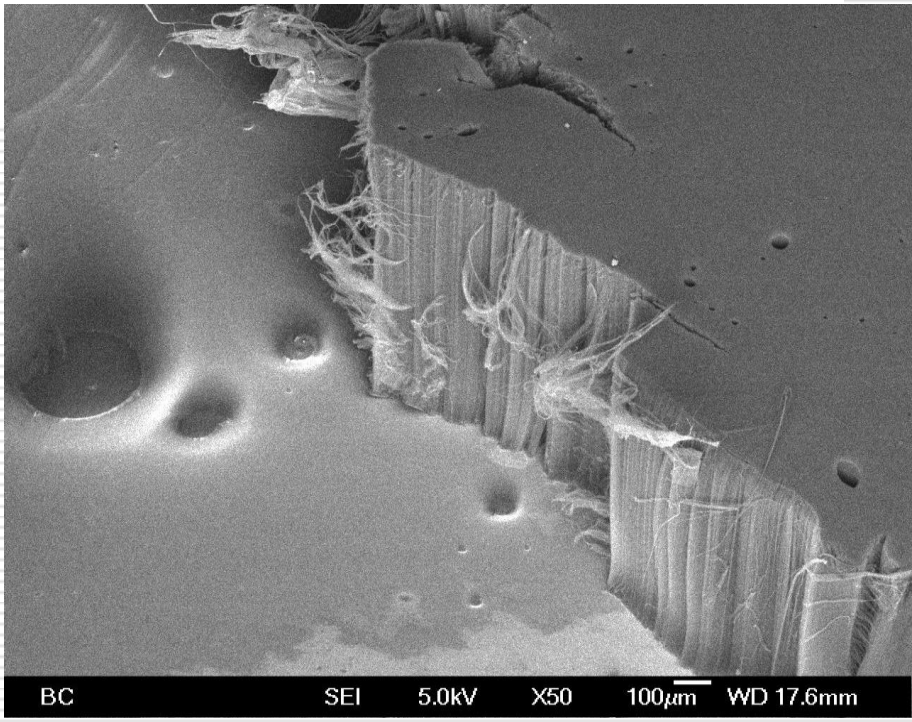
Nanostructured Optical Black Coatings

NASA SBIR Phase II Contract NNX13CP46C

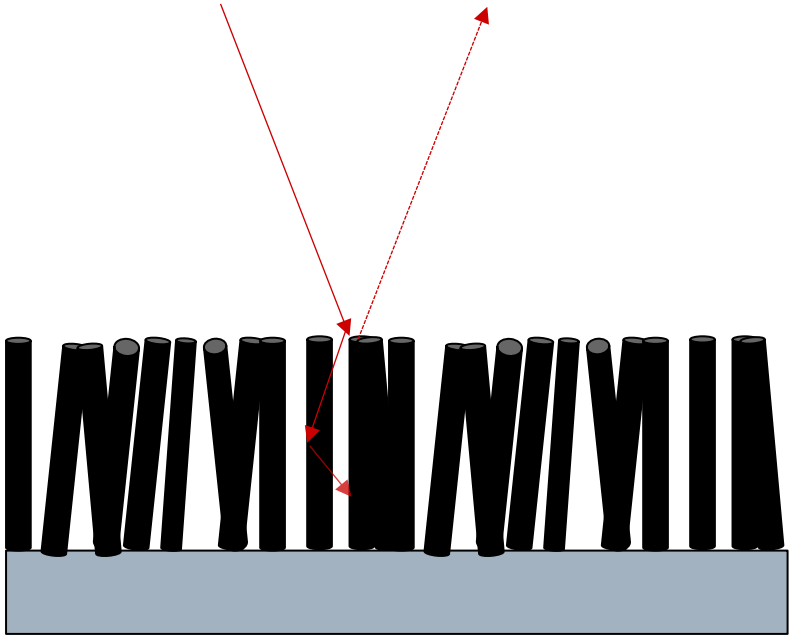
PI: David Carnahan
NanoLab, Inc.
179 Bear Hill Rd.
Waltham, MA 02451
dcarnahan@nano-lab.com
Phone 781 609 2722

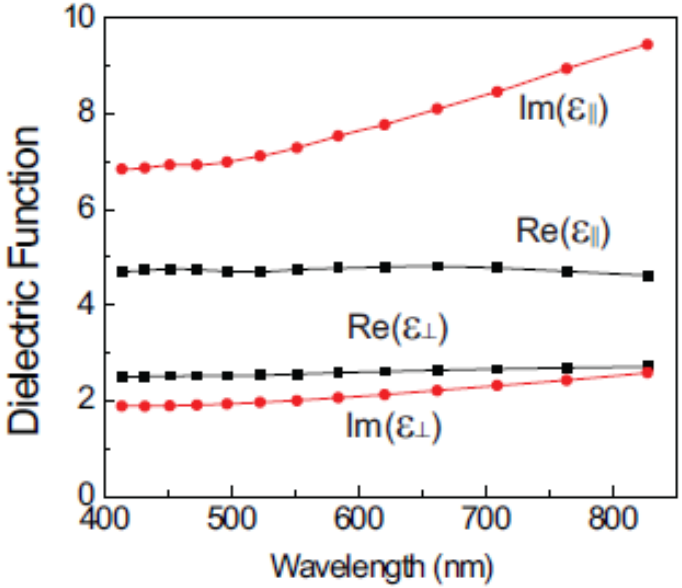
Sub: Beth Kelsic
Ball Aerospace
1600 Commerce St
Boulder, CO 80301
bkelsic@ball.com



Why are aligned nanotubes really black?

- Low density of array (~5vol%) means low index mismatch at interface (low reflection)
- Spacing between CNT can be sub-λ
- CNT are sub-λ in diameter, & supra-λ in length.
- Dielectric constant is directionally dependent



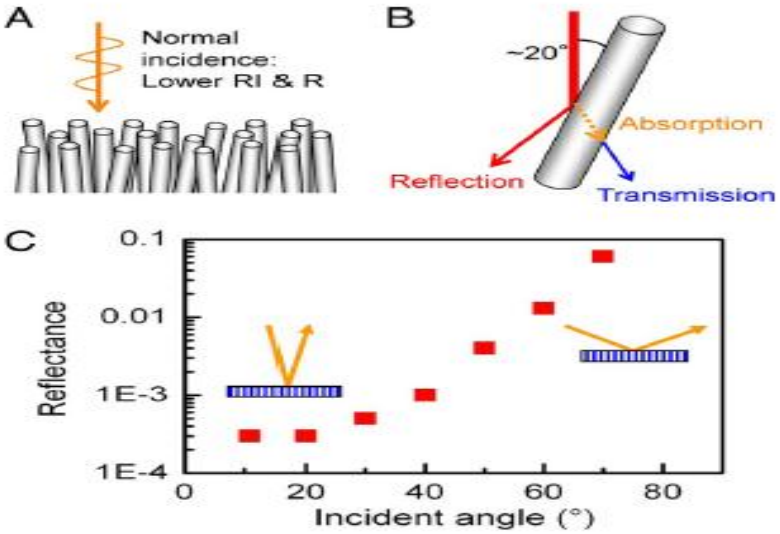


Hua-Bao, Xiu Lin Ran, Timothy Fisher, "Optical properties of vertical arrays of multiwalled carbon nanotubes from FTDT simulations" 15 March 2010 / Vol. 18, No. 6 / OPTICS EXPRESS 6353

Phase II Technical Objectives

1. Correlate the optical properties of nanotube arrays to their growth parameters; determining the influence of:

   diameter
   site density
   alignment
   length
   graphitization



2. Develop adhesion and scratch resistant treatments.
3. Scale processes for on flexible substrates. (Titanium, Stainless steel, mica, etc.)
4. Develop processes for complex 3D parts

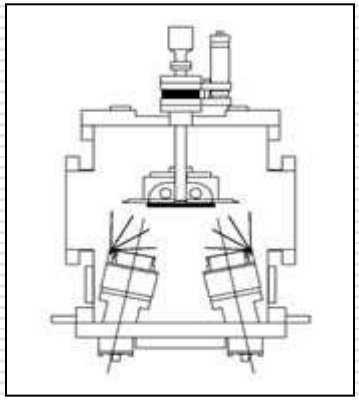
Ref: Mizuno PNAS, 2009, 106, 15

Outline

1. Catalyzation & CVD growth on flexible substrates & parts
    1.1 Catalyzation
    1.2 Aligned Array Growth
2. Resulting Morphologies
    2.1 Optical and Electron Microscopy
3. Characterization
    3.1 Optical Reflectance vs. wavelength (UV-Vis, FITR)
    3.3 Adhesion & Toughening
4. Scaleup for large substrate deposition
5. Conclusions

1.1 Substrate Catalyzation

- Options for catalysis:
  - Cleanroom
    - Sputtering (LOS)
    - Evaporation (LOS)
    - ALD (3D)
  - Low-cost options
    - Electro-plating (R2R or 3D)
    - Spray-coating (LOS)
    - Spin Coating (Planar)

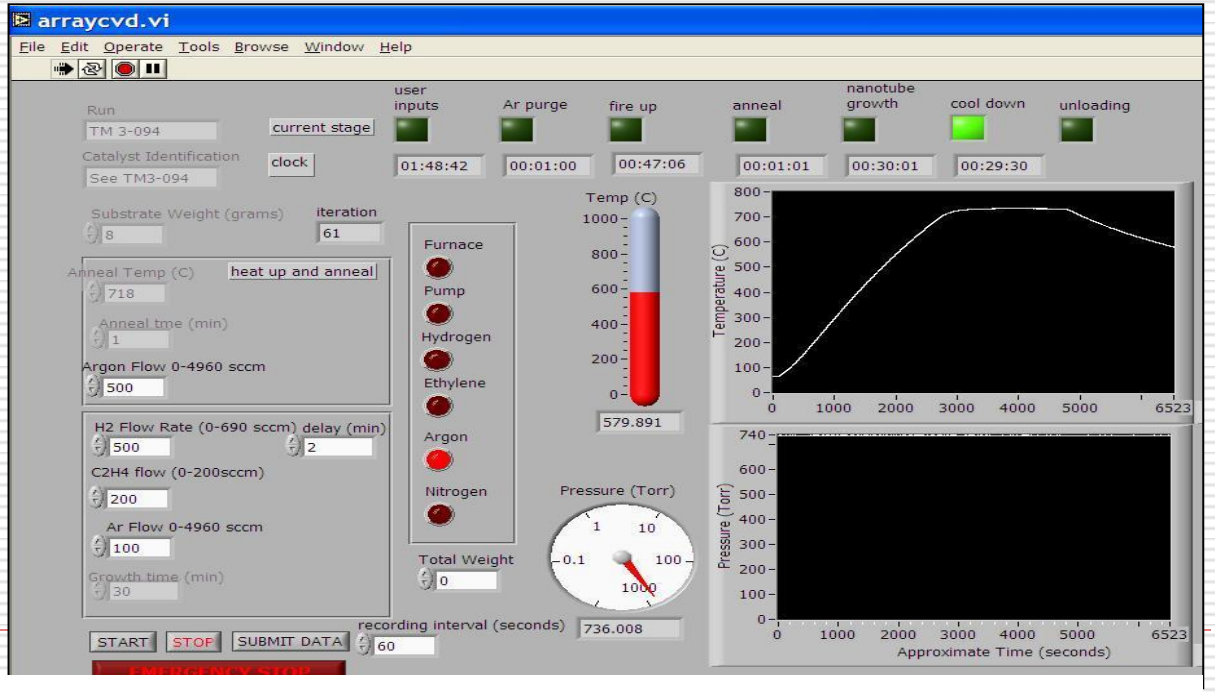


Substrates: SS sheet, Ti sheet, mica sheet, carbon veil, complex parts

1.2 CVD Growth of Carbon Nanotubes

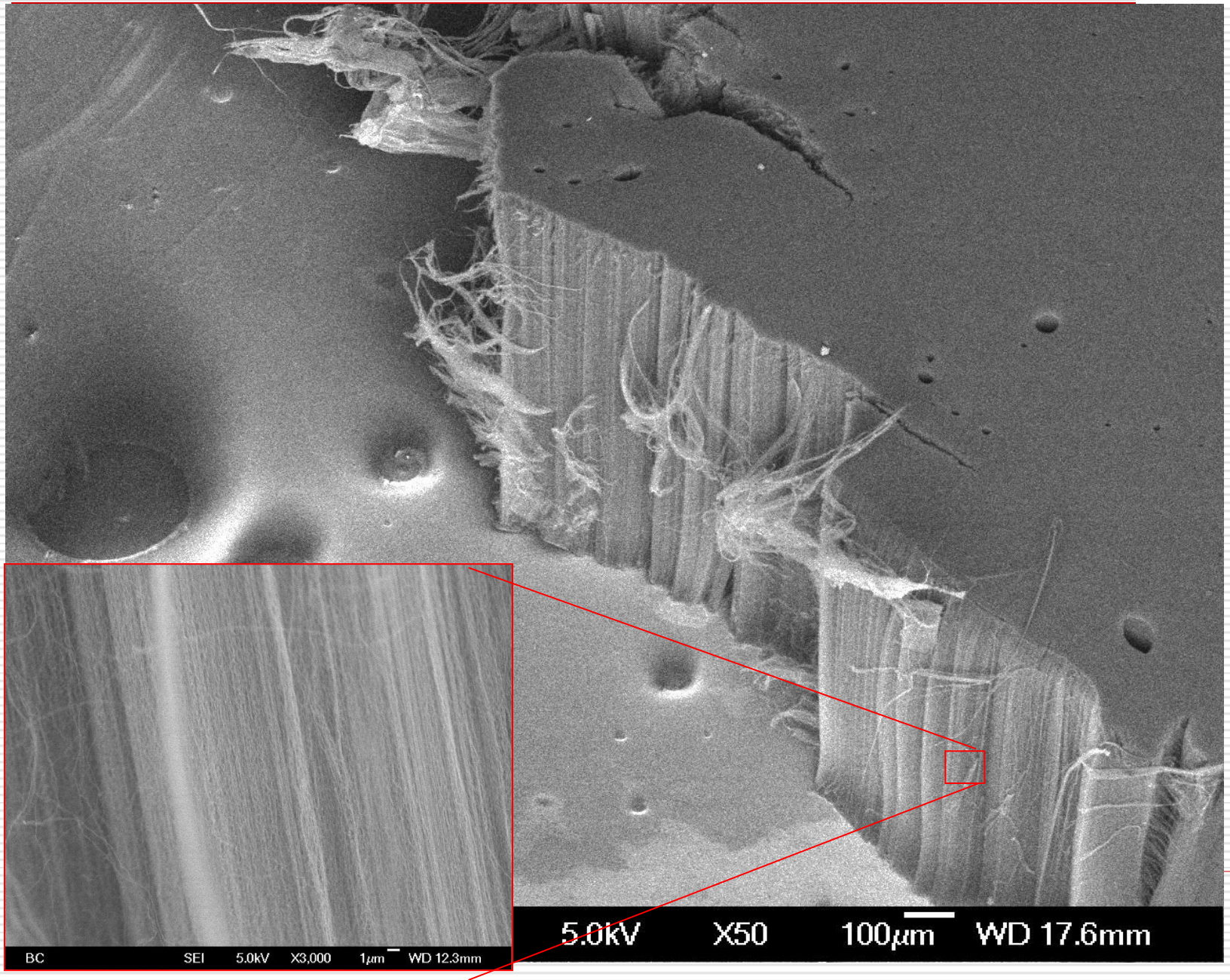
- Lindberg tube furnace, 36” heated length, 3 zones
- Quartz tube 54mm x 2m
- MKS mass flow controllers
  - Ar, H2, C2H4
- Automated with LabView

7 Step Program
1. Insert
2. Chamber Purge
3. Heat-up
4. Anneal
5. Growth
6. Cool
7. Unload



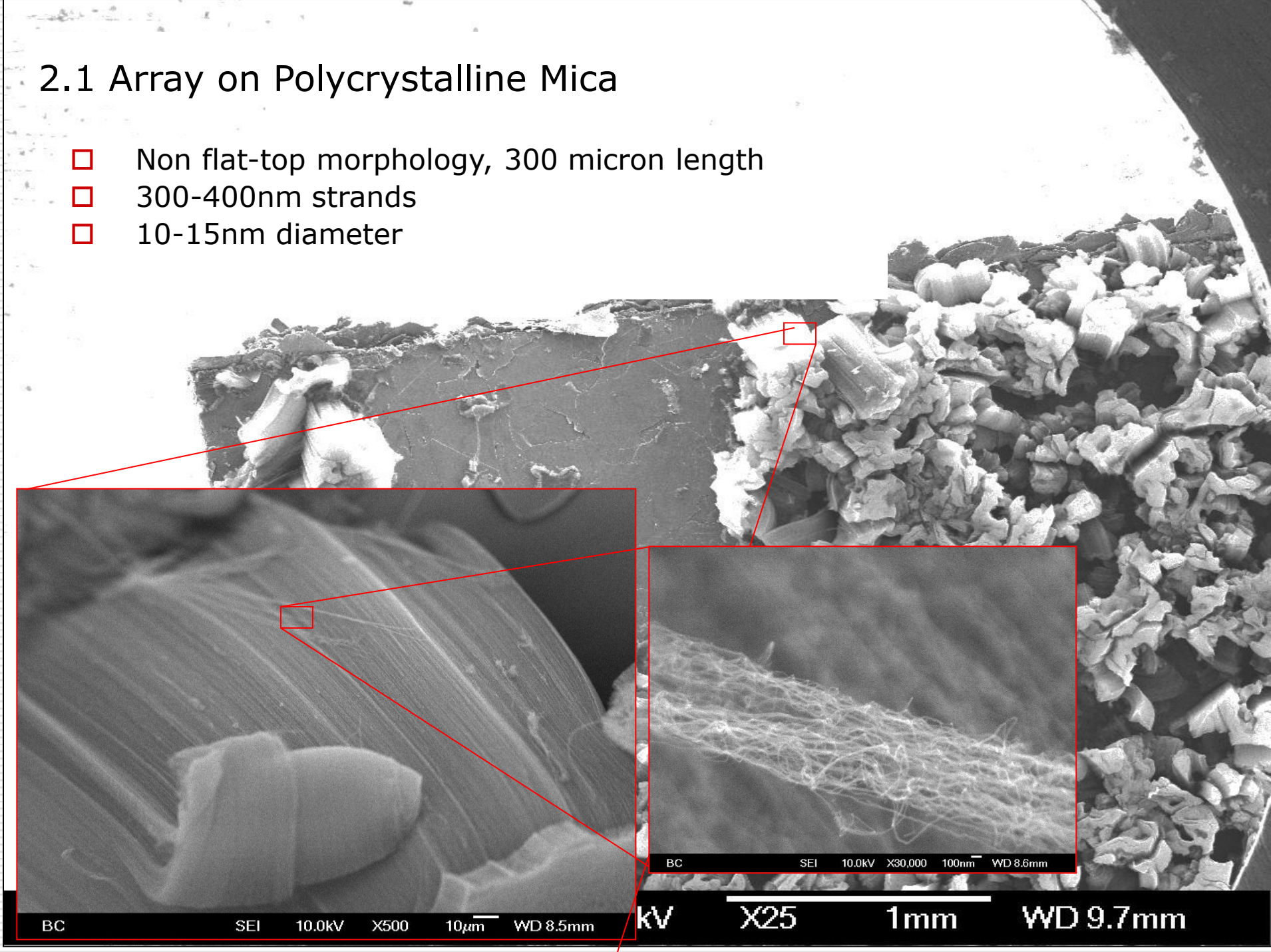
Scaling to 4” dia, then 9” dia, then roll to roll system

2.1 Resulting Morphology: Standard Arrays on Si

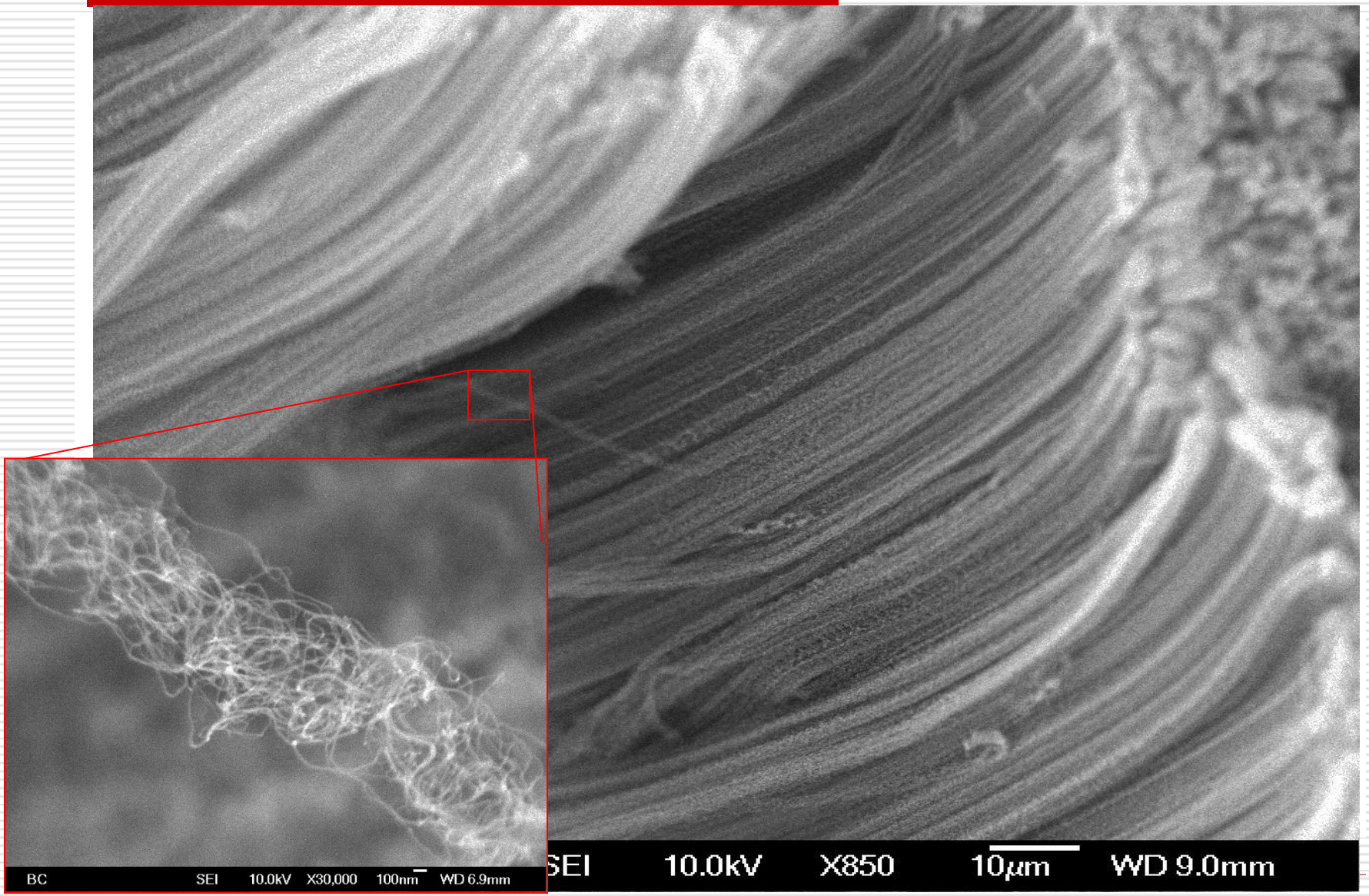


2.1 Array on Polycrystalline Mica

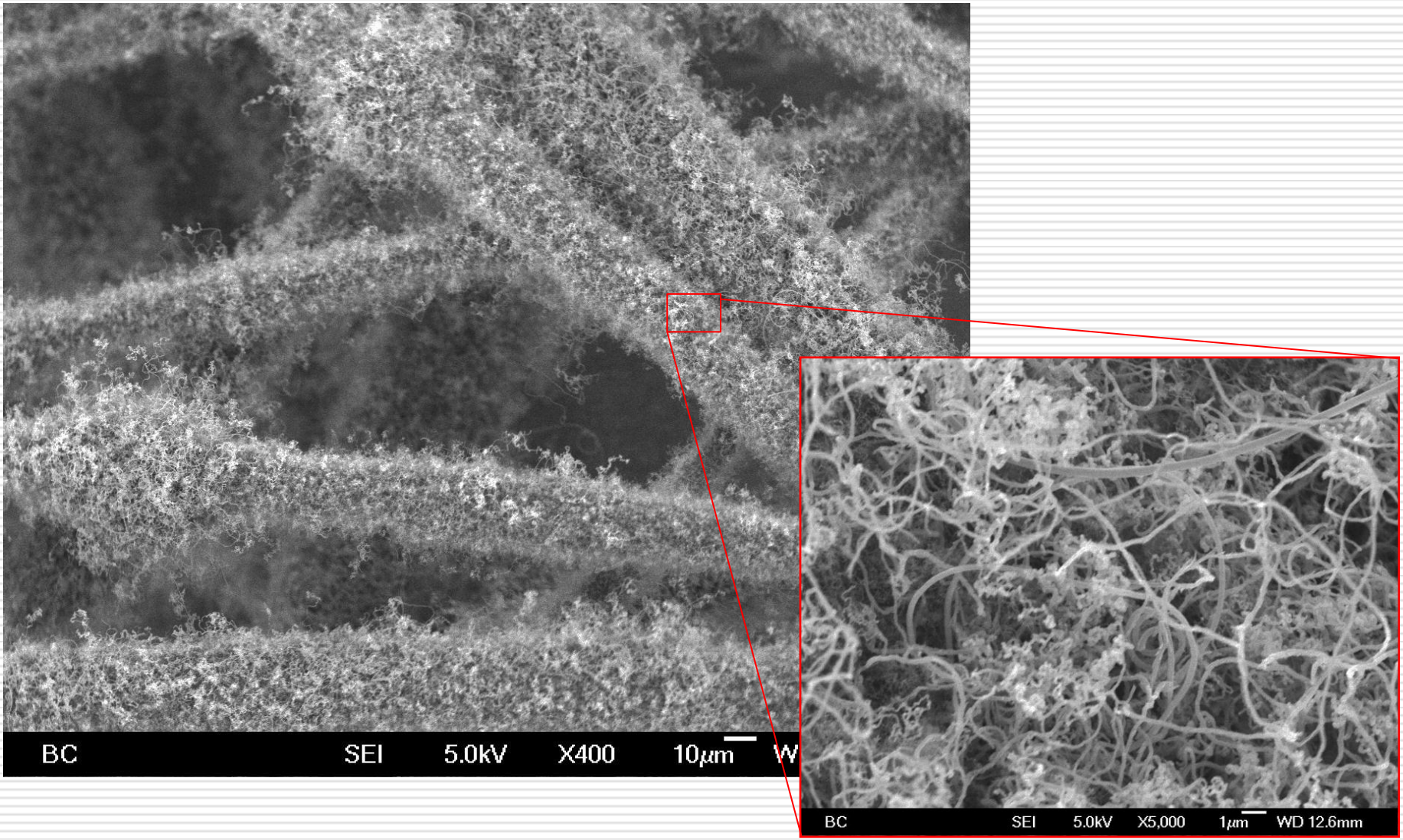
- Non flat-top morphology, 300 micron length
- 300-400nm strands
- 10-15nm diameter



2.1 Array on Stainless steel



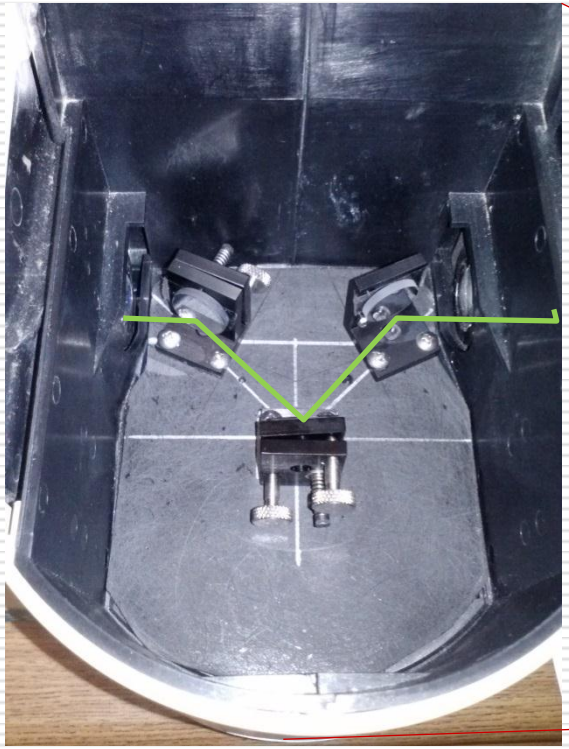
2.1 Carbon Nanotube- Carbon Veil



3. Characterization and Correlation

Type	Technique	What We Learn
Optical		
	UV-Vis	Specular Reflectance in 300-1000nm range
	DRIFT	Diffuse Reflectance Infrared from 2.5 to 25 um
Morphological		
	SEM	Diameter, alignment, Length, Site density
Chemical		
	Raman	Amorphous carbon and D:G ratio
Structural		
	Tape	Adhesion
	Scratch	Damage tolerance

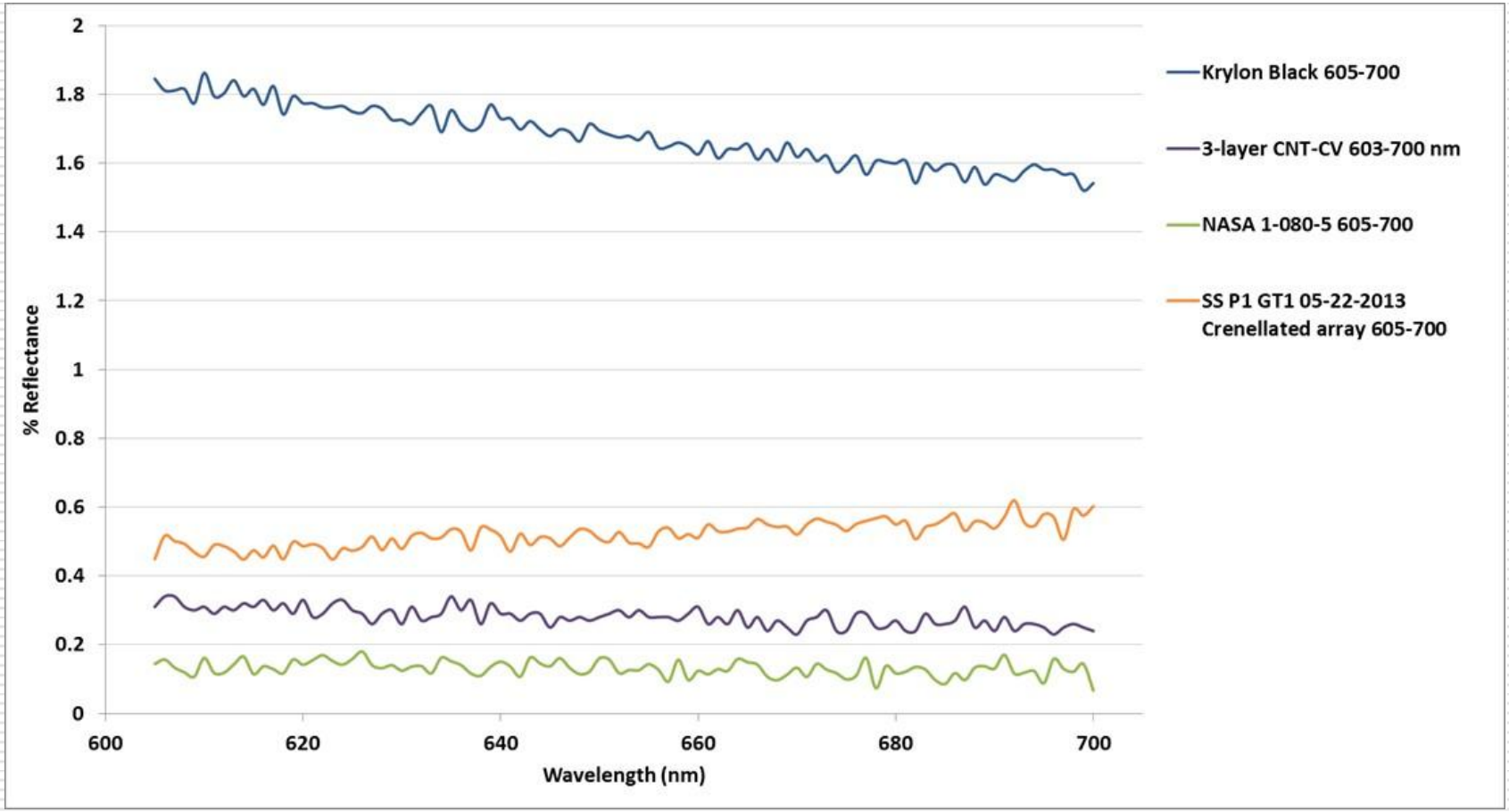
3.1 UV-VIS Spectroscopy



Fixed angle reflection, 72 degree incident angle to substrate. Samples are mounted on the middle mirror, allowing us to collect reflectance from 190-1100nm, using both lamps (deuterium (UV) and tungsten (Visible)).

3.1 UV-Vis Data, 70 degrees AOI

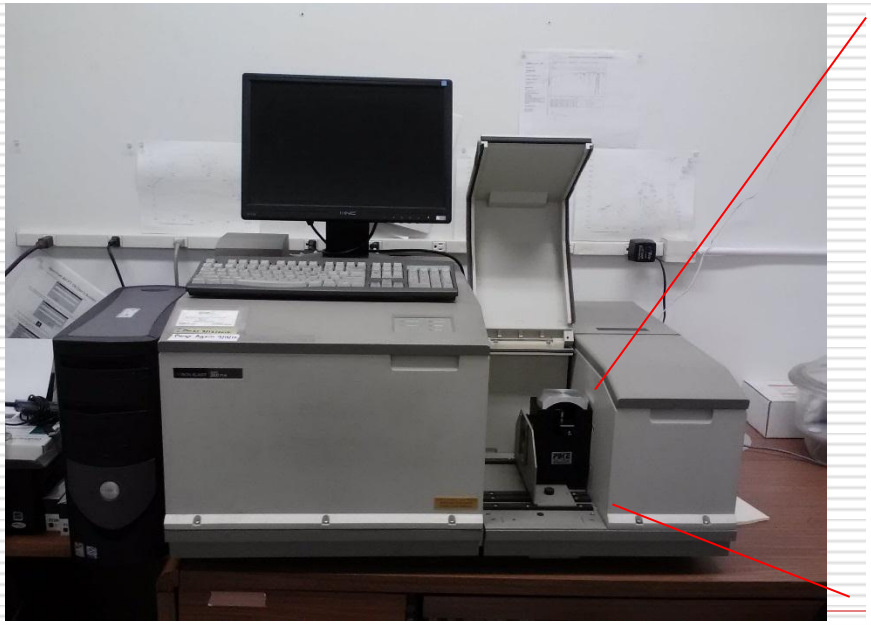
- Best performers are <0.1% reflectance in the optical, using our system

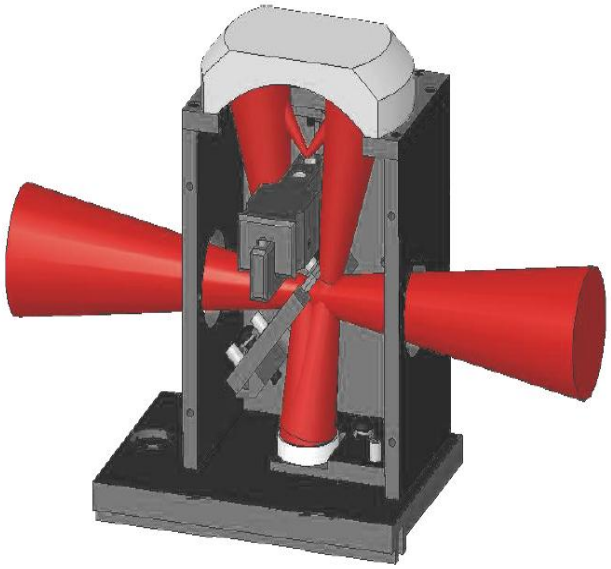


3.2 DRIFTS

We needed a rapid method to grade the coatings in the IR. Our FTIR system, equipped with a diffuse reflectance accessory (Pike EasiDiff) gives us a way to compare the relative reflectance of our nanotube arrays.

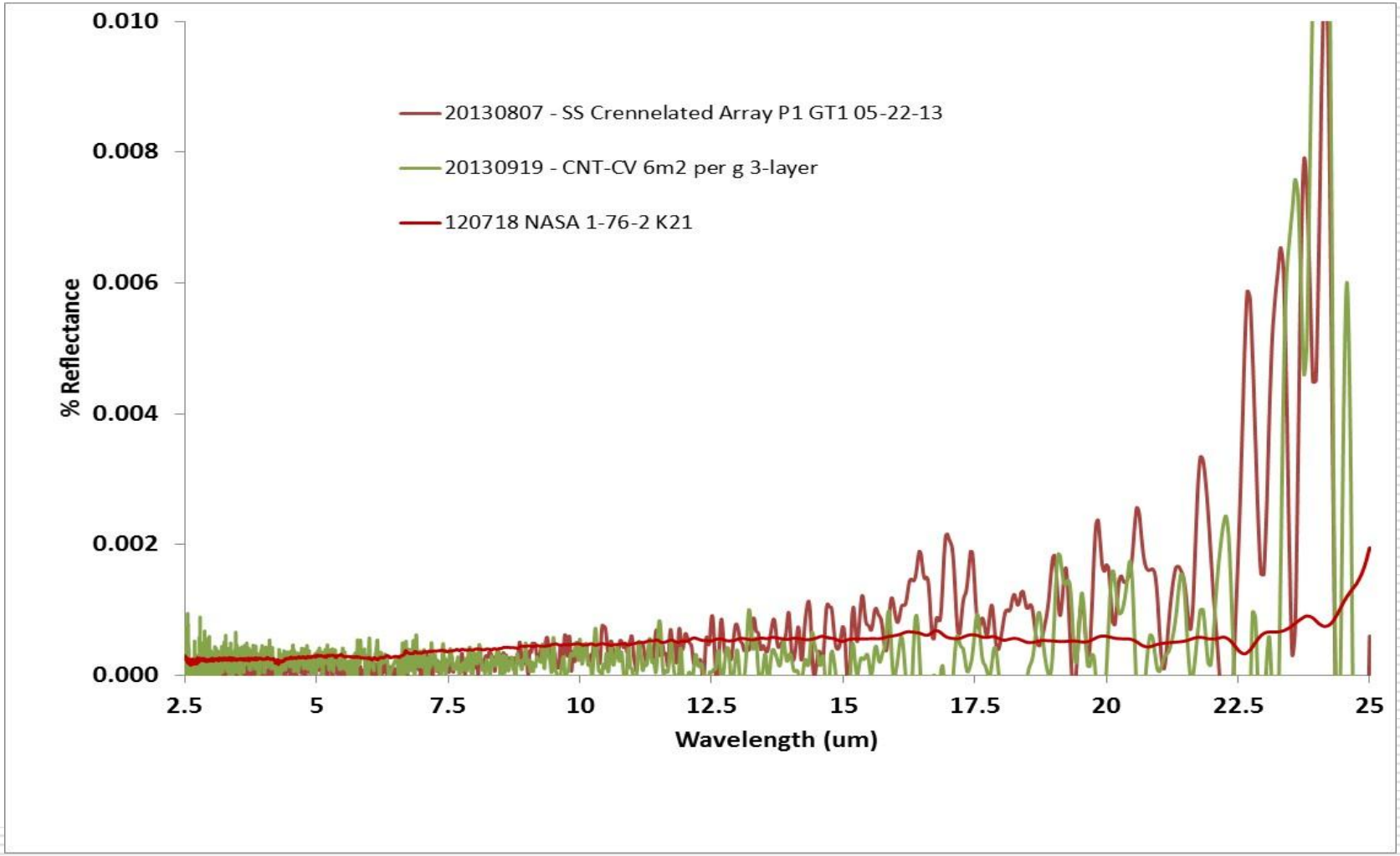
- We measure:
  1. Reflected energy spectrum from 2.5-25 microns
  2. Beam Energy (BE) which is a rough average across the range.
     - A mirror gives a BE ~6000
     - Krylon flat black on mica, BE = 324
     - Our best arrays, BE= 2



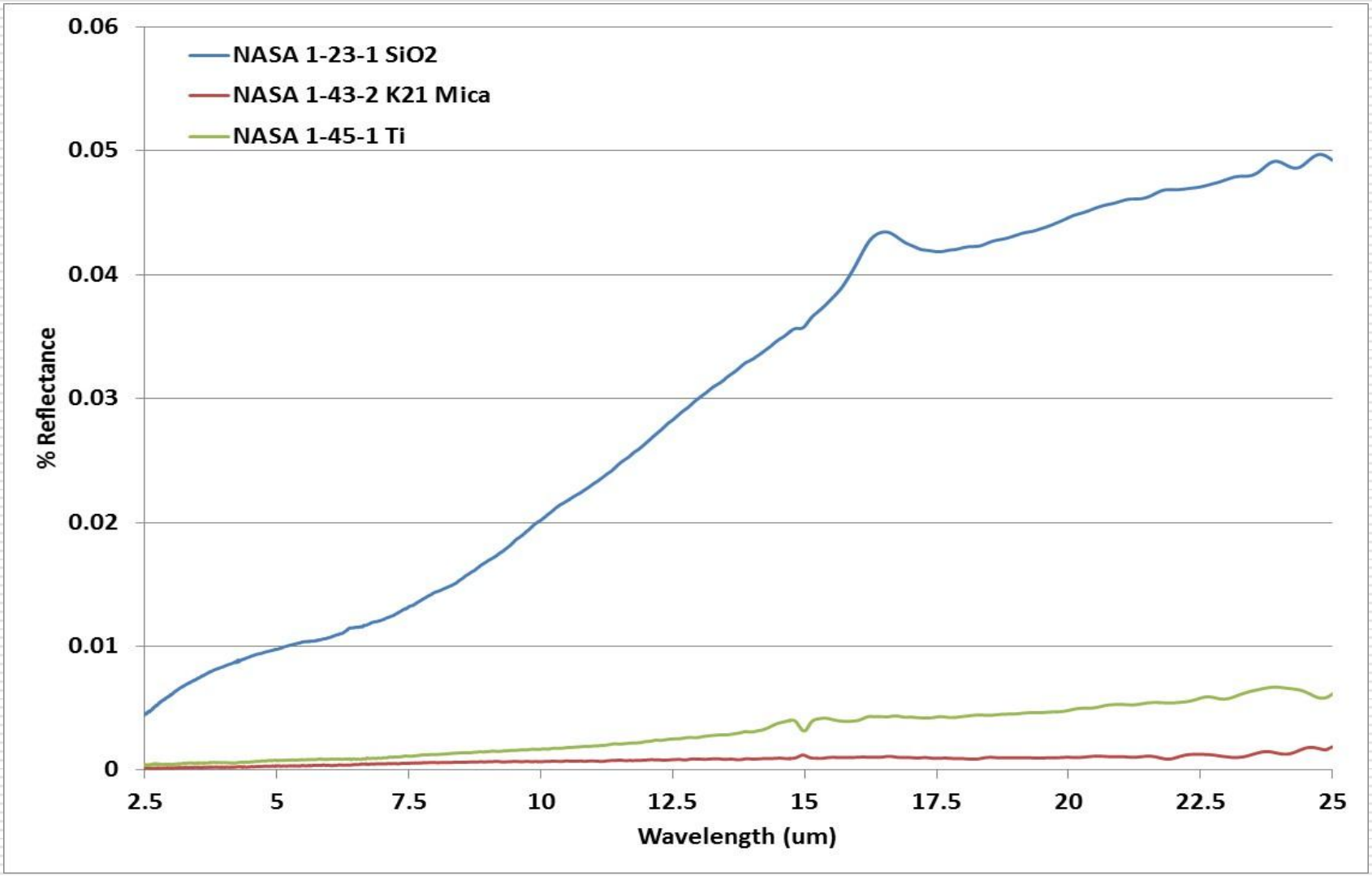


3.2 DRIFTS

- Three avenues for array growth give 99.99+ Absorbtion



Phase I Top Performers- DRIFTS



3.3 Modifying adhesion & scratch resistance

The arrays pass Scotch-tape style adhesion tests, but only because few nanotubes actually contact the adhesive. However, the arrays have negligible scratch resistance, unless we modify them.

Several approaches are being investigated to toughen the nanotube arrays:

Pre-growth

Geometric

Surface Roughness

Pillars

Patterning

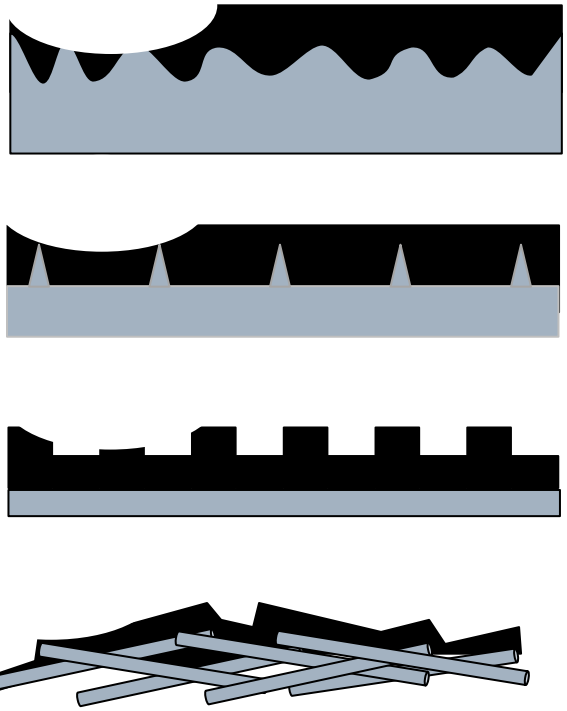
Crenellation

Post-Processing

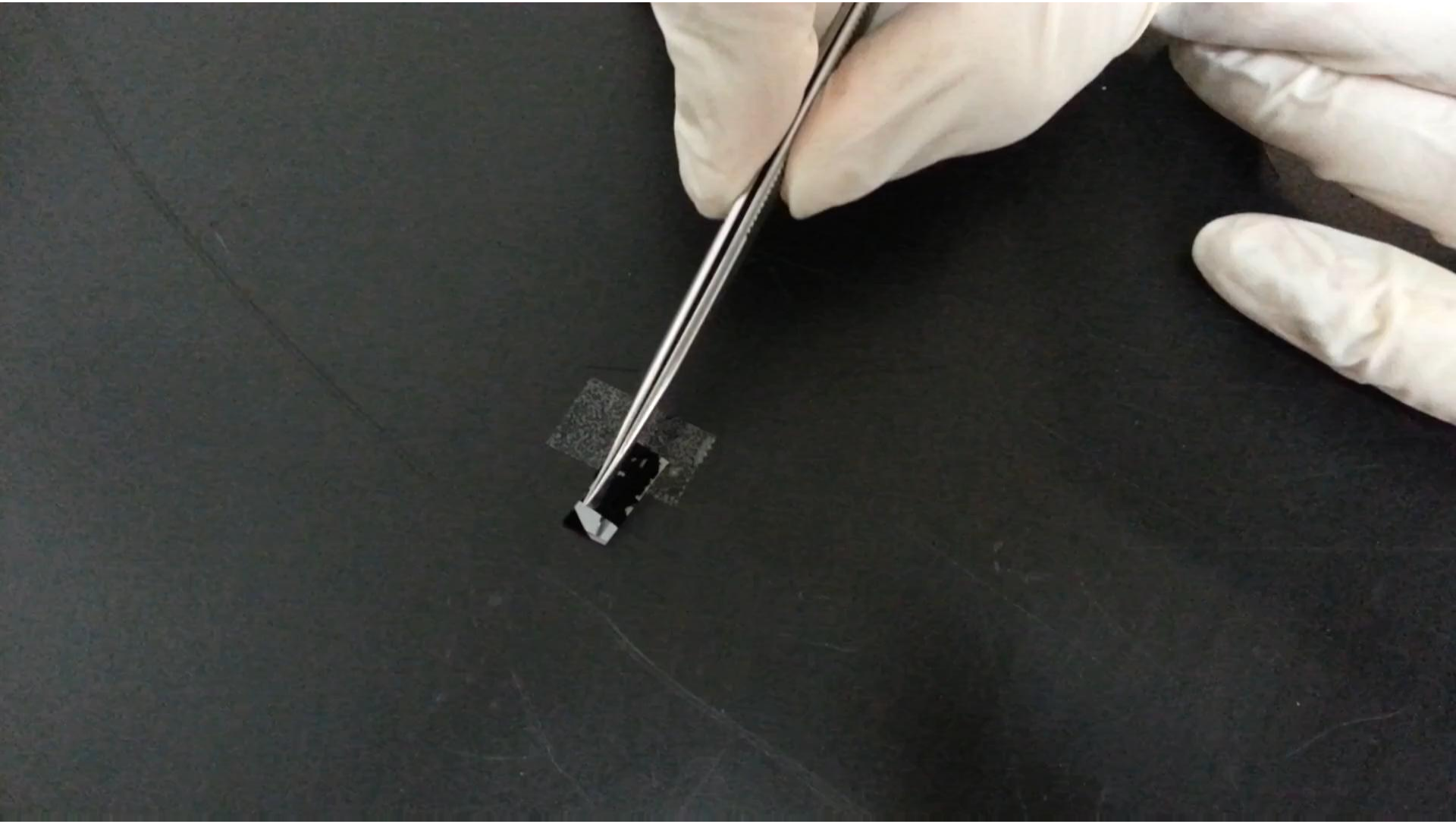
Develop scratch resistant treatments

Alternatives

Veil morphologies



3.3 Abrasion- Initial-no treatment



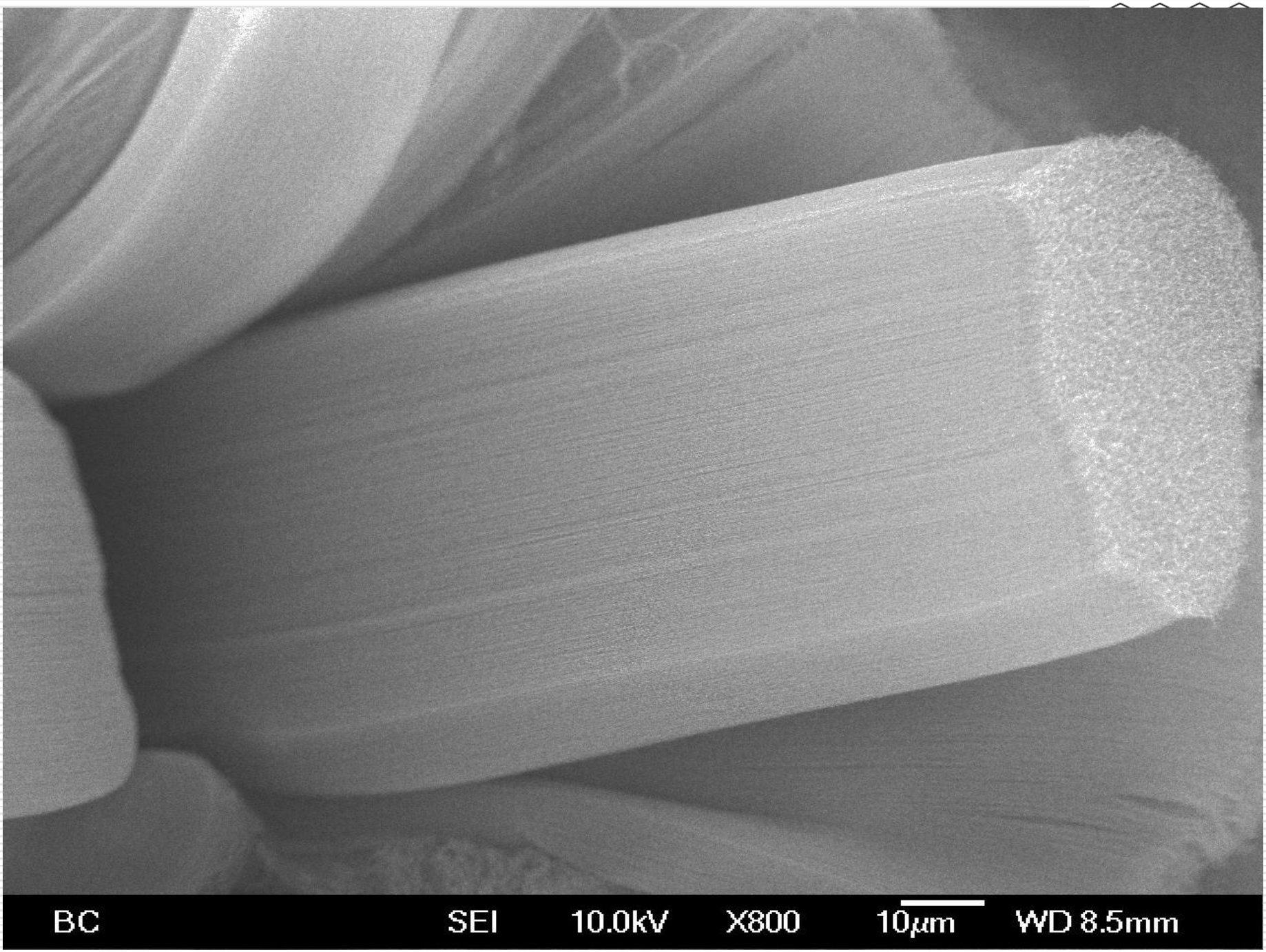
3.3 Abrasion- after treatment

4. Scaleup Effort

- Scale-up just beginning:
- Concerns
  - Effects of flow (turbulence v. laminar)
  - Gas scaling effects
  - Chamber material (stainless v. quartz)
  - Roll to Roll mechanics

5. Conclusion

- Highly black coatings can be achieved on a number of substrates, materials, and complex parts.
- Adhesion-modifying treatments make a significant difference in the scratch resistance of the films.
- We are building our correlative understanding between growth parameters and the optical response.
- Next steps
  - Scale-up
  - Pre-qualification tests
    - Vibration
    - Outgassing
    - Cleaning
- Questions?


BC
SEI
10.0kV
X800
10μm
WD 8.5mm