Vertically Aligned Carbon Nanotubes Embedded in Ceramic Matrices for Hot Electrode Applications

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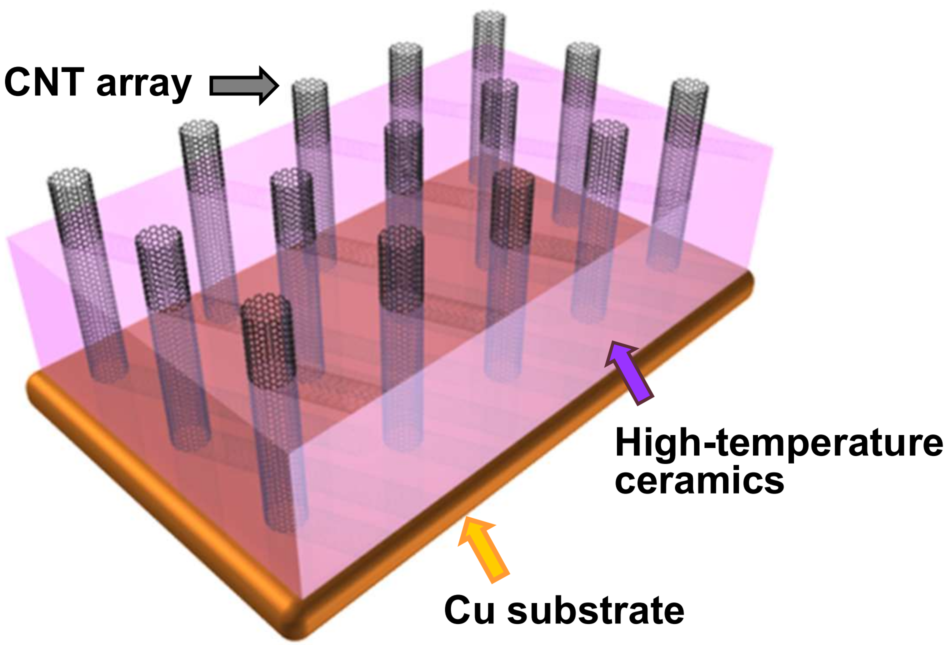
Project Title

Project Title:	Vertically Aligned Carbon Nanotubes Embedded in Ceramic Matrices for Hot Electrode Applications
Grant Number:	DE-FE0023061
Project Investigator:	Yongfeng Lu
Recipient Organization:	University of Nebraska - Lincoln
Project Period:	10/01/2014 – 09/30/2018

Goal and Objectives

Primary goal: Develop carbon nanotubes-ceramic (CNT-C) composite structures in which vertically aligned CNTs (VA-CNTs) are embedded in ceramic matrices for hot electrode applications in magnetohydrodynamics (MHD) power systems.



CNTs: T_m > 1726 ˚C
Oxidation resistance ~ 700 ˚C
$\sigma = 10^6 – 10^7$ S/m
K = 200 – 30,000 W/(m·K)

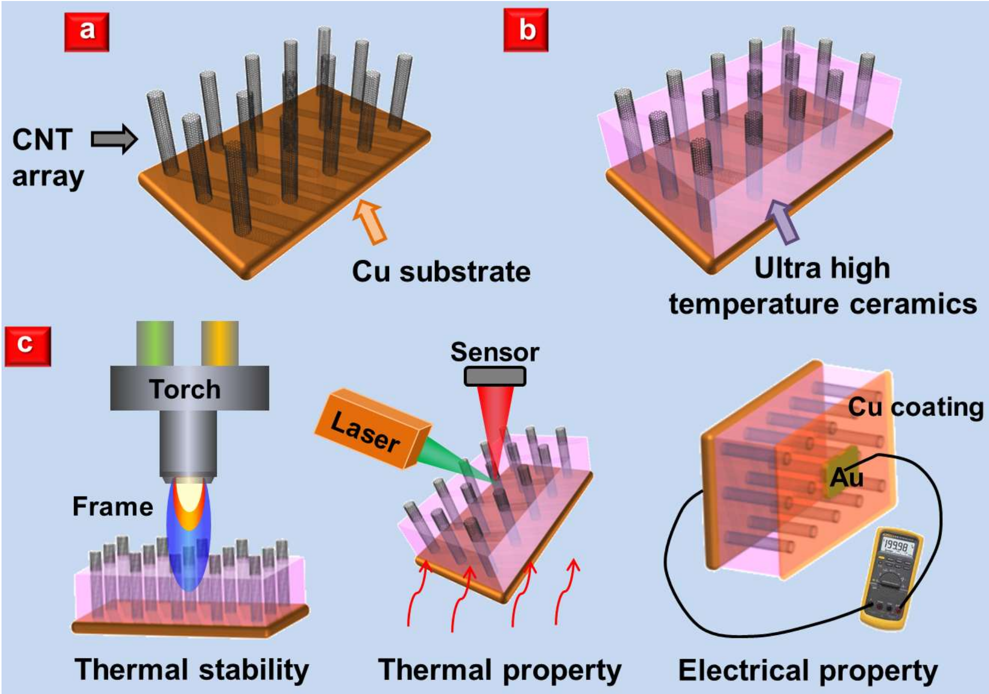
BN: T_m > 2900 ˚C
Oxidation resistance ~ 1500 ˚C
Insulator
K = 600 - 740 W/(m·K)

Cu: T_m = 1084 ˚C
Oxidation resistance < 200 ˚C
$\sigma = 59.6 \times 10^6$ S/m
K = 401 W/(m·K)

Goal and Objectives

Objectives:

1. Super growth of VACNT carpets
2. Fabrication of CNT-BN composite structures
3. Stability and resistance studies of the CNT-BN composite structures
4. Thermionic emissions from the CNT-BN composite structures



Goal and Objectives

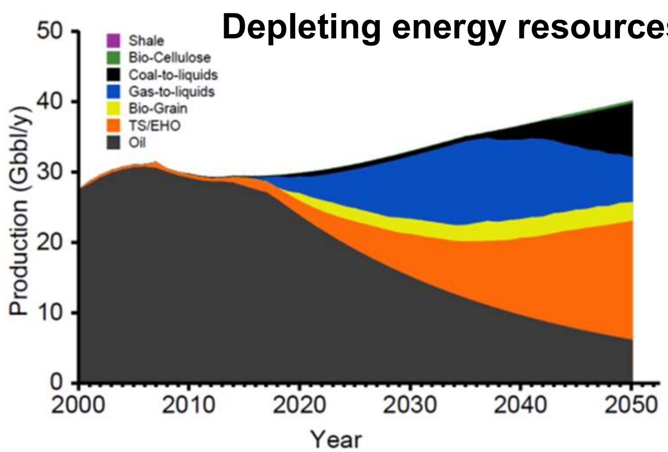
Milestone of the project

Tasks	Milestone	Planned Completion Date
1. Project Management and Planning	Successful completion of the proposed project within the 3-year period.	09/30/2017
2. Super Growth of Vertically Aligned CNT Carpets	Achieve the growth of VA-CNT carpets on Cu substrates with CNT lengths up to 1 cm.	09/30/2015
3. Fabrication of CNT-BN Composite Structures	Achieve uniform and dense growth of BN matrices wrapping VA-CNTs.	03/31/2016
4. Stability and Resistance Studies of the CNT-BN Composite Structures	Determine the stability and resistance of the CNT-BN composite structures	09/30/2016
	Determine the electrical and thermal conductivities of the CNT-BN composite structures.	09/30/2017
5. Thermionic Emissions from the CNT-BN Composite Structures	Determine the thermionic emission performance of the CNT-BN composite structures.	09/30/2018

Outline

1. **Background and Motivations**
2. **Accomplishments**
   1) Improving BN growth using the chemical vapor deposition method
   2) Structural and elemental analysis of grown BN
   3) Fabricating VACNT-BN structure and testing its oxidation stability
   4) Determining the infiltration of BN into VACNT arrays
   5) Tested gas erosion ability of CNT-BN at extreme temperatures
   6) Tested thermal and electrical conductivity of CNT-BN composite structure
3. **Deliverables**
4. **Status and Future Work**
5. **Student Training**

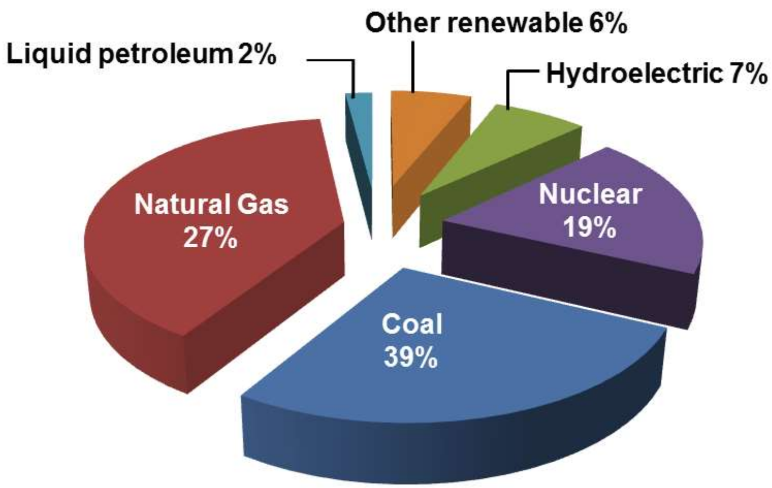
1. Background and Motivations



How are we going to satisfy future energy needs?

1. Background and Motivations

U.S. Electricity Generation (2013)



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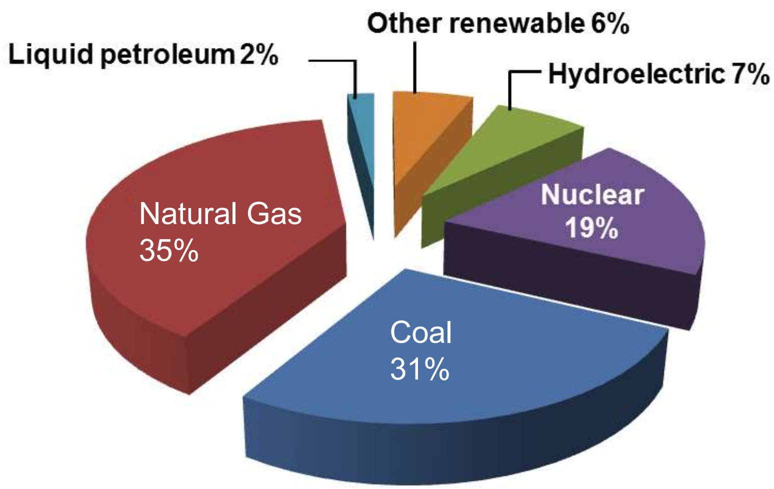
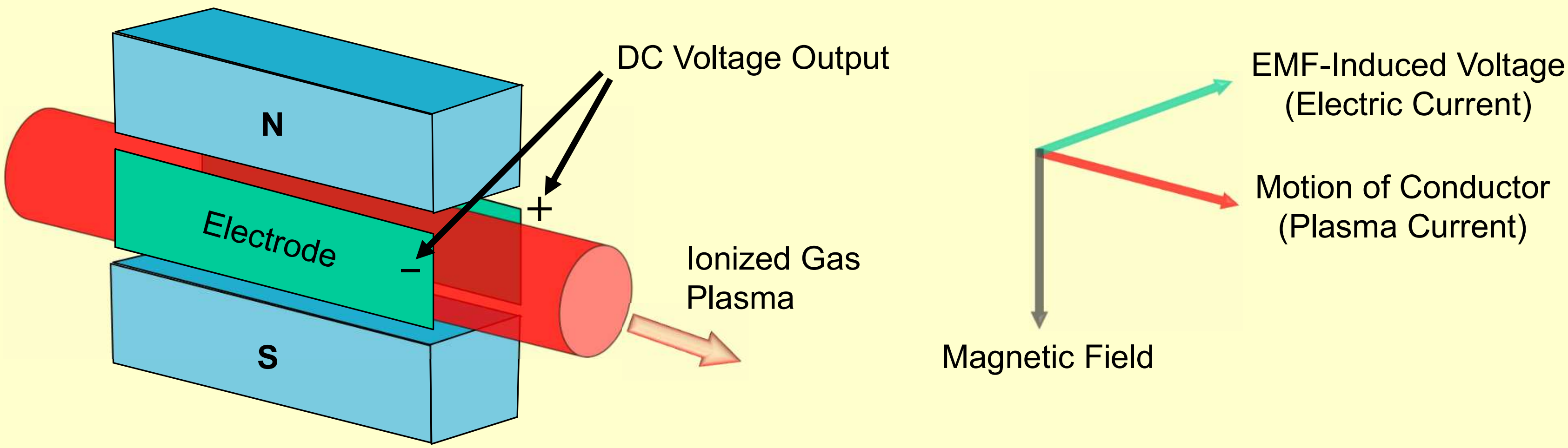


Method	Efficiency (%)	References
Nuclear	33 – 36	Efficiency in Electricity Generation, EURELECTRIC "Preservation of Resources" Working Group's "Upstream" Sub-Group in collaboration with VGB, 2003
Coal	39 – 47	
Natural gas	< 39	
MHD	**~ 65**	**http://www.mpoweruk.com/mhd_generator.htm**

1. Background and Motivations

Principle of Magnetohydrodynamic Power Generation



Advantages:

1) **Only working fluid is circulated without moving mechanical parts.**
2) **The ability to reach full power level almost directly.**
3) **Lower infrastructure cost than conventional generators.**
4) **A very high efficiency (60% for a closed cycle MHD).**

http://en.wikipedia.org/wiki/Magnetohydrodynamic_generator#Generator_efficiency

1. Background and Motivations

Material Challenges for a MHD Generator

Requirement	Remarks
Electrical conductivity (σ)	$\sigma > 1$ S/m, flux ≈ 1 amp/cm^2
Thermal conductivity (k)	High heat flux from the combustion fluids at 2400 K
Thermal stability	Melting point (T_m) above 2400 K
Oxidation resistance	Resistant to an oxygen partial pressure about 10^{-2} atm at 2400 K
Corrosion resistance	Potassium seeds and aluminosilicate slags
Erosion resistance	High velocity hot gases and particulates
Thermionic emission	The anode and cathode should be good acceptor and emitters, respectively.

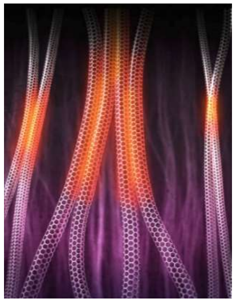
1. Background and Motivations

Property	CNTs
Electrical conductivity (σ)	$10^6 – 10^7$
Thermal conductivity (k)	200 – 3000
Thermal stability	T_m > 1726 ˚C
Oxidation resistance	~ 700 ˚C
Corrosion resistance	Yes
Erosion resistance	Yes
Thermionic emission	Yes

Y. Won, Y. Gao et al., PNAS, 2013, 110(51), 20426-20430.

1000 × current density of copper
5 × electrical conductivity of copper
15 × thermal conductivity of copper
1/7 density of copper and ½ or Al

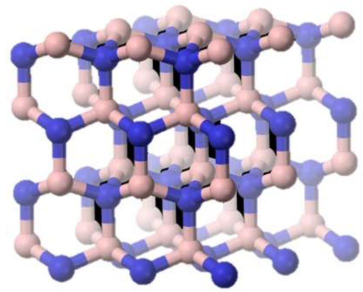
3,500 pounds of Cu and 147,000 pounds of Al in a Boeing 747



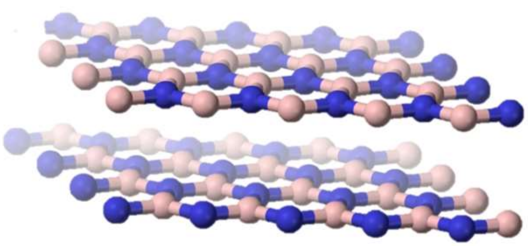
1. Background and Motivations

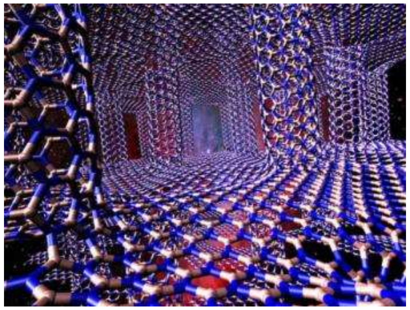
Property	BN
Electrical conductivity (σ)	Insulating
Thermal conductivity (k)	600 - 740
Thermal stability	T_m = 2973
Oxidation resistance	~ 1500 ˚C
Corrosion resistance	Yes
Erosion resistance	Yes
Thermionic emission	N.A.

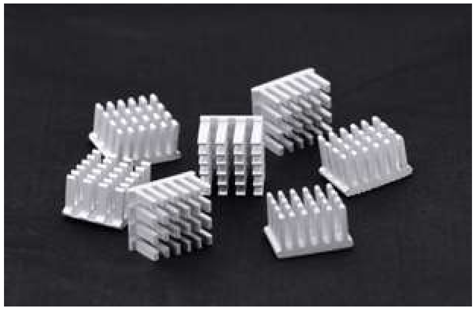
C-BN



h-BN

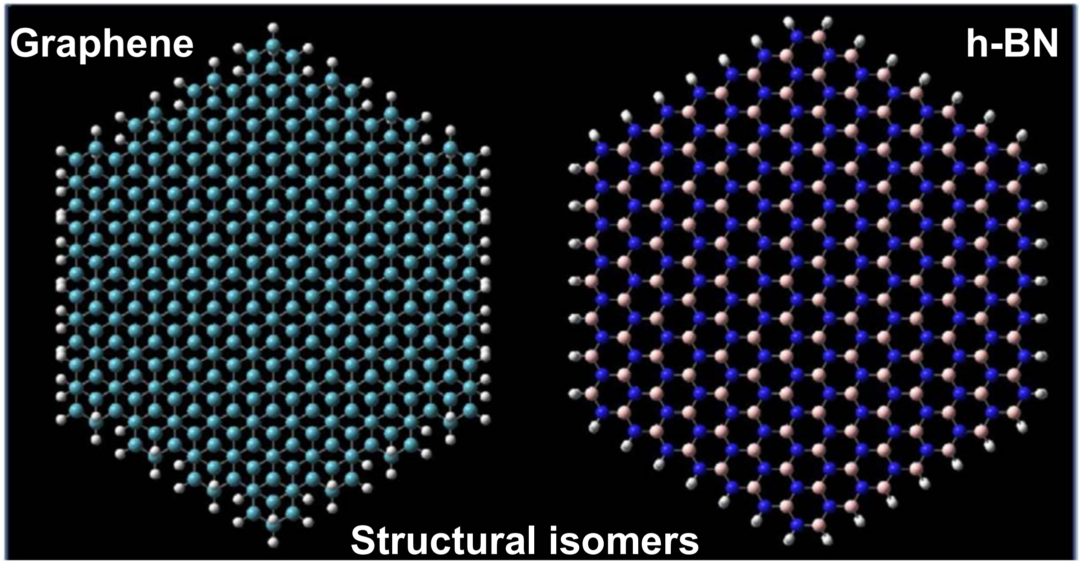






http://www.graphene-info.com/3d-white-graphene-could-cool-electronics

1. Background and Motivations

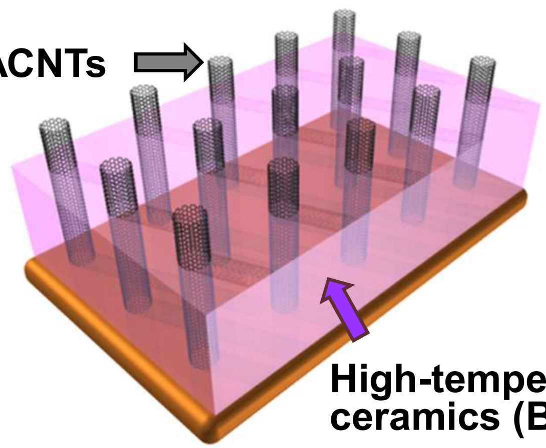


	Graphene	h-BN
Space group	P_{63}	P_{63}
Lattice constant, *a* (Å)	2.46	2.50
Lattice constant, *c* (Å)	6.70	6.66
Thermal expansion coefficient (10^{-6} ˚C^{-1})	-1.5 ‖, 25 ⊥	-2.7 ‖, 38 ⊥

Within the basal planes (‖) and perpendicular to them (⊥)

1. Background and Motivations

Proposed Solution: CNT-BN Composite Structures



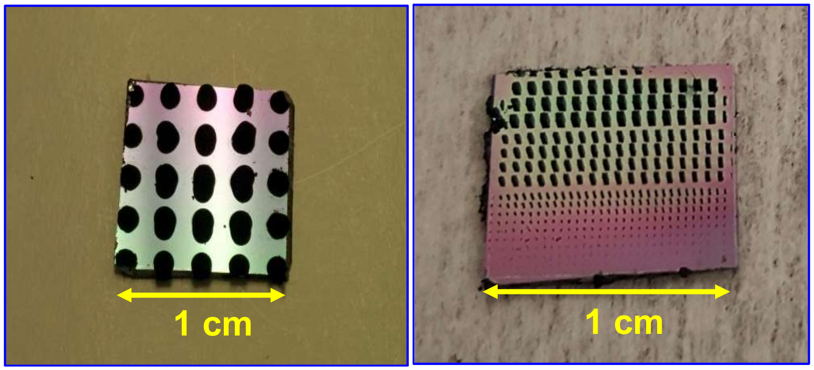
VACNTs: **Electrical and thermal conductive channels.**

BN: **Protective layer shielding CNTs from erosive and corrosive environments.**

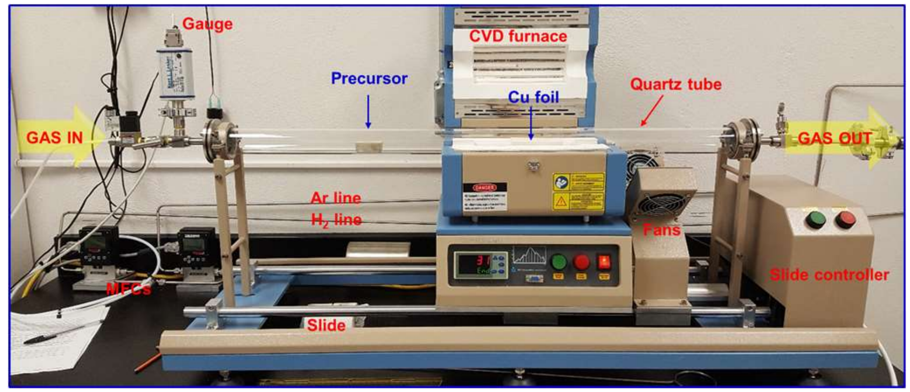
Property	BN	CNTs
Melting point (˚C / K)	2973 / 3246	> 1726 / 2000
Chemical inertness	Inert to acids but soluble in alkaline molten salts and nitrides	Yes
Oxidation resistance in open air (˚C / K)	1500 / 1773	< 700 / 973
Electrochemical passiveness	Yes. Used as electrode.	Yes.
Electrical conductivity (S/m)	Insulating	10^6 - 10^7
Thermal conductivity [W/(m·K)]	600 - 740	Up to 3000

A review of previous research

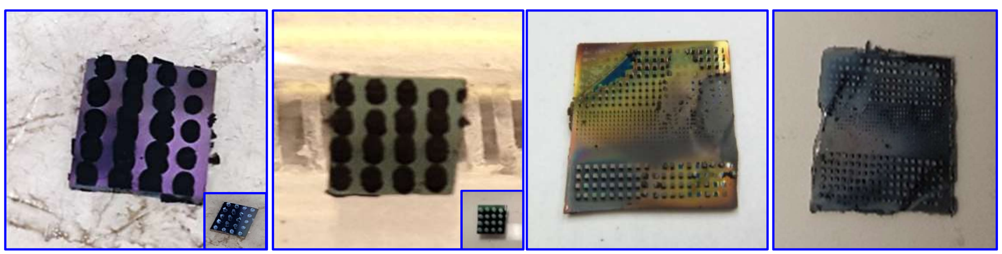
1) Obtained patterned VACNTs



2) Built a CVD system for BN growth



3) Obtained various VACNT-Ceramic (Si, GaN, BN) structure



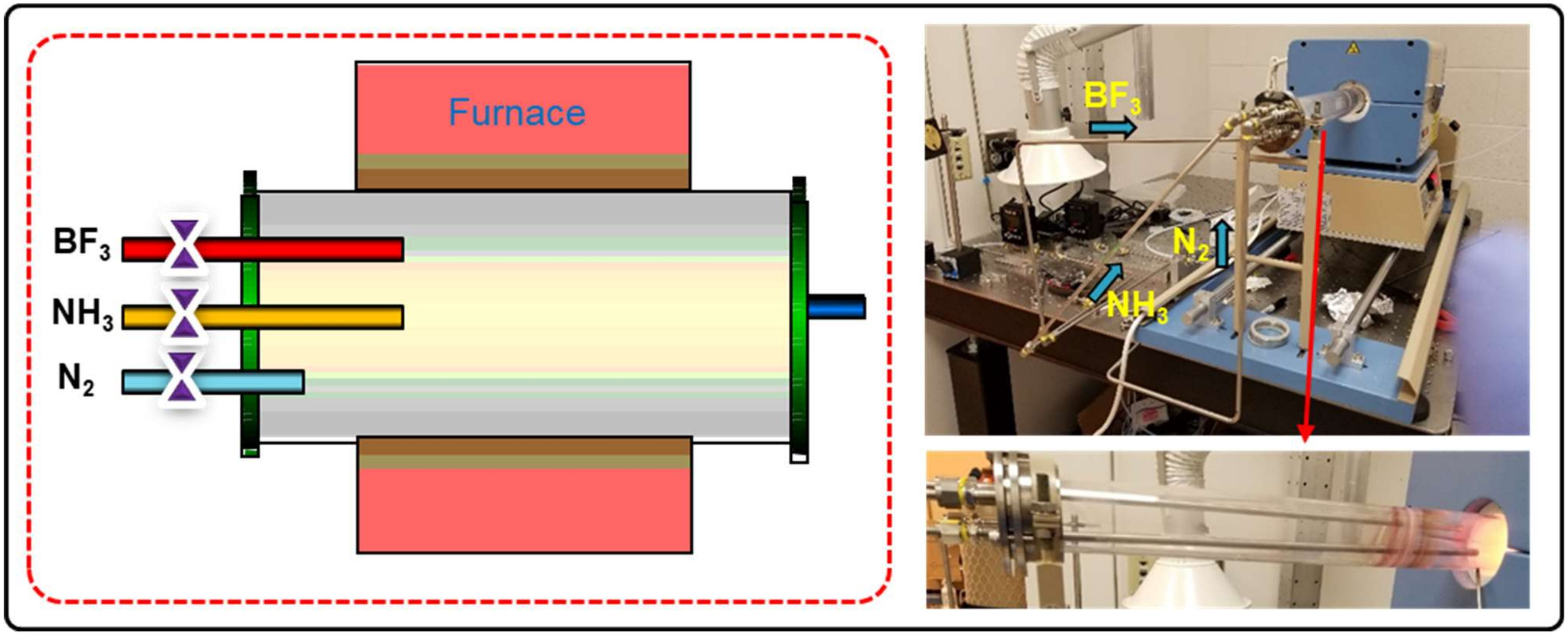
4) Tested anti-oxidation ability of CNT-Ceramic (Si, GaN, BN)

2. Accomplishments

1) **Improving BN growth using the chemical vapor deposition method**
2) Structural and compositional analysis of grown BN
3) Oxidation stability of grown BN
4) Infiltration of BN into VACNT arrays
5) Fabricating VACNT-BN infiltrated structure and testing its oxidation stability
6) Gas erosion resistance of CNT-BN at extreme temperatures
7) Thermal and electrical conductivity of CNT-BN composite structure

2. Accomplishments
- Improving BN using thermal CVD method

Improving thermal CVD system for BN growth



BF_3 and NH_3 are separately fed into the hot zone to prevent undesired reaction at low temperature

2. Accomplishments
- Improving BN using thermal CVD method

Improving thermal CVD system for BN growth

	N_2 Flushing	Heating	Growth	Cooling
T (°C)	RT		1100 ° C	RT
Time (min)	20	60	180	>60
N_2 (Torr)	10			10
NH_3 (sccm)		100	100	
BF_3 (sccm)			75	

Growth Parameter	Value
Precursor	NH_3(100 sccm) BF_3 (75 sccm)
Temperature	1000-1100 °C
Chamber pressure	2-3 Torr
Growth time	30-180 min
Substrate	SiO_2/Si

2. Accomplishments

1) Improving BN growth using the chemical vapor deposition method
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2. Accomplishments

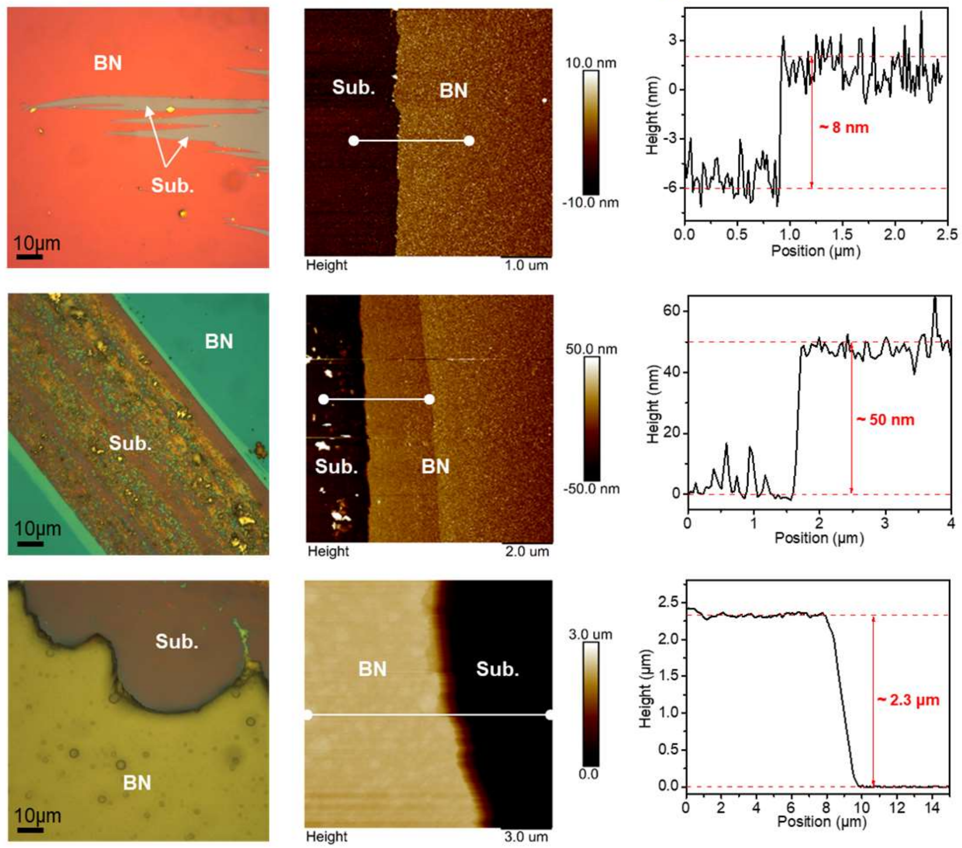
- Structural and compositional analysis of grown BN

Structural analysis: Thin BN film on SiO_2/Si (Optical images & AFM)

10 min

20 min

30 min

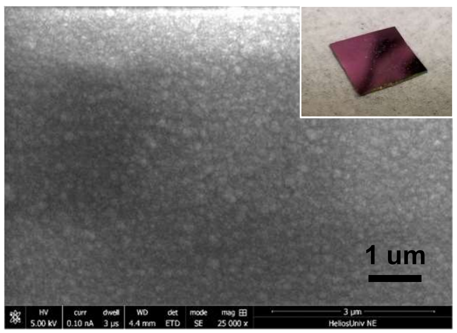


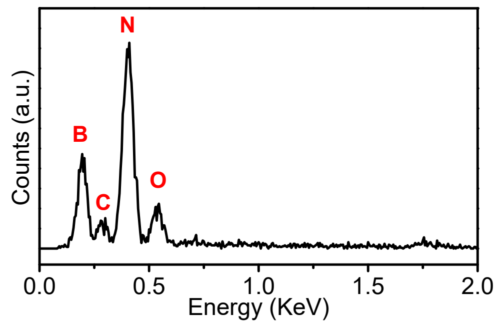
2. Accomplishments
- Structural and compositional analysis of grown BN

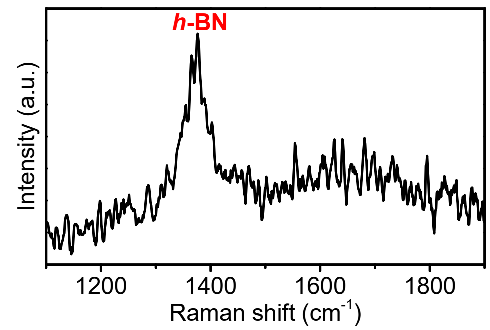
Composition analysis: Thin BN on SiO_2/Si

SEM image | **EDS** | **Raman spectrum**

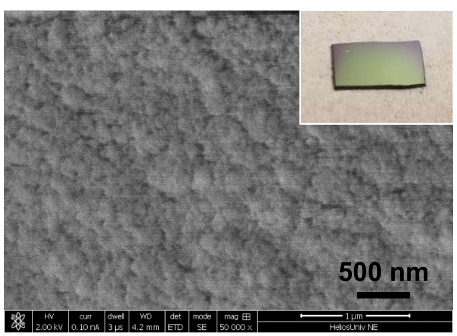
10 min

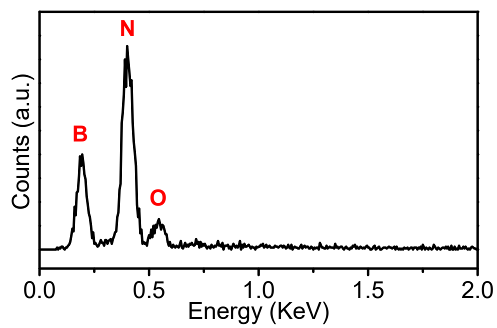


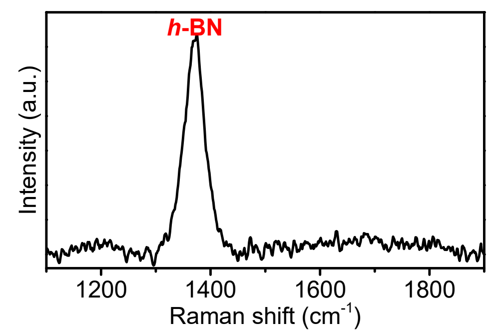




30 min

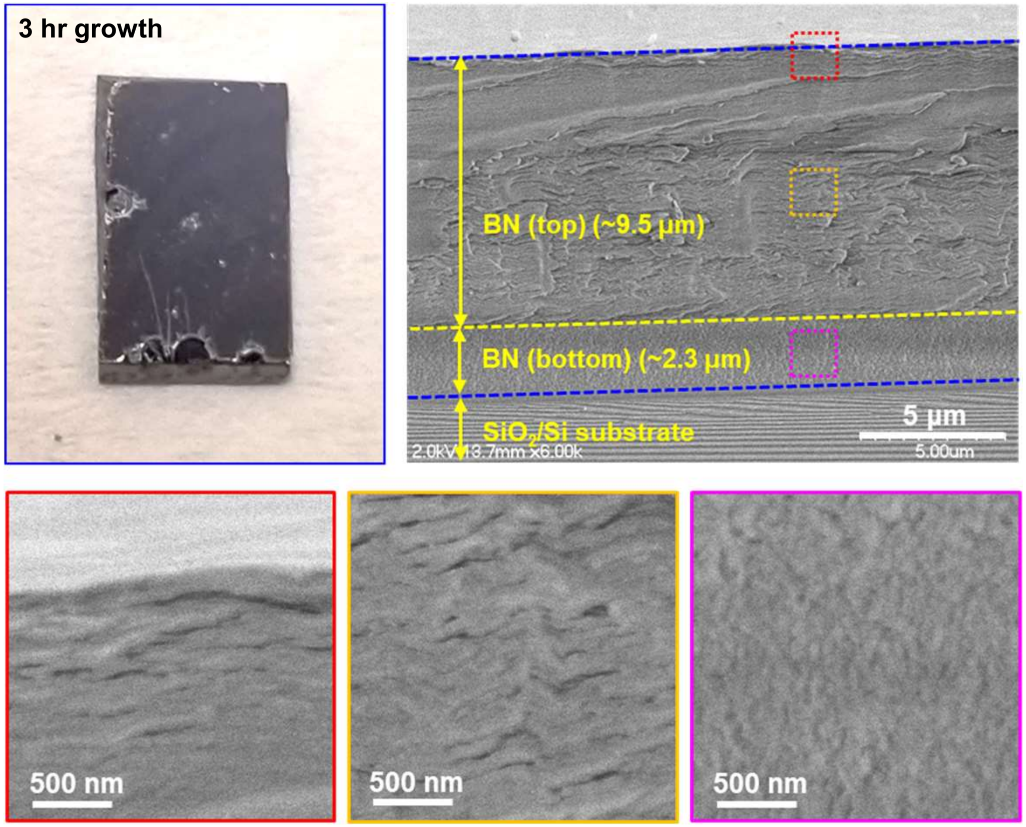






2. Accomplishments
- Structural and compositional analysis of grown BN

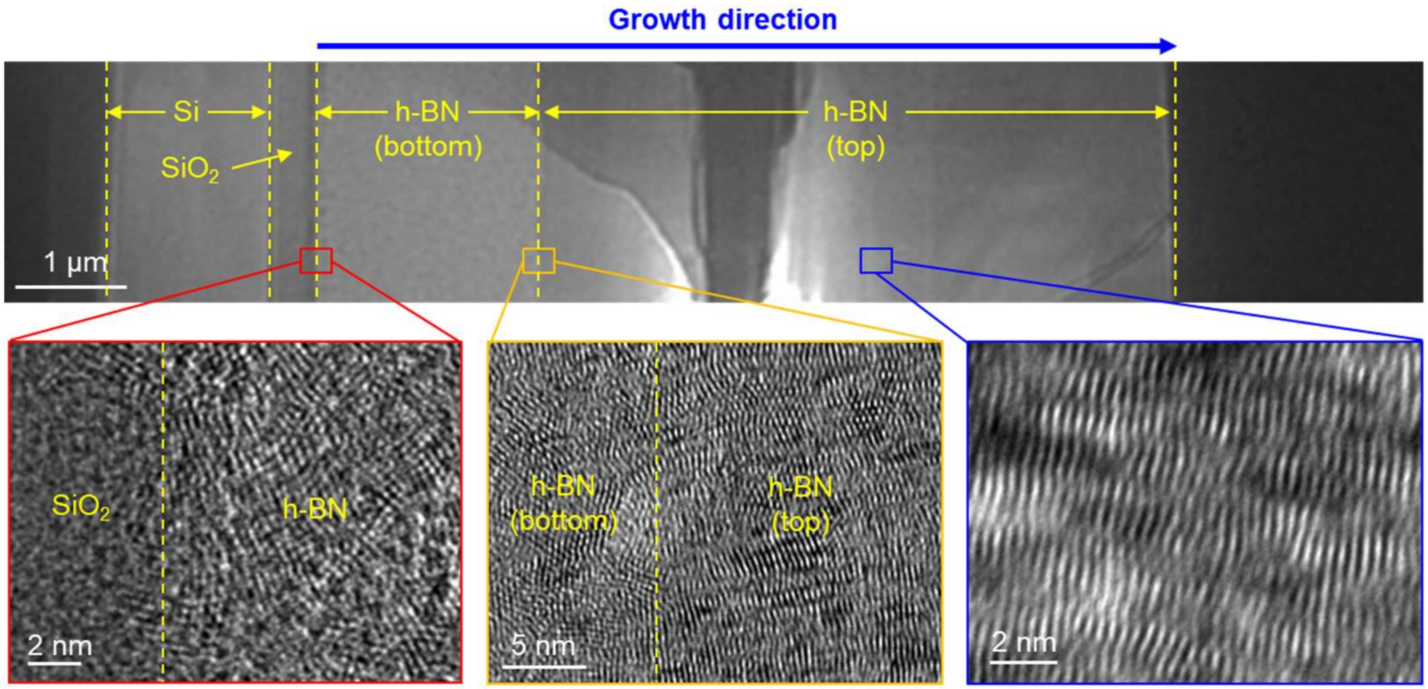
Structural analysis: Thick BN film on SiO_2/Si



2. Accomplishments

- Structural and compositional analysis of grown BN

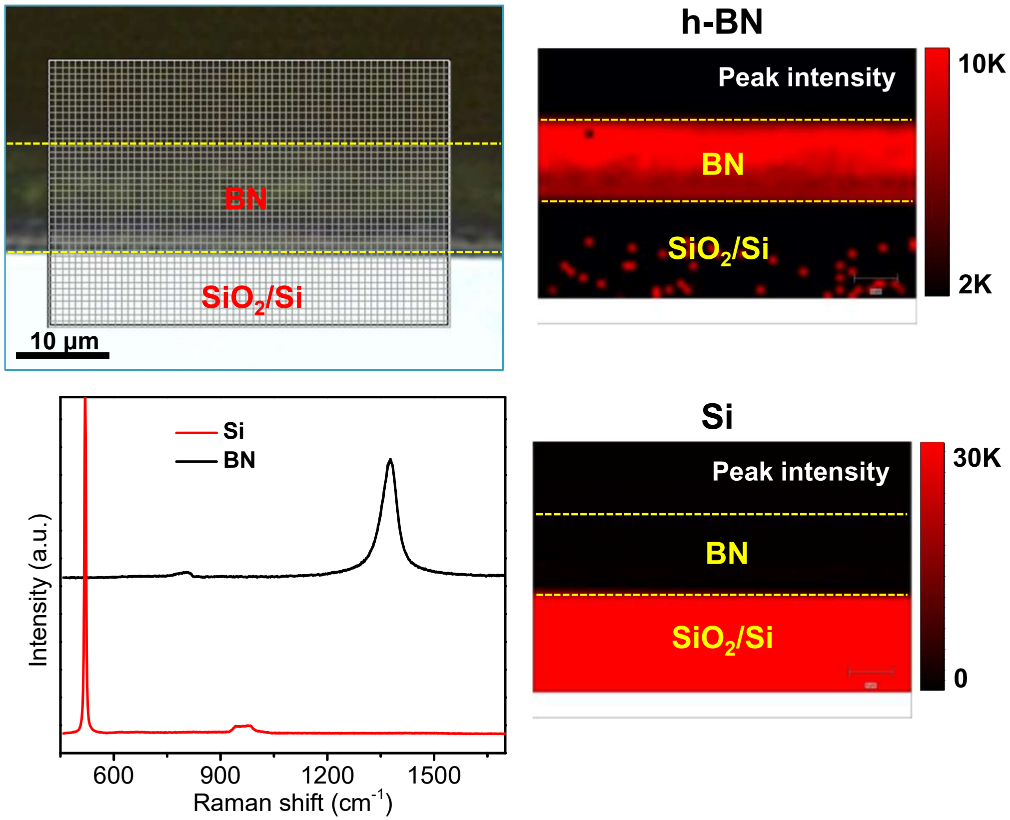
Structural analysis: Thick BN film on SiO_2/Si (HRTEM)



2. Accomplishments

- Structural and compositional analysis of grown BN

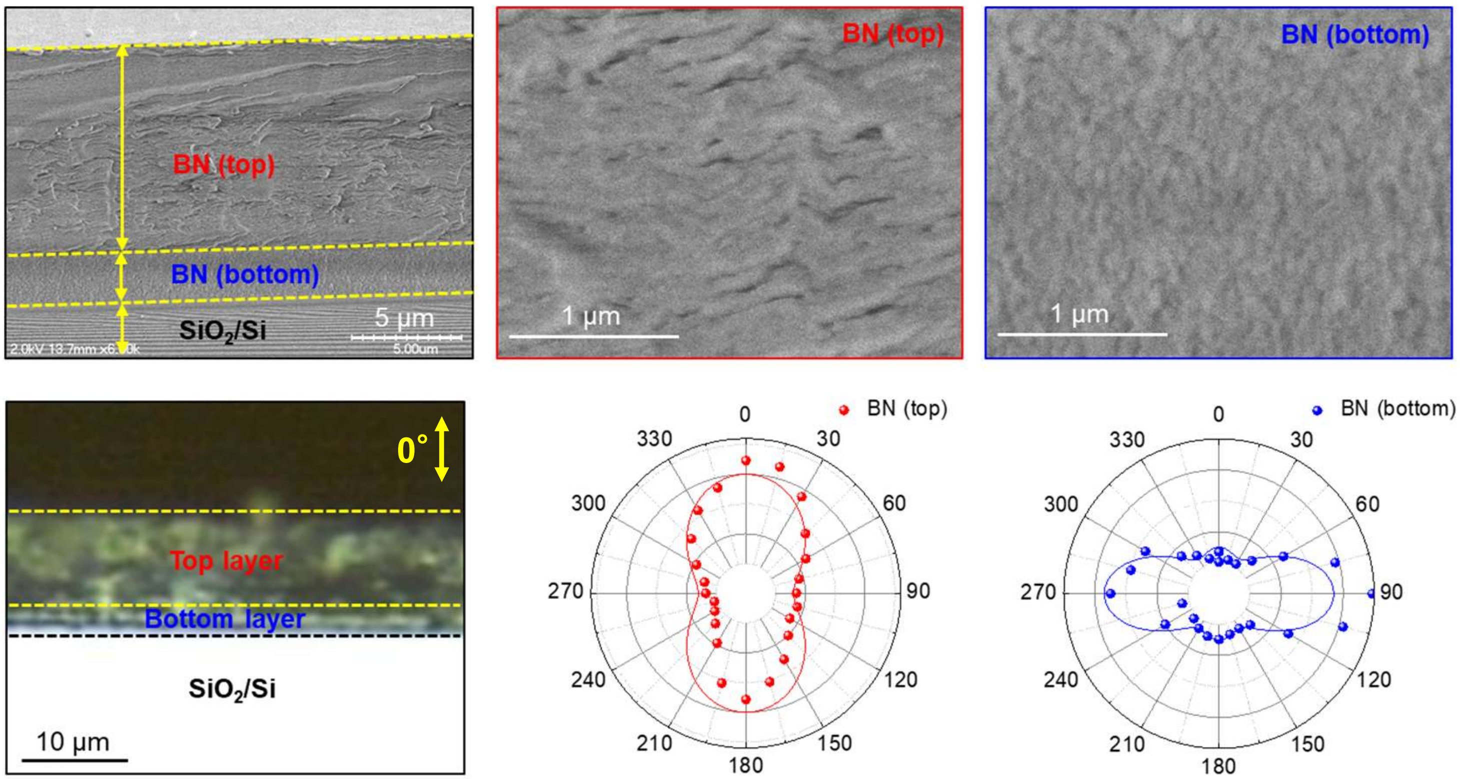
Composition analysis: Thick BN film on SiO_2/Si (Raman mapping)



2. Accomplishments

- Structural and compositional analysis of grown BN

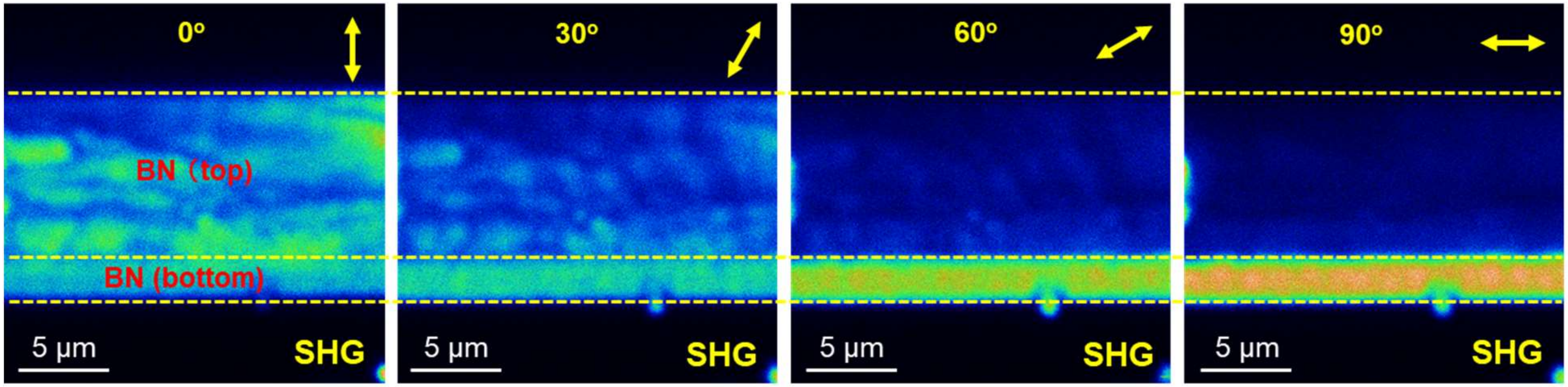
Composition analysis: Thick BN film on SiO_2/Si (Polarized Raman)



2. Accomplishments

- Structural and compositional analysis of grown BN

Composition analysis: Thick BN film on SiO_2/Si (Polarized CARS)

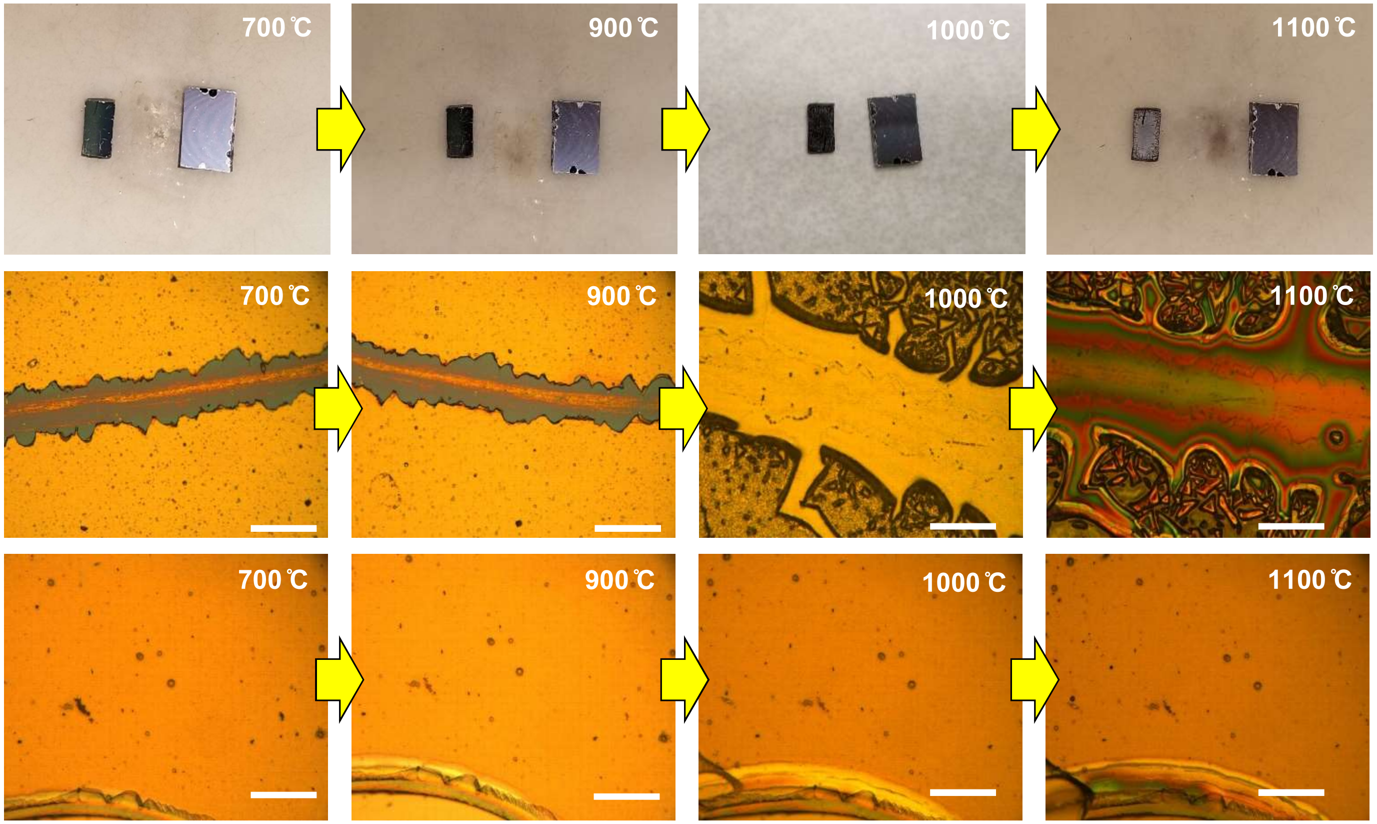


2. Accomplishments

1) Improving BN growth using the chemical vapor deposition method
2) Structural and compositional analysis of grown BN
3) **Oxidation stability of grown BN**
4) Infiltration of BN into VACNT arrays
5) Fabricating VACNT-BN infiltrated structure and testing its oxidation stability
6) Gas erosion resistance of CNT-BN at extreme temperatures
7) Thermal and electrical conductivity of CNT-BN composite structure

2. Accomplishments
- Oxidation stability of grown BN

Oxidation stability of as-grown thick h-BN (in air)

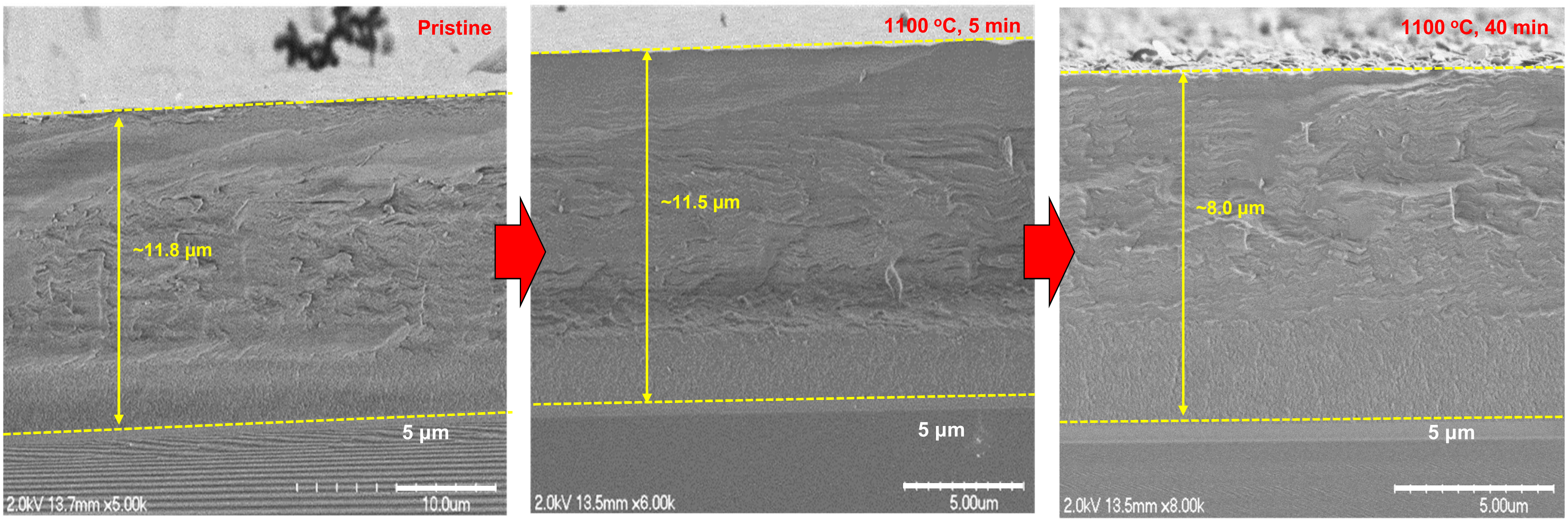


Scale bars: 100 um

2. Accomplishments

- Oxidation stability of grown BN

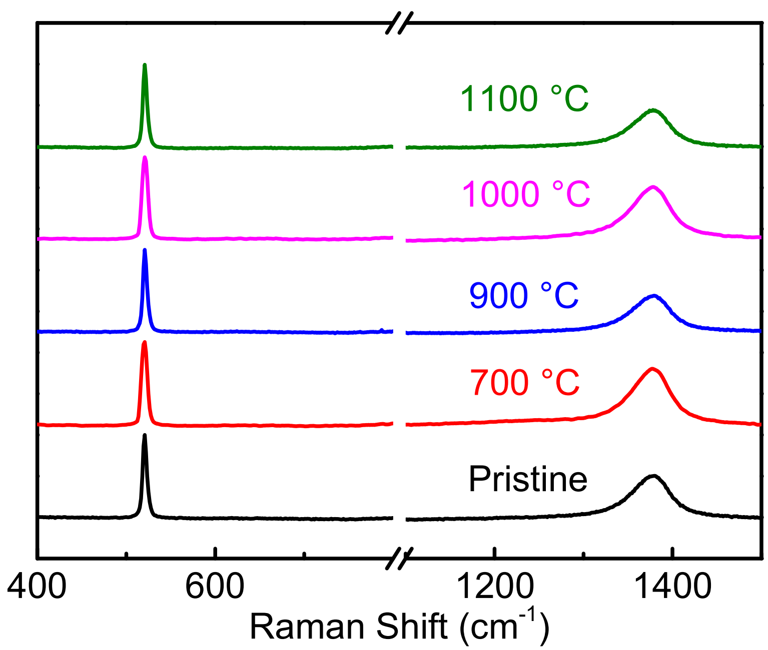
Oxidation stability of as-grown thick h-BN (in air)

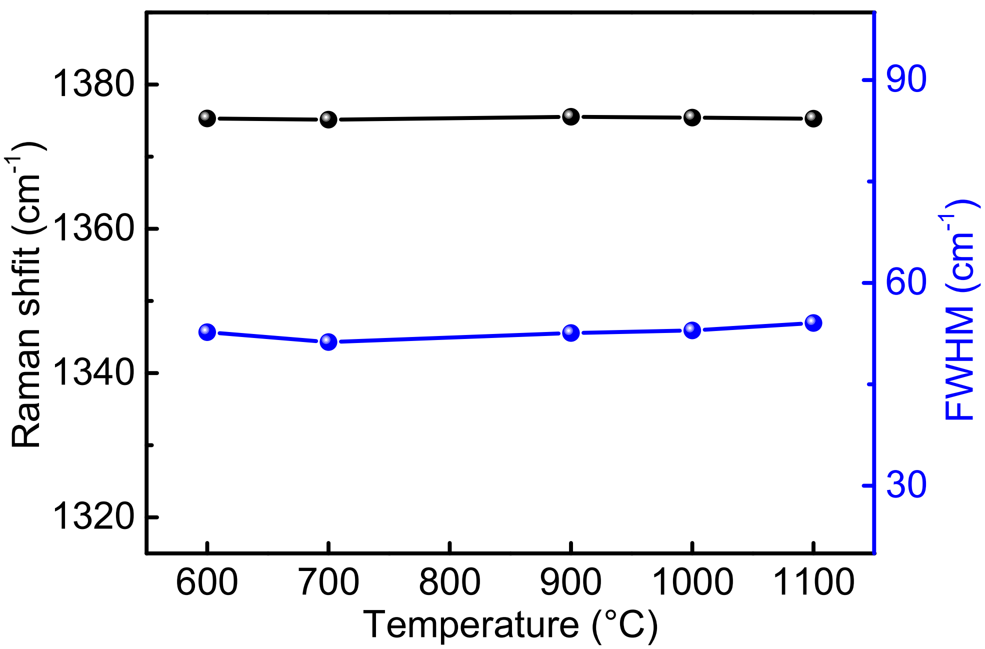


Slight decrease in thickness

2. Accomplishments
- Oxidation stability of grown BN

Oxidation stability of as-grown h-BN (in air)





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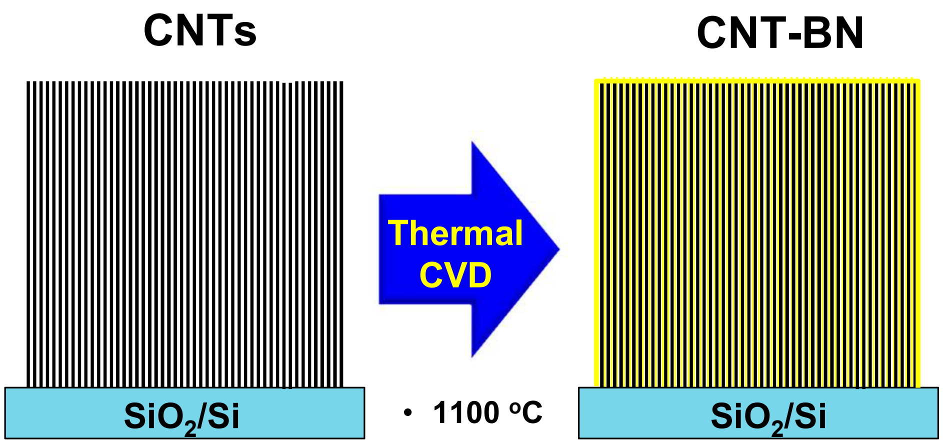
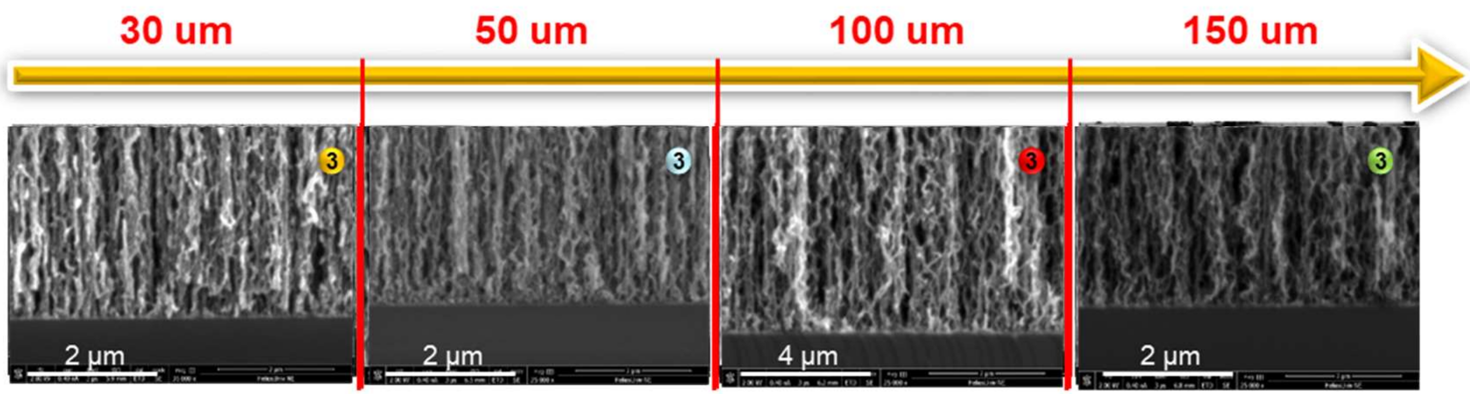
2. Accomplishments
- Infiltration of BN into VACNT array

Infiltration of BN into VACNT array



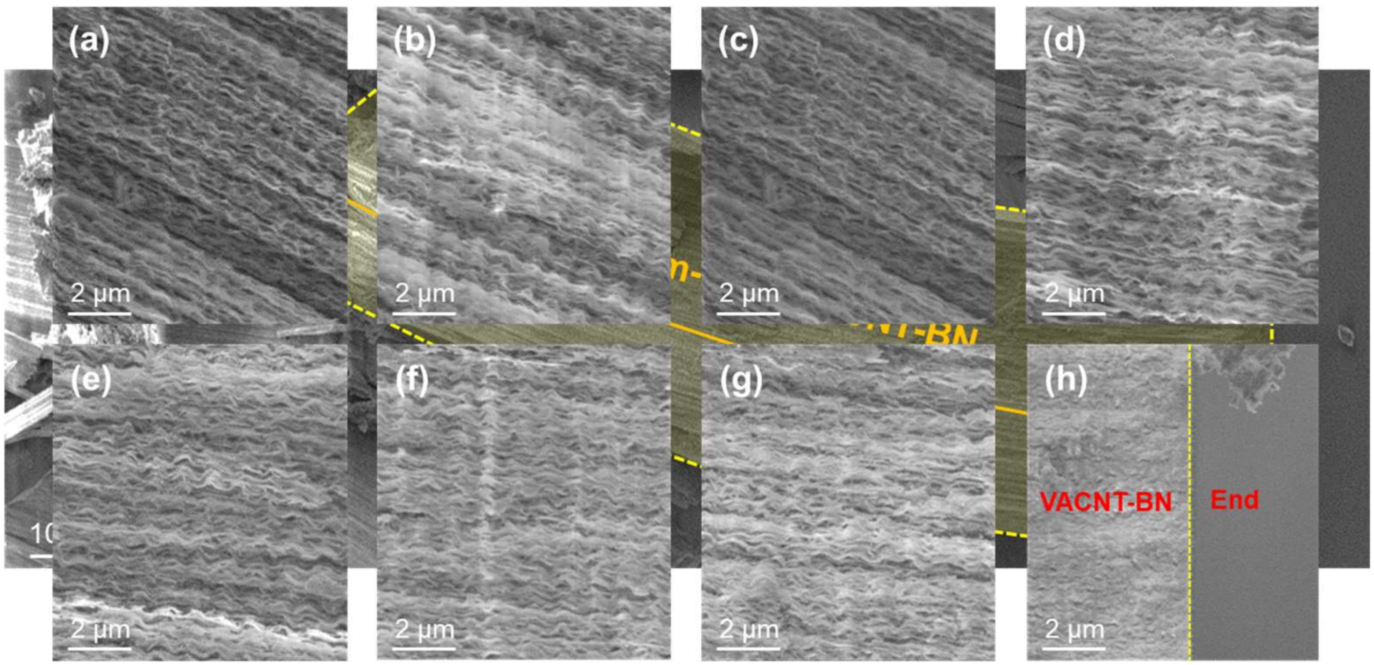
2. Accomplishments
- Infiltration of BN into VACNT array

Infiltration of BN into VACNT arrays with different height



2. Accomplishments
- Infiltration of BN into VACNT array

Infiltration of BN into long VACNT arrays



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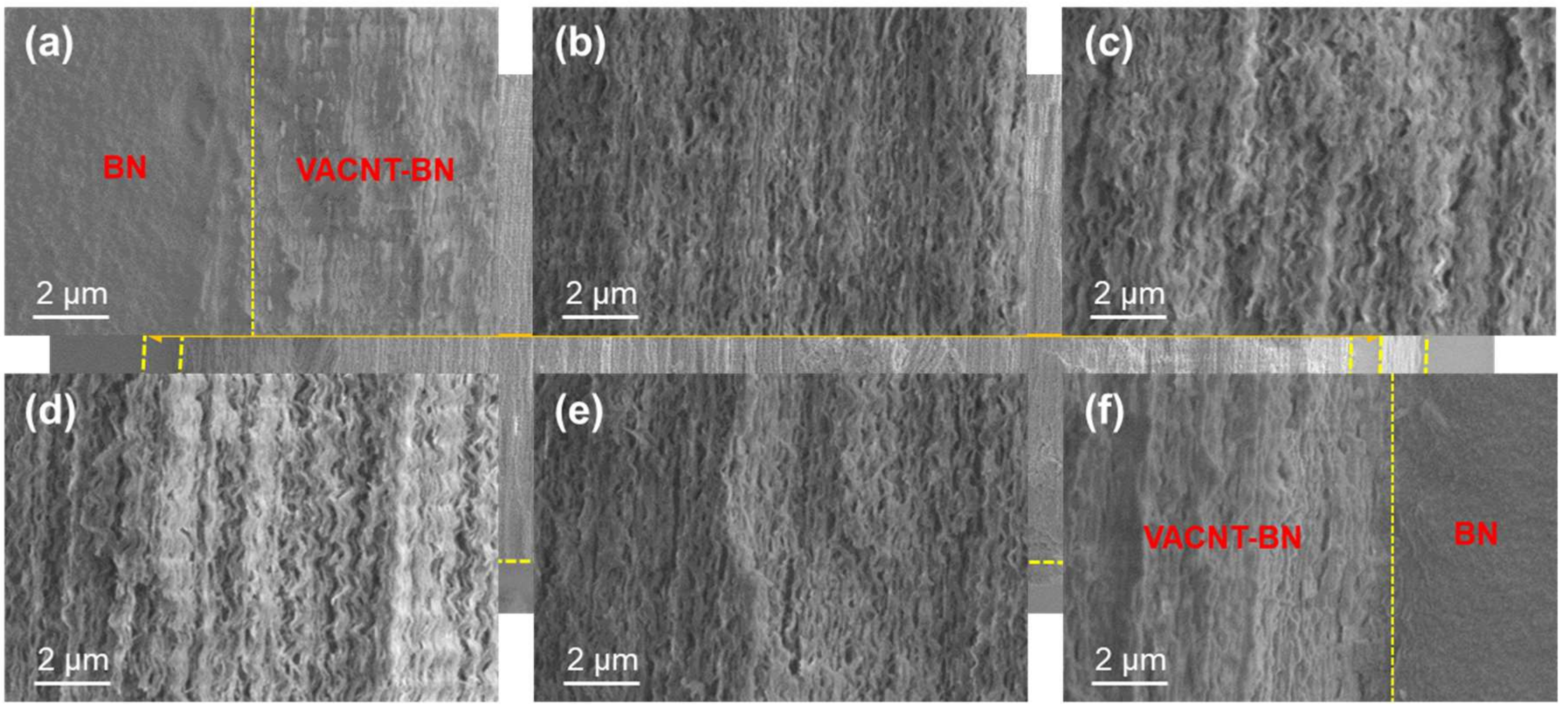
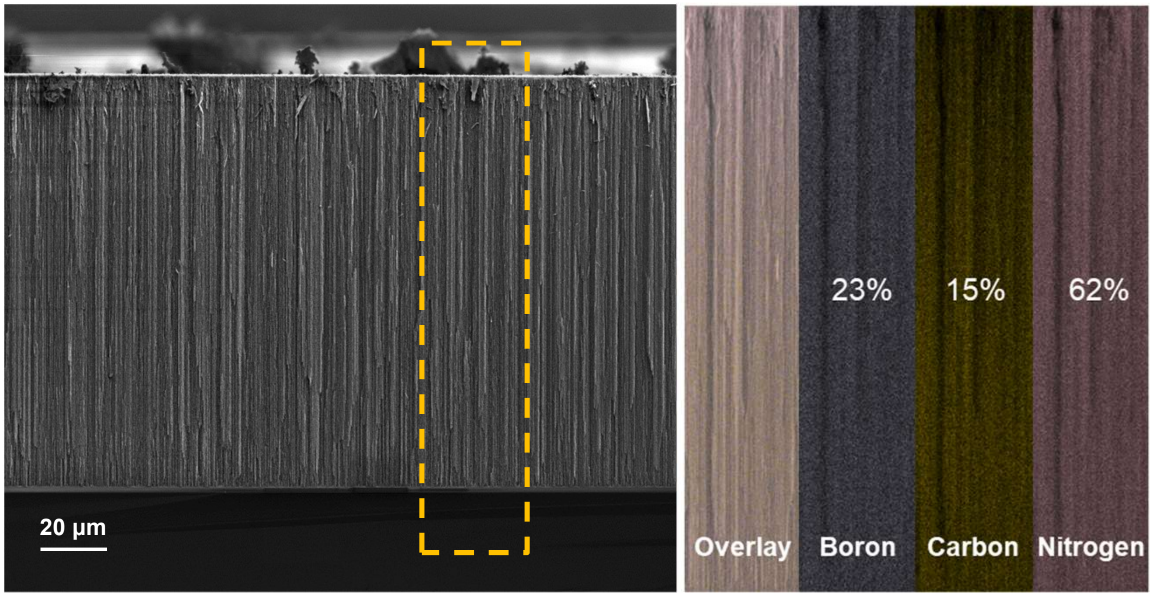
Infiltration of BN into long VACNT arrays



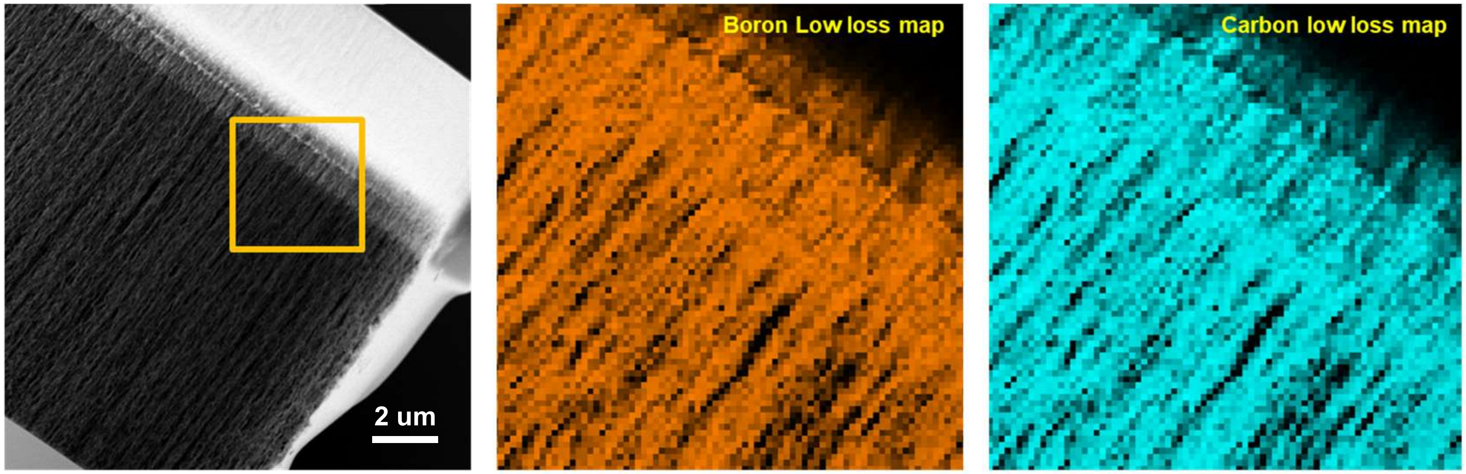
2. Accomplishments
- Infiltration of BN into VACNT array

Infiltration of BN into VACNT arrays (EDS mapping)



2. Accomplishments
- Infiltration of BN into VACNT array

Infiltration of BN into VACNT arrays (EELS mapping)



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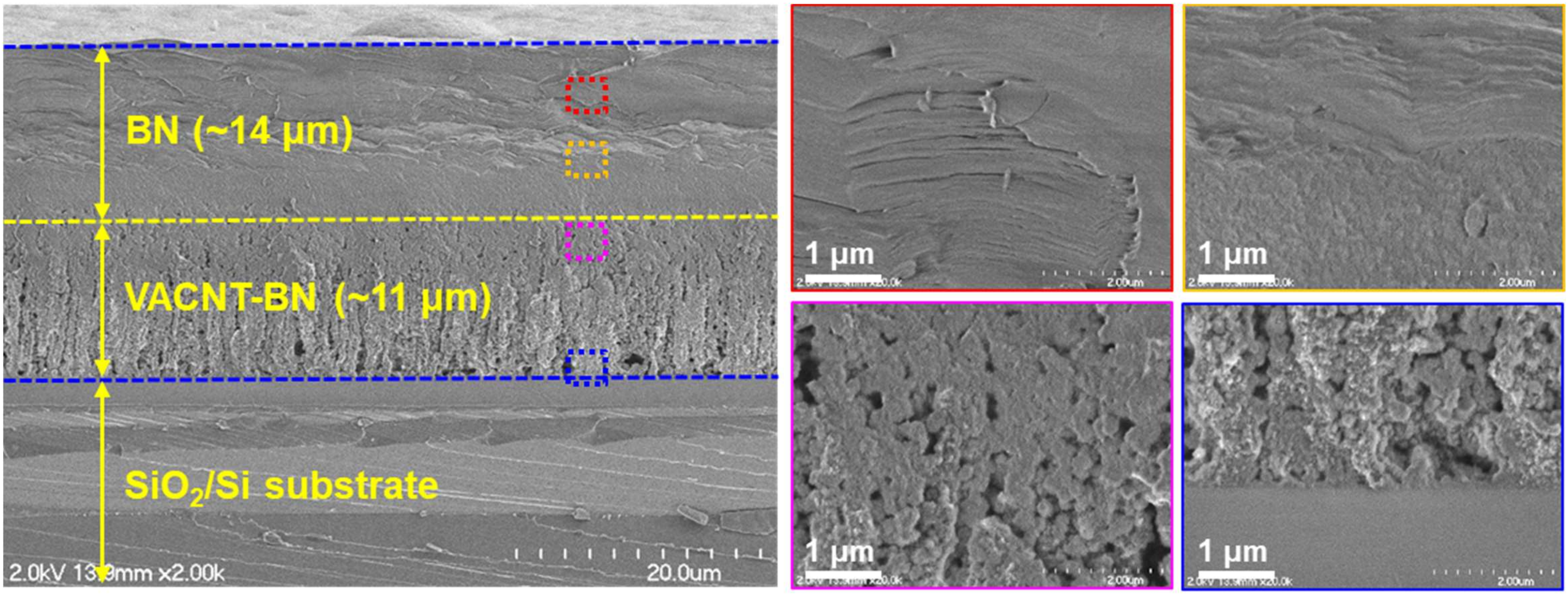
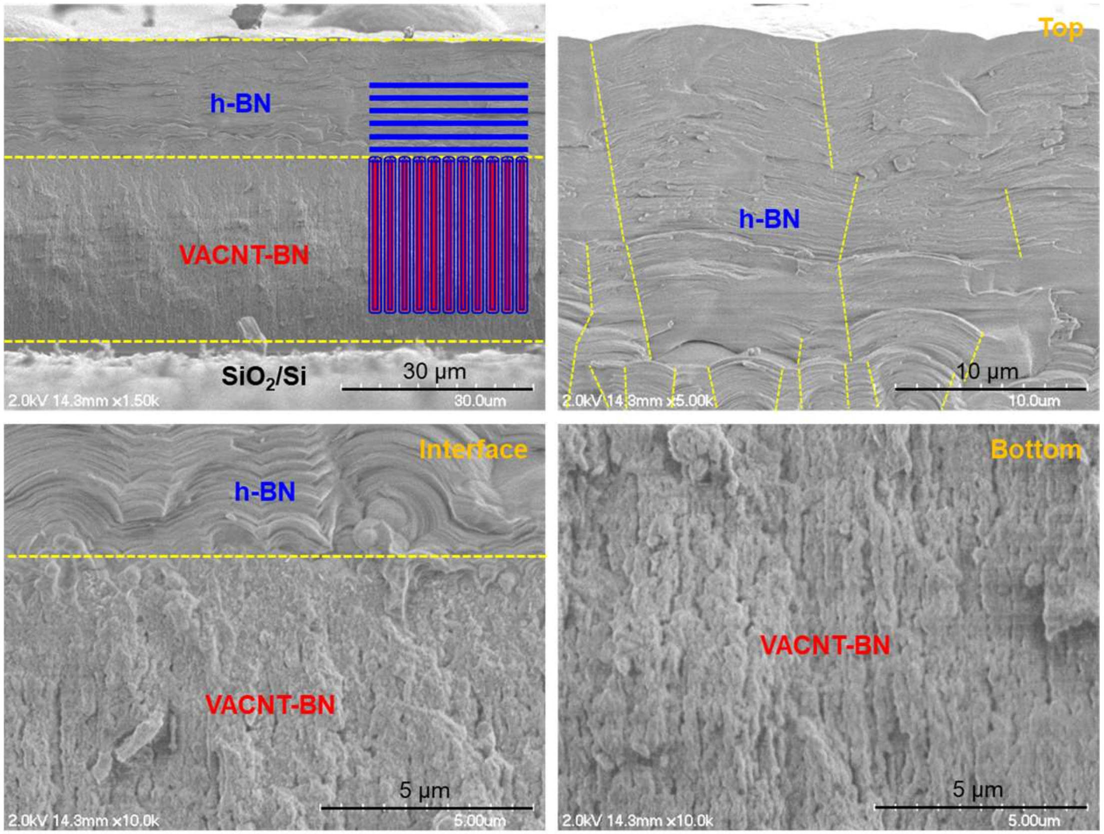
2. Accomplishments
- Fabricating VACNT-BN infiltrated structure

Thin VACNT-BN film (Cross-sectional SEM)



2. Accomplishments
- Fabricating VACNT-BN infiltrated structure

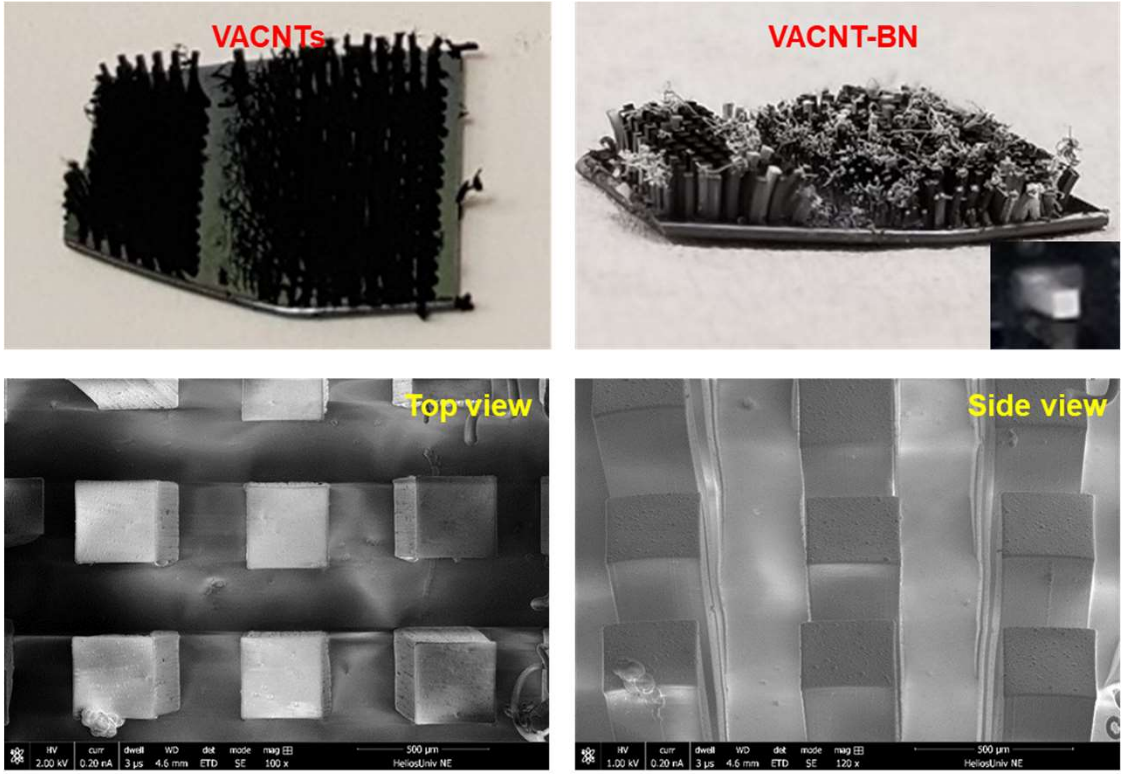
Thick VACNT-BN film (Cross-sectional SEM)



2. Accomplishments

- Fabricating VACNT-BN infiltrated structure

Fabricating milimeter long VACNT-BN (~2mm)

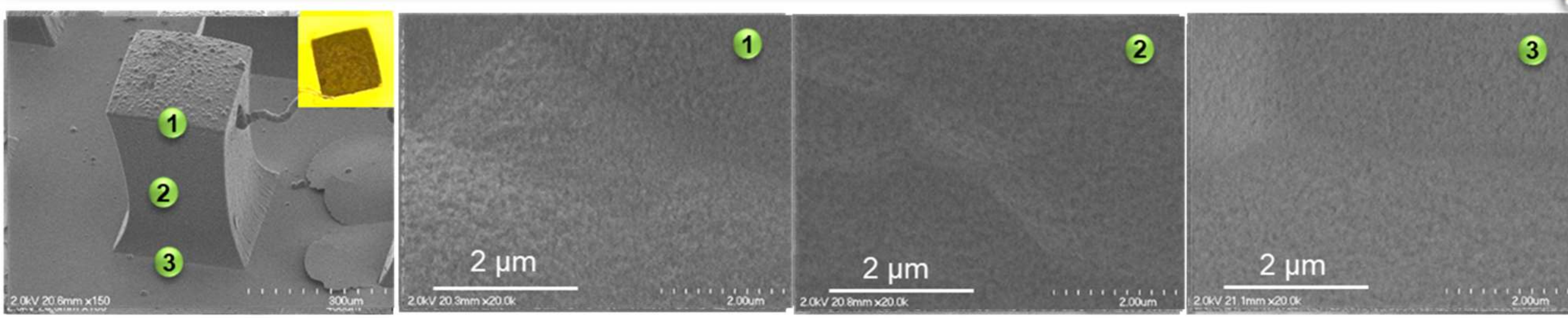


2. Accomplishments

- Fabricating VACNT-BN infiltrated structure

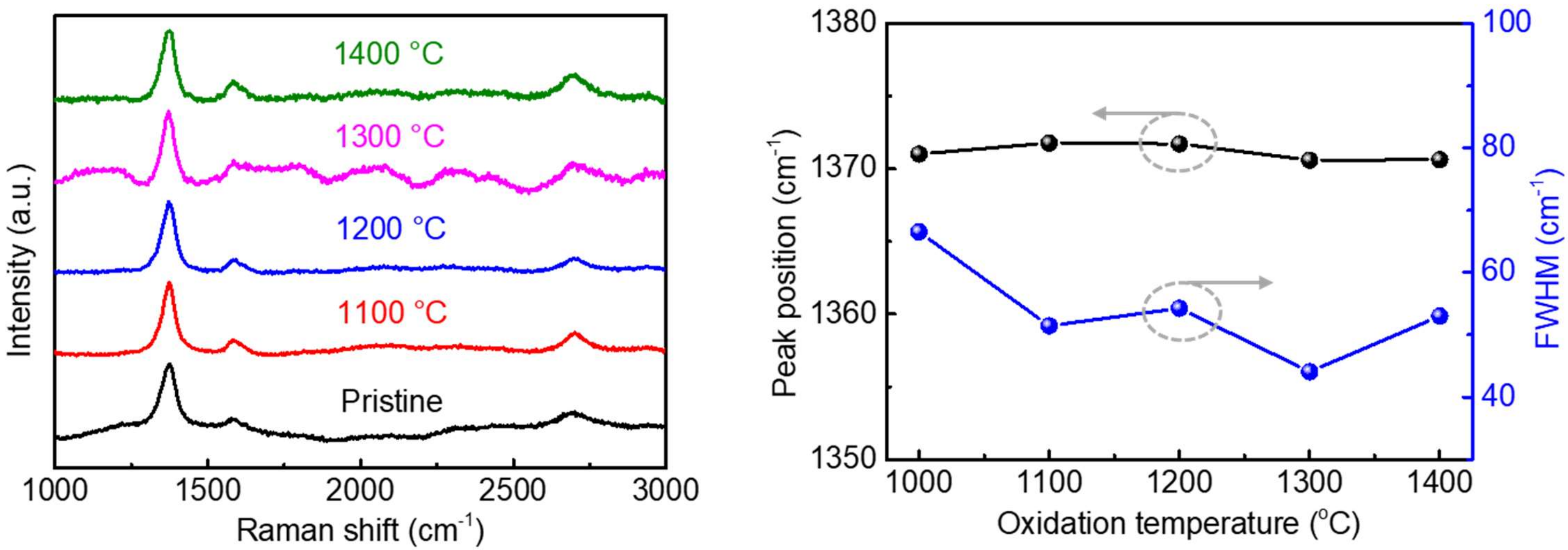
Thermal stability of VACNT-BN (O_2 100 mTorr)

1200 °C



2. Accomplishments
- Fabricating VACNT-BN infiltrated structure

Thermal stability of VACNT-BN (O_2 100 mTorr)



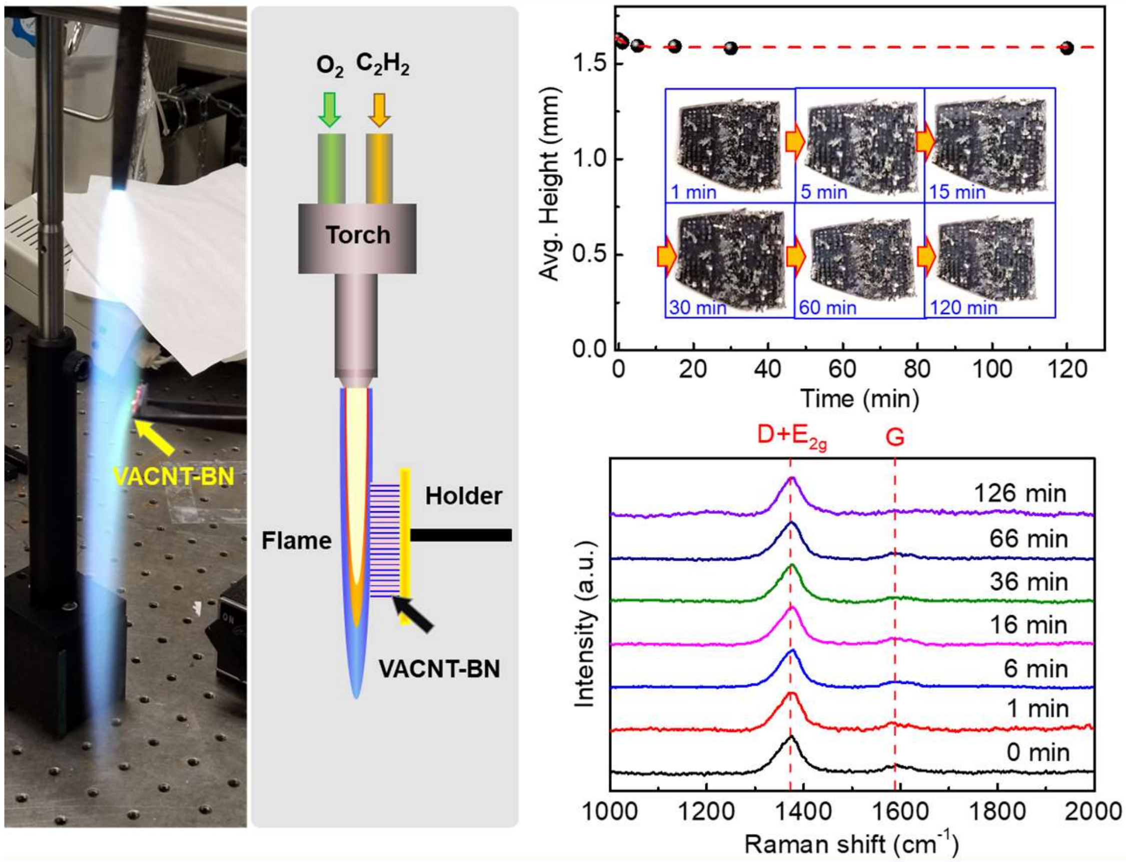
2. Accomplishments

1) Improving BN growth using the chemical vapor deposition method
2) Structural and compositional analysis of grown BN
3) Oxidation stability of grown BN
4) Infiltration of BN into VACNT arrays
5) Fabricating VACNT-BN infiltrated structure and testing its oxidation stability
6) **Gas erosion resistance of CNT-BN at extreme temperatures**
7) Thermal and electrical conductivity of CNT-BN composite structure

2. Accomplishments

- Gas erosion ability of CNT-BN at extreme temperatures

Gas erosion ability of CNT-BN at extreme temperatures



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2. Accomplishments

- Thermal conductivity of VACNT-ceramic infiltrated structure

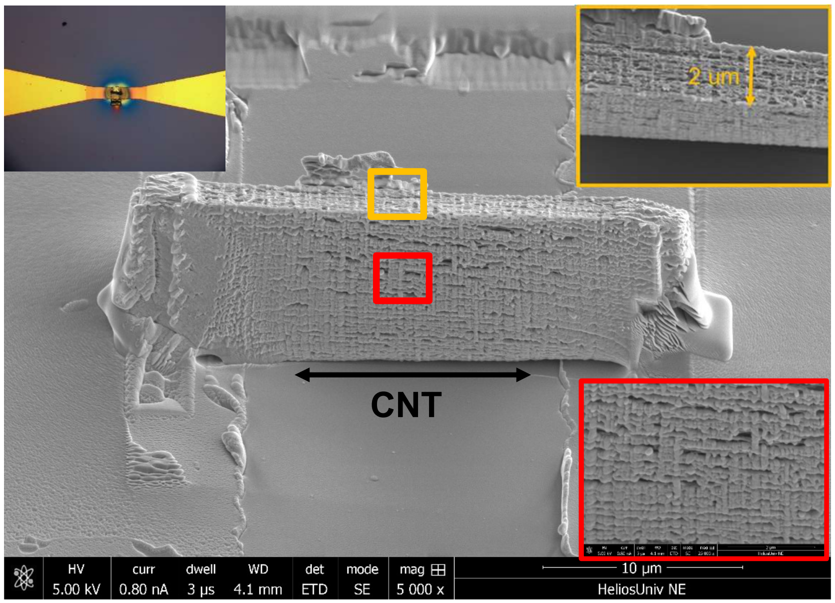
Thermal conductivity the VACNT-BN infiltrated structure

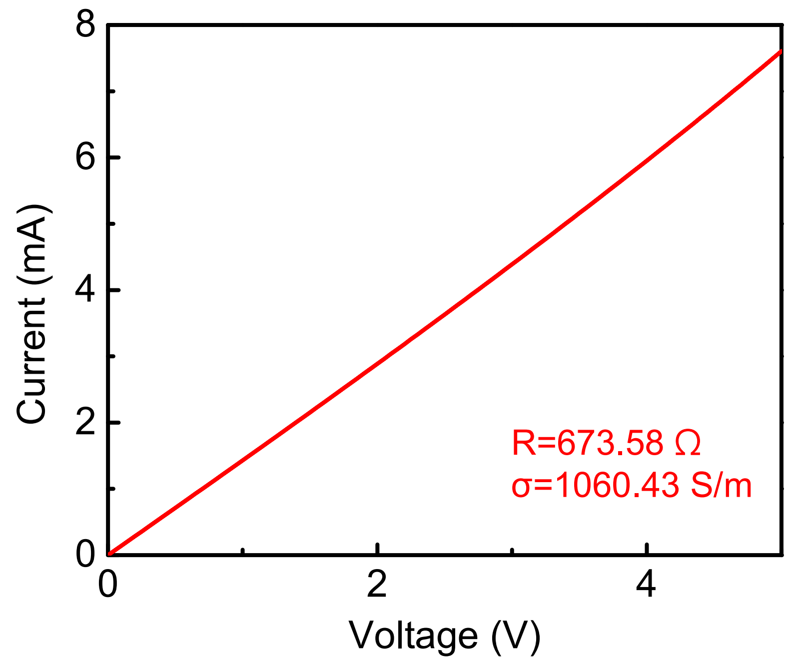
Parameter	h-BN	G-band
χ_p(cm^{-1}/mW)	3.57	4.24
χ_T (cm^{-1}/K)	0.0094	0.014
$\Delta\bar{T}$(K/mW)	379.79	302.86
k[W/(m·K)]	**438.83**	**550.31**

2. Accomplishments

- Electrical conductivity of VACNT-ceramic infiltrated structure

Room-temperature electrical conductivity the VACNT-BN infiltrated structure





- **15 × 2 × 10 um^3 (L W H)**

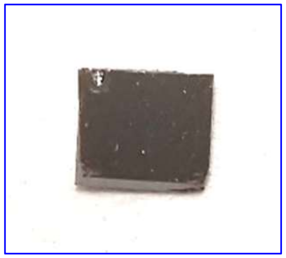
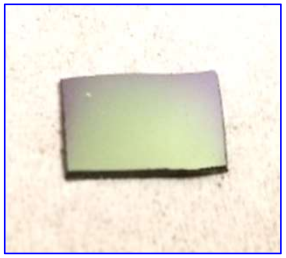
A CNT-BN device is attached to gold electrodes.

2. Accomplishments
- Summary

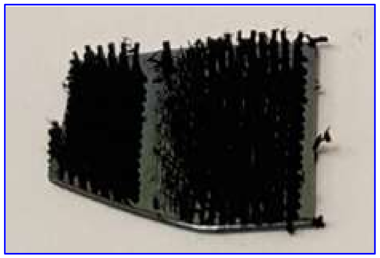
1) Improved BN growth method via thermal CVD
2) Obtained good quality BN films on SiO_2/Si
3) Obtained infiltrated VACNT-BN structures (both films and cubic patterns)
4) Tested VACNT-BN structures with good oxidation stability (1400 ^{o}C)
5) Tested VACNT-BN structures with good thermal conductivity and excellent electrical conductivity
6) Tested VACNT-BN structures with good hot gas erosion resistance (126 min)

3. Deliverables

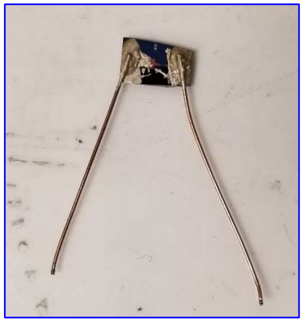
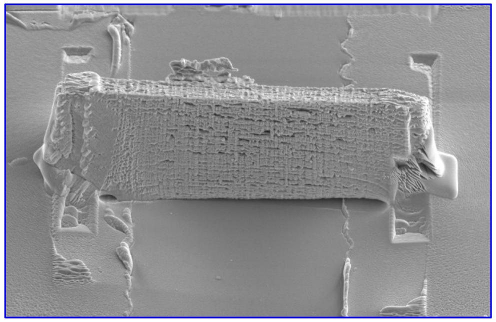
1) BN films


2) VACNT, VACNT-BN infiltrated composite structures



3) VACNT-BN device

4. Future work

- Status of the project

Goals	Milestone	Planned Completion Date	Status
Super Growth of Vertically Aligned Carbon Nanotube (VACNT) Carpets	Achieving the growth of VACNT carpets on Cu substrates with CNT lengths up to 1 cm.	09/30/15	Obtaining millimeter long VA-CNT carpets (up to 4 mm)
Fabrication of CNT-Boron-Nitride (CNT-BN) Composite Structures	Achieving uniform and dense growth of BN matrices wrapping VA-CNTs.	03/31/16	Obtaining CNT-BN infiltrated composite structures
Stability and Resistance Studies of the CNT-BN Composite Structures	Determining the stability and resistance of the CNT-BN composite structures.	09/30/17	Determined the high-temperature stability/oxidation resistance (1400 ^{o}C) of CNT-BN infiltrated composite structures
Thermionic Emissions from the CNT-BN Composite Structures	Determining the electrical and thermal conductivities of the CNT-BN composite structures.	09/30/18	Determined thermal and electrical conductivity; testing thermionic emission of CNT-BN infiltrated composite structures;

4. Future work

- Planned Activities in the Next-Phase

Tasks	Methods	Millstones	Planned Completion Date
Chemical stability of CNT-BN composite structures	Chemical corrosion	Achieving CNT-Si_3N_4 infiltrated composite structures	09/30/18
High temperature electrical conductivity studies of the CNT-BN composite structures	Home-made electrical conductivity measurement system (77 K to 1800 K)	Electrical conductivity: > 1 S/m; thermal conductivity: > 50 W/m·K	09/30/18
Thermionic emission current measurement of the CNT-BN composite structures	Acetylene torch with tungsten electrodes in air.	CNT-BN composite structures can be used as good emitters	09/30/18

5. Student Training

Student	Program	Training
Qiming Zou	PhD student at UNL	Under the support of this project, he was trained with all required experiments and data analysis related to fabricating and characterizing patterned VACNTs, BN, GaN, VACNT-BN, VACNT-Al_2O_3, VACNT-GaN, VACNT-GaN-Si composite structures.

Acknowledgements

We would like to express our heartfelt thankfulness for the Department of Energy and National Energy Technology Laboratory (Grant Number: DE-FE0023061) for the generous financial support.

Thank you!