Air Sampling Approaches for Engineered Nanoparticles used in the Semiconductor Industry

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Workplace Exposure Assessment

Consider risks from **engineered nanomaterials (ENMs)** across the product lifecycle, applying a management system framework:

Hazard Characterization

Evaluate data on physiochemical properties and toxicity.

Exposure Assessment

Apply the most practical method to identify and evaluate data on exposure scenarios.

Air sampling to quantify exposures

Risk Characterization

Follow banding models, screening methods, other recommended approaches. Consider uncertainty.

Risk Management

Apply the hierarchy of controls and confirm protection. Communicate risks and controls. Periodically re-evaluate and improve.

Air Sampling Approaches

Screening level to more comprehensive approaches, depending on objectives. Common metrics include:

- Number
- Mass
- Size

**Particle surface area is a key factor in toxicity but not as commonly measured in workplace exposure assessments.*

Screening with direct-reading instruments → Filter-based samples: mass and composition → Electron microscopy (TEM/EDX): size, shape, number, composition

See the AIHA Fact Sheet: Nanoparticle Sampling and Analysis (2016)

Air Sampling Challenges

Measurement

- Commonly involves multiple methods/instruments
- Electron microscopy methods resource-intensive
- Validated methods limited
- Time-resolved devices non-specific
- Background characterization for number metric
- Differentiation from incidental ultrafine particles

Results Interpretation

- Metrics and correlation to biological activity
- Consensus lacking on size ranges to include and data analysis methods
- Comparative values limited

Images: TSI CPC; TSI SMPS

Workplace Exposure Scenario: Semiconductor Fabrication

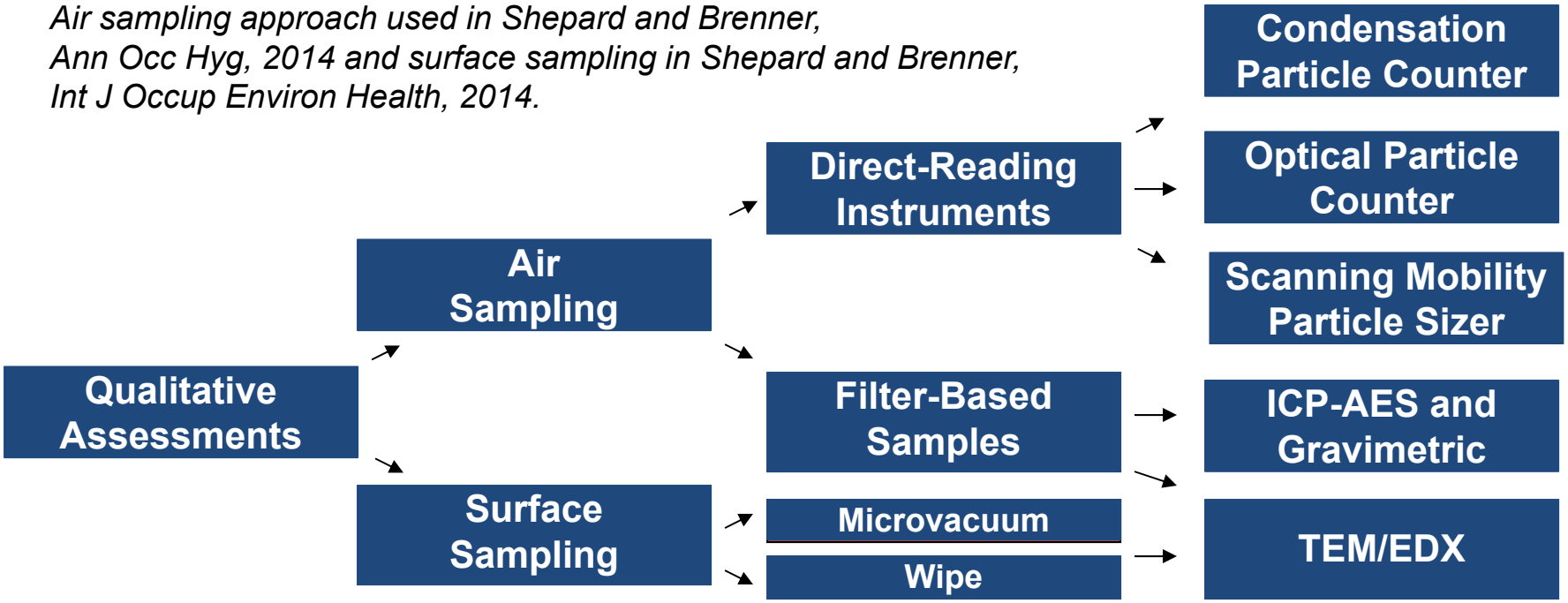
Chemical Mechanical Planarization (CMP)

- ENMs are used as abrasives in wafer polishing processes in semiconductor fabrication
- Product formulations: typically include amorphous silica, aluminum oxide, or cerium oxide nanoparticles
- Physical forms at semiconductor fabs: slurry, powder depending on site
  **or embedded on pad*

Activity	Duration	Frequency
1.Operate bulk slurry delivery system	0.25-1 hr	Daily/ weekly
2.Operate CMP Tool	2-8 hrs	Daily
3.Set up CMP Tool	< 0.5 hr	Daily
4.Conduct PM on CMP Tool	2-8 hrs	Monthly
5.Change pre-filter on CMP WWT system	~ 0.5 hr	Monthly
6.Clean up slurry overflow or spill	< 1 hr	As needed

Exposure Assessment Approach used for an academic research project

Sampling approach applied in a semiconductor workplace.
Air sampling approach used in Shepard and Brenner, Ann Occ Hyg, 2014 and surface sampling in Shepard and Brenner, Int J Occup Environ Health, 2014.



ICP-AES: inductively coupled plasma - atomic emission spectroscopy.
TEM/EDX: transmission electron microscopy/energy dispersive x-ray spectroscopy.

Figure: Shepard M. © 2014

Applicable Reference Values: Number

- Benchmark levels above background exposures for biopersistent particles 1-100 nm (IFA, 2009, 2011)
  - 20,000 p/cc for granular ENMs with density > 6,000 kg/m^3
  - 40,000 p/cc for granular ENMs with density < 6,000 kg/m^3
- 20,000 p/cc above background (BSI, 2007)

Applicable Reference Values: Mass

- 0.3 mg/m^3 TWA for nanoscale titanium dioxide, for up to 10 hours (NIOSH CIB 63, 2011)
- 0.3 mg/m^3 TWA as an upper bound categorical guideline adjusted for other poorly soluble low toxicity (PSLT) nanoparticles (Schulte et al., *J Nanopart Res* 2010; NIOSH CIB 63, 2011)
- 0.06 x Bulk OEL for insoluble, non-fibrous ENMs (BSI, Nanotechnologies-Part 2, 2007)

Screening Approach
used by EHS practitioners

Sampling approach currently being applied at three semiconductor manufacturing sites in the U.S.

Considerations in selecting initial assessment approach:

- Materials of interest: ubiquitous (silica, alumina)
- Clean environments with high degree of process control
- Short duration tasks with potential for inhalation exposure
- Limited budget/resources (for TEM or multiple DRI sets)
- Limits of detection and instrument specifications
- Instruments available for rental
- No site-specific baseline data

Screening Approach used by EHS practitioners

Screening Methods and Action Limits:

- **Number**: task measurements with condensation particle counter; probe positioned in worker breathing zone
  - 20,000 p/cc above background
  - Safety factors: measuring particles 20 to~1000 nm and comparing to reference value for particles ≤100 nm; non-specific
- **Mass**: personal breathing zone task measurements with laser photometer with cyclone
  - 0.03 mg/m^3 TWA
  - Instrument lower size range: 0.1 µm
  - Safety factors: set at 10% of NIOSH REL for nanoscale TiO2; measuring respirable particle mass; non-specific

Progress and Future Directions

- General increase in amount and quality of data from toxicology studies
- Improved capability to collect, evaluate and interpret air sampling data with advances in:
  - Occupational exposure limits (OELs) or banding approaches
  - Method for setting OELs
  - Instrumentation/sampling devices
  - Guidelines for air sampling and analysis

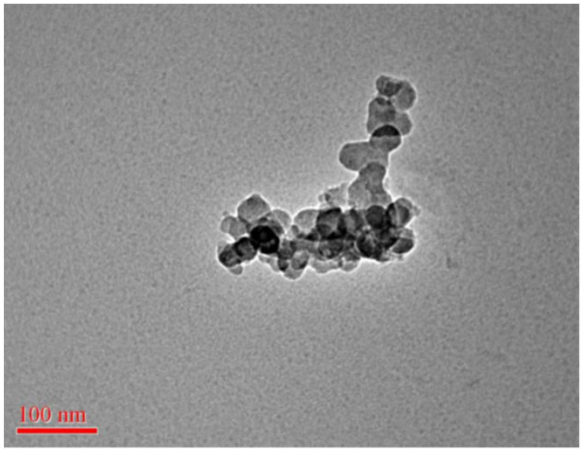


Image credit: NIOSH. Agglomerates/aggregates of amorphous silica nanoparticles. [NIOSH Nanotechnology Field Team report to CNSE, 10.25.11]

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No information presented is intended to provide consulting advice on specific scenarios or applications; any use or adaptation of this information is at the risk of the user.

This presentation is intended to share experiences and observations on air sampling methods used to assess and quantify airborne concentrations and potential workplace exposures to engineered nanoparticles, and references current guidelines and standards.

Questions or comments:

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