Understanding the Physicochemical Properties, Behavior and Toxicity Threshold Limit of Bound and Unbound Engineered Nanomaterials (*Task Number: 425.051*)

PIs:

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Other Researchers:

- **Steven Crawford, Research Technician, Nanoengineering, NC A&T**

Cost Share (other than core ERC funding):

- **25% cost-share (in cash) from JSNN (collaboration between NCA&T and UNC-G)**

Previous Funding

- Conducted comprehensive physical and chemical characterization of four model slurries, bound ENs and few "real" slurries along with dried micro and NPs of comparable size and method of synthesis
- Investigated NP interaction with a mammalian cell
    - Surface Interaction, cellular uptake and internalization, interaction with nucleus (NP-induced DNA damage, Comet assay)
- With model slurries
    - Silica NP slurries NPs showed dose and time - dependent toxicity (both colloidal and fumed silica NPs), NP aggregation major factor in toxicity
    - Acute toxicity observed in case of Ceria slurry NPs and Alumina slurry NPs showed no significant toxicity.
    - Significant increase in production of intracellular ROS, indicating that silica NPs cause cellular toxicity via oxidative stress.
    - Raman Spectroscopy of cellular uptake was used and showed the internalization and inhomogeneous distribution of ceria NPs in cells
- With "real" slurries – preliminary physiochemical, toxicity and uptake data

Rationale and Objectives

- **Rationale**
  - Characteristics of spent CMP NPs, waste and bound ENs in biological media are expected to be very different in their state of aggregation, dispersibility and charge, compared to pre-CMP NP slurries.
- **Overall/long-term objectives (Year 1 –3)**
  - Building on current understanding on cell toxicity and uptake, along with a validated set of analytical, metrology and microscopy techniques, we will study the following ENs and EN mixtures
  - EN systems – (1) pre-CMP slurries ("real" or model), (2) spent waste and rinse water (post-CMP), (3) CMP waste (from SRC members), (4) bound ENs in CNT-polymer and Boron Nitride-epoxy composites
    - Determine toxicity threshold limit and EN behavior that is directly correlated to physicochemical data of spent CMP waste, dried residues on CMP tools and waste treatment systems and bound ENs
    - Determine recommended exposure and discharge limits from CMP processes and semiconductor packages with bound ENs

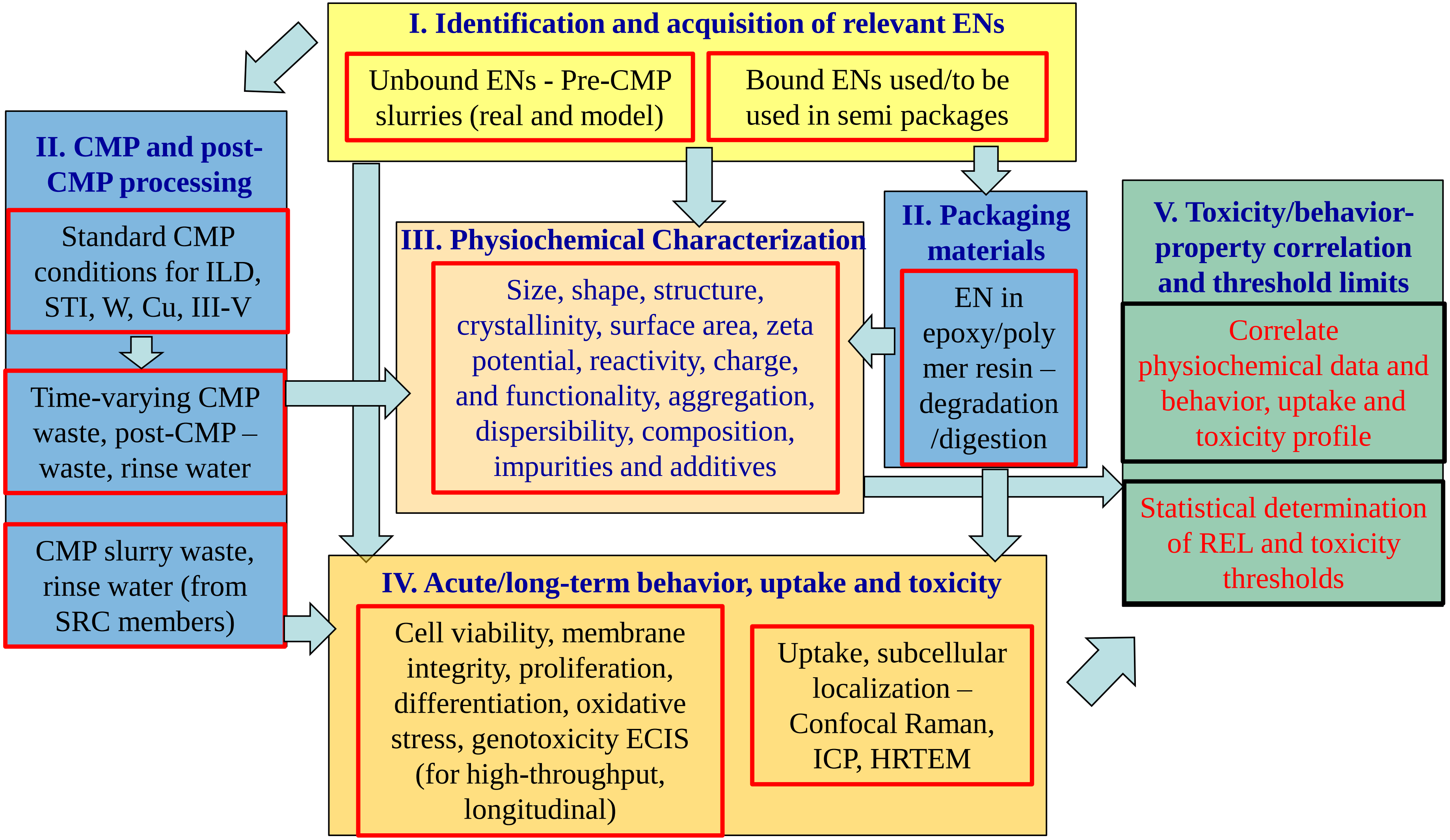
Objectives (contd..)

- **Short-term objectives (Year 1)**
  - Identification, acquisition and/or generation of relevant CMP NP slurries ("real" and model), spent CMP waste, rinse water and other bound ENs used/to be used in semiconductor packages
  - Comprehensive physiochemical characterization of ENs and other constituents in pre- and post-processed CMP mixtures and in bound ENs using a validated set of analytical, metrology and microscopic techniques
  - Conduct CMP and post-CMP processing of test wafers of inter-layer dielectric (HDP oxide), copper, tungsten, STI and III-V materials

ESH Metrics and Impact

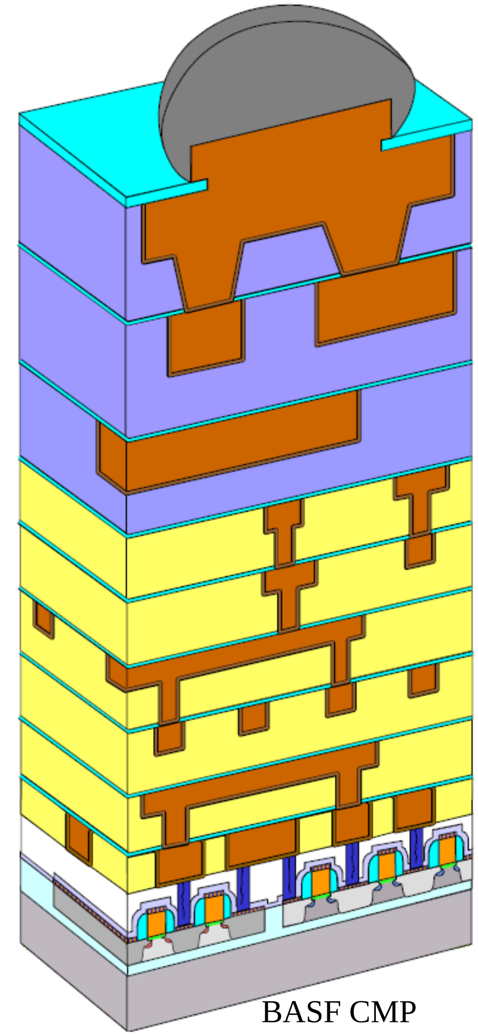
1. **Reduction in the use or replacement of ESH-problematic materials**
   - Quantitative correlation of EN behavior and toxicity potential in relevant ESH media to physicochemical properties of M1
2. **Reduction in emission of ESH-problematic material to environment**
   - Determination of recommended exposure limit (REL) and discharge thresholds for bound and unbound ENs in spent CMP waste, rinse water, dried residues and packages
3. **Reduction in the use of natural resources (water and energy)**
   - Results from Metric 2 will provided information on efficient use of water for dilution and/or neutralization processes
4. **Reduction in the use of chemicals**

Experimental Plan and Approach



I. Identification/Acquisition of relevant ENs

- **CMP slurries – Unbound ENs**
  - Cu CMP for 3D TSV
    - Front and back side
  - Cu CMP for Interconnect
  - Barrier CMP for Interconnect
  - Interlayer dielectric (ILD)
  - Shallow trench isolation (STI)
    - Nitride and poly Si stopping
  - High K metal Gate
    - Poly Si opening
  - Emerging front-end/high-mobility channel materials
    - III-V materials - GaAs, InGaAs and InP
    - Hazardous residues in spent CMP waste/rinse water



BASF CMP

- **Bound NPs in polymer composites**
  - CNT-polymer and BN-epoxy as polymer composite packaging materials

I. Identification/Acquisition of relevant ENs

#	Name	Applications	pH	Size (nm)	Solid %	DLS (nm)	Measured pH	Zeta
1	Ultrasol 200S; Colloidal Silica	Si, GaAs, InP, Ge other IR materials	9.5	30	24	23.96	9.06	
2	Dow Klebosol 15 01-50; Colloidal silica	ILD, STI	10.9	50	30	65.43	10.5	37.8
3	Dow Klebosol 30 H50; Colloidal silica	W, Cu	2.0	50	30			
4	Ultrasol 3005; Ceria	STI, ILD, BK7, Fused Silica, Glass	8.8	550	10	319.9	8.56	-89.3
5	Ultrasol 200A; Alumina	Al, CdZn, Te, GaAs, InP, Ni, Spinel, ZnSe Chalcogenides	4.0	100	20	281	3.19	54
6	Cabot Semi-Sperse® 12E Fumed Silica	ILD, PMD, polysilicon, STI	10.9	140	10	158.7	8.57	-63.2

- Selection criteria (a) applications, (b) pH and (c) close to model slurries

II. CMP and Post-CMP Cleans

IPEC Avanti 472 CMP. Inset shows 8” polishing pad/surface (right) Lam DSS-200 Series II Brush Cleaner for post-CMP cleaning

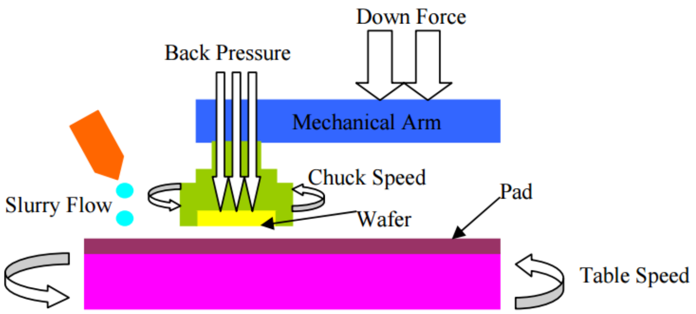
- **CMP metrics - MRR, WIWNU, defects, surface analysis – AFM, XPS**
- **Control of polishing conditions**

  (1) Platen Speed (2) Platen temp

  (3) Carrier/platen speed (4) Polishing time

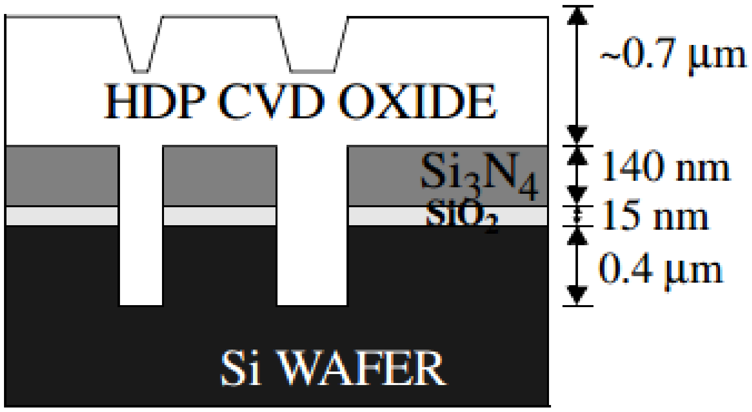
  (5) Dow® IC1000™ K-groove polishing pad

  (6) Downforce (7) Slurry flow rate

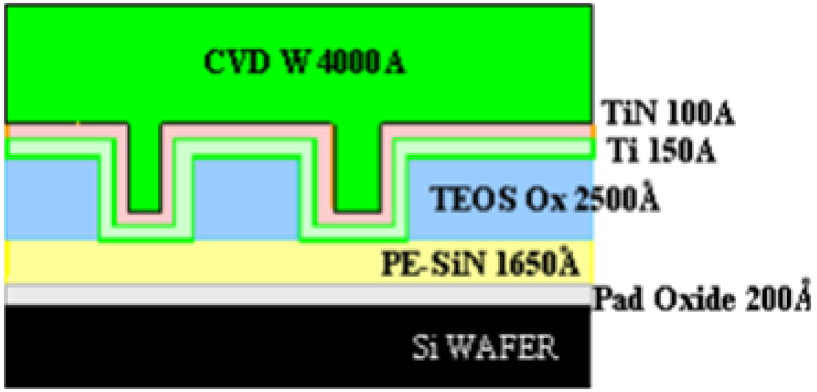


Nanolab, UC-Berkeley

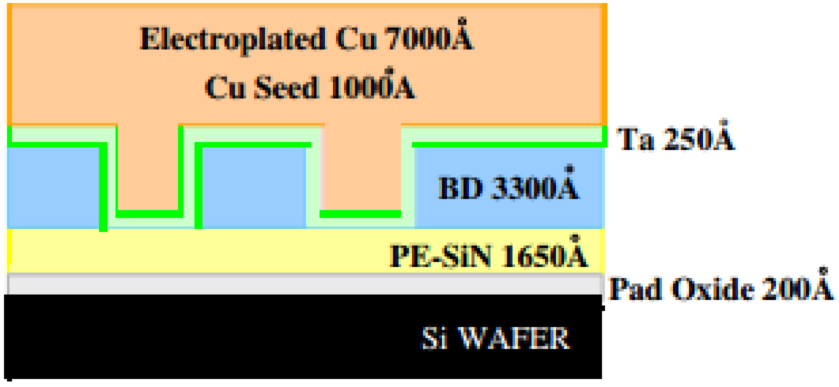
II. CMP and Post-CMP Cleans



CMP of HDP oxide – STI, ILD



CMP of CVD W

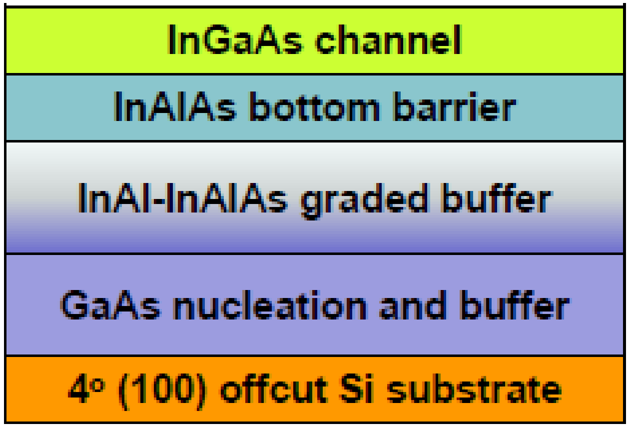


CMP of electroplated Cu

- Obtained test wafers with blanket (HDP Oxide, CVD W and e-Cu) and CMP characterization mask set (SKW Associates, Advantiv Technologies and Silyb Wafer)
  Characterization masks - MIT864 and MIT854
- Minimum line width – 0.18 µm

II. CMP and Post-CMP Processes

- **CMP of GaAs/InGaAs**
  - EPI 930 solid source MBE system (available at JSNN) used to grow In0.53Ga 0.47As n-channels.
  - 10 nm of In0.15Al0.85As/GaAs superlattice with 2-3 repeats with about 300 nm GaAs buffer layer (threading dislocation filter) will be grown on SiGe wafer, which is graded to 100% Ge.
  - Ge has a mismatch of only 0.4% with respect to GaAs; Off-cut wafers will be used to control the antiphase boundaries.
  - Evolution of toxic arsenic trihydride and phosphine (from InP CMP) gases will be monitored, along with measuring the concentration of indium in discharge.

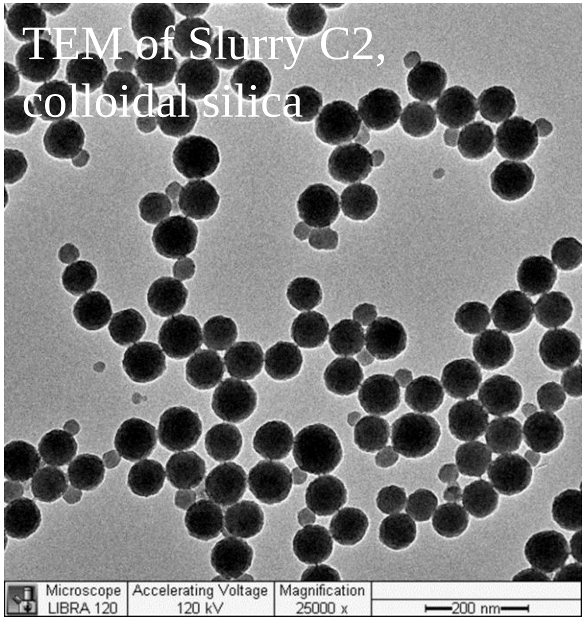


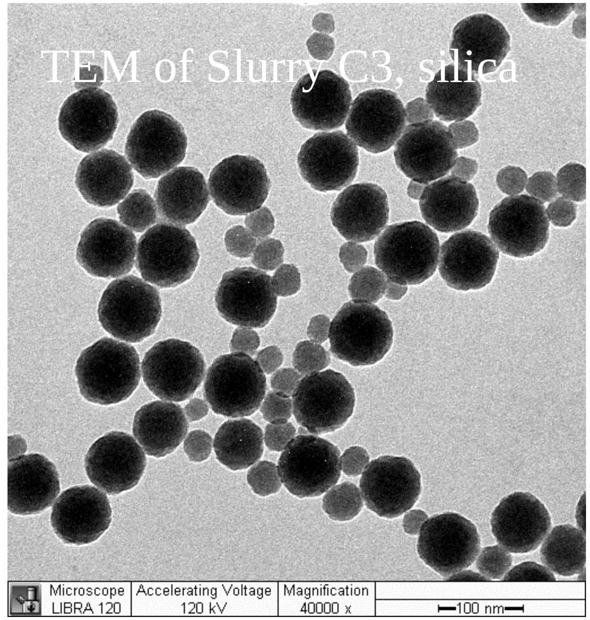
III-V (InGaAs) Channel Design (J. Oh, SEMATECH)

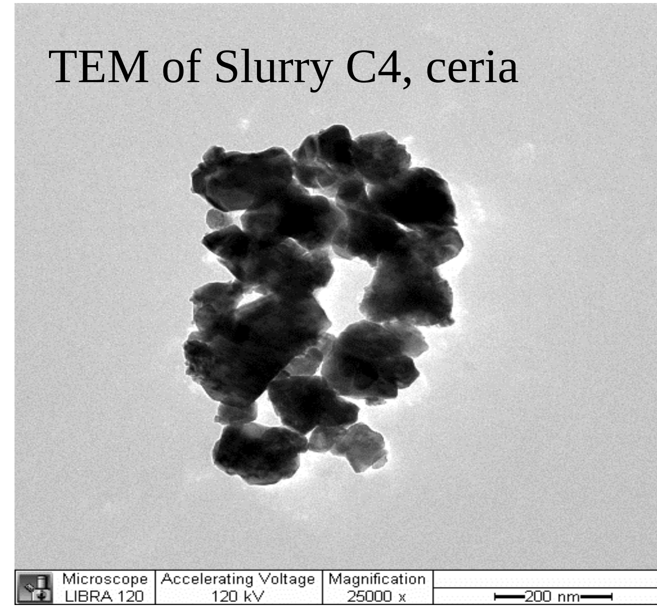
III. Physiochemical Characterization

- **Physiochemical properties**
  - Size, shape, structure, crystallinity, surface area, zeta potential, reactivity, charge, and functionality, aggregation, dispersibility, composition, impurities, additives, surface analysis – AFM, XPS
- **Comparison of complete NP slurries, supernatants and dried ENs**
- **Techniques**
  - DLS, zeta, NTA (NP under flow), XRD, SEM/EDS, HRTEM, Helium ion microscope, BET-surface area, FTIR, UV-Vis, Confocal Raman, ICP-MS/OES, NMR. ion chromatography and mass spectrometry

III. Physiochemical Characterization



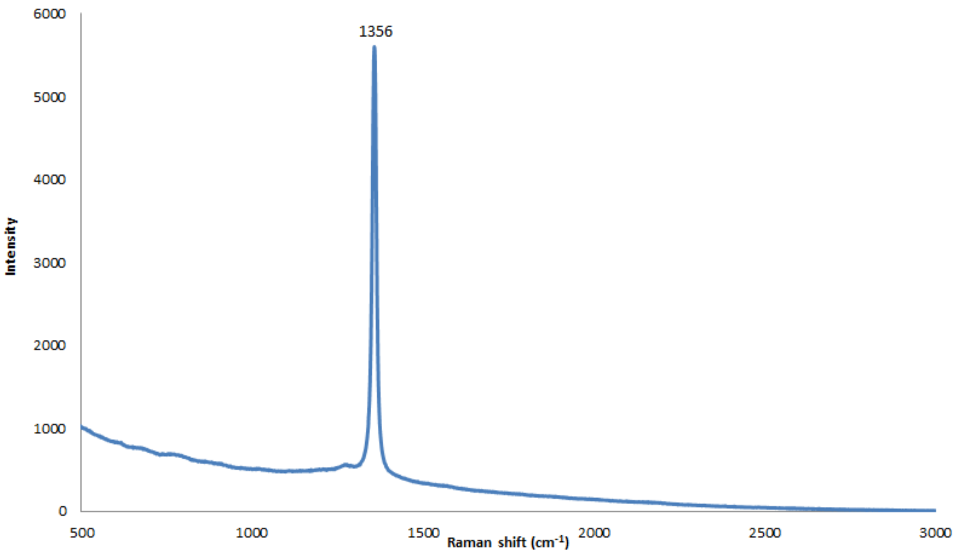




III. Physiochemical Characterization

- Hexagonal Boron Nitride powder (hBN) of sizes 70, 500, 1500 nm were purchased from Lower friction Lubricants/M K Impex Corp (suggested by Chris Lee (TI)/UNT)

SEM image of h-BN powder

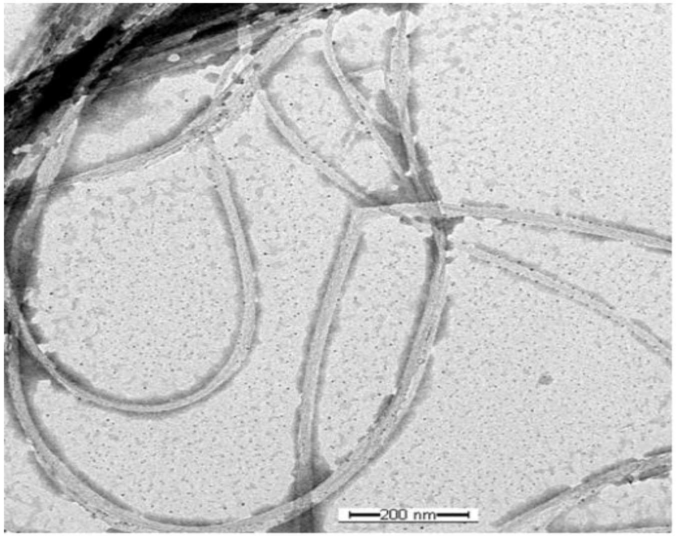


Raman spectra of h-BN powder

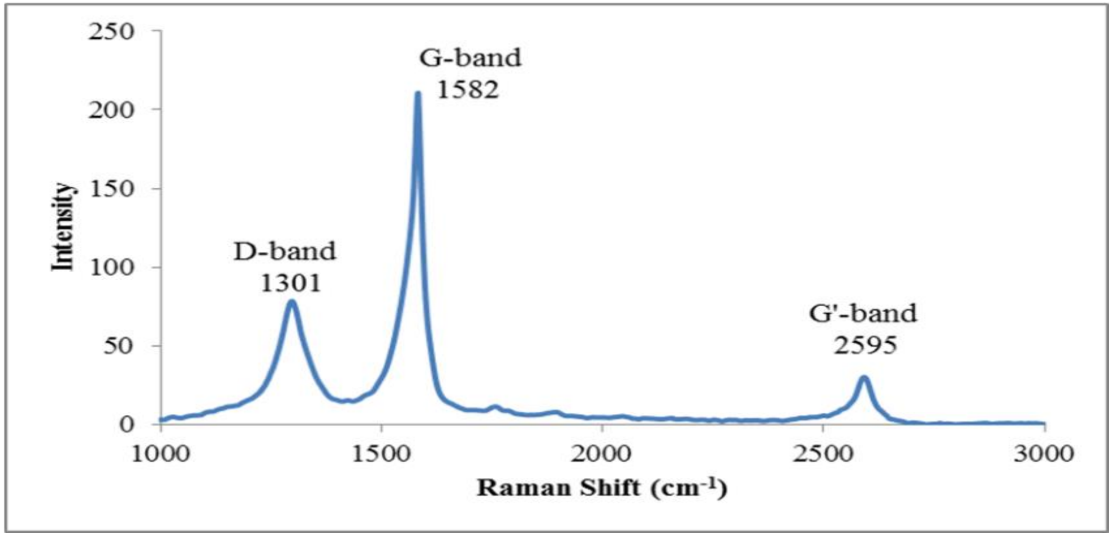
- Flow ability, thermal conductivity and flexural properties of boron nitride (BN) filled EPON 8281 and DEN 431 epoxy composites

III. Physiochemical Characterization

- CNTs dispersed in 1% pluronic F-68



TEM image of CNTs in surfactant



Raman spectra of CNTs

IV. Acute and Long-term Behavior, Uptake and Toxicity Studies

- In vitro cell culture studies with different cell types
  - Phagocytes (macrophages); non-phagocytes (A459 lung, Hep G2 liver, Pk15 kidney cells)
- EN samples
  - Pre-CMP slurries (real/model), supernatants, dried ENs, post-CMP waste/rinse water, CMP waste (from SRC members), bound ENs in CNT-polymer matrix and Boron Nitride-epoxies – degraded/digested
- Mechanistic short-term and long-term (>10 days) studies
  - Cell viability (MTT), membrane integrity (LDH), proliferation, differentiation, oxidative stress (ROS), genotoxicity (Comet), ECIS (for high-throughput, longitudinal studies)
- EN behavior and cellular uptake
  - Bioavailability, transport, uptake and accumulation
  - Confocal Raman, ICP and ultrastructural - HRTEM

V. Toxicity/Behavior-Property Correlation and Threshold Limits

- Study the tole of aggregation, dispersibility, composition, additives and medium (cell culture media, rinse water, whole blood) on EN behavior and toxicity
- Establish correlation of varying physiochemical properties with EN behavior and toxicity data
- Statistical determination of REL and toxicity thresholds
  - Determine IC50 values, ANOVA, student's t-test

Deliverables and Timeline

Deliverables/Timeline	6	12	18	24	30	36
Comprehensive Physiochemical Characterization of Bound and Unbound EN and Other Constituents in Pre- and Post-Processed Mixtures	→	→				
Influence of Varying Physicochemical Properties from Different CMP Processing Conditions on Short- and Long-term (> 10 days Behavioral and Toxicity Measurements		→	→	→		
Correlation of Physicochemical Data with Behavioral and Toxicity Measurements			→	→	→	
Determination of Recommended Exposure Limit (REL) and Discharge Thresholds for Specific Set of EN Physiochemical Properties				→	→	→
Formulation of Predictive Toxicology Guidelines for any Set of EN Physiochemical Data					→	→
Dissemination			→	→	→	→

Industrial Interactions and Technology Transfer

- Continue collaboration with SRC/ERC Nanotoxicity consortium
  - Provide "real" post-CMP slurries to other consortium members for round-robin studies
- Work with SRC member companies and technical liaisons (Global Foundries, IBM and TI) to obtain "real" CMP spent waste from fab line
- Possible collaboration with RTI Nanotox/SEMATECH ESH
- Value to industry
  - Nanomaterial occupational safety and health information: determination of toxicity threshold and information on safe handling practices for CMP and other bound nanomaterials
  - Chemical information on emerging materials and processes: High throughput screening for physiochemical properties, toxicity and behavior of materials of interest to the industry

Thank You