SUNY POLYTECHNIC INSTITUTE

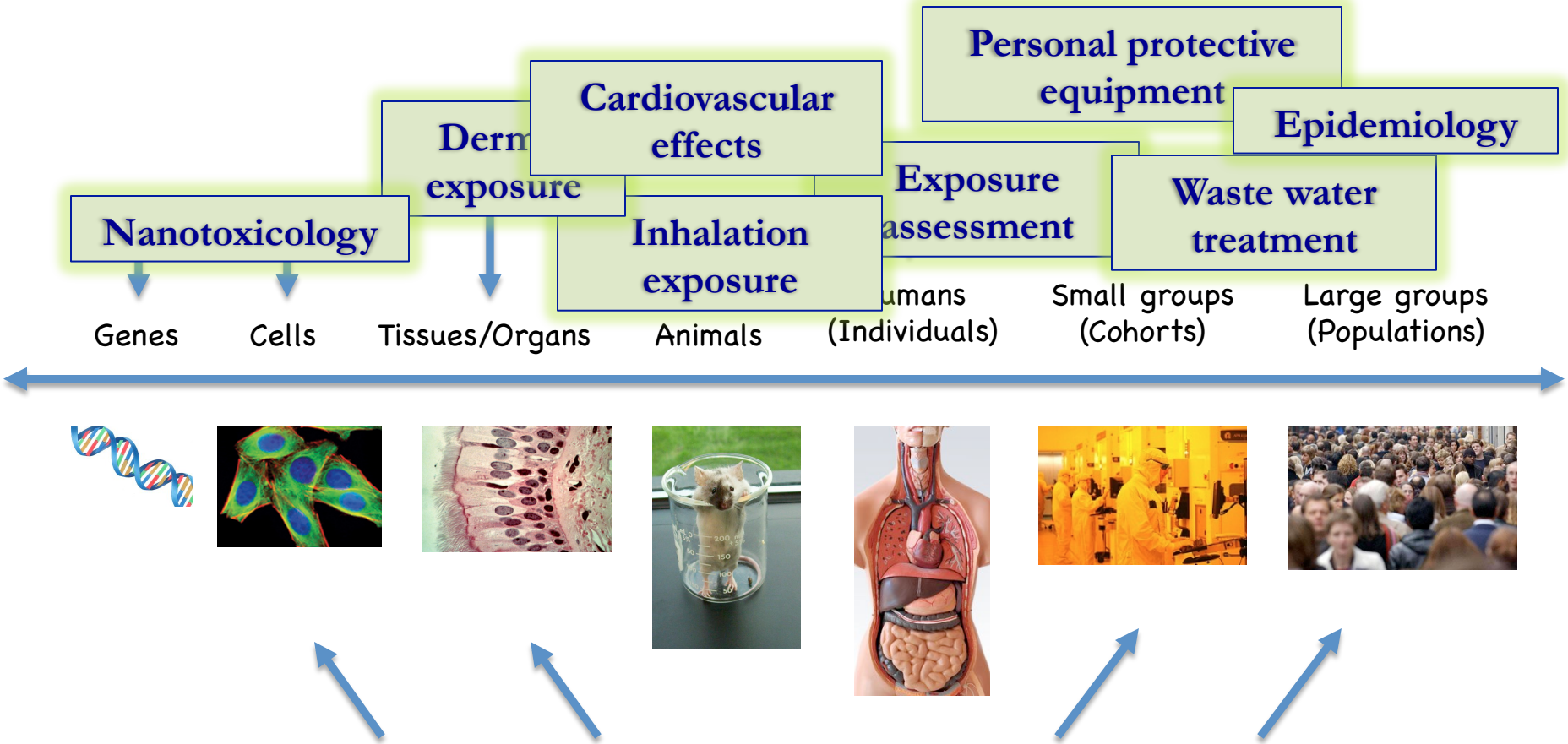
Concurrent Session: Epidemiology: the exposure-health interface

Field-based exposure assessment: tailoring your approach to maximize and obtain key data for each worker

COLLEGES OF NANOSCALE SCIENCE + ENGINEERING
SUNY POLYTECHNIC INSTITUTE

Sara Brenner, MD, MPH
Asst Vice President for NanoHealth
Asst Professor of Nanobioscience
Co-Director, MD/PhD program in Nanomedicine

NanoHealth & Safety Research



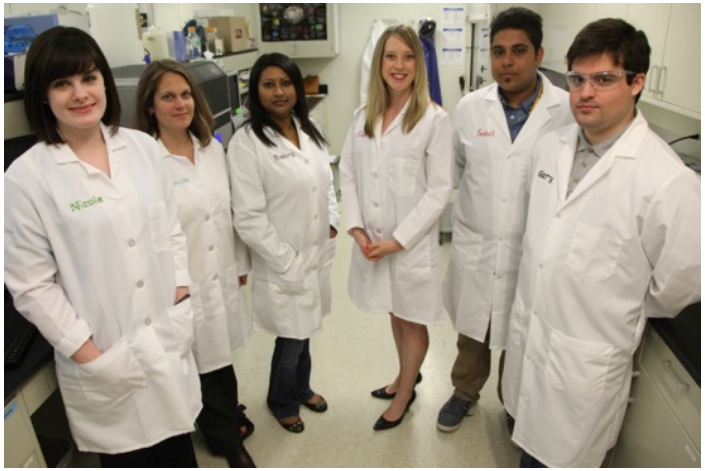
Metrology: nanoparticle characterization and quantification in exposure scenarios

Stebounova LV, Morgan H, Grassian VH, **Brenner S**. Health and safety implications of occupational exposure to engineered nanomaterials. *WIREs Nanomedicine & Nanobiotechnology* 2012, 4:310-321

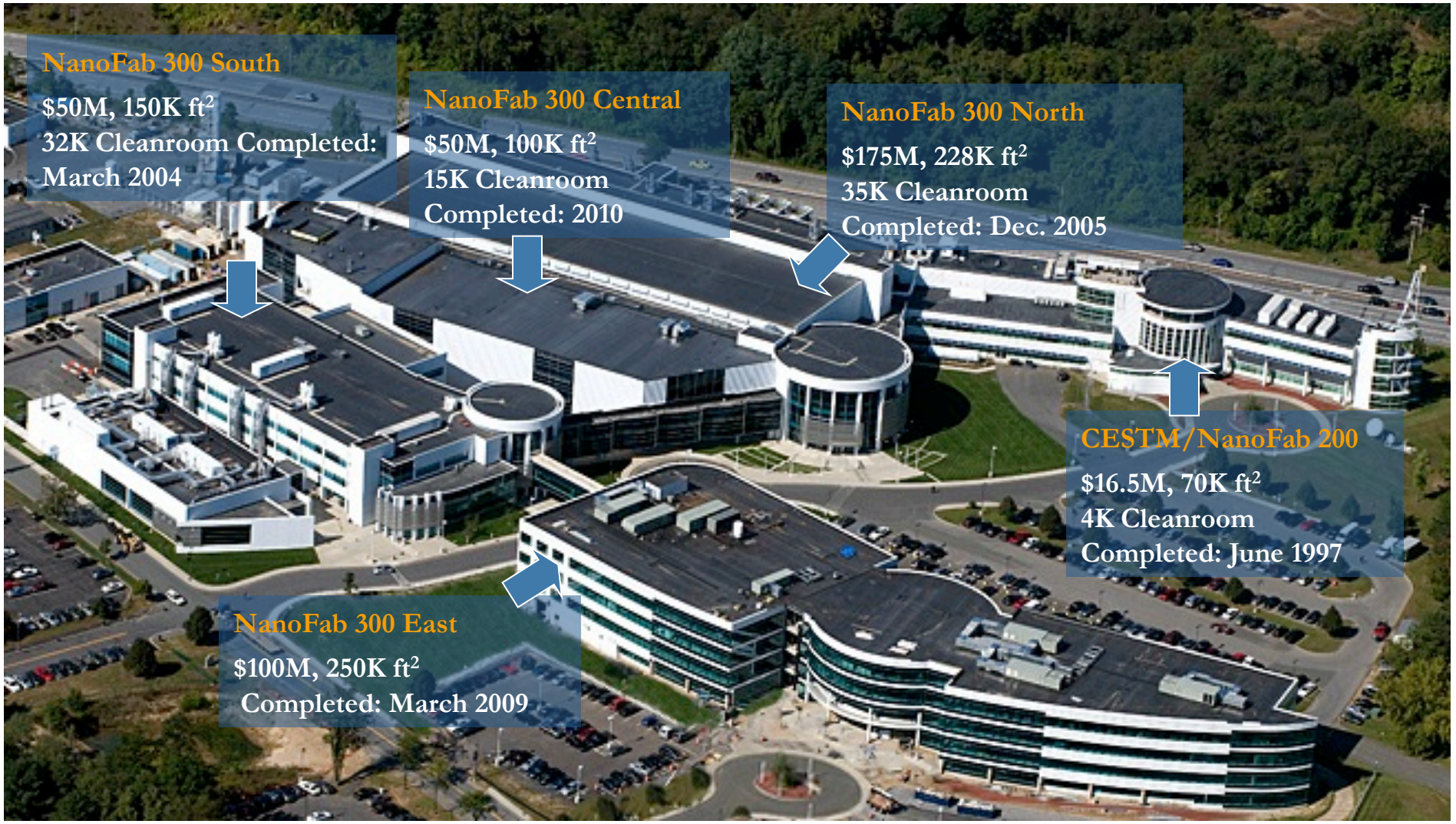
Occupational and Environmental Health & Safety of Engineered Nanomaterials

Scope: The integration of occupational and environmental medicine, exposure science, industrial hygiene, materials science, and metrology to investigate the human health and safety implications of exposure to engineered nanomaterials

Goal: To proactively address the emerging needs of health and safety research related to engineered nanomaterials, seeking to develop in real-time the innovative technologies and methodologies needed to assess, monitor, and safely accelerate nanotechnology R&D worldwide



SUNY POLYTECHNIC INSTITUTE — CNSE Albany Nanotech Complex



- $20+ billion high-tech investments to date
- 3,500+ employees on-site
- 300+ global corporate partners to date
- 1.3 million ft² total facility space to date

SUNY Polytechnic Institute

CNSE Albany Nanotech Complex

Presidential visit to CNSE

Albany, NY

May 8, 2012

NIOSH Top 10 Nanotechnology Research Needs

1. Exposure Assessment
2. Toxicity and Internal Dose
3. Epidemiology and Surveillance
4. Risk Assessment
5. Measurement Methods
6. Engineering Controls and Personal Protective Equipment
7. Fire and Explosion Safety
8. Recommendations and Guidance
9. Communication and Information
10. Applications

CDC Centers for Disease Control and Prevention

National Institute for Occupational Safety and Health NIOSH

Risk = Hazard x Exposure

In order to characterize the potential risks to human and environmental health, we must evaluate both exposures and hazards.

Hazard → inherent properties of a substance with the potential to cause adverse, or harmful, effects

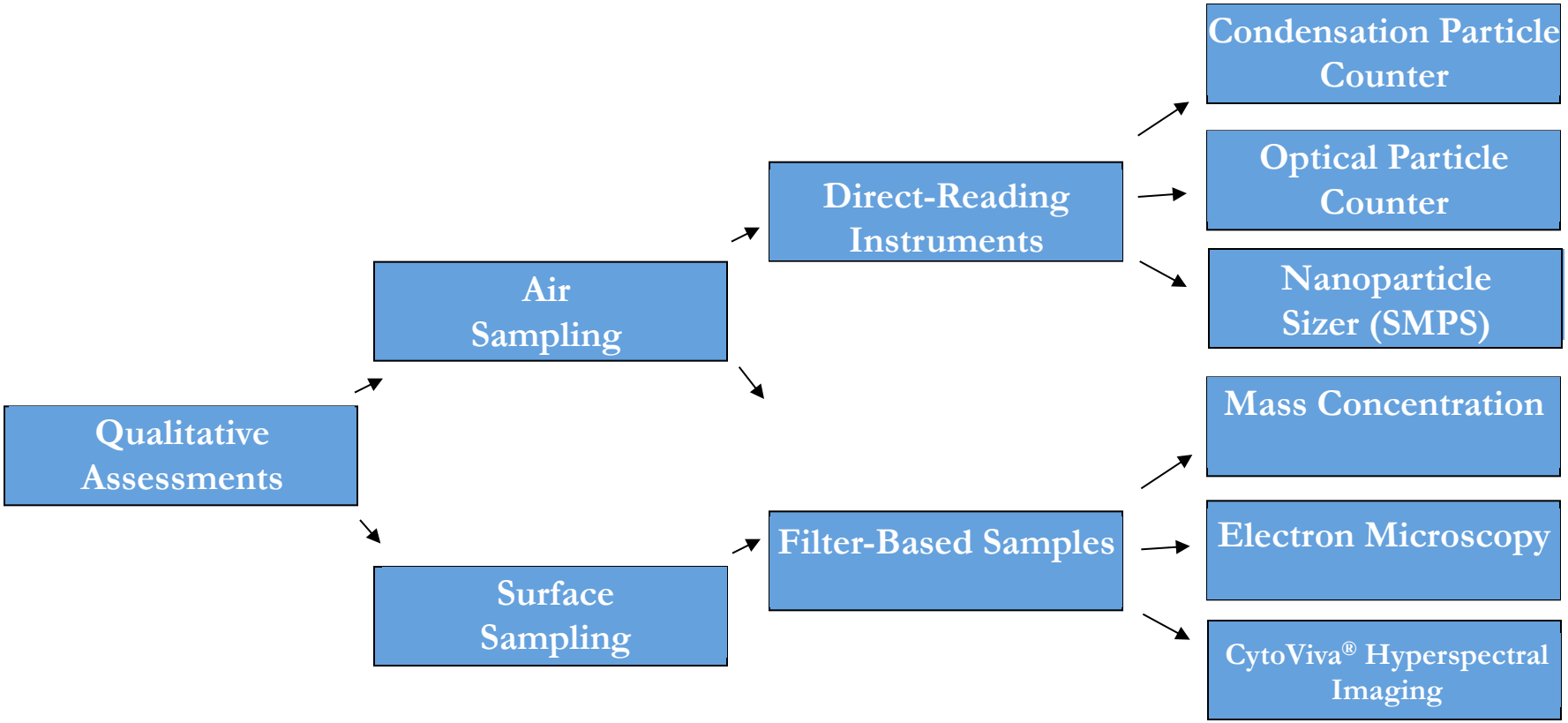
Exposure → quantitative measurement of the extent to which a given hazard is present

Risk → probability that an adverse effect will occur to someone if exposed to the hazard

Occupational Health & Safety: Nanoelectronics Workforce

Work proactively with industry partners and collaborators to monitor, assess, and document the exposure to and potential health effects associated with nanomaterials prior to commercialization and introduction to market.

Exposure Assessment Sampling Approach



Brenner SA, Neu-Baker NM, Caglayan C, Zurbenko IG. Occupational exposure to airborne nanomaterials: as assessment of worker exposure to aerosolized metal oxide nanoparticles in semiconductor wastewater treatment. *Journal of Occupational and Environmental Hygiene*. Accepted January 2015. Article in press.

Air Sampling Approach

Instrument/Device	Type	Size Range	Metric
Condensation particle counter (CPC)	Size integrated, time resolved	10 - ~1000 nm	Number conc.
Optical particle counter (OPC)	Size and time resolved	300nm-20μm	Number size dist.
Aerosol photometers	Size integrated, time resolved	250nm-20μm	Mass conc.
Filter collection and off-line analysis (gravimetric, ICP, XRD)	Off-line analysis; Size and time integrated	Depends on method	Mass conc., chem
Electron microscopy (ESEM, SEM, TEM) *EDX/EDS –chem composition	Off-line analysis; Size and time integrated	Depends on device	Morph, size, number

Slide credit: Michele Shepard, PhD, MS, CIH

Surface Sampling Approach

- Wipe / Vacuum samples
  - MCE filters
  - PC filters
- Used modified approaches to identify nanoparticles of interest (as Si, Al, or Ce):
  - ASTM D5755 Standard Test Method for Microvacuum Sampling and Indirect Analysis of Dust by Transmission Electron Microscopy for Asbestos Structure Number Surface Loading
  - ASTM D6480 Standard Test Method for Wipe Sampling of Surfaces, Indirect Preparation, and Analysis for Asbestos Structure Number Concentration by Transmission Electron Microscopy

Slide credit: Michele Shepard, PhD, MS, CIH

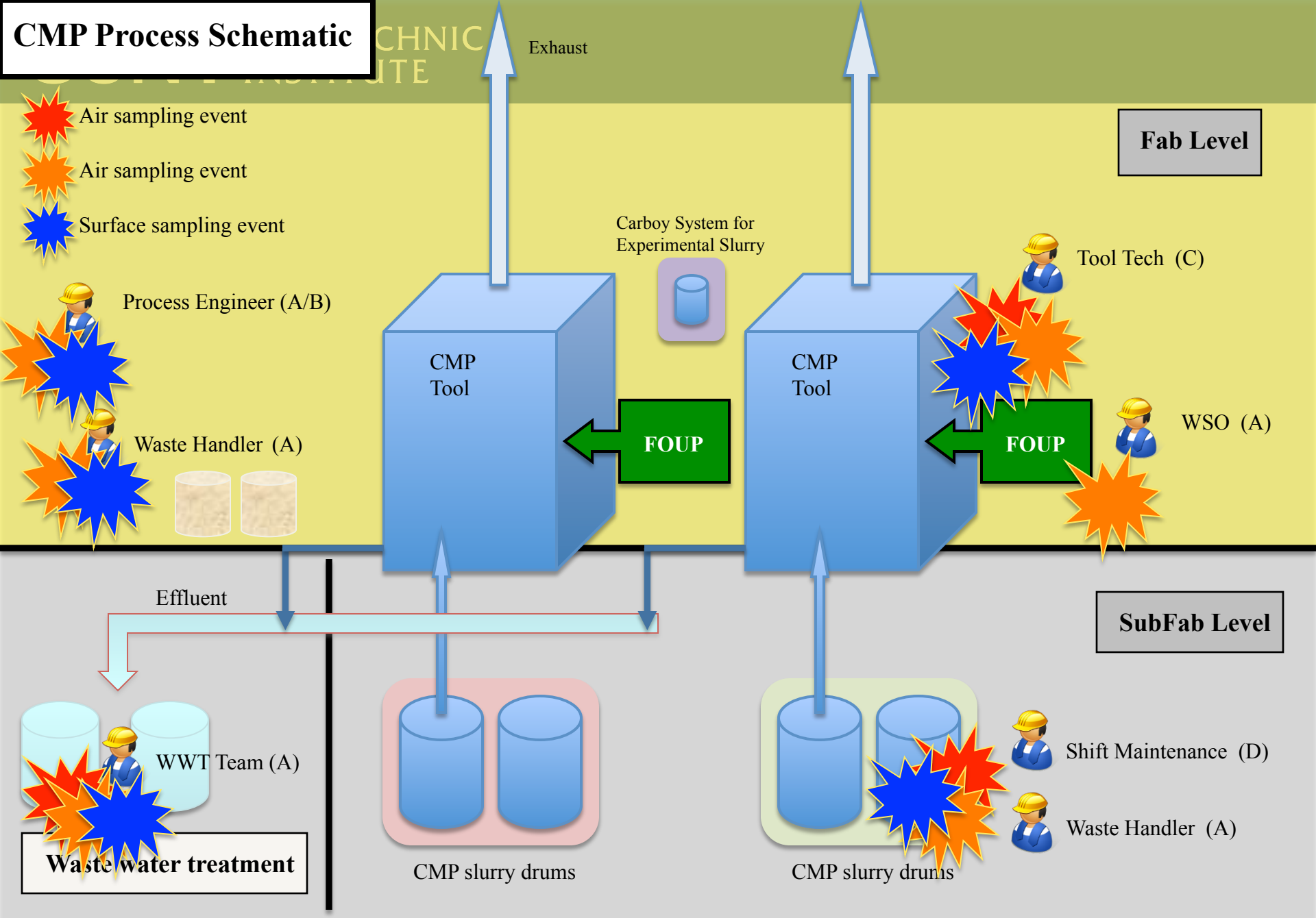
Job Tasks and Exposures

*selected examples for illustrative purposes

Job Title	Task(s)/Location	Airborne Exposure Potential (Monitoring Priority Based on Qualitative Risk Assessment)
Workstation operator	Operate CMP Tool/Fab	Low – Normal operations
Tool technician	Maintain CMP Tool/Fab	Low – Set-up Moderate – Change-out of consumables Moderate to High – Entry into tool for PM
Process engineer	Mixing experimental slurries/ Chem Mix Room	Moderate to High – Prepare slurry formulations for experimental use
Shift maintenance	Operate and maintain slurry distribution system/Subfab	Low – Routine operations Moderate to High – Overflows, drum washout, slurry delivery system cleanout
Waste handler	Remove waste for offsite shipment/Subfab to Storage	Low to moderate – Periodic waste pick-ups
Wastewater treatment operator	Treat and manage process wastewater/Subfab to Mech-WWT1	Low - Routine operations Moderate – PM to change copper filter

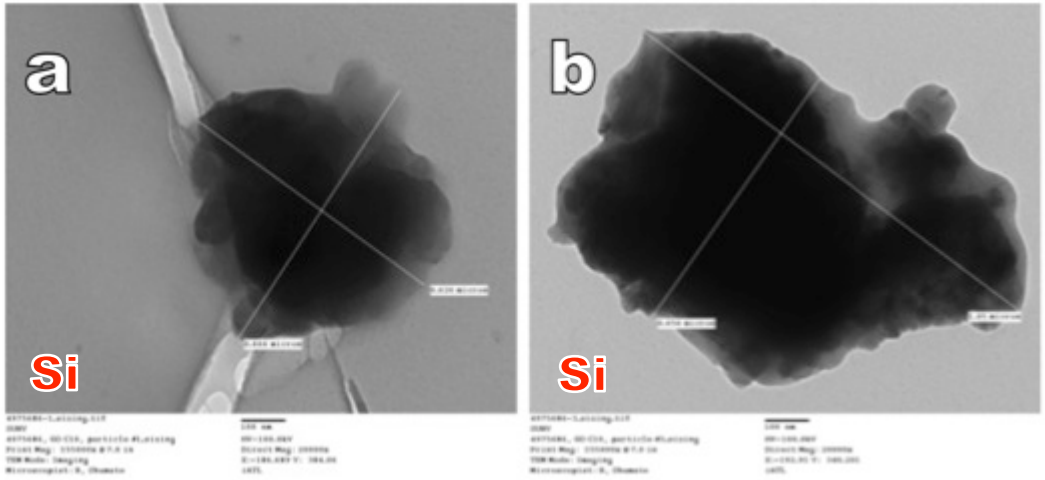
Shepard MN, **Brenner S**. An occupational exposure assessment for engineered nanoparticles used in semiconductor fabrication. *Annals of Occupational Hygiene* 2014, 58(2):251-265.

CMP Process Schematic



Brenner, S. A., Neu-Baker, N. M., Caglayan, C., & Zurbenko, I.G. Occupational Exposure to Airborne Nanomaterials: An Assessment of Worker Exposure to Aerosolized Metal Oxide Nanoparticles in Semiconductor Wastewater Treatment. *Journal of Occupational and Environmental Hygiene*. Accepted January 2015. Article in press.

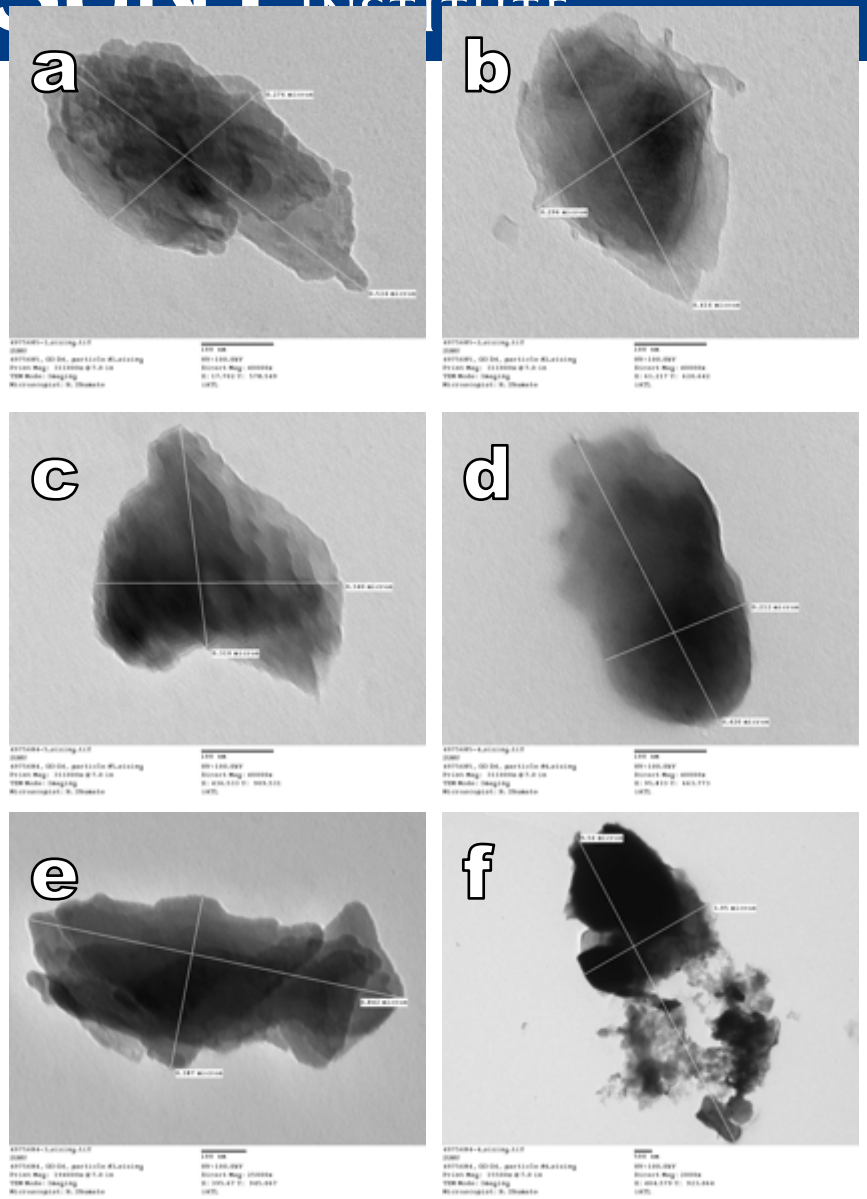
Fab surface sampling



Microvacuum surface samples from below the CMP tool door were acquired during preventive maintenance tasks in the fab (February 2013). a) Particulate containing **Si**. Size: 666nm×626nm. EDS: **Si**, Mg, P, S, Cl, Sn, Ca, Cr, Fe. b) Particulate containing **Si**. Size: 656nm×1,050nm. EDS: **Si**, Cl, Sn, Cr, Fe. Both imaged at iATL (Mt. Laurel, NJ) by R. Shumate.

Brenner SA, Neu-Baker NM. Occupational exposure to nanomaterials: assessing the potential for cutaneous exposure to metal oxide nanoparticles in a semiconductor facility. *Journal of Chemical Health and Safety.* Available online 15 November 2014. Article in press. doi:10.1016/j.jchas.2014.11.001.

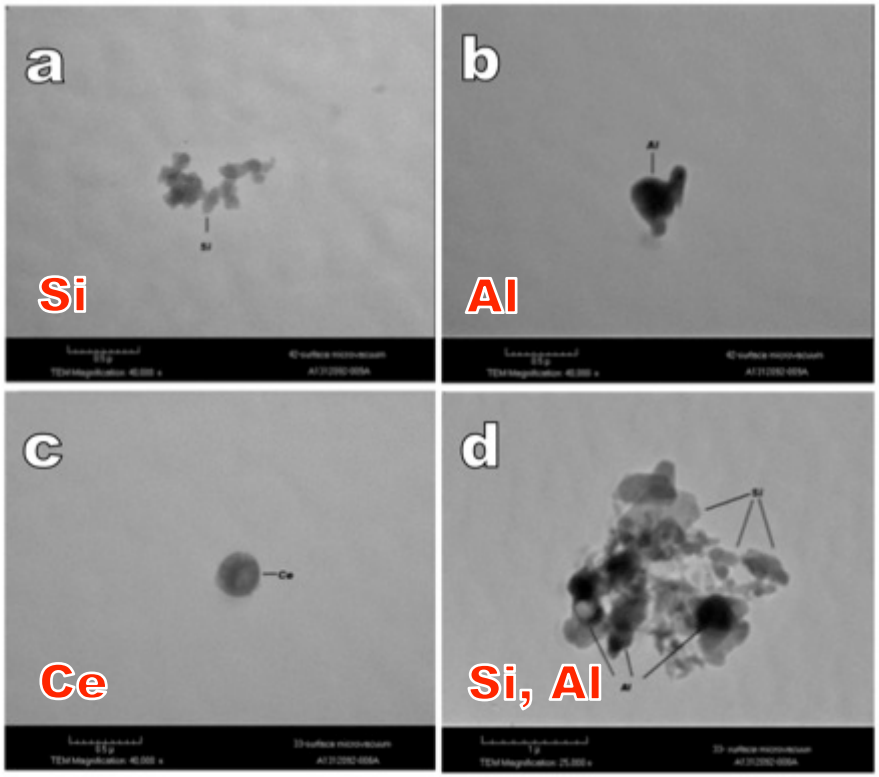
Subfab surface sampling



Microvacuum surface samples from the door hatch to a slurry loading tool were acquired during preventive maintenance and quality control tasks in the subfab (February 2013). a) Particulate containing Si. Size: 276nm×524nm. EDS: **Si**, Cr. b) Particulate containing Si and Al. Size: 276nm×524nm. EDS: Mg, **Si**, **Al**, P, Cr. c) Particulate containing Si only. Size: 310nm×340nm. EDS: **Si**. d) Particulate containing Si. Size: 276nm×524nm. EDS: **Si**, P, Ca. e) Particulate containing Si and Al. Size: 387nm×842nm. EDS: **Si**, **Al**, Cr. f) Particulate containing Si and Al. Size: 9,560nm×3,950nm. EDS: Mg, **Si**, **Al**, K, Fe. a) – f) imaged at iATL (Mt. Laurel, NJ) by R. Shumate.

Brenner SA, Neu-Baker NM. Occupational exposure to nanomaterials: assessing the potential for cutaneous exposure to metal oxide nanoparticles in a semiconductor facility. *Journal of Chemical Health and Safety.* Available online 15 November 2014. Article in press. doi:10.1016/j.jchas.2014.11.001.

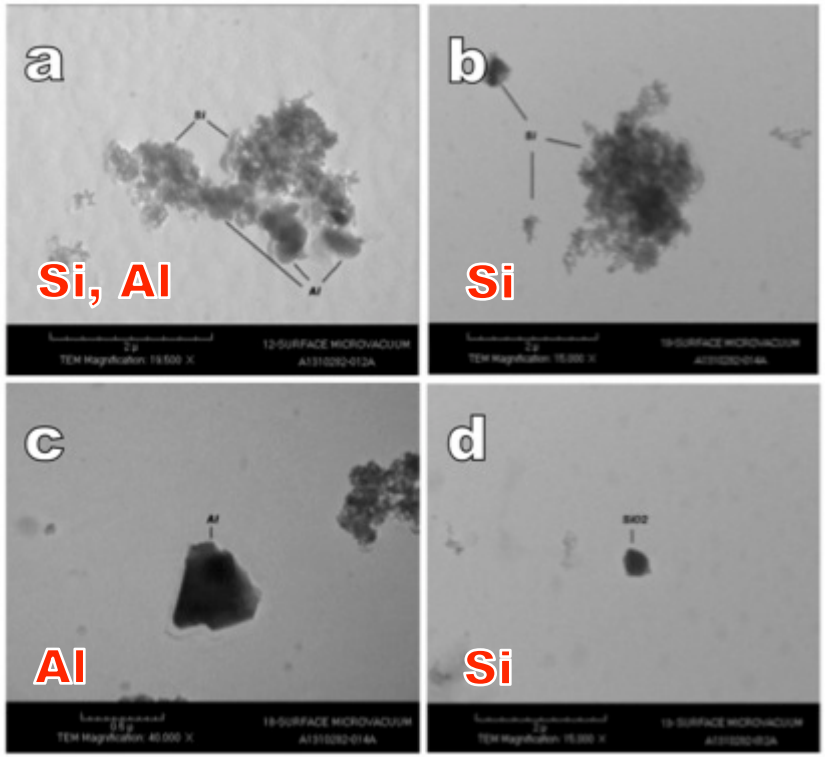
Subfab surface sampling



Microvacuum surface samples were acquired during preventive maintenance and quality control tasks in the subfab (October 2013). All samples were acquired from the outside door to filter boxes that load slurry. a) Agglomerate containing **Si**. b) Particulate containing **Al**. c) **Ce** particle. d) Agglomerate containing **Si** and **Al**. a) – d) imaged at BVNA (Kennesaw, GA) by N. Gapon.

Brenner SA, Neu-Baker NM. Occupational exposure to nanomaterials: assessing the potential for cutaneous exposure to metal oxide nanoparticles in a semiconductor facility. *Journal of Chemical Health and Safety.* Available online 15 November 2014. Article in press. doi:10.1016/j.jchas.2014.11.001.

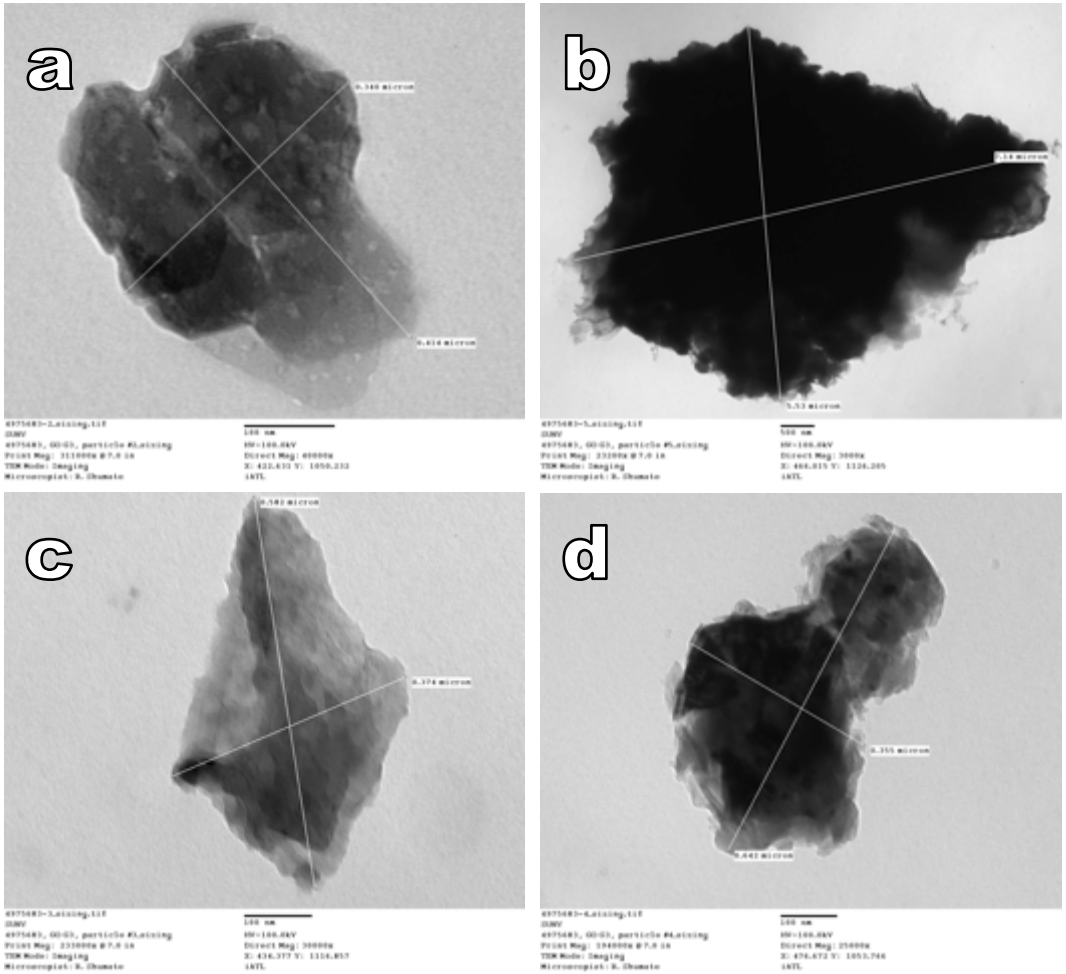
WWT surface sampling



Microvacuum surface samples from WWT during filter changes and sump pump clean-out (October 2013). a) Agglomerate containing **Si** and **Al** from the plastic wall covering next to the sump pump valve during a pump clean-out. b) Particulate containing **Si** from the floor next to the base filter tank. c) Particulate containing **Al** only from the floor next to the base filter tank. d) Particulate containing **SiO_2** from the floor next to the acid filter tank. a) – d) imaged at BVNA (Kennesaw, GA) by N. Gapon.

Brenner SA, Neu-Baker NM. Occupational exposure to nanomaterials: assessing the potential for cutaneous exposure to metal oxide nanoparticles in a semiconductor facility. *Journal of Chemical Health and Safety.* Available online 15 November 2014. Article in press. doi:10.1016/j.jchas.2014.11.001.

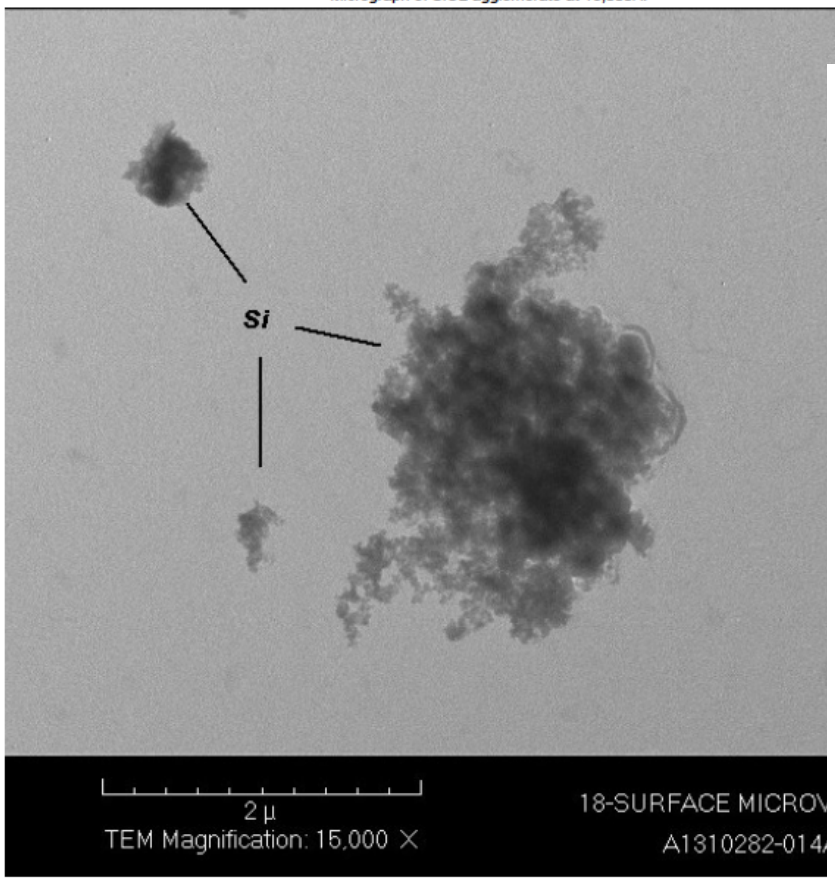
WWT surface sampling

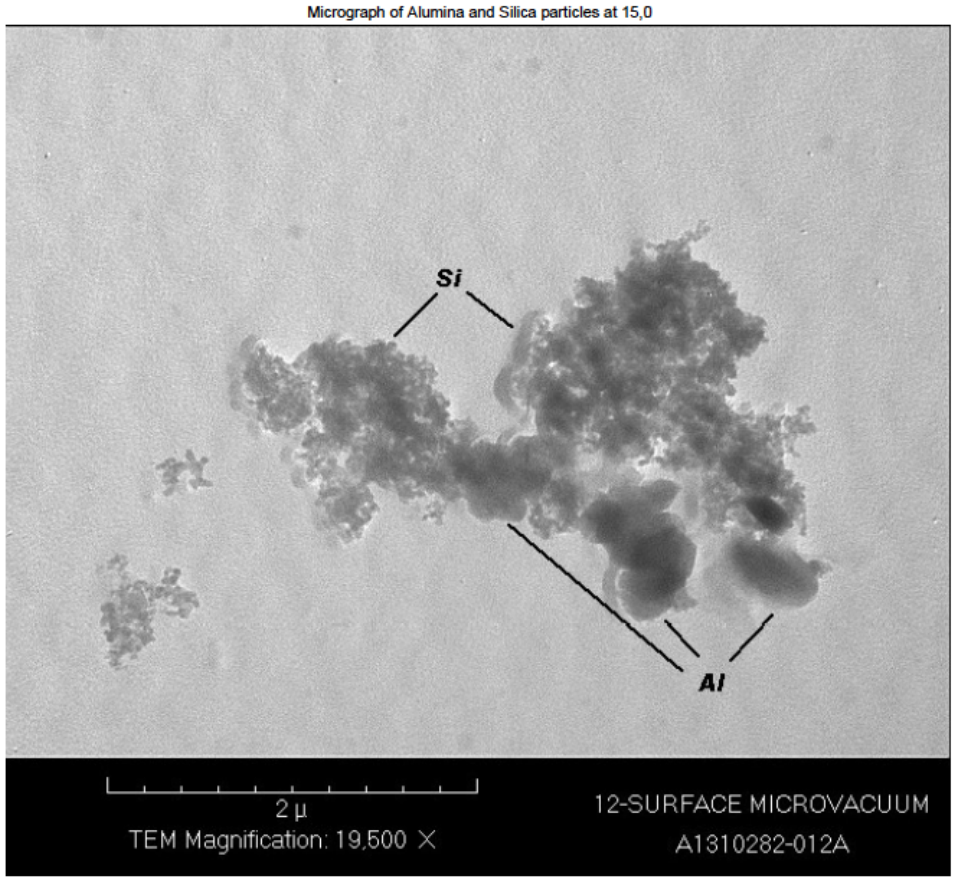


Microvacuum surface samples from the hatch to the acid filter tank in WWT (February 2013). a) Particulate containing Al and Si. Size: 340nm×414nm. EDS: **Si**, **Al**, Fe. b) Particulate containing Si and Al. Size: 5,530nm×7,140nm. EDS: Mg, **Si**, **Al**, K, Ti, Cr. c) Particulate containing Si only. Size: 374nm×582nm. EDS: **Si**. d) Particulate containing Si only. Size: 642nm×355nm. EDS: **Si**. a) – d) imaged at iATL (Mt. Laurel, NJ) by R. Shumate.

Brenner SA, Neu-Baker NM. Occupational exposure to nanomaterials: assessing the potential for cutaneous exposure to metal oxide nanoparticles in a semiconductor facility. *Journal of Chemical Health and Safety.* Available online 15 November 2014. Article in press. doi:10.1016/j.jchas.2014.11.001.

WWT surface sampling



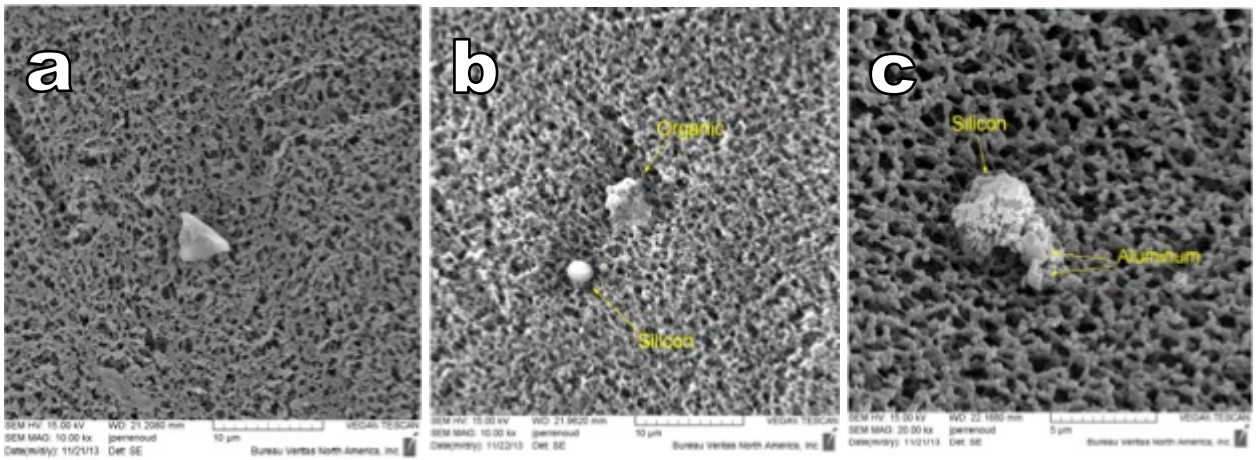


SiO2 nanoparticle agglomerate: surface: floor by base filter tank (WWT)

Alumina and silica nanoparticle agglomerate: surface: plastic sheet by valve (CUB)

Source for TEM Images: Imaged by Nadiya Gapon, BVNA

WWT surface sampling

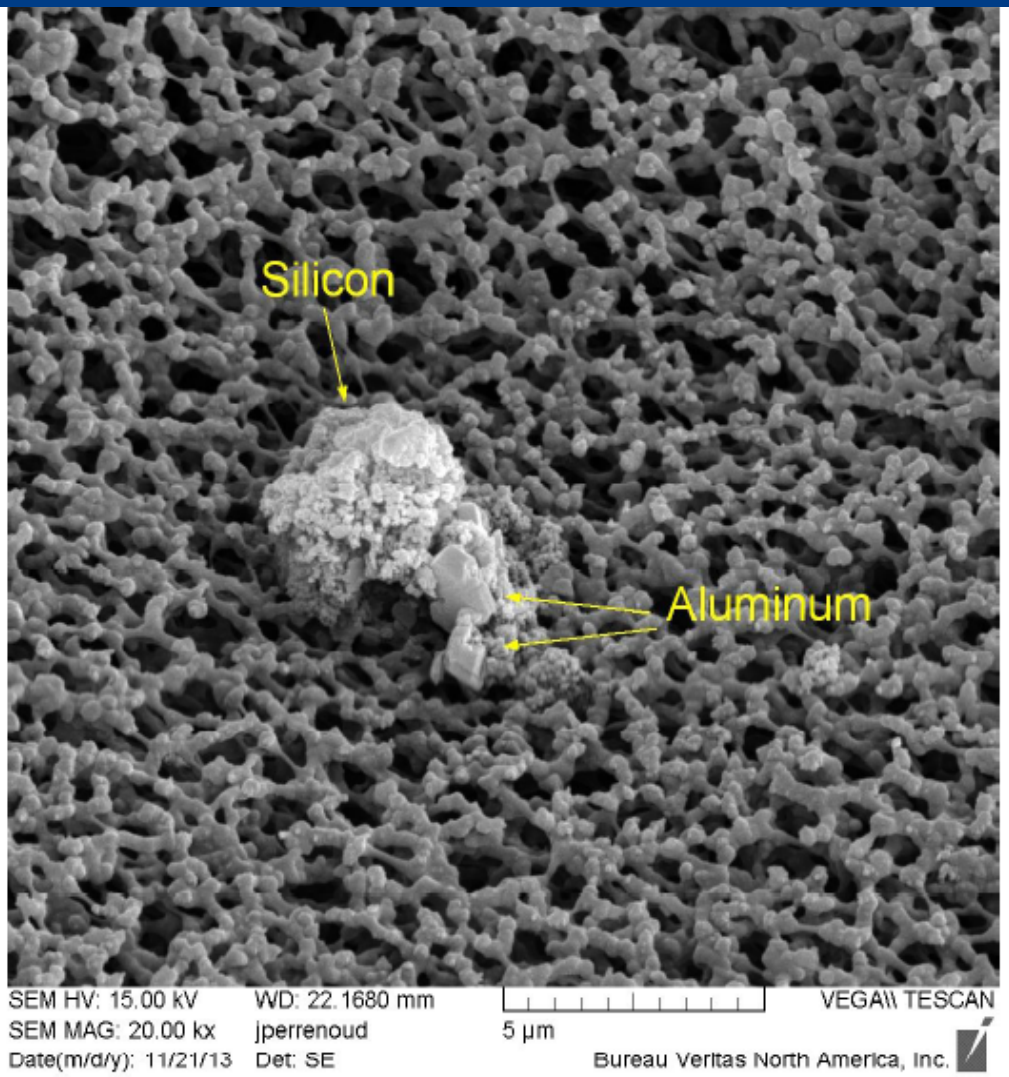


Microvacuum surface samples from WWT during filter changes and sump pump clean-out (October 2013). a) **Si** particle from the floor next to the acid filter tank. b) Particulate containing **Si** (bottom particle) and organic material (top particle) from the floor next to the base filter tank. c) Particulate containing **Si** and **Al** from the plastic wall covering next to the sump pump valve during a pump clean-out. a) – d) imaged at BVNA (Kennesaw, GA) by J. Perrenoud.

Brenner SA, Neu-Baker NM. Occupational exposure to nanomaterials: assessing the potential for cutaneous exposure to metal oxide nanoparticles in a semiconductor facility. *Journal of Chemical Health and Safety.* Available online 15 November 2014. Article in press. doi:10.1016/j.jchas.2014.11.001.

WWT surface sampling

Silicon and aluminum nanoparticles: Surface: plastic sheet by valve in CUB

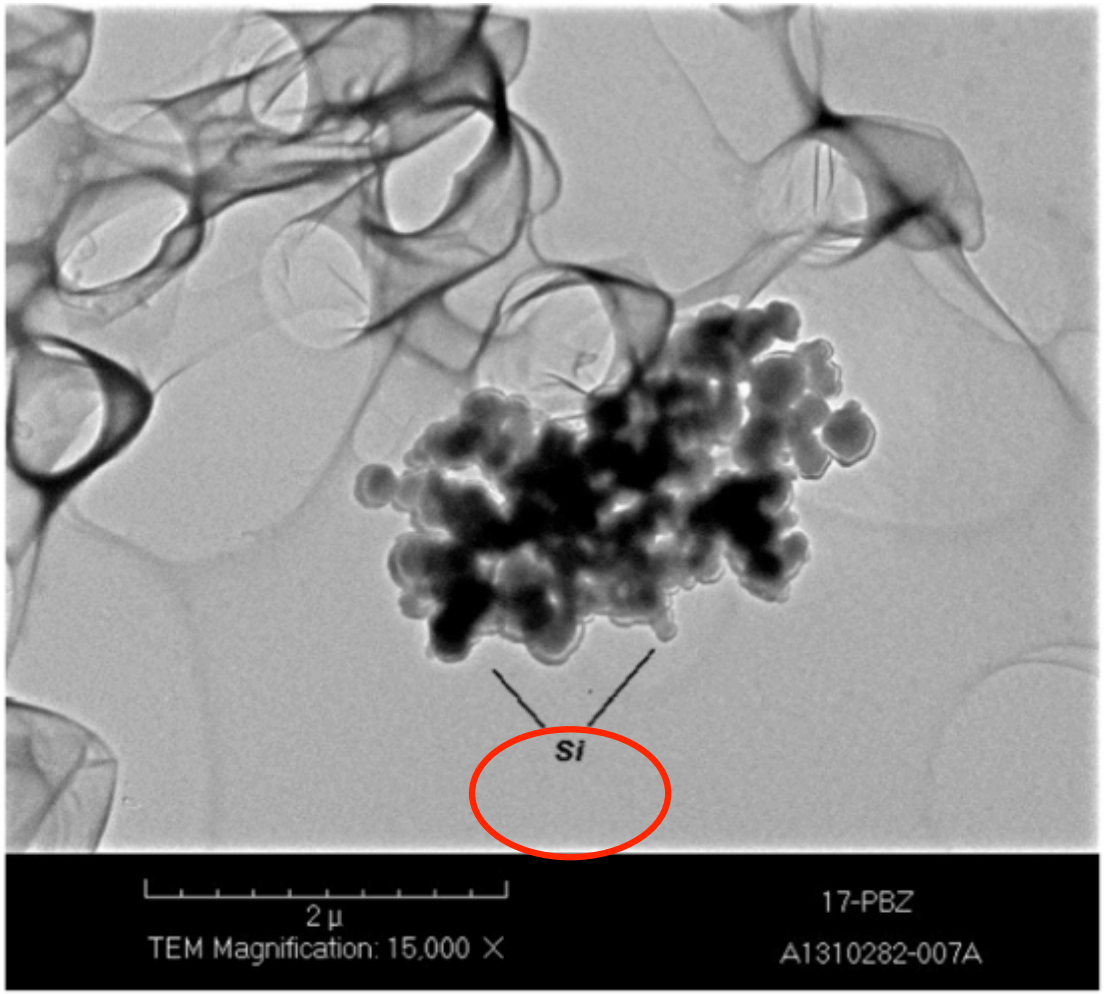


Photomicrograph at 20,000X of Sample 12-Surface Microvacuum showing aluminum and silicon particles.

Source for SEM Images: Imaged by Jon Perrenoud, BVNA

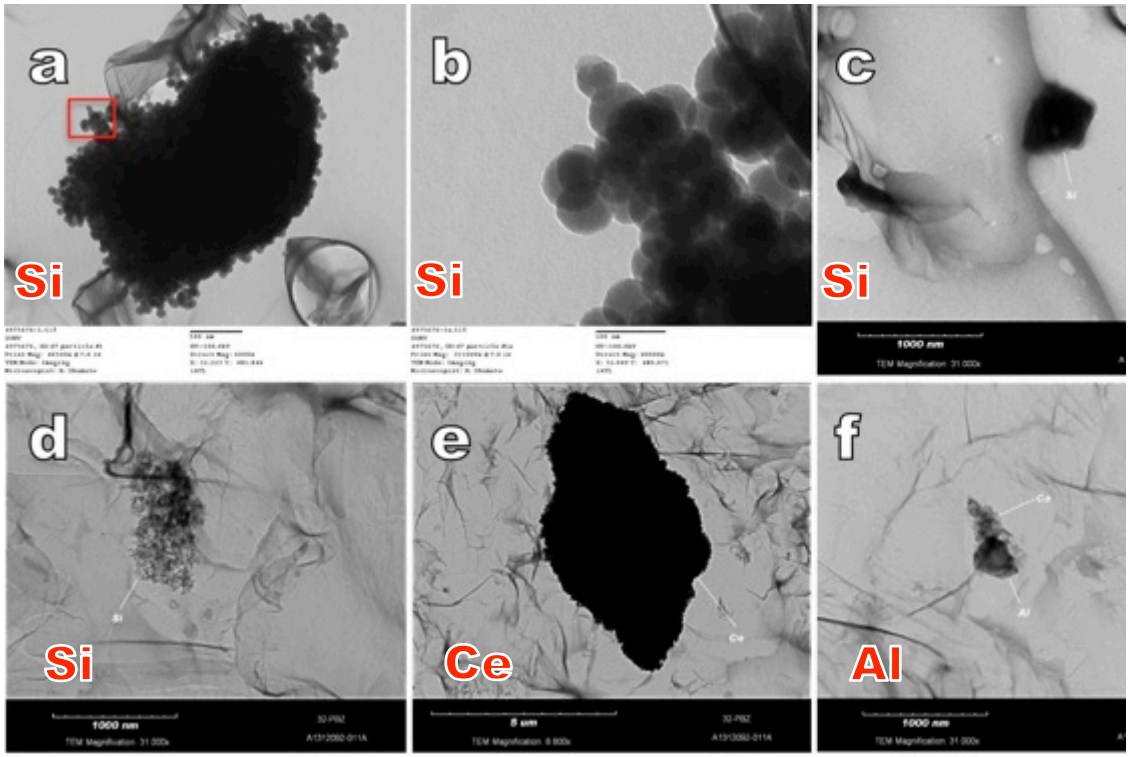
WWT air sampling

TEM image of **Si** agglomerate composed of smaller **Si** nanoparticles, collected from a worker PBZ during a sump pump clean-out in the CUB. Imaged at BVNA (Kennesaw, GA) by N. Gapon, November 2013.



Brenner SA, Neu-Baker NM, Caglayan C, Zurbenko IG. Occupational exposure to airborne nanomaterials: an assessment of worker exposure to aerosolized metal oxide nanoparticles in semiconductor wastewater treatment. *Journal of Occupational and Environmental Hygiene*. Accepted January 2015. Article in press.

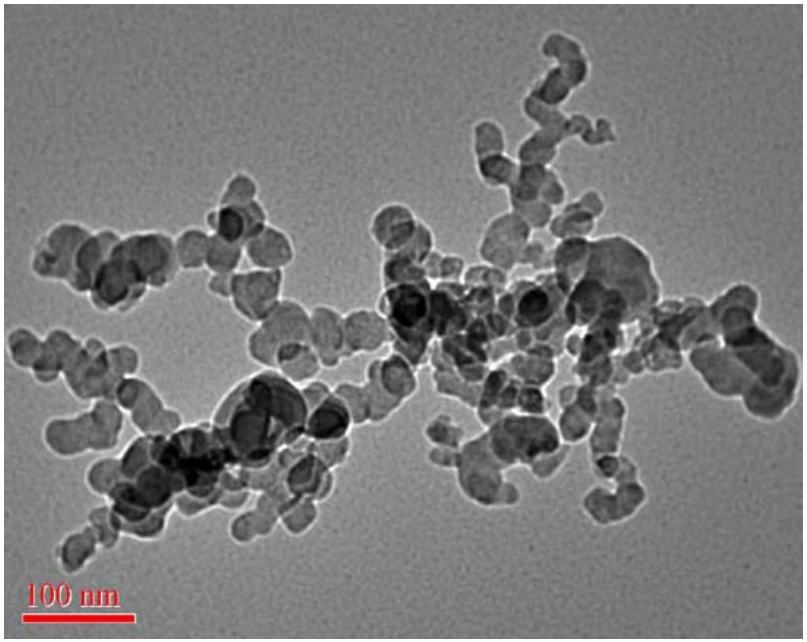
Fab air sampling



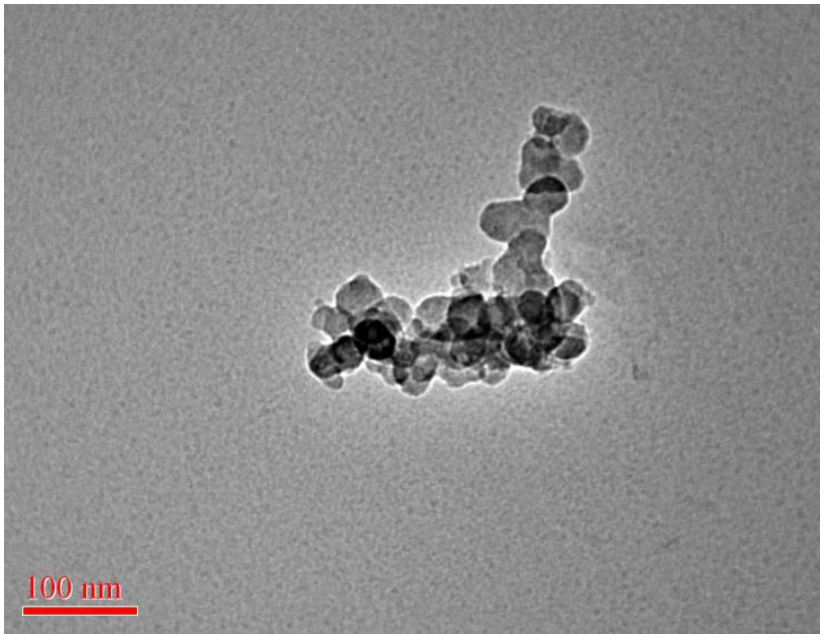
Selected TEM images from worker PBZ samples obtained in the fab during preventive maintenance and consumable change-out tasks and in the chemical mix room during slurry mixing tasks. a) Image of mixed agglomerate containing **Si** collected from a worker PBZ during monthly preventive maintenance in the fab. Particle size: 1,940nm × 3,230nm. EDS: **Si**, Cr. b) Higher magnification image of area indicated by a red box in a). Representative sub-particle diameter: 75.2nm. EDS: **Si**, Cr. c) **Si** particle collected from a worker PBZ during a consumable change-out. Particle size: 35nm × 280nm. d) **Si** agglomerate collected from a worker PBZ during slurry mixing in the chemical mix room. Particle size: 1,390nm × 760nm. e) **Ce** agglomerate from a worker PBZ during slurry mixing in the chemical mix room. Particle size: 7,640nm × 3,470nm. f) Agglomerate containing **Al** from a worker PBZ during slurry mixing in the chemical mix room. Particle size: 350nm × 280nm. EDS: **Al**, Ca. (a – b) imaged at iATL (Mt. Laurel, NJ) by R. Shumate, May 2013. (c – f) imaged at BVNA (Kennesaw, GA) by K. Parikh, December 2013.

Brenner SA, Neu-Baker NM, Caglayan C, Zurbenko IG. (under review). Occupational exposure to airborne nanomaterials: an assessment of worker exposure to aerosolized metal oxide nanoparticles in a semiconductor fab and subfab. *Journal of Occupational and Environmental Hygiene*.

Air sampling



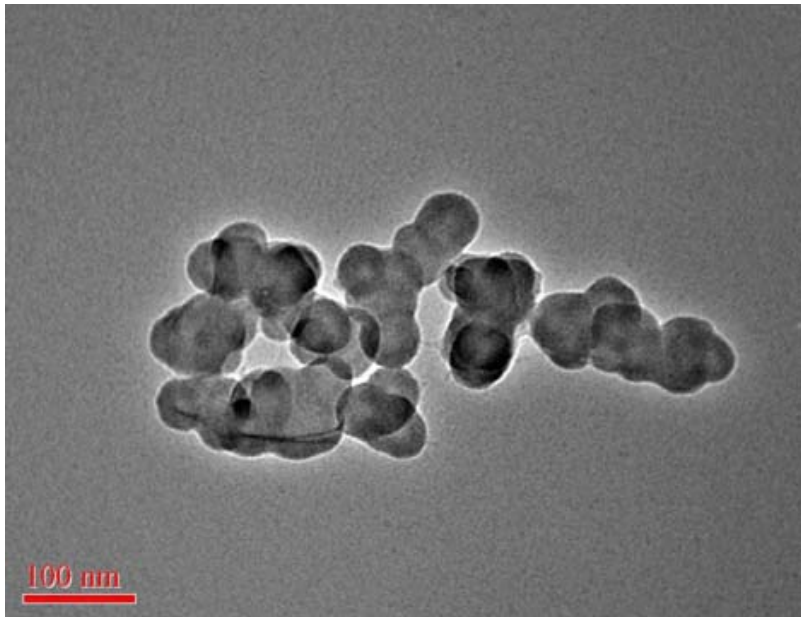
Amorphous silica nanoparticles collected in the task area sample in the SubFab area



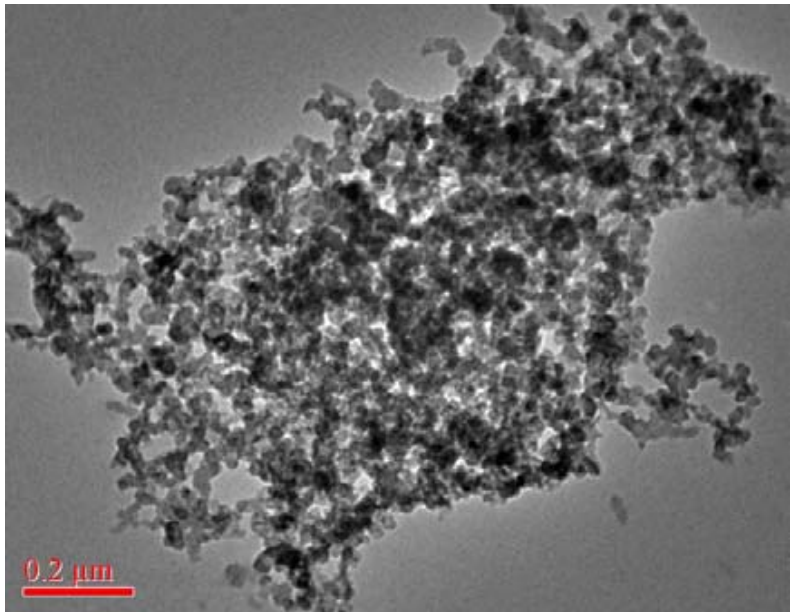
Amorphous silica nanoparticles collected in worker breathing zone sample in wastewater treatment

TEM Images: NIOSH Nanotechnology Field Research Team, 10/25/11 Final Report

Air sampling



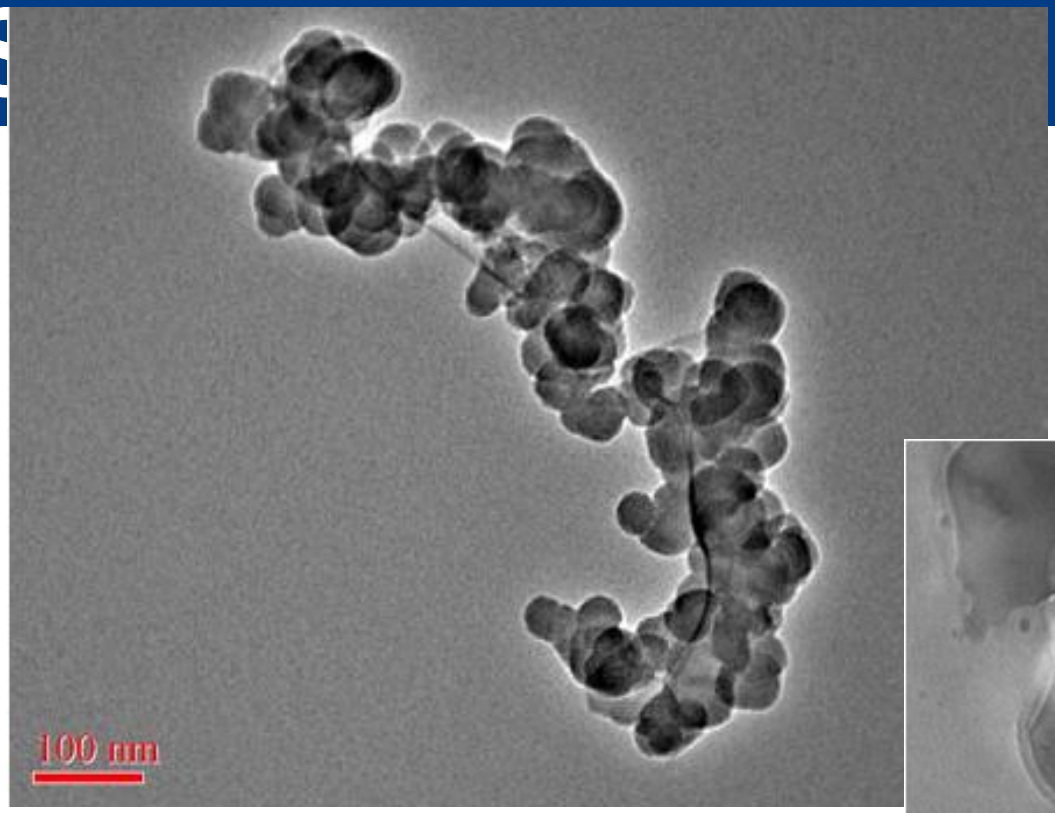
Aluminum oxide nanoparticles collected in the cleanroom on the CMP WSO worktable



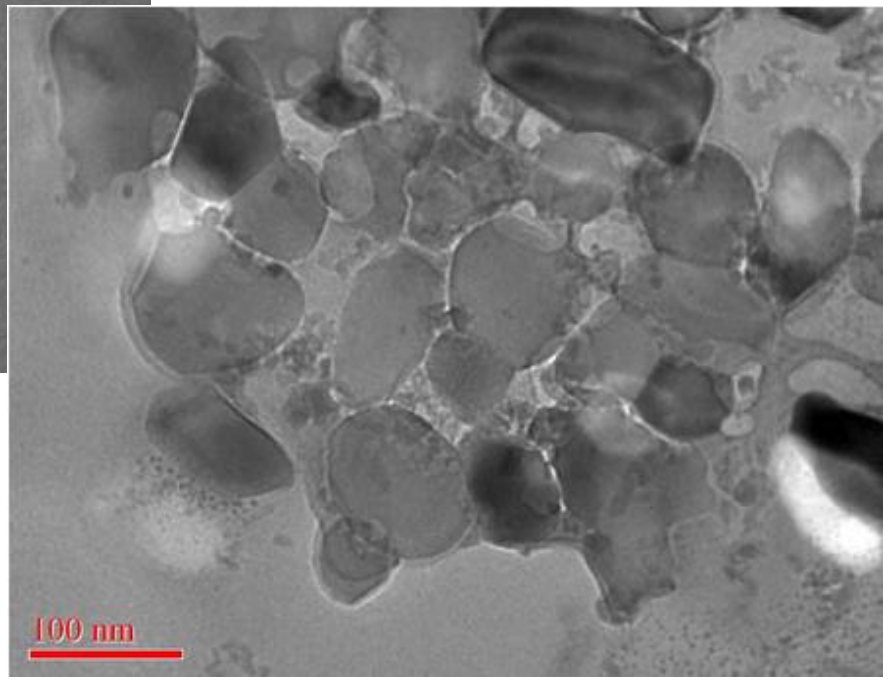
Mixed aluminum and silica particles collected in wastewater treatment

TEM Images: NIOSH Nanotechnology Field Research Team, 10/25/11 Final Report

Air sampling

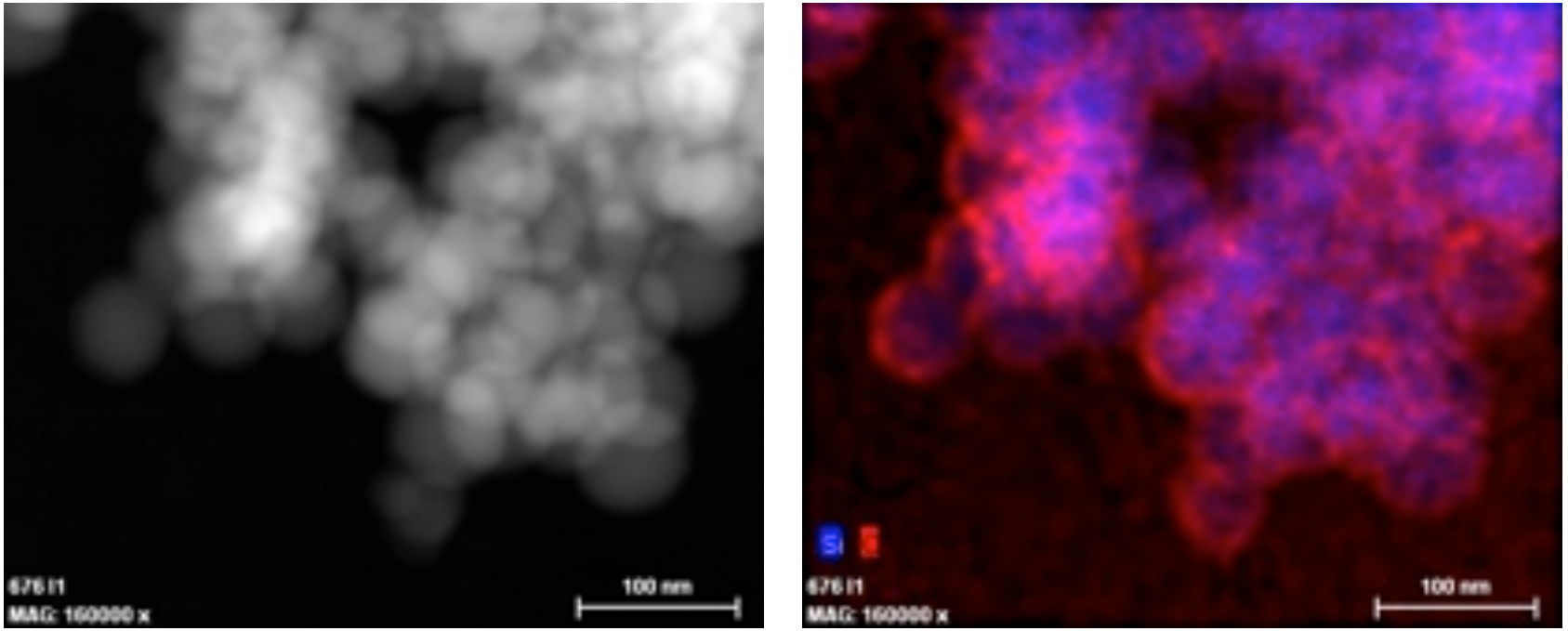


Amorphous silica nanoparticles (agglomerate)



Amorphous aluminum oxide nanoparticles (agglomerate)

TEM Images: NIOSH Nanotechnology Field Research Team, 10/25/11 Final Report

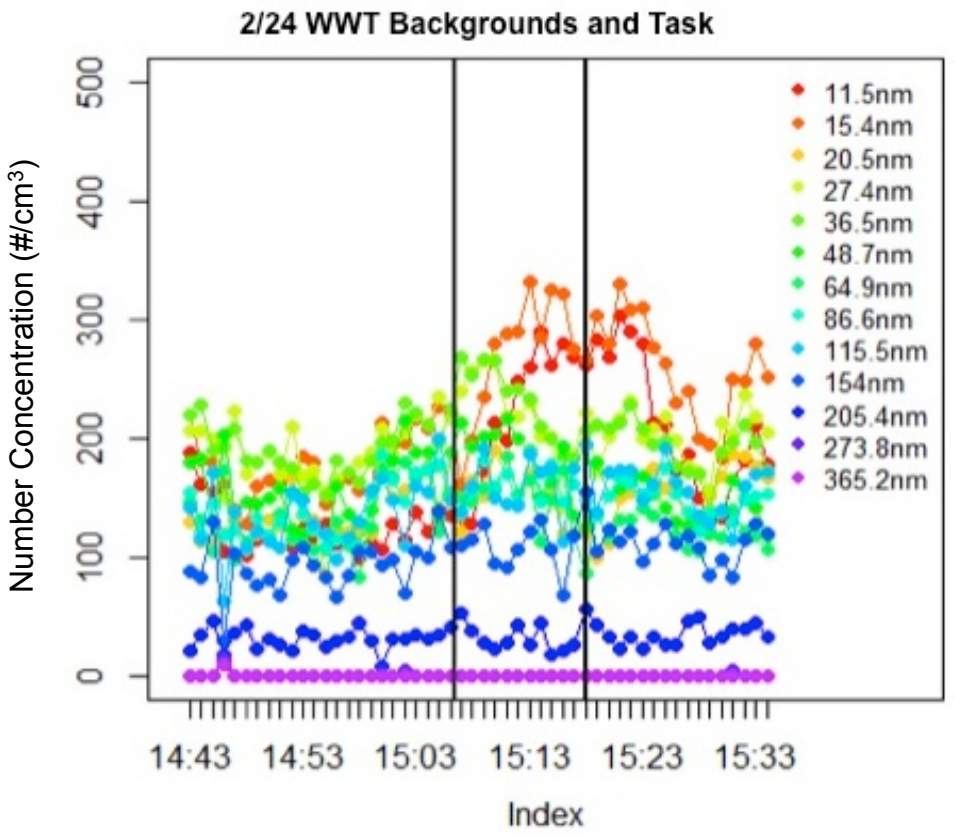


Imaging by Prof Kathleen Dunn, PhD – SUNY Poly CNSE

STEM image (left) and EDX mapping (right) of a cluster of nanoparticles obtained from a worker's personal breathing zone (PBZ) during monthly preventative maintenance on a CMP tool. The particulates are primarily silica (oxygen map not shown), with a 10 nm "rind" of carbon.

→ *imaging and elemental localization possible using high angular dark field (HAADF) in an aberration-corrected 300kV FEI Titan^3 STEM*

WWT air sampling



This plot shows **three distinct periods: a pre-task background, an acid and base filter change task** (the period in between the two black vertical lines), **and a post-task background** (field measurement). All measurements were obtained by SMPS over the course of one day (data not shown). **This data represents one representative sampling event (2/24/14) where we observed increased particle number concentrations after the task began, particularly in the smaller size channels, with some delay in time.** After the completion of the task, we observed some slow stabilization for these particle number concentrations **back to original pre-task background levels**. In order to draw more definitive conclusions, additional sampling is needed.

Brenner SA, Neu-Baker NM, Caglayan C, Zurbenko IG. Occupational exposure to airborne nanomaterials: an assessment of worker exposure to aerosolized metal oxide nanoparticles in semiconductor wastewater treatment. *Journal of Occupational and Environmental Hygiene*. Accepted January 2015. Article in press.

Exposure Data

- All sampling studies to date identified the presence of metal oxide particulates and agglomerates **on surfaces frequently contacted by workers and in PBZs** (Si>Al>Ce)
- It is **more difficult** to determine the source of materials found on **surfaces** than in air, based on morphology and composition
- Nearly all samples contained particles of **mixed composition**
- The majority of particles captured in air and surface samples were in the **>100nm** size range
- In many cases, **aggregates or agglomerates** of smaller particles were collected (non-uniform dimensions, measured in the micron range)
- *Continuing to employ precautionary measures to minimize ENM exposure is suggested, particularly as research in nanotoxicology and exposure science for nanomaterials is ongoing*

Considerations

- **Nanomaterial-specific, validated methods for occupational exposure assessment for this work force are desperately needed.**
  - *The TEM and SEM methods used (NIOSH 7402 for TEM; ASTM D5755-09) were developed decades ago for micron-sized asbestos and have been minimally modified for ENMs and therefore may not be sufficient for analysis of materials in the sub-micron range.*

- **A fundamental hurdle holding back the field of exposure science for the nanotechnology workforce is the lack of validated analytical techniques that consistently, reliably, and accurately identify and characterize ENMs captured in the occupational settings.**
  - *Additionally, the associated costs, time, and lack of standardization and validation of methods make it difficult at this point for industries to implement an occupational exposure assessment program for workers who handle ENMs, or attempt to comply with recommended occupational exposure limits (ROELs) for ENMs.*

Further Considerations

- **Contamination issues** identified in 2011 with MCE filters also occurred intermittently with PC filters during the sampling period

- In a **complex industrial environment**, other ongoing tasks and processes may influence the results of exposure assessment for a particular job task, if it is not separated sufficiently by space and time

- Related work in 2015 focuses on the liberation of materials of interest from surfaces by workers during tasks, into the personal breathing zone
    - *A major limitation is the lack of a single air sampling instrument that collects data on morphology, composition, agglomeration state, and particle size. Ideally, such an instrument would also provide fine size resolution ranging from nanoscale particles to ultrafine particles.*

- Despite the current limitations and challenges, we believe that **a proactive approach** to exposure assessment for the nanotechnology workforce is particularly important given the knowledge gaps both in sampling methodology and toxicology.

Context

- Since the **effectiveness of current PPE** in protecting workers from ENMs is not yet fully understood, research is needed to investigate their efficacy under conditions that simulate occupational use

- Evaluating the materials of interest **along their entire lifecycle** is important

- Although this work targets ENMs employed in the **semiconductor industry**, the knowledge gained from studying these model systems can be extrapolated to improve the health and safety environment for workers in **a variety of industries** that utilize ENMs

- It is critical to interpret **exposure assessment data** alongside data from **toxicology studies** (hazard assessment) in order to accurately and appropriately assess risk to workers
  → *elemental composition, size, size distribution, shape/morphology, aspect ratio, degree of agglomeration, specific surface area, and surface composition*

- Toxicology research investigating **these real-world exposures** is also ongoing concurrently with collaborators (not included in this presentation)

NIOSH and SUNY Poly CNSE Launch Nano Health & Safety Consortium

CNSE press release:
http://www.sunycnse.com/Newsroom/NewsReleases/Details/15-05-20/SUNY_Poly_CNSE_and_NIOSH_Launch_Federal_Nano_Health_and_Safety_Consortium.aspx

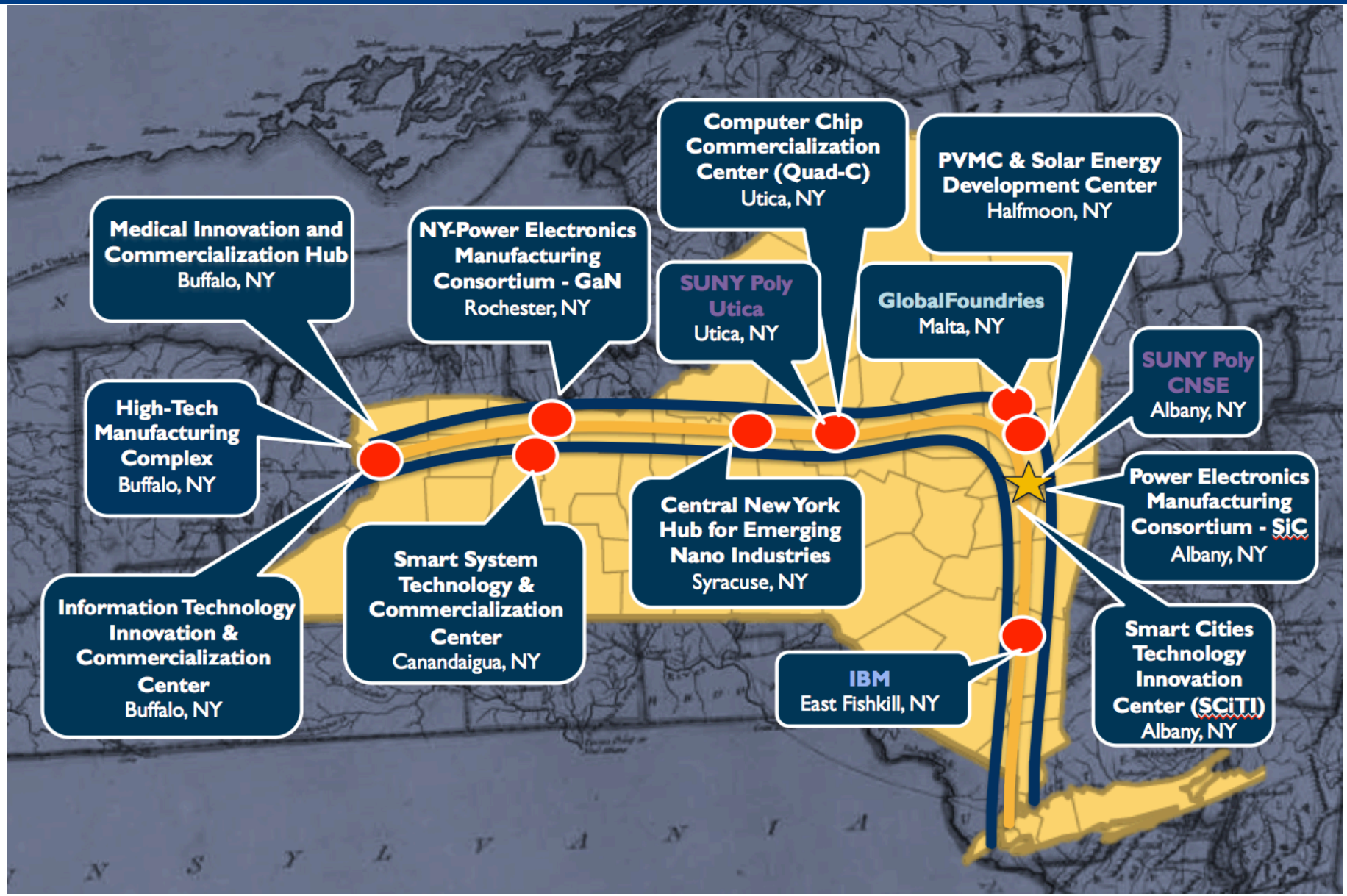
NIOSH press release:
http://www.cdc.gov/niosh/updates/upd-05-20-15.html

WHBlog post:
https://www.whitehouse.gov/blog/2015/05/20/new-initiatives-accelerate-commercialization-nanotechnology

Nano.gov post:
http://nano.gov/May2015Forum

SUNY Polytechnic Institute

New York's Nanotech Corridor



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2015 Brenner Research Team (Graduate Students & Staff)

SUNY Polytechnic Institute

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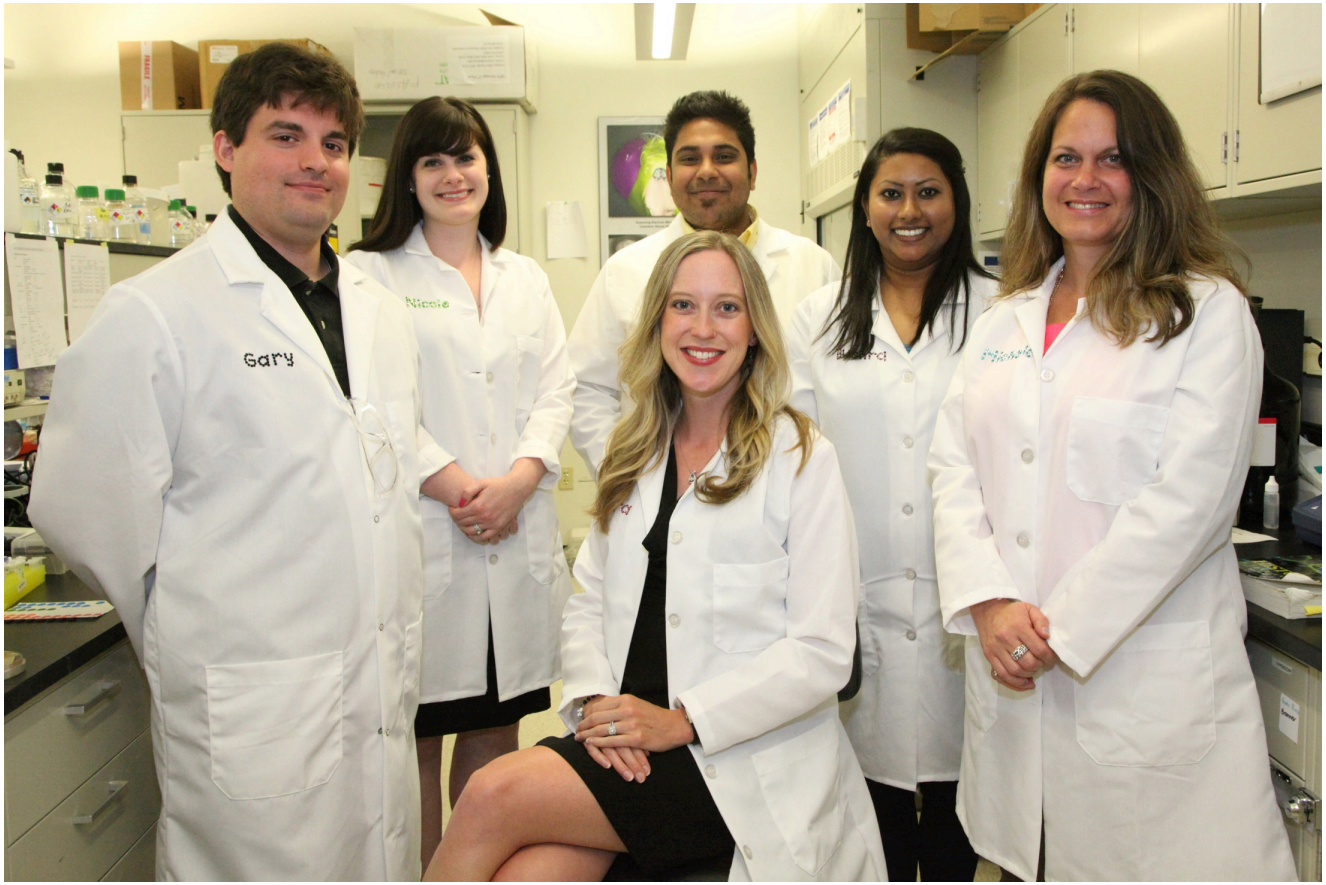

Current Staff & Students

Bushra Alam, MS
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Pilar Sosa
James Dillon
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Marissa Guttenberg
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Arun Nallainathan
Danielle Attanasio
Julia Martinez
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Support

• Nanoparticle Exposure Assessment during CMP Operation and Maintenance (CDC-NIOSH)

• EPA STAR Fellowship-Risk Assessment and Life Cycle Analysis of Nanoscale Metal Oxides used in Semiconductor Wafer Fabrication (U.S. Environmental Protection Agency [EPA])

• Nanoparticle Exposure Assessment during CMP Operation and Maintenance Phase IV (SEMATECH/NYS)

• Identification and Determination of Fate of SiO_2 Nanoparticles in Conventional Wastewater Treatment Phase III (SEMATECH/NYS)

• Efficacy of Personal Protective Equipment (PPE) in Preventing Dermal and iNhalation Exposure to Nanoparticles and Nanoagglomerates Phase III (SEMATECH/NYS)

• Acute vs. Subchronic Health Effects of Inhalation Exposure to Engineered Metal Oxide Nanoparticles in a Rat Model Phase III (SEMATECH/NYS)

• Development of Advanced Imaging and Analytical Techniques for Occupational Exposure to Nanomaterials (CDC-NIOSH)

Former Staff & Students

Gary Roth, PhD, MS; Michele Shepard, PhD, CIH; Nickie Johnston, MPH; Hallie Morgan, MPH, MA; Jean McMahon, MD, MPH; Julielynn Wong, MD; John Ling, MD; Stephanie Reed, RN, MPH; Selina Osei, MPH; Tanya Pick, MPH; Jason Condro, MPH; Caroline Boisclair, MSPH; Pascale Houanche; Allison Pastel; Leo Albert; Stephanie Collins-Finn; Henry Herbol; Alex Talamo; Patricia Massa; Olivia Obicheta; Logan Fischer; Molly Goodman; Radha Urribarri; Benjamin Denn; Eunice Chou; Sara Wong; Sam Rosis; Ahlam Abudawad

https://sunypoly.edu/research/team-brenner/