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**

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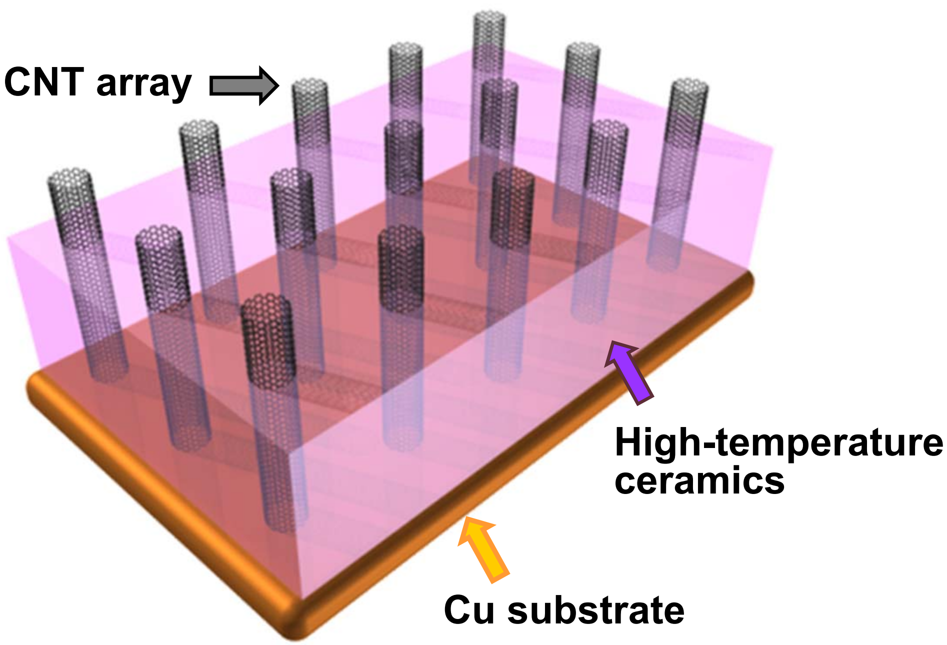
Project Investigator: Yongfeng Lu

Recipient Organization: University of Nebraska - Lincoln

Project Period: 10/01/2014 – 09/30/2017

Goal and Objectives

Primary goal: Develop carbon nanotubes-ceramic 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)

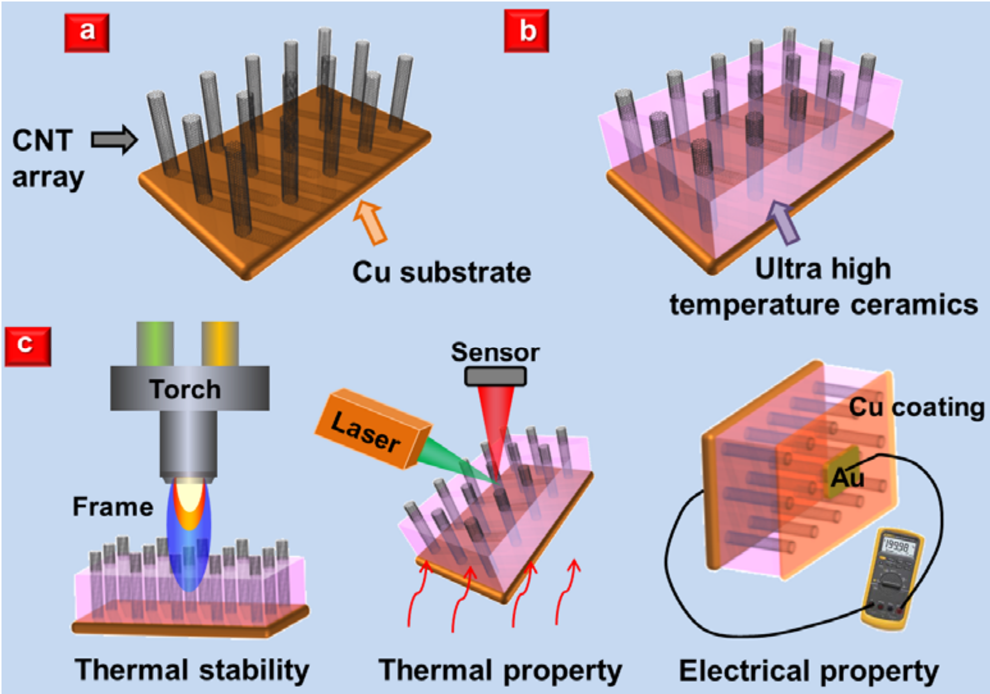
BN: $T_m > 2900$ ˚C
Oxidation resistance ~ 1500 ˚C
Insulator
$K = 600 - 740$ W/(m·K)

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



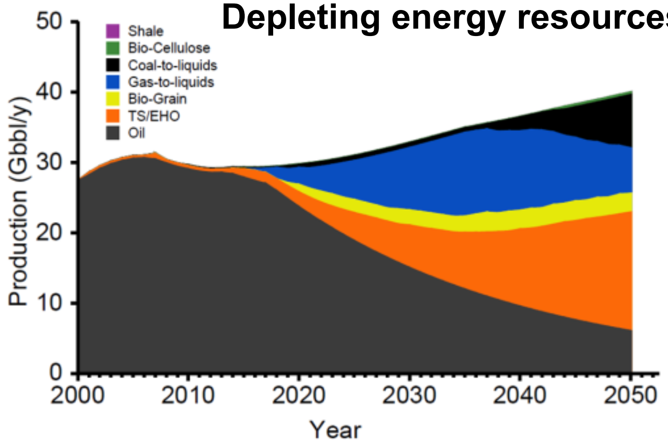
Outline

1. **Background and Motivations**
2. **Accomplishments**
   1) Measuring structure and electrical conductivity of the VACNTs
   2) Growing VACNT patterns
   3) Growing BN using the chemical vapor deposition method
   4) Fabricating VACNT-BN structure and testing its oxidation stability
   5) Fabricating VACNT-Al_2O_3 structure and testing its oxidation stability
   6) Fabricating VACNT-GaN structure and testing its oxidation stability
   7) Fabricating VACNT-GaN-Si structure and testing its oxidation stability
   8) Fabricating VACNT-SiN_x infiltrated composite structure
3. **Deliverables**
4. **Status and Future Work**
5. **Student Training**

1. Background and Motivations

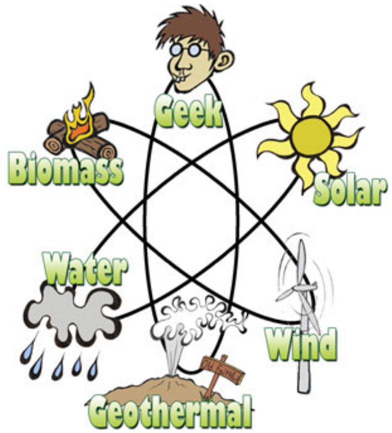
Soaring energy demand !

Depleting energy resources !



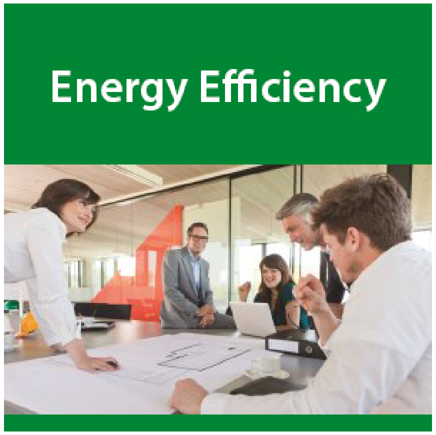
How are we going to satisfy future energy needs?

1. Background and Motivations



New Energy Sources

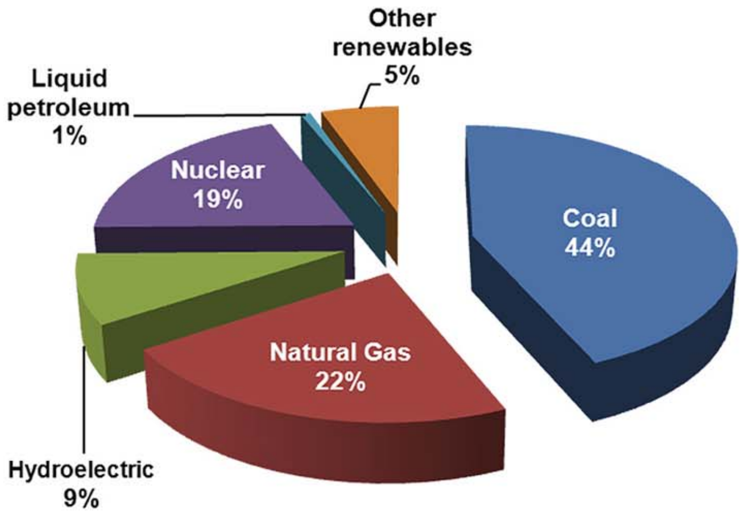
Search for solutions



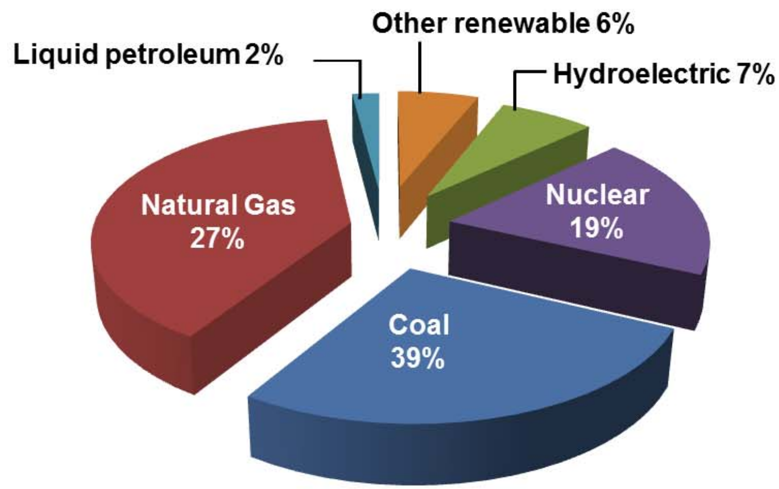
High Energy Efficiency

1. Background and Motivations

U.S. Electricity Generation (2010)



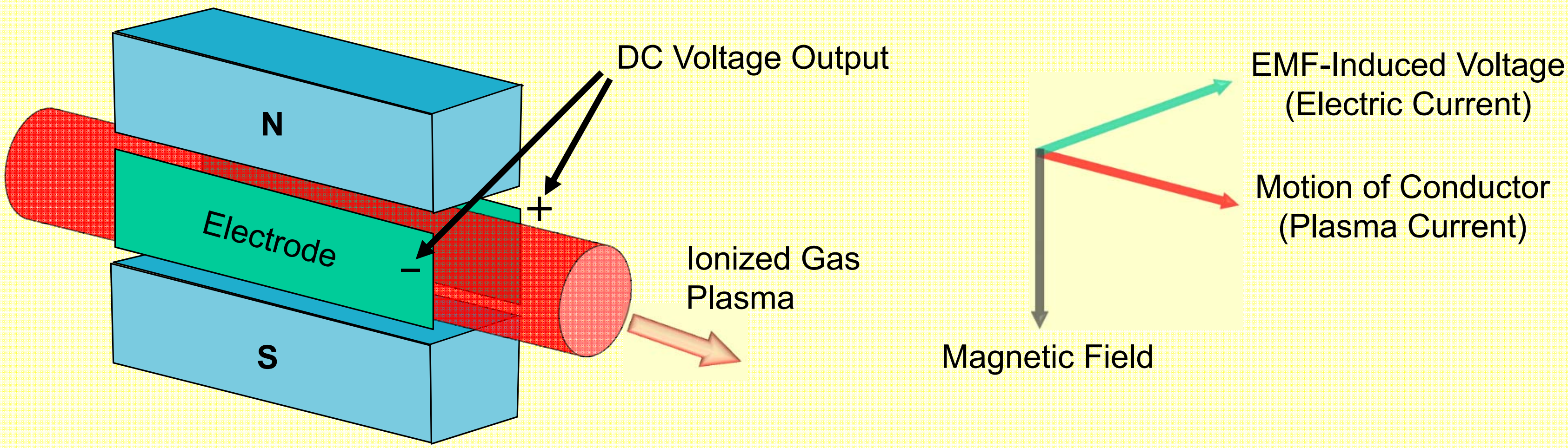
U.S. Electricity Generation (2013)



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).**

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.

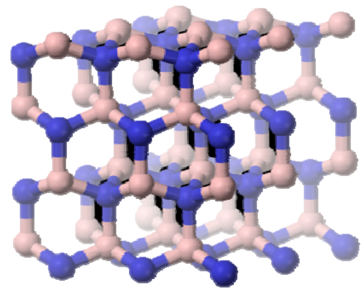
1000 × current density of copper
5 × electrical conductivity of copper
15 × thermal conductivity of copper
1/7 density of copper and **½** or Al

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

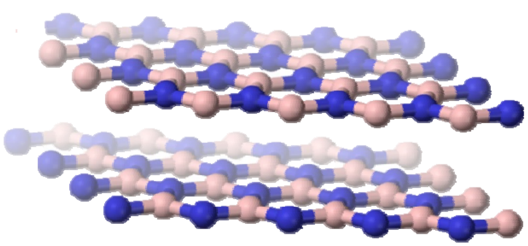
1. Background and Motivations

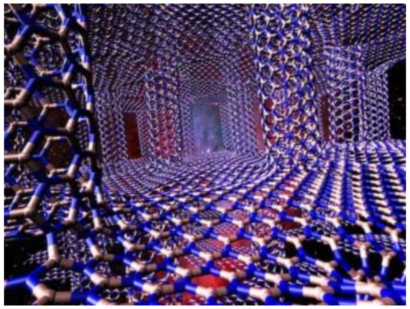
Property	BN
Electrical conductivity (σ)	Insulating
Thermal conductivity (k)	600 - 740
Thermal stability	T_m = 2973
Oxidation resistance	~ 1500 ˚C
Corrosion resistance	Yes
Erosion resistance	Yes
Thermionic emission	N.A.

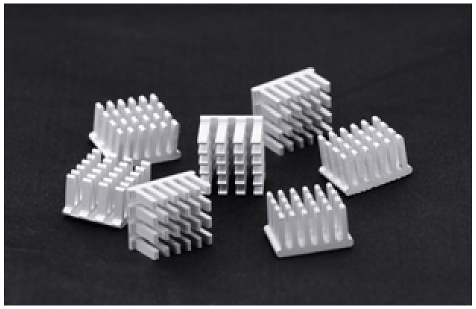
C-BN



h-BN

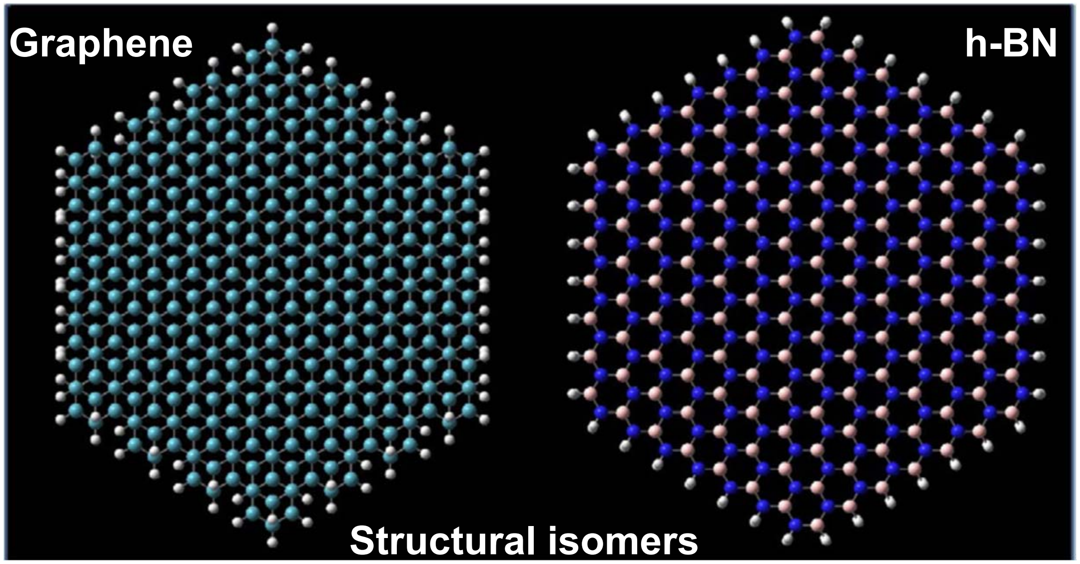






http://www.graphene-info.com/3d-white-graphene-could-cool-electronics

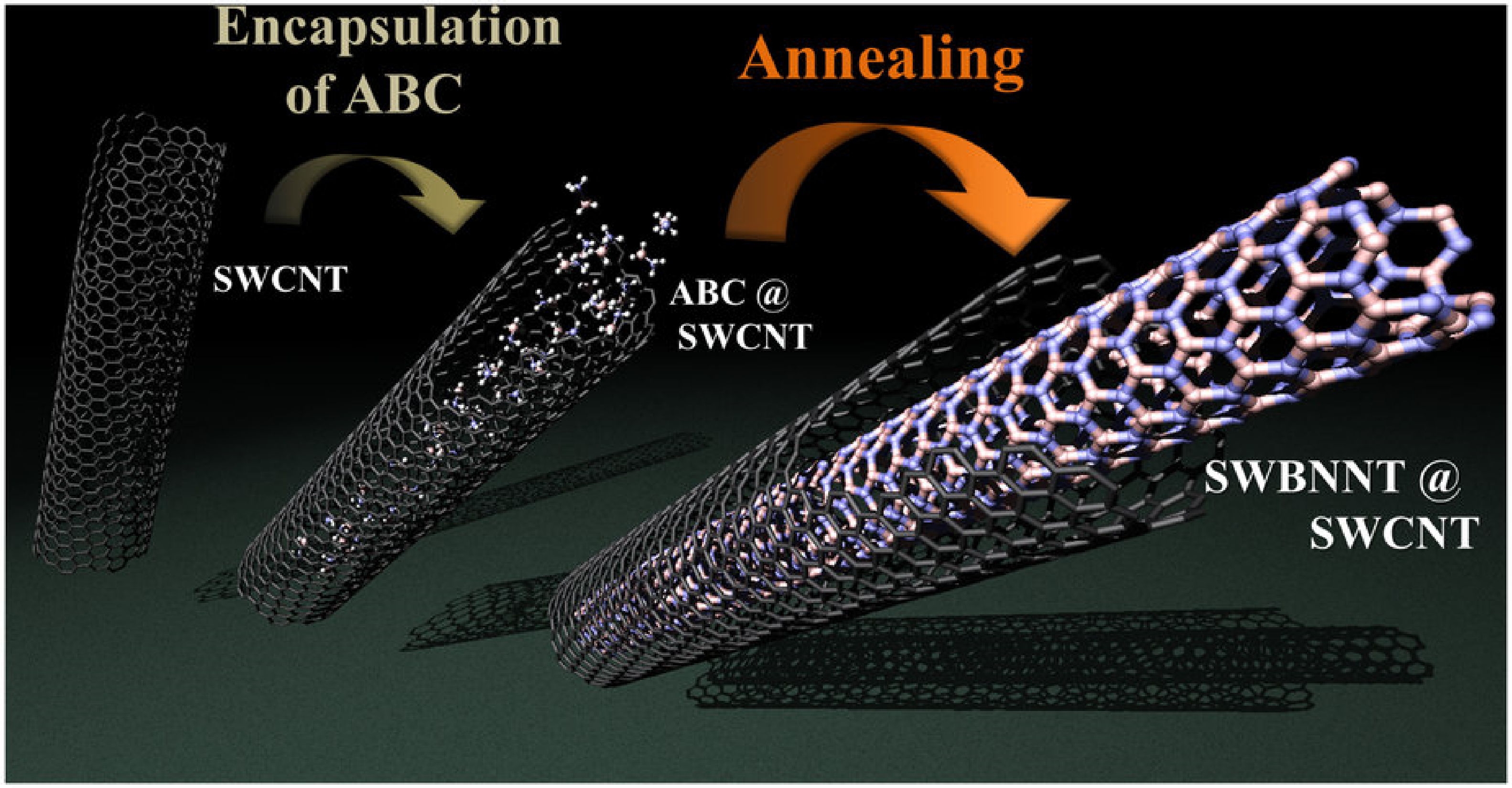
1. Background and Motivations



	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 (⊥)

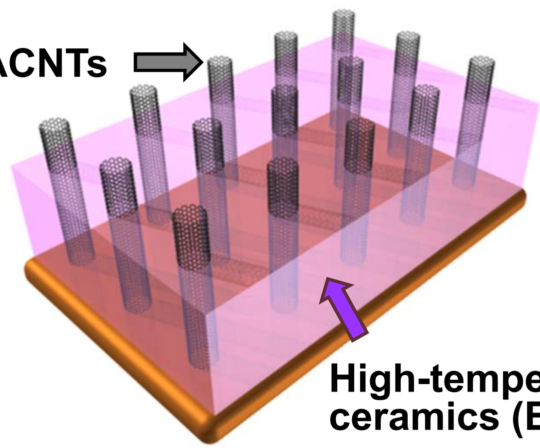
1. Background and Motivations



It is feasible to insert BNNTs in CNTs, and vice verse.

1. Background and Motivations

Proposed Solution: CNT-BN Composite Structures



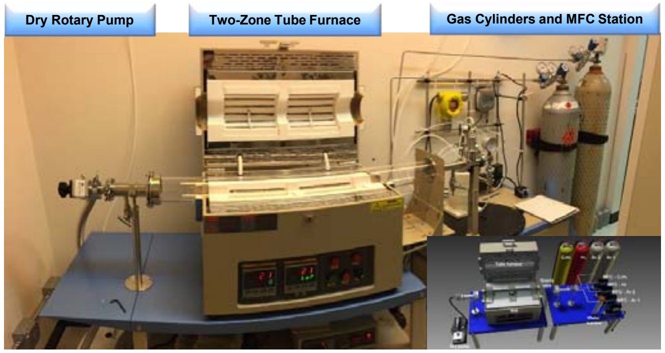
VACNTs: Electrical and thermal conductive channels.

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

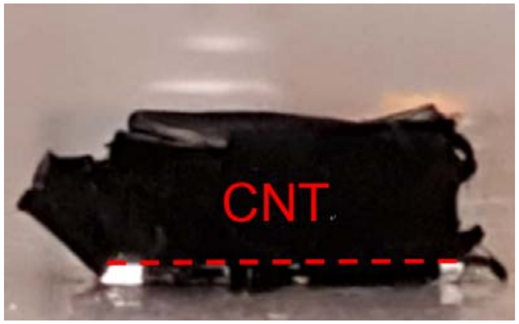
Property	BN	CNTs
Melting point (˚C / K)	2973 / 3246	> 1726 / 2000
Chemical inertness	Inert to acids but soluble in alkaline molten salts and nitrides	Yes
Oxidation resistance in open air (˚C / K)	1500 / 1773	< 700 / 973
Electrochemical passiveness	Yes. Used as electrode.	Yes.
Electrical conductivity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

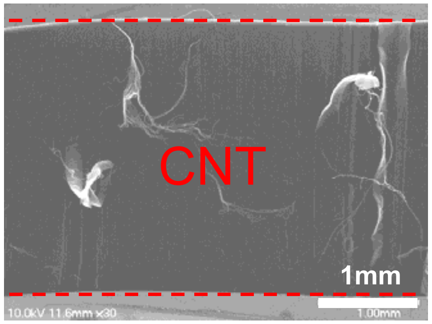
A review of previous research

1) Established a WVA-CVD system

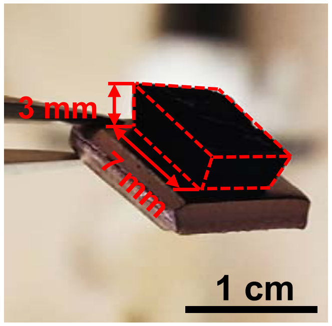


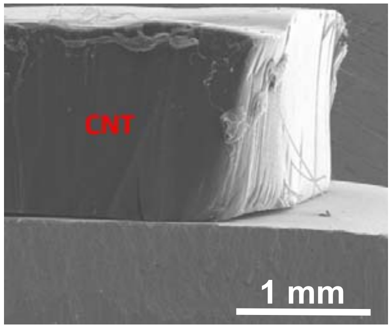
2) Obtained ultralong VACNTs up to 4 mm long



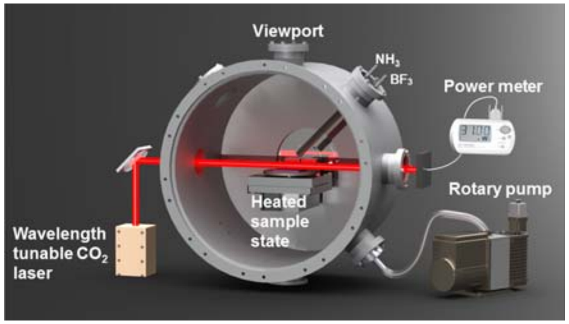


3) Obtained VACNT-Cu structure





4) Established a LCVD system



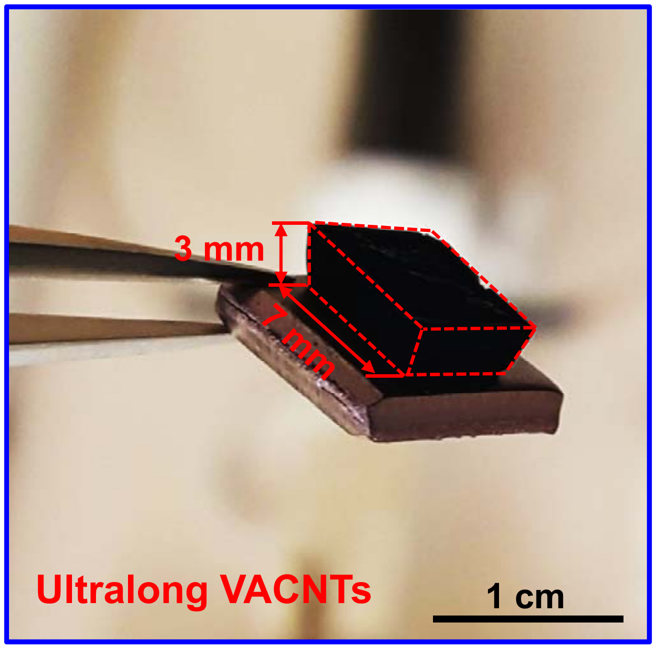
2. Accomplishments

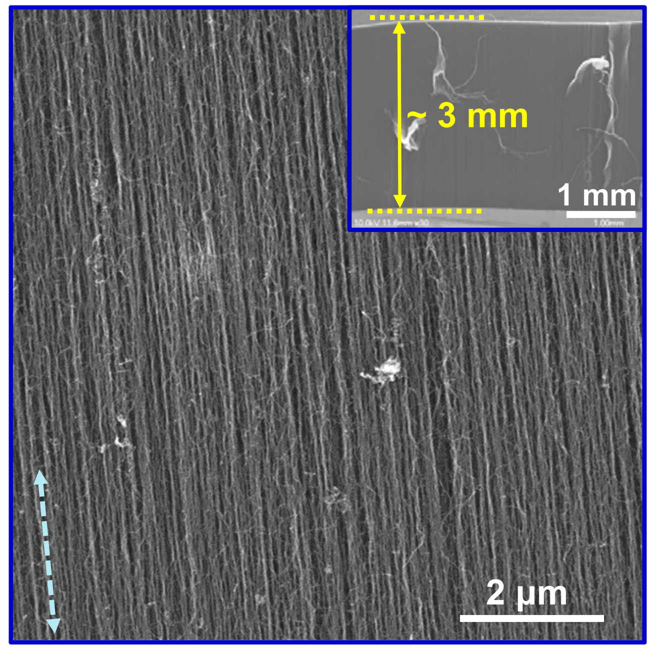
1) Measuring structure and electrical conductivity of the VACNTs
2) Growing VACNT patterns
3) Growing BN using the chemical vapor deposition (CVD) method
4) Fabricating VACNT-BN structure and testing its oxidation stability
5) Fabricating VACNT-Al_2O_3 structure and testing its oxidation stability
6) Fabricating VACNT-GaN structure and testing its oxidation stability
7) Fabricating VACNT-GaN-Si structure and testing its oxidation stability
8) Fabricating VACNT-SiN_x infiltrated composite structure (in progress)

2. Accomplishments

- Measuring structure and electrical conductivity of the VACNTs

Structure characterization

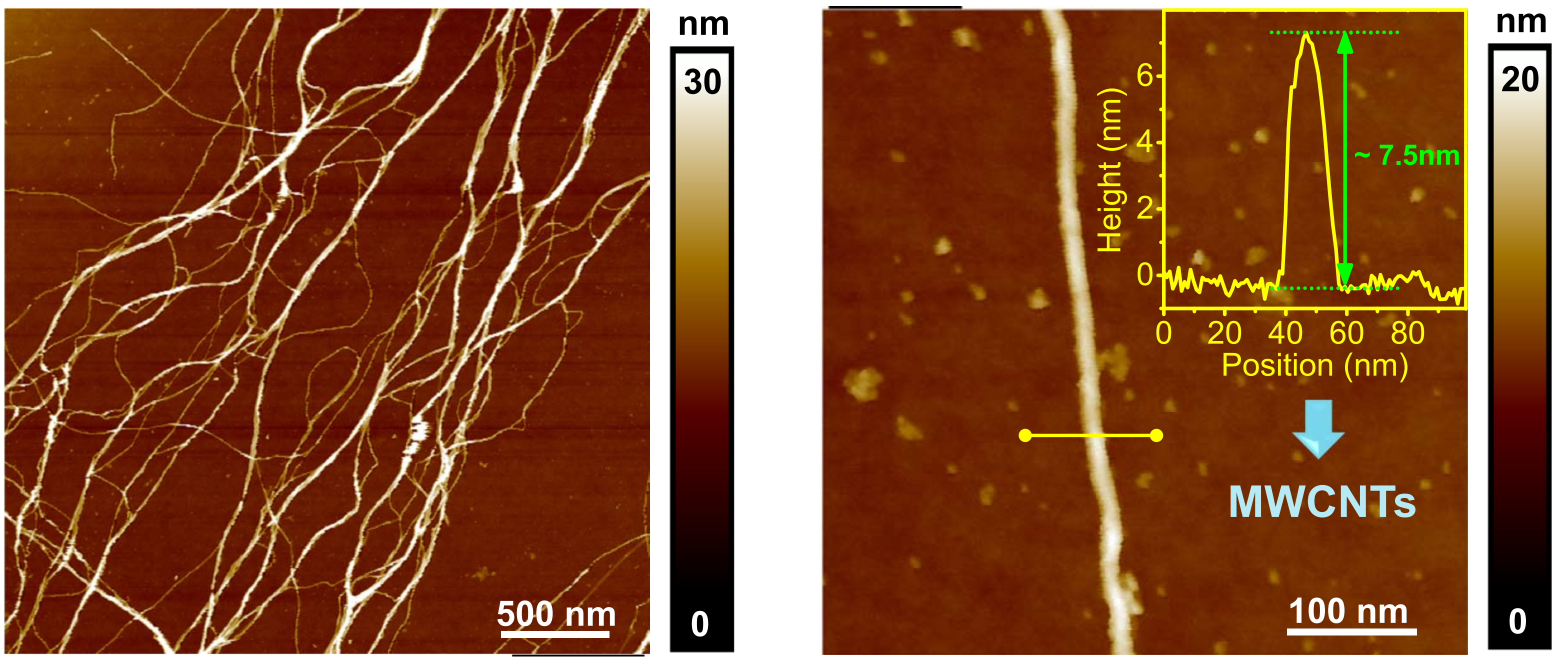




2. Accomplishments

- Measuring structure and electrical conductivity of the VACNTs

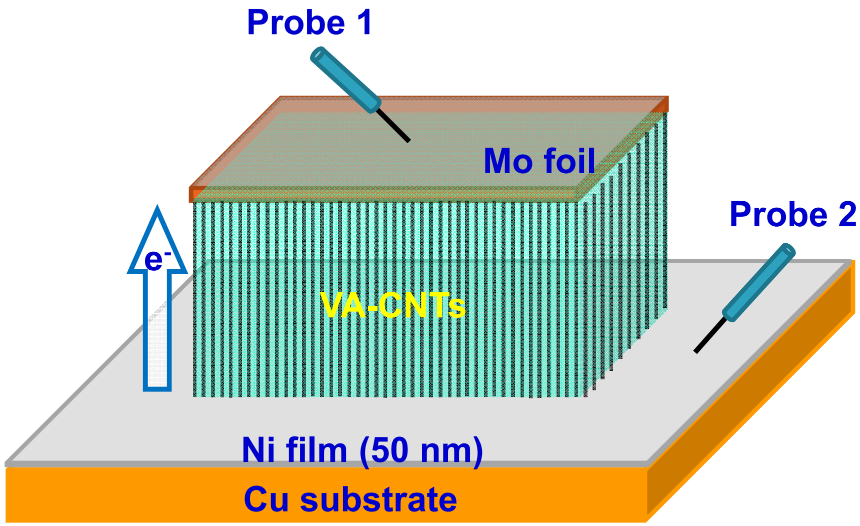
Structure characterization



2. Accomplishments

- Measuring structure and electrical conductivity of the VACNTs

Room-temperature electrical conductivity

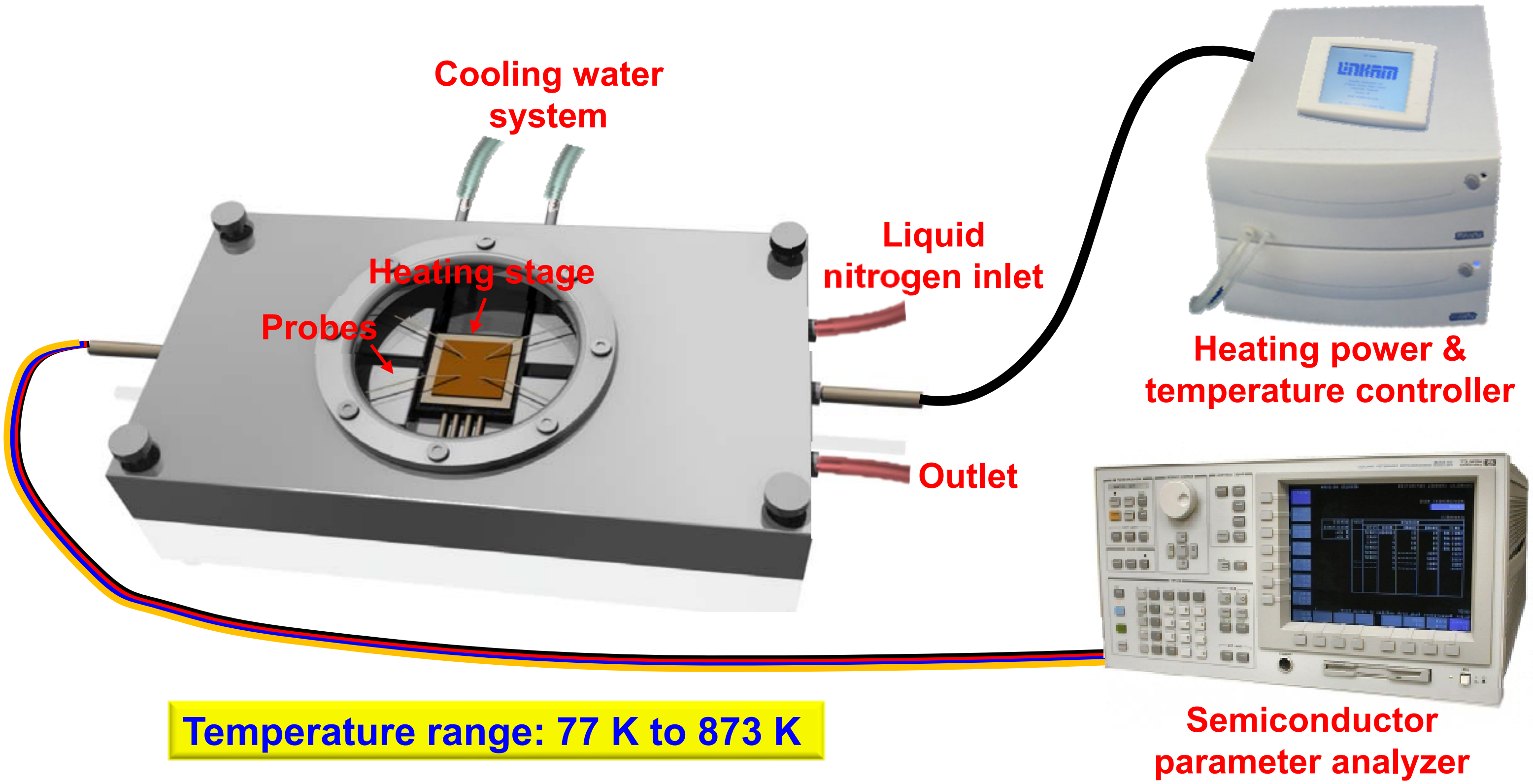


- 3 × 7 × 5 mm^3 (H L W)

2. Accomplishments

- Measuring structure and electrical conductivity of the VACNTs

Building a high-temperature electrical conductivity measurement system

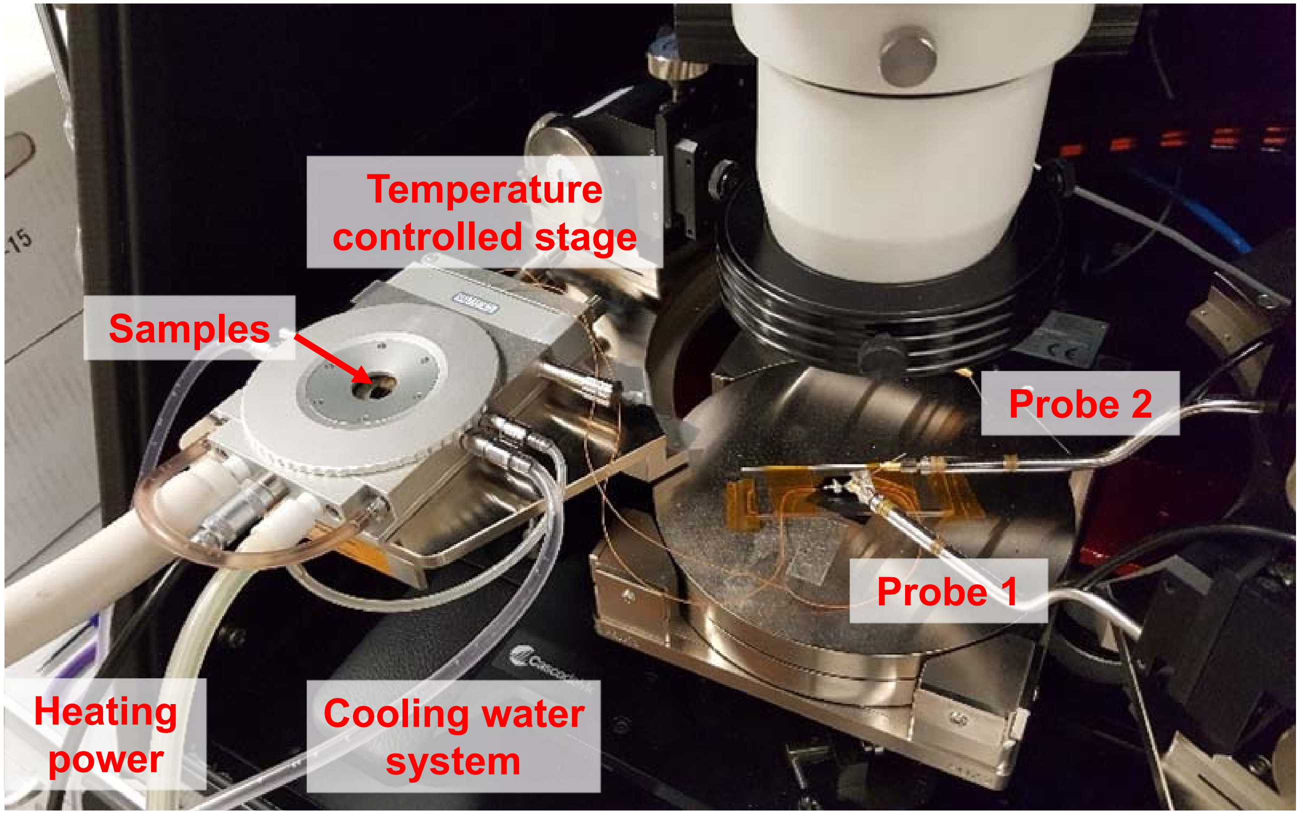


Temperature range: 77 K to 873 K

2. Accomplishments

- Measuring structure and electrical conductivity of the VACNTs

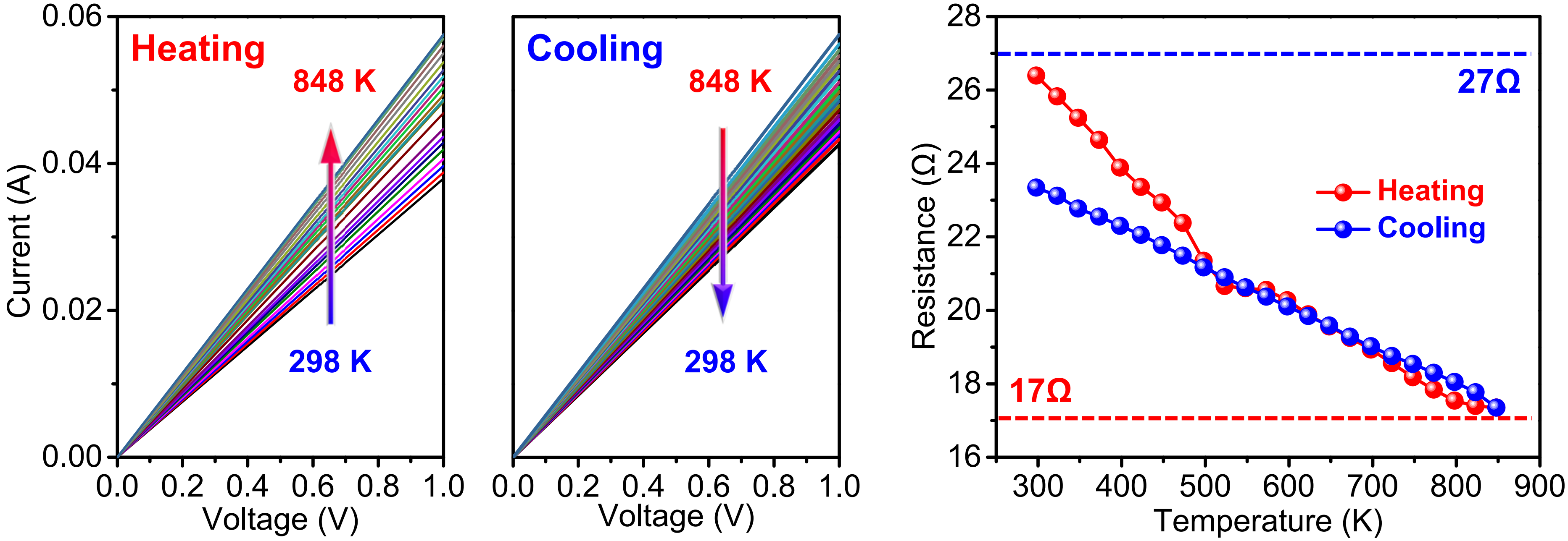
Building a high-temperature electrical conductivity measurement system



2. Accomplishments

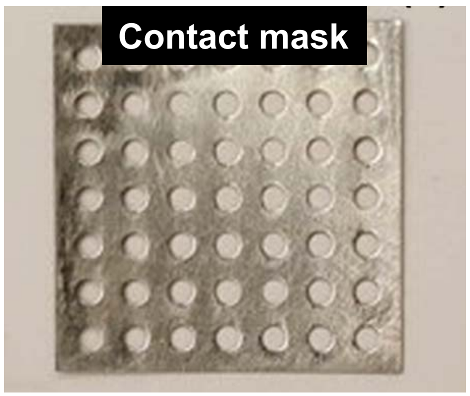
- Measuring structure and electrical conductivity of the VACNTs

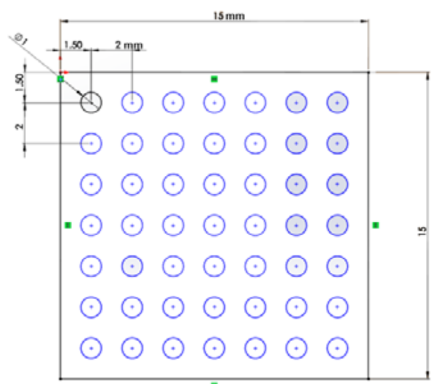
High-temperature electrical conductivity of the VACNTs

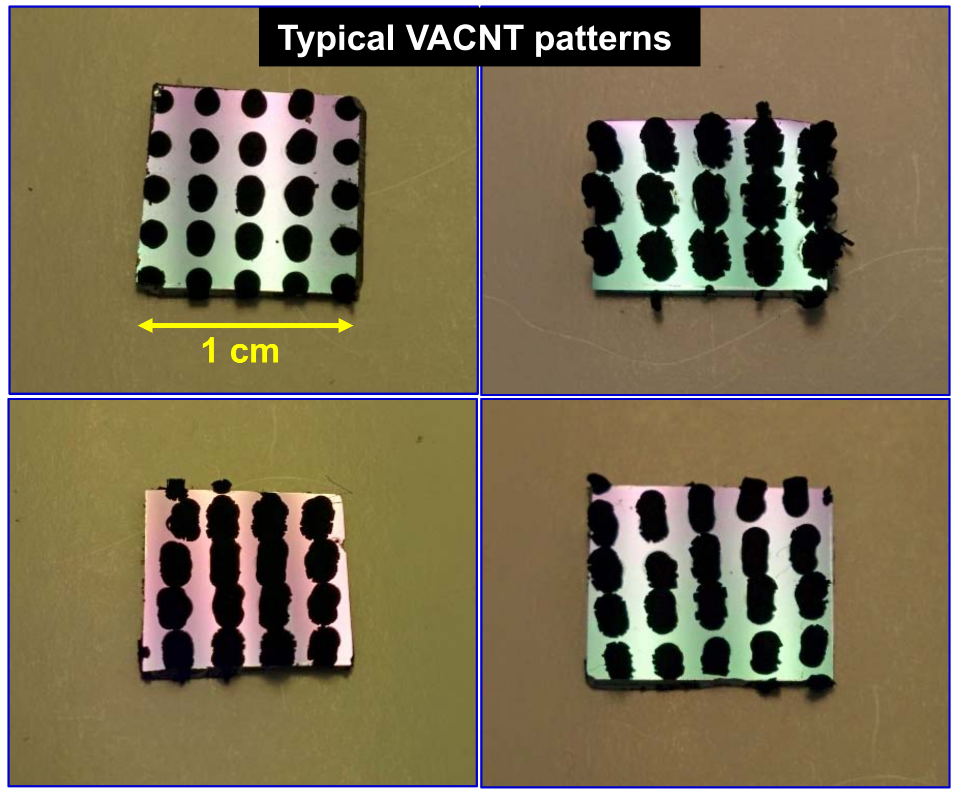


2. Accomplishments
- Growing VACNT patterns

Large VACNT patterns



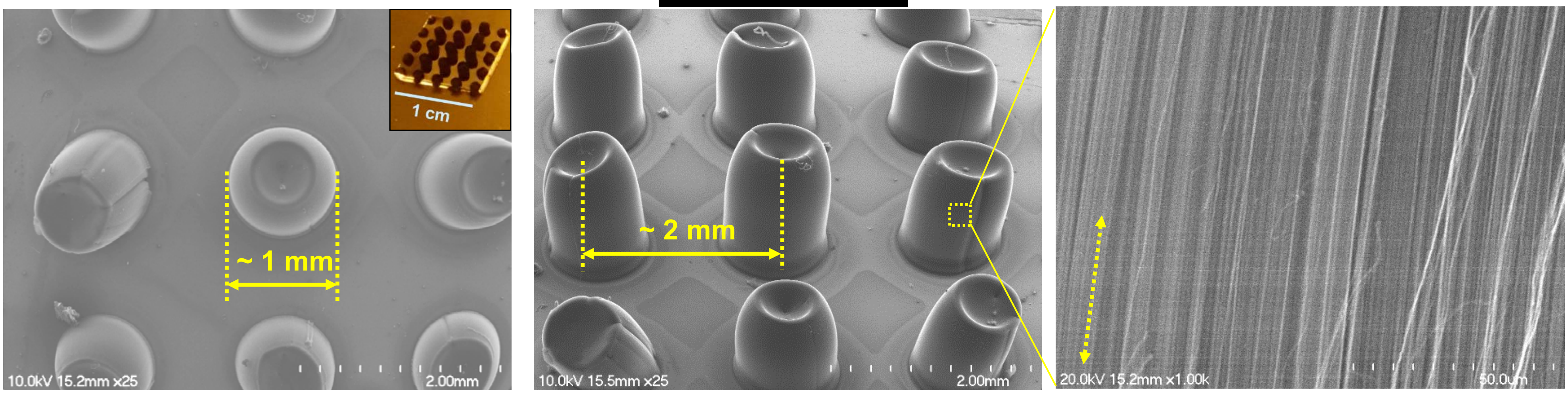




2. Accomplishments
- Growing VACNT patterns

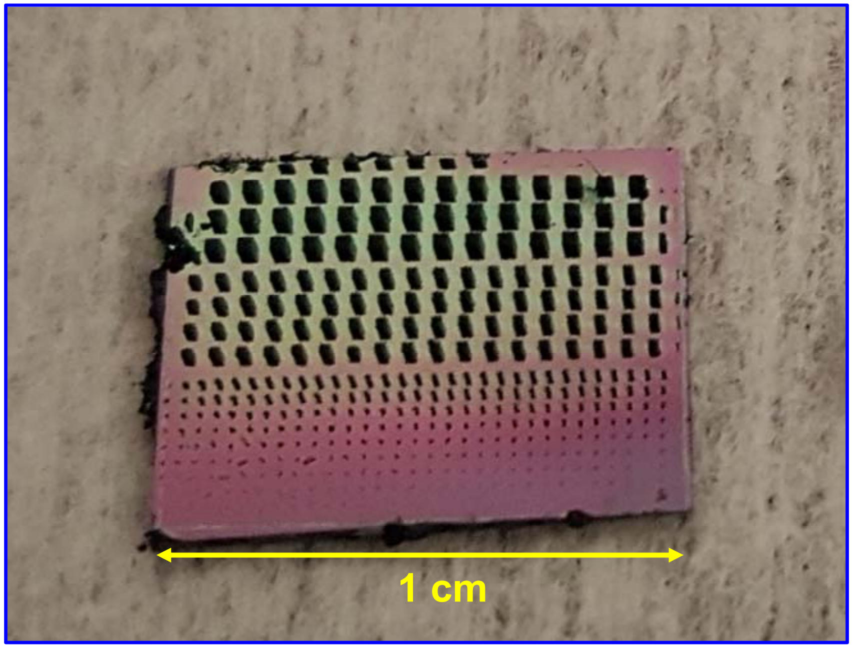
Large VACNT patterns

SEM micrograph



2. Accomplishments
- Growing VACNT patterns

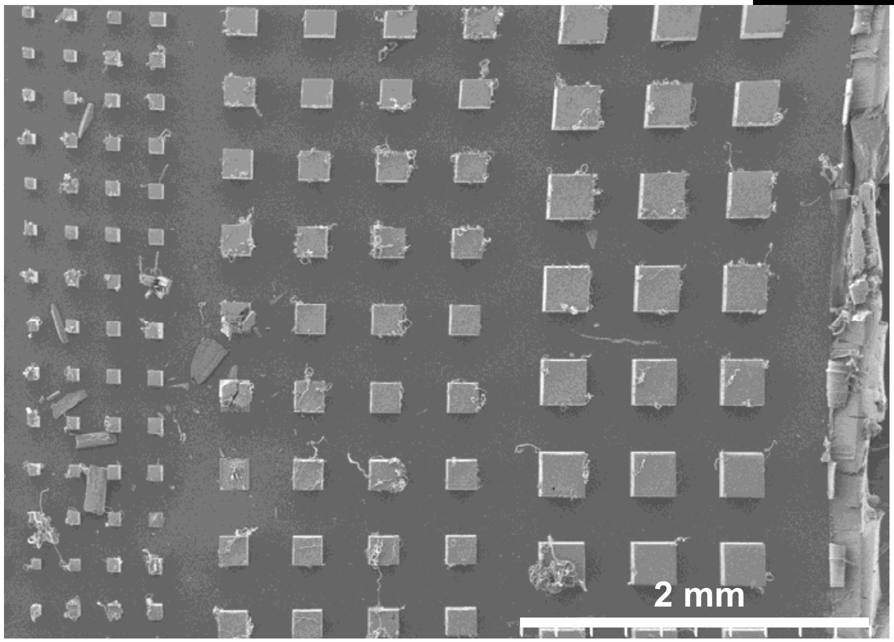
Small VACNT patterns

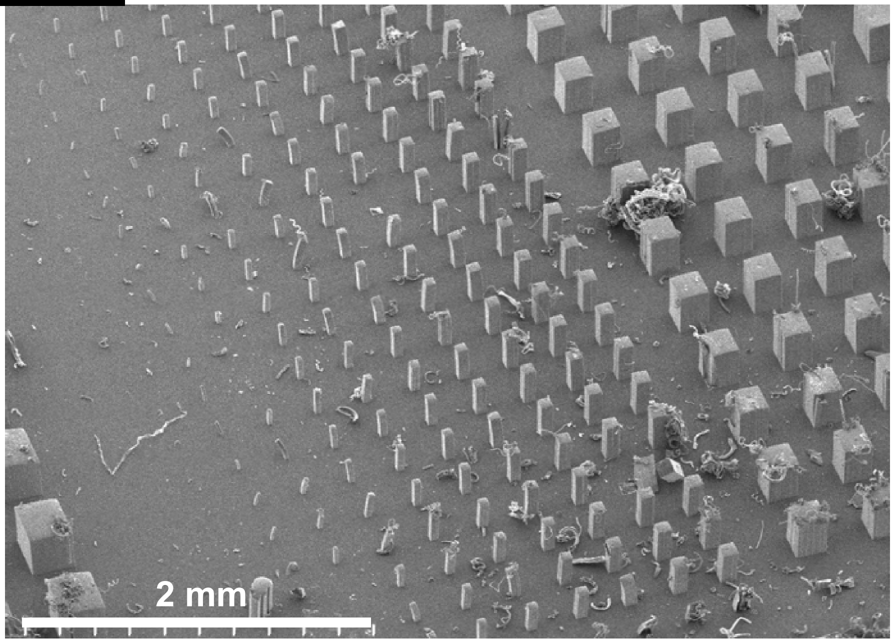


2. Accomplishments
- Growing VACNT patterns

Small VACNT patterns

SEM micrograph

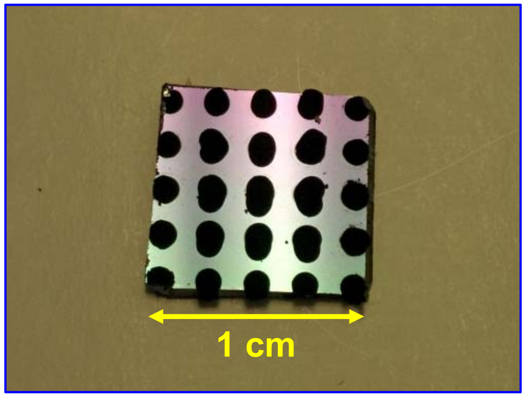


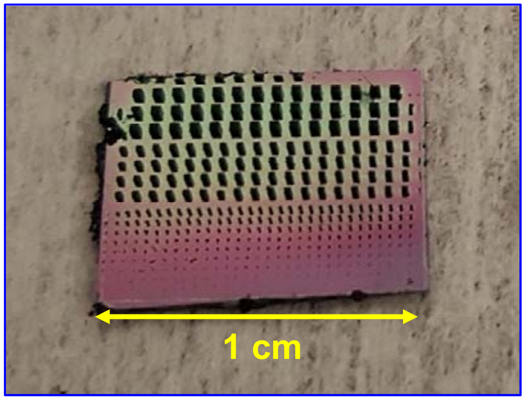


2. Accomplishments

- Growing VACNT patterns

Large and small VACNT patterns were obtained.

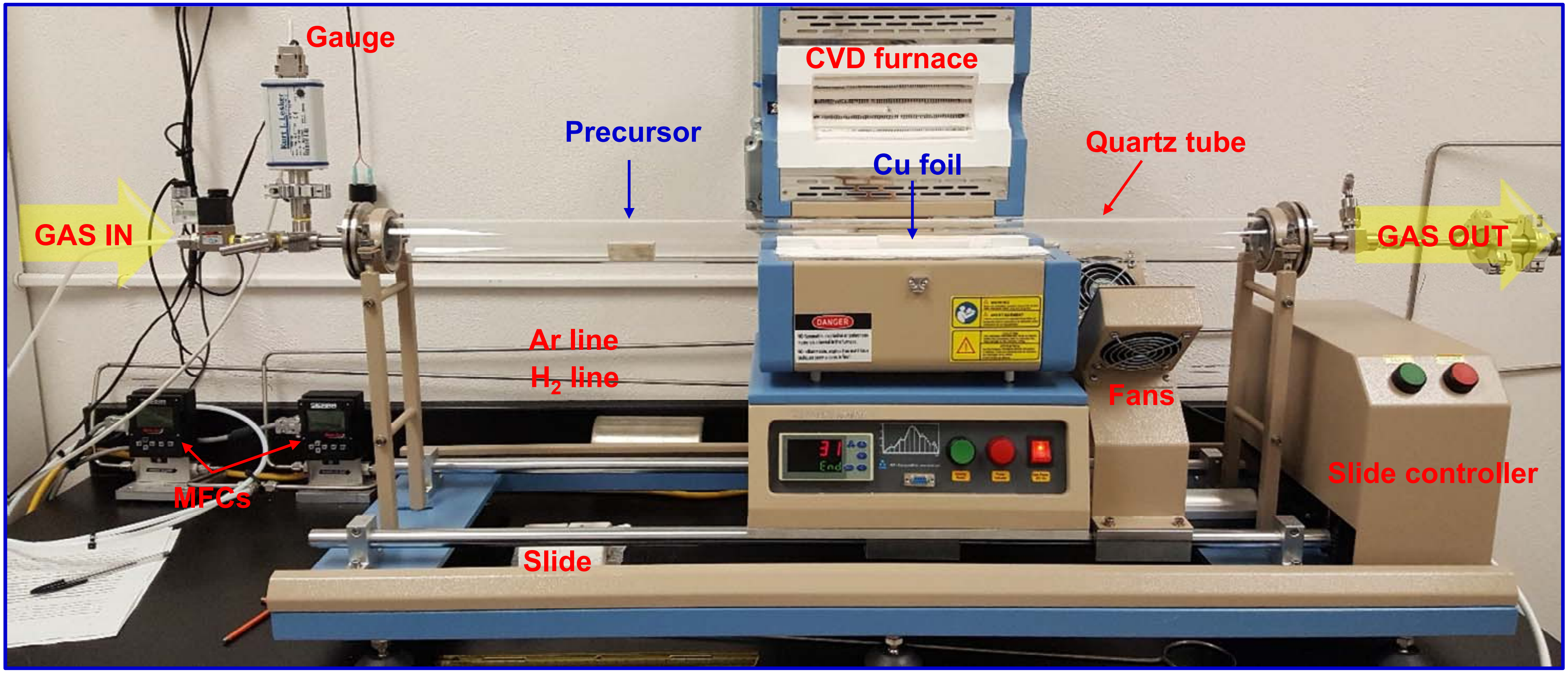




2. Accomplishments

- Growing BN using thermal CVD method

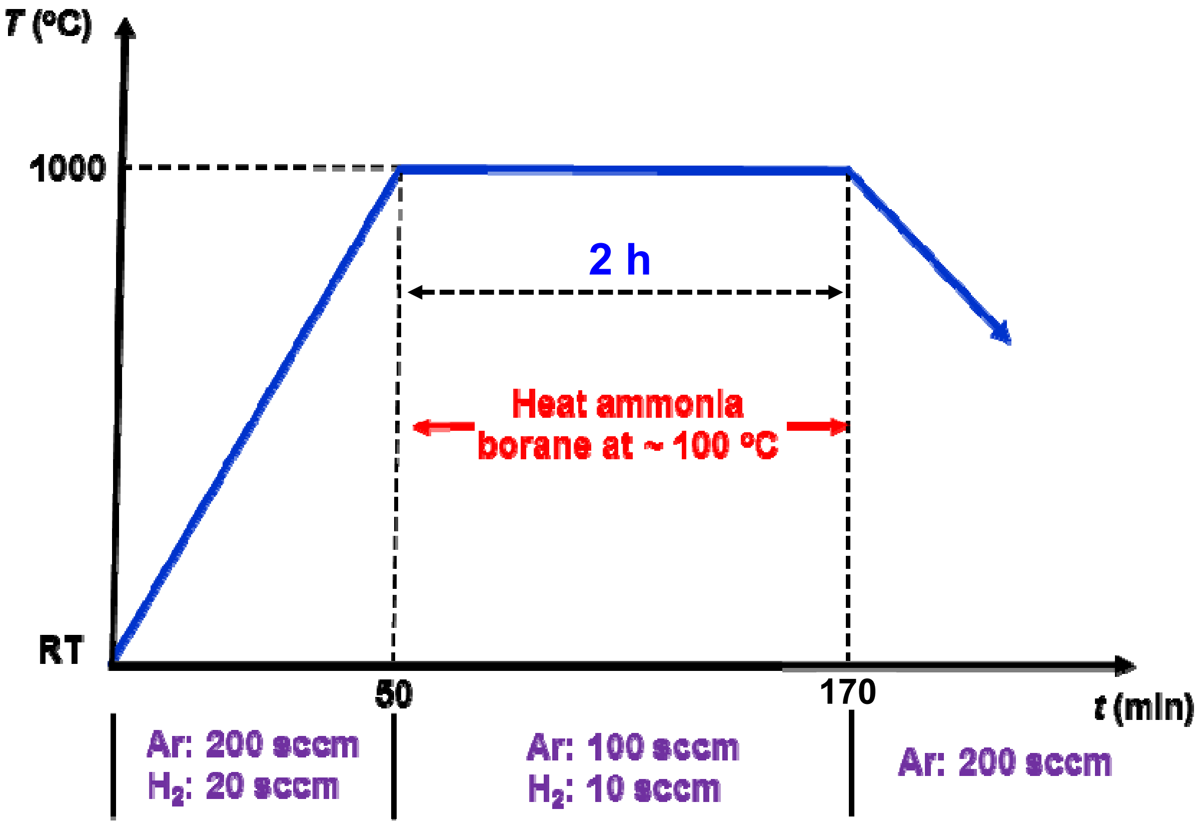
Building a thermal CVD system for BN growth



2. Accomplishments

- Growing BN using thermal CVD method

BN on Cu foil using thermal CVD

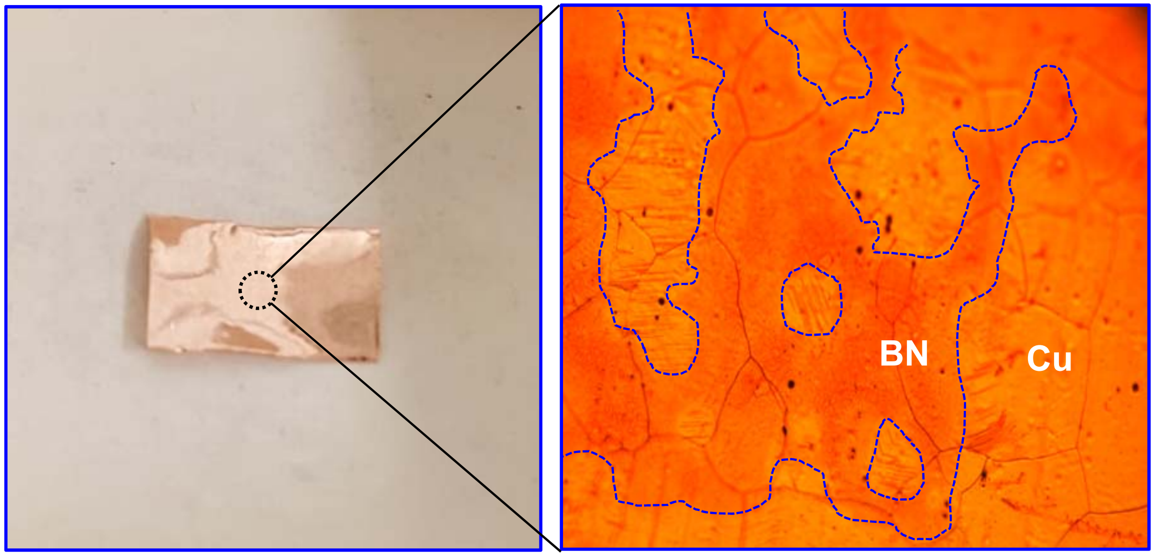


2. Accomplishments

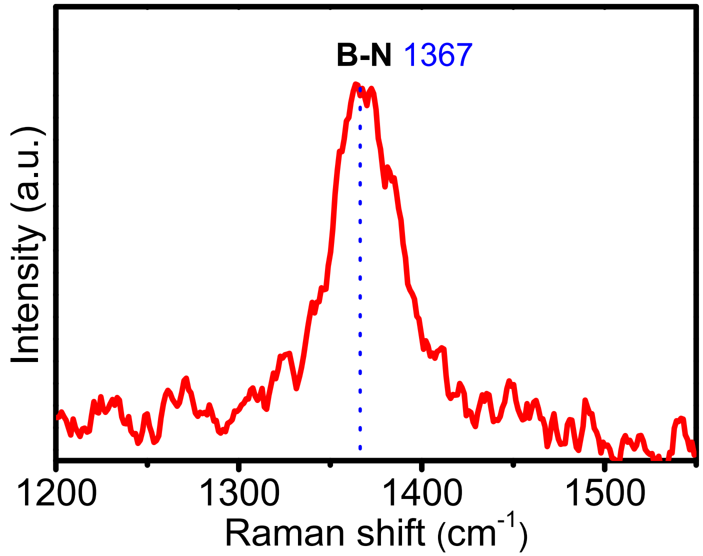
- Growing BN using thermal CVD method

BN on Cu foil using thermal CVD

Optical image



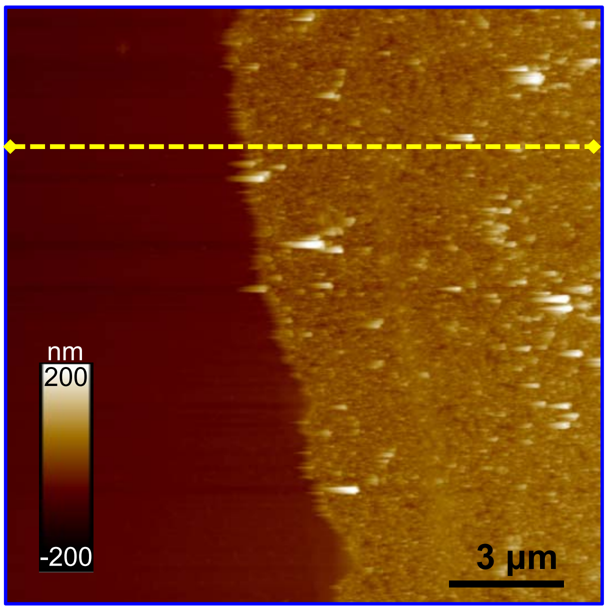
Raman spectrum

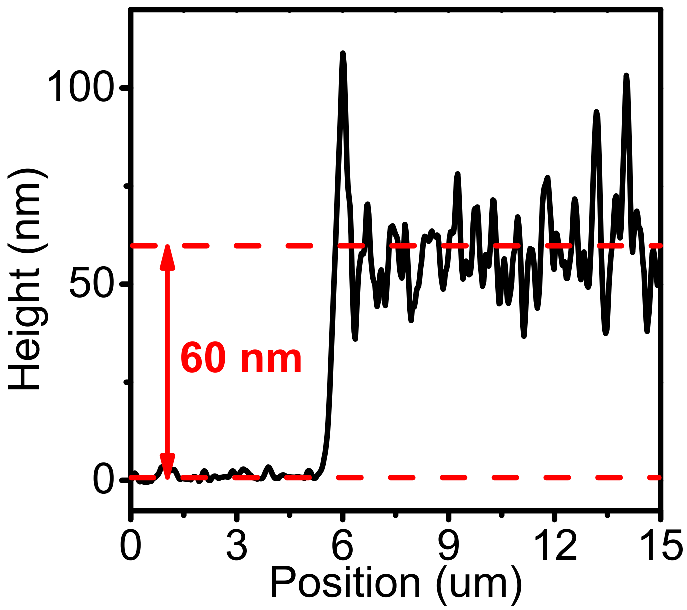


2. Accomplishments
- Growing BN using thermal CVD method

Structure characterization

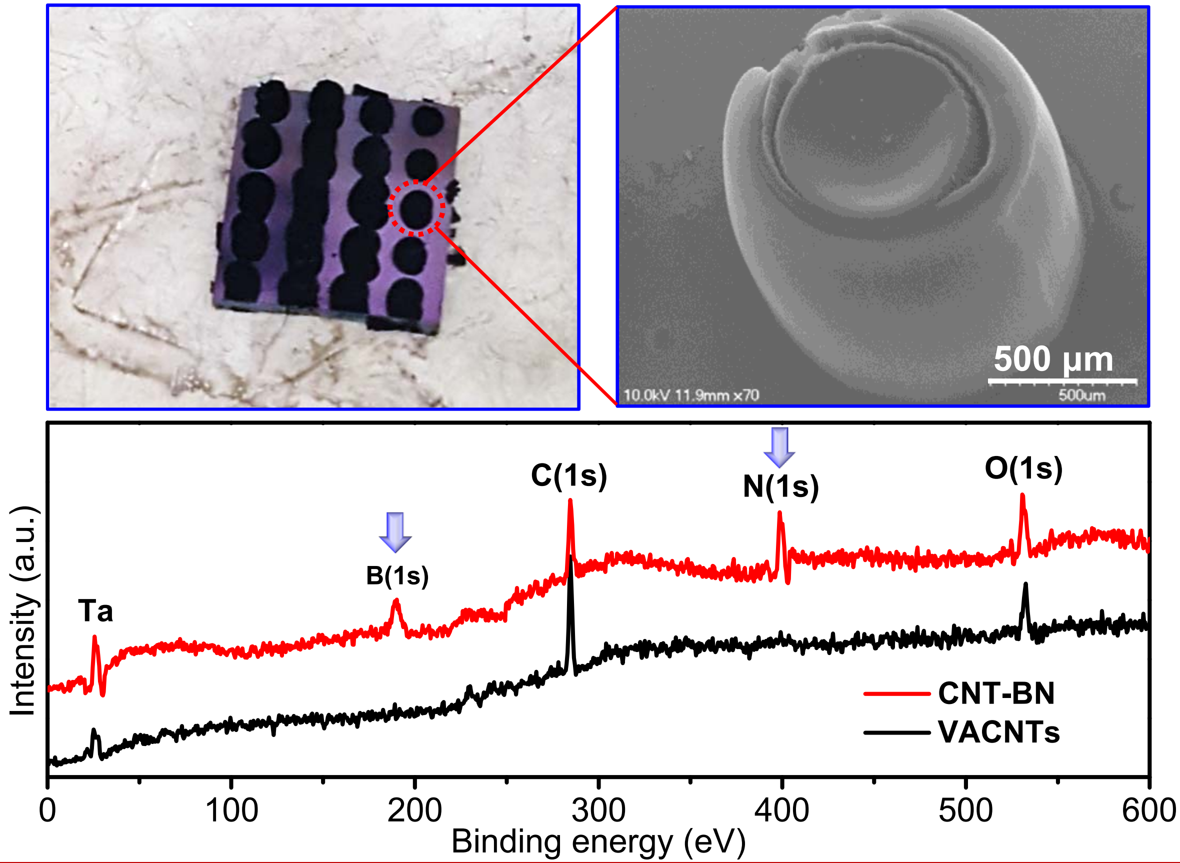
AFM image





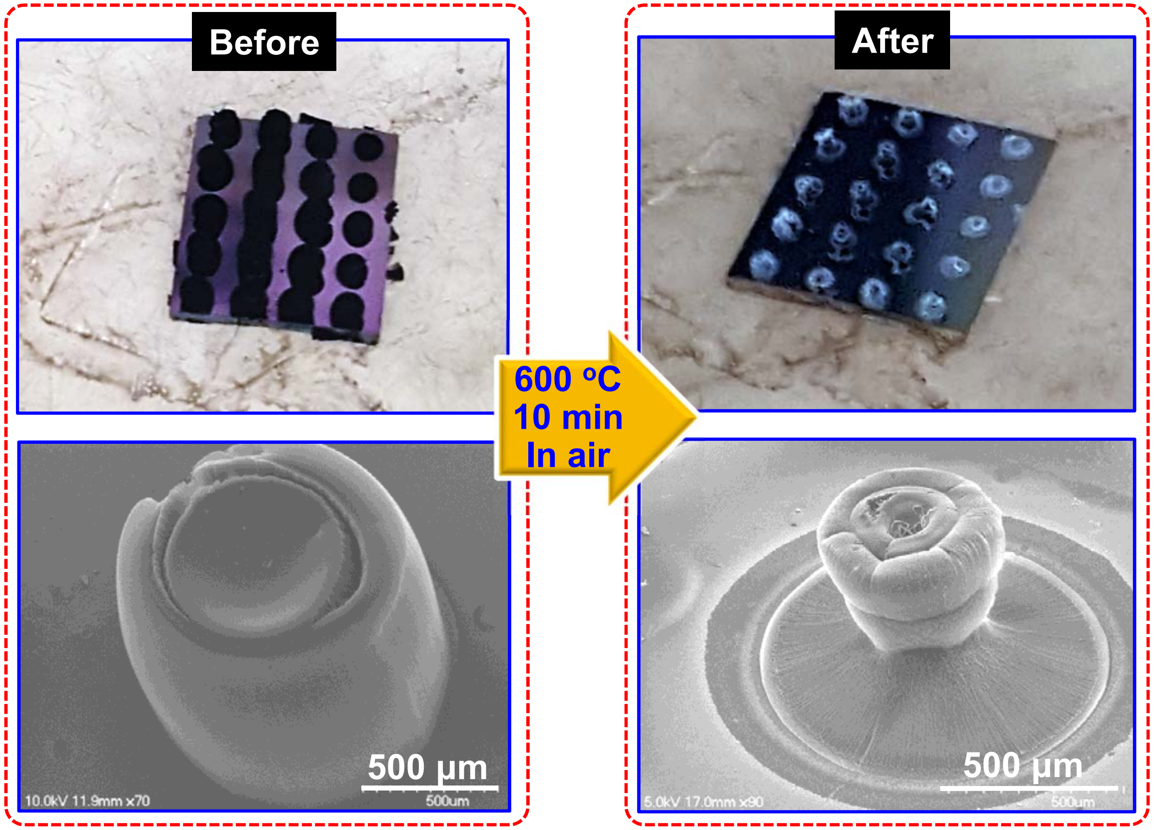
2. Accomplishments
- Fabricating VACNT-BN structure

VACNT-BN patterns



2. Accomplishments
- Fabricating VACNT-BN structure

Oxidation resistance test



2. Accomplishments
- Fabricating VACNT-BN structure

Poor oxidation resistance properties of VACNT-BN patterns.

Growth of thick BN on VACNT patterns is a very challenging task.

2. Accomplishments

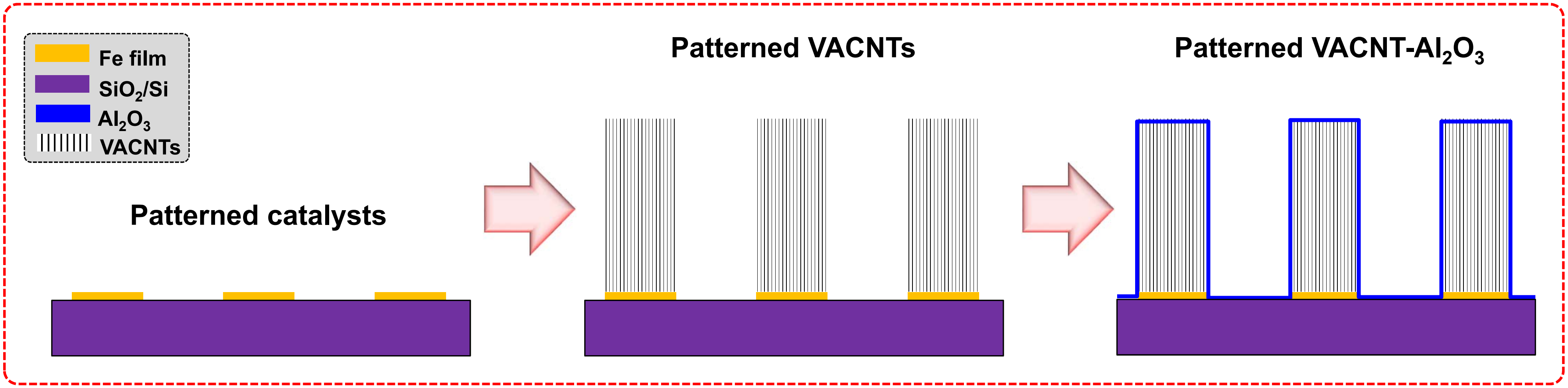
- Comparison of properties of BN, Al_2O_3, SiO_2, GaN

Property	c-BN	h-BN	Al_2O_3	Si/SiO_2	GaN	Si_3N_4
Bandgap (eV)	6.4	5.2	/	/	3.4	/
Melting point (°C)	2973 (sublimation)	2600 (decomposition)	2072	1713	2500	1900
Thermal conductivity ($mW \cdot cm^{-1}k^{-1}$)	740	600 ∥, 30 ⊥	300	120 ∥, 68 ⊥	1300	300
Lattice parameters (Å)	a = 2.5 c = 6.66	a = 3.6157	a = 4.785 c = 12.991	a = 4.9133 c = 5.4053	a = 4.526	a = 7.6165 c = 2.9109
Density (g/cm^3)	3.45	2.1	3.95-4.1	2.648	6.15	3.2
Electron mobility ($cm^2/V \cdot s$)	< 200	< 200	/	/	< 500	/
Refractive index	2.17	1.8	1.768	1.544	2.29	2.016
Thermal expansion ($10^{-6}/K$)	1.2	−2.7 ∥, 38 ⊥	8.4	12.3 (quartz) 0.4 (fused silica)	a: 5.59	3.3

2. Accomplishments

- Fabricating VACNT-Al_2O_3 structure

Fabricating VACNT-Al_2O_3 patterns using sputtering method

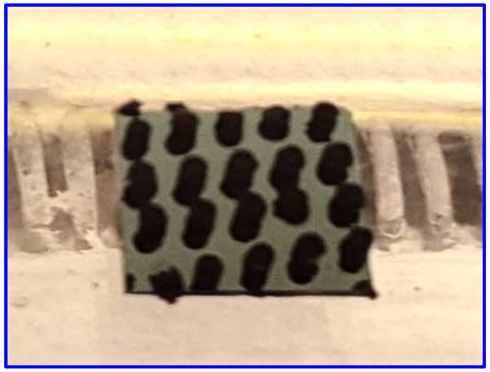


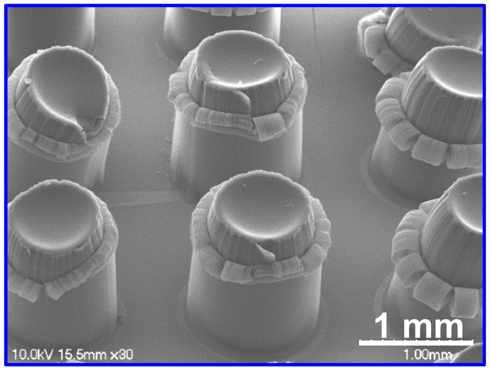
Target	Chamber pressure	Deposition time	Power	Atmosphere
Al_2O_3	5.5 mTorr	120 min	200 W	Argon (99.999%)

2. Accomplishments
- Fabricating VACNT-Al_2O_3 structure

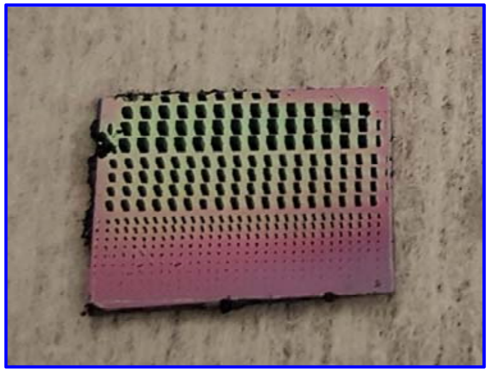
VACNT-Al_2O_3 patterns

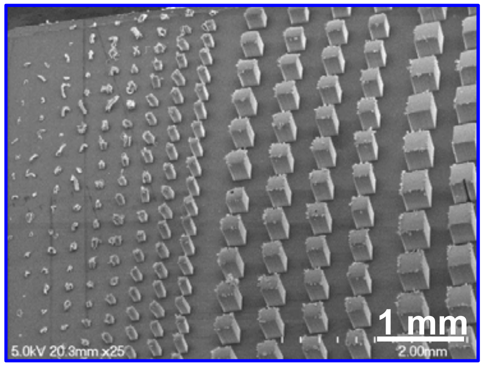
Sample 1





Sample 2





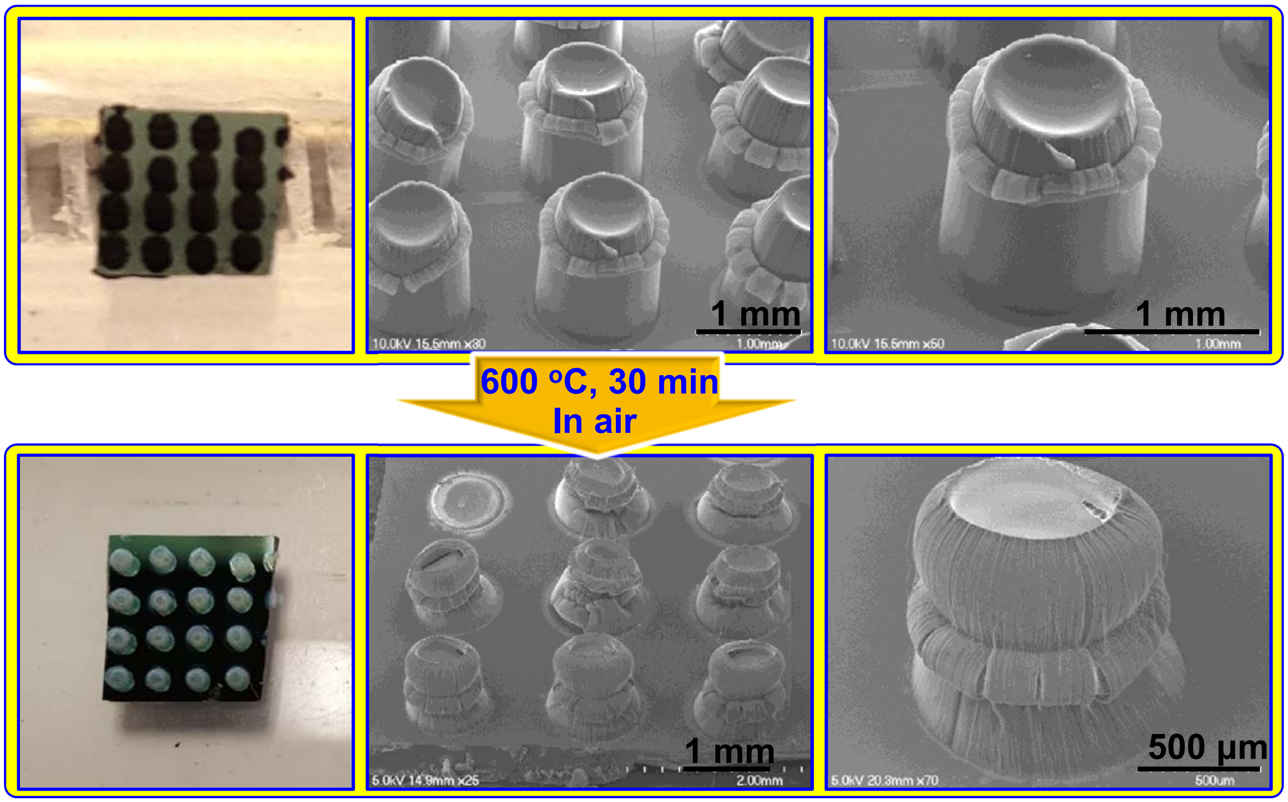
2. Accomplishments

- Fabricating VACNT-Al_2O_3 structure

Oxidation resistance test (Sample 1)

Before

After



2. Accomplishments

- Fabricating VACNT-Al_2O_3 structure

Oxidation resistance test (Sample 2)

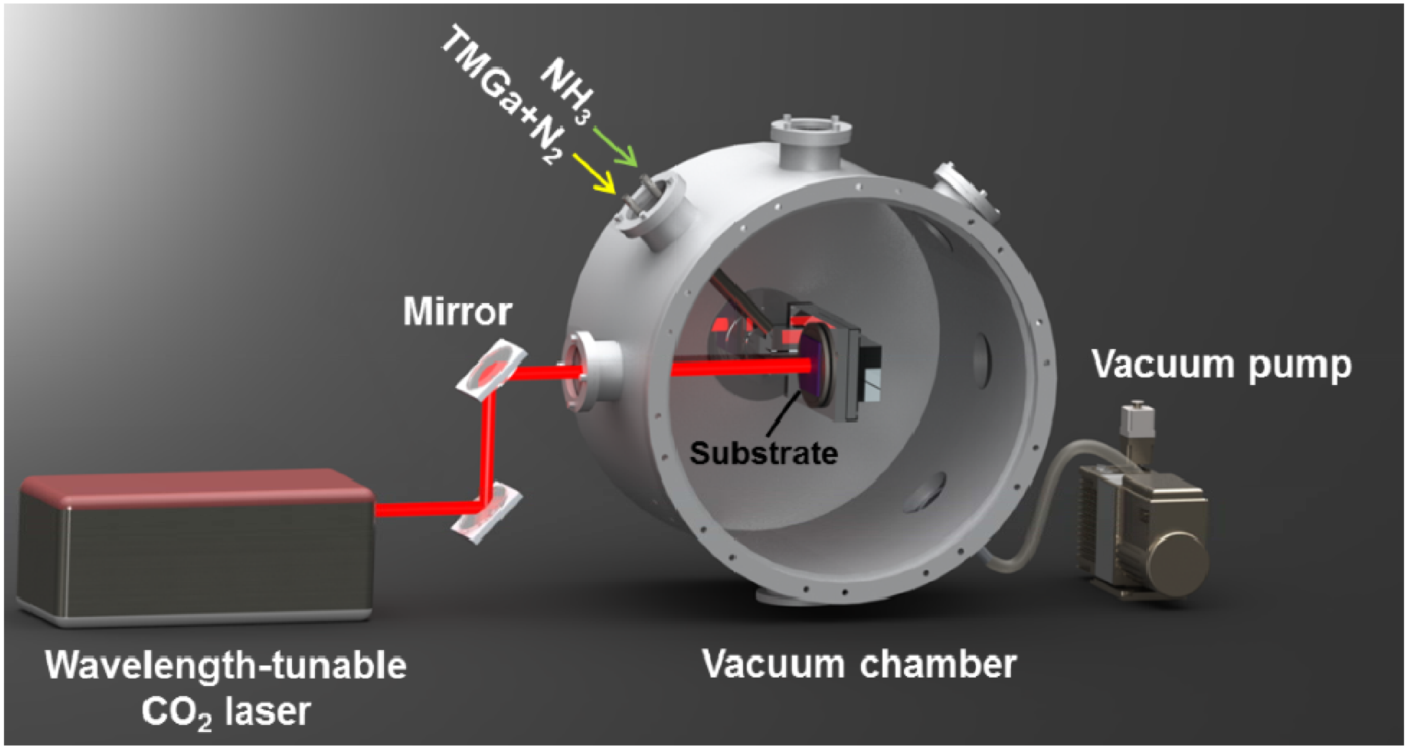
2. Accomplishments
- Fabricating VACNT-Al_2O_3 structure

Poor oxidation resistance properties of VACNT-Al_2O_3 patterns.

Similar to BN, growth of thick Al_2O_3 on VACNT patterns is very challenging.

2. Accomplishments
- Fabricating VACNT-GaN structure

Building a Laser-assisted MOCVD system for GaN growth



2. Accomplishments

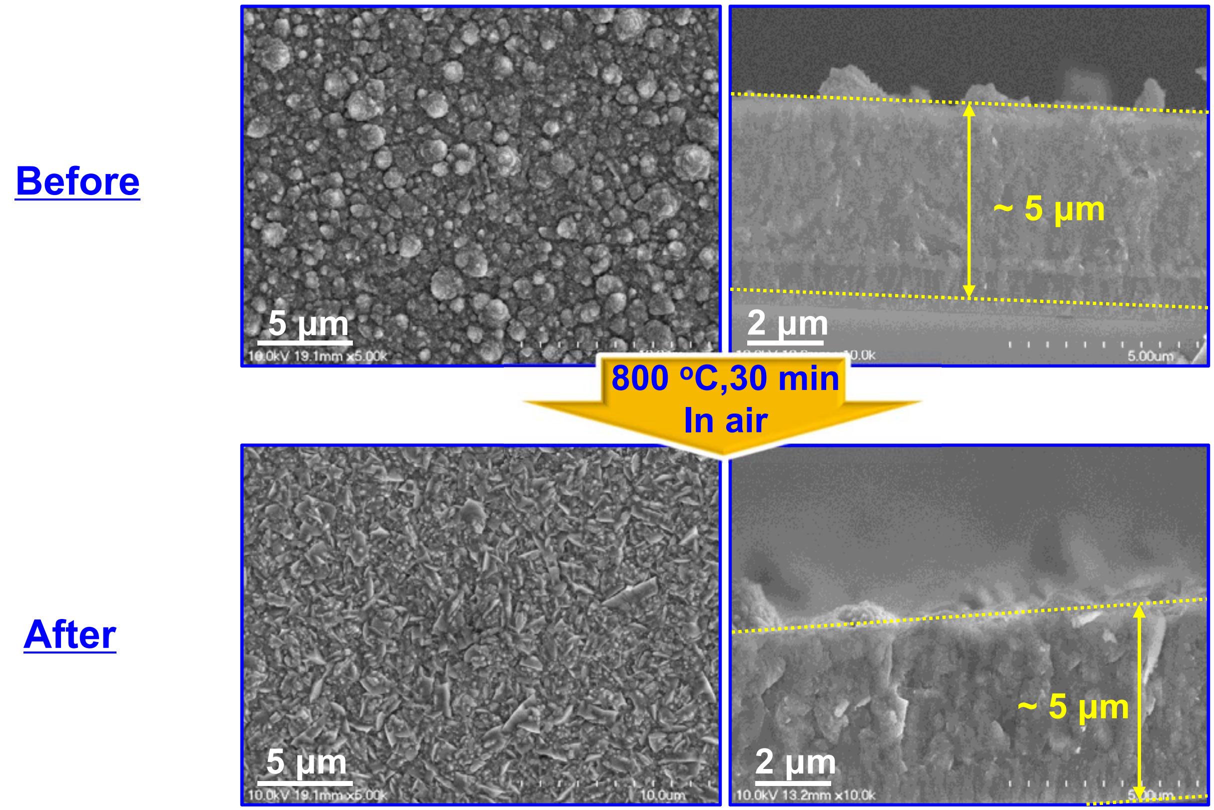
- Fabricating VACNT-GaN structure

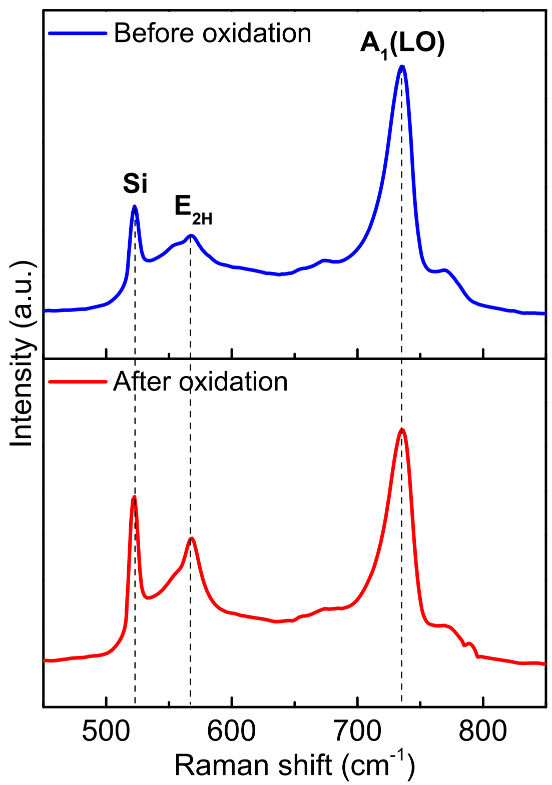
Optimized parameters used for GaN growth

Parameters	Values
Laser power	100 W
Laser wavelength	9.201 μm
Growth temperature	900 ^{o}C
Growth time	5 min
Precursors	TMGa + N_2, NH_3
NH_3 flow rate	54 mmol/min
Carrier gas (flow rate)	N_2 (88 μmol/min)
Chamber pressure	100 Torr
Direction	Laser was irradiated in backside of the sample

2. Accomplishments
- Fabricating VACNT-GaN structure

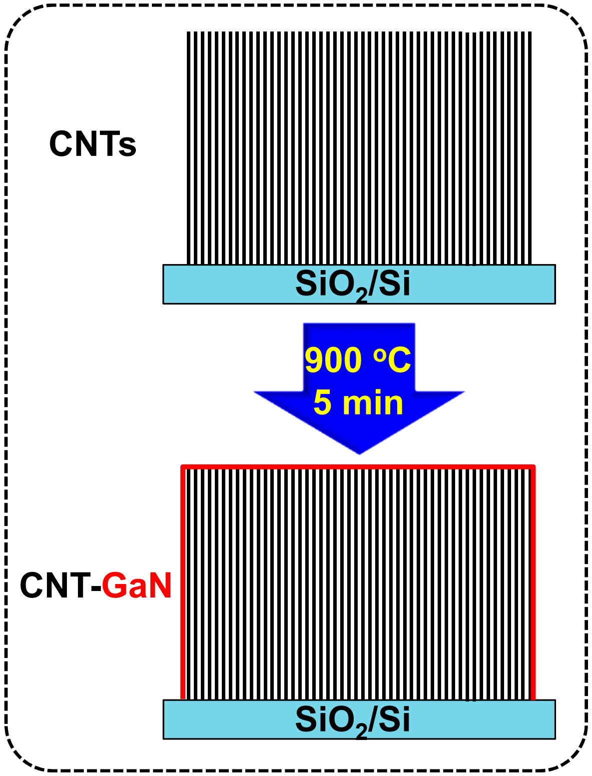
Oxidation resistance properties of GaN

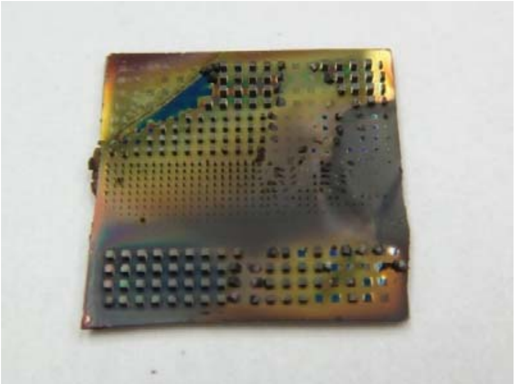


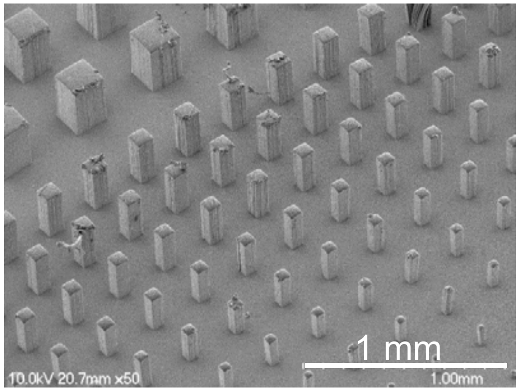


2. Accomplishments
- Fabricating VACNT-GaN structure

VACNT-GaN patterns fabricated using LMOCVD method

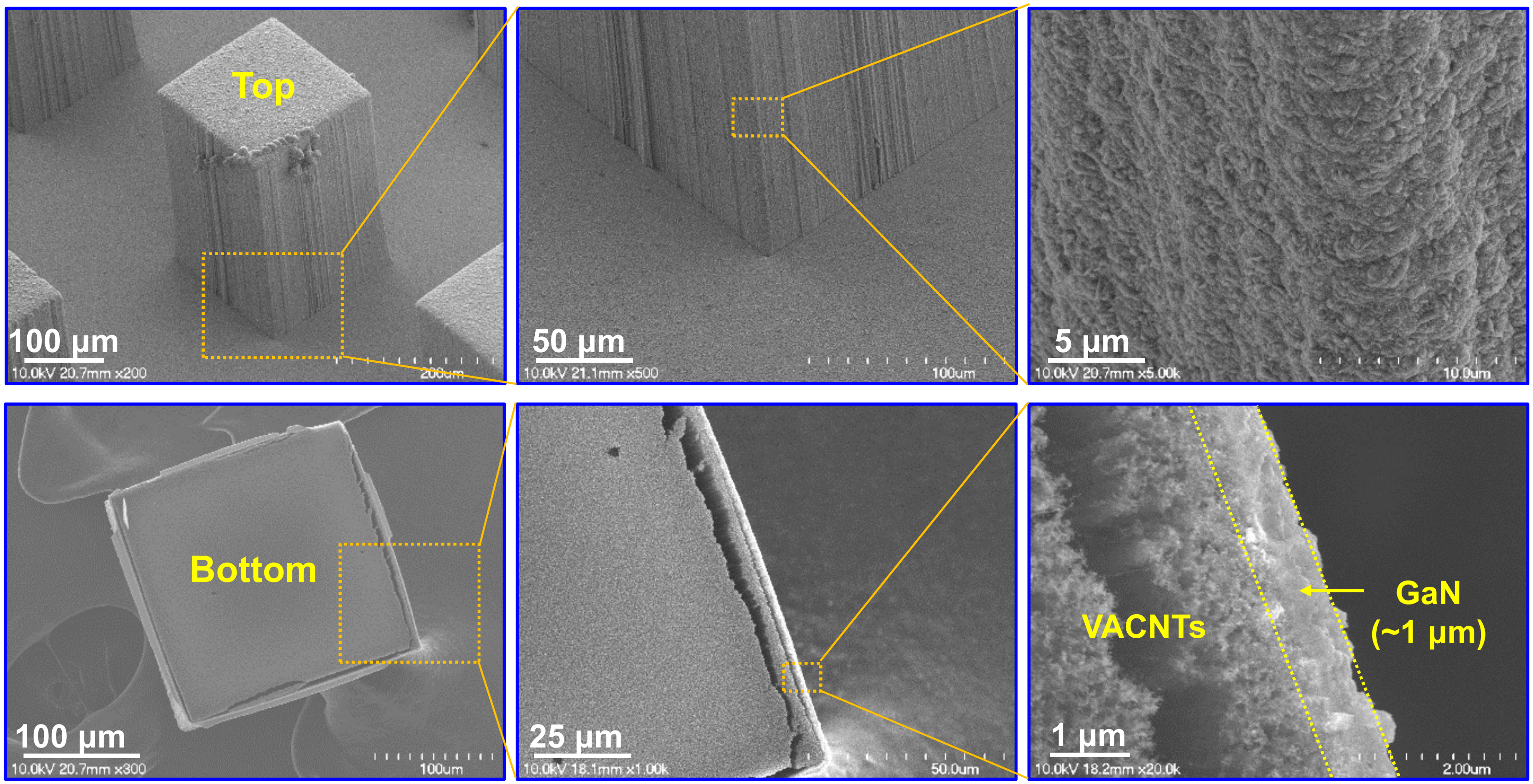






2. Accomplishments
- Fabricating VACNT-GaN structure

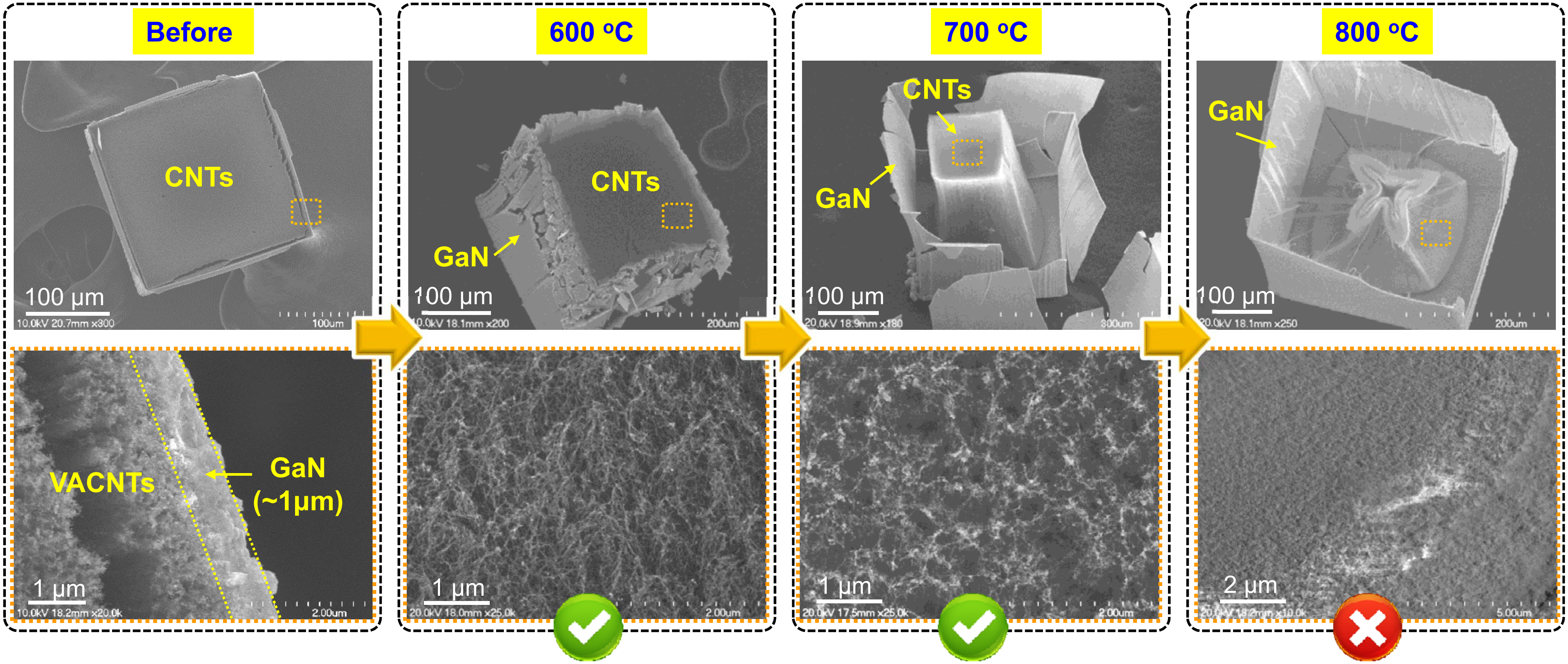
VACNT-GaN patterns fabricated using LMOCVD method



2. Accomplishments

- Fabricating VACNT-GaN structure

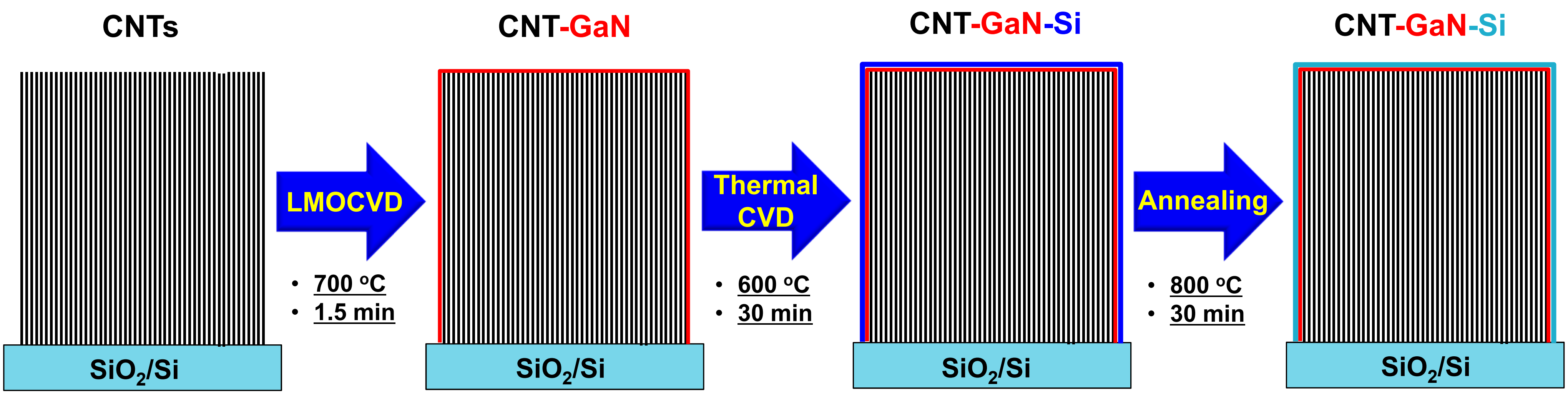
Oxidation resistance test



2. Accomplishments
- Fabricating VACNT-GaN structure

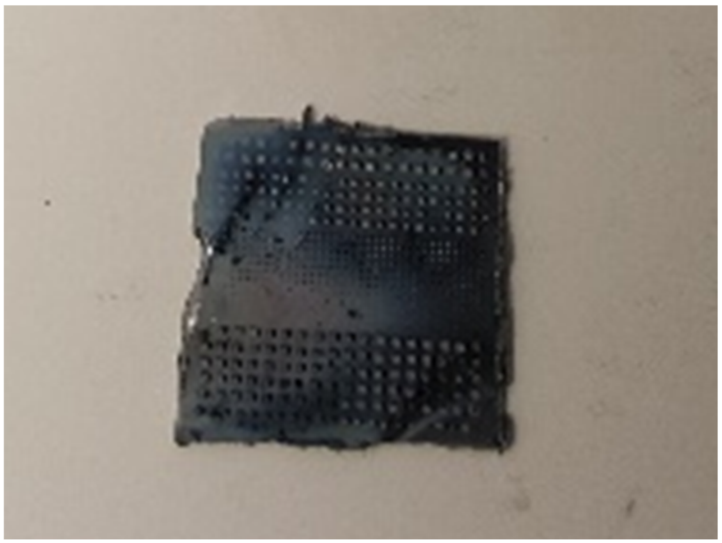
How to improve the oxidation resistance properties of VACNT-GaN patterns.

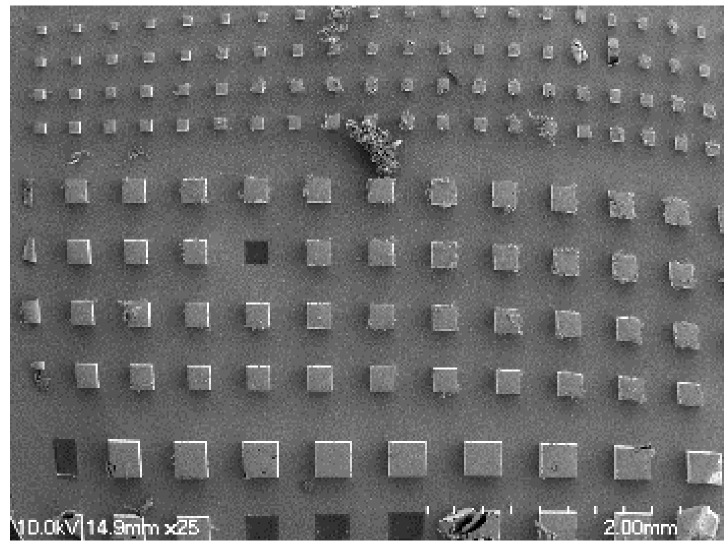
2. Accomplishments
- Fabricating VACNT-GaN-Si structure



2. Accomplishments
- Fabricating VACNT-GaN-Si structure

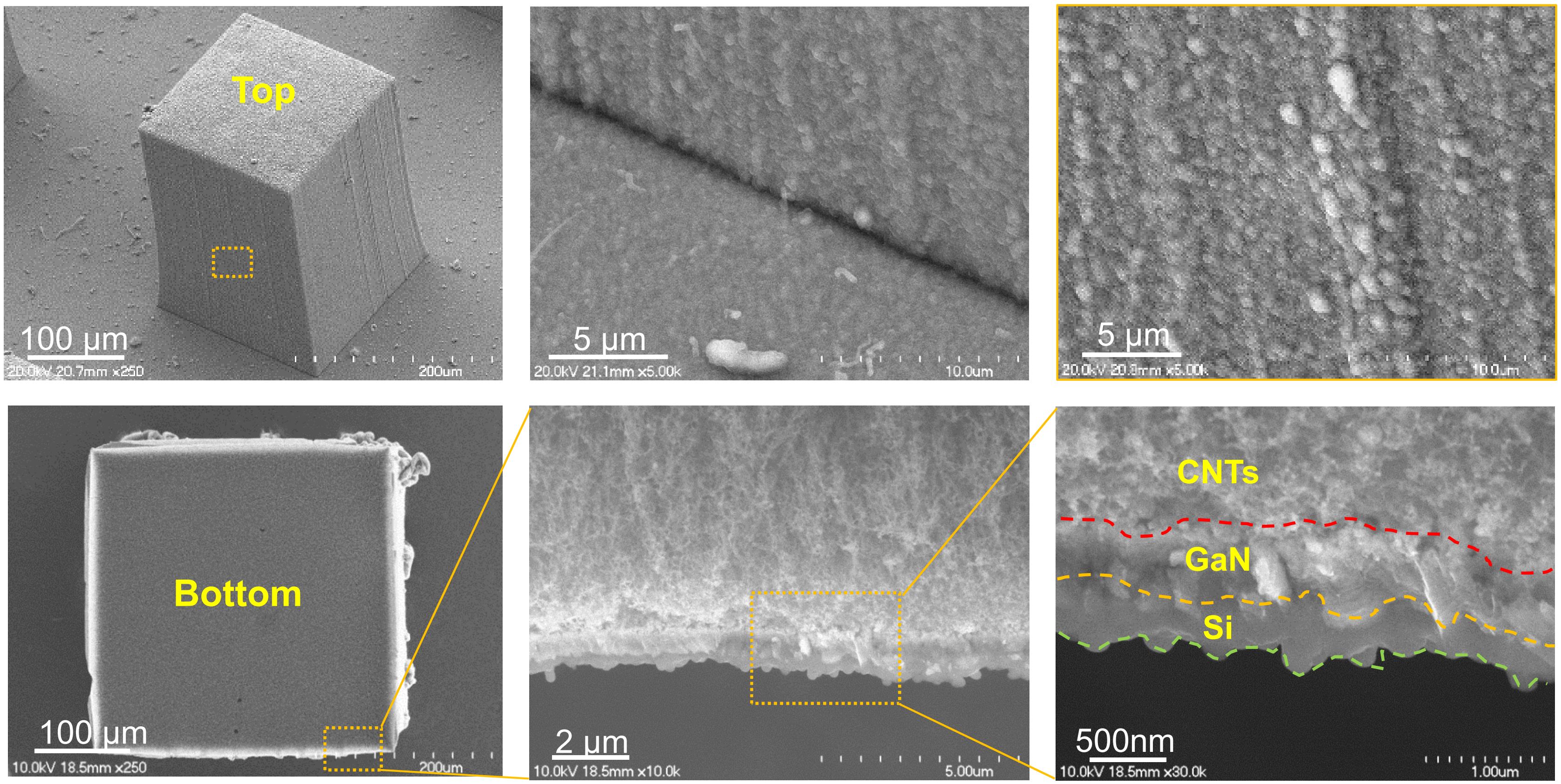
VACNT-GaN-Si patterns





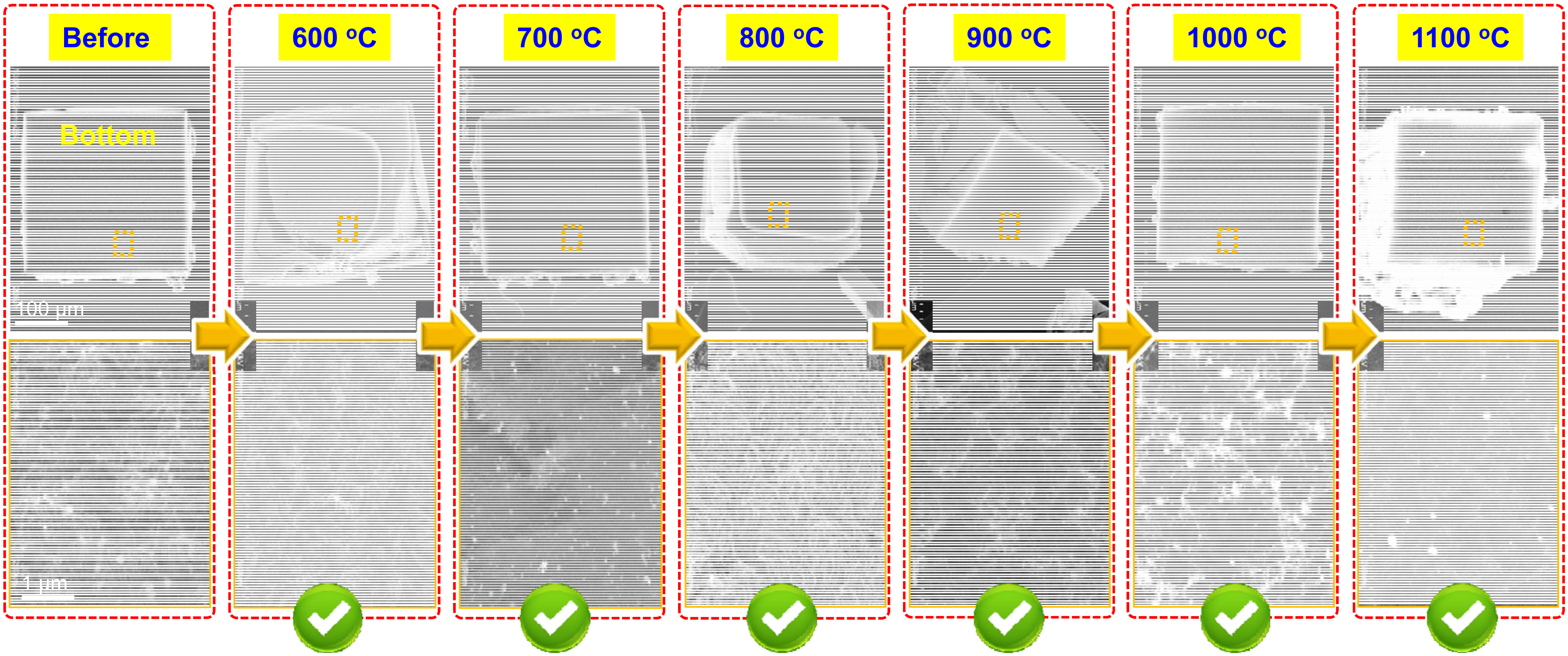
2. Accomplishments
- Fabricating VACNT-GaN-Si structure

VACNT-GaN-Si patterns



2. Accomplishments
- Fabricating VACNT-GaN-Si structure

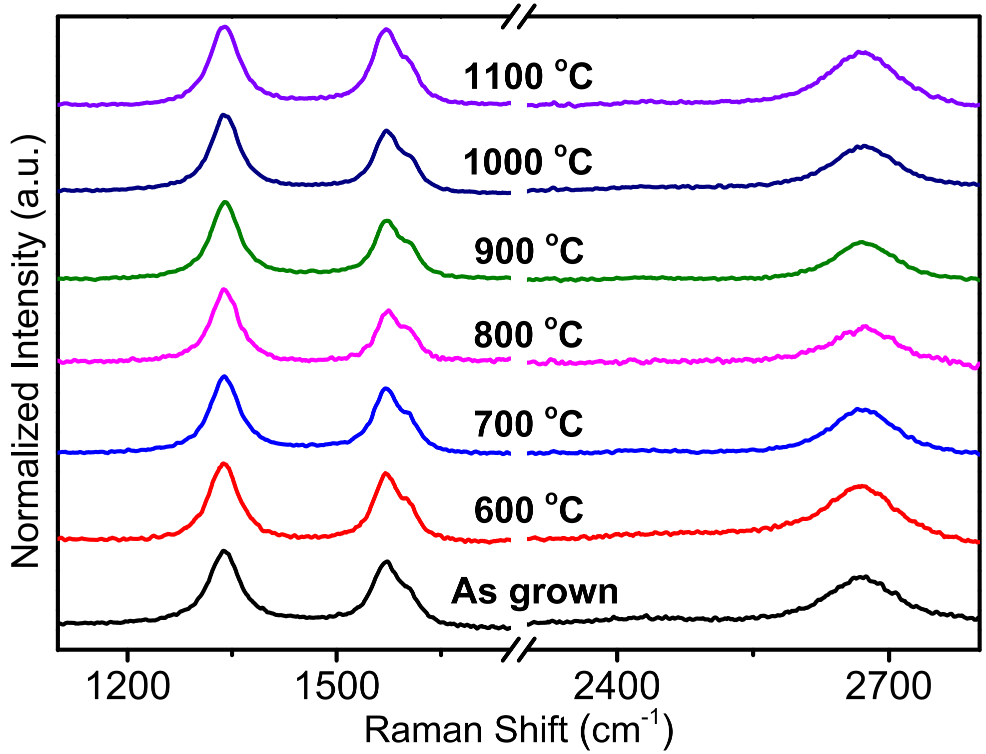
Oxidation resistance test



2. Accomplishments

- Fabricating VACNT-GaN-Si structure

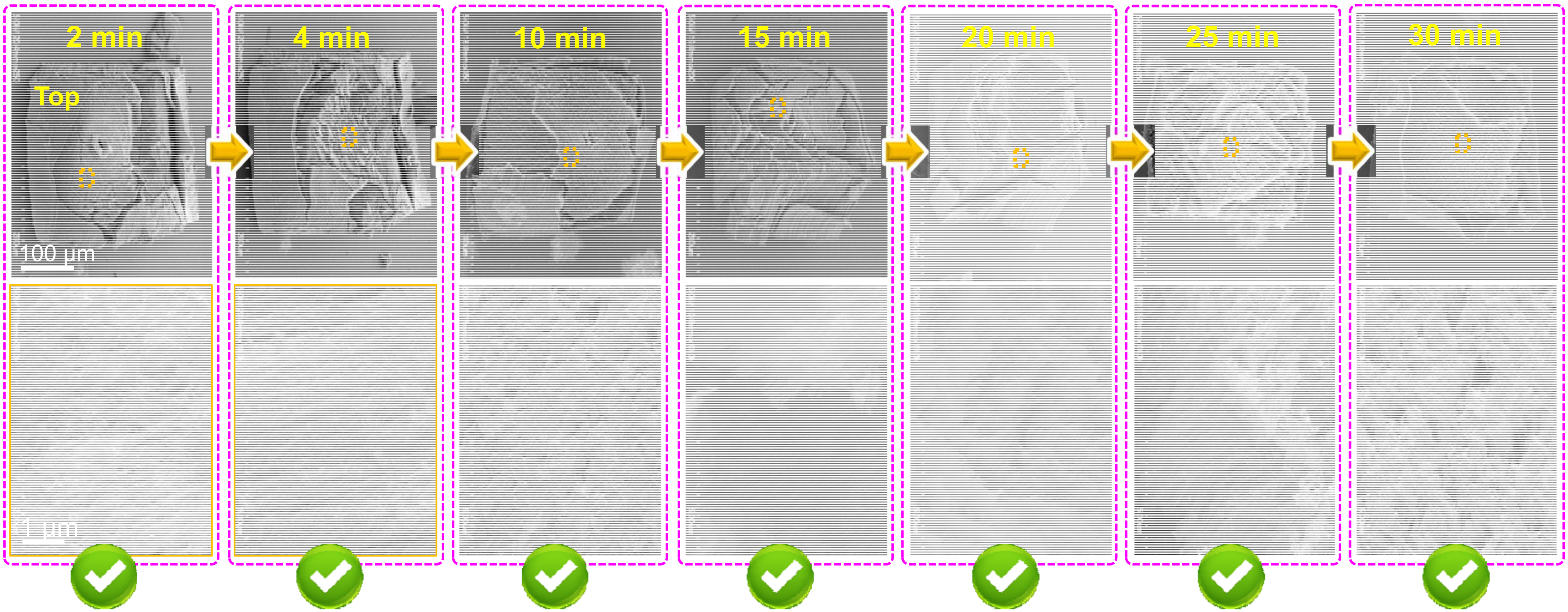
Oxidation resistance test



2. Accomplishments

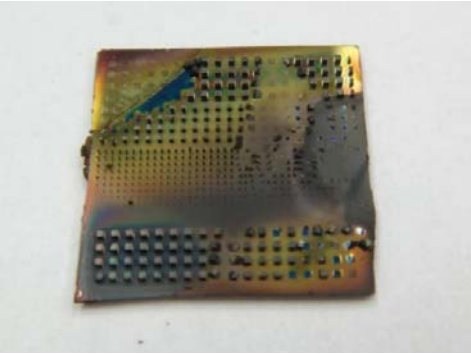
- Fabricating VACNT-GaN-Si structure

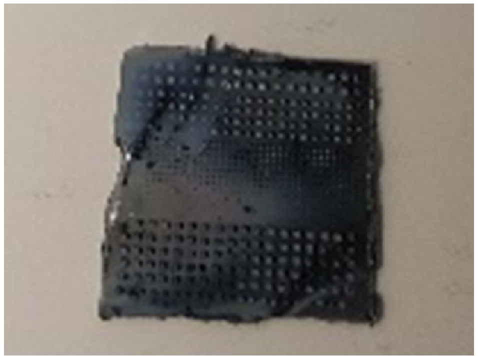
Time-dependent oxidation resistance at high temperature (1000 °C)



2. Accomplishments
- Fabricating VACNT-GaN-Si structure

VACNT-GaN and VACNT-GaN-Si structures were obtained.





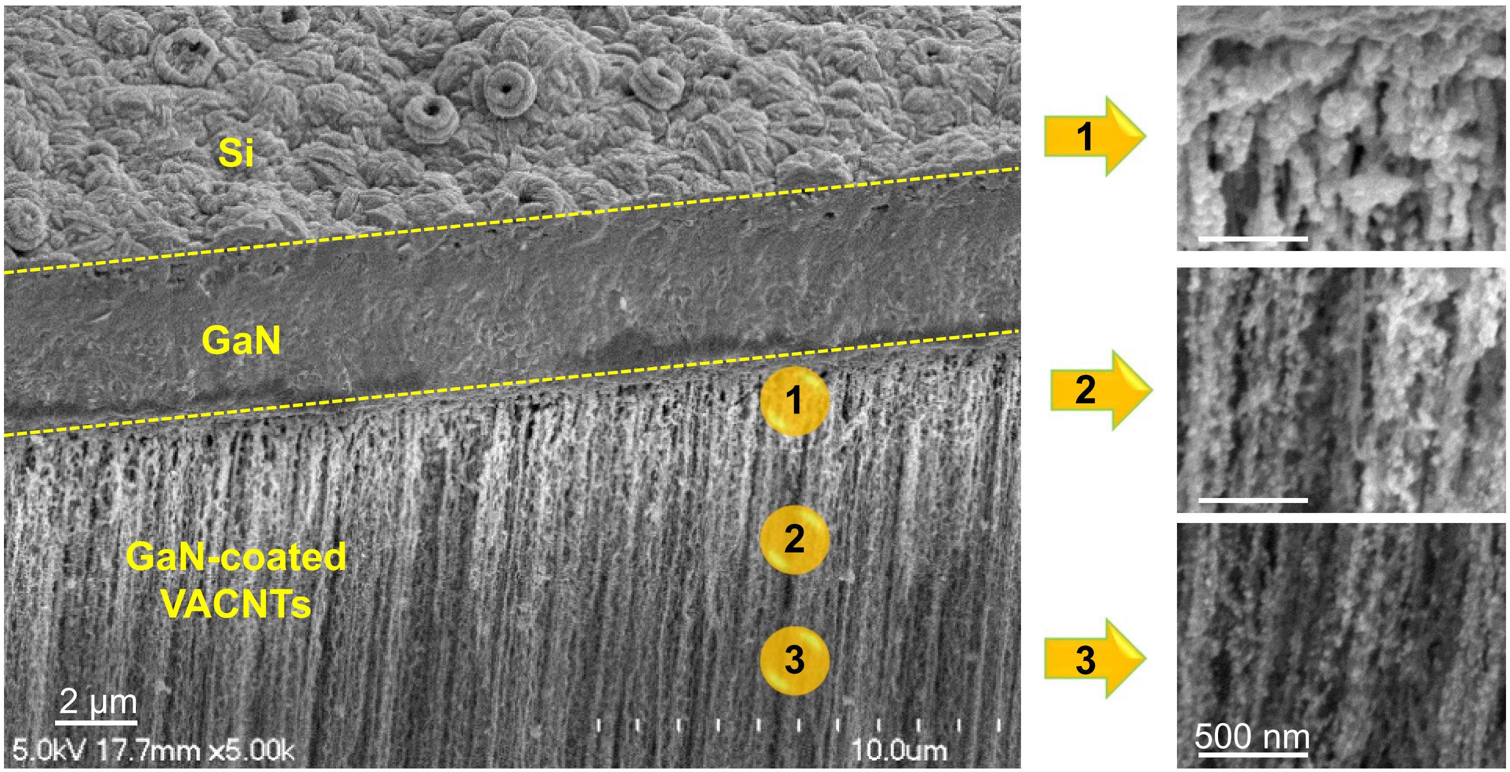
2. Accomplishments
- Fabricating VACNT-GaN-Si structure

How to realize VACNT-ceramic infiltrated structure.

2. Accomplishments

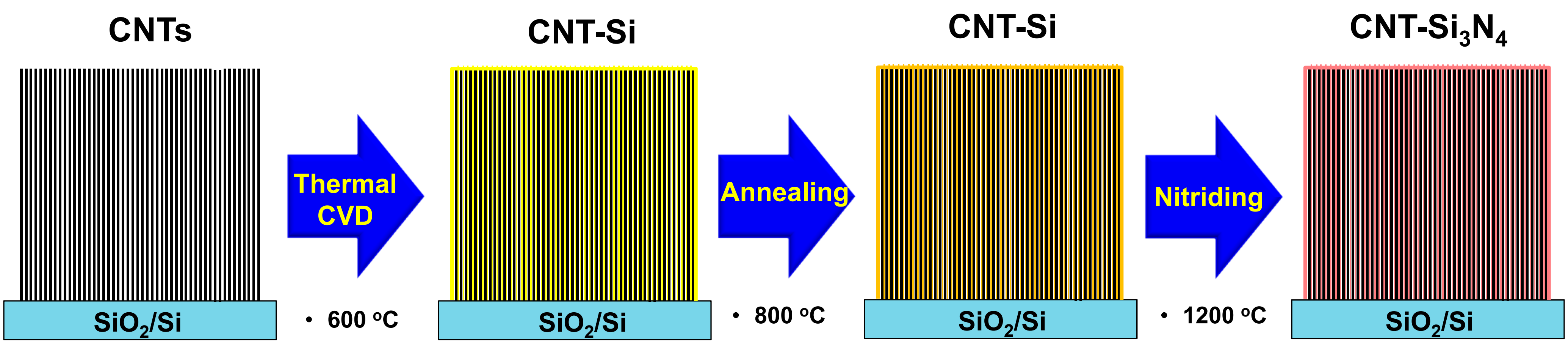
- Fabricating VACNT-ceramic infiltrated structure

Is it possible to realize VACNT-GaN-Si infiltrated structure ???



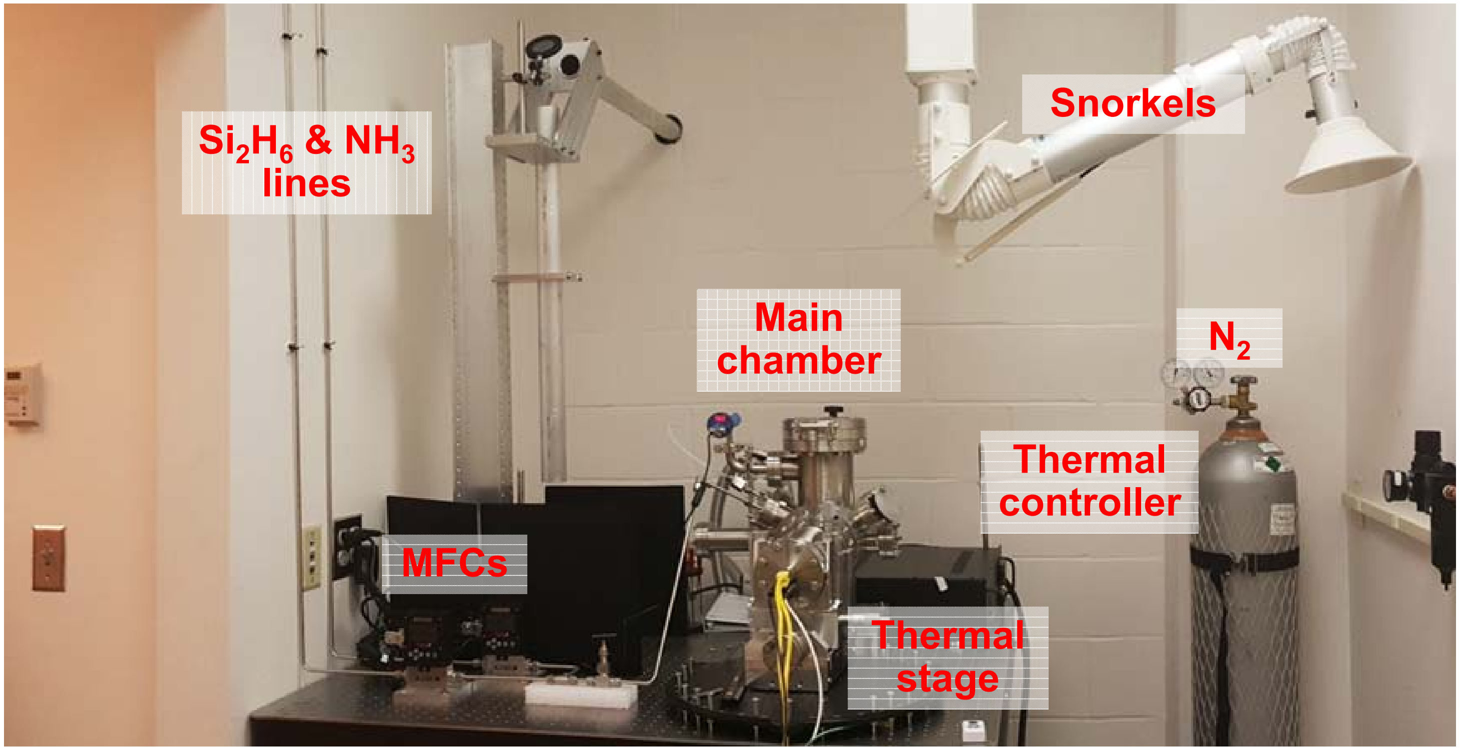
2. Accomplishments
- Fabricating VACNT-ceramic infiltrated structure

Fabricating VACNT-Si_3N_4 infiltrated structure



2. Accomplishments
- Fabricating VACNT-ceramic infiltrated structure

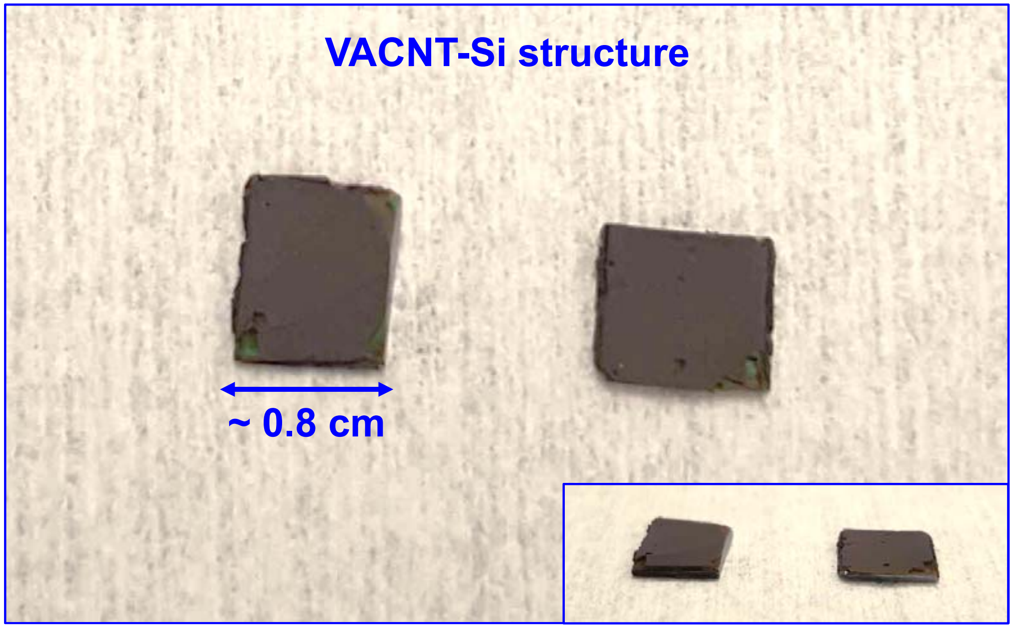
Vacuum thermal CVD system used for Si (Si_3N_4) deposition

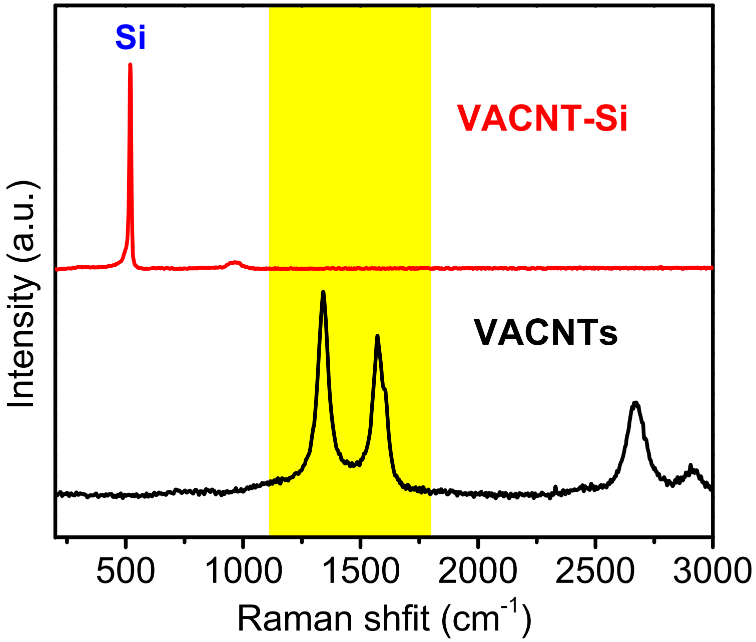


Parameter	Value
Precursor	Si_2H_6 (10%)
Carrier gas	N_2 (90%)
Temperature	600 °C
Chamber pressure	1 Torr
Heating rate	120 °C/min
Growth time	30 min

2. Accomplishments
- Fabricating VACNT-ceramic infiltrated structure

Fabricating VACNT-Si structure

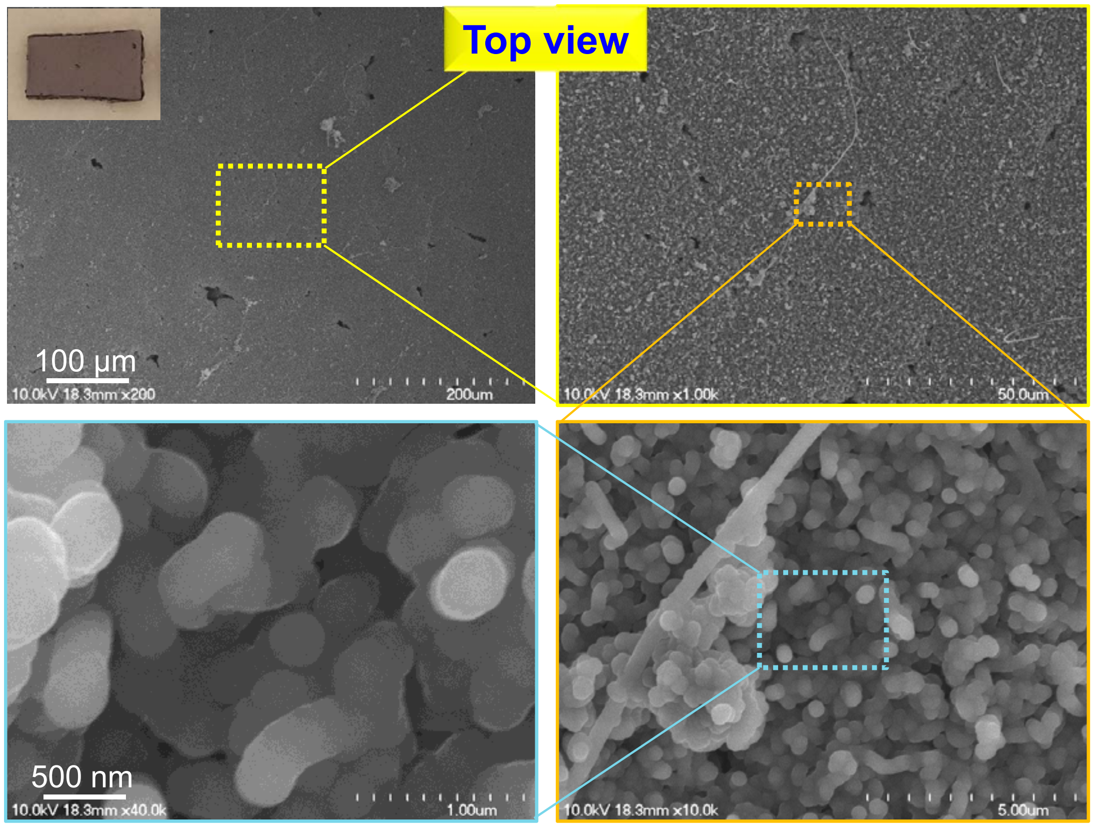




2. Accomplishments

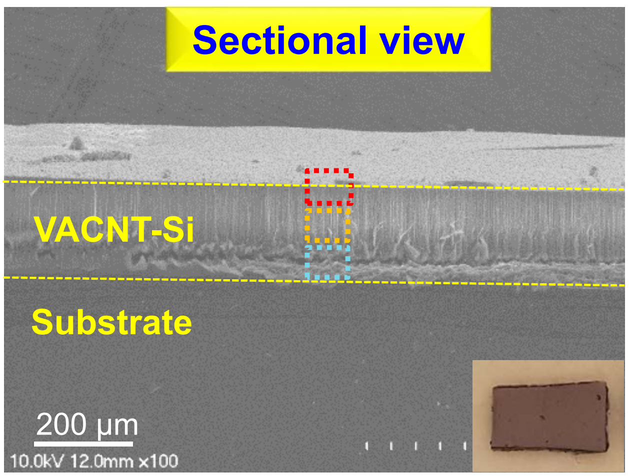
- Fabricating VACNT-ceramic infiltrated structure

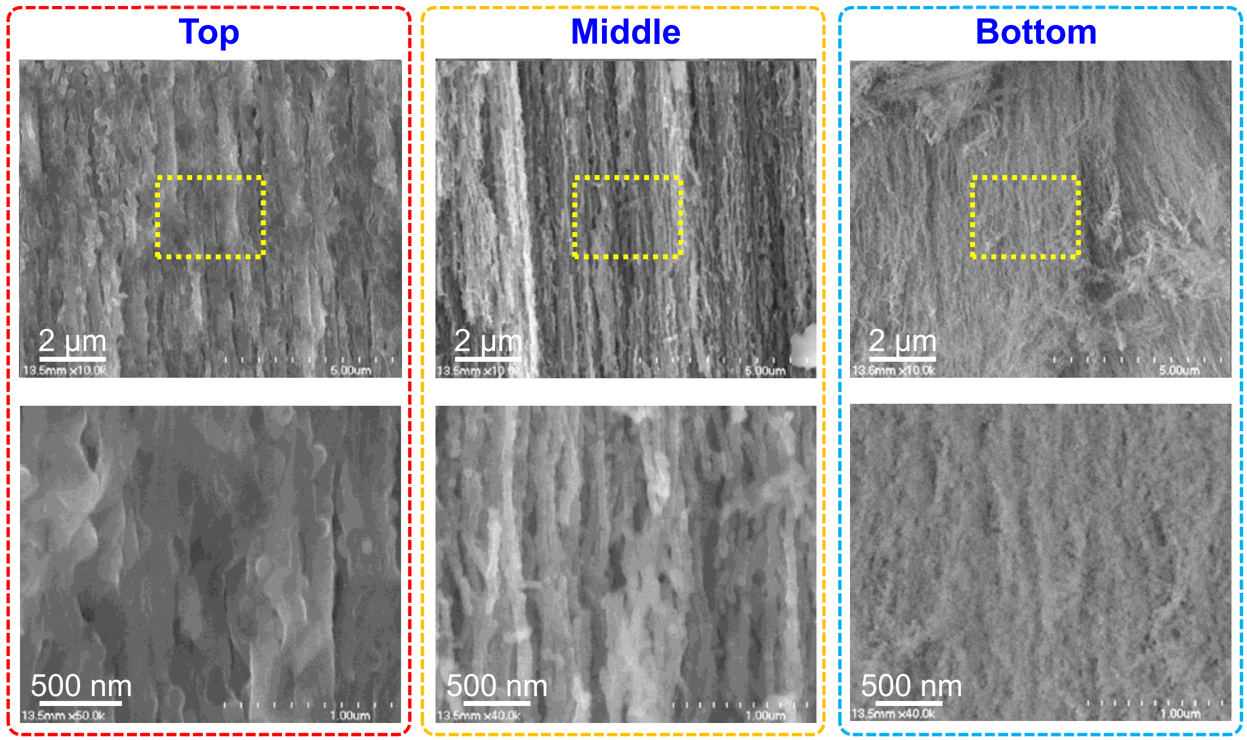
Fabricating VACNT-Si structure



2. Accomplishments
- Fabricating VACNT-ceramic infiltrated structure

Fabricating VACNT-Si structure

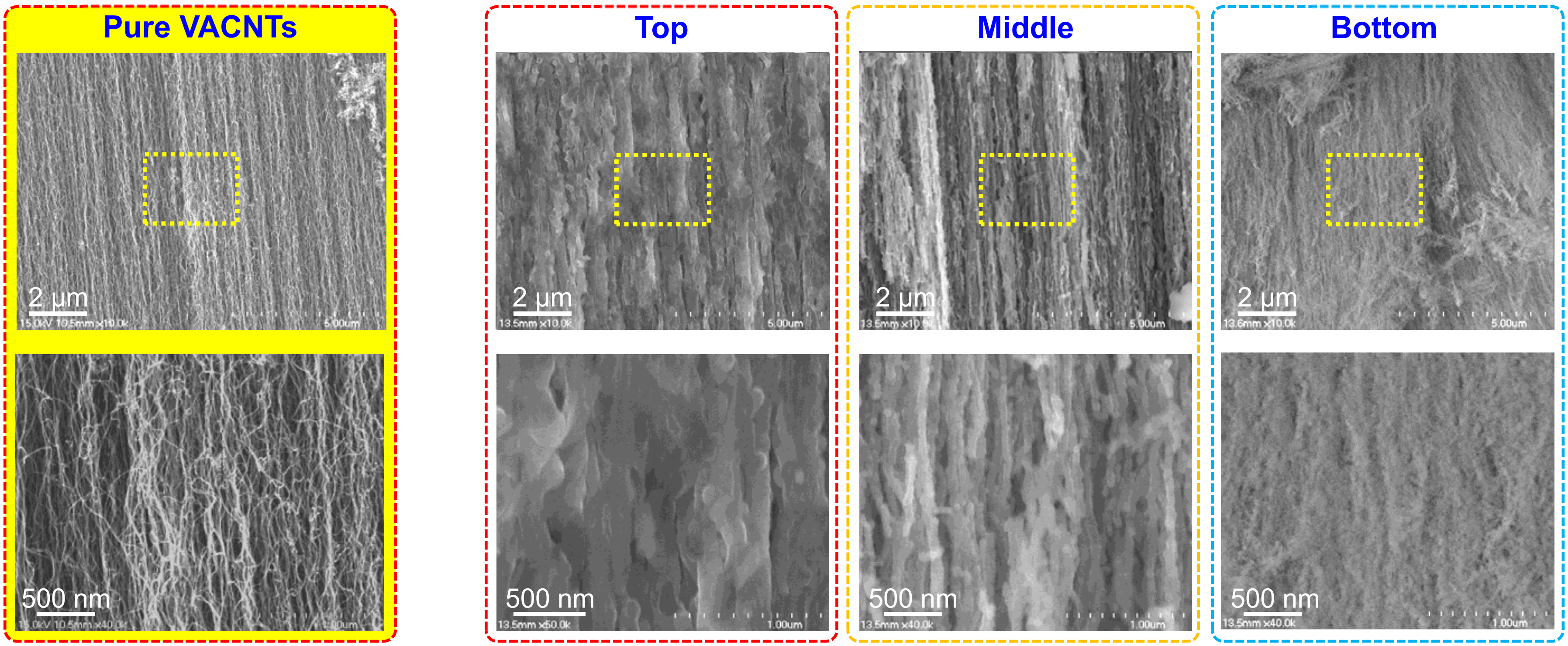




2. Accomplishments

- Fabricating VACNT-ceramic infiltrated structure

Fabricating VACNT-Si structure

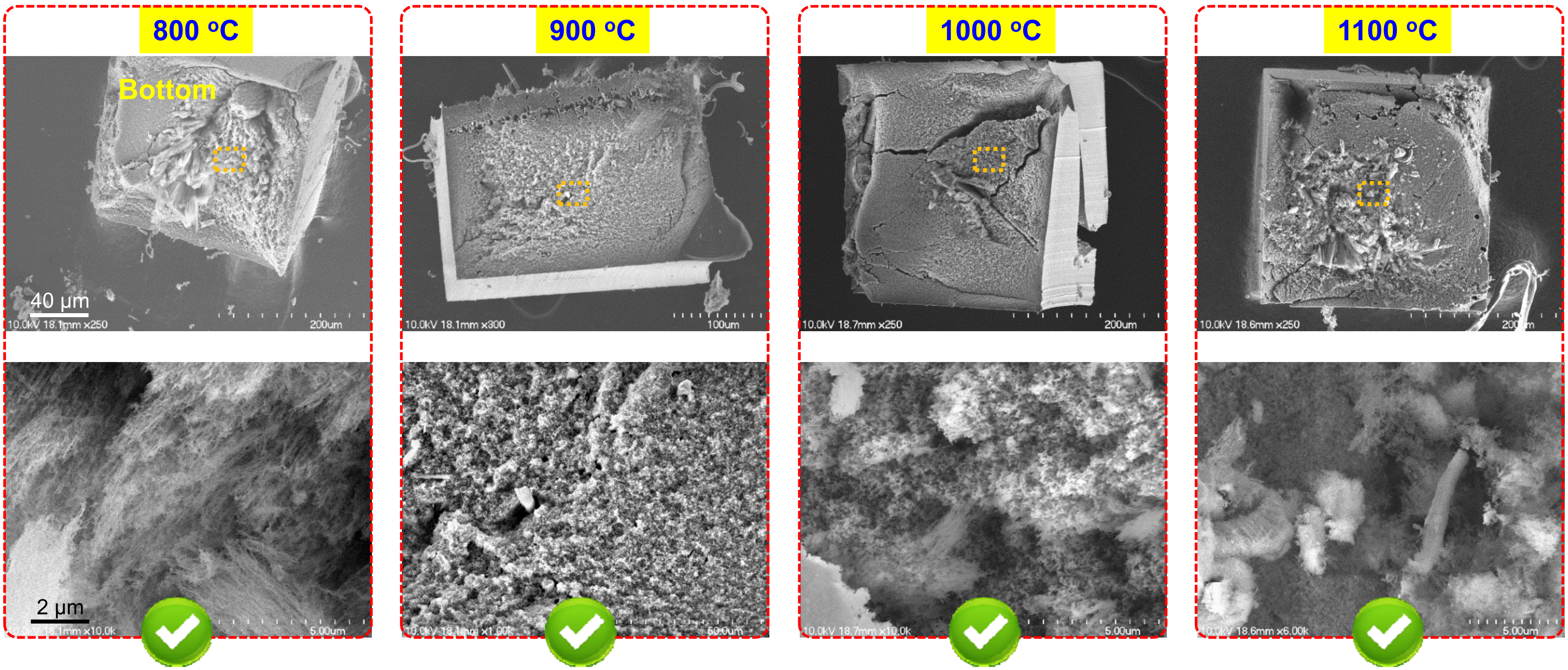


VACNT-Si infiltrated structures were obtained.

2. Accomplishments

- Fabricating VACNT-ceramic infiltrated structure

Oxidation resistance of VACNT-Si infiltrated structure



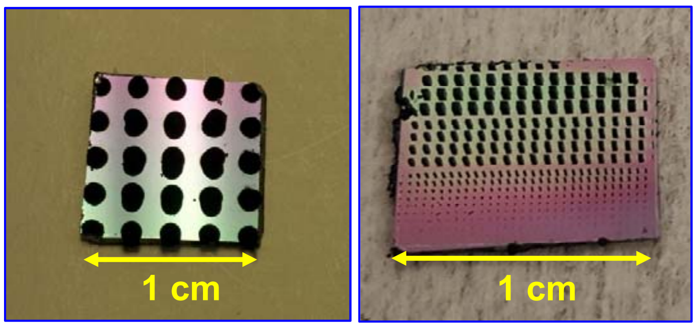
2. Accomplishments

- Summary

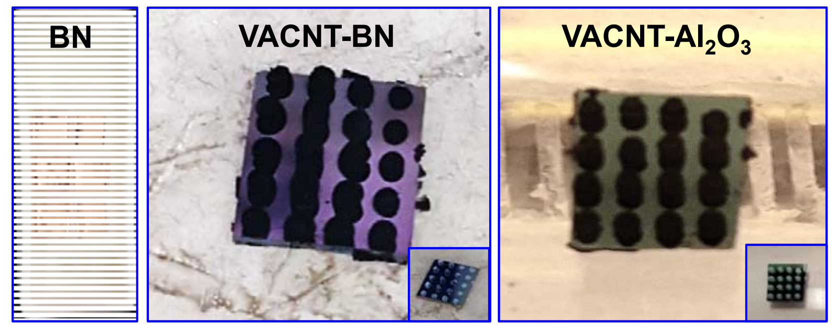
1) Obtained large and small VACNT patterns
2) Obtained BN film on Cu foil
3) Obtained patterned VACNT-BN and VACNT-Al_2O_3 structures with poor oxidation stability
4) Obtained patterned VACNT-GaN-Si structure with good oxidation stability (1100 ^oC)
5) Obtained high-temperature electrical conductivity of the VACNTs
6) Obtained VACNT-Si infiltrated composite structure with high oxidation stability/electrical conductivity

3. Deliverables

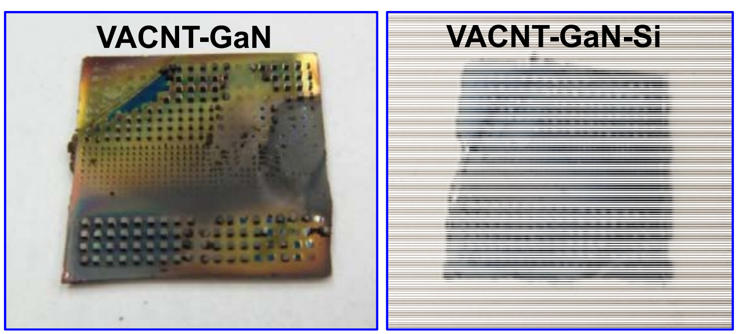
1) Large and small VACNT patterns



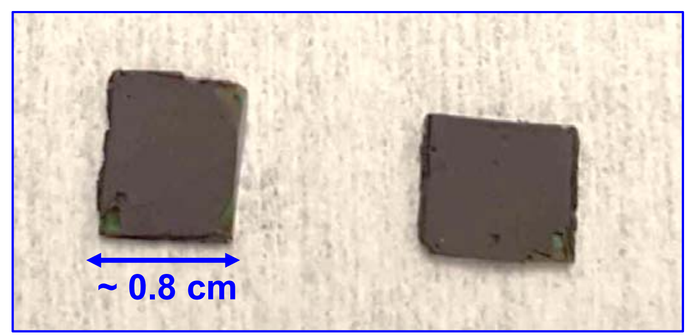
2) BN, VACNT-BN and VACNT-Al_2O_3 structures



3) VACNT-GaN and VACNT-GaN-Si structures



4) VACNT-Si infiltrated composite structures



4. Future work

- Planned Activities in the Next-Phase

Tasks	Methods	Millstones	Planned Completion Date
Fabrication of CNT-Si_3N_4 composite structures	Chemical vapor infiltration using a home-made thermal CVD system	Achieving CNT-Si_3N_4 infiltrated composite structures	04/15/17
Stability studies of the CNT-Si_3N_4 composite structures	High-temperature furnace and TGA	Thermal and oxidation stabilities: ≥ 1800 K	05/15/17
Electrical and thermal conductivity studies of the CNT-Si_3N_4 composite structures	Home-made electrical conductivity measurement system (77 K to 1800 K)	Electrical conductivity: > 1 S/m; thermal conductivity: > 50 W/m·K	07/01/17
Thermionic emission current measurement of the CNT-Si_3N_4 composite structures	Acetylene torch with tungsten electrodes in air.	CNT-Si_3N_4 composite structures can be used as good emitters	09/30/17

5. Student Training

Student	Program	Training
Qiming Zou Lydia Wemhoff Dawei Li	PhD student Undergrad student Postdoc researcher	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!