2023 Research Needs Document: Environmental Safety and Health

Semiconductor Research Corp. (SRC)
Research Triangle Park, NC 27703

Introduction

This document is prepared to accompany the Call-for-Research in the research program of Environment Safety and Health (ESH). The research needs in this area are very broad. We present here selected areas of high priority as identified by our sponsor members.

Semiconductor fabrication processes have evolved enormously with time, largely driven by the demand for advanced device architectures and increased performance. To continue to drive innovation and to achieve the desired electrical functionality required by today's market, the industry relies on a number of highly sophisticated chemicals and materials. However, the potential environmental, health and safety risks associated with the use of some new chemistries may not be fully understood or available at the time our suppliers introduce chemicals to the market. This requires the industry to invest in proactive environmental, safety, and health (ESH) research and development (R&D). Proactive ESH R&D is necessary to enable new technology, address new information from evolving health and environmental science studies, assure compliance with government regulations, and prevent the need for expensive and disruptive corrective measures.

This *research-needs* document identifies materials of high concern (MoHC) that we believe need to be evaluated and addressed proactively with ESH R&D. Where feasible, safer more benign substitutes should be developed for MoHC. Where substitution of a more benign material is not feasible, process technology should be developed and optimized for minimal use with maximum protections that mitigate risks. Likewise, cost-effective treatment and abatement processes are needed to assure that wastewater effluents, air emissions, and other waste streams, all have minimal environmental impacts.

The ESH R&D needs are addressed in four sub-categories as follows:

A. ESH impact analysis of materials.
B. Aqueous effluent management.
C. Air emissions management.
D. Alternative materials analysis.

The Global Research Collaboration (GRC) division of SRC focuses on research in a timeframe five or more years ahead of technology release. Research on advanced tools and techniques such as modeling, simulation, and characterization can be of value with implementation timelines as low as one to two years post project completion. This timeframe represents the "sweet spot" for pre-competitive, collaborative research, after which the industry focuses on proprietary development for technology differentiation. Successful research proposals will need to match this timing.

SRC has released a document called the Decadal Plan for Semiconductors (www.src.org/about/decadal-plan/) which describes five Seismic Shifts facing the electronics industry in the coming decade. Research should address issues arising from at least one of them:

- Smart Sensing – The Analog Data Deluge
- Memory & Storage – The Growth of Memory and Storage Demands
- Communication – Communication Capacity vs. Data Generation
- Security – Information & Communications Technology (ICT) Security Challenges
- Energy Efficiency – Compute Energy vs. Global Energy Production

Moving forward, the SRC is also embarking on an effort to broaden participation in its funded research programs. This aggressive agenda will help us drive meaningful change in advanced ICT that seem impossible today. In the programs we lead, we must increase the participation of women and under-represented minorities as well as strike a balance between U.S. and non-U.S. citizens, creating an inclusive atmosphere that unlocks the talents inherent in all of us. Please visit https://www.src.org/about/broadening-participation/ for more information about the 2030 Broadening Pledge.

With the expected growth of semiconductor chip manufacturing in the coming years, it is imperative that the chemicals, materials, and processes involved in their manufacturing are as sustainable as possible. Therefore, research must take into consideration the environmental and human health impacts of new chemistries and focus on the development of more environmentally preferable materials and processes that are more efficient, more effective, and safer. In general, processes that are known to use chemicals that are persistent, bio-accumulative, or toxic will benefit from more environmentally benign substitutions.

Research Needs

A. ESH impact analysis of materials.

New and novel chemicals are introduced to the semiconductor industry by chemical and tool suppliers at a rapid rate that sometimes outpaces the rate at which the suppliers can provide fundamental information on the physicochemical properties, toxicity, and environmental fate and behavior characteristics of the purchased chemicals, and/or the reactive products that are created within manufacturing processes. This presents a risk of unanticipated hazardous conditions, and/or unexpected regulatory actions on chemicals used in critical applications. In light of these concerns, proposals are encouraged that provide knowledge and solutions for the following:

a. **Evaluate EUV and other photolithography chemistries for toxicity, environmental fate, and behavior characteristics**. A wide variety of potential photolithography chemical systems are under evaluation for EUV and other photolithography applications. These include conventional triarylsulfonium and diaryliodonium type photoresists, as well as novel metal-based nanoparticle resists, among others. The development and application of methods to characterize potential emissions, occupational exposure routes, and waste streams is needed for photolithography chemicals and their degradation products. The development of structure – toxicity and/or structure-behavior relationships is also of interest. For instance, expanded knowledge of the influence of structural modifications (i.e., the cation, alkyl chain length, functional groups, anion) to the toxicity and environmental fate of onium photo acid generators and their decomposition products, would help identify more benign chemicals that pose lower risk to human health and the environment.

b. **Development of predictive toxicology tools for cationic species.** Currently, there is a lack of appropriate *in silico* models available to delineate the toxicity potential of cationic species such as those commonly used in certain photolithography applications (e.g., triarylsulfonium and diaryl iodonium). Developing computational methods for estimating the toxicity potential of these chemicals would be useful toward identifying safer more benign substitutes.

c. **Develop information regarding the behavior, toxicity, treatment, monitoring and/or alternatives to per- and polyfluorinated (PFAS) chemicals used in semiconductor manufacturing.** The semiconductor industry and its suppliers have worked hard to minimize and/or eliminate the use of long chain perfluorochemicals like PFOS and PFOA because of their defined environmental and health risks. However, in the meantime, thousands of new PFAS compounds have been introduced to commerce, many under the claim of being safer and more environmentally benign, but few with definitive data to back the claims. For instance, recent information and controversy over short chain fluorinated chemicals like Gen-X highlight the need for chemical substitutions to be well informed and backed by solid data. Research that provides fundamental data on the behavior, toxicity and fate of PFAS that are in current use and/or targeted for future use in photolithography would be very valuable. Improved knowledge of the factors that cause PFAS to be toxic would be helpful toward identifying potentially more benign substitutes. The development and validation of occupational exposure monitoring and analytical methods for PFAS is desired. Presently available analytical methods identify only a small fraction of the total spectrum of fluorinated organic chemicals that are potentially present in samples. Proposals should describe analytical capabilities and limitations. Proposals should also describe how the proposed work would produce actionable information that the industry can put to effective use. PIs are encouraged to partner with photolithography suppliers, device makers, and/or government institutions, many of whom are working to understand this broad class of chemicals.

d. **Validate and expand the capability of analytical methods to measure and control chemicals of concern in the working environment, wastewater, and air emissions streams.** Chemicals of concern include PFAS, TMAH, nMP, azoles, HF, nanoparticles, oniums, organosilicons, total oxidizers (H_2O_2 + H_2SO_4), and a variety of inorganics, among others. Relevant media include air, water, waste, and solids. In addition to conventional in-lab analytical analysis of samples, there is interest in the development of small-scale detectors/sensor for integration into light weight, highly portable detection devices. Similarly, there is interest in sensor/analytical devices, that provide continuous monitoring for flow streams and work environments. Work plans for the development of novel detection/analytical methods should include validation against existing conventional methods with potential agency involvement (NIOSH) in the validation.

B. Aqueous effluent management.

A wide variety of wastewater constituents represent emerging concerns because of their bioinhibitory, refractory, and/or potential PBT characteristics, and require removal/treatment. Chemicals of concern include PFAS, PAG cations, azoles, and TMAH, among others. Often the chemicals of concern are present at low concentrations in waste streams that have high flow rates, such that conventional destructive treatment of the targeted chemical may not be viable without the use of a process step that removes and concentrates the chemical of concern for more cost-effective destructive treatment. The viability of a wastewater treatment process for given target compound is often highly dependent on the presence and composition of other constituents that occur in a wastewater (matrix effects. It is essential therefore that wastewater technology development addresses real fab wastewater early in the game. In light of these considerations, proposals are encouraged that:

a. **Develop technology and information for effective wastewater treatment of residual photolithography effluent streams.** The vast majority of photoresist and photoacid generator (PAG) is recovered into solvent waste systems for recovery or incineration, with generally only a small quantity of residual organics reaching wastewater from the developer step, and post resist strip rinses. Presently, a consortium of semiconductor manufacturers and photolithography chemical suppliers are working with the US EPA and a university to investigate new concerns regarding the toxicity and environmental fate and behavior of onium based PAGs. Depending on the results of these investigations, there may be a need to develop cost effective technology for the removal of low concentrations of triarylsulfonium and diaryliodonium compounds (which typically are cations) and/or their photodegradation products from fab wastewater streams that often typically high concentrations of tetramethylammonium cation.

b. **Develop and/or validate effective and complete destruction of fluorinated organic chemicals and gases (PFASs & PFCs) in incineration and fuel blending operations.** At present there is equivocal information regarding the temperature, residence time and other process conditions necessary to assure effective and complete destruction (mineralization) of fluorinated organic chemicals (i.e., PFAS and PFC gases) during waste incineration. Research, that ideally combines controlled laboratory testing, and thermokinetic modeling, with testing at commercial incinerators, of relevant waste compositions, is needed to define incinerator design and operating conditions that provide effective destruction of PFAS, with complete mineralization and fluorine balance; as well as minimization of criteria pollutants (NOx, SOx, CO, PM (particulates), and Volatile Organics). Because of the analytical challenges associated with phase changes and the wide variety of known and potential byproducts (CF_4, C_2F_6, trifluoracetic acid, etc), proposals should feature their chemical analytical plan and capabilities.

c. **Develop information that fabs and POTWs can use to determine what organic chemicals can be effectively treated by biotreatment processes.** Currently there is uncertainty and/or equivocal information regarding the extent to which residual organic chemicals like nMP, TMAH, azoles, and isothiazolinones, amongst others, can be effectively removed in the conventional activated sludge processes used by most POTWs that receive residual fab wastewater. The ability of a particular POTW to treat an organic chemical is believed to vary with SRT, biomass, target chemical concentration, and other factors; but these factors--and how they vary between chemicals and as a function of POTW design and operating conditions--are poorly characterized. PIs are encouraged to partner with device makers and/or government POTWs to better characterize the capability of biological wastewater treatment processes to remove chemicals of interest.

d. **Evaluate/develop concentrating techniques for separation of water/solvent and other mixtures to reduce hazardous waste generation.** Separation of mixtures represents a challenge. For instance, some semiconductor waste streams are composed of 50:50 water/organic, organic/inorganic, or ammonia/ sulfuric acid/ peroxide mixtures that are difficult and expensive to handle and treat. High hydrogen peroxide concentrations, for instance, can be unstable and represent reactive safety hazards. R&D is needed to develop solutions to the handling and treatment of mixed waste streams that can reduce hazardous waste generation and shipping. Potential solutions might include static and dynamic (in-line) separation techniques, among other approaches.

e. **Develop technology for minimizing the use of organic cleaning solvents.** The industry has seen some shifting over time from aqueous and inorganic cleaning agents to organic and organic/inorganic mixtures for newer technologies. Improved knowledge of the technology drivers for increased uses of organic or organic/inorganic mixes of cleaning chemistries, including the physics and surface science that has driven their use, may help minimize use and/or provide alternatives. PIs should also investigate technically viable alternatives and optimization techniques that could reduce the use of these types of substances, and/or shift to alternatives that are “greener” and have a lower total cost of ownership.

C. Air emissions management.

Achieving cost effective treatment of fab air emissions is challenging. Important challenges include limitations in emissions measurement capabilities, an absence of demonstrated cost effective alternatives and limited exhaust abatement solutions. In light of these considerations, proposals are encouraged that:

a. **Develop and validate improved air emission measurement techniques for stacks.** Dilute exhaust emissions are difficult to quantify using FTIR and other established EPA-preferred analytical techniques. The use of novel specialty materials drives the need for new and better measurement techniques. FTIR measurements are hampered by equipment clogging and sampling size limitation that require remedy. Improved online (real-time) capability is needed particularly for Cl_2, N_2O, and other chemicals of interest.

b. **Evaluate methods for N_2O removal from air emissions.** N_2O is one of the largest unabated GWG emissions in the industry. Although the GWP of N_2O is relatively low, there is a need for effective N_2O reduction systems that do not produce large amounts of NO_x. It would be helpful to understand information on potential catalytic and other transformation capabilities that might lead to more efficient use with lower operating costs. PIs should consider engaging/partnering with abatement system vendors to comprehend current capabilities and gaps of leading-edge equipment. PIs might also want to consider this topic in combination with the next topic, NOx abatenment.

c. Investigate NOx abatement options for POU (point of use) or house (end of pipe) abatement of exhaust emissions. Many end-of-pipe or point-of-use treatment exhaust emissions control devices use thermal abatement to treat target chemicals and can result in significant production of NOx. It would be helpful to develop information on generation and/or behavior in typical semiconductor abatement systems and evaluate various mechanisms to eliminate generation of NOx or derive options to convert NOx to a non-regulated species.

d. **Evaluate and develop low to zero GWP heat transfer fluids (HTFs) for Semiconductor equipment chiller use. Industry needs alternative HTFs with** Low GWP that can also fulfill a wide range of performance requirements. These materials are needed as substitutes for higher GWP chemicals, and must not be criteria pollutants (e.g. volatile organic compounds [VOCs]). The upper performance range of existing available low GWP materials is typically 30-50 degrees lower than currently used higher GWP materials and need improvement. HTFs represent a very large portion of the GWGs pareto (EPA estimates 13-15% of U.S. total) so finding etter HTFs presents a large opportunity. PIs might consider working with Tool/Equipment suppliers such as Applied Materials, LAM Research, Tokyo Electron (TEL), etc., as well as device makers to evaluate options.

e. **Evaluate cleaning-time changes to yield in plasma tools - characterize how to set end of recipe limits.** Nozzle flushing (at start) and post endpoint for cleaning/etching uses tend to use excessive quantities of PFCs leading to higher emissions. Excessive run-time on such recipe steps is typically related to fear of yield issues. Projects are needed to develop appropriate empirical models for predicting optimal use of PFCs for non-processing/cleaning steps on CVD/Etch tools.

f. **Evaluate methods and technologies for exhaust switching.** Semiconductor tools employ multiple chemistries, and therefore multiple exhaust system connections that require exhaust switching in order to route the emissions to the appropriate treatment systems. One needed focus is on the reduction or elimination of drag-out of chemical to inappropriate exhaust connections. When this occurs, it can have negative effects such as reduction in 'house' abatement removal efficiency, or cause fouling. PIs should consider engaging/partnering with exhaust/abatement system vendors to comprehend current capabilities and gaps of leading-edge equipment.

g. **Develop and/or validate effective and complete destruction of organic per- and polyfluorinated chemicals and gases (PFASs & PFCs) in incineration and fuel blending operations.** [Please see combined needs in aqueous effluent management section above.]

D. Alternative materials analysis.

The industry strives to use the most benign material that is effective for a given application. However, the task of identifying, demonstrating, and implementing more benign and cost-effective substitutes is challenging. Projects that develop fundamental information on chemical behavior, process technology, and/or toxicity help pave the pathway for innovation. The ideal projects might involve partnering with a chemical or tool supplier who can help demonstrate the technical viability of proposed alternatives. We encourage research proposals that:

a. **Evaluate alternative etchant or cleaning gases and processes that are effective and safe.** At present, a variety of fluorinated gases like CF_4, C_2F_6, SF_6 , and HFCs are used for plasma etching and chamber cleaning. These chemicals can be hazardous, have high global warming potentials (GWPs), and can be difficult to destroy via conventional thermal abatement technology. The evaluation of more fundamentally simple starting gases such as individual carbon, hydrogen and fluorine sources, rather than as PFC or HFC gas, represent potential promise for reducing the amount of PFC and HFC usage and emissions. Such technologies are new, and/or need evaluation of their performance capabilities, safety considerations, emissions factors, and operational sustainability in order for the industry to adopt their use more broadly.

b. **Develop alternatives for more benign photolithography formulations**: Reduction or ideally elimination of PFAS from photolithography formulations could help the industry reduce its environmental footprint and costs. Effective substitutes that have no, or minimal fluorine, and which are known to be benign, need to be identified, validated, and implemented. The ideal project would involve partnering with a photolithography chemical supplier and/or fab who can help demonstrate the viability of proposed alternatives at the wafer-level on tools. Collaboration with a toxicologist who can help prevent “regrettable substitutions” would also be desirable. Proposals should describe how a proposed alternative would be demonstrated to be both benign and viable.

c. **Evaluate more benign and/or easily treatable metal passivating agents.** Currently a wide variety of azoles compounds are used in CMP and wet chemical processes to aid in selective etching/materials removal. However, azoles are potent nitrification inhibitors, biorefractory, and can exert aquatic toxicity. The development of more benign metal passivating agents could save millions of dollars per year in waste treatment costs. Likewise, the development of fundamental information regarding the mechanism by which metal passivating agents work in CMP, wet chemical, and corrosion control might lead to more effective, efficient and benign applications.

d. **Investigate availability of more benign or easily treatable biocides.** Currently a variety of biocides, including various isothiazolinones, are used to prevent microbial growth in carbon-rich wet chemical formulations, and to protect cooling water and cooling tower systems. However, these can be potent nitrification inhibitors, biorefractory, and exert aquatic toxicity. Fundamental information on the use, mode of action, and behavior of biocides may aid in developing more efficient dosing and blowdown regimens. Likewise, the development of more benign and/or readily treatable biocides could save millions of dollars per year in waste treatment costs.

e. **Evaluate less-toxic substitutes for TMAH (tetramethylammonium hydroxide).** TMAH is a strong organic base that is in widespread use as developer and in various wet etch applications as both etchant and pH adjuster. In general, there is a need for strong organic bases that can be used in applications like silicon etching and other wet chemical formulations and photolithography. Fundamental studies on the mechanism of TMAH toxicity may also be of interest to the extent that they help the industry identify more benign alternatives and/or improve the protections and controls on existing uses of TMAH.

f. **Evaluate alternatives to nMP for use in photolithography.** Currently nMP is the subject of an EPA risk analysis, and there is a desire for more benign alternative solvents that can serve as an effective substitute for NMP in photoresist and resist stripping applications. An evaluation of alternative chemistries needs to be conducted for common semiconductor applications like photoresist and photoresist stripping, to establish technical feasibility and reliability.

g. Evaluate alternatives to N_2O for use in deposition processes. N_2O is used extensively in deposition processes and is difficult to abate. As such, it represents one of the largest unabated GWG emissions in the industry. An evaluation of other feasible deposition mechanisms for leading edge semiconductor use that reduces or eliminates N_2O needs to be conducted to establish technical feasibility and reliability.

Contributors

Reed Content (GLOBALFOUNDRIES)
John Currier (Intel)
Chris Lee (TI)
Robert Leet (Intel)
Jennifer Politsch (Intel)
Dave Speed (GLOBALFOUNDRIES)
Brooke Tvermoes (IBM)
Sarah Wallace (TI)
Kevin Wolfe (Intel)
Tim Yeakley (TI)
Ralph Dammel (EMD)
Stefan Uhlenbrock (Micron)
Mansour Moinpour (EMD)
David Palsulich (Micron)