# Comparative Study of the Environmental Impact of Depositing Al 2 O 3 by Atomic Layer Deposition and Spatial Atomic Layer Deposition

Muhammad Farooq Khan Niazi, David Munoz-Rojas, Damien Evrard, Matthieu Weber

# Comparative study of the environmental impact of depositing $Al_2O_3$ by Atomic Layer Deposition and Spatial Atomic Layer Deposition.

Muhammad Farooq Khan Niazi,[1] David Muñoz Rojas, [1] Damien Evrard,[2,*] Matthieu Weber[1,*]

1 Univ. Grenoble Alpes, CNRS, Grenoble INP, LMGP, Grenoble F- 38000, France

2 Univ. Grenoble Alpes, CNRS, Grenoble INP, G-SCOP, Grenoble F- 38000, France

* damien.evrard@grenoble-inp.fr ; matthieu.weber@grenoble-inp.fr

*Keywords: Atomic layer deposition (ALD); Spatial ALD; Life Cycle Assessment; trimethylaluminum (TMA)*

**Abstract**

With increasing concerns about the environmental impacts of human activities, novel nanotechnologies and nanomaterials are being explored as key solutions to tackle pollution and pave the way for a more sustainable future. One such technology that has gained attention is Atomic Layer Deposition (ALD), which can be used to prepare thin films with precise control over thickness and composition. Spatial ALD (SALD), in particular, presents high deposition rates and can be performed at high pressure, and has emerged as a promising alternative to conventional ALD. However, to the best of our knowledge, there is no literature reporting on its environmental performance compared to that of ALD. Herein, we present a comparative life cycle assessment (LCA) study between conventional ALD and SALD to quantify and compare their environmental impacts. The study focuses on the deposition of a 20 nm alumina thin film from TMA (trimethylaluminum) and water at 200 °C as the functional unit, considering the use of typical lab-scale reactors, the SALD being based on the close-proximity approach. Different region-based scenarios were evaluated, considering the film production in Europe, in France and in Taiwan. The assessments obtained revealed that electricity consumption was the primary contributor to most impact categories for both ALD and SALD processes, followed by the TMA precursor. The results indicated that, for the alumina process and the assumptions considered, SALD had a notably better environmental performance than ALD for the majority of assessed impact categories, in all three regions considered.

## Introduction

Our different ecosystems are facing an ever-increasing peril due to human impact on the environment, including rising resource consumption and environmental alterations. To sustain our societies, more ambitious conservation and proactive emission reduction efforts are required. Researchers should develop eco-friendly technologies, analyze their environmental impacts, and reduce pollutants to contribute to the global effort required.[1-5] Particularly, the sustainability of nanotechnologies and nanomaterials is a growing concern and needs to be assessed.[6]

Atomic Layer Deposition (ALD) is a vapor phase deposition technique that can be used to deposit a wide range of nanomaterials, with an excellent control over the thickness, composition and uniformity of the films. The basic principle of ALD involves the sequential exposure of a substrate to two or more gaseous chemical precursors, and due to the self-limiting nature of the process, this deposition route allows for the creation of complex nanostructures with atomic-level precision.[7–9]

ALD typically takes place in a vacuum chamber; the substrate being heated to a specific temperature to ensure proper reactivity of precursor molecules. The first step of ALD is the introduction of precursor molecules into the chamber. These molecules react with the substrate surface, in a self-limiting fashion. The chamber is then purged with an inert gas to remove the excess of precursors and the by-products generated. Then, a second precursor or co-reactant is introduced, reacting with the surface, and forming the desired sub-monolayer. The chamber is finally purged again, to remove the unreacted species. This cycle is repeated multiple times until the desired film thickness is achieved. Thus, ALD offers precise control over film thickness by adjusting the number of cycles, enabling the precise layer-by-layer growth of uniform and conformal nanomaterials.[7–9]

Thanks to its unique assets, the deployment of ALD in industrial applications has ramped up during the last few decades and is primarily focused on high-volume manufacturing in two industrial sectors, namely semiconductor and photovoltaics.[10,11] Many other applications and products could benefit from the implementation of ALD, such as batteries, membranes, or fuel cells for example.[12–14] ALD is highly efficient in producing functional layers with atomic precision, thereby maximizing the utility of materials in the final products. However, the process itself is energy intensive, and a significant amount of precursors and gases are wasted during their synthesis and in the midst of the ALD process itself. Therefore, it is crucial to assess and quantify the environmental impact of ALD, and to find paths to lower it. In a recent work, our group provided a summary of relevant findings in the literature evaluating the environmental impact of ALD and discussed the principles of green chemistry when applied to ALD process.[12] The studies reviewed indicate that the use of ALD has the most significant environmental impact in the fossil fuels category, primarily due to its energy demand, which is mainly caused by the duration of the process, the temperature, the materials utilized and wasted. Several strategies that can help promote sustainable ALD practices have been suggested, including optimizing reactor and processing parameters, designing more sustainable precursor chemicals, and utilizing high-throughput techniques like SALD.[12]

SALD is a high-throughput ALD approach that results in faster deposition rates, up to 2 orders of magnitude, reducing production costs and time.[13,14] Such faster deposition rates make SALD suitable for industrial implementation since it reduces production costs, as illustrated in the photovoltaics industry, the initial application of SALD[13,15].

Just like conventional ALD, SALD was patented by Suntola et al.[16] This alternative approach involves the continuous injection of precursors molecules in distinct regions, enabling deposition rates significantly faster than conventional ALD, sometimes by several orders of magnitude, and can be conducted at atmospheric pressure. The route can be implemented amongst various approaches depending on the type of sample being coated (e.g., roll to roll), making the process as efficient as possible. In this work, we focus on a close proximity SALD approach which was initially developed by Eastman Kodak[17]. This approach ensures precursors separation by keeping a small (<100 μm) distance between the substrate and the manifold head through which the precursors are dosed continuously (see Figure 1). The deposition is accomplished by moving either the head or the substrate to expose it to the various flows. This method thus considers the reaction chamber as the space between the head and the substrate and allows for depositions at atmospheric pressure and even in open air without a deposition chamber.[18] However, it does come with a drawback of higher precursor and inert gas usage compared to conventional ALD.[12] Figure 1 depicts the close-proximity SALD approach considered in this work.

Assessing the environmental impact of ALD and SALD processes is crucial in identifying the resource consumption and subsequently for developing strategies to minimize their environmental impact. Recently, investigations have been conducted to tackle the environmental aspects and potential effects of ALD processes. Notably, the team led by Yuan at the University of Wisconsin Milwaukee (USA) has made significant strides in this emerging field, conducting extensive life cycle assessments and other environmental evaluations for ALD of $Al_2O_3$ based on TMA and water.[19–22]

While the advantages of SALD have been widely discussed,[15,23,24] to the best of our knowledge, there is no literature reporting on its environmental performance compared to that of ALD. In fact, if SALD has emerged as a faster alternative to conventional ALD, its higher consumption of inert and precursor gas poses challenges to its sustainability. It is thus necessary to provide the necessary data to evaluate the environmental performance of SALD in comparison to ALD, and to determine if it indeed delivers on its promise of a lower environmental footprint.

In this study, we investigate and compare the environmental impacts of ALD and SALD, by conducting comprehensive and comparative life cycle assessments of the well-known alumina processes based on TMA and water. The close-proximity SALD process carried out in our lab was taken as the Life Cycle Assessment (LCA) reference system with a cradle-to-gate system boundary, while a similar model was established for the ALD process, based on the existing literature already reported on the ALD environmental footprint. To the best of our knowledge, this is the first time that an in-depth analysis of the environmental performance of SALD is carried out, depending on the processes and the regions where the process is carried out.

## Experimental Methodology

### Life Cycle Assessment

Life Cycle Assessment is a comprehensive analysis methodology that assesses the associated environmental impact of a product/production system from its creation to its disposal, considering all upstream and downstream processes involved. The purpose of conducting an LCA is to gain insight into the life cycle stages and specific inputs that have the greatest environmental, economic, and social impact.[25] This allows practitioners to mitigate/minimize these risks through process or product optimization. LCA follows a standardized procedure in accordance with the ISO Standard (ISO 14044:2006), which includes 4 major steps as shown in Figure 2.[26]

Defining the goal and scope is the first step in the process. It includes the purpose, determines the system boundaries, defines the impact indicators to be studied, establishes a functional unit, calculates the reference flow, and includes all the assumptions taken for the analysis.

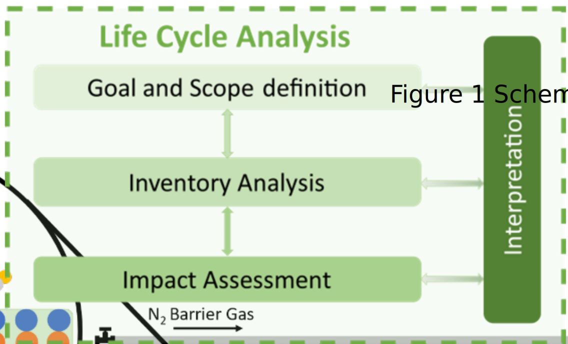


Figure 2 Steps of a life cycle analysis.

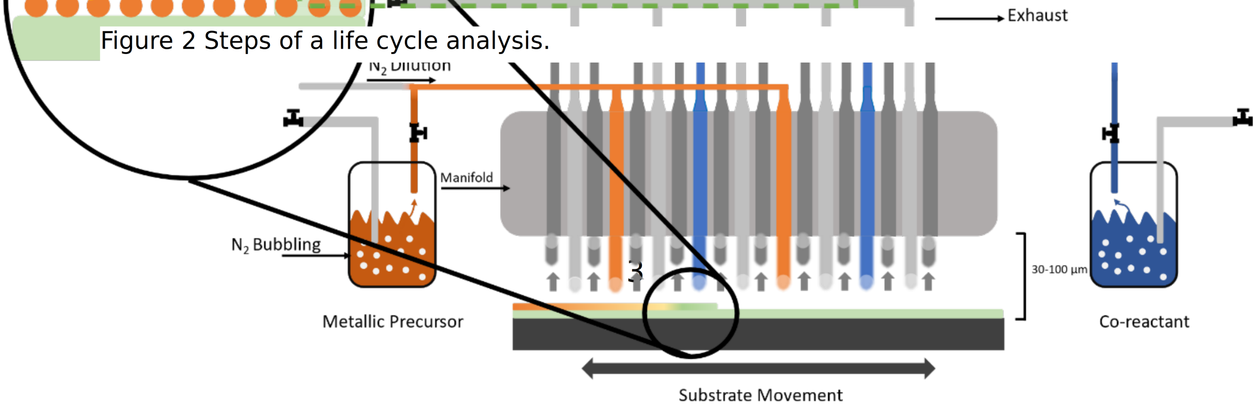


Figure 1 Schematic representation of a close-proximity SALD c

Once the Goal and Scope are defined, the next step is to create and analyze the inventory, with the help of databases (e.g., Ecoinvent). Subsequently, using specific calculation methods, the impacts are assessed, categorized, and interpreted. Finally, additional steps such as sensitivity and uncertainty analysis can make the assessment more precise.

## Goal and Scope

Functional Unit

The functional unit chosen for this study is the 'deposition of a 20 nm alumina film from TMA and water on an 80 $cm^2$ substrate surface'. The process based on TMA and water to prepare alumina has been chosen because it is well known and widely studied in the community.[27–30] The area of 80 $cm^2$ corresponds to a typical 4-inch wafer. This functional unit was selected to allow for a direct comparison of the SALD process studied with research previously published on ALD. The LCA study follows the Type B systems approach as established by Bauer C. *et al.*,[27] which is used to compare two different manufacturing alternatives performing the same function.

## System Boundaries

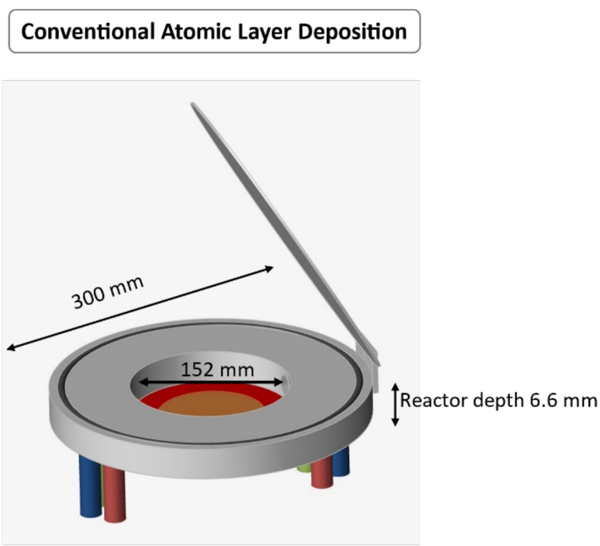
The system boundaries for this study are defined as cradle-to-gate, which includes life cycle phases from raw material extraction to the point of leaving the factory gate. By focusing on these phases, the study can draw a clear comparison between the techniques as the final use in both cases remains the same regardless of the manufacturing methodology.

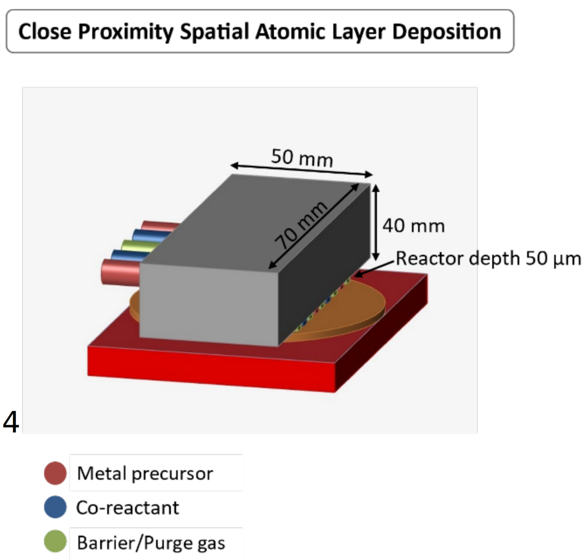
To produce an alumina film via ALD and SALD, multiple inputs are required, including specialized equipment, specific precursor gases, and energy in the form electricity. The ALD reactor considered is based on the reported literature present for deposition on a 4-inch silicon wafer, whereas the SALD reactor considered is based on a close proximity approach and is the one used in our laboratory. Section on 'Inventory analysis' provides the inventories with specific details on the equipment, the precursors, and their production.

## Assumptions for Processing Parameters

For ALD, the process considered is based on the successive pulses of TMA and water at a temperature of 200 °C under vacuum, as reported by Yuan C. et al[28]. The authors comprehensively described the deposition process, providing a detailed breakdown of precursor and energy inputs required for the formation of an alumina film. In this ALD process, the film deposition occurs through two half reactions, where the precursors are transported by a flow of nitrogen gas of 10 sccm. Each precursor is pulsed into the deposition chamber for a duration of 1 second, followed by a subsequent purge step of 5 seconds. This sequential pulsing and purging procedure constitute a single ALD cycle, which has a total duration of 12 seconds and results in a growth rate of 0.1 nm/cycle. To form a 20 nm alumina film, this process requires 200 cycles, taking around 40 minutes.

For SALD, the process is also based on TMA and water, and carried out at the same temperature of 200 °C. The process takes place in atmospheric pressure. The bubbling and dilution flowrates of nitrogen through the TMA bubbler are 100 and 270 sccm respectively, and 30 and 350 sccm for water. The barrier gas used is also nitrogen, with a total flow of 1000 sccm through multiple channels. This process allows to achieve growth rates up to 0.5 nm/s with a total deposition time in the range of one minute. The precursor usage



is overestimated in our analysis, as considered equal to the bubbling rate of nitrogen gas flow through the precursor[29]. The energy required to deposit the thin film was measured using a wattmeter (Atorch electric energy meter) and included all the electricity used from the startup of the machine to the end of the deposition, which encompass the system heating, stabilization, and deposition phase. The system heating duration was 25 minutes whereas the stabilization phase applied was 60 minutes long. The coating was assumed to be dense and uniform.

## Equipment assumptions for Reactors

The ALD and SALD reactors considered are lab-scale tools and are illustrated in Figure 3. They were considered to have a similar outer shell based on stainless steel, with notable differences in reactor size, as depicted in Figure 3. Some of the assumptions made for the ALD and SALD reactors are summarized in Table 1.

**Table 1 Equipment assumptions for Life Cycle Analysis.**

| | |
|---|---|
| **Assumptions** | The ALD reactor is assumed to be cylindrical with a diameter 152.4 mm and a height of 12.7 mm[30] |
| | The SALD reactor manifold is precisely measured to be 50 mm x 70 mm x 40 mm |
| | Equipment Life for high wear parts assumed to be 1000 depositions of 20 nm film |
| | Equipment Life for low wear parts assumed to be 10000 depositions of 20 nm film |
| | Both machines considered to have a similar aluminum frame |

## Inventory analysis

The life cycle assessment encompasses both primary and secondary life cycle inventories (LCI). The primary data collected in the lab includes machine specifications, process details, precursor utilization and energy requirement for the SALD equipment. The secondary data for ALD is extracted from literature.

Figure 3 Reactor Volume Comparison of ALD (left) vs SALD (right).

OpenLCA, an open-source software, was used to list all material and energy inputs for the relevant processes. The Ecoinvent 3.8 database was used for machine and energy LCI data in this study. However, datasets on metal-organic precursors such as TMA are limited in LCI databases. Therefore, the synthesis of the precursors using their base chemicals and reactions present in the Ecoinvent 3.8 database has been considered, as this approach highlights environmental impacts, which might be overlooked if a chemical with a similar composition, already present in the database, is substituted instead of the abovementioned approach.

For this assessment, the energy provider selected was RER (an acronym for Europe in Ecoinvent) to obtain an overview of the deposition process in Europe. When not specified otherwise, RER was selected as the provider for all processes unless it was not available in the database, in which case the provider was kept as Global (GLO).

## Inventory for ALD Equipment

The ALD equipment was divided into two segments: (a) Low wear parts, which comprised of parts with high lifespan (b) High wear parts, which comprised of parts that need maintenance and replacing. The low wear parts are assumed to last 10,000 deposition cycles, whereas the high wear parts are assumed to last 1,000 deposition cycles. Details on the parts considered are given in Table S1 and Table S2. To create the inventory for ALD equipment, the size of the lab-scale reactor was obtained from the work of Zhou T. et al.[31] A 3D model of the reactor was drawn as shown in Figure 3, which was used to also estimate the weight of the reactor. The ALD equipment also required the inclusion of a vacuum pump.

## Inventory for SALD Equipment

The inventory for SALD equipment was created by measuring and/or estimating the materials required to fabricate the equipment used in our lab. As for the conventional ALD, the SALD equipment's parts were divided into two segments. Subdividing the inventory allows for a more accurate evaluation of the impact close to a real-world scenario. The SALD equipment included more parts in the high wear segment than ALD, as the manifold head has a shorter lifespan (it is likely to be clogged/blocked after certain number of deposition). The inventory for SALD equipment is detailed in Table S3 and Table S4.

## Inventory for Synthesis of TMA

Different synthetic procedures exist for the preparation of trimethylaluminum (TMA), as described in the works of Pasynkiewicz et al.[32] and Smith et al.[33] Although both synthetic routes could be considered, as the base chemicals and intermediate compounds used in the Pasynkiewicz's procedure were not available in the database, the method outlined by Smith *et al.* has been considered in this work. This synthetic procedure is well described in the literature, as shown by various publications including a study encompassing a life cycle assessment model (see process flow in Figure 4). This method was deemed preferable for our work as well, due to its reliability and availability in existing literature and higher purity of the precursor obtained.

To synthesize trimethylaluminum (TMA) by this method, the inputs required are shown in Table 2. However, all the chemicals necessary to synthesize TMA were not present in the Ecoinvent 3.8 database. Therefore, additional subprocesses were created for Anhydrous Aluminum Chloride and Methyl Aluminum Sesquichloride as detailed in Table S5-7. The TMA produced is 98% pure, to further increase the purity another process block was created as described in annex. This yielded 99.95% pure TMA, which was then used as the metallic precursor in the processes and in the LCA carried out.

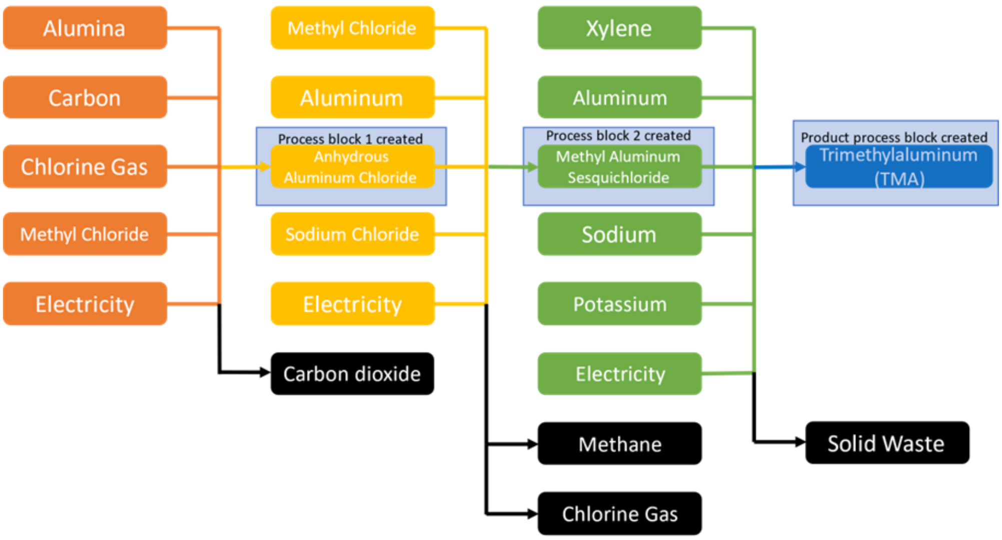



Figure 4 Process Flow for synthesizing TMA based on the work of Smith et al. [32]

**Table 2 Inventory for Synthesis of TMA by Smith et al.[32]**

| Input Flow | Amount | Unit | Provider | Description |
|---|---|---|---|---|
| **electricity, low voltage** | 82 | Wh | market group for electricity, low voltage \| electricity, low voltage \| Cutoff, S - RER | Stirring |
| **electricity, low** | 5.1 | kWh | market group for electricity, | Kept near 150°C for 7 |

| | | | | |
|---|---|---|---|---|
| **voltage** | | | low voltage \| electricity, low voltage \| Cutoff, S - RER | hours, |
| **electricity, low voltage** | 8 | Wh | market group for electricity, low voltage \| electricity, low voltage \| Cutoff, S - RER | Vacuum distillation |
| **methyl aluminum sesquichloride** | 82.6 | kg | methyl aluminum sesquichloride | Process block created |
| **nitrogen, liquid** | 0.825 | kg | market for nitrogen, liquid \| nitrogen, liquid \| Cutoff, S - RER | |
| **sodium** | 27 | kg | market for sodium \| sodium \| Cutoff, S - GLO | Potassium unavailable in ecoinvent, use mass of sodium |
| **xylene** | 153.1 | kg | market for xylene \| xylene \| Cutoff, S - RER | Estimated mass, no re-use |
| **Output Flow** | | | | |
| **triethylaluminium (TMA) 98%** | 30 | kg | | 68% yield |
| **hazardous waste, for incineration** | 26 | kg | | unreacted methyl aluminum sesquichloride |
| **hazardous waste, for incineration** | 48 | kg | | Sodium Chloride |
| **hazardous waste, for incineration** | 153.1 | kg | | Lost Solvent |

## Inventory for Alumina deposition using ALD

Using the process created by Yuan C. et al.[28] and the estimate of the ALD reactor described before, the inventory for alumina deposition using ALD was created.

Briefly, it considers the amount of energy, nitrogen, TMA, and water as well as the ALD reactor inputs to produce alumina film and methane as the outputs (details are given in Table S8). The locations of dataset used for the input flows were the same for ALD and SALD (see Table 3), to allow a direct comparison between the techniques.

## Inventory for Alumina deposition using SALD

The SALD equipment considered uses a close proximity approach in which a movable injector head with channels through which a constant flow of precursors and barrier gas is passed to deposit a thin layer of alumina onto a substrate. The barrier gas used is nitrogen whereas the precursors are water and trimethylaluminum (TMA) for alumina deposition.

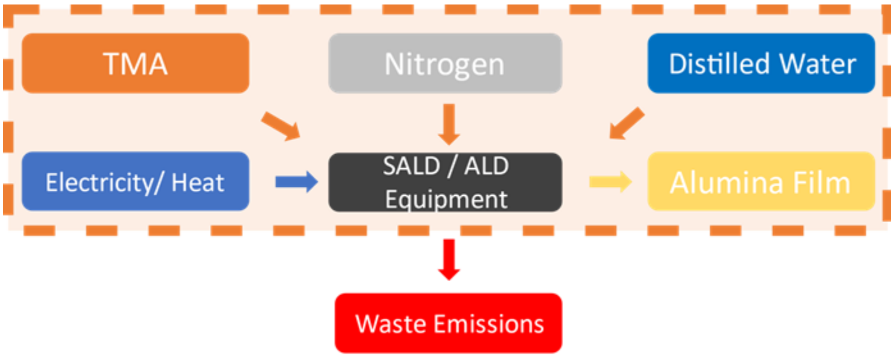



Figure 5 Schematic representation of inputs and outputs in a deposition process

After creating the process blocks for the precursor and machine, the alumina deposition process was established as shown in Figure 5. The amount of inventory used is primary data gathered through experimentation conducted in the laboratory. The input data used is compiled in a table shown in Table S9. The parameters utilized for the calculation of input data necessary for a 20 nm alumina film deposition included gas flows, deposition temperatures, substrate velocity and distance between substrate and manifold. The inventory for alumina deposition using SALD can be seen in Table 3.

**Table 3 Inventory for alumina deposition process using SALD.**

| Input Flow | Amount | Unit | Provider | Description |
|---|---|---|---|---|
| **electricity, low voltage** | 1.569 | MJ | market group for electricity, low voltage \| electricity, low voltage \| Cutoff, S - RER | Power utilization measured in lab |
| **nitrogen, liquid** | 0.00333152 | kg | market for nitrogen, liquid \| nitrogen, liquid \| Cutoff, S - RER | Liquid nitrogen amount calculated in Kg by converting from sccm using ideal gas assumption |
| **SALD r** | | | | nents that replacement more often hence have higher impact. |
| **SALD machine parts (Low wear)** | 0.00001 | Item(s) | SALD Machine parts (low wear) - FR | Components of the machine that do not wear out |
| **trimethylaluminum (TMA) 99.95%** | 0.000572 | kg | trimethylaluminium (TMA) 99.95% | TMA process block created |
| **water, deionized** | 0.0000429 | kg | market for water, | Precursor 2 used is |

| | | | | |
|---|---|---|---|---|
| | | | deionized \| water, deionized \| Cutoff, S - Europe without Switzerland | water |
| **Output Flow** | | | | |
| **alumina film** | 0.000000632 | kg | | 20 nm alumina film |
| **methane** | 0.000000595 | kg | | Byproduct |

### Limitations of the Study

It is important to consider the constraints imposed by the lab-scale process that served as the foundation for this Life cycle analysis study. A conscious effort was made to consider these limitations during the assessment; however, it is crucial to acknowledge that uncertainties still exist in our findings. The limitations of this study are described below.

As the data on complex precursors was not readily available in the database, the TMA precursor had to be 'synthesized' using the available data. This synthesis of the precursors induces uncertainty and human error, which can lead to a difference in impacts.

While this study provides a baseline for environmental performance of SALD, when a lab scale process study is extrapolated to an industrial scale it introduces uncertainties due to the difference in equipment and operating conditions. Scaling up will possibly reduce the environmental impacts but it needs to be quantified and cannot be directly assumed.

As a lab-scale process is well defined it does not have operational variability similar to that of an industrial process. The maintenance and potential pieces replacements were not considered. The variability in the industrial process can lead to a fluctuation in the environmental impacts.

Since close-proximity SALD is still in the development phase, technological uncertainties, including process optimization and scalability exist.

## Results and discussion

### Life cycle impact assessment

The obtained Life Cycle Inventories were analyzed using a relevant impact assessment method, known as the "EF 3.0 Method (adapted)", as it is an EU recommended method to quantify the environmental impacts of products.[34] The categories covered by the Environmental Footprint (EF) 3.0 Method are as follows: (1) Climate change, total (2) Ozone depletion (3) Human toxicity, cancer (4) Human toxicity, non-cancer (5) Particulate matter (6) Ionizing radiation, human health (7) Photochemical ozone formation, human health (8) Acidification (9) Eutrophication, terrestrial (10) Eutrophication, freshwater (11) Eutrophication, marine (12) Ecotoxicity, freshwater (13) Land use (14) Water use (15) Resource use, minerals and Metals (16) Resource use, fossils. The total environmental impact of the deposition known as the 'eco-indicator', or 'footprint' was estimated by normalizing and weighting the results of all the above-mentioned categories into a single point score as well. This footprint allows for a direct comparison between products, but it must be interpreted along with individual category results.

## Interpretation

### Comparative LCA

Before drawing a comparison, both ALD and SALD processes were separately studied to gain further insight on the effect of the inputs of the process. A comprehensive analysis of alumina deposition via ALD is reflected in the contribution tree results in Figure S1. Apart from 2 categories out of 16, the results show that more than 90% of the contribution is attributed to electricity, due to the high consumption of electrical energy in the process. Conversely, the impact of precursor and purging gas is very low due to the lower consumption ,compared to SALD, during the process. The contribution tree also suggests that the ALD reactor equipment has more contribution to the footprint than the precursors. These findings stress the importance of reducing energy consumption in ALD processes and reactor manufacturing to reduce environmental footprint and promote sustainability.

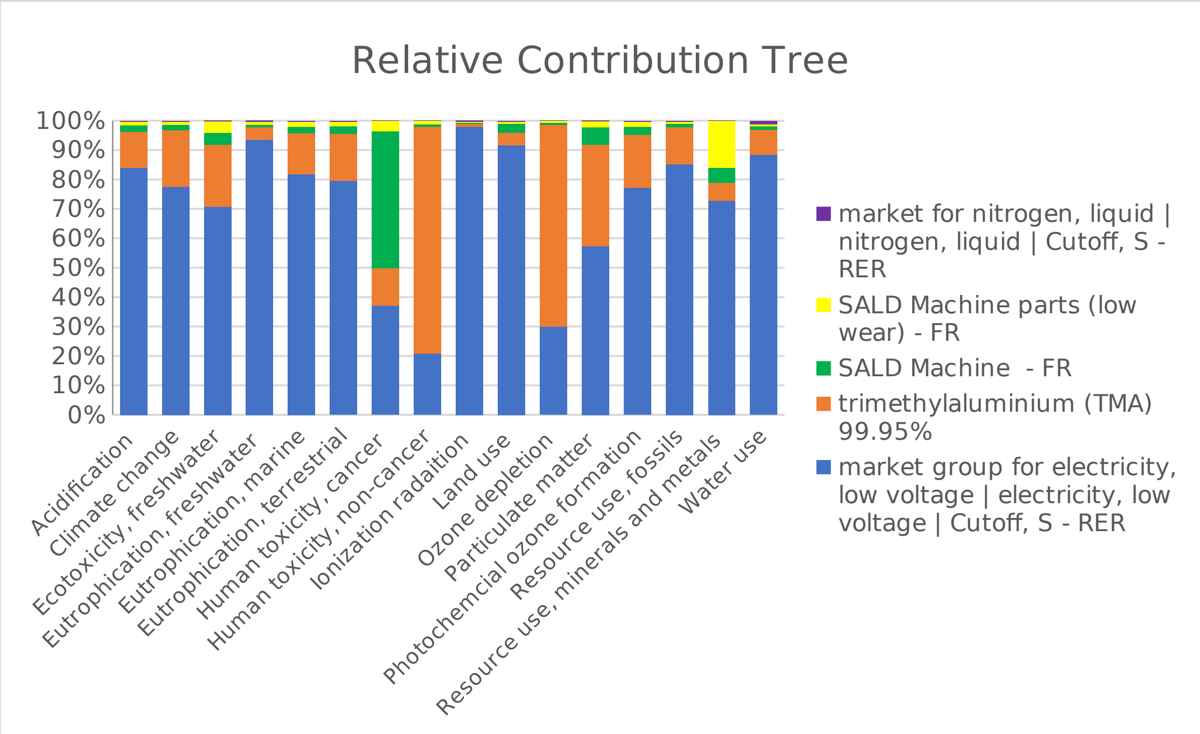



Figure 6 Contribution Tree of Alumina Film Deposition using SALD Process

For SALD the relative contribution tree in the analysis revealed that the highest contributor to most impact categories was electricity consumption as well, accounting for an average of 70% of the overall impact per category. The second largest contributor was the TMA precursor. Interestingly, the relative contribution of nitrogen, which was initially assumed to be a concern due to its potential excess use as a barrier and carrier gas, was found to be less than 1% in most categories as shown in Figure 6. To further investigate the impact of excessive barrier gas usage, nitrogen was substituted with argon, a gas known to have a bigger carbon footprint. It was found out that even when using argon, the contribution of the barrier gas does not exceed more than 2.5% in most categories as shown in Figure S2.

In addition to the relative contribution tree, the normalized scores were also studied to gain further insights into the most affected categories. As shown in Figure 7a, by the normalization score the top four affected impact categories are: ecotoxicity, eutrophication freshwater, resource use fossil and resource use minerals and metals. The contribution tree shows that the consumption of electricity is a primary driver for the majority of the impact in these categories. By interpreting normalization score along with relative contributions it can be deduced that electricity consumption has the most significant impact. This is followed by the impact of TMA precursor, which has the second highest impact score attributed to it due to the excessive usage when compared to ALD.

A detailed comparison between SALD and ALD was plotted to evaluate the environmental footprint of each process. The evaluation was conducted using a combination of relative LCIA results, normalized results, and single score results. The comparative results, present in Figure 7, indicate that for the process considered and the assumptions made, SALD is more environmentally friendly when compared to ALD for 14 categories out of 16 evaluated. SALD shows inferior performance in two categories: Ozone Depletion and Human toxicity, non-cancer.

While the relative Life Cycle Inventory Assessment (LCIA) results suggest a higher impact of Ozone Depletion for SALD, an in-depth analysis of the normalized scores shows that ozone depletion has the lowest value amongst all the categories, with a value two orders of magnitude lower than most other categories, thus making its effect negligible.

"Human toxicity, non-cancer" emerges as a relative hotspot for SALD as evident from figure 7a, due to the excessive use and overestimation of precursor utilization in this analysis. This impact category is precursor dependent making it possible to achieve significant reduction by optimizing the process to enhance precursor utilization and implementing a mechanism for recycling excess precursors.

Overall, it can be seen that apart from the aforementioned impact categories, ALD has a worst score in all other categories when compared to SALD.

The differences in magnitudes between the two techniques varied across different impact categories with SALD consistently displaying superior environmental performance.

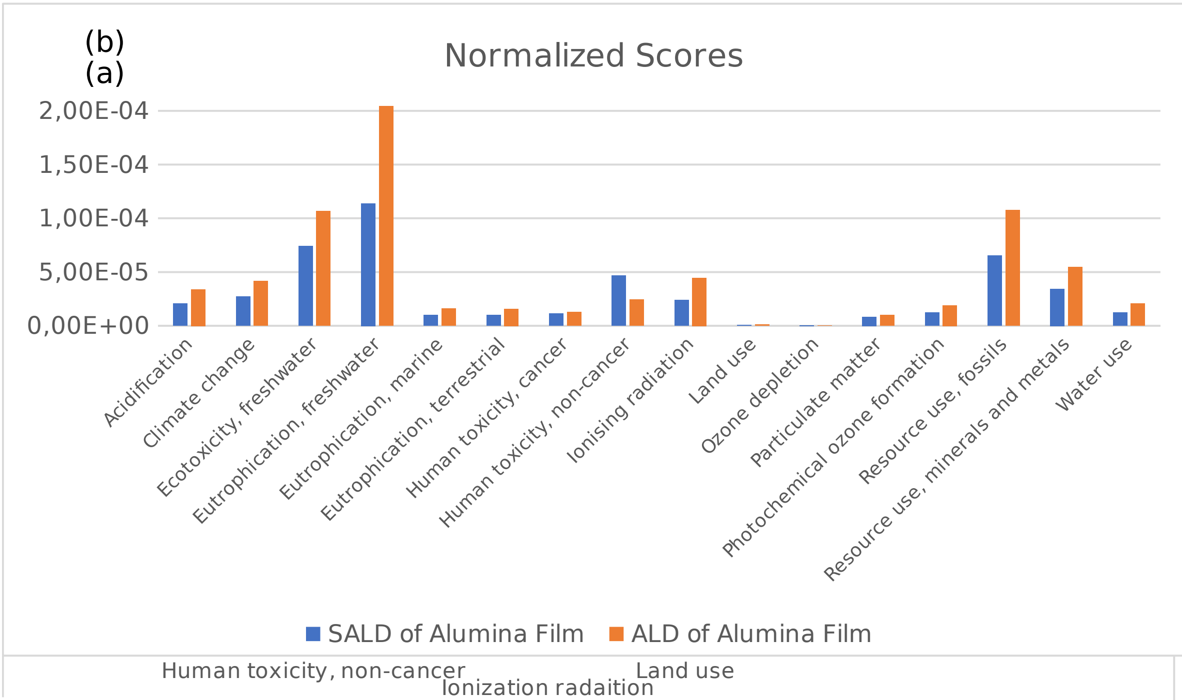


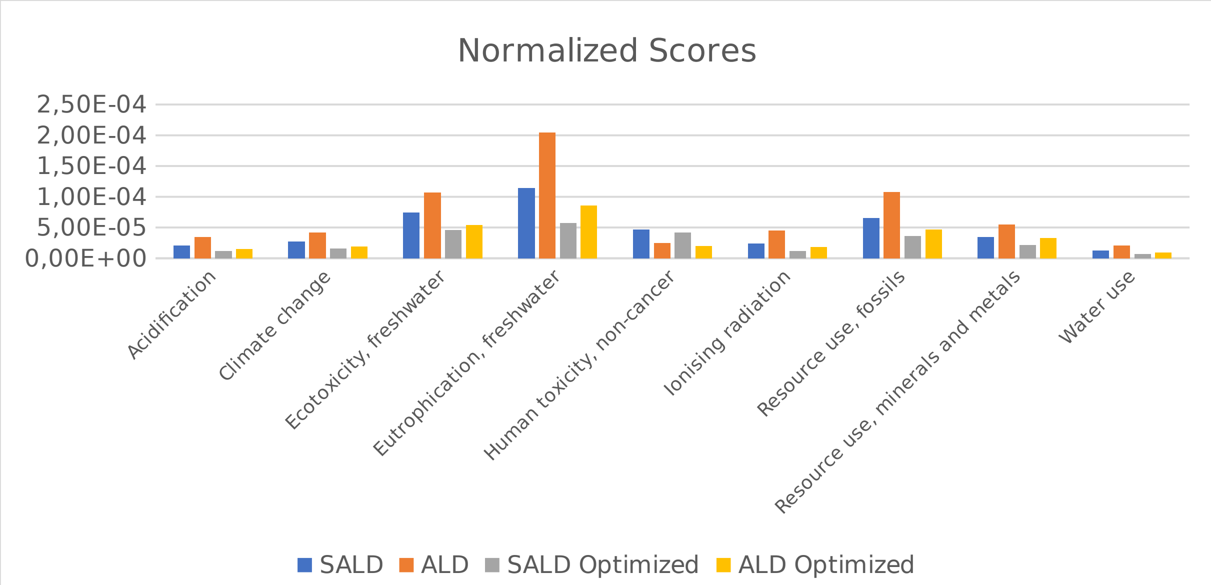

Figure 7 (a) Relative LCIA results shown in a Radar graph (b) Normalized Bar chart shows a detailed analysis between SALD and ALD.

## Optimization

The major contributor in the ALD and SALD processes considered is electricity consumption. Various strategies exist to reduce this consumption, such as limiting the process duration or the deposition temperature. In one of their work, Yuan C. et al.[30] optimized the ALD process for alumina deposition by reducing the cycle time, making it faster and thus reducing the energy consumption from 2.9MJ to 1.2 MJ (for 20 nm alumina film deposition) compared to their prior studies.

Similarly, the process for alumina deposition was optimized to produce the film at a lower temperature of 130 °C at the same fast rate of 0.50 nm/s. This reduced the energy consumption from 1.57 MJ to just 0.76 MJ, as the majority of the energy is used in the substrate heating and stabilization.

In view of these optimizations, a sensitivity analysis was conducted to study the environmental impact of using the faster optimized ALD and the optimized SALD processes in comparison with the base processes. This decrease in energy of the optimized process is significant from the base ALD process as we see a 2.4 times reduction in energy consumption and even slightly less energy than the base SALD process. Despite the lower consumption of the optimized ALD process, when compared to the optimized SALD process it still consumes 65% more energy, SALD consuming just 0.73 MJ of energy per 20 nm of alumina film deposition.




Even though the environmental impact of SALD is overestimated due to precursor usage considerations, its overall environmental footprint remains lower than that of optimized ALD process. This is attributed to the significant difference in energy consumption of both processes.

While the optimized ALD process represents a significant improvement over the base process, as evidenced by the halving of the single score (as shown in Figure S3), it still falls short when compared to the close proximity SALD approach. Figure 8 illustrates that the optimized ALD process yields results that are relatively similar to those of SALD in various impact categories, indicating close competition between the two approaches. Figure S4 contains the extended graph with all 16 impact categories.

It is worth noting that further optimization of the precursor usage for SALD has the potential to yield an even lower environmental impact. As the process evolves the precursor usage as well as the energy consumption decrease leading to an improved process and reduced environmental footprint associated with SALD. However, it is important to note that the decrease will not be linear.[35]

Figure 8 Graph depicting a comparison between SALD, ALD and optimized SALD and ALD with a lower energy input.

## Regionalization

To understand the broader impact of industrialization of ALD and SALD, three region-based scenarios were considered. The first scenario was focused on producing alumina thin films in Europe, while the second and third scenarios were considering France and Taiwan, the world industrial hub for semiconductor production.[36] Each scenario considers the effect of varying the input providers of the process inventory, considering their respective locations and how they affect the results.

As depicted in Figure 9 (and detailed in Figure S5) it has been found that in the

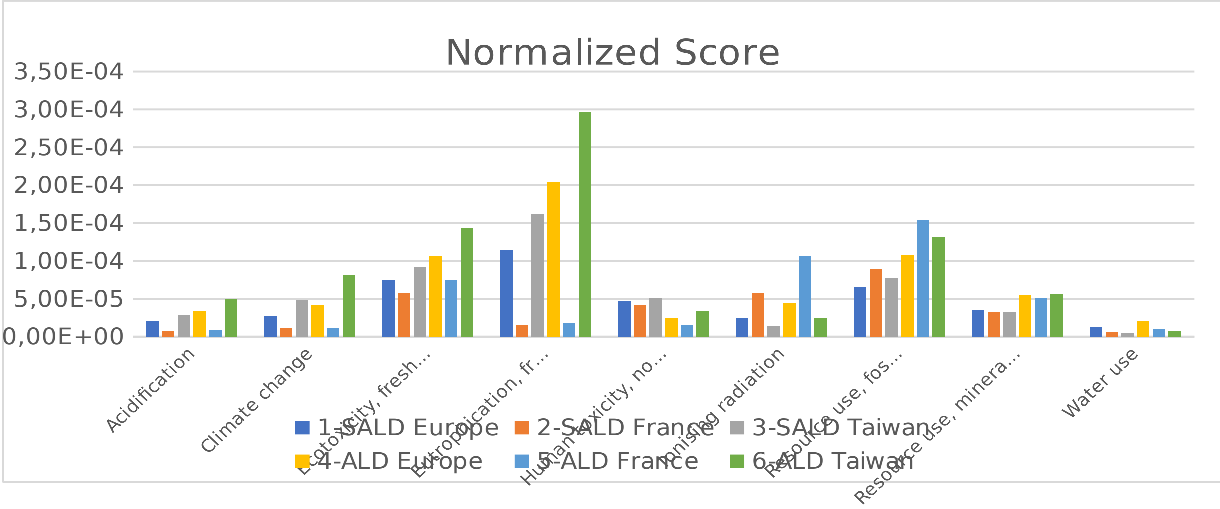



Figure 9 Effect of Regionalization of ALD and SALD to France Europe and Taiwan.

ALD process impact categories can vary significantly, as they are primarily dependent on energy consumption. These variations can be attributed to the differences in the energy mix of the regions where the ALD is performed, e.g., in France, most of the electricity is provided by nuclear plants. When carried out in Taiwan, it has a significantly higher impact on Climate Change as well as Eutrophication is freshwater due to the use of fossil sources.

## Effect of the substrate

In order to gain a deeper understanding of the environmental footprint contribution of thin film deposition on a substrate, we included a silicon wafer in our inventory as the substrate material. This allowed us to compare the impacts of the thin film deposition process with the impact of the substrate production itself. We conducted a comparative analysis for both ALD and SALD, considering scenarios with and without the substrate included in the inventory.

The silicon wafer included in the life cycle inventory was specifically chosen for its relevance to the production of photovoltaic cells. This selection was motivated by the use of trimethylaluminum (TMA) in depositing alumina films as passivation layers in silicon photovoltaic cells.[19] By considering this use case, we aimed to obtain practical insights into the environmental implications of thin film deposition processes in the renewable energy sector.

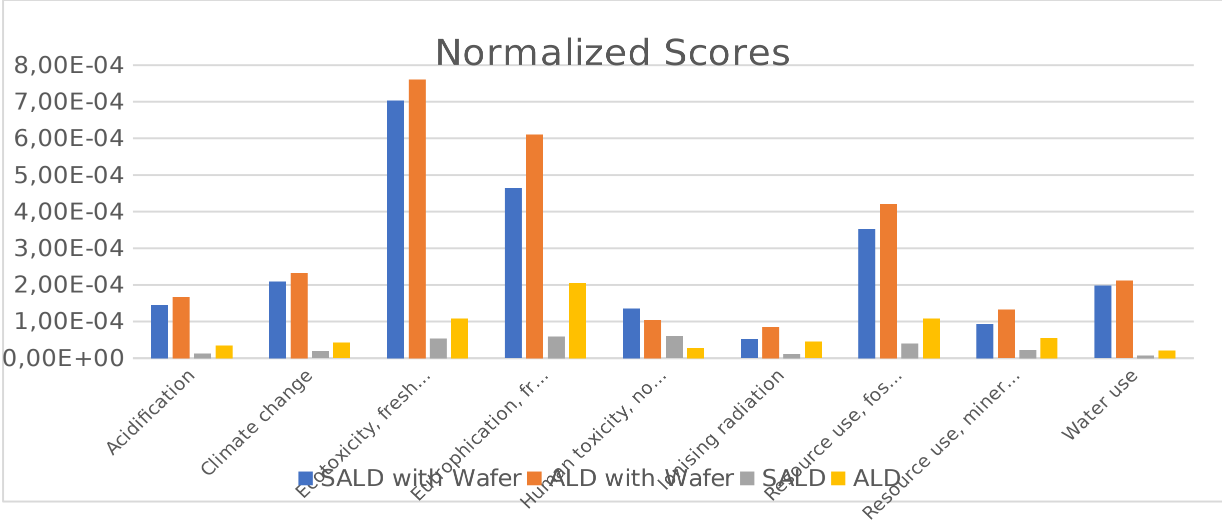
Overall, the lowest environmental footprint is obtained when conducting SALD in the French region, whereas the highest is observed in Taiwan. Interestingly, although the impact of SALD is highest in Taiwan, it has a 20% smaller environmental footprint when compared to ALD in Europe, and a 60% smaller footprint when compared to a similar model for ALD in Taiwan. These findings suggest that SALD has a lower environmental footprint than ALD even when considering regions with higher impacts.

Comparing the scenarios for both ALD and SALD with and without the wafer, it becomes apparent that the wafer plays a significant role in the overall process, as indicated by both the contribution tree (Figure S6 and Figrue S7) and the normalized scores. In the case of SALD, the normalized score for the thin film deposition across multiple impact categories ranges from only 4-25% with majority of the categories under 10%, with the exception of Human toxicity, non-cancer which is 44%, versus the deposition with wafer included.

Similarly, for ALD, the normalized score without the wafer for all impact categories is between 9-53 %, with the majority of the impacts being in 20-25% range when compared with the ALD with wafer included. As shown in Figure 10 and detailed in Figure S8 the difference of adding the wafer to the inventory is immediately visible. These findings highlight the significant influence of the wafer on the overall impact in both deposition processes, underscoring its importance as a contributing factor in environmental assessments.



Figure 10 Effect of inclusion of the footprint of a silicon waf




## Conclusion

In this work, we performed a comparative LCA of the SALD and ALD techniques for deposition of 20 nm thick alumina films using TMA to evaluate them on an ecological level. The findings of this study show that close-proximity SALD has a lower environmental footprint when compared to ALD, which is mainly due to its lower energy consumption. Conversely to the initial concerns, the impact of excessive nitrogen utilization does not contribute to a major percentage of the environmental footprint. However, high use of TMA precursor shows a significant impact in Human toxicity, non-cancer. Overall, even with the significant impact in Human toxicity, non-cancer, SALD performs significantly better than ALD with environmental footprint being approximately 40% of the one obtained for ALD.

It has to be precised that SALD process has room for optimization, which can further reduce precursor and energy consumption by implementing the following:

The energy consumption for SALD was calculated for deposition of one film, which included the machine start up and heating phase as well. This represents the majority of electricity consumption. Once the machine is in operating condition, multiple depositions could be considered, leading to a much lower average energy consumed per deposition when a batch process is considered. In order to have a projection of the results in a more “production-like” setting, a LCA calculation has been performed by considering a 50-deposition batch process. As shown in Figure S9, a significant reduction in the environmental footprint is observed when comparing the 50-deposition batch process to a one-piece flow process with the same number of depositions. This reduction is attributed to the decrease in electricity consumption. Crucially, it was observed when analyzing the relative contribution tree of the batch process that even at lower electricity consumption, nitrogen does not play a significant role in the overall environmental footprint as shown in Figure S10. In contrast, the impact of TMA becomes relatively more pronounced.

In addition, the precursor use in the SALD process has been overestimated, if lowered the environmental impact would be further reduced. Precursor recycling and efficient use can reduce the environmental footprint by reducing waste and improving efficiency.[37]

Simulation studies can optimize the process by calculating the exact amount of precursor required, further reducing the impact.

A sensitivity analysis was also conducted with an optimized ALD process that used 1.2 MJ of energy compared to 2.96 MJ. The results still favor SALD with an overall reduction of 10% of the impacts compared to the optimized ALD cycle. Regionalization of ALD and SALD showed varied impacts in multiple categories due to the energy mix in the grids of the respective countries. However, the total impact of SALD was still lower than the impact of ALD in all three scenarios. The higher nitrogen gas and precursor consumption in SALD also have an economical aspect, but it must be compared with the cost of energy consumed which was not in the scope of this study. A lifecycle costing can be conducted to further expand on this study.

To conclude, assessing the environmental impact of processes such as ALD is important to develop strategies to minimize their environmental impact, but proactive measures should be pursued to identify less detrimental approaches across the wide spectrum of manufacturing processes, as they could yield to substantial benefits in terms of reducing the overall worldwide carbon footprint.

## Author contribution

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

## Supporting Information

Table S1: Inventory of high wear parts of ALD machine ; Table S2: Table Inventory of low wear parts of ALD ; Table S3: Inventory of high wear parts of SALD ; Table S4: Inventory of low wear parts of SALD ; Table S5: Production of Anhydrous Aluminum Chloride ; Table S6: Production of Methyl Aluminum Sesquichloride ; Table S7: Purification of TMA 99.95% ; Table S8: ALD of Alumina Process ; Table S9: Process parameters of alumina preparation ; Figure S1 : Complete Contribution Tree of Alumina Deposition via ALD ; Figure S2: Contribution Tree of SALD via TMA and water with argon as the barrier gas ; Figure S3: Single Score Chart of Sensitivity Analysis ; Figure S4: Normalized scores comparison between SALD, ALD and ALD with a lower energy ; F igure S5: Regionalization Results (normalized scores) ; Figure S6: Complete contribution tree of alumina deposition with wafer via SALD ; Figure S7: Complete Contribution Tree of Alumina Deposition with wafer via ALD ; Figure S8: Effect of inclusion of the footprint of a silicon wafer to ALD and SALD processes shown in normalized scores ; Figure S9: Comparison of environmental footprint of 50 depositions batch process vs one-piece flow of SALD shown in normalized scores ; Figure S10: Contribution Tree of 50 depositions using SALD process.

## Funding sources

The authors would like to thank the French National research agency (ANR) for funding, through the project REACTIVE (ANR-21-CE08-0047, DFG-DE-790-28-1). The RESILEX project (Horizon Europe Innovation Action Grant n°101058583) is also acknowledged.

## Acknowledgements

The authors would like to thank the French National research agency (ANR) for funding, through the project REACTIVE (ANR-21-CE08-0047, DFG-DE-790-28-1). The RESILEX project (Horizon Europe Innovation Action Grant n°101058583) is also acknowledged.

## Abbreviations

ALD, Atomic Layer Deposition; SALD, Spatial Atomic Layer Deposition; LCA, Life Cycle Assessment; LCI, Life Cycle Inventory; TMA, trimethylaluminum; GLO, Global; RER, Europe; FR, France; TW, Taiwan.

## References

1. Ceballos, G., Ehrlich, P. R. & Dirzo, R. Biological annihilation via the ongoing sixth mass extinction signaled by vertebrate population losses and declines. *Proc Natl Acad Sci U S A* **114**, E6089–E6096 (2017). A*ccessed 2023-07-01.*

2. Steffen, W., Broadgate, W., Deutsch, L., Gaffney, O. & Ludwig, C. The trajectory of the anthropocene: The great acceleration. *Anthropocene Review* **2**, 81–98 (2015).

3. Díaz, S. *et al.* Set ambitious goals for biodiversity and sustainability. *Science* **370**, 411–413 (2020).

4. Tilman, D. *et al.* Future threats to biodiversity and pathways to their prevention. *Nature 2017 546:7656* **546**, 73–81 (2017).

5. Charpentier, A. *et al.* Losses and lifetimes of metals in the economy. *Nat Sustain* 717–726 (2022) doi:10.1038/s41893-022-00895-8ï.

6. Battisti, R. & Corrado, A. Evaluation of technical improvements of photovoltaic systems through life cycle assessment methodology. *Energy* **30**, 952–967 (2005).

7. Leskelä, M. & Ritala, M. Atomic layer deposition (ALD): from precursors to thin film structures. *Thin Solid Films* **409**, 138–146 (2002).

8. George, S. M. Atomic layer deposition: An overview. *Chem Rev* **110**, 111–131 (2010).

9. Weber, M. J., Mackus, A. J. M., Verheijen, M. A., Marel, C. Van Der & Kessels, W. M. M. Supported core/shell bimetallic nanoparticles synthesis by atomic layer deposition. *Chemistry of Materials* **24**, 2973–2977 (2012).

10. Zhang, X. H. *et al.* High-performance pentacene field-effect transistors using $Al_2O_3$ gate dielectrics prepared by atomic layer deposition (ALD). *Org Electron* **8**, 718–726 (2007).

11. Kong, X. Y., Yu, D., Huang, Z., Shen, W. & Dai, N. Atomic layer deposition for photovoltaics: applications and prospects. *Light, Energy and the Environment 2015 (2015), paper PTu3B.1* PTu3B.1 (2015) doi:10.1364/PV.2015.PTU3B.1.

12. Weber, M. *et al.* Assessing the Environmental Impact of Atomic Layer Deposition (ALD) Processes and Pathways to Lower It. *ACS Materials Au* (2023) doi:10.1021/acsmaterialsau.3c00002.

13. Muñoz-Rojas, D. & Macmanus-Driscoll, J. Spatial atmospheric atomic layer deposition: a new laboratory and industrial tool for low-cost photovoltaics. *Mater Horiz* **1**, 314–320 (2014).

14. Poodt, P. *et al.* Spatial atomic layer deposition: A route towards further industrialization of atomic layer deposition. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **30**, 010802 (2012).

15. Poodt, P. *et al.* High-Speed Spatial Atomic-Layer Deposition of Aluminum Oxide Layers for Solar Cell Passivation. *Advanced Materials* **22**, 3564–3567 (2010).

16. *United States Patent (19) Suntola et al. 54 METHOD FOR PRODUCING COMPOUND*.

17. Levy, D. H., Nelson, S. F. & Freeman, D. Oxide Electronics by Spatial Atomic Layer Deposition. *J. Display Technol.* **5**, 484–494 (2009).

18. Levy, D. H., Freeman, D., Nelson, S. F., Cowdery-Corvan, P. J. & Irving, L. M. Stable ZnO thin film transistors by fast open air atomic layer deposition. *Appl Phys Lett*

**92**, (2008).

19. Wang, F., Li, T., Zhang, H.-C. & Yuan, C. Y. Exergy Analysis of Atomic Layer Deposition for $Al_2O_3$ Nano-film Preparation. in *Re-engineering Manufacturing for Sustainability* 285–290 (Springer Singapore, 2013). doi:10.1007/978-981-4451-48-2_47.

20. Ma, L., Pan, D., Xie, Y. & Yuan, C. Atomic layer deposition of $Al_2O_3$ process emissions. *RSC Adv* **5**, 12824–12829 (2015).

21. Ma, L., Pan, D., Xie, Y., Wang, F. & Yuan, C. Experimental Study of Process Emissions From Atomic Layer Deposition of $Al_2O_3$ Under Various Temperatures and Purge Time. *J Manuf Sci Eng* **139**, (2017).

22. Wang, E. & Yuan, C. A hybrid life cycle assessment of atomic layer deposition process. *J Clean Prod* **74**, 145–154 (2014).

23. Muñoz-Rojas, D. *et al.* Spatial Atomic Layer Deposition (SALD), an emerging tool for energy materials. Application to new-generation photovoltaic devices and transparent conductive materials. *C R Phys* **18**, 391–400 (2017).

24. Muñoz-Rojas, D. *et al.* Speeding up the unique assets of atomic layer deposition. *Mater Today Chem* **12**, 96–120 (2019).

25. Brusseau, M. L. Sustainable Development and Other Solutions to Pollution and Global Change. *Environmental and Pollution Science* 585–603 (2019) doi:10.1016/B978-0-12-814719-1.00032-X.

26. Curran, M. A. *US EPA Life Cycle Assessment: Principles and Practice*. (2006).

27. Bauer, C. *et al.* Towards a framework for life cycle thinking in the assessment of nanotechnology. *J Clean Prod* **16**, 910–926 (2008).

28. Yuan, C. Y. & Dornfeld, D. Environmental performance characterization of atomic layer deposition. in *IEEE International Symposium on Electronics and the Environment* (2008). doi:10.1109/ISEE.2008.4562943.

29. Viet Huong, N. *et al.* Impact of Precursor Exposure in Spatial Atomic Layer Deposition on Process Efficiency and Film Properties. *Chemical Engineering Journal* **403**, 126234 (2021).

30. Yuan, C. Y. & Dornfeld, D. A. Integrated sustainability analysis of atomic layer deposition for microelectronics manufacturing. *J Manuf Sci Eng* **132**, 0309181–0309187 (2010).

31. Zhou, T. *et al.* Single wafer atomic layer deposition reactor design. in *Advanced Materials Research* vol. 668 767–770 (2013).

32. Pasynkiewicz, S. & Boleslawski, M. Synthesis of trimethylaluminium. Journal of Organometallic Chemistry, **25**, 1, 11 (1970).

33. Smith, B. L. *Development and Life Cycle Assessment of Advanced-Concept III-Development and Life Cycle Assessment of Advanced-Concept III-V Multijunction Photovoltaics***.(2018)** Rochester Institute of Technology. https://scholarworks.rit.edu/theses/9877. A*ccessed 2023-07-01.*

34. Marc-Andree W., Kirana C. et al. International Reference Life Cycle Data System (ILCD) Handbook – General guide for Life Cycle Assessment – Detailed guidance. *Constraints* 417 (2010).

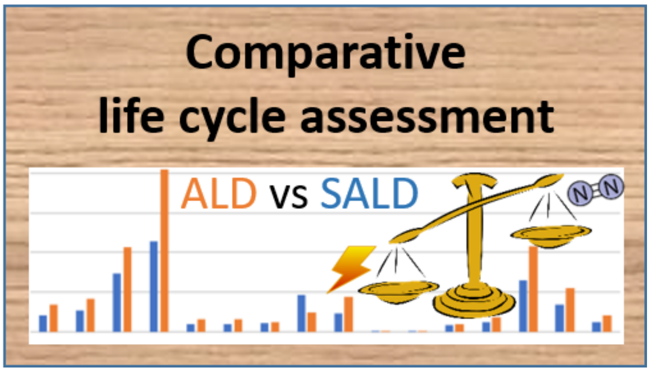
35. Piccinno, F., Hischier, R., Seeger, S. & Som, C. From laboratory to industrial scale: a scale-up framework for chemical processes in life cycle assessment studies. *J Clean Prod* **135**, 1085–1097 (2016).

36. Rasiah, R., Shahrivar, R. B. & Yap, X. S. Institutional support, innovation capabilities and exports: Evidence from the semiconductor industry in Taiwan. *Technol Forecast Soc Change* **109**, 69–75 (2016).

37. Pedersen, H., Barry, S. T. & Sundqvist, J. Green CVD—Toward a sustainable philosophy for thin film deposition by chemical vapor deposition. *Journal of Vacuum Science & Technology A* **39**, 51001 (2021).

For Table of Contents Use Only

TOC graphical image




Synopsis:

Comparative LCA of ALD and SALD helps achieving more sustainable choices by identifying the options with minimal environmental impact.