text{ of CIGS}} \quad (3)$$

where I_{total} refers to the total normalized environmental impact for a CIGS solar cell, I_{CIGSu} refers to the normalized environmental impact that the CIGS solar cell has during its lifetime, I_{1kWh} refers to the normalized environmental impact of the production of 1 kWh for each country, affected by its energy mix, $\eta_{CIGS \text{ solar cell}}$ refers to the efficiency of the solar cell, t refers to time (in hours) and $I_{Manufacturing \text{ of CIGS}}$ refers to the normalized environmental impact of manufacturing a CIGS solar cell. This equation was used for both non-passivated and passivated CIGS solar cells, translating the total environmental impact required to produce 1 kWh of energy as a function of time. Efficiency values of 11.90 % and 13.23 % were assumed for non-passivated and passivated CIGS solar cells, respectively. [49] Table 7 presents the total normalized environmental impact of producing 1 kWh of electricity in the considered world's leading countries in installed PV capacity per capita.

Table 7 - Total normalized impact of the production of 1 kWh.

Country	Total normalized impact per kWh
Australia	2.46×10^{-11}
Germany	1.14×10^{-11}
Japan	7.37×10^{-12}
Netherlands	5.11×10^{-12}
Portugal	6.33×10^{-12}

4 RESULTS AND DISCUSSION

The present study focused first on calculating the environmental impact of the passivation process carried out by the NOA group at INL, including the Characterization and Normalization steps. To have a holistic perspective and given the potential for the industrial implementation of this process, the obtained results were recalculated considering that the passivation process was carried out in the world leading countries of PV cells production, *i.e.* China, United States of America, Malaysia, and South Korea. Then, to be able to assess if the passivation process is beneficial or not, in environmental terms, the results were translated into the necessary years to neutralize the environmental impact brought by the passivation process, compared to standard CIGS solar cells, *i.e.*, manufactured without passivation treatment. In other words, the avoided environmental impact due to renewable electricity production from solar energy was estimated comparatively to the current environmental impact caused by the production of 1 kWh in the world leading countries of PV electricity production. Finally, a brief comparison was made with the literature to better understand if the obtained results are reasonable taking into account other similar works in the field. Nevertheless, it is important to note that the goal and scope definition of this study limits its comparison with other studies, due to the almost non-existing literature regarding LCA studies on CIGS solar cells, and particularly regarding passivation processes. From that perspective, the obtained results highlight the importance of this work to the field of GIGS solar cells, enabling them to have a deeper understanding of their environmental impact, while helping to identify the critical processes that need to be optimized.

4.1 ENVIRONMENTAL IMPACT OF THE NOA PASSIVATION PROCESS

As mentioned before, the CML-IA baseline methodology was used for the environmental impact calculations. Integrated into the SimaPro software, this baseline allowed obtaining the environmental impact for environmental impact categories listed in Table 8 and depicted in Figure 17.

Table 8 - Studied Environmental Categories and their respective units of measurement.

Environmental Impact Categories	Unit of Measurement
Global Warming	kg CO ₂ eq
Abiotic Depletion	kg Sb eq
Abiotic Depletion - Fossil Fuels	MJ
Ozone Layer Depletion	kg CFC-11 eq
Fresh Water Ecotoxicity	kg 1-4 DB eq
Marine Water Ecotoxicity	kg 1-4 DB eq
Terrestrial Ecotoxicity	kg 1-4 DB eq
Human Toxicity	kg 1-4 DB eq
Eutrophication	kg 1-4 DB eq
Acidification	kg SO ₂ eq
Photochemical Oxidation	kg C ₂ H ₄ eq

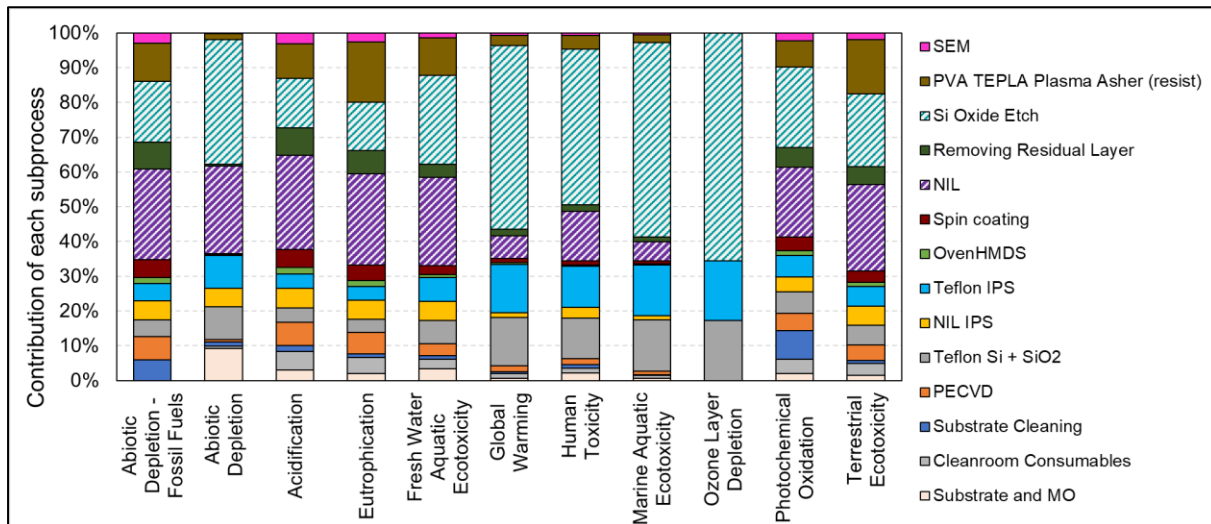


Figure 17 - Impact of each phase from the passivation process from all the studied environmental impact categories.

From Figure 17, it is perceptible that the silicon oxide etch (Si oxide Etch) and the NIL subprocesses have the greatest contributions for almost all environmental impact categories, being a preliminary indicator that these are the critical subprocesses in terms of environmental performance.

The Si oxide etch contributes especially to the ozone layer depletion (65.54% contribution) and to the marine aquatic ecotoxicity (55.88 % contribution). The ozone layer depletion refers to the thinning of the ozone layer present in the stratosphere (located at *ca.* 20-30 km high), mainly due to the reaction of chlorine and bromine atoms with the ozone molecules.[70] On the other hand, the Marine Aquatic Ecotoxicity category refers to the impacts of toxic substances on marine aquatic ecosystems. All the categories mentioned

before were analysed in detail, and their characterized values are present in Annex C and the respective graphics are presented in Annex E. The impactful contribution of the Si oxide etch process to these categories is mainly related to the need of repeating several times this subprocess due to equipment limitations. Almost all equipment of the INL Clean Room facilities is adapted to Si wafers with a diameter of 20 cm; it is important to mention that this equipment is pre-industrial units and has to be adapted for each purpose. For the case of the Si oxide etch, the process has to be repeated seven times for fourteen SLG substrates, since the equipment can only handle two SLG substrates at a time, therefore totalling a seven-time process to give continuity to the whole passivation process. With this said, it is important to note that the Si oxide etch process uses a considerable amount of C_4F_8 (octafluorocyclobutane). This organofluorine compound is obtained from the dimerization of tetrafluoroethylene and the reductive coupling of 1,2-dichloro-1,1,2,2-tetrafluoroethane should, resulting in long atmospheric lifetimes and altering Earth's radiative budget. Although PFAS (Per- and Polyfluoroalkyl Substance) do not directly affect the ozone layer due to the lack of chlorine atoms, chemical reactions that occur in the atmosphere can transform C_4F_8 into ozone layer depleting and global warming gases.[48][49][50] Also, this substance has a high environmental impact on fresh and saltwater ecotoxicity, according to the Global Harmonized System (GHS), including the hazardous label GHS09, which refers to "Hazardous to Aquatic Environment". Finally, C_4F_8 contains fluorinated greenhouse gases (F-GHG), which are the most potent and long-lasting greenhouse gases emitted by human activities.[49]

The NIL subprocess suffers from the same problem, being performed four times to a total of fourteen substrates, resulting in the usage of 1.469 kg of compressed air, which translates into a huge consumption of electricity and, subsequently, in an impactful contribution to related environmental impact categories. It is important to emphasize that NIL techniques are being used for producing the passivation layers of CIGS solar cells.

The two Teflon subprocesses performed have a very high impact, despite being performed only one time, due to the usage of C_4F_8 , a PFAS; as a matter of fact, this substance is the main common material in three of the most impactful subprocesses, Si Oxide Etch and the two Teflon subprocesses.

Figure 18 demonstrates the passivation processes and what category they affect the most.

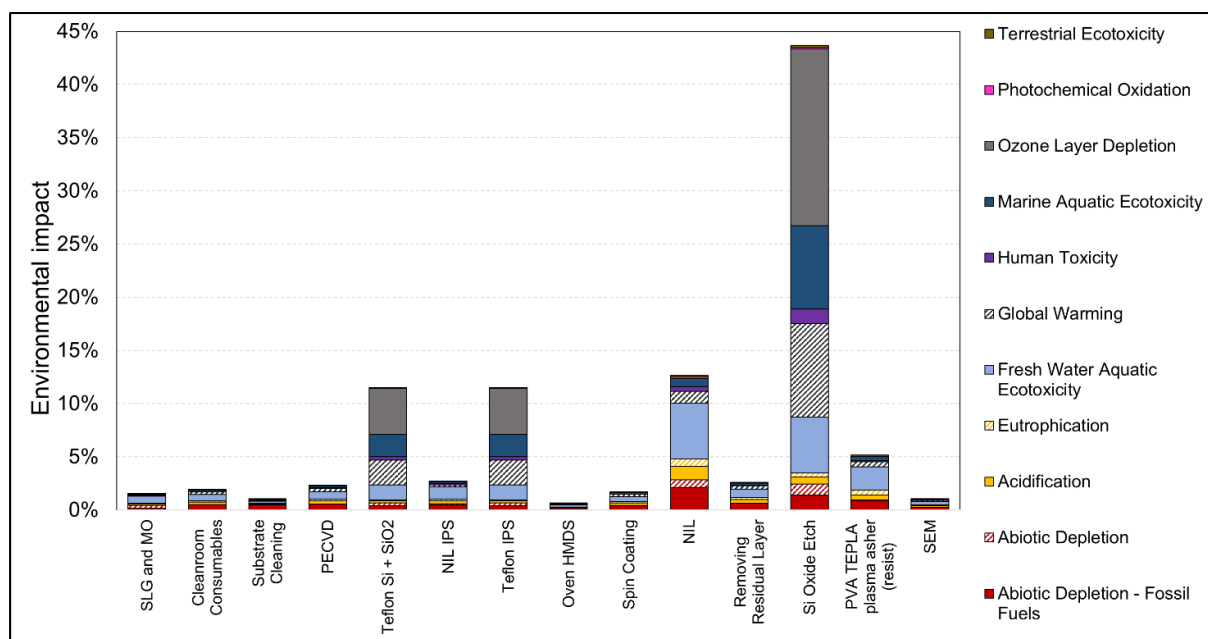


Figure 18 - Environmental impact of each subprocesses involved in the passivation of CIGS solar cells.

From the normalized impact graph, it is perceptible that the silicon oxide etch is the subprocess with the greatest contribution to the total environmental impact, totalling 43.68 %, followed by NIL (12.66 %), and by the subprocesses that use Teflon (11.52 %). The normalized values of all subprocesses for the studied categories are showcased in Annex H. The subprocess that presents the lowest normalized impact is the oven HMDS, with a total contribution of 0.63 %. This might sound somehow strange at a first glance, given that processes that require the use of ovens usually have a high environmental impact due to the considerable power consumption. However, in the present case, the oven is used only once and 1 mL of HMDS gas can be used for *ca.* 200 wafers, making its impact almost negligible. This reinforces the importance of performing each step at once. As an example, the normalized environmental impact was recalculated considering that the silicon oxide etch could be performed at once - Figure 19.

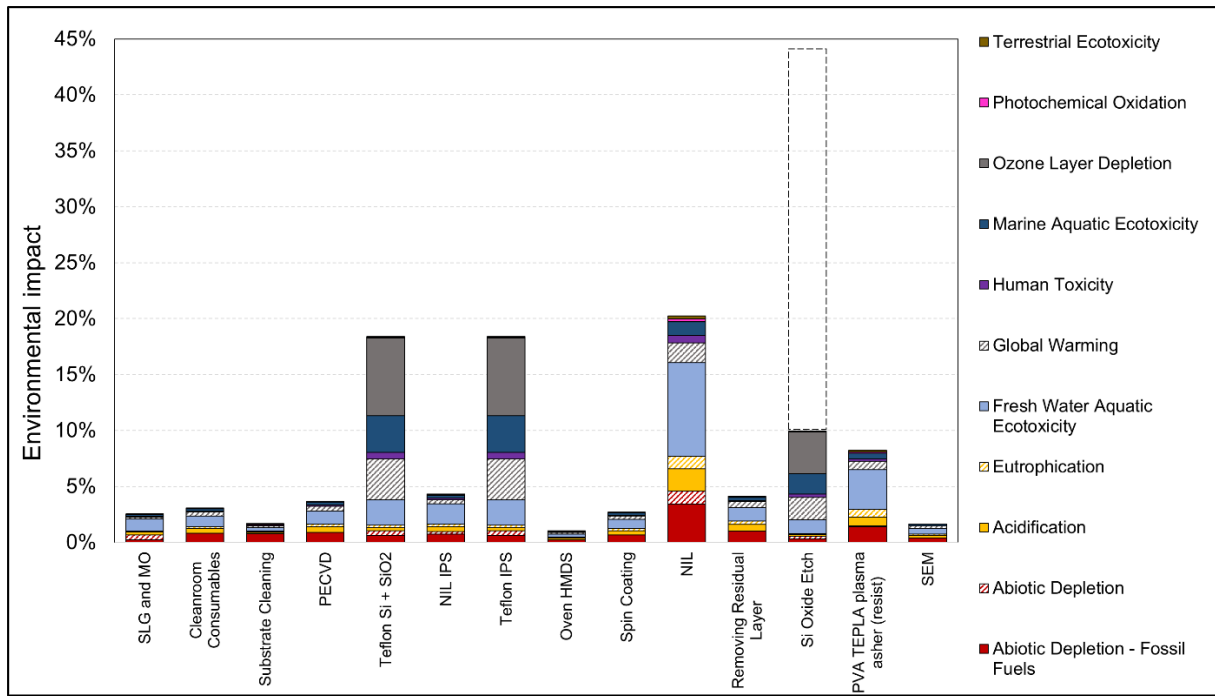


Figure 19 - Environmental impact associated with all subprocesses, considering that the Si oxide etch is performed only once.

Performing the Si oxide etch at once for fourteen SLG substrates would result in an impact reduction of 37.44 %. In this case, the subprocess with the largest contribution to the overall environmental impact would be the NIL, with a recalculated contribution of 20.24%. Following this approach, it becomes obvious that the most effective and impactful environmental impact mitigation strategy is the optimization of the NOA process for substrates that allow fully using of the available active area of the clean room equipment, or the repurposing of the clean room equipment for this specific process, *e.g.*, by using different sample holders. It is important to note that when industrialization is brought into sight, all subprocesses would be fully optimized for the used machinery, which means that the harmful effect of repeating subprocesses would be eliminated. Still, for this particular work, such an assumption should not be simply extrapolated since the whole process was optimized for fourteen SLG substrates with specific dimensions and the inventory data collection was performed considering this baseline. On the other hand, all processes conducted at the clean room facilities of INL have an industrial perspective on sight; all equipment is pre-industrial units, aiming at replicating what would be an industrial production line. Therefore, removing the need of repeating subprocess must be considered, at least, for future aims. In this case, the subprocesses with the greatest contribution to the total environmental impact are those that use Teflon. As so, another mitigation strategy should be the search for alternative materials to PTFE, especially because PFAS are expected to be banned from use in Europe in the upcoming years. [71]

After normalization, the contribution of the NOA passivation process to each environmental impact category was analysed in detail - Figure 20. Annex D showcases the substances with the highest impact in each of the studied categories.

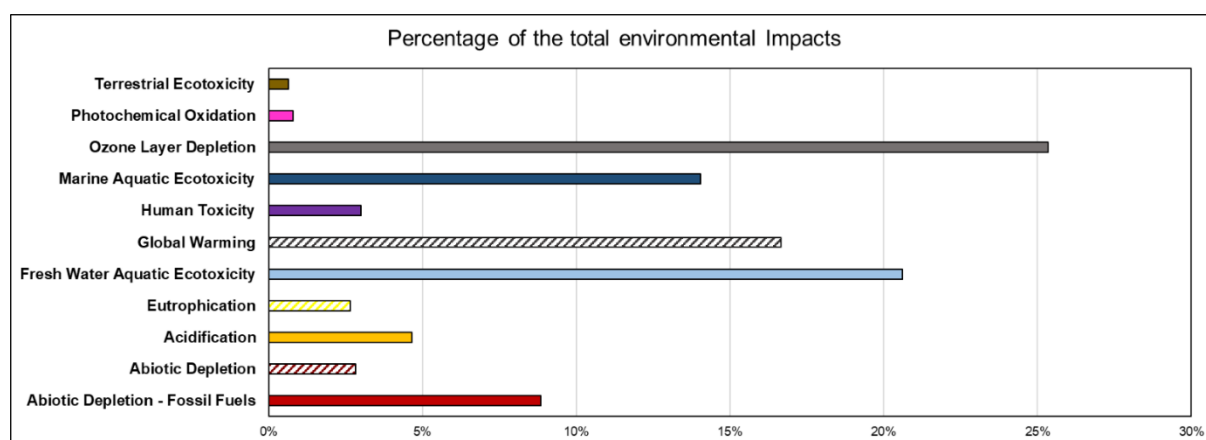


Figure 20 - Categories with the most environmental impact associated.

Considering the baseline scenario, which includes the repetition of some subprocesses, the NOA's passivation process contributes mostly to ozone layer depletion (25.34 %), fresh water ecotoxicity (20.61 %) and global warming (16.66 %). LCA studies on CIGS solar cells have also identified the freshwater ecotoxicity as one of the most critical environmental impact categories, but the other categories that are more frequently mentioned as being critical for this technology are human toxicity and abiotic depletion, which were not observed for the present case study. It is important to note that most LCA studies on CIGS solar cells consider a cradle-to-grave approach, assuming a 20-year lifetime (for solar energy production) and disposal in landfills as end-of-life activity. This study focused only on a specific manufacturing process, *i.e.*, the interface passivation, being, therefore, a small part of the entire manufacturing of CIGS solar cells. Given that CIGS solar cells comprise several critical raw materials and toxic elements (Cd, In, Ga, Se), when the whole life cycle is considered, higher impacts are expected for toxicity-related and resource depletion categories. As an example, indium lung disease is recognized as a potentially fatal disease caused by the inhalation of indium-containing particles; also, exposure to gallium halide complexes can result in acute toxicity, as soluble gallium salts can result in nephrotoxicity in animals.[72] However, cadmium presents naturally the highest concerns both in human and environmental terms, being present in the CdS layer in CIGS solar cells. Inhalation of cadmium particles can result in chemical pneumonitis, pulmonary edema, and death. Kidney damage has been described to be the main problem for patients chronically exposed to cadmium.[73] Cadmium is also referred as a strong environmental hazard. Global warming potential has been identified as one of the most critical categories for many common manufacturing processes due to the extensive use of fossil fuels to supply the energy

consumption of large manufacturing plants, especially in developing countries, such as China, India, or Malaysia.[74] Nevertheless, for the NOA passivation process, the large contribution to the ozone layer depletion can be attributed to the extensive use of C_4F_8 in the silicon oxide etch and in the anti-sticking layer deposition processes. Also, PFAS have a high bio cumulative effect, being, therefore, an impactful pollutant to aquatic compartments.[75]

4.2 HOLISTIC ANALYSIS TO THE NOA'S PASSIVATION PROCESS

As already mentioned, the clean room processes carried out at INL always have industrial applications on sight. As so, it is interesting to investigate what would be the environmental impact if this process was conducted in some of the world-leading countries of PV cells manufacturing. To perform this study, the SimaPro software was used with the same inventory considered for the NOA passivation process carried out at INL, *i.e.*, in Portugal, is only possible to change the origin of the electricity. As so, the specific energy mix of each country was selected as energy input, and the environmental impact was recalculated for China, USA, Malaysia, and South Korea. Figure 21 and Figure 22 show the relative contribution of each subprocess to the ozone layer depletion and fresh water ecotoxicity, respectively, since these are the two most affected impact categories (as depicted in Figure 20).

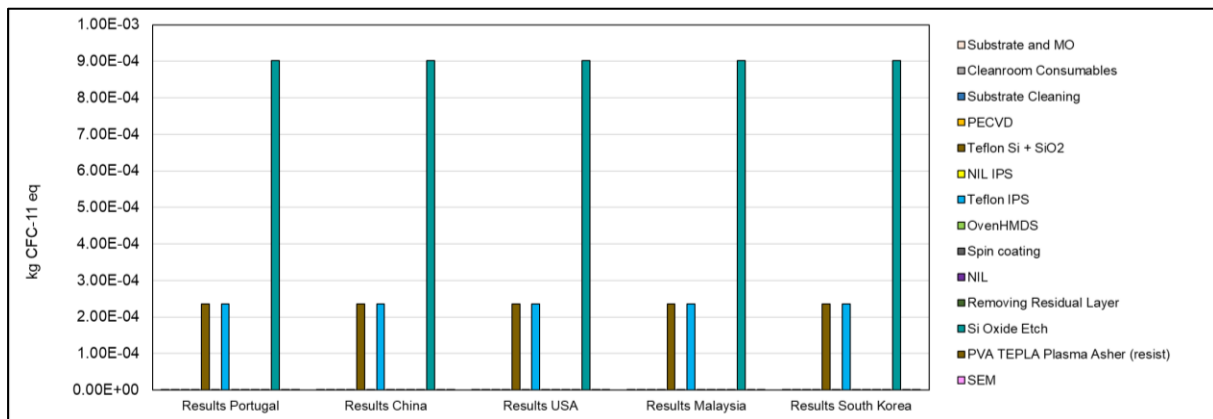


Figure 21 - Impact on the Ozone Layer Depletion of the NOA process in the world's leading PV solar cells producers.

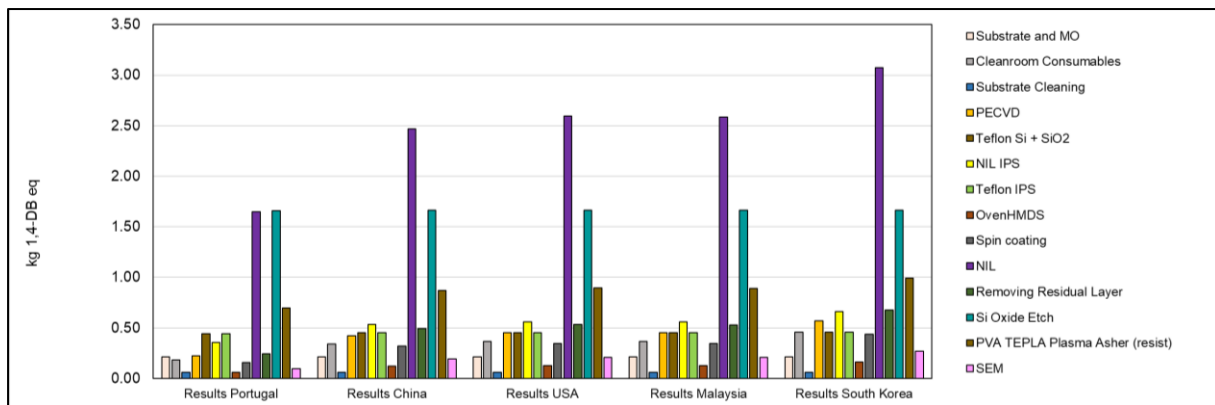


Figure 22 - Impact on the Fresh Water Aquatic Ecotoxicity of the NOA process in the world leading PV solar cells producers.

Changing the origin of the electricity affects all impact categories. As an example, a higher share of coal in the energy mix can lead to a significant contribution to photochemical ozone creation, eutrophication, acidification, and abiotic depletion, apart from the expected contribution to the global warming potential. [76] Therefore, the environmental impact of high-power consuming subprocesses is more vulnerable to the origin of the electricity, and its contribution to the total normalized impact can change accordingly. This camouflaged effect is shown in Figures 21 and 22. Despite the ozone layer depletion and fresh water ecotoxicity are the two most affected categories considering the entire process, both are highly dependent on the Si oxide etch and Teflon deposition, which are low energy consumers (see Table 3). Therefore, it is not expected to observe significant changes in ozone layer depletion and fresh water ecotoxicity by changing the origin of electricity. On the other hand, the two subprocesses with the highest energy consumption are NIL and the removal of the residual layer, and these processes highly contribute to acidification, eutrophication, and abiotic depletion of fossil fuels (Figure 17). Subsequently, performing the NOA's passivation process in different countries, and changing the energy mix, accordingly, is expected to have a major effect on these impact categories, which can be confirmed in Figures 23, 24 and 25.

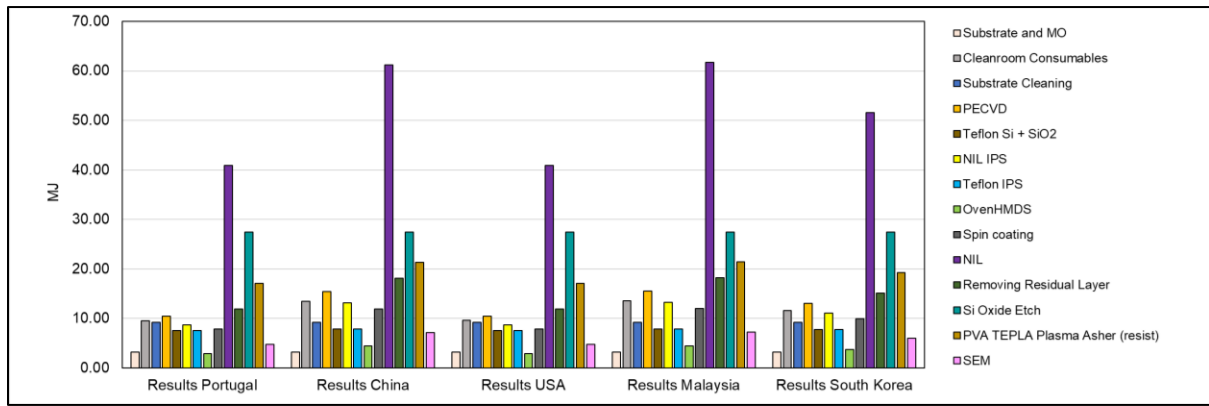


Figure 23 - Impact in the Abiotic Depletion - Fossil Fuels of the NOA process in the world's leading PV solar cells producers.

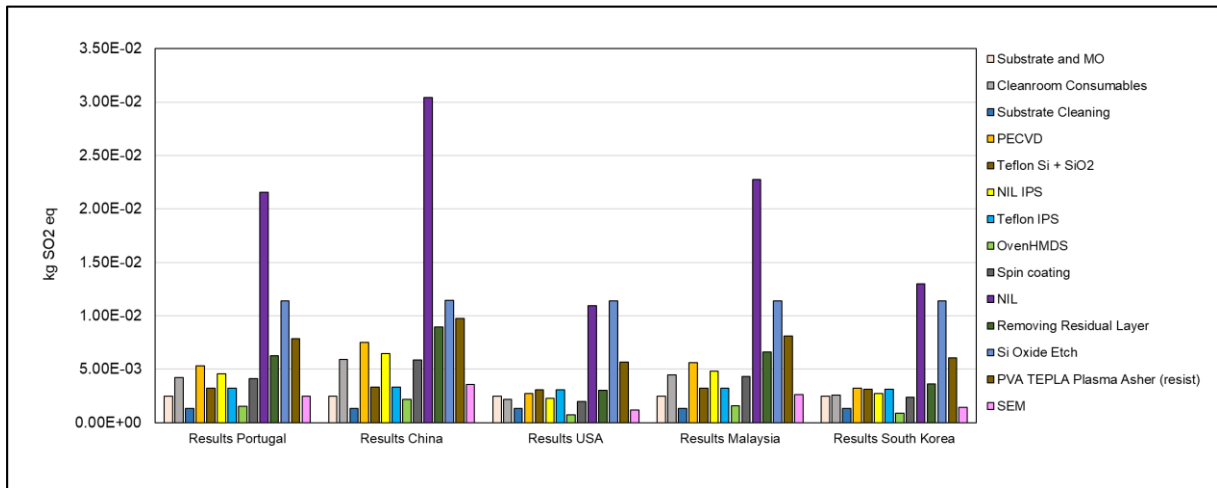


Figure 24 - Impact in Acidification of the NOA process in the world's leading PV solar cells producers.

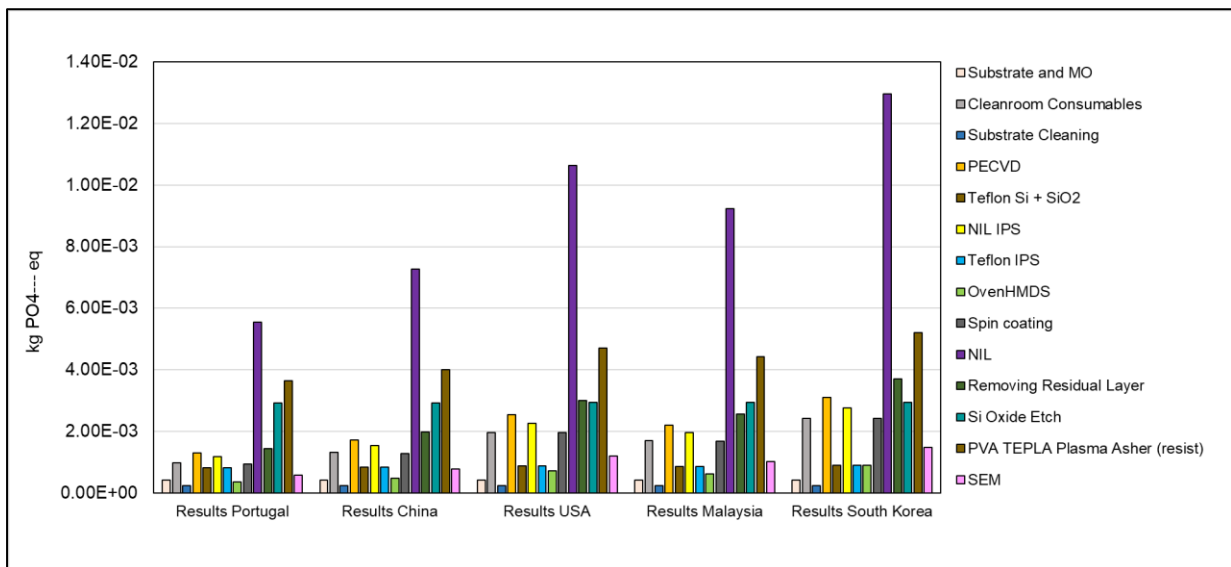


Figure 25 - Impact in Eutrophication of the NOA process in the world's leading PV solar cells producers.

Regarding the environmental categories plotted in Figures 23-25, clear changes are observed between countries. The abiotic depletion of fossil fuels and eutrophication are particularly relevant for China, given the intensive use of coal in the energy mix (see Annex F). Eutrophication assumes particular relevance in South Korea, possibly due to the high share of nuclear power in the energy mix (Annex F), which is associated with thermal pollution, a significant inducer of eutrophication. [77]

Finally, the total normalized impact of the NOA passivation process was recalculated for the world's leading PV cells manufacturers and plotted in Figure 26.

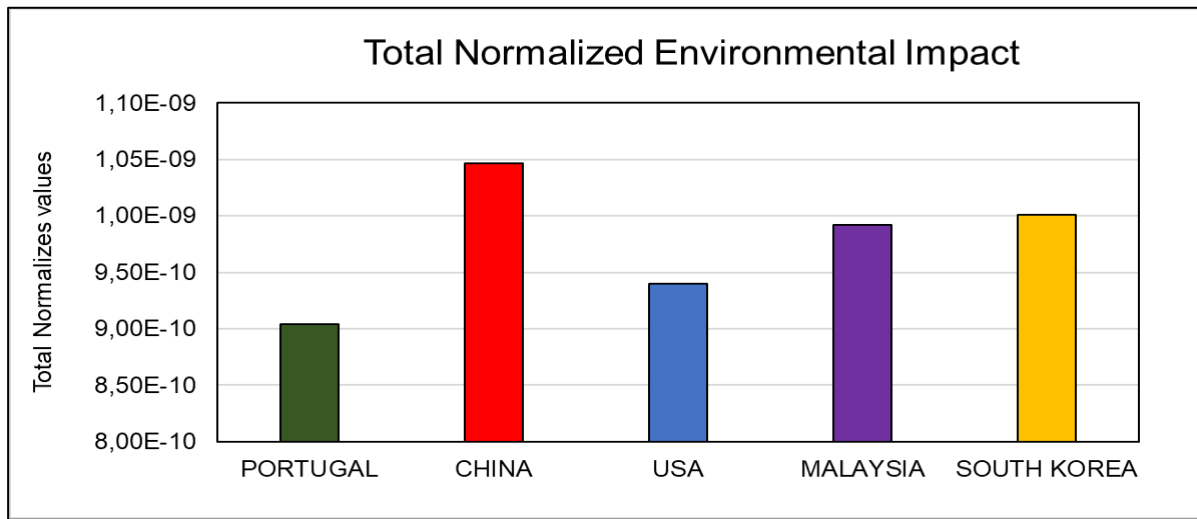


Figure 26 - Total Normalized Impact of the NOA passivation process, assuming that it would be carried out in the world leading countries of PV cells manufacturing.

From Figure 26 it can be seen that the countries from the Asian Continent have the highest normalized environmental impact, and Portugal is the country with the lowest impact. As already explained, since only the source of the electricity was changed between countries, it is expected that those with the highest share of renewables should present the lowest impact. In this case, this can be confirmed by the fact that Portugal presents the lowest environmental impact, and it is simultaneously the country with the highest share of renewables (ca. 58.82 % - Annex F). The contribution of each subprocess to the total impact for the remaining categories and the countries under study is presented in Annex G. Overall, it can be inferred that performing the NOA passivation process in countries with a high share of renewables in their energy mix is a predictive mitigation strategy, helping to make the CIGS solar cells manufacturing more environmentally friendly. On the other hand, considering the high probability that, in case this passivation process is successfully transferred to the industry, it would be carried out in China, Malaysia or South Korea, reducing power consumption, or making the manufacturing process as efficient as possible,

this would be the only way to compensate the inevitable high environmental impact associated with the use of fossil fuels to supply the grid.

4.3 ASSESSMENT OF THE ENVIRONMENTAL PERFORMANCE OF PASSIVATED CIGS SOLAR CELLS

One of the main goals of this thesis is to assess if the passivation process developed by the NOA group is beneficial from an environmental point of view. In other words, adding an interface passivation process to the CIGS solar cells manufacturing carries an additional environmental impact with it. However, passivated cells are more efficient than standard ones, which translates into additional production of renewable electricity from solar energy, allowing to reduce the contribution of fossil fuels to the energy mix and reducing land use for the generation of a certain amount of solar power. To answer this question, it becomes necessary to compare the total normalized impact of standard CIGS solar cells and passivated CIGS cells, the second corresponding to the first with the addition of the environmental impact of the passivation process. The environmental impact of standard CIGS solar cells was obtained from Stamford *et al.* [23] Then, the environmental impact of producing 1 kWh was obtained for the world's leading countries of installed PV capacity per capita, aiming at calculating the avoided environmental impact arising from the increase in renewable solar energy production due to the efficiency increase. Finally, using equation 3, together with the total normalized values from table 6 and the normalized environmental impact of producing 1 kWh in different countries, it was possible to calculate how much time is needed to compensate for the environmental impact of the CIGS solar cells manufacturing. The obtained results are presented in Table 9.

Table 9 - Environmental payback time of standard CIGS solar cells and passivated CIGS solar cells using the NOA process, expressed in the necessary years to neutralize the environmental impact of the manufacturing process relative to the avoided environmental impact of energy production in world leading countries of installed PV capacity per capita.

	Environmental payback time of standard CIGS solar cells (years)	Environmental payback time of passivated CIGS solar cells (years)
Australia	0.27	0.39
Germany	0.59	0.83
Japan	0.91	1.29
Netherlands	1.32	1.86
Portugal	1.07	1.50

From table 9, and considering the Portuguese scenario, it takes on average 10 months for the CIGS solar cells to overcome the environmental impact associated with their manufacturing, and 14 months (one year and two months) for the passivated CIGS to become environmentally neutral. It is not surprising that the most pollutant countries take the least

amount of time for the process to be worth it (Germany and Australia) since it was assumed that the CIGS solar panels do not cause any significant environmental impact during their life usage; so, the only environmental impact associated with the CIGS solar panels is that calculated before the usage phase in their life cycle. It becomes then clear that producing green electricity from CIGS solar panels is more impactful in less green countries, where any increase in efficiency is highly relevant, easily surpassing the negative contribution of the passivation process. Moreover, it should be emphasized that the passivation processes not only increase the efficiency of the CIGS solar cells but also their stability; nowadays, they already have a lifetime of more than 25 years.

5 CONCLUSIONS

The main goal of this thesis was to assess the environmental impact of the passivation process of CIGS solar cells implemented by the NOA group at INL. To attain this goal an LCA study was performed. SimaPro software, the ecoinvent database, the CML-IA methodology and the EU 25 normalization factors were used during the calculation steps.

The subprocess with the greatest contribution to the total environmental impact is the Si oxide etch, followed by the Nanoimprint lithography (NIL). These two subprocesses have to be repeated more times, due to equipment limitations, which was considered to be the main reason for their high environmental impact. Most of the clean room equipment are pre-industrial units, optimized for Si wafers with a diameter of 20 cm, and not for small size square samples. Apart from the repetition issue, the high environmental impact of the Si oxide etch subprocess is also related to the use of C_4F_8 ; indeed, three of the subprocesses with the highest impact use this gas, which is an impactful pollutant of the atmospheric and aquatic compartments. Regarding the NIL subprocess, the high environmental impact was mainly attributed to the significant use of compressed air, requiring high electricity consumption. Overall, the passivation process contributes mainly to ozone layer depletion (25.34 %), freshwater ecotoxicity (20.61 %) and global warming (16.66 %).

Given that repeating some subprocesses was a critical contributor to the total environmental impact, an obvious mitigation strategy should be the full optimization of the clean room equipment for holding multiple small-size samples at once or adapting the passivation process to larger substrates. As an example, performing the Si oxide etch at once would result in a 37.44 % decrease in the total environmental impact. Another important mitigation strategy, for example, relies on the use of other anti-sticking layers than C_4F_8 , especially because PFAS are expected to be banned in Europe in the upcoming years.[71]

To have a holistic overview of the obtained results, the environmental impact was recalculated for the world's leading PV producers, *i.e.*, considering that the passivation process would be carried out in those countries. It was observed that the environmental impact would be higher in Asian countries, with China presenting the highest value, corresponding to a 17.63 % increase comparatively to Portugal. This was mainly attributed to the large share of coal in China's energy mix (60.75 %), generating considerably more pollution.

Finally, it was estimated how much time is needed to neutralize the additional environmental impact brought by the passivation process, considering that this process allows having an increase in the CIGS efficiency of *ca.* 1.33 %, which translates into higher renewable energy production. This analysis was made for the world's leading countries of installed PV capacity per capita, assuming the current environmental impact generated by the production of 1 kWh as the baseline. For the Portuguese scenario, it was concluded that

passivated CIGS solar cells require 4 additional months of green electricity production to compensate for the environmental impact of the passivation process, whereas for Australia, the country that presented the lowest environmental payback time, only 1 month and 2 weeks are required.

6 CLOSING REMARKS AND SUGESTIONS FOR FUTURE WORK

From a global perspective, the main goal was fully achieved, *i.e.*, the environmental impact of the NOA passivation process was fully assessed and quantified. The main steps of the LCA study were successfully addressed, being possible to obtain the normalized environmental impact. More important, despite the tight timeline, this dissertation went well beyond the pre-defined work plan, including: i) a comparative study based on the estimation of the environmental impact of the passivation process carried out in the world-leading countries in PV cells manufacturing, assuming the Portuguese case as baseline; ii) a comparative analysis of the environmental impact of electricity production in the world-leading countries in PV installed capacity per capita, followed by the estimation of the environmental payback time for those countries, where a hypothetical CIGS solar cells field is more likely to be installed; *i.e.*, it was estimated how much time is needed to compensate the environmental impact added by the passivation process, based on the extra green energy production brought by the increase in efficiency.

During the work performed throughout this dissertation it was possible to identify some important limitations, listed as follows: i) the lack of a full inventory at INL regarding the clean room equipment, especially in what concerns power and water consumption, generated emissions and waste, and basic specifications of the equipment; ii) the lack of literature data on LCA studies regarding the manufacturing processes of CIGS solar cells and, particularly, passivation processes; iii) limited access to the full potential of SimaPro software, since the available license was an educational one, restricting the access to some important menus or options; iv) lack of data for some materials in the ecoinvent database, forcing to perform some approximations and assumptions; v) absence of standardized methodologies to compare different normalization factors between studies on LCA of CIGS solar cells; vi) the non-existence of weighing factors especially conceived for the solar energy field; and vii) the lack of time to perform the dissertation work more calmly, allowing to study the obtained results more in detail and, above all, allowing for a comparative study with the literature aiming at understanding how the obtained results compare with others reported within the topic.

Based on the aforementioned limitations, it was possible to identify important suggestions for future work. First, to properly assess the environmental benefits of the NOA passivation process, and to calculate the necessary time to overcome the additional impact, detailed LCI data should be obtained for the complete manufacturing of CIGS solar cells, in this case, for the manufacturing processes carried out by Uppsala University. Therefore, it would be interesting to test some mitigation strategies aiming at reducing the environmental impact of the most harmful subprocesses. As an example, it would be quite interesting to search for alternatives to the use of C_4F_8 and PTFE, to test them, and finally to conclude if they are

viable and how much environmental impact they avoid. Another important weak point that can be easily addressed is the lack of vital information regarding the clean room equipment. It is highly recommended to strengthen the available database of that equipment, especially regarding power and water consumption and how the generated emissions and waste are treated. For the particular case of air emissions, it should be investigated what are the INL building specifications regarding gaseous emissions, *i.e.*, where the exhaust gases generated from different machines go and if there are filters in the chimneys. Finally, the NOA group is currently studying the stability of passivated CIGS solar cells, especially regarding the NIL technique. As so, in the case it is found that the NOA's interface passivation allows increasing the stability of these cells, a broader LCA study and environmental payback assessment should be performed, including the whole lifetime of the cells, and not only the manufacturing step. Regarding the LCA study itself, it is recommended to perform a sensitivity analysis to validate the significance of the obtained values. Additionally, a more complete approach should consider the possibility of repeating the resist deposition in case it reveals to be in bad condition.

Overall, this dissertation work highlighted the difficulty of performing complete and scrutinized LCA studies on solar cells. This might explain why there are so few studies on the topic. The research community is mostly focused on understanding the fundamentals of CIGS solar cells and on improving their efficiency, rather than reducing their overall impact. This is somehow paradoxical, given that the ultimate objective of this technology is to contribute to the decarbonization of the energy sector and to contribute to sustainable development, which cannot be truly achieved if the technology is not produced in the most environmentally friendly and efficient way. As so, this study is particularly relevant to the field since, to my best knowledge, this is the first LCA study addressing

passivation processes of thin film solar cells. Additionally, this was the first LCA study conducted at the NOA group, opening the door to similar studies. More importantly, this work allowed identifying the most critical subprocesses of CIGS solar cells passivation, being a helpful contribution to further improve it and support future decision-making steps for viable applications.

Solar energy harvesting is currently in the spotlight, so, developing new and more efficient manufacturing processes has never been so relevant. This work gave me insights into the complexity of the laboratorial side involved in this research field and their environmental and economic side, vital for achieving further technological advancements.

7 REFERENCES

1. IEA, *World Energy Outlook 2021*. 2021.
2. Paris, I., *Global Energy Review 2021*. 2021.
3. Al-Ghussain, L., *Global warming: review on driving forces and mitigation*. Environmental Progress & Sustainable Energy, 2019. **38**(1): p. 13-21.
4. Kweku, D.W., et al., *Greenhouse effect: Greenhouse gases and their impact on global warming*. Journal of Scientific research and reports, 2017: p. 1-9.
5. Rhode, R., *Global Temperature Report for 2021*. 2022, Berkeley Earth.
6. Ritchie, H. and M. Roser, *CO₂ and greenhouse gas emissions*. Our world in data, 2020.
7. Institute., W.R., *Climate Watch Historical GHG Emissions*. 2021.
8. EC, *COMMUNICATION FROM THE COMMISSION TO THE EUROPEAN PARLIAMENT, THE EUROPEAN COUNCIL, THE COUNCIL, THE EUROPEAN ECONOMIC AND SOCIAL COMMITTEE AND THE COMMITTEE OF THE REGIONS The European Green Deal*. 2019.
9. COP, *Paris Agreement*, E. Union, Editor. 2016.
10. EU, *GREEN PAPER A 2030 framework for climate and energy policies*, E. Union, Editor. 2013.
11. EC, *COMMUNICATION FROM THE COMMISSION TO THE EUROPEAN PARLIAMENT, THE COUNCIL, THE EUROPEAN ECONOMIC AND SOCIAL COMMITTEE AND THE COMMITTEE OF THE REGIONS A policy framework for climate and energy in the period from 2020 to 2030*. 2014.
12. Agency, I.E. *Global Energy Review 2021 Renewables*. 2021 [cited 2021; Available from: <https://www.iea.org/reports/global-energy-review-2021/renewables>].
13. Van de Krol, R. and M. Grätzel, *Photoelectrochemical hydrogen production*. Vol. 90. 2012: Springer.
14. BP, *bp Statistical Review of World Energy 2021*. 2021: BP.
15. IRENA. *Renewable Energies Technologies*. 2022 [cited 2022; Available from: <https://www.irena.org/Statistics/View-Data-by-Topic/Capacity-and-Generation/Technologies>].
16. Dipankar Deb, K.B., *Chapter 1 - Introduction to photovoltaics*, in *Degradation, Mitigation, and Forecasting Approaches in Thin Film Photovoltaics*, K.B. Dipankar Deb, Editor. 2021, Academic Press. p. 1-18.
17. Luísa Andrade, T.L., Helena Aguilar Ribeiro, Adélio Mendes, *Transient phenomenological modeling of photoelectrochemical cells for water splitting - Application to undoped hematite electrodes*, in *International Journal of Hydrogen Energy*. 2011. p. Pages 175-188,.
18. Amato, A. and F. Beolchini, *End-of-life CIGS photovoltaic panel: A source of secondary indium and gallium*. Progress in Photovoltaics: Research and Applications, 2019. **27**(3): p. 229-236.
19. Energy, U.O.o.E.E.R. *Crystalline Silicon Photovoltaics Research*. 2021; Available from: <https://www.energy.gov/eere/solar/crystalline-silicon-photovoltaics-research>.
20. Curado, M.A., et al., *Front passivation of Cu (In, Ga) Se₂ solar cells using Al₂O₃: Culprits and benefits*. Applied Materials Today, 2020. **21**: p. 100867.
21. Kaelin, M., D. Rudmann, and A. Tiwari, *Low cost processing of CIGS thin film solar cells*. Solar Energy, 2004. **77**(6): p. 749-756.
22. Cunha, J.M., et al., *High-Performance and Industrially Viable Nanostructured SiO_x Layers for Interface Passivation in Thin Film Solar Cells*. Solar RRL, 2021. **5**(3): p. 2000534.
23. Stamford, L. and A. Azapagic, *Environmental impacts of copper-indium-gallium-selenide (CIGS) photovoltaics and the elimination of cadmium through atomic layer deposition*. Science of the Total Environment, 2019. **688**: p. 1092-1101.
24. Tsoutsos, T., N. Frantzeskaki, and V. Gekas, *Environmental impacts from the solar energy technologies*. Energy policy, 2005. **33**(3): p. 289-296.
25. Roy, P., et al., *A review of life cycle assessment (LCA) on some food products*. Journal of food engineering, 2009. **90**(1): p. 1-10.
26. van der Hulst, M.K., et al., *A systematic approach to assess the environmental impact of emerging technologies*.
27. Administration, U.S.E.I. *Solar explained Photovoltaics and electricity*. 2021 [cited 2021; Available from: <https://www.eia.gov/energyexplained/solar/photovoltaics-and-electricity.php>].
28. Knier, G. *How do Photovoltaics Work?* 2008 [cited 2021; Available from: <https://science.nasa.gov/science-news/science-at-nasa/2002/solarcells>].
29. energy, s. *HOW DO SOLAR PANELS WORK? THE SCIENCE OF SOLAR EXPLAINED*. 2021 [cited 2021; Available from: <https://solect.com/the-science-of-solar-how-solar-panels-work/>].

- 30.Celik, I., et al., *Environmental analysis of perovskites and other relevant solar cell technologies in a tandem configuration*. Energy & Environmental Science, 2017. 10(9): p. 1874-1884.
- 31.Bye, G. and B. Ceccaroli, *Solar grade silicon: Technology status and industrial trends*. Solar Energy Materials and Solar Cells, 2014. 130: p. 634-646.
- 32.Yan, D., *Siemens Process*, in *Handbook of Photovoltaic Silicon*, D. Yang, Editor. 2019, Springer Berlin Heidelberg: Berlin, Heidelberg. p. 37-68.
- 33.Pizzini, S., *Towards solar grade silicon: Challenges and benefits for low cost photovoltaics*. Solar energy materials and solar cells, 2010. 94(9): p. 1528-1533.
- 34.Fraas, L.M., *History of solar cell development*, in *Low-cost solar electric power*. 2014, Springer. p. 1-12.
- 35.Ohl, R.S., *Light-sensitive electric device*. 1946, Google Patents.
- 36.Nogueira, C.E.C., et al., *Performance of monocrystalline and polycrystalline solar panels in a water pumping system in Brazil*. Renewable and Sustainable Energy Reviews, 2015. 51: p. 1610-1616.
- 37.[Comparison] *Monocrystalline vs Polycrystalline Solar Panels*. 2020 [cited 2021; Available from: <https://solarmagazine.com/solar-panels/monocrystalline-vs-polycrystalline-solar-panels/>].
- 38.Dobrzański, L., et al., *Electrical properties mono-and polycrystalline silicon solar cells*. Journal of Achievements in Materials and Manufacturing engineering, 2013. 59(2): p. 67-74.
- 39.ENERGY, O.o.E.E.R. *Cadmium Telluride*. 2022; Available from: <https://www.energy.gov/eere/solar/cadmium-telluride>.
- 40.Ramanujam, J., et al., *Flexible CIGS, CdTe and a-Si: H based thin film solar cells: A review*. Progress in Materials Science, 2020. 110: p. 100619.
- 41.Kronik, L., D. Cahen, and H.W. Schock, *Effects of sodium on polycrystalline Cu (In, Ga) Se₂ and its solar cell performance*. Advanced Materials, 1998. 10(1): p. 31-36.
- 42.Kazmerski, L., F. White, and G. Morgan, *Thin-film CuInSe₂/CdS heterojunction solar cells*. Applied Physics Letters, 1976. 29(4): p. 268-270.
- 43.Colombara, D., et al., *Sodium enhances indium-gallium interdiffusion in copper indium gallium diselenide photovoltaic absorbers*. Nature communications, 2018. 9(1): p. 1-12.
- 44.Dhere, N.G., *Toward GW/year of CIGS production within the next decade*. Solar Energy Materials and Solar Cells, 2007. 91(15-16): p. 1376-1382.
- 45.Cooray, N.F., et al., *Large area ZnO films optimized for graded band-gap Cu (InGa) Se₂-based thin-film mini-modules*. Solar Energy Materials and Solar Cells, 1997. 49(1-4): p. 291-297.
- 46.Harper, G.D.J. *CIGS solar cell technology*. 2016 [cited 2021; Available from: <https://www.britannica.com/technology/CIGS-solar-cell>].
- 47.Eisenberg, D.A., et al., *Comparative alternative materials assessment to screen toxicity hazards in the life cycle of CIGS thin film photovoltaics*. Journal of hazardous materials, 2013. 260: p. 534-542.
- 48.Salome, P.M., et al., *Passivation of interfaces in thin film solar cells: Understanding the effects of a nanostructured rear point contact layer*. Advanced Materials Interfaces, 2018. 5(2): p. 1701101.
- 49.Oliveira, K., et al. *SiO_x patterned based substrates implemented in Cu (In, Ga) Se₂ ultrathin solar cells: optimum thickness*. in *2021 IEEE 48th Photovoltaic Specialists Conference (PVSC)*. 2021. IEEE.
- 50.Klöppfer, W., *Life cycle assessment*. Environmental Science and Pollution Research, 1997. 4(4): p. 223-228.
- 51.Hauschild, M.Z., R.K. Rosenbaum, and S.I. Olsen, *Life cycle assessment*. Vol. 2018. 2018: Springer.
- 52.Curran, M.A., *Life cycle assessment: a review of the methodology and its application to sustainability*. Current Opinion in Chemical Engineering, 2013. 2(3): p. 273-277.
- 53.ISO, *Environmental management – Life cycle assessment – Principles and framework*, I.O.f. Standardization, Editor. 2006.
- 54.ISO, *Environmental management – Life cycle assessment – Requirements and guidelines*, I.O.f. Standardization, Editor. 2006.
- 55.Jonker, G. and J. Harmsen, *Engineering for sustainability: a practical guide for sustainable design*. 2012: Elsevier.

56. Associations, T.I.C.o.C. *How to Know If and When Its Time to Commission a Life Cycle Assessment*. 2021 [cited 2021; Available from: <https://icca-chem.org/resources/how-to-know-if-and-when-its-time-to-commission-a-life-cycle-assessment/>].
57. Zalasiewicz, J., et al., *Scale and diversity of the physical technosphere: A geological perspective*. The Anthropocene Review, 2017. 4(1): p. 9-22.
58. Matthews, H.S., C.T. Hendrickson, and D.H. Matthews, *Life cycle assessment: Quantitative approaches for decisions that matter*. Retrieved June, 2015. 1: p. 2016.
59. 2022 [cited 2022; Available from: <https://gabi.sphera.com/international/index/>].
60. 2022; Available from: <https://simapro.com/>.
61. Ecology, C.-D.o.I. *CML-IA Characterisation Factors*. 2016; Available from: <https://www.universiteitleiden.nl/en/research/research-output/science/cml-ia-characterisation-factors>.
62. EPA, *Tool for Reduction and Assessment of Chemicals and Other Environmental Impacts (TRACI)*. 2022.
63. Sustainability, P. *ReCiPe*. 2016 [cited 2022; Available from: <https://pre-sustainability.com/articles/recipe/>].
64. Sleeswijk, A.W., et al., *Normalisation in product life cycle assessment: An LCA of the global and European economic systems in the year 2000*. Science of the total environment, 2008. 390(1): p. 227-240.
65. Mancia, G., et al., *2013 Practice guidelines for the management of arterial hypertension of the European Society of Hypertension (ESH) and the European Society of Cardiology (ESC): ESH/ESC Task Force for the Management of Arterial Hypertension*. Journal of hypertension, 2013. 31(10): p. 1925-1938.
66. Sala, S., B. Ciuffo, and P. Nijkamp, *A systemic framework for sustainability assessment*. Ecological Economics, 2015. 119: p. 314-325.
67. Koumi Ngoh, S. and D. Njomo, *An overview of hydrogen gas production from solar energy*. Renewable and Sustainable Energy Reviews, 2012. 16(9): p. 6782-6792.
68. Jaganmohan, M. *Global PV module manufacturing share 2019 by country*. 2021 [cited 2022; Available from: <https://www.statista.com/statistics/668749/regional-distribution-of-solar-pv-module-manufacturing/>].
69. Statistics, R.C., Available online: https://www.irena.org/-/media/Files/IRENA/Agency/Publication/2020/Mar.IRENA_RE_Capacity_Statistics_2020.pdf (accessed on 5 May 2020), 2020.
70. UNEP. *About Montreal Protocol*. 2022; Available from: <https://www.unep.org/ozonaction/who-we-are/about-montreal-protocol>.
71. Secretariat, C.-I.C. *EU puts 200 PFAS out of business - but thousands remain*. 2021 [cited 2022; Available from: <https://chemsec.org/eu-puts-200-pfas-out-of-business-but-thousands-remain/>].
72. Flora, S.J., G.M. Kannan, and P. Kumar, *Selenium effects on gallium arsenide induced biochemical and immunotoxicological changes in rats*. Chemico-biological interactions, 1999. 122(1): p. 1-13.
73. White, S.J.O. and J.P. Shine, *Exposure potential and health impacts of indium and gallium, metals critical to emerging electronics and energy technologies*. Current environmental health reports, 2016. 3(4): p. 459-467.
74. Watkins, A., et al., *National innovation systems and the intermediary role of industry associations in building institutional capacities for innovation in developing countries: A critical review of the literature*. Research Policy, 2015. 44(8): p. 1407-1418.
75. Council, I.T.a.R. *Human and Ecological Health Effects of select PFAS*. 2021 [cited 2022; Available from: <https://pfas-1.itrcweb.org/7-human-and-ecological-health-effects-of-select-pfas/>].
76. Wang, J., et al., *Life cycle assessment and environmental cost accounting of coal-fired power generation in China*. Energy Policy, 2018. 115: p. 374-384.
77. Grigoryeva, I., et al., *Influence of thermal pollution on the ecological conditions in cooling reservoirs*. Water Resources, 2019. 46(1): p. S101-S109.
78. Hannah Ritchie, M.R., "Energy". 2020: OurWorldInData.

ANNEX A - OVERVIEW OF THE INVENTORY OF THE PASSIVATION PROCESS

1st Step	Substrate and MO	System	Time under use	Used Materials	Quantity	Number of times used
		Wafer and Mask Blank Store	NA	SLG wafer	0,266 kg	once
2nd Step	Cleanroom Procedure	Cleanrom Changing Room	30	Gloves	0,008 kg	once
				Shoe covers	0,009 kg	
				Head protectors	0,0068 kg	
				Water	0,85 l	
3rd Step	Substrate Cleaning	System	Time under use	Used Materials	Quantity	Number of times used
		Wet Bench	10 min in acetone	Acetone	25 mL	once
			5 min in H2O	H2O	25 mL	
			10 min in IPA(alcohol)	IPO	25 mL	
4th Step	Silicon Oxide deposition PECVD	System	Time under use	Used Materials	Quantity	Number of times used
		SPTS CVD (LIMS-ID 00000005	45 a 50 s	Silicon Oxide	47,07 mm/min	4
				N2O	1420 sccm or 1,42l/min	
				SiH4	10 sccm or 0,1 l/min	
				N2	392 sccm or 0,39l/min	
5th Step	Teflon Si + SiO2	System	Time under use	Used Materials	Quantity	Number of times used
		SPTS Pegasus	10 s	C4F8	200 sccm or 0,2 l/min	once
6th Step	NIL IPS	System	Time under use	Used Materials	Quantity	Number of times used
		Obducat Eitre 8	6 min and 40 s	Compressed Air	40 l/min	once
				Nitrogen	0,3 l/min	
				Cooling Water	----	
7th Step	Teflon IPS	System	Time under use	Used Materials	Quantity	Number of times used
		SPTS Pegasus			200nm	once
8th Step	HMDS Oven	System	Time under use	Used Materials	Quantity	Number of times used
		Forno HMDS	20-25 min	HMDS	NA	once
9th Step	Spin Coating	System	Time under use	Used Materials	Quantity	Number of times used
		E-beam Photoresist Track	5 min, 30 s is the RESIST deposition	5 mL for a 5 by 5 sample	200nm	14
9,5th Step	PVA TEPLA Plasma Asher	System	Time under use	Used Materials	Quantity	Number of times used
		Plasma Asher	8 min	O2	600 sccm or 0,60l/min	3
				Argon	50 sccm or 0,050l/min	
10th Step	Nanoimprint lithography NIL	System	Time under use	Used Materials	Quantity	Number of times used
		Obducat Eitre 8	7 min 45 s	SLG wafer	NA	4
11th Step	Removing residudal layer	System	Time under use	Used Materials	Quantity	Number of times used
		SPTS Pegasus	30-45 s	O2	115 sccm or 0,115 l/min	7
12th Step	Silicon oxide etch	System	Time under use	Used Materials	Quantity	Number of times used
		SPTS APS (LIMS-ID 00000005	22 s	C4F8	50 sccm or 0,050l/min	7
				He	200 sccm or 0,2 l/min	
				H2	30 sccm or 0,03 l/min	
13th Step	PVA TEPLA Plasma Asher(Retirar RESIST)	System	Time under use	Used Materials	Quantity	Number of times used
		Plasma Asher	8 min	O2	600 sccm or 0,60l/min	3
				Argon	50 sccm or 0,050l/min	
14th Step	SEM	System	Time under use	Used Materials	Quantity	Number of times used
		SEM	30 min	NA	NA	once

Figure A -1 - Inventory of the 14 subprocesses that occur during the passivation process.

ANNEX B - INTERIM STEPS OF SIMAPRO

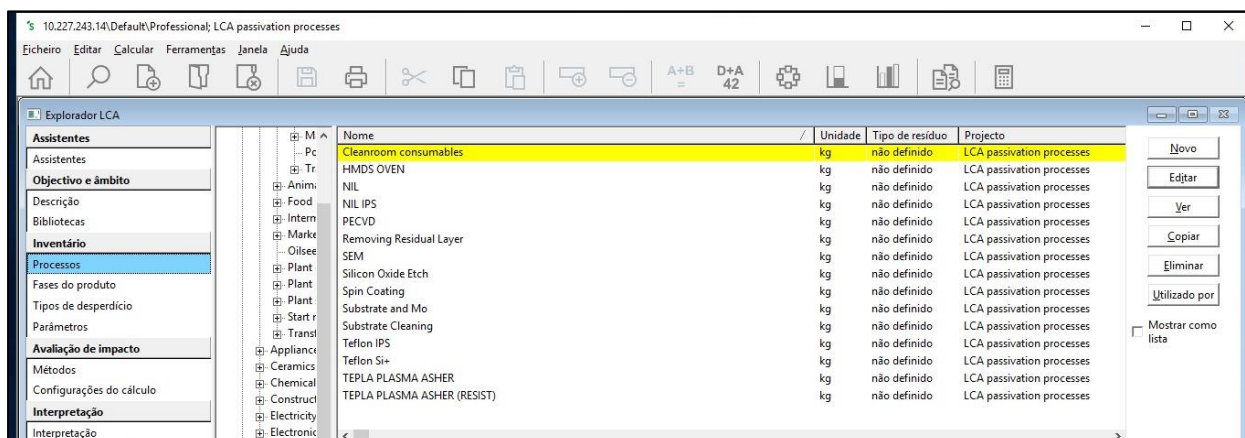


Figure B-1 - Screen that shows where all the studied subprocesses are located.

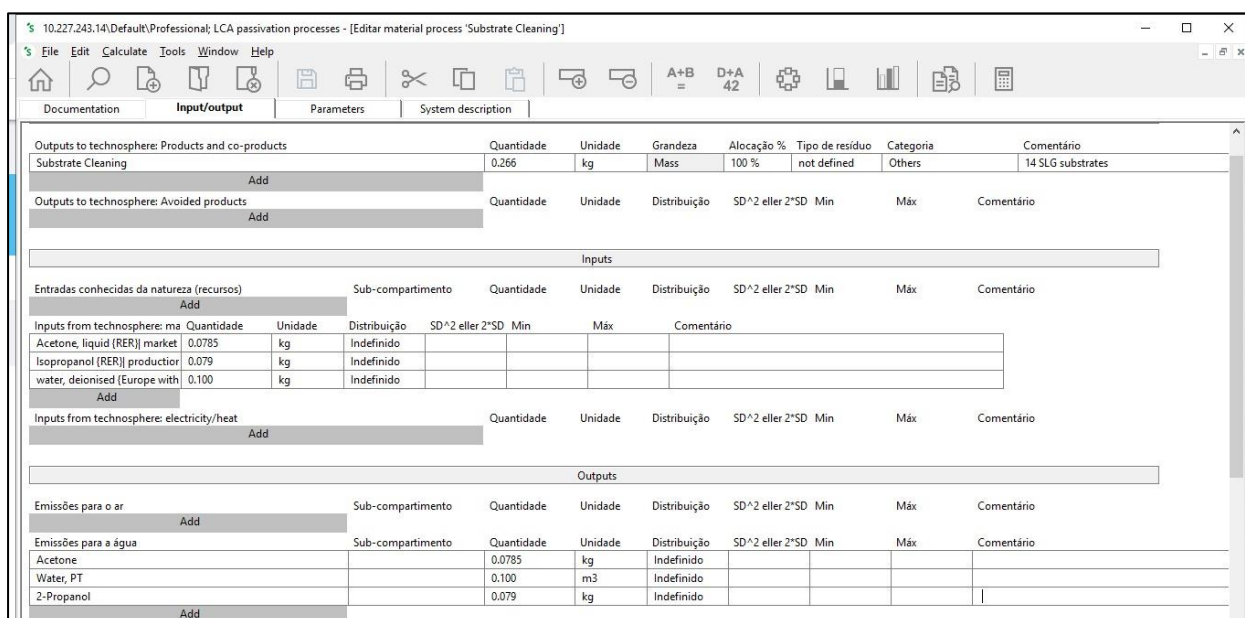


Figure B-2 - Insertion of the collected data in its corresponding position.

Name

LCA PASSIVATION PROCESSES IN THIN FILM SOLAR CELLS

Comment

Calculation function

Rede

Arvore

Analisar

Comparar

Method

CML-IA baseline V3.06 / EU25

Product	Amount	Unit	Project	Comment
Substrate and Mo	0.266	kg	LCA passivation processes	
Cleanroom consumables	0.266	kg	LCA passivation processes	
Substrate Cleaning	0.266	kg	LCA passivation processes	
PECVD	0.266	kg	LCA passivation processes	
Teflon Si+	0.266	kg	LCA passivation processes	
NIL IPS	0.266	kg	LCA passivation processes	
Teflon IPS	0.266	kg	LCA passivation processes	
HMDS OVEN	0.266	kg	LCA passivation processes	
Spin Coating	0.266	kg	LCA passivation processes	
NIL	0.266	kg	LCA passivation processes	
Removing Residual Layer	0.266	kg	LCA passivation processes	
Silicon Oxide Etch	0.266	kg	LCA passivation processes	
TEPLA PLASMA ASHER (RESIST)	0.266	kg	LCA passivation processes	
SEM	0.266	kg	LCA passivation processes	

Current library

Suffix

Help

Calculate

Figure B-3 - Calculation of the results using the CML-IA baseline v2.06 with the EU 25 normalization factors.

ANNEX C - CHARACTERIZED VALUES OF THE NOA SUBPROCESSES REGARDING THE STUDIED ENVIRONMENTAL CATEGORIES

Factor	UNIT	Substrate and MO	leanroom Consumable	Substrate Cleaning	PECVD	Teflon Si + SiO2	NIL IPS	Teflon IPS	OvenHMDS	Spin coating	NIL	Removing Residual Layer	Si Oxide Etch	PVA TEPLA Plasma Asher (resist)	SEM	TOTAL
Abiotic Depletion - Fossil Fuels	MJ	3.12	9.54	9.16	10.42	7.57	8.71	7.57	2.87	7.81	40.89	11.86	27.39	17.02	4.70	168.63
	contribution to the category	1.85%	5.66%	5.43%	6.18%	4.49%	5.16%	4.49%	1.70%	4.63%	24.25%	7.03%	16.24%	10.09%	2.78%	100.00%
Abiotic Depletion	kg Sb eq	1.35E-05	9.88E-07	1.72E-06	9.96E-07	1.36E-05	7.93E-06	1.36E-05	1.92E-07	5.13E-07	3.68E-05	7.80E-07	5.20E-05	2.54E-06	3.08E-07	1.46E-04
	contribution to the category	9.25%	0.68%	1.18%	0.68%	9.37%	5.45%	9.37%	0.13%	0.35%	25.29%	0.54%	35.76%	1.74%	0.21%	100.00%
Acidification	kg SO2 eq	2.45E-03	4.21E-03	1.33E-03	5.32E-03	3.20E-03	4.56E-03	3.20E-03	1.51E-03	4.10E-03	2.15E-02	6.26E-03	1.14E-02	7.88E-03	2.48E-03	7.95E-02
	contribution to the category	3.09%	5.30%	1.67%	6.69%	4.03%	5.74%	4.03%	1.90%	5.16%	27.12%	7.88%	14.35%	9.91%	3.12%	100.00%
Eutrophication	kg PO4--- eq	4.05E-04	9.80E-04	2.29E-04	1.30E-03	8.15E-04	1.17E-03	8.15E-04	3.49E-04	9.42E-04	5.55E-03	1.44E-03	2.92E-03	3.65E-03	5.71E-04	2.11E-02
	contribution to the category	1.92%	4.64%	1.08%	6.14%	3.86%	5.54%	3.86%	1.65%	4.46%	26.25%	6.83%	13.82%	17.26%	2.70%	100.00%
Fresh Water Aquatic Ecotoxicity	kg 1,4-DB eq	0.21	0.18	0.06	0.22	0.44	0.36	0.44	0.06	0.16	1.65	0.24	1.66	0.70	0.10	6.48
	contribution to the category	3.30%	2.84%	0.93%	3.44%	6.83%	5.48%	6.83%	0.90%	2.42%	25.44%	3.74%	25.62%	10.74%	1.48%	100.00%
Global Warming	kg CO2 eq	0.29	0.69	0.33	0.86	7.06	0.69	7.06	0.23	0.63	3.34	0.97	26.84	1.45	0.38	50.81
	contribution to the category	0.57%	1.36%	0.65%	1.68%	13.89%	1.35%	13.89%	0.46%	1.25%	6.57%	1.90%	52.82%	2.85%	0.75%	100.00%
Human Toxicity	kg 1,4-DB eq	0.32	0.19	0.13	0.24	1.66	0.43	1.66	0.06	0.16	2.01	0.25	6.30	0.57	0.10	14.07
	contribution to the category	2.24%	1.35%	0.94%	1.68%	11.78%	3.06%	11.78%	0.43%	1.16%	14.26%	1.79%	44.78%	4.02%	0.71%	100.00%
Marine Aquatic Ecotoxicity	kg 1,4-DB eq	5.70E+02	8.86E+02	1.37E+02	1.16E+03	1.46E+04	1.17E+03	1.46E+04	3.20E+02	8.57E+02	5.45E+03	1.32E+03	5.55E+04	2.30E+03	5.23E+02	9.94E+04
	contribution to the category	0.57%	0.89%	0.14%	1.16%	14.67%	1.18%	14.67%	0.32%	0.86%	5.48%	1.33%	55.88%	2.31%	0.53%	100.00%
Ozone Layer Depletion	kg CFC-11 eq	2.76E-08	7.42E-09	8.71E-09	1.13E-08	2.36E-04	8.62E-09	2.36E-04	2.47E-09	6.24E-09	4.02E-08	9.64E-09	9.01E-04	4.16E-08	3.81E-09	1.37E-03
	contribution to the category	0.00%	0.00%	0.00%	0.00%	17.17%	0.00%	17.17%	0.00%	0.00%	0.00%	0.00%	65.64%	0.00%	0.00%	100.00%
Photochemical Oxidation	kg C2H4 eq	8.12E-05	1.67E-04	3.29E-04	1.99E-04	2.51E-04	1.70E-04	2.51E-04	5.62E-05	1.53E-04	8.08E-04	2.32E-04	9.28E-04	3.05E-04	9.20E-05	4.02E-03
	contribution to the category	2.02%	4.16%	8.19%	4.95%	6.24%	4.23%	6.24%	1.40%	3.80%	20.08%	5.78%	23.07%	7.58%	2.29%	100.00%
Terrestrial Ecotoxicity	kg 1,4-DB eq	2.71E-04	6.56E-04	1.56E-04	8.51E-04	1.07E-03	1.01E-03	1.07E-03	2.30E-04	6.17E-04	4.70E-03	9.51E-04	3.95E-03	2.92E-03	3.76E-04	1.88E-02
	contribution to the category	1.44%	3.49%	0.83%	4.53%	5.66%	5.36%	5.66%	1.22%	3.28%	24.98%	5.06%	20.97%	15.52%	2.00%	100.00%

Figure C-1 - Characterized values of the entire passivation process for the environmental categories under study.

ANNEX D - SUBSTANCES WITH THE HIGHEST CONTRIBUTION FOR EACH ENVIRONMENTAL CATEGORY

Substance	Compartment	Unit	Substrate and Mo	Cleanroom consumables	Substrate Cleaning	PECVD	Teflon Si+	NIL IPS	Teflon IPS	HMDS OVEN	Spin Coating	NIL	Removing Residual Layer	Silicon Oxide Etch	TEPLA PLASMA ASHER (RESIST)	SEM	TOTAL
Tellurium	Raw Material	kg Sb eq	1.01E-05	6.69E-07	1.10E-06	6.93E-07	7.35E-06	5.81E-06	7.35E-06	1.38E-07	3.64E-07	2.70E-05	5.62E-07	2.80E-05	1.86E-06	2.22E-07	9.12E-05
Gold	Raw Material	kg Sb eq	3.93E-07	1.11E-07	2.84E-07	9.50E-08	1.85E-06	8.06E-07	1.85E-06	1.22E-08	3.20E-08	3.74E-06	4.93E-08	7.07E-06	1.52E-07	1.95E-08	1.65E-05
Copper	Raw Material	kg Sb eq	7.94E-07	7.00E-08	1.12E-07	7.45E-08	1.00E-06	5.88E-07	1.00E-06	1.43E-08	3.79E-08	2.73E-06	5.85E-08	3.83E-06	1.91E-07	2.31E-08	1.05E-05
Silver	Raw Material	kg Sb eq	2.33E-07	3.46E-08	6.52E-08	3.37E-08	1.22E-06	2.16E-07	1.22E-06	6.00E-09	1.58E-08	1.00E-06	2.44E-08	4.66E-06	8.04E-08	9.65E-09	8.82E-06
Lead	Raw Material	kg Sb eq	1.03E-07	1.91E-08	2.54E-08	1.98E-08	1.11E-06	6.25E-08	1.11E-06	4.19E-09	1.11E-08	2.92E-07	1.71E-08	4.23E-06	4.97E-08	6.77E-09	7.06E-06
Molybdenum	Raw Material	kg Sb eq	5.79E-07	2.03E-08	3.30E-08	2.11E-08	2.20E-07	1.74E-07	2.20E-07	4.23E-09	1.12E-08	8.09E-07	1.73E-08	8.40E-07	5.63E-08	6.83E-09	3.01E-06
Zinc	Raw Material	kg Sb eq	4.03E-08	7.44E-09	9.79E-09	7.67E-09	4.24E-07	2.42E-08	4.24E-07	1.62E-09	4.30E-09	1.13E-07	6.63E-09	1.62E-06	1.91E-08	2.62E-09	2.71E-06
Selenium	Raw Material	kg Sb eq	2.36E-07	1.74E-08	2.86E-08	1.80E-08	1.91E-07	1.51E-07	1.91E-07	3.58E-09	9.44E-09	7.01E-07	1.46E-08	7.29E-07	4.84E-08	5.76E-09	2.34E-06
Chromium	Raw Material	kg Sb eq	3.03E-08	1.81E-08	1.88E-08	1.87E-08	1.23E-07	5.91E-08	1.23E-07	4.44E-09	1.19E-08	2.74E-07	1.83E-08	4.66E-07	3.72E-08	7.25E-09	1.21E-06
Tin	Raw Material	kg Sb eq	9.31E-07	2.14E-09	4.69E-09	1.95E-09	2.94E-08	5.81E-09	2.94E-08	4.59E-10	8.29E-10	2.70E-08	1.28E-09	1.12E-07	2.84E-09	5.06E-10	1.15E-06
Sulfur	Raw Material	kg Sb eq	1.87E-08	1.32E-08	3.10E-08	5.67E-09	7.77E-08	1.96E-08	7.77E-08	8.43E-10	1.04E-08	9.11E-08	3.40E-09	2.97E-07	8.24E-09	1.35E-09	6.56E-07
Nickel	Raw Material	kg Sb eq	2.92E-09	1.87E-09	1.75E-09	2.26E-09	1.32E-08	5.97E-09	1.32E-08	5.17E-10	1.38E-09	2.77E-08	2.13E-09	5.01E-08	3.95E-09	8.43E-10	1.28E-07
Cadmium	Raw Material	kg Sb eq	1.37E-09	2.50E-10	3.31E-10	2.59E-10	1.43E-08	8.12E-10	1.43E-08	5.48E-11	1.45E-10	3.77E-09	2.24E-10	5.47E-08	6.43E-10	8.86E-11	9.12E-08
Uranium	Raw Material	kg Sb eq	6.36E-10	1.66E-09	1.06E-09	2.21E-09	1.99E-09	2.31E-09	1.99E-09	5.71E-10	1.53E-09	1.07E-08	2.37E-09	7.28E-09	2.06E-08	9.35E-10	5.59E-08
Antimony	Raw Material	kg Sb eq	2.06E-10	6.00E-11	8.68E-11	5.83E-11	4.23E-09	9.57E-11	4.23E-09	1.22E-11	3.22E-11	4.44E-10	4.97E-11	1.62E-08	8.82E-11	1.97E-11	2.58E-08
Barium	Raw Material	kg Sb eq	8.67E-10	7.40E-10	2.33E-10	9.88E-10	2.45E-09	8.28E-10	2.45E-09	2.68E-10	7.18E-10	3.84E-09	1.11E-09	9.21E-09	1.56E-09	4.39E-10	2.57E-08

Figure D-1 - Quantity of the subproducts by subprocesses, on the Abiotic Depletion category.

Substance	Compartment	Unit	Substrate and Mo	Cleanroom consumables	Substrate Cleaning	PECVD	Teflon Si+	NILIPS	Teflon IPS	HMDS OVEN	Spin Coating	NIL	Removing Residual Layer	Silicon Oxide Etch	TEPLA PLASMA ASHER (RESIST)	SEM	TOTAL
Gas, natural/m3	Raw Material	MJ	1.50E+00	3.23E+00	4.02E+00	3.95E+00	4.74E+00	3.24E+00	4.74E+00	1.07E+00	2.86E+00	1.51E+01	4.41E+00	1.76E+01	6.12E+00	1.74E+00	7.43E+01
Coal, hard	Raw Material	MJ	3.23E-01	4.16E+00	3.75E-01	5.48E+00	1.84E+00	4.67E+00	1.84E+00	1.55E+00	4.15E+00	2.17E+01	6.40E+00	6.15E+00	7.12E+00	2.53E+00	6.83E+01
Oil, crude	Raw Material	MJ	1.21E+00	1.32E+00	4.70E+00	7.85E-01	6.55E-01	6.77E-01	6.55E-01	2.14E-01	5.71E-01	3.15E+00	8.81E-01	2.39E+00	1.23E+00	3.49E-01	1.88E+01
Coal, brown	Raw Material	MJ	8.49E-02	5.26E-02	5.53E-02	1.02E-01	3.11E-01	1.26E-01	3.11E-01	1.46E-02	3.87E-02	5.81E-01	6.09E-02	1.18E+00	2.42E+00	2.36E-02	5.36E+00
Gas, mine, off-gas, process, coal mining/m3	Raw Material	MJ	5.56E-03	7.64E-02	3.77E-03	1.01E-01	3.08E-02	8.69E-02	3.08E-02	2.88E-02	7.72E-02	4.04E-01	1.19E-01	1.02E-01	1.32E-01	4.72E-02	1.25E+00
Energy, from gas, natural	Raw Material	MJ	0	3.27E-01	0	0	0	6.31E-02	0	0	5.97E-02	3.15E-02	0	0	0	0	4.81E-01
Energy, from oil	Raw Material	MJ	0	3.30E-01	0	0	0	1.70E-02	0	0	4.84E-02	8.49E-03	0	0	0	0	4.04E-01
Energy, from coal	Raw Material	MJ	0	4.09E-02	0	0	0	1.50E-02	0	0	7.95E-03	7.52E-03	0	0	0	0	7.14E-02
Energy, from coal, brown	Raw Material	MJ	0	8.57E-03	0	0	0	5.98E-03	0	0	6.68E-08	2.99E-03	0	0	0	0	1.75E-02

Figure D-2 - Quantity of the subproducts by subprocesses, on the Abiotic Depletion-Fossil Fuel category.

Substance	Compartment	Unit	Substrate and Mo	Cleanroom consumables	Substrate Cleaning	PECVD	Teflon Si+	NIL IPS	Teflon IPS	HMDS OVEN	Spin Coating	NIL	Removing Residual Layer	on Oxide	TEPLA PLASMA ASHER (RESIST)	SEM	TOTAL
Sulfur dioxide	Air	kg SO ₂ eq	1.74E-03	3.31E-03	1.04E-03	4.15E-03	2.59E-03	3.61E-03	2.59E-03	1.19E-03	3.23E-03	1.69E-02	4.93E-03	9.23E-03	6.20E-03	1.95E-03	6.27E-02
Nitrogen oxides	Air	kg SO ₂ eq	6.20E-04	8.50E-04	2.80E-04	1.09E-03	5.51E-04	9.49E-04	5.51E-04	3.07E-04	8.24E-04	4.41E-03	1.27E-03	1.93E-03	1.59E-03	5.03E-04	1.57E-02
Ammonia	Air	kg SO ₂ eq	9.33E-05	3.60E-05	4.16E-06	7.20E-05	3.54E-05	4.65E-05	3.54E-05	1.30E-05	3.48E-05	2.16E-04	5.36E-05	1.28E-04	8.87E-05	2.12E-05	8.78E-04
Sulfur trioxide	Air	kg SO ₂ eq	6.21E-08	3.64E-08	3.60E-06	4.11E-08	2.95E-05	6.95E-08	2.95E-05	7.04E-09	1.79E-08	3.22E-07	2.76E-08	1.13E-04	1.29E-07	1.09E-08	1.76E-04
Nitrogen dioxide	Air	kg SO ₂ eq	0.00	2.20E-05	0	0	0	3.67E-05	0	0	6.14E-06	1.84E-05	0	0	0	0	8.33E-05
Sulfuric acid	Air	kg SO ₂ eq	1.58E-09	4.59E-10	7.03E-10	5.00E-10	2.72E-08	1.26E-09	2.72E-08	9.16E-11	2.42E-10	5.87E-09	3.73E-10	1.04E-07	7.19E-10	1.48E-10	1.70E-07
Nitrogen monoxide	Air	kg SO ₂ eq	8.75E-12	3.72E-11	3.47E-12	3.45E-11	2.05E-10	1.19E-11	2.05E-10	1.20E-12	3.19E-12	5.49E-11	4.92E-12	7.83E-10	9.09E-12	1.95E-12	1.36E-09

Figure D-3 - Quantity of the subproducts by subprocesses, on the Acidification category.

Substance	Compartment	Unit	Substrate and Mo	Cleanroom consumables	Substrate Cleaning	PECVD	Teflon Si+	NIL IPS	Teflon IPS	HMDS OVEN	Spin Coating	NIL	Removing Residual Layer	Silicon Oxide Etch	TEPLA PLASMA ASHER (RESIST)	SEM	TOTAL
Phosphate	Water	kg PO ₄ --- eq	1.92E-04	6.99E-04	9.50E-05	9.27E-04	6.19E-04	8.94E-04	6.19E-04	2.53E-04	6.83E-04	4.15E-03	1.05E-03	2.23E-03	3.08E-03	4.14E-04	1.59E-02
Nitrogen oxides	Air	kg PO ₄ --- eq	1.61E-04	2.21E-04	7.27E-05	2.84E-04	1.43E-04	2.47E-04	1.43E-04	7.99E-05	2.14E-04	1.15E-03	3.31E-04	5.03E-04	4.13E-04	1.31E-04	4.09E-03
Nitrate	Water	kg PO ₄ --- eq	4.78E-06	2.25E-05	2.72E-06	2.98E-05	1.96E-05	2.53E-05	1.96E-05	8.12E-06	2.18E-05	1.25E-04	3.36E-05	7.03E-05	1.04E-04	1.33E-05	5.01E-04
COD (Chemical Oxygen Demand)	Water	kg PO ₄ --- eq	2.04E-05	1.49E-05	3.34E-05	8.24E-06	1.80E-05	-1.93E-06	1.80E-05	2.02E-06	5.42E-06	4.19E-05	8.30E-06	6.76E-05	1.49E-05	3.29E-06	2.54E-04
Ammonia	Air	kg PO ₄ --- eq	2.04E-05	7.87E-06	9.11E-07	1.57E-05	7.73E-06	1.02E-05	7.73E-06	2.85E-06	7.60E-06	4.73E-05	1.17E-05	2.80E-05	1.94E-05	4.64E-06	1.92E-04
Dinitrogen monoxide	Air	kg PO ₄ --- eq	7.86E-07	4.74E-06	3.73E-07	6.23E-06	3.55E-06	5.07E-06	3.55E-06	1.73E-06	4.65E-06	2.53E-05	7.18E-06	1.26E-05	1.30E-05	2.84E-06	9.15E-05
Ammonium, ion	Water	kg PO ₄ --- eq	1.18E-06	6.32E-07	2.91E-07	2.49E-05	2.57E-06	6.42E-07	2.57E-06	2.74E-07	3.67E-07	2.98E-06	5.66E-07	9.73E-06	1.14E-06	2.24E-07	4.81E-05
Phosphorus	Solo	kg PO ₄ --- eq	6.60E-07	2.14E-06	2.29E-07	2.78E-06	1.18E-06	2.48E-06	1.18E-06	7.94E-07	2.13E-06	1.15E-05	3.29E-06	4.09E-06	6.16E-06	1.30E-06	3.99E-05
Phosphorus	Water	kg PO ₄ --- eq	3.65E-06	1.56E-07	2.35E-05	7.12E-08	2.89E-07	6.71E-08	2.89E-07	1.90E-08	4.93E-08	3.11E-07	7.61E-08	1.09E-06	1.26E-07	3.01E-08	2.98E-05
Phosphorus	Air	kg PO ₄ --- eq	1.07E-07	3.04E-07	4.28E-08	3.98E-07	1.49E-07	3.54E-07	1.49E-07	1.13E-07	3.03E-07	1.65E-06	4.67E-07	5.06E-07	9.17E-07	1.85E-07	5.64E-06
Nitrite	Water	kg PO ₄ --- eq	1.72E-08	7.58E-09	2.27E-09	5.33E-09	3.42E-08	7.15E-09	3.42E-08	1.42E-09	3.78E-09	3.32E-08	5.83E-09	1.30E-07	1.03E-08	2.31E-09	2.95E-07

Figure D-4 - Quantity of the subproducts by subprocesses, on the Eutrophication category.

Substance	Compartment	Unit	Substrate and Mo	Cleanroom consumables	Substrate Cleaning	PECVD	Teflon Si+	NIL IPS	Teflon IPS	HMDS OVEN	Spin Coating	NIL	Removing Residual Layer	Silicon Oxide Etch	TEPLA PLASMA ASHER (RESIST)	SEM	TOTAL
Copper	Water	kg 1,4-DB eq	1.24E-01	2.74E-02	2.40E-02	3.24E-02	2.13E-01	1.36E-01	2.13E-01	7.86E-03	2.10E-02	6.33E-01	3.24E-02	8.09E-01	1.14E-01	1.28E-02	2.40
Nickel	Water	kg 1,4-DB eq	2.23E-02	6.37E-02	1.07E-02	8.49E-02	7.17E-02	8.76E-02	7.17E-02	2.30E-02	6.17E-02	4.07E-01	9.52E-02	2.61E-01	2.71E-01	3.77E-02	1.57
Beryllium	Water	kg 1,4-DB eq	3.14E-02	3.28E-02	1.29E-02	4.33E-02	6.06E-02	5.30E-02	6.06E-02	1.15E-02	3.09E-02	2.46E-01	4.77E-02	2.25E-01	1.29E-01	1.89E-02	1.00
Vanadium	Water	kg 1,4-DB eq	9.35E-03	3.51E-02	4.92E-03	2.99E-02	3.56E-02	3.12E-02	3.56E-02	7.68E-03	2.06E-02	1.45E-01	3.18E-02	1.32E-01	8.04E-02	1.26E-02	6.11E-01
Cobalt	Water	kg 1,4-DB eq	8.66E-03	1.48E-02	3.17E-03	1.96E-02	2.29E-02	2.31E-02	2.29E-02	5.27E-03	1.41E-02	1.07E-01	2.18E-02	8.47E-02	6.52E-02	8.62E-03	4.22E-01
Barium	Water	kg 1,4-DB eq	4.74E-03	2.42E-03	1.22E-03	3.38E-03	1.24E-02	6.07E-03	1.24E-02	7.63E-04	2.04E-03	2.82E-02	3.15E-03	4.71E-02	9.36E-03	1.24E-03	1.35E-01
Thallium	Water	kg 1,4-DB eq	8.07E-03	1.03E-03	1.38E-03	1.14E-03	1.30E-02	7.20E-03	1.30E-02	2.37E-04	6.28E-04	3.34E-02	9.70E-04	4.97E-02	3.00E-03	3.84E-04	1.33E-01
Zinc	Water	kg 1,4-DB eq	2.57E-03	2.47E-03	7.21E-04	3.17E-03	6.10E-03	4.52E-03	6.10E-03	8.55E-04	2.29E-03	2.10E-02	3.53E-03	2.29E-02	8.97E-03	1.40E-03	8.65E-02
Selenium	Water	kg 1,4-DB eq	4.68E-04	2.03E-03	3.00E-04	2.71E-03	1.86E-03	2.62E-03	1.86E-03	7.34E-04	1.97E-03	1.22E-02	3.04E-03	6.70E-03	8.62E-03	1.20E-03	4.63E-02
Molybdenum	Water	kg 1,4-DB eq	4.42E-04	5.64E-04	1.34E-04	7.47E-04	1.03E-03	9.51E-04	1.03E-03	1.98E-04	5.31E-04	4.42E-03	8.21E-04	3.83E-03	2.44E-03	3.25E-04	1.75E-02
Cadmium	Water	kg 1,4-DB eq	7.33E-04	3.59E-04	1.61E-04	3.98E-04	1.42E-03	8.99E-04	1.42E-03	1.04E-04	2.77E-04	4.18E-03	4.27E-04	5.38E-03	1.10E-03	1.69E-04	1.70E-02

Figure D-5 - Quantity of the subproducts by subprocesses, on the Fresh Water Aquatic Ecotoxicity category.

Substance	Compartment	Unit	Substrate and Mo	Cleanroom consumables	Substrate Cleaning	PECVD	Teflon Si+	NIL IPS	Teflon IPS	HMDS OVEN	Spin Coating	NIL	Removing Residual Layer	Silicon Oxide Etch	TEPLA PLASMA ASHER (RESIST)	SEM	TOTAL
Methane, trifluoro-, HFC-23	Air	kg CO2 eq	2.67E-07	1.57E-07	3.35E-07	4.83E-07	4.52E+00	1.04E-06	4.52E+00	1.99E-08	5.16E-08	4.80E-06	7.96E-08	1.73E+01	2.02E-07	3.15E-08	2.63E+01
Carbon dioxide, fossil	Air	kg CO2 eq	2.76E-01	6.08E-01	2.76E-01	7.91E-01	4.37E-01	6.68E-01	4.37E-01	2.17E-01	5.81E-01	3.10E+00	8.96E-01	1.55E+00	1.35E+00	3.55E-01	1.15E+01
Methane, dichlorodifluoro-, CFC-12	Air	kg CO2 eq	1.29E-07	6.19E-07	1.01E-07	5.07E-07	9.20E-01	3.85E-07	9.20E-01	1.43E-06	3.32E-07	2.69E-06	5.12E-07	3.52E+00	9.19E-07	2.03E-07	5.36E+00
Methane, chlorodifluoro-, HCFC-22	Air	kg CO2 eq	1.32E-05	2.45E-05	1.72E-05	3.57E-05	7.91E-01	2.92E-05	7.91E-01	9.00E-06	2.40E-05	1.36E-04	3.71E-05	3.02E+00	5.93E-05	1.47E-05	4.60E+00
Methane, tetrachloro-, CFC-10	Air	kg CO2 eq	2.43E-07	3.84E-07	3.28E-07	4.83E-07	2.89E-01	8.97E-07	2.89E-01	7.56E-08	1.97E-07	2.42E-06	3.04E-07	1.10E+00	7.36E-07	1.20E-07	1.68E+00
Methane, fossil	Air	kg CO2 eq	8.86E-03	4.30E-02	5.55E-02	5.20E-02	3.90E-02	4.30E-02	3.90E-02	1.40E-02	3.74E-02	2.00E-01	5.77E-02	1.42E-01	7.25E-02	2.28E-02	8.26E-01
Chloroform	Air	kg CO2 eq	4.91E-09	5.94E-09	7.55E-09	1.04E-08	2.69E-02	4.55E-08	2.69E-02	1.16E-09	3.07E-09	8.19E-08	4.75E-09	1.03E-01	1.76E-08	1.88E-09	1.56E-01
Dinitrogen monoxide	Air	kg CO2 eq	7.72E-04	4.65E-03	3.66E-04	6.11E-03	3.49E-03	4.97E-03	3.49E-03	1.70E-03	4.57E-03	2.48E-02	7.05E-03	1.24E-02	1.27E-02	2.79E-03	8.98E-02
Ethane, 1,1,1,2-tetrafluoro-, HFC-134a	Air	kg CO2 eq	2.54E-07	1.03E-06	1.25E-07	1.09E-06	1.50E-02	1.07E-06	1.50E-02	2.99E-07	8.02E-07	4.96E-06	1.24E-06	5.73E-02	5.96E-06	4.90E-07	8.73E-02
Carbon dioxide, land transformation	Air	kg CO2 eq	9.17E-05	3.99E-03	4.93E-05	5.11E-03	7.70E-04	4.49E-03	7.70E-04	1.51E-03	4.06E-03	2.09E-02	6.27E-03	2.10E-03	5.92E-03	2.48E-03	5.85E-02
Methane, trichlorofluoro-, CFC-11	Air	kg CO2 eq	3.48E-10	2.04E-10	4.37E-10	6.30E-10	5.90E-03	4.64E-07	5.90E-03	2.60E-11	6.72E-11	2.27E-07	1.04E-10	2.25E-02	2.63E-10	4.10E-11	3.43E-02

Figure D-6 - Quantity of the subproducts by subprocesses, on the Global Warming category.

Substance	Compartment	Unit	Substrate and Mo	Cleanroom consumables	Substrate Cleaning	PECVD	Teflon Si+	NIL IPS	Teflon IPS	HMDS OVEN	Spin Coating	NIL	Removing Residual Layer	Silicon Oxide Etch	TEPLA PLASMA ASHER (RESIST)	SEM	TOTAL
Hydrogen fluoride	Air	kg 1,4-DB eq	1.90E-02	3.88E-02	1.85E-03	5.13E-02	9.77E-01	4.44E-02	9.77E-01	1.45E-02	3.90E-02	2.06E-01	6.01E-02	3.73E+00	7.20E-02	2.38E-02	6.25E+00
Thallium	Water	kg 1,4-DB eq	2.27E-01	2.88E-02	3.88E-02	3.19E-02	3.66E-01	2.02E-01	3.66E-01	6.66E-03	1.77E-02	9.38E-01	2.73E-02	1.39E+00	8.42E-02	1.08E-02	3.74E+00
Chromium VI	Air	kg 1,4-DB eq	1.68E-02	1.71E-02	1.37E-02	2.10E-02	8.87E-02	4.56E-02	8.87E-02	4.99E-03	1.33E-02	2.11E-01	2.06E-02	3.36E-01	5.19E-02	8.14E-03	9.38E-01
Selenium	Water	kg 1,4-DB eq	8.97E-03	3.90E-02	5.75E-03	5.20E-02	3.56E-02	5.03E-02	3.56E-02	1.41E-02	3.77E-02	2.34E-01	5.83E-02	1.28E-01	1.65E-01	2.30E-02	8.88E-01
Barium	Water	kg 1,4-DB eq	1.32E-02	6.71E-03	3.39E-03	9.37E-03	3.44E-02	1.68E-02	3.44E-02	2.12E-03	5.65E-03	7.80E-02	8.73E-03	1.30E-01	2.59E-02	3.45E-03	3.72E-01
Vanadium	Water	kg 1,4-DB eq	3.29E-03	1.24E-02	1.73E-03	1.05E-02	1.26E-02	1.10E-02	1.26E-02	2.71E-03	7.25E-03	5.09E-02	1.12E-02	4.65E-02	2.83E-02	4.43E-03	2.15E-01
Methane, tetrachloro-, CFC-10	Air	kg 1,4-DB eq	3.09E-08	4.88E-08	4.17E-08	6.15E-08	3.67E-02	1.14E-07	3.67E-02	9.61E-09	2.51E-08	3.08E-07	3.87E-08	1.40E-01	9.36E-08	1.53E-08	2.14E-01
Molybdenum	Water	kg 1,4-DB eq	5.12E-03	6.52E-03	1.56E-03	8.65E-03	1.19E-02	1.10E-02	1.19E-02	2.30E-03	6.15E-03	5.11E-02	9.50E-03	4.44E-02	2.82E-02	3.76E-03	2.02E-01
Nickel	Air	kg 1,4-DB eq	3.51E-03	1.04E-02	5.56E-03	1.29E-02	7.63E-03	1.19E-02	7.63E-03	3.63E-03	9.79E-03	5.53E-02	1.50E-02	2.71E-02	1.86E-02	5.94E-03	1.95E-01
Nickel	Water	kg 1,4-DB eq	2.28E-03	6.50E-03	1.10E-03	8.67E-03	7.33E-03	8.95E-03	7.33E-03	2.35E-03	6.30E-03	4.16E-02	9.72E-03	2.67E-02	2.77E-02	3.85E-03	1.60E-01
Beryllium	Water	kg 1,4-DB eq	4.81E-03	5.03E-03	1.97E-03	6.63E-03	9.30E-03	8.13E-03	9.30E-03	1.77E-03	4.74E-03	3.77E-02	7.31E-03	3.46E-02	1.98E-02	2.89E-03	1.54E-01

Figure D-7 - Quantity of the subproducts by subprocesses, on the Human Toxicity category.

Substance	Compartment	Unit	Substrate and Mo	Cleanroom consumables	Substrate Cleaning	PECVD	Teflon Si+	NIL IPS	Teflon IPS	HMDS OVEN	Spin Coating	NIL	Removing Residual Layer	Silicon Oxide Etch	TEPLA PLASMA ASHER (RESIST)	SEM	TOTAL
Hydrogen fluoride	Air	kg 1,4-DB eq	2.72E+02	5.54E+02	2.64E+01	7.32E+02	1.39E+04	6.33E+02	1.39E+04	2.08E+02	5.57E+02	2.95E+03	8.59E+02	5.32E+04	1.03E+03	3.40E+02	8.93E+04
Beryllium	Water	kg 1,4-DB eq	1.85E+02	1.94E+02	7.59E+01	2.55E+02	3.58E+02	3.13E+02	3.58E+02	6.81E+01	1.82E+02	1.45E+03	2.81E+02	1.33E+03	7.61E+02	1.11E+02	5.93E+03
Nickel	Water	kg 1,4-DB eq	1.55E+01	4.42E+01	7.45E+00	5.90E+01	4.99E+01	6.08E+01	4.99E+01	1.60E+01	4.28E+01	2.83E+02	6.61E+01	1.82E+02	1.88E+02	2.62E+01	1.09E+03
Vanadium	Water	kg 1,4-DB eq	8.94E+00	3.35E+01	4.71E+00	2.86E+01	3.41E+01	2.98E+01	3.41E+01	7.35E+00	1.97E+01	1.38E+02	3.04E+01	1.26E+02	7.69E+01	1.20E+01	5.85E+02
Cobalt	Water	kg 1,4-DB eq	1.11E+01	1.90E+01	4.07E+00	2.52E+01	2.94E+01	2.97E+01	2.94E+01	6.76E+00	1.81E+01	1.38E+02	2.80E+01	1.09E+02	8.37E+01	1.11E+01	5.42E+02
Barium	Water	kg 1,4-DB eq	1.74E+01	8.88E+00	4.48E+00	1.24E+01	4.54E+01	2.22E+01	4.54E+01	2.80E+00	7.47E+00	1.03E+02	1.15E+01	1.72E+02	3.43E+01	4.56E+00	4.92E+02
Copper	Water	kg 1,4-DB eq	2.50E+01	5.51E+00	4.83E+00	6.52E+00	4.28E+01	2.74E+01	4.28E+01	1.58E+00	4.22E+00	1.27E+02	6.51E+00	1.63E+02	2.29E+01	2.57E+00	4.83E+02
Thallium	Water	kg 1,4-DB eq	2.68E+01	3.40E+00	4.59E+00	3.77E+00	4.33E+01	2.39E+01	4.33E+01	7.87E-01	2.09E+00	1.11E+02	3.22E+00	1.65E+02	9.96E+00	1.27E+00	4.42E+02
Selenium	Water	kg 1,4-DB eq	4.05E+00	1.76E+01	2.60E+00	2.35E+01	1.61E+01	2.27E+01	1.61E+01	6.36E+00	1.71E+01	1.06E+02	2.63E+01	5.80E+01	7.47E+01	1.04E+01	4.01E+02
Molybdenum	Water	kg 1,4-DB eq	1.94E+00	2.47E+00	5.90E-01	3.28E+00	4.53E+00	4.18E+00	4.53E+00	8.71E-01	2.33E+00	1.94E+01	3.60E+00	1.68E+01	1.07E+01	1.43E+00	7.67E+01
Selenium	Air	kg 1,4-DB eq	1.55E-01	1.50E+00	8.55E-02	1.99E+00	8.15E-01	1.74E+00	8.15E-01	5.61E-01	1.51E+00	8.11E+00	2.32E+00	2.80E+00	2.99E+00	9.20E-01	2.63E+01

Figure D-8 - Quantity of the subproducts by subprocesses, on the Marine Aquatic Ecotoxicity category.

Substance	Compartment	Unit	Substrate and Mo	Cleanroom consumables	Substrate Cleaning	PECVD	Teflon Si+	NIL IPS	Teflon IPS	HMDS OVEN	Spin Coating	NIL	Removing Residual Layer	Silicon Oxide Etch	TEPLA PLASMA ASHER (RESIST)	SEM	TOTAL
Methane, tetrachloro-, CFC-10	Air	kg CFC-11 eq	1.02E-10	1.62E-10	1.38E-10	2.04E-10	1.22E-04	3.78E-10	1.22E-04	3.19E-11	8.33E-11	1.02E-09	1.28E-10	4.66E-04	3.11E-10	5.08E-11	7.09E-04
Methane, dichlorodifluoro-, CFC-12	Air	kg CFC-11 eq	1.26E-11	6.07E-11	9.88E-12	4.97E-11	9.02E-05	3.77E-11	9.02E-05	1.41E-10	3.25E-11	2.64E-10	5.02E-11	3.45E-04	9.01E-11	1.99E-11	5.25E-04
Methane, chlorodifluoro-, HCFC-22	Air	kg CFC-11 eq	3.74E-10	6.96E-10	4.90E-10	1.01E-09	2.25E-05	8.30E-10	2.25E-05	2.56E-10	6.83E-10	3.86E-09	1.05E-09	8.59E-05	1.69E-09	4.17E-10	1.31E-04
Methane, trichlorofluoro-, CFC-11	Air	kg CFC-11 eq	7.47E-14	4.38E-14	9.37E-14	1.35E-13	1.27E-06	-9.97E-11	1.27E-06	5.57E-15	1.44E-14	-4.86E-11	2.22E-14	4.84E-06	5.64E-14	8.80E-15	7.37E-06
Methane, bromochlorodifluoro-, Halon 1211	Air	kg CFC-11 eq	1.08E-08	2.11E-08	4.56E-09	2.76E-08	1.99E-08	2.39E-08	1.99E-08	7.89E-09	2.12E-08	1.11E-07	3.26E-08	7.16E-08	4.72E-08	1.29E-08	4.32E-07
Methane, bromotrifluoro-, Halon 1301	Air	kg CFC-11 eq	1.63E-08	8.33E-09	3.49E-09	1.14E-08	1.54E-08	9.11E-09	1.54E-08	2.90E-09	7.76E-09	4.23E-08	1.20E-08	5.74E-08	1.67E-08	4.74E-09	2.23E-07
Ethane, 1,1,2-trichloro-1,2,2-trifluoro-, CFC-113	Air	kg CFC-11 eq	2.82E-11	1.78E-10	2.33E-11	2.27E-10	1.60E-10	2.39E-10	1.60E-10	6.56E-11	1.76E-10	1.11E-09	2.71E-10	5.76E-10	5.07E-10	1.07E-10	3.83E-09
Methane, monochloro-, R-40	Air	kg CFC-11 eq	8.30E-12	9.46E-12	3.29E-12	2.93E-11	1.19E-10	1.19E-11	1.19E-10	1.88E-12	4.90E-12	5.51E-11	7.58E-12	4.54E-10	4.52E-11	2.99E-12	8.71E-10
Ethane, 1,1,1-trichloro-, HCFC-140	Air	kg CFC-11 eq	1.88E-12	2.14E-12	7.45E-13	6.65E-12	2.69E-11	2.69E-12	2.69E-11	4.27E-13	1.11E-12	1.25E-11	1.72E-12	1.03E-10	1.03E-11	6.78E-13	1.97E-10
Ethane, 2-chloro-1,1,1,2-tetrafluoro-, HCFC-124	Air	kg CFC-11 eq	3.28E-13	3.29E-12	1.63E-13	4.21E-12	8.43E-13	3.83E-12	8.43E-13	1.24E-12	3.33E-12	1.78E-11	5.15E-12	2.53E-12	9.74E-12	2.04E-12	5.53E-11
Methane, bromo-, Halon 1001	Air	kg CFC-11 eq	7.37E-13	1.45E-13	2.52E-13	1.71E-13	1.39E-12	3.79E-12	1.39E-12	2.74E-14	7.28E-14	1.76E-11	1.12E-13	5.31E-12	2.49E-13	4.44E-14	3.13E-11

Figure D-9 - Quantity of the subproducts by subprocesses, on the Ozone Layer Depletion category.

Substance	Compartment	Unit	Substrate and Mo	Cleanroom consumables	Substrate Cleaning	PECVD	Teflon Si+	NIL IPS	Teflon IPS	HMDS OVEN	Spin Coating	NIL	Removing Residual Layer	Silicon Oxide Etch	TEPLA PLASMA ASHER (RESIST)	SEM	TOTAL
Sulfur dioxide	Air	kg C2H4 eq	6.96E-05	1.32E-04	4.16E-05	1.66E-04	1.04E-04	1.44E-04	1.04E-04	4.77E-05	1.29E-04	6.78E-04	1.97E-04	3.69E-04	2.48E-04	7.81E-05	2.51E-03
Methanol	Air	kg C2H4 eq	9.98E-09	4.22E-08	6.50E-09	3.28E-08	7.20E-05	2.94E-08	7.20E-05	9.65E-09	2.42E-08	1.38E-07	3.73E-08	2.75E-04	5.20E-08	1.48E-08	4.20E-04
Chloroform	Air	kg C2H4 eq	7.06E-12	8.54E-12	1.09E-11	1.49E-11	3.86E-05	6.55E-11	3.86E-05	1.67E-12	4.42E-12	1.18E-10	6.82E-12	1.48E-04	2.53E-11	2.70E-12	2.25E-04
Methane, fossil	Air	kg C2H4 eq	1.90E-06	9.22E-06	1.19E-05	1.11E-05	8.37E-06	9.22E-06	8.37E-06	2.99E-06	8.01E-06	4.28E-05	1.24E-05	3.04E-05	1.55E-05	4.89E-06	1.77E-04
Carbon monoxide, fossil	Air	kg C2H4 eq	4.72E-06	6.60E-06	9.11E-06	7.89E-06	1.05E-05	7.91E-06	1.05E-05	1.97E-06	5.26E-06	3.67E-05	8.12E-06	3.91E-05	1.79E-05	3.21E-06	1.70E-04
Propene	Air	kg C2H4 eq	1.26E-07	2.24E-07	1.58E-04	1.62E-07	2.28E-07	1.36E-07	2.28E-07	3.97E-08	1.08E-07	6.32E-07	1.63E-07	8.50E-07	2.62E-07	6.44E-08	1.61E-04
2-Propanol	Air	kg C2H4 eq	8.43E-09	6.25E-08	9.93E-05	2.06E-08	4.31E-08	2.04E-08	4.31E-08	6.01E-09	1.54E-08	9.49E-08	2.38E-08	1.62E-07	2.96E-08	9.41E-09	9.99E-05
Ethane	Air	kg C2H4 eq	6.28E-07	1.67E-06	3.63E-07	2.33E-06	2.16E-06	1.85E-06	2.16E-06	6.21E-07	1.66E-06	8.85E-06	2.56E-06	7.90E-06	3.84E-06	1.02E-06	3.76E-05
Pentane	Air	kg C2H4 eq	4.09E-07	1.59E-06	3.34E-07	2.10E-06	1.55E-06	1.76E-06	1.55E-06	5.87E-07	1.57E-06	8.30E-06	2.43E-06	5.61E-06	3.49E-06	9.61E-07	3.23E-05
Butane	Air	kg C2H4 eq	2.41E-07	1.19E-06	2.58E-07	1.58E-06	1.20E-06	1.29E-06	1.20E-06	4.41E-07	1.18E-06	6.21E-06	1.83E-06	4.34E-06	2.56E-06	7.23E-07	2.43E-05
Toluene	Air	kg C2H4 eq	2.25E-07	6.42E-07	1.85E-07	1.00E-06	2.48E-06	7.00E-07	2.48E-06	2.19E-07	5.86E-07	3.26E-06	9.03E-07	9.39E-06	1.44E-06	3.57E-07	2.39E-05

Figure D-10 - Quantity of the subproducts by subprocesses, on the Photochemical Oxidation category.

Substance	Compartment	Unit	Substrate and Mo	Cleanroom consumables	Substrate Cleaning	PECVD	Teflon Si+	NIL IPS	Teflon IPS	HMDS OVEN	Spin Coating	NIL	Removing Residual Layer	Silicon Oxide Etch	TEPLA PLASMA ASHER (RESIST)	SEM	TOTAL
Mercury	Air	kg 1,4-DB eq	8.12E-05	4.80E-04	6.18E-05	6.27E-04	4.70E-04	5.98E-04	4.70E-04	1.77E-04	4.76E-04	2.79E-03	7.34E-04	1.70E-03	1.17E-03	2.90E-04	1.01E-02
Chromium VI	Solo	kg 1,4-DB eq	5.24E-05	2.22E-05	3.50E-05	4.26E-05	2.86E-04	1.95E-04	2.86E-04	3.93E-06	1.02E-05	9.05E-04	1.65E-05	1.09E-03	1.31E-03	6.26E-06	4.26E-03
Mercury	Water	kg 1,4-DB eq	3.83E-05	5.63E-05	1.49E-05	7.39E-05	9.55E-05	9.03E-05	9.55E-05	2.00E-05	5.36E-05	4.20E-04	8.27E-05	3.54E-04	2.40E-04	3.27E-05	1.67E-03
Chromium VI	Air	kg 1,4-DB eq	1.48E-05	1.51E-05	1.21E-05	1.86E-05	7.83E-05	4.03E-05	7.83E-05	4.40E-06	1.18E-05	1.87E-04	1.82E-05	2.97E-04	4.59E-05	7.19E-06	8.29E-04
Nickel	Air	kg 1,4-DB eq	1.16E-05	3.45E-05	1.84E-05	4.28E-05	2.53E-05	3.94E-05	2.53E-05	1.20E-05	3.24E-05	1.83E-04	4.97E-05	9.00E-05	6.17E-05	1.97E-05	6.46E-04
Zinc	Air	kg 1,4-DB eq	5.53E-06	2.94E-06	5.23E-06	3.72E-06	4.00E-05	4.63E-06	4.00E-05	9.67E-07	2.59E-06	2.15E-05	4.00E-06	1.52E-04	8.25E-06	1.58E-06	2.93E-04
Cypermethrin	Solo	kg 1,4-DB eq	6.08E-06	1.84E-05	1.62E-06	1.11E-05	1.37E-05	9.43E-06	1.37E-05	2.89E-06	7.72E-06	4.38E-05	1.19E-05	5.08E-05	1.91E-05	4.72E-06	2.15E-04
Zinc	Solo	kg 1,4-DB eq	5.24E-06	4.45E-06	1.23E-06	4.94E-06	7.38E-06	4.84E-06	7.38E-06	1.38E-06	3.67E-06	2.25E-05	5.67E-06	2.74E-05	1.10E-05	2.24E-06	1.09E-04
Barium	Solo	kg 1,4-DB eq	4.29E-06	4.04E-06	1.02E-06	5.37E-06	5.03E-06	4.51E-06	5.03E-06	1.44E-06	3.86E-06	2.10E-05	5.96E-06	1.84E-05	8.84E-06	2.36E-06	9.12E-05
Mercury	Solo	kg 1,4-DB eq	2.57E-06	1.65E-06	5.27E-07	1.62E-06	9.98E-06	2.11E-06	9.98E-06	4.00E-07	1.04E-06	9.78E-06	1.60E-06	3.79E-05	2.73E-06	6.33E-07	8.25E-05
Lead	Air	kg 1,4-DB eq	1.66E-06	1.39E-06	6.40E-07	1.86E-06	8.61E-06	2.53E-06	8.61E-06	4.60E-07	1.23E-06	1.18E-05	1.90E-06	3.27E-05	4.19E-06	7.52E-07	7.83E-05

Figure D-11 - Quantity of the subproducts by subprocesses, on the Terrestrial Ecotoxicity category.

ANNEX E - RELATIVE CONTRIBUTION OF EACH SUBPROCESS OF THE NOA PASSIVATION PROCESS FOR DIFFERENT ENVIRONMENTAL IMPACT CATEGORIES

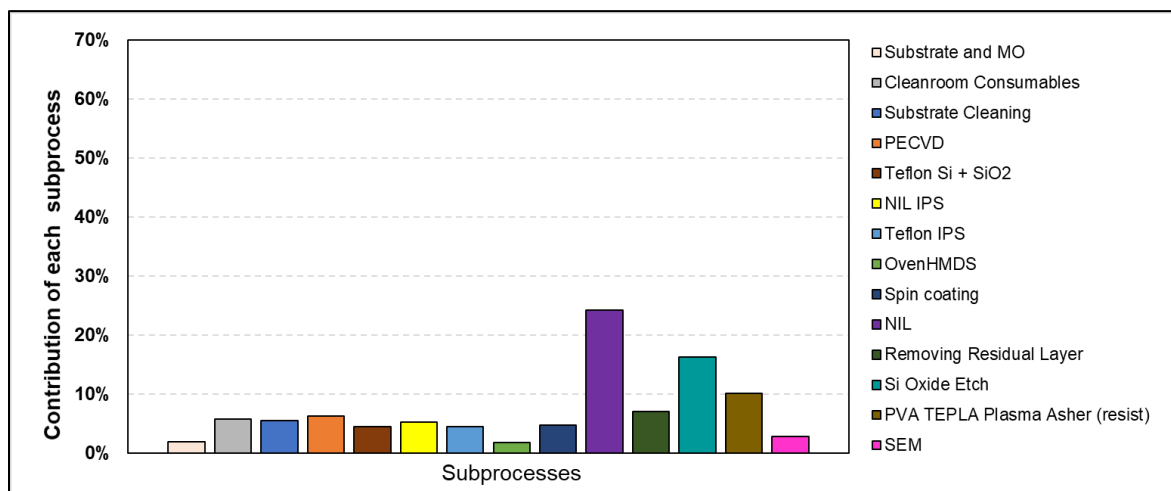


Figure E-1 - Relative contribution of the passivation subprocesses to Abiotic Depletion - Fossil Fuels.

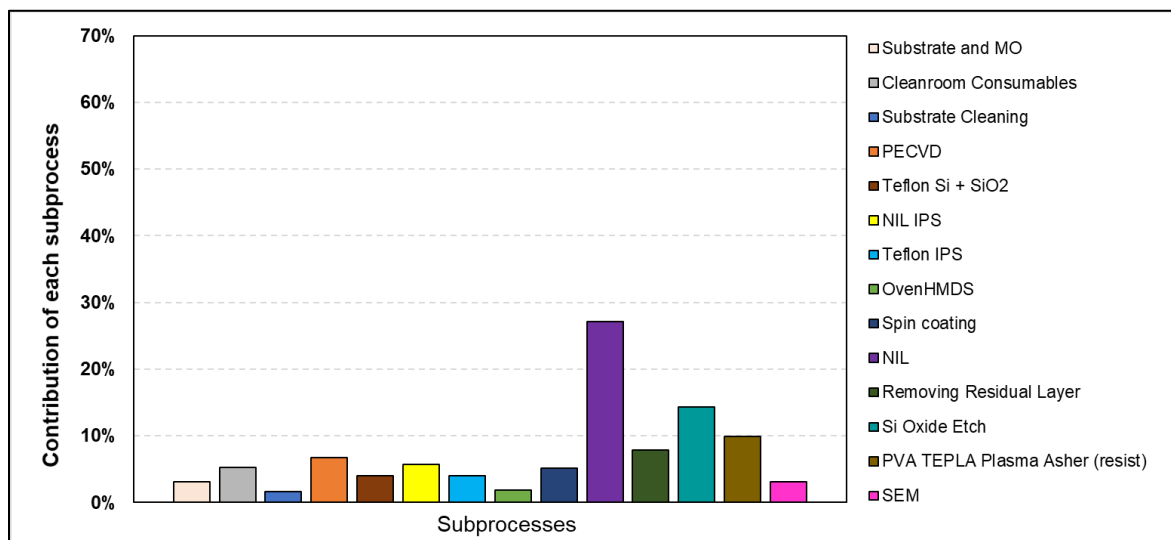


Figure E-2 - Relative contribution of the passivation subprocesses to Acidification.

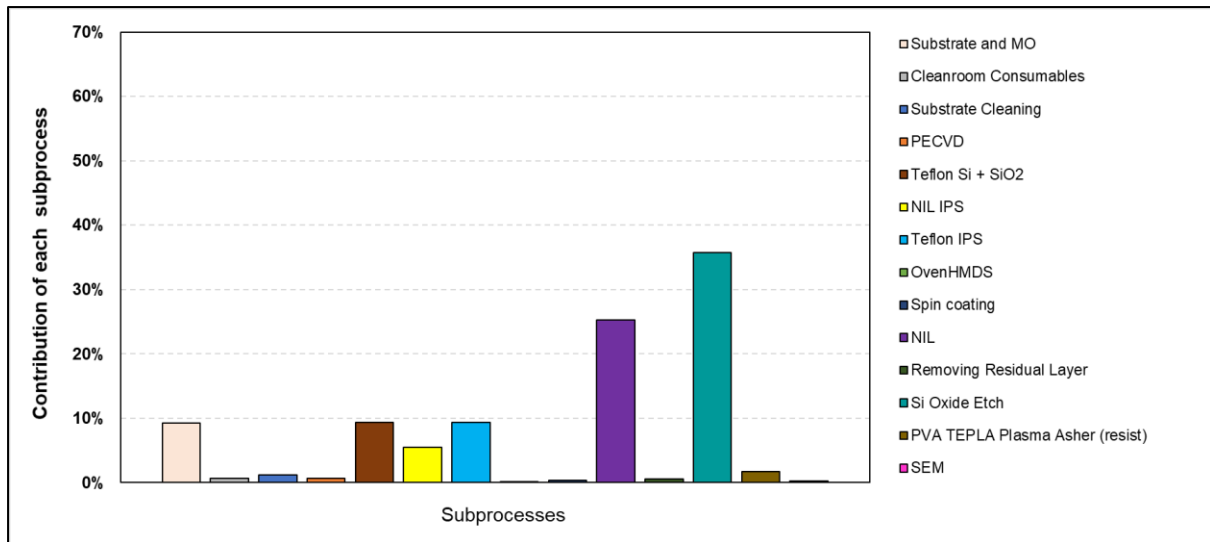


Figure E-3 - Relative contribution of the passivation subprocesses to Abiotic Depletion.

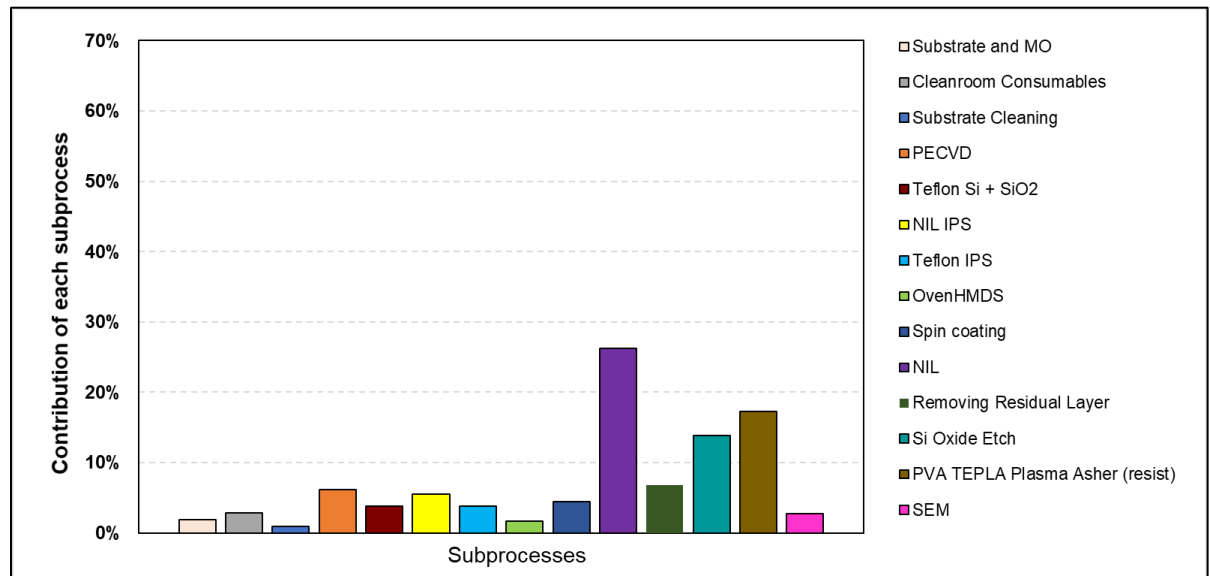


Figure E-4 - Relative contribution of the passivation subprocesses to Eutrophication.

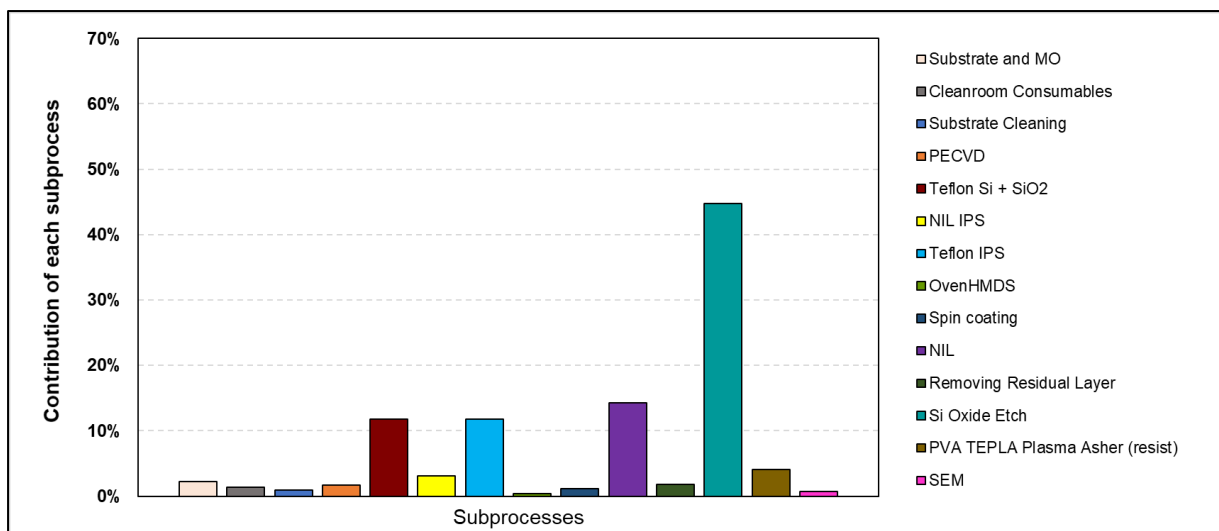


Figure E-5 - Relative contribution of the passivation subprocesses to Human Toxicity.

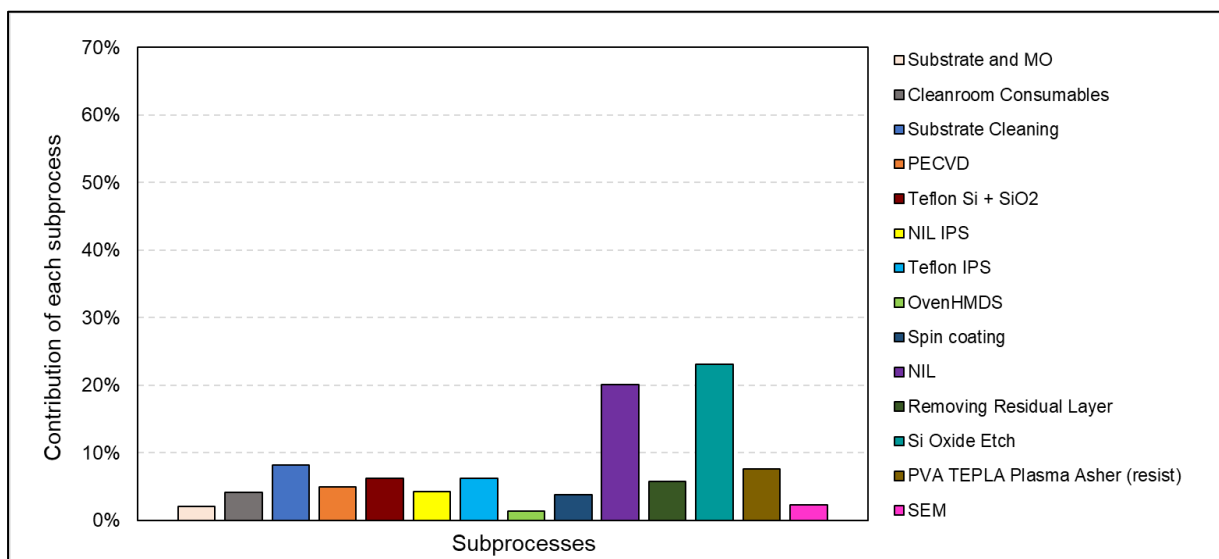


Figure E-6 - Relative contribution of the passivation subprocesses to Photochemical Oxidation.

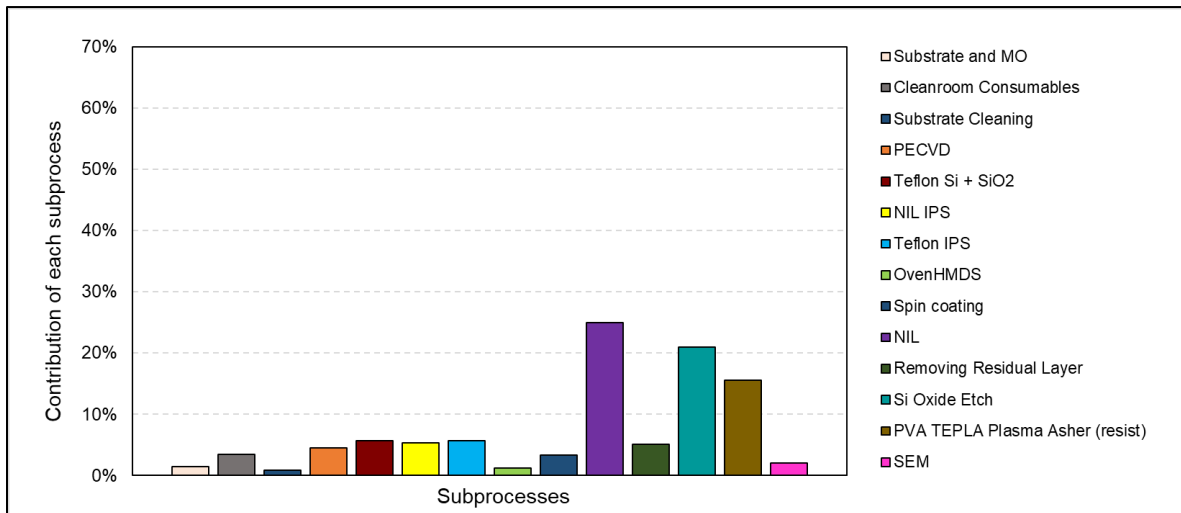


Figure E-7 - Relative contribution of the passivation subprocesses to Terrestrial Ecotoxicity.

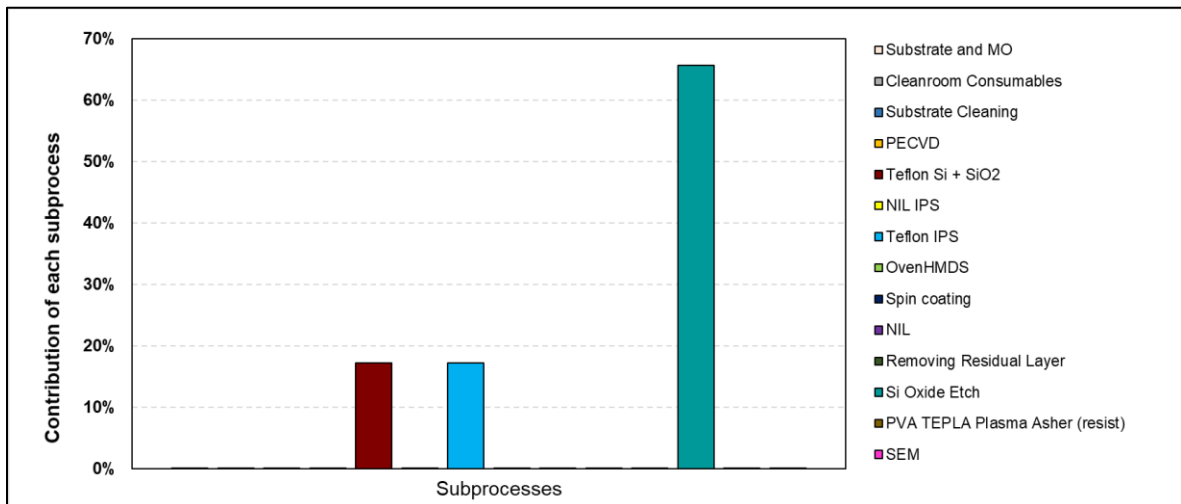


Figure E-8 - Relative contribution of the passivation subprocesses to Ozone Layer Depletion.

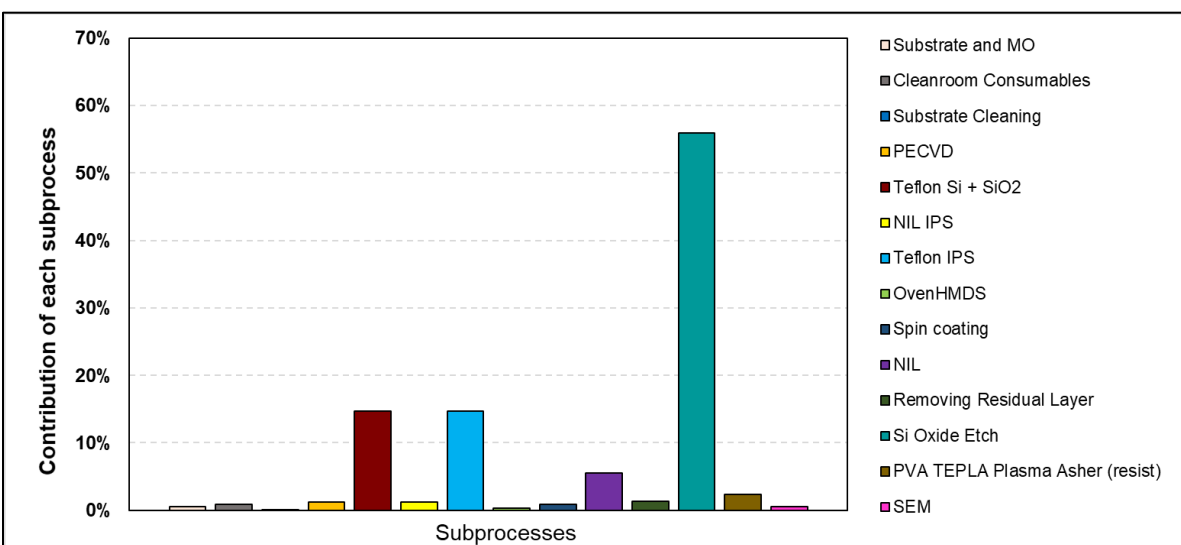


Figure E-9 - Relative contribution of the passivation subprocesses to Marine Aquatic Ecotoxicity.

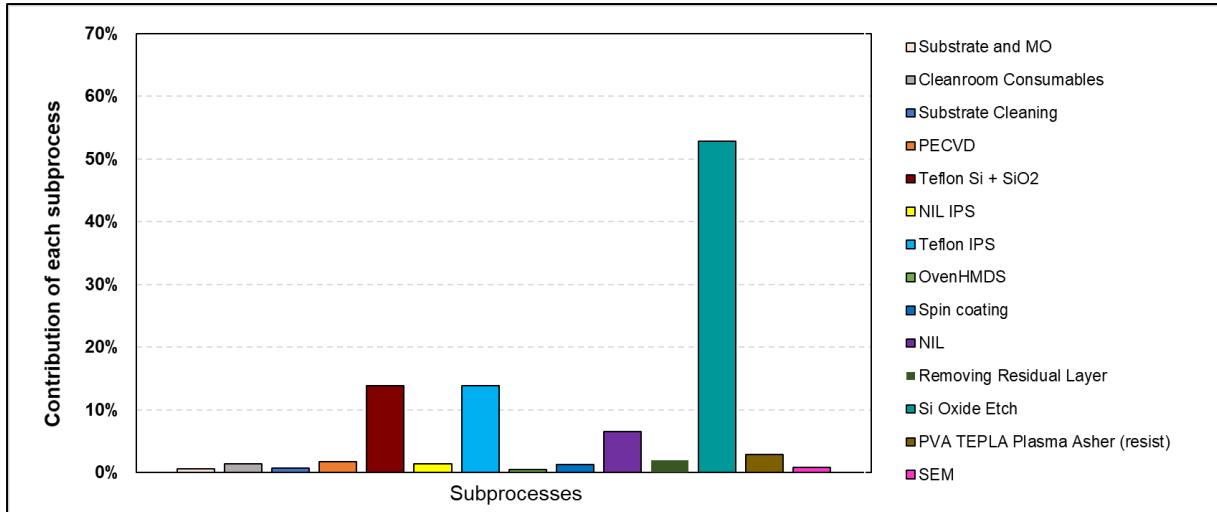


Figure E-10 - Relative contribution of the passivation subprocesses to Global Warming.

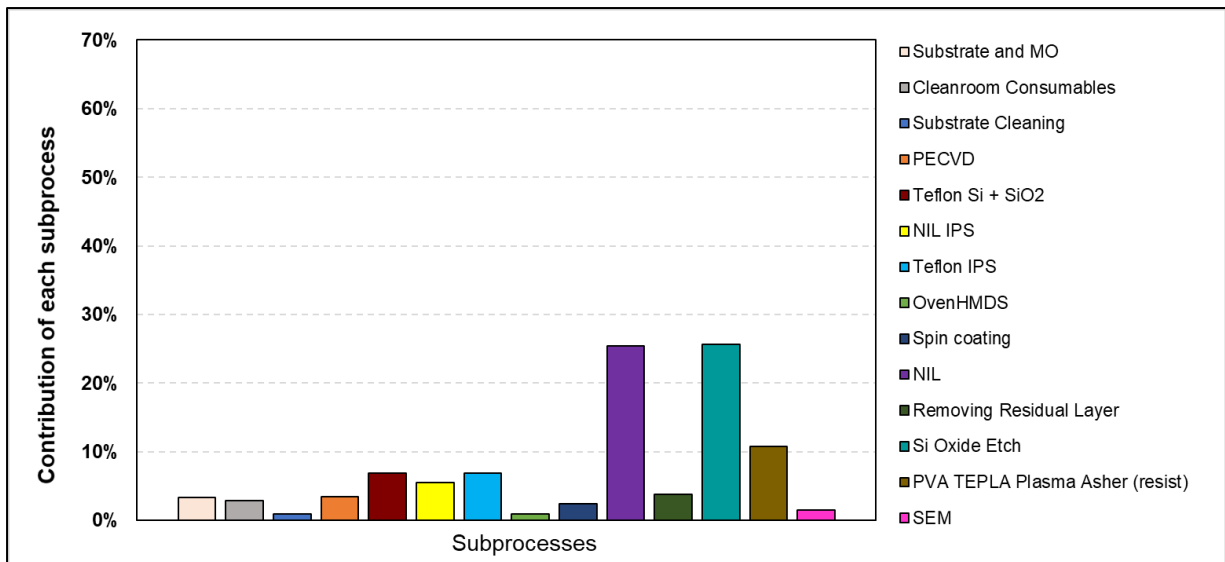


Figure E-11 - Relative contribution of the passivation subprocesses to Fresh Water Aquatic Ecotoxicity.

ANNEX F - ENERGY MIX FOR PORTUGAL, CHINA, USA, MALAYSIA, AND SOUTH KOREA.

Table F-1 - Distribution of the energy mix of Portugal, China, USA, Malaysia, and South Korea [78].

	Solar	Wind	Hydropower	Nuclear	Oil	Gas	Coal	Other Renewable Sources	Total	Unit	%Renewable
Portugal	1.45	12.32	12.61	0	1.04	17.32	3.06	4.21	52.01	Terawatt-hour	58.82%
	2.79%	23.69%	24.25%	0.00%	2.00%	33.30%	5.88%	8.09%	100.00%		
China	261.10	466.52	1355.21	366.23	160.32	253.43	4631.21	129.74	7623.7	Terawatt-hour	29.02%
	3.42%	6.12%	17.78%	4.80%	2.10%	3.32%	60.75%	1.70%	100.00%		
USA	132.63	336.53	285.79	789.92	28.95	1629.24	773.81	72.98	4049.85	Terawatt-hour	20.44%
	3.27%	8.31%	7.06%	19.50%	0.71%	40.23%	19.11%	1.80%	100.00%		
Malaysia	0.81	0.00	26.73	0.00	2.43	64.65	66.87	1.55	163.03	Terawatt-hour	17.84%
	0.49%	0.00%	16.40%	0.00%	1.49%	39.66%	41.02%	0.95%	100.00%		
South Korea	17.67	2.94	3.98	153.14	18.55	142.49	191.67	5.75	536.19	Terawatt-hour	5.66%
	3.30%	0.55%	0.74%	28.56%	3.46%	26.57%	35.75%	1.07%	100.00%		

ANNEX G – RELATIVE CONTRIBUTION OF THE PASSIVATION SUBPROCESSES TO THE TOTAL NORMALIZED IMPACT CALCULATED FOR THE WORLD LEADING COUNTRIES IN PV SOLAR PANELS MANUFACTURING

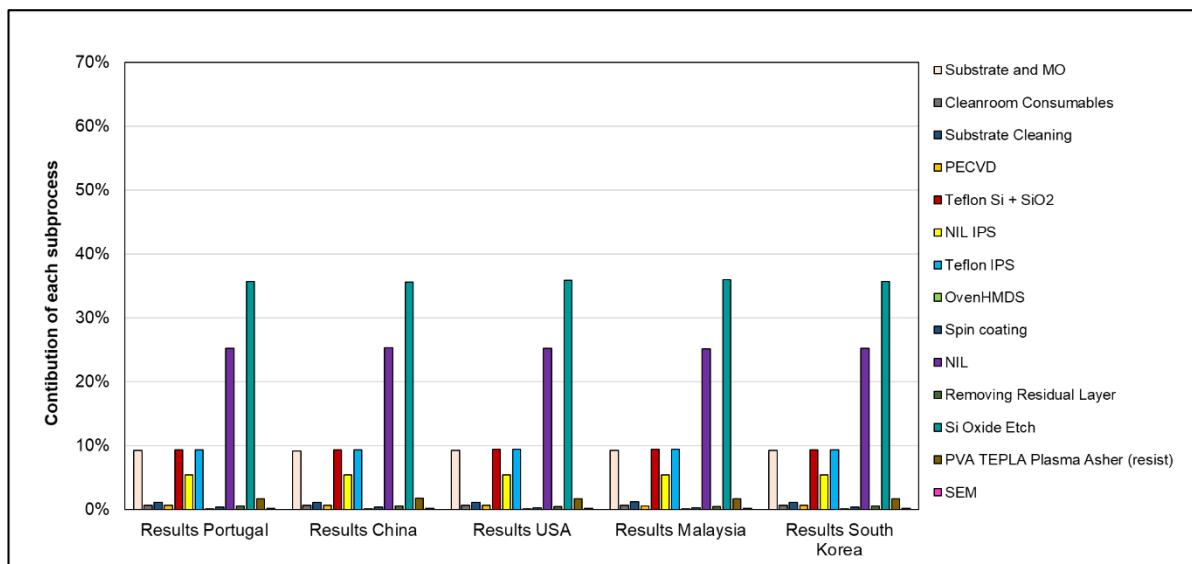


Figure G-1 - Relative contribution of the passivation subprocesses to Abiotic Depletion in the world leading countries of PV panels' production.

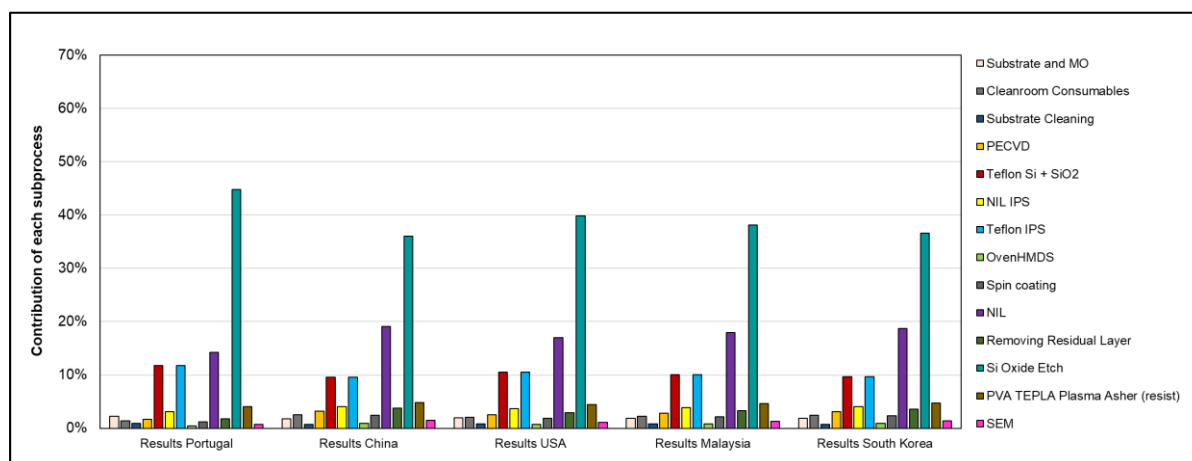


Figure G-2 - Relative contribution of the passivation subprocesses to Human Toxicity in the world leading countries of PV panels' production.

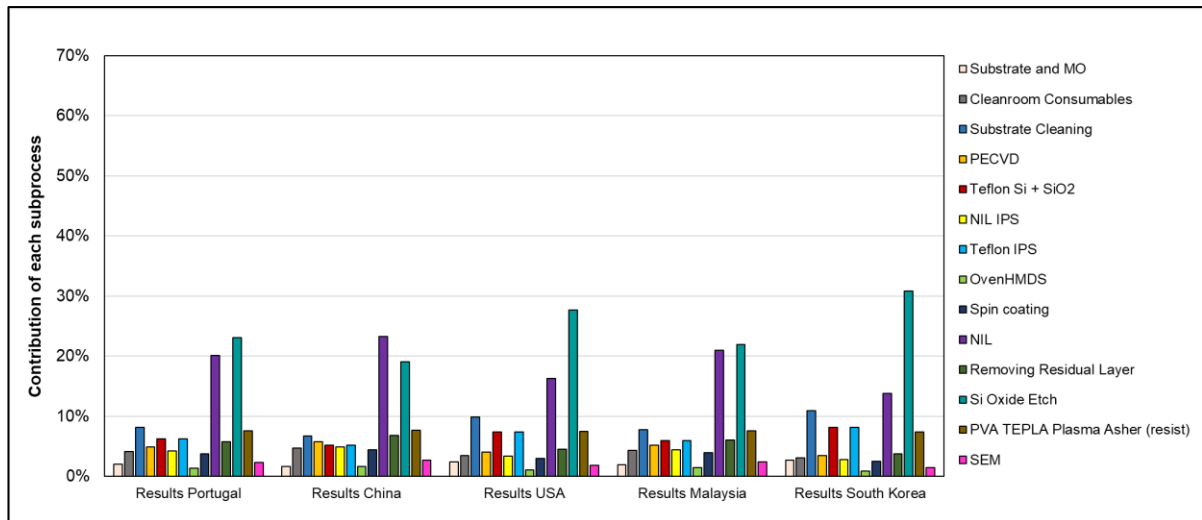


Figure G-3 - Relative contribution of the passivation subprocesses to Photochemical oxidation in the world leading countries of PV panels' production.

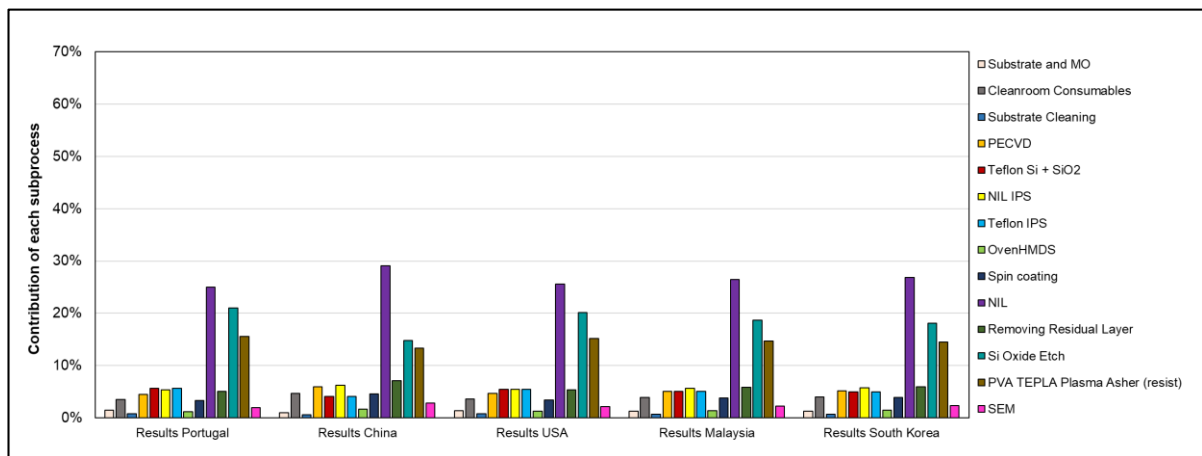


Figure G-4- Relative contribution of the passivation subprocesses to Terrestrial ecotoxicity in the world leading countries of PV panels' production.

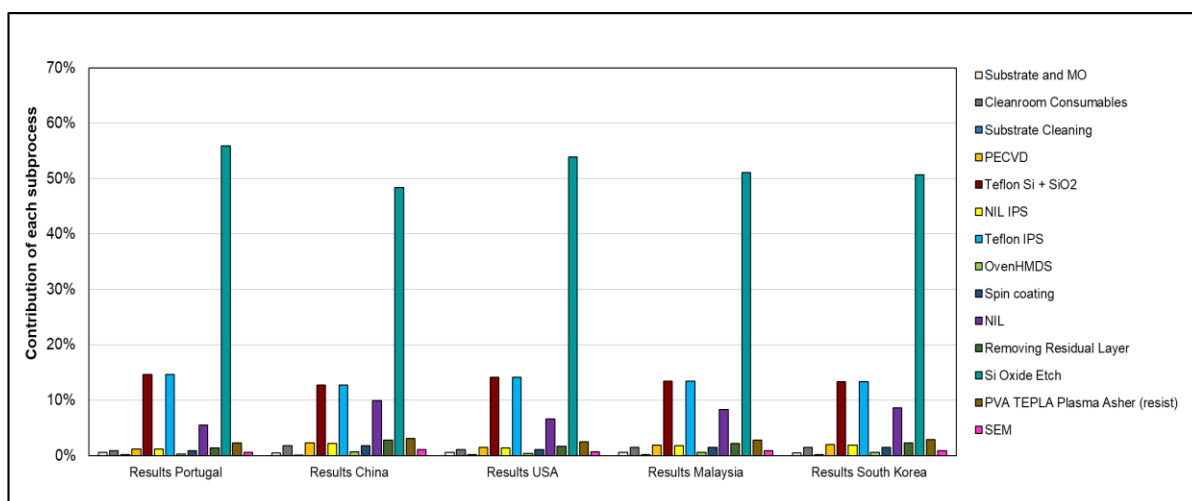


Figure G-5 - Relative contribution of the passivation subprocesses to Marine aquatic ecotoxicity in the world leading countries of PV panels' production.

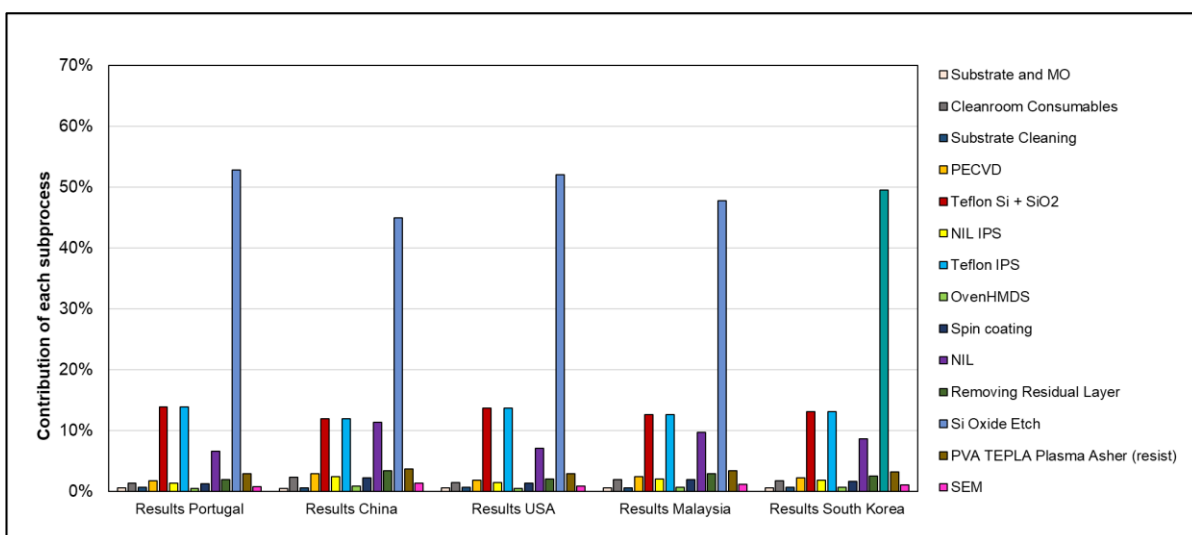


Figure G-6 - Relative contribution of the passivation subprocesses to Global Warming in the world leading countries of PV panels' production.

ANNEX H - NORMALIZED ENVIRONMENTAL IMPACT VALUES FOR THE ENVIRONMENTAL IMPACT CATEGORIES UNDER STUDY

Table H-1 - Normalization results for the whole passivation process.

Factor	Substrate and MO	Cleanroom Consumables	Substrate Cleaning	PECVD	Teflon Si + SiO2	NIL IPS	Teflon IPS	OvenHMDS
Abiotic Depletion - Fossil Fuels	9.935E-14	3.035E-13	2.913E-13	3.314E-13	2.408E-13	2.769E-13	2.408E-13	9.124E-14
Abiotic Depletion	1.588E-13	1.166E-14	2.026E-14	1.175E-14	1.610E-13	9.357E-14	1.610E-13	2.260E-15
Acidification	8.709E-14	1.496E-13	4.709E-14	1.888E-13	1.138E-13	1.620E-13	1.138E-13	5.370E-14
Eutrophication	3.073E-14	7.428E-14	1.738E-14	9.843E-14	6.180E-14	8.880E-14	6.180E-14	2.644E-14
Fresh Water Aquatic Ecotoxicity	4.130E-13	3.548E-13	1.158E-13	4.308E-13	8.552E-13	6.855E-13	8.552E-13	1.132E-13
Global Warming	5.737E-14	1.376E-13	6.605E-14	1.702E-13	1.404E-12	1.365E-13	1.404E-12	4.657E-14
Human Toxicity	4.071E-14	2.444E-14	1.698E-14	3.056E-14	2.137E-13	5.559E-14	2.137E-13	7.882E-15
Marine Aquatic Ecotoxicity	4.885E-14	7.593E-14	1.173E-14	9.899E-14	1.249E-12	1.005E-13	1.249E-12	2.740E-14
Ozone Layer Depletion	3.087E-16	3.415E-16	9.755E-17	4.540E-16	2.641E-12	3.842E-16	2.641E-12	1.264E-16
Photochemical Oxidation	9.578E-15	1.974E-14	3.885E-14	2.349E-14	2.961E-14	2.005E-14	2.961E-14	6.629E-15
Terrestrial Ecotoxicity	5.587E-15	1.352E-14	3.218E-15	1.754E-14	2.195E-14	2.077E-14	2.195E-14	4.739E-15

Table H-2 - Normalization results for the whole passivation process (continuation from Table H-1).

Factor	Spin coating	NIL	Removing Residual Layer	Si Oxide Etch	PVA TEPLA Plasma Asher (resist)	SEM	TOTAL	TOTAL %
Abiotic Depletion - Fossil Fuels	2.482E-13	1.300E-12	3.772E-13	8.710E-13	5.411E-13	1.493E-13	5.362E-12	8.83%
Abiotic Depletion	6.057E-15	4.343E-13	9.202E-15	6.142E-13	2.994E-14	3.639E-15	1.718E-12	2.83%
Acidification	1.455E-13	7.649E-13	2.222E-13	4.049E-13	2.796E-13	8.796E-14	2.821E-12	4.65%
Eutrophication	7.139E-14	4.206E-13	1.094E-13	2.215E-13	2.765E-13	4.328E-14	1.602E-12	2.64%
Fresh Water Aquatic Ecotoxicity	3.032E-13	3.183E-12	4.680E-13	3.206E-12	1.344E-12	1.851E-13	1.251E-11	20.61%
Global Warming	1.263E-13	6.644E-13	1.926E-13	5.341E-12	2.880E-13	7.624E-14	1.011E-11	16.66%
Human Toxicity	2.110E-14	2.588E-13	3.255E-14	8.126E-13	7.296E-14	1.288E-14	1.815E-12	2.99%
Marine Aquatic Ecotoxicity	7.346E-14	4.670E-13	1.133E-13	4.760E-12	1.971E-13	4.484E-14	8.518E-12	14.03%
Ozone Layer Depletion	3.349E-16	1.788E-15	5.167E-16	1.009E-11	7.451E-16	2.045E-16	1.538E-11	25.34%
Photochemical Oxidation	1.803E-14	9.529E-14	2.742E-14	1.095E-13	3.596E-14	1.085E-14	4.746E-13	0.78%
Terrestrial Ecotoxicity	1.271E-14	9.681E-14	1.960E-14	8.129E-14	6.018E-14	7.752E-15	3.876E-13	0.64%