Research Priorities from SIA Gap Analysis & SRC Summer Study

1.0 Introduction

The June 2013 SRC Summer Study identified 5 priority areas where focused environmental, health, and safety (EHS) research and development is needed in order to enable the semiconductor industry technology roadmap:

- Nanomaterial occupational safety & health
- Nanomaterial environmental discharges
- Energetic materials characterization, handling, and safety
- III-V EHS Enablement
- Chemical information on emerging materials & processes

This document provide recommendations regarding specific aspects of the R&D that is needed to address these 5 gap areas. The intent is to identify the need for actionable information, but not to presume the content of specific research programs.

2.0 Fundamental EHS Goals

Although the focus of this document is on the five specific areas of research need, it is a universal semiconductor industry goal for all materials to be used efficiently, and in a manner that is protective of human health and the environment. In consideration of these universal goals, the five above priorities were derived from the following basic set of EHS requirements supporting the safe and environmentally sound use of materials, as they apply to the semiconductor technology roadmap.

a) Chemical handling, usage, and safety:
1. Knowledge of hazardous properties and risks
2. Well-defined safe handling practices
3. Well-understood and optimized process
4. Use of the least hazardous material that is effective for the application (based on well-defined hazard evaluation methodologies)
5. Substitution of known or potentially restricted process chemicals

b) Occupational exposures and controls:
1. Knowledge of exposure routes
2. Defined measurement and detection methods, including metrology for substances in relevant matrices
3. Knowledge of protective exposure threshold values

4. Appropriate Personal Protective Equipment (PPE) for relevant exposure routes
5. Appropriate engineering controls for relevant exposure routes

c) Environmental discharges and controls:
1. Characterized air, water, and waste effluent streams
2. Metrology for the substance in relevant matrices
3. Protective discharge/emissions levels
4. Cost effective effluent and discharge controls
5. Known fate and behavior in the environment

d) Environmental and Safety Aspects of Materials Contained in Products:
1. Substitution of known or potentially restricted substances which are contained in products at levels relevant to regulatory thresholds
2. Well-defined alternatives assessment methodologies to avoid substitutions with materials that themselves become targets of future bans/restrictions or which are subsequently shown to be hazardous
3. Knowledge of potential for release of chemicals during product use and disposal
4. Sustainable end-of-life strategies (to the extent applicable to semiconductor devices)

3.0 Nanomaterial Occupational Safety & Health

Nanomaterials have a wide variety of potential applications in semiconductor technology, but presently the alumina, ceria and silica nanoparticles (NPs) used in Chemical Mechanical Planarization (CMP) processes constitute the predominant usage. Silver NPs, carbon nanotubes (CNTs) and other nanomaterials may be used for thermal interfacing and device applications. Various other nanomaterials are under consideration for applications in photoresists and self-assembling material formulations, among others. In view of the current and likely increasing importance of nanomaterials to semiconductors, there is a need for a balanced research portfolio that addresses the current use of nanoscale particles in CMP processes while also paving the way for the safe use of nanomaterials in future applications.

At present, outside of CNTs and TiO_2, there is little regulatory guidance and a general lack of directly actionable information or standards (e.g. particle-specific threshold limit values for occupational exposure), to guide the safe use of engineered NPs. The effectiveness of safe handling practices, PPE, and engineering controls are predicated on knowledge of toxicity thresholds and degree of exposure, which in turn are predicated on the availability of validated procedures for their quantification in relevant media. Moreover, there are a range of alternative workplace exposure metrics such as mass concentration, particle number, particle surface area concentration, and particle size distribution, whose toxicological significance and inter-relation are not well understood (Oberdorster, 2010; Nel et al, 2013) . NP research sponsored by the semiconductor industry must therefore be collaborative, well informed, and targeted to produce actionable information that address the industry’s most pressing questions.

In light of the inherent and well-characterized hazards of acids, bases and other conventional chemicals used in CMP formulations, the CMP tools and slurry formulation and distribution systems that are typically employed in fabs are designed to provide a high degree of isolation from workers. Work conducted collaboratively with NIOSH has determined that occupational exposures to CMP particles in CMP processing areas at the Albany Nanotech facility are generally low, but also highlight the challenges in developing occupational exposure monitoring methods for nanoparticles (Shepard and Brenner, 2013).

Toxicity evaluations that have been conducted on alumina, ceria, amorphous silica and other NPs generally vary widely depending upon the particular aspects of the particles being assessed (particle size, physiochemical properties, dispersion state) as well as the particular toxicity assessment method being utilized (dose, cell lines, exposure protocols, and assay end points) (Kroll et al, 2011; Maynard et al, 2011). The industry would benefit from metastudies that synthesize the available data and which relate them to relevant occupational exposure scenarios. To the extent that toxicity evaluations are conducted, the results should be expressed in context of the existing body of toxicity information relevant to semiconductor materials and operations.

To aid in such evaluations, a set of 4 test slurries comprising the 4 basic types of particles (alumina, ceria, precipitated silica and pyrolytic silica) have been formulated and are available to PI’s via a materials transfer agreement with SRC/ERC. These “model slurries" represent the simplest possible stable dispersion of particles in water. While it should be recognized that commercial CMP slurries are formulated with a wide variety of additional ingredients—including surface active and redox active chemicals which are intended to influence particle behavior—the model slurries serve as fully characterized test subjects to develop analytical techniques and assess toxicity.

In consideration of existing information gaps regarding toxicity and physicochemical characterization methodologies for engineered NPs that are currently used or likely to be used by the semiconductor industry, the industry encourages research proposals which:

- Address first the EHS characteristics of CMP particles and then secondarily the portfolio of the nanomaterials which are most likely to be used in future semiconductor industry applications.
- Determine toxicity threshold limits that are directly relevant to potential occupational exposures and which provide a technical basis for the establishment of occupational exposure limits.
- Develop and validate methods for occupational exposure monitoring.
- Inform safe handling practices for CMP and other nanomaterials.
- Develop and apply test methods for evaluating the efficacy of existing PPE relative to materials of interest for semiconductor manufacturing.
- Develop and validate improved PPE and engineering controls, to the extent that improvements are needed.
- Evaluate the role of chemical additives, compositional dependencies, and environmental media (e.g. pre- vs. post-process) on particle behavior, toxicity, and the efficacy of PPE and engineering controls.

4.0 Nanomaterial Environmental Controls and Impacts

Many types of naturally occurring NPs (including alumina, ceria, and silica) are believed to be ubiquitous in natural water systems, and intertwined with a variety of natural geologic and biological processes. A deeper understanding of background concentrations of these naturally occurring nanomaterials, the geochemical processes that govern their occurrence and behavior, and how biota respond to them, may provide important context for evaluating potential impacts of NP wastewater discharges, and thereby determining appropriate discharge standards or guidelines, which currently do not exist.

Efforts to characterize NPs in both waste materials and natural water systems face difficult metrology challenges. There is a need for standardized and validated methodologies which can discriminate quantitatively between individual types of nanomaterials, and evaluate concentration by size, number count and mass concentration within real environmental matrices.

Published evaluations of NP removal from CMP wastewaters have primarily addressed municipal-style biological wastewater treatment processes; whereas relatively little information is available regarding NP removal in the types of physicochemical treatment processes that are often used in fabs to pre-treat wastewaters prior to discharge. The existing literature indicates that alumina and ceria, but not silica[1], typically have a high level of removal in conventional biological wastewater treatment processes (Limbach et al, 2008; Jarvie et al, 2009). However, the fate and ultimate stability of NPs that are removed into waste solids is an important consideration that needs to be addressed.

Commercial CMP slurries are formulated with a variety of surface-active and other additives that are added with the intent of influencing particle behavior. The fate of these and other constituents that may occur within fab waste treatment systems may also exert important influences on the treatability of NPs, whose behavior might otherwise be fundamentally described using modified DLVO (Derjaguin and Landau, Verwey and Overbeek) or similar phenomenological approaches (Elimelech et al, 1995).

In consideration of the principal types, characteristics, quantities, and uses of engineered NPs; the nature of waste streams; the absence of standardized and validated methods for characterizing NP in complex matrices; and the absence of data on ecotoxicity, environmental fate and impact, we encourage research proposals which:

- Develop and validate methods for characterizing NP concentration, fate, and behavior in waste streams and in natural water systems
- Determine and/or provide a synthesis of information (meta studies) on the threshold concentrations at which selected NPs demonstrate toxicity and/or other negative impacts on natural water bodies that receive treated aqueous wastes
- Develop and recommend tests and criteria for establishing effluent discharge threshold limits for NP if necessary
- Determine the concentrations at which CMP NP wastes demonstrate toxic and/or inhibitory effects on the microbes resident in conventional biological wastewater treatment processes
- Characterize NP removal mechanisms within existing waste treatment processes, and explain the observed removal in terms of fundamental engineering principles that can be used to design and/or optimize waste treatment processes
- Develop new technology for NP removal from fab waste streams in a manner that quantifies the performance of the new technology relative to existing methods, and which advances a fundamental understanding of engineering principles, practices, and methodologies for NP removal.
- Evaluate the stability of NPs in waste solids, their long term stability and fate, and best practices for sustainable treatment and disposal processes.

---

[1] The removal of silica NP in treatment processes is likely related to its low pH_{zpc}, and/or the potentially lower affinity of surface organics for the surface of silica particles.

5.0 III-V EHS Enablement

There is considerable interest in incorporating III-V film structures into silicon wafers as a means of providing enhanced IC device performance in wafers manufactured using sub-10 nm technology nodes. Certain combinations of the elements As, Ga, In, Sb, and P yield high electron mobility, with wide and/or adjustable band gaps, and the potential for reduced power consumption. Although many of these same materials have long been used as dopants in Si-based devices, and composite GaAs wafers have long been used in certain applications (e.g. optoelectronics and microwave components), the incorporation of III-V materials into Si wafers presents a variety of EHS challenges related to new materials usage, tool design, and wafer fabrication processes.

In wet etch/clean tools, for instance, a variety of wet chemical acid, base and oxidizer formulations will be used to clean and/or etch III-V film surfaces. Similarly, CMP tools will use a variety of abrasive slurry formulations to planarize III-V film surfaces. Likewise, metal-organic chemical vapor deposition (MOCVD) processes will be used to deposit III-V films, and plasma etch tools will be used to etch high aspect ratio features within III-V film structures.

Whereas the hazards of elemental arsenic and arsine are well known, the potential hazards of less widely used and characterized III-V elements, like indium, are less well understood. For instance, recent health study information indicates an incidence of lung disease among indium workers, and recent toxicological information suggests that inhalation threshold limits for indium may need to be made more restrictive (Cummings et al, 2013; Hines et al, 2013). Likewise, the combinations of acids, bases, oxidizers and reductants hold the potential to generate III-V chemical species that are not well characterized and which may be volatile or exhibit unique partitioning properties. Whereas arsine and phosphine are well understood reaction products of certain wet chemical applications, with readily available chemical analytical monitoring methods, little information exists regarding the spectrum of As, Ga, Ge, In, and Sb species that could be produced under potentially relevant processing conditions. Knowledge regarding the process conditions under which potentially hazardous chemical species may be formed, and how to monitor for them, is necessary to provide appropriate monitoring and protection.

In consideration of the III-V elements that are under development for use in silicon wafers, the chemical processing mixtures and conditions to which they will be subject, and the absence of physicochemical and health information on potentially materials, we encourage proposals which:

- Determine Indium toxicity threshold limits that are directly relevant to potential occupational exposures and which provide a technical basis for the establishment of occupational exposure limits.
- Identify potentially hazardous and/or volatile III-V species and the conditions under which they may be produced in appreciable quantities
- Develop and validate analytical methods and/or instruments to characterize volatile III-V species which may be produced,
- Characterize the process conditions under which relevant hazards are produced, and identify process boundaries which prevent or mitigate the formation of hazardous constituents.
- Determine relevant EHS characteristics for under-characterized III-V species
- Determine the efficacy with which existing conventional wastewater treatment processes remove relevant III-V species.
- Determine the efficacy with which existing air emissions abatement processes (point-of-use and centralized) remove relevant III-V species

- Develop and validate new air, water and waste treatment methods for relevant III-V species if necessary.
- Where justified by projected usage quantities develop and demonstrate feasible processes for recovery/recycling of III-V materials.

6.0 Energetic Materials Characterization, Handling, and Safety

Certain semiconductor fabrication steps entail the use of highly energetic and/or reactive chemicals. When these chemicals must be used, it is essential that their physicochemical and reactive properties be well-characterized and that there be well-considered engineering analysis and methodologies for designing processes that comprehend and effectively mitigate the risk.

A wide variety of reactive chemicals are currently used, including silanes, metal hydrides, and an increasing diversity of organometallic precursors. Typical applications involve the deposition of atomic scale films using methods like MOCVD (Metal Organic Chemical Vapor Deposition), ALD (Atomic Layer Deposition), CVD, and ion implantation. As the dimensions of the fabricated device structures become finer, involve more complicated non-planar geometries (like fins in FinFET devices), and require more precision of placement and increased purity, there is a trend towards use of precursor chemicals which are capable of delivering and depositing metals under lower temperatures and less reactive process conditions. These requirements tend to drive the use of increasingly specialized, and often reactive, chemicals. Moreover, it has been observed that where unplanned chemical reaction events do occur, they tend to involve mixtures of energetic byproducts, downstream of the actual reaction chamber.

A review of the technical literature indicates a lack of consensus regarding which characterization methodologies are most appropriate for certain types of reactive chemical hazards (Crowl and Elwell, 2004; Carreto-Vazquez et al, 2010). For instance, differential scanning calorimetry (DSC), differential thermal analysis (DTA), and automated pressure tracking adiabatic calorimeters (APTAC), have different relative merits, depending upon the nature of the particular chemical reaction hazard (Kossoy, 2005).

In consideration of the nature of the reactive and energetic materials used by the semiconductor industry, experience with energetic events, and the state of the science for characterizing, evaluating and mitigating reaction hazards, we encourage research proposals which:
- Develop rapid, efficient, and inexpensive methods and/or test apparatus for characterizing reactive materials and their reaction hazards
- Address the role of reactive mixtures and byproducts that may occur within exhaust systems and other infrastructure downstream of semiconductor tool reaction chambers
- Develop predictive methods and software tools which aid in the estimation of chemical properties and hazards of reactive and energetic materials.
- Develop and or/advance fundamental understanding and engineering analysis of reaction hazards.
- Develop methods and tools available for the analysis and mitigation of reaction hazards.
- Develop “green chemistry” methodologies for more benign precursor materials.

7.0 Chemical Information on Emerging Materials & Processes

Chemical information, including physicochemical properties, toxicity, and behavior, is essential to the safe use of chemicals, selection of benign alternatives, development of effective treatment & disposal methods, and virtually any "green" chemistry effort. However, there is a significant data gap between the tens to hundreds of thousands of chemicals used in commerce, and the relatively few for which comprehensive and reliable EHS property and toxicity data are available. For instance, of the ~90,000 chemicals for which the evaluation of EHS characteristics are required under the EU REACH regulations, there exists a full set of measured EHS data for only 91 chemicals; microbial degradation half-lives for only 216; bioconcentration data for 995; acute aquatic toxicity data for 2,198; chronic aquatic toxicity data for 241; and octanol-water partition coefficient (K_{ow}) data for 13,349 (Strempel et al, 2012).

In the absence of measured data, various chemical property prediction relationships may be employed, but their predictive capability depends upon the class of chemical under consideration and whether training sets of measured data were available to derive the predictive relationships. For instance, many existing tools are not able to produce reliable estimates for certain types of salts, inorganic compounds, organometallics, and surface active compounds, or those with non-standard SMILES **(**Simplified Molecular-Input Line-Entry System codes).

The conventional means of determining the toxicity of chemicals to humans is via animal toxicity evaluations that typically require 2 to 3 years and several million dollars; a paradigm that does not provide for the tens of thousands of chemicals that require evaluation. Moreover, standard *in vivo* methodologies are often not informative regarding the mechanisms by which a chemical exerts toxicity. However, where in vitro and/or predictive techniques are developed, they generally must be validated against conventional in vivo techniques in order to be useful and provide actionable information.

In recognition of these concerns, there are extensive efforts worldwide to develop high-throughput screening (HTS) assays and improve the capability of computational algorithms for predicting toxicological and ecotoxicological properties. These efforts, however, are largely prioritized toward high production volume chemicals, and therefore sometimes overlook important classes of chemicals that are used by the semiconductor industry. Conventional prediction tools have, for instance, failed in the past to effectively anticipate hazards associated with perfluorinated chemicals like PFOS and PFOA, or quaternary ammonium compounds like TMAH.

In consideration of the chemicals used by the semiconductor industry, the essential importance of chemical information to using chemical safely, and the state of the science for predicting and evaluating chemicals, proposals are encouraged which:

- Evaluate existing chemical environmental property and ecotoxicity estimation software to optimize applicability to the chemicals of principal interest to the semiconductor industry.
- Develop/advance predictive capability for physicochemical properties, toxicity, ecotoxicity and environmental behavior.
- Evaluate and validate the use of HTS (high throughput screening) for predicting the toxicity of chemicals that are of principal interest to the semiconductor industry, including nanomaterials and emerging research materials.
- Develop and validate quantitative tools or methodologies for aiding evaluations of chemical alternatives. For instance, by evaluating the influence of permutations in a quaternary

ammonium compound’s structure on its physicochemical properties, EHS characteristics and toxicity.
- Address the effects that permutations in the composition of a chemical mixture have on the physicochemical properties and behavior of that chemical mixture and its ESH characteristics and toxicology.
- Aid the identification of chemicals or chemical mixtures that provide a certain function or set of effects (i.e., selective etching of certain types of materials, dissolution and/or destruction of certain types of photoresists).

8.0 Mini and Meta-studies

There are a number of topics for which a short term mini- or meta- study might reveal key information and work scope definition that could enable highly targeted and cost-effective future research projects. This section provides suggestions for a few such studies. In the context below, a mini study is one that produces new information, perhaps from a survey or preliminary set of experiments, and which might either direct or discourage a more comprehensive study. A meta-study is one that synthesizes existing information into conclusions and possibly a workplan recommendation. For instance, a meta-study on the toxicity of alumina, ceria and silica NPs, might for instance consist of a critical literature review, and proposed work scope for key information that might be needed in order to recommend exposure threshold limit criteria as follows:

- What information regarding toxicity thresholds is available, and what certainty and relevance can be attached to the existing body of data?
- Is sufficient information available from the existing literature to inform the establishment of exposure threshold levels?
- Absent the availability of an adequate body of published information, can a specific set of toxicity tests and endpoints be recommended to establish threshold exposure values for dermal and respiratory exposure?
- What information is available within the published literature regarding the methods for evaluating the efficacy of gloves and/or respirators as PPE for the NPs used by the semiconductor industry, and is it sufficiently informative to conduct PPE testing?
- What information is available regarding the efficacy of engineering controls for mitigating workplace exposures to the NPs used by the semiconductor industry, and is it sufficient for the industry’s needs?
- Absent the availability of an adequate body of published information, can a workplan for developing and validating appropriate test methodology be recommended?

9.0 Prioritization, Proposal Content, and Deliverables

Critical Review and context: The proposals should provide context regarding how the proposed work is informed by the existing body of published research and how it will advance the state of the science.

Prioritization: Research activities must be attuned to the list of materials that industry is, or will most likely be, using, and prioritized according to the anticipated technology insertion schedule and projected usage quantities.

Actionable Information: Research necessarily involves addressing, producing, and integrating diverse information, but ultimately we are most in need of information that enables us to take specific actions to protect human health and the environment.

Development of validated methods: A key objective of industry-supported EHS research is the development of validated characterization methods that can inform future research, as well as reliable validated methods that member companies can employ at their fabs.

10.0 References

Carreto-Vazquez, V., I. Herandez, W. Rogers, M. Mannan (2010). Inclusion of pressure hazards into NFPA 704 instability rating system. Journal of Loss Prevention in the Process Industries. Vol. 23. p. 30-38.

Crowl, D., and T. Elwell (2004). Identifying criteria to classify chemical mixtures as “highly hazardous” due to chemical reactivity. Journal of Loss Prevention. Vol. 17. p. 279-289

Cummings, K.J, M. Nakano, K. Omae, et al (2012). Indium Lung Disease. Chest. 2012 June; 141(6): 1512–1521. doi: 10.1378/chest.11-1880PMCID: PMC3367484

Elimelech, M., J. Gregory, X. Jia, R. A. Williams (1995). Particle Deposition and Aggregation Measurement: Modeling and Simulation. Elsevier Publishers.

Hines, C.J., J. Roberts, R. Andrews, M. Jackson. And J. Deddens (2013) Use of and Occupational Exposure to Indium in the United States. Journal of Occupational and Environmental Hygiene. Vol. 10(12). P 723-733.

Jarvie et al (2009). Fate of Silica Nanoparticles in Simulated Primary Wastewater Treatment. ES&T Vol 43 p.8622-8628

Kossoy, A., A. Benin, and Y. Akhmetshin (2005). An advanced approach to reactivity rating. Journal of Hazardous Materials. Vol. A118. p. 9-17

Kroll, A., C. Dierker, C. Rommel, D. Hahn, W. Wohlleben, C. Schulze-Isfort, C. Göbbert, M. Voetz, F. Hardinghaus, and J. Schnekenburger. Cytotoxicity screening of 23 engineered nanomaterials using a test matrix of ten cell lines and three different assays. Particle and Fibre Toxicology 2011, 8:9.

Limbach, L., R. Bereiter, E. Muller, R. Krebs, R. Galli, and W. Stark (2008). Removal of oxide nanoparticels in a model wastewater treatment plant: influence of agglomeration and surfactants on clearing efficiency. Eviron. Sci. Technol. Vol. 42. p. 5828-58

Maynard, A., D. Warheit, and M. Philbert (2011). The new toxicology of sophisticated materials: nanotoxicology and beyond. Toxicological sciences. Vol 120(S1). P.S109-S129

Nel, A.E., E. Nasser, H. Godwin, D. Avery, T. Bahadori. L. Bereson. E. Beryt, J. Bonner. D. Boverhof, J. Carter, V. Castranova, J. DeShazo, S. Hussain. A. Kane, F. Klaessig, E. Kuempel. M. Lafranconi. R. Landsiedel., T. Mally, M.B. Miller, J. Morris, K. Moss. G. Oberdorster, K. Pinkerton. R. Pleus., J.A. Shatkin, R. Thomas. T. Tolaymat, A. Wang, J. Wong (2013). A Multi-Stakeholder Perspective on the Use of Alternative Test Strategies for Nanomaterial Safety Assessment. ACS Nano, 2013, 7 (8), pp 6422

Oberdörster G. (2010). Safety assessment for nanotechnology and nanomedicine: concepts of nanotoxicology. Journal of internal medicine. Vol. 267(1):89-105

Shepard, M., and S. Brenner (2013). An Occupational Exposure Assessment for Engineered Nanoparticles Used in Semiconductor Fabrication. Ann Occup Hyg (2013) doi: 10.1093/annhyg/met064

Strempel, S. , M. Scheringer, C. Ng , and K. Hungerbühler (2012). Screening for PBT Chemicals among the “Existing” and “New” Chemicals of the EU. Environ. Sci. Technol., 2012, 46 (11), pp 5680–5687.