Research Needs Document: ESH

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Introduction

In semiconductor manufacturing, it is a universal industry goal for all materials and processes to be used efficiently, and in a manner that is protective of human health and the environment. This is not only necessary to comply with government rules, but to avoid corrective measures which are expensive and disruptive. With the necessity of the continuing introduction of new materials and nanoparticles in technology innovation, we have to address their potential impact on the environment and human health to ensure a sustainable industry. The semiconductor industry requires proactive R/D efforts leading to a coordinated worldwide reduction of fab greenhouse gas emissions, elimination of chemicals of concern such as perfluorooctane sulfonate (PFOS), and development of industry ESH standards for development of manufacturing tools to protect employees and the environment.

Here we list the needs into six sub-categories as:

5a) ESH aspects of short chain PFAS and Polyfluorinated materials chemicals used in lithography.
5b) Treatment of fab process wastewaters and emissions (including understanding removal of pollutants in conventional activated sludge treatment systems).
5c) Energetic compounds and prevention of uncontrolled reactions.
5d) Nanomaterial/nanoparticle occupational safety and health, and environmental discharges.
5e) Development of ESH-preferable material and process alternatives (e.g. s**u**stainable materials and green chemistries).
5f) Improved portable electronic detector capability for semiconductor chemical air/exposure sampling.

The details for each sub-category can be found below.

5a) ESH aspects of chemicals used in lithography.

Photolithography is essential to the fabrication of semiconductors, with KrF and ArF exposure tools and photoresist chemical systems being the current work horses of the industry. A massive effort is underway to enable efficient manufacturing with EUV (13 nm) photolithography processes, and has introduced entirely new photoresist chemistry systems, along with highly complex and energy intensive EUV exposure tools. In light of these considerations, proposals are encouraged that:

- Evaluate, characterize and optimize the energy and chemical efficiency of EUV processes. EUV tools use large quantities of energy, tin, and hydrogen. Potentially as EUV tools and processes mature, there may be significant opportunities to optimize for reduced energy consumption and waste.

- Evaluate EUV photoresist chemistries for toxicity, environmental fate and behavior characteristics. A wide variety of potential resist chemistry systems are under evaluation for EUV photolithography, including conventional diphenyl iodonium type resists, and novel metal based nanoparticle resists, among others. A systematic evaluation of potential emissions, occupational exposure routes, and waste streams would help fabs and photolithography suppliers assure that effective controls are in place as necessary to enable this rapidly evolving technology.

- Develop technology and information for effective wastewater treatment of residual photolithography effluent streams. The vast majority of photoresist and PAG is recovered into solvent waste systems for recovery or incineration, with only a small quantity of residual organics reaching wastewater streams through the developer step, and post resist strip rinses. Additionally, in a small number of scenarios an aqueous photoresist system exists where all waste goes to the industrial wastewater. Despite the low expected concentrations, a consortium of semiconductor manufacturers and photolithography chemical suppliers are currently working with the US EPA and a university to investigate new concerns regarding the toxicity and environmental fate and behavior of onium based photoacid generator compounds (PAGs). Depending on the results of these investigations, there may be a need to develop cost effective technology for the removal of these compounds and/or their photodegradation products from complex fab wastewater streams. How for instance does one remove very low concentrations of organic cations like triphenylsulfonium or a substituted diphenyliodonium from a wastewater drain system that contains very high concentrations of tetramethylammonium cation?

- Develop information and/or technology on the behavior, toxicity, and treatment of per and polyfluorinated chemicals used in photolithography. 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 environmental and health risks. In many cases, shorter chain perfluorinated and/or novel per and polyfluorinated chemicals have been introduced with the intent that they provide more benign substitutes. However, recent controversy over short chain fluorinated chemicals like GenX make it ever clearer that chemical substitutions must be well informed and backed by solid data. Research that provides fundamental data on the behavior, toxicity and fate of per and polyfluorinated chemicals that are in current use and/or targeted for use in photolithography would be very valuable. Similarly, research that leads to, and ideally demonstrates, the efficacy of wastewater treatment technology for the removal of these compounds from real fab waste streams would be very valuable. Selecting relevant compounds and wastewater matrices would be an essential aspect of generating research results that are useful and actionable by the semiconductor industry. Towards that end, PI are encouraged to partner with photolithography suppliers and/or device makers.

- Provide characterization and predictive capability for the behavior, environmental behavior, toxicity, and treatment of organic cations and anions.

- Provide characterization and predictive capability for the behavior, environmental behavior, and toxicity of per and polyfluorinated chemicals. PFOS and PFOA are well characterized, but shorter chain chemicals like PFBS and similar shorter chain and/or branched species are less well characterized.

- Provide characterization and predictive capability for the behavior, environmental behavior, toxicity, and treatment of organosilane materials

5b) Treatment of fab process wastewaters and emissions.
Cost effective treatment of fab wastewater effluents and exhaust emissions has become an increasing challenge due to the bioinhibitory, refractory, and/or potential PBT characteristics of some of these compounds. In light of these considerations, proposals are encouraged that:

- Develop cost effective and safe means for treating wastewaster streams that contain high concentrations of hydrogen peroxide. Some fab waste water streams may contain 20 wt % or more of residual H_2O_2, which represents a reactive hazard that can be surprisingly difficult and expensive to treat safely.

- Develop and/or validate effective and complete destruction of organic per and polyfluorinated chemicals in incineration and fuel blending operations. At present there is equivocal information regarding the temperature, residence time and potential other process conditions necessary to assure effective and complete destruction of per and polyfluoroalkyl substances (PFAS) in a manner that does not generate significant amounts of undesirable daughter products like CF_4 and C_2F_6. Ideally, the project would include commercial scale test burns as well as laboratory and theoretical evaluations.

- 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 treated in the conventional activated sludge processes used by most POTWs that receive residual fab wastewater. It is generally appreciated that the ability of a particular POTW to treat an organic chemical may 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.

- Develop technology and information that Fabs can use to determine what organic chemicals can be effectively destroyed by advanced oxidation or other means of treating aqueous wastes. There are a wide variety of advanced oxidation techniques but generally little quantitative information or definitive guidance regarding whether a given chemical may be effectively destroyed within a particular wastewater matrix. In some cases it has been determined that the partial decomposition products resulting from an AOP represent only relatively minor rearrangements of the target molecule, which in some cases are more toxic than the parent compound.

5c) Energetic compounds and prevention of uncontrolled reactions.
Certain semiconductor fabrication steps entail the use of highly energetic and/or reactive chemicals. When these chemicals must be used, it is essential that the reactive and hazardous properties of the materials and their decomposition products be well-characterized; and that processes within which they are used be designed in a manner that comprehends and effectively mitigates the hazards. Based on industry statistics, the majority of reactive events that occur during semiconductor manufacturing operations are associated with deposited or condensed materials in the foreline and exhaust systems downstream of CVD and ALD/ALE deposition tools. In light of these considerations, we encourage research that:

- Develops ex-situ monitoring techniques which could be used to detect and forewarn of the potential accumulation of hazardous depositions downstream of CVD and similar manufacturing tools.

- Provides chemical behavior models and predictive tools that can be used to help mitigate the deposition of hazardous/energetic materials downstream of deposition tools.

- Provides practical and safe methodology for collecting samples of reactive deposits from the interior surface of a duct; transporting the sample to a laboratory; and loading it into an instrument. At present, the lack of suitable apparatus and methodology is an impediment to efforts to characterize the accumulation of potentially reactive materials downstream of deposition tools.

- Provides practical and safe methodology for removing, transporting and cleaning piping and parts that have accumulated post-deposition byproducts.
- Provides improved methodology for characterizing the energetic properties of precursor materials, and managing the reactive hazards downstream of deposition tools. Currently used methods like the instantaneous power density (IPD) presume a purely thermal event, and may not appropriately account for the relevant reactive conditions and/or role of co-reactants like oxygen and moisture.

5d) Nanomaterial/nanoparticle occupational safety and health, and environmental discharges.
At present the alumina, ceria and silica particles used in CMP processes represent the principal use of engineering nanoparticles by the semiconductor industry. However, research is trending towards the use of nano metallic EUV photoresists, graphene, quantum dots, and other nano sized materials. At present, efforts to characterize potential workplace exposures of airborne nanoparticles is hampered by limitations in the available methodology and instrumentation. In light of these considerations, we encourage proposals that:

- Determine toxicity threshold limits that are actionable and relevant to potential occupational exposures and which provide a technical basis for the establishment of occupational exposure limits.
- Develop and validate methods for nanoparticle occupational exposure monitoring.
- Develop and apply test methods for evaluating the efficacy of existing PPE relative to nano materials of interest for semiconductor manufacturing.

5e) Development of ESH-preferable material and process alternatives (e.g. sustainable materials and green chemistries).
Employing the most benign material that is effective for a given application is an important but not always readily achievable goal. We encourage research proposals that:

- Develop 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 may 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.
- Develop 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.
- Develop 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.

- Develop alternative etchant gases and processes that are effective and safe. At present, a variety of fluorinated gases like CF_4, C_2F_6, and SF_6 are used for plasma etching and CVD 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 development of more fundamental information on their use and/or behavior in abatement systems, along with potential catalysts, might lead to more efficient use with lower operating costs.

- Develop more efficient wet chemical processes. An industry trend from the use of batch wafer cleaning tools to single wafer cleaning tools has been driven by the need to provide effective wafer cleaning for more advanced technology nodes. However, the trend to single wafer wets tools may cause increased fab chemical usage. Investigation of fundamental wafer cleaning mechanisms may help provide more effective and efficient processes and tool usage (e.g. high efficiency spray nozzles) that use less water and chemical, and produce less wastewater. Depending on the research pursuit, partnering with tool suppliers might provide the most direct route to achieving high impact results.

- Develop more benign alternatives to nMP for use in photolithography. Currently nMP is the subject of an U.S. EPA risk analysis, and there is a desire for more benign alternative solvents that still achieve effective cleaning of photomasks and other organic thin films.

5f) Improved portable electronic detector capability for semiconductor chemical air/exposure sampling.

Having efficient and effective exposure detection and analysis for Fabs is an ongoing need that is not always met with legacy, large scale "portable" devices, industrial hygiene samples or after-the-fact tests on pull-samples. We encourage research proposals that:

- Develop small-scale detectors for integration into light weight, highly portable detection devices, or for use as standalone devices. These should focus on common semiconductor chemicals (e.g. HF, HCl, Arsine, nMP, etc.) and categorically focus on organics, fluorides, caustics, nanomaterials, etc.

- Development of highly portable detection devices that can provide detection of multiple types of chemicals or have the flexibility to interchange detectors in order to test for varying chemicals in any exposure scenario.

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