Green Chemistry

PERSPECTIVE ARTICLE

# Opportunities and perspectives for green chemistry in semiconductor technologies

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Semiconductor chip manufacturing has one of the highest environmental footprints within the electronics life cycle. This sector offers a plethora of technological challenges and opportunities for implementing green chemistry principles more extensively. In addition to technical solutions, a renewed collaborative focus on green chemistry throughout the ecosystem of the semiconductor industry, particularly in the pre-competitive stage, will be fundamental to seeing those solutions through to implementation.

## Background

The pervasive use of modern integrated circuits have turned the semiconductor industry into a very large share of the worldwide economy, projected to reach a volume of just under $500 billion US dollars in total revenue in 2019, as shown in **Fig. 1**[1]. As Moore's Law is slowing down[2], the drive for miniaturization of electronics is not only as strong as ever, but it is also extending to less traditional areas such as photonics, energy, communications and a vast range of integrated sensors - from chemical to physical and imaging micro-sensors[3]. Indeed, the demand for micro-integrated, portable and interconnected systems (or "smart sensors") is only getting more pervasive as the Internet of Things, Big Data and Artificial Intelligence start underpinning most aspects of modern life[4]. Although alternate manufacturing paths such as 3D printing are now also available, it is expected that a substantial part of the miniaturisation effort of such systems will still rely on wafer –level semiconductor manufacturing processes[5].

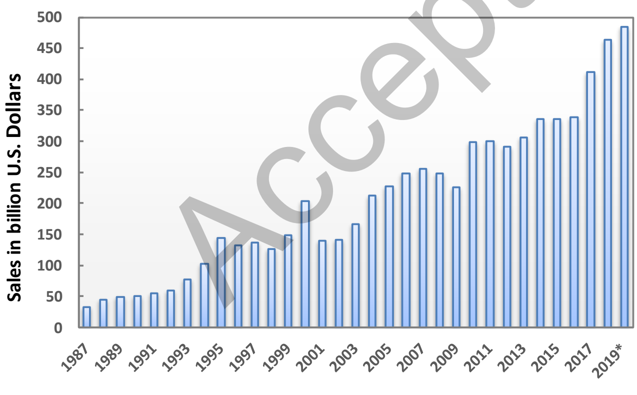


**Fig.** 1 Historical and projected market size for semiconductor industry. Data from Statista/ WSTS Semiconductor Market Forecast Spring 2018[1]

Hence, although semiconductor industry focuses on microscale products, the volume of its market is such that any small "green" improvement along the electronics lifecycle would lead to a large positive impact. Several major companies, such as Intel[6], include sustainability aspects in their corporate responsibility. The general lifecycle and landscape of electronics is quite complex and its environmental footprint is spread across an extensive vertical industrial ecosystem and several different stages, as illustrated in **Fig. 2**[7]. On –wafer chip manufacturing is only one of the stages, strongly dependent on the supply chain of raw materials, as well as on the subsequent packaging and assembly steps, and product distribution. The lifecycle of electronics ends usually with disposing of the product after its useful life, which is usually just a few years for consumable electronics. Unfortunately, only a small percentage of the discarded electronic (E-waste) is ever recycled[8]. When considering that per year several tens of millions metric tonnes of E-waste are generated[9], in addition to the fact that an increasingly high variety of elemental materials are being incorporated in microelectronic products, some of which being particularly rare and/or toxic, the benefit that could be brought through more efforts into recycling of E-waste appears evident.

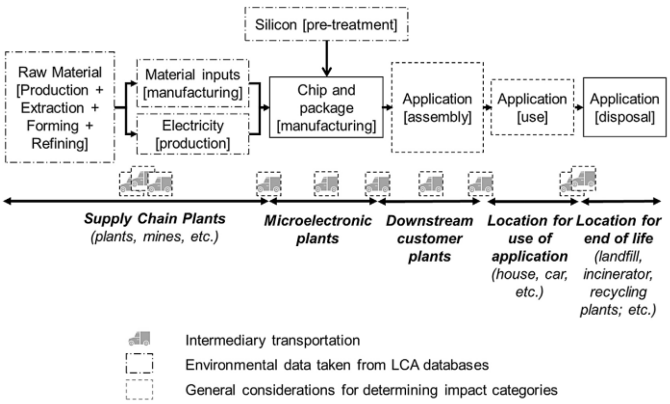


**Fig. 2** The microelectronics ecosystem. Reprint with permission from Elsevier[7]

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In this respect, it is important to mention the ongoing efforts towards greener semiconductor materials, devising biodegradable components, as well as circuits and potentially batteries using novel inorganic, polymeric and biomaterials.[10] While these approaches may take a more prominent role in the future, the bulk of the current semiconductor technologies are still mostly based on non –biodegradable materials. Here following, we will focus on the mainstream semiconductor (chip) manufacturing stage, its environmental impact and the potential opportunities for green chemistry for a more sustainable industry.

## Semiconductor Manufacturing

ICs or semiconductor microchips are central to most modern electronic products, as they perform the key functions of data processing/computation (logic chip), data storage (memory chip), and electrical power management (power chip). In addition, as discussed, semiconductor chips are taking on increasingly new functions, such as sensing and actuation using semiconductor –based MEMS, optoelectronics for data communication /transmission, and a multitude of additional functions thanks to More Than Moore[11] and 3D IC technologies[7]. All of these vastly different chips are manufactured in a semiconductor fab (microelectronic plant), using the same wafer –level approach and specific infrastructure that is at the core of semiconductor manufacturing.

Chip fabrication is also the stage of electronics life cycle having the largest documented environmental footprint[7, 12] and thus focus of this perspective.

The basic principle of semiconductor manufacturing is the fabrication in parallel of a high –number of chips on the same semiconductor substrate (wafer, generally but not exclusively silicon), which are then separated by mechanical or laser dicing at the end of the wafer –level fabrication process. The parallel processing is a key feature of semiconductor fabrication that allow feature sizes as small as tens of nanometers to be uniformly printed over wafers of up to 300mm diameter, with largely reduced costs than if each chip was fabricated separately[13]. The reason is that the fabrication is based on thin –film subtractive processes, and takes place as a precise sequence of hundreds of basic wafer –level steps ranging from surface cleaning, film deposition, doping, patterning (via photolithography and etching) to planarization processes (see **Fig. 3**). All of those steps are based on highly specialised processes, consumables and equipment, taking place in an extensive dedicated cleanroom facility (fab) under strict rules to avoid microparticle and material cross-contamination. While a detailed description of the fabrication processes can be found in several reference books[14], here we will focus on the aspects relevant to environmental impact and opportunities for green chemistry.

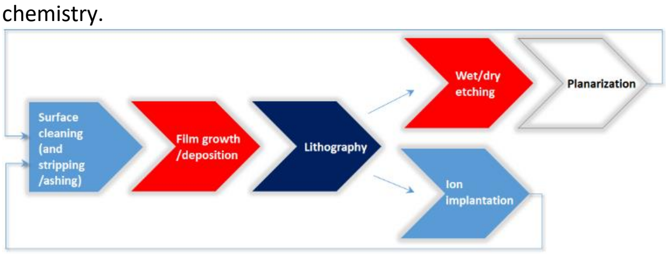


**Fig. 3** Schematic description of the basic processes sequences for semiconductor manufacturing.

### Key environment indicators of environmental footprint for semiconductor manufacturing

Running a semiconductor fab is extremely intensive in terms of resources, facilities and support required. This translates into a significant and wide-ranging environmental footprint, categorised by Williams[15] into 3 broad impact areas of chemical emissions, worker health, and high materials intensity. More recently, Villard et al.[7] suggested a set of 7 indicators for a complete impact assessment of a semiconductor fab.

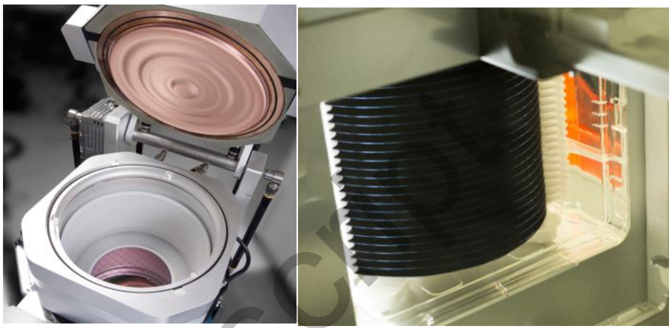

**Fig. 4** On the left, a typical example of wafer –scale process step, in this case metal sputtering deposition. On the right, the picture shows how the wafers are handed throughout the manufacturing processes. The wafer cassette is nowadays a sealed container that is automatically transported from equipment to equipment along the sequence of the manufacturing flow. (*Images courtesy of Applied Materials*)

Some are linked to the intensive use of resources as input flows into a fab: abiotic depletion (namely rare gasses, metals and rare earth elements), imported volume of raw water (demand for ultrapure deionized water) and local electricity consumption. The remaining indicators are mostly related to the output flows of a fab, covering: global warming, summer smog, water eutrophication and human eco-toxicity. These indicators assess the impact of gas emissions and waterwaste on the ambient, as well as harmful exposure for workers. Note that the last aspect has been dramatically reduced by the full automation of modern semiconductor fabs[16]. While there is some contribution in the form of NOX and VOCs from the fab infrastructure and support facility (air treatment, etc), the core of the environmental impact of the output flows of a fab originate from the manufacturing processes.

As we described in the previous section, semiconductor manufacturing relies on the sequence of extremely specialized wafer –level fabrication steps, most of them heavily relying on highly specific and finely tailored chemical reagents and physico-chemical reactions. In the next section we will briefly review the range of processes involved in wafer -level manufacturing, and the corresponding types of chemicals utilised and waste generated, linking them back to their environmental impact. For each family of processes, current approaches and limitations to "replace, reduce, neutralize, recycle" strategies will be reviewed.

### Manufacturing processes: impact and opportunities

The consumable substances at the basis of manufacturing processes range from solid (mainly silicon) to liquid (acids, bases, solvents, resins) and gas compounds of countless kinds. The output generated thus also ranges from solid to liquid waste and gas emissions, and it is usually a combination of reacted/used input consumables and newly generated compounds. As this section will explain more into detail, a large range of highly reactive, rare, and/or hazardous material is present in both input and output substances of a semiconductor manufacturing fab. We will analyse briefly the reasons for this, as well as the current status and perspectives in the context of a *replace* (input), *reduce* (input), *neutralize* (output) and *recycle* (output) strategy for such problematical substances.

Many of the key semiconductor manufacturing steps are based on vacuum processes where a very controlled amount of material is first deposited or grown on a substrate (thin –film deposition) and then selectively removed with high location precision (dry etching) according to high –resolution patterns (currently defining physical sizes as small as 10nm) defined via photolithography.

Thin –film deposition or growth processes take usually place as physical (PVD) or chemical (CVD) vapour deposition processes. CVD approaches, with many different variations, are usually the most common in manufacturing environments because of their superior control on the crystallinity of the films, and rely on the availability of volatile precursors as the sources of the material to be grown or deposited. Precursors have the ability to be easily broken down by temperature and/or plasma bombardment[17]. Widespread gaseous precursors in semiconductor manufacturing fabs are those used for the growth of silicon compounds, such as silane ($SiH_4$), di- or tri-chlorosilane ($H_2Cl_2Si$ and $SiHCl_3$)[18]. Most silicon precursors are highly flammable and show different extents of toxicity[19], as well as the doping precursors which are often simultaneously employed to grow doped silicon, such as phosphine, arsine and diborane, which are all extremely toxic in low doses[20]. Due to the advancements of CMOS technologies such as strained silicon, germanium is also used in semiconductor fabs to form SiGe, with its main precursor germane ($GeH_4$) being extremely hazardous[21]. There is therefore a strong drive to employing and developing safer CVD sources, and liquid precursors for silicon such as tetraethyl orthosilicate (TEOS), as well as for germanium[22] are generally considered to be safer, but also considerably more expensive.

Several compound semiconductors of the III-V group are nowadays taking a prominent place in manufacturing as well, namely GaAs for RF and optoelectronics, as well as nitrides such as AlN and GaN for optoelectronics and power electronics applications. They are grown using metal-organic CVD (MOCVD) processes, which make use of liquid organometallic precursors, like trimethyl-gallium, -indium and -aluminium (TMG, TMI, TMA) for the metal element of the compound, but also of the problematic gaseous phosphine and arsine precursors for III-V phosphides and arsenides.

Finally, the introduction of high k dielectrics in CMOS technologies, and the advent of CVD processes such as the Atomic Layer Deposition (ALD), have reignited substantial efforts into the development of precursors for a large range of elements and materials[23, 24]. As Roy Gordon from MIT mentions, "*Ideally, the precursors should be non-flammable, non-corrosive, non-toxic, simple and non-hazardous to make and inexpensive*"[25]. There are certainly still lot of challenges to reach such goals, but there also has never been a stronger technological drive to develop adequate solutions.

Patterning processes, particularly dry or plasma etching via reactive ion etching (RIE) and its many variations[26] are another class of processes associated with input and output of problematic gasses. RIE etching is widespread in semiconductor manufacturing as opposed to standard gas or wet –based etching because of its capability to be made extraordinarily anisotropic, which is a key requirement to create patterns with adequate resolution. Therefore, etching input gasses are generally a mixture of highly reactive gasses which can atomically combine with the material to be removed and form volatile compounds, with different moderately reactive or inert carrier gasses, the most common being $H_2$, $N_2$, $O_2$, Ar, He. The function of the heavier elements in the plasma is to contribute via ion-assisted etching, which combines the chemical etching action with the physical bombardment to obtain the best directionality. The chemical action in RIE etching of silicon or silicon –based materials is commonly achieved using halogen –based chemistries, and particularly fluorine- and/or and chlorine- based chemistries. Fluorine chemistries include $SF_6$, hydrofluorocarbons (HFCs) such as $CHF_3$, perfluorocarbons (PFCs) such as $CF_4$, $C_3F_4$, $C_4F_8$, as well as $XeF_2$. Chlorine chemistries include $Cl_2$ and $SiCl_2$. $SF_6$, as well as most HFCs and PFCs are known as greenhouse gasses with high global warming potential (GWP)[27]. As they are long –lived, their impact in the atmosphere is longer –lasting than $CO_2$, and as such their use has been restricted since the Montreal Protocol of 1987[28].

Increasingly efficient RIE equipment designs, accompanied by the efficient use of endpoint detection systems, have vastly improved the efficacy of the processes so that less of the high GWP etching gases are required and released unreacted per process[29]. However, in terms of replacing such halogen chemistries with environmentally friendlier ones, the situation has not substantially changed over the last decades, as halogens so far are the only chemistries capable of leading efficiently to volatile silicon by-products such as $SiF_4$, $SiCl_4$, etc[30]. $H_2$ alone is unfortunately not efficient for RIE etching of silicon, but it may be used in the etching gas mixture with fluorine and/or chlorine –based chemistries. Bromine –based chemistries are another alternative being recently investigated more into detail[31], but their by-products may lead to even more severe environmental consequences as they would directly contribute to atmospheric ozone depletion[28]. Silicon etching chemistries are hence an area truly ripe for an out-of-the-box disruption.

In the meantime, downstream gas abatement systems are the most efficient counter-measure. The destruction removal efficiencies may be as high as 99%, but this is highly dependent on the abatement technology used, the gas and process flows, as well as the specific halogen compound. $CF_4$ for example tends to be the most difficult to abate for some PFC abatement technologies, requiring higher temperatures and therefore more energy, which would likely be supplied from hydrocarbon fuels[32]. The abatement fuels may hence also contribute to greenhouse gas emissions, although with impact a couple orders of magnitude lower than the targeted species. In addition, the operation of abatement itself, may produce undesirable by-products like NOx and carbon oxides[33].

As silicon and its oxide will continue to be a major component in IC manufacturing, moving away completely from fluorinated chemicals will not be an easy undertaking. Meanwhile, the selection of fluorinated compounds which are easier to treat downstream or have a lower global warming potential should be highly encouraged.

Reactive gasses are not the only source of problematic input and output substances in semiconductor manufacturing. Several of the key processing steps make use of sensible quantities of reactive wet chemistries, resins and solvents. For example photolithography needs a range of photosensitive resins, development plus stripping agents, silicon surface cleaning makes use of a range of acid, bases and solvents (see for example the RCA cleaning[34], and planarization steps like chemical –mechanical polishing requires oxides and copper slurries, which are tailored suspensions of abrasive microparticles in proprietary liquid mixtures[35].

In terms of reduction of the amount of toxic input materials, again this relies on the improvement of the efficiency of the individual process steps. Regarding their potential replacement, it is worth mentioning for example that the surface cleaning steps could greatly benefit from the basic and industrial advancement of several types of UV-ozone[36] and supercritical fluid cleaning, such as $CO_2$[37]. In addition, there has been quite a lot of recent development in the area of green solvents[38], which could also greatly help to reduce the environmental footprint of semiconductor manufacturing, also advanced by the increasing research efforts around processing of polymeric semiconductors[39] and organic solar cells.[40]

All of the above- mentioned liquid substances and their by-products contribute to a large range of environmental impact risk, from the release of toxic compounds in wastewater, in air, or as hazardous solid waste. We have already briefly covered abatement systems for gas emission control. In parallel, semiconductor fabs require sophisticated wastewater treatment systems to neutralise the waste water stream to an appropriate pH[41]. Fluorides are typically flocculated before discharge in order to comply with regulatory limits[42].

#### Impact of fab support facilities

Chemical choice and process design are certainly avenues for managing the environmental impact of semiconductor manufacturing. However, there is a significant opportunity in the facilities and support equipment for the process tools. Studies show that the overall fab energy consumption remains largely unchanged with production. Some equipment manufacturers have sought to take advantage of this this opportunity by developing controllers that would synchronize the facilities support equipment, such as abatement and pumps with the state of the process tools. As such the resources used to support the process tools, (energy, fuel, industrial water, waste treatment, etc.) would correlate to process starts. Additionally, it was found that when the support equipment is synchronised to the state of the tool, there was not only a reduction in utilities usage, but a reduction in emissions such as NOx and VOC, tied to the operation of the support equipment[43].

Other areas where manufacturing support facilities can play a role in reducing the environmental impact of IC manufacturing, is in recycling and reclamation of process by-products, for example from gas exhaust[44]. When it comes to highly toxic by-products, like for example arsenic –containing species, mitigation will likely occur closer to the tool level-before it gets to the general facilities waste water treatment[45]. This can take the form of trapping or binding to media, and the further development of adsorption technologies that may enable such substances to be recycled would be greatly beneficial[46]. Ideally, mitigating technologies should allow for recovery of the species like heavy metals or rare earths from by-products or un-utilised process chemistries also from wastewater through appropriate membranes[47]. Pursuing such an option would come with the challenge of dealing with a waste stream originating from multiple sources with a wide range of process chemistries. Designing the ability to segregate process waste streams with reclamation in mind could make such an option more feasible.

Finally, in a similar way as artificial intelligence is being increasingly used nowadays to predict and enhance chip yield in semiconductor fabs[48], one would reasonably expect AI to play a major role in the automated operation, synchronisation and optimisation of fab support facilities as described above, helping to further reduce the environmental footprint of the fab of the future.

## Perspectives

As we briefly discussed, semiconductor manufacturing has a large environmental footprint and there are plenty of process technology areas that would greatly benefit from a continued focus on green chemistry. How to foster thus an increasingly green and efficient semiconductor manufacturing?

In addition to the purely scientific and technical challenges and opportunities, as Clark et al recently discuss: *"Many published articles claim to provide green alternatives to existing processes, often by stating how their research complies with one or more of the green principles. Winterton argues that such strategies are in fact "green herrings", and consideration must be given to the larger context, particularly in terms of scalability, economics, and regulatory constraints. This viewpoint is in accordance with sustainable chemistry, which takes a more holistic approach to the development of chemical technologies"*[49].

Because of the very complex nature of the semiconductor R&D and manufacturing ecosystem, extending from raw and refined materials suppliers, to equipment suppliers, foundries, integrated device manufacturers and fabless design houses, and at the same time the need for a specific process to have broad uptake to be economically viable, pre-competitive R&D cooperation across all vertical and horizontal sectors of the supply chain is a must. Advances in green chemistry are no exception, and corporate responsibility in sustainability should be a major drive in this direction.

Influential international centres for semiconductor R&D such as IMEC (Belgium) and others start taking the lead in the discourse on environmental impact of semiconductors, which is key to obtain stronger support for green chemistry along the whole value chain. Finally, because of the technological complexity of semiconductor industry, any substantial change to current processes or materials would require 5-10 years of R&D and qualifications, so there is a long lag between a scientific breakthrough in green chemistry and its potential implementation[50]. The International Roadmap working groups, ITRS in the past, and since 2017 the International Roadmap for Devices and Systems (IRDS)[51], also play a key role in shaping and steering the evolution of semiconductor industry. The fact that green chemistry appears as a central theme of the relevant chapter of IRDS[51] confirms that this aspect is high on the agendas of corporate responsibilities in semiconductor industry.

## Conflicts of interest

There are no conflicts to declare.

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