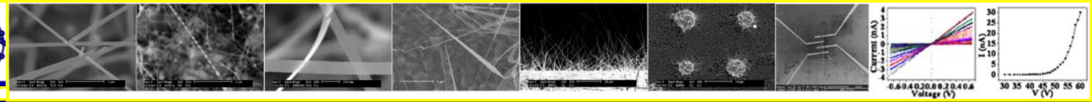
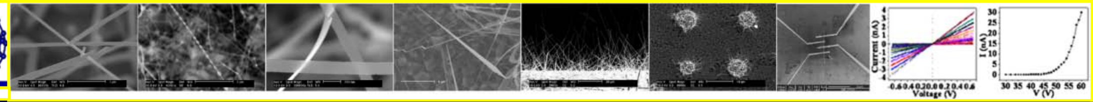


Boron Nanowires for Flexible Electronics and Field Emission

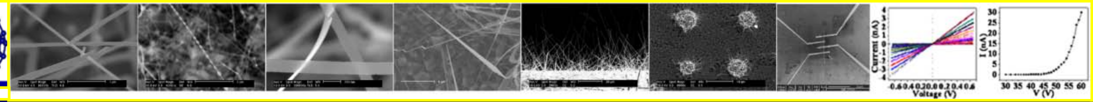
Hongjun Gao and Jifa Tian

Institute of Physics, CAS, Beijing, China



OUTLINE

- Introduction
- Four Probe STM Setup: Imaging and I-V Measurements
- Boron Nanostructures: synthesis and characterization
- Properties of Boron Structures: electrical, mechanical and field emission
- Conclusions



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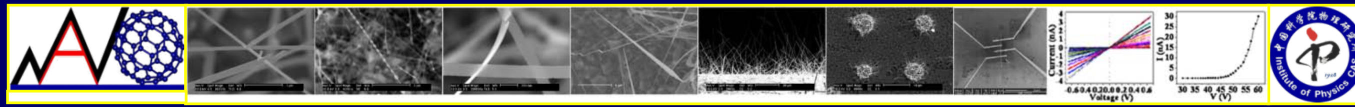
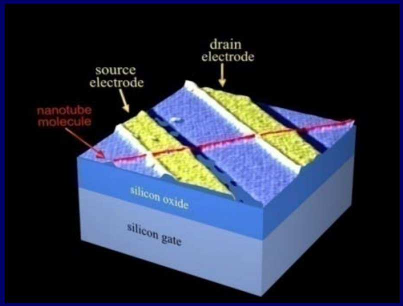
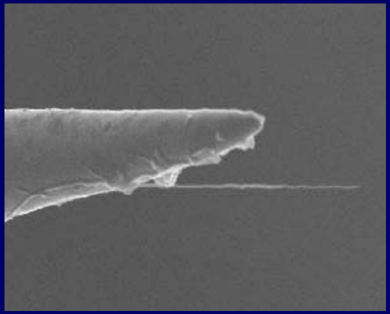


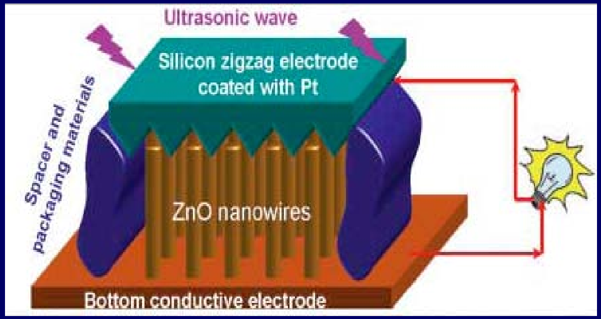
1D Semiconductor Nanostructures

- Nanotechnolgy: Work at the atomic, molecular and supramolecular levels, in order to understand and creat materials , devices and systems with fundamentally new properties and functions becasue of their small structures.
- 1D nanostructures: 1/1000 the size of a human hair, high surface area to volume ratio, ranges from 10 nm to 100 nm in diameter
- Synthesis techniques: laser ablation, CVD, MOVPE, CBE, MBE....
- Applications: Nanotransistors, field emitters, energy and charge Storage …

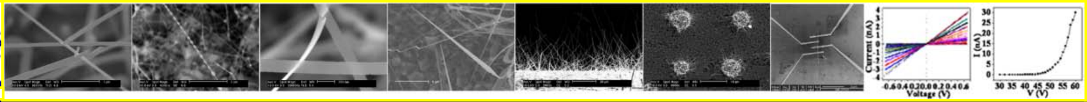


Nature 393 (1998)


IPN CNT group



Science 316 (2207)



Flexible Technology and Field Emission

Circuits

Displays

Flexible nanomaterials: inorganic semiconductors and organic conducting materials.

Challenge: (1) The high-performance inorganic electronic materials such as silicon tend to fracture under 1% tensile strain. (2) Carbon nanotubes have shown great promise for applications in flexible electronics, ill control of structural chirality makes them a big challenge for being useful in high-performance integrated circuits.

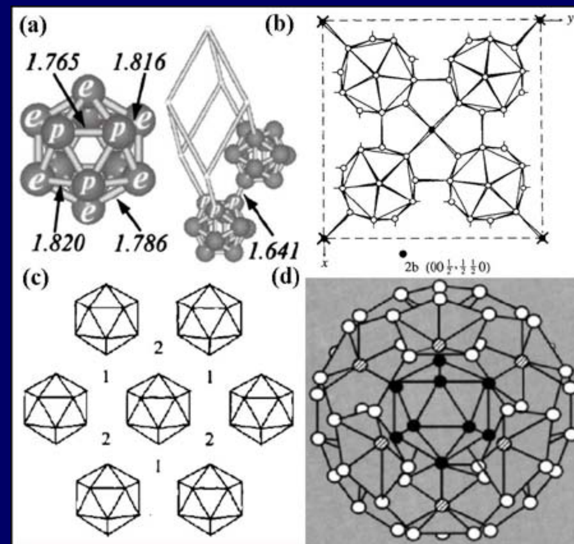
New materials and techniques need to be developed!

Boron

Properties:

- Low density，2.364 g/cm^3 ；
- High melting point，2300 ℃；
- Large bulk Young's modulus of 380–400 GPa
- Extreme hardness close to diamond
- Only non-metallic element that has fewer than 4 electrons in its outer shell；
- Unusual three-center sp2 hybrid valence bond
- Electron configuration is 1s22s22p
- Poor conductor at room temp but good at high temps

Structures:



(a) B_{12} icosahedron

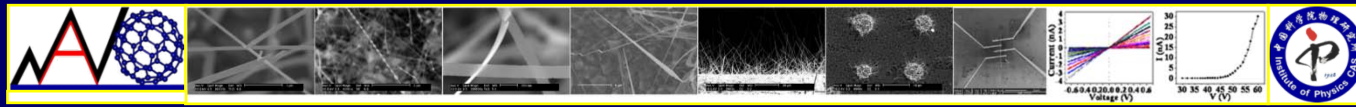
(b) Tetragonal B

(c) α- rhombohedral B

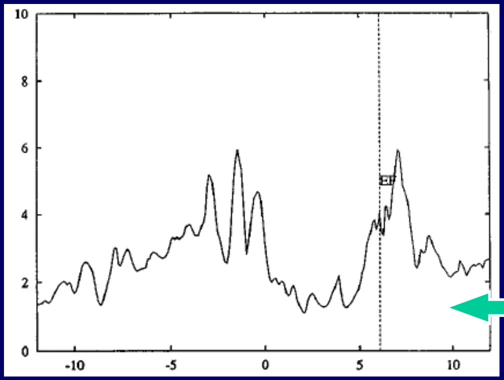
(d) β- rhombohedral B

Applications:

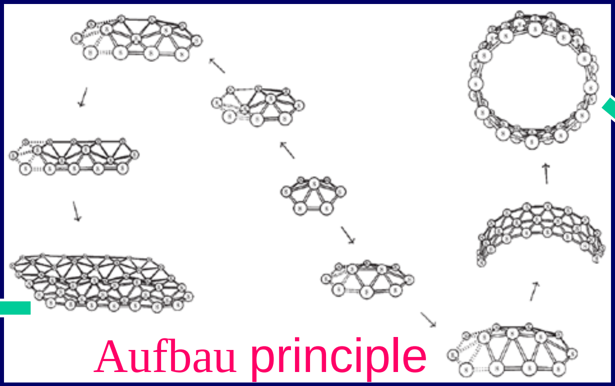
- **Lightweight coating；**
- **High-temperature semiconductor devices；**
- **Neutron absorbent；**
- **Surface catalyst**



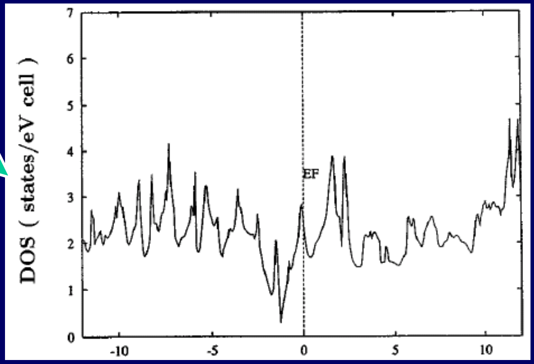
Theoretical Work on Boron Nanostructures



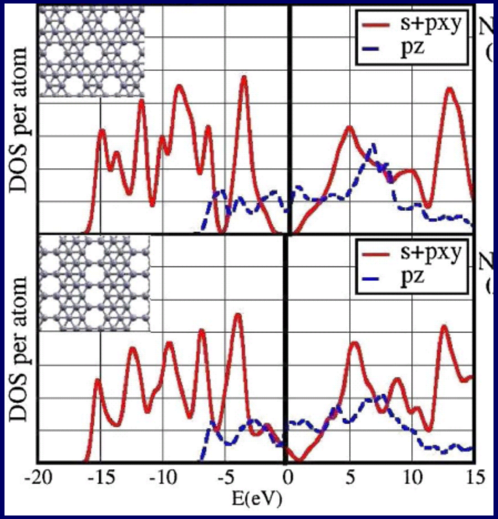
J. Chem. Phys. 110 (1999) 3176



Boron NT and sheet can be formed by B_7 cluster.

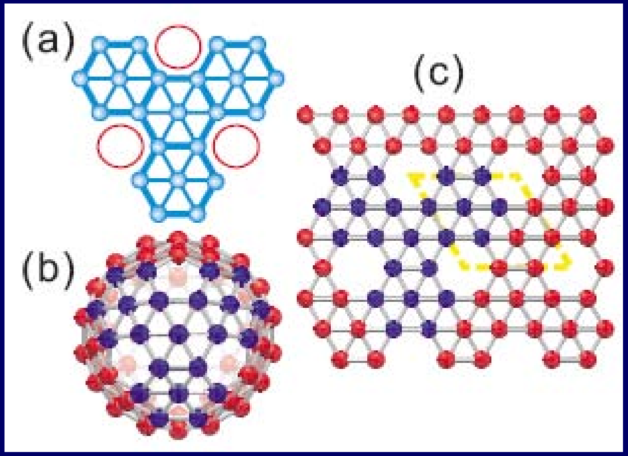


ChemPhysChem 6 (2005) 2001

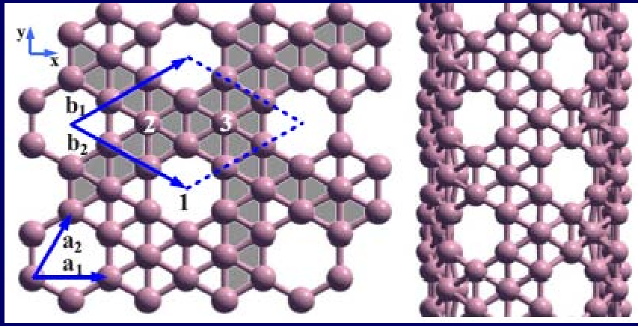


Chirality

PRL 99 (2007) 115501

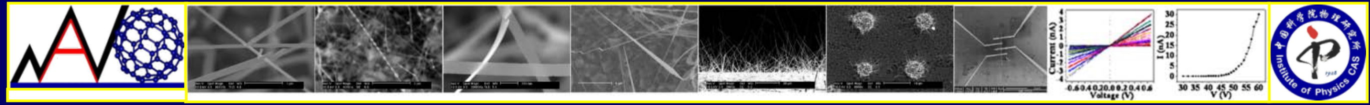


PRB 78 (2008) 201401



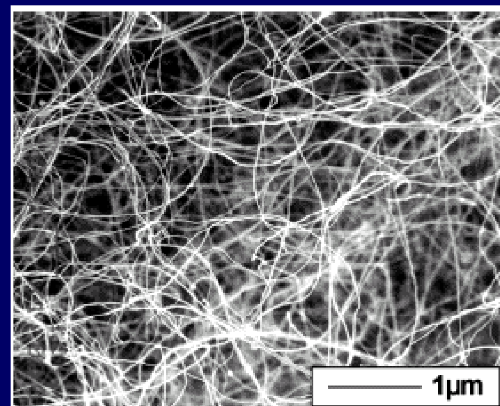
PRB 77 (2008) 041402

Can boron nanotube be synthesized?

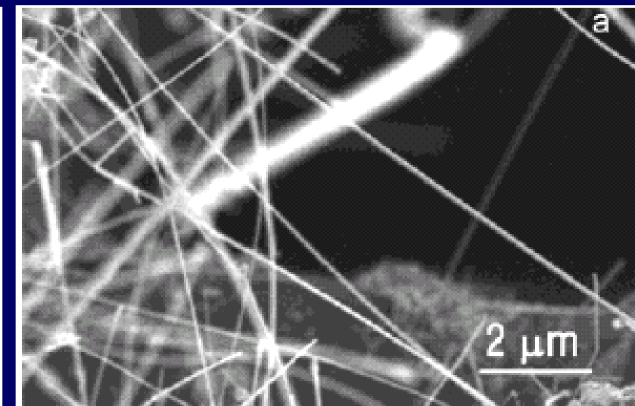


Experimental Work on 1D Boron

Adv. Mater. 2001 *13* 1701

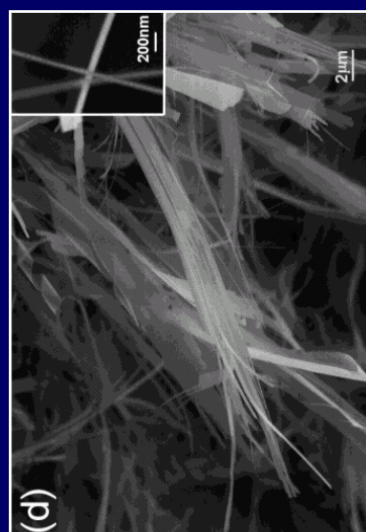


Adv. Mater. 2001 *13* 1487



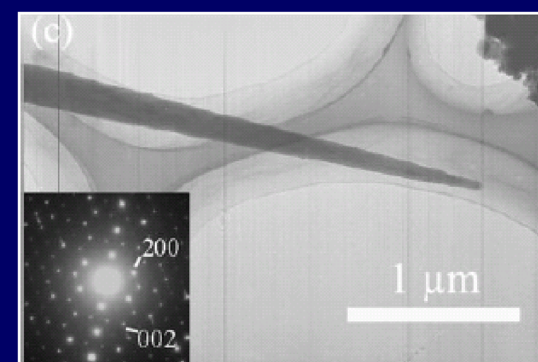
J Am. Chem. Soc. 2002 *124* 4564

Chem. Comm. 2002 2806



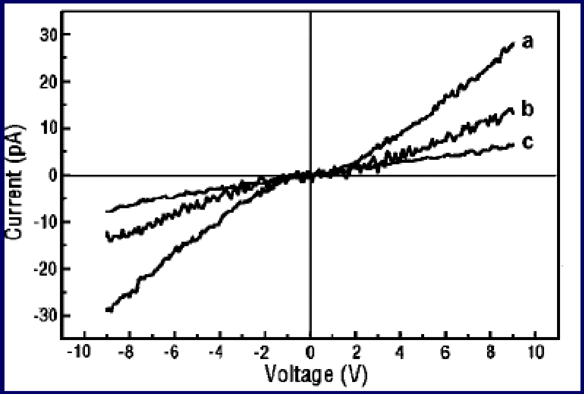
Nano Lett 2004 *4* 963

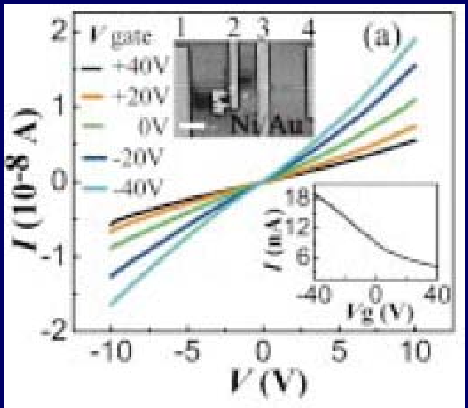
Nano Lett 2006 *6* 385

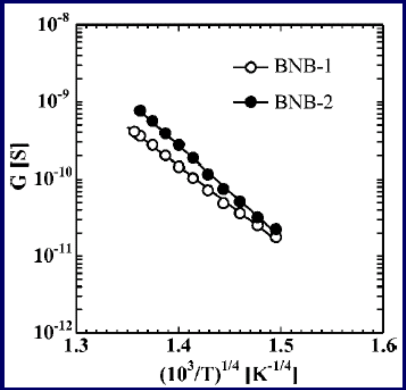


H. J. Gao *et al.*
Adv. Mater 2007 *19* 4480

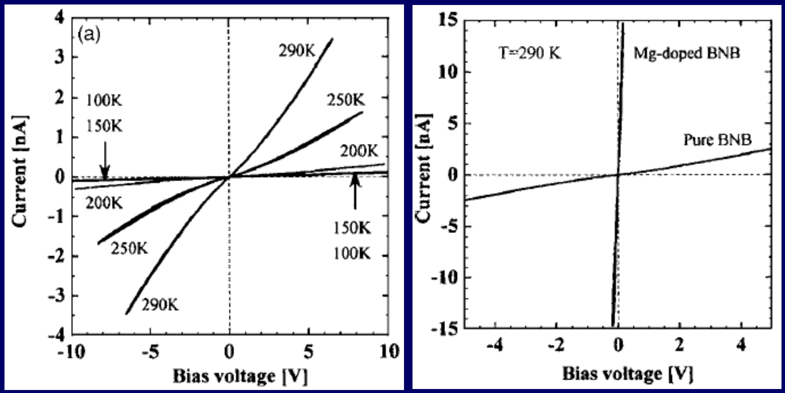
Properties of Boron Nanostructures

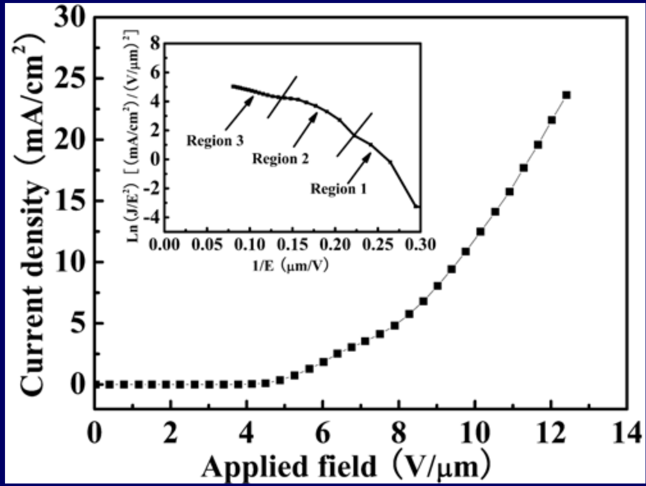






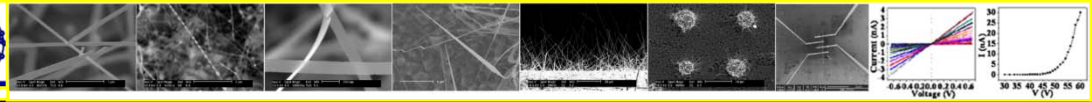
J AM CHEM SOC 2002 124 4564 Appl. Phys. Lett. 2003 83 5280 Appl. Phys. Lett. **86**, 212101 (2005)





J. Vac. Sci. Technol. B 23 2005 2510

H. J. Gao *et al*. Adv. Mater 2007 *19* 4480



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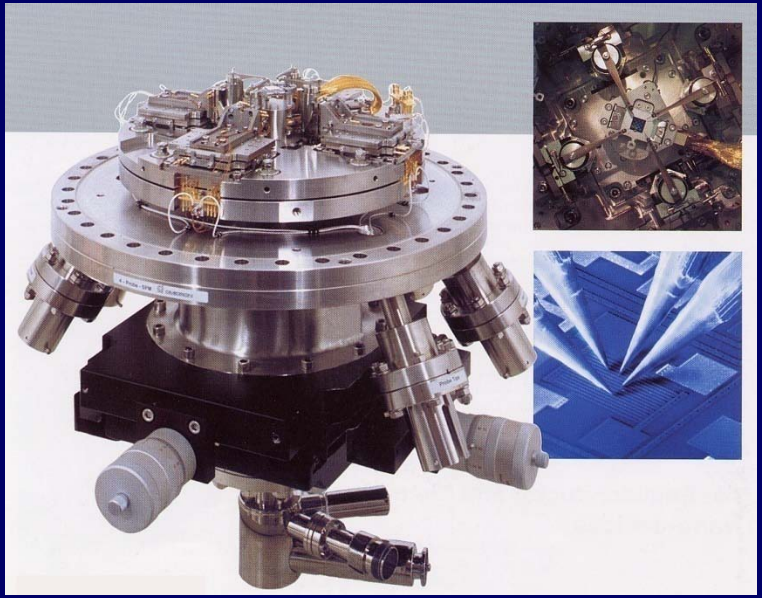
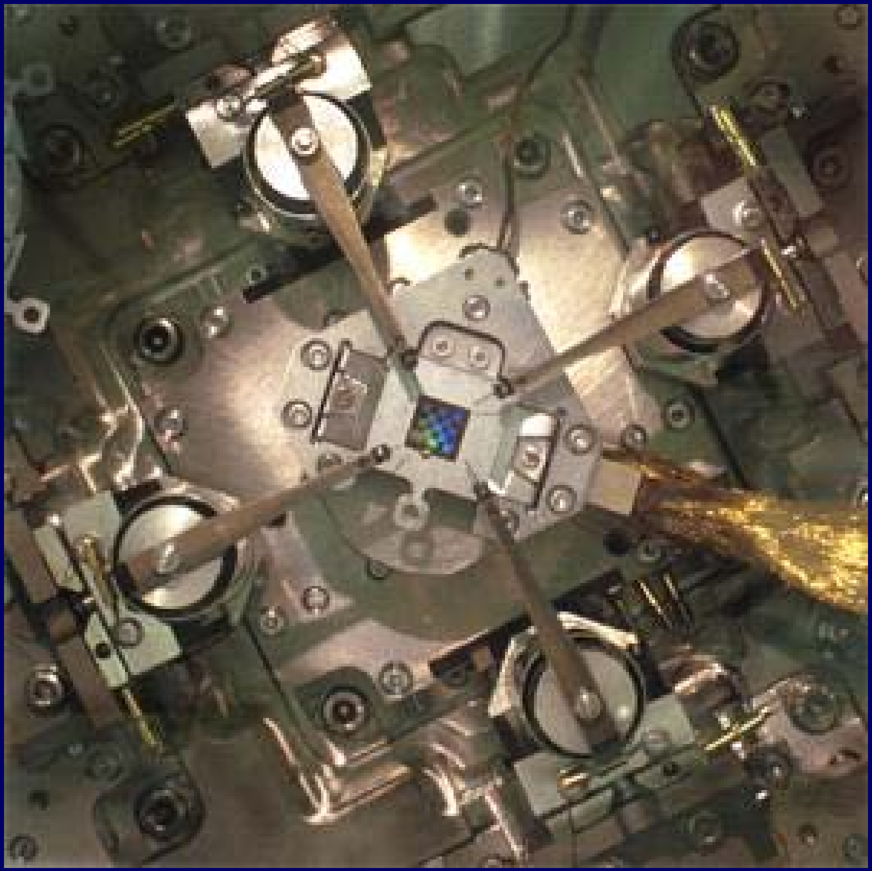
MBE-FSTM Combined System

MBE

Four probe STM

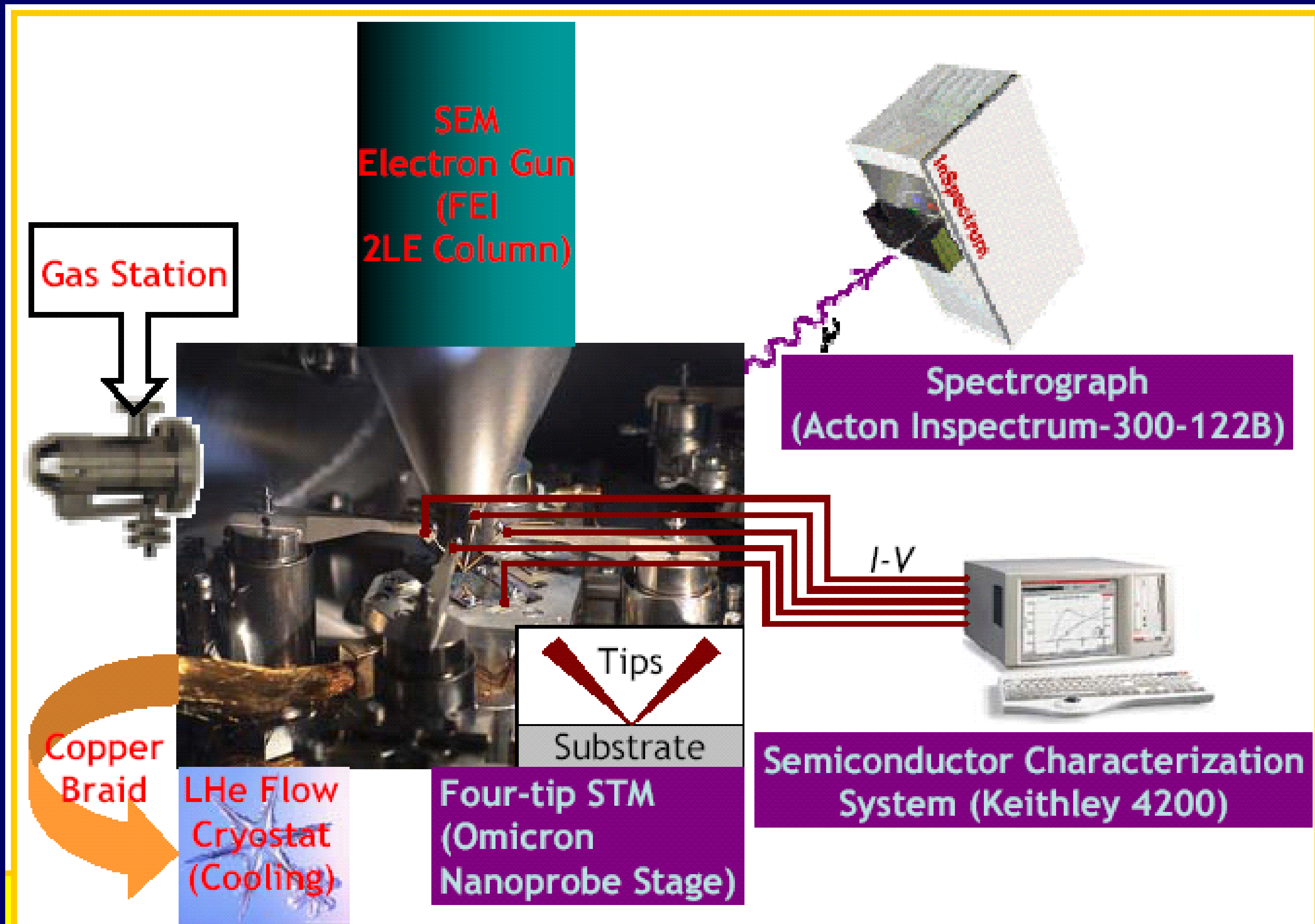
Nanoprobe Stage





- Four independent STMs
- Atomic resolution
  (with IDE air spring)
- Temperature: from 30K to 500K
  (with CryoVac)

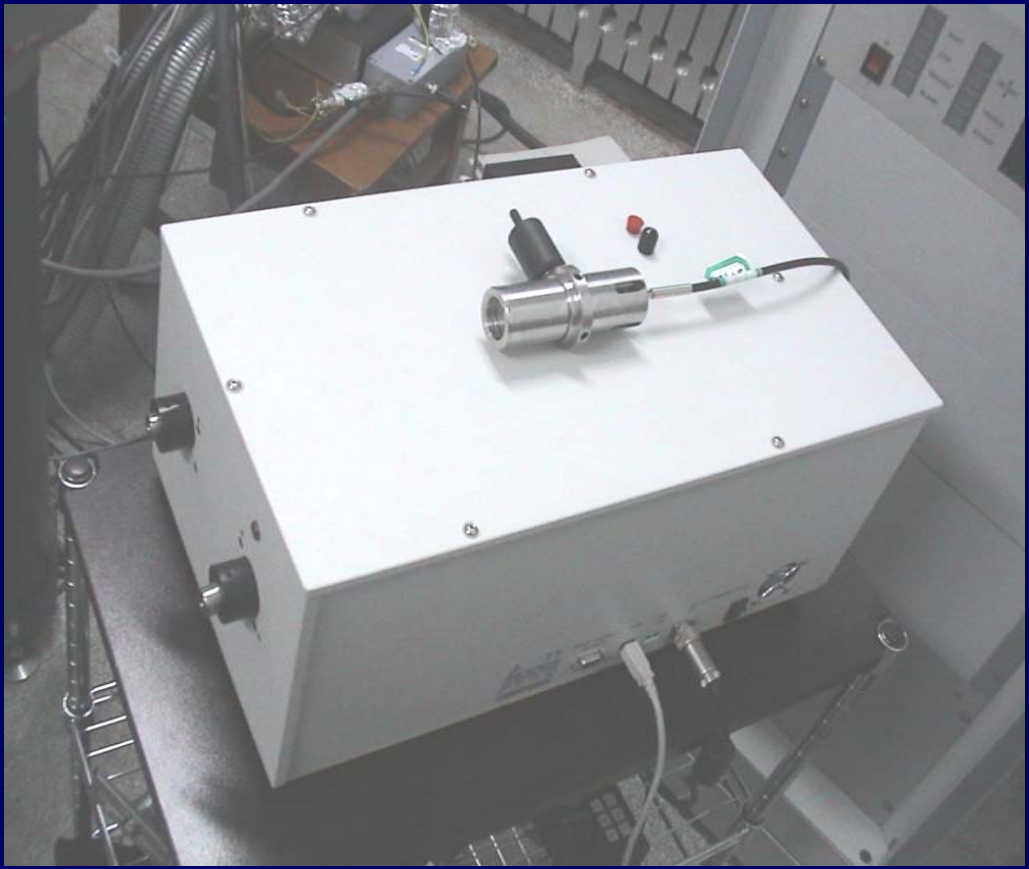
Four Probe STM System



I-V Measurements with Keithley SCS-4200

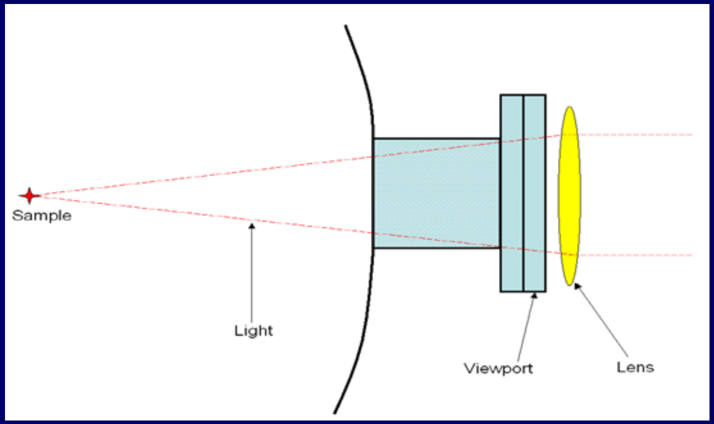
- Three independent source-measure units (SMUs) and their preamplifiers (PAs)
- Common ground unit (GNDU)
- Capable for four-terminal-method
- Current resolution: 1E-15A
- Programmable for auto

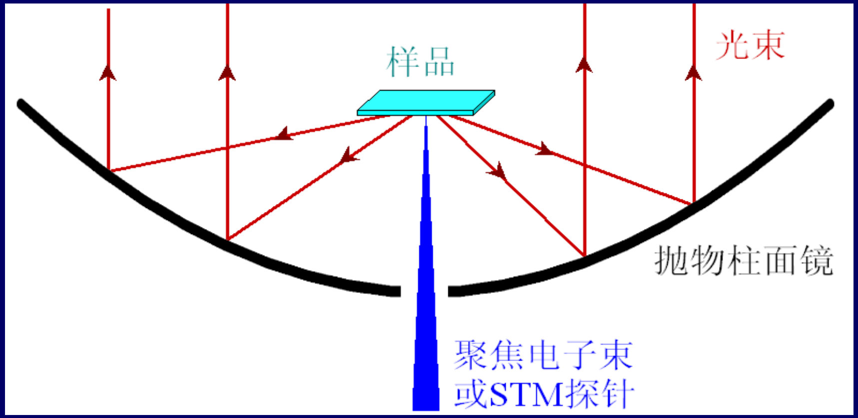
Optical Property Measurements with Acton Inspectrum-300-122B

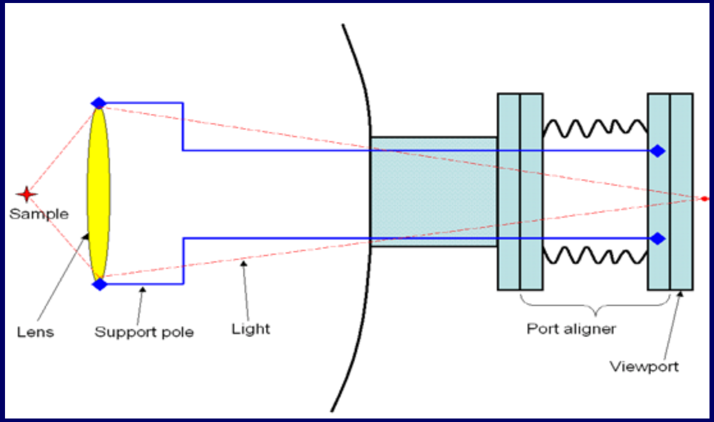


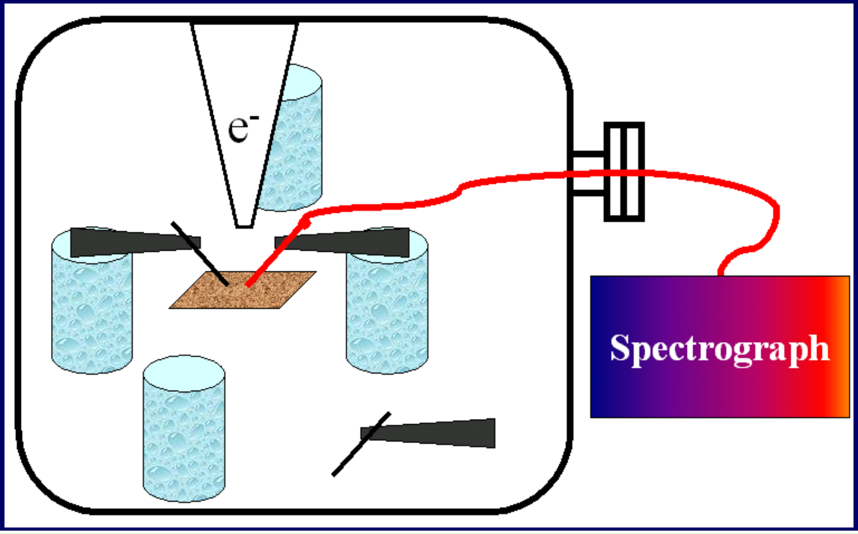
- Wavelength: 200 ~ 900nm
- Resolution: 0.2nm
- CL spectrum (SEM) & tunneling current induced photon emission (STM)
- Others after slight alteration in inducing source

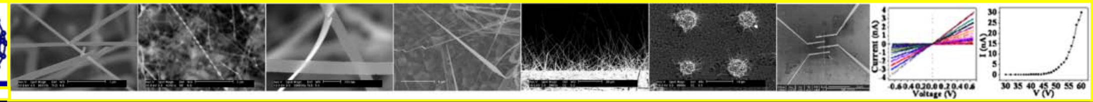
Optical Measurements Setup



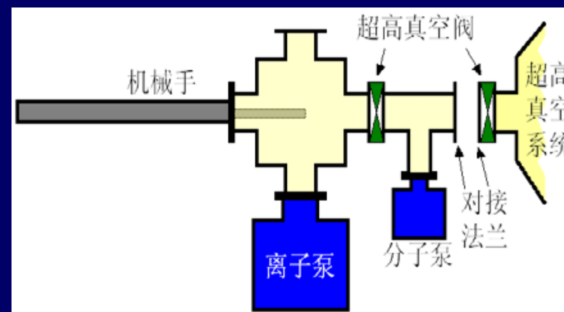


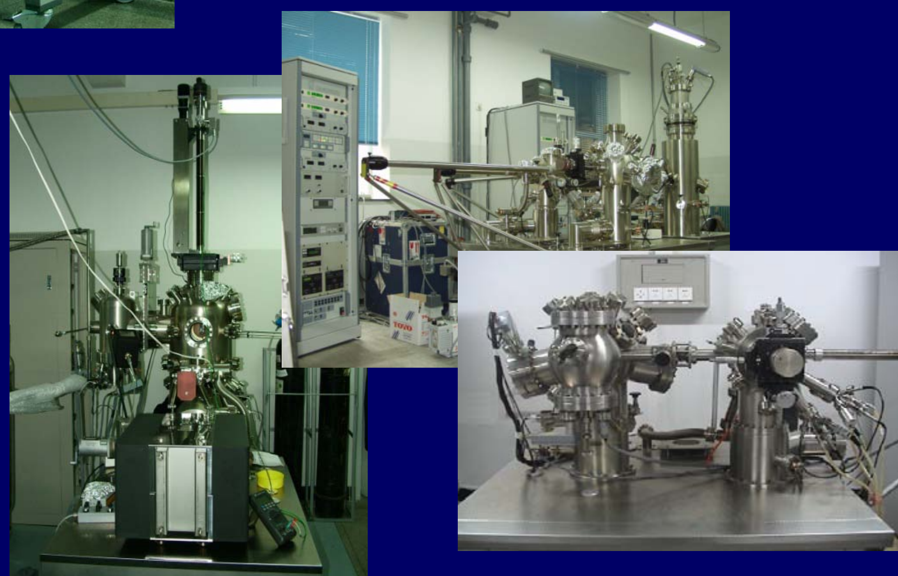


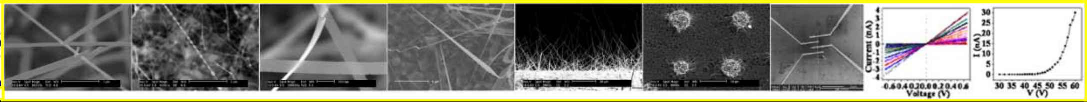




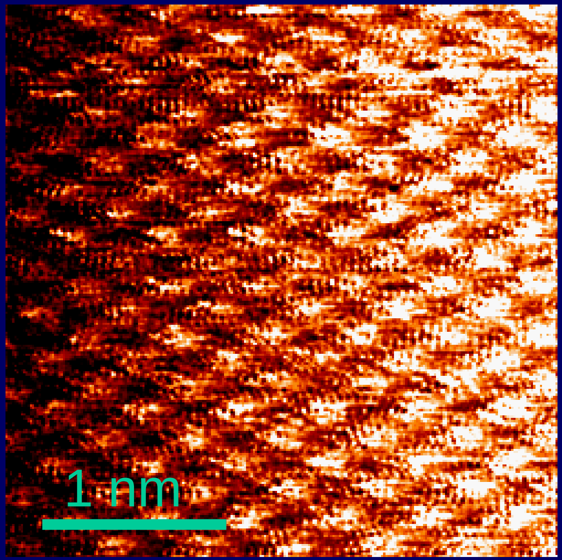
Vacuum System and Other UHV-MBE-STMs



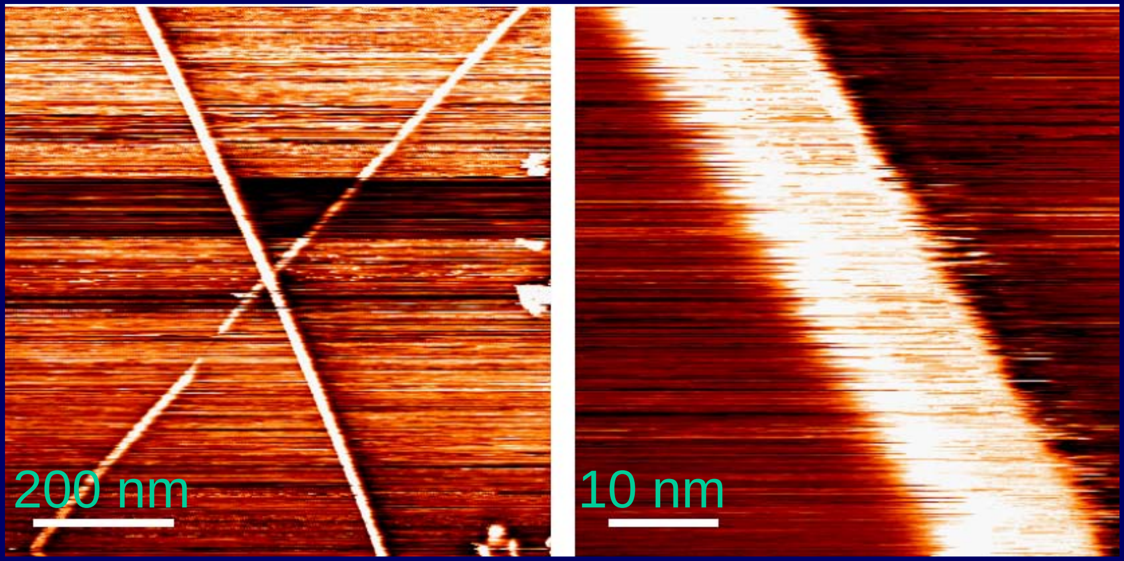




STM Imaging: Atomic Resolution Capability

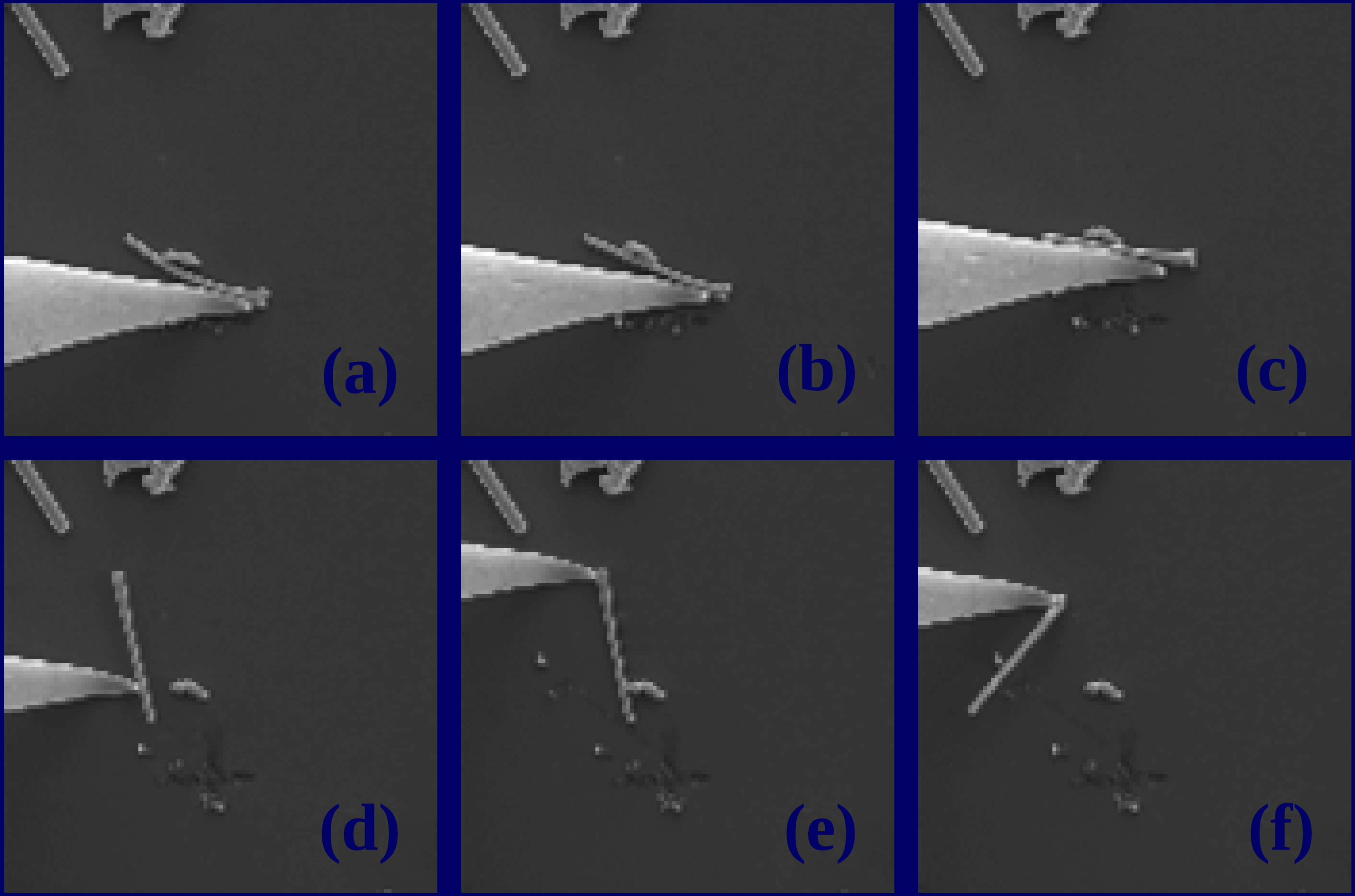


HOPG
I=500pA, V=70mV

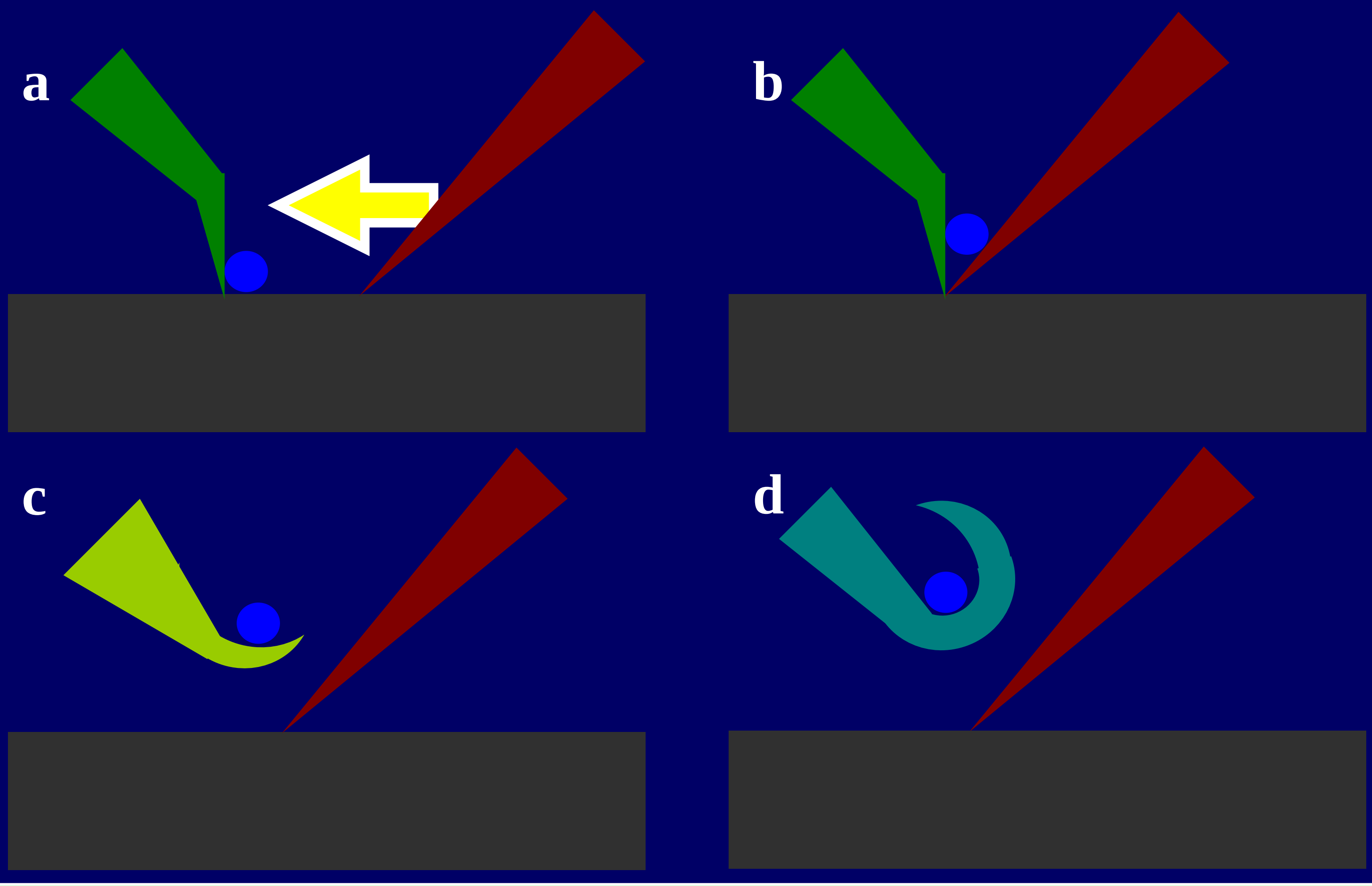


B nanowire on HOPG
I=500pA, V=300mV

Manipulation of Nanowires: Pushing



Manipulation of Nanowires: Hocking

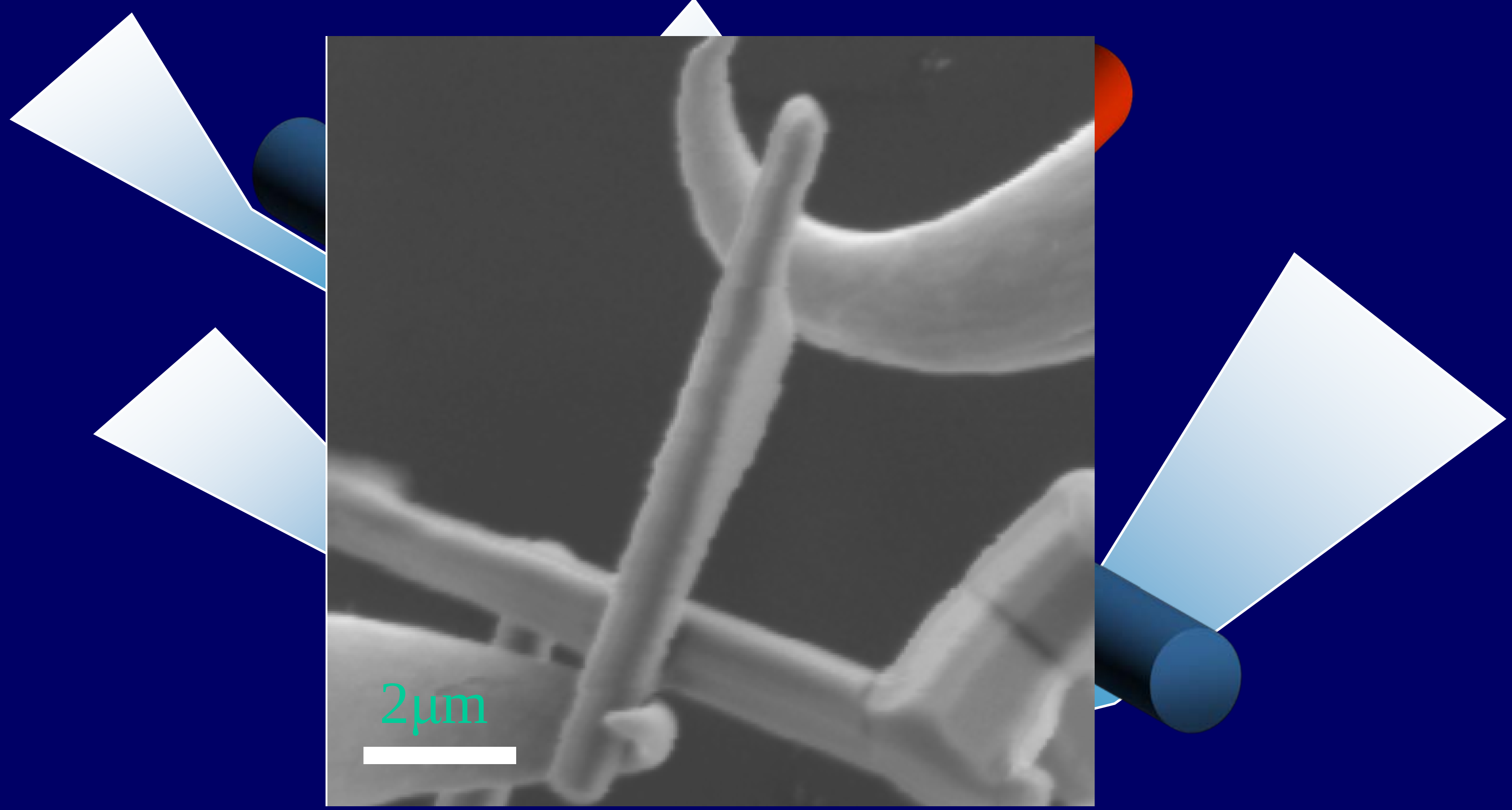


Manipulation of Nanowires: Hocking

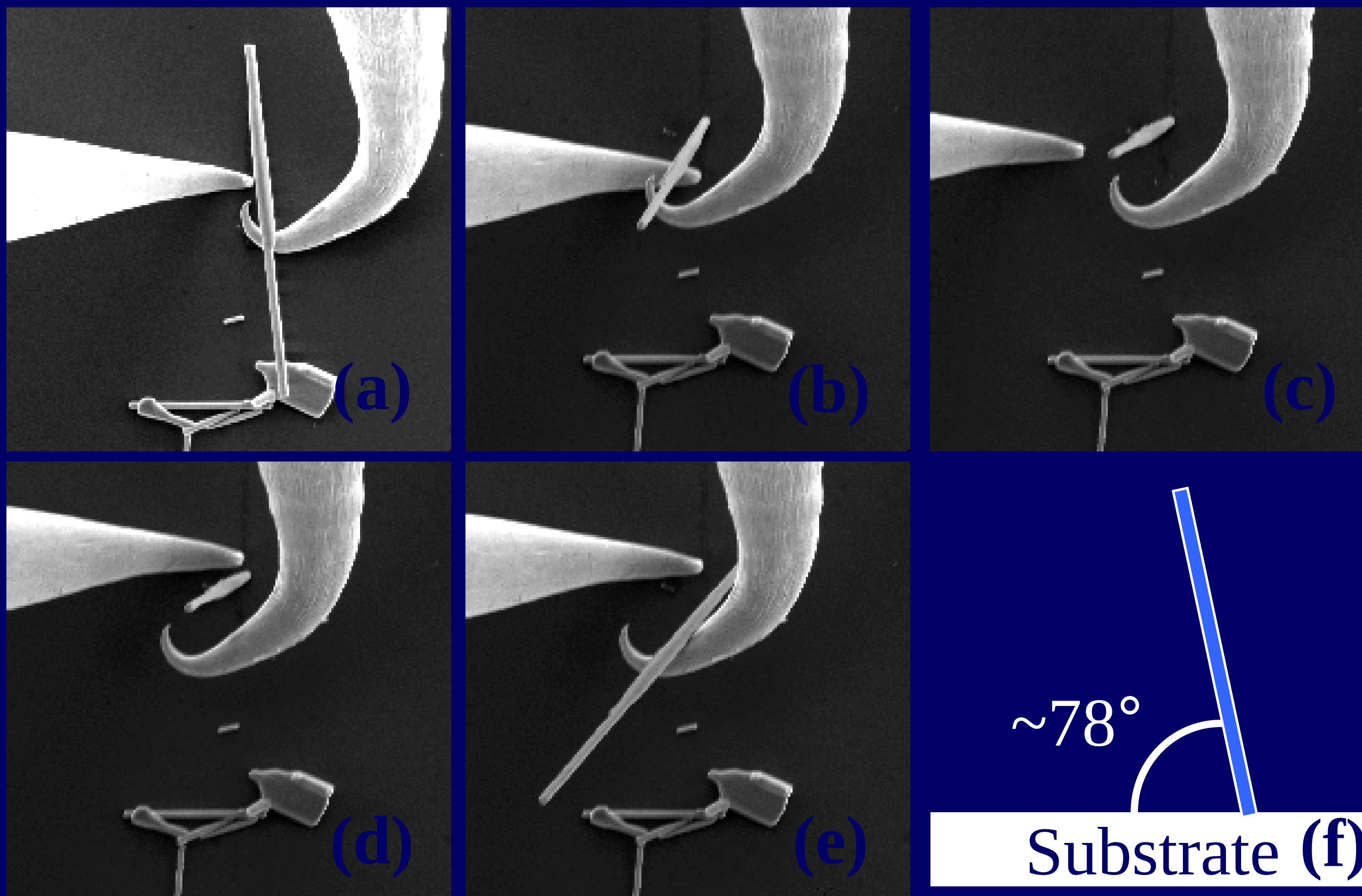
SEM image: 7µm x … x 7µm

SEM image: 2µm x 2µm

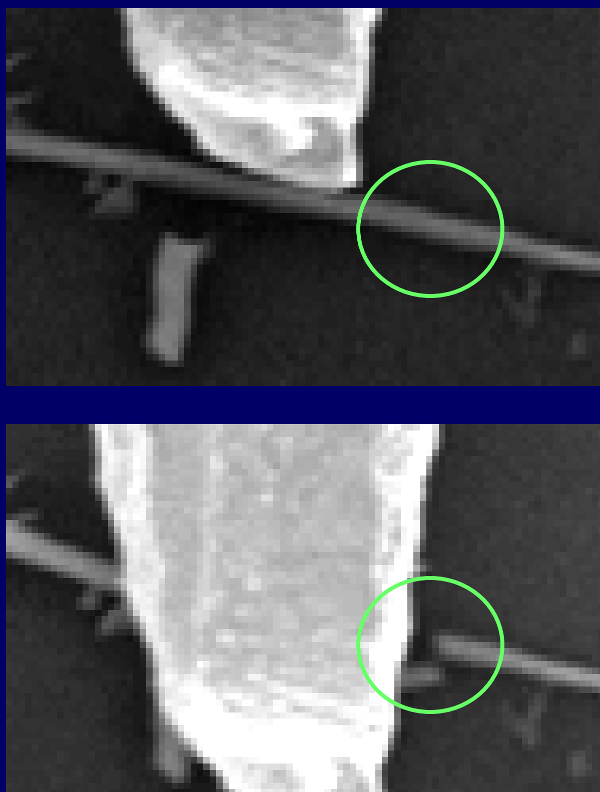
Manipulation of Nanowires and I-V Measurements



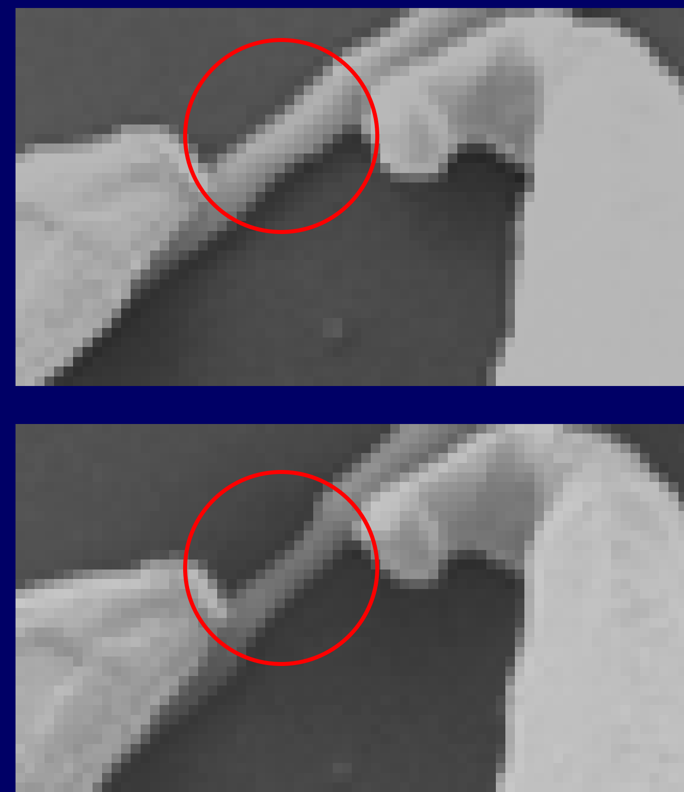
Manipulation of Nanowires: I-V Measurements



Manipulation of Nanowires: Cutting and Annealing

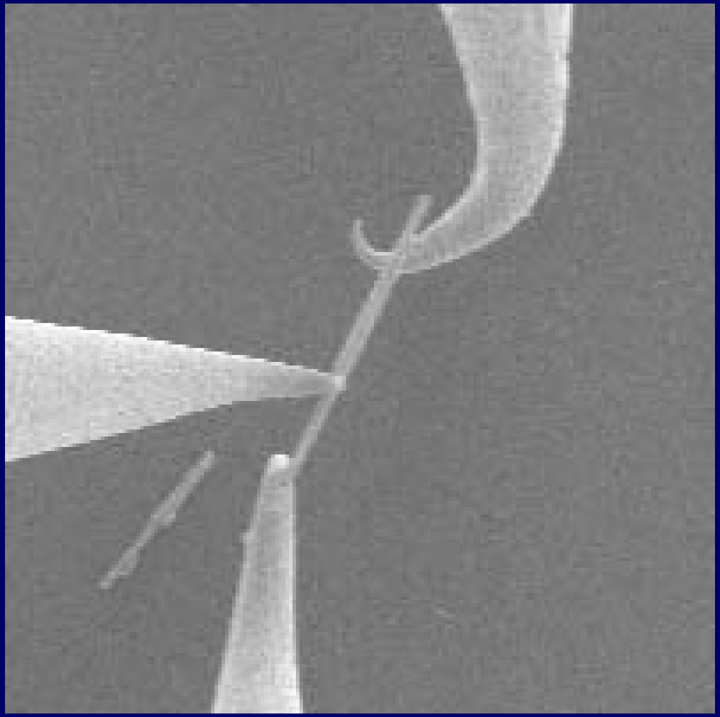


Cutting

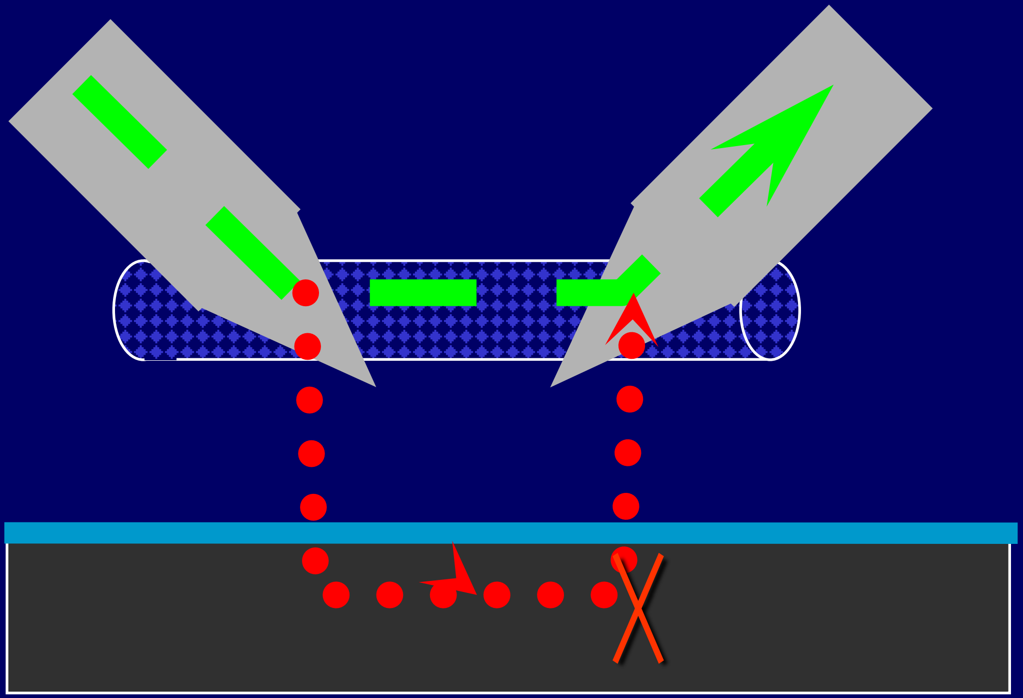


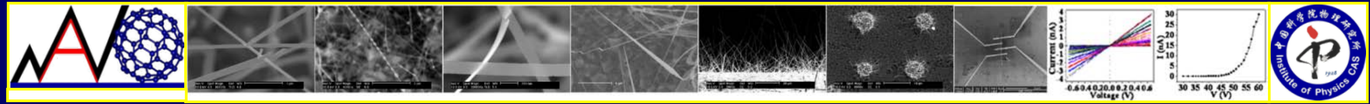
Sublimation

Manipulation of Nanowires: I-V Measurements

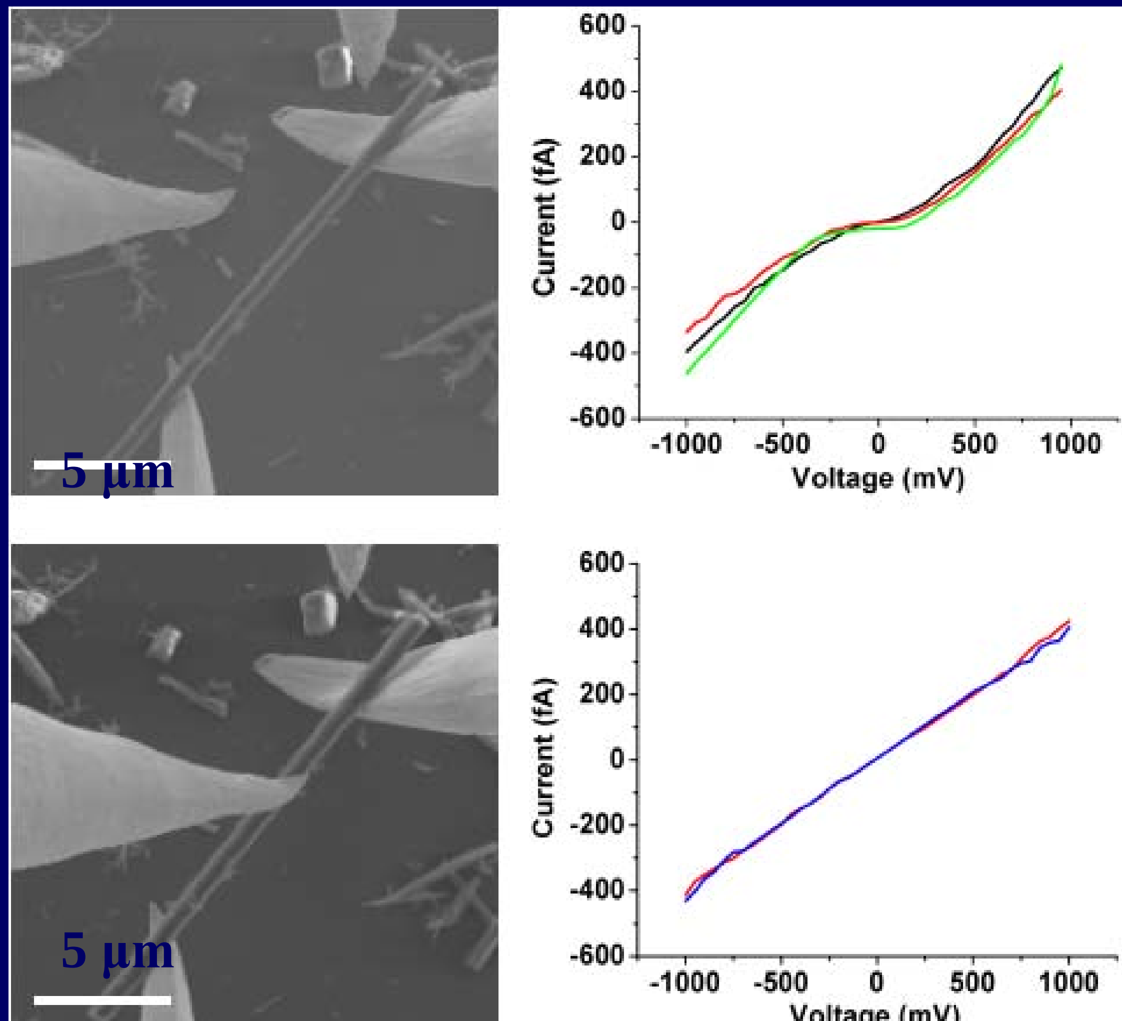


SEM image: 25μm x 25μm

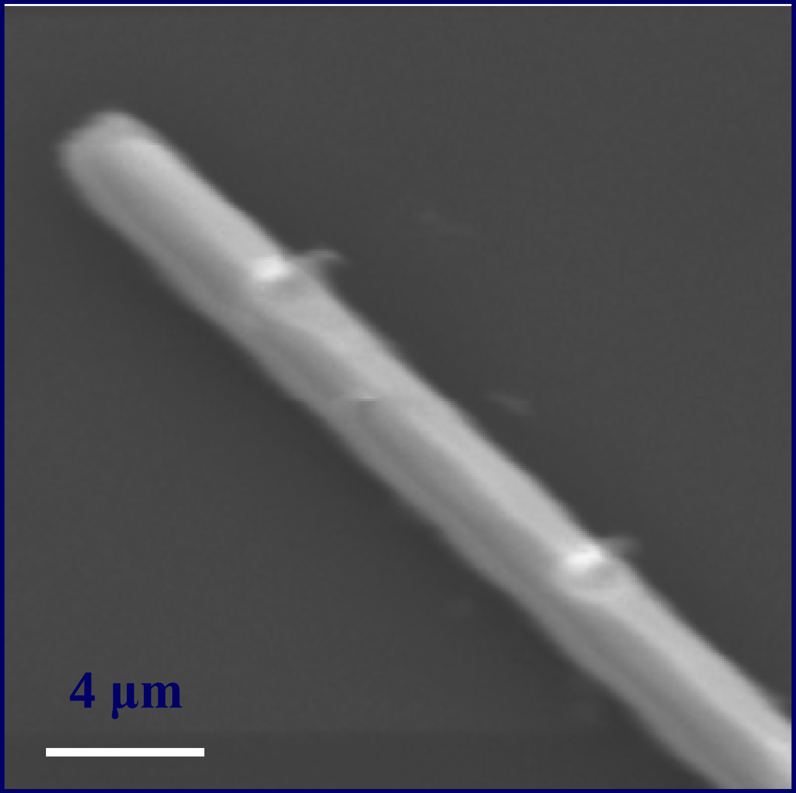


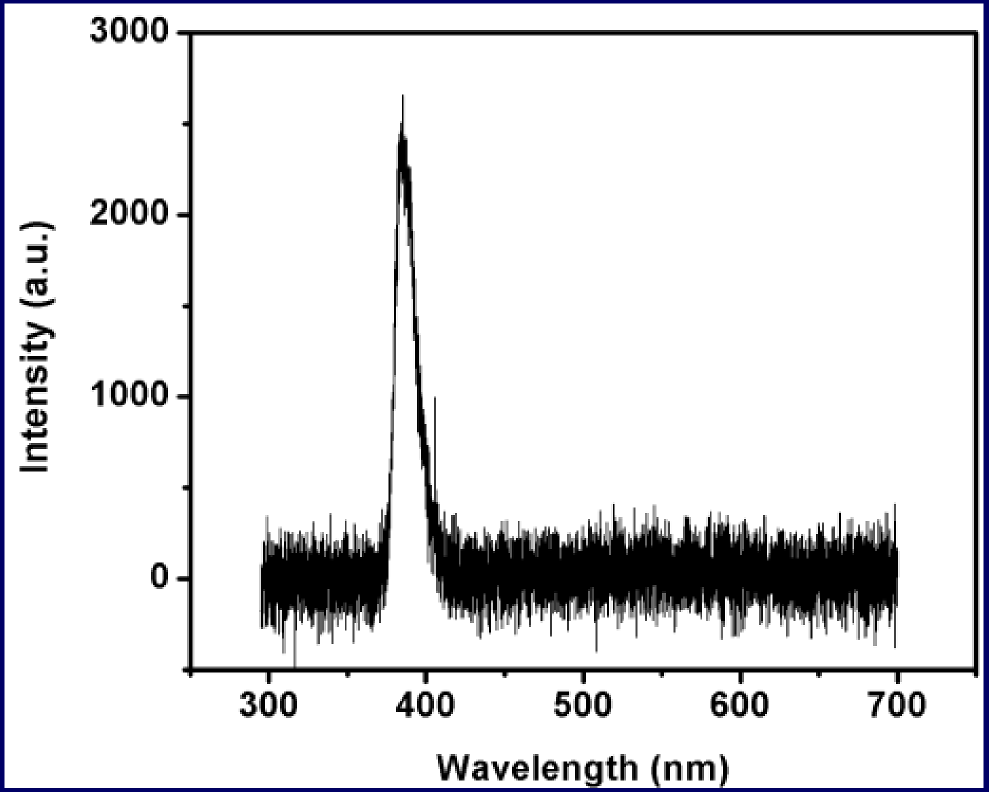


Manipulation of Nanowires: I-V measurements

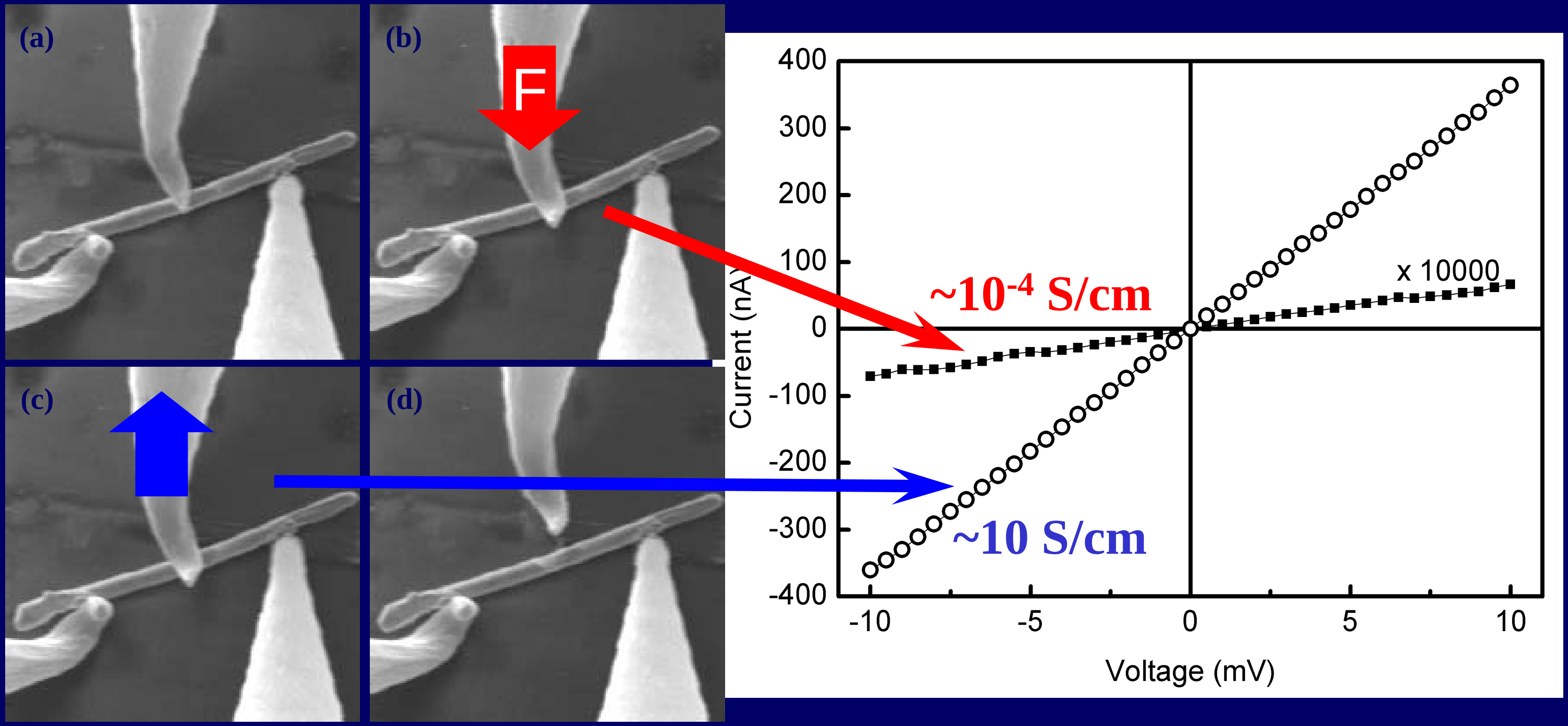


CL Property of ZnO Nanowires

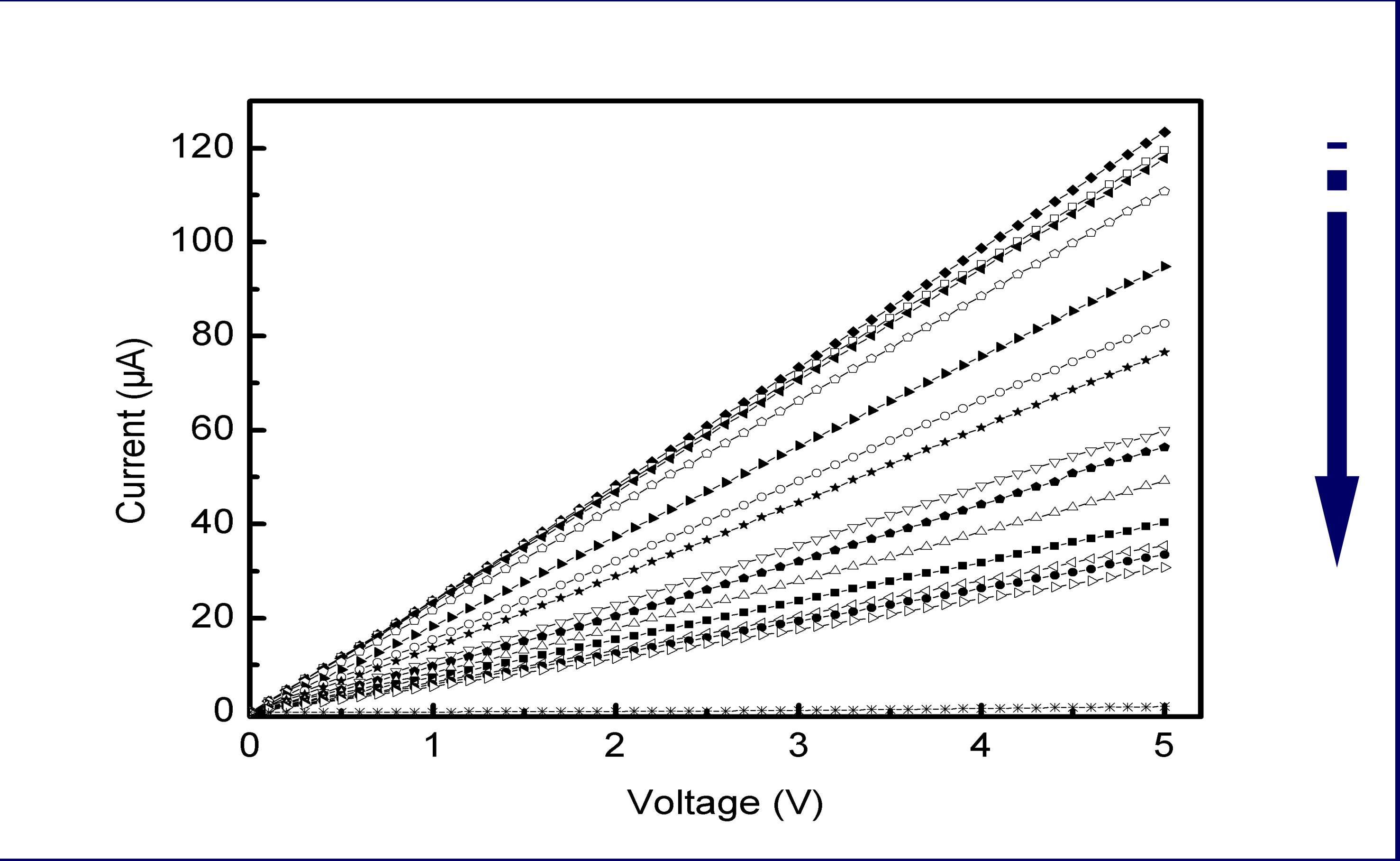


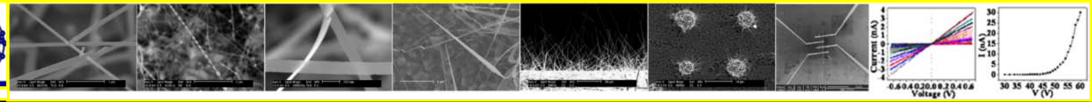


I-V Measurements of Strained ZnO Nanowires

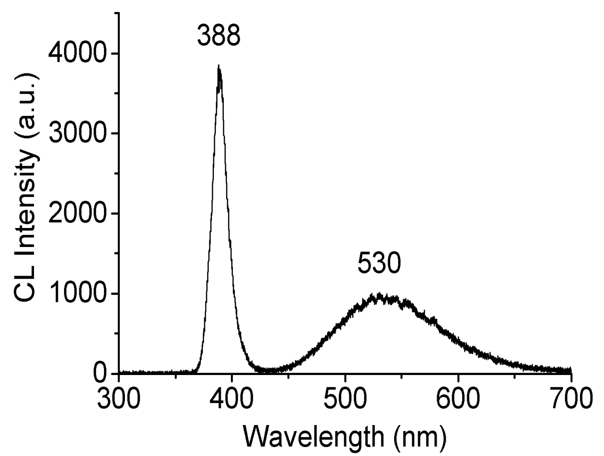


I-V Properties of A Strained Nanowire during Bending Process

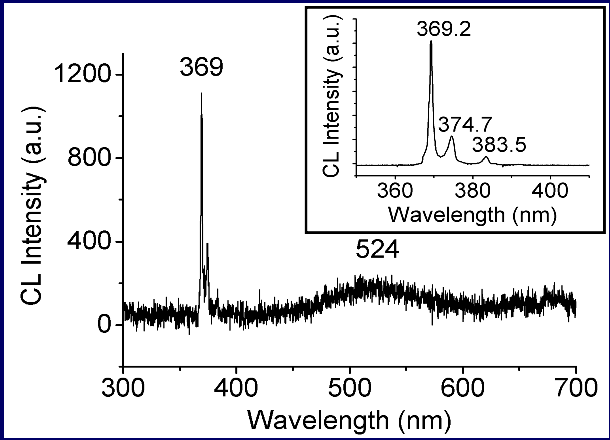




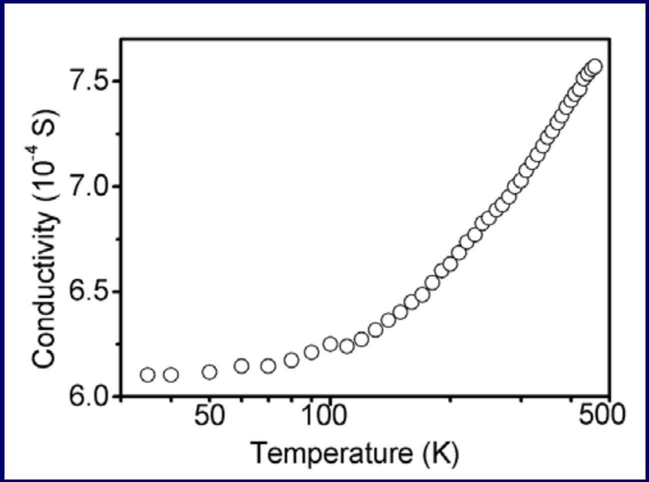
CL Property and Temperature- Conductance Relationship Of ZnO Nanowires



Room temperature (300K)



Low temperature (30K)



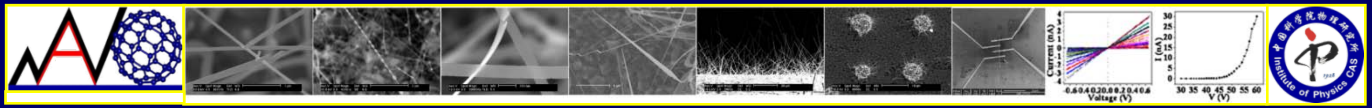
❖Strong emission of green-light

❖High electrical conductance

❖Slight change during T change

❖R is proportional to lnT at LT

2D metal-like characteristic



Theoretical Considerations

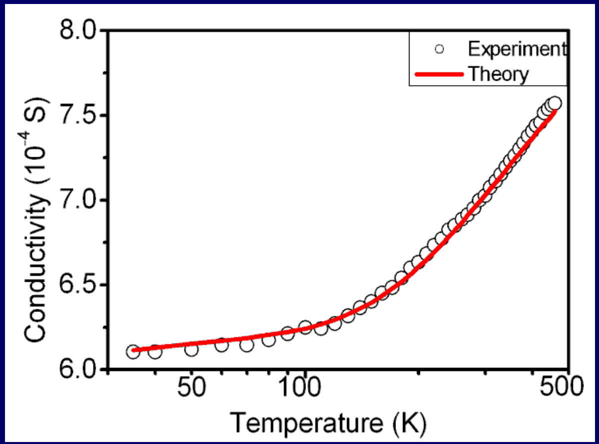
Weak localization: $R \propto -p \ln T$

$$\sigma = \alpha \ln T + \frac{\beta}{1 + \exp\left(\Delta E / K_B T\right)} + \gamma \qquad \left(\alpha = \frac{e^2 p}{\pi h} = 1.2 \times 10^{-5} \times p\right)$$

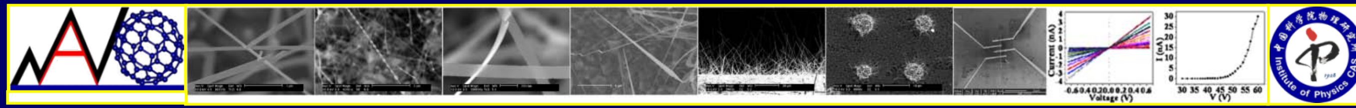
$$\sigma = 1.0 \times 10^{-5} \ln T + \frac{0.00048}{1 + \exp\left(530.2 / T\right)} + 0.00056$$

$$\alpha = 1.0 \times 10^{-5}$$

$$\Delta E = 45.7 meV$$



X. Lin/H.J. Gao et al., APL 2007



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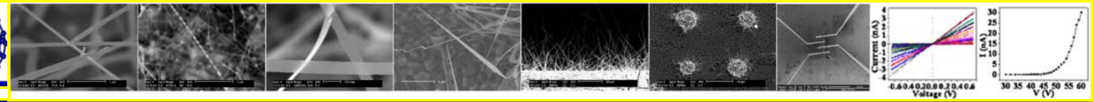


Experimental Details: Thermo-reduction of boron-oxygen compounds with active metal

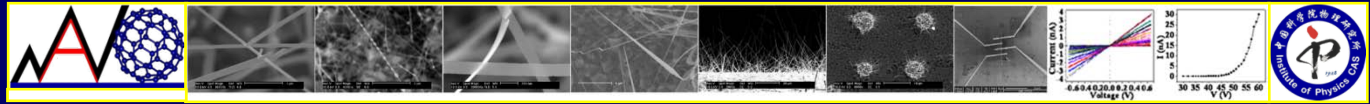
Precursors: B, B_2O_3 and Mg

Catalyst: Fe_3O_4 nanoparticles

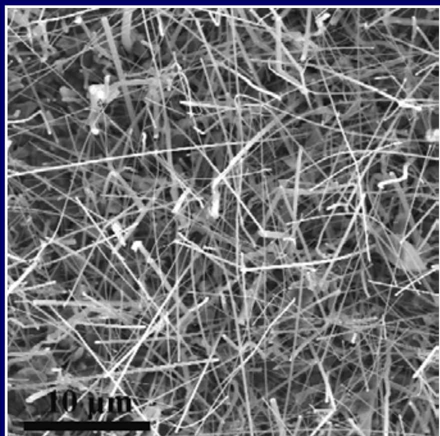
Substrate: Si (111) and STM tips

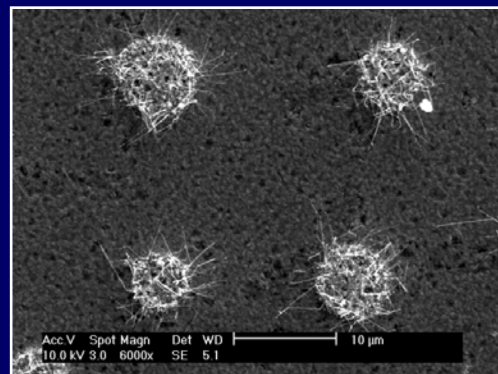
Carrier gases: 5 ~ 10% H_2/Ar

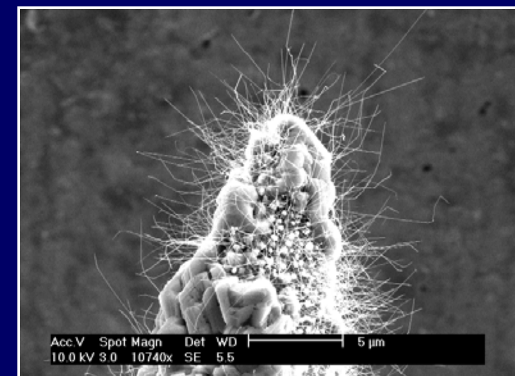
Reaction temperature: 400 ^{o}C for 30 min ; 1100 ~ 1200 ^{o}C for 2 h

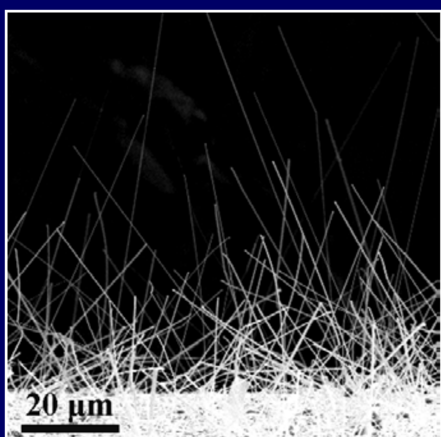


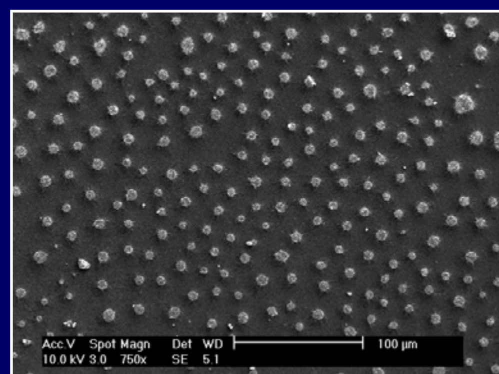
Controllable Growth of Boron Nanowires

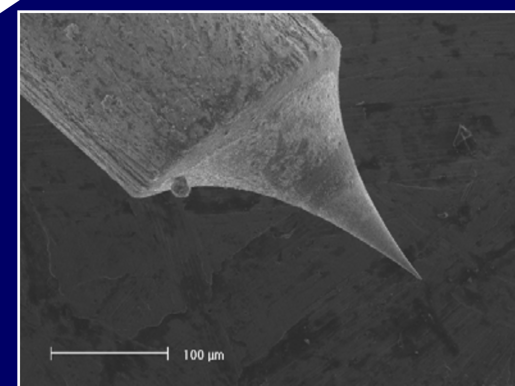








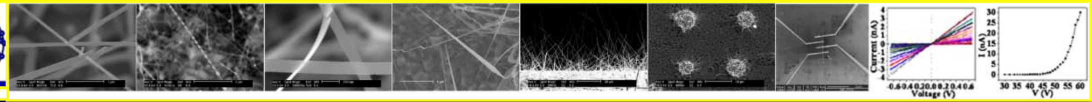




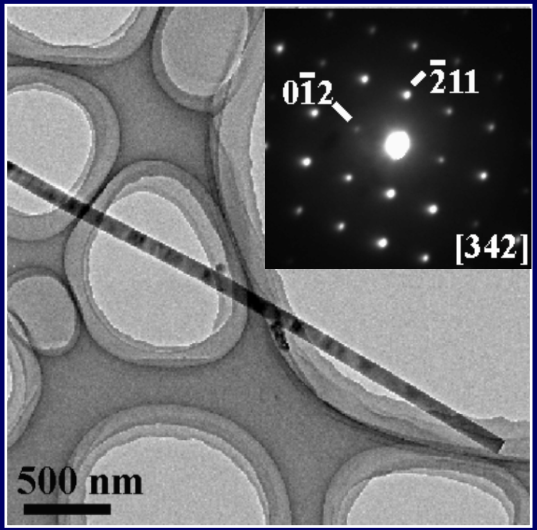
High density

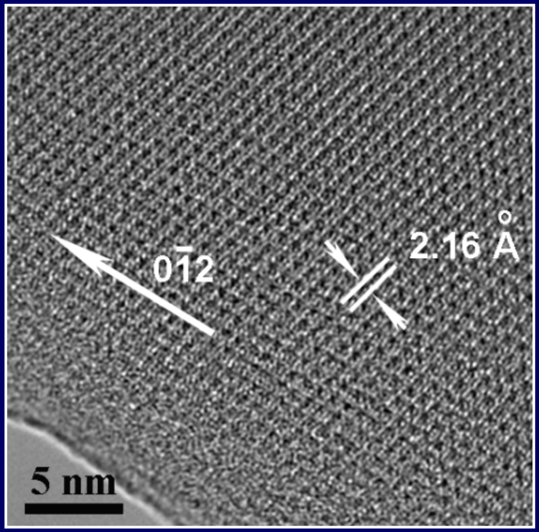
Pattern

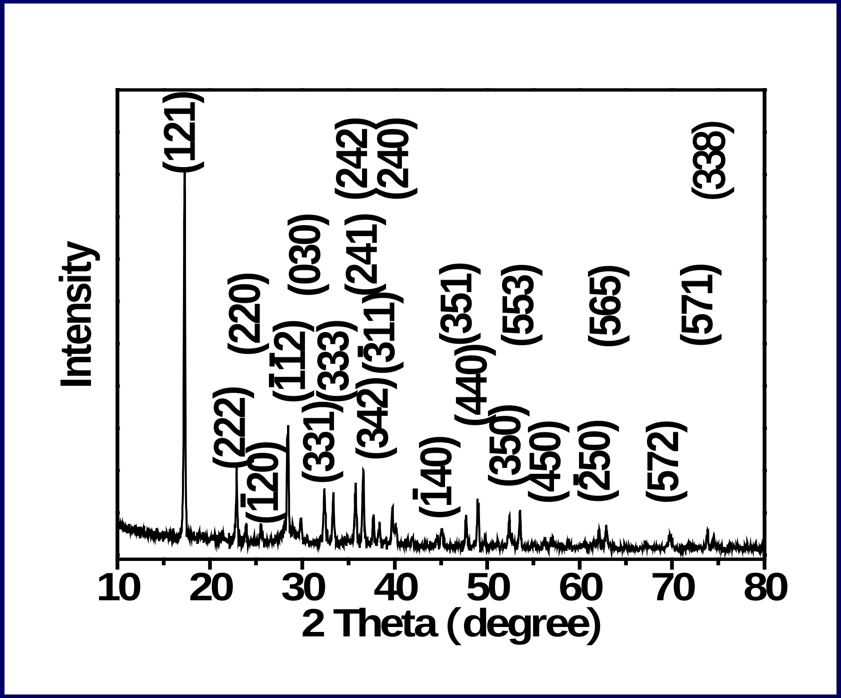
STM tip



Structures of Boron Nanowires





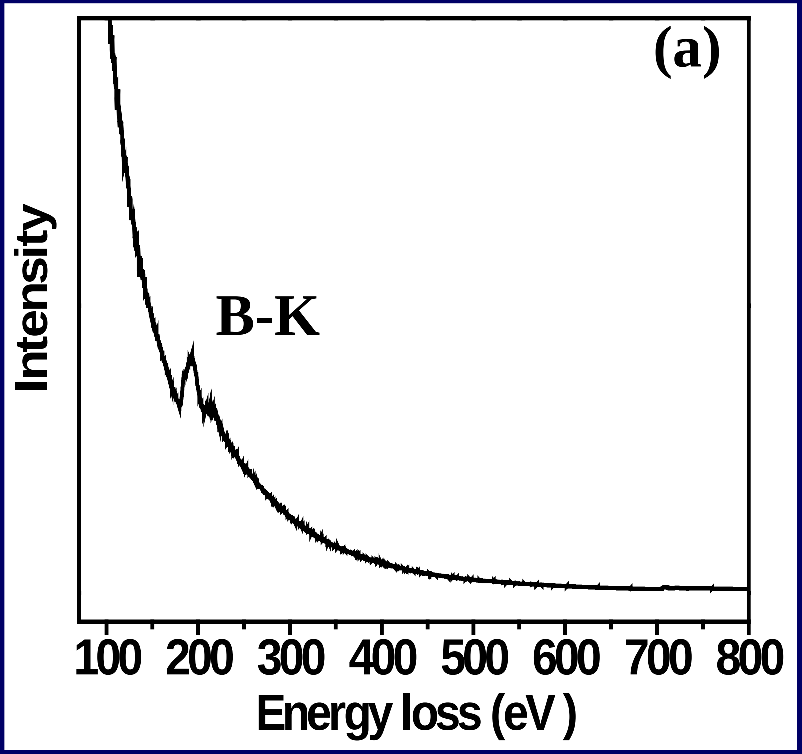


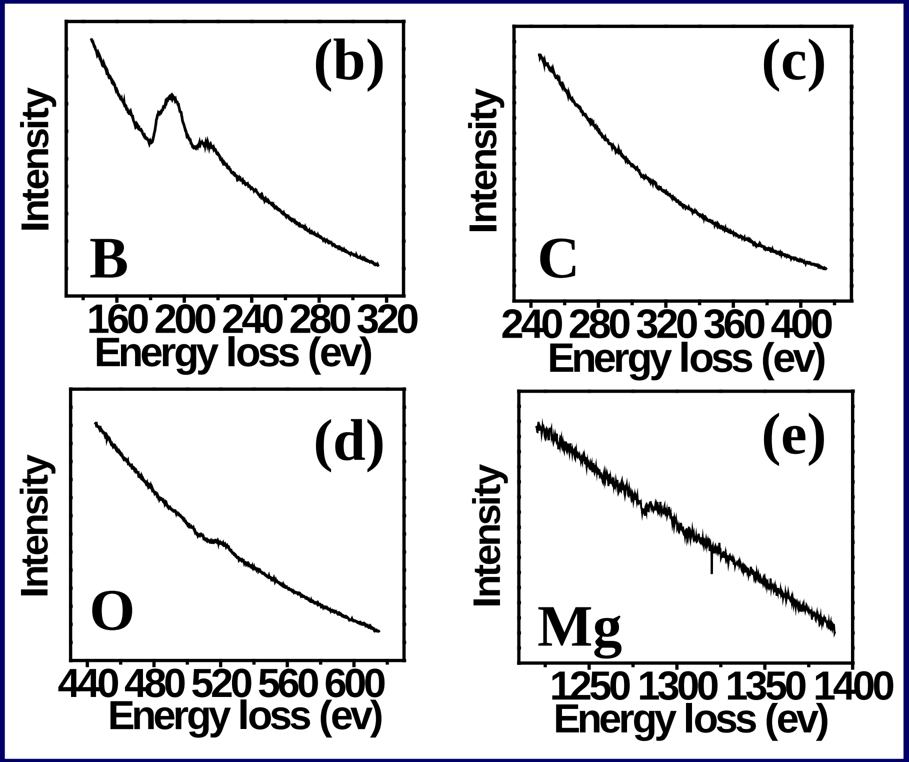
β-rhombohedral：JCPDS：85-0409

a=b=c=10.17 Å；**α=β=γ=** 65.12°

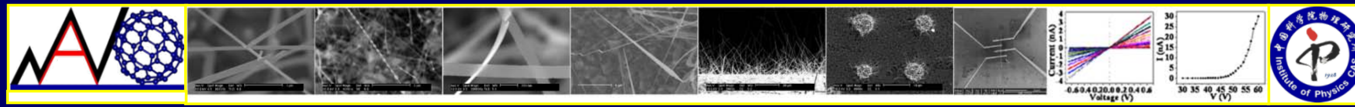
- Diameter: 50-200nm
- Lenghth up to several μm
- Rhombohedral structure
- Growth direction [01̄2]

The Composition of Boron Nanowires

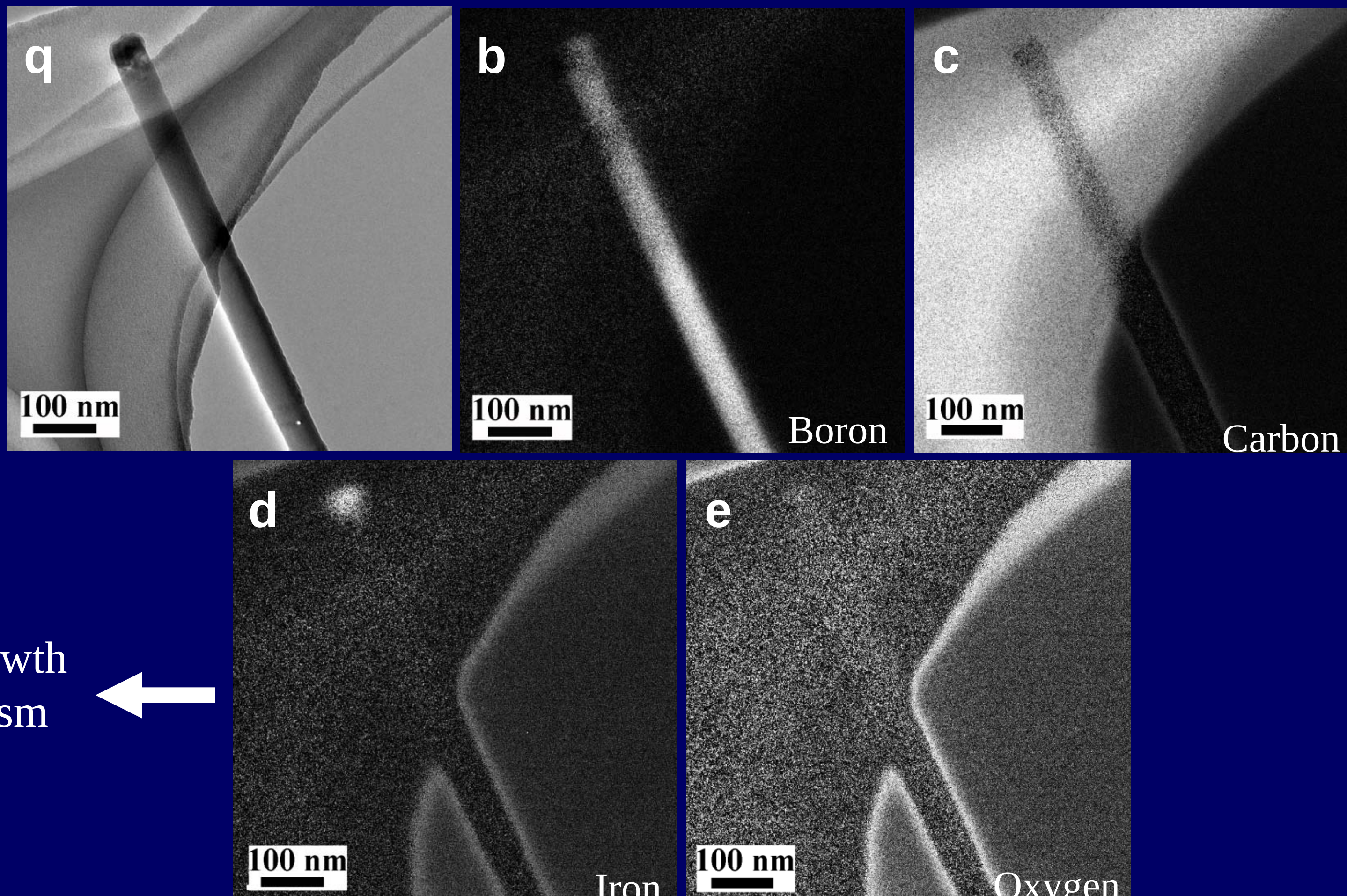




a) A typical EELS spectum from individual nanowire; b) K-shell ionization edge of the boron is clearly seen at about 188 eV; c, d, e) The EELS for possible impurities of carbon (284 eV), oxygen (532 eV) and magnesium (1305 eV), respectively.

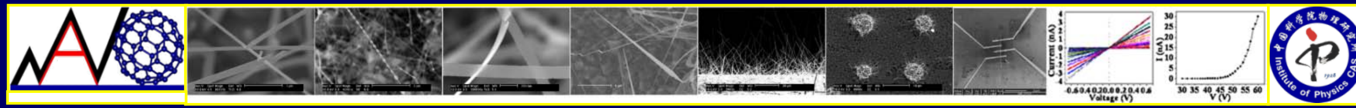


The EFTEM Image of Boron Nanowire



VLS growth mechanism ←

a) Typical TEM image of boron nanowire; Elemental mappings of b) boron, c) carbon, d) iron and e) oxygen.



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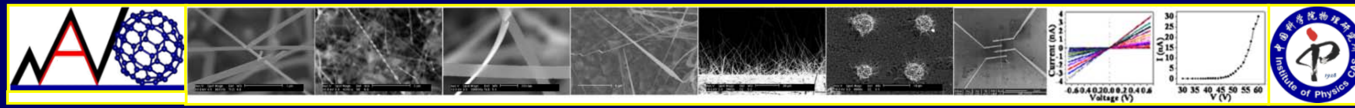
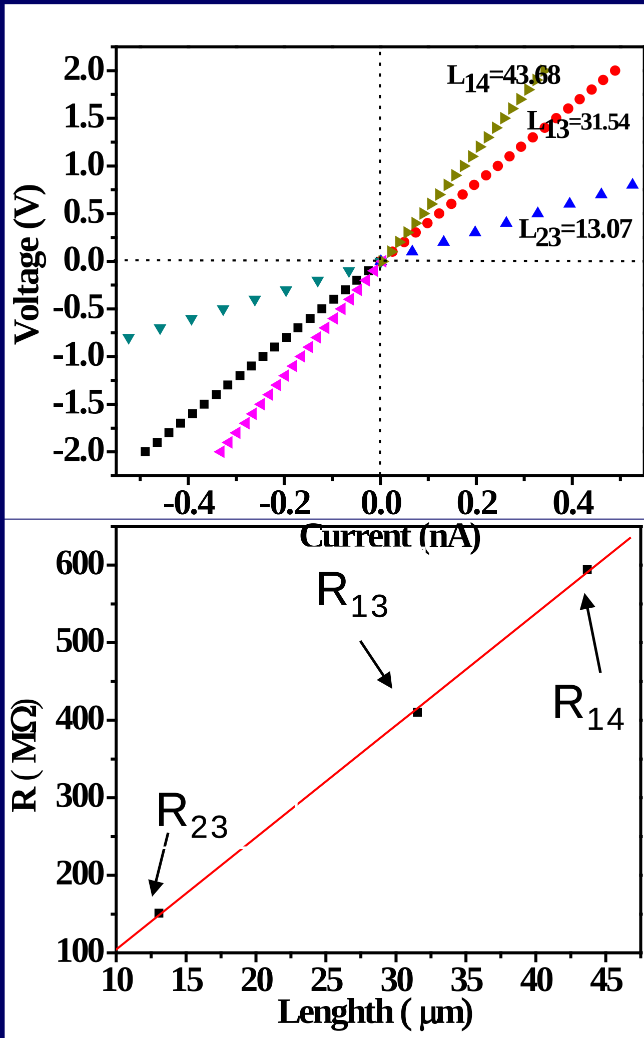


I-V characteristics : Ohmic contact
(two terminal measurement -23,13,14) (Electrodes are Pt)



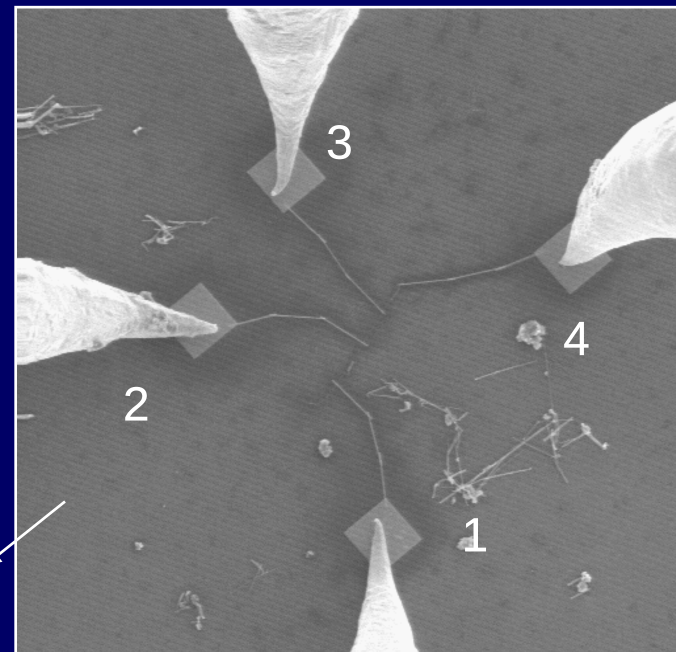
L23=13.07 μ m

L13=31.54 μ m

L14=43.68 μ m

D=200nm

Made by FIB

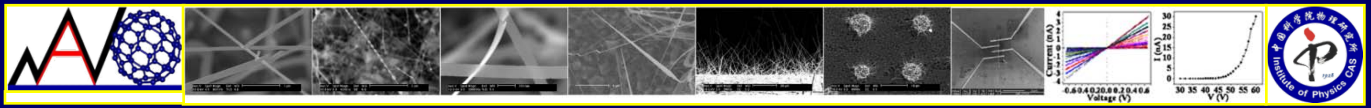


10kV, 250μm×250μm

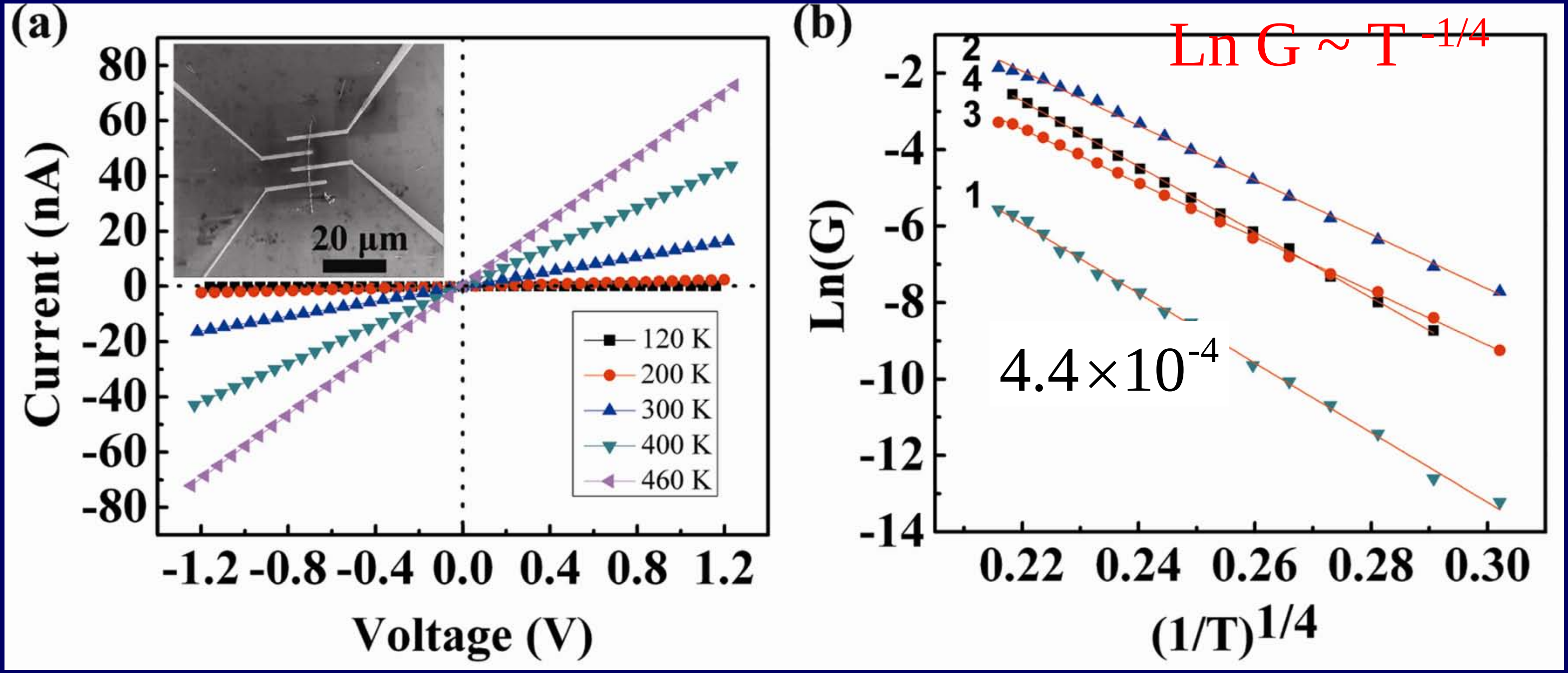
Work function: Φ_{Pt} =5.3eV >Φ_{B} =4.3eV

B NW has Ohmic contact with Pt

B is a p-type semiconductor



The Temperature Dependent Behavior of B NWs



Mott's law

$$G = G_0 \exp\left\{-\left(\frac{T_0}{T}\right)^{1/4}\right\}$$

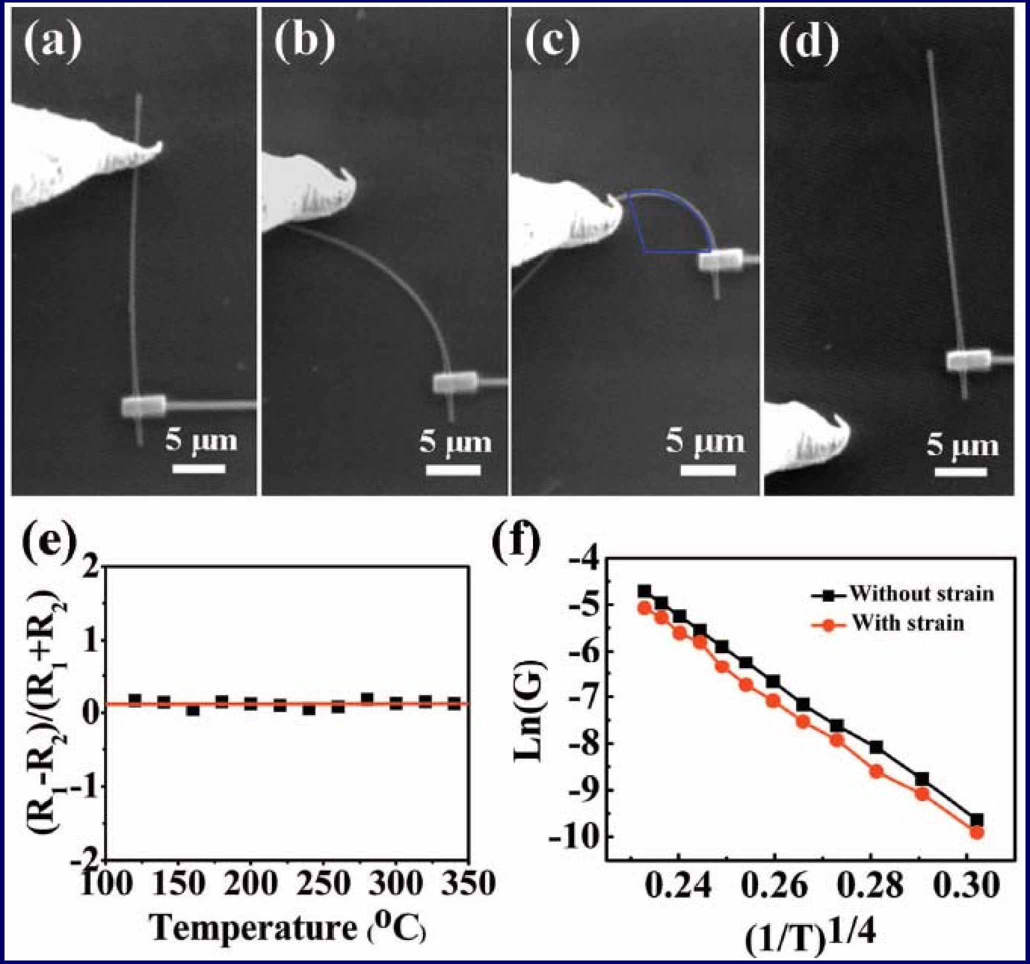
$$T_0 = \frac{60}{\pi k_B \ell^3 N(E_F)},$$

for the three-dimensional VRH

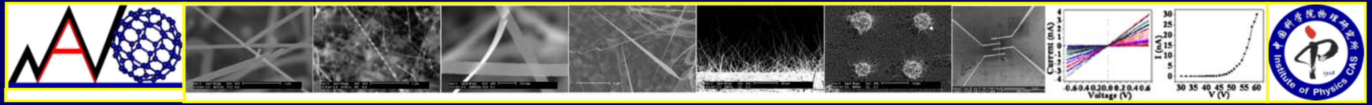
T_0 of the four devices

samples	β-rh. B (polycrystalline)	β-rh. B (single-crystal)	Device 1	Device 2	Device 3	Device 4
T_0 (K)	5.1 x 10^9	8.7 x 10^7	6.8 x 10^7	2.56x 10^7	2.47 x 10^7	5.4 x 10^7

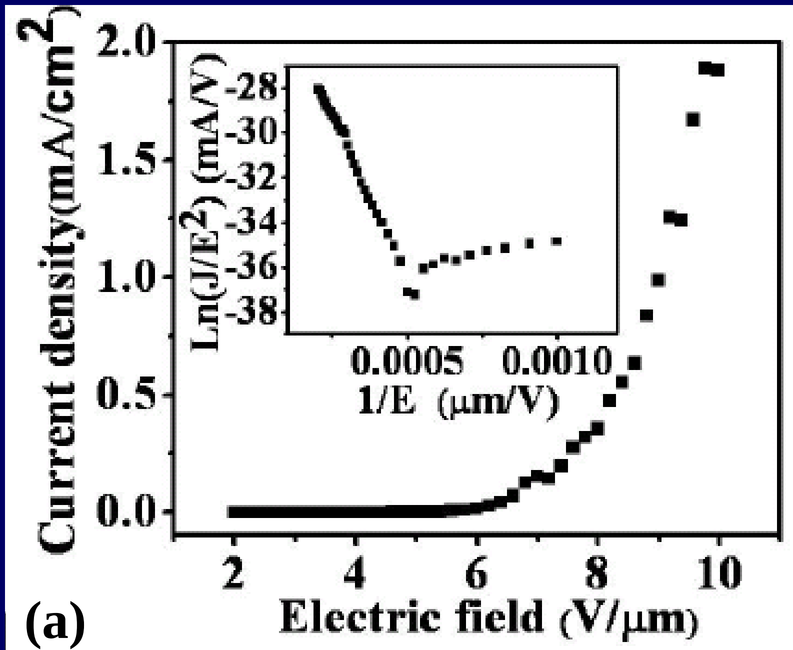
Robust Conductance and Flexibilty of B NWs

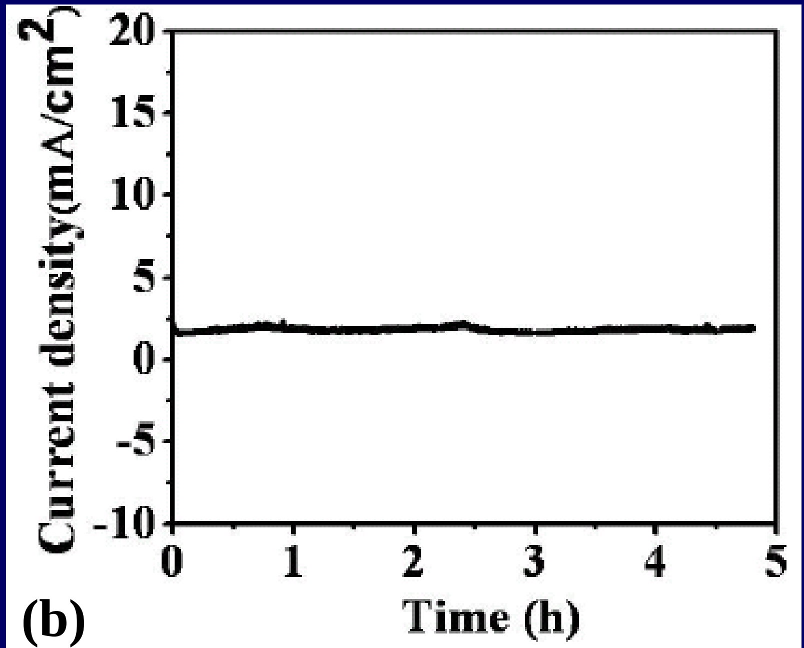


a) ρ=139.3Ω·cm, effective length L_{effect}=23.45 μm, diameter d=150 nm.
b) ρ=143.8 Ω·cm, L_{effect}=20.08 μm.
c) ρ=142.4Ω·cm, L_{effect}=20.44 μm, and the distortion of the nanowire is 3%.
d) After releasing the strain.
e) R_1-R_2 / R_1+R_2 vs T, where R_1 and R_2 are the resistances of boron nanowire without and with 3% strain
f) Temperature dependence.



Field Emission---High Density B NWs Film

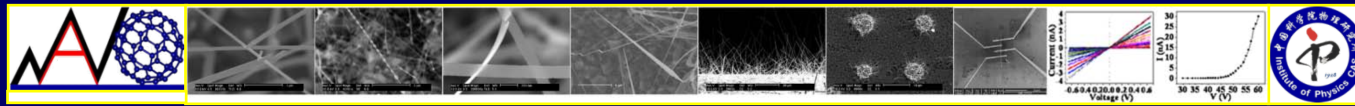




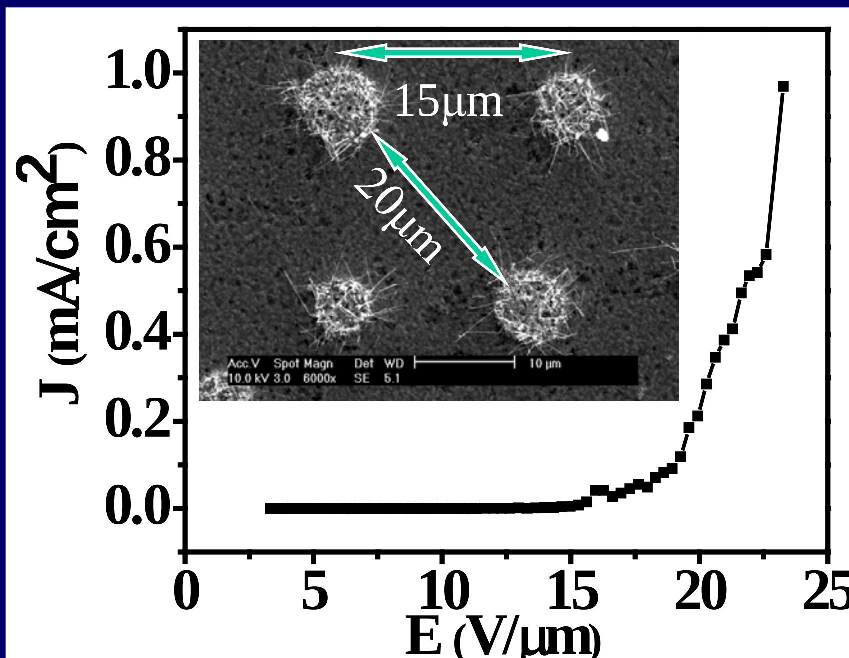
Turn-on Field：the applied field when the emission current gets to 10μA/cm^2.

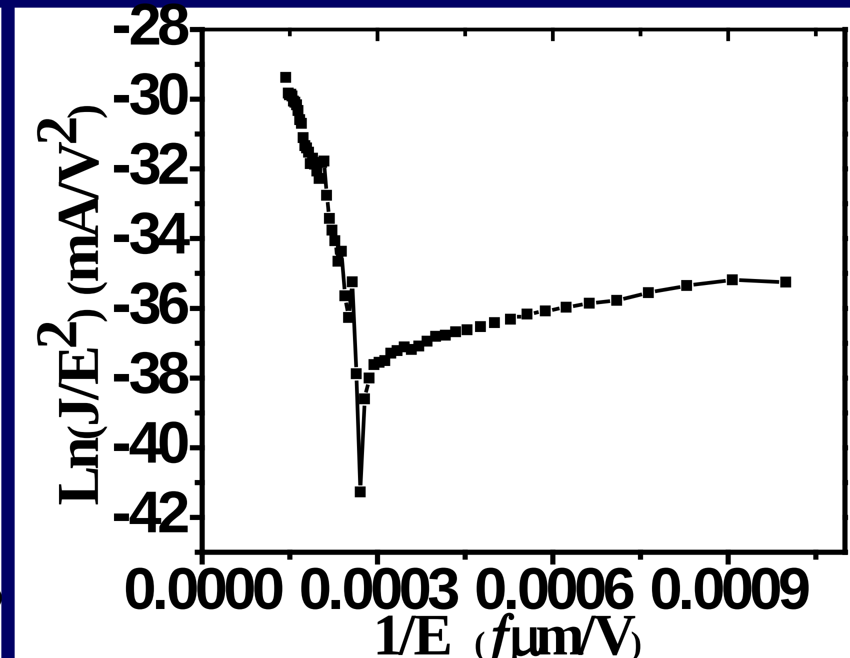
Threshold Field：the applied field when the emission current gets to 1 mA/cm^2.

	B nanocone	AlN nanocone	CNT
E_{on}=5.7 V/ μm	3 V/ μm	12 V/ μm	2.5 V/ μm
E_{th}=9 V/ μm	5.3 V/ μm		



Field Emission of Patterned B NWs Film





Patterned Boron (PB) { E_{on} : 15 V/ μm; E_{th} : 22.5 V/ μm

High density Boron (HB) { E_{on}=5.7 V/ μm; E_{th}=9 V/ μm

Length of B NW: L=5 μm

Distance of patterns: D=15-20 μm

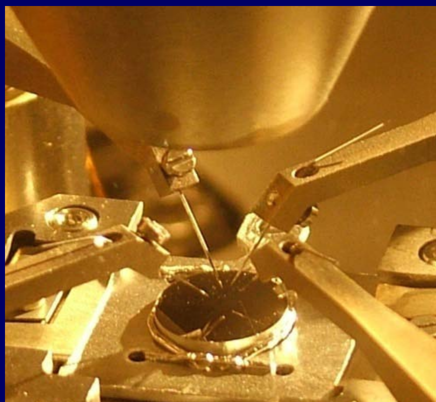
} D / L=3, 4

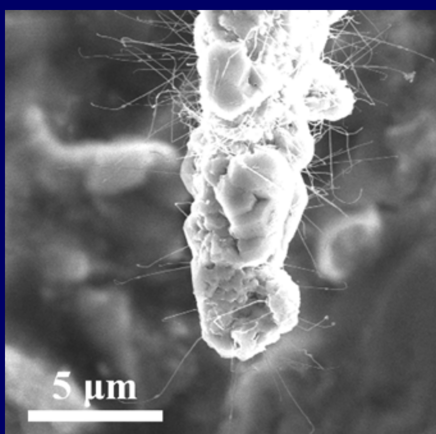
PB: HB

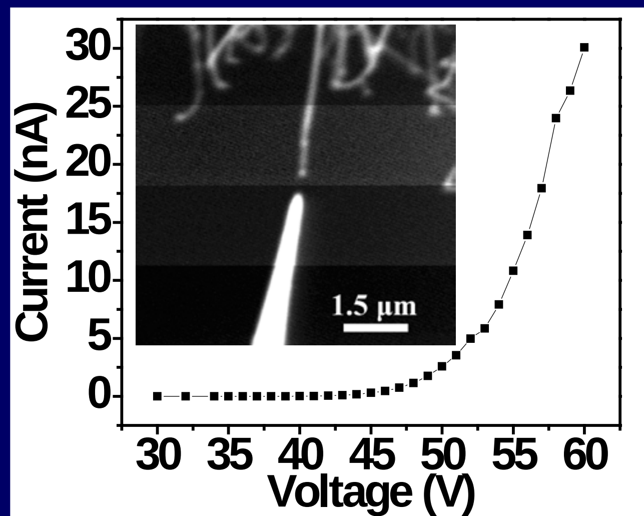
Desity: 1 : 10

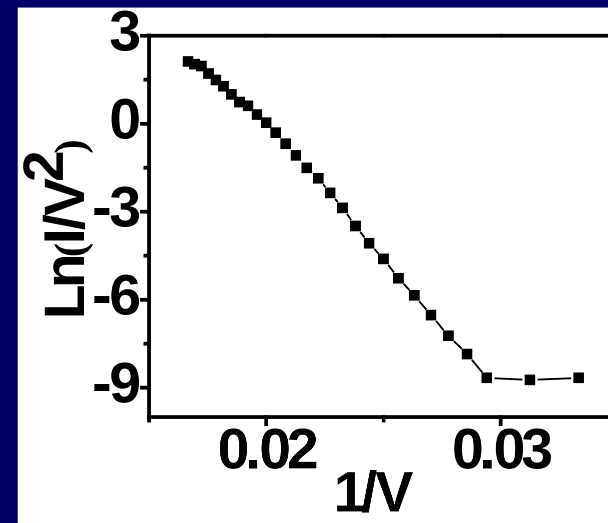
FE: 1 : 2.6

Field Emission Properties of A Single B Nanowire









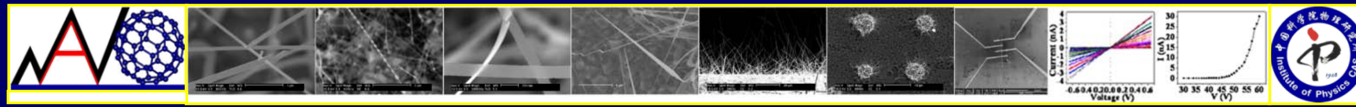
Emission current density: 10^4 A/cm^2 at 60 V ⟷

Single carbon NT: 10^4~10^6

ZnO nanowire: 10^2~10^3

LaB_6 NW: 10^3~10^4

Turn on field : 70 V/ μm at 500 nm



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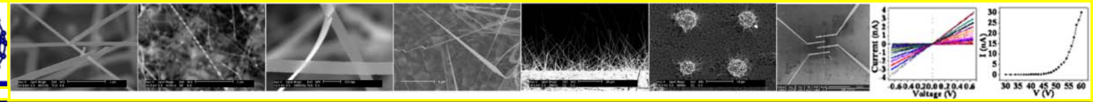
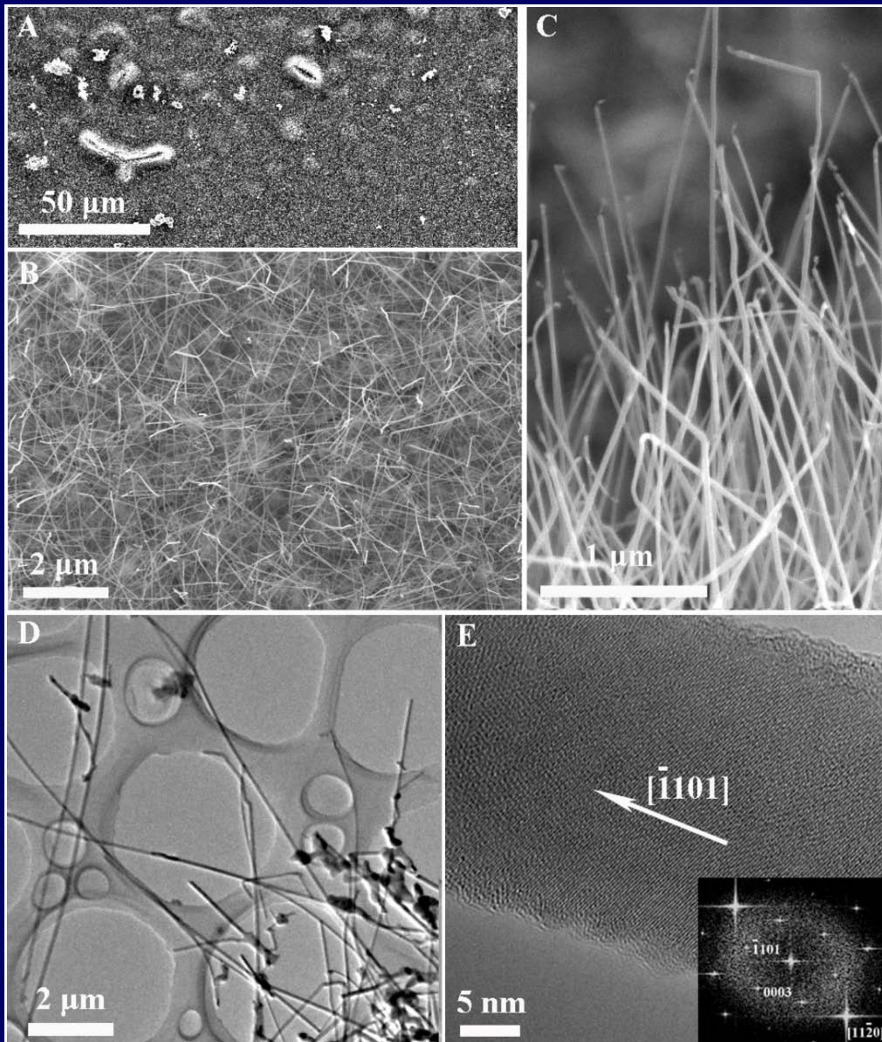


SEM and TEM Structure of B_4C Nnaowires



A) The SEM image of large-scale boron carbide nanowires.

B) The SEM image of high density boron carbide nanowires with higher magnification.

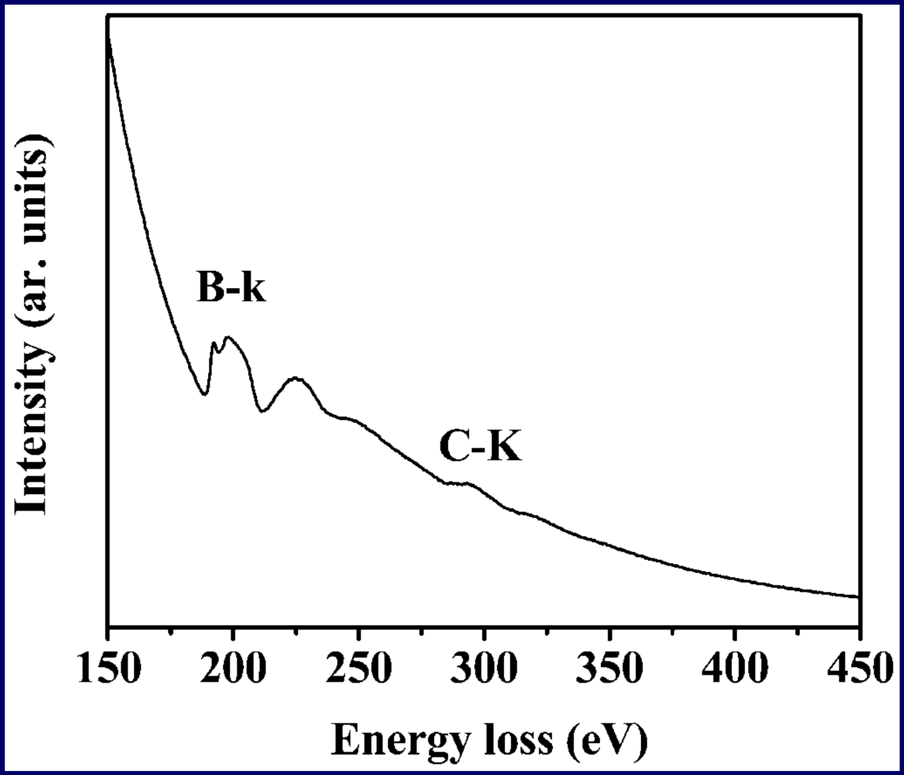
C) The side-view SEM image showing some protrusions of boron carbide nanowires.

D) The TEM image of boron carbide nanowires.

E) The HRTEM image of boron carbide nanowire, the inset is the corresponding FFT pattern from the HRTEM image.

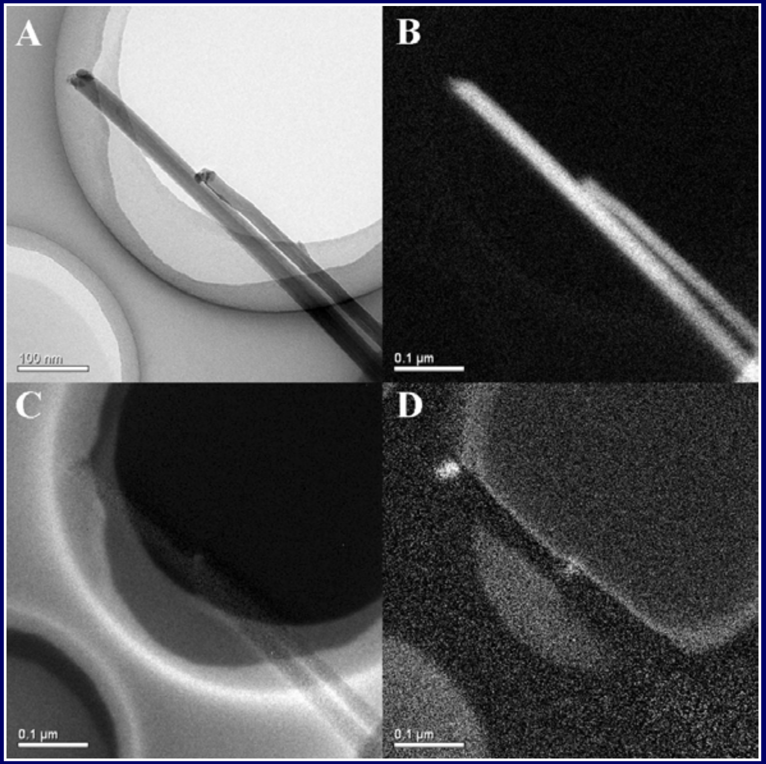
1). 1100 ºC; 2). 20 - 30 nm; 3). Crystalline; 4). Nanowires.

Composition and Distribution of B_4C nanowires



The EELS from Boron carbide nanowire showing characteristic B and C K-edges at 188 eV and 284 eV.

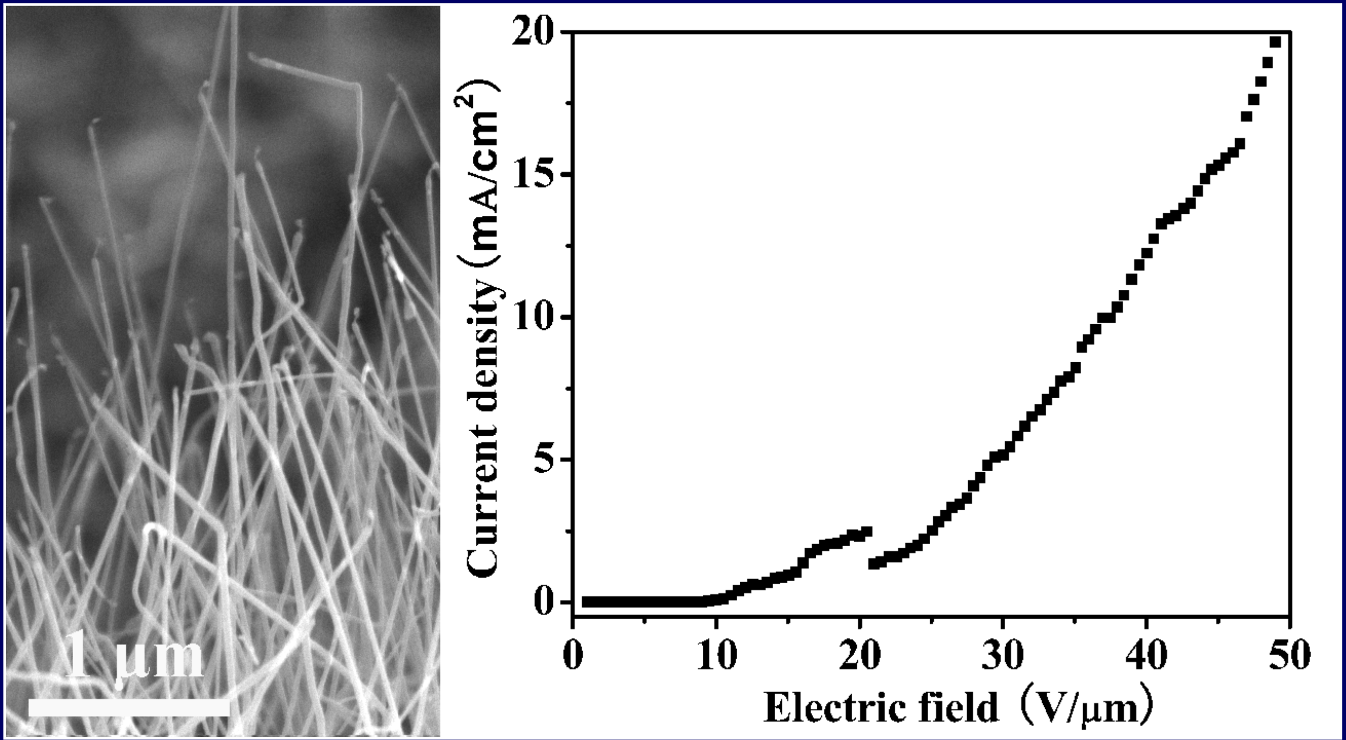
B : C = 4.08



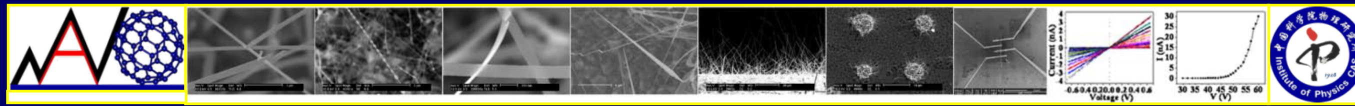
(A) TEM image. (B) The mapping image of boron. (C) Carbon. (D) Iron.

VLS growth mechanism

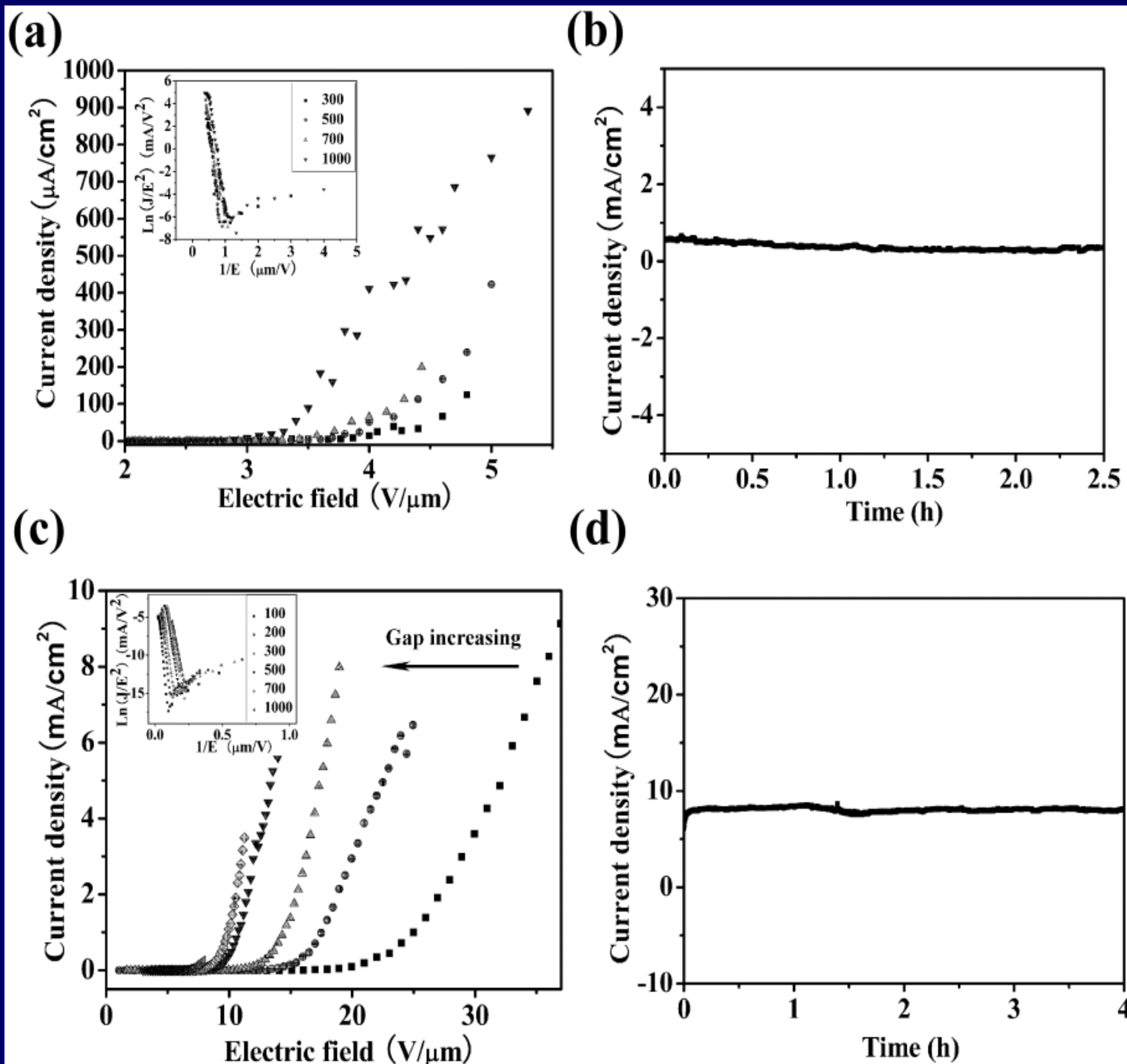
Field Emission Property of B_4C Nanostructure Films



The FE current density (J) is turned on at 4.0 V/μm and steadily increases to 2.48 mA/cm² at 20.6 V/μm. Then it experiences a sudden drop to 1.43 mA/cm² when the applied field (E) passes 20.6 V/μm.



Field Emission Property of B_4C Nanowire Films



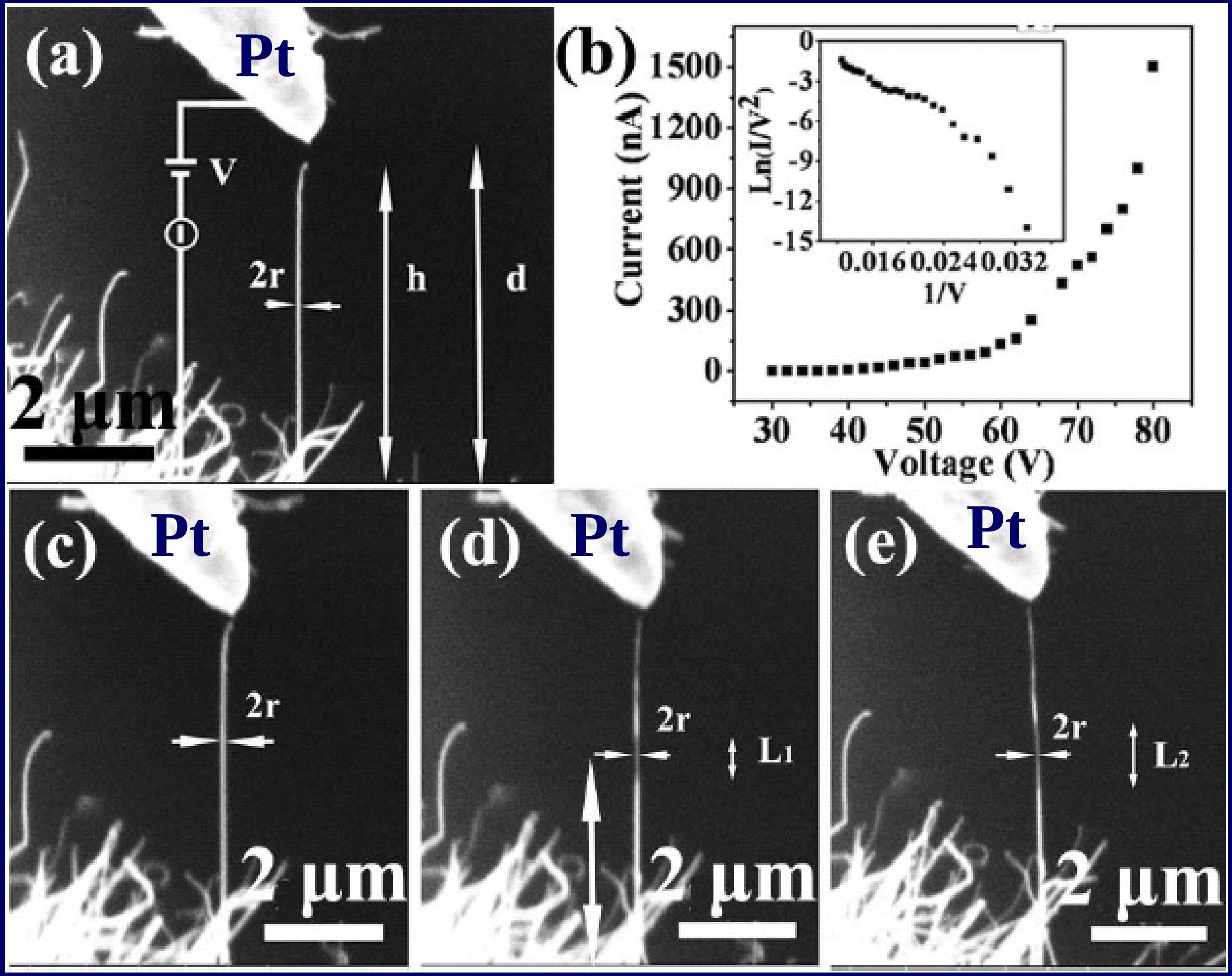
The turn-on field was decreased from 3.8 V/μm to 3 V/μm corresponding to the vacuum gaps increased from 300 μm to 1000 μm. The current fluctuation is less than 9%.

The turn-on fields decreases (16 V/μm to 6.3 V/μm) with increasing vacuum gaps (100 μm to 1000 μm).

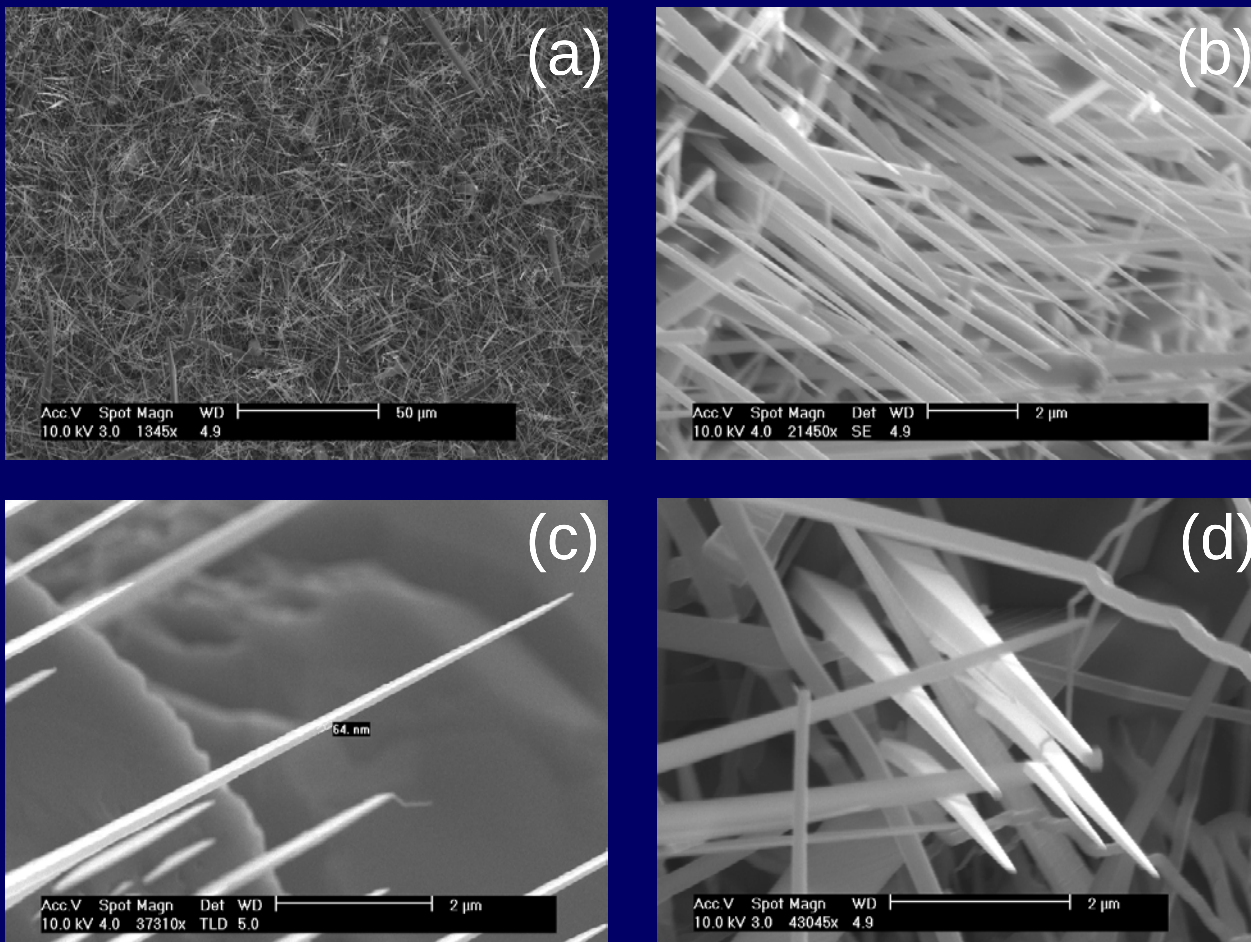
The high field emission current of B_4C nanowires is very stable with fluctuation below 5%.

There is no current decline during a long-term emission.

Field Emission Property of a Single B_4C Nanowire

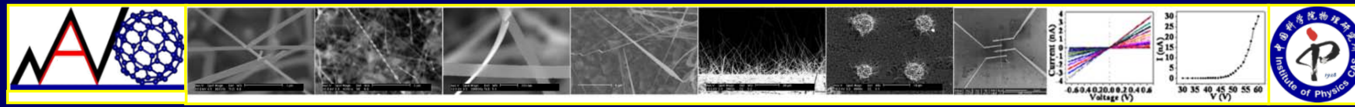


Boron Nanoswords: Growth and Properties



1) 400℃，0.5h，
   $8.0X10^2$ Pa；
2) 1200℃，2h，
   $5.5X10^3$ Pa。

- 10-5 nm
- Thickness:
  a few tens nm

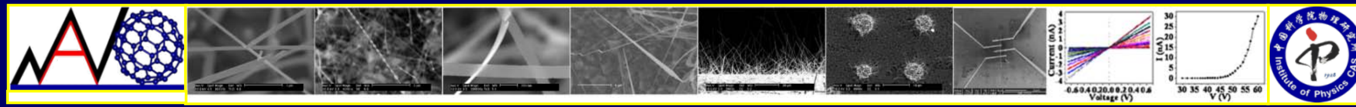


Conclusions

- We have developed a novel synthetic route for controllable growth of high quality boron nanowires.

- The electrical transport of single boron nanowires shows room temperature conductivity of 4.4 x 10^{-4} $(\Omega\bullet cm)^{-1}$, and follows the Mott's VRH mechanism. This electrical conductivity is very robust under mechanical strain up to 3% which indicted that boron nanowires show excellent flexibility.

- FE characteristic of boron nanowires film, patterned boron nanowires film and a single boron nanowire reveal a high field emission current density from them. Boron nanowire material is a good candidate for field emission applications.



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IOP CAS, China

Feng Liu, *Utah U., USA*
Qian Niu, *UT-Austin, USA*
X.C. Xie, *IOP/ASU*
Werner Hofer, *Liverpool Univ., UK*
Hong Guo, *Mcgill U., Canada*
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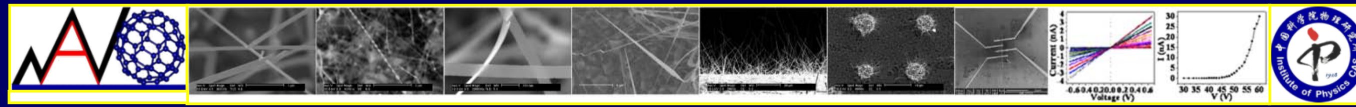

Thank you for your attention!