ROADMAP

NANOMATERIALS: STRATEGIES FOR SAFETY ASSESSMENT IN ADVANCED INTEGRATED CIRCUITS MANUFACTURING

HORIZON 2020

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This roadmap can be downloaded from:

http://www.nanostreem.eu/

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Who should read this roadmap?

If you are an Environmental, Health and Safety (EHS) professional, technologist, researcher or work in the semiconductor industry, you will obtain an overview of the safety of working with nanomaterials within the context of semiconductor manufacturing.

If you are a policy maker, member of a national competent authority, or a member of the European Chemicals Agency (ECHA), you will get an insight into the semiconductor industry's programme in utilising nanomaterials.

Finally, if you have a natural curiosity regarding nanomaterials and their safety regarding worker exposure or the environment, this roadmap will inform you about the current safety/environmental protocols in place and those that will need to be developed for the future use of nanomaterials.
Objectives

Understanding properties of nanoparticles and how they behave in living systems is a relatively new area of scientific study. As a result, a precautionary approach has been utilised when handling and using these materials where exposure cannot be avoided.

From a semiconductor manufacturing perspective, this project aims to identify what nanomaterials are in use today and identify their use in future technologies in order to determine possible worker/environmental exposure.

Between current and possible future use of nanomaterials, an holistic view of the nano-hazards and the associated process risk is critical for the successful pragmatic integration of nano-safety aspects in an overall risk management methodology for semiconductor manufacturing.
Executive Summary

The European Semiconductor Industry has demonstrated throughout the years to be a leader in Environmental Health and Safety Management. As an industry that is always on the cutting edge of scientific discovery, it is predisposed to having to resolve novel EHS topics.

One such subject concerns comprehending the unique characteristics of nanomaterials in relation to worker health and environmental consequences. In this roadmap, growing EHS knowledge in how to identify the presence of nanoparticles in the workplace and how to minimise exposure to workers and the environment is forefront to the output of the NanoStreeM project.

NanoStreeM’s learnings/findings illustrate potential worker or environmental exposure to nanoparticles to be very low for the two semiconductor processes that were evaluated – Chemical Mechanical Polish and Coloured Resist.

Recommendations regarding the availability of nanomaterial toxicological information on safety data sheets, communication of findings regarding tasks with high potential for exposure, exposure scenario identification of strategic nanomaterials and the continued dissemination of information generated in NanoStreeM is important to advance pragmatic tools/solutions to aid in the mitigation of potential nanoparticle exposure in the workplace/environment.

For those readers interested in more detailed information regarding NanoStreeM and all of its work packages, please refer the our website at http://www.nanostreem.eu/
What are Nanomaterials?

Nanomaterials are chemical substances or materials that have structures ranging from approximately 1 to 100nm in at least one dimension. The European Union defines nanomaterials as:

“A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm.”

Given their unique characteristics when compared with the same substance or material with larger scale structures, nanomaterials can differ in their physico-chemical properties.

Nanotechnology as a discipline has grown exponentially in the last number of years with nanomaterials present in products ranging from cosmetics to computers. It is the unknowns regarding nanomaterial properties that has given rise to health and environmental concerns.
Nanomaterial Risk Assessment – Current State

Nanomaterials are regulated by REACH and CLP in European Union countries. However, the required information regarding nanomaterials is rarely provided on safety data sheets.

From a rudimentary chemical/material approval perspective, the basic information needed by Environmental, Health and Safety professionals such as nano specific structure, physical-chemical and toxicological information is not readily available through the regular channels.

In addition, the ability to measure exposure to nanomaterials in the workplace via air and or water sampling, by personal monitoring or waste water sampling is certainly more complicated than for larger scale structures.
Nanomaterials currently in use in the semiconductor industry

Across Europe’s semiconductor industry, nanomaterials fall into two categories. Those nanomaterials that are purchased from a supplier and are typically used in what is known as a “slurry”. These are stable suspensions of nanomaterials dispersed in water with other chemicals and are used for abrasive surface preparation. The other nanomaterials are those that are generated via the manufacturing process itself through unintended spillings of deposits.

**Purchased Nanomaterials**

- Silica slurry: 70%
- Ceria slurry: 19%
- Alumina slurry: 9%
- Colored resist: 2%

**Suspected Generation of Nanomaterials**

16 different scenarios submitted:

- Opening of process chambers or exhaust lines during **maintenance activities**
- Etch
- Diffusion,
- CMP (Chemical Mechanical Polish)
- CVD (Chemical Vapour Deposition)
- Wafer grinding and splitting operations
Nanomaterials currently in use in the semiconductor industry

Through the NanoStreeM project, nanomaterials were identified in specific use cases:

- Chemical Mechanical Polish (CMP)
- Coloured Resist
- Scenarios related to nanoparticles generated in the manufacturing process
- Nanoparticles generated from alumina silicate ceramic fibre isolation material through thermal treatment.
- Environmental exposure scenarios were also given consideration.

This allowed for the development of an inventory containing 47 nanomaterials used in today’s semiconductor industry within Europe.
The semiconductor industry – a special working environment

Semiconductor devices are manufactured in very special working environments. These are known as cleanrooms.

There are several standards available that classify a cleanroom by the number of particles found in the cleanroom’s air or put another way, the cleanliness of the air.

How clean is a cleanroom?. In essence the cleanest cleanrooms have low figures, such as Class 1, Class 10 etc.

To help compare these work environments, a typical hospital operating theatre is some 10,000 times “dirtier” than most high volume manufacturing semiconductor cleanrooms.

Keeping cleanrooms free as possible from particles is one of the reasons why people who work in a cleanroom need to wear special clothing known as Bunny Suits.
Chemical Mechanical Polish

CMP is by far the area within semiconductor manufacturing that utilises the greatest quantities of nanomaterials. The function of CMP is to improve the performance of semiconductor devices by polishing their surfaces to be perfectly flat, smooth and flawless. Without this process, devices would have wiring causing shorts and opens resulting in the device’s failure to operate correctly.

A total of 16 different tasks with relevant exposure scenarios for workers were identified across normal operations, preventative and corrective maintenance tasks and in accidental operating mode.

Approximately half of the tasks had low amounts of nanoparticles available for exposure and these had a low potential for dust or aerosol formation. Of the remaining tasks, they did have higher amounts of nanoparticles (>1g) available for exposure but with low potential for dispersion through aerosol formation. There was just one task that had a high potential for dispersion through aerosol formation (accidental spray of slurry while disconnecting from a dispense system under pump pressure). Also the tasks with higher nanoparticle exposure were found to be undertaken on a very low frequency (1 to 2 times per annum) apart from just one (removal of dried sludge or solids from filters) which is undertaken on a daily basis.

Given the combination of high nanoparticles available for exposure with a daily frequency of undertaking the task, this scenario poses the greatest exposure dose for workers in the CMP area.
CMP Process Overview
Coloured Resist

In semiconductor manufacturing, one of the processes is called Photolithography. This is the process during which the geometric pattern that produces the desired electrical behaviour is transformed to the surface of the silicon wafer. A “resist” is a chemical substance containing light-sensitive mater in suspension in a solvent. It is utilised to etch the films and materials used in semiconductor manufacturing.

A total of 9 tasks involving the use of coloured resist were identified that had tasks with exposure scenarios for workers. All of the tasks apart from 1 (drain cleaning inside equipment with solvents and wipes) had low amounts (<1g) of nanoparticles available for exposure. There were several tasks (connecting/disconnecting resist bottles, collection of accumulated resist bottles and cleaning equipment nozzles inside the equipment) that had daily frequencies but had low amounts of nanoparticles available for exposure. In summary, the highest possible exposure for workers is either during drain cleaning inside of equipment or in the collection of empty resist bottles.
Scenarios Related to Nanoparticles Generated in the Manufacturing Process

A total of 5 tasks were identified where workers could be exposed to nanoparticles generated during various manufacturing processes. All of these tasks were maintenance related.

All of the tasks have high amounts of nanoparticles available for exposure apart from one. These were i. opening and disassembly of foreline particles released on pipe connections, ii. opening chambers without a pump purge before opening, iii. Opening the scrubber (cyclone type) to remove powder and iv. Opening and disassembly of exhaust ducts containing solid layers or powder particles.

The tasks dealing with cyclone type scrubbers or exhaust ducts have a high potential for dust or aerosol formation. Finally, the scrubber task given its high level of nanoparticles available for exposure, high dispersion probability in conjunction with the frequency of the task (daily) make it the task with the potential for the highest exposure dose.
Nanoparticles Generated From Alumina Silicate Ceramic Fibre Isolation Material Through Thermal Treatment

Although not unique to semiconductor manufacturing, the use of electrical heater elements with insulation material consisting of ceramic fibres in certain tools for thermal treatment have been highlighted as 3 tasks had nanoparticles available for exposure.

All 3 tasks were maintenance related which involved opening the heater element’s safety covers which allowed exposure to the ceramic fibres.
A total of 8 relevant environmental exposure scenarios were identified. 2 of the scenarios were related to the collection of empty packages or waste from cleaning.

5 scenarios were related to nanoparticles in waste water which was to be treated in an on-site waste water treatment plant or it was to be treated in a local municipal waste water centre. The presence of nanoparticles in waste water was the most prevalent form of environmental exposure and is related to the amount of nanoparticles in the CMP process.

The final environmental exposure scenario is related to the nanoparticles generated in thermal processes. These are then pumped to the exhausts, scrubbed by different techniques depending upon the process and eventually emitted to air.
Gaps in our knowledge

In order to highlight tasks that have potential for exposure to nanoparticles, tasks had to be aggregated to enable the identification of potential exposure scenarios on an industry wide basis. Potential exposure to workers from nanoparticles in the manufacturing process suggests a comprehensive degree of knowledge with respect to relevant risk assessments and associated controls.

However, due to the complexities associated with the identification of nanoparticles in process waste water, knowledge at an industry level is not as comprehensive as that for potential worker exposure. Nonetheless, it is important that the semiconductor industry addresses these gaps through a combination of engineering and administrative controls.

On a more tactical level, the NanoStreeM consortium identified significant gaps in information related to generated nanoparticles. This gap included the chemical composition, type, amount and their dispersive behaviour. It was noted that all these characteristics were very heavily influenced by factors such as process type, process parameters, type of semiconductor tool used and available scrubbing techniques.

With respect to the purchased nanomaterials, there was a better alignment of the data as there is less of an influence on their characteristics by factors such as the process or tool type.
Risk assessment and risk mitigation

As described previously, nanomaterials pose novel EHS management challenges. With the typical sources of data for risk assessments such as safety data sheets not incorporating sufficient information regarding nanomaterials along with the complexity of sampling waste water, air sampling and undertaking personal monitoring, it became clear that some level of standardised risk assessment protocol was necessary to develop and deploy across the semiconductor industry.

This gap was addressed by the NanoSteeM project. A total of 32 risk assessment tools/approaches were identified under quantitative and qualitative methodologies. A tiered approach for the risk assessment was developed.
Risk assessment and risk mitigation

The first tier involved the use of ISO TS 12901/2’s the control banding approach. This proved to be highly beneficial. This approach was found to be user-friendly, required limited, and readily available (nano of bulk) parameter information and included risk mitigation measures. The second tier, which involved the Advanced Reach Tool (ART) showed to be the most promising tool for modelling semiconductor exposure scenarios. The third tier assessment was based on measured data. The need for standardised measuring protocols for the semiconductor industry was recognised by the consortium as a crucial element for risk assessment improvement.
Risk assessment and control methodology

Graphical illustration of the “Tiered Approach” utilised in the risk assessment
Tools to aid risk assessment and risk mitigation

The NanoStreeM consortium undertook much testing of “off the shelf” air sampling and monitoring equipment that had the potential to be used for nanomaterials.

It was found that Condensation Particle Counters (CPCs) were found to be the most accurate and could be used for personal, indoor and outdoor monitoring so long as the model did not have an internal background feature.

The use of Dynamic Light Scattering in conjunction with Scanning/Transmission Electron Microscopy was successfully used to determine for the presence of nanomaterials in process waste water.

The chemical composition of nanomaterials found in process waste water could be determined by utilising Energy Dispersion X-Ray Spectroscopy (EDX) or X-Ray Photoelectron Spectroscopy (XPS).
Strategic nanomaterials in the semiconductor industry for the future

There is a growing body of data related to potential exposure scenarios both to the worker and environment for nanomaterials currently in use in semiconductor manufacturing. However, given the strong research culture within this industry, attention needs to be afforded to those nanomaterials that are of a strategic importance to the sector in order to ensure their appropriate environmental and safety management.

Through the NanoStreeM project, a “Search Strategy” was developed to identify those nanomaterials that potentially will be selected for manufacturing processes in the coming months and years. A total of 1,070 journal articles had been reviewed. This resulted in the identification of seven distinct material classes for future use.
Future nanomaterials

The seven nanomaterial classes are illustrated below with their forecasted application and handling.

<table>
<thead>
<tr>
<th>Materials class</th>
<th>Application</th>
<th>NM handling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group IV-Materials</td>
<td>Transistor channel</td>
<td>Standard ULSI techniques, Epitaxial growth</td>
</tr>
<tr>
<td>Si / Ge / SiGe / SiC (to some extent)</td>
<td>Memory</td>
<td></td>
</tr>
<tr>
<td>Carbon Allotropes</td>
<td>Transistor channel</td>
<td>Transfer, dispersion, Epitaxial growth</td>
</tr>
<tr>
<td>Fullerenes, CNTs, Graphene</td>
<td>Wiring, Sensor other</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-D materials</td>
<td>Transistor channel</td>
<td>Transfer</td>
</tr>
<tr>
<td>hBN, black Phosphorus, MoS₂, WSe, ...</td>
<td></td>
<td></td>
</tr>
<tr>
<td>III-V / II-V</td>
<td>Photonics, Transistor channel</td>
<td>Dispersion, Epitaxial growth</td>
</tr>
<tr>
<td>GaAs / GaN / InP / ...</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heavy metal quantum dots</td>
<td>Photonics</td>
<td>Dispersion</td>
</tr>
<tr>
<td>SC Metal oxides</td>
<td>Sensors</td>
<td>Dispersion</td>
</tr>
<tr>
<td>others, e.g. transition and noble</td>
<td></td>
<td></td>
</tr>
<tr>
<td>metals</td>
<td></td>
<td></td>
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The main conclusions from the consortium’s analysis of in excess of 1,000 journal articles are:

Ultra Large Scale Integration processing schemes impose very high demands on the integration of new materials and device features in terms of reproducibility and yield.

Materials that can be manufactured by means of common technologies will be introduced preferably.

New nanomaterials and device approaches will not add additional hazards to people or the environment due to their specific nature.
Strategic nanomaterials in the semiconductor industry for the future – graphical illustration

Background & Motivation

- **NanoStreem**
  - Environmental, Safety, and Health (ESH) risks of nanomaterials cannot be derived from their bulk properties
  - Precautionary approaches in order to avoid exposure
  - Promote good practices, identify gaps in methodologies, and support risk assessment to protect human health

- Acquire a comprehensive overview on the utilization and technological issues of particulate nanomaterials in current and future semiconductor manufacturing

Key benefits of nanomaterials

- Nanomaterials have proven capabilities for ultimately scaled or post-silicon devices due to 0D, 1D, and 2D nano-size effects
- Nanowire transistors
- Nanomaterials modify matrix (bulk) materials to give enhanced performance
  - Physical properties: low-k dielectrics
  - Processing: high-NA immersion litho
- Improve manufacturability as process medium: CMP

Integration of particulate nanomaterials

- Application of nanoparticle powders and dispersions
  - Functional fillers
  - Dispersions
  - Preparation from bulk or direct growth
  - Unintended release during deposition, etching, waste treatment, end-of-life

Summary

- Particulate nanomaterials already in use in process media, packaging, and assembly
- Use cases can guide introduction to other areas

Parts of this compilation have been derived from the ITRS chapters on ESH and Emerging Research Materials
EHS training regarding nanomaterials

When the NanoStreeM consortium members reviewed the training available with respect to EHS aspects of nanomaterials, only 4 partners (1 industrial and 3 research) had training specific for nanomaterials. The remaining consortium partners followed safety guidelines as applied to general chemical safety.

This resulted in the need to develop comprehensive nanomaterial specific training materials. NanoStreeM developed three distinct training packages:

1. Internal training package for operators and maintenance engineers within the consortium.
2. Training package for safety professionals to conduct risk banding, risk assessments and monitoring.
3. “Train the Trainer” package for safety professionals which effectively could be used as a toolbox for training and communication.

These training packages were developed to cater for instructor lead or web based training platforms.
Horizon 2020 and Nanomaterial safety

The NanoStreeM project co-funded by Horizon 2020 Framework Programme of the European Union, is providing the European Semiconductor Industry the opportunity to grow its knowledge regarding its utilisation of nanomaterials. Through the identification of exposure scenarios for the current use and potential future use of nanomaterials, the industry has been able to identify those tasks that have the potential to generate nanoparticles which could result in worker or environmental exposure.

The Consortium, a mix of industrial, research and academic partners have worked together to develop semiconductor standards for the sampling, health monitoring, water and waste water characterisation, risk assessment methodology and training of employees in the sector with respect to nanomaterials.
Recommendations

1. Communicate the findings from the use cases to the semiconductor industry.

2. Policy makers enable the provision of detailed toxicological information on Safety Data Sheets relating to nanomaterials.

3. Continue the dissemination of the information generated in the NanoStreeM project to external sources such as conferences and journals (academic and industry).

4. Develop a standardised occupational air measuring protocol for the semiconductor industry.

5. Deploy the training material within the NanoStreeM consortium both in an instructor lead and on line format to cater for enhanced safety training in nanomaterials.
The Consortium

[Logos of various companies]

- CEA
- Fraunhofer IISB
- Intel
- imec
- UCF Foundry
- NXP
- Premed
- ST
- Soitec
- Texas Instruments
- TNO
- Tyndall National Institute

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