



HAL
open science

Assessing the Environmental Impact of Atomic Layer Deposition (ALD) Processes and Pathways to Lower It

Matthieu Weber, Nils Boysen, Octavio Graniel, A. Sekkat, Christian Dussarrat, Paulo Wiff, Anjana Devi, David Muñoz-Rojas

► **To cite this version:**

Matthieu Weber, Nils Boysen, Octavio Graniel, A. Sekkat, Christian Dussarrat, et al.. Assessing the Environmental Impact of Atomic Layer Deposition (ALD) Processes and Pathways to Lower It. ACS Materials Au, 2023, 3 (4), pp.274 - 298. 10.1021/acsmaterialsau.3c00002 . hal-04303432

HAL Id: hal-04303432

<https://hal.science/hal-04303432v1>

Submitted on 23 Nov 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

Assessing the Environmental Impact of Atomic Layer Deposition (ALD) Processes and Pathways to Lower It

Matthieu Weber,* Nils Boysen, Octavio Graniel, Abderrahime Sekkat, Christian Dussarrat, Paulo Wiff, Anjana Devi, and David Muñoz-Rojas



Cite This: *ACS Mater. Au* 2023, 3, 274–298



Read Online

ACCESS |



Metrics & More



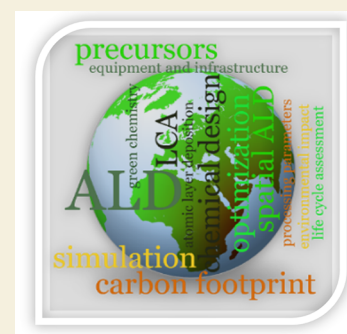
Article Recommendations



Supporting Information

ABSTRACT: Due to concerns on resources depletion, climate change, and overall pollution, the quest toward more sustainable processes is becoming crucial. Atomic layer deposition (ALD) is a versatile technology, allowing for the precise coating of challenging substrates with a nanometer control over thickness. Due to its unique ability to nanoengineer interfaces and surfaces, ALD is widely used in many applications. Although the ALD technique offers the potential to tackle environmental challenges, in particular, considerations regarding the sustainability of renewable energy devices urge for greater efficiency and lower carbon footprint. Indeed, the process itself has currently a consequential impact on the environment, which should ideally be reduced as the technique is implemented in a wider range of products and applications. This paper reviews the studies carried out on the assessment of the environmental impact of ALD and summarizes the main results reported in the literature. Next, the principles of green chemistry are discussed, considering the specificities of the ALD process. This work also suggests future pathways to reduce the ALD environmental impact; in particular, the optimization of the reactor and processing parameters, the use of high throughput processes such as spatial ALD (SALD), and the chemical design of greener precursors are proposed as efficient routes to improve ALD sustainability.

KEYWORDS: atomic layer deposition, green chemistry, spatial ALD, precursors, synthesis



1. INTRODUCTION

According to recent global assessments of living nature, our planet is experiencing a huge and fast decline of biodiversity,¹ and the human alteration of the environment in the last decades has triggered a drastic acceleration of species extinctions.^{1–3} The consumption of most resources continues to rise and sustainability considerations urge greater efficiency and recycling implementation.⁴ The decline of nature and resources has negative and cascading consequences on ecosystems, which are vital to sustain our global civilization. As recent data shows, more ambitious conservation efforts and more aggressive emission reduction actions are needed to reduce threats to biodiversity and to ensure the continuity of our global civilization.^{5–10} As an illustration, Figure S1 shows the CO₂ emissions growth in the last decades and the drastic reduction of carbon emissions required for limiting anthropogenic warming to 1.5 or 2 °C. In parallel to policy makers, academic and industrial researchers should focus on the development of innovative routes enabling pollution reduction while producing energy and goods with more environmentally friendly technologies.^{11,12} In a quest for consistency and role models, researchers should analyze and quantify the environmental impact of their activities and debate on reduction options.^{13,14} The assessment of the environmental impact of a given technology, along with the design of a plan to reduce the

generation and emissions of pollutants, will directly contribute to the required global effort.

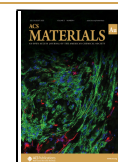
Nanotechnologies and novel nanomaterials are often highlighted as key solutions enabling to treat pollution generated by human activities and enabling a sustainable future in which less energy is consumed and a larger fraction of it is renewable.^{15,16} Atomic layer deposition (ALD) is an important and versatile technology that enables the manufacturing of material layers at the nanoscale. This vapor phase deposition technique enables the synthesis of a wide variety of nanomaterials such as oxides,^{17–19} nitrides,^{20,21} sulfides,^{22,23} and metals,^{24,25} with a subnanometer thickness control.^{26–28} ALD can be used to precisely coat challenging 3D substrates with a conformal and uniform layer down to the angstrom level, a unique capability among film deposition techniques.^{26–29} ALD is therefore very relevant for the design and fabrication of new energy (and other) devices in which the nanoengineering of surfaces and interfaces is key for optimizing their performance. ALD-grown materials can be used to tackle various environmental challenges,³⁰ as they

Received: January 4, 2023

Revised: March 27, 2023

Accepted: March 28, 2023

Published: April 27, 2023



can be applied in niche applications for the improvement of photovoltaics,^{31–33} membranes,^{34,35} batteries, or fuel cell technologies.^{36,37}

The ALD process is based on successive pulses of one or more chemical precursors and co-reactant gases in a vacuum reactor, separated by purge steps. Using these so-called “ALD cycles”, the ideal process enables the surface-limited, self-terminated atomic layer-by-layer growth of nanomaterials. The ALD chemistry is based on volatile precursors, which are typically metal centers surrounded by ligands that contain a wide variety of functional groups, and on co-reactants whose chemistry depends on the nature of the material to be deposited. For example, water or oxygen gas are typically used as co-reactants for the preparation of oxides.^{26–28,38} The schematic illustration of one ALD cycle is given in Figure 1.

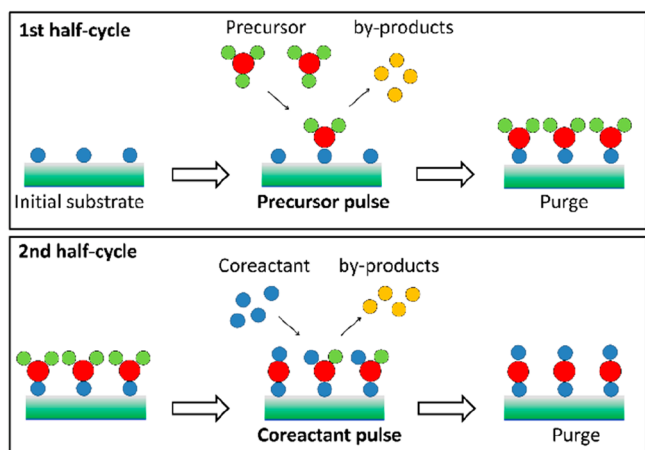


Figure 1. Schematic illustration of one ALD cycle. The first half-cycle consists in exposing the substrate to the precursor, followed by a purge step to remove the excess precursor and the byproduct molecules. Next, in the second half-cycle, the co-reactant is introduced, followed by a final purge step, allowing for the deposition of one material monolayer.

The layer-by-layer type growth of nanomaterials enabled by ALD can be directly used to minimize the incorporation of elements and materials into the manufactured product, and thus the technology could in principle be seen as an intrinsically green chemistry synthetic method, through the “atomically precise reactions” it allows.¹² ALD has been mainly developed for microelectronics applications,³⁹ which rely on an industry with important and growing energy demand and greenhouse gas emissions.^{40,41} Even if some recent work estimating the emissions of processing tools in the semiconductor industry showed that the energy demands for ALD were among the lowest (especially when compared to lithography equipment),^{42,43} the typical chemical precursors used in ALD and the byproducts generated in the reaction are often toxic and present negative environmental impacts. In addition, only a small proportion of the precursors react with the surface of the substrate, while most of the precursors never interact with the substrate in the gas–solid interface and are thus wasted during the process.

The assessment of the environmental impacts associated with ALD technology is important as it can help to detect the main sources of pollution while also finding a path toward their reduction.⁴⁰ Processing at the atomic scale has become increasingly critical for state-of-the-art microelectronic devices, and ALD is still to be implemented for many applications and

products. It appears essential to apply it by considering the environmental impact from an early phase of the manufacturing process. The ALD technology involves several advanced components including the chemical precursors and gases, as well as complex hardware equipment and infrastructures, and the generation of wastes and gaseous emissions should also be considered. Therefore, the assessment of the global environmental impact of ALD is a challenging task.

Several studies have been carried out in the past aiming to analyze the associated material or energy flows, the greenhouse gas (GHG) emissions, or to carry out the life cycle assessment (LCA) of a given ALD process.^{44–49} However, the studies did not consider the same parameters, and the models used to assess the impacts of the processes differ from each other in their basic modeling principles, scopes, and outcomes. The differences are often hard to reconcile, and the different assessment models and selection of boundaries of the components considered make it difficult to compare the data resulting from these studies. Herein, we present a global overview and summarize the main results gathered in the different studies reported in the literature.

From this analysis, in the second part, we attempt to provide ways to reduce the environmental impact associated with the industrial utilization of ALD. After depicting the potential and beneficial use of the principles of green chemistry to ALD, three main mitigation routes are identified: First, the optimization of the processing parameters, which can minimize the environmental impact through computational optimization for example. Second, to favor high throughput ALD processes such as spatial ALD (SALD), as they offer the possibility to reduce the time required to prepare the layers, among other assets. Third, to optimize the precursor chemistry, because it defines the number of initial synthetic steps, the deposition temperature, the toxicity of byproducts, and the process duration and efficiency. Finally, an industrial point of view will be given, as ALD is becoming a key component also in high-performance energy-related applications playing a significant role in the mitigation of greenhouse gas emissions. Ultimately, this work will hopefully lead to the development of more sustainable ALD processes.

2. OVERVIEW AND DISCUSSION

2.1. Definitions

The assessment of the environmental impacts of any product, or technology, can be based on different methodologies, data inputs, and assumptions. For example, material and energy analysis can be carried out as first approximations. This section aims to give some basics to understand the two mostly used assessments: Life Cycle Assessment (LCA) and greenhouse gas (GHG) emissions analysis, more commonly called carbon footprint. LCA considers a large range of environmental impact categories (e.g., acidification, ozone depletion, ecotoxicity, etc.), whereas carbon footprint only considers the GHG caused by and/or emitted from the system.

LCA is an internationally standardized methodology (ISO 14040),⁵⁰ addressing the potential environmental impacts such as the use of resources and the environmental consequences of releases throughout a product’s “life cycle”, from the acquisition of raw materials through production, use, end-of-life treatment, eventual recycling, and final disposal (i.e., “cradle-to-gate” or “cradle-to-grave”, see Figure 2).

The scope of an LCA, including the system boundary and level of detail, depends on the subject and the intended use of the study.⁵⁰ The process-based LCA is the mostly used

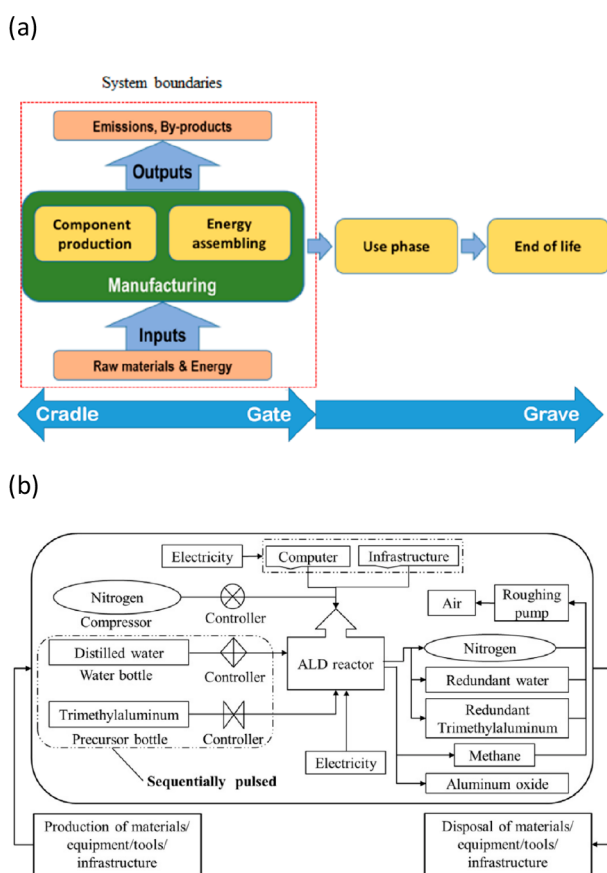


Figure 2. (a) LCA boundaries cradle-to-gate/grave. Reprinted from ref 51 with permission under an open access Creative Commons CC BY license. Copyright 2020 MDPI. (b) LCA boundaries (cradle-to-grave) of an ALD process of alumina, based on trimethylaluminum (TMA) and water. Reprinted with permission from ref 45. Copyright 2014 Elsevier.

methodology for measuring the life cycle environmental burden of products and processes. This approach aims to break down the whole life cycle of a product into defined and operable functional unit processes with quantifiable inputs (e.g., energy, resources, etc.) and outputs (e.g., emissions, wastes, etc.).⁵²

The term “carbon footprint” is commonly used to describe the concept of relating a certain amount of GHG emissions to a certain activity, product, or technology. There are numerous definitions for a carbon footprint, all attempting to relate to a certain suite of GHG emissions.^{53,54} The inclusion of CO₂ and CH₄ often forms the basis of the definition of a carbon footprint, but considering more GHGs is obviously more accurate. For example, the Kyoto Protocol requires the reporting of six gases or family of gases: CO₂, CH₄, N₂O, hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and SF₆, whereas the European Emissions Trading Scheme (EUETS) only requires the reporting of CO₂ emissions.^{53–55} Thus, the total GHG emissions consider a wide family of gases, usually expressed in “equivalent of CO₂” or simply “carbon footprint”.

2.2. Overview of Environmental Assessments Related to ALD Processes

Several studies have been carried out to address the environmental aspects and potential environmental impacts of ALD processes. In particular, Yuan’s group at the University of Wisconsin Milwaukee (USA) has performed a considerable

amount of work in this upcoming field by carrying out extensive LCA and other environmental assessments for ALD of alumina.^{44–49} Just like ALD processes, CVD (chemical vapor deposition) processes make use of chemical reactions of gaseous reactants in a vacuum chamber to obtain a coating with defined properties at the surface of a substrate. The main difference between the processes is that in ALD the precursors are injected separately and the process is performed at a lower temperature, allowing for a slower but desired layer-by-layer growth. The ambitions to develop CVD processes with lower carbon footprints are thus also relevant for ALD processes. Considering this common goal, the overview presented below will also include some relevant studies focusing on the environmental assessments of specific CVD processes. Table 1 summarizes the studies carried out in the literature for the environmental assessment of ALD and relevant CVD processes.

The studies presented in Table 1 provide data to analyze and understand the potential environmental impacts of ALD, and the next logical step is to find routes to limit and reduce them as much as possible.

The team of Yuan et al. has pioneered research toward more environmentally sustainable ALD manufacturing. They first intended to analyze and prevent pollution by considering the energy flows and material utilization efficiency of the ALD technology. Their results indicated that the material use efficiency was always below 20% and that the energy inputs for ALD process operations were as high as 1.2×10^6 J to deposit a 20 nm Al₂O₃ film on a 4-in. Si wafer (functional unit used). Using energy flows analysis, the authors have also shown that the ALD process energy consumption was mainly determined by the ALD cycle time rather than the process temperature for this process (200 °C).^{44,63} The energy flows diagram used for this study is illustrated in Figure 3.

According to Yuan and Dornfeld, when assessing ALD of alumina at 200 °C, the energy consumption of the process is mainly affected by the operating temperature (40%) and by the pumping system of the ALD reactor (29%), whereas the electronics, compressed air, and computer represented energy demands of 15, 8, and 6%, respectively.⁶⁴ In the work of Wang and Yuan, the authors carried out a thorough LCA for the ALD of alumina, considering a functional unit as the deposition of 1 g Al₂O₃ on a 4-in. silicon wafer (cradle-to-grave boundaries). The LCA results obtained showed that the process’s largest impact was in the category of fossil fuels when compared to the other life cycle impacts such as water pollution or air acidification.⁴⁵ The authors reported that the largest carbon emission sources were from the infrastructure, equipment, and tools supporting the ALD operations. The cycle time is therefore important, as it is directly related to the power consumption of the different pieces of equipment. They concluded the work by proposing to improve the efficiency of the deposition and increasing the batch size to limit the pollution generated.⁴⁵

By considering the deposition of a ZnO film on a 1 cm² surface as a functional unit, Zieminska-Stolarska et al. confirmed that the main impact of ALD is related to electricity, whereas the impact produced by the material is of minor importance.⁵⁸ In their recent study, focusing on the minimization of the environmental impact of transparent conductive oxide layer (TCO) deposition processes, they found that for the films deposited by CVD and ALD, the main impact is related to energy or nitrogen consumption, whereas for PVD (physical vapor deposition) to energy and raw material of TCO.⁵⁸

Table 1. Studies Focusing on the Environmental Assessment of ALD and Relevant CVD Processes

process studied	methodology	assessment boundaries	main findings of the study	ref
ALD of Al ₂ O ₃	energy analysis	precursor utilization, methane emissions, and nanowaste generations	energy flow analysis demonstrates that the ALD process energy consumption is mainly determined by the ALD cycle time rather than the process temperature	44
ALD of Al ₂ O ₃	exergy analysis	energies associated with material, heat, and work flow	utilization of energy is extremely low in ALD Al ₂ O ₃ process	49
ALD of Al ₂ O ₃	LCA	cradle-to-grave	ALD produces the highest environmental impact in the category of fossil fuel use; the impacts associated with the auxiliary infrastructure, equipment, and tools for ALD operation are intensive mainly due to the slow ALD cycling process	45
ALD of Al ₂ O ₃	gas and aerosol emissions analysis	process emissions at the exhaust	CH ₄ and C ₂ H ₆ generated, emissions of ultrafine particles (diameter <100 nm) reduce with longer purging time	46
ALD of Al ₂ O ₃	DFT calculations on process wastes and methane emissions	chemical reaction of the process: 2Al(CH ₃) ₃ + 3H ₂ O → Al ₂ O ₃ + 6CH ₄	high material waste (up to 60% of precursors); waste generated and methane emissions increase with pulse time; the moderate temperature of the chamber (200 °C) leads to less waste	47
ALD of Al ₂ O ₃	gas and nanoparticles emissions analysis	process emissions at the exhaust	93% of TMA is discarded as waste; nanoparticles generated are harmful to humans; emissions decrease with purge time	48
ALD of Al ₂ O ₃	computational analysis	10-wafer ALD processing system emissions	Al ₂ O ₃ nanowastes generated from the ALD production system are grave concerns	56
ALD of Zn(O ₂ S) to replace CdS as buffer layer in CIGS photovoltaic cells	LCA	front end of a CIGS module	ALD has 19–26 times lower environmental impacts than chemical bath deposition (CBD) of CdS for all categories but metal depletion (2.65 higher)	57
ALD of ZnO	LCA	gate-to-gate	majority of the impact is related to electricity consumption, and material usage is of minor importance	58
Plasma-enhanced CVD (PECVD) of amorphous silicon (a-Si:H)/nc-SiO _x /SiN _x and ALD of Al ₂ O ₃ for silicon heterojunction solar cells	LCA	complete solar PV installation	new SHJ designs based on PECVD and ALD have a better environmental performance compared to the reference SHJ design; PECVD requires more energy for thin film deposition than ALD	59
low-pressure CVD (LPCVD) of TiO ₂	material and energy consumptions analysis	material consumption: Ti(OC ₂ H ₅) ₄ (g) + 2H ₂ O(g) → TiO ₂ (s) + 4C ₂ H ₅ OH(g) Energy consumption: Energy for heating the reactor, energy for pumping, energy absorbed by the input gases, and energy of the chemical reaction	precursor and energy utilization efficiencies < 1%	60
plasma-assisted CVD (PA-CVD) of SiO _x	LCA	1 m ² surface protected by a layer with a thickness of 1 μm	PA-CVD involves high gross energy requirement (GER) and global warming potential (GWP) values	61
CVD of TiCN-TiN-Al ₂ O ₃	LCA	cradle-to-gate	thin film deposition process accounts for less than 10% of the total manufacturing energy of inserts for cutting tools; CVD is more energy-demanding than PVD	62

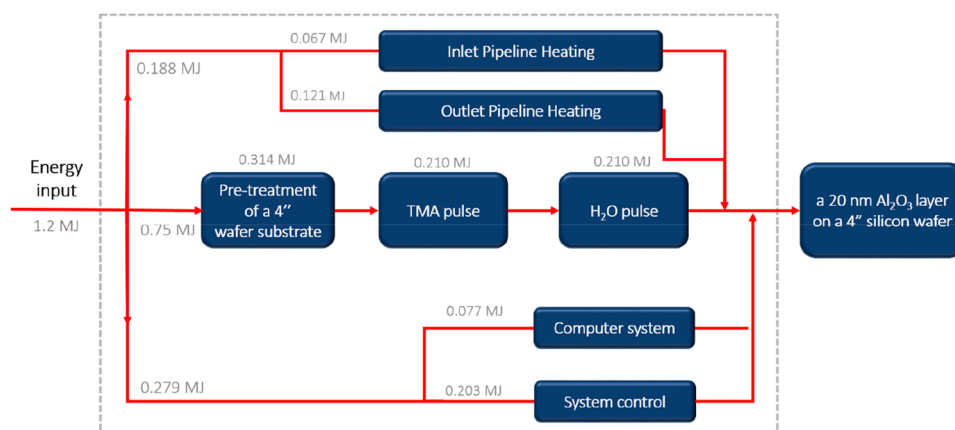


Figure 3. Energy flow diagram of a 200 cycles ALD process at 200 °C. The data was extracted from ref 44.

Focusing solely on the emissions of the ALD Al₂O₃ process (considering total emissions after ALD 25 cycles), Ma et al. reported the generation of CH₄ and C₂H₆ GHG, as well as the undesired production of ultrafine particles (diameter <100 nm) that poses risks to the users. The number of particles emitted from the ALD reduced with a longer purging time.⁴⁶ As the purge time modifies the time of reaction as well as the degree of gas phase mixing, it greatly influences ALD particle emissions. In addition, after studying CH₄ and nanoparticles emissions from ALD Al₂O₃ reactions they found that $(2-9) \times 10^4$ nanoparticles in the range of 10 and 100 nm are generated after just one ALD cycle.⁵⁶ The amount of ALD precursor waste generated relates to the process pulse time, carrier gas flow rate, temperature, and the surface area ratio between the substrates and the ALD reactor's internal surface. Thus, the optimization of the reactor design and processing parameters is highly recommended.

When assessing the impact of CVD of TiO₂, Wang et al. studied the material and energy consumption of the process. Their study revealed that the material utilization efficiency is very low (less than 1%) and increases with higher temperature and lower pressure, whereas the energy analysis showed that the energy efficiency was extremely low (less than 0.1%) but increased with decreasing temperature and increasing pressure. In this work, the authors calculated this energy efficiency by dividing the “useful energy” by the “total input energy”. The useful energy is described as the energy absorbed by the input gases and the chemical reaction energy, and the total input energy depicts the energy used for reactor heating and pumping. Concerning this specific TiO₂ CVD process, an optimal reaction condition was obtained at a temperature of 350 °C and a pressure of 500 Pa.⁶⁰ In a study conducted to evaluate PVD and CVD coating systems in metal cutting processes, one of the key findings was that the investigated PVD process is considerably less consuming in respect to gases and electrical energy as compared to the CVD process.⁶²

The growing development of low-carbon energy technologies required comparative studies between various processes, to identify eco-design opportunities.⁶⁵ For example, the rapid expansion of solar photovoltaic (PV) systems has fueled a strong interest in ALD and CVD thin film technologies to help reduce the overall environmental impact involved in their manufacturing. Toward that goal, Stamford and Azapagic⁵⁷ compared the environmental footprint of replacing the cadmium sulfide (CdS) buffer layer prepared by CBD (chemical bath deposition) with zinc oxysulfide (Zn(O,S)) deposited by ALD in copper indium

gallium-selenide (CIGS) PV modules. The study shows that ALD of Zn(O,S) has between 19 and 26 times lower environmental impacts (e.g., biogenic carbon, fine particulate matter formation, fossil fuel depletion) than CBD of CdS. However, the use of stainless steel for building ALD equipment contributes to a 2.65-factor increase in the metal depletion category when compared to CBD. Still, when considering the whole life cycle, the higher metal depletion value of ALD compared to CBD becomes less important as the overall impact increases by only 0.01%. Moreover, due to its toxicity, cadmium has been restricted in many industrial applications and thus, its replacement remains of utmost importance. Similarly, Louwen et al. performed an LCA on four different silicon heterojunction (SHJ) PV cell designs to provide a fabrication process with a low environmental footprint while increasing cell efficiency.⁵⁹ Among the designs, the one based on Al₂O₃ by ALD (and ZnO by sputtering) had a lower footprint when compared with the reference and multifunctional emitter designs that are mostly based on plasma-enhanced CVD (PECVD). This is mainly due to the lower energy consumption of ALD equipment when compared to a PECVD one (almost 90% lower).⁵⁹ Finally, the study also reported the fact that the majority of the environmental impacts of such PV systems results from the silicon wafer and its feedstock (about 38–40%).

When comparing the different growth techniques based on the studies reported in Table 1, it can be deduced that the low energy and material utilization efficiency of ALD processes are directly related to the environmental impact of the technique. The CBD and PVD processes are overall less demanding in terms of energy and resources than CVD/ALD-based routes, but the latter techniques present unique advantages when considering the thin films prepared. Figure 4 presents a comparison between different growth techniques, in terms of material and energy utilization efficiency, electricity and nitrogen demand, process duration, and uniformity and conformality of the deposits. It is however important to note that this comparison (and the environmental impact of any manufacturing process) is highly dependent on the specific details of the processes, tools, and materials involved.

To sum up, as seen in Table 1, so far, only a few environmental impact studies have been undertaken. Comparative analysis of alternatives for other materials besides Al₂O₃ has not been performed, as reflected in the low number of reports found in the literature. This shortage of work can be partially explained by factors such as the slow adoption of ALD in industrial processes

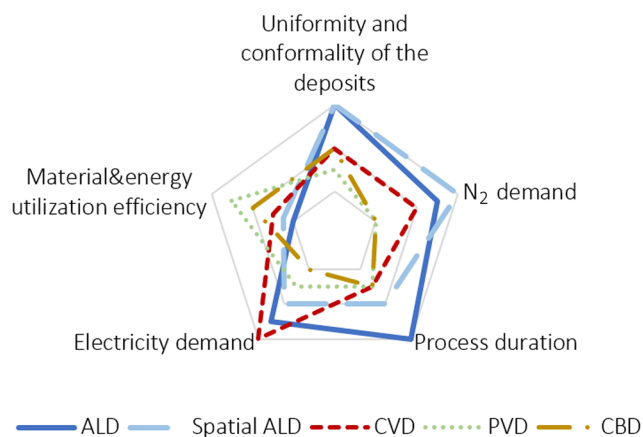


Figure 4. Comparison between different growth techniques, in terms of material and energy utilization efficiency, electricity and nitrogen demand, process duration, and uniformity and conformance of the deposits.

(besides the electronics industry) and inherent problems of LCA studies (e.g., the overall complexity of the systems, lack of available data, different calculation techniques, availability of impact coefficients).⁶⁶

The studies summarized demonstrate that ALD produces the highest environmental impact in the category of fossil fuels use (mainly related to energy demand) and that the impacts mainly originate from the duration, the temperature, and the materials utilized (and wasted) during the ALD process and the associated emissions. When extending the scope considering the materials used in ALD, one should not forget the substrates, which can represent a large carbon footprint (e.g., silicon wafers).⁵⁹ The equipment itself and the associated infrastructure also are at the origin of many emissions, as they require a considerable amount of energy and materials for their production and use. However, an ALD equipment is made of several advanced components, and the number of emissions and overall pollution generated for each component is subject to large error margins and is highly usage and system-dependent. Ideally, the equipment and associated infrastructure should be as simple and light as possible, and the process energy requirements, duration, material wastes and emissions must be limited while maintaining a high deposition rate of high-quality materials. Figure 5 sums up the different impacts associated with the ALD processes, equipment, and infrastructure (“xTime” represents the duration

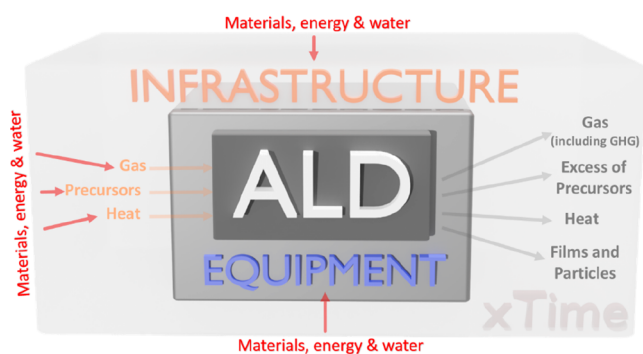


Figure 5. Schematic representation of the environmental impacts associated with ALD processes.

of a given process, for which all the materials and energy are necessary).

Expanding the scope of ALD to other fast-growing and relevant markets like PV and other energy-related applications should boost the interest in performing LCA and environmental assessments of other materials prepared by ALD than alumina, and to find paths to limit their carbon footprint as much as possible. Allowing for the design of products and processes that reduce or eliminate the use and generation of hazardous substances, the principles of green chemistry can be employed as guidelines to help us find and define ALD processes with lower environmental impact.

2.3. Principles of Green Chemistry Applied to ALD

Green chemistry aims to design products and processes that minimize or even eliminate the use and generation of hazardous substances. Taking the 12 principles of green chemistry¹² (Figure 6) and relating them to the specificities and the main environmental burdens of ALD processes, several paths can be defined to reduce the associated cradle-to-grave impacts.

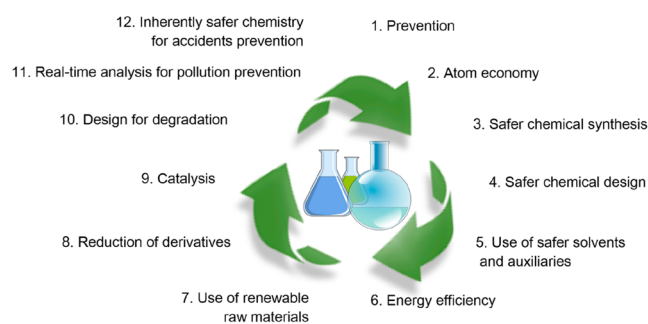


Figure 6. Schematic representation of the 12 principles of green chemistry, as described by Anastas and Eghbali.^{12,67}

(1) The Prevention Principle. The first principle of green chemistry describes the fact that preventing waste is better than treating it after it is created. The overview presented in the previous part has shown that, even if better than for industrial CVD processes,⁶⁸ ALD processes present a very high precursor material and energy waste, and generate the emission of GHG and nanoparticles. In addition, the bulk gases (e.g., N₂) used in the processes are injected through the reactor without reacting, generating huge waste. Even if nitrogen release in the atmosphere poses no environmental concern, its initial production using air separation units involves the generation of CO₂ emissions, and avoiding N₂ waste is hence desired.

Thus, better optimization of the process could help to reduce the amount of waste. The efforts on optimization should be carried out to limit the use of precursors and the duration of the process as much as possible, to minimize the environmental impact. These efforts could aim to decrease the consumption of precursors and co-reactant gases, as well as compressed air, which is another energy consumer in ALD, as it is used to control the valves for pulsing, purging, and pumping. In fact, the generation of compressed air also requires important energy inputs.⁶⁹

In addition, the development of more “atom efficient” ALD chemistries would also enable the reduction of waste. The precursors could also be designed to be “reused”, in the sense that their recapture and recycling could be achieved, either by recycling unreacted precursor molecules or by recycling atoms, e.g., the metal atom in the precursor.^{40,70} It is important to note

that the reuse of the core metals of precursors could be environmentally beneficial and also economically relevant, depending on the elements considered. In particular, Pd could be recycled from hydrogen membranes, Pt from fuel cells, or Co from Li-battery cathodes.

(2) The Atom Economy. The second principle is the so-called “atom economy”, which aims to maximize the incorporation of all materials used in the process into the final product. The atomic layer-by-layer growth enabled by ALD is in this way very powerful, as atomically precise functional layers can be prepared, maximizing the use of the materials in the final devices. However, the synthesis of the precursors often requires several steps, and the amount of precursor and gases wasted during the process is considerable, as a lot of atoms (especially from ligands) are not incorporated in the films.

(3) Less Hazardous Chemical Synthesis. Synthetic routes such as ALD should be designed to use and generate substances that possess little or no toxicity to human health or the environment. As ALD precursors need to be very reactive, the synthetic approaches themselves might be intrinsically dangerous to conduct not only due to the high reactivity (e.g., pyrophoricity) of the precursors but also due to the high reactivity of the employed reagents. Moreover, most solvents used during the synthesis of precursors need to be chemically inert. Solvents such as THF, hexane, and diethyl ether are toxic but might be hard to replace with less hazardous solvents.

(4) Designing Safer Chemicals. This principle is intrinsically related to the third point and promotes the need to develop less toxic precursors. However, minimizing the toxicity of ALD precursors, while maintaining their chemical function and efficiency at low temperatures is highly challenging. Highly reactive chemicals are used because they are very effective in affecting molecular transformations. However, they are very often also more toxic, as they are likely to react with (unintended) biological targets, resulting in environmental burdens. Thus, more fundamental research should be carried out to develop alternative precursors and ALD chemistries, as will be described in more details in section 2.6.

(5) Safer Solvents and Auxiliaries. The fifth principle states that auxiliary substances such as solvents should be made unnecessary whenever applicable, and innocuous when used. In conventional ALD, the process does not make use of any solvent. In some specific processes, the precursors are introduced in the chamber using direct injection systems (DLI), that make use of (little) amounts of solvents.⁷¹ Liquid ALD also uses (more) solvents to bring the precursors to the substrate surfaces.⁷² However, these two particular ALD techniques present other advantages, such as the broadening of the potential precursors that can be used, and the materials that can be deposited. When extending the scope boundaries, the solvents used in the synthesis of the precursor itself should also be considered. Most precursor syntheses rely on salt metathesis reactions which are typically carried out in some moderately polar, nonaqueous solvent, and can require several reaction and purification steps.^{73,74} Thus, efforts should also be made to limit the use of solvents and increase the overall efficiency of the synthetic procedure as specified in section 2.6.

(6) Design for Energy Efficiency. As the massive use of current energy sources presents a high environmental impact, the use of mild ALD process conditions, such as low temperature and ambient pressure, is preferable. When a considerable thermal budget is required, the ALD process should be properly optimized to limit the cycle duration at elevated temperatures,

and the reactor should have proper thermal isolation to reduce the energy demand. The energy required to reach the adequate temperature (including heat-up and cool-down steps) generates other impacts as it may require the use of cooling systems and other subreactor level equipment. Eventually, the excess heat generated could be harvested and reused to heat other parts of the system such as pipes or some other tools, or even to be reemployed in the building heating system.

Developing an ALD chemistry allowing for low-temperature deposition of materials is thus very attractive to limit the energy required. For example, the use of plasmas as co-reactants enables lower deposition temperatures, and metals, as well as oxides, have been deposited by ALD at room temperature.^{75–78} Fast ALD at ambient pressure can also be achieved, for example by using high throughput approaches such as Spatial ALD (SALD). This alternative to conventional ALD, in which the precursors are continuously injected in different areas, allows deposition rates up to several orders of magnitude faster than conventional ALD and can easily be performed at atmospheric pressure, removing the need for vacuum-related equipment.^{79–81} Other approaches to enhance the speed of ALD processing such as batch ALD and reactor/process engineering (e.g., parallel precursor wave technology⁸²) can also contribute to limiting the environmental impact of the technique.⁸¹

(7) Use of Renewable Feedstocks. This principle states that raw materials and feedstock should be renewable rather than depleting. In ALD, different routes could be undertaken to achieve more sustainable use of feedstocks. First, the precursors could be synthesized using biosourced solvents and even reactants, for example, by making use of chelants from biomass.^{83,84} Bulk gases used either as carrier precursors or as co-reactants (e.g., Ar, N₂, and O₂) should be easily available and could be supplied in different optimized ways according to the installation size. Thus, lab installations would prefer the use of high-pressure cylinders because transport cost tends to be small compared to the total operational cost at the facility. Whereas at industrial and semi-industrial scales, the use of onsite production by using air separation units (ASU), cryogenic storages tanks, and evaporators is preferable, to secure a continuous supply, high purity, and the minimization of the logistics and pollution associated with the transport activities. As shown in Figure 7, the economic feasibility of onsite installations strongly depends on the cost and easy access to energy and more recently on its carbon footprint calculated from its direct emissions (scope 1) energy-related emissions (scope 2) and indirect up/downstream stream (scope 3).⁸⁵

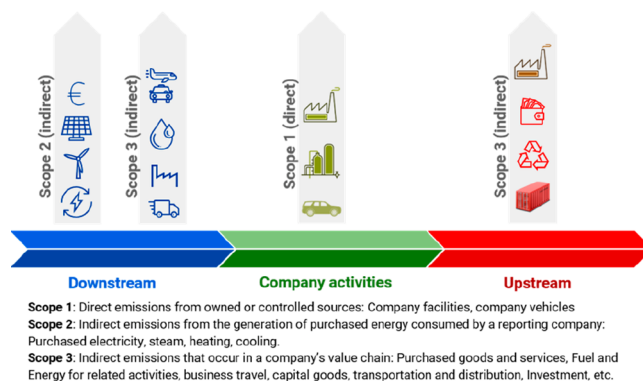


Figure 7. Schematic representation of the emissions associated with the different scopes across the value chain.

Finally, renewable energy (e.g., solar, hydroelectric, wind power) should preferably be used to its maximum extent to produce all the energy required for the ALD process, from the precursor synthesis to the reactor substrate heater and related equipment (e.g., vacuum pump, compressed air, computer).

(8) Reduce Derivatives. This principle of green chemistry aims to decrease the use of derivatives and protecting groups in the synthesis of molecules, such as ALD precursors in our case. The synthesis of the desired precursor molecules and in particular the synthesis of organic ligands surrounding the metal center atom should be carried out using a minimal number of steps and make use of green synthesis methods when possible. For example, these novel green chemistry routes include physical methods such as ultrasound-assisted and hydrothermal processes, microwave heating, or ball milling, often in combination with biosourced precursors, as well as solventless and biosynthesis techniques. Applying more exotic biological routes making use for example of bacteria or algae also perfectly fit to the green chemistry synthesis.^{83,84,86} Overall, the transition from fossil-based chemicals manufacturing to more sustainable biomass-based production is desired and should be more investigated.⁸⁶ Therefore, these novel synthesis techniques could be explored for ALD purposes.

(9) Catalysis. The ninth principle recommends the use of catalysis. Catalysis can be applied to ALD, by making the precursor synthesis more efficient and less energy-demanding using catalytic transformations within the synthetic approaches to produce ligands (see section 2.6). In fact, catalytic reagents and catalysts are superior to stoichiometric reagents and enable the reaction to take place at lower energy. Furthermore, when applicable, the ALD process can also be carried out on a catalytic substrate, which typically allows for lower deposition temperatures (at least for the first cycles). In addition, the use of catalytic surfaces also permits to achieve area selective deposition (ASD), for example for the preparation of precisely tuned core/shell nanoparticles or layers at defined areas.^{87–90} ASD can also limit the overall emissions of a manufacturing process, as it could limit the use of lithography and etching steps in certain cases.⁸⁷

(10) Design for Degradation. The tenth principle advises designing chemical products so that at the end of their function they break down into innocuous products and do not persist in the environment. Again, it is in the ALD precursor synthesis method itself that this principle could be applied. Understanding the decomposition pathways and anticipated byproducts for a precursor in a particular process would lead to an effective design strategy. The synthesis should be carried out to reach the formation of environmentally friendly precursor molecules, but also the byproducts and other decomposition-created molecules should be innocuous.

(11) Real-Time Analysis for Pollution Prevention. Analytical *in situ* methods need to be further developed to permit real-time, in-process monitoring of the formation of potentially hazardous substances. In ALD, the processes are often monitored to control the growth of the layers prepared, for example by using *in situ* spectroscopic ellipsometry^{91,92} or quartz microbalance (QCM).⁹³ However, more efforts should be carried out to develop the *in situ* monitoring of polluting emissions generated by the process,^{46,48} and to detect and limit the pollutants or enhance their capture or destruction.

(12) Inherently Safer Chemistry for Accident Prevention. The final principle of green chemistry is known as the “safety” principle. The control of recognized hazards should be

mastered to achieve an acceptable level of risk. In ALD, the reactive precursors are often toxic or pyrophoric, thus leading to a certain level of risk. This risk could be reduced by developing nonpyrophoric precursors, and alternatives have been proposed for this purpose, e.g., to replace the pyrophoric but widely used TMA.^{94,95} For example, Mai et al. developed a nonpyrophoric intramolecular stabilized aluminum precursor class, that permitted the low-temperature ALD of alumina, while limiting the risks of fire or explosions.⁹⁴ More details on this topic are given in section 2.6.

From the studies carried out on the environmental impacts assessments (summarized in Table 1) and the green principles applied to ALD described above, the key applicable routes to reach ALD processes with lower environmental impact that can be deduced are the:

- Process optimization
- High throughput processes, e.g., spatial ALD
- Chemical design of greener precursors

2.4. Process Optimization

Optimizing the ALD reactor design and the processing parameters can enable minimizing the precursors' consumption and the byproducts released, and also drastically decrease the ALD cycle duration and thermal budget.⁸¹ These optimizations can thus limit the pollution generated. To achieve this, *in situ* process monitoring and modeling are of great help.

2.4.1. Reactor and Infrastructure. There are a plethora of different reactor designs and geometries that can be used to prepare ALD films, depending on the substrates to be coated. For example, the geometries can be adapted to coat a single or a large number of wafers,⁹⁶ particles,⁹⁷ or even astronomical mirrors.⁹⁸ An integrated optimal ALD chamber design considers many geometry optimizations, such as the inlet tubes, the feed nozzles and showerhead, and of course the main chamber. The dimensions and the geometry of the reactor will have a profound impact on the gas-phase dynamics and surface reaction kinetics, which are critical for the ALD process optimization. In addition, as the energy consumption of an ALD process is mainly driven by the operating temperature, optimized thermal management of the heated chamber and the heating elements is key to saving electricity and reducing the carbon footprint. Computational fluid dynamics (CFD) and Monte Carlo (MC) simulations can be used to model and design optimized ALD reactors. The simulated models can provide precious insights and understanding into the flow physics related to the transport of the precursor species from the inlets, through wafer feed nozzles, into the wafer regions, and finally through the outlet.⁹⁹ The CFD modeling can thus advantageously be applied to the optimization of the chamber and overall reactor design. For example, Zhang et al. recently designed an optimal configuration of reactor geometry which enabled a considerable reduction of the half-cycle time.^{100,101} Then, for specific ALD reactor geometries, dynamic modeling, and computational simulations can also be of great assistance in the determination of processing parameters.¹⁰² Based on an analysis of the limiting factors of conventional cross-flow reactors, parallel precursor wave technology systems have been developed as well, enabling to minimize precursor consumption and reactor chamber dimensions.¹⁰¹ Considering the infrastructure, the example of semiconductor foundries (fabs) is worth noting. The rise of energy costs and the quest to achieve lower GHG emissions set by the World Semiconductor Council,¹⁰³ have led the main fabs to reduce their total energy consumption. At each technology

node, new processing steps (including ALD) are added, and improvements and optimizations are carried out to infrastructure and facility equipment, such as the water chillers or exhaust pumps, allowing for overall reduced energy consumption. Therefore, in parallel to the improvement of performance, the specific energy consumption per area of silicon consumed was roughly the same in 2005 as in 1995, approximately 1.5 kWh/cm².^{104–106}

2.4.2. In Situ Process Monitoring. Establishing the best processing parameters, such as the set of timings for the reactants pulses and purge steps to reach the saturation in a minimum amount of time, at a minimal temperature (within the temperature window), along with the appropriate pressures and flows is a challenging and time-consuming task. Thus, *in situ* measurement techniques and physics-based models have been developed by different research groups to optimize the parameters of various ALD processes. An expanding number of tools can be applied for the *in situ* monitoring of ALD processes, providing some insights into these processes and the reaction mechanisms taking place.¹⁰⁷ For example, QCM and ellipsometry are often used to measure the thickness of the growing films.^{92,93} A QCM device measures very small changes in mass, whereas ellipsometry measures a change in the optical properties of the growing films. When these techniques are applied *in situ*, they enable to directly relate the processing parameters and the resulting film growth per cycle. The self-limiting nature of the surface reactions can also be tested and saturation curves can easily be established when using these *in situ* thickness measurements. An *in situ* equipment such as ellipsometry can provide key data of the initial steps and further cycles toward optimization of the process, as it has been shown for the preparation of tin sulfides, for example.¹⁰⁸ Other instruments enable to study the ALD reaction mechanisms. For example, quadrupole mass spectrometer (QMS) and infrared spectroscopy (IR) measurements can be used to determine the composition of a gas, and gain insights on the gas phase reaction products generated in the ALD reactor.^{97,109} These *in situ* tools enable to probe the reaction products generated during an ALD process, and these gas phase species may contain relevant pollutants to measure (e.g., GHG). For plasma-activated processes, optical emission spectroscopy (OES) can be used to obtain information on the plasma species being generated.¹¹⁰ Thus, these techniques can also be applied to study the polluting emissions when they are created. Despite the availability of these tools and the pressing environmental challenges, there are only a few papers that focused on studying the emissions of pollutants issued from ALD processes. For example, when measuring the gaseous emissions generated by ALD of alumina, Ma et al. found that in addition to the expected CH₄, C₆H₆, which is also GHG and toxic, was generated by the process.⁴⁶ More research could benefit from *in situ* studies using these tools and others, to measure and understand the generation of environmentally impacting species and lower their emission.

2.4.3. Modeling. Apart from *in situ* process monitoring, modeling can also be of great assistance to optimize the process. To gain understanding of the ALD chemistry and optimize the processing parameters, a wide array of models has been developed, based on different theories and physical details. Diffusion models can be used to analyze the effects of the processing parameters on the coating kinetics, and apply the model to assess the optimal parameters to achieve the conformal coating of ultrahigh aspect ratio structures.^{111,112} For example, Gayle et al. developed a reaction-diffusion process model to

quantify the trade-offs between excess precursor utilization and process time when coating high-aspect-ratio structures.¹¹³ Atomic-scale simulations employing *ab initio* methods have been widely used to predict ALD reaction mechanisms, as they considered the precursor adsorption, ligand elimination, film densification, and the various reactions taking place at the substrate surface.¹¹⁴ Density functional theory (DFT) is often applied to these mechanistic studies, and the main processes studied are ALD of high-k oxides and nitrides, which are typically applied in the semiconductor industry.¹¹⁴ These methods permit to investigate the reaction mechanisms and predict the energetically favored reaction pathways at each stage of ALD. Combining DFT and kinetic MC simulations helps quantify the kinetics of the film nucleation and growth,^{115,116} and different surface reaction models have been developed to estimate the growth kinetics¹¹⁷ and the effects of processing parameters such as precursor exposure time or temperature.^{102,117,118}

In recent years, machine learning (ML) based modeling has been explored as well by different teams to optimize ALD processing parameters. For example, Ding et al. applied machine-learning modeling using multiscale CFD model data to characterize the film growth dynamics with a feed-forward artificial neural network model. This multiscale data-driven model helped to assess the dependence of deposition rate on the different processing parameters, such as the precursor feed flow rate, the pressure, and the temperature.¹¹⁹ Magness et al. used a combined approach of kinetic MC and ML to simulate the growth mechanisms of metal oxide layers grown by ALD and to assess the role of different processing parameters such as the pulse/purge times, the temperature, and the pressure.¹²⁰ Recently, Paulson et al. demonstrated the efficiency of optimization algorithms in determining optimal dose/purge timings for different ALD processes, as their machine-learning-based Bayesian optimization quickly enabled them to approach the optimal timings. In their study, QCM thickness measurements were utilized as inputs to the intelligent agents developed, but other *in situ* data could have been used.¹²¹ Figure 8 illustrates the approach developed by Paulson et al.,¹²¹ making use of *in situ* data (GPC obtained from QCM) and artificial intelligence to optimize a given ALD process.

Yanguas-Gil also explored machine learning and artificial intelligence to optimize ALD processes, and the results obtained showed that for the optimization of a single precursor, the

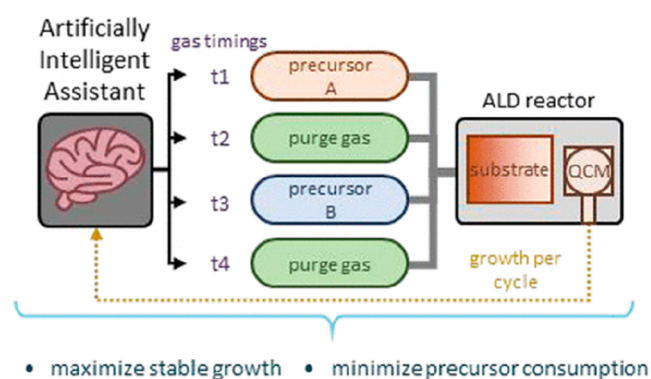


Figure 8. Illustration of the combination of artificially intelligent assistance and *in situ* GPC data to optimize the gas timing parameters of a given ALD process.¹²¹ Reproduced from ref 121. Copyright 2019 ACS.

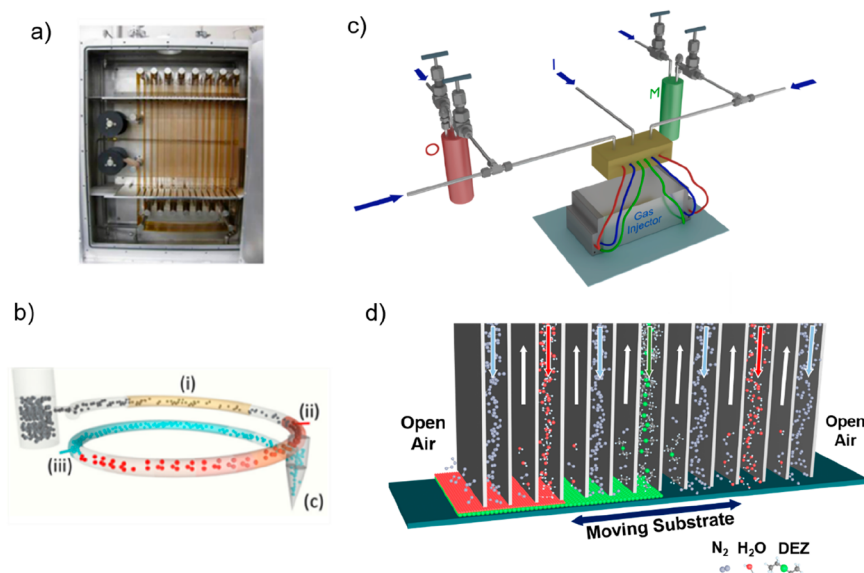


Figure 9. Schematic representation of different SALD systems. (a) SALD prototype based on three chambers containing the different precursors and the inert gas in between, designed for flexible substrates in a roll-to-roll mode. Reprinted with permission from reference.¹²⁶ Copyright 2012 American Vacuum Society. (b) Fluidized SALD system designed to coat particles. Reprinted with permission from ref 127. Copyright 2015 American Vacuum Society. (c) Scheme of the SALD approach based on a close-proximity head. Reprinted with permission from ref 128. Copyright 2020 Wiley & Sons. (d) Transversal cross section of the bottom of a close proximity head showing the different channels containing the precursors and inert gas (along with the exhaust channels) and the forming films as the substrate oscillates below the head. Reprinted with permission from ref 128. Copyright 2020 Wiley & Sons.

saturation times can be precisely predicted by neural networks using just a single growth profile and dosing time as inputs.¹²²

As seen above, making use of *in situ* process monitoring and advanced modeling has beneficial and practical outcomes. However, there is still room for the development of more *in situ* studies, models, and simulations, focusing on the reduction of pollutant emissions, and the limitation of the gas feed, and thermal and energy budget required for given ALD processes.

As the energy consumption by vacuum and heating systems is high, atmospheric pressure processes with limited duration are preferred. Thus, Spatial ALD can be seen as an energy-efficient branch of the classic ALD.

2.5. High Throughput Processes, e.g., Spatial ALD

As depicted above, identified key factors affecting the carbon footprint of ALD processes are the cycle time and the thermalization of the reactor. Apart from their environmental impact, these factors also have an important economic impact. While these different aspects can be tackled separately to reduce the carbon footprint of ALD processes, it would be ideal to develop processes in which all these factors are optimized. As stated above, different high-throughput ALD approaches can be used to reduce the processing duration,^{81,82,101} and SALD appears as a very appealing variant since it translates into faster depositions by its intrinsic mode of operation, as described in this section.

Despite being included in the initial ALD patent,¹²³ the concept of having a continuous flow of the precursors being injected in different locations of the reactor separated by inert gas flows has only been developed from 2008, both at the laboratory and industrial scales.¹²⁴ The first main difference and advantage of SALD with respect to the temporal scheme of conventional ALD is that the process becomes faster, up to 2 orders of magnitude depending on the process and substrates.^{31,79,81} Such faster deposition rates make SALD advanta-

geous for industrial implementation since it reduces production costs, as illustrated in the photovoltaics industry, the initial application of SALD, where cost is a key parameter.³¹ A faster deposition has also a tremendous impact in research since the fabrication and optimization of thin film materials is much faster. Regarding the environmental impact of ALD, processes that can be several orders of magnitude faster have a huge and beneficial impact on the process LCA.

The SALD concept can be implemented in different approaches,⁷⁹ which is good to adapt to the type of sample to be coated and make the process more efficient (see examples of SALD systems designed to coat flexible substrates and particles in Figure 9a and b). In addition, efficient precursor separation and high deposition rate can be performed at high pressures, thus eliminating the equipment and energy associated with vacuum processes, again contributing to a process with a lower carbon footprint. Therefore, SALD, being faster and performed at high pressure, responds to green chemistry principle 6. SALD still offers more potential, as many approaches are based on a variation of a close-proximity concept originally patented by D. Levi et al.¹²⁵ In this approach, precursors are carried by a N₂ flow to a gas manifold where the different flows are distributed along parallel channels with exhaust channels placed in between to evacuate the gas being injected (see the schemes of the close-proximity concept in Figure 9c and 9d). By placing the head at close proximity of the substrate (50 μm to several cm depending on the injector design), an efficient precursor separation is ensured. In this approach, the reaction chamber can be seen as the volume corresponding to the gap between the head and the substrate. As a result, this approach enables depositions at atmospheric pressure and even in the open air (i.e., with no deposition chamber). The deposition is performed by exposing the substrate to the different flows by moving the head or the substrate.

In the close-proximity concept, as shown in the scheme in Figure 9c and d, the precursors are directly injected on top of the substrate. This means that much less precursor molecules are used since they are only exposed to the substrate surface (conversely to conventional ALD where precursors can also react with the chamber walls).³¹ The excess of precursor is then collected along with the reaction products through the exhaust channels and could potentially be recycled and reused in an industrial process. Thus, close proximity SALD addresses very efficiently the green chemistry principles 1 and 7. In addition, the system can be easily adapted to the substrate geometry by modifying the design and size of the head, while the rest of the system remains equal. An example is the development of a SALD cylindrical head to coat tubular membranes.¹²⁹ Several heads could be even combined in a modular approach yielding even higher throughput and contributing to lower precursor waste.^{130–134} By adjusting the design of the head, the deposition can also be limited to a certain zone, thus having Area-Selective Deposition (ASD) without the need to prepattern the substrate (i.e., reducing the fabrication steps). Muñoz-Rojas' team has, for example, shown that a head based on concentric channels can be used to deposit free-from patterns with resolution in x-y in the order of the cm.¹²⁸ Other teams have later shown that it is possible to reach micrometric resolution.^{135,136} In fact, SALD/CVD approaches offer a huge potential for the fast fabrication of miniaturized complex patterns at a high rate with reduced energy demands.^{128,137}

As discussed in section 2.4., both modeling and *in situ* characterization are powerful tools to optimize the amount of precursor injected. Modeling has already been extensively used to optimize different SALD processes^{132,138–145} and could be readily applied toward the optimization of precursor utilization. Regarding the implementation of *in situ* characterization, again SALD, and the close-proximity approach in particular, are very appealing as *in situ* characterization tools can readily be added thanks to the lack of chamber and the atmospheric processing, and the fact that gases can be easily collected through the exhaust for analysis.^{130,136,146–148}

Another advantage of close-proximity SALD approaches is that the thermalization/plasma activation can be limited to the head/substrate volume, thus limiting energy consumption.^{149–152,152–155}

Despite all the advantages of SALD when considering the faster and “greener” aspects of the approach, operating at atmospheric pressure can also have detrimental effects. For example, not all the precursors that would be suitable for vacuum-based ALD approaches can be used in SALD, due to a lower vapor pressure in ambient conditions. The dedicated heating of the precursor and the line leading to the head are thus necessary and should be designed to minimize the thermal budget. Alternative volatilization processes such as laser volatilization of precursors could also be used, as has been done for CVD.¹⁵⁶ Another potential drawback of SALD is the need for larger flows of inert carrier gas such as N₂ (also partially compensated by the faster growth rate). When justified by the size of operations, onsite air separation units (ASU) are suitable to supply the continued demand of N₂; however, their environmental impact could be affected by the carbon footprint of energy and cooling systems, among other items.¹⁵⁷ Figure 10 depicts a schematic representation in which the intrinsic and potential benefits of SALD toward processes with lower environmental impact are shown.

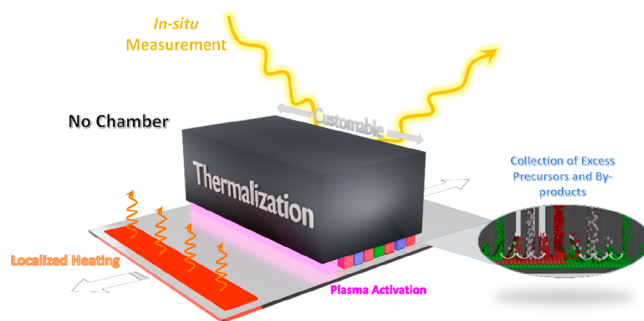


Figure 10. Schematic representation of the intrinsic and potential benefits of SALD toward processes with lower environmental impact.

Even if SALD effectively allows for reduced cycle times and depositions orders of magnitude faster, the process duration (and thereby the energy consumption and emissions) scales linearly with batch size, whereas this is not the case for classical (batch) reactors in which placing a large number of wafers is possible. The advantages of SALD versus batch ALD needs to be evaluated and it will surely depend on the specific process and material deposited substrates. Other high-throughput ALD approaches could thus also be used to reduce the processing duration and related emissions.^{81,82,101} In addition, most of the data extracted from the literature are gathered from lab-scale tools, which usually are less energy efficient than industrial ones. Therefore, it is essential to validate the LCA results with ALD and SALD equipment used in production.

2.6. Chemical Design of Greener Precursors

As illustrated by the application of green chemistry principles to ALD, precursor chemistry is a key parameter. Precursors allowing for low-temperature deposition of materials are very attractive to limit the thermal budget required. Ideally, their synthesis should be achieved by using a minimal number of efficient steps and making use of green synthesis methods when possible. In fact, from the raw materials extraction and refinement, which are highly energy demanding and sometimes very complicated to achieve (e.g., certain mines of metals are located in conflicts zones) to the pure targeted organometallic precursor species, the synthesis of ALD precursors has a large number of steps and a consequent impact on the environment.

The physicochemical characteristics of the precursors that are highly important for a successful implementation in ALD processes are high volatility, thermal stability, and reactivity. Precursors such as TMA (trimethyl aluminum), DEZ (diethyl zinc), or HfCl₄ are readily available as industrial bulk chemicals and are conveniently used in ALD processes, thanks to their desirable physicochemical properties for ALD applications, and because they do not require complicated synthetic approach. TMA is a liquid at room temperature (RT), provides a more than sufficient vapor pressure at RT, is highly reactive, and delivers Al-containing high-quality films.¹⁵⁸ Despite being highly pyrophoric, TMA might be seen as a role model for precursor chemists and ALD experts due to its desirable properties. Also, the synthesis of TMA can be considered highly optimized from an industrial standpoint and proceeds in two discrete synthetic steps. It typically involves the reaction of elemental aluminum and chloroform to produce dimethylaluminumchloride which is further converted to TMA in a melt by a reaction with sodium. The TMA is distilled from the reaction mixture afterward.^{159–161} However, for the deposition of material systems other than Al₂O₃, ZnO, or HfO₂ by ALD, more complicated

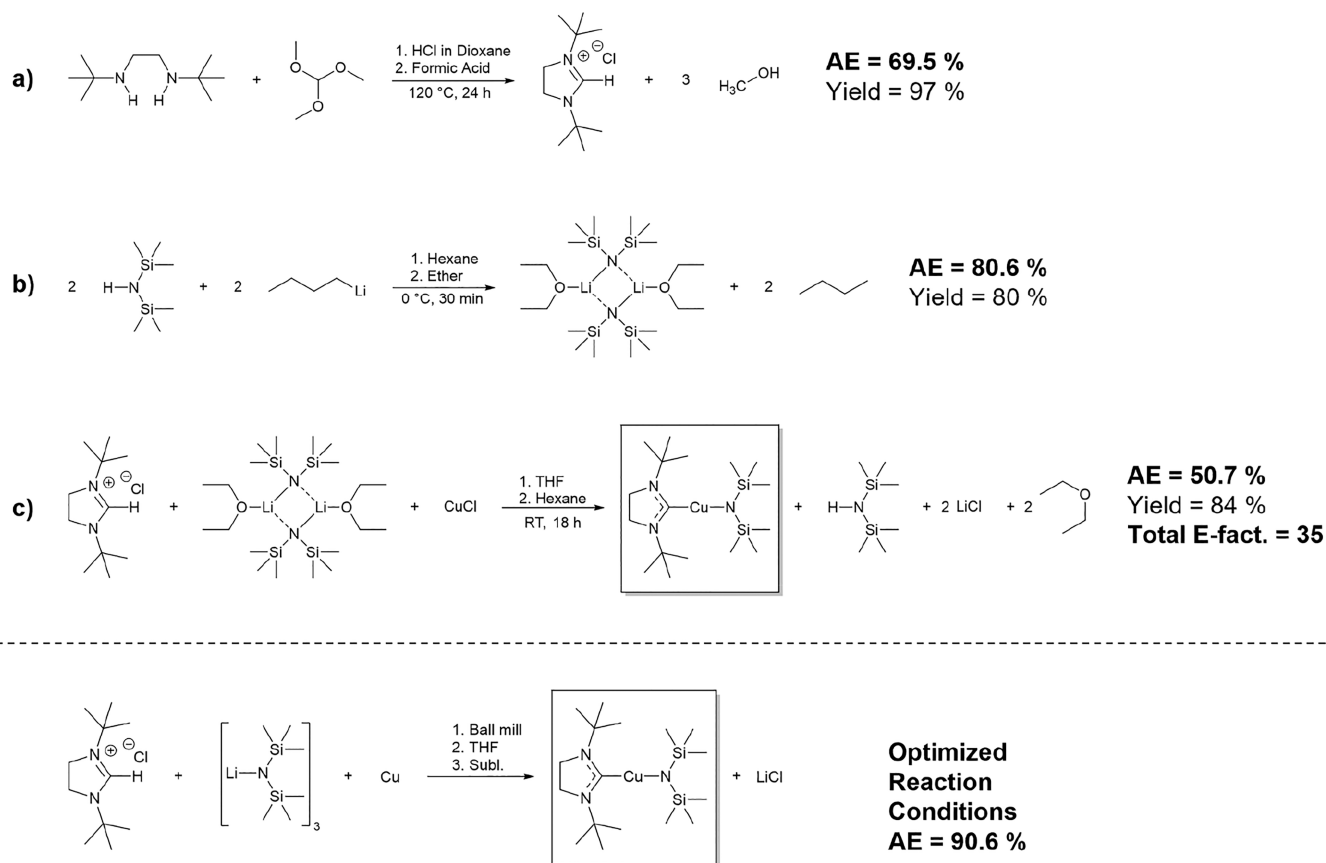


Figure 11. Synthetic steps involved in the synthesis of the $[\text{Cu}(\text{NHC})(\text{hmds})]$ precursor. Parameters for the initial (a), intermediate (b), and final (c) reactions are denoted next to the reactions. AE: Atom economy.

chemistries and thus synthetic approaches are normally needed to obtain the desired physicochemical properties of an ALD precursor.^{162,163} For example, when considering the formation of metallic Ag layers, small molecules such as AgCl or Ag(CH₃) cannot be employed for a well-functioning ALD process as they are either not volatile or highly unstable, respectively.¹⁶⁴ Thus, the pertinent design of ligands increasing volatility and thermal stability needs to be considered, which arguably renders the overall environmental impact of the synthesis and consequently whole ALD process chain more challenging. It should be highlighted that the environmental aspect of precursor chemistry is highly specific and bound to the resulting material systems, which makes an overall assessment of the impact of precursor chemistry on the environment challenging. Interestingly, and to the best of our knowledge, an assessment of the typically employed green chemistry principles and their implications on the ALD precursor chemistry is not discussed in the literature so far, and only scarcely evaluated for CVD.¹⁶⁵ Hereafter, we provide case studies, from the perspective of academic R&D, on how the impact of precursor synthesis and chemistry on the environment can be potentially minimized while respecting the principles of green chemistry and retaining the important physicochemical properties of ALD precursors.

2.6.1. Synthetic Aspects: E-Factor and Solvents. As stated above, the synthesis of the precursor is the first step toward a well-functioning ALD process. The synthesis not only includes the final conversion of ligands and metals to the targeted organometallic species, but also the synthesis of starting materials such as ligands or other reagents themselves. Most of

the synthetic approaches for the creation of precursors are dominated by the excessive use of organic solvents with considerable environmental impacts, such as tetrahydrofuran, hexane, or diethyl ether.¹⁶⁶ Solvents that are considerably less harmful to the environment such as ethanol, water, or supercritical CO₂ are mostly ruled out as the targeted organometallic precursor molecules might be highly reactive toward protic, highly polar solvents and noninert conditions. Additionally, commonly employed solvents such as hexane or ethers must be purified, dried, and stored in an inert-gas atmosphere which considerably adds to their environmental impact, even when reused. One of the key principles of green chemistry is to avoid the waste that might be produced during the synthesis of the desired compound, which is in our case the organometallic precursor employed in the ALD process. An established metric for the assessment of waste produced during the synthesis of pharmaceutical-relevant molecules is the so-called E-Factor introduced by Sheldon et al.,^{167–169} which relates the mass of the overall waste to the mass of the obtained product. Generally, lower E-Factors are thus desirable for a precursor chemist as they consequently indicate less production of waste. For example, when considering the synthesis of Cu^I and Ag^I NHC-based precursors of the general type $[\text{M}(\text{NHC})(\text{hmds})]$ (M = Cu, Ag) which have been successfully established in spatial ALD for the deposition of metallic Cu and Ag layers,^{152,154,170} the E-Number can indeed be calculated to assess the amount of waste that is produced during the synthesis. Notably, over 16 different chemicals in three different synthetic steps are involved in the synthesis of $[\text{Cu}(\text{NHC})(\text{hmds})]$

(Figure 11). The yields of the reactions a) to c) can be considered on the higher side, while each reaction itself is a one-pot reaction and in that respect highly optimized if the principles of green chemistry are considered.

However, if the masses of the employed chemicals are considered, it should be directly apparent that the solvents employed in the synthesis have the largest impact on the E-factor. In total, for the production of ≈ 12 g of $[\text{Cu}(\text{NHC})(\text{hmds})]$, approximately 420 g of chemicals are wasted during the process if they are not reused. This results in an E-factor of 35 which is in the same range as commonly known pharmaceutical and fine-chemical industry according to a classification by Sheldon.¹⁶⁸ A promising optimization of the E-factor might be accessible by reducing the amount of solvent used, or by the use of alternative solvents.¹⁷¹ Hypothetically, such optimization is especially promising for steps (b) and (c), as in this case ether is only used for coordination and crystallization in step (b) while hexane is used for extraction of the product after salt metathesis reaction in step (c). Most interestingly, Et_2O is not needed to isolate a stable $[\text{Li}(\text{hmds})]_3$ intermediate which can be directly crystallized from the reaction mixture and could most probably be used in step c) without further considerations.^{172,173} Additionally, $[\text{Cu}(\text{NHC})(\text{hmds})]$ might be sublimed out of the crude reaction mixture without the prior extraction of hexane, other reagents which might be leftover in the reaction mixture such as the imidazolium chloride should not present significant volatility. The optimization of the THF solvent quantity that is needed for step c) might lead to further minimization of solvent usage. When considering no Et_2O , no hexane, and only half the amount of THF is used to synthesize the final precursor $[\text{Cu}(\text{NHC})(\text{hmds})]$, the E-factor decreases to 11 and only 128 g of waste is produced.

If the solvents are potentially indispensable for the desired reaction protocols, efforts should at least be undertaken to replace the solvents by alternatives reducing the environmental impact. THF can for example be replaced by 2-Methyltetrahydrofuran (2-Me-THF) and hexane by heptane, among other potential alternatives that have been thoroughly discussed in recent literature.^{166,174} This example highlights that optimizations can be carried out for established reactions and that alternative synthetic protocols might result in a considerable minimization of (toxic) waste, thus reducing the overall environmental impact of the ALD precursor synthesis.

2.6.2. Atom Economy. The atom economy (AE) as introduced by Trost¹⁷⁵ needs to be considered as well for the optimization of a reaction protocol with regard to its environmental impact. According to the concept of AE, the chemical reactions can be ranked in several different regimes (see Figure 12), where 100% is the most desirable and 0% is the worst case (complete decomposition of the reactants and no formation of the product at all). Addition reactions, rearrangements, and insertion reactions typically result in an AE of 100% as no other products are formed. Catalytic reactions, such as coupling reactions typically also avoid the formation of condensation or other elimination products, resulting in high AE percentages. The organometallic reactions used for the synthesis of precursors mostly, rely on salt-metathesis reactions. This elimination-type reaction, which is exemplarily used in the formation of $[\text{Cu}(\text{NHC})(\text{hmds})]$ by the elimination of LiCl, highlights that not all employed atoms from the starting materials ultimately end up in the molecular composition of the Cu precursor. Together with the elimination of LiCl, also Et_2O and hmds are formed through substitution or as a result of LiCl

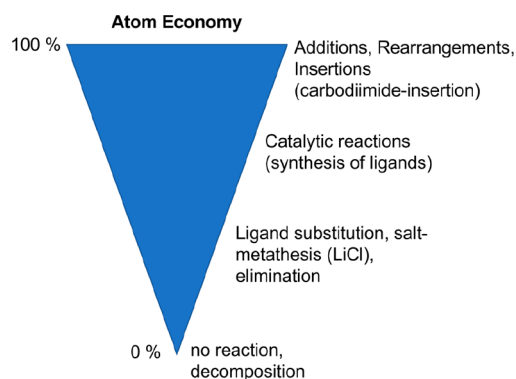


Figure 12. Schematic representation for the concept of atom economy. Different types of reaction protocols can be roughly assigned to their overall degree of potential obtainable atom economy values, from 0% to 100%. Adapted and modified from ref 179 with permission under a Creative Commons Attribution-Share Alike 4.0 International license. Copyright 2017 Wikimedia Commons.

elimination, respectively. The corresponding AE for this reaction step in Figure 11c) can thus be considered as mostly mediocre with a value of 50.7%. Generally, the optimization of the AE can be achieved by switching the reaction type from elimination or substitution reactions to catalyzed transformations or addition and insertion-type reactions (Figure 12). Insertion-type reactions can ensure reaching an AE of 100% as no additional trivial byproducts are created. Hence, the production of $[\text{Cu}(\text{NHC})(\text{hmds})]$ in reaction step c) could hypothetically be optimized by generating the $[\text{Cu}(\text{NHC})\text{Cl}]$ intermediate through mechanochemistry methods (ball-milling) of elemental copper with the respective imidazolium chloride which was described for similar $[\text{Cu}(\text{NHC})\text{Cl}]$ -type complexes in recent literature.^{176–178} This insertion-type reaction would not only increase the AE, but also circumvents the usage of solvents like THF or dichloromethane for the first step of the reaction. Yet, for the second part of the reaction and salt metathesis reaction of $[\text{Cu}(\text{NHC})\text{Cl}]$ and $[\text{Li}(\text{hmds})]_3$, solvents like THF are needed and LiCl is expelled, so that wastes are not fully avoidable, but can be minimized. Through the optimized reaction steps in terms of AE, an optimized value of 90.6% could in principle be achieved for this reaction.

2.6.3. Catalysis for Ligand Synthesis. As described before, catalytically enhanced transformations through, e.g., transition-metal catalysis can in principle enhance the AE further and reduce the amount of waste that is potentially produced. Catalysis has shown to be a beneficial route in various synthetic pathways, especially for the synthesis of ligands used for organometallic complexation of the metal ions.

The preparation of *N*-alkyl substituted formamidines, which are very promising ligands for Yttrium and Indium precursors,^{180–182} will be considered as an example. The synthesis can be achieved through two separate routes (Figure 13), a conventional and catalyzed procedure.^{183–185} In the first route, two equivalents of a *N*-alkyl substituted amine together with acetic acid and triethylorthoformate as the reagent and solvent can be transformed to an *N*-alkyl substituted formamidinium acetate species through vigorous heating of the reaction mixture and removal of the employed residual reactant and byproducts. As an alternative, the second route employs a PdCl_2 -catalyzed insertion of triethylsilane into an *N*-alkyl substituted carbodiimide species forming a triethylsilylformamide through H–Si bond activation. The reaction can be

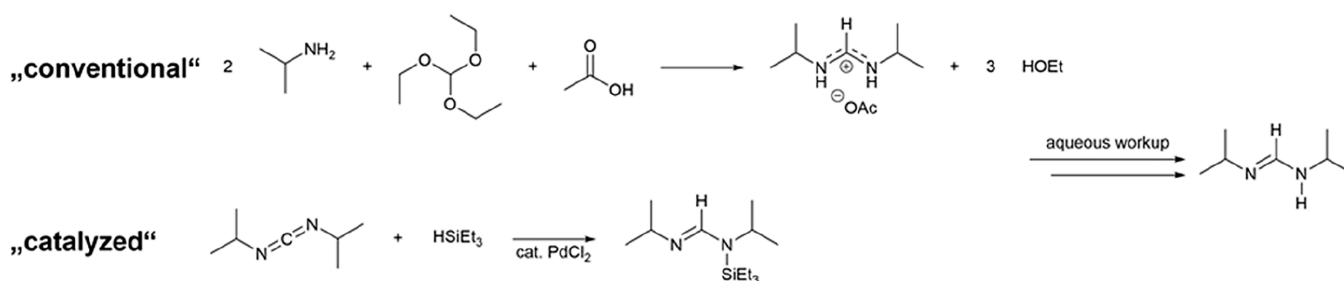


Figure 13. Synthetic procedure of formamidine using two different routes.

conducted without the use of a solvent in an autoclave reactor, at a similar temperature. Thus, thanks to the use of a catalyst and the insertion-type reaction protocol, the AE can be increased from 58.2% to 100% with the latter route. Both intermediate species, namely the formamidinium acetate and the triethylsilylformamide, can be converted to the final *N*-alkyl substituted formamidine ligand under aqueous alkaline conditions and consecutive crystallization or distillation.

As seen from this representative example, it is generally beneficial to find substitutional pathways for the formation of different types of ligands under catalytic enhancement to increase AE and decrease waste production and thus the environmental impact of such reactions.

2.6.4. Precursor Purity and Physicochemical Properties. For some ALD processes, the use of precursors with a reduced purity may be sufficient (e.g., 97% instead of 99.9%) to obtain good quality films, which limits the purification/recrystallization steps to be carried out. This might be especially interesting if the impurities are not volatile and stay behind in the precursor container so that an inclusion inside the films is nearly impossible. Sublimation experiments with the slightly impure precursor mixture can be beneficial in this case to clarify if the impurities do not volatilize together with the precursor. The recuperation of precursors in excess should also be more developed, for example using a condensation step.

Another important aspect is the evaluation of the physicochemical characteristics of the precursors. This includes the assessment of its volatility, thermal stability, reactivity, and melting point, among other parameters that are discussed in a later section. When considering spatial ALD processes operated at atmospheric conditions, the physicochemical properties of the precursors are even more important than for vacuum-based temporal ALD processes, as the volatility of the precursors is not boosted using overall low process pressures. Assessment of volatilities and thermal stabilities can be conveniently approached by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).¹⁸⁶ In an ideal case, the precursor provides a sufficiently high volatility (0.1 Torr) down to room temperature, while still being thermally robust at high temperatures and providing good reactivity. High reactivity and volatility lead to lower processing temperatures and shorter processing times. Accordingly, the energy and carbon footprint of the process can be directly influenced and optimized by the rational design of ligands and resulting precursors.

The guanidinate, amidinate, and formamidinate ligand classes can be projected as representative examples, as they have been used in comparative precursor and process studies for Indium and Yttrium precursors. Specifically, a study by Kim et al.¹⁸² comparatively investigated the thermal properties of tris(*N,N'*-diisopropylamidinato)indium(III) and tris(*N,N'*-diisopropylformamidinato)indium(III), whereby the latter

enabled the growth of high-quality In₂O₃ thin films by ALD with water in the lowest and widest ALD window known in recent literature. Further, the length of the water pulse during the ALD process could be minimized. The reasons for the higher performing nature of the formamidinate-type complex can be attributed to its higher volatility, thermal stability, and reactivity compared to its amidinate-type congener. Ultimately, the smaller –H substituent within the endocyclic backbone of the indium formamidinate enables these promising properties of the precursor. Very similar results could be obtained for isostructural Yttrium complexes, where the formamidinate-type complex features superior physicochemical properties and thus enables a low and wide ALD window for the deposition of Y₂O₃ thin films with water, compared to the amidinate- and guanidinate-type yttrium complexes.^{180,181}

2.6.5. Potential Hazards: Pyrophoricity and Toxicity.

To assess the environmental impact of precursor chemistry, the potentially hazardous nature of the precursor should also be considered. A school case example is the hazardous TMA, a highly pyrophoric and potentially corrosive substance, which certainly needs to be handled with special care and by highly trained staff. Despite the possibility to synthesize the precursor at an industrial scale as known in the literature for decades, the inherent pyrophoric nature of TMA unfortunately caused a series of accidents around the world.^{187,188} Therefore, alternatives should be explored, and interestingly, there are numerous candidates to replace TMA, which are not pyrophoric, while mostly retaining high volatility, thermal stability, and reactivity as needed for well-functioning ALD processes. Alternatives such as aluminum alcoholates [Al(OR)₃],^{189–196} aluminum (dimethylamino)propyls [Al(DMP)-R],^{197,198} and aluminum amides [Al(NR₂)₃] have been successfully used for the formation of Al₂O₃ thin films by ALD.^{199–207} It should be mentioned that the functionalization of TMA toward nonpyrophoric precursors involves more synthetic steps and thus certainly causes a higher production of chemical waste if the corresponding synthetic procedures for the creation of alternative TMA precursors are not optimized with respect to the principles of green chemistry. From a “green” chemistry perspective, the creation and usage of AlCl₃ as an alternative precursor might be beneficial,^{208–210} as no lengthy synthetic procedures for the functionalization are needed. However, the high melting point of this precursor and the production of corrosive HCl vapor during the ALD process might hinder its application as a suitable alternative to TMA.^{211,212} Several alternative examples are also known for the pyrophoric precursor diethylzinc, commonly applied for the formation of Zn-containing thin films.^{213,214} Recent efforts were undertaken to drastically reduce the pyrophoricity by employing (dimethylamino)propyl ligands in [Zn(DMP)₂],²¹⁵ similar to those employed for Al precursors, while retaining a high

reactivity that enabled the growth of functional ZnO films at mild deposition temperatures in PEALD (60–150 °C). Other efforts were also undertaken to limit the pyrophoric nature of Zn-based precursors, employing acetate, β -ketoiminate and chlorides,^{216–218} although the properties of the precursors in terms of volatility, thermal stability and reactivity are a considerable drawback for the above-mentioned alternatives. Overall, the number of reported alternative Zn precursors is still very limited and efforts should be undertaken to explore and identify more alternatives.

Another important aspect is the toxicity of the employed precursor. Optimizing the employed precursor to reduce its toxicity might not be easily accessible and is, as discussed before, constrained by other parameters like volatility, thermal stability, and reactivity of the precursor. The intrinsic toxicity of the employed metal ions, which mostly depends on the employed ligands and the oxidation state of the metal itself, but also on the type of exposure to the human body among many other factors, can thus not be conveniently optimized. During precursor synthesis, the contamination of the solvent wastes with metal ions and ligands might even further enhance the toxicity of the employed solvent mixture and resulting wastage. It is thus directly apparent that solvents should be only used minimally and, if possible, should be avoided at all as discussed already in other sections. Moreover, the modification of the precursor during the ALD process, namely by the reaction with the co-reactant or partial decomposition and ligand-cleavage on the surface or change of oxidation state will result in potentially toxic wastages even if the employed precursor itself might only be mildly toxic. As an example, the LD₅₀ value (rats) for Cr(acac)₃ (3360 mg/kg),²¹⁹ a precursor used for the deposition of Cr-containing thin films by ALD,^{220–223} is considerably higher compared to CrCl₃ (440 mg/kg), or CrO₃ (52 mg/kg) which might be a possible oxide-based material that is formed by ALD or after the disposal of the precursor in the ambient. A change of the oxidation state can thus severely enhance the toxicity of the metal ion after ALD processing. A commonly known issue when using carbonyl-based precursors might be the formation of highly toxic CO gas during the ALD process and/or precursor decomposition over time. For other more sophisticated precursor chemistries, the formation and identification of potential toxic byproducts might be more difficult and should be explored in future studies by *in situ* techniques such as residual gas analysis (RGA). The reader is referred to an interesting review by Egorova and Ananikov²¹⁹ that thoroughly summarizes different aspects of the toxicity of metal compounds and how different variables influence their toxicity. The assessment and comparison between different precursors' environmental impact remains challenging, as small molecules such as halides need a lower number of synthetic steps compared to more complex organometallic compounds but might present a higher toxicity as discussed already for different chromium precursors.

The co-reactants used in ALD might also present a highly toxic nature. For the formation of transition metal sulfides, which are especially relevant for the production of 2D materials such as MoS₂ or WS₂ for next-generation microelectronics, hydrogen sulfide (H₂S) is commonly employed as the co-reactant in the respective ALD processes.^{224–230} Even though safety protocols such as gas sensors, protective equipment, and highly trained personnel can substantially minimize the risk of possible accidents with H₂S, the substitution of H₂S as a reactant in ALD is the most sustainable approach, ultimately. Efforts to

circumvent its usage for thin film metal sulfide deposition were originally evaluated in numerous studies about MOCVD processes using elemental Sulfur.²³¹ It should be critically noted, however, that the use of elemental sulfur in ALD might be ultimately difficult as its allotropes that might be formed at different evaporation temperatures affect physicochemical properties such as evaporation rates and melting points of the substance, which are not desirable. Such a precursor is also more challenging to use in atmospheric SALD approaches and also, residues of elemental sulfur in the reaction chamber and exhaust might be undesirable. Other alternatives to H₂S, namely, mercaptans and thioethers, have been used for the formation of, e.g., MoS₂, ZnS, or NiS_x.^{232–238} Notably, the toxicity of these compounds is mostly still considerably increased compared to elemental sulfur, but significantly less hazardous than gaseous H₂S. A design of alternative sulfur precursors might be a promising pathway to consider to reduce the toxicity of sulfur precursors while retaining important properties as desired for ALD applications. For example, molecular layer deposition approaches using ethane-1,2-dithiol (EDT) have been developed to prepare tin sulfides,¹⁰⁸ to eliminate the use of H₂S, but the process requires an annealing step at high temperatures, which is detrimental to the overall environmental friendliness of the process.

All things considered, the efforts on developing precursors with “greener” chemistry approaches can still be significantly higher as only a few reports are known in literature yet. Exploring substitutional pathways for the formation of different types of ligands and precursor under optimized protocols using e.g. catalysis or mechanochemistry should become a priority. The development of novel precursors chemically designed for having less environmental impact is challenging but desired, as they would enable to reach ALD processes with a lower carbon footprint.

2.7. Industrial Perspective

ALD is mainly applied in the semiconductor industry, which suffers from a very significant carbon footprint,⁴¹ and there is thus a drastic need to develop novel processes with lower environmental impact. In the latest ten years, some of the major companies in the field are trying to reduce their environmental impact and increase their efforts toward this reduction. In particular, efforts are focusing on energy efficiency, water recyclability, and material use. The quest to achieve lower GHG emissions has been set by the World Semiconductor Council already decades ago,¹⁰³ and the sustainable semiconductor technologies and systems research program led by the Interuniversity Microelectronics Centre (IMEC) and reuniting most of the major semiconductor companies is worth noting as well.^{239,240}

The U.S. Department of Energy, in its Quadrennial Technology Review on the Assessment of Energy Technologies,²⁴¹ described new manufacturing approaches based on process intensification (PI), which involves combining separate unit operations into a single piece of equipment. This type of technology could be readily applied to the production of ALD precursors by combining reactors and separators, thereby increasing the efficiency and cleanliness of the process while reducing its overall operating costs. The European Chips Act, representing €43 billion of policy-driven investment until 2030, aims to bolster Europe's resilience in semiconductor technologies and help achieve both the digital and green transition,²⁴² representing also a considerable opportunity for

the development of ALD processes with lower environmental impact.

On the other hand, ALD has been used also in high-performance energy-related applications playing a significant role in the mitigation of GHG emissions, such as photovoltaics, membranes, batteries, fuel cells, or electrolyzers. It is important to ensure that the development and deployment of these technologies take place with as low environmental impacts as possible, and the eco-design of energy-related technologies is a crucial factor in the EU strategy (Directive 2009/125/EC). As illustrated below, the use of ALD is key to improving the performance of these upcoming technologies, but it remains crucial to perform thorough LCA studies with ALD equipment used in production to validate the overall environmental benefits.

The use of ALD technology in solar photovoltaics is not new,²⁴³ however, recent advances allowed the fabrication of a novel interdigitated back-contacted solar cell concept (IBC) as the bottom cell of a three-terminal tandem device.²⁴⁴ This new concept of three-terminal tandem could be capable of increasing the solar cell efficiency by over 30% due to the possibility to extract two photocurrents from a single tandem.²⁴⁵ Controlled deposition of transition metal oxides (TMOs) such as molybdenum (MoO_x), titanium (TiO_x), and vanadium (VO_x) oxides has been widely evaluated to avoid the utilization of high temperature and flammable gases in the np-based or a-Si:H junction of solar cells. In that sense, ALD represents a clear advantage over the conventional fabrication process such as CVD due to its excellent control of TMO film growth. Nonetheless, its main challenge still lies in the low deposition rates. Fortunately, high throughput ALD could surge as a suitable method to attain higher deposition rates required at the industrial scale.^{246,247} For example, it has been shown that Cu_2O p-layers can replace a-Si(p) in silicon heterojunction cells and still provide high efficiencies on $3 \times 3 \text{ cm}^2$ cells.²⁴⁸ In the same line, the fast deposition and mild temperatures involved in SALD have proven to be advantageous to deposit blocking and passivating layers in hybrid perovskite solar cells.^{249,250}

Membranes, typically used in the industry to purify mixtures without using heat, allow the lowering of global energy use, carbon emissions, and overall pollution. Due to its unique assets, ALD has also been explored for the tuning of membranes, such as the atomic-level tuning of pore dimensions and the functionalization of various materials at the pore surface. The ALD-modified membranes were aimed at many applications, including water filtration, gas separation, biosensing, and catalysis.^{35,251–253}

Batteries and fuel cells are other fields where advanced ALD coatings are able to trigger a game changer behavior thanks to the unique advantage of ALD to fabricate complex functional or catalyst layers by successive and alternating single-atoms processing.

A key issue in the batteries, especially in lithium-ion batteries (LiB), is the degradation reaction taking place at the electrolyte interface, causing the formation of a passivation layer at the surface of the negatively charged electrode.^{254–256} Previous ALD-based reports showed that the deposition of ultrathin buffer layers on electrode materials is effective to reduce the passivation layer formation and promote a rapid electron transfer.²⁵⁷ Typical ALD deposited layers are based on oxide materials such Al_2O_3 , ZnO , or HfO_2 ,²⁵⁸ all of them improving the battery lifetime during long-term cycles. Further research efforts toward the use of more ionic conductive materials, such

as zirconate and niobates, remain active. Moreover, ALD is been also evaluated for use in the next battery generation, the so-called solid-state battery, to enhance the current density thanks to the high effectiveness of depositing conformal films in high-aspect-ratio substrates.²⁵⁹

ALD is also opening opportunities in the fabrication of catalyst and buffer layers for low-temperature^{260,261} and high-temperature fuel cells.^{262,263} Low-temperature fuel cells, so-called proton-exchange membrane fuel cells (PEMFC), are extensively used in commercial applications such as light-duty vehicles, residential cogeneration systems (electricity and heat production) like the ENE-FARM in Japan with more than 300 000 units installed by 2019,²⁶⁴ and emergency power units for disaster events. One of the main obstacles to the spread of this technology is the high cost of components, especially the Pt catalyst used for the oxygen reduction reaction. ALD has been used to deposit a minimum Pt amount on different types of substrates. The small Pt particles deposited with a homogeneous spatial distribution can mitigate the cell degradation caused by the Pt dissolution during cycling operation, which can effectively reduce the pressure on this noble metal.²⁶⁵ High-temperature fuel cells, so-called solid oxide fuel cells (SOFC), operate between 600 and 800 °C to get sufficient ion and electric conductivity through their ceramic components and increase the kinetics of the electrochemical reactions. Unfortunately, high-temperature operation also triggers adverse reactions in the materials. ALD has shown promising results in fabricating nanostructured layers to reduce the SOFC component thickness and operating temperature, and fabricating defect-free thin layers acting as buffer or electrolyte layers.^{266–268} ALD is also useful to improve the oxidation–reduction reaction at the SOFC cathode materials, by improving the formation of active sites, via the homogeneous dispersion of active phases or catalyst materials such as CeO_2 for example.^{269–271} Hydrogen and oxygen reactants used during the energy-related devices manufacturing, or their utilization, need to be produced in environmentally benign processes. Electrolysis techniques appear to be promising to obtain cost-effective and low-carbon hydrogen and oxygen molecules. Among these techniques, the development of Solid Oxide Electrolysis Cell (SOEC) technology,^{272,273} working in a reverse principle of SOFC, is particularly attractive, and the nanoengineering capabilities offered by ALD could permit increasingly efficient SOEC, helping the production of low-carbon hydrogen.

3. CONCLUSIONS AND OUTLOOK

The quest for sustainability is becoming vital. In the last decades, ALD technology has been implemented in a wide range of applications, from microelectronics to solar cells. However, when considering its environmental impact, this thin film deposition route has still some challenges to tackle, due to its high energy and materials consumption and its emission of GHG and nanoparticles. In addition, the emissions generated constitute a health risk to ALD equipment users. This work presents different studies on the environmental assessments of ALD processes and proposes several routes to reduce the footprint of this innovative technology based on the literature and the principles of green chemistry. The main conclusions that can be drawn are the following:

First, there are still too few environmental impact assessments of ALD processes in the literature, and additional research efforts should be done to achieve LCA of other processes besides ALD of alumina. The impact of the precursor synthesis, the

equipment manufacturing, and the ALD process itself should be evaluated in combinatorial and comparative LCA approaches, especially for systems used in production. In the future, even if the precise assessment of the environmental impact of an ALD process stays very complex and highly system dependent, a more solid collection of studies could enable one to reach a precious database, that could be used to compare the different processes from an environmental point of view.

Second, since the infrastructure, equipment, and tools that support ALD operations have a significant environmental impact, they should be manufactured with novel high-efficiency and energy-saving equivalents and be as simple as possible. As the energy consumption of the process is mainly dictated by the operating temperature, optimized thermal management of the heated chamber and heated elements is also key to reducing the carbon footprint of the process. The use of renewable energy is also recommended to power equipment and infrastructures, as well as ALD processes. The recycling and reuse of heat, precursors, gases and water issued from the process should become a common practice in ALD systems as it is already adopted in similar industrial processes.^{274–276}

Third, based on the literature review and the green principles applied to ALD depicted in this work, three main routes toward ALD processes with lower environmental impact could be deduced and should be applied where possible:

- (i) The thorough optimization of the processing parameters and the reactor design and its infrastructure would drastically lower the undesired wastes and emissions. Computational simulations, machine learning, and artificial intelligence can, for example, be applied to optimize ALD processes faster than ever, as the saturation times can be precisely predicted using these innovative tools.
- (ii) High throughput processes such as SALD applied at atmospheric pressure could lead to depositions that are orders of magnitude faster and lower the overall energy budget and related emissions.
- (iii) The chemical design of greener precursors would have the largest impact as it could reduce the overall environmental impact: from the raw material extracted and the (limited) number of greener chemistry synthetic steps resulting in the precursor molecules to the thermal budget related to the deposition temperature, and to the emissions of less polluting byproducts.

ALD is already being used and is becoming a key component in high-performance devices playing a significant role in the mitigation of greenhouse gas emissions, such as photovoltaic cells, membranes, batteries, fuel cells, or electrolyzers. If the ALD processes used for energy-related devices manufacturing are applied with the environmental considerations discussed before, a lower carbon footprint of the process could truly help to reduce the pollution generated by the manufacturing of these devices.

However, strong incentives through public policies are required to efficiently go toward the implementation of processes with lower carbon footprint, as new links are needed between existing institutional frameworks to oversee responsible minerals and chemical sourcing, precursor synthesis, and overall environmental and sustainable practices.

Finally, as highlighted in the previous sections, there is still much room for improvement to limit the energy demand and the carbon footprint of the ALD process. We hope that the ALD

community, at both the academic and the industrial level, will foster and increase the number of works to assess the impact of their processes, but also and more importantly will present novel strategies and recommendations to achieve ALD processes with lower environmental impact.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmaterialsau.3c00002>.

Figures depicting the temporal evolution of historical CO₂ emissions between 1980 and 2021, and current emissions trends and predictions of reductions needed for limiting anthropogenic warming to a few degrees (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Matthieu Weber – Univ. Grenoble Alpes, CNRS, Grenoble INP, LMGP, Grenoble F- 38000, France; orcid.org/0000-0003-2490-6168; Email: matthieu.weber@grenoble-inp.fr

Authors

Nils Boysen – Inorganic Materials Chemistry, Ruhr University Bochum, 44801 Bochum, Germany; Fraunhofer IMS, 47057 Duisburg, Germany; orcid.org/0000-0002-6931-8506

Octavio Graniel – Univ. Grenoble Alpes, CNRS, Grenoble INP, LMGP, Grenoble F- 38000, France

Abderrahime Sekkat – Univ. Grenoble Alpes, CNRS, Grenoble INP, LMGP, Grenoble F- 38000, France; Laboratoire de Génie Chimique, Université de Toulouse, CNRS, F-31030 Toulouse, France

Christian Dussarrat – Air Liquide Research and Development, Yokosuka 239-0847 Kanagawa, Japan

Paulo Wiff – Air Liquide Research and Development, Yokosuka 239-0847 Kanagawa, Japan

Anjana Devi – Inorganic Materials Chemistry, Ruhr University Bochum, 44801 Bochum, Germany; Fraunhofer IMS, 47057 Duisburg, Germany

David Muñoz-Rojas – Univ. Grenoble Alpes, CNRS, Grenoble INP, LMGP, Grenoble F- 38000, France; orcid.org/0000-0003-1234-0814

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acsmaterialsau.3c00002>

Author Contributions

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

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to thank the French National research agency (ANR) and German Research Foundation (DFG) for funding, through the projects ALD4MEM (ANR-20-CE09-0008), REACTIVE (ANR-21-CE08-0047, DFG-DE-790-28-1)) and DFG-DE-790-18-1. We also would like to thank Paul Poodt (SparkNano) for fruitful discussion. The Global Monitoring Laboratory (www.ourworldindata.org) is also acknowledged for providing the updated CO₂ emissions data

used in Figure S1. The RESILEX project (Horizon Europe Innovation Action Grant n°101058583) is also acknowledged.

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.* **2017**, *114* (30), E6089–E6096.
- (2) UN Report: Nature's Dangerous Decline 'Unprecedented'; Species Extinction Rates 'Accelerating.' <https://www.un.org/sustainabledevelopment/blog/2019/05/nature-decline-unprecedented-report/> (12/01/2023).
- (3) Almond, R. E. A.; Grooten, M.; Petersen, T. *Living Planet Report 2020 - Bending the Curve of Biodiversity Loss*; Gland, Switzerland, 2020.
- (4) Charpentier Poncelet, A.; Helbig, C.; Loubet, P.; Beylot, A.; Muller, S.; Villeneuve, J.; Laratte, B.; Thorenz, A.; Tuma, A.; Sonnemann, G. Losses and Lifetimes of Metals in the Economy. *Nat. Sustain.* **2022**, *5*, 717–726.
- (5) Díaz, S.; Zafra-Calvo, N.; Purvis, A.; Verburg, P. H.; Obura, D.; Leadley, P.; Chaplin-Kramer, R.; De Meester, L.; Dulloo, E.; Martín-López, B.; et al. Set Ambitious Goals for Biodiversity and Sustainability. *Science* **2020**, *370* (6515), 411–413.
- (6) Chapin, F. S., III; Zavaleta, E. S.; Eviner, V. T.; Naylor, R. L.; Vitousek, P. M.; Reynolds, H. L.; Hooper, D. U.; Lavorel, S.; Sala, O. E.; Hobbie, S. E.; Mack, M. C.; Diaz, S.; et al. Consequences of Changing Biodiversity. *Nature* **2000**, *405* (6783), 234.
- (7) Tilman, D.; Clark, M.; Williams, D. R.; Kimmel, K.; Polasky, S.; Packer, C. Future Threats to Biodiversity and Pathways to Their Prevention. *Nature* **2017**, *546* (7656), 73.
- (8) Ali, S. H.; Giurco, D.; Arndt, N.; Nickless, E.; Brown, G.; Demetriades, A.; Durrheim, R.; Enriquez, M. A.; Kinnaird, J.; Littleboy, A.; et al. Mineral Supply for Sustainable Development Requires Resource Governance. *Nature* **2017**, *543* (7645), 367–372.
- (9) Peters, G. P.; Andrew, R. M.; Canadell, J. G.; Friedlingstein, P.; Jackson, R. B.; Korsbakken, J. I.; Le Quéré, C.; Pregon, A. Carbon Dioxide Emissions Continue to Grow amidst Slowly Emerging Climate Policies. *Nat. Clim. Change* **2020**, *10* (1), 3–6.
- (10) Liu, Z.; Deng, Z.; Davis, S. J.; Giron, C.; Ciais, P. Monitoring Global Carbon Emissions in 2021. *Nat. Rev. Earth Environ.* **2022**, *3*, 217–219.
- (11) Zimmerman, J. B.; Anastas, P. T.; Erythropel, H. C.; Leitner, W. Designing for a Green Chemistry Future. *Science* **2020**, *367* (6476), 397–400.
- (12) Anastas, P.; Eghbali, N. Green Chemistry: Principles and Practice. *Chem. Soc. Rev.* **2010**, *39* (1), 301–312.
- (13) Aujoux, C.; Blanchard, O.; Kotera, K. How to Assess the Carbon Footprint of a Large-Scale Physics Project. *Nat. Rev. Phys.* **2021**, *3* (6), 386–387.
- (14) Bousema, T.; Burtscher, L.; van Rij, R. P.; Barret, D.; Whitfield, K. The critical role of funders in shrinking the carbon footprint of research. *The Lancet Planetary Health* **2022**, *6*, No. e4–e6.
- (15) Graphene as "the philosopher's stone": Turning waste into gold. <https://nano-magazine.com/news/2022/8/18/graphene-as-the-philosophers-stone-turning-waste-into-gold> (12/01/2023).
- (16) Carroll, M. Nanoparticles increase light scattering, boost solar cell performance. <https://phys.org/news/2022-08-nanoparticles-boost-solar-cell.html> (12/01/2023).
- (17) Ritala, M.; Kukli, K.; Rahtu, A.; Räisänen, P. I.; Leskelä, M.; Sajavaara, T.; Keinonen, J. Atomic Layer Deposition of Oxide Thin Films with Metal Alkoxides as Oxygen Sources. *Science* **2000**, *288* (5464), 319–321.
- (18) Hämäläinen, J.; Ritala, M.; Leskelä, M. Atomic Layer Deposition of Noble Metals and Their Oxides. *Chem. Mater.* **2014**, *26* (1), 786–801.
- (19) Sekkat, A.; Liedke, M. O.; Nguyen, V. H.; Butterling, M.; Baiutti, F.; Sirvent Veru, J. de D.; Weber, M.; Rapenne, L.; Bellet, D.; Chichignoud, G. Chemical Deposition of Cu₂O Films with Ultra-Low Resistivity: Correlation with the Defect Landscape. *Nat. Commun.* **2022**, *13* (1), 1–11.
- (20) Kim, H. Atomic Layer Deposition of Metal and Nitride Thin Films: Current Research Efforts and Applications for Semiconductor Device Processing. *J. Vac. Sci. Technol. B Microelectron. Nanometer Struct. Process. Meas. Phenom.* **2003**, *21* (6), 2231–2261.
- (21) Weber, M.; Coy, E.; Iatsunskyi, I.; Yate, L.; Miele, P.; Bechelany, M. Mechanical Properties of Boron Nitride Thin Films Prepared by Atomic Layer Deposition. *CrystEngComm* **2017**, *19* (41), 6089–6094.
- (22) Dasgupta, N. P.; Meng, X.; Elam, J. W.; Martinson, A. B. Atomic Layer Deposition of Metal Sulfide Materials. *Acc. Chem. Res.* **2015**, *48* (2), 341–348.
- (23) Mattinen, M.; Leskelä, M.; Ritala, M. Atomic Layer Deposition of 2D Metal Dichalcogenides for Electronics, Catalysis, Energy Storage, and Beyond. *Adv. Mater. Interfaces* **2021**, *8* (6), 2001677.
- (24) Aaltonen, T.; Ritala, M.; Tung, Y.-L.; Chi, Y.; Arstila, K.; Meinander, K.; Leskelä, M. Atomic Layer Deposition of Noble Metals: Exploration of the Low Limit of the Deposition Temperature. *J. Mater. Res.* **2004**, *19* (11), 3353–3358.
- (25) Mackus, A. J. M.; Weber, M. J.; Thissen, N. F.; Garcia-Alonso, D.; Vervuurt, R. H.; Assali, S.; Bol, A. A.; Verheijen, M. A.; Kessels, W. M. M. Atomic Layer Deposition of Pd and Pt Nanoparticles for Catalysis: On the Mechanisms of Nanoparticle Formation. *Nanotechnology* **2016**, *27* (3), 034001.
- (26) George, S. M. Atomic Layer Deposition: An Overview. *Chem. Rev.* **2010**, *110* (1), 111–131.
- (27) Johnson, R. W.; Hultqvist, A.; Bent, S. F. A Brief Review of Atomic Layer Deposition: From Fundamentals to Applications. *Mater. Today* **2014**, *17* (5), 236–246.
- (28) Parsons, G. N.; George, S. M.; Knez, M. Progress and Future Directions for Atomic Layer Deposition and ALD-Based Chemistry. *MRS Bull.* **2011**, *36* (11), 865–871.
- (29) Detavernier, C.; Dendooven, J.; Pulinthanathu Sree, S.; Ludwig, K. F.; Martens, J. A. Tailoring Nanoporous Materials by Atomic Layer Deposition. *Chem. Soc. Rev.* **2011**, *40* (11), S242–S253.
- (30) Marichy, C.; Bechelany, M.; Pinna, N. Atomic Layer Deposition of Nanostructured Materials for Energy and Environmental Applications. *Adv. Mater.* **2012**, *24* (8), 1017–1032.
- (31) Munoz-Rojas, D.; MacManus-Driscoll, J. Spatial Atmospheric Atomic Layer Deposition: A New Laboratory and Industrial Tool for Low-Cost Photovoltaics. *Mater. Horiz.* **2014**, *1* (3), 314–320.
- (32) Van Delft, J. A.; Garcia-Alonso, D.; Kessels, W. M. M. Atomic Layer Deposition for Photovoltaics: Applications and Prospects for Solar Cell Manufacturing. *Semicond. Sci. Technol.* **2012**, *27* (7), 074002.
- (33) Chang, N. L.; Poduval, G. K.; Sang, B.; Khoo, K.; Woodhouse, M.; Qi, F.; Dehghanimadvar, M.; Li, W. M.; Egan, R. J.; Hoex, B. Techno-economic Analysis of the Use of Atomic Layer Deposited Transition Metal Oxides in Silicon Heterojunction Solar Cells. *Prog. Photovolt. Res. Appl.* **2023**, *31*, 414–428.
- (34) Weber, M.; Julbe, A.; Ayril, A.; Miele, P.; Bechelany, M. Atomic Layer Deposition for Membranes: Basics, Challenges, and Opportunities. *Chem. Mater.* **2018**, *30* (21), 7368–7390.
- (35) Weber, M.; Julbe, A.; Kim, S. S.; Bechelany, M. Atomic Layer Deposition (ALD) on Inorganic or Polymeric Membranes. *J. Appl. Phys.* **2019**, *126* (4), 041101.
- (36) Ji, S.; Cho, G. Y.; Yu, W.; Su, P.-C.; Lee, M. H.; Cha, S. W. Plasma-Enhanced Atomic Layer Deposition of Nanoscale Ytria-Stabilized Zirconia Electrolyte for Solid Oxide Fuel Cells with Porous Substrate. *ACS Appl. Mater. Interfaces* **2015**, *7* (5), 2998–3002.
- (37) Jiang, X.; Huang, H.; Prinz, F. B.; Bent, S. F. Application of Atomic Layer Deposition of Platinum to Solid Oxide Fuel Cells. *Chem. Mater.* **2008**, *20* (12), 3897–3905.
- (38) Leskelä, M.; Ritala, M. Atomic Layer Deposition (ALD): From Precursors to Thin Film Structures. *Thin Solid Films* **2002**, *409* (1), 138–146.
- (39) Hwang, C. S. Atomic Layer Deposition for Microelectronic Applications. *At. Layer Depos. Nanostructured Mater.* **2011**, 159–192.
- (40) Pedersen, H.; Barry, S. T.; Sundqvist, J. Green CVD—Toward a Sustainable Philosophy for Thin Film Deposition by Chemical Vapor Deposition. *J. Vac. Sci. Technol. Vac. Surf. Films* **2021**, *39* (5), 051001.

- (41) Gupta, U.; Kim, Y. G.; Lee, S.; Tse, J.; Lee, H.-H. S.; Wei, G.-Y.; Brooks, D.; Wu, C.-J. Chasing Carbon: The Elusive Environmental Footprint of Computing. *IEEE Micro* **2022**, *42* (4), 37–47.
- (42) Bardon, M. G.; Wuytens, P.; Ragnarsson, L.-Å.; Mirabelli, G.; Jang, D.; Willems, G.; Mallik, A.; Spessot, A.; Ryckaert, J.; Parvais, B. DTCO Including Sustainability: Power-Performance-Area-Cost-Environmental Score (PPACE) Analysis for Logic Technologies. In *2020 IEEE International Electron Devices Meeting (IEDM)*; IEEE, 2020; pp 41–44.
- (43) Ragnarsson, L. A.; Bardon, M. G.; Wuytens, P.; Mirabelli, G.; Jang, D.; Willems, G.; Parvais, B. Environmental Impact of CMOS Logic Technologies. *IEEE Electron Devices Technol. Manuf. Conf. EDTM* **2022**, 82–84.
- (44) Yuan, C. Y.; Dornfeld, D. A. Integrated Sustainability Analysis of Atomic Layer Deposition for Microelectronics Manufacturing. *J. Manuf. Sci. Eng. Trans. ASME* **2010**, *132* (3), 0309181–0309187.
- (45) Wang, E.; Yuan, C. A Hybrid Life Cycle Assessment of Atomic Layer Deposition Process. *J. Clean. Prod.* **2014**, *74*, 145–154.
- (46) Ma, L.; Pan, D.; Xie, Y.; Yuan, C. Atomic Layer Deposition of Al₂O₃ Process Emissions. *RSC Adv.* **2015**, *5* (17), 12824–12829.
- (47) Pan, D.; Guan, D.; Jen, T. C.; Yuan, C. Atomic Layer Deposition Process Modeling and Experimental Investigation for Sustainable Manufacturing of Nano Thin Films. *J. Manuf. Sci. Eng. Trans. ASME* **2016**, *138* (10), 1–9.
- (48) Ma, L.; Pan, D.; Xie, Y.; Wang, F.; Yuan, C. Experimental Study of Process Emissions from Atomic Layer Deposition of Al₂O₃ under Various Temperatures and Purge Time. *J. Manuf. Sci. Eng. Trans. ASME* **2017**, *139* (5), 2–8.
- (49) Wang, F.; Li, T.; Zhang, H.-C.; Yuan, C. Y. *Exergy Analysis of Atomic Layer Deposition for Al₂O₃ Nano-Film Preparation*; Springer, 2013; pp 285–290.
- (50) ISO. 14040: Environmental Management-Life Cycle Assessment—Principles and Framework. *Int. Organ. Stand.* **2006**, *2006*, <https://www.iso.org/standard/37456.html>.
- (51) Díaz-Ramírez, M. C.; Ferreira, V. J.; García-Armingol, T.; López-Sabirón, A. M.; Ferreira, G. Environmental Assessment of Electrochemical Energy Storage Device Manufacturing to Identify Drivers for Attaining Goals of Sustainable Materials 4.0. *Sustainability* **2020**, *12* (1), 342.
- (52) Williams, E. Energy Intensity of Computer Manufacturing: Hybrid Assessment Combining Process and Economic Input- Output Methods. *Environ. Sci. Technol.* **2004**, *38* (22), 6166–6174.
- (53) Wiedmann, T.; Minx, J. A Definition of ‘Carbon Footprint.’ *Ecol. Econ. Res. Trends* **2008**, *1*, 1–11.
- (54) Wright, L. A.; Kemp, S.; Williams, I. ‘Carbon Footprinting’: Towards a Universally Accepted Definition. *Carbon Manag.* **2011**, *2* (1), 61–72.
- (55) Finkbeiner, M. Carbon Footprinting—Opportunities and Threats. *International Journal of Life Cycle Assessment*. **2009**, *14*, 91–94.
- (56) Yuan, C. Y.; Sheng, Y. Sustainable Scale-up Studies of Atomic Layer Deposition for Microelectronics Manufacturing. *Proc. 2010 IEEE Int. Symp. Sustain. Syst. Technol. ISSST 2010* **2010**, 53201, 1–6.
- (57) Stamford, L.; Azapagic, A. Environmental Impacts of Copper-indium-gallium-Selenide (CIGS) Photovoltaics and the Elimination of Cadmium through Atomic Layer Deposition. *Sci. Total Environ.* **2019**, *688*, 1092–1101.
- (58) Zieminska-Stolarska, A.; Pietrzak, M.; Zbicinski, I. Comparative Lca Analysis for Replacement of Materials to Reduce Environmental Impact. *Chem. Eng. Trans.* **2022**, *96*, 145–150.
- (59) Louwen, A.; Van Sark, W.; Schropp, R. E. I.; Turkenburg, W. C.; Faaij, A. P. C. Life-cycle Greenhouse Gas Emissions and Energy Payback Time of Current and Prospective Silicon Heterojunction Solar Cell Designs. *Prog. Photovolt. Res. Appl.* **2015**, *23* (10), 1406–1428.
- (60) Wang, F.; Zhu, N.; Li, T.; Zhang, H.-C. Material and Energy Efficiency Analysis of Low Pressure Chemical Vapor Deposition of TiO₂ Film. *Procedia Cirp* **2014**, *15*, 32–37.
- (61) DeBenedetti, B.; Grassini, S.; Maffia, L. Comparison between Eco-Profiles of Innovative PA-CVD and Traditional Galvanic Coatings. In *Proceedings of International Conference on Materials for Advanced Technologies ICMAT*; 2005; p 1.
- (62) Klocke, F.; Döbeler, B.; Binder, M.; Kramer, N.; Grüter, R.; Lung, D. Ecological Evaluation of PVD and CVD Coating Systems in Metal Cutting Processes. *11th Glob. Conf. Sustain. Manuf.* **2013**, *12* (3), 381–386.
- (63) Yuan, C.; Zhai, Q.; Dornfeld, D. A Three Dimensional System Approach for Environmentally Sustainable Manufacturing. *CIRP Ann. - Manuf. Technol.* **2012**, *61* (1), 39–42.
- (64) Yuan, C. Y.; Dornfeld, D. Environmental Performance Characterization of Atomic Layer Deposition. In *2008 IEEE International Symposium on Electronics and the Environment*; IEEE: San Francisco, CA, 2008; pp 1–6. DOI: 10.1109/ISEE.2008.4562943.
- (65) Chatzisisideris, M. D.; Espinosa, N.; Laurent, A.; Krebs, F. C. Ecodesign Perspectives of Thin-Film Photovoltaic Technologies: A Review of Life Cycle Assessment Studies. *Sol. Energy Mater. Sol. Cells* **2016**, *156*, 2–10.
- (66) Westkämper, E.; Alting, L.; Arndt, G. Life Cycle Management and Assessment: Approaches and Visions towards Sustainable Manufacturing. *Proc. Inst. Mech. Eng. Part B J. Eng. Manuf.* **2001**, *215* (5), 599–626.
- (67) de Marco, B. A.; Rechelo, B. S.; Tófoli, E. G.; Kogawa, A. C.; Salgado, H. R. N. Evolution of Green Chemistry and Its Multidimensional Impacts: A Review. *Saudi Pharm. J.* **2019**, *27* (1), 1–8.
- (68) Pedersen, H.; Barry, S. T.; Sundqvist, J. Green CVD—Toward a Sustainable Philosophy for Thin Film Deposition by Chemical Vapor Deposition. *J. Vac. Sci. Technol. A* **2021**, *39* (5), 051001.
- (69) Yuan, C. Y.; Zhang, T.; Rangarajan, A.; Dornfeld, D.; Ziemba, B.; Whitbeck, R. A Decision-Based Analysis of Compressed Air Usage Patterns in Automotive Manufacturing. *J. Manuf. Syst.* **2006**, *25* (4), 293–300.
- (70) Suzuki, G. J.; Leusink, F. R. M. Method and System for Refurbishing a Metal Carbonyl Precursor. WO2006104783A1, 2006.
- (71) Vahlas, C.; Caussat, B.; Gladfelter, W.; Senocq, F.; Gladfelter, E. Liquid and Solid Precursor Delivery Systems in Gas Phase Processes. *Recent Pat. Mater. Sci.* **2015**, *8* (2), 91–108.
- (72) Graniel, O.; Puigmartí-Luis, J.; Muñoz-Rojas, D. Liquid Atomic Layer Deposition as Emergent Technology for the Fabrication of Thin Films. *Dalton Trans.* **2021**, *50* (19), 6373–6381.
- (73) Aspinall, H. C.; Bickley, J. F.; Gaskell, J. M.; Jones, A. C.; Labat, G.; Chalker, P. R.; Williams, P. A. Precursors for MOCVD and ALD of Rare Earth Oxides- Complexes of the Early Lanthanides with a Donor-Functionalized Alkoxide Ligand. *Inorg. Chem.* **2007**, *46* (15), 5852–5860.
- (74) Potts, S. E. Precursor Synthesis and Chemical Vapour Deposition of Transition Metal Nitrides and Carbonitrides. Doctoral Thesis, University of London, January 2009.
- (75) Potts, S. E.; Profijt, H. B.; Roelofs, R.; Kessels, W. M. M. Room-Temperature ALD of Metal Oxide Thin Films by Energy-Enhanced ALD. *Chem. Vap. Depos.* **2013**, *19* (4–6), 125–133.
- (76) Mackus, A. J. M.; Garcia-alonso, D.; Knoops, H. C. M.; Bol, A. A.; Kessels, W. M. M. Room-Temperature Atomic Layer Deposition of Platinum. *Chem. Mater.* **2013**, *25* (9), 1769.
- (77) Profijt, H. B.; Potts, S. E.; van de Sanden, M. C. M.; Kessels, W. M. M. Plasma-Assisted Atomic Layer Deposition: Basics, Opportunities, and Challenges. *J. Vac. Sci. Technol. Vac. Surf. Films* **2011**, *29* (5), 050801.
- (78) Knoops, H. C. M.; Faraz, T.; Arts, K.; Kessels, W. M. M. Status and Prospects of Plasma-Assisted Atomic Layer Deposition. *J. Vac. Sci. Technol. Vac. Surf. Films* **2019**, *37* (3), 030902.
- (79) Poodt, P.; Cameron, D. C.; Dickey, E.; George, S. M.; Kuznetsov, V.; Parsons, G. N.; Roozeboom, F.; Sundaram, G.; Vermeer, A. Spatial Atomic Layer Deposition: A Route towards Further Industrialization of Atomic Layer Deposition. *J. Vac. Sci. Technol. Vac. Surf. Films* **2012**, *30* (1), 010802.
- (80) Hoye, R. L. Z.; Muñoz-Rojas, D.; Nelson, S. F.; Illiberi, A.; Poodt, P.; Roozeboom, F.; MacManus-Driscoll, J. L. Research Update: Atmospheric Pressure Spatial Atomic Layer Deposition of ZnO Thin Films: Reactors, Doping, and Devices. *APL Mater.* **2015**, *3* (4), 040701.

- (81) Muñoz-Rojas, D.; Maindrón, T.; Esteve, A.; Pierrat, F.; Kools, J. C. S.; Decams, J.-M. Speeding up the Unique Assets of Atomic Layer Deposition. *Mater. Today Chem.* **2019**, *12*, 96–120.
- (82) Kools, J. Modular Gas Injection Device. Patent US20160319426A1.
- (83) Kharissova, O. V.; Kharisov, B. I.; Oliva González, C. M.; Méndez, Y. P.; López, I. Greener Synthesis of Chemical Compounds and Materials. *R. Soc. Open Sci.* **2019**, *6* (11), 191378.
- (84) Asemave, K. *Alternative bio-derived chelating agents (chelants)*. PhD Report, University of York, 2015.
- (85) *Greenhouse Gas Protocol: Corporate Value Chain (Scope 3) Accounting and Reporting Standard: Supplement to the GHG Protocol Corporate Accounting and Reporting Standard*; World Resources Institute; World Business Council for Sustainable Development: Washington, DC; Geneva, Switzerland, 2011.
- (86) Sheldon, R. A. Fundamentals of Green Chemistry: Efficiency in Reaction Design. *Chem. Soc. Rev.* **2012**, *41* (4), 1437–1451.
- (87) Mackus, A. J. M.; Merckx, M. J. M.; Kessels, W. M. M. From the Bottom-Up: Toward Area-Selective Atomic Layer Deposition with High Selectivity. *Chem. Mater.* **2019**, *31* (1), 2–12.
- (88) Weber, M. J.; Verheijen, M. A.; Bol, A. A.; Kessels, W. M. M. Sub-Nanometer Dimensions Control of Core/Shell Nanoparticles Prepared by Atomic Layer Deposition. *Nanotechnology* **2015**, *26* (9), 094002.
- (89) Lu, J.; Low, K.-B.; Lei, Y.; Libera, J. A.; Nicholls, A.; Stair, P. C.; Elam, J. W. Toward Atomically-Precise Synthesis of Supported Bimetallic Nanoparticles Using Atomic Layer Deposition. *Nat. Commun.* **2014**, *5*, 3264.
- (90) Weber, M. J.; MacKus, A. J. M.; Verheijen, M. A.; van der Marel, C.; Kessels, W. M. M. Supported Core/Shell Bimetallic Nanoparticles Synthesis by Atomic Layer Deposition. *Chem. Mater.* **2012**, *24* (15), 2973–2977.
- (91) Langerreis, E.; Heil, S. B. S.; Knoops, H. C. M.; Keuning, W.; Van de Sanden, M. C. M.; Kessels, W. M. M. In Situ Spectroscopic Ellipsometry as a Versatile Tool for Studying Atomic Layer Deposition. *J. Phys. Appl. Phys.* **2009**, *42* (7), 073001.
- (92) Leick, N.; Weber, J. W.; Mackus, A. J. M.; Weber, M. J.; Van de Sanden, M. C. M.; Kessels, W. M. M. In Situ Spectroscopic Ellipsometry during Atomic Layer Deposition of Pt, Ru and Pd. *J. Phys. Appl. Phys.* **2016**, *49* (11), 115504.
- (93) Elam, J. W.; Groner, M. D.; George, S. M. Viscous Flow Reactor with Quartz Crystal Microbalance for Thin Film Growth by Atomic Layer Deposition. *Rev. Sci. Instrum.* **2002**, *73* (8), 2981–2987.
- (94) Mai, L.; Boysen, N.; Zanders, D.; de Los Arcos, T.; Mitschker, F.; Mallick, B.; Grundmeier, G.; Awakowicz, P.; Devi, A. Potential Precursor Alternatives to the Pyrophoric Trimethylaluminum for the Atomic Layer Deposition of Aluminium Oxide. *Chem.—Eur. J.* **2019**, *25* (31), 7489–7500.
- (95) Potts, S. E.; Dingemans, G.; Lachaud, C.; Kessels, W. M. M. Plasma-Enhanced and Thermal Atomic Layer Deposition of Al₂O₃ Using Dimethylaluminum Isopropoxide, [Al(CH₃)₂(μ-OiPr)]₂, as an Alternative Aluminum Precursor. *J. Vac. Sci. Technol. Vac. Surf. Films* **2012**, *30* (2), 021505.
- (96) Granneman, E.; Fischer, P.; Pierreux, D.; Terhorst, H.; Zagwijn, P. Batch ALD: Characteristics, Comparison with Single Wafer ALD, and Examples. *Surf. Coat. Technol.* **2007**, *201* (22–23), 8899–8907.
- (97) King, D. M.; Spencer II, J. A.; Liang, X.; Hakim, L. F.; Weimer, A. W. Atomic Layer Deposition on Particles Using a Fluidized Bed Reactor with in Situ Mass Spectrometry. *Surf. Coat. Technol.* **2007**, *201* (22–23), 9163–9171.
- (98) Fryauf, D. M.; Phillips, A. C.; Bolte, M. J.; Feldman, A.; Tompa, G. S.; Kobayashi, N. P. Scaling Atomic Layer Deposition to Astronomical Optic Sizes: Low-Temperature Aluminum Oxide in a Meter-Sized Chamber. *ACS Appl. Mater. Interfaces* **2018**, *10* (48), 41678–41689.
- (99) Thiruppathiraj, S.; Ryu, S.-M.; Uh, J.; Raja, L. L. Direct-Simulation Monte Carlo Modeling of Reactor-Scale Gas-Dynamic Phenomena in a Multiwafer Atomic-Layer Deposition Batch Reactor. *J. Vac. Sci. Technol. A* **2021**, *39* (5), 052404.
- (100) Zhang, Y.; Ding, Y.; Christofides, P. D. Multiscale Computational Fluid Dynamics Modeling of Thermal Atomic Layer Deposition with Application to Chamber Design. *Chem. Eng. Res. Des.* **2019**, *147*, 529–544.
- (101) Kools, J. High Throughput Atomic Layer Deposition for Encapsulation of Large Area Electronics. *ECS Trans.* **2011**, *41* (2), 195.
- (102) Travis, C. D.; Adomaitis, R. A. Dynamic Modeling for the Design and Cyclic Operation of an Atomic Layer Deposition (ALD) Reactor. *Processes* **2013**, *1* (2), 128–152.
- (103) World Semiconductor Council (WSC). <http://www.semiconductorcouncil.org/> (accessed 2022-07-08).
- (104) Williams, E. D.; Ayres, R. U.; Heller, M. The 1.7 Kilogram Microchip: Energy and Material Use in the Production of Semiconductor Devices. *Environ. Sci. Technol.* **2002**, *36* (24), 5504–5510.
- (105) *Statistics for Industry Groups and Industries, Annual Survey of Manufacturers*; U.S. Census Bureau: Washington, DC, 2005.
- (106) Boyd, S. B. *Life-Cycle Assessment of Semiconductors*; Springer: New York, 2011.
- (107) Knapas, K.; Ritala, M. In Situ Studies on Reaction Mechanisms in Atomic Layer Deposition. *Crit. Rev. Solid State Mater. Sci.* **2013**, *38* (3), 167–202.
- (108) Chatmaneerungcharoen, B.; Fraccaroli, M.; Martin, F.; Guedj, C.; Nolot, E.; Rouchon, D.; Vaxelaire, N.; Templier, R.; Grenier, A.; Papon, A.-M. Synthesis of In-Plane Oriented Tin Sulfides by Organosulfur-Mediated Sulfurization of Ultrathin SnO₂ Films. *Chem. Mater.* **2022**, *34* (13), 5842–5851.
- (109) Goldstein, D. N.; McCormick, J. A.; George, S. M. Al₂O₃ Atomic Layer Deposition with Trimethylaluminum and Ozone Studied by In Situ Transmission FTIR Spectroscopy and Quadrupole Mass Spectrometry. *J. Phys. Chem. C* **2008**, *112* (49), 19530–19539.
- (110) Mackus, A. J. M.; Heil, S. B. S.; Langereis, E.; Knoops, H. C. M.; Van de Sanden, M. C. M.; Kessels, W. M. M. Optical Emission Spectroscopy as a Tool for Studying, Optimizing, and Monitoring Plasma-Assisted Atomic Layer Deposition Processes. *J. Vac. Sci. Technol. Vac. Surf. Films* **2010**, *28* (1), 77–87.
- (111) Dendooven, J.; Deduytsche, D.; Musschoot, J.; Vanmeirhaeghe, R. L.; Detavernier, C. Modeling the Conformality of Atomic Layer Deposition: The Effect of Sticking Probability. *J. Electrochem. Soc.* **2009**, *156* (4), 63.
- (112) Yazdani, N.; Chawla, V.; Edwards, E.; Wood, V.; Park, H. G.; Utke, I. Modeling and Optimization of Atomic Layer Deposition Processes on Vertically Aligned Carbon Nanotubes. *Beilstein J. Nanotechnol.* **2014**, *5* (1), 234–244.
- (113) Gayle, A. J.; Berquist, Z. J.; Chen, Y.; Hill, A. J.; Hoffman, J. Y.; Bielinski, A. R.; Lenert, A.; Dasgupta, N. P. Tunable Atomic Layer Deposition into Ultra-High-Aspect-Ratio (> 60000:1) Aerogel Monoliths Enabled by Transport Modeling. *Chem. Mater.* **2021**, *33* (14), 5572–5583.
- (114) Elliott, S. D. Atomic-Scale Simulation of ALD Chemistry. *Semicond. Sci. Technol.* **2012**, *27* (7), 074008.
- (115) Alam, M. A.; Green, M. L. Mathematical Description of Atomic Layer Deposition and Its Application to the Nucleation and Growth of HfO₂ Gate Dielectric Layers. *J. Appl. Phys.* **2003**, *94* (5), 3403–3413.
- (116) Puurunen, R. L.; Vandervorst, W. Island Growth as a Growth Mode in Atomic Layer Deposition: A Phenomenological Model. *J. Appl. Phys.* **2004**, *96* (12), 7686–7695.
- (117) Lim, J.-W.; Park, H.-S.; Kang, S.-W. Kinetic Modeling of Film Growth Rate in Atomic Layer Deposition. *J. Electrochem. Soc.* **2001**, *148* (6), C403.
- (118) Travis, C. D.; Adomaitis, R. A. Modeling ALD Surface Reaction and Process Dynamics Using Absolute Reaction Rate Theory. *Chem. Vap. Depos.* **2013**, *19* (1–3), 4–14.
- (119) Ding, Y.; Zhang, Y.; Ren, Y. M.; Orkoulas, G.; Christofides, P. D. Machine Learning-Based Modeling and Operation for ALD of SiO₂ Thin-Films Using Data from a Multiscale CFD Simulation. *Chem. Eng. Res. Des.* **2019**, *151*, 131–145.
- (120) Magness, D.; Justus, E.; Timalisina, B.; Wu, J.; Sakidja, R. Applications of Kinetic Monte Carlo Simulations and Machine

Learning to Model Atomic Layer Deposition (ALD) of Metal Oxides. *Bull. Am. Phys. Soc.* **2021**, *66*, 1.

(121) Paulson, N. H.; Yanguas-Gil, A.; Abuomar, O. Y.; Elam, J. W. Intelligent Agents for the Optimization of Atomic Layer Deposition. *ACS Appl. Mater. Interfaces* **2021**, *13* (14), 17022–17033.

(122) Yanguas-Gil, A. Exploring the Potential of Machine Learning and AI for ALD Process Optimization. In *ECS Meeting Abstracts*; IOP Publishing, 2021; p 875.

(123) Suntola, T.; Antson, J. Method for Producing Compound Thin Films. Patent US4058430A, November 15, 1977.

(124) Muñoz-Rojas, D.; Nguyen, V. H.; Huerta, C. M.; Jiménez, C.; Bellet, D. Spatial Atomic Layer Deposition. *Chem. Vap. Depos. Nanotechnol. Intechopen* **2019**, *1*, 1–26.

(125) 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.* **2008**, *92* (19), 192101.

(126) Dickey, E.; Barrow, W. A. High Rate Roll to Roll Atomic Layer Deposition, and Its Application to Moisture Barriers on Polymer Films. *J. Vac. Sci. Technol. Vac. Surf. Films* **2012**, *30* (2), 021502.

(127) van Ommen, J. R.; Kooijman, D.; Niet, M. de; Talebi, M.; Goulas, A. Continuous Production of Nanostructured Particles Using Spatial Atomic Layer Deposition. *J. Vac. Sci. Technol. Vac. Surf. Films* **2015**, *33* (2), 021513.

(128) de la Huerta, C. A. M.; Nguyen, V. H.; Sekkat, A.; Crivello, C.; Toldra-Reig, F.; Veiga, P. B.; Quessada, S.; Jimenez, C.; Muñoz-Rojas, D. Gas-Phase 3D Printing of Functional Materials. *Adv. Mater. Technol.* **2020**, *5* (12), 2000657.

(129) Toldra-Reig, F.; Lausecker, C.; Weber, M.; Bechelany, M.; Muñoz-Rojas, D. Custom 3D Printed Spatial Atomic Layer Deposition Manifold for the Coating of Tubular Membranes. *ACS Sustain. Chem. Eng.* **2022**, *10* (43), 14112–14118.

(130) Yersak, A. S.; Lee, Y. C.; Spencer, J. A.; Groner, M. D. Atmospheric Pressure Spatial Atomic Layer Deposition Web Coating with in Situ Monitoring of Film Thickness. *J. Vac. Sci. Technol. Vac. Surf. Films* **2014**, *32* (1), 01A130.

(131) Ryan Fitzpatrick, P.; Gibbs, Z. M.; George, S. M. Evaluating Operating Conditions for Continuous Atmospheric Atomic Layer Deposition Using a Multiple Slit Gas Source Head. *J. Vac. Sci. Technol. Vac. Surf. Films* **2012**, *30* (1), 01A136.

(132) Wang, X.; Li, Y.; Lin, J.; Shan, B.; Chen, R. Modular Injector Integrated Linear Apparatus with Motion Profile Optimization for Spatial Atomic Layer Deposition. *Rev. Sci. Instrum.* **2017**, *88* (11), 115108.

(133) Sharma, K.; Hall, R. A.; George, S. M. Spatial Atomic Layer Deposition on Flexible Substrates Using a Modular Rotating Cylinder Reactor. *J. Vac. Sci. Technol. Vac. Surf. Films* **2015**, *33* (1), 01A132.

(134) Franke, S.; Baumkötter, M.; Monka, C.; Raabe, S.; Caspary, R.; Johannes, H.-H.; Kowalsky, W.; Beck, S.; Pucci, A.; Gargouri, H. Alumina Films as Gas Barrier Layers Grown by Spatial Atomic Layer Deposition with Trimethylaluminum and Different Oxygen Sources. *J. Vac. Sci. Technol. Vac. Surf. Films* **2017**, *35* (1), 01B117.

(135) Kundrata, I.; Barr, M. K.; Tymek, S.; Döhler, D.; Hudec, B.; Brüner, P.; Vanko, G.; Precner, M.; Yokosawa, T.; Spiecker, E.; et al. Additive Manufacturing in Atomic Layer Processing Mode (Small Methods 5/2022). *Small Methods* **2022**, *6* (5), 2270028.

(136) Mistry, K.; Jones, A.; Kao, M.; Yeow, T. W.-K.; Yavuz, M.; Musselman, K. P. In-Situ Observation of Nucleation and Property Evolution in Films Grown with an Atmospheric Pressure Spatial Atomic Layer Deposition System. *Nano Express* **2020**, *1* (1), 010045.

(137) Midani, L.; Ben-Yahia, W.; Salles, V.; Marichy, C. Nanofabrication via Maskless Localized Atomic Layer Deposition of Patterned Nanoscale Metal Oxide Films. *ACS Appl. Nano Mater.* **2021**, *4* (11), 11980–11988.

(138) Poodt, P.; van Lieshout, J.; Illiberi, A.; Knaapen, R.; Roozeboom, F.; van Asten, A. On the Kinetics of Spatial Atomic Layer Deposition. *J. Vac. Sci. Technol. Vac. Surf. Films* **2013**, *31* (1), 01A108.

(139) Pan, D.; Jen, T.-C.; Yuan, C. Effects of Gap Size, Temperature and Pumping Pressure on the Fluid Dynamics and Chemical Kinetics of

in-Line Spatial Atomic Layer Deposition of Al₂O₃. *Int. J. Heat Mass Transfer* **2016**, *96*, 189–198.

(140) Deng, Z.; He, W.; Duan, C.; Chen, R.; Shan, B. Mechanistic Modeling Study on Process Optimization and Precursor Utilization with Atmospheric Spatial Atomic Layer Deposition. *J. Vac. Sci. Technol. Vac. Surf. Films* **2016**, *34* (1), 01A108.

(141) Li, Z.; Cao, K.; Li, X.; Chen, R. Computational Fluid Dynamics Modeling of Spatial Atomic Layer Deposition on Microgroove Substrates. *Int. J. Heat Mass Transfer* **2021**, *181*, 121854.

(142) Masse de la Huerta, C.; Nguyen, V. H.; Dedulle, J.-M.; Bellet, D.; Jiménez, C.; Muñoz-Rojas, D. Influence of the Geometric Parameters on the Deposition Mode in Spatial Atomic Layer Deposition: A Novel Approach to Area-Selective Deposition. *Coatings* **2019**, *9* (1), 5.

(143) Poodt, P.; Illiberi, A.; Roozeboom, F. The Kinetics of Low-Temperature Spatial Atomic Layer Deposition of Aluminum Oxide. *Thin Solid Films* **2013**, *532*, 22–25.

(144) Nguyen, V. H.; Sekkat, A.; Jimenez, C.; Munoz, D.; Bellet, D.; Munoz-Rojas, D. Impact of Precursor Exposure in Spatial Atomic Layer Deposition on Process Efficiency and Film Properties. *Chem. Eng. J.* **2021**, *403*, 126234.

(145) Cong, W.; Li, Z.; Cao, K.; Feng, G.; Chen, R. Transient Analysis and Process Optimization of the Spatial Atomic Layer Deposition Using the Dynamic Mesh Method. *Chem. Eng. Sci.* **2020**, *217*, 115513.

(146) Jones, A.; Mistry, K.; Kao, M.; Shahin, A.; Yavuz, M.; Musselman, K. P. In-Situ Spatial and Temporal Electrical Characterization of ZnO Thin Films Deposited by Atmospheric Pressure Chemical Vapour Deposition on Flexible Polymer Substrates. *Sci. Rep.* **2020**, *10* (1), 1–10.

(147) Mione, M. A.; Engeln, R.; Vandalon, V.; Kessels, W. M. M.; Roozeboom, F. Infrared and Optical Emission Spectroscopy Study of Atmospheric Pressure Plasma-Enhanced Spatial ALD of Al₂O₃. *Appl. Phys. Lett.* **2019**, *115* (8), 083101.

(148) Mione, M. A.; Vandalon, V.; Mameli, A.; Kessels, W. M. M.; Roozeboom, F. Atmospheric-Pressure Plasma-Enhanced Spatial ALD of SiO₂ Studied by Gas-Phase Infrared and Optical Emission Spectroscopy. *J. Phys. Chem. C* **2021**, *125* (45), 24945–24957.

(149) van den Bruele, F. J.; Smets, M.; Illiberi, A.; Creighton, Y.; Buskens, P.; Roozeboom, F.; Poodt, P. Atmospheric Pressure Plasma Enhanced Spatial ALD of Silver. *J. Vac. Sci. Technol. Vac. Surf. Films* **2015**, *33* (1), 01A131.

(150) Mione, M. A.; Katsouras, I.; Creighton, Y.; Van Boekel, W.; Maas, J.; Gelinck, G.; Roozeboom, F.; Illiberi, A. Atmospheric Pressure Plasma Enhanced Spatial ALD of ZrO₂ for Low-Temperature, Large-Area Applications. *ECS J. Solid State Sci. Technol.* **2017**, *6* (12), N243.

(151) Creighton, Y.; Illiberi, A.; Mione, A.; Van Boekel, W.; Debernardi, N.; Seitz, M.; van den Bruele, F.; Poodt, P.; Roozeboom, F. Plasma-Enhanced Atmospheric-Pressure Spatial ALD of Al₂O₃ and ZrO₂. *ECS Trans.* **2016**, *75* (6), 11.

(152) Boysen, N.; Hasselmann, T.; Karle, S.; Rogalla, D.; Theirich, D.; Winter, M.; Riedl, T.; Devi, A. An N-Heterocyclic Carbene Based Silver Precursor for Plasma-Enhanced Spatial Atomic Layer Deposition of Silver Thin Films at Atmospheric Pressure. *Angew. Chem., Int. Ed.* **2018**, *57* (49), 16224–16227.

(153) Zoubian, F.; Rabat, H.; Aubry, O.; Dumuis, N.; Dozias, S.; Muñozrojas, D.; Hong, D. *Development and Characterization of an Atmospheric Pressure Plasma Reactor Compatible with Spatial ALD*; IOP Publishing, 2019; Vol. 1243, p 012002.

(154) Boysen, N.; Misimi, B.; Muriqi, A.; Wree, J.-L.; Hasselmann, T.; Rogalla, D.; Haeger, T.; Theirich, D.; Nolan, M.; Riedl, T.; Devi, A. A Carbene Stabilized Precursor for the Spatial Atomic Layer Deposition of Copper Thin Films. *Chem. Commun.* **2020**, *56* (89), 13752–13755.

(155) Illiberi, A.; Katsouras, I.; Gazibegovic, S.; Cobb, B.; Nekovic, E.; van Boekel, W.; Frijters, C.; Maas, J.; Roozeboom, F.; Creighton, Y.; et al. Atmospheric Plasma-Enhanced Spatial-ALD of InZnO for High Mobility Thin Film Transistors. *J. Vac. Sci. Technol. Vac. Surf. Films* **2018**, *36* (4), 04F401.

(156) Loho, C.; Darbandi, A. J.; Djenadic, R.; Clemens, O.; Hahn, H. CO₂-Laser Flash Evaporation as Novel CVD Precursor Delivery

- System for Functional Thin Film Growth. *Chem. Vap. Depos.* **2014**, *20* (4–5–6), 152–160.
- (157) *Environmental Impacts of Air Separation Units*; European Industrial Gases Association AISBL: Brussels, 2017.
- (158) Puurunen, R. L. Surface Chemistry of Atomic Layer Deposition: A Case Study for the Trimethylaluminum/Water Process. *J. Appl. Phys.* **2005**, *97* (12), 121301.
- (159) Pasynkiewicz, S.; Boleslawski, M. Synthesis of Trimethylaluminum. *J. Organomet. Chem.* **1970**, *25* (1), 29–32.
- (160) Drissi-Amraoui, S. Trimethylaluminum. *Synlett* **2015**, *26* (10), 1424–1425.
- (161) Krause, M. J.; Orlandi, F.; Saurage, A. T.; Zietz, J. R., Jr Aluminum Compounds, Organic. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley, 2000. DOI: 10.1002/14356007.a01_543.
- (162) Leskelä, M.; Ritala, M. Atomic Layer Deposition (ALD): From Precursors to Thin Film Structures. *Thin Solid Films* **2002**, *409* (1), 138–146.
- (163) Devi, A. 'Old Chemistries' for New Applications: Perspectives for Development of Precursors for MOCVD and ALD Applications. *Coord. Chem. Rev.* **2013**, *257* (23), 3332–3384.
- (164) Semerano, G.; Riccoboni, L. Beitrag Zur Kenntnis Der Metallorganischen Verbindungen, I. Mitteil.: Silbermethyl, Silber-Äthyl Und Silber- *n*-Propyl. *Berichte Dtsch. Chem. Ges. B Ser.* **1941**, *74* (7), 1089–1099.
- (165) Pedersen, H.; Barry, S. T.; Sundqvist, J. Green CVD—Toward a Sustainable Philosophy for Thin Film Deposition by Chemical Vapor Deposition. *J. Vac. Sci. Technol. A* **2021**, *39* (5), 051001.
- (166) Clarke, C. J.; Tu, W.-C.; Levers, O.; Bröhl, A.; Hallett, J. P. Green and Sustainable Solvents in Chemical Processes. *Chem. Rev.* **2018**, *118* (2), 747–800.
- (167) Sheldon, R. A. The E Factor 25 Years on: The Rise of Green Chemistry and Sustainability. *Green Chem.* **2017**, *19* (1), 18–43.
- (168) Sheldon, R. A. The E Factor: Fifteen Years On. *Green Chem.* **2007**, *9* (12), 1273.
- (169) Sheldon, R. A. Organic Synthesis - Past, Present and Future. *Chem. Ind.* **1992**, *23*, 903–906.
- (170) Boysen, N.; Philip, A.; Rogalla, D.; Karppinen, M.; Devi, A. Role of Anionic Backbone in NHC-Stabilized Coinage Metal Complexes: New Precursors for Atomic Layer Deposition. *Chem. - Eur. J.* **2022**, *28* (16), e202103798.
- (171) Sheldon, R. A. Green Solvents for Sustainable Organic Synthesis: State of the Art. *Green Chem.* **2005**, *7* (5), 267.
- (172) *Inorganic Syntheses*; Holtzlaw, H. F., Ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 1966. DOI: 10.1002/9780470132395.
- (173) Hämäläinen, J.; Munnik, F.; Hatanpää, T.; Holopainen, J.; Ritala, M.; Leskelä, M. Study of Amorphous Lithium Silicate Thin Films Grown by Atomic Layer Deposition. *J. Vac. Sci. Technol. Vac. Surf. Films* **2012**, *30* (1), 01A106.
- (174) Byrne, F. P.; Jin, S.; Paggiola, G.; Petchey, T. H. M.; Clark, J. H.; Farmer, T. J.; Hunt, A. J.; Robert McElroy, C.; Sherwood, J. Tools and Techniques for Solvent Selection: Green Solvent Selection Guides. *Sustain. Chem. Process.* **2016**, *4* (1), 7.
- (175) Trost, B. The Atom Economy—A Search for Synthetic Efficiency. *Science* **1991**, *254* (5037), 1471–1477.
- (176) Beillard, A.; Métro, T.-X.; Bantreil, X.; Martinez, J.; Lamaty, F. Cu(0), O₂ and Mechanical Forces: A Saving Combination for Efficient Production of Cu-NHC Complexes. *Chem. Sci.* **2017**, *8* (2), 1086–1089.
- (177) Do, J.-L.; Friščić, T. Mechanochemistry: A Force of Synthesis. *ACS Cent. Sci.* **2017**, *3* (1), 13–19.
- (178) James, S. L.; Adams, C. J.; Bolm, C.; Braga, D.; Collier, P.; Friščić, T.; Grepioni, F.; Harris, K. D. M.; Hyett, G.; Jones, W.; Krebs, A.; Mack, J.; Maini, L.; Orpen, A. G.; Parkin, I. P.; Shearouse, W. C.; Steed, J. W.; Waddell, D. C. Mechanochemistry: Opportunities for New and Cleaner Synthesis. *Chem. Soc. Rev.* **2012**, *41* (1), 413–447.
- (179) Atom Economy. https://commons.wikimedia.org/wiki/File:Atom_economy_V3_en.svg (12/01/2023).
- (180) Beer, S. M. J.; Boysen, N.; Muriqi, A.; Zanders, D.; Berning, T.; Rogalla, D.; Bock, C.; Nolan, M.; Devi, A. A Study on the Influence of Ligand Variation on Formamidinate Complexes of Yttrium: New Precursors for Atomic Layer Deposition of Yttrium Oxide. *Dalton Trans.* **2021**, *50* (37), 12944–12956.
- (181) Boysen, N.; Zanders, D.; Berning, T.; Beer, S. M. J.; Rogalla, D.; Bock, C.; Devi, A. Atomic Layer Deposition of Dielectric Y₂O₃ Thin Films from a Homoleptic Yttrium Formamidinate Precursor and Water. *RSC Adv.* **2021**, *11* (5), 2565–2574.
- (182) Kim, S. B.; Jayaraman, A.; Chua, D.; Davis, L. M.; Zheng, S.; Zhao, X.; Lee, S.; Gordon, R. G. Obtaining a Low and Wide Atomic Layer Deposition Window (150–275 °C) for In₂O₃ Films Using an In^{III} Amidinate and H₂O. *Chem. - Eur. J.* **2018**, *24* (38), 9525–9529.
- (183) Taylor, E. C.; Ehrhart, W. A. A Convenient Synthesis of Formamidinate and Acetamidinate Acetate. *J. Am. Chem. Soc.* **1960**, *82* (12), 3138–3141.
- (184) Dunsford, J. J.; Tromp, D. S.; Cavell, K. J.; Elsevier, C. J.; Kariuki, B. M. N-Alkyl Functionalised Expanded Ring N-Heterocyclic Carbene Complexes of Rhodium(i) and Iridium(i): Structural Investigations and Preliminary Catalytic Evaluation. *Dalton Trans.* **2013**, *42* (20), 7318.
- (185) Ojima, I.; Inaba, S. Reduction of Isocyanates and Carbodiimides via Hydrosilylation. *J. Organomet. Chem.* **1977**, *140* (1), 97–111.
- (186) Multia, J.; Khayami, A.; Heiska, J.; Karppinen, M. Low-Pressure Thermogravimetric Analysis for Finding Sublimation Temperatures for Organic Precursors in Atomic/Molecular Layer Deposition. *J. Vac. Sci. Technol. A* **2020**, *38* (5), 052406.
- (187) Lowe, D. Trimethylaluminum Explosion in Massachusetts. *Science*, January 7, 2016. <https://www.science.org/content/blog-post/trimethylaluminum-explosion-massachusetts> (accessed 2022-04-04).
- (188) Die Gefahrstoffschnellauskunft Informiert Zu Trimethylaluminium. *Umweltbundesamt*. <https://www.umweltbundesamt.de/themen/die-gefahrstoffschnellauskunft-informiert-zu> (accessed 2022-04-04).
- (189) Cao, L.; Mattelaer, F.; Sajavaara, T.; Dendooven, J.; Detavernier, C. A Liquid Alkoxide Precursor for the Atomic Layer Deposition of Aluminium Oxide Films. *J. Vac. Sci. Technol. A* **2020**, *38* (2), 022417.
- (190) Cho, W.; Sung, K.; An, K.-S.; Sook Lee, S.; Chung, T.-M.; Kim, Y. Atomic Layer Deposition of Al₂O₃ Thin Films Using Dimethylaluminum Isopropoxide and Water. *J. Vac. Sci. Technol. Vac. Surf. Films* **2003**, *21* (4), 1366–1370.
- (191) Hiltunen, L.; Kattelus, H.; Leskelä, M.; Mäkelä, M.; Niinistö, L.; Nykänen, E.; Soininen, P.; Tiittä, M. Growth and Characterization of Aluminium Oxide Thin Films Deposited from Various Source Materials by Atomic Layer Epitaxy and Chemical Vapor Deposition Processes. *Mater. Chem. Phys.* **1991**, *28* (4), 379–388.
- (192) Potts, S. E.; Dingemans, G.; Lachaud, C.; Kessels, W. M. M. Plasma-Enhanced and Thermal Atomic Layer Deposition of Al₂O₃ Using Dimethylaluminum Isopropoxide, [Al(CH₃)₂(μ-OⁱPr)]₂, as an Alternative Aluminium Precursor. *J. Vac. Sci. Technol. Vac. Surf. Films* **2012**, *30* (2), 021505.
- (193) Tiittä, M.; Nykänen, E.; Soininen, P.; Niinistö, L.; Leskelä, M.; Lappalainen, R. Preparation and Characterization of Phosphorus-Doped Aluminium Oxide Thin Films. *Mater. Res. Bull.* **1998**, *33* (9), 1315–1323.
- (194) Cho, W.-T.; Kiwhan, S.; Kim, Y. Preparation of Al₂O₃ Thin Films by Atomic Layer Deposition Using Dimethylaluminum Isopropoxide and Water and Their Reaction Mechanisms. *Bull. Korean Chem. Soc.* **2003**, *24* (11), 1659–1663.
- (195) Xia, X.; Taylor, A.; Zhao, Y.; Guldin, S.; Blackman, C. Use of a New Non-Pyrophoric Liquid Aluminium Precursor for Atomic Layer Deposition. *Materials* **2019**, *12* (9), 1429.
- (196) Hashemi, F. S. M.; Cao, L.; Mattelaer, F.; Sajavaara, T.; van Ommen, J. R.; Detavernier, C. Aluminium Tri-Isopropoxide as an Alternative Precursor for Atomic Layer Deposition of Aluminium Oxide Thin Films. *J. Vac. Sci. Technol. A* **2019**, *37* (4), 040901.
- (197) Mai, L.; Boysen, N.; Zanders, D.; de los Arcos, T.; Mitschker, F.; Mallick, B.; Grundmeier, G.; Awakowicz, P.; Devi, A. Potential Precursor Alternatives to the Pyrophoric Trimethylaluminum for the Atomic Layer Deposition of Aluminium Oxide. *Chem. - Eur. J.* **2019**, *25* (31), 7489–7500.

- (198) Mai, L.; Gebhard, M.; de los Arcos, T.; Giner, I.; Mitschker, F.; Winter, M.; Parala, H.; Awakowicz, P.; Grundmeier, G.; Devi, A. Unearthing [3-(Dimethylamino)Propyl]Aluminum(III) Complexes as Novel Atomic Layer Deposition (ALD) Precursors for Al_2O_3 : Synthesis, Characterization and ALD Process Development. *Chem. - Eur. J.* **2017**, *23* (45), 10768–10772.
- (199) Katamreddy, R.; Inman, R.; Jursich, G.; Soulet, A.; Takoudis, C. ALD and Characterization of Aluminum Oxide Deposited on Si(100) Using Tris(Diethylamino) Aluminum and Water Vapor. *J. Electrochem. Soc.* **2006**, *153* (10), C701.
- (200) Majumder, P.; Katamreddy, R.; Takoudis, C. Atomic Layer Deposited Ultrathin HfO_2 and $\text{Al}[\text{Sub } 2]\text{O}[\text{Sub } 3]$ Films as Diffusion Barriers in Copper Interconnects. *Electrochem. Solid-State Lett.* **2007**, *10* (10), H291.
- (201) Katamreddy, R.; Inman, R.; Jursich, G.; Soulet, A.; Takoudis, C. Atomic Layer Deposition of HfO_2 , Al_2O_3 , and HfAlO_x Using O_3 and Metal(Diethylamino) Precursors. *J. Mater. Res.* **2007**, *22* (12), 3455–3464.
- (202) Katamreddy, R.; Inman, R.; Jursich, G.; Soulet, A.; Takoudis, C. Controlling Interfacial Reactions between HfO_2 and Si Using Ultrathin Al_2O_3 Diffusion Barrier Layer. *Appl. Phys. Lett.* **2006**, *89* (26), 262906.
- (203) Katamreddy, R.; Inman, R.; Jursich, G.; Soulet, A.; Takoudis, C. Effect of Film Composition and Structure on the Crystallization Point of Atomic Layer Deposited HfAlO_x Using Metal (Diethylamino) Precursors and Ozone. *Acta Mater.* **2008**, *56* (4), 710–718.
- (204) Majumder, P.; Katamreddy, R.; Takoudis, C. Effect of Film Thickness on the Breakdown Temperature of Atomic Layer Deposited Ultrathin HfO_2 and Al_2O_3 Diffusion Barriers in Copper Metallization. *J. Cryst. Growth* **2007**, *309* (1), 12–17.
- (205) Katamreddy, R.; Inman, R.; Jursich, G.; Soulet, A.; Nicholls, A.; Takoudis, C. Post Deposition Annealing of Aluminum Oxide Deposited by Atomic Layer Deposition Using Tris(Diethylamino)-Aluminum and Water Vapor on Si(100). *Thin Solid Films* **2007**, *515* (17), 6931–6937.
- (206) Wade, C. R.; Silvernail, C.; Banerjee, C.; Soulet, A.; McAndrew, J.; Belot, J. A. Tris(Dialkylamino)Aluminums: Syntheses, Characterization, Volatility Comparison and Atomic Layer Deposition of Alumina Thin Films. *Mater. Lett.* **2007**, *61* (29), 5079–5082.
- (207) Buttera, S. C.; Mandia, D. J.; Barry, S. T. Tris(Dimethylamido)-Aluminum(III): An Overlooked Atomic Layer Deposition Precursor. *J. Vac. Sci. Technol. Vac. Surf. Films* **2017**, *35* (1), 01B128.
- (208) Hiltunen, L.; Kattelus, H.; Leskelä, M.; Mäkelä, M.; Niinistö, L.; Nykänen, E.; Soininen, P.; Tiittä, M. Growth and Characterization of Aluminium Oxide Thin Films Deposited from Various Source Materials by Atomic Layer Epitaxy and Chemical Vapor Deposition Processes. *Mater. Chem. Phys.* **1991**, *28* (4), 379–388.
- (209) Kattelus, H.; Ylilampi, M.; Saarihahti, J.; Antson, J.; Lindfors, S. Layered Tantalum-Aluminum Oxide Films Deposited by Atomic Layer Epitaxy. *Thin Solid Films* **1993**, *225* (1–2), 296–298.
- (210) Ritala, M.; Saloniemi, H.; Leskelä, M.; Prohaska, T.; Friedbacher, G.; Grasserbauer, M. Studies on the Morphology of Al_2O_3 Thin Films Grown by Atomic Layer Epitaxy. *Thin Solid Films* **1996**, *286* (1–2), 54–58.
- (211) *CRC Handbook of Chemistry and Physics: A Ready-Reference Book of Chemical and Physical Data*, 92nd ed., 2011–2012.; Haynes, W. M.; Lide, D. R., Eds.; CRC Press: Boca Raton, FL, 2011.
- (212) Ovanesyan, R. A.; Filatova, E. A.; Elliott, S. D.; Hausmann, D. M.; Smith, D. C.; Agarwal, S. Atomic Layer Deposition of Silicon-Based Dielectrics for Semiconductor Manufacturing: Current Status and Future Outlook. *J. Vac. Sci. Technol. A* **2019**, *37* (6), 060904.
- (213) Lujala, V.; Skarp, J.; Tammenmaa, M.; Suntola, T. Atomic Layer Epitaxy Growth of Doped Zinc Oxide Thin Films from Organometals. *Appl. Surf. Sci.* **1994**, *82–83*, 34–40.
- (214) Cai, J.; Ma, Z.; Wejinya, U.; Zou, M.; Liu, Y.; Zhou, H.; Meng, X. A Revisit to Atomic Layer Deposition of Zinc Oxide Using Diethylzinc and Water as Precursors. *J. Mater. Sci.* **2019**, *54* (7), 5236–5248.
- (215) Mai, L.; Mitschker, F.; Bock, C.; Niesen, A.; Ciftiyurek, E.; Rogalla, D.; Mickler, J.; Erig, M.; Li, Z.; Awakowicz, P.; Schierbaum, K.; Devi, A. From Precursor Chemistry to Gas Sensors: Plasma-Enhanced Atomic Layer Deposition Process Engineering for Zinc Oxide Layers from a Nonpyrophoric Zinc Precursor for Gas Barrier and Sensor Applications. *Small* **2020**, *16* (22), 1907506.
- (216) Kaiya, K.; Yoshii, N.; Omichi, K.; Takahashi, N.; Nakamura, T.; Okamoto, S.; Yamamoto, H. Atmospheric Pressure Atomic Layer Epitaxy of ZnO Using a Chloride Source. *Chem. Mater.* **2001**, *13* (6), 1952–1956.
- (217) O' Donoghue, R.; Peeters, D.; Rogalla, D.; Becker, H.-W.; Rechmann, J.; Henke, S.; Winter, M.; Devi, A. Systematic Molecular Engineering of Zn-Ketoiminates for Application as Precursors in Atomic Layer Depositions of Zinc Oxide. *Dalton Trans.* **2016**, *45* (47), 19012–19023.
- (218) Tammenmaa, M.; Koskinen, T.; Hiltunen, L.; Niinistö, L.; Leskelä, M. Zinc Chalcogenide Thin Films Grown by the Atomic Layer Epitaxy Technique Using Zinc Acetate as Source Material. *Thin Solid Films* **1985**, *124* (2), 125–128.
- (219) Egorova, K. S.; Ananikov, V. P. Toxicity of Metal Compounds: Knowledge and Myths. *Organometallics* **2017**, *36* (21), 4071–4090.
- (220) Haukka, S.; Lakomaa, E.-L.; Suntola, T. Chemisorption of Chromium Acetylacetonate on Porous High Surface Area Silica. *Appl. Surf. Sci.* **1994**, *75* (1–4), 220–227.
- (221) Puurunen, R. Chromium(III) Supported on Aluminum-Nitride-Surfaced Alumina: Characteristics and Dehydrogenation Activity. *J. Catal.* **2003**, *213* (2), 281–290.
- (222) Hakuli, A.; Kytökiivi, A.; Krause, A. O. I. Dehydrogenation of *i*-Butane on $\text{CrO}_x/\text{Al}_2\text{O}_3$ Catalysts Prepared by ALE and Impregnation Techniques. *Appl. Catal. Gen.* **2000**, *190* (1–2), 219–232.
- (223) Lindblad, M.; Haukka, S.; Kytökiivi, A.; Lakomaa, E.-L.; Rautiainen, A.; Suntola, T. Processing of Catalysts by Atomic Layer Epitaxy: Modification of Supports. *Appl. Surf. Sci.* **1997**, *121–122*, 286–291.
- (224) Wu, Y.; Raza, M. H.; Chen, Y.-C.; Amsalem, P.; Wahl, S.; Skrodzky, K.; Xu, X.; Lokare, K. S.; Zhukush, M.; Gaval, P.; Koch, N.; Quadrelli, E. A.; Pinna, N. A Self-Limited Atomic Layer Deposition of WS_2 Based on the Chemisorption and Reduction of Bis(*t*-Butylimino)Bis(Dimethylamino) Complexes. *Chem. Mater.* **2019**, *31* (6), 1881–1890.
- (225) Mattinen, M.; Hatanpää, T.; King, P. J.; Meinander, K.; Mizohata, K.; Jalkanen, P.; Räisänen, J.; Ritala, M.; Leskelä, M. Crystalline Tungsten Sulfide Thin Films by Atomic Layer Deposition and Mild Annealing. *J. Vac. Sci. Technol. A* **2019**, *37* (2), 020921.
- (226) Balasubramanyam, S.; Shirazi, M.; Bloodgood, M. A.; Wu, L.; Verheijen, M. A.; Vandalon, V.; Kessels, W. M. M.; Hofmann, J. P.; Bol, A. A. Edge-Site Nanoengineering of WS_2 by Low-Temperature Plasma-Enhanced Atomic Layer Deposition for Electrocatalytic Hydrogen Evolution. *Chem. Mater.* **2019**, *31* (14), S104–S115.
- (227) Cao, Y.; Wu, Y.; Badie, C.; Cadot, S.; Camp, C.; Quadrelli, E. A.; Bachmann, J. Electrocatalytic Performance of Titania Nanotube Arrays Coated with MoS_2 by ALD toward the Hydrogen Evolution Reaction. *ACS Omega* **2019**, *4* (5), 8816–8823.
- (228) Nandi, D. K.; Sen, U. K.; Dhara, A.; Mitra, S.; Sarkar, S. K. Intercalation Based Tungsten Disulfide (WS_2) Li-Ion Battery Anode Grown by Atomic Layer Deposition. *RSC Adv.* **2016**, *6* (44), 38024–38032.
- (229) Jurca, T.; Moody, M. J.; Henning, A.; Emery, J. D.; Wang, B.; Tan, J. M.; Lohr, T. L.; Lauhon, L. J.; Marks, T. J. Low-Temperature Atomic Layer Deposition of MoS_2 Films. *Angew. Chem., Int. Ed.* **2017**, *56* (18), 4991–4995.
- (230) Shen, C.; Raza, M. H.; Amsalem, P.; Schultz, T.; Koch, N.; Pinna, N. Morphology-Controlled MoS_2 by Low-Temperature Atomic Layer Deposition. *Nanoscale* **2020**, *12* (39), 20404–20412.
- (231) Tripathi, T. S.; Lahtinen, J.; Karppinen, M. Atomic Layer Deposition of Conducting CuS Thin Films from Elemental Sulfur. *Adv. Mater. Interfaces* **2018**, *5* (9), 1701366.
- (232) Cadot, S.; Renault, O.; Frégnaux, M.; Rouchon, D.; Nolot, E.; Szeto, K.; Thieuleux, C.; Veyre, L.; Okuno, H.; Martin, F.; Quadrelli, E. A. A Novel 2-Step ALD Route to Ultra-Thin MoS_2 Films on SiO_2

- through a Surface Organometallic Intermediate. *Nanoscale* **2017**, *9* (2), 538–546.
- (233) Ko, D.-H.; Kim, S.; Jin, Z.; Shin, S.; Lee, S. Y.; Min, Y.-S. A Novel Chemical Route to Atomic Layer Deposition of ZnS Thin Film from Diethylzinc and 1,5-Pentanedithiol: A Novel Chemical Route for ZnS ALD. *Bull. Korean Chem. Soc.* **2017**, *38* (7), 696–699.
- (234) Zhang, T.; Wang, Y.; Xu, J.; Chen, L.; Zhu, H.; Sun, Q.; Ding, S.; Zhang, D. W. High Performance Few-Layer MoS₂ Transistor Arrays with Wafer Level Homogeneity Integrated by Atomic Layer Deposition. *2D Mater.* **2018**, *5* (1), 015028.
- (235) Jin, Z.; Shin, S.; Kwon, D. H.; Han, S.-J.; Min, Y.-S. Novel Chemical Route for Atomic Layer Deposition of MoS₂ Thin Film on SiO₂/Si Substrate. *Nanoscale* **2014**, *6* (23), 14453–14458.
- (236) Li, H.; Zhao, R.; Zhu, J.; Guo, Z.; Xiong, W.; Wang, X. Organosulfur Precursor for Atomic Layer Deposition of High-Quality Metal Sulfide Films. *Chem. Mater.* **2020**, *32* (20), 8885–8894.
- (237) Włodarski, M.; Chodorow, U.; Józwiak, S.; Putkonen, M.; Durejko, T.; Sajavaara, T.; Norek, M. Structural and Optical Characterization of ZnS Ultrathin Films Prepared by Low-Temperature ALD from Diethylzinc and 1,5-Pentanedithiol after Various Annealing Treatments. *Materials* **2019**, *12* (19), 3212.
- (238) Jeon, W.; Cho, Y.; Jo, S.; Ahn, J.-H.; Jeong, S.-J. Wafer-Scale Synthesis of Reliable High-Mobility Molybdenum Disulfide Thin Films via Inhibitor-Utilizing Atomic Layer Deposition. *Adv. Mater.* **2017**, *29* (47), 1703031.
- (239) IMEC. *Sustainable Semiconductor Technologies and Systems | imec*. <https://www.imec-int.com/en/expertise/cmos-advanced/sustainable-semiconductor-technologies-and-systems-ssts> (accessed 2022-06-22).
- (240) Freeman, D. How Do We Reduce the Semiconductor Carbon Footprint?. *3D InCites*. <https://www.3dincites.com/2021/12/how-do-we-reduce-the-semiconductor-carbon-footprint/> (accessed 2022-06-22).
- (241) US Department of Energy. Chapter 6: Innovating Clean Energy Technologies in Advanced Manufacturing. *Quadrennial Technology Review*; US Department of Energy, 2015, 45.
- (242) *European Chips Act* https://ec.europa.eu/info/strategy/priorities-2019-2024/europe-fit-digital-age/european-chips-act_en (accessed 2022-07-08).
- (243) Agostinelli, G.; Delabie, A.; Vitanov, P.; Alexieva, Z.; Dekkers, H. F. W.; De Wolf, S.; Beaucarne, G. Very Low Surface Recombination Velocities on P-Type Silicon Wafers Passivated with a Dielectric with Fixed Negative Charge. *Sol. Energy Mater. Sol. Cells* **2006**, *90* (18), 3438–3443.
- (244) Masmitjà, G.; Ros, E.; Almache-Hernández, R.; Pusay, B.; Martín, I.; Voz, C.; Saucedo, E.; Puigdollers, J.; Ortega, P. Interdigitated Back-Contacted Crystalline Silicon Solar Cells Fully Manufactured with Atomic Layer Deposited Selective Contacts. *Sol. Energy Mater. Sol. Cells* **2022**, *240*, 111731.
- (245) Warren, E. L.; McMahon, W. E.; Rienäcker, M.; VanSant, K. T.; Whitehead, R. C.; Peibst, R.; Tamboli, A. C. A Taxonomy for Three-Terminal Tandem Solar Cells. *ACS Energy Lett.* **2020**, *5* (4), 1233–1242.
- (246) Poodt, P.; Cameron, D. C.; Dickey, E.; George, S. M.; Kuznetsov, V.; Parsons, G. N.; Roozeboom, F.; Sundaram, G.; Vermeer, A. Spatial Atomic Layer Deposition: A Route towards Further Industrialization of Atomic Layer Deposition. *J. Vac. Sci. Technol. A* **2012**, *30* (1), 010802.
- (247) Muñoz-Rojas, D.; MacManus-Driscoll, J. Spatial Atmospheric Atomic Layer Deposition: A New Laboratory and Industrial Tool for Low-Cost Photovoltaics. *Mater. Horiz.* **2014**, *1* (3), 314–320.
- (248) Nguyen, V. S.; Sekkat, A.; Bellet, D.; Chichignoud, G.; Kaminski-Cachopo, A.; Muñoz-Rojas, D.; Favre, W. Open-Air, Low-Temperature Deposition of Phase Pure Cu₂O Thin Films as Efficient Hole-Transporting Layers for Silicon Heterojunction Solar Cells. *J. Mater. Chem. A* **2021**, *9* (29), 15968–15974.
- (249) Raninga, R. D.; Jagt, R. A.; Béchu, S.; Huq, T. N.; Li, W.; Nikolka, M.; Lin, Y.-H.; Sun, M.; Li, Z.; Li, W. Strong Performance Enhancement in Lead-Halide Perovskite Solar Cells through Rapid, Atmospheric Deposition of n-Type Buffer Layer Oxides. *Nano Energy* **2020**, *75*, 104946.
- (250) Alshehri, A. H.; Loke, J. Y.; Nguyen, V. H.; Jones, A.; Asgarimoghaddam, H.; Delumeau, L.; Shahin, A.; Ibrahim, K. H.; Mistry, K.; Yavuz, M. Nanoscale Film Thickness Gradients Printed in Open Air by Spatially Varying Chemical Vapor Deposition. *Adv. Funct. Mater.* **2021**, *31* (31), 2103271.
- (251) Graniel, O.; Weber, M.; Balme, S.; Miele, P.; Bechelany, M. Atomic Layer Deposition for Biosensing Applications. *Biosens. Bioelectron.* **2018**, *122*, 147–159.
- (252) Weber, M.; Drobek, M.; Rebière, B.; Charmette, C.; Cartier, J.; Julbe, A.; Bechelany, M. Hydrogen Selective Palladium-Alumina Composite Membranes Prepared by Atomic Layer Deposition. *J. Membr. Sci.* **2020**, *596*, 117701.
- (253) Yang, H.-C.; Waldman, R. Z.; Chen, Z.; Darling, S. B. Atomic Layer Deposition for Membrane Interface Engineering. *Nanoscale* **2018**, *10* (44), 20505–20513.
- (254) Croguennec, L.; Palacin, M. R. Recent Achievements on Inorganic Electrode Materials for Lithium-Ion Batteries. *J. Am. Chem. Soc.* **2015**, *137* (9), 3140–3156.
- (255) Karki, K.; Zhu, Y.; Liu, Y.; Sun, C.-F.; Hu, L.; Wang, Y.; Wang, C.; Cumings, J. Hoop-Strong Nanotubes for Battery Electrodes. *ACS Nano* **2013**, *7* (9), 8295–8302.
- (256) Jin, L.; Shen, C.; Wu, Q.; Shellikeri, A.; Zheng, J.; Zhang, C.; Zheng, J. P. Pre-Lithiation Strategies for Next-Generation Practical Lithium-Ion Batteries. *Adv. Sci.* **2021**, *8* (12), 2005031.
- (257) Riyanto, E.; Martides, E.; Pikra, G.; Atmaja, T. D.; Pramana, R. I.; Purwanto, A. J.; Santosa, A.; Junianto, E.; Darussalam, R.; Saepudin, A.; Susatyo, A.; Subekti, R. A.; Utomo, Y. S.; Subagio, D. G.; Fudholi, A.; Abimanyu, H.; Radiansah, Y.; Sudibyo, H.; Kusnadi; Rajani, A.; Suprpto; Prawara, B. A Review of Atomic Layer Deposition for High Lithium-Ion Battery Performance. *J. Mater. Res. Technol.* **2021**, *15*, 5466–5481.
- (258) Lu, W.; Liang, L.; Sun, X.; Sun, X.; Wu, C.; Hou, L.; Sun, J.; Yuan, C. Recent Progresses and Development of Advanced Atomic Layer Deposition towards High-Performance Li-Ion Batteries. *Nanomaterials* **2017**, *7* (10), 325.
- (259) Liu, J.; Zhu, H.; Shiraz, M. H. A. Toward 3D Solid-State Batteries via Atomic Layer Deposition Approach. *Front. Energy Res.* **2018**, *6*, 10.
- (260) Lee, W.-J.; Bera, S.; Kim, C. M.; Koh, E.-K.; Hong, W.-P.; Oh, S.-J.; Cho, E.; Kwon, S.-H. Synthesis of Highly Dispersed Pt Nanoparticles into Carbon Supports by Fluidized Bed Reactor Atomic Layer Deposition to Boost PEMFC Performance. *NPG Asia Mater.* **2020**, *12* (1), 1–13.
- (261) Juang, R.-S.; Hsieh, C.-T.; Hsiao, J.-Q.; Hsiao, H.-T.; Tzou, D.-Y.; Huq, M. M. Size-Controlled Platinum Nanoparticles Prepared by Modified-Version Atomic Layer Deposition for Ethanol Oxidation. *J. Power Sources* **2015**, *275*, 845–851.
- (262) Paige, J. M.; Cheng, Y.; Pepin, P. A.; Curran, C. D.; Sun, D.; Chen, M. U.; McIntosh, S.; Vohs, J. M.; Gorte, R. J. Surface Modification of SOFC Cathodes by Co, Ni, and Pd Oxides. *Solid State Ion.* **2019**, *341*, 115051.
- (263) Cheng, Y.; Raman, A. S.; Paige, J.; Zhang, L.; Sun, D.; Chen, M. U.; Vojvodica, A.; Gorte, R. J.; Vohs, J. M. Enhancing Oxygen Exchange Activity by Tailoring Perovskite Surfaces. *J. Phys. Chem. Lett.* **2019**, *10* (14), 4082–4088.
- (264) Nagashima, M. Japan's Hydrogen Society Ambition: 2020 Status and Perspectives. In *Notes de l'Ifri*; Ifri, 2020.
- (265) Zhang, S.; Yuan, X.-Z.; Hin, J. N. C.; Wang, H.; Friedrich, K. A.; Schulze, M. A Review of Platinum-Based Catalyst Layer Degradation in Proton Exchange Membrane Fuel Cells. *J. Power Sources* **2009**, *194* (2), 588–600.
- (266) Shin, J. W.; Go, D.; Kye, S. H.; Lee, S.; An, J. Review on Process-Microstructure-Performance Relationship in ALD-Engineered SOFCs. *J. Phys. Energy* **2019**, *1* (4), 042002.
- (267) Holme, T. P.; Lee, C.; Prinz, F. B. Atomic Layer Deposition of LSM Cathodes for Solid Oxide Fuel Cells. *Solid State Ion.* **2008**, *179* (27), 1540–1544.

(268) Gong, Y.; Palacio, D.; Song, X.; Patel, R. L.; Liang, X.; Zhao, X.; Goodenough, J. B.; Huang, K. Stabilizing Nanostructured Solid Oxide Fuel Cell Cathode with Atomic Layer Deposition. *Nano Lett.* **2013**, *13* (9), 4340–4345.

(269) Wiff, J. P.; Jono, K.; Suzuki, M.; Suda, S. Improved High Temperature Performance of La_{0.8}Sr_{0.2}MnO₃ Cathode by Addition of CeO₂. *J. Power Sources* **2011**, *196* (15), 6196–6200.

(270) Kan, C. C.; Kan, H. H.; Assche, F. M. V.; Armstrong, E. N.; Wachsmann, E. D. Investigating Oxygen Surface Exchange Kinetics of La_{0.8}Sr_{0.2}MnO_{3-δ} and La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} Using an Isotopic Tracer. *J. Electrochem. Soc.* **2008**, *155* (10), B985.

(271) Armstrong, E. N.; Duncan, K. L.; Oh, D. J.; Weaver, J. F.; Wachsmann, E. D. Determination of Surface Exchange Coefficients of LSM, LSCF, YSZ, GDC Constituent Materials in Composite SOFC Cathodes. *J. Electrochem. Soc.* **2011**, *158* (5), B492.

(272) Cassir, M.; Ringuedé, A.; Niinistö, L. Input of Atomic Layer Deposition for Solid Oxide Fuel Cell Applications. *J. Mater. Chem.* **2010**, *20* (41), 8987–8993.

(273) Vora, S.; Williams, M. Projections for Solid Oxide Electrolysers for Water Electrolysis. *ECS Meet. Abstr.* **2021**, MA2021-03 (1), 185.

(274) Jouhara, H.; Khordehgah, N.; Almahmoud, S.; Delpech, B.; Chauhan, A.; Tassou, S. A. Waste Heat Recovery Technologies and Applications. *Therm. Sci. Eng. Prog.* **2018**, *6*, 268–289.

(275) Lin, F.; Lin, S.-W.; Lu, W.-M. Dynamic Eco-Efficiency Evaluation of the Semiconductor Industry: A Sustainable Development Perspective. *Environ. Monit. Assess.* **2019**, *191* (7), 435.

(276) Eng, C. Y.; Yan, D.; Withanage, N.; Liang, Q.; Zhou, Y. Wastewater Treatment and Recycle from a Semiconductor Industry: A Demo-Plant Study. *Water Pract. Technol.* **2019**, *14* (2), 371–379.