

# Three-Tiered Risk Assessment for Engineered Nanomaterials. A Use Case for the Semiconductor Industry

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**Abstract.** Safety of engineered nanomaterials is a new scientific field, which draws increasing attention in the literature. Among the challenges the field is facing are the insufficient amount and quality of nanotoxicological data and the ambiguity in the metrics describing the exposure. This results in substantial difficulties in the actual quantification of risk in terms of exposure limits, which is a cornerstone of the regulatory chemical risk assessment. While there is no golden standard for risk assessment and management several pragmatic systems have come into being. All of these employ some form of categorization and grouping of materials into hazard groups. This paper outlines the risk assessment approach developed within the H2020 project NanoStreeM, which is based on a combination of categorical and quantitative risk assessment tools implemented in a 3-tier system. The approach includes the use of existing tools, such as ART, Consexpo and NanoSafer, in combination with the ISO standard ISO/TS 12901-2:2014 and field measurements. The paper outlines the experience with these tools for risk assessment of typical exposure scenarios present in semiconductor manufacturing.

## 1. Introduction

Nanomaterials offer a wide range of possibilities for new applications in major economic sectors, for example automotive, cosmetics, consumer electronics. At the same time, the industrial use of novel manufactured nanomaterials raises questions about potential unintended risks for the workers, consumers or the environment. Among the challenges the field of nanosafety is facing are the insufficient amount and quality of nanotoxicological data and the ambiguity in the metrics describing the exposure. This results in substantial difficulties in the actual quantification of risk in terms of dose-response relationships and exposure limits, which is a cornerstone of chemical risk assessment.

Challenges in the traditional chemical risk assessment approach can be traced to the assumption that the hazard and the risk can be quantified absolutely. Since hazard profile data for novel materials are inherently uncertain, the risk can be estimated only in a relative way. A way to do that is by introducing a grouping of materials based on certain similarity metrics. Such an approach favors categorical or qualitative risk assessment tools, which results in a classification into hazard and control bands for the process under investigation. The risk assessment approach developed in the NanoStreeM consortium focuses on the specific conditions present in the semiconductor industry – notably almost particle-free



working environment. NanoStreeM is funded by the H2020 Research and Innovation program of the European Union. The goal of the project is to promote good practices by identifying and implementing standards, identify gaps in methodologies and directions for further investigations to support governance of the occupational risk induced by the use of nanomaterials in the semiconductor industry.

## 2. The NanoStreeM risk assessment approach

This paper outlines the 3-tier risk assessment approach developed within NanoStreeM. The tiered risk assessment approach is depicted in Fig. 1. The method can be summarized as follows. Tier 0 consists of hazard and risk categorization. As Tier 0 method the consortium has identified the ISO Technical Standard ISO/TS 12901-2:2014 “Nanotechnologies - Occupational risk management applied to engineered nanomaterials” [1]. The standard is focused on intentionally produced nano-objects, such as nanoparticles, nanopowders, nanotubes, nanowires, as well as of aggregates and agglomerates and is focused on the management of the inhalation hazard. The standard defines 5 nano-hazard groups which combine with 4 exposure bands (see Table 1). This is constrained by 5 control bands, which identify measures to be implemented in order to reduce the risk for the personnel.

ISO Hazard class	Definition	Examples
Category A	No significant risk to health	Non-toxic soluble nanoparticles
Category B	Slight Hazard – Slightly toxic	-
Category C	Moderate Hazard	-
Category D	Serious hazard	-
Category E	Severe hazard	Carcinogenic insoluble nanoparticles, insoluble fibers, such as carbon nanotubes

Table 1. Engineered nanomaterial hazard grouping according to ISO/TS 12901.

Tier 1 consists of risk scenario modeling, however, without performing emission measurements. The outcome of this tier is an indicative estimate of the expected exposure (for example a Nano Reference Value) and a prescription on how the exposure can be controlled. Finally, Tier 2 consists of designating of specific monitoring and control strategies for the exposure or emission of nanomaterials, which confirms the identified control strategies.

The rationale behind the approach is to be able to refine the prescribed control measures and to reduce uncertainty as the risk assessment progresses along tiers.

## 3. Evaluation of some tools prescribed for semiconductor-specific scenarios

The project partners have identified a limited number of scenarios where exposure to the nanomaterials used in the semiconductor industry may occur. The data have been collected during a structured survey conducted among the industrial project partners for several typical semiconductor facilities across Europe [2-5]. Based on the frequency and the scale of different activities, it was decided that Chemical Mechanical Polishing (CMP) as the process of choice to be used in tools evaluations (Table 2).

The semiconductor fabrication process involves a series of steps involving the processing of Si wafers. A wafer is produced in a disk shape from semiconductor base material (i.e. Si or Ge). The integrated circuits are patterned on the surface of the wafer and finally, they are diced and packaged into the final chips. CMP is a ubiquitous step in all kinds of chip manufacturing technologies. After a certain number of processing steps the surface roughness of the wafer increases, so to keep the yield a wafer needs to go through a polishing process - CMP, for it to obtain again a very flat surface. During CMP, a wafer is turned upside down to face the polishing pad and slurries (i.e. suspensions containing nanoparticles of cerium oxide (CeO<sub>2</sub>), silicon dioxide (SiO<sub>2</sub>) or aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) are applied during the abrasion. CMP slurries are a well-established set of products containing nanomaterials that are used within the semiconductor sector. Accordingly, they have constituted the largest number of submissions in NanoStreeM (Table 3, [2]).

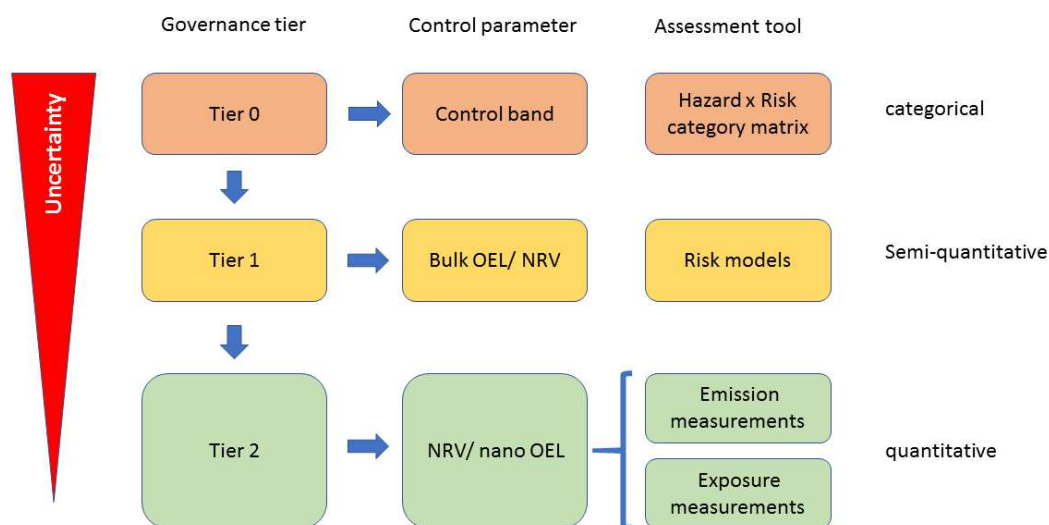


Figure 1. NanoStreeM tiered risk assessment and control approach.

Task	Scenario	Duration (Hours)	Frequency
Pad and/or filter change	During pad change: exposure from mechanical dispersion of dried out residues on a pad, platen, chuck, pad conditioner or other parts	1	Daily
Corrective maintenance (CM) after interruption or broken wafer	During corrective maintenance: exposure from mechanical dispersion of dried out residues from regular operation - broken wafer parts - small internal leakages not rinsed or cleaned enough before maintenance	1-3	Monthly

Table 2. Scenarios selected for evaluation in Consexpo, ART, and NanoSafer

Purchased Nanomaterial Type	Number of products
Silica slurry for CMP	33
Ceria slurry for CMP	9
Alumina slurry for CMP	4
Coloured Resist	1

Table 3. Summary of the submissions for the purchased ENM used in processing

A specific implementation of the approach tested in the project is presented in Fig. 2. Tier 0 recommended the use of two tools: the ISO TS 12901-2:2014 and Stoffenmanager-nano [6], which are both risk-banding methodologies. Three tools providing quantitative exposure estimates have been recommended for use in Tier 1: Consexpo [7], ART [8], and NanoSafer [9]. ConsExpo is not a nano-specific tool, which is developed by RIVM to estimate exposure to substances from consumer products such as paint, cleaning agents and personal care products. ConsExpo estimates the inhalation exposure to vapors of the liquid or to liquid aerosols (airborne droplets of the product). The Advanced Reach Tool (ART) is a quantitative exposure model developed for non-nano substances. ART provides either a task-based personal exposure level or an 8-hour Time Weighted Average (TWA) exposure level. ART contains a mechanistic exposure model that is applied to probabilistically calculate exposure levels in mass concentrations. NanoSafer is an online nano-specific control banding and risk management tool developed by the Danish National Research Centre for the Working Environment (NRCWE) for exposure situations to dry nano-powders during the production and use in specific workplace scenarios

and to emissions from nanoparticle-forming processes. Finally, in comparison with field particle emission measurements was recommended in Tier 2.

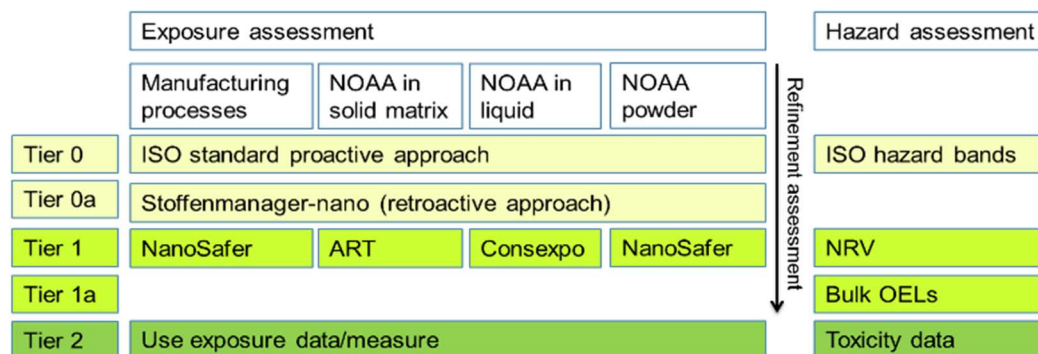


Figure 2. Different risk assessment tools evaluated in NanoStreeM. NOAA – nano-objects and their aggregates and agglomerates; NRV – nano reference value; OEL – occupational exposure limit

#### 4. Summary of the evaluation

The evaluation procedure consisted of using the prescribed tools according to the developed guidelines and available operational safety expertise within the consortium. The purpose of the activity was to evaluate the suitability of the tools for semiconductor processing applications. The evaluation can be summarized as follows:

**Tier 0:** The ISO Standard ISO/TS 12901-2:2014 required toxicological information about the bulk material, which was made available from the safety data sheets. The use of the ISO standard required collection of detailed information, which is not required for the risk categorization and was not readily available even for well-established slurries on the market. Stoffenmanager Nano required toxicological information about the nanoforms, which was not present in available sources. Therefore, the tool was not used further.

**Tier 1:** Consexpo was found to be unsuitable for the selected scenarios, as none of them involved spraying. NanoSafer was designed to assess continuous dust emissions (i.e. pouring activities) and not fast transient particle sources as observed. No tool could be used to assess exposure from liquid dispersions of ENM.

**Tier 2:** Only two literature sources of data have been identified [10, 11]. ART provided a mass estimate for the expected emissions, which without assumptions about particle size and density, could not be compared to available data. Worst case scenario estimates conducted with ART indicated a low absolute amount of exposure for the CMP scenarios. It is, therefore, recommended to calibrate ART for use in low emission conditions, notably in the semiconductor clean rooms.

The detailed results are summarized in a project deliverable, which will be published separately.

#### 5. Conclusion and Perspectives

In conclusion, the exposure to workers during production is likely in only a limited number of operations and it was estimated to be low for CMP. Consistent use of ART would require collecting particle size distribution in all cases, which may not be practical. Moreover, ENM toxicological properties are likely to depend on the surface area and not on the mass. The consortium has encountered several substantial data gaps, which impede the use of recommended risk assessment tools, notably:

- Only a limited number of tools providing quantitative information was identified, and none was so far used or validated in semiconductor industrial settings.
- Many nanotoxicity databases developed to date are not available for public use or the available data cover only a few materials which are not used in the semiconductor device manufacturing
- Many 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 without adaptation for the selected typical scenarios. Such adaptations would require targeted field measurement campaigns. A prerequisite for doing so would be to establish a harmonized protocol for nanoparticle emission measurements in semiconductor clean rooms. Furthermore, it is important to obtain reliable toxicological information about the nanomaterials used by the semiconductor industry. This also represents a clear direction of future research, since the ENM currently used in semiconductor manufacturing are not well studied at present.

## 6. Acknowledgment

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