凝聚态物理-北京大学周五论坛

一维纳米材料物性及相关器件

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http://Nano.pku.edu.cn

人类发展历史

- 。。。石器时代。。。
- 。。。青铜时代。。。
- 。。。钢铁时代。。。
- 1968年：硅（微电子）时代
  - 科学家关于硅材料研究的科技论文超过了关于钢铁研究的论文~500篇
- 2003年：微→纳米时代
  - 科学家关于纳米研究的科技论文超过了关于微米和硅技术研究的论文~15000篇
- 2004年：纳米时代（？）
  - 科学家关于纳米研究的科技论文超过了30000篇
  - 中国科学家在这个重要的研究领域发表的科技论文在全世界排名第二

The NANO age?

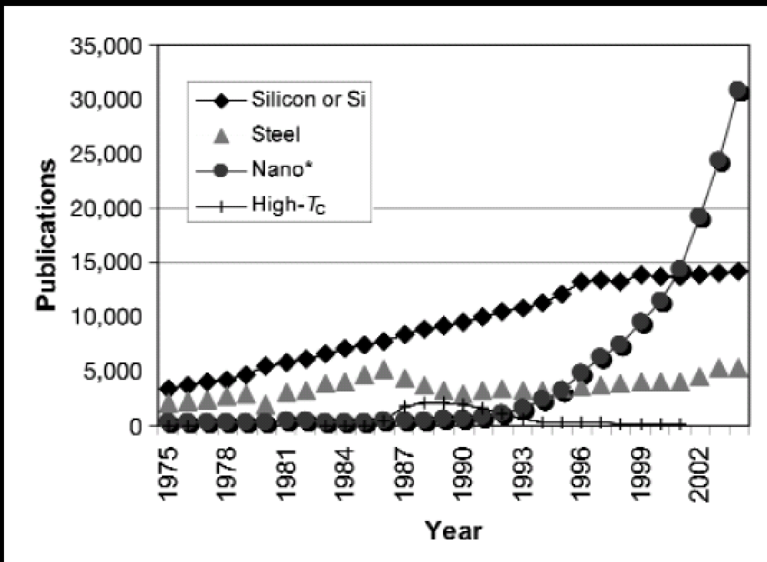


Figure 1. Publications over time by material topic.

Simon Sze famously announced that the end of the Iron Age and the beginning of the Silicon Age was in 1968, when the scientific community published more papers on silicon than on steel. In 2004, papers on *nano* outran publications on silicon by 2:1. Have we taken leave of the Silicon Age already?

论文数和产业的关系

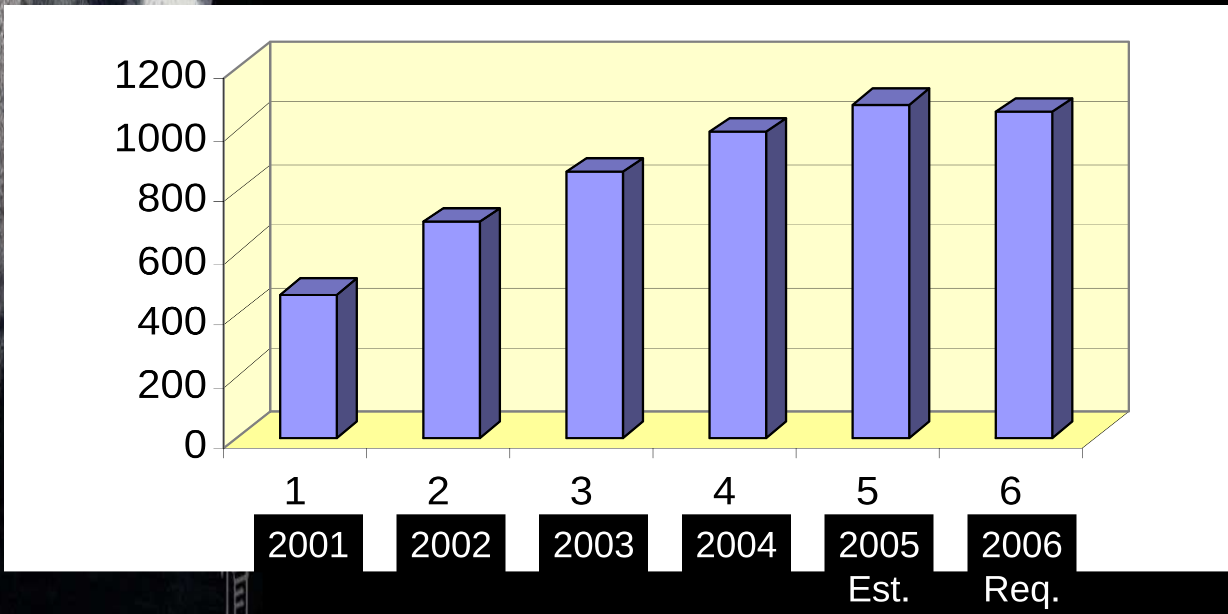
Table I: Correlation of Publications to Economic Activity.

Topic	2004 Papers	2004 Revenue ($ Billions)	2004 Ratio (paper/$1B revenue)	Growth	2010 Revenue ($ Billions)	2010 Ratio (paper/$1B revenue)
Silicon	14,185	160	88.7	10%	290	49
III-V	1300	13	100.0	17%	33	39
Steel	5354	205	26.1	3%	245	22
Nitrides	1200	2.5	480.0	47%	25	48
Nano	30,828	?	?	?	?	?

虽然科技论文数不能完全代表相关产业的发展，纵观历史我们可以发现其实科技论文数和相关产业的大小是有着非常密切的关联性的。例如对于成熟的产业，例如钢铁，这个比值大约是约30篇科技论文对应10亿美金的产值。对于不那么成熟的产业，这个比例要大些。例如对于硅基产业这个比例目前大致为90，预计到2010年将进一步降低至50左右。纳米科技目前的发展还相当不成熟，这个比例还相当高。美国基金会以及若干欧洲的研究机构的估算和预测都表明10年内和纳米科技相关的产业将达到2万亿美金的水平。 .

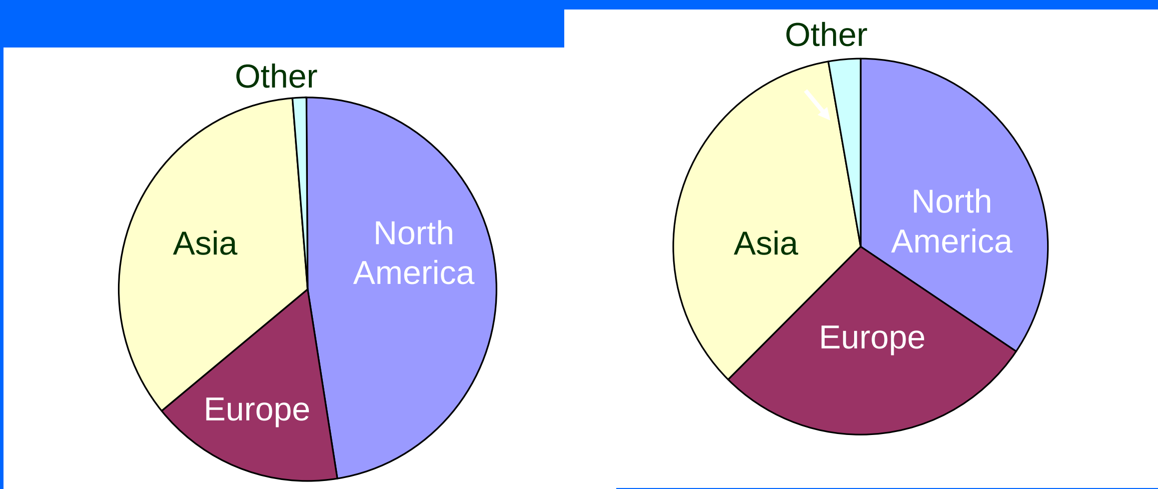
NNI Budgets

Estimated spending in 2006 is over $1.3 billion.



The 2007 NII budget is nearly $1.3 billon, an increase of 21% over the 2006 request.

Global investments in 2004 (Total=$8.6 billion)



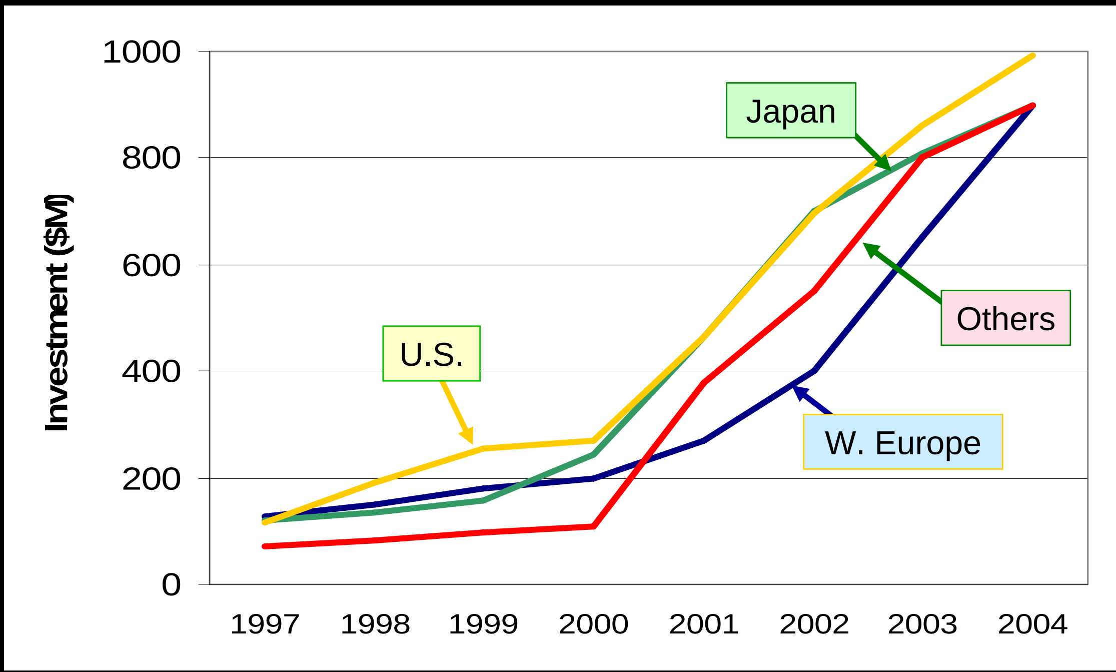
Private (Corp. + VC)
Total = $4 billion

Public (National, regional, state)
Total = $4.6 billion

Source: Lux Research

2005年民间投资将超过政府投资政府

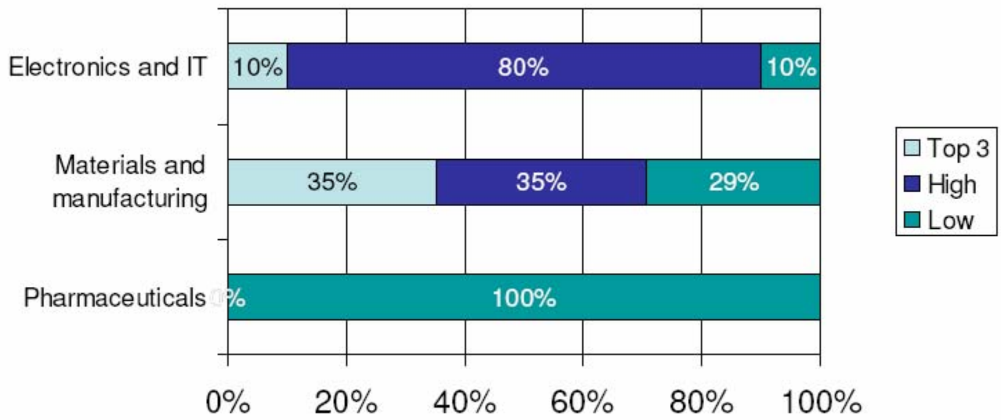
International government spending



Source: National Science Foundation

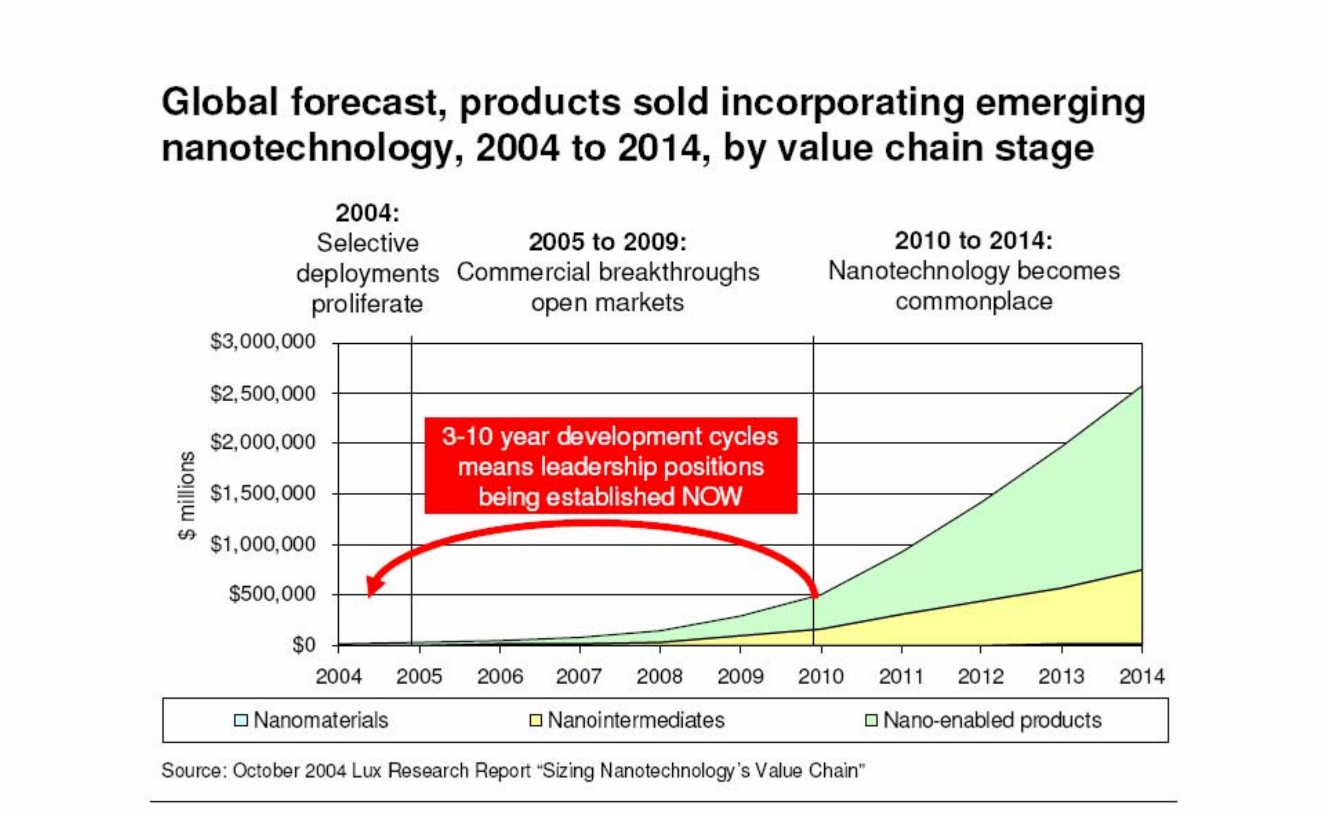
大约90%的电子信息公司的执行总裁认为纳米科技对于他们公司的发展非常重要！！！

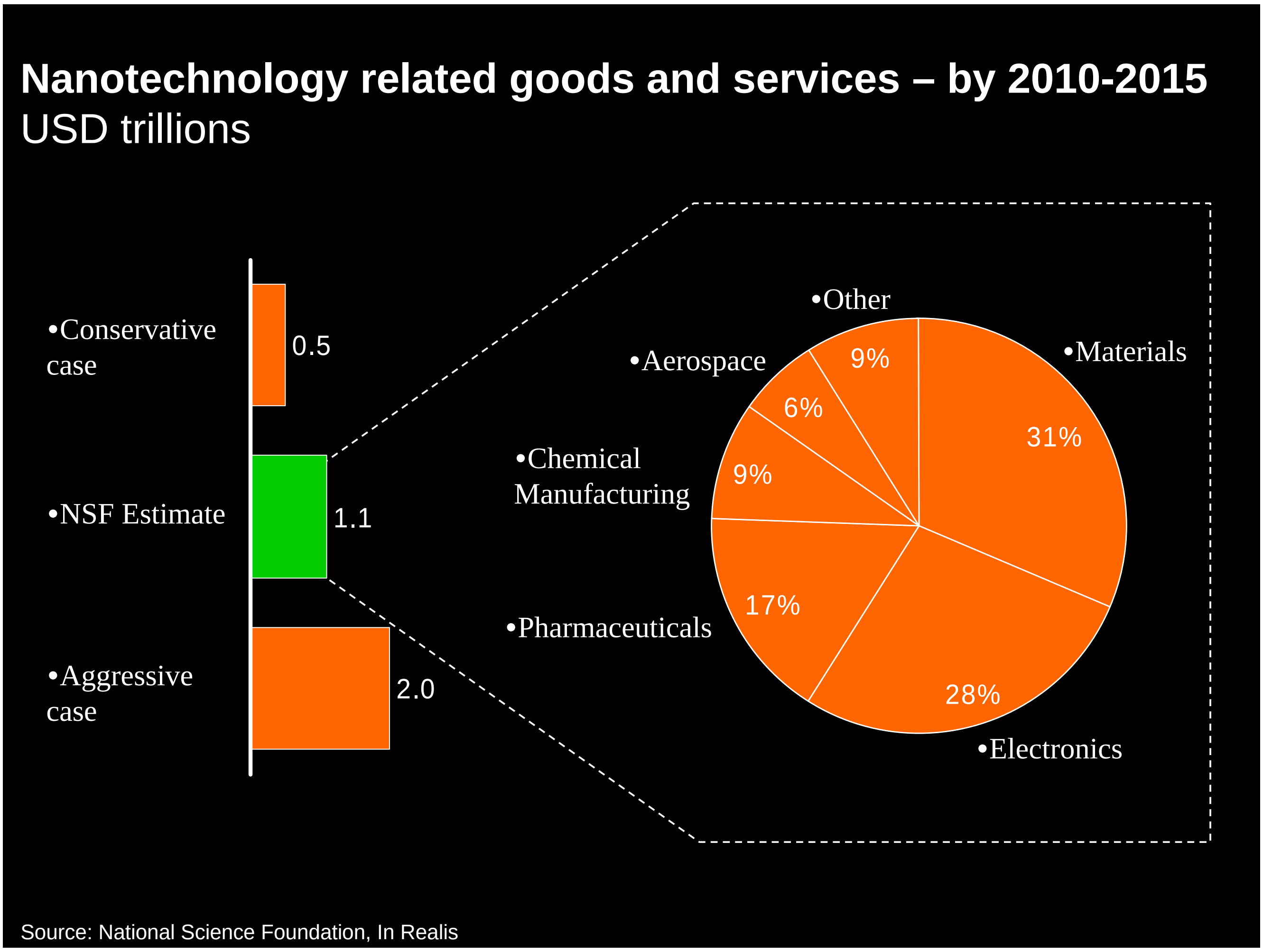
"How big a priority is nanotechnology at your company today?"



Base: 33 global corporations with more than $5B in annual revenue; median $30B revenue and 46,000 employees
Source: December 2004 Lux Research Report "The CEO's Nanotechnology Playbook"

10年以内发展成为万亿美圆的产业！！！





中国与世界的比较（美国人的统计）

J. Nanoparticle Research 2006 Vol 8, Issue 1

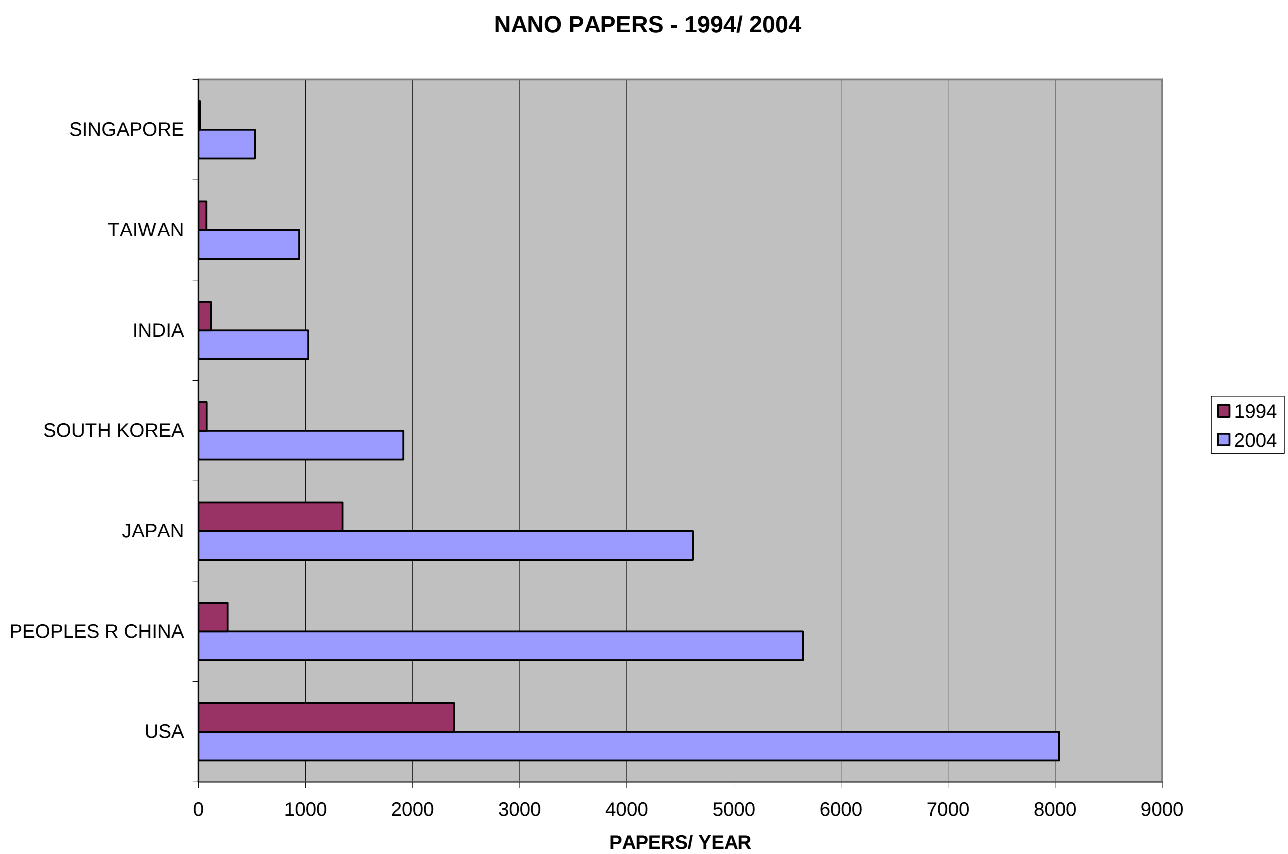
- 2004年大陆已经成为了世界上在纳米领域发表论文第二的国家（在过去的10年内发表论文数增加了21倍），仅次于美国；
- 一般来讲,发表论文多的国家一般拥有发明专利的数量也多.但中国是一个例外.以美国专利为例,2003年中国仅排20名.
- 美国2004年在纳米科技领域发表了8037篇论文，占所发表论文总数的2.7%； 中国2004在纳米科技发表论文总数为5644，占总论文数的10%；
- 在美国的<科学>杂志里纳米科技论文所占的比例为2-3%，但高影响因子论文所占比例高达40%；

The Key Words

- NANOPARTICLE* OR NANOTUB* OR NANOSTRUCTURE* OR NANOCOMPOSITE* OR NANOWIRE* OR NANOCRYSTAL* OR NANOFIBER* OR NANOFIBRE* OR NANOSPHERE* OR NANOROD* OR NANOTECHNOLOG* OR NANOCLUSTER* OR NANOCAPSULE* OR NANOMATERIAL* OR NANOFABRICAT* OR NANOPOR* OR NANOPARTICULATE* OR NANOPHASE OR NANOPOWDER* OR NANOLITHOGRAPHY OR NANO-PARTICLE* OR NANODEVICE* OR NANODOT* OR NANOINDENT* OR NANOLAYER* OR NANOSCIENCE OR NANOSIZE* OR NANOSCALE* OR ((NM OR NANOMETER* OR NANOMETRE*) AND (SURFACE* OR FILM* OR GRAIN* OR POWDER* OR SILICON OR DEPOSITION OR LAYER* OR DEVICE* OR CLUSTER* OR CRYSTAL* OR MATERIAL* OR ATOMIC FORCE MICROSCOP* OR TRANSMISSION ELECTRON MICROSCOP* OR SCANNING TUNNELING MICROSCOP*)) OR QUANTUM DOT* OR QUANTUM WIRE* OR ((SELF-ASSEMBL* OR SELF-ORGANIZ*) AND (MONOLAYER* OR FILM* OR NANO* OR QUANTUM* OR LAYER* OR MULTILAYER* OR ARRAY*)) OR NANOELECTROSPRAY* OR COULOMB BLOCKADE* OR MOLECULAR WIRE*

2004年各国发表论文比较

COUNTRY	2004 NANO PAP	2004 TOT PAP	2004 NANPAP/ TOTPAP	1994 NANO PAP	1994 TOT PAP	1994 NANPAP/ TOTPAP	2004/1994 NANPAP	2004/1994 TOTPAP
USA	8037	294762	0.027266	2388	283530	0.008422	3.365578	1.039615
CHINA	5644	54024	0.104472	271	8976	0.030192	20.82657	6.018717
JAPAN	4617	71411	0.064654	1346	49524	0.027179	3.430163	1.441947
GERMANY	3120	65358	0.047737	928	45686	0.020313	3.362069	1.430591
FRANCE	1954	46647	0.041889	519	35346	0.014683	3.764933	1.319725
SOUTH KOREA	1912	22284	0.085801	77	3450	0.022319	24.83117	6.45913
ENGLAND	1465	57134	0.025641	467	43254	0.010797	3.137045	1.320895
RUSSIA	1300	23992	0.054185	249	24737	0.010066	5.220884	0.969883
ITALY	1115	35561	0.031355	204	21054	0.009689	5.465686	1.689038
INDIA	1025	21117	0.048539	115	12129	0.009481	8.913043	1.741034
TAIWAN	941	13456	0.069932	73	5244	0.013921	12.89041	2.56598
SPAIN	829	26302	0.031519	114	12548	0.009085	7.27193	2.096111
CANADA	785	35630	0.022032	246	29200	0.008425	3.191057	1.220205
SWITZERLAND	598	14552	0.041094	175	9882	0.017709	3.417143	1.472576
NETHERLANDS	584	20176	0.028945	207	14376	0.014399	2.821256	1.40345
POLAND	582	12968	0.04488	67	5878	0.011398	8.686567	2.206193
SINGAPORE	527	5348	0.098542	14	1378	0.01016	37.64286	3.880987
SWEDEN	471	15021	0.031356	128	11167	0.011462	3.679688	1.345124
BRAZIL	462	14631	0.031577	47	4368	0.01076	9.829787	3.349588
AUSTRALIA	462	22789	0.020273	101	14392	0.007018	4.574257	1.583449



从1994年2004年,中国科学家发表的论文数量增加了21倍!

中国科学的地位

北京大学在世界的排名（5年）

INSTITUTION RANKINGS IN (ALL FIELDS)

Display items with at least: 0 Citation(s)

Sorted by: Citations SORT AGAIN

381 - 400 (of 3342) [11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20] Page 20 of 168

	View	Institution	Papers	Citations	Citations Per Paper
381		NATL INST MED RES	2,563	77,517	30.24
382		INDIAN INST TECHNOL	21,423	77,322	3.61
383		AMGEN	2,181	77,321	35.45
384		NOVARTIS PHARMA AG	3,678	76,703	20.85
385		FOX CHASE CANC CTR	2,897	76,699	26.48
386		UNIV BUENOS AIRES	11,368	76,532	6.73
387		INST CANC RES	3,027	76,338	25.22
388		BEIJING UNIV	16,702	76,336	4.57
389		NATL CTR ATMOSPHER RES	4,067	75,975	18.68

中国在世界的排名（10年）

COUNTRY/TERRITORY RANKINGS IN (ALL FIELDS)

Display items with at least: 0 Citation(s)

Sorted by: Citations SORT AGAIN

1 - 20 (of 146) [1 | 2 | 3 | 4 | 5 | 6 | 7 | 8] Page 1 of 8

	View	Country/Territory	Papers	Citations	Citations Per Paper
1		USA	2,784,437	36,571,232	13.13
2		ENGLAND	632,645	7,307,398	11.55
3		GERMANY	711,362	7,242,783	10.18
4		JAPAN	759,619	6,090,783	8.02
5		FRANCE	513,012	4,997,969	9.74
6		CANADA	375,968	4,049,152	10.77
7		ITALY	351,590	3,245,707	9.23
8		NETHERLANDS	211,248	2,572,057	12.18
9		AUSTRALIA	236,244	2,189,849	9.27
10		SWITZERLAND	151,435	2,096,082	13.84
11		SPAIN	249,372	1,964,621	7.88
12		SWEDEN	163,060	1,894,248	11.62
13		PEOPLES R CHINA	387,753	1,402,090	3.62

中国的物理学

COUNTRY/TERRITORY RANKINGS IN PHYSICS

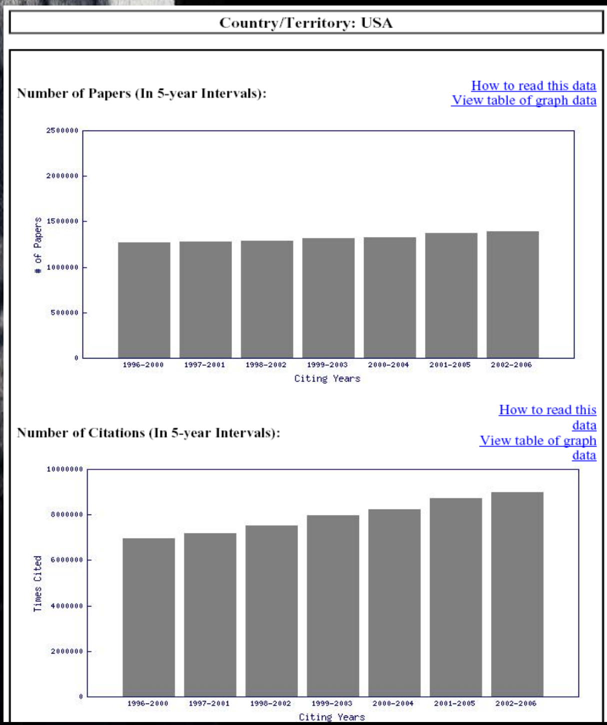
Display items with at least: 0 Citation(s)

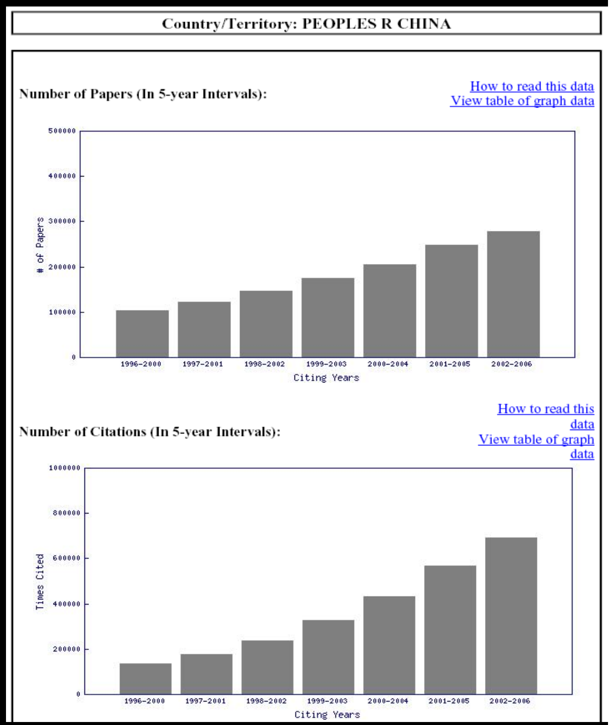
Sorted by: Citations SORT AGAIN

1 - 20 (of 86) [1 | 2 | 3 | 4 | 5] Page 1 of 5

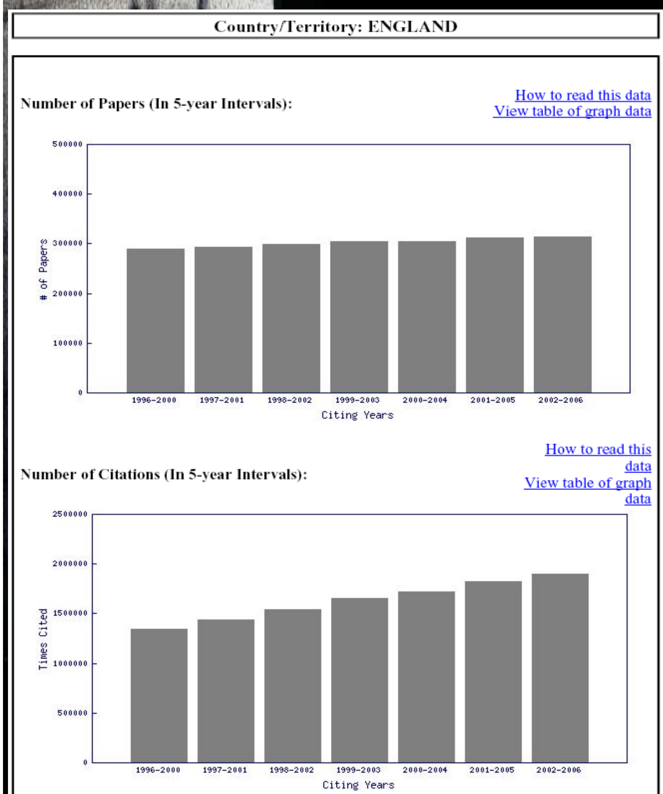
	View	Country/Territory	Papers	Citations	Citations Per Paper
1		USA	205,593	2,402,741	11.69
2		GERMANY	99,369	963,678	9.70
3		JAPAN	111,624	789,209	7.07
4		FRANCE	70,433	599,735	8.51
5		ENGLAND	52,303	502,598	9.61
6		RUSSIA	78,819	406,752	5.16
7		ITALY	46,392	390,849	8.42
8		SWITZERLAND	20,991	269,541	12.84
9		PEOPLES R CHINA	69,632	262,441	3.77
10		SPAIN	25,600	217,516	8.50

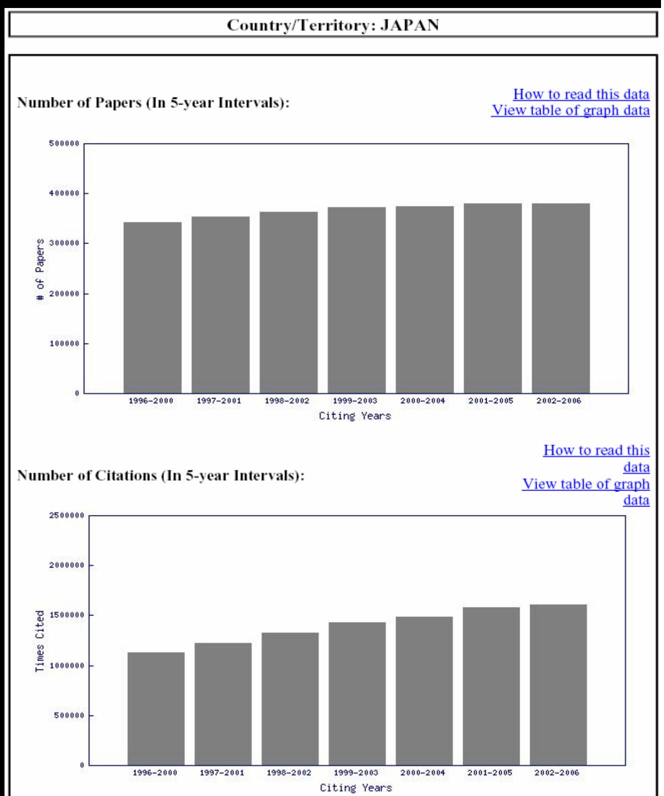
科学的发展：美国 vs 中国





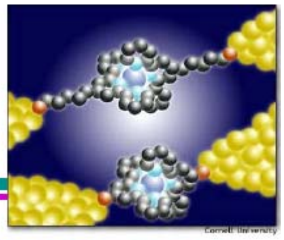
科学的发展：英国 vs 日本





Nanotechnology

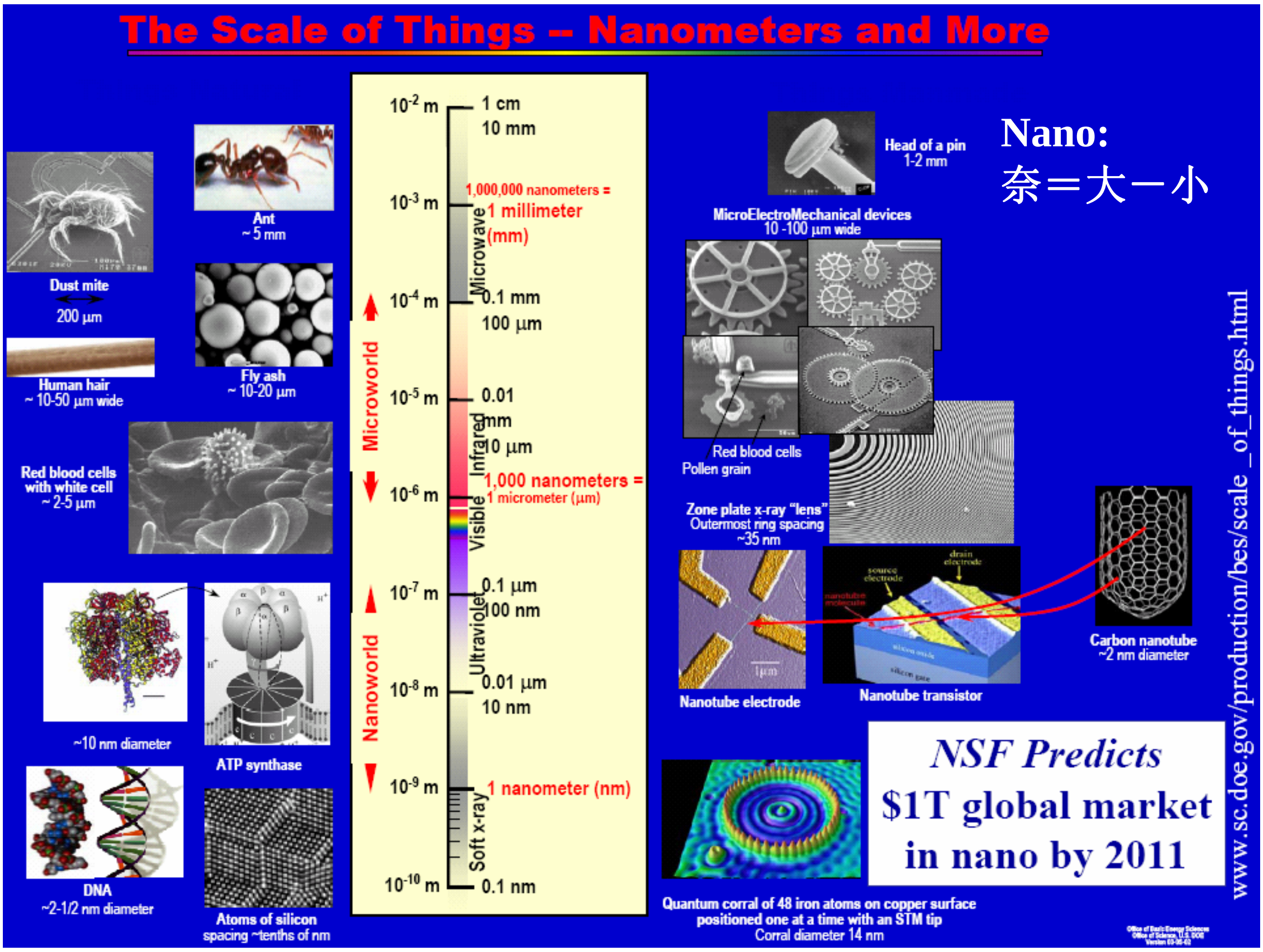
Definition on www.nano.gov/omb_nifty50.htm (2000)



- Working at the atomic, molecular and supramolecular levels, in the length scale of approximately 1 – 100 nm range, in order to understand and create materials, devices and systems with fundamentally new properties and functions because of their small structure
- **NNI definition encourages new contributions that were not possible before.**
  - novel phenomena, properties and functions at nanoscale, which are nonscalable outside of the nm domain
  - the ability to measure / control / manipulate matter at the nanoscale in order to change those properties and functions
  - integration along length scales, and fields of application

MC. Roco, 5/17/04

纳米尺度的测量、控制和操纵，纳米尺度的新现象、新性质和功能



物理学家喜欢谈的纳米科技发展的版本

http://www.zyvex.com/nanotech/feynman.html

On December 29th 1959 at the annual meeting of the American Physical Society at the California Institute of Technology (Caltech), Nobel Laureate Richard Feynman invited physicists to create a new field of scientific research

There's Plenty of Room at the Bottom

An Invitation to Enter a New Field of Physics

by Richard P. Feynman

There's Plenty of Room at the Bottom

An Invitation to Enter a New Field of Physics

by Richard P. Feynman

In this classical talk, Feynman drew attention to the huge benefits to be gained from the ability to produce computers and machines on a molecular scale. He speculated that at some time in the future these would be assembled at the atomic level, observing that the principles of physics do not speak against the possibility of manoeuvring things atom by atom.

纳米为何现在热（固体电子学家的版本）？

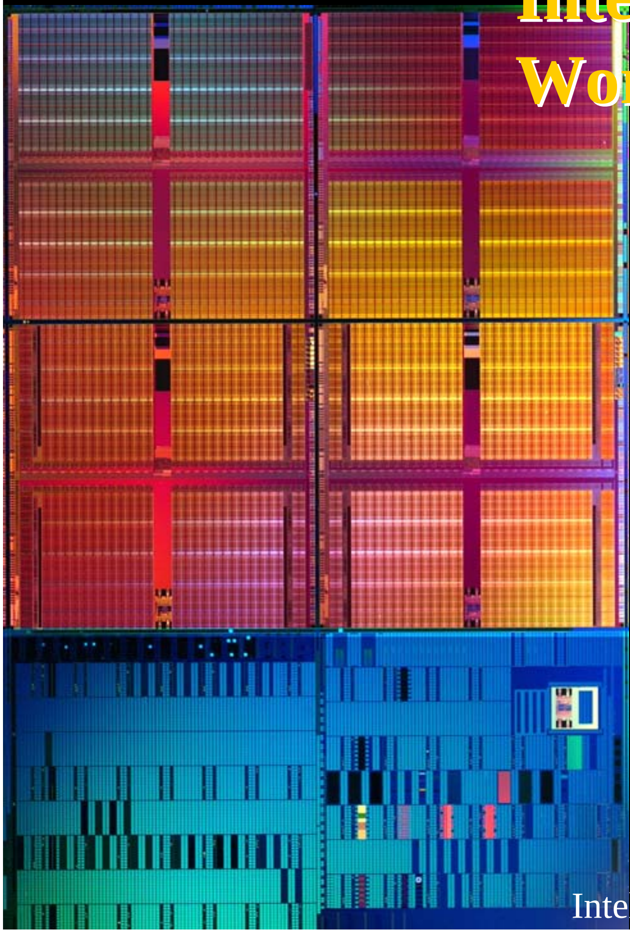
Modern Computers

- The first generation of computers used vacuum tubes;
- The second generation of computers used transistors;
- The third generation of computers used integrated circuits;
- The fourth generation of computers used microprocessors;
- The fifth generation ?????

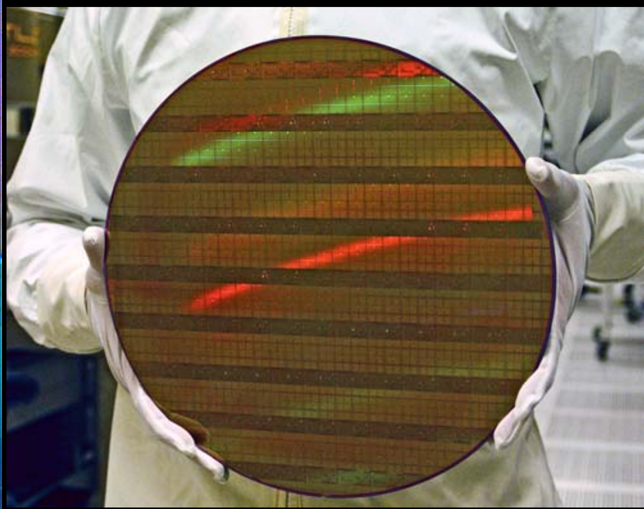
The best way
to predict the future
is to invent it.

Alan Kay

Intel First to Demonstrate Working 45nm Chips

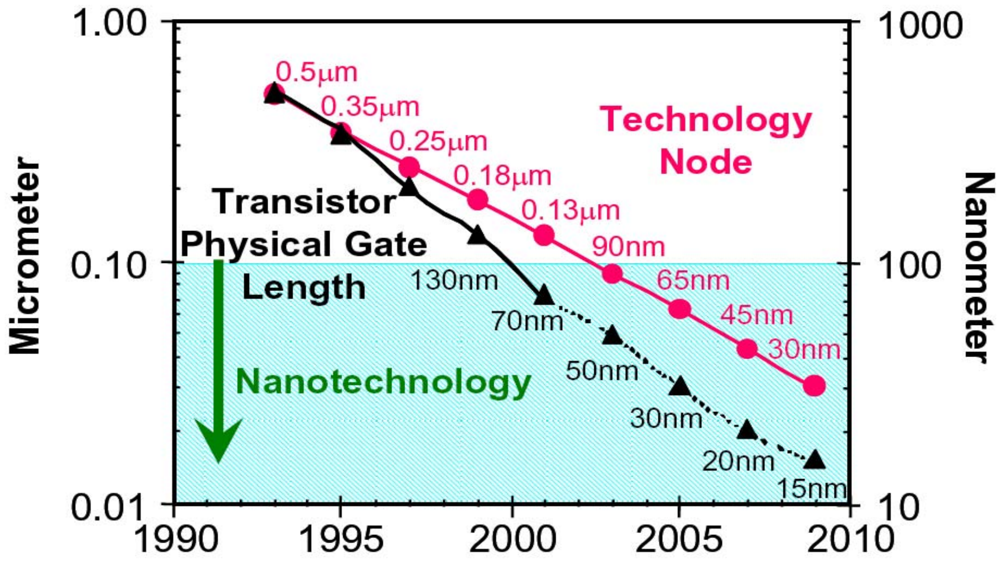


SANTA CLARA, Calif., Jan. 25, 2006 – Intel Corporation today announced it has become the first company to reach an important milestone in the development of 45 nanometer (nm) logic technology.



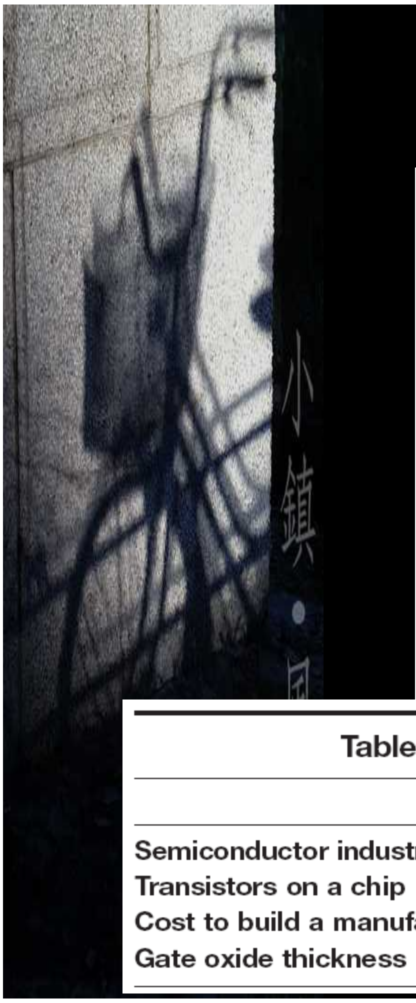
Intel® 300 mm wafer with 45 nm shuttle test chips

Intel's vision on Transistor Scaling



Transistor physical gate length will reach ~15 nm before end of this decade, and ~10 nm early next decade

The Scaling of CMOS



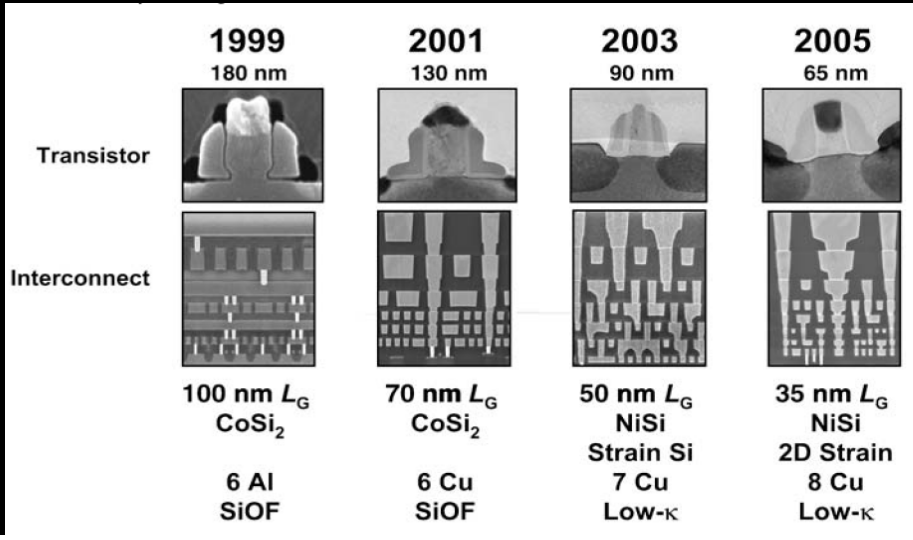


Table I: The Semiconductor Industry—Then and Now.

	1993	2006
Semiconductor industry revenue	$77 billion	$230 billion
Transistors on a chip	10 million	1.7 billion
Cost to build a manufacturing plant	$1 billion	$3 billion
Gate oxide thickness	80 Å	12 Å

nature

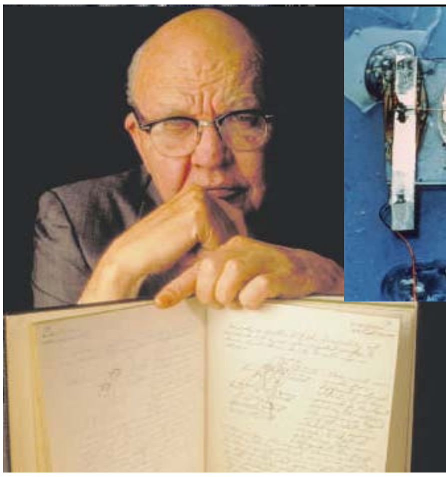
BUSINESS

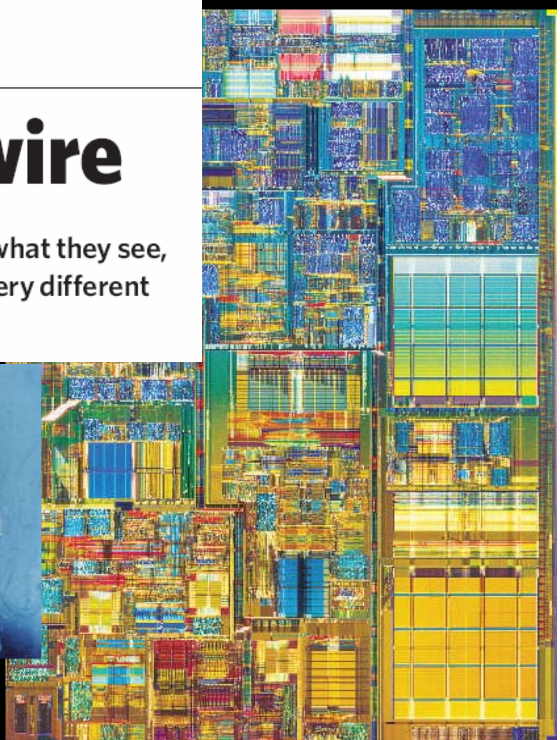
Nature 7, July 2005

Silicon down to the wire

Microchip-makers are starting to look beyond silicon, and what they see, reports **Colin Macilwain**, is a semiconductor industry of a very different complexion — but not for some time yet.

Roadmap 2005





First integrated circuit by ←Jack Kilby

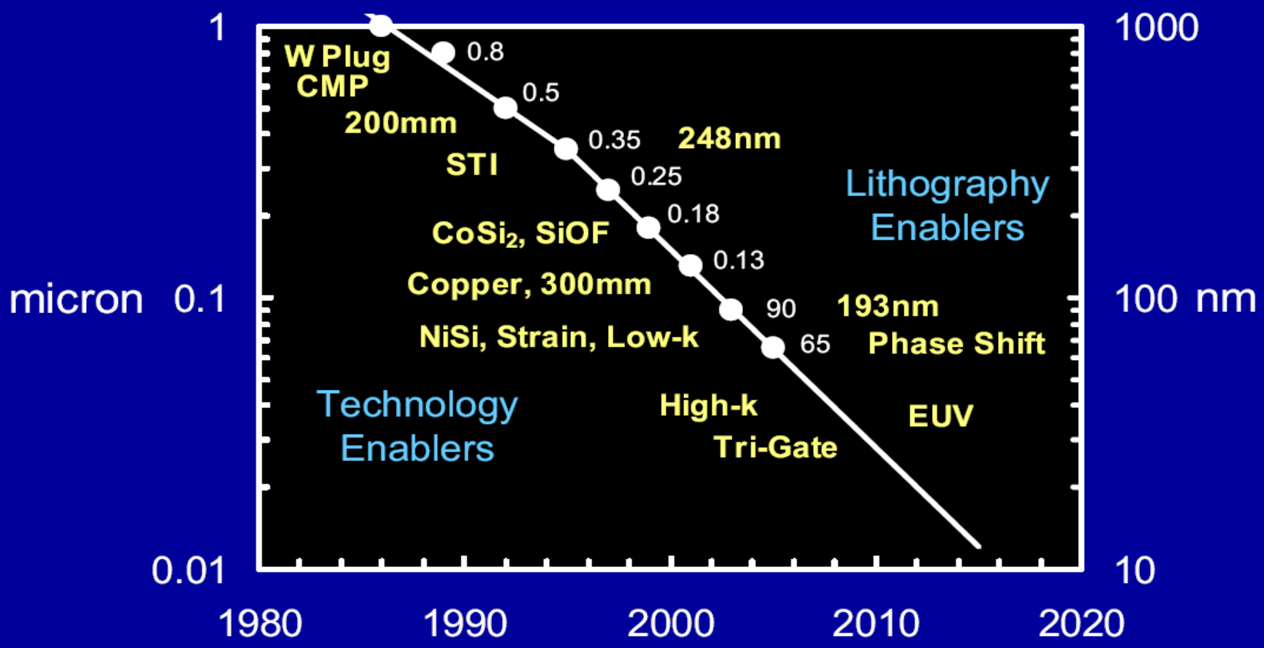
Pentium 4

The scaling cannot go on forever …

The limits to the Moore's law are often said to be lithography …

It turns out that materials are now a key constrain …

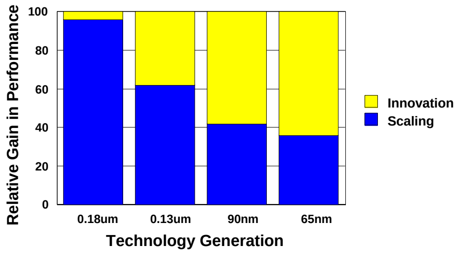
Scaling Gets Tougher at Smaller Dimensions

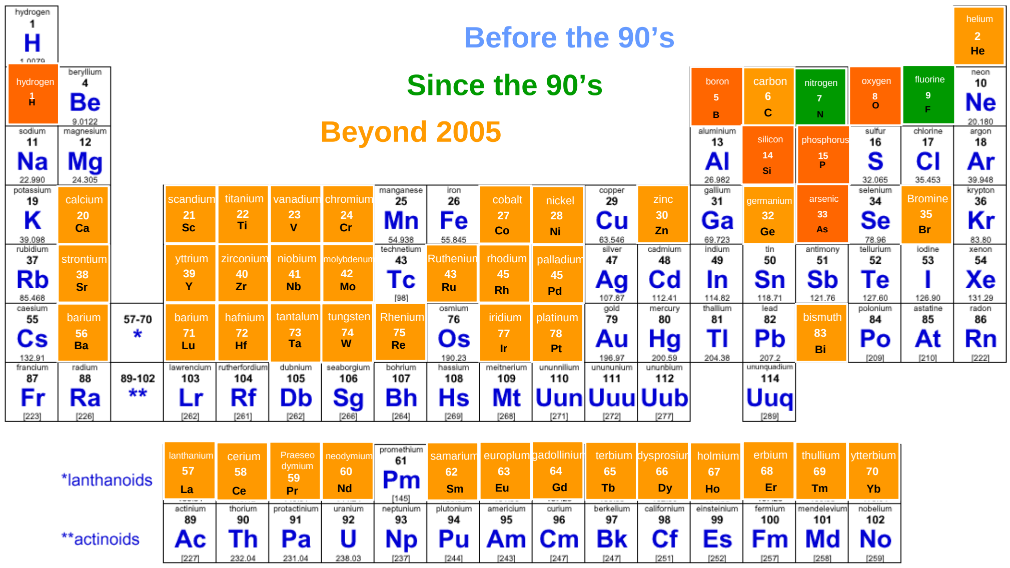


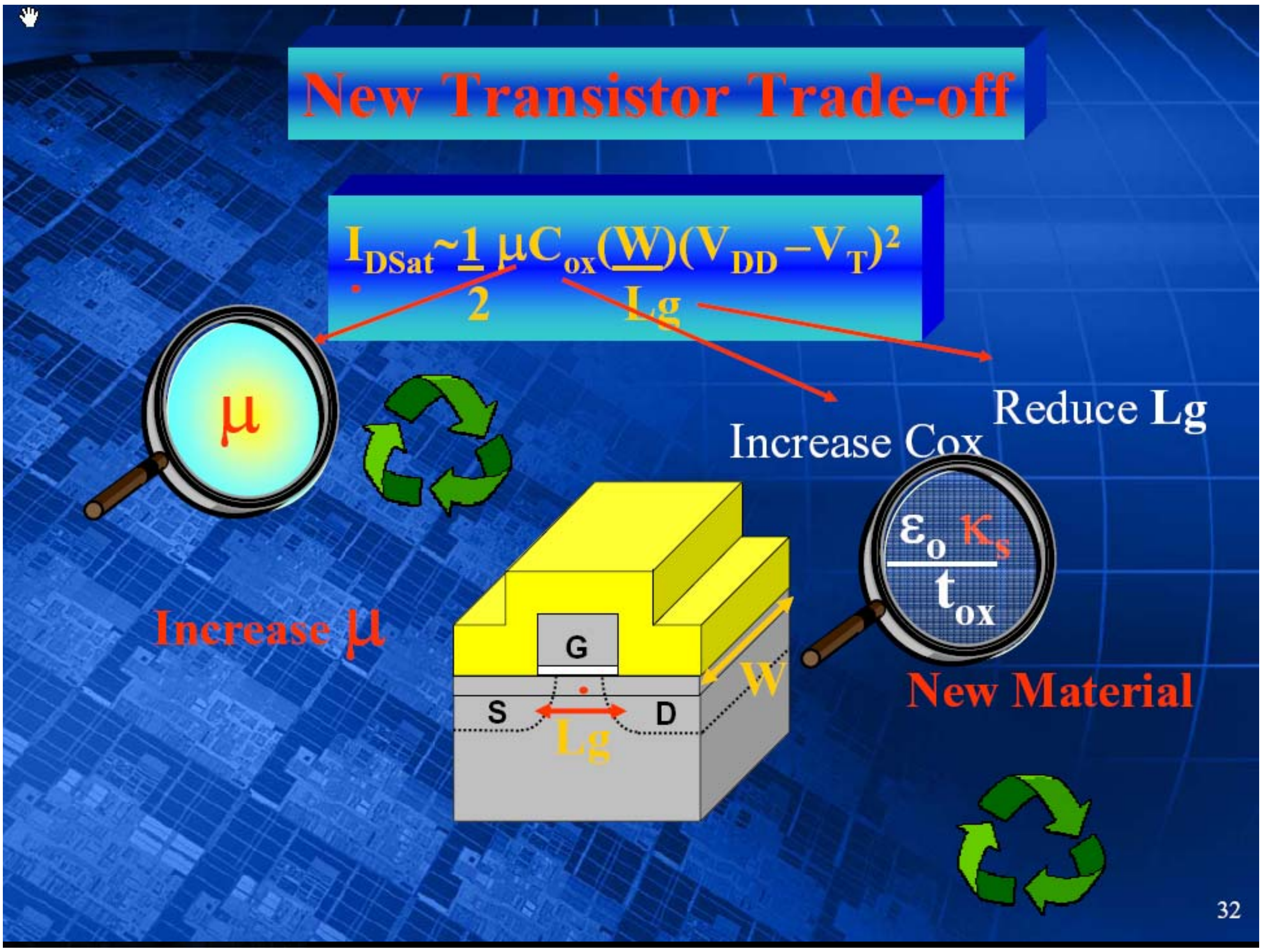
New materials and structures needed to meet the challenge

Improving Performance

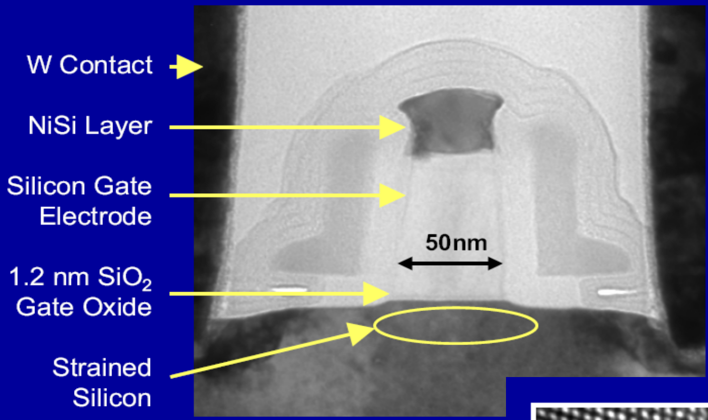
- No longer possible by scaling alone
  - New Device Structures
  - New Device Design point
  - New Materials

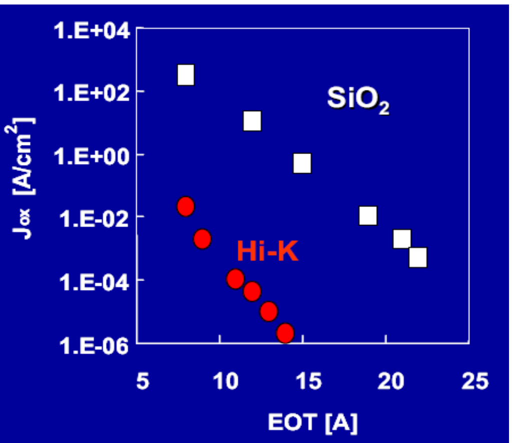






90 nm Generation Transistor



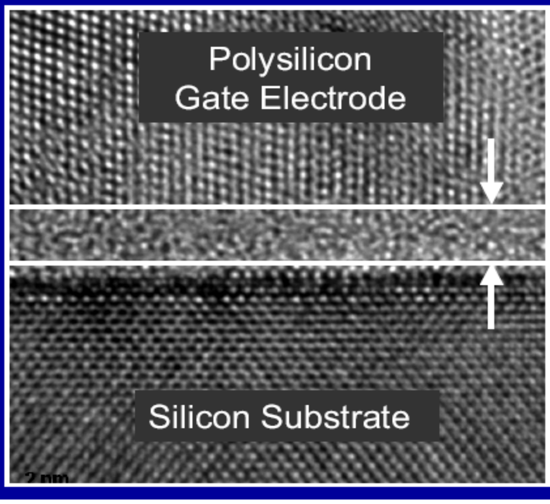


With higher mobility μ

SiO_2 scaling limited by leakage below 1.2 nm

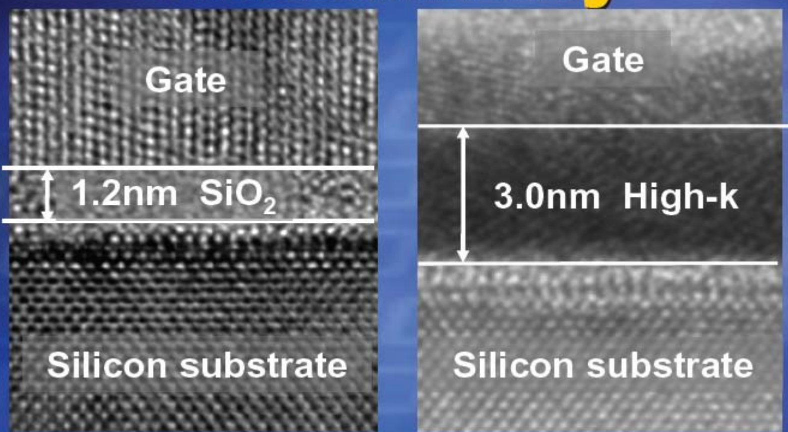
Quantum limit →

Poly gate depletion limits electrical gate oxide scaling



1.2 nm SiO_2

High-k Dielectric reduces leakage substantially



Benefits compared to current process technologies

	High-k vs. SiO_2	Benefit
Capacitance	60% greater	*Much faster transistors*
Gate dielectric leakage	> 100x reduction	*Far cooler*

intel

Continuation of Moore's Law

With known solution up to 2011, at the 22nm node with physical gate length ~ 10nm

Process Name	P856	P858	Px60	P1262	P1264	P1266	P1268	P1270
1st Production	1997	1999	2001	2003	2005	2007	2009	2011
Process Generation	0.25μm	0.18μm	0.13μm	90 nm	65 nm	45 nm	32 nm	22 nm
Wafer Size (mm)	200	200	200/300	300	300	300	300	300
Inter-connect	Al	Al	Cu	Cu	Cu	Cu	Cu	?
Channel	Si	Si	Si	Strained Si	Strained Si	Strained Si	Strained Si	Strained Si
Gate dielectric	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	High-k	High-k	High-k
Gate electrode	Poly-silicon	Poly-silicon	Poly-silicon	Poly-silicon	Poly-silicon	Metal	Metal	Metal

Introduction targeted at this time

Subject to change

Intel found a solution for High-k and metal gate

Implications of using high-k

- Good FETs require
  - Short channel length Lg
  - High mobility μ → strained Si (90, 65nm nodes)
  - Large Cox → high k, metal gate (45 nm node)
  - New geometries → Fin- and Tri-FETs (32, 22nm node)
  - After 2011 ???
- Golden combination
  - Si+SiO_2, not so much about Si, it is all about SiO_2!!!
  - Si is only an ordinary semiconductor
  - Other semiconductors + high k ???

更高的迁移率

Picking the Right High-μ Material

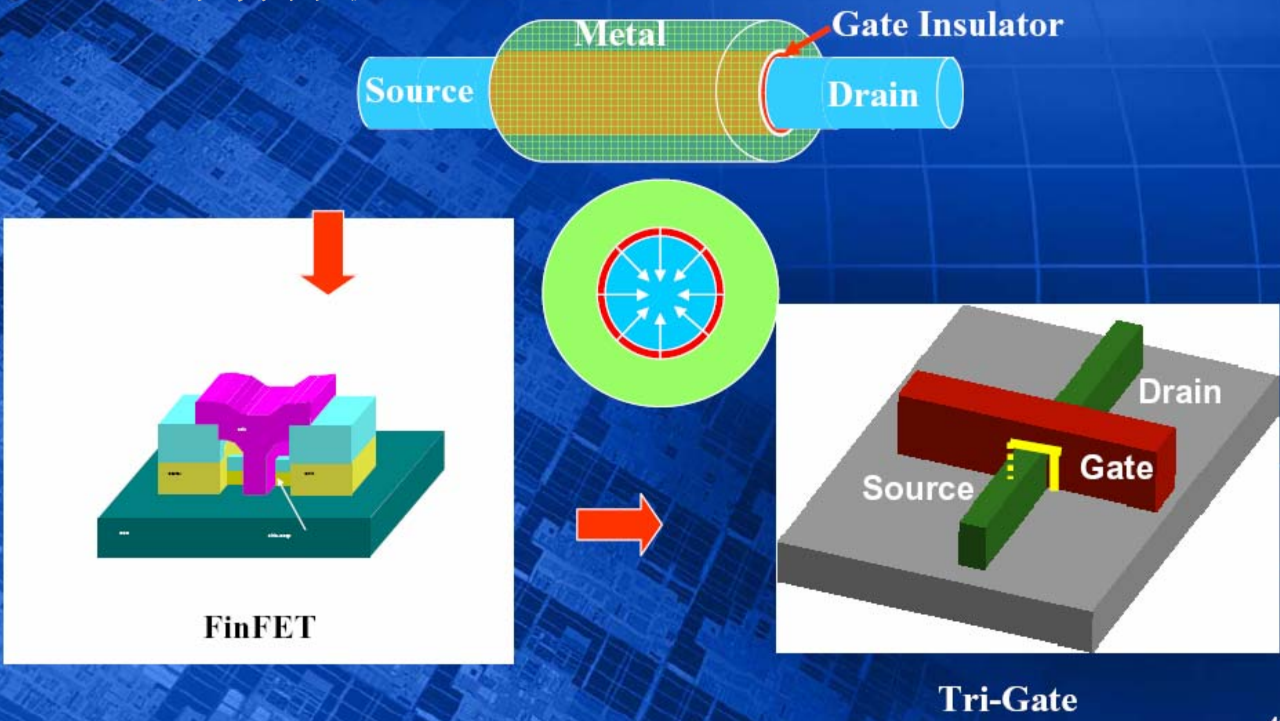
Material ⇒ Property ⇓	Si	Ge	GaAs	InAs	InSb	CNT
Electron mobility	1600	3900	9200	40000	77000	>100000
Hole mobility	430	1900	400	500	850	
Bandgap (eV)	1.12	0.66	1.424	0.36	0.17	1-2eV
Dielectric constant	11.8	16	12.4	14.8	17.7	

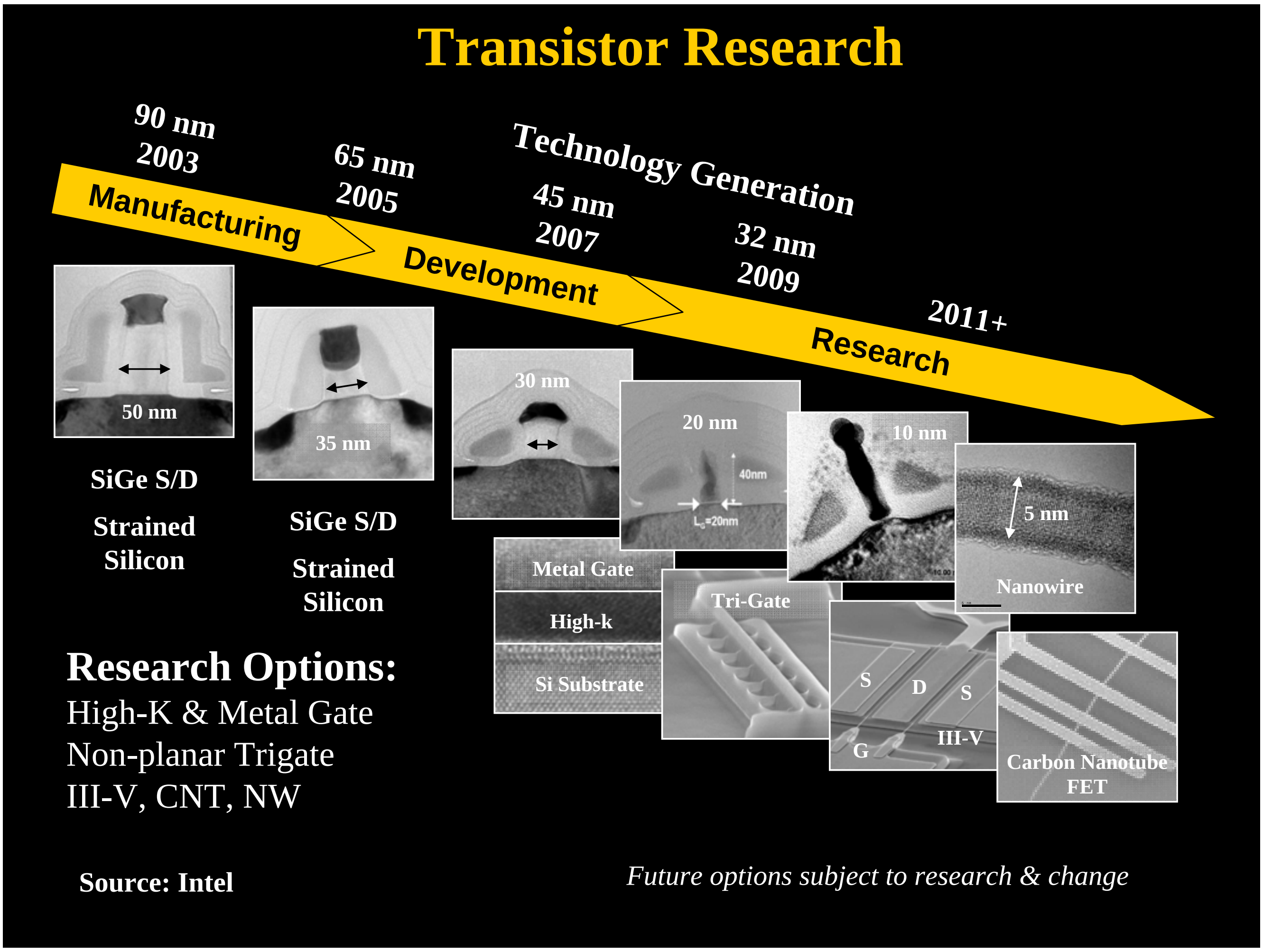
As a semiconductor, Si has an average performance, but in most cases SiO_2 is an excellent insulator.

更好的电容偶合（栅极控制）

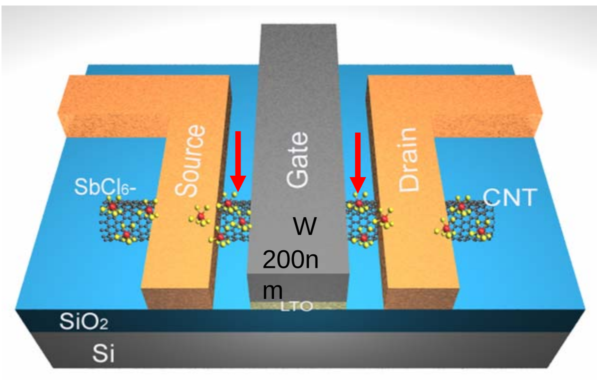
Surrounding the Semiconductor

一维材料最理想

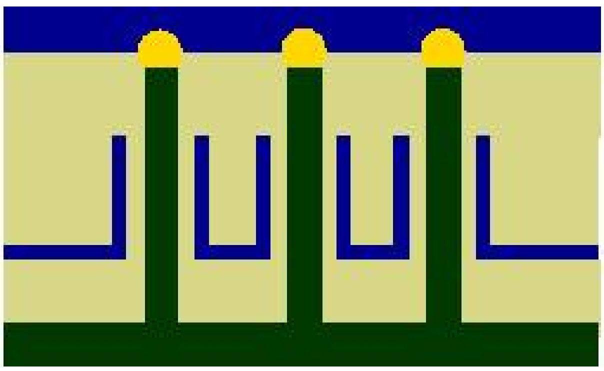




Post-Silicon CMOS: The Quest for the Ultimate FET



Self-Aligned Carbon Nanotube FET:
Extension Contacts Based on
Charge-Transfer Chemical Doping



Vertical Transistor
Based on Semiconductor Nanowires

- The "ultimate FET" may not contain silicon.

纳米科技和介观物理之比较

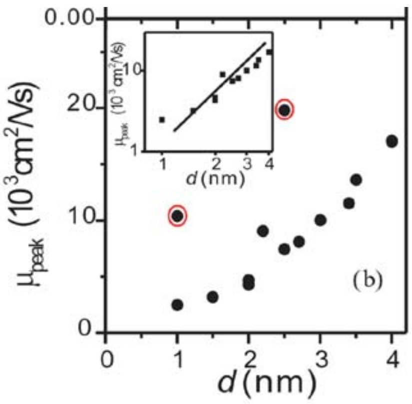
- 纳电子材料与器件
  - 纳米科技、微电子的下一代，长远应用背景的牵引
  - 主要研究方式为自下而上
  - 主要研究对象为各类纳米管、线等（主要是一维材料）
  - 接触或电极问题，可控度（结构和搀杂）差
  - 材料丰富，制备简单和便宜
- 介观物理
  - 介观尺度的新物理现象，人类对于未知的探索
  - 主要研究方式为自上而下
  - 主要研究对象为半导体量子井、超晶格、2维电子气、量子点等（主要是零维和二维材料）
  - 基本无接触或电极问题，高度可控
  - 有限种类的半导体材料

The performance limit of SWCNT

(P. McEuen et al., PRL 95 (2005) 146805)

$$\mu_{\mathrm{FE}} = (L/C_g^l)(dG/dV_g)$$

Localized states may result in extremely large μ via ~L

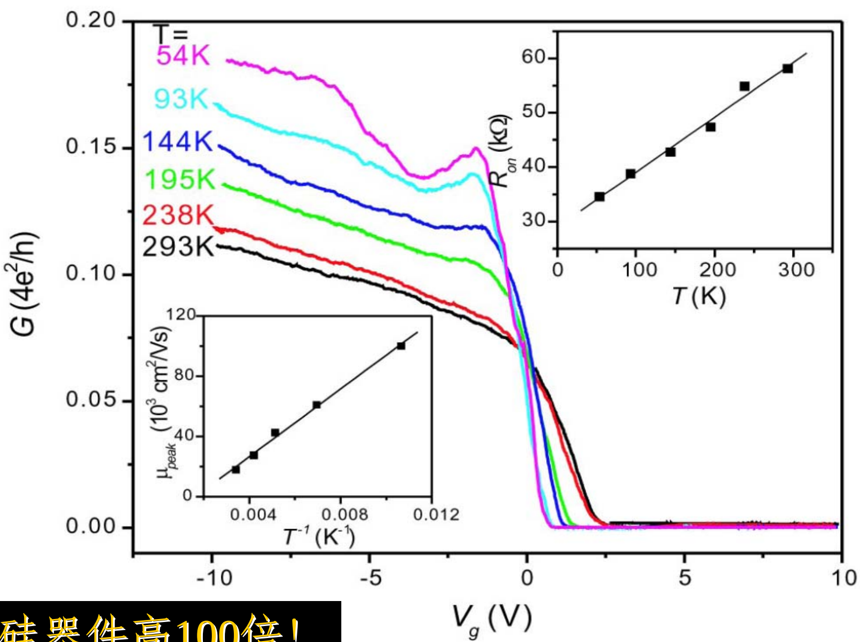


Room Temperature

$$\mu_{\text{peak}} = 0.48 \frac{e v_0}{\hbar \alpha} \frac{d^2}{T}$$

$$G_{\max} = \frac{4e^2 v_0}{h \alpha L} \frac{d}{T}.$$

For comparison, field-effect mobilities achieved in silicon MOSFETs are ~ 1000 cm²/Vs



比硅器件高100倍！

μ_{FE} ~ 1/T, and d^2

reaching 100 000 cm²/Vs at 50K for d=4nm

Intrinsic Switching Speed of CNFETs

Cut-off Frequency $f_T = \dfrac{g_m}{2\pi C_g}$ C_g : gate capacitance

	Lin et al. (IBM)	Javey et al. (Stanford)	Seidel et al. (Infineon)
Diameter	~ 1.8 nm	~ 1.7 nm	~ 1.1 nm
Gate Dielectric	10-nm SiO_2	8-nm HfO_2	12-nm SiO_2
Maximum g_m	12.5 μS	27 μS	3.5 μS
C_g/L	38 pF/m	120 pF/m	32 pF/m
f_T @ L_g = 65 nm	**800 GHz**	550 GHz	260 GHz

Yu-Ming Lin *et al.* (IBM), EDL 2005

高频响应比所有半导体都优越

AC Performance: toward a ballistic THz CNT transistor

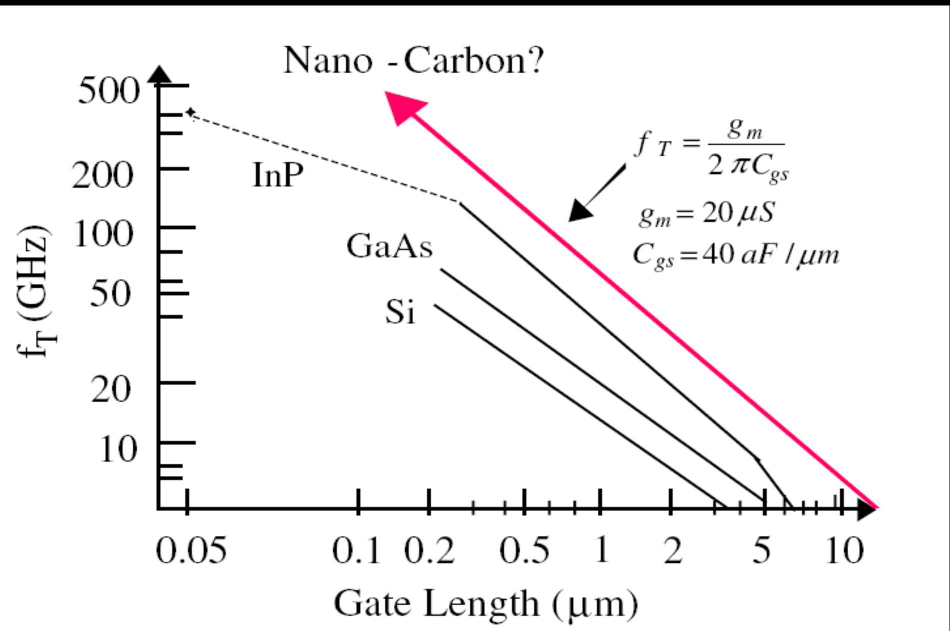
(P.J. Burke, Solid-State Communications 48 (2004) 1981)

RC time for CNT: $1/(2\pi RC) \sim 6.3$THz

Transconductance: $g_m/(2\pi C_{gs}) \sim 400$GHz

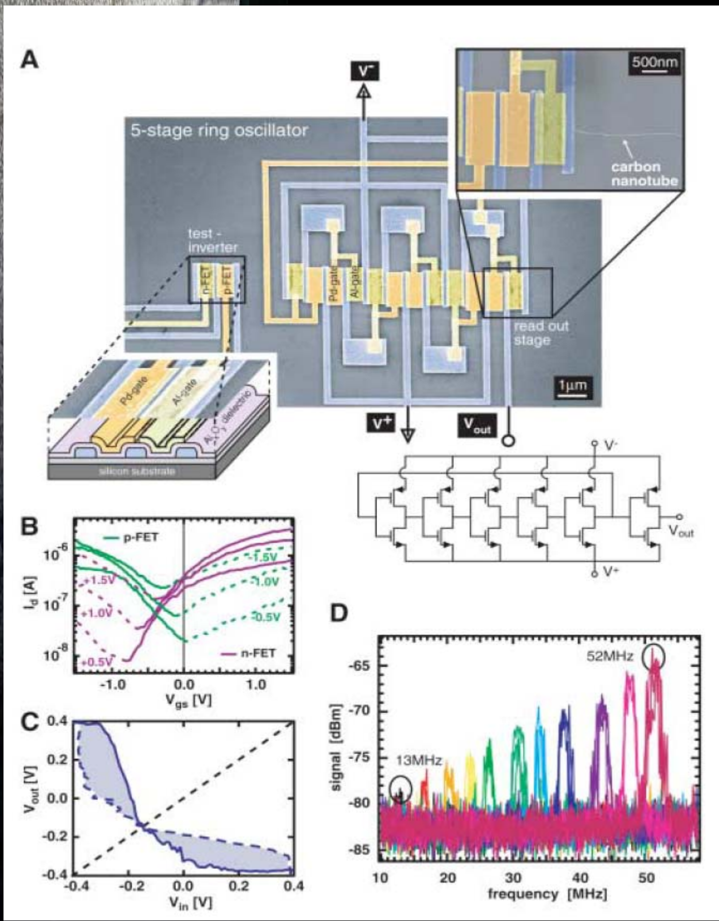
For small-signal equivalent circuit

$$f_T = \frac{80\ \text{GHz}}{L_{gate}\ (\mu\text{m})}$$



f_T: cut off frequency at which the current gain falls to unit.

An Integrated Logic Circuit Assembled on a Single CNT



IBM的研究人员在一根18微米长的碳管上实现了5阶环形振荡器, Science 311 (March 2006) 1735**.**

(A) Scanning electron microscope image of a SWCNT ring oscillator consisting of five CMOS inverter stages. A test inverter was added to determine the parameter set for the actual measurement. (B) Characteristics for the p-type FET with Pd metal gate and n-type FETwith Al gate. (C) Inverter characteristics and its mirrored curve. (D) Voltage-dependent frequency spectra. From the left to the right, the respective supply voltages are as follows: *V*dd 0 0.5 V and 0.56 V to 0.92 V (in 0.4-V increments).

碳纳米管与硅材料之比较

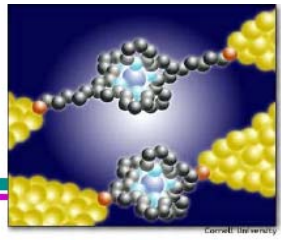
- 许多硅材料目前和将要遇见的问题并不存在于碳纳米管材料中
  - 电子输运是一维的→弹道输运，低功耗， f_T～THz
  - 无悬挂键→不必局限于SiO_2绝缘层，可用高k和晶体绝缘材料，可用于构建三维结构
  - 极强的C=C共价键→优异的机械和热稳定性，非常强的抗电致迁移性→电流密度$10^9 A/cm^2$
  - 理想的静电学控制，关键的尺寸是通过化学而不是通过传统的加工技术来控制的
  - 直接带隙材料→可实现光电器件
  - 从原理来讲，器件单元和互联接都能用碳纳米管来做。
- 碳纳米管电子器件与其他化学、机械以及生物系统的集成
  - 碳纳米管电子器件在生物环境（例如盐水）中工作良好，其尺度和典型的生物分子尺度（例如DNA）相当→理想的单生物分子传感器

纳电子器件结构加工和测量

1. 多种纳米结构原位加工、操纵和实时测量方法
2. 单根碳纳米管的原位场电子发射测量
3. 一维纳米材料I-V曲线的测量和定量分析
4. 单壁和双壁碳纳米管晶体管

Nanotechnology

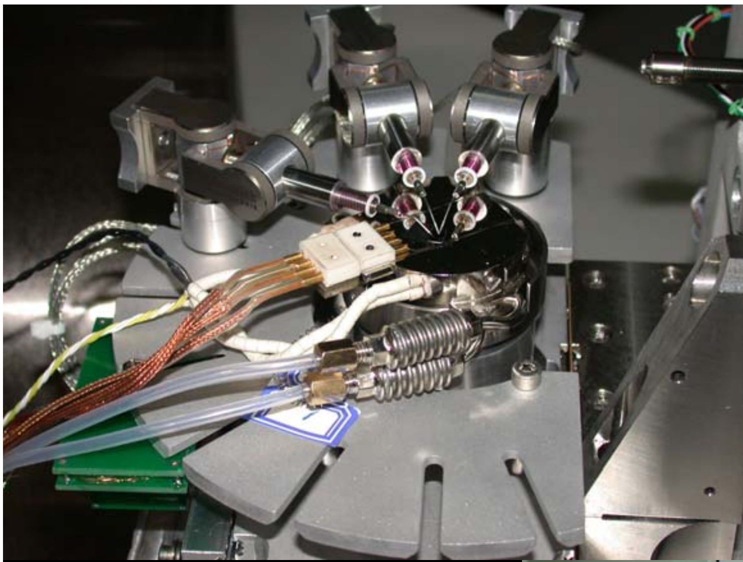
Definition on www.nano.gov/omb_nifty50.htm (2000)

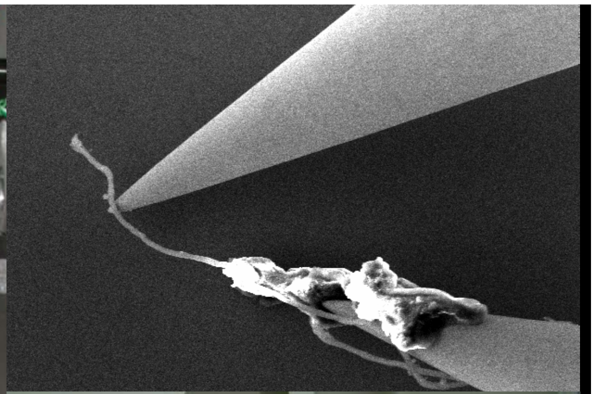


- Working at the atomic, molecular and supramolecular levels, in the length scale of approximately 1 – 100 nm range, in order to understand and create materials, devices and systems with fundamentally new properties and functions because of their small structure
- **NNI definition encourages new contributions that were not possible before.**
  - novel phenomena, properties and functions at nanoscale, which are nonscalable outside of the nm domain
  - the ability to measure / control / manipulate matter at the nanoscale in order to change those properties and functions
  - integration along length scales, and fields of application

MC. Roco, 5/17/04

纳米尺度的测量、控制和操纵，纳米尺度的新现象、新性质和功能



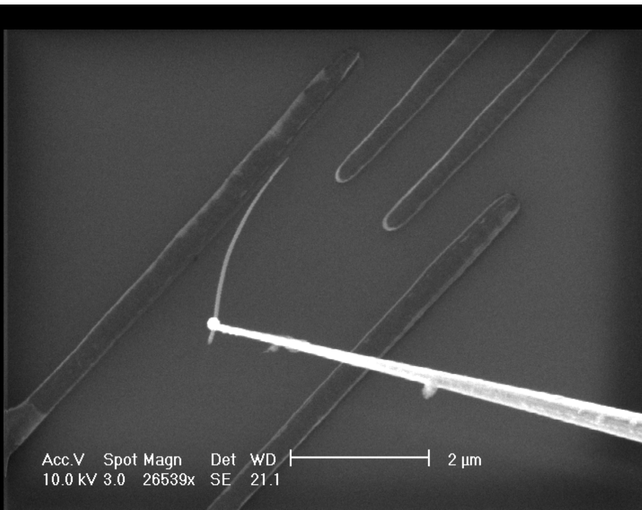


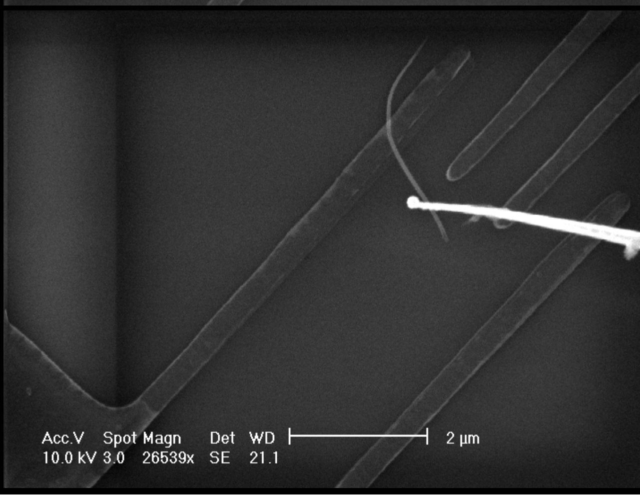
扫描电镜中的纳米探针

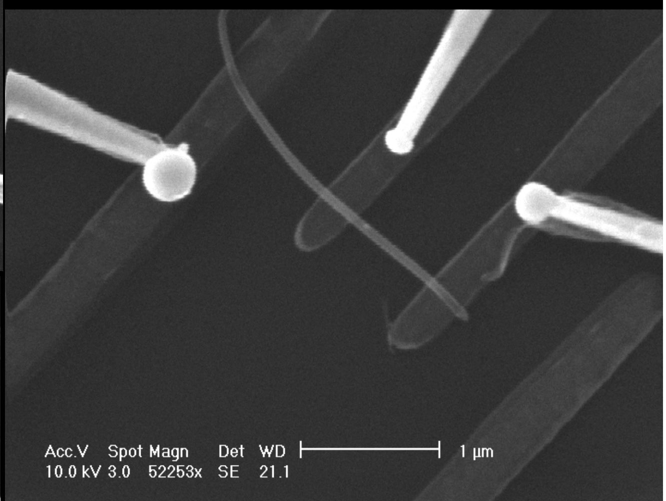
扫描电镜中单个纳米结构的电学和力学性能测量；纳米精度的操纵

原位电学测量

(X.L. Wei, Q. Chen et al.)



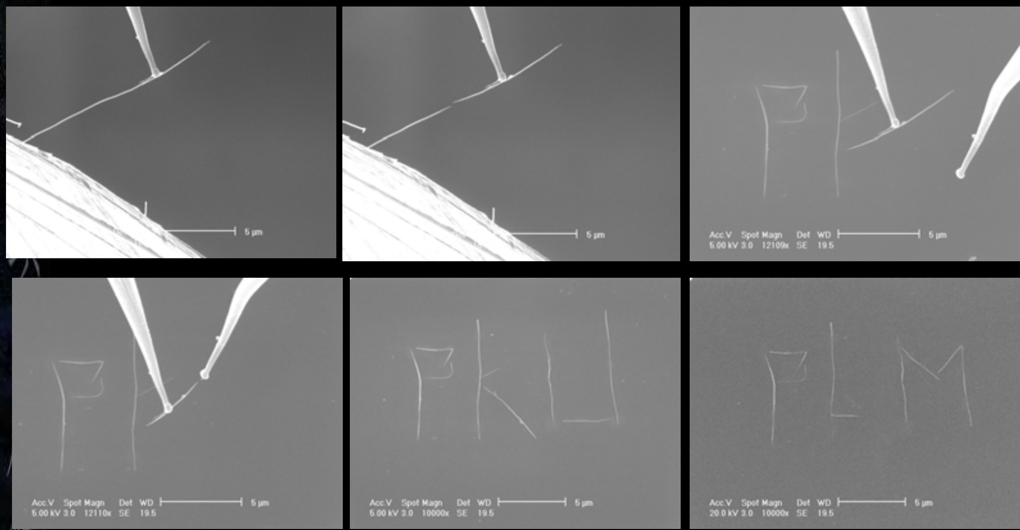




可以搬迁碳纳米管，变换基底，开展原位的实时电性能测量。

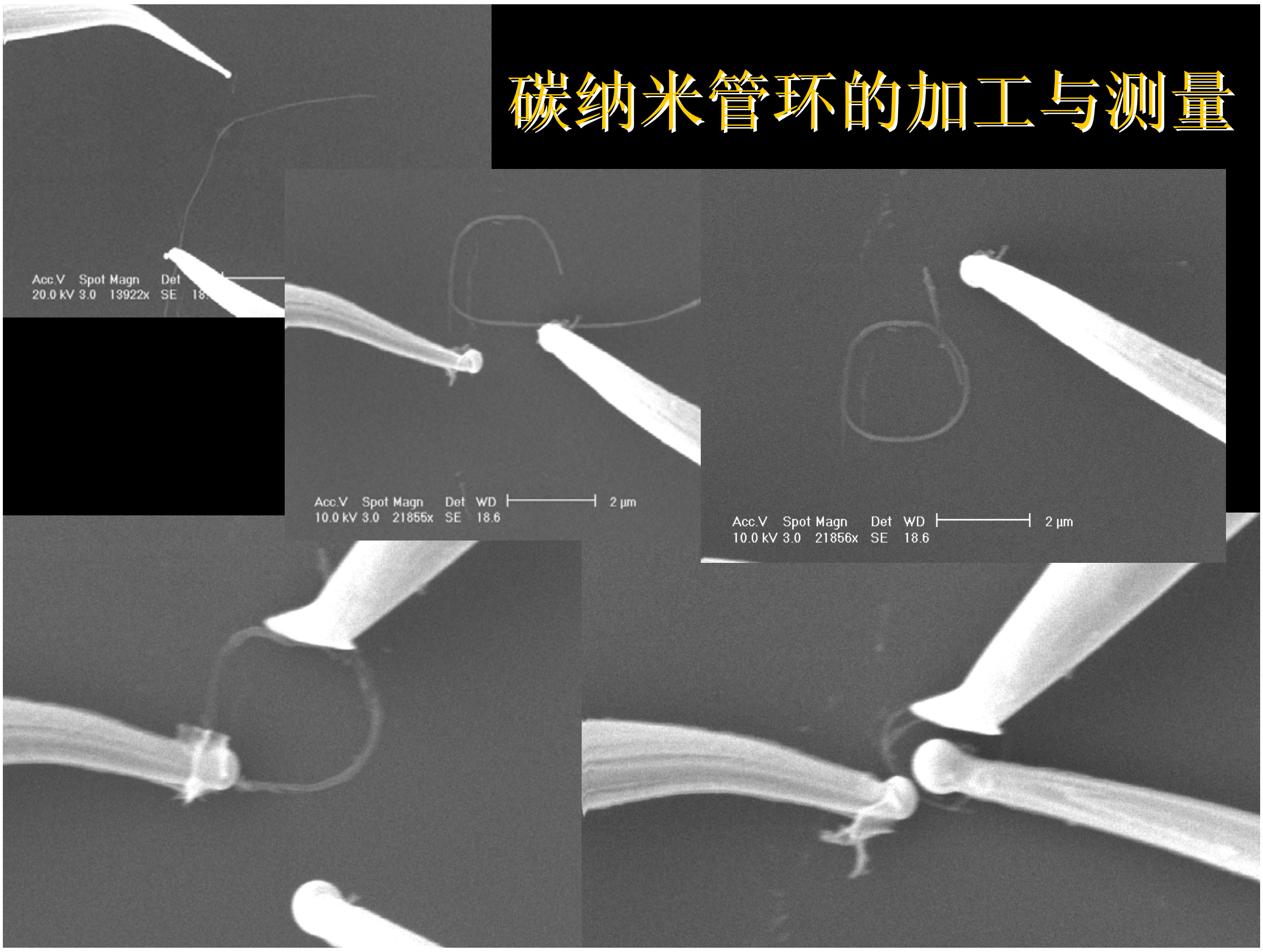
Writing with carbon nanotubes

多探针操纵



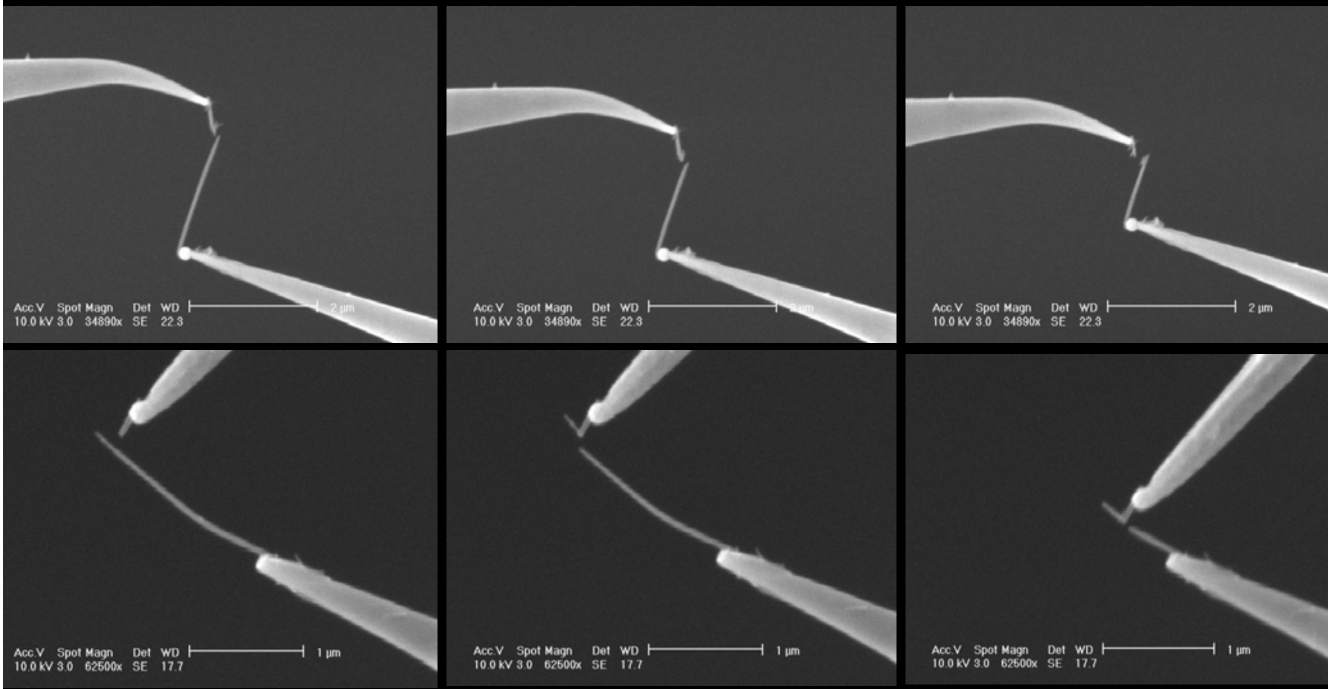
PeKing University　Peng Lian-Mao

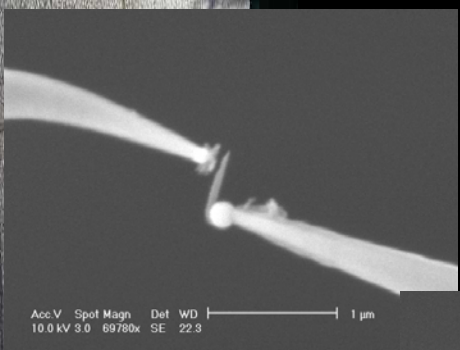
碳纳米管环的加工与测量



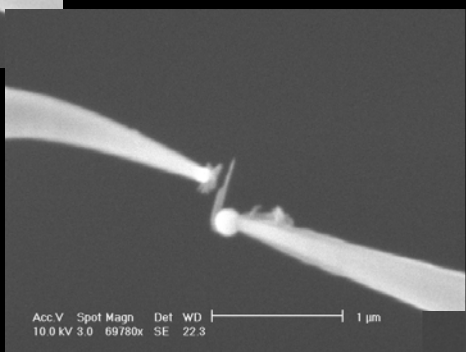
利用碳纳米管做刀将另一碳纳米管切短

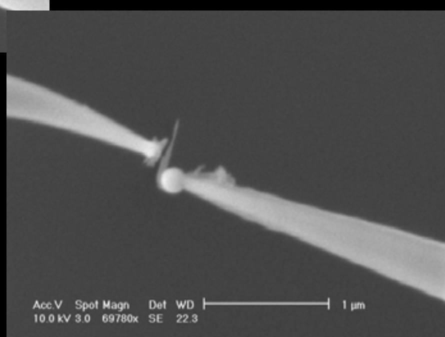
X.L. Wei, Q. Chen et al. (unpublished)

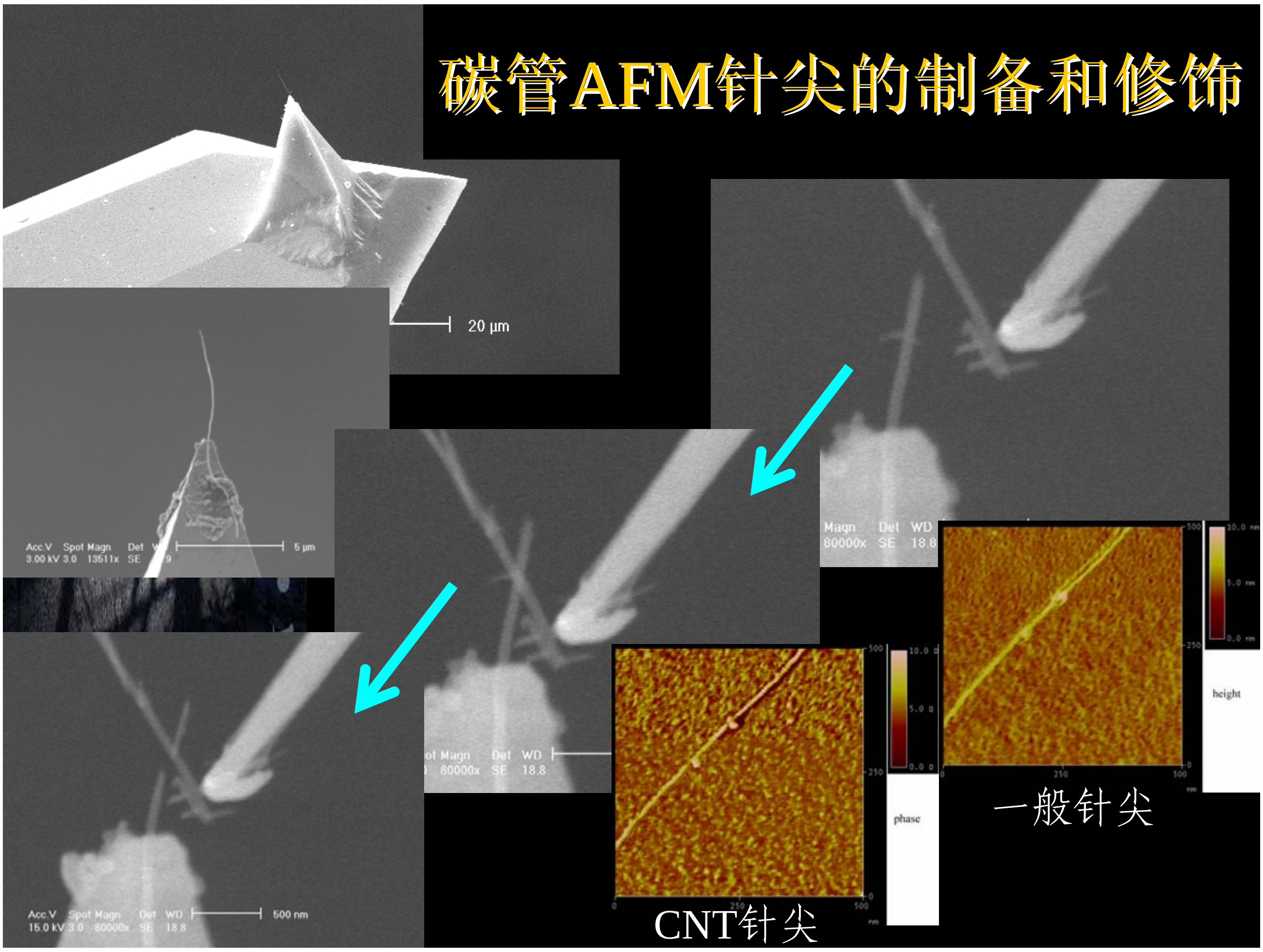


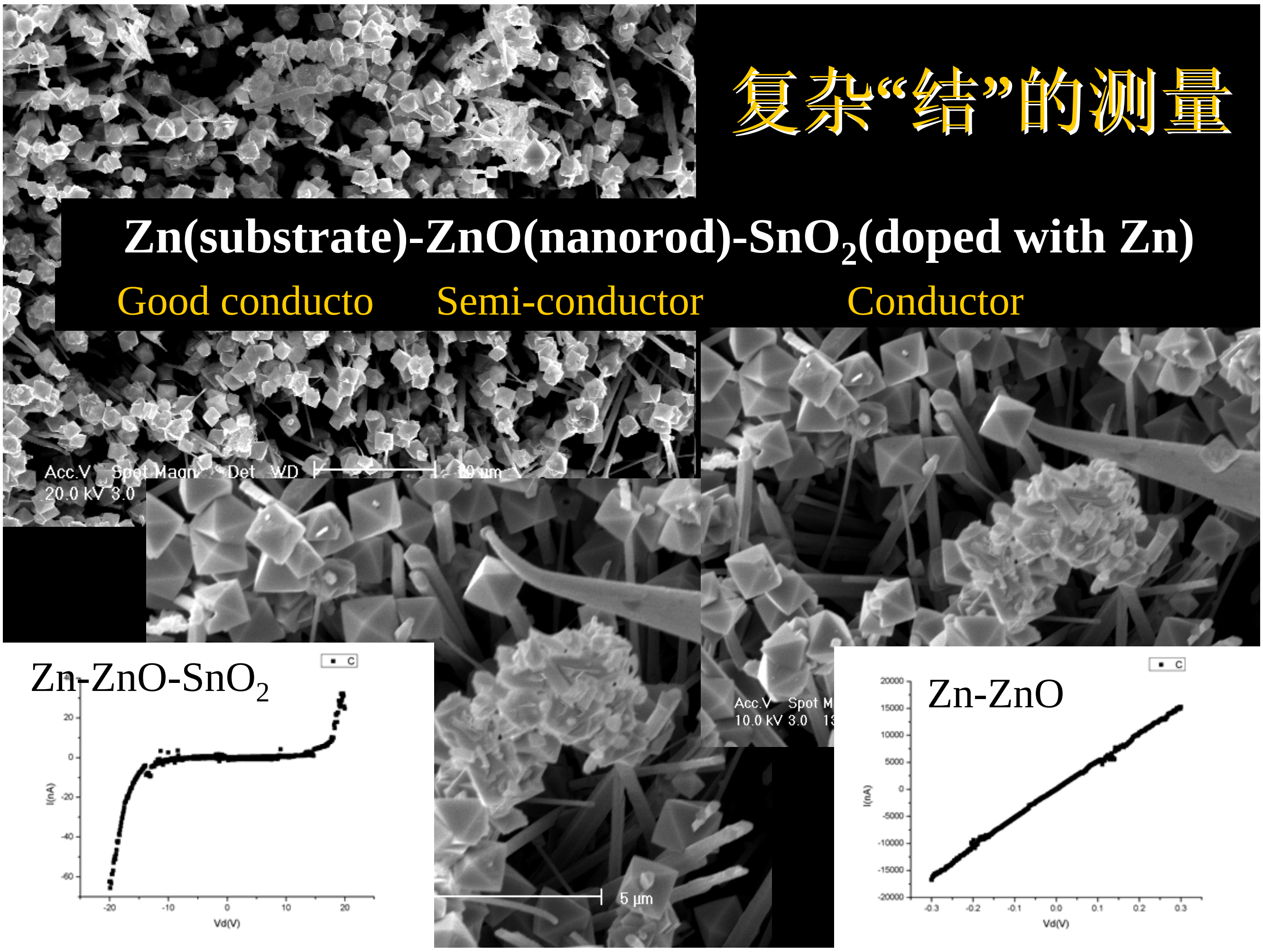


修饰尖端形状



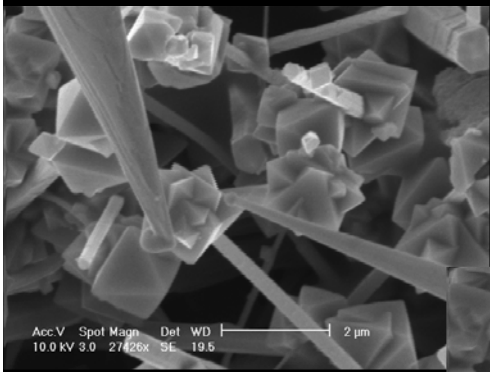


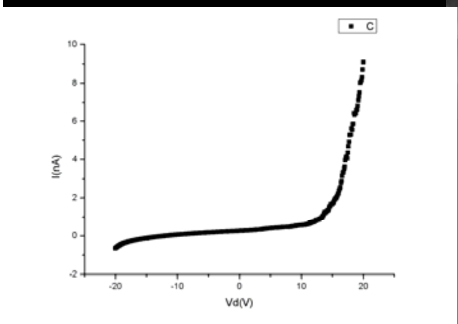

碳管AFM针尖的制备和修饰
20 µm
500 nm
一般针尖
CNT针尖
height
phase


复杂“结”的测量
Zn(substrate)-ZnO(nanorod)-SnO2(doped with Zn)
Good conducto
Semi-conductor
Conductor
5 µm
Zn-ZnO-SnO2
Zn-ZnO
I(nA)
Vd(V)

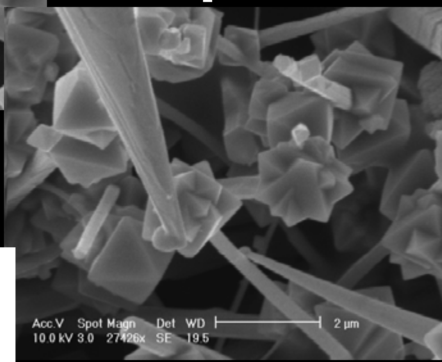
复杂"结"的多探针测量

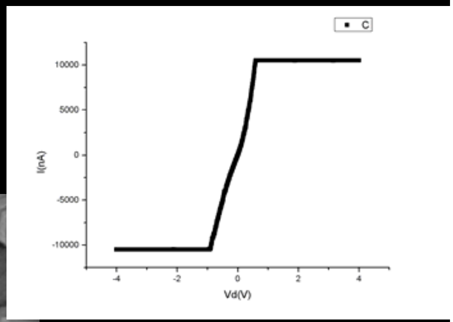
W-SnO_2-W



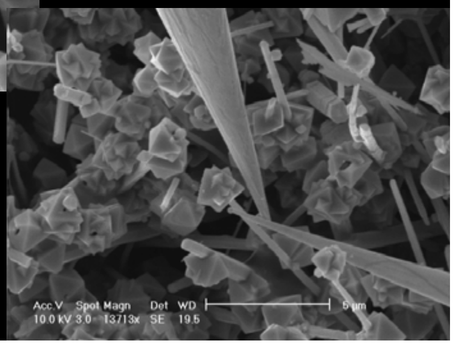


W-SnO_2-ZnO-(W)-Zn

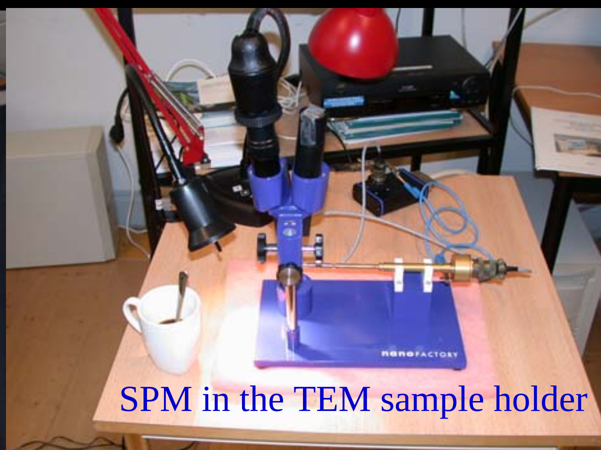




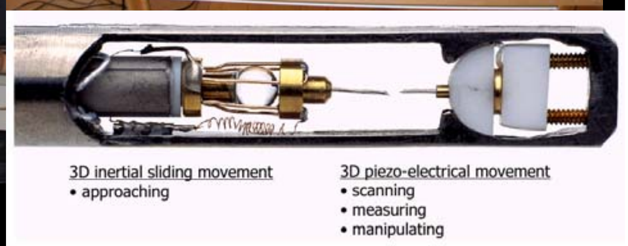
W-ZnO-(W)-Zn



透射电镜中的STM探针

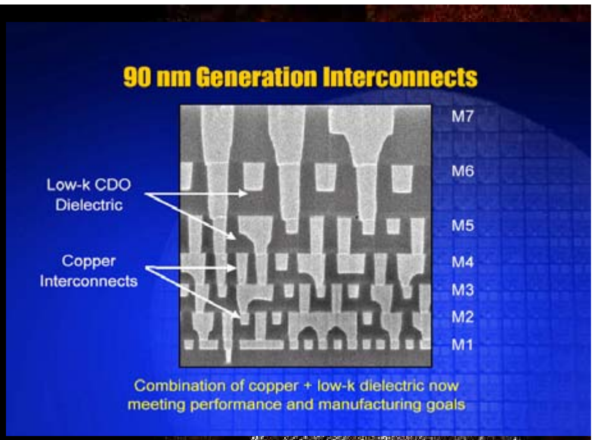


SPM in the TEM sample holder



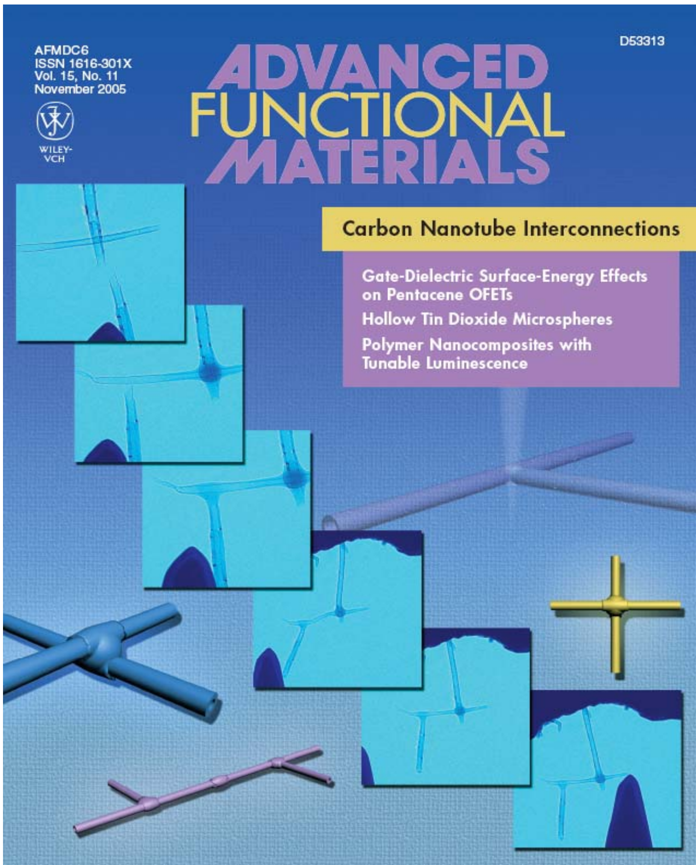
透射电镜中纳米结构的原位加工和实时电学性能测量

Interconnecting wires



Metal wires, currently about 250nm

- There is as yet no good way to remove the heat produced by the devices, so packing them in more tightly will only lead to rapid overheating
- As metal wires get smaller, the gust of electrons moving through them becomes strong enough to bump the metal atoms around, and before long the wires fail like blown fuses



M.S. Wang et al.,
Adv. Func. Mater. 2005, 15, 1825

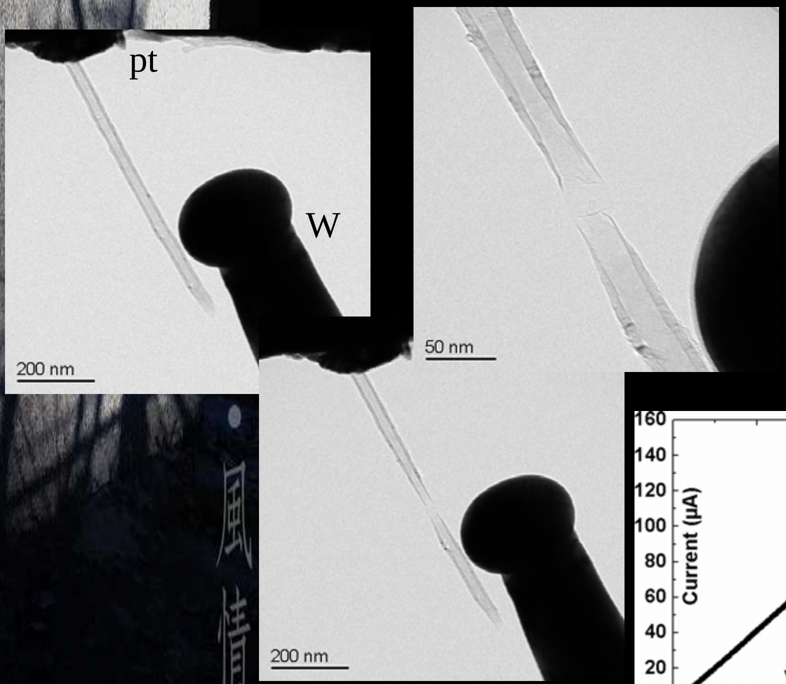
Carbon nanotubes can be ballistic and conduct heat nearly as well as diamond or sapphire. So nanotubes could efficiently cool very dense arrays of devices

Because the bonds among carbon atoms are so much stronger than those in any metal, nanotubes can transport terrific amount of electric current

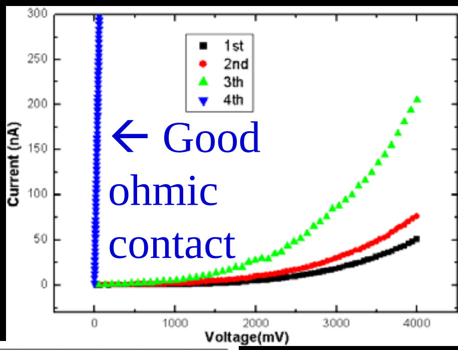
→ ideal interconnecting wires

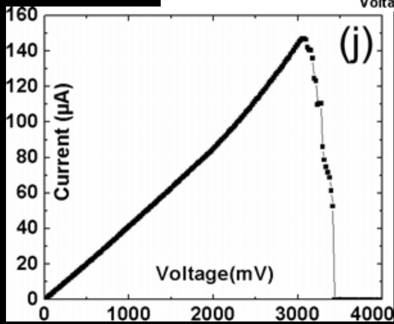
•How to connect CNTs into desired configuration???

Contacting and cutting a CNT



I-V sweeps

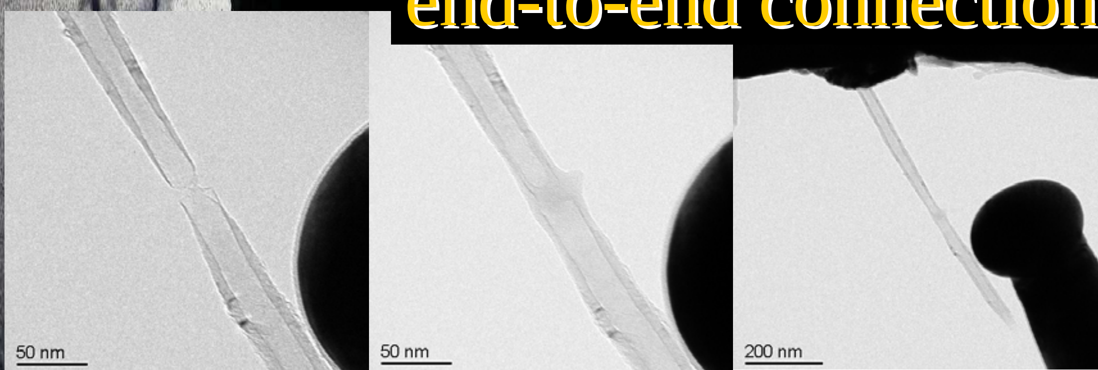


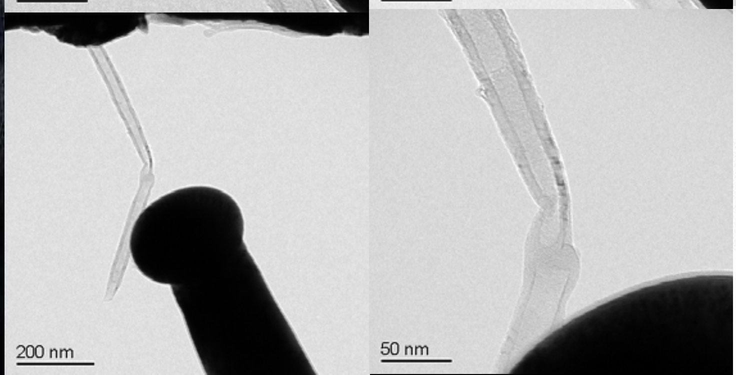


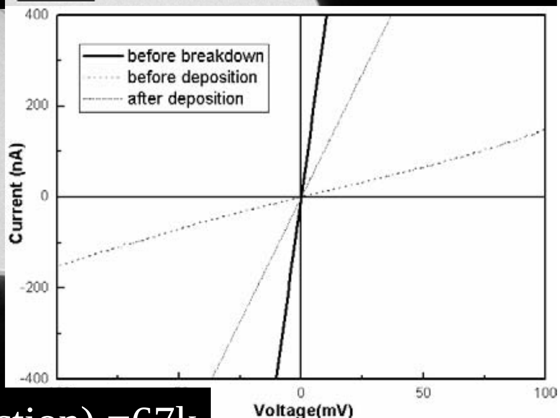
Cutting CNT via a large current

I > 140μA
For a single CNT

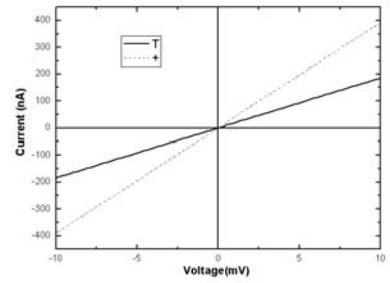
Soldering together CNTs end-to-end connection



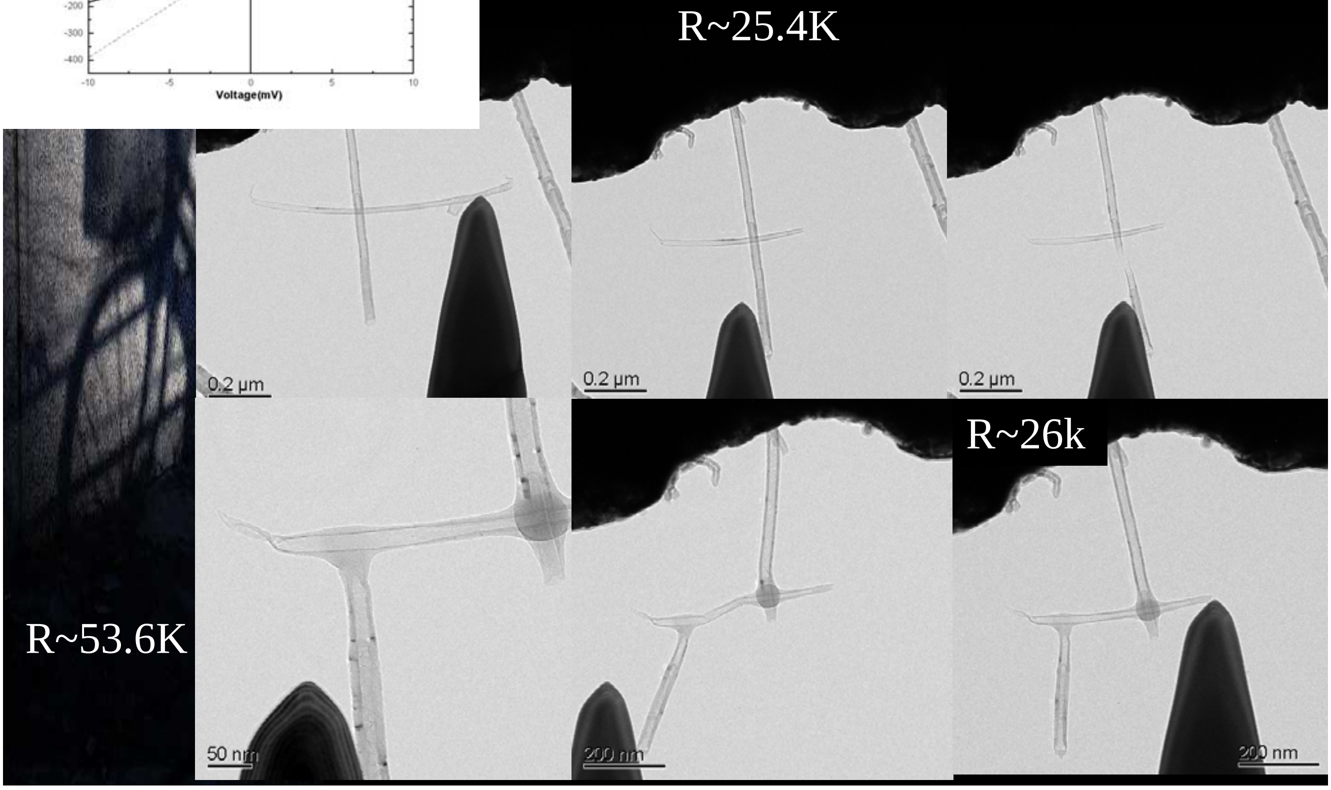




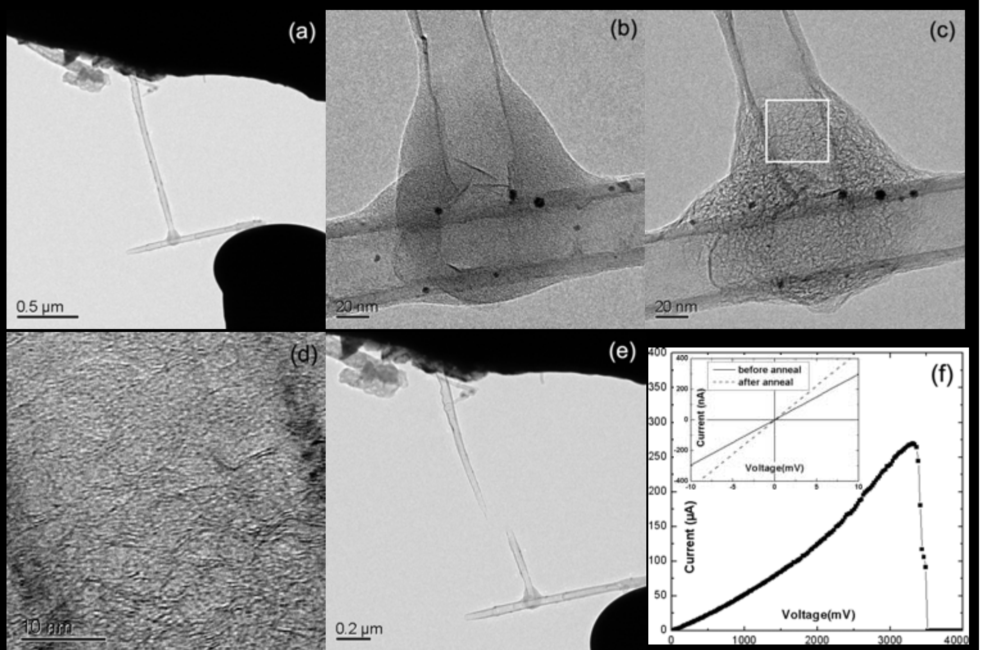
R(perfect)=25k, R(after)=92k → R(junction) =67k



CNT network



Improving conductance: Current induced graphitization



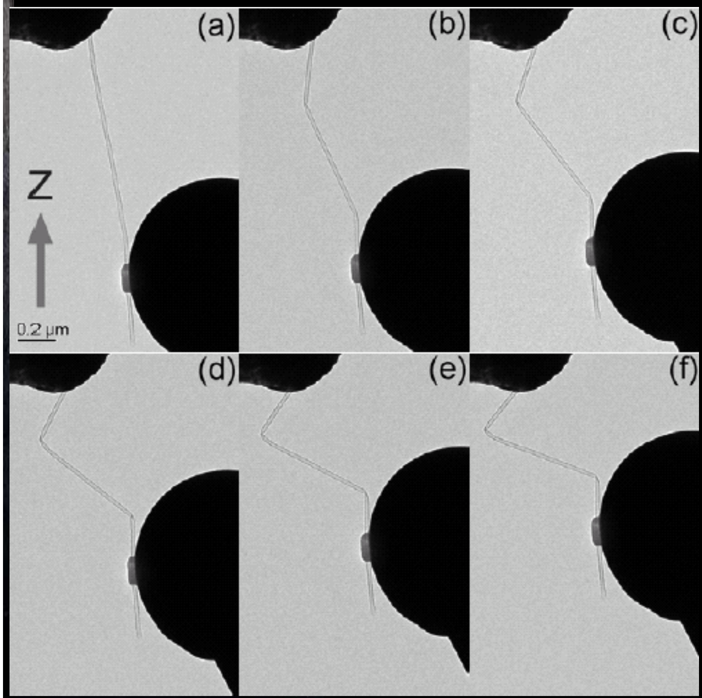
Total resistance of the system: R(junction) ~ a few kΩ or less

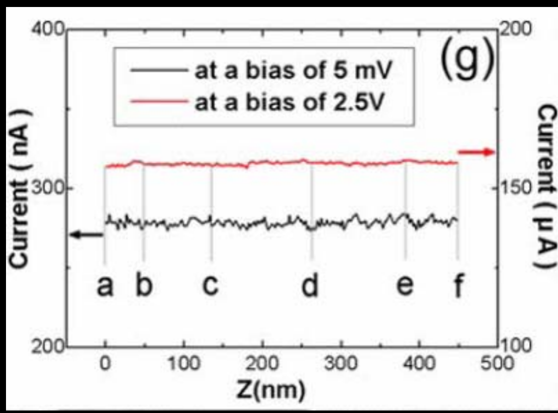
34kΩ (before graphitization) → 22kΩ (after graphitization)

Conductance vs bending

M.S. Wang et al., Adv. Func. Mater. 16 (2006) 1462

R=18kΩ



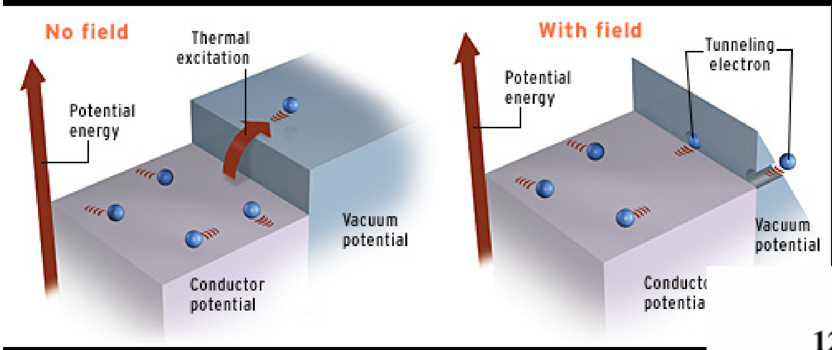


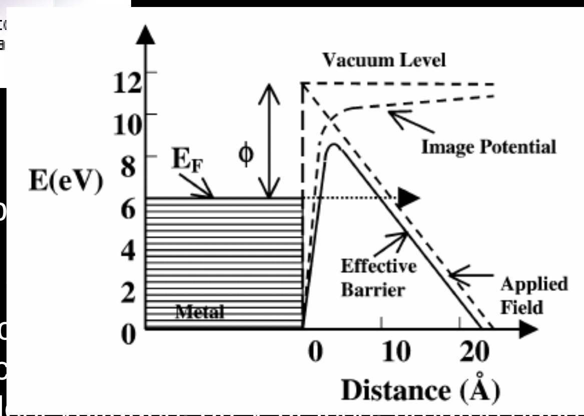
The conductions of the nanotube shows no notable dependence on the bending and the amorphous carbon deposition on the nanotube → Multiwall CNT can be shaped and used as nano-interconnections in complicated circuit.

Eg ~ 0.8/d, for a CNT of 40nm, Eg ~ 20meV, it is basically metallic at RT

碳纳米管的场电子发射性能与应用

Electron Field-emission

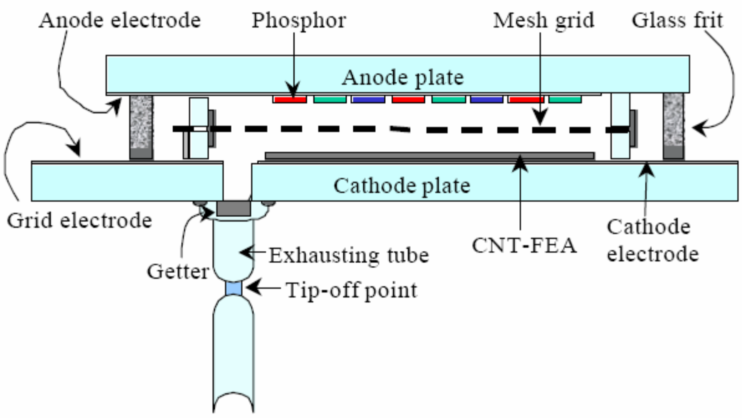


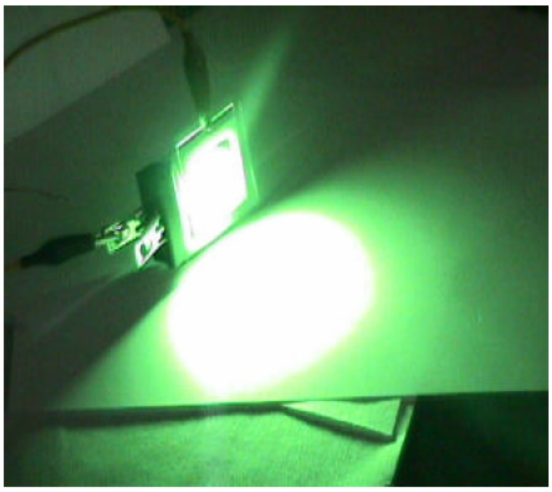


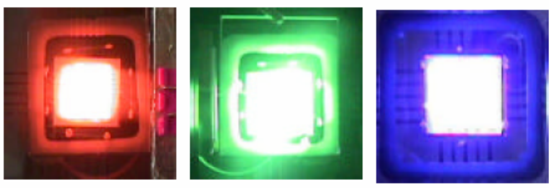
Unless a conductor is in the shape of a sp
is not distributed uniformly across its surface.
places of greatest curvature—in other words,
charge will be found at the tip, effectively conc
If a small, but similarly pointy, negatively c
emission display, the application of even modest voltages, 50 V or less, creates such a concentrated electric field at the tip—10^7 to 10^8 V/cm—that electrons can engage in a phenomenon known as tunneling and escape into free space without the traditional CRT's need to heat the cathode to release electrons.

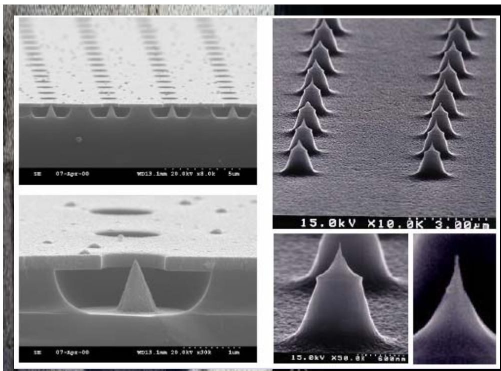
CNT field-emission display

http://diana.kist.re.kr

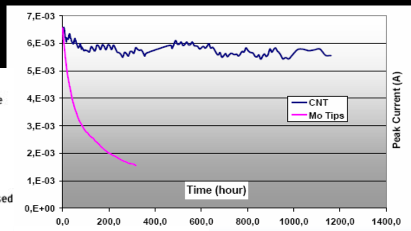






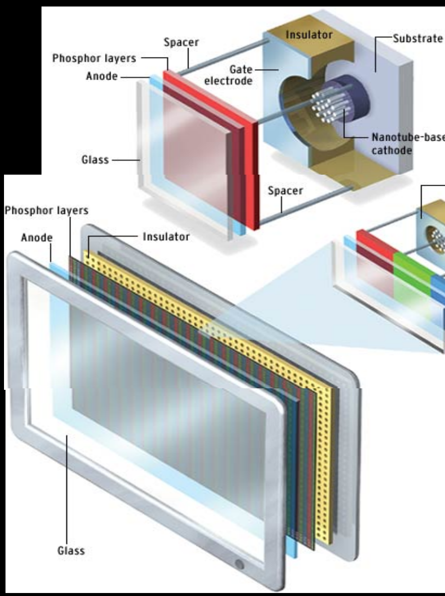


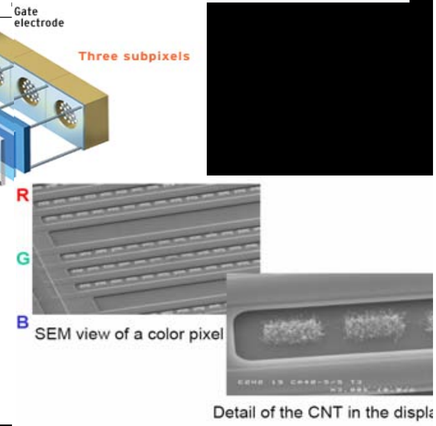
Carbon nanotube field emission display and TV



Why CNTs:

(1) good conductivity;
(2) ideal pointed shape;
(3) doesn't suffer from a resistive heating feedback cycle;
(4) isn't chemically reactive;
(5) can withstand high temperatures without deforming.





Field-emission from individual CNTs: The First Report

REPORTS

Unraveling Nanotubes: Field Emission from an Atomic Wire

A. G. Rinzler, J. H. Hafner, P. Nikolaev, L. Lou, S. G. Kim, D. Tománek, P. Nordlander, D. T. Colbert, R. E. Smalley

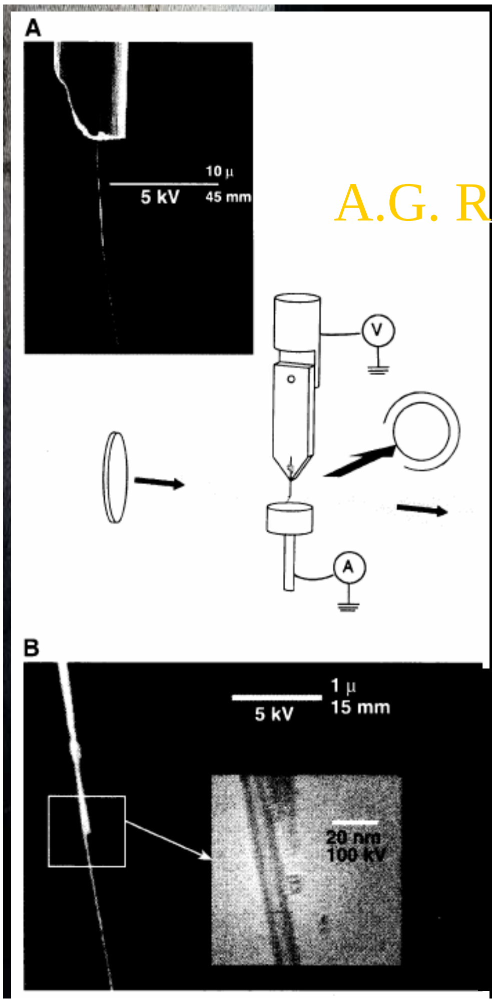
Field emission of electrons from individually mounted carbon nanotubes has been found to be dramatically enhanced when the nanotube tips are opened by laser evaporation or oxidative etching. Emission currents of 0.1 to 1 microampere were readily obtained at room temperature with bias voltages of less than 80 volts. The emitting structures are concluded to be linear chains of carbon atoms, C_n (n = 10 to 100), pulled out from the open edges of the graphene wall layers of the nanotube by the force of the electric field, in a process that resembles unraveling the sleeve of a sweater.

A.G. Rinzler et al., Science 269 (1995) 150

Unraveling Nanotubes:

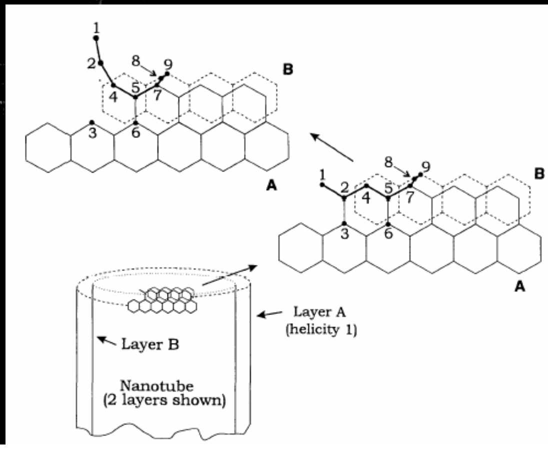
Field emission from an atomic wire

A.G. Rinzler et al., Science 269 (1995) 150



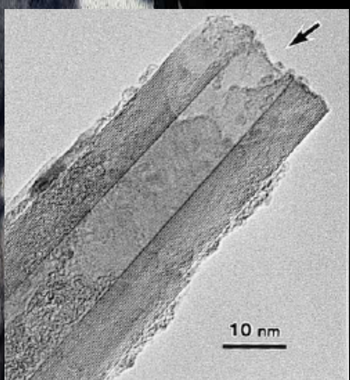
CNT became shorter during electron field emission, and the current is much larger than would be expected for the diameter of the CNT.

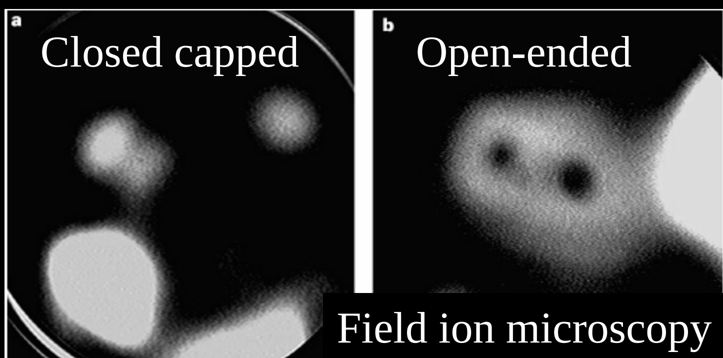
Either a protrusion of tens nm at the tip (unlikely), or 1D carbon chain to give such strong emission.



Conical beams from open nanotubes

(Y. Saito et al., Nature 389 (1997) 554)



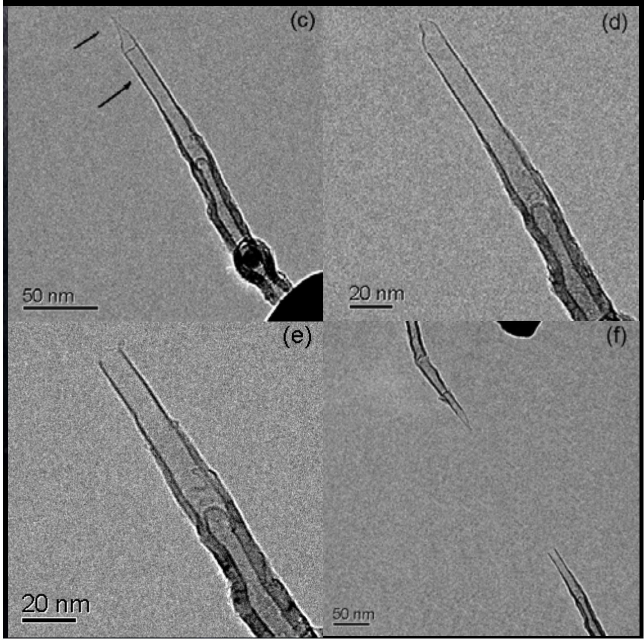


Field ion microscopy

"Contrary to their (Rinzler et al.) report, we saw no sharp contrast corresponding to the atomic chain in our emission patterns. Electron emission seems to occur from the circular edges of the graphitic layers of a nanotube."

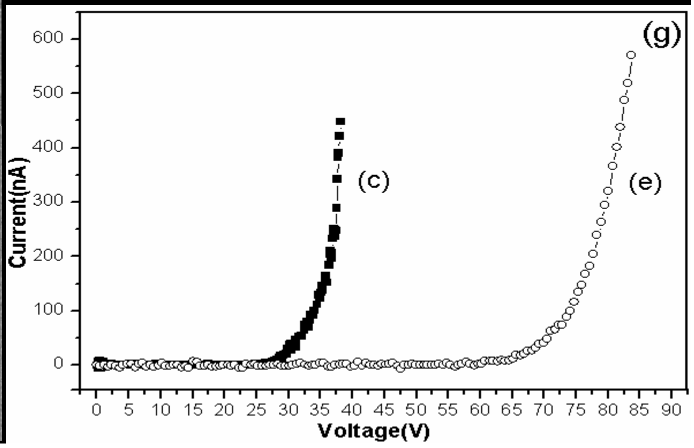
1D carbon chain vs sharp tip (protrution of tens nm)

Graphitic protrusions of tens of nm may occur at the tip of the CNT



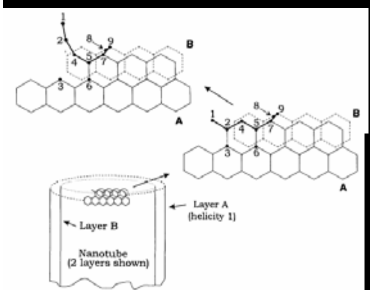
The emission characteristics of the CNT depends sensitively on the tip structure of the CNT!!!

For the same open CNT, the onset of (c) is about half that of (e).

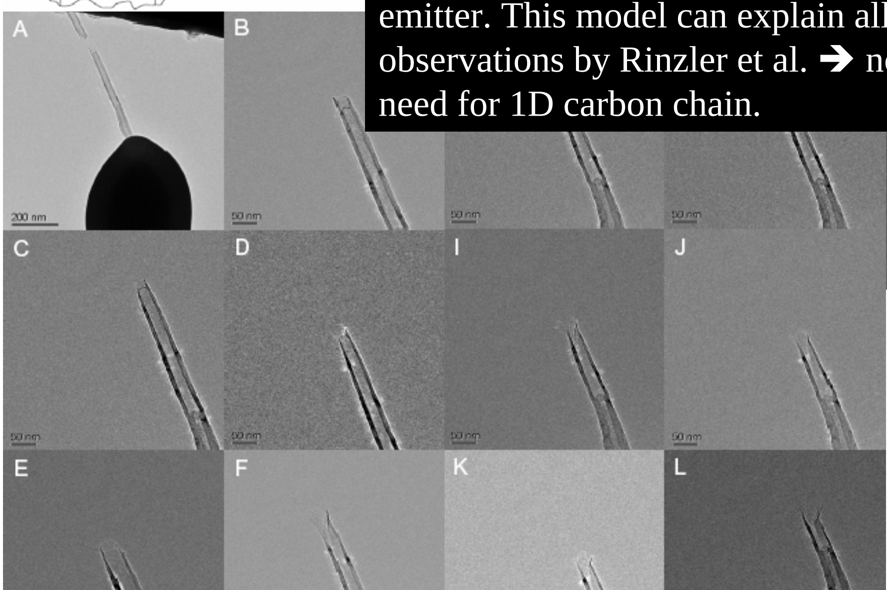


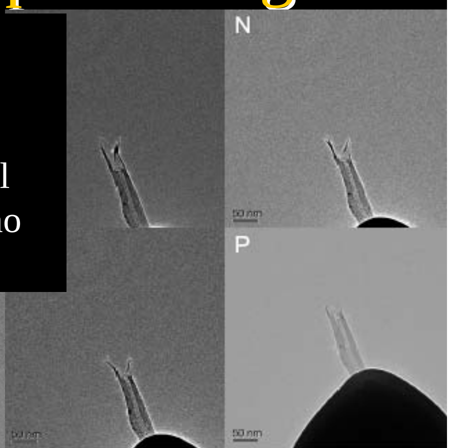
A.G. Rinzler et al.

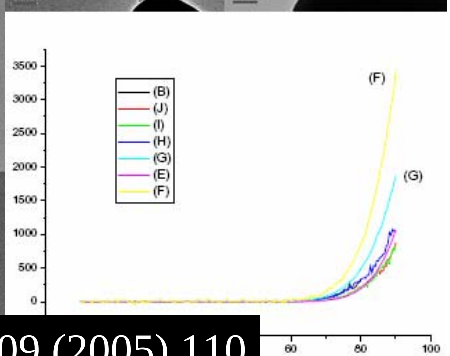
Field evaporation & etching atomic wire vs graphitic fragment



A CNT becomes short via the evaporation of the sharp graphitic protrusions at the tip of the CNT emitter. This model can explain all observations by Rinzler et al. ➔ no need for 1D carbon chain.







M.S. Wang, L.-M. Peng et al., J Chem. Phys. B109 (2005) 110

Open vs capped CNT?

J.-M. Bonard et al., Solid State Electronics 45 (2001) 893

Capped CNTs have lower onset voltage, and are better emitter than open CNTs.

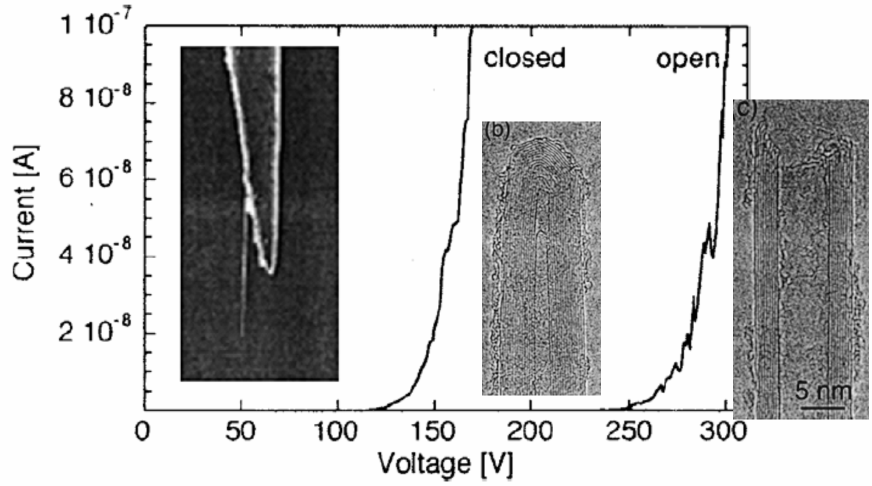


Fig. 9. Field emission *I–V* curves acquired on a single closed and open MWNT mounted on the apex of an etched gold fiber of 20 μm diameter as shown in the inset.

Open vs capped CNT

Saito et al., Carbon 38 (2000) 169

Field emission properties of the four kinds of carbon nanotubes[a]

Carbon nanotubes	Threshold voltage[b] (V)	Saturation current (nA)
Capped MWNT	900–1000	0.5–3.0
Nanografiber	700–800	70.0–100.0
Open MWNT	500–600	400.0–900.0
SWNTs	600–700	50.0–300.0

Saito et al.: The open MWNTs began to emit electrons at the lowest tip voltage and sustained the highest current density.

Bonard et al.: Open tubes emitted at about twice the voltage needed for the closed ones!

Which one is correct ???

← Different samples

← Different measurement environments

Field-emission of CNT: open vs capped

Freshly created CNT emitters

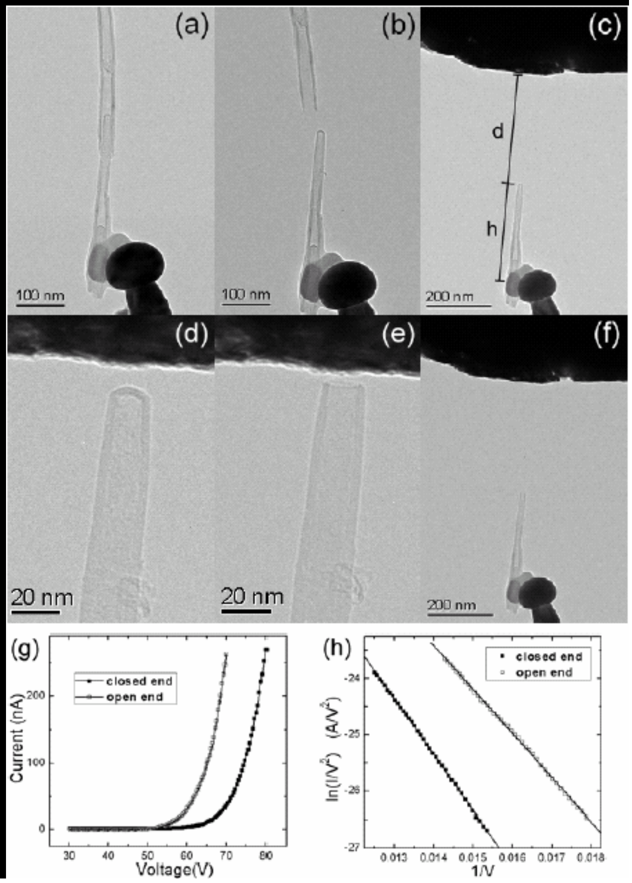
High vacuum, heated CNT → not much absorbates

Singe CNT: no screening

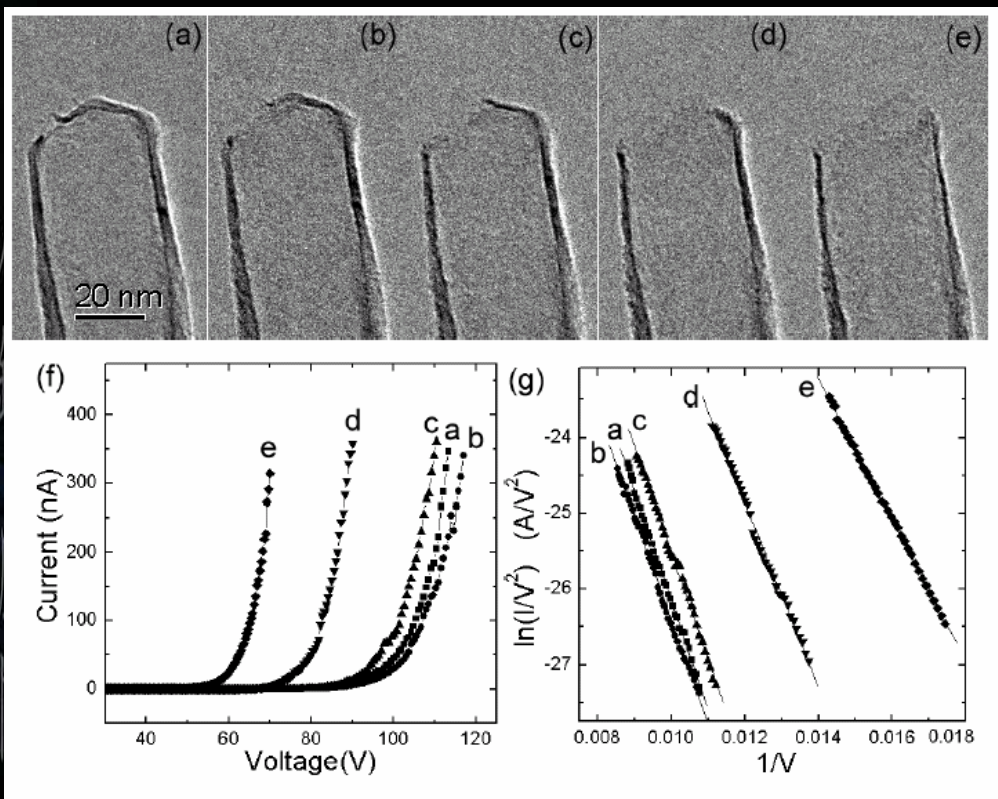
Same CNT, same measurement environment, only different tips

The onset voltage of the open tube is consistently smaller than that of the capped tube.

M.S. Wang et al., J. Phys. Chem. B. 110 (2006) 9397



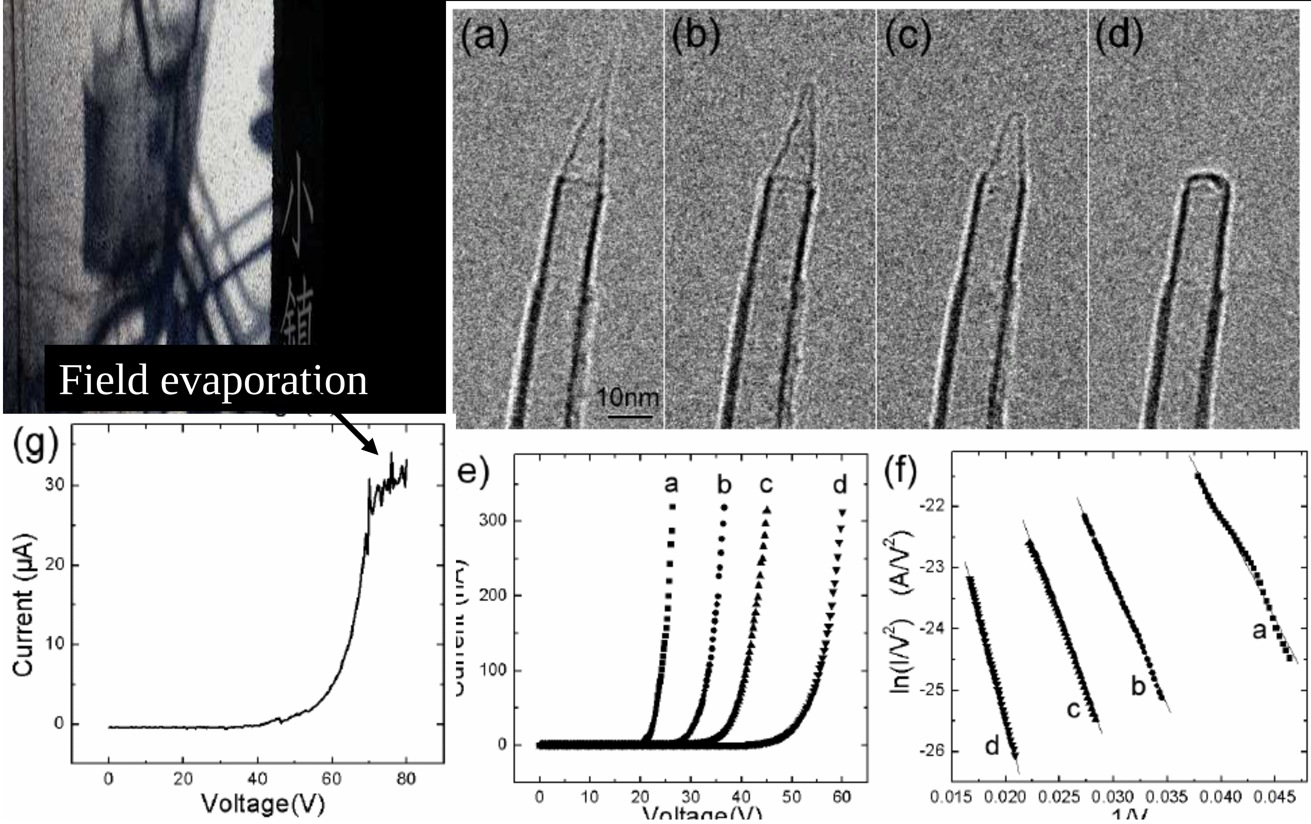
Controlled opening of a CNT



An opened CNT (e) has a much smaller onset voltage than a caped CNT (a).

Engineering the cap structure

M.S. Wang et al., Appl. Phys. Lett. 88 (2006) 243108



The Fowler-Nordheim Theory

Electron Emission in Intense Electric Fields

R. H. Fowler; L. Nordheim

Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character, Vol. 119, No. 781 (May 1, 1928), 173-181.

Stable URL:
http://links.jstor.org/sici?sici=0950-1207%2819280501%29119%3A781%3C173%3AEEIIEF%3E2.0.CO%3B2-N

Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character is currently published by The Royal Society.

The F-N model

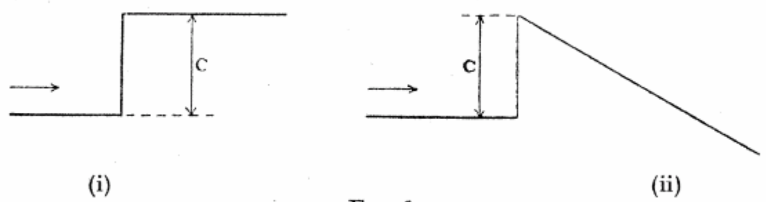


Fig. 1.

In order to study the emission through the potential energy step of fig. 1 we have only to solve the wave equations

$$\frac{d^2\psi}{dx^2} + \kappa^2 (\mathrm{W} - \mathrm{C} + \mathrm{F}x)\, \psi = 0 \qquad (x > 0), \tag{4}$$

$$\frac{d^2\psi}{dx^2} + \kappa^2 \mathrm{W} \psi = 0 \qquad (x < 0), \tag{5}$$

subject to the conditions that ψ and $d\psi/dx$ are continuous at $x = 0$ and that for $x > 0$ ψ represents a stream of electrons progressing to the right only. The constant κ is defined by

$$\kappa^2 = 8\pi^2 m/h^2. \tag{6}$$

$$\mathrm{I} = \frac{\varepsilon}{2\pi h} \frac{\mu^{\frac{1}{2}}}{(\chi + \mu)\, \chi^{\frac{1}{2}}} \mathrm{F}^2 e^{-4\kappa\chi^{\frac{3}{2}}/3\mathrm{F}}. \tag{21}$$

The χ of this equation is necessarily and exactly the thermionic work function.†

The effect of the image force

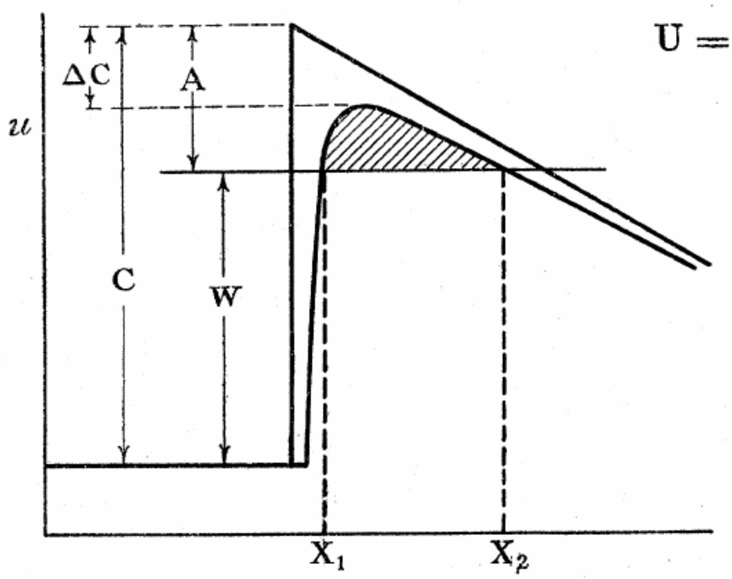
$$2\mathrm{Q} = 2\kappa \int_{x_1}^{x_2} (\mathrm{U} - \mathrm{W})^{\frac{1}{2}}\, dx,$$

with

$$\mathrm{U} = \mathrm{C} - e^2/4x - \mathrm{F}x \qquad \text{for } x > x_0$$

$$\mathrm{U} = 0 \qquad \text{for } x < x_0,$$

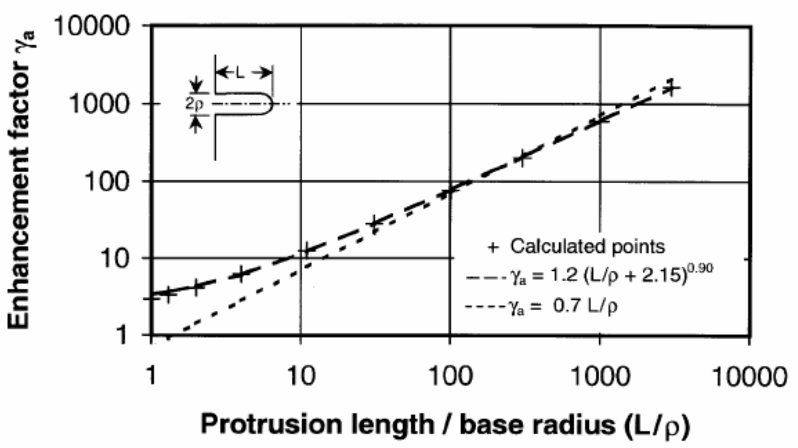
$$e^2/4x_0 = \mathrm{C},$$



$$\mathrm{I} = \text{const } \mathrm{F}^2\, e^{-2\mathrm{Q}},$$

L.W. Nordheim,
Proc. R. Soc. London
121 (1928) 626-639

Field enhancement



In geometrical configurations resembling a parallel-plate capacitor, the *macroscopic field* F_M is defined by

$$F_M = V/d, \quad (1)$$

where V is the voltage applied across a gap of thickness d. The *local field* F is the field, close to the emitting surface (within 1–2 nm of the surface atoms), that determines the barrier through which field-emitted electrons tunnel. This field F is sometimes called the *barrier field*. F is typically a few V/nm, and is often significantly higher than F_M. Their ratio defines a *field-enhancement factor* γ

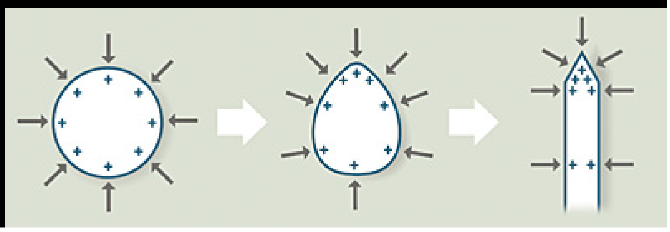
$$\gamma = F/F_M. \quad (2)$$

In the range $4 \leqslant \nu \leqslant 3000$

$$\gamma_a \simeq 1.2(2.15 + \nu)^{0.90}.$$

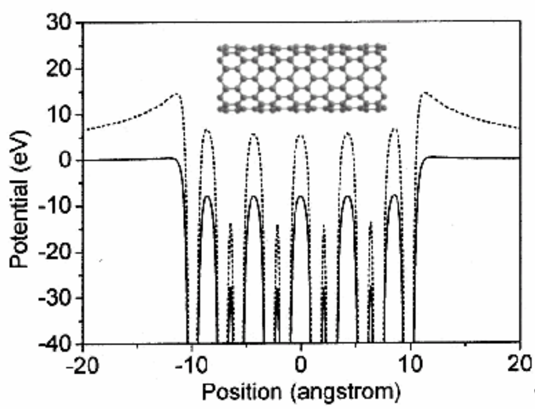
for smaller values of ν.

$$\gamma_a \simeq 2 + L/\rho = 3 + \ell/\rho.$$



Formation of potential barriers and field-electron emission

Charge accumulation at the tip →strong local field→narrower barrier



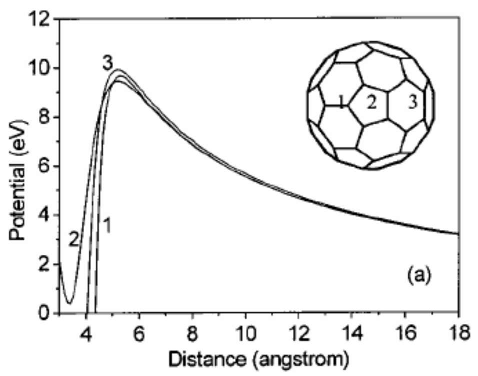


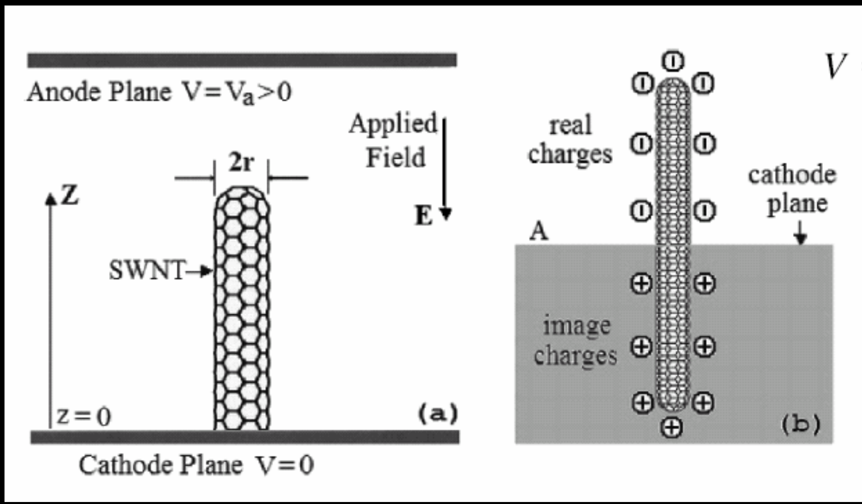
TABLE I. Transmission coefficient T, potential barrier width W, and the maximum end field F of the four-electron-charged model (a) in Fig. 2, calculated from the potential barriers illustrated in Fig. 3(a). T and W are for the HOMO energy.

Direction	1	2	3
T	0.0029	0.0020	0.0014
W (Å)	4.5	4.8	4.9
F (V/Å)	1.4	1.1	1.4

J. Luo, L.-M. Peng et al.
Phys. Rev. B66 (2002) 155407
Phys. Rev. B66 (2002) 115415

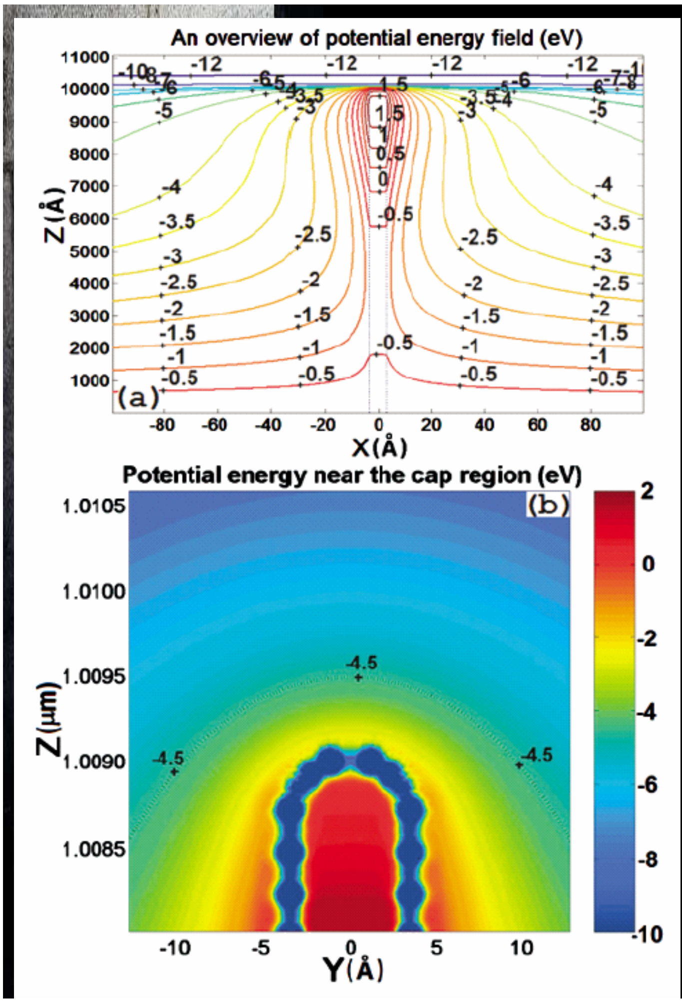
Quantum mechanical modellings

(G.H. Chen et al., PRL 92 (2004) 106803)



$$V = \begin{cases} V_a > 0 & \text{anode,} \\ 0 & \text{cathode.} \end{cases}$$

In contrast to the classical field-emission model where the CNT is treated as a bulk metal having the same electrostatic potential as the cathode, the SWNT in our model is taken as a quantum object subjected to the following boundary condition as depicted in the above figure.



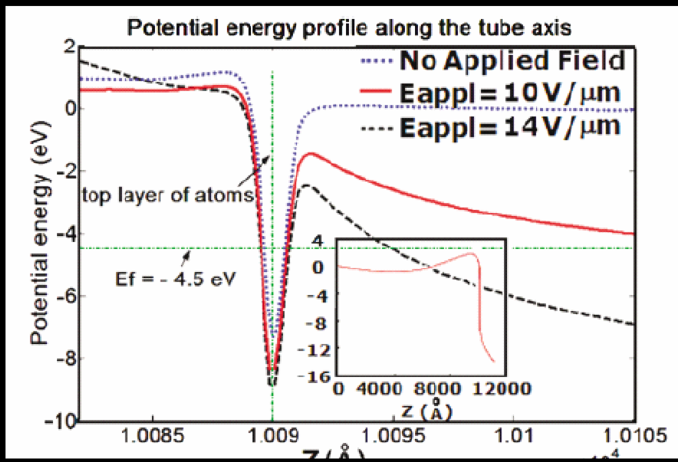
Potential energy contours

a (5,5) SWCNT, E_f=-4.5V

(1) Potential drop concentrates mostly at the tip region → electric field penetrates strongly at the tip.
(2) The variation of electrostatic potential along most of the tube is only about 2V, much less than the applied voltage.
(3) The Fermi energy is below the potential barriers around the tip. Potential barriers on the side wall are much higher and thicker than that in front of the cap.
(4) The electrostatic field is much stronger outside the tube as compared to that inside.

Potential barriers

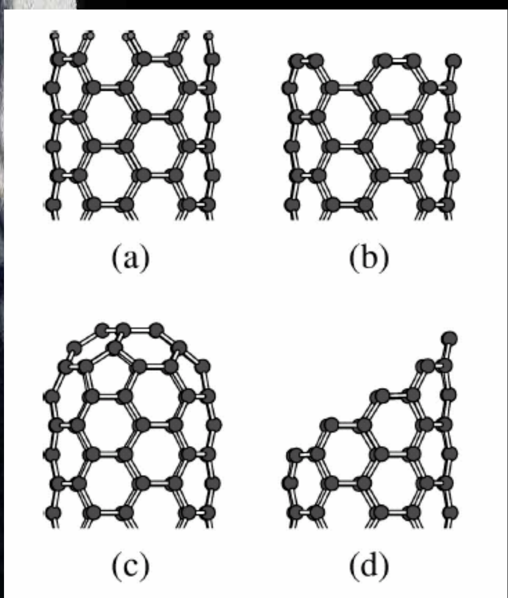
The effective field-enhancement β is field dependent!!!
β depends not only on the slop of the potential barrier but also on the field penetration and therefore the lowering of the barrier (very sensitive to the tip structure).

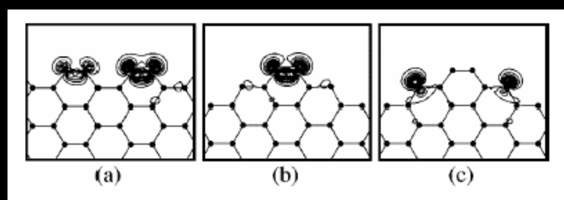


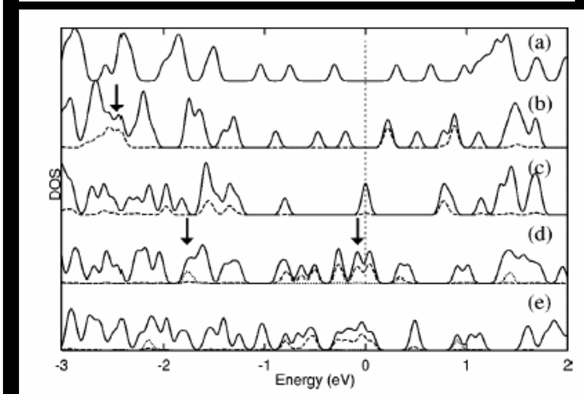
(a) The barrier height is lowered as E_{appl} is increased, BUT the barrier height depends nonlinearly on the external field.
(b) The local field is defined as the average in front of the tip (from z=10091.5 to 100095) → ratios of the local field to the applied field of 310 and 410 respectively for the two E_{appl}.
(c) The lowering of the barrier height due to the field penetration increases further the effective field enhancement factors to 500 and 1200

The importance of the tip structure

S. Han et al. PRB 61 (2000) 9986

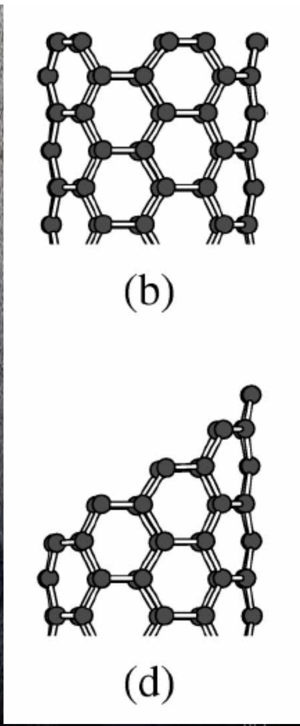


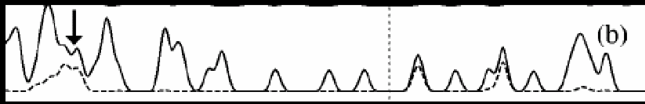




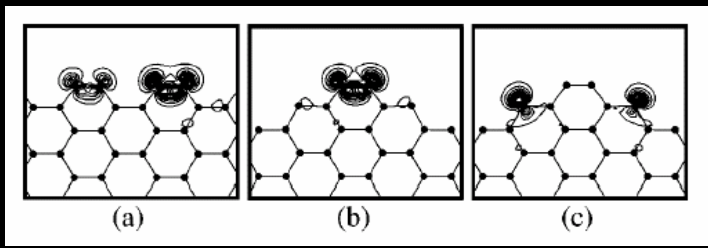
Different tip structures → different DOS at the E_f, and different coupling with vacuum wave → different emission current.

Nature of the localized states

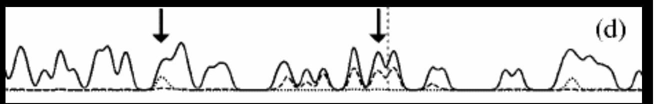




Paired dangling bonds→bonding and antibonding splitting →no DOS at E_f



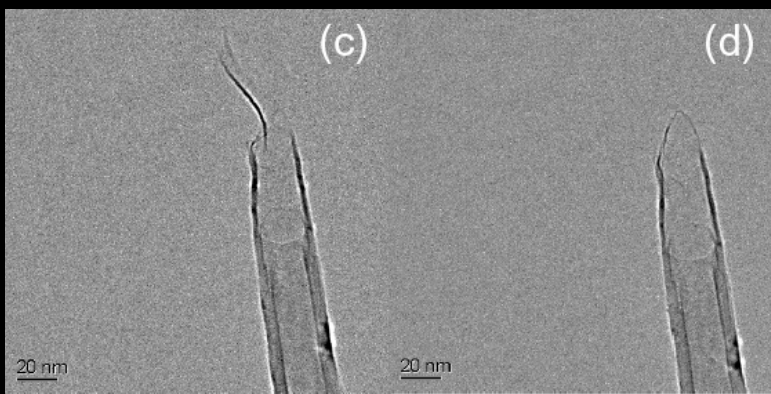
Unpaired dangling bonds →weak interaction →large DOS at E_f

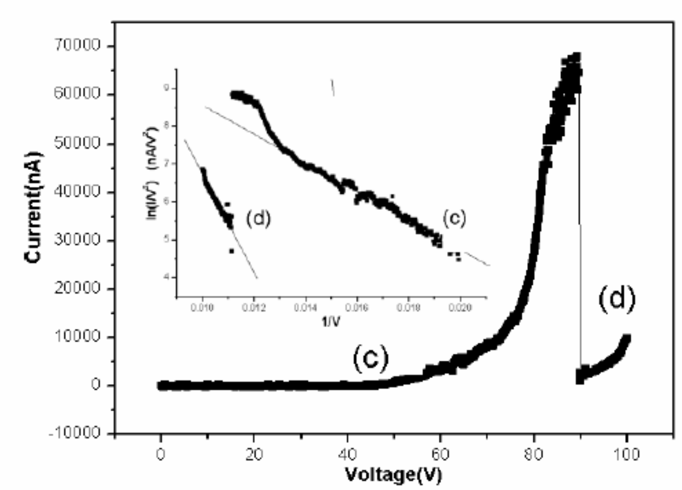


The most favorable tip geometry for FE is the open tube with zigzag edge where unsaturated dangling bond states can exist.

It is the dangling bond states around the edge of the graphitic fragments that make the CNT such good field emitters.

General CNT with no ideal circular end > capped CNT > ideal zigzag CNT without dangling bond states

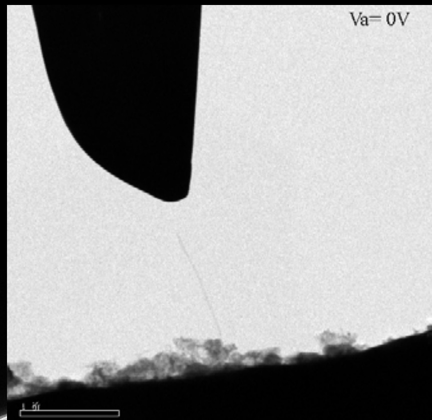




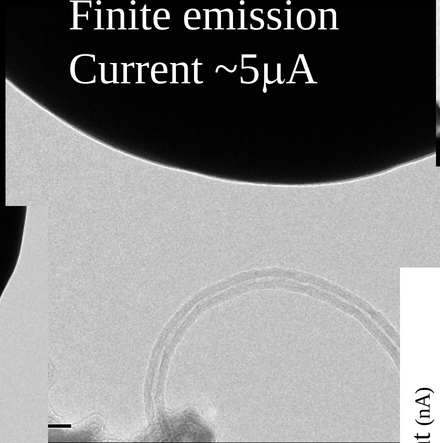
Structure vs emission current

Field-emission geometry top vs side emission

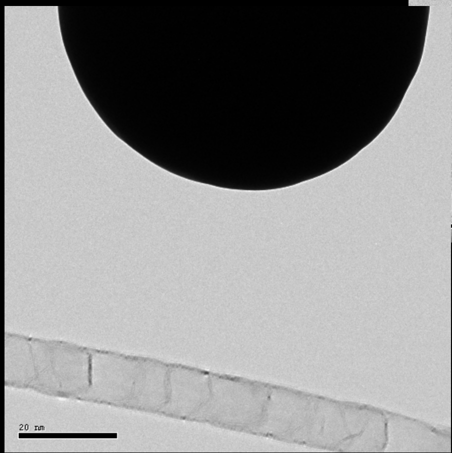
For CNTs, the top emission geometry is the favorable emission geometry.



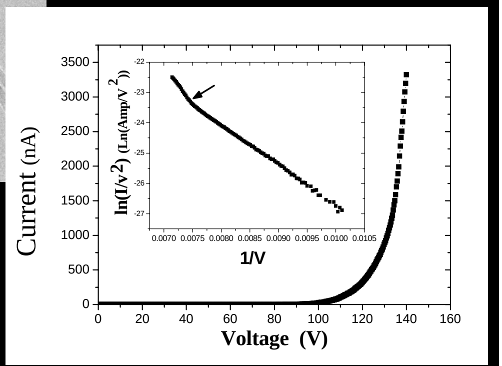
Best emission geometry
Current ~ 45μA



Finite emission
Current ~5μA

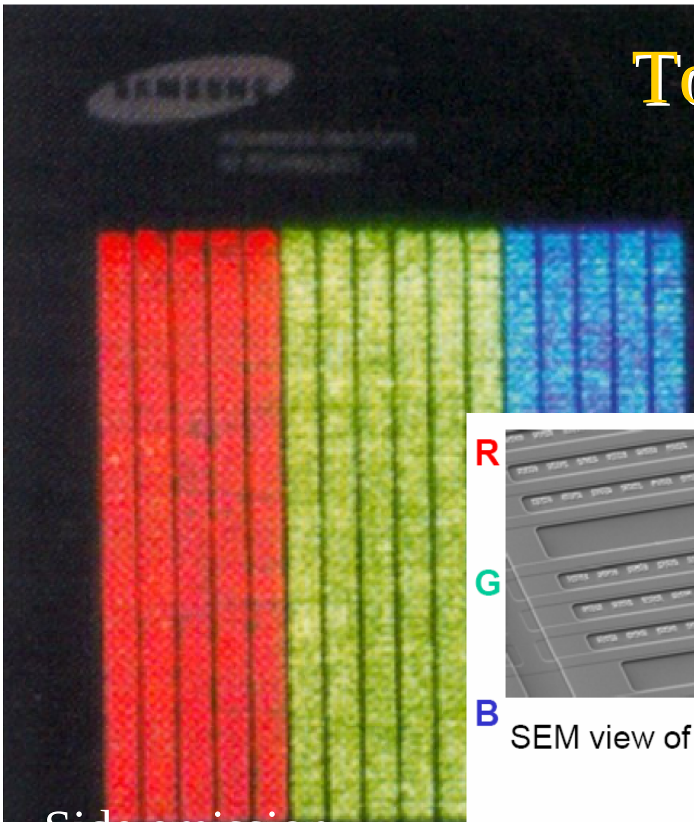


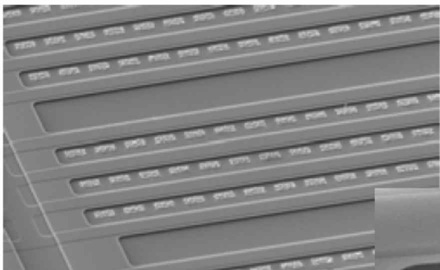
No field-emission current



C.Jin et al., Carbon 43 (2005) 1026

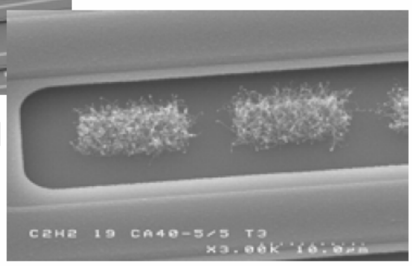
Top vs side emission geometry





SEM view of a color pixel

Top geometry,
high T processing

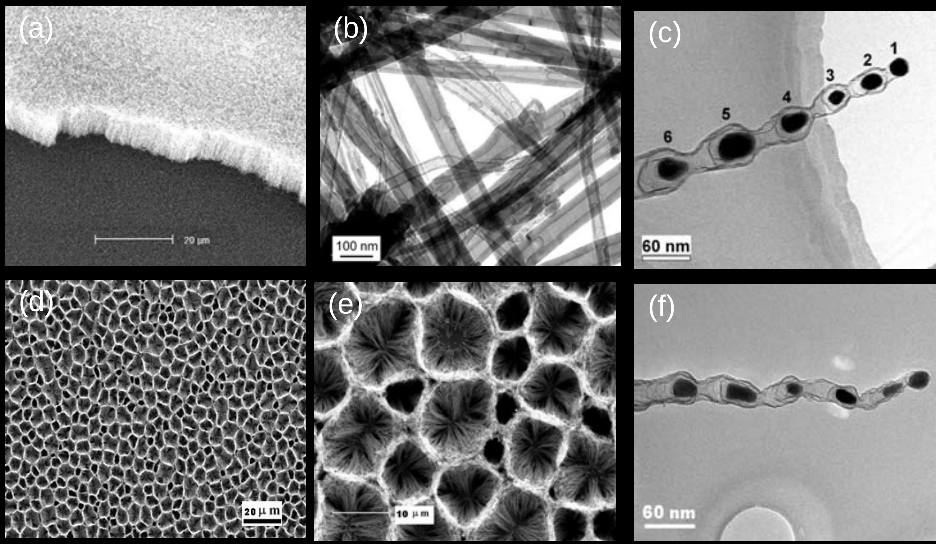


Detail of the CNT in the display

Side emission,
low T processing,
but additional deflection system

Vertically aligned and horizontally grown CNT films

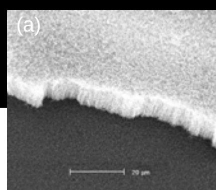
Vertically aligned nanotubes



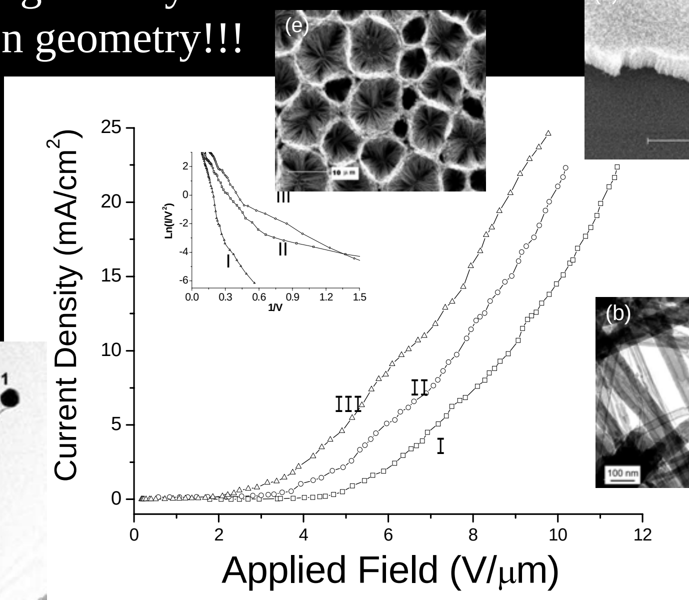
Horizontally grown nanotubes

Top and side electron field-emission

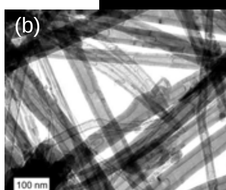
II. Vertically aligned peapod nanotubes

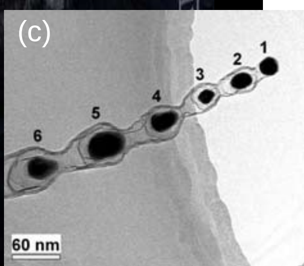


The side emission geometry is the better emission geometry!!!



I. CNT

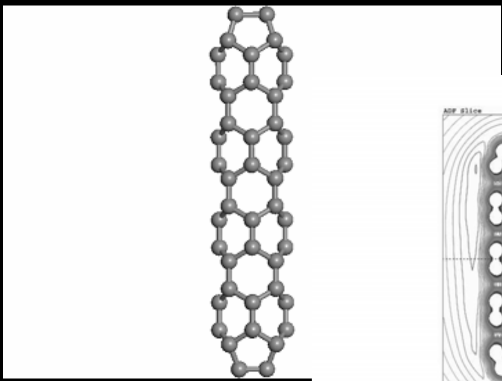


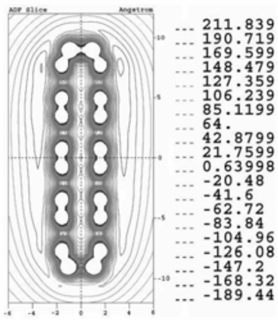


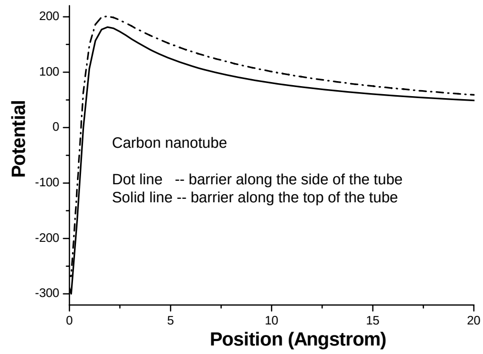
WHY???

III. Horizontally grown peapod nanotubes.

Field electron emission from a CNT



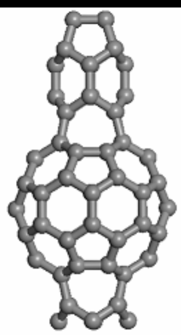


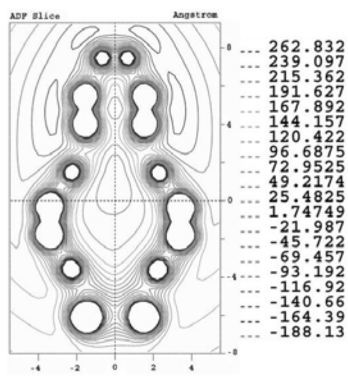


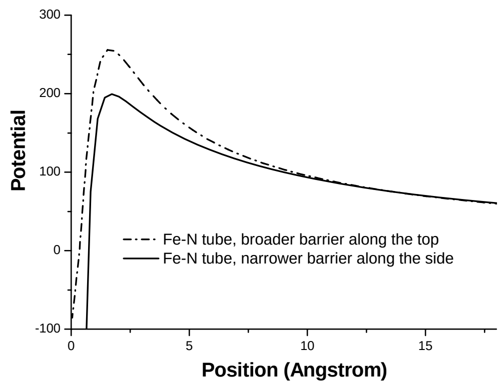
Potential barrier along the top is lower and narrower than that along the side of the CNT → top emission

Top emission

Field-emission from a deformed CNT



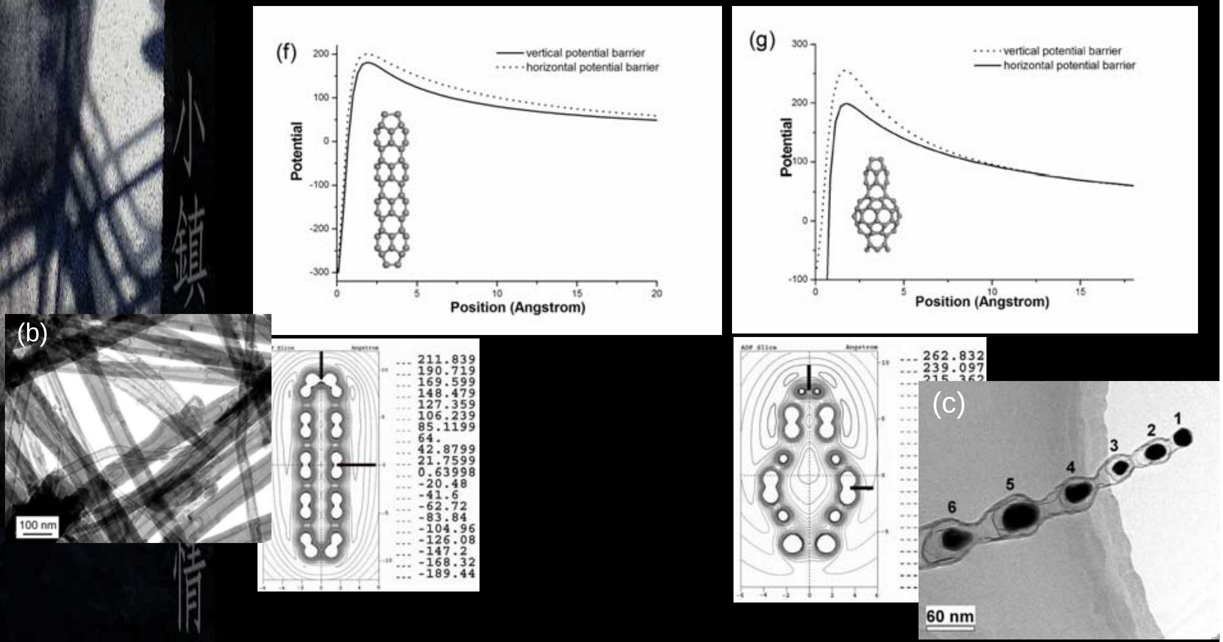




Potential barrier along the top is higher and broader than that along the side of the CNT → side emission

Side emission

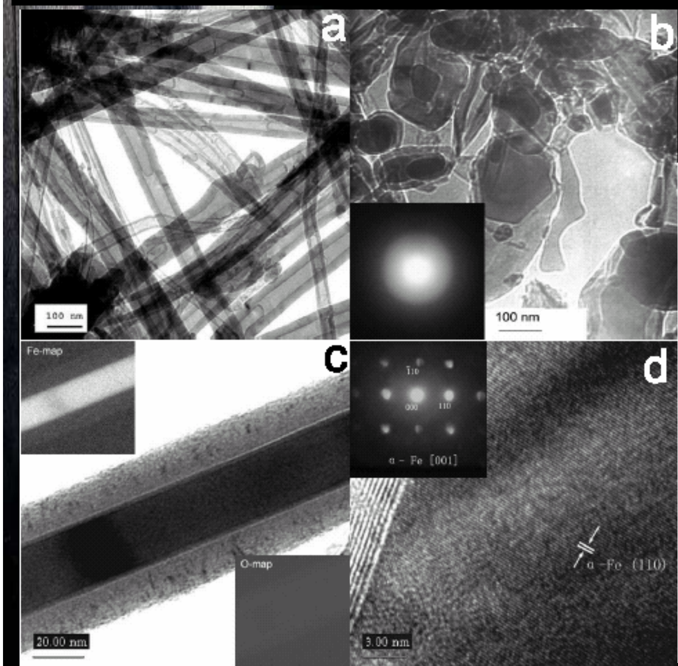
CNT models and electrostatic potential



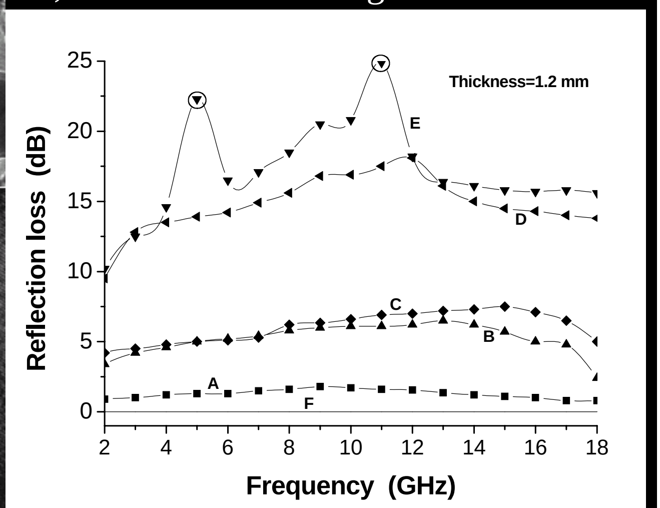
R.C. Che, L.-M. Peng, M.S. Wang, Appl. Phys. Lett. 85 (2004) 4753

Microwave absorption (微波吸收)

RAM: Radar absorbent material

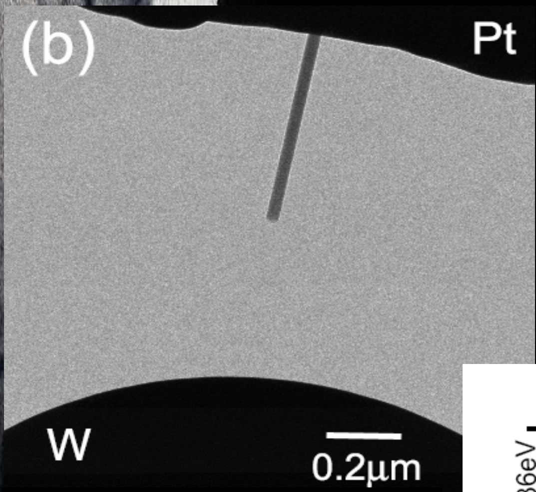


F: a pure sheet of Fe
A: pure CNT
B,C: α-Fe in carbon cages and tubes
D,E: α-Fe in carbon cages and tubes



R. Che, L.-M. Peng et al., Advanced Materials 16 (2004) 401

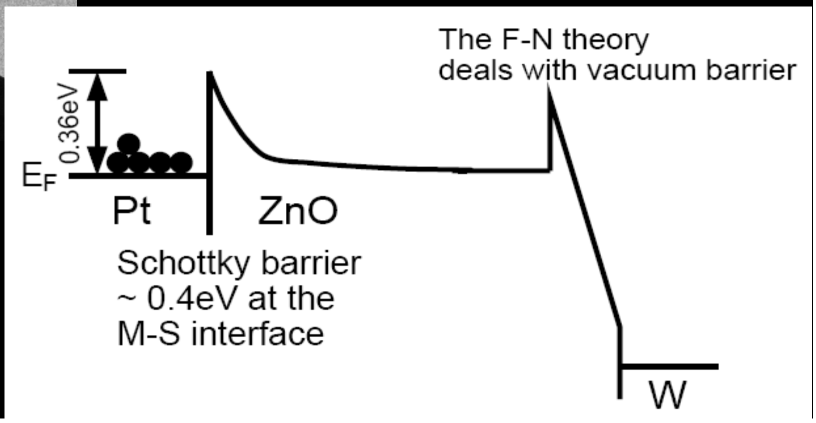
Schottky Barrier Switches
一种新型的电子开关



Basically composed of:
- Pt-NW: Schottky barrier
  → electron injection into NW
- NW-Vacuum:
  The Fowler-Nordheim formula
  → electron field emission

一般的晶体管中电流是通过控制栅极电压改变载流子浓度来控制的。

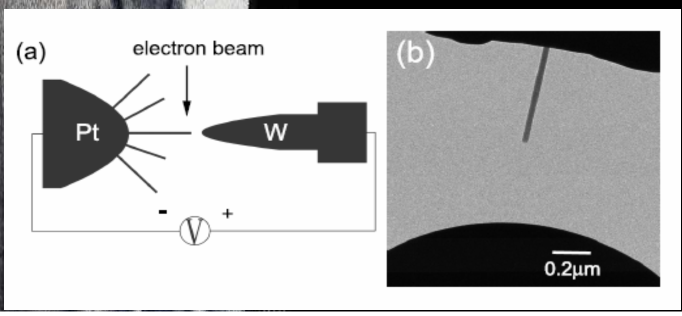
控制电子的注入效率来控制电流？

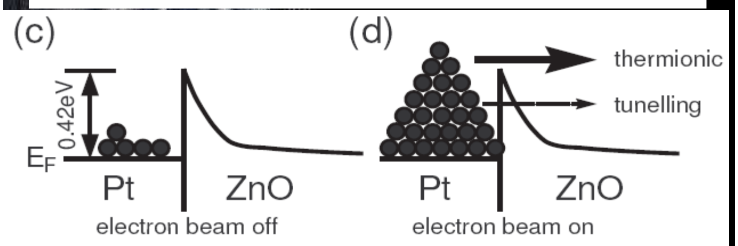


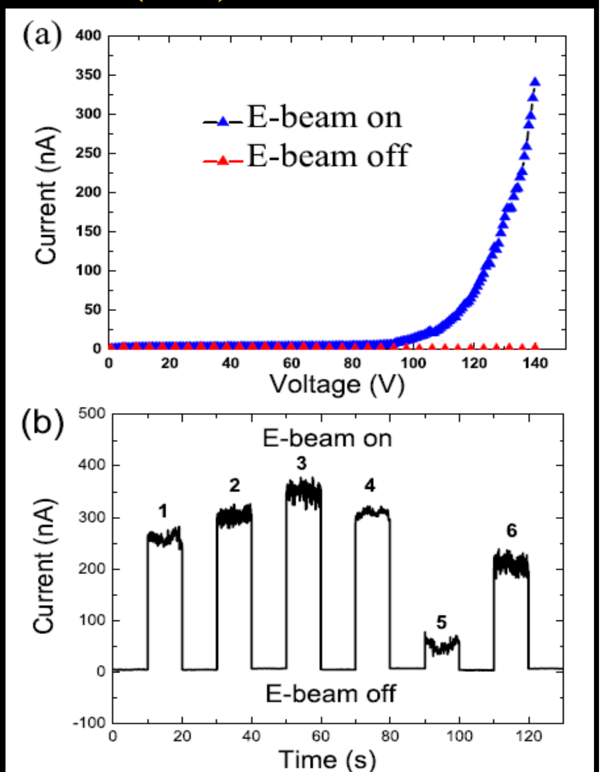
Schottky Barrier Switches

利用电子束激发我们证明了电子的注入效率是可以调制的。

C.H. Jin et al., Appl. Phys. Lett. 89 (2006) 213108





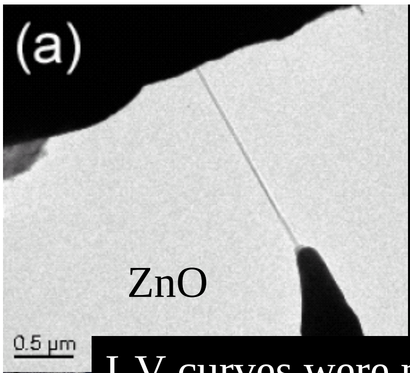


Most electronic appliances are based on digital electronics, which in essence just require a lot of switches working together in an organized fashion.

一维半导体纳米线的电学特性测量及应用

Background

- Many new semiconductor nanowires are routinely being fabricated → aiming to be used as the building block of future nanoelectronics.
- The above nanoelectronic applications of semiconducting nanowires require desired electric properties of the nanowires: high carrier mobility, conductivity etc.
- How to characterize the electric properties of semiconducting nanowires?
  - Choosing suitable electrode materials → linear I-V curve → resistivity (but no information on the doping concentration, mobility etc.)
  - Fabrication of nanotransistors: most widely used method, but not easy, requires high quality gate oxide etc.
  - Low-temperature magneto-resistance measurement: only provide reliable results for low-temperature (~4K) characteristics
  - **Our method: quantitative full I-V curve fitting via a simple MSM model**

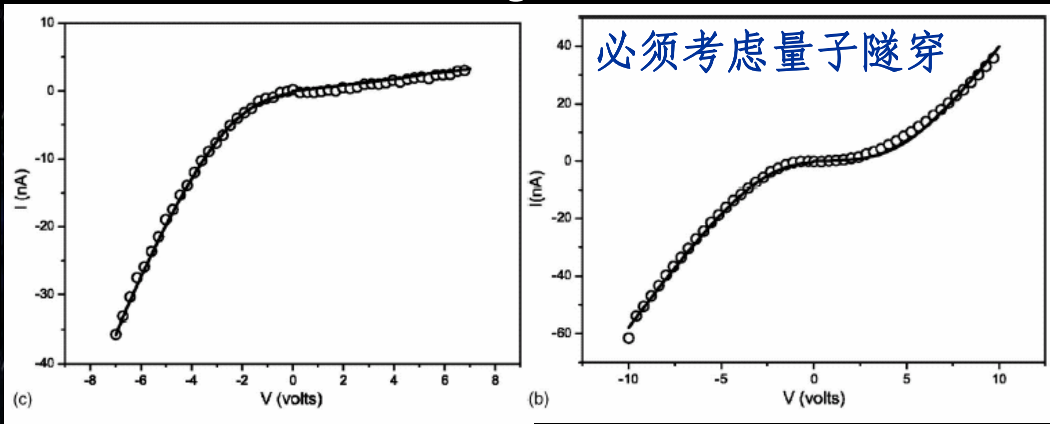


Quantitative analysis of I-V curves of semiconducting NWs

Z.Y. Zhang et al., Appl. Phys. Lett. 88 (2006) 073102

I-V curves were measured in-situ in high vacuum in TEM 10^{-5} Pa.

Experimental I-V curves are very sensitive to the contact. How to analyze them?



1. Linear I-V, both Schottky barriers ~ 0
2. Almost rectifying, one Schottky barrier is effective
3. Almost symmetric ??? Both Schottky barriers are effective, why?

Metal-semiconductor junction

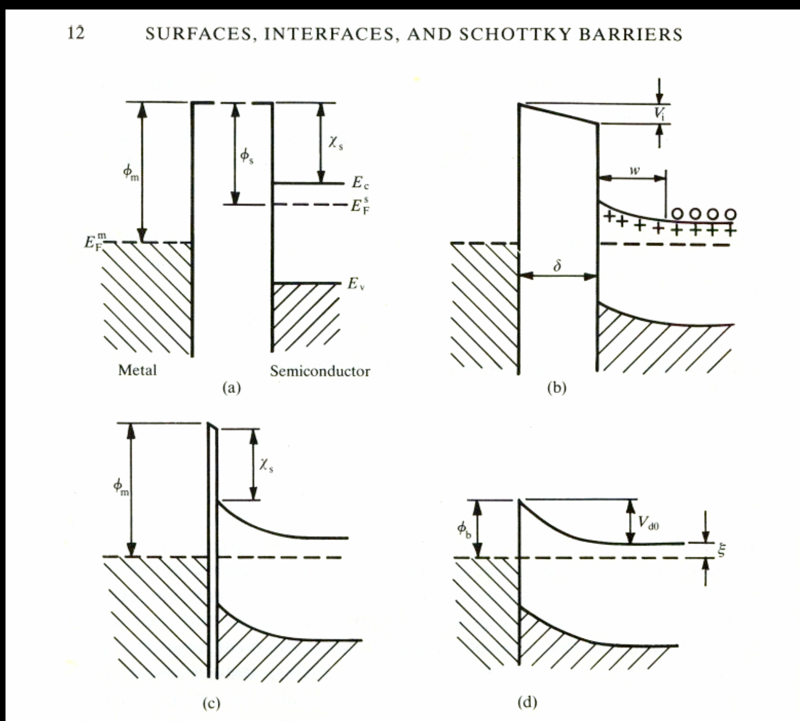


Fig. 1.7 Formation of a barrier between a metal and a semiconductor (a) neutral and isolated, (b) electrically connected, (c) separated by a narrow gap, (d) in perfect contact. ○ denotes electron in conduction band; + denotes donor ion.

The barrier

$\phi_b = \phi_m - \chi_s$

The planar Schottky barrier

The barrier height:

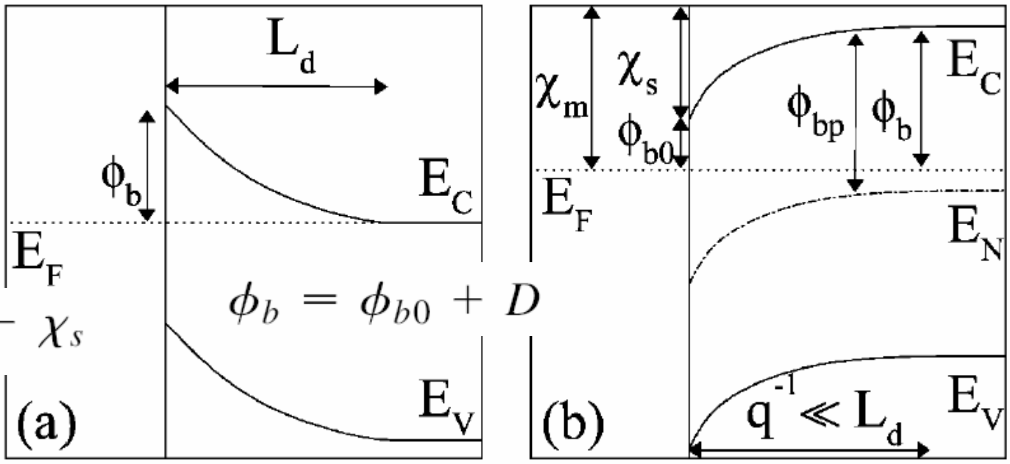
$$\phi_b = E_C - E_F$$

If there were no MIGS

$$\phi_{b0} = \chi_m - \chi_s$$

MIGS give a dipole at the interface

$$\phi_b = \phi_{b0} + D$$



$$\phi_b = \phi_{b0} + D$$

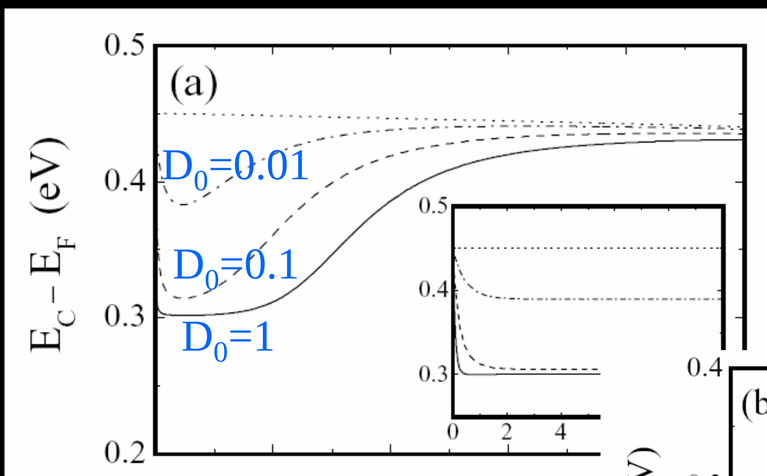
FIG. 2. Schematic band diagram for planar Schottky barrier, showing energy of Fermi level and local band edges vs distance ... interface (vertical line). (a) Large scale, showing band bending over length L_d due to doping. (b) Closeup of interface region, showing dipole (spread over length q^{-1}) due to MIGS.

The depletion length L_d is long compared to other length scales.

The dipole at the interface: the NT

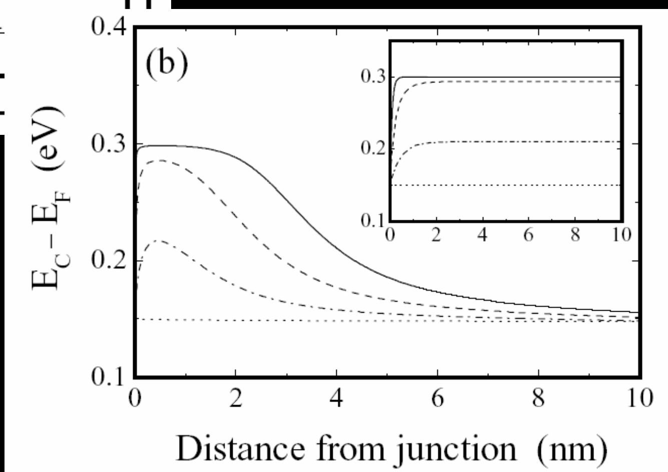
$$\chi_m > \chi_s + \phi_{bp}$$

$\Phi_{bo}=0.45$



The inserts: different dipole gives different potential at distance from the interface.

$\Phi_{bo}=0.15$



Local conduction band edge: For a dipole model

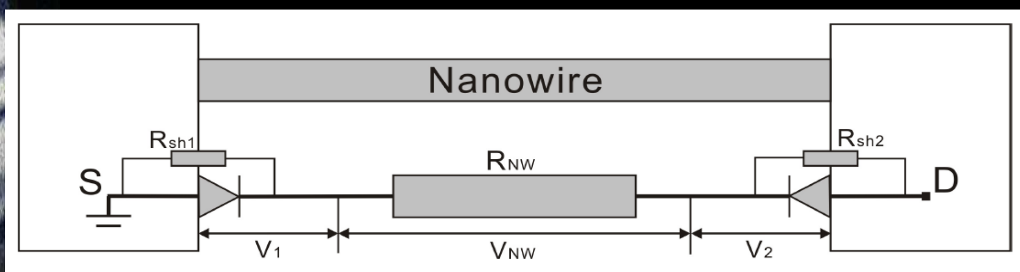
$$\sigma(z) = D_0(E_N - E_F)e^{-qz}$$

All states in the band gap decay exponentially with distances

The dipole: a comparison

- For the planar junctio, the dipole is a sheet, so it shifts the semiconductor bands relative to the metal Fermi level even at "infinite" distances.
- In contrast, for the NT the dipole is localized in all three directions, so its effect on the potential decays as z $^{-2}$ at distances larger than 2 nm.
- Thus for the NT, the Fermi-level pinning has no effect on the Schottky barrier height. Rather the barrier height is controlled by the metal work function.

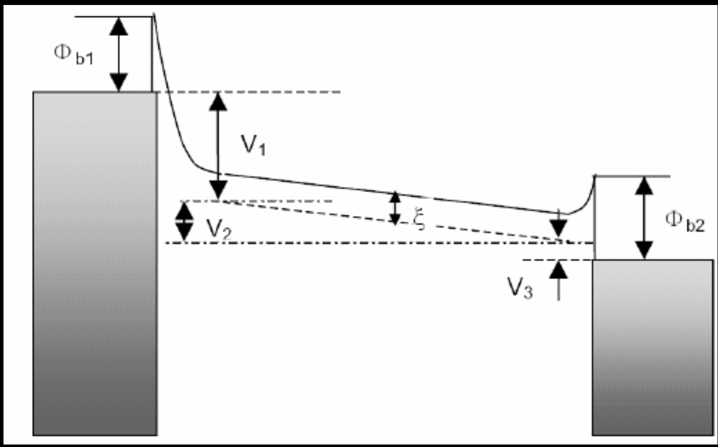
A M-S-M model



$$
\begin{aligned}
I_1 &= S_1 J_r(V_1) + V_1/R_{sh1} \\
I_2 &= S_2 J_f(V_2) + V_2/R_{sh2} \\
I_{NW} &= V_{NW}/R_{NW},
\end{aligned}
$$

考虑了隧穿、镜像力等

$$I_1 = I_2 = I_{NW}.$$



Electron thermionic field-emission model

$$V = V_1 + V_2 + V_3,$$

The reverse biased Schottky barrier:

$$J_1(V, \phi_b) = -J_s(V, \phi_b)\exp\left[V\left(\frac{q}{kT} - \frac{1}{E_0}\right)\right]$$

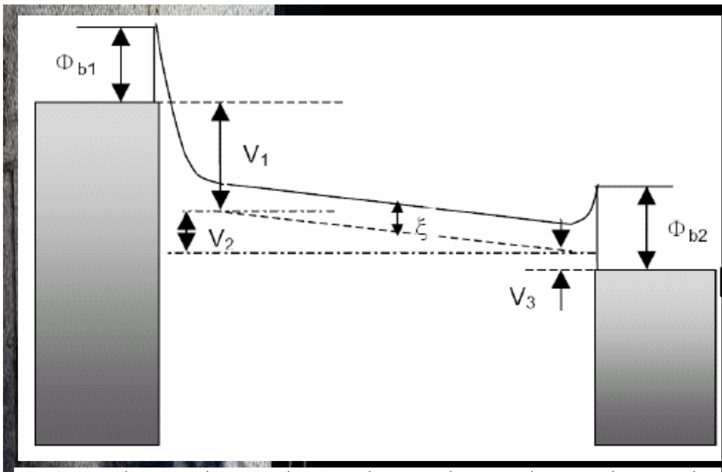
Tunneling current ~ tens nA, important in nano!

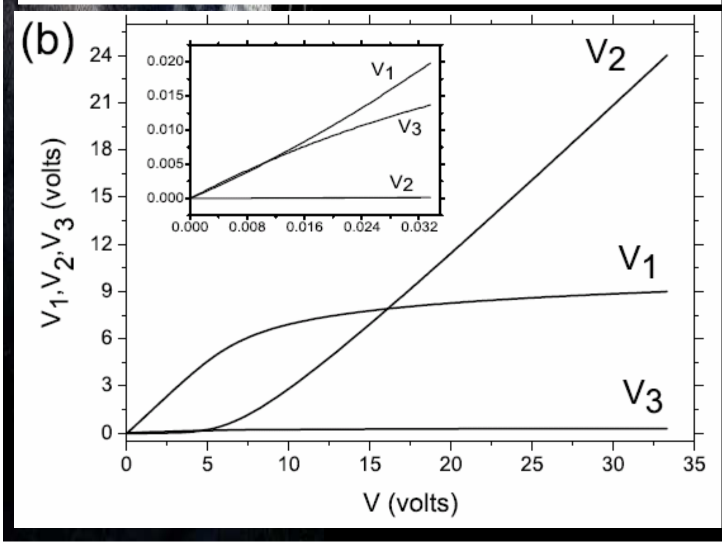
The forward-biased Schottky barrier:

$$J_2(V, \phi_b) = A^*T^2 exp\left(-\frac{q\phi_b}{kT}\right)\left\{\exp\left(\frac{qV}{kT}\right) - 1\right\}.$$

→ normal rectifying I-V characteristics

The total current: $I = S_1 J_1(V_1, \phi_{b1}) = V_2/R = S_2 J_2(V_3, \phi_{b2}),$





Potential distribution

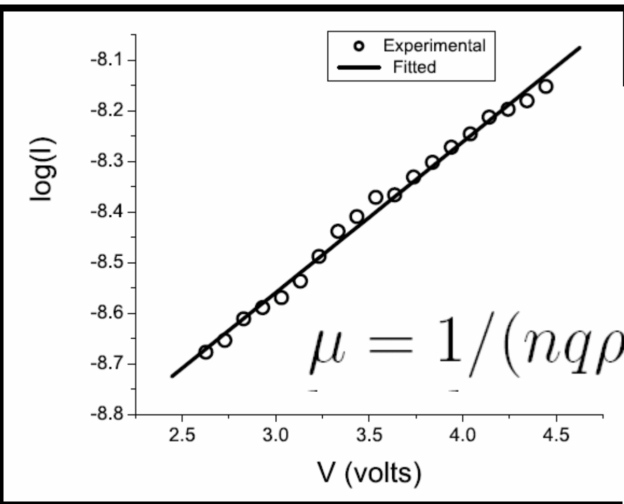
1. At very small bias, voltage drop occurs largely at the two Schottky barriers, i.e. V1 and V3 dominate;
2. At intermediate bias, voltage drop occurs largely at the reverse-biased Schottky barrier → V1, and also at the nanowire →V2;
3. At large voltage, the voltage drops at both Schottky barriers saturate, and increased bias is applied mainly at the nanowire.

Parameter retrieval

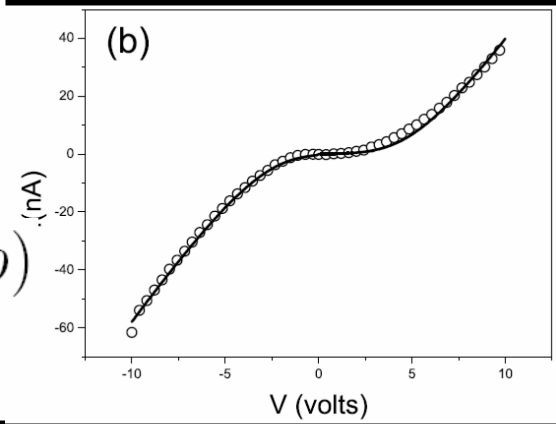
$$E_0 = E_{00} \coth\left(\frac{qE_{00}}{kT}\right),$$

$$E_{00} = \frac{\hbar}{2}\left[\frac{N_d}{m^*\epsilon_s}\right]^{1/2},$$

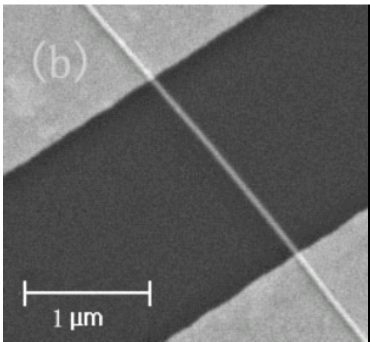
$$\log I = \log(S_1 J_1) = \log S_1 + V\left(\frac{q}{kT} - \frac{1}{E_0}\right) + \log J_s.$$



$$\mu = 1/(nq\rho)$$



At large bias, dV/dI→R→ρ, at intermediate bias, slop of logI vs V → E_0 → Electron density $n=N_d$→μ mobility etc., and at small bias, curve fitting → Schottky barrier height at the M-S interface etc.

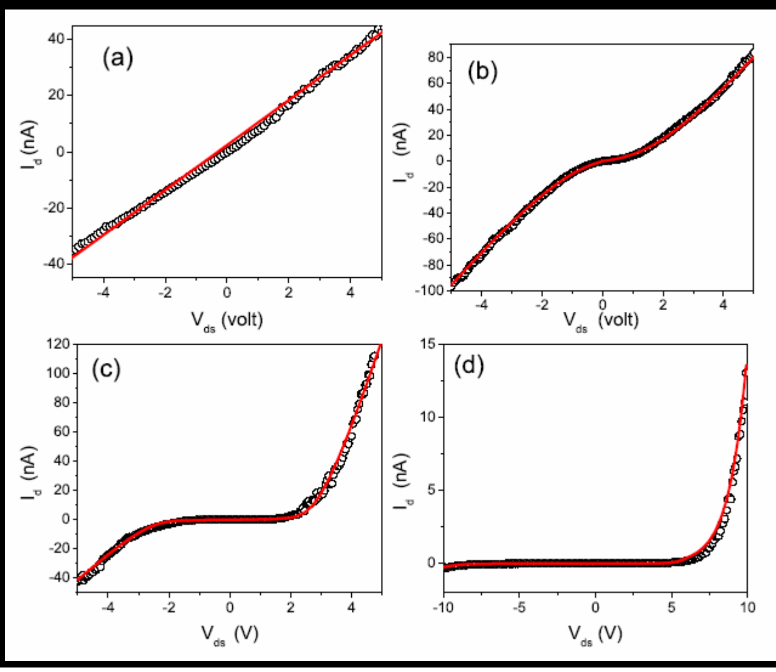


Application to Bi_2S_3 nanowire field-effect transistors (FETs)

Z.Y. Zhang et al., Adv. Func. Mater. (2006) in press

Different doping level →different Fermi surface → different contact → different I-V.

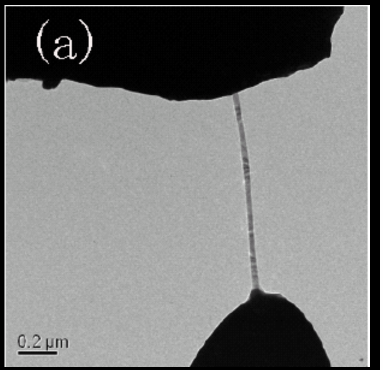
Our model can decouple effects due to contacts → intrinsic properties of semiconducting nanowires.

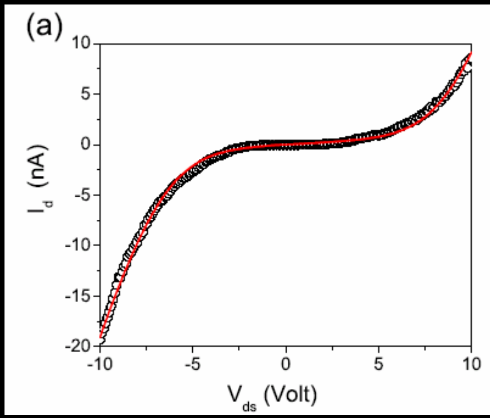


Two-terminal vs three-terminal FET method

Easy, free of substrate effect, and a quantitative tool.

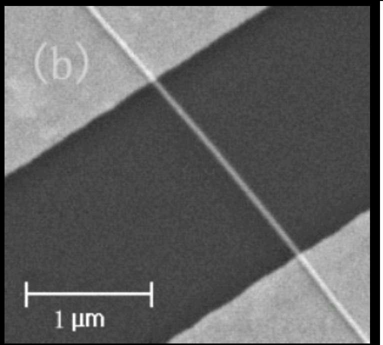
μ=1.23cm^2/(V.s)

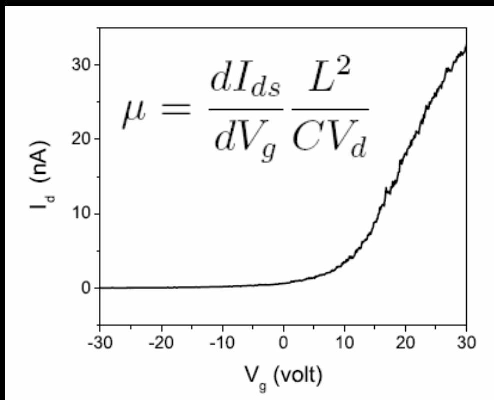




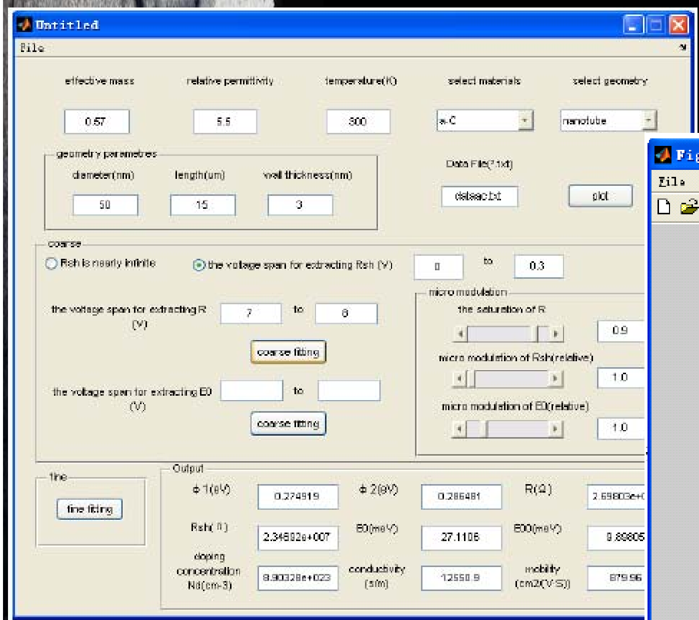
Fabrication of high quality field-effect transistor: effect of gate insulating layer, e.g. trapped charges

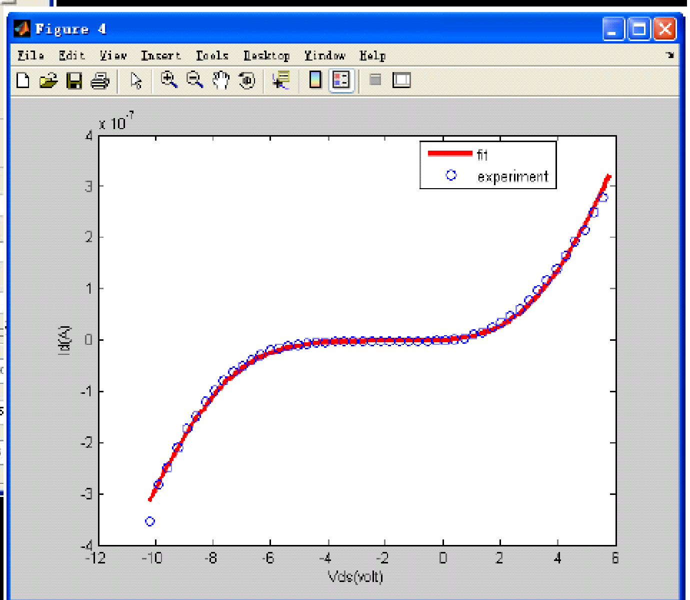
μ=1.10cm^2/(V.s)





A Peking University M-S-M (PKUMSM) Program





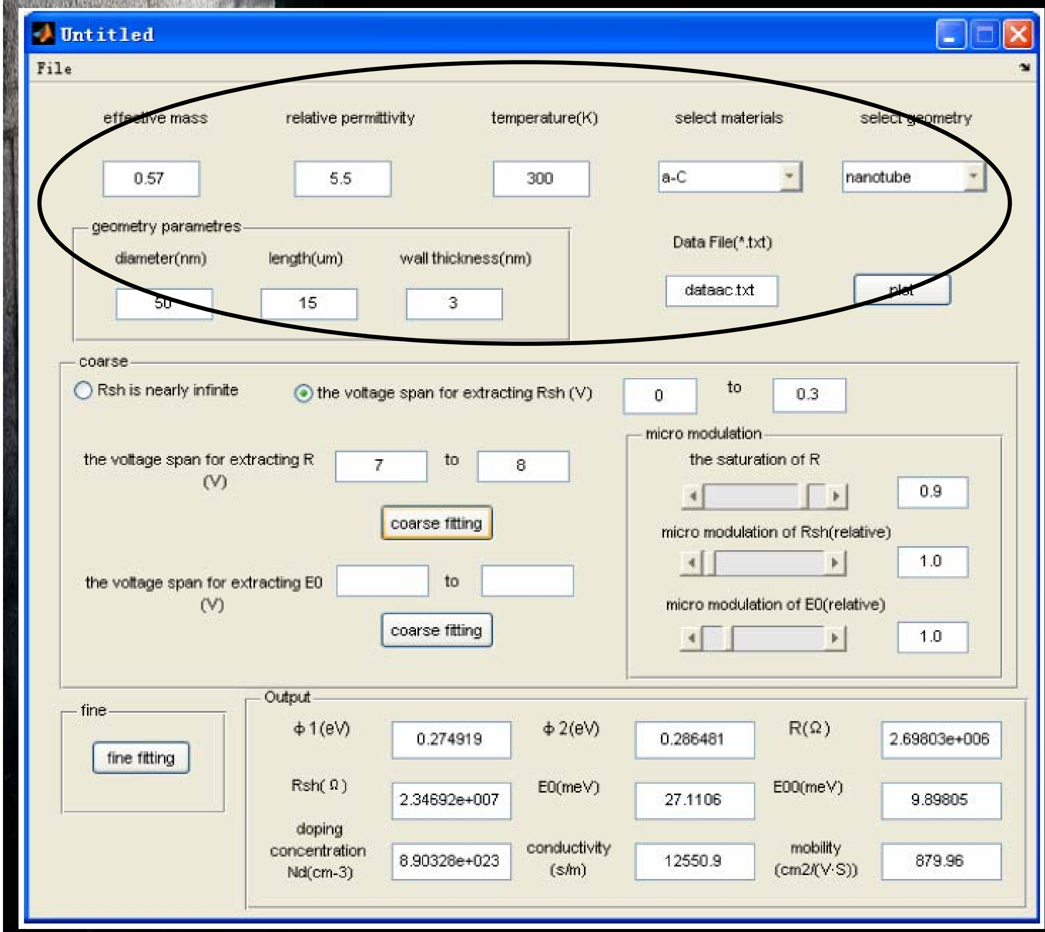
Totally six fitting parameters:
Two Schottky barriers,
NW resistance, shunt resistances, doping concentration

The parameters

- The known parameters
  - Geometry: nanotube or nanowire
  - Composition: effective mass and dielectric constants
- Uncertain parameters
  - The contact geometry and area: can vary from experiment to experiment
  - The Schottky barriers: affected by a range of things, including the work functions of both the metal electrode and nanowires, image force, the Fermi level of the nanowire, the interface composition and geometry, interface density → Fermi level pinning
- **Intrinsic parameters: those we aim to retrievel**
  - **Carrier (or doping) density, mobility, resistivity**

Parameter Retrieval: Two Schottky barriers, NW resistance, shunt resistances, doping concentration

- First, two to three parameters are estimated
  - The nanowire resistance at large bias
  - The shunt resistance at zero bias
  - The doping concentration at intermediate bias via ln(I) vs V plot
- Coarse refinement
  - Using two estimated parameters (Rs, R_NW or Nd), carry out three parameter fitting of the full I-V curve
- Fine refinement
  - Using the retrieved parameters from the coarse refinement and carry out full five parameter refinement.

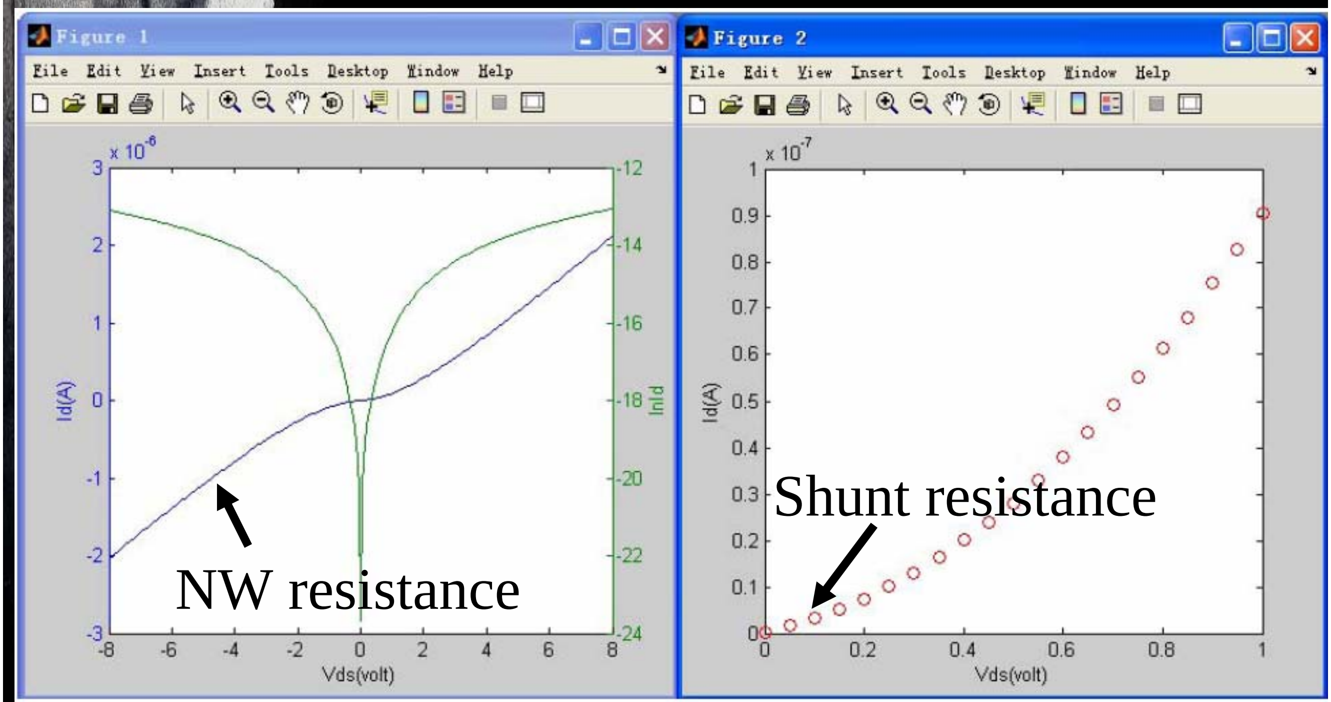


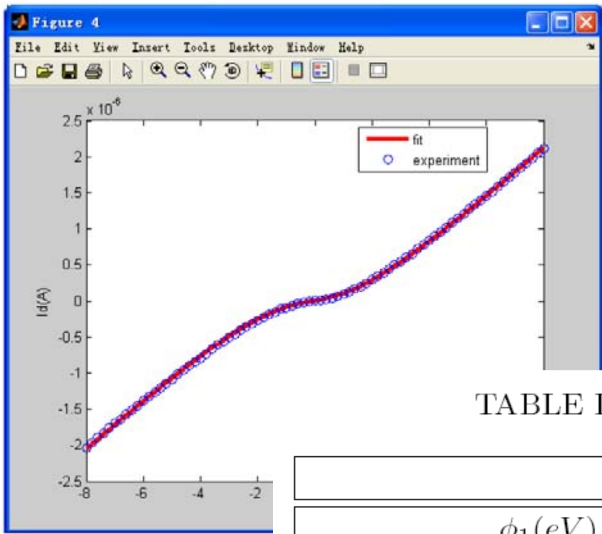
Input data:
Effective mass
Etc.

Coarse
fitting (3P)

Fine
fitting (6P)

Estimation of R_{NW}, E_{shunt} etc.





Output from quantitative whole curve fitting

TABLE II: Output from fine fitting for a-CNT

	value	standard error	relative error
$\phi_1(eV)$	0.226225	0.000755	0.002535
$\phi_2(eV)$	0.238582	0.000777	0.002496
$E_0(meV)$	26.749389	0.000096	0.000004
$E_{00}(meV)$	8.328692	0.000453	0.000054
$R_{NW}(\Omega)$	2.782970e+006	6.923187e+003	0.002488
$R_{sh1}(\Omega)$	2.244418e+007	3.150222e+006	0.140358
$R_{sh2}(\Omega)$	4.177945e+007	1.496908e+008	3.582881
$N_d(cm^{-3})$	2.991451e+016	3.253197e+012	0.000109
$conductivity(s/m)$	1.216785e+004	3.026991e+001	0.002488
$mobility(\frac{cm^2}{VS})$	2.539038e+004	6.322390e+001	0.002490
objective function χ^2	3.094868e-015		

Relevant parameters for CdS, ZnO, Bi_2S_3 nanowires

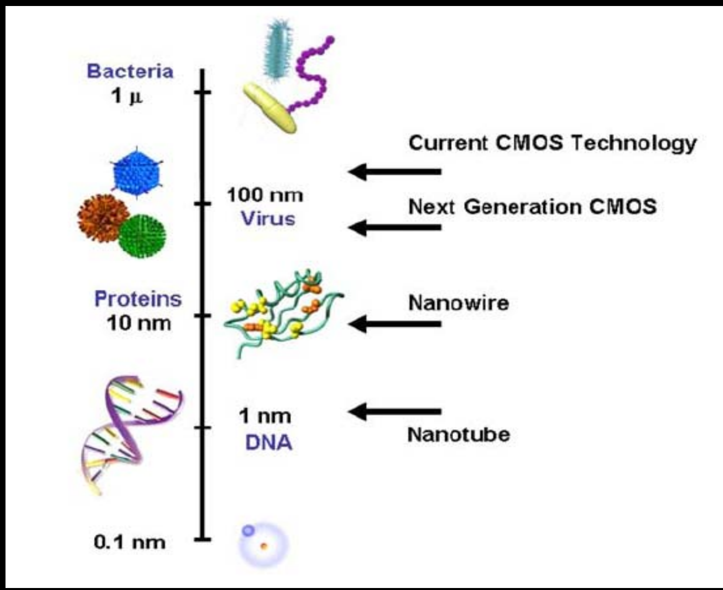
	CdS	ZnO	Bi_2S_3
Bandgap [eV] 300K	2.42	3.35	1.30
Permittivity [ε_0]	9.12	8.75	120.00
Effective mass [m_0]	0.21	0.27	0.59
Mobility (bulk) [$cm^2/(V.s)$]	340	200	200
Length [μm]	0.98	1.78	2.89
Diameter [nm]	42.2	40.8	73.8
E_0 [meV]	29.2	26.6	26.5
E_{00} [meV]	16.2	7.5	6.9
Electron concentration [$/cm^3$]	3.7E17	1.0E17	8.0E17
ϕ_{b1} [eV]	0.34	0.41	0.40
ϕ_{b2} [eV]	0.80	0.35	0.44
Resistivity [Ω.cm]	0.52	7.06	0.75
Mobility [$cm^2/(V.s)$]	32.20	8.85	10.47

Z.Y. Zhang, L.-M. Peng et al., Appl. Phys. Lett. 88 (2006) 073102

Nanosensing applications

Advantages of electronic detection (utilizing nanoscale devices):

1. Size compatibility;
2. Most biological processes involve electrostatic interaction and charge transfer → allowing electronic detection and the eventual merging of biology and electronics.



Ref: G. Gruner, Anal Bioanal Chem (2006) 384:322

Working principle

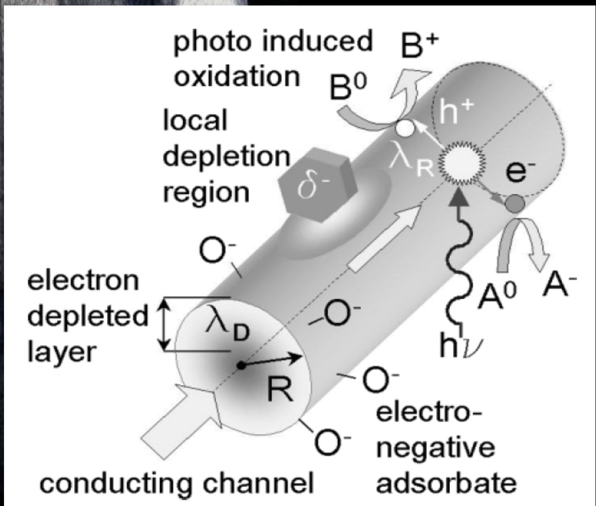


Figure 3 A summary of a few of the electronic, chemical, and optical processes occurring on metal oxides that can benefit from reduction in size to the nanometer range.

- The working principle of solid-state sensors is based on the transduction of the binding of an analyte at the active surface of the sensor to a measurable signal that most often is a change in the resistance, capacitance, or temperature of the active element.

Advantages of Nanosensors

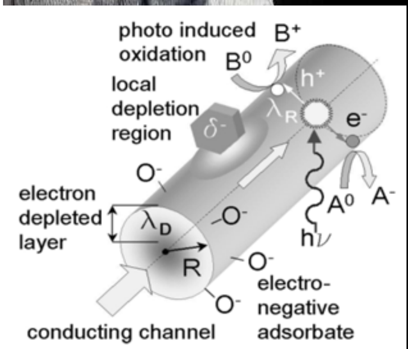


Figure 3 A summary of a few of the electronic, chemical, and optical processes occurring on metal oxides that can benefit from reduction in size to the nanometer range.

- A large surface-to-volume ration
  - meaning that a significant fraction of the atoms (or molecules) in such systems are surface atoms that can participate in surface reaction.

  The Debye length λ_D (a measurement of the field-penetration into the bulk) for most semiconducting oxide nanowires is comparable to the radius over a wide temperature and doping range, causing their electronic properties to be strongly influenced by processes at their surface.
  - ➔ better sensitivity (~ 10^5-fold greater than those of comparable solid film devices for In_2O_3 nanowires) and selectivity.
- The average time it takes photo-excited carriers to diffuse from the interior of an oxide nanowire to its surface (~10^{-12} – 10^{-10}s) is greatly reduced with respect to electron-hole recombination time (~ 10^{-9} – 10^{-8}s)
  - Surface photoinduced redox reaction with quantum yield close to unity are routinely possible on nanowires.
  - Allowing the analyte to be rapidly photo-desorbed from the surface (~ a few seconds) even at room temperature ➔ much reduced recovery and response times of the sensor.

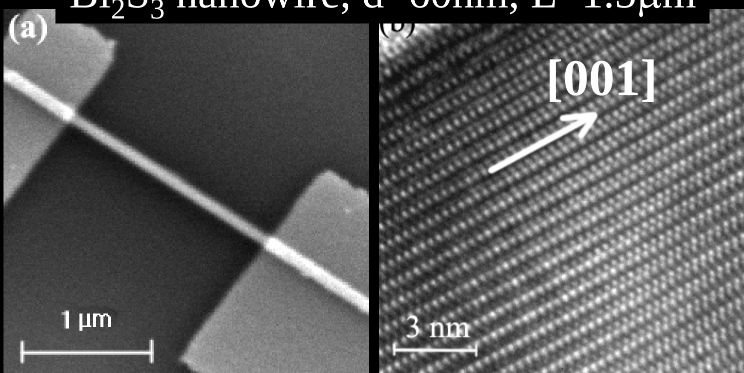
H_2 Gas Sensing
surface or contact effects?

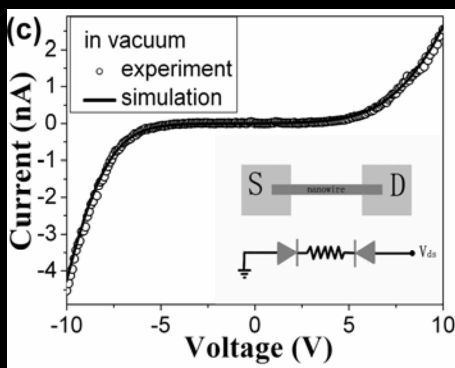
Vacuum: 2.5×10^{-2}Pa

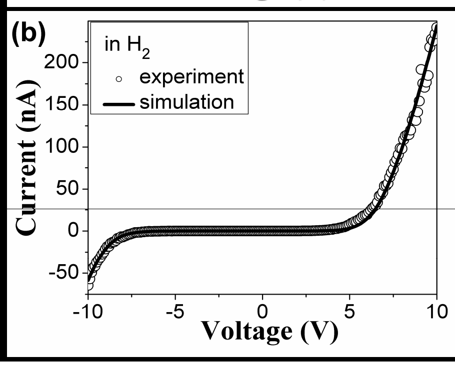
H_2 gas: ~ 1atm

正向电流增加了上百倍

Bi_2S_3 nanowire, d~60nm, L~1.5μm







In vacuum:

μ=0.029cm^2/Vs, n=2.8×10^{15}cm^{-3}

In H_2 gas:

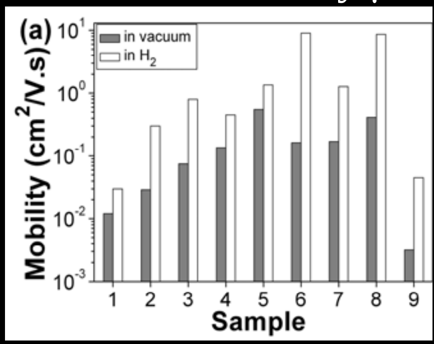
μ=0.3cm^2/Vs, n=5.6×10^{15}cm^{-3}

迁移率增加了１０多倍，载流子浓度增加了１倍.

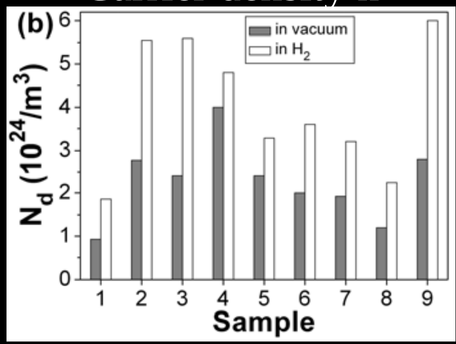
Effects of H_2

(K. Yao et al., J. Phys. Chem. B 110 (2006) 21408)

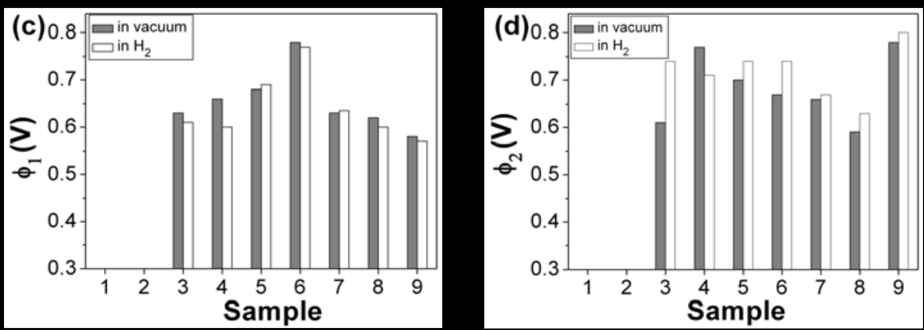
Electron mobility μ



Carrier density n



Schottky barrier heights ϕ_1 and ϕ_2



9 FET devices

2 with ohmic contact, and 7 with non-ohmic contact

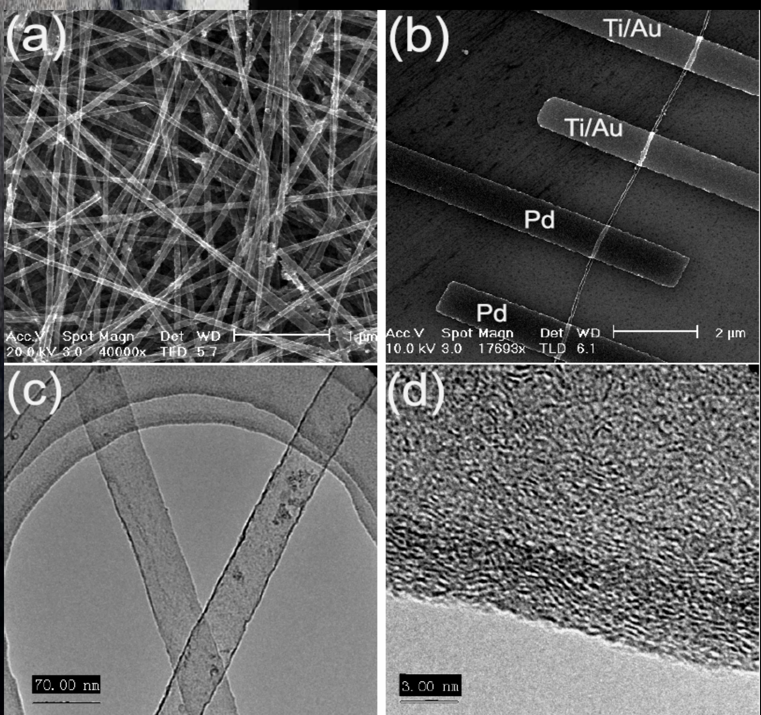
H_2 increases
μ ~10 times
n ~ 2 times
φ ~ hardly

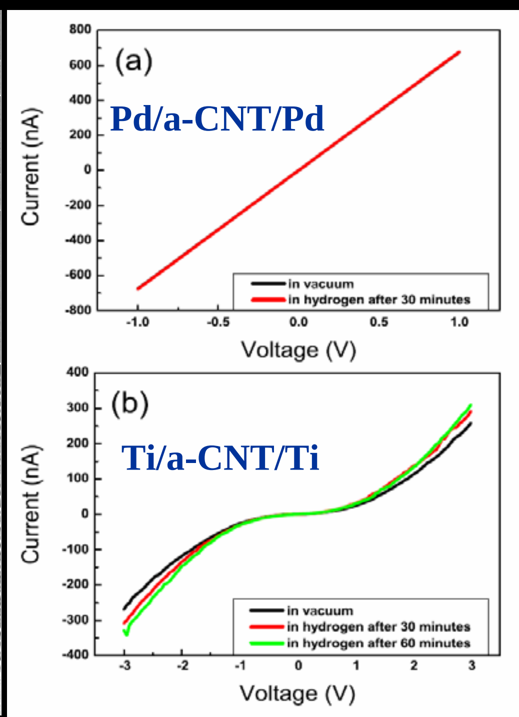
氢气主要是消除表面悬挂键，降低了表面散射，增加了载流子浓度。

How ???

H_2 gas sensing: effects of contacts

(Y.F. Hu et al., Appl. Phys. Lett. 88 (2006) 063113)

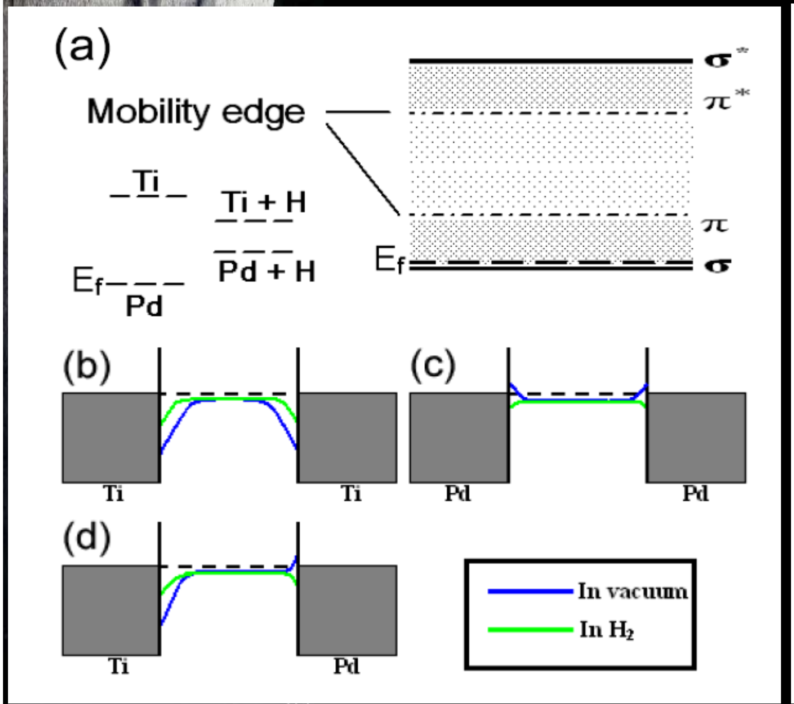


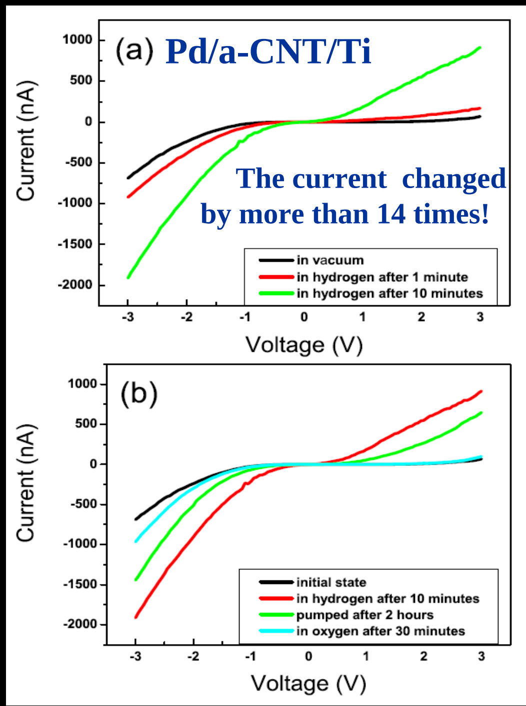


For symmetrically contacted devices, H_2 hardly changes the current.

Asymmetrically contacted devices

Y.F. Hu et al., Appl. Phys. Lett. 88 (2006) 063113

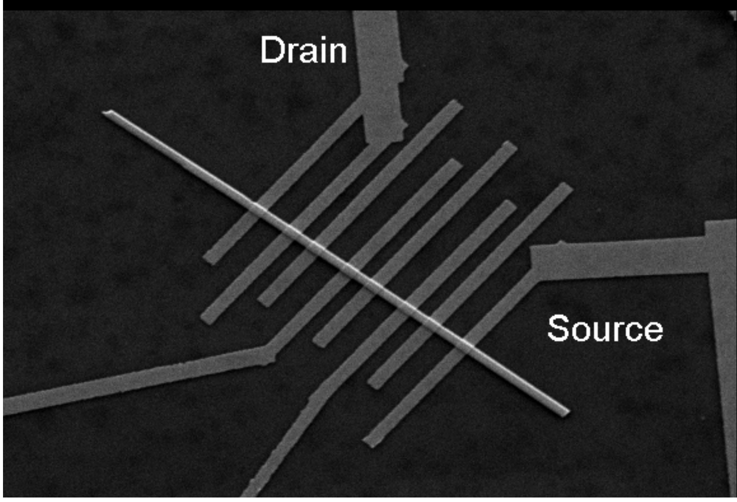




Asymmetrically contacted a-CNT devices: Pd/a-CNT/Ti: the current changed more than 14 times.

The changes in the current is mainly due to the changes in the contacts (via workfunctions).

单壁和双壁碳纳米管场效应晶体管器件

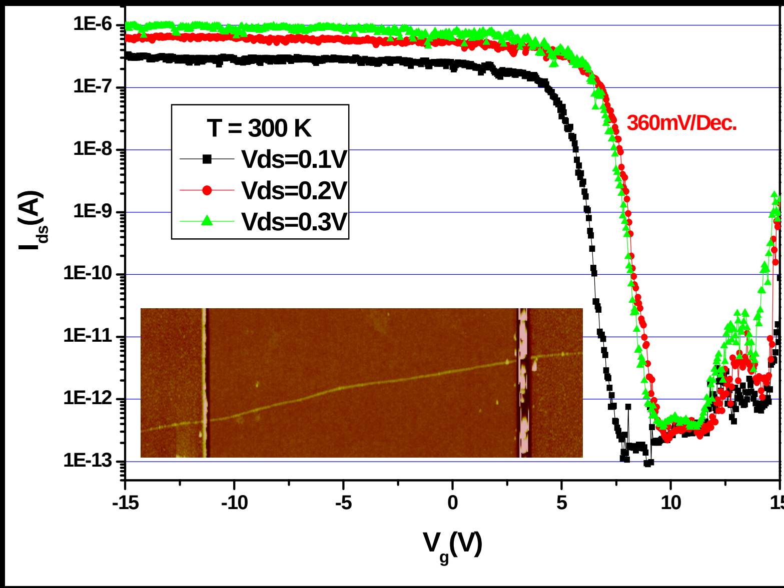


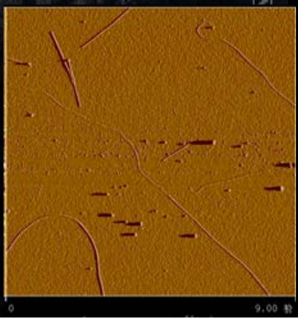
1.4纳米单壁碳纳米管晶体管

通过一根半导体性碳管的电流开关比达到了10^6。
通过一根金属性碳管的电导超过了$3.7G_0$。

p-type SWCNT FET

Back gate 100nm SiO_2
室温下开关电流比 > 10^6



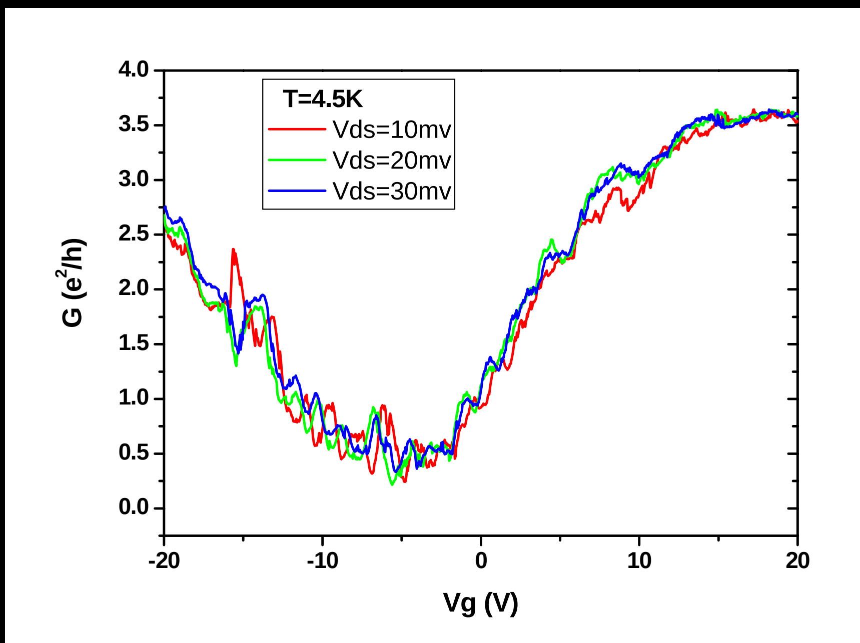


←直径~1.4纳米 （北京大学化学院张锦教授）

金属性SWCNT中的弹道输运（L~500nm）

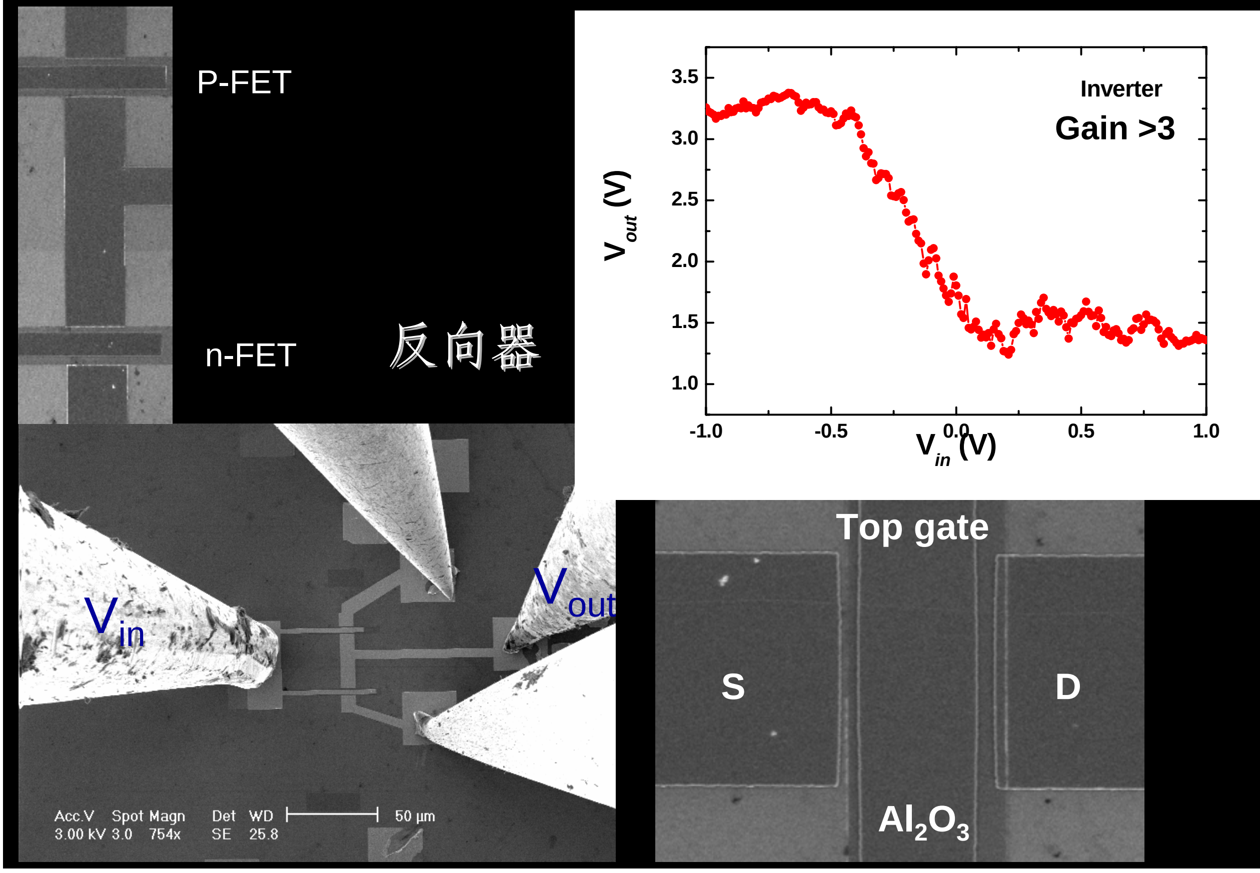
金属型碳管电导低温下的准周期性振荡反映了电子波在碳管中的量子相干行为。

The energies of standing waves $\Delta E=h\nu_F/2L$,
Rapid:
500nm long tube
Slow:
localized states



弹道输运：金属型碳管低温电导可达$3.7G_0$ ($G_0=e^2/h$)，已接近弹道输运的理论极限$4G_0$.

单根单壁碳纳米管CMOS器件



器件性能和国际最好水平比较

（可比，但仍有差距）

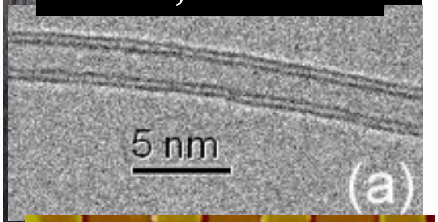
	Cees Dekker	IBM (p-type)		H. Dai		Infineon Technologies	Our	
		Back-gated	Top-gated	Back-gated	Top-gated		Back-gated	Top-gated
Gate length (nm)	100	1030	260	300nm~3μm	>50nm	Sub 20nm	500nm~2μm	~3-5μm
Gate thickness (nm)	几nm	150	15	67nm	8nm~几十nm	12nm	100-200nm	12-15nm
Gate dielectrics	Al_2O_3	SiO_2	SiO_2	SiO_2	ZrO_2, HfO_2	SiO_2	SiO_2	Al_2O_3
ON state Resistance	26MΩ	~ MΩ	~ MΩ	10~40kΩ	~50kΩ	30~100kΩ	20~300kΩ	~ MΩ
ON state current	100nA	nA~μA	nA~μA	~10μA	>20μA	1~十几μA	>10μA	nA~μA
ON/OFF current ratio	$\sim10^5$	$\sim10^5$	$\sim10^6$	$\sim10^6$	$\sim10^6$	$>10^6$	$>10^6$	$\sim10^3$
Subthreshold Slope (mV/dec)		730	130	150~170	~70(p-type) ~80(n-type)	170~200	~360(p-type) ~95(n-type)	~210(p-type) ~500(n-type)
Gain of Inverter	~2	>1		~3.5 (back gate) >60 (top gate,high K,ALD)			>3	

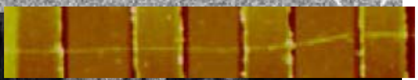
双壁碳纳米管晶体管场效应

S. Wang et al., J. Phys. Chem. B (2005)

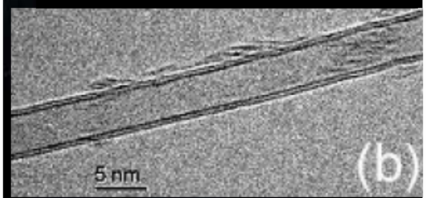
批量制备了几百个器件,成功率达到了60%.

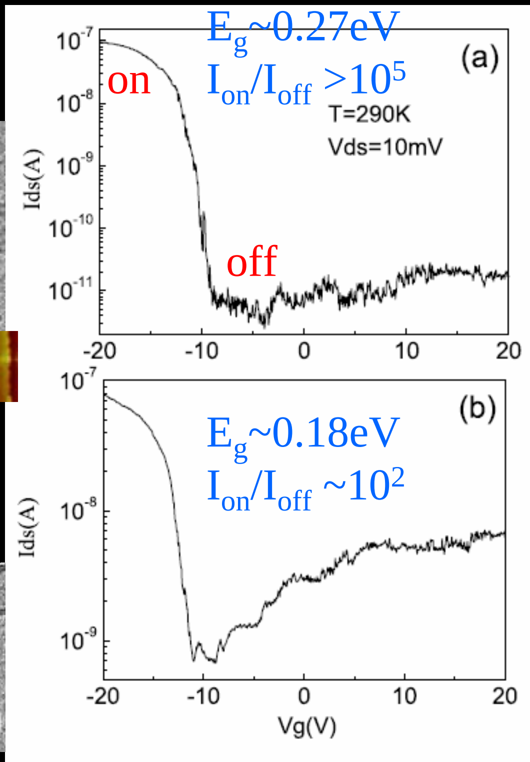
d=3nm, L=500nm





d=4.5nm, L=800nm





DWCNT:

M,S

M,S

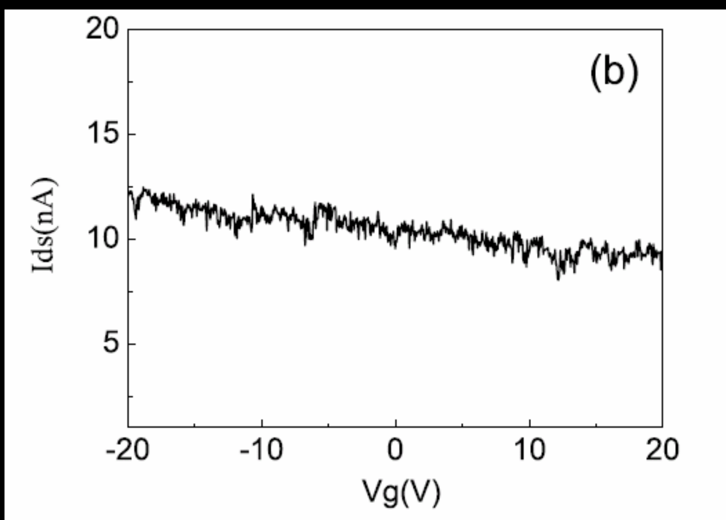
Four possibilities: SS, SM, MS, MM

Almost completely depleted of carriers at off states → both shells are semiconducting, i.e. the tube is SS

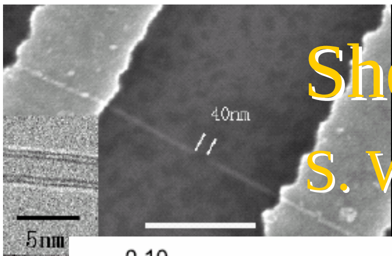
For larger tube, it is more difficult to turn it completely off.

Metallic-Metallic DWCNT

d=4.5nm
L=0.8μm
M-M or
M-S tube

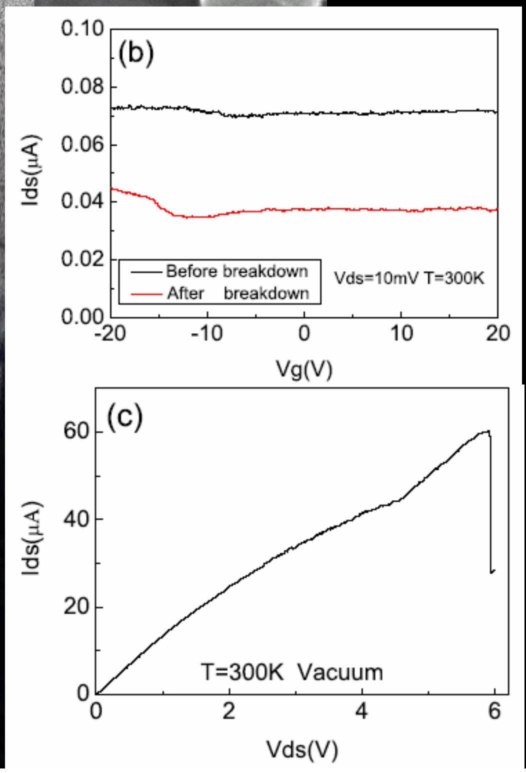


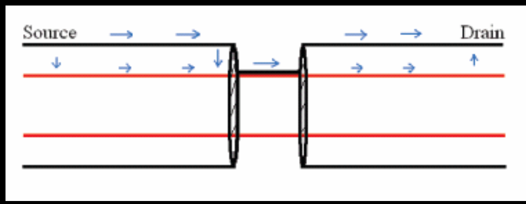
Hardly shows any modulation by V_G
→dominated by metallic outer shell →M-M or M-S tube.

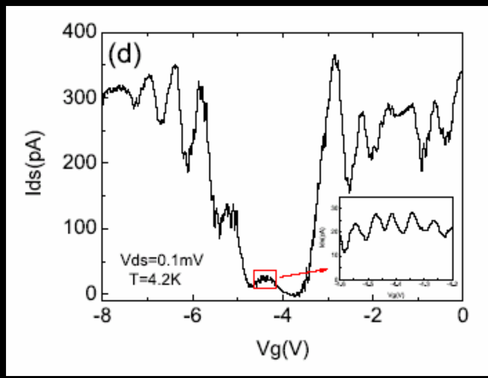


Shell by shell breakdown (MM)

S. Wang et al., Carbon (2007) in press

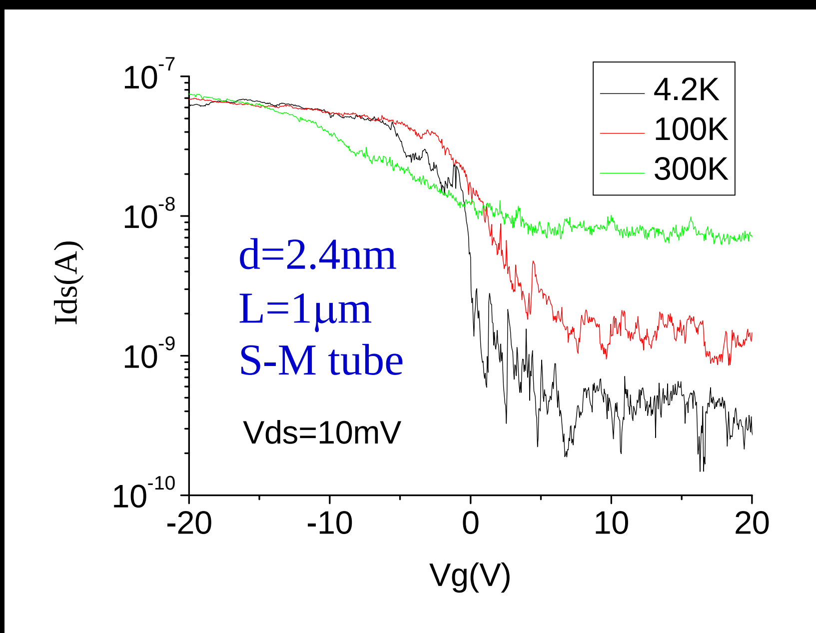






Fast oscillation → L~250nm, tube length
Slow oscillation → L~27nm, gap

Semiconducting-Metallic DWCNTs

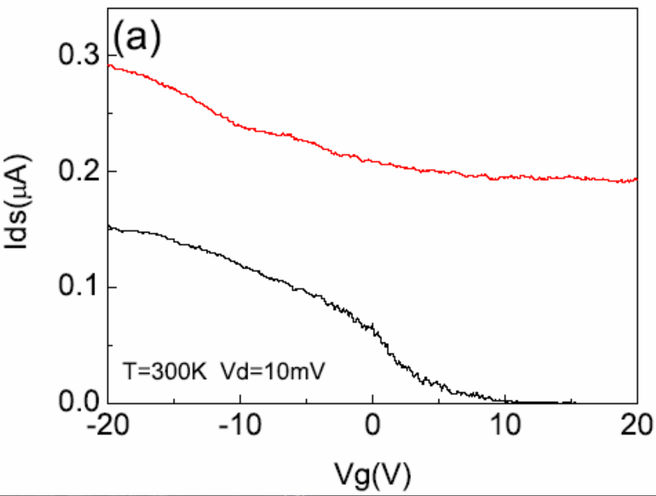


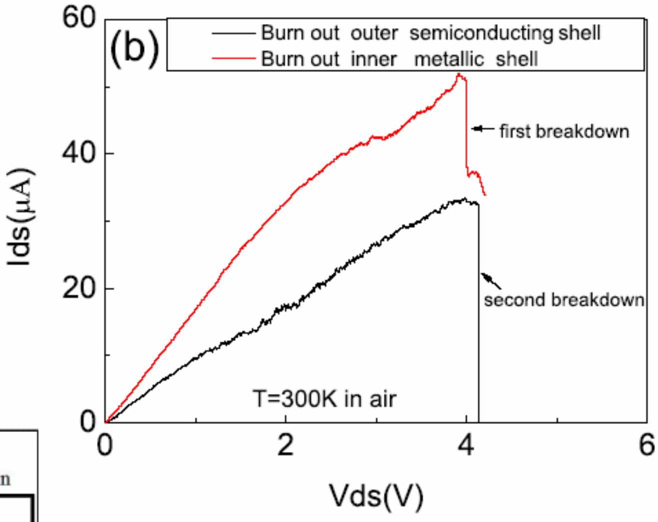
Strong screening effect due to residual electrons in the inner shell → less effective gate → current cannot be completely turn off

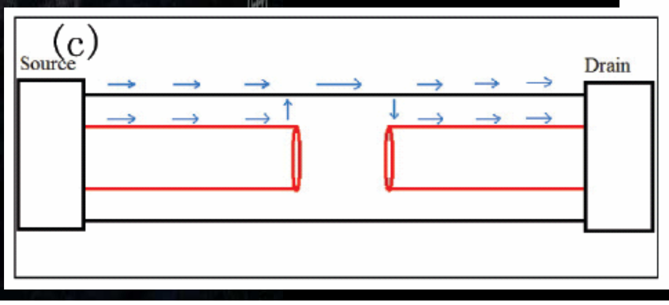
p-region, dominated largely by the outer semiconducting shell.

The outer S-shell is turned off (at low temperature)

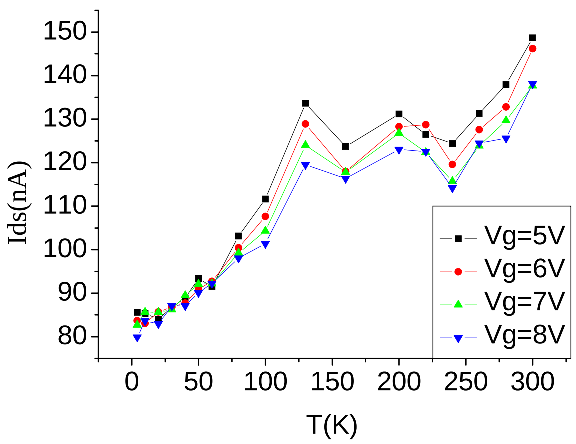
Shell by shell breakdown (SM)



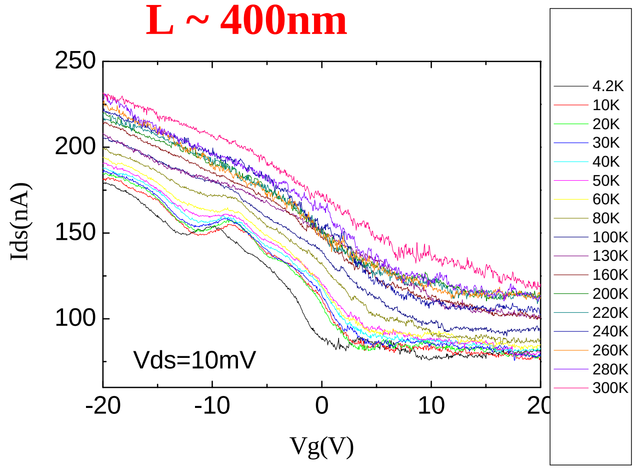




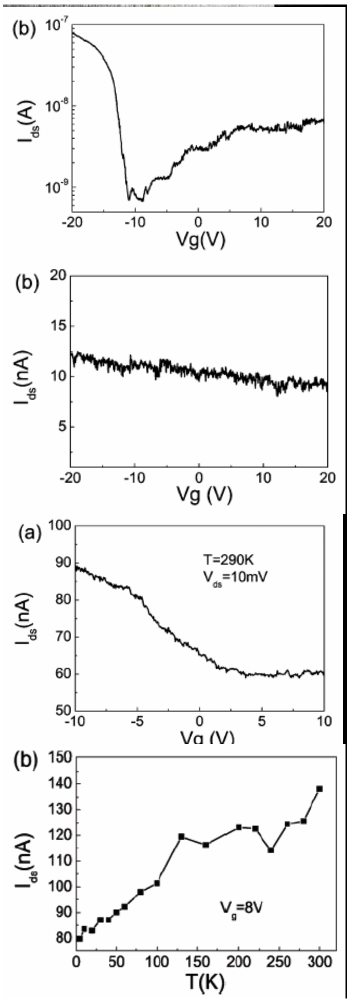
Temperature dependent charge transfer



L ~ 400nm



These results seem to suggest that the charge injection into the inner shell is temperature dependent.



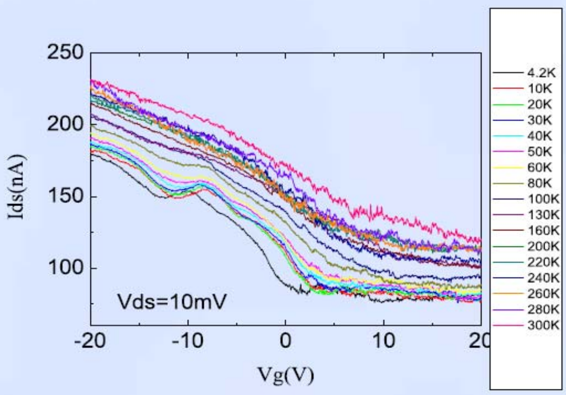
Summary: DWCNT-FET

- Totally over 200 devices were fabricated, and 125 were found to work properly.
- Three distinct behaviors were found
  - 52 SS devices (4/9 were expected , i.e. 55)
    - Large I_{on}/I_{off} ratio, 10^2-10^5, behavior similar to SWCNTs
  - 44 MM or MS devices (3/9→42)
    - Current hardly modulated by Vg, dominated by metallic conductance
  - 29 SM devices (2/9→28)
    - Lower I_{on}/I_{off} ratio, typically less than 10, high conductance in p-region, and the current cannot be turn “off” completely, or turn “on” again in the n-region→screening effect due to the inner metallic shell.
- Interlayer coupling was found to be temperature dependent.

Strange FEC of S-M DWCNT --- *Our Focus*

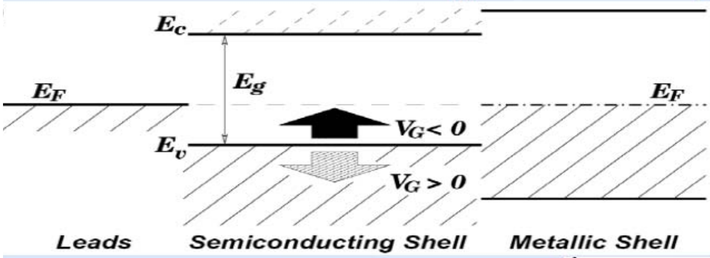
- I_{on}/I_{off} is order of 10^1 or 10^2 , in contrast with order of 10^5 for S-S ones.
- $I_{sd} \sim V_G$ curve is NOT exponential in transition region.
- Transition region is much WIDER than usual semiconductors.

Under different T:



奇异场效应是由于内层电子的screening造成的。

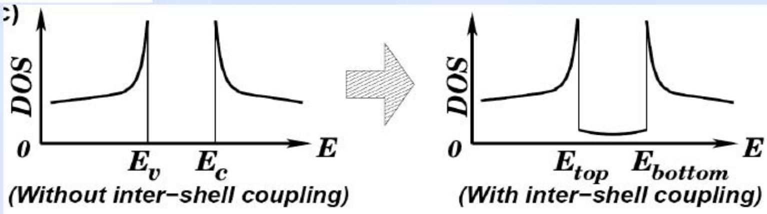
Physical picture



Anomalous FECs of S-M DWCNT

Crucial points:

inter-shell coupling



e-WFs in the inner shell penetrate into the outer one

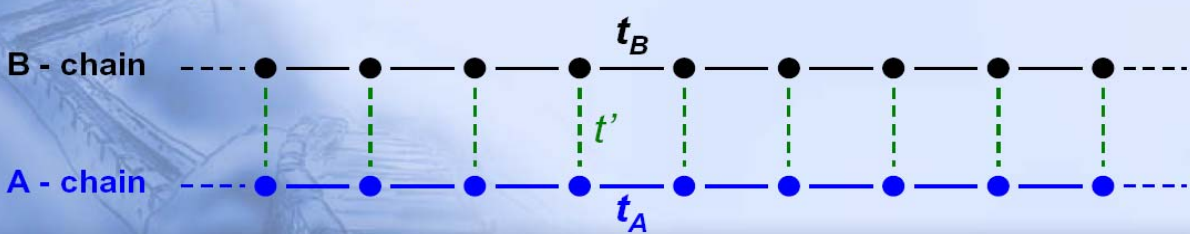
LDOS of outer s-shell in its original gap region becomes non-zero

Outer s-shell becomes a weak metal (proximity effect)

奇异场效应的定量理论是和香港科技大学王向荣教授合作完成的。

Modelling

1-D two-leg tight-binding Model



Hamiltonian can be written as:

$$H = \sum_{\alpha,i} (\frac{1}{2}\varepsilon_\alpha c^\dagger_{\alpha,i} c_{\alpha,i} + t_\alpha c^\dagger_{\alpha,i} c_{\alpha,i+1}) + \sum_i t' c^\dagger_{A,i} c_{B,i} + h.c.$$

Two eigen energy branches:

$$E_{\pm,k} = \frac{1}{2}(\varepsilon_A + \varepsilon_B) + (t_A + t_B)\cos k \pm \frac{1}{2}\sqrt{[(\varepsilon_A - \varepsilon_B) + 2(t_A - t_B)\cos k]^2 + 4|t'|^2}$$

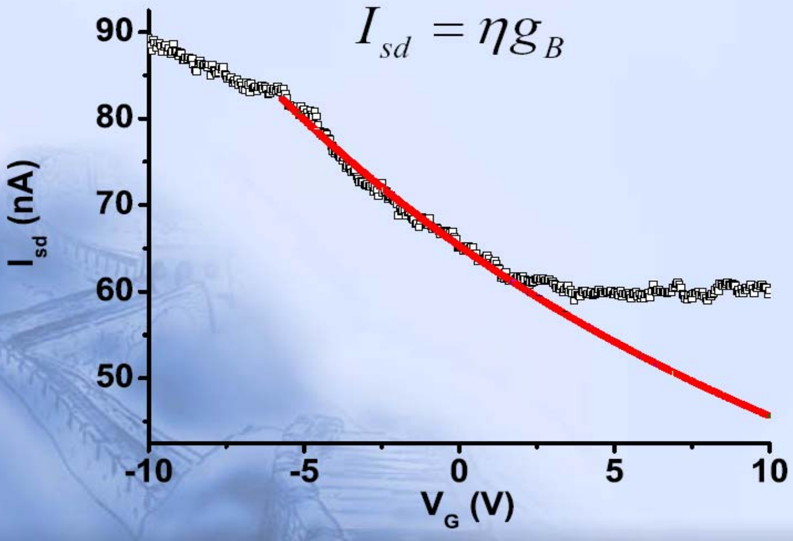
With: ε_A $fixed$ **--- Fermi level pinning**

$$\varepsilon_B = U_0 - e\beta V_G, \qquad \beta = C_1/(C_1 + C_2)$$

Fitting between model and experimental data at T=4.2K

$$\varepsilon_A - \varepsilon_B = -U_0 + \beta e V_G$$

$$I_{sd} = \eta g_B$$

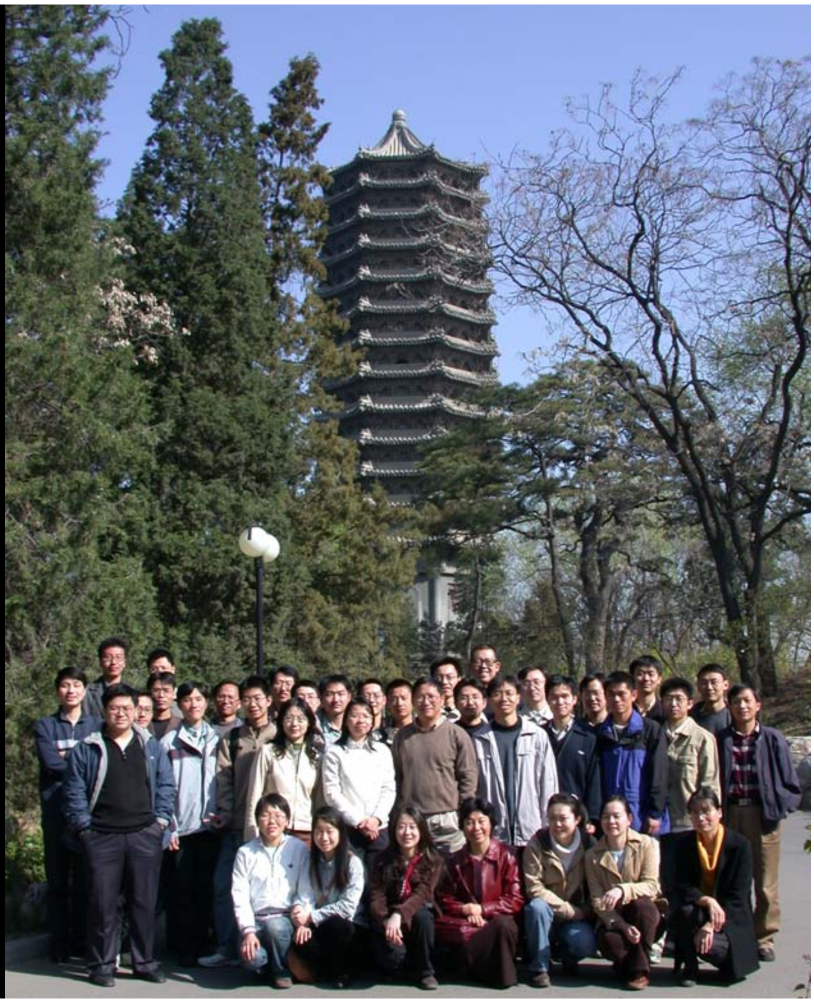


t_A =0.95eV;
t_B =0.44eV;
t' =0.42eV;
U_0=-1.05eV;
β =0.025;
η =3.1 μ A*eV.
ε_A=0.11eV

L.M. Peng *et al.*

J. Phys. Chem. B v109 (No.37) p17361

纳米材料与器件
研究组
2005年初春



结束语

- 主要是由美国科学家发展起来的硅基CMOS技术经过40余年的高速发展已经到达了一个转折点
  - 呼唤新的类似固体晶体管的纳电子开关的出现
- 中国的科技经过多年后备席的韬光养晦，正在开始走向前台
  - 呼唤更多的优秀物理学子积极参与前沿科技研究，催生作为科技大国的中国的诞生
- 时势造英雄
  - 现在势在中国，英雄也将出于中国

谢谢！