

SAFETY OF ENGINEERED NANOMATERIALS USED IN SEMICONDUCTOR MANUFACTURING

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Safety of engineered nanomaterials used in semiconductor manufacturing

The safety of engineered nanomaterials used in semiconductor manufacturing is placed under the spotlight in this extensive and informative analysis by NanoStreeM, a consortium that comprises of 14 partners from six European countries

The semiconductor industry uses a growing variety of materials, as companies seek to further improve devices' performance to meet increasing market demand in a constant process of innovation. At present, there are more than 200 chemical compounds consisting of elements, such as silicon, germanium, copper, gold, hafnium, indium and many others, which are present in most computer and mobile phone chips (Figure 1). In some manufacturing processes, engineered nanomaterials (ENM) enable superior yields and performance.

Understanding the properties of these innovative materials and nanoforms, and how they interact with living systems and the environment, often comes years after the materials have been introduced in manufacturing. Such an inherent uncertainty brings about multiple challenges in the governance of the occupational and environmental risks. This is a common situation for many technology-intensive sectors, and it requires a systematic risk reduction approach. This understanding was the driving force behind the NanoStreeM project, which was funded by the European Union (EU) from 2016 until 2018. The objectives of the project were to:

- Build inventories of materials, research topics and applications relevant for nanomaterial use and exposure in nano-electronics manufacturing;
- Identify gaps in knowledge and methodologies to assess the risk of engineered or accidentally produced nanomaterials and;
- To inform stakeholders in order to support decision-making and governance of the risks related to the use of nanomaterials and nanoforms in the semiconductor fabrication process.

The NanoStreeM consortium comprises 14 partners from six European countries and combines unique expertise throughout the research and development chain: from the academic labs via technology development through the semiconductor application side. The companies represented in the consortium have some of the largest fabrication facilities in Europe and are globally representative. The consortium included leading centra of semiconductor research, such as Imec, CEA, Fraunhofer, and the Tyndall National Institute and several other academic institutions.

ENMs possess unique properties, which enable broad industrial applications. The risk assessment of chemicals and by extension ENMs, used by the industry is a legal obligation of the employers in the EU. At present, no mandatory Occupational Exposure Limits (OEL) for ENMs are prescribed at EU or Member State level. On the

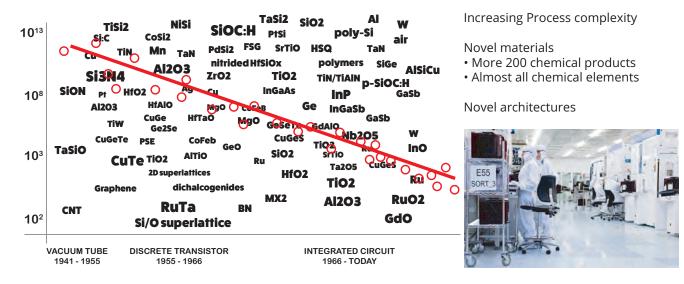


Fig. 1: Occupational Health and Safety challenges in the Information and Communication Technologies (ICT) innovation chain.

other hand, some member states have introduced registries tracing ENM use in the supply chain. The NanoStreeM consortium established for the first time how and where ENMs are used in semiconductor manufacturing. Major project findings can be summarised as follows:

Use of nanomaterials throughout semiconductor processing

The industrial partners composed a database comprising information about which ENM-containing products are used in the semiconductor fabrication facilities in Europe. The database includes 47 products containing nanoforms, most of them suspensions of nanoparticles dispersed in water (slurries), used for abrasive surface preparation.

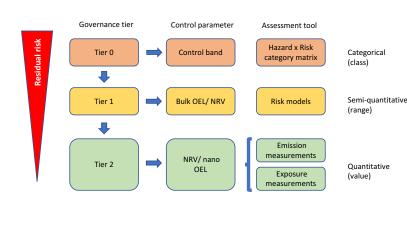
Summary of the findings

- > Most of the nanoforms contain $SiO_{2'}$ CeO_{2'} or Al_2O_3 nanoparticles.
- > ENMs are used in two main types of operations – Chemical Mechanical Polish (CMP), having slurries as polishing agents, and photolithography using coloured photoresist for wafer patterning.

- In some other well-defined production steps, nanomaterials can be generated as process residues.
- > Size and shape information for all ENMs could be collected.
- > Finished products (i.e. computer chips) do not contain ENM.

Encountered data gaps

- The physicochemical and toxicological properties necessary to perform a safety assessment of nanomaterials are not readily available for the safety professional. The standard safety data sheets for chemical products do not contain information about the eventual presence of nanoforms and their characteristics.
- > In most of the cases acute and chronic toxicity information of the bulk material for the assessed products was absent.
- Many generic nanotoxicity databases developed to date are not available for public use or the available data only covers a few materials, which are not used in semiconductor device manufacturing.



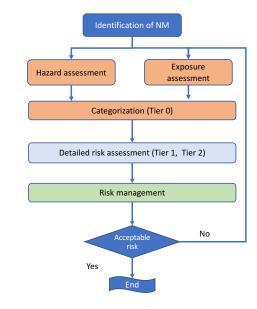


Fig. 2: NanoStreeM risk assessment and control methodology.

What is the impact on the industry and society?

- > NanoStreeM demonstrated for the first time where ENMs are used in a representative sample of the manufacturing facilities in Europe.
- > NanoStreeM collected the most common and typical exposure scenarios.
- > The overall use of ENM in semiconductor manufacturing is limited to a few well-defined operations.

How can we perform a risk assessment of operations involving ENM?

Unique properties of ENMs entail dependence of the toxic effects on the size and shape of the nanoparticle and not to unit mass. The toxic effects can be substantially modified by applied surface functionalisation. Therefore, the current expert opinion agrees that conventional risk assessment tools have limited applicability to nanomaterials or nanoforms. At present, there are more than 30 risk state-of-the-art assessment tools providing quantitative and qualitative methodologies for risk assessment. Therefore, detailed guidance for risk assessment was produced. The applicability of the risk assessment guidance was evaluated by the industrial partners. The consortium has encountered several substantial gaps which impede the use of recommended risk assessment tools.

The NanoStreeM tiered risk assessment approach

- > NanoStreeM developed a three-tier approach for risk assessment (see Figure 2).
 - Tier 0: Use of risk banding approaches to categorise risk: The ISO Standard ISO/TS 12901-2:2014 or StoffenManager Nano.
 - Tier 1: Use of (semi) quantitative tools to give exposure estimated: NanoSafer, Consexpo and Advanced REACH Tool (ART)
 - Tier 2: Use of detailed emission measurement data to check the conclusions of Tier 1.

Data gaps

> The ISO Standard ISO/TS 12901-2:2014 requires a collection of detailed information, which is not required for the risk categorisation and is not readily available even for wellestablished slurries on the market.

- > Many other control banding tools require toxicological information about the nanoform without prescribing clear workarounds if such information is absent.
- NanoSafer, Consexpo, and ART could not be used for the selected typical scenarios. This represents a clear direction for future tool development.

What is the impact on society?

- > Exposure to workers during production is likely in only a limited number of operations and it was estimated to be low for CMP.
- > It is necessary to establish a harmonised protocol for emission/exposure measurements in semiconductor clean rooms.
- > It is important to produce reliable toxicological information about the nanomaterials used by the semiconductor industry

How to measure nanoparticle emissions in air and water

The absence of particle background is a major advantage of the clean room and it facilitates and enhances the measurement sensitivity. Several wearable devices suitable for individual monitoring were identified. Contamination risk of the clean room by the measurement instruments is not a real concern, as most of the devices do not generate particles or their emissions can be controlled.

Gaps identified

- Recommended devices provide number concentrations, which can be linked only indirectly to mass-based exposure limits if such are available. Use of air nanoparticle emission measurement devices and the interpretation of the obtained results need special training of the staff.
- Only the DLS (dynamic light scattering) technique was identified as suitable for routine wastewater analysis. However, DLS does not provide concentration readout. Identified

analysis techniques for wastewater containing nanomaterials are available in research settings but cannot be applied routinely by the industry due to a lack of training.

What is the impact on the industry?

- > The usual methods for nanomaterials monitoring are suitable for a clean room environment.
- The OECD tiered exposure measurement approach was recommended for use in clean rooms.

Competences development and training needs

Definite needs for competences development were established in terms of informing about the physicochemical properties of nanomaterials, a dedicated nanotoxicology knowledge base, and about the limitations of the traditional occupational chemical risk assessment. To meet these needs, the project composed nanosafety training packages, as one of its major outcomes. The project partners Tyndall, CEA and Imec composed three dedicated training courses focusing on semiconductor industry processes and the clean room environment. The topics of the training are as follows:

- > An induction training package for technical personnel first-time users of nanomaterials with no prior experience.
- A training package for safety professionals to aid in their formative education concerning the properties of nanomaterials and available risk assessment methodologies.
- "Train the trainer" guideline for deployment of the training.

Developed training packages will be used by the semiconductor industry and the partnering institutions after the end of the project. The packages are available upon request via the European Semiconductor Industry Association or via the project coordination office at Imec.



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