Do silício ao carbono: novos rumos para o transporte eletrônico?

Caio Lewenkopf - UFF

Prêmio Nobel de Física - 2010

"por experimentos pioneiros relacionados ao material bidimensional grafeno"

Andre Geim

Konstantin Novoselov

Nem sempre foi assim...

Eur. J. Phys. 18 (1997) 307–313. Printed in the UK

PII: S0143-0807(97)84689-2

Of flying frogs and levitrons

M V Berry† and A K Geim‡

† H H Wills Physics Laboratory, Tyndall Avenue, Bristol BS8 1TL, UK
‡ High Field Magnet Laboratory, Department of Physics, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Prêmio Ignobel

Física 2000

A. Geim e M. Berry

Nem sempre foi assim...

Eur. J. Phys. 18 (1997) 307–313. Printed in the UK PII: S0143-0807(97)84689-2

Of flying frogs and levitrons

M V Berry† and A K Geim‡

† H H Wills Physics Laboratory, Tyndall Avenue, Bristol BS8 1TL, UK
‡ High Field Magnet Laboratory, Department of Physics, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Microfabricated adhesive mimicking gecko foot-hair

A. K. Geim, K. S. Novoselov e outros

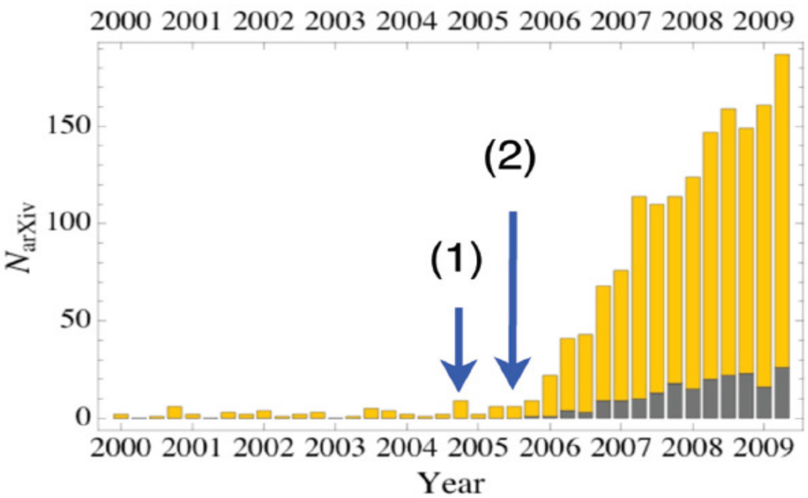
Nature Materials **2**, 461 - 463 (2003)

Nascimento de um campo de pesquisa

Science **306**, 666 (2004)

Electric Field Effect in Atomically Thin Carbon Films

K. S. Novoselov,[1] A. K. Geim,[1*] S. V. Morozov,[2] D. Jiang,[1] Y. Zhang,[1] S. V. Dubonos,[2] I. V. Grigorieva,[1] A. A. Firsov[2]



Vol 438|10 November 2005|doi:10.1038/nature04233

Two-dimensional gas of massless Dirac fermions in graphene

K. S. Novoselov[1], A. K. Geim[1], S. V. Morozov[2], D. Jiang[1], M. I. Katsnelson[3], I. V. Grigorieva[1], S. V. Dubonos[2] & A. A. Firsov[2]

O que nanotecnologia?

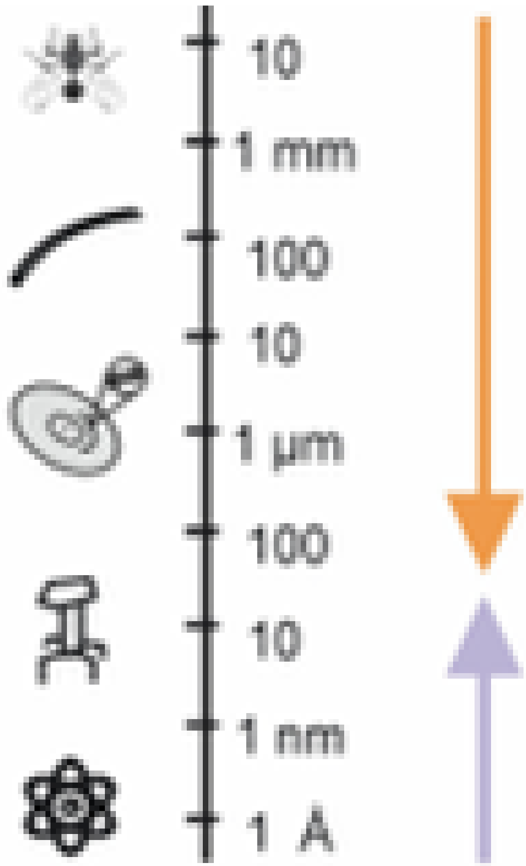
Mosca

Cabelo humano

Estruturas micrométricas

Virus

Átomos e moléculas



Abordagens “top-down”

(física, engenharias)

Abordagens “bottom-up”

(química, biologia)

De onde surgiu a idéia?

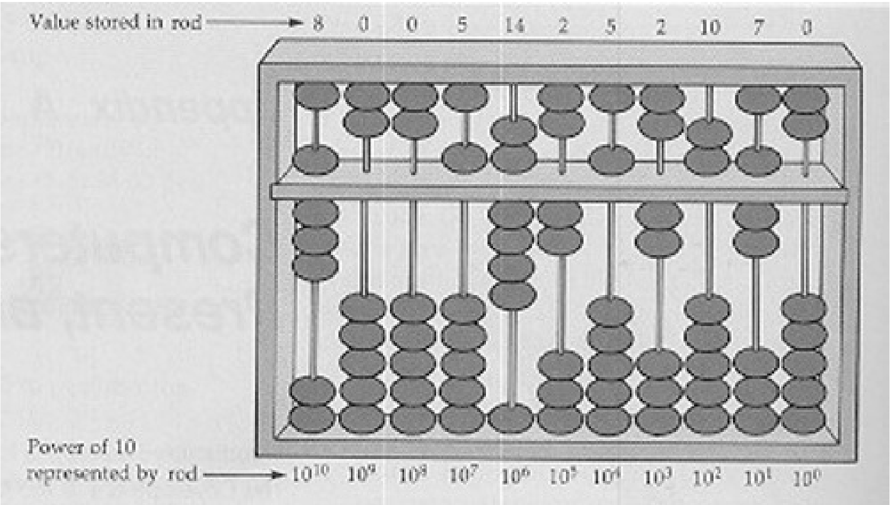
Richard P. Feynman

palestra na Caltech, EUA (1959)

"Há muito espaço embaixo"

- Por que não podemos transcrever toda Enciclopédia Britânica na cabeça de um alfinete?
- Por que não podemos reduzir o tamanho de motores elétricos para escalas de comprimento moleculares?

Física e a revolução na informação



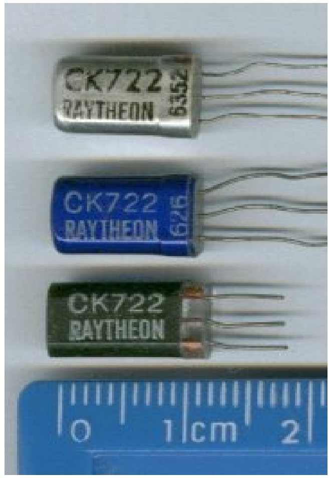
ábaco – 500 A.C. – 10 adições / min

Intel Core i5 – 2010 D.C. – 10^{9} adições / s

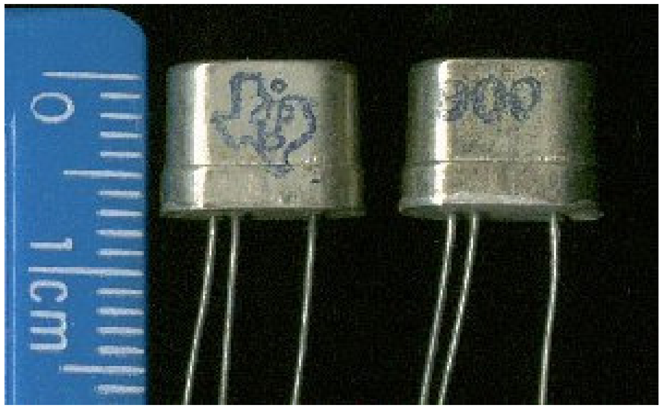
Evolução dos transistores

1948- Schockly
inventa o transistor de junção de Ge

1949- Raytheon CK703
Primeiro transistor comercial de Ge



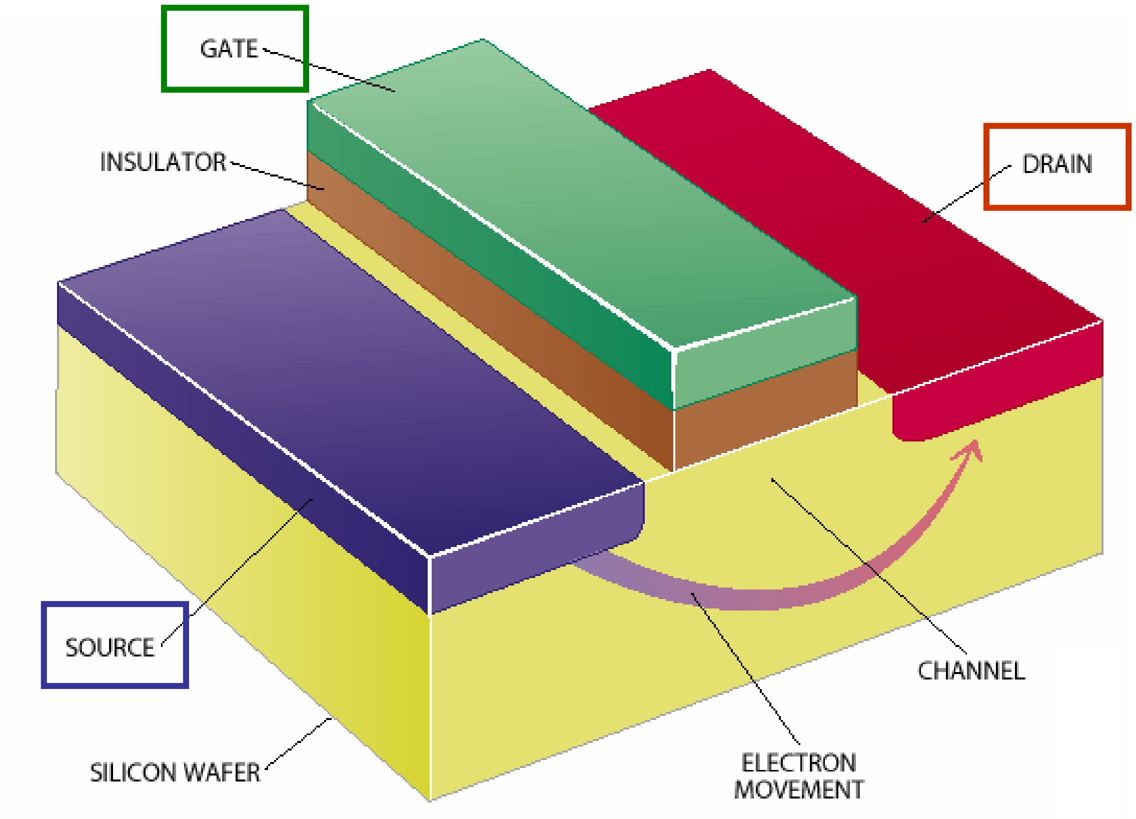
1953 - Raytheon CK722
Primeiro transistor de Ge produzido em massa

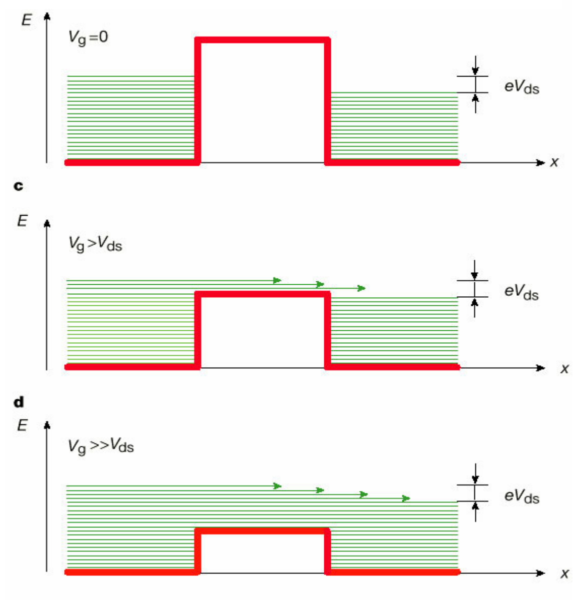


1955 - Texas Instruments 900
Primeiro transistor comercial de Si

Transistor como amplificador & chave

Transitor de efeito de campo (FET)





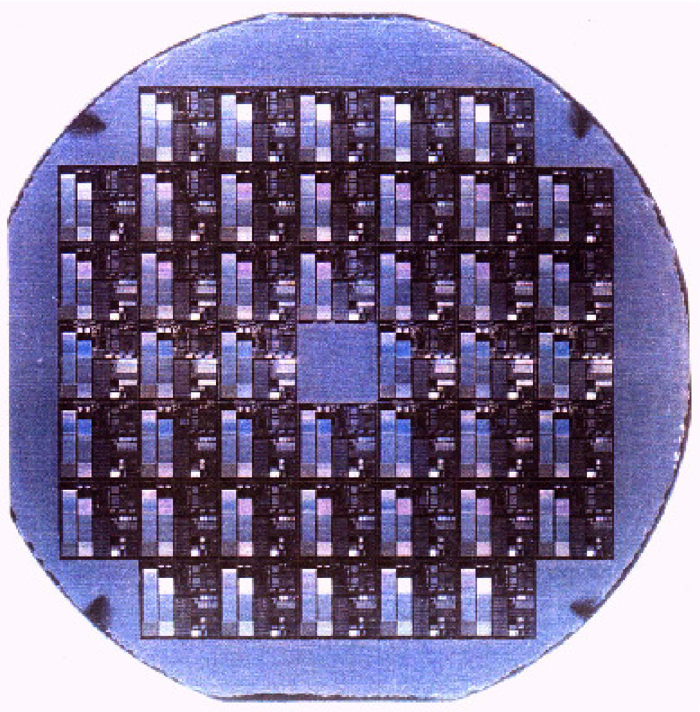
pequena voltagem de *porta* controla uma grande corrente de *dreno*

inventando o *circuito integrado*

- muitos transistores e circuitos complexos em um único substrato -

Primeiro circuito integrado produzido pela Texas Instruments

1958 - Jack Kilby e Robert Noyce



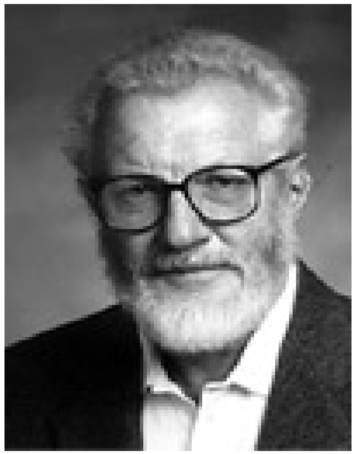
circuito integrado moderno
cada chip contem muitos milhões de transistores

Prêmio Nobel de Física - 2000

"pelo trabalho fundamental em informação e tecnologia de comunicação"

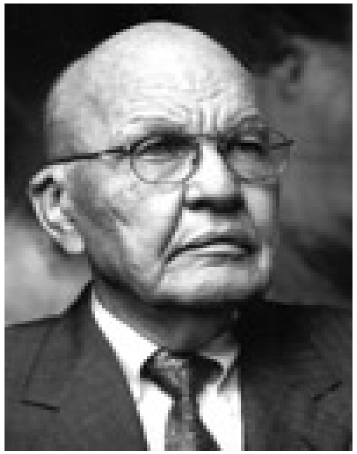
"pelo desenvolvimento de heteroestruturas semicondutoras usadas em aplicações de alta velocidade e opto-eletrônica"

Zhores I Alferov



Herbert Kroemer

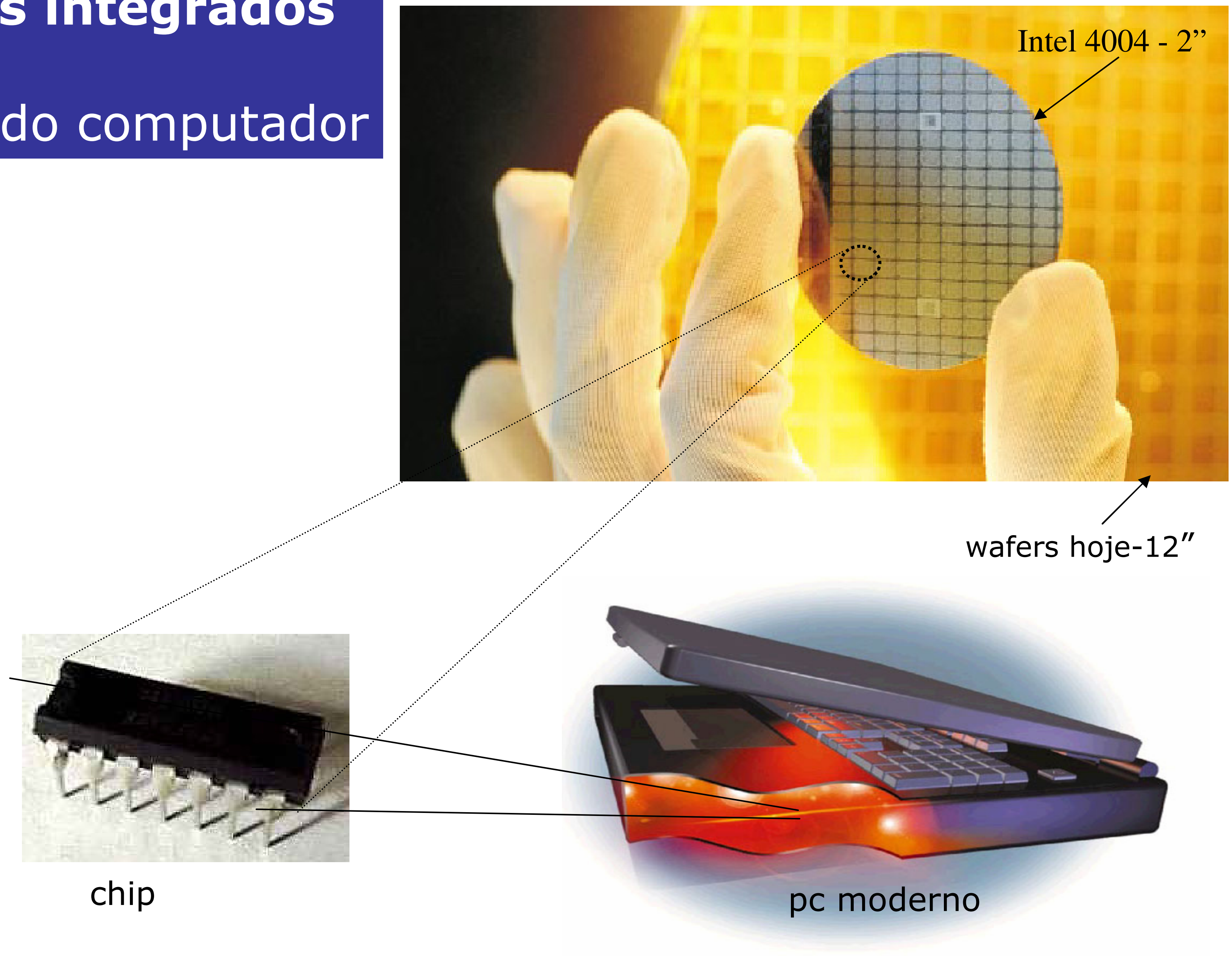
"pela sua atuação na invenção do circuito integrado"



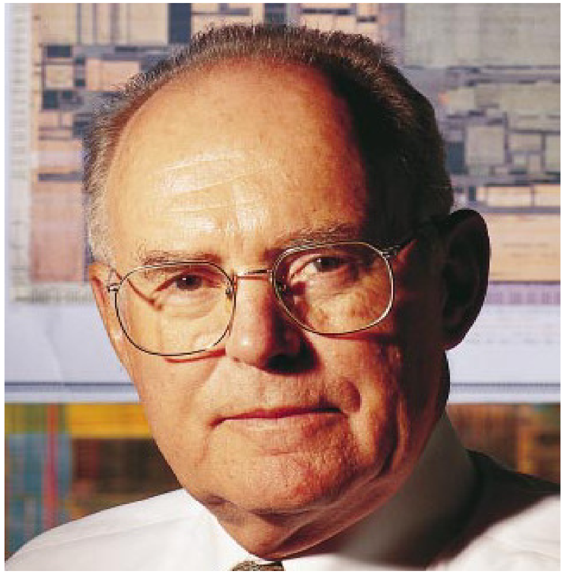
Jack S Kilby

circuitos integrados

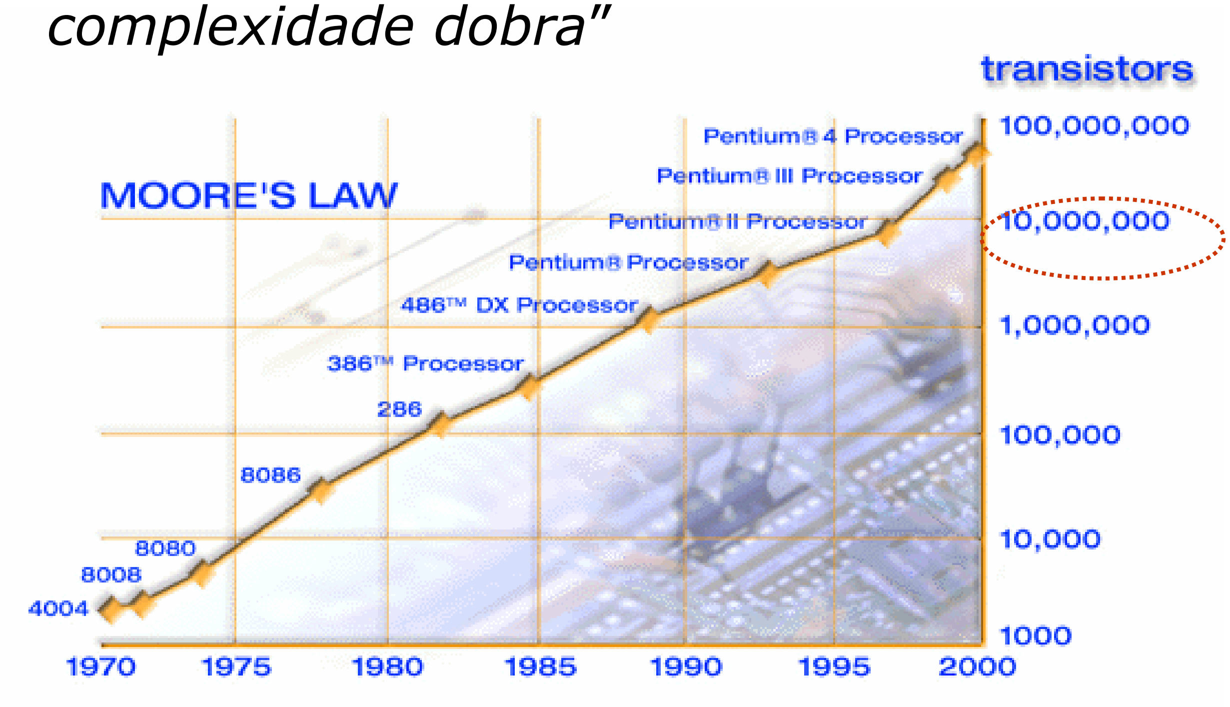
coração do computador



Lei de Moore

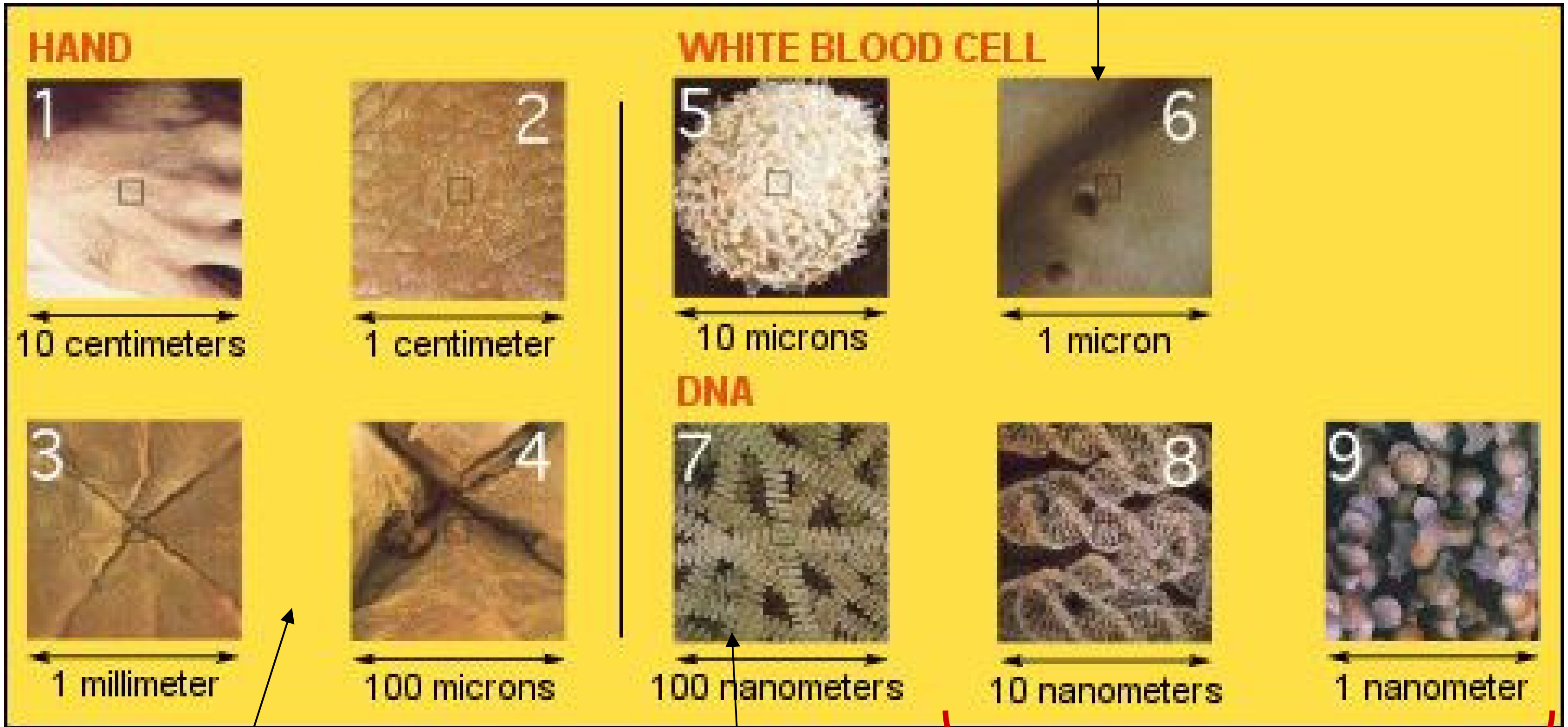


Gordon Moore
"a cada 1,5 anos a complexidade dobra"



Continuando o processo de “scale down”

microelectrônica de ontem



macroeletrônica nos anos 1950’s

microeletrônica hoje

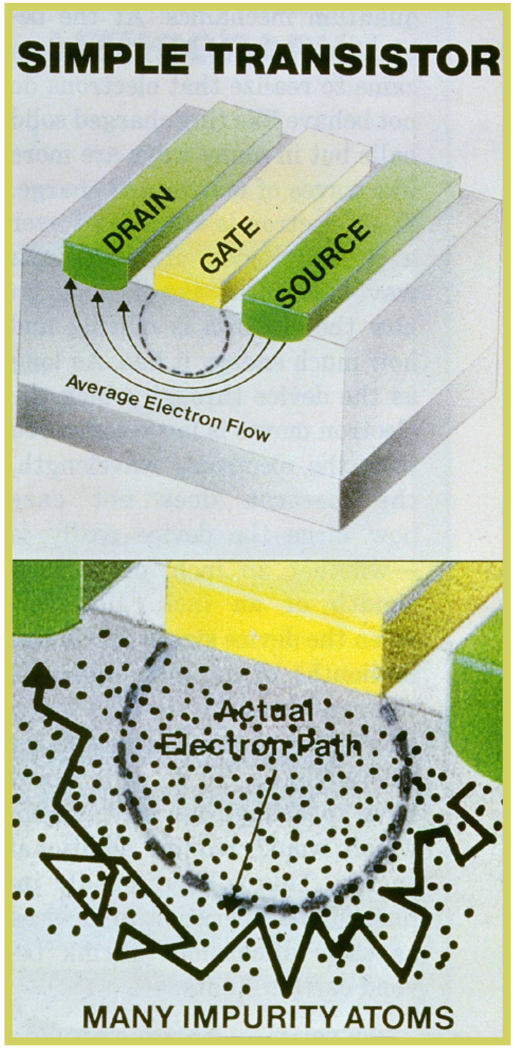
futura nanoelectrônica

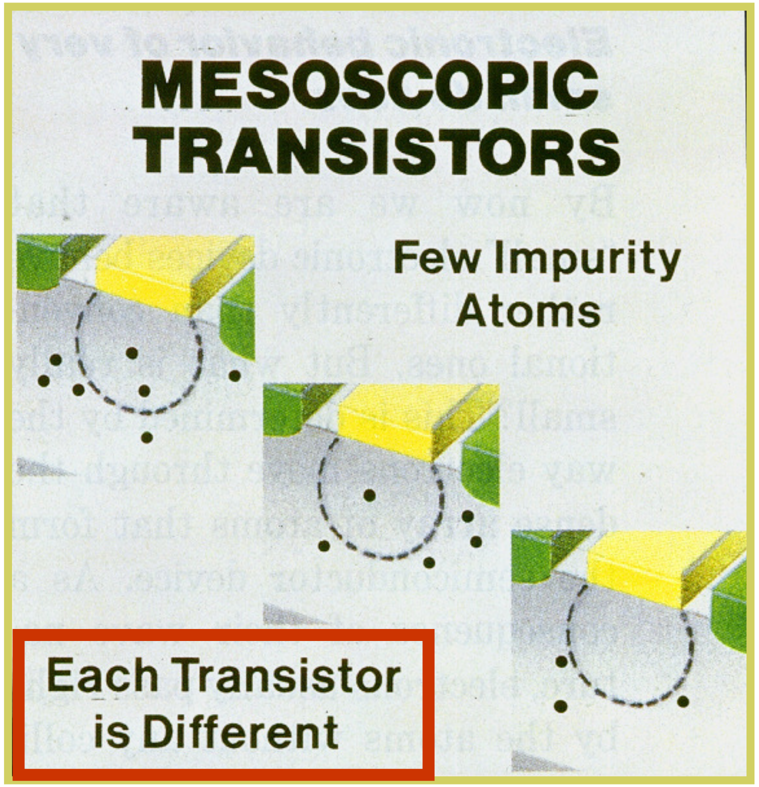
Quais as novidades conceituais da nanoeletrônica ?

Um problema imediato: simples estatística

hoje

futuro

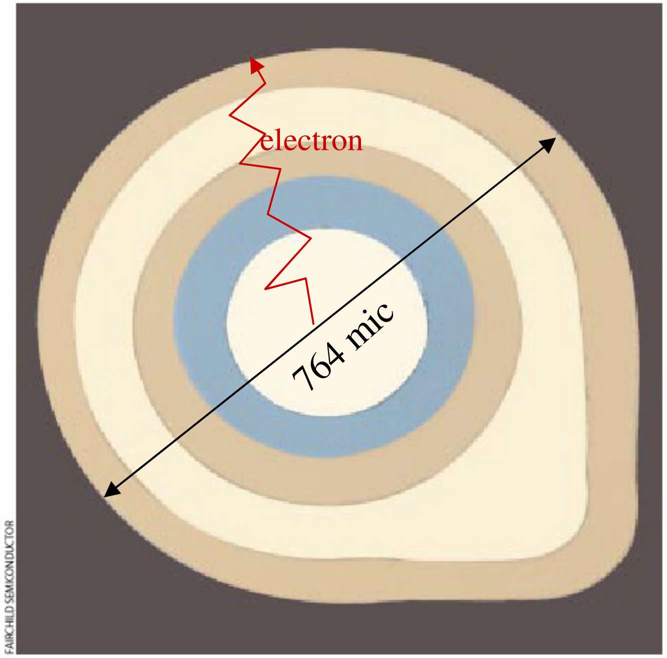




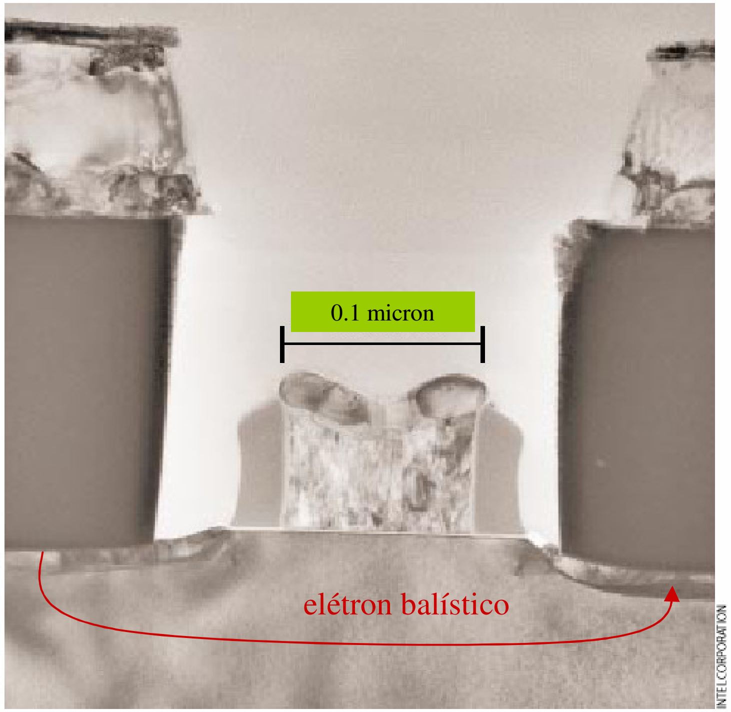
todos transistores são similares
por causa de *self averaging*

De muitas impurezas ... para muito poucas

Fairchild - 1959

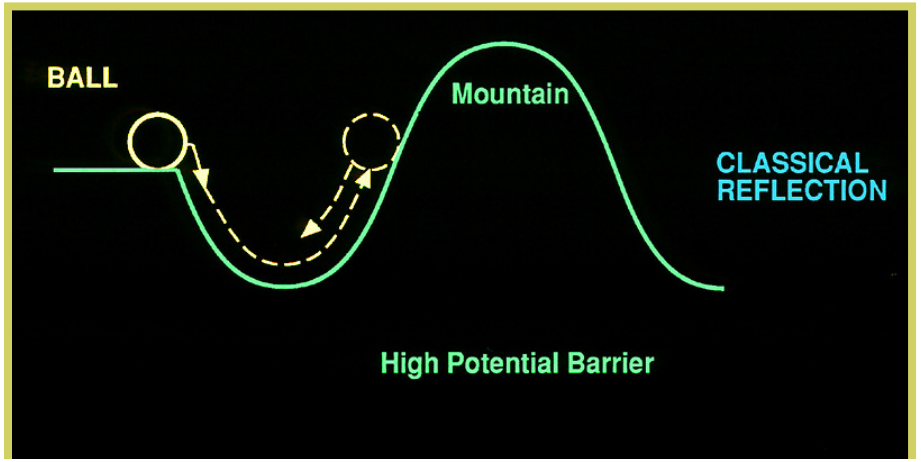


Intel - 2004

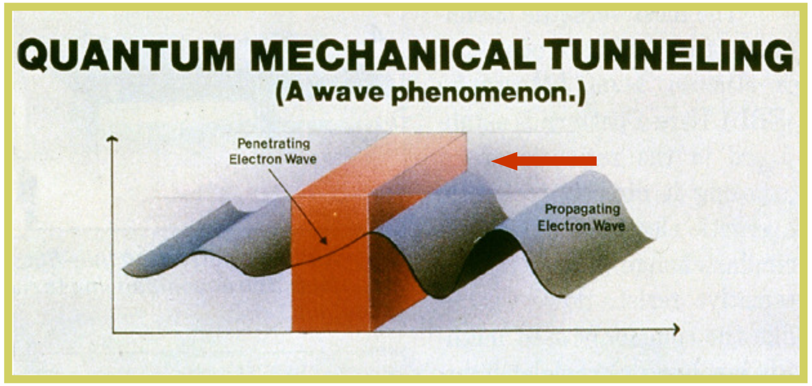


elétrons movendo-se sem colisões

Uma das maravilhas da mecânica quântica:
Efeito túnel



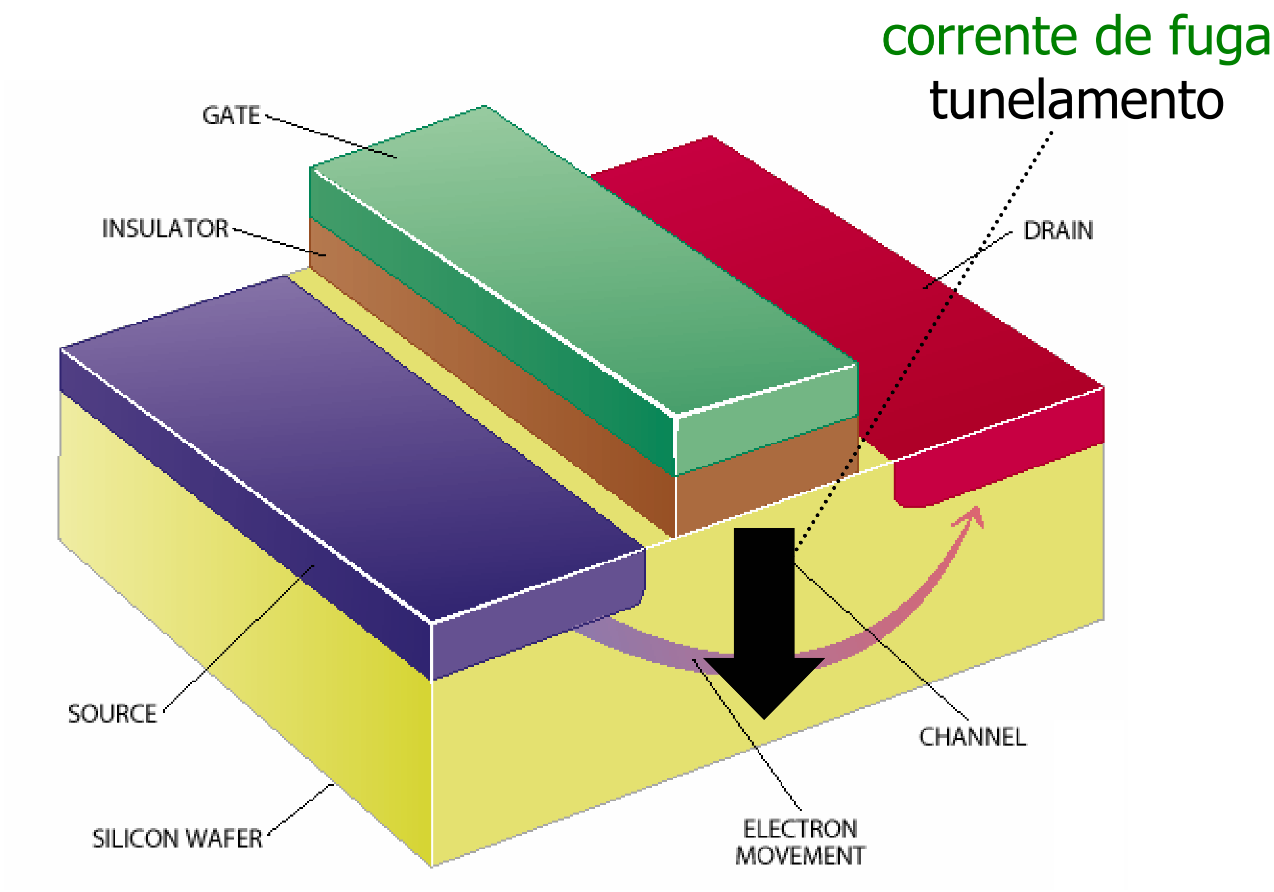
natureza ondulatória dos elétrons



Tunelamento: consequências

pequenas currentes fluem
através
de circuitos ABERTOS

tunelamento: limite para a miniaturização de dispositivos

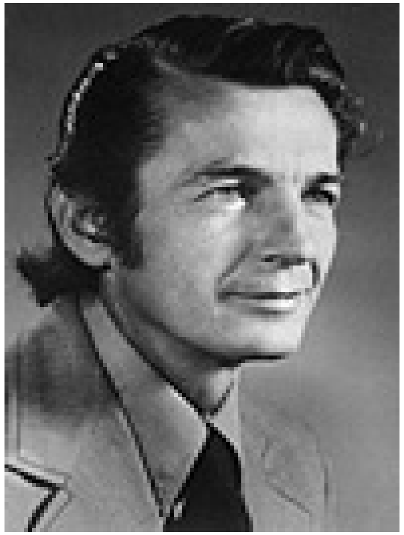


Prêmio Nobel de Física - 1973

“por suas descobertas experimentais de fenômenos de tunelamento em semi-condutores e em super-condutores respectivamente"

“por sua predição teórica das propriedades de uma supercorrente através de uma barreira de tunelamento, em particular dos fenômenos que são geralmente conhecidos como efeitos Josephson"

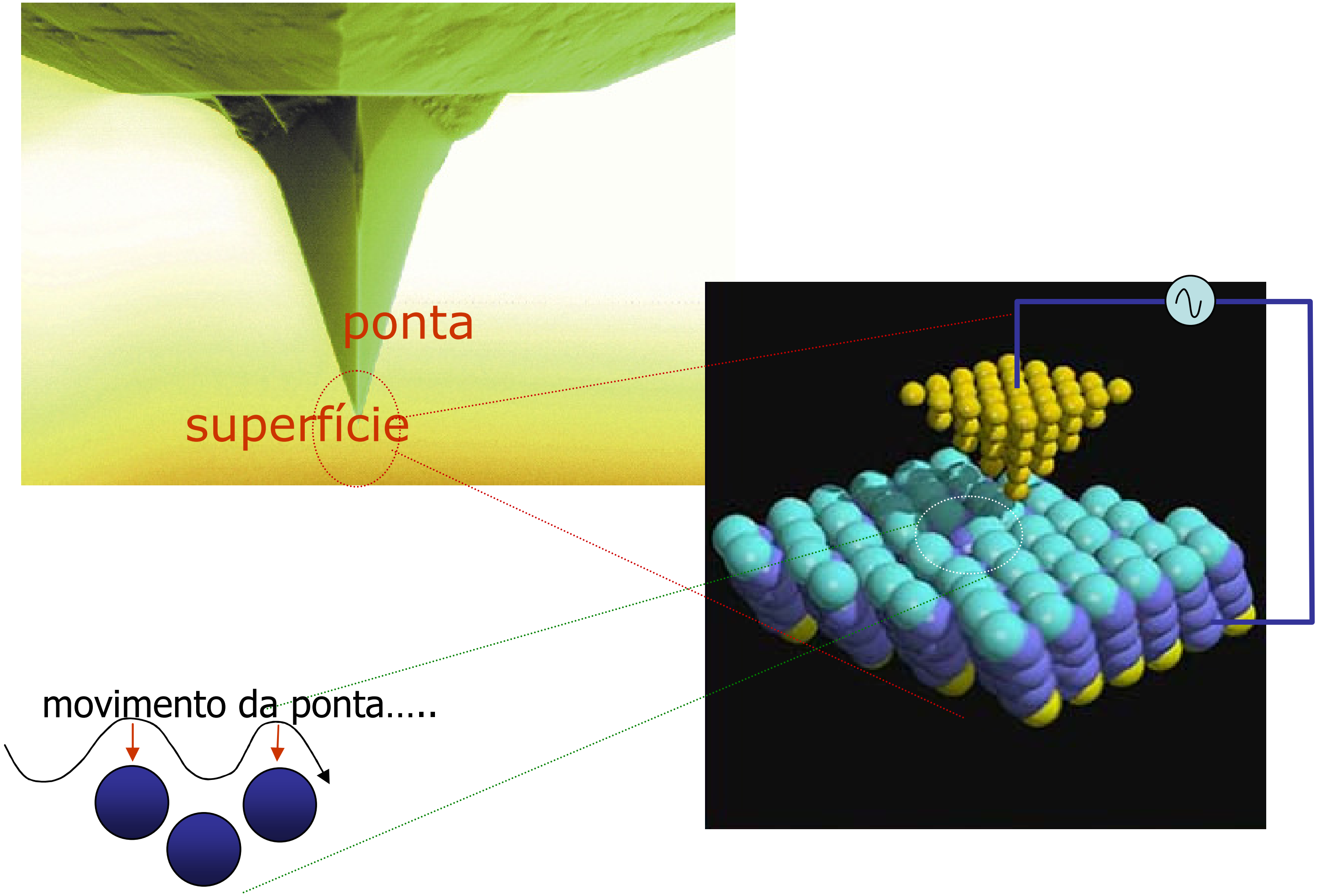
Leo Esaki



Ivar Giaever

Brian Josephson

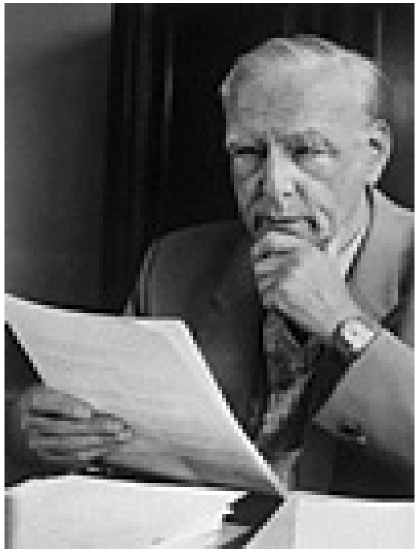
Revolução do tunelamento: Scanning Tunneling Microscope



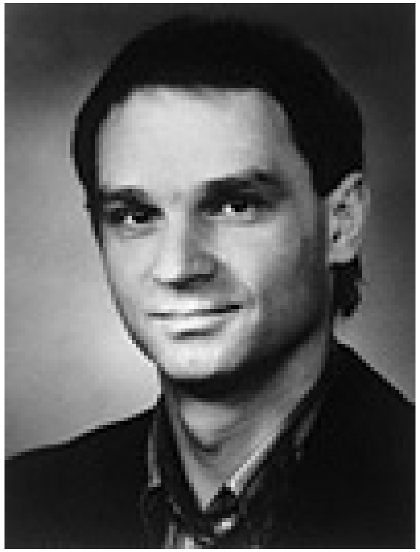
Prêmio Nobel de Física - 1986

"por seu trabalho fundamental em ótica eletrônica e pelo desenho do primeiro microscópio eletrônico"

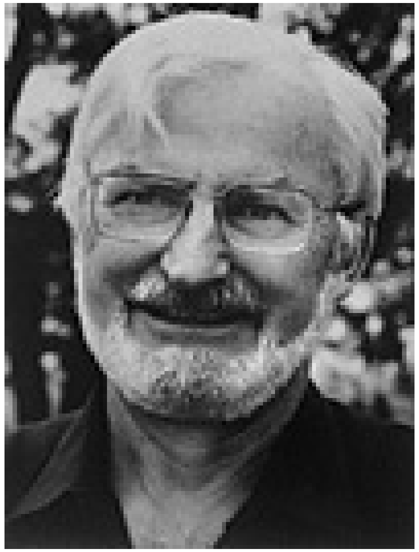
"pelo seu desenho do microscópio de tunelamento de varredura"



Ernst Ruska



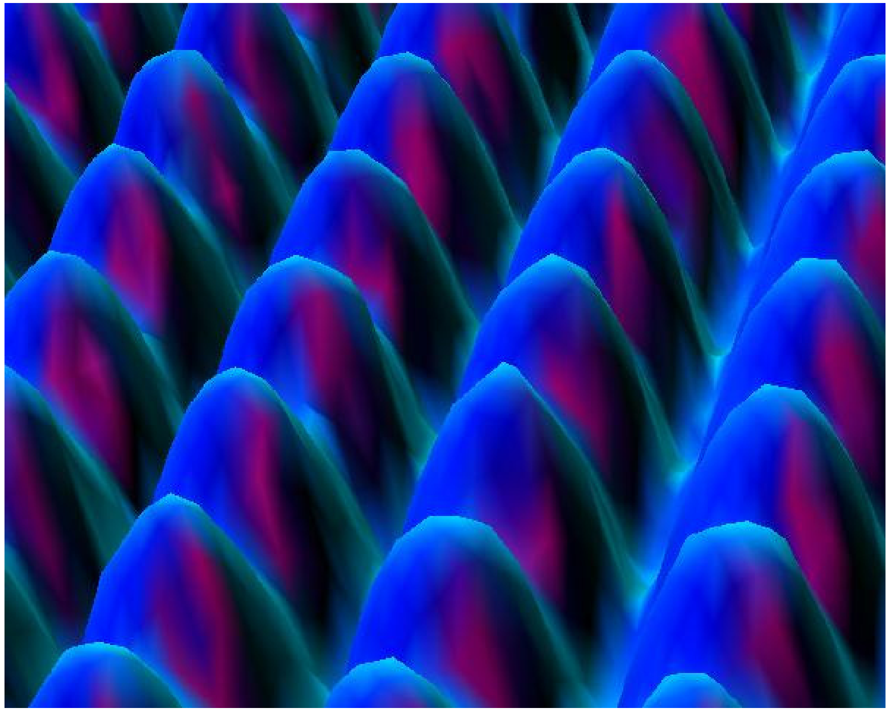
Gerd Binnig



Heinrich Rohrer

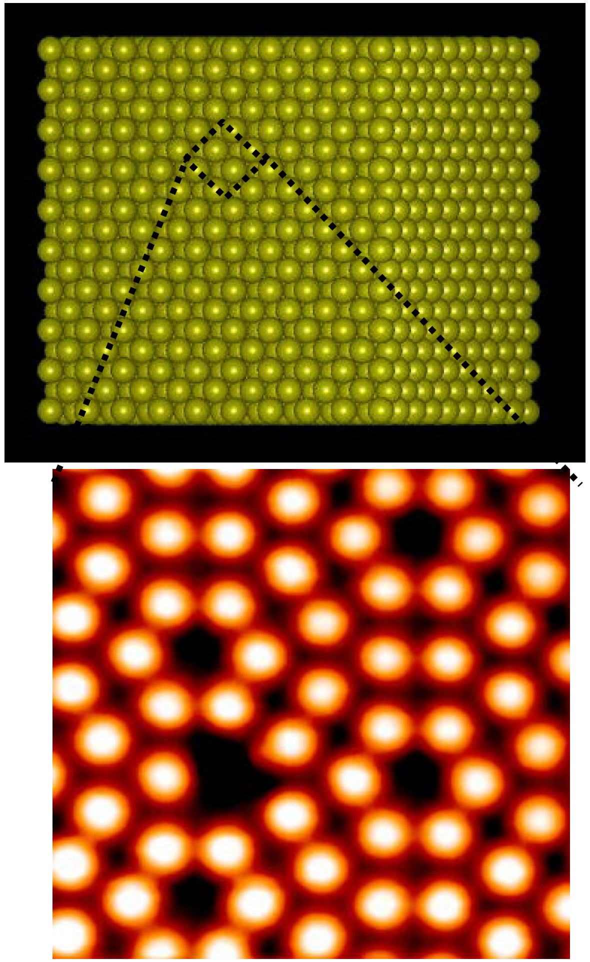
STM observando superfícies

níquel

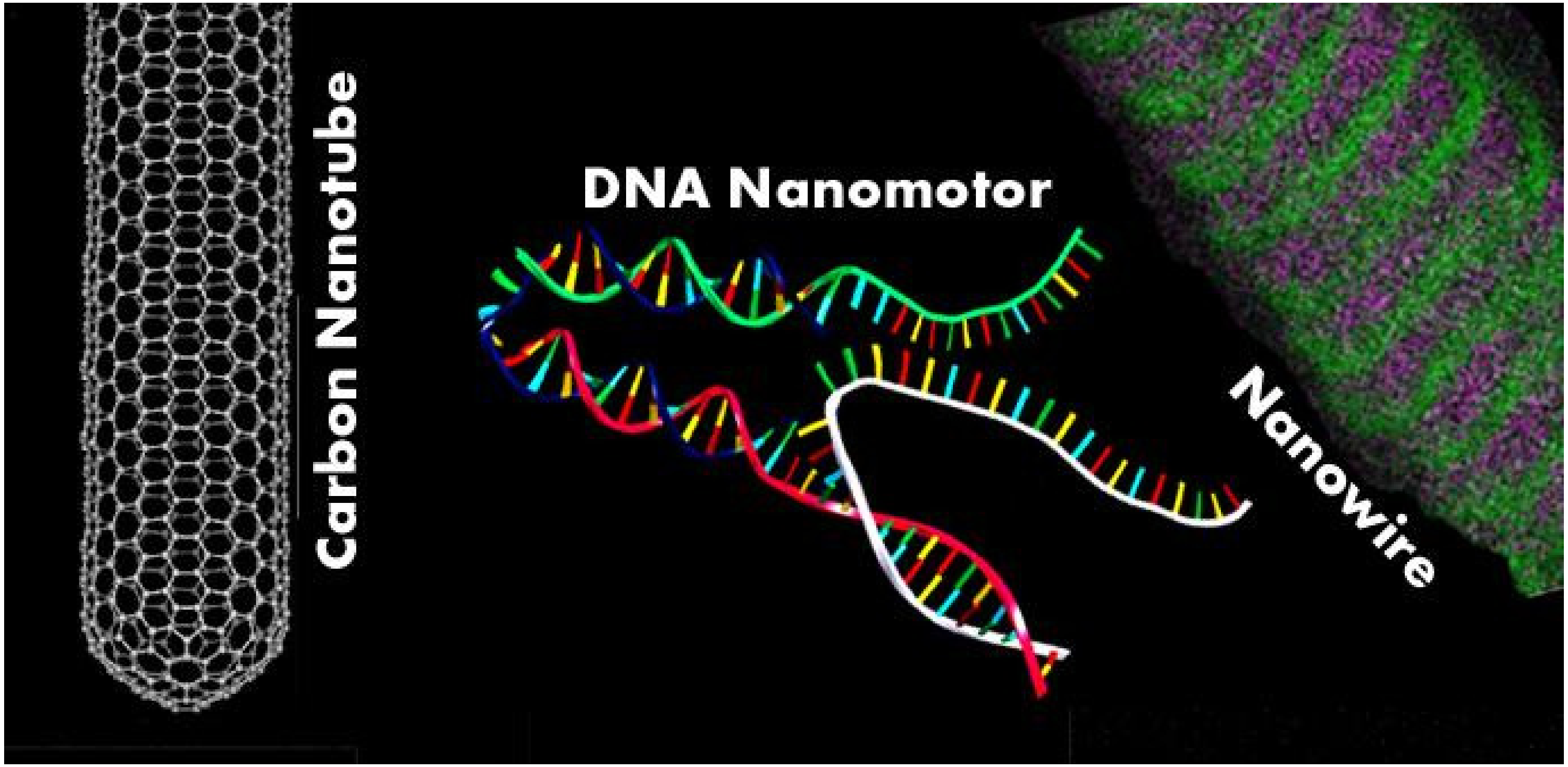


3 Angstroms = 0.3 nm

silício



Bottom-up: começando pelos constituintes básicos



Eletrônica molecular – outra palestra

Estruturas com nanotubos

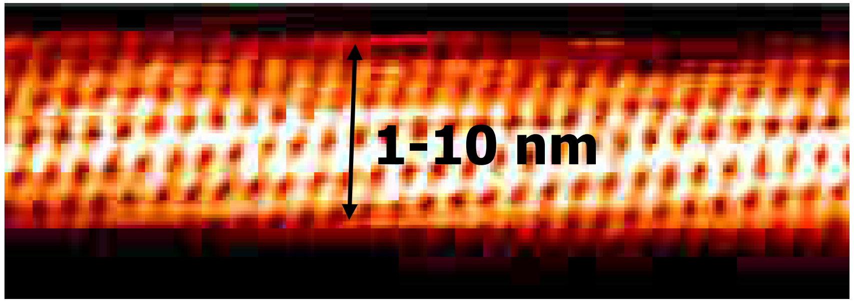
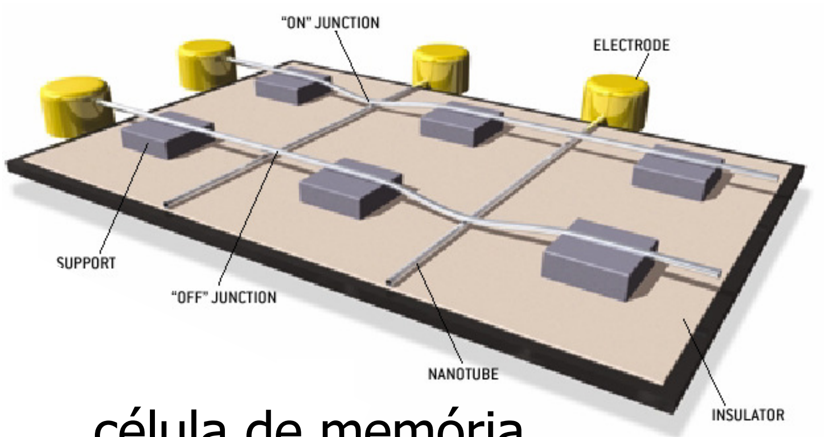
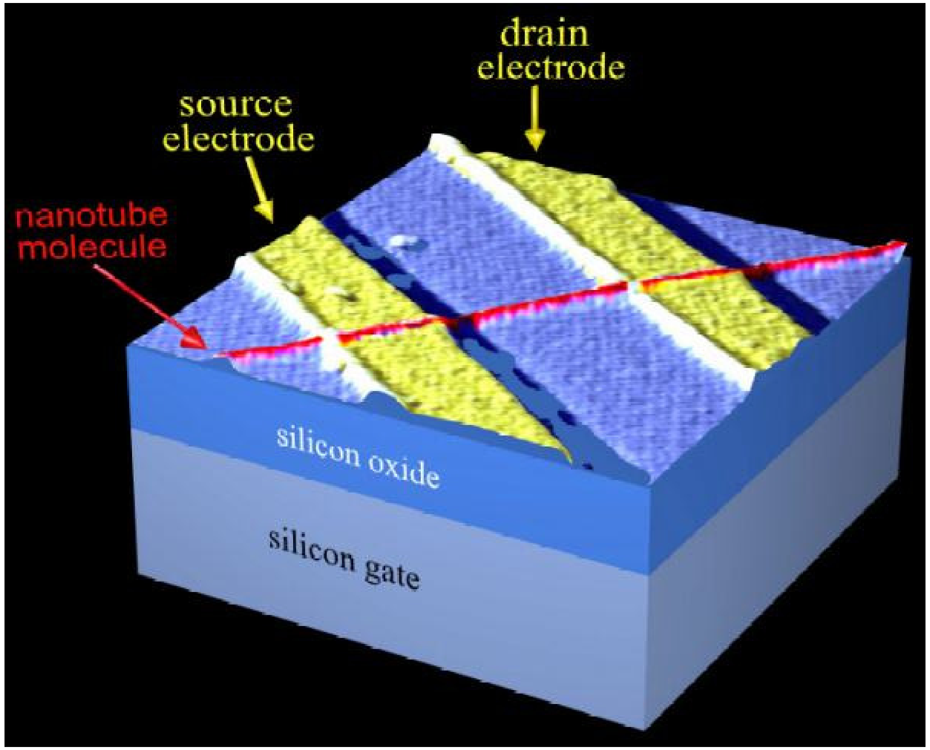


imagem de nanotubo

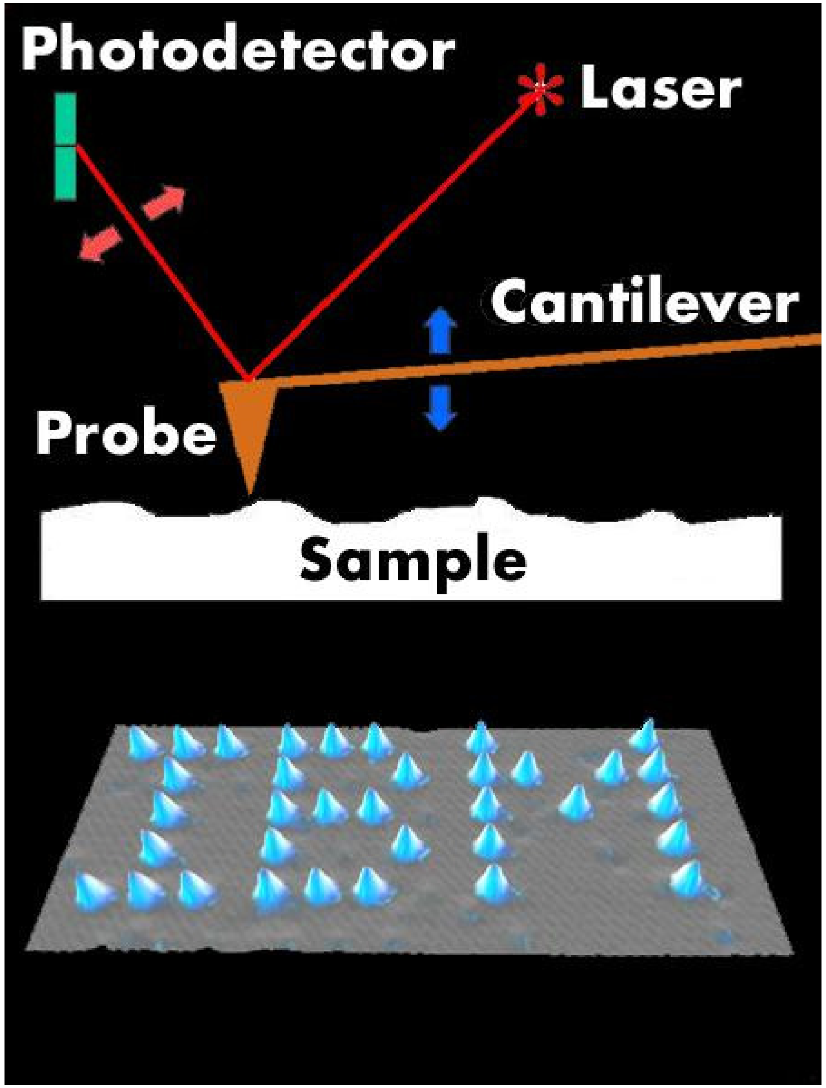


célula de memória

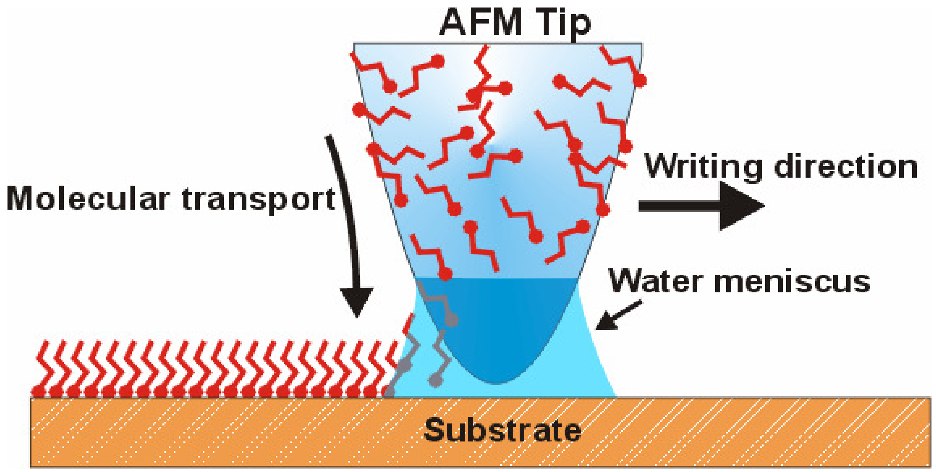


transistor unidimensional

Pegar e colar

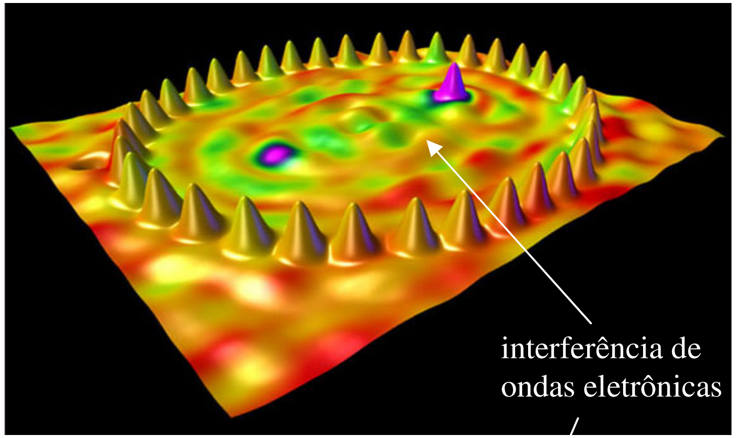


escrever

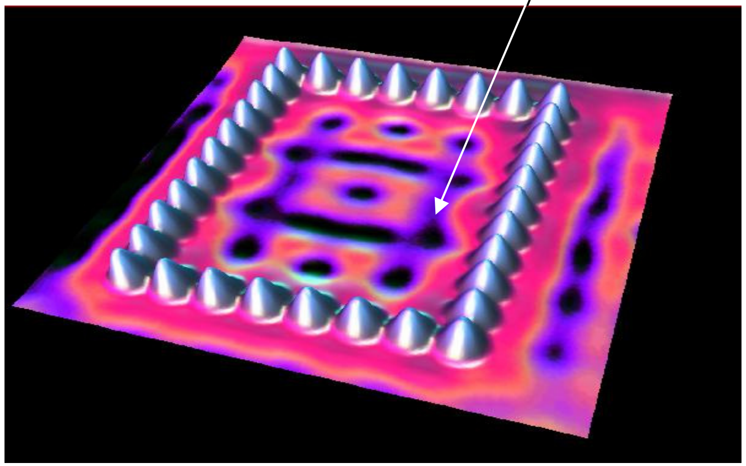


ponta AFM (como STM)

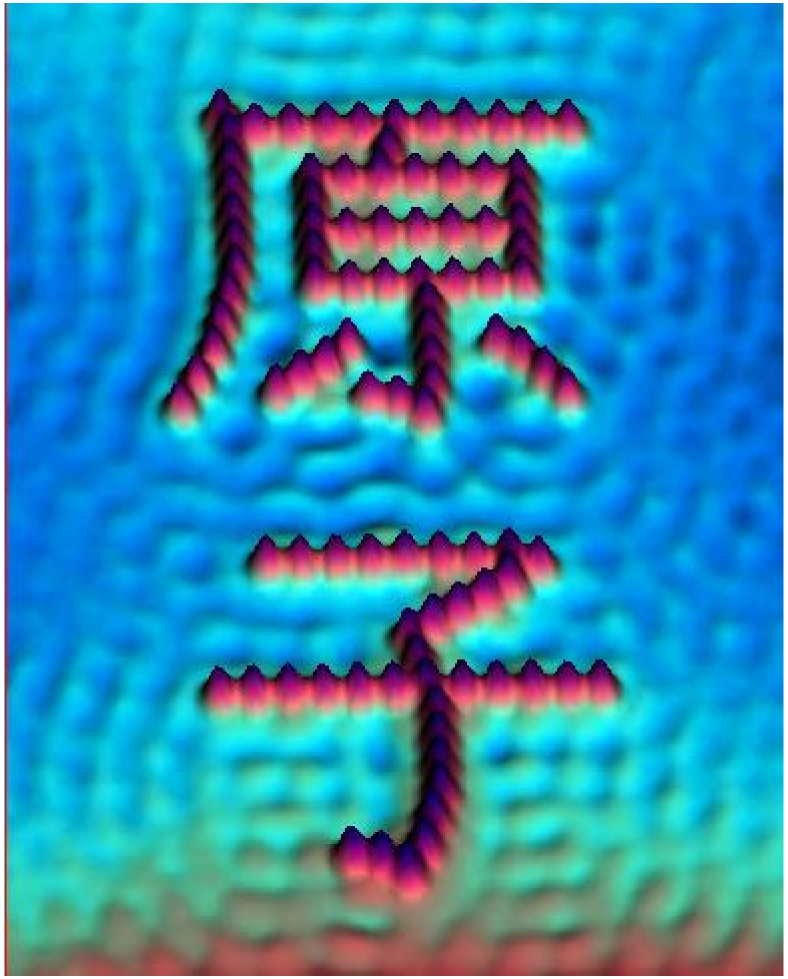
Pegar e colar



estádio circular



estádio quadrado



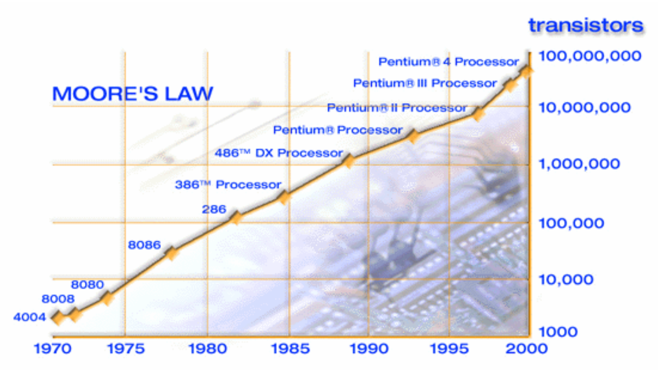
Kanji para *ÁTOMO*

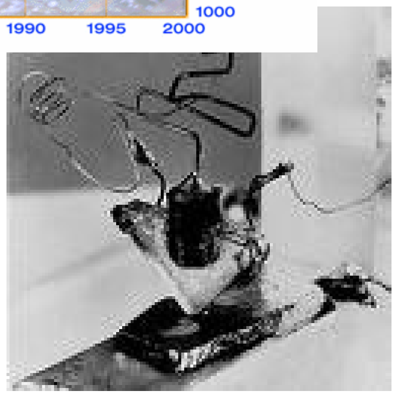
Lei de Moore e o Silício

- Dissipação de calor.
  - No momento, micro-processadores de 500 MHz com 10 milhões de transistores emitem quase 100W
- Vazamento de um dispositivo para o outro
  - A estrutura de bandas do silício possibilita uma grande variedade de energias para os electrons. Alguns eletrons podem ganhar energia suficiente para tunelar de um dispositivo para outro
- Acoplamento capacitivo entre os dispositivos.
- Métodos de fabricação (fotolitografia).
  - O tamanho do dispositivo é limitado pela difração – aproximadamente meio comprimento de onda da luz utilizada no processo de litografia.
- ‘Silicon Wall’
  - Para comprimentos de 50 nm ou menores não é possível dopar o silício uniformemente (isto é o fim da linha para o comportamento tipo bulk).

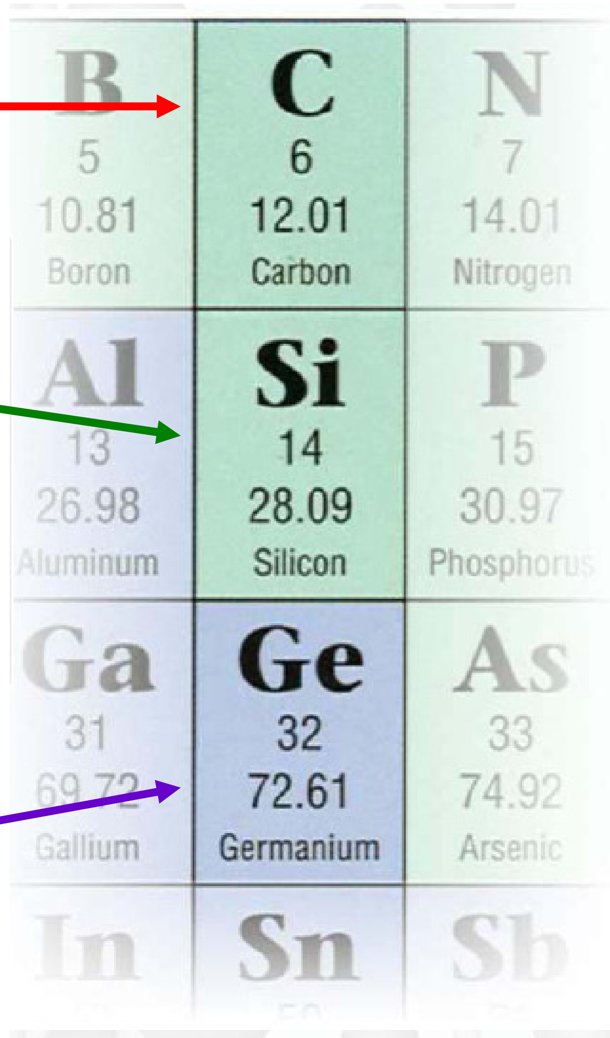
Mapa tecnológico de semicondutores

Por que não pensar em materiais que não o Si?





1947
William Shockley
John Bardeen
Walter Brattain



Carbono e eletrônica: por que é interessante?

Where we stand in the push for miniaturization and higher speeds :

Materials technology metrics*

2012 ↓

Table FEP2 — *Starting Materials Technology Requirements—Near and Long-term Years*

Year of Production	*2007*	*2008*	*2009*	*2010*	*2011*	*2012*
DRAM ½ Pitch (nm) (contacted)	68	59	52	45	40	36
MPU/ASIC Metal 1 (M1) ½ Pitch (nm)(contacted)	68	59	52	45	40	36
MPU Physical Gate Length (nm)	32	29	27	24	22	20
DRAM Total Chip Area (mm^2)	107	81	61	93	74	59
DRAM Active Transistor Area (mm^2)	33.4	25.3	19.2	29.1	23.1	18.3
MPU High-Performance Total Chip Area(mm^2)	310	246	195	310	246	195
MPU High-Performance Active Transistor Area(mm^2)	31.7	25.1	20.0	31.7	25.1	20.0
General Characteristics * (99% Chip Yield)						
Maximum Substrate Diameter (mm) ~~High-volume Production (>20K wafer starts per month)~~	300	300	300	300	300	450
Edge exclusion (mm)	2	2	2	2	2	2
Front surface particle size (nm), latex sphere equivalent (A)	[illegible symbol]65	[illegible symbol]65	[illegible symbol]65	[illegible symbol]65	[illegible symbol]65	[illegible symbol]45
Particles (cm^{-2})	≤ 0.33	≤ 0.33	≤ 0.32	≤ 0.15	≤ 0.15	≤ 0.32
Particles (#/wf)	≤ 228	≤ 228	≤ 219	≤ 105	≤ 105	≤ 496
Site flatness (nm), SFQR 26mm x 8 mm Site Size	≤68	≤59	≤52	≤45	≤40	≤36
Nanotopography, p-v, 2 mm dia. analysis area (I)	≤17	≤15	≤13	≤11	≤10	≤9
Epitaxial Wafer * (99% Chip Yield)						
Large structural epi defects (DRAM) (cm^{-2}) (B)	≤ 0.009	≤ 0.012	≤ 0.016	≤ 0.011	≤ 0.014	≤ 0.017
Large structural epi defects (MPU) (cm^{-2}) (B)	≤ 0.003	≤ 0.004	≤ 0.005	≤ 0.003	≤ 0.004	≤ 0.005
Small structural epi defects (DRAM) (cm^{-2}) (C)	≤ 0.019	≤ 0.025	≤ 0.033	≤ 0.022	≤ 0.027	≤ 0.034
Small structural epi defects (MPU) (cm^{-2}) (C)	≤ 0.006	≤ 0.008	≤ 0.010	≤ 0.006	≤ 0.008	≤ 0.010
Silicon-On-Insulator Wafer* (99% Chip Yield)						
Edge exclusion (mm)	2	2	2	2	2	2
Starting silicon layer thickness (Partially Depleted) (tolerance ± 5%, 3σ) (nm) (D)	58-100	54-93	50-76	46-71	43-65	40-60
Starting silicon layer thickness (Fully Depleted) (tolerance ± 5%, 3σ) (nm) (E)				16-31	16-20	15-19
Buried oxide (BOX) thickness (Fully Depleted) (tolerance ± 5%, 3σ) (nm) (F)				36-60	34-56	30-50
D_{LASOI}, Large area SOI wafer defects (DRAM) (cm^{-2}) (G)	≤ 0.009	≤ 0.012	≤ 0.016	≤ 0.011	≤ 0.014	≤ 0.017
D_{LASOI}, Large area SOI wafer defects (MPU) (cm^{-2}) (G)	≤ 0.003	≤ 0.004	≤ 0.005	≤ 0.003	≤ 0.004	≤ 0.005
D_{SASOI}, Small area SOI wafer defects (DRAM) (cm^{-2}) (H)	≤ 0.150	≤ 0.198	≤ 0.262	≤ 0.173	≤ 0.218	≤ 0.274
D_{SASOI}, Small area SOI wafer defects (MPU) (cm^{-2}) (H)	≤ 0.159	≤ 0.200	≤ 0.252	≤ 0.159	≤ 0.200	≤ 0.252

- manufactorable solutions exist
- manufactorable solutions known
- manufactorable solutions unknown

* International Technology Roadmap for Semiconductors - 2008 Revision (http://www.itrs.net/)

Carbono e eletrônica: por que é interessante?

Where we stand in the push for miniaturization and higher speeds :

Materials technology metrics*

2012 ↓ … 2020 ↓

Table FEP2 — *Starting Materials Technology Requirements—Near and Long-term Years*

Year of Production	*2007*	*2008*	*2009*	*2010*	*2011*	*2012*	*2013*	*2014*	*2015*	*2016*	*2017*	*2018*	*2019*	*2020*
DRAM ½ Pitch (nm) (contacted)	68	59	52	45	40	36	32	28	25	23	20	18	16	14
MPU/ASIC Metal 1 (M1) ½ Pitch (nm)(contacted)	68	59	52	45	40	36	32	28	25	23	20	18	16	14
MPU Physical Gate Length (nm)	32	29	27	24	22	20	18	17	15	14	13	12	11	10
DRAM Total Chip Area (mm^2)	107	81	61	93	74	59	93	74	59	93	74	59	93	74
DRAM Active Transistor Area (mm^2)	33.4	25.3	19.2	29.1	23.1	18.3	29.1	23.1	18.3	29.1	23.1	18.3	29.1	23.1
MPU High-Performance Total Chip Area(mm^2)	310	246	195	310	246	195	310	246	195	310	246	195	310	246
MPU High-Performance Active Transistor Area(mm^2)	31.7	25.1	20.0	31.7	25.1	20.0	31.7	25.1	20.0	31.7	25.1	20.0	31.7	25.1
*General Characteristics * (99% Chip Yield)*														
Maximum Substrate Diameter (mm) ~~High-volume Production (>20K wafer starts per month)~~	300	300	300	300	300	450	450	450	450	450	450	450	450	450
Edge exclusion (mm)	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Front surface particle size (nm), latex sphere equivalent (A)	65	65	65	65	65	45	45	45	32	32	32	22	22	22
Particles (cm^{-2})	≤ 0.33	≤ 0.33	≤ 0.32	≤ 0.15	≤ 0.15	≤ 0.32	≤ 0.16	≤ 0.16	≤ 0.31	≤ 0.16	≤ 0.16	≤ 0.33	≤ 0.17	≤ 0.17
Particles (#/wf)	≤ 228	≤ 228	≤ 219	≤ 105	≤ 105	≤ 496	≤ 248	≤ 248	≤ 490	≤ 245	≤ 245	≤ 518	≤ 259	≤ 259
Site flatness (nm), SFQR 26mm x 8 mm Site Size	≤68	≤59	≤52	≤45	≤40	≤36	≤32	≤28	≤25	≤23	≤20	≤18	≤16	≤14
Nanotopography, p-v, 2 mm dia. analysis area (I)	≤17	≤15	≤13	≤11	≤10	≤9	≤8	≤7	≤6	≤6	≤5	≤4	≤4	≤4
*Epitaxial Wafer * (99% Chip Yield)*														
Large structural epi defects (DRAM) (cm^{-2}) (B)	≤ 0.009	≤ 0.012	≤ 0.016	≤ 0.011	≤ 0.014	≤ 0.017	≤ 0.011	≤ 0.014	≤ 0.017	≤ 0.011	≤ 0.014	≤ 0.017	≤ 0.011	≤ 0.014
Large structural epi defects (MPU) (cm^{-2}) (B)	≤ 0.003	≤ 0.004	≤ 0.005	≤ 0.003	≤ 0.004	≤ 0.005	≤ 0.003	≤ 0.004	≤ 0.005	≤ 0.003	≤ 0.004	≤ 0.005	≤ 0.003	≤ 0.004
Small structural epi defects (DRAM) (cm^{-2}) (C)	≤ 0.019	≤ 0.025	≤ 0.033	≤ 0.022	≤ 0.027	≤ 0.034	≤ 0.022	≤ 0.027	≤ 0.034	≤ 0.022	≤ 0.027	≤ 0.034	≤ 0.022	≤ 0.027
Small structural epi defects (MPU) (cm^{-2}) (C)	≤ 0.006	≤ 0.008	≤ 0.010	≤ 0.006	≤ 0.008	≤ 0.010	≤ 0.006	≤ 0.008	≤ 0.010	≤ 0.006	≤ 0.008	≤ 0.010	≤ 0.006	≤ 0.008
Silicon-On-Insulator Wafer (99% Chip Yield)*														
Edge exclusion (mm)	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Starting silicon layer thickness (Partially Depleted) (tolerance ± 5%, 3σ) (nm) (D)	58-100	54-93	50-76	46-71	43-65	40-60	38-56	35-52	33-48	31-45	29-42	28-39	26-37	25-34
Starting silicon layer thickness (Fully Depleted) (tolerance ± 5%, 3σ) (nm) (E)				16-31	16-20	15-19	15-18	14-16	13-16	13-15	13-15	13-14	12-14	12-14
Buried oxide (BOX) thickness (Fully Depleted) (tolerance ± 5%, 3σ) (nm) (F)				36-60	34-56	30-50	28-46	26-42	24-38	22-36	20-32	18-30	16-26	14-24
D_{LASOI}, Large area SOI wafer defects (DRAM) (cm^{-2}) (G)	≤ 0.009	≤ 0.012	≤ 0.016	≤ 0.011	≤ 0.014	≤ 0.017	≤ 0.011	≤ 0.014	≤ 0.017	≤ 0.011	≤ 0.014	≤ 0.017	≤ 0.011	≤ 0.014
D_{LASOI}, Large area SOI wafer defects (MPU) (cm^{-2}) (G)	≤ 0.003	≤ 0.004	≤ 0.005	≤ 0.003	≤ 0.004	≤ 0.005	≤ 0.003	≤ 0.004	≤ 0.005	≤ 0.003	≤ 0.004	≤ 0.005	≤ 0.003	≤ 0.004
D_{SASOI}, Small area SOI wafer defects (DRAM) (cm^{-2}) (H)	≤ 0.150	≤ 0.198	≤ 0.262	≤ 0.173	≤ 0.218	≤ 0.274	≤ 0.173	≤ 0.218	≤ 0.274	≤ 0.173	≤ 0.218	≤ 0.274	≤ 0.173	≤ 0.218
D_{SASOI}, Small area SOI wafer defects (MPU) (cm^{-2}) (H)	≤ 0.159	≤ 0.200	≤ 0.252	≤ 0.159	≤ 0.200	≤ 0.252	≤ 0.159	≤ 0.200	≤ 0.252	≤ 0.159	≤ 0.200	≤ 0.252	≤ 0.159	≤ 0.200

- manufactorable solutions exist
- manufactorable solutions known
- manufactorable solutions unknown

* International Technology Roadmap for Semiconductors - 2008 Revision (http://www.itrs.net/)

Carbono e eletrônica: por que é interessante?

Propriedades desejadas:

Capacidade de suportar correntes latas, alta condução de calor, carbono é mais robusto que silício, alta mobilidade, geometria permite escalar agressivamente, etc..

Workshop on Maturity Evaluation for Selected "Beyond CMOS" Technologies, (San Franscisco, CA, USA, July 12-13, 2008), co-sponsored by the National Science Foundation. Excerpts from the final report:

2008 Update: Working Group Summaries 29

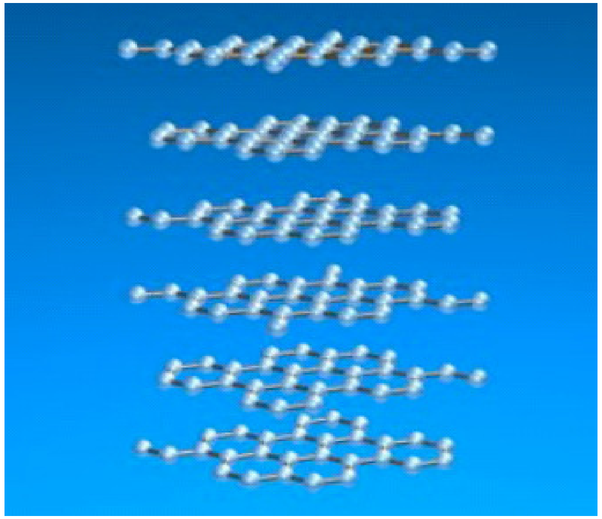
The final outcome of this study is the ERD/ERM working groups chose Carbon-based Nanoelectronics as their recommended "Beyond CMOS" technology for accelerated development and more detailed roadmapping in the 2009 ITRS.

Carbon-based Nanoelectronics has a major advantage in that the science and technologies resulting from accelerated development of CNTs and GNRs for MOSFET applications can provide a substantial basis for exploring and developing new physical phenomena in these materials for "Beyond CMOS" information processing paradigms. The field of

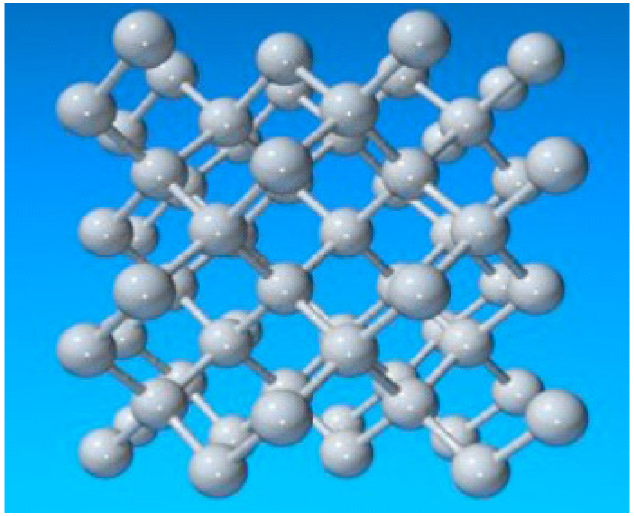
Formas de ligação de carbono

grafite

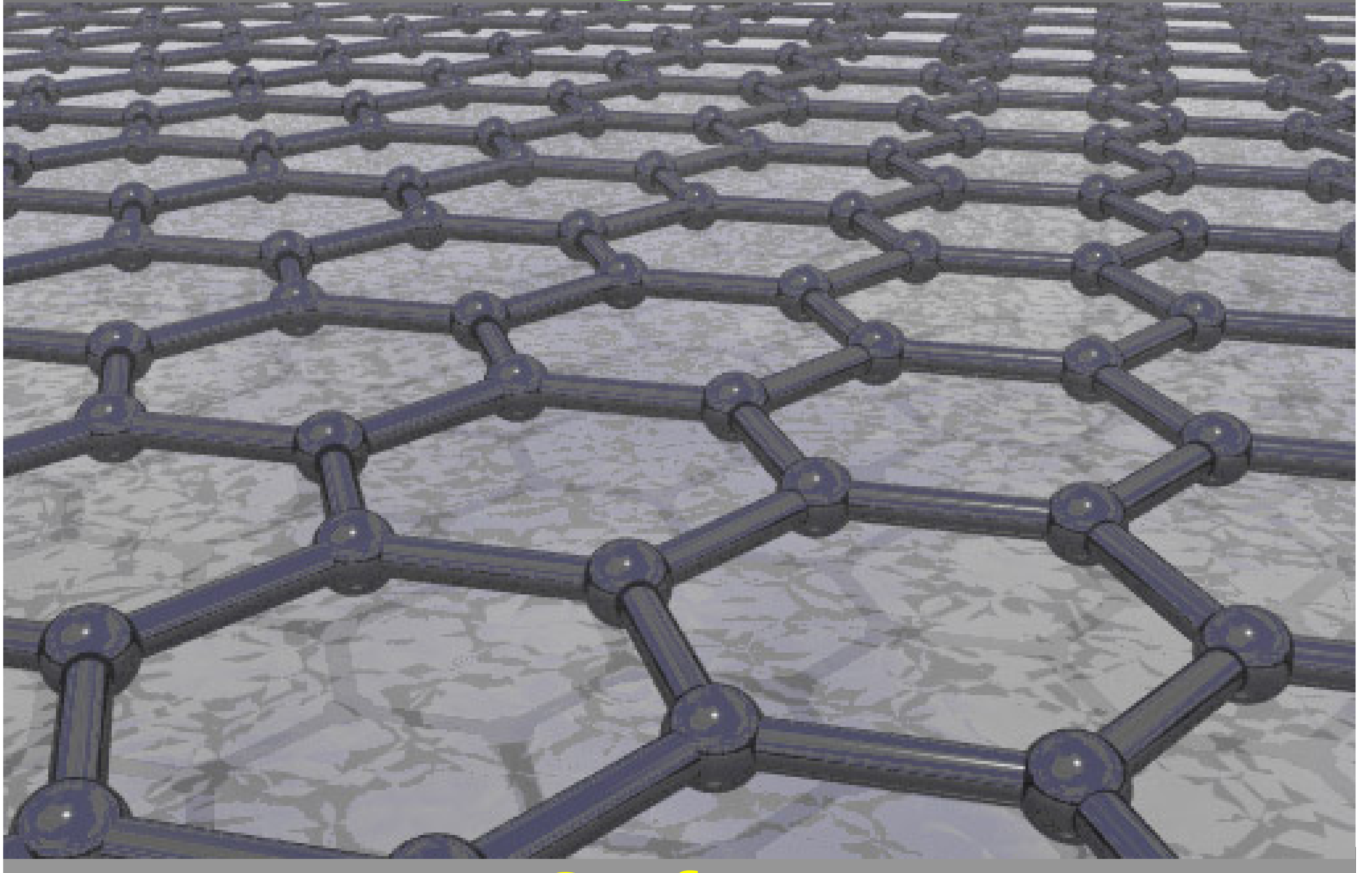
diamante



Ligação flexível: riqueza de estruturas



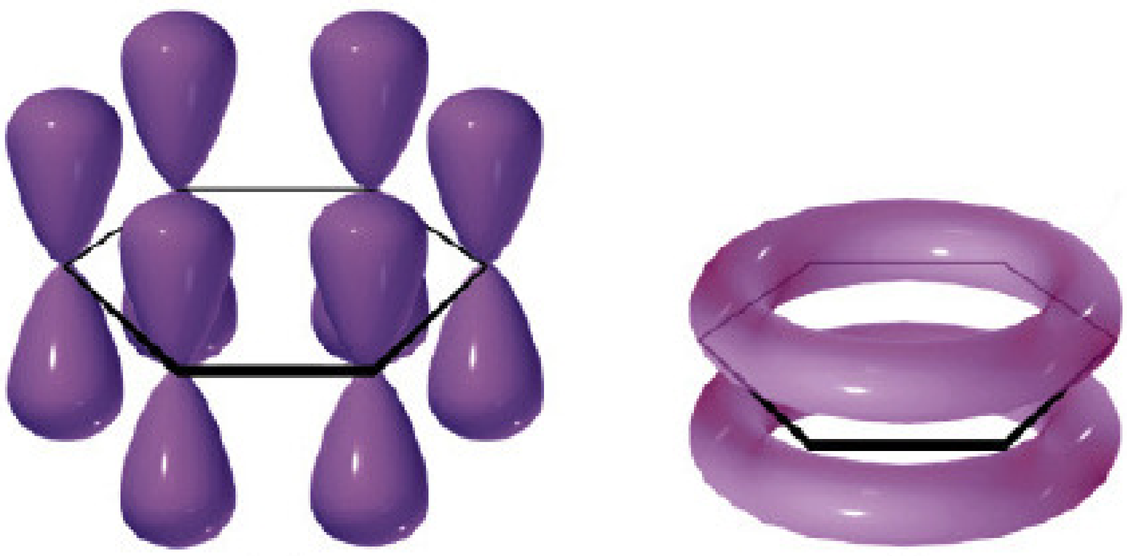
Personagem central



Grafeno

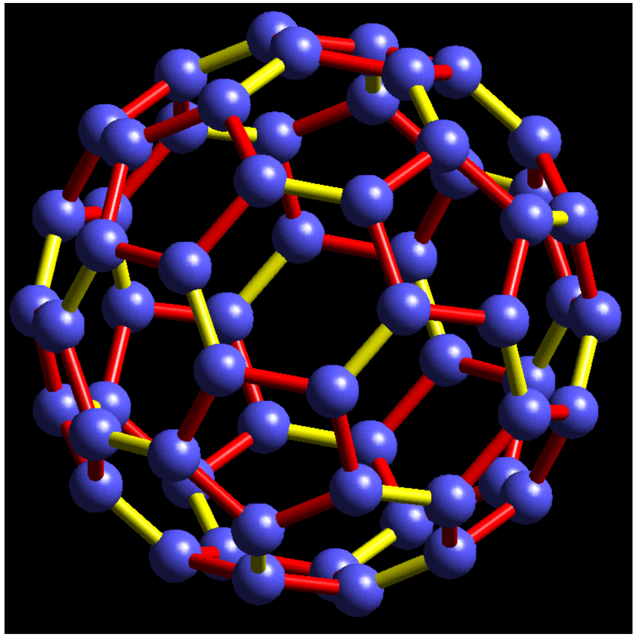
Elemento de construção: molécula de benzeno

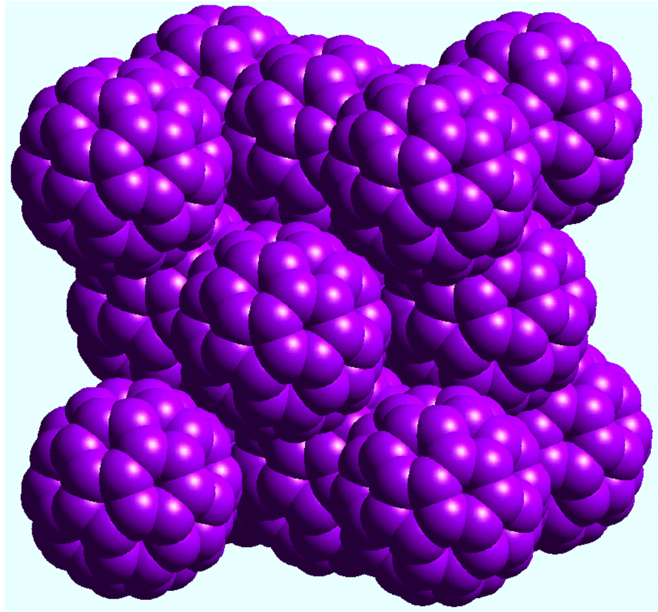
estados p estado π

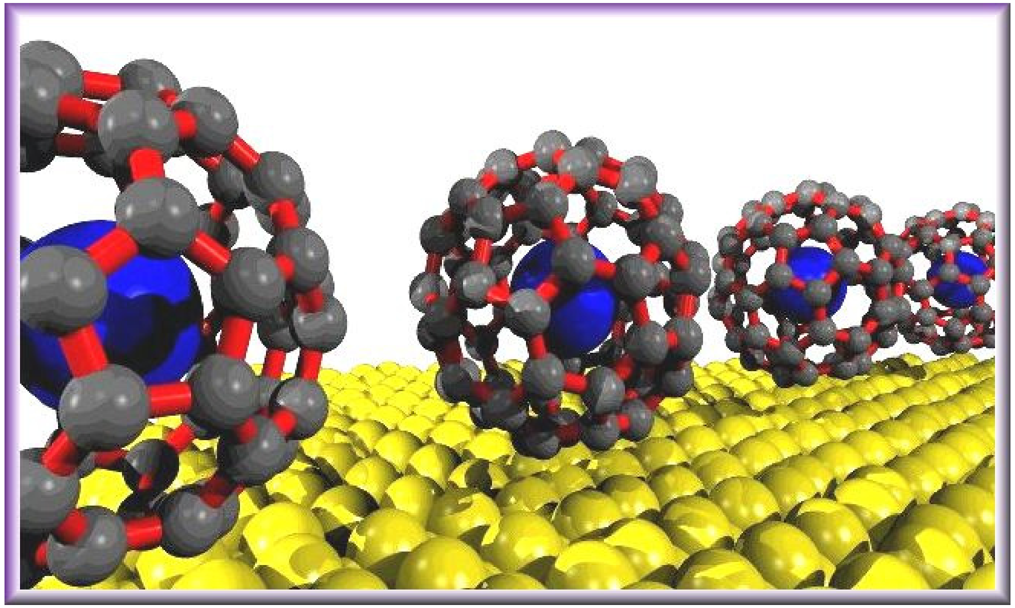


(a) (b)

Linus Pauling, The nature of the chemical bond, pg 234-235 (1957)

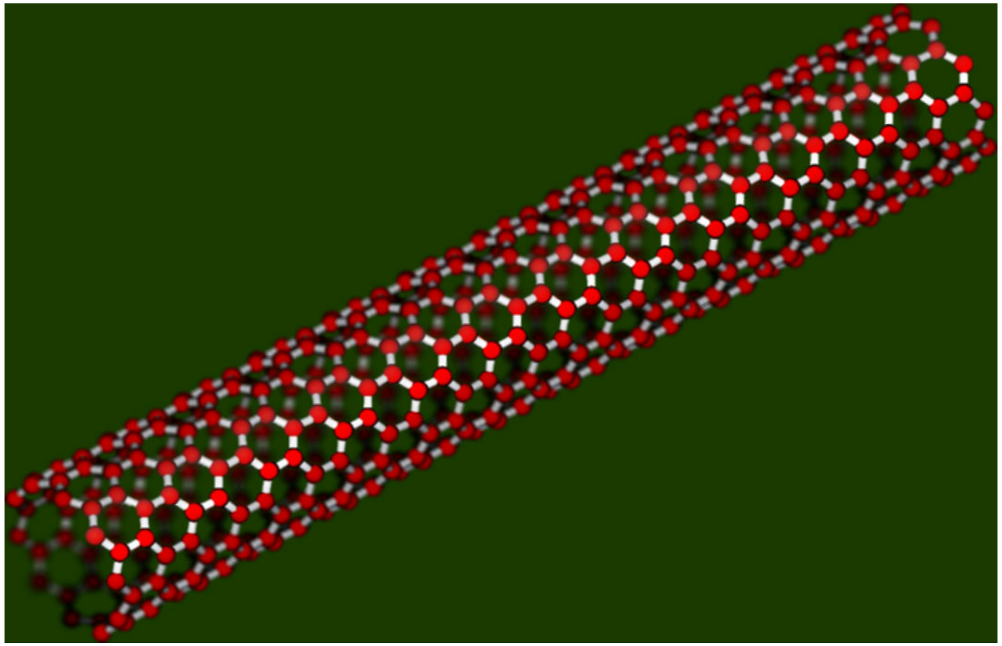


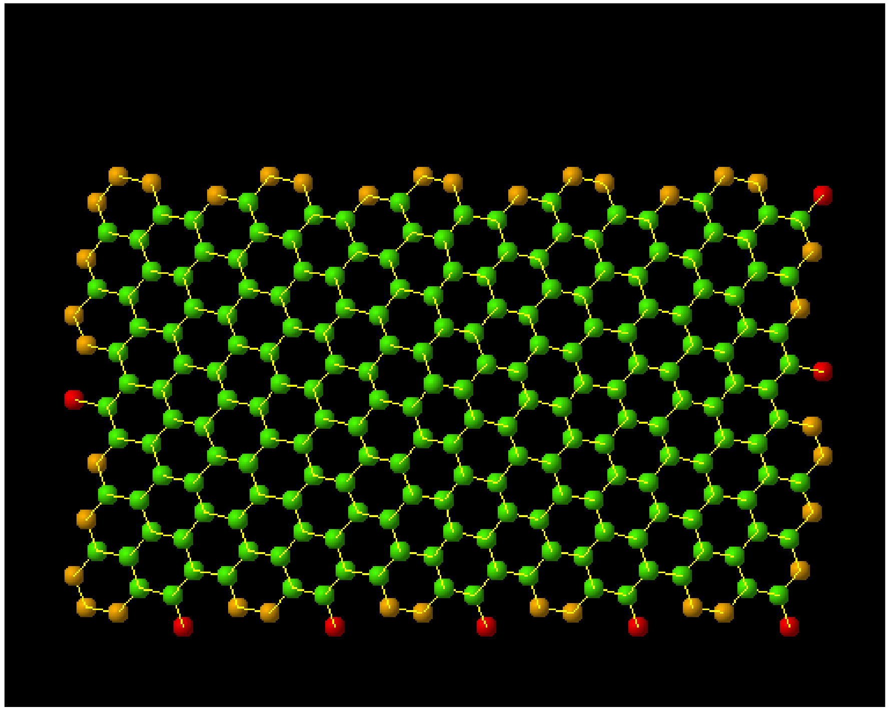


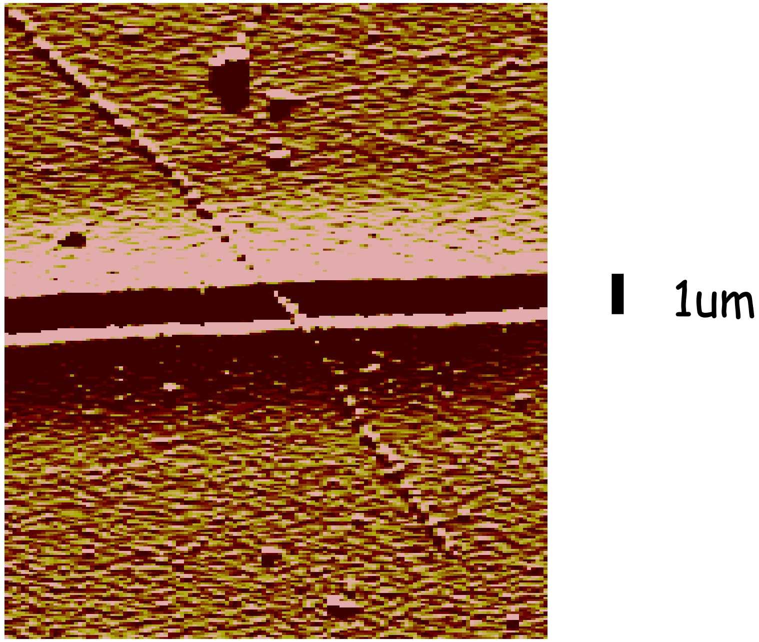


dimensão zero: fulerenos

grafeno dobrado

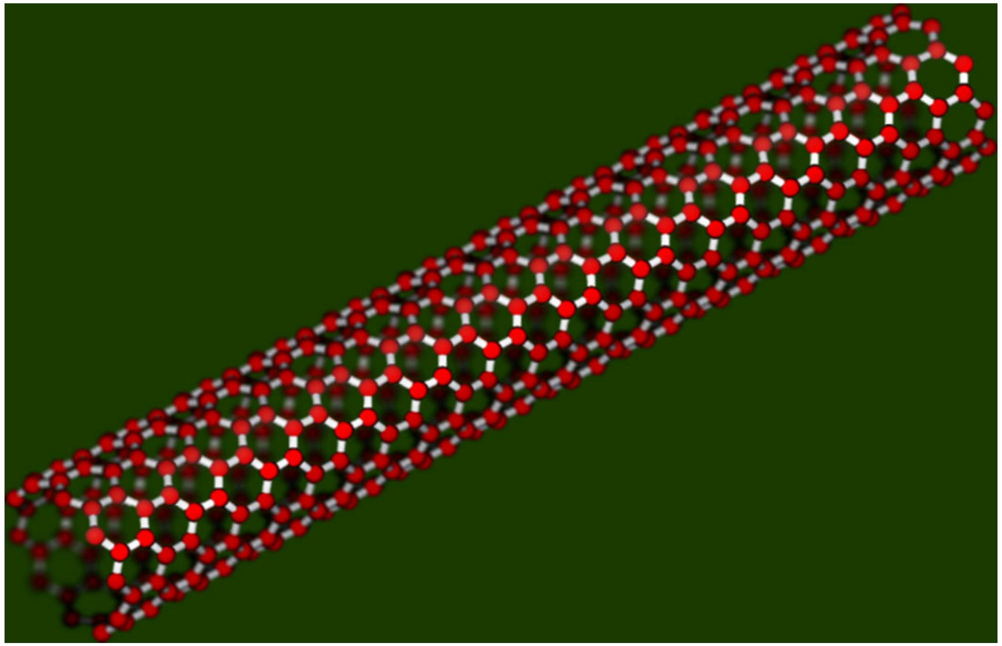


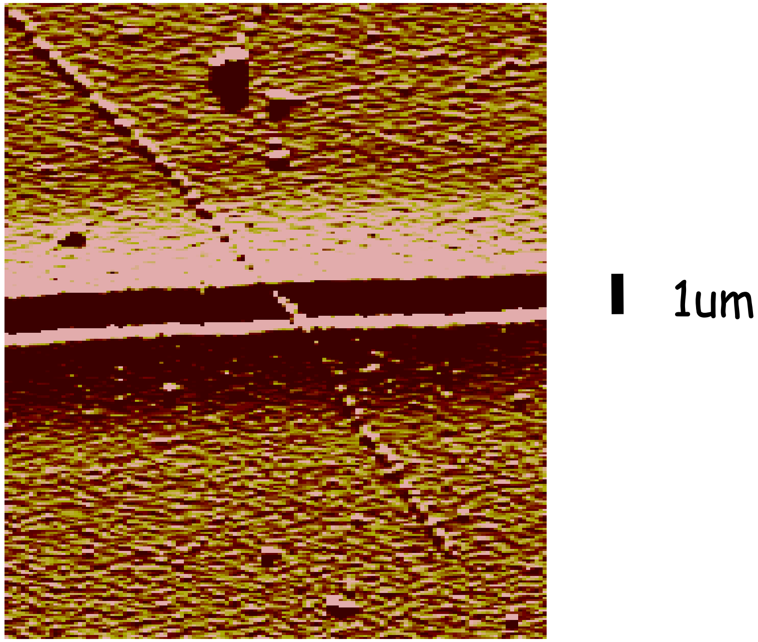


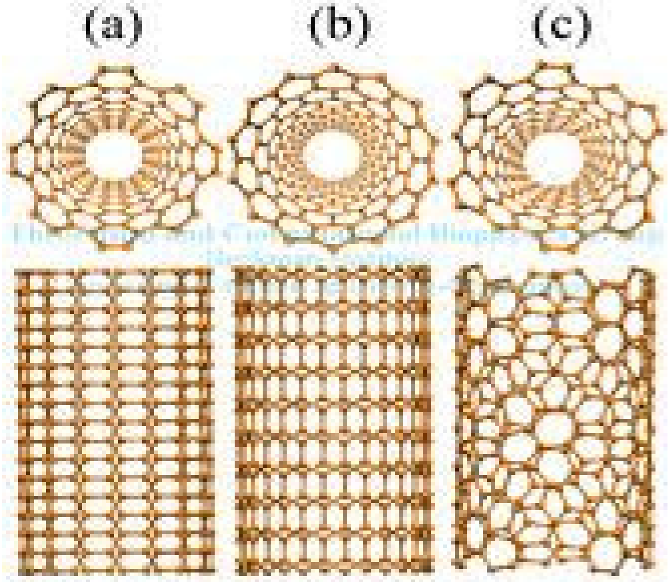


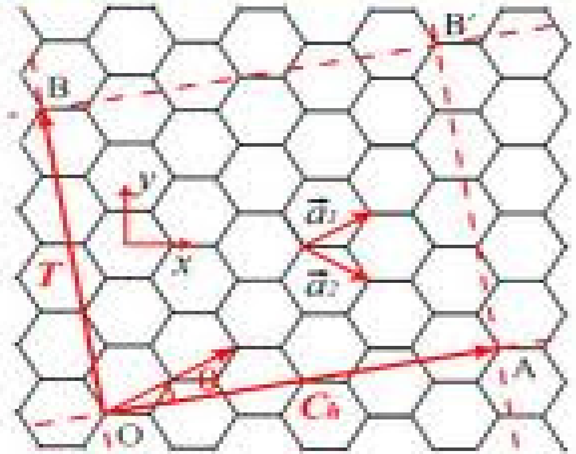
Unidimensional:
nanotubos de carbono

Grafeno enrolado

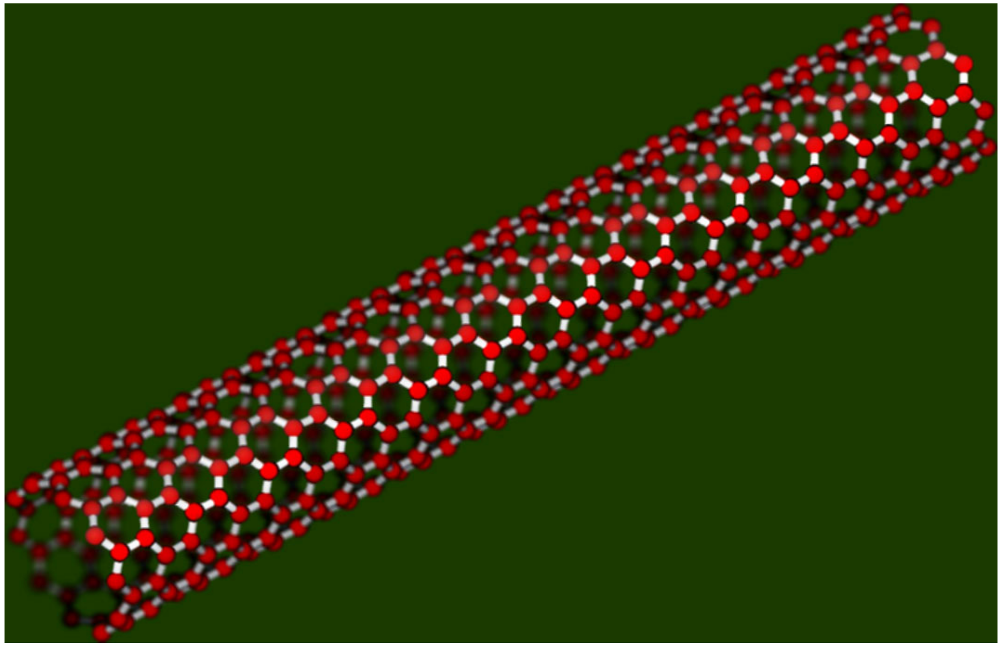


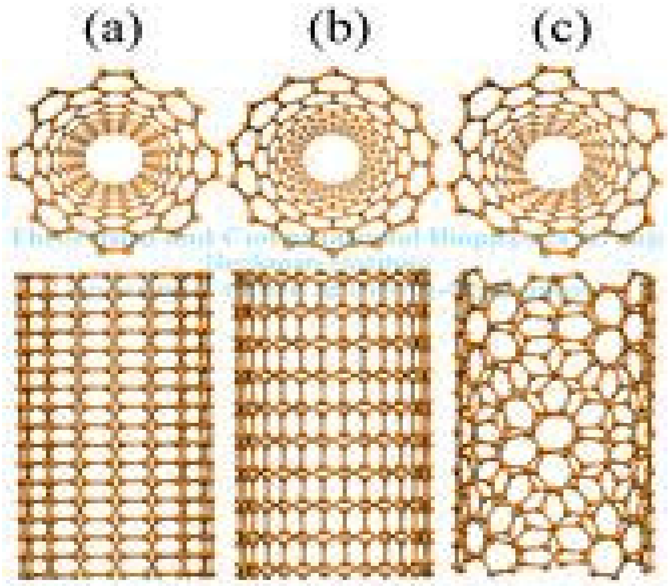


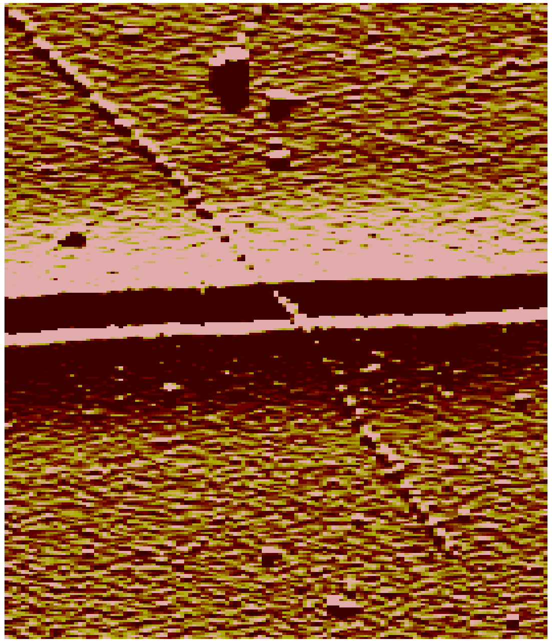




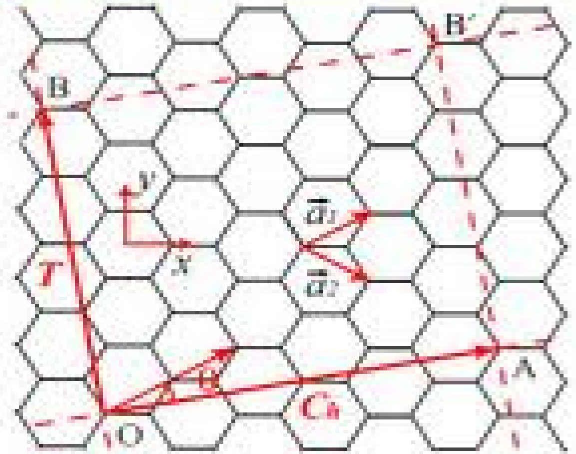
Unidimensional: nanotubos de carbono



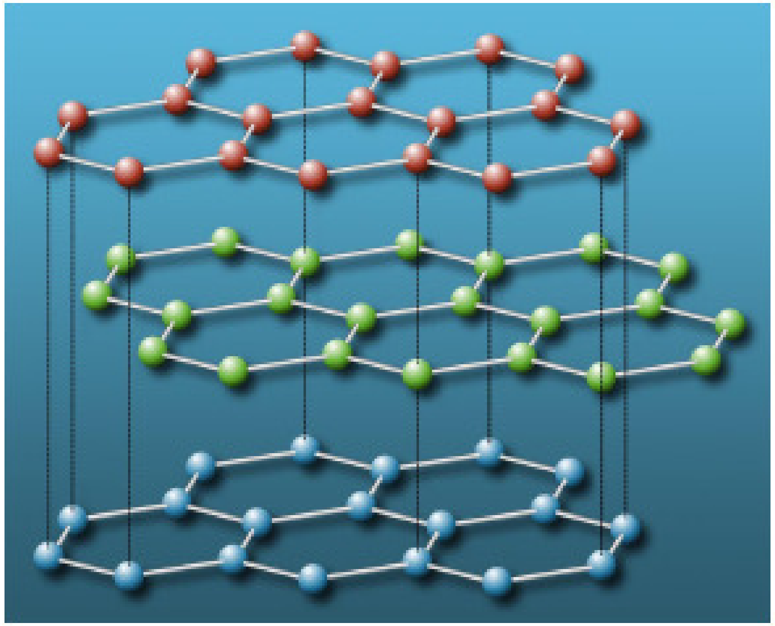


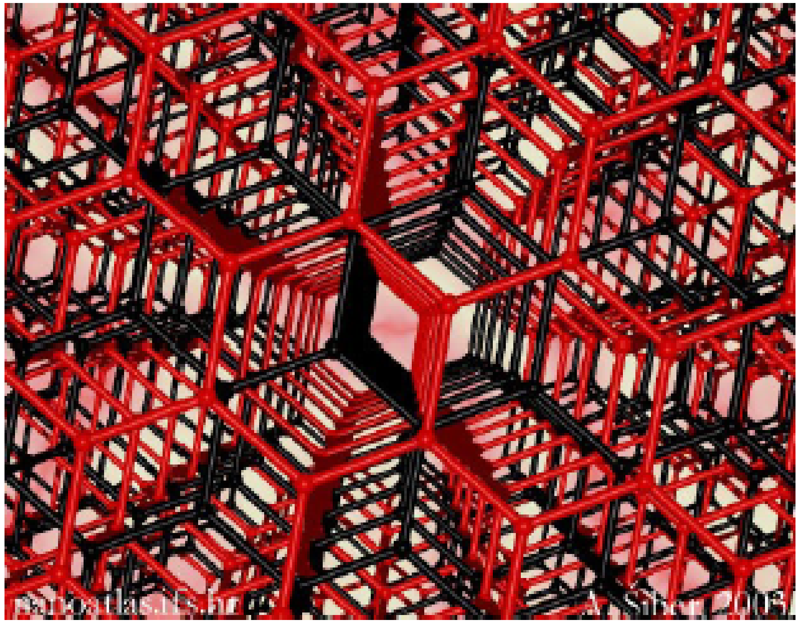


1um



grafeno enrolado





Tridimensional: grafite

grafeno empilhado

Grafeno é o pai
de todos eles.

Teoria de 60 anos.

PHYSICAL REVIEW VOLUME 71, NUMBER 9 MAY 1, 1947

The Band Theory of Graphite

P. R. Wallace*
National Research Council of Canada, Chalk River Laboratory, Chalk River, Ontario

(Received December 19, 1946)

Exercício

2. ZONE STRUCTURE OF A SINGLE HEXAGONAL LAYER

Since the spacing of the lattice planes of graphite is large (3.37A) compared with the hexagonal spacing in the layer (1.42A), a first approximation in the treatment of graphite may be obtained by neglecting the interactions between planes, and supposing that conduction takes place only in layers.

Graphite possesses four valence electrons. Three of these form tight bonds with neighboring atoms in the plane. Their wave functions are of the form

$$\frac{1}{\sqrt{3}}(\psi_c(2s)+\sqrt{2}\psi_c(\sigma_i 2p)) \quad (i=1, 2, 3),$$

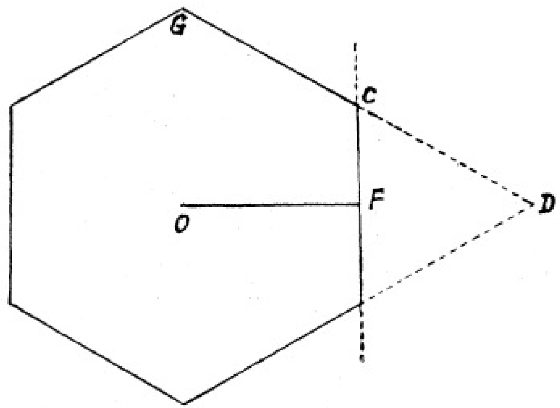
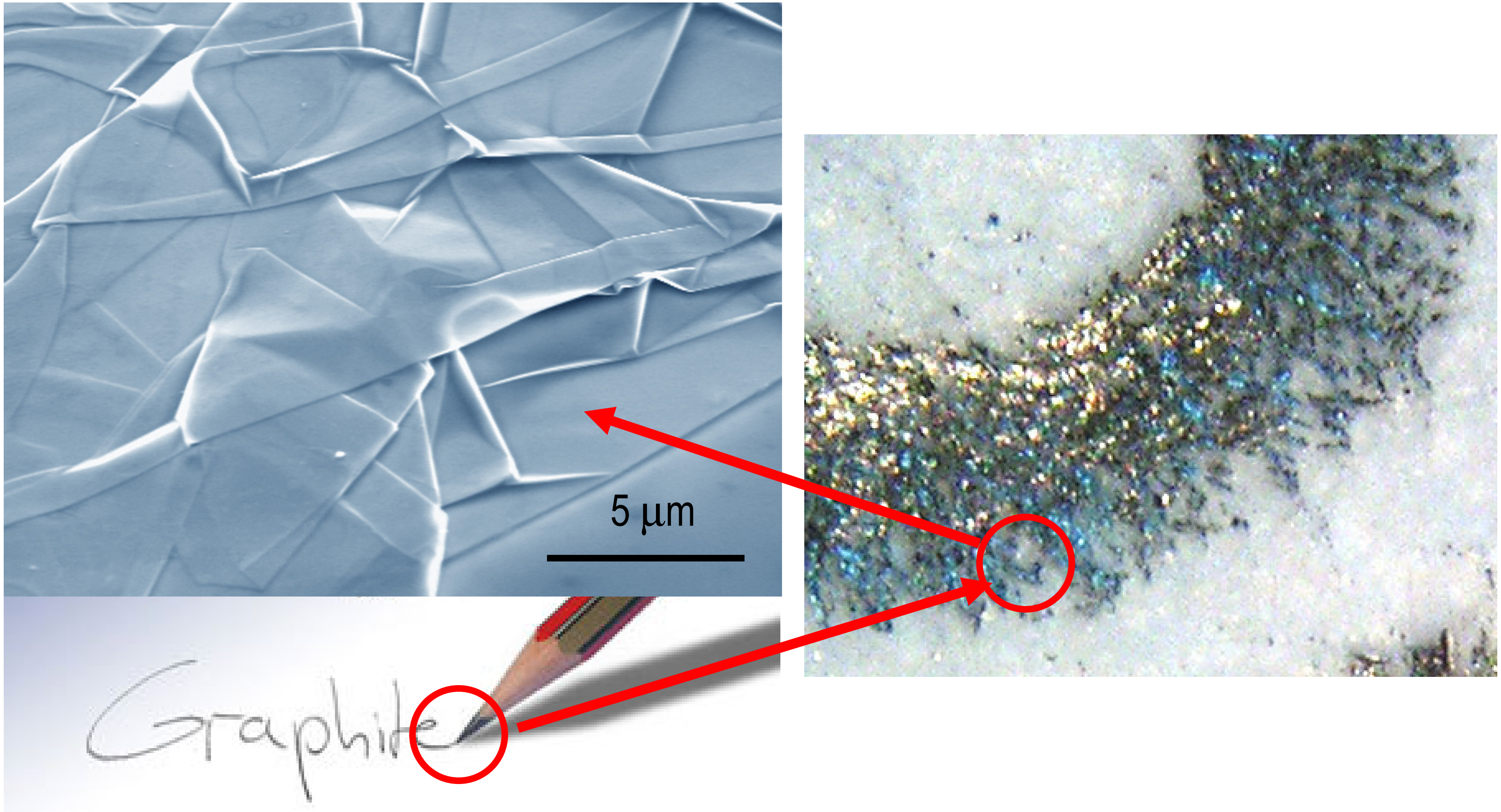


Fig. 2.

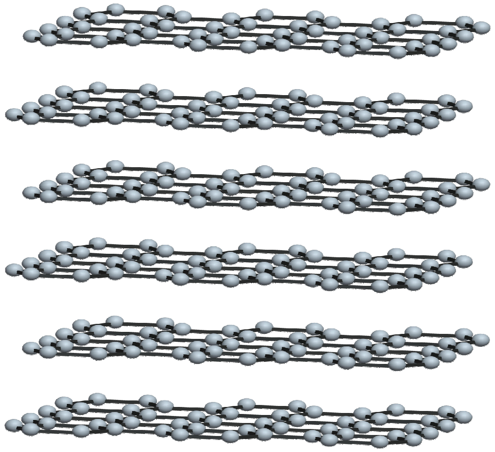
hexagon (Fig. 2) whose sides are distant $1/\sqrt{3}a$ from its center. It is easily shown that this zone contains one electron per atom, for the density

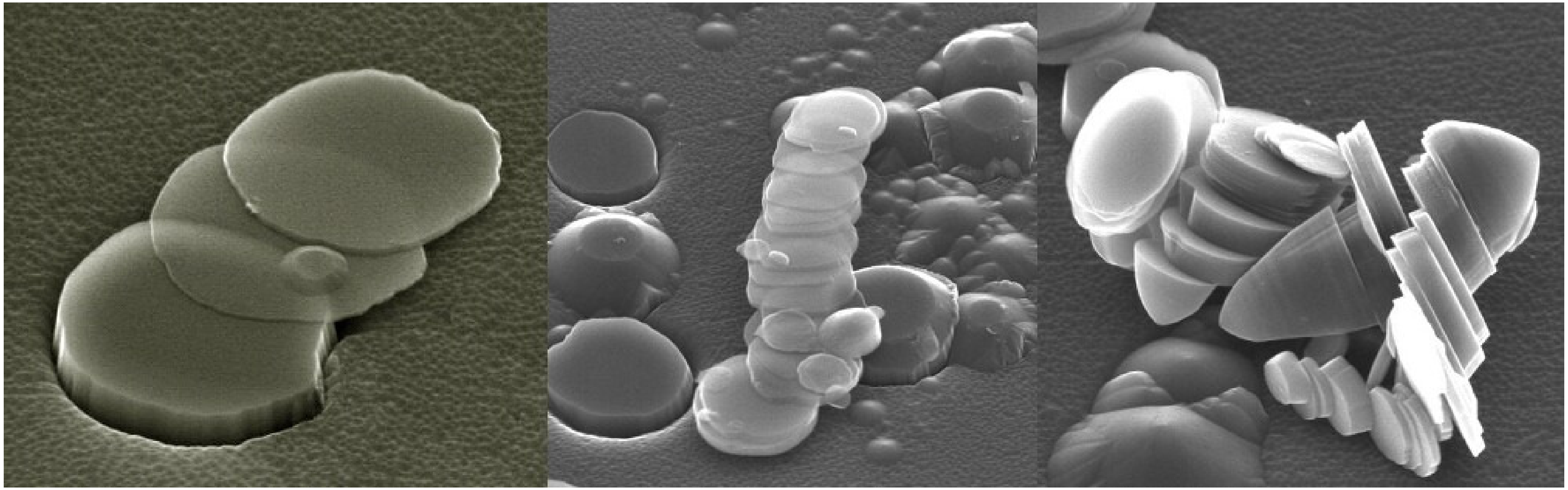
Grafeno: fácil de fazer, difícil de achar



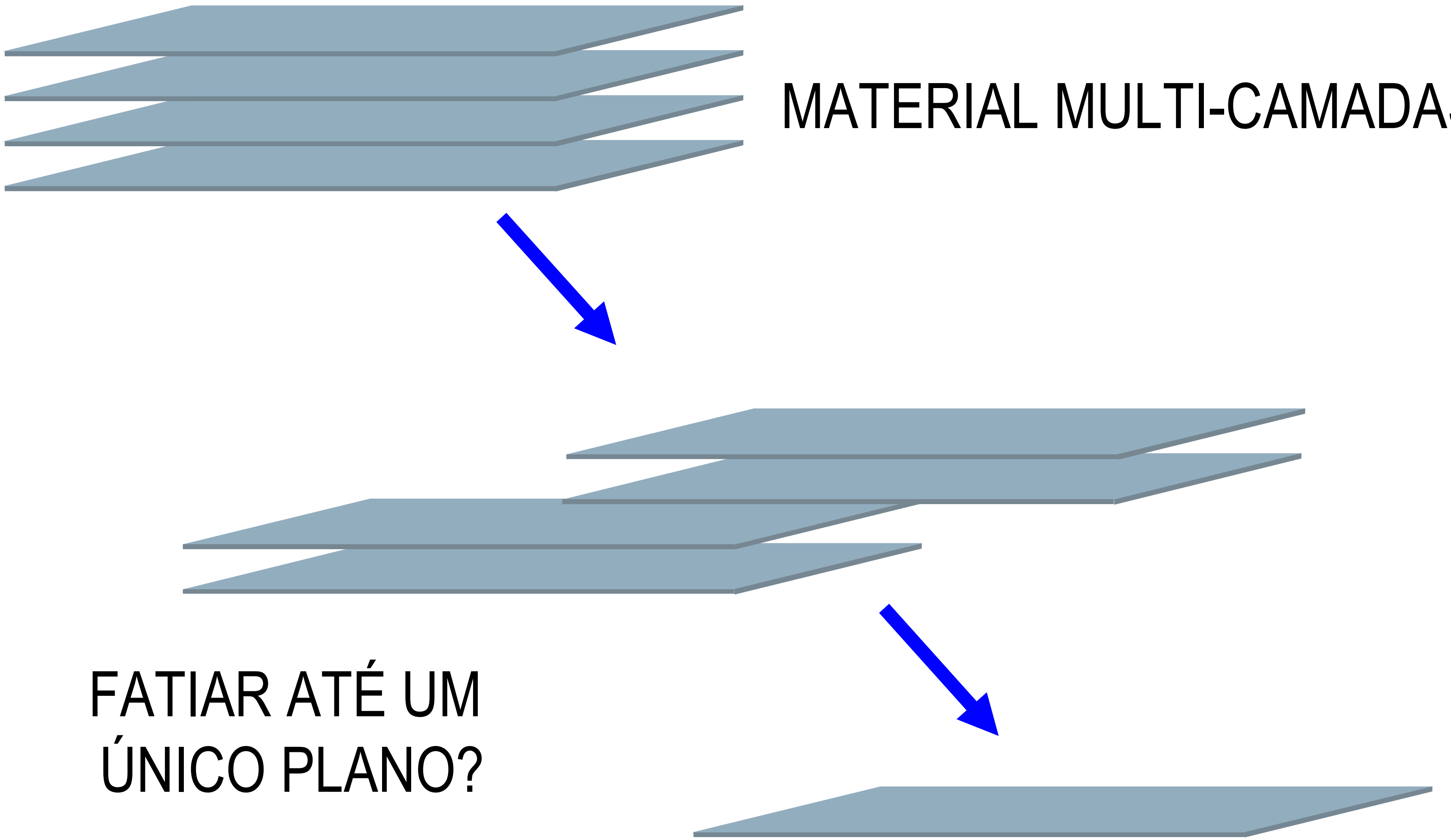
Quão fino podemos fatiar grafite?

Estrutura de camadas do grafite

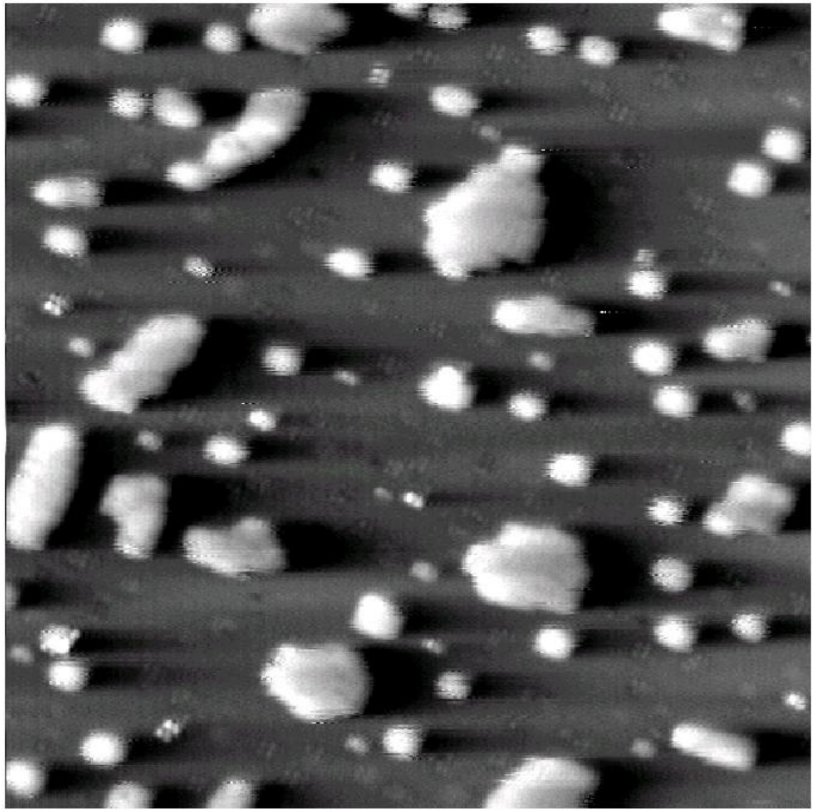




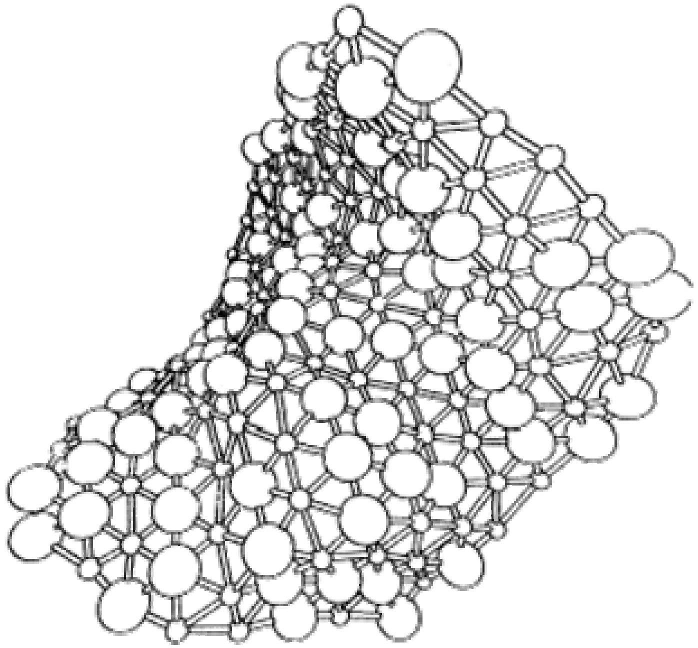
Podemos isolar uma única camada?



A natureza “odeia” baixas dimensões



“crescimento de ilhas”
aglomerados de filmes finos

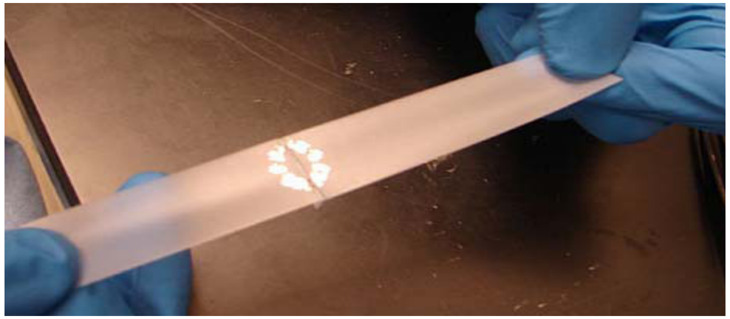


Precursores de 2D rapidamente formam estruturas 3D

Peierls; Landau; Mermin-Wagner; ….

Clivagem mecânica

"Descascando" camadas de grafite com fita adesiva



Transferência para substrato (em geral SiO_2)

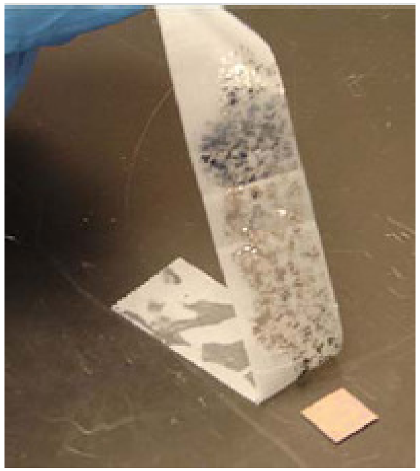
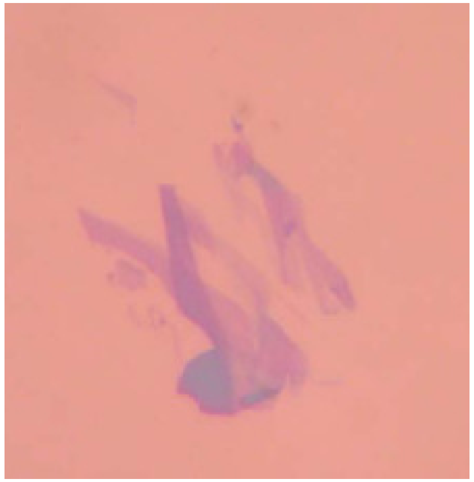


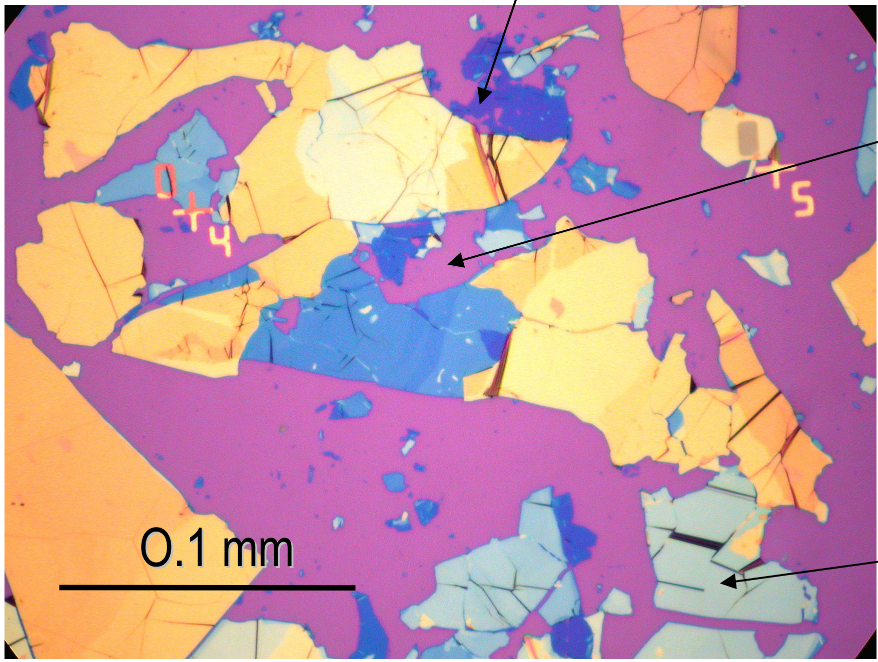
Imagem de microscópio ótico dos flocos resultantes



Técnica da "fita adesiva"

1 a 5 camadas – Manchester 04

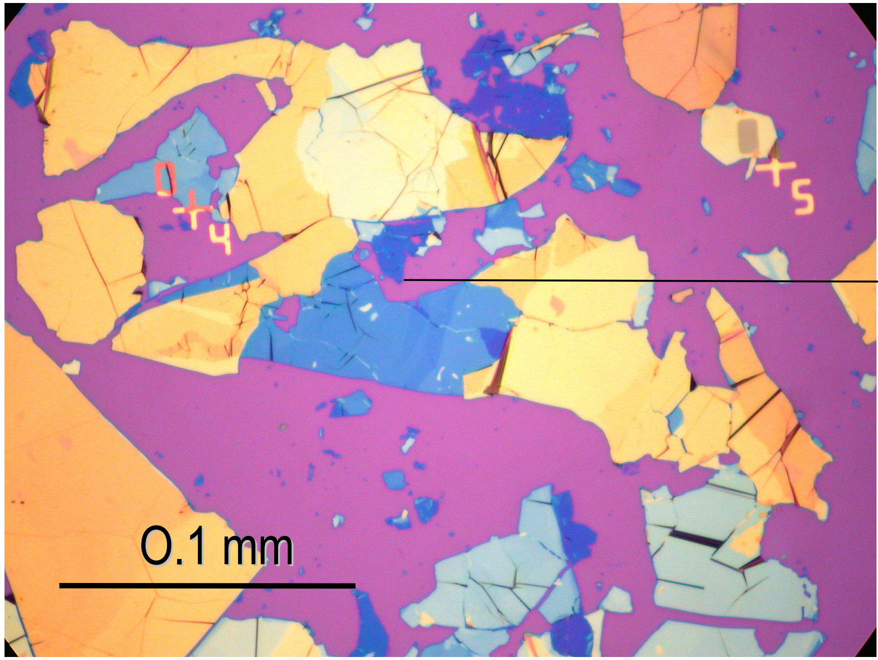
10 a 20 camadas – Columbia 02

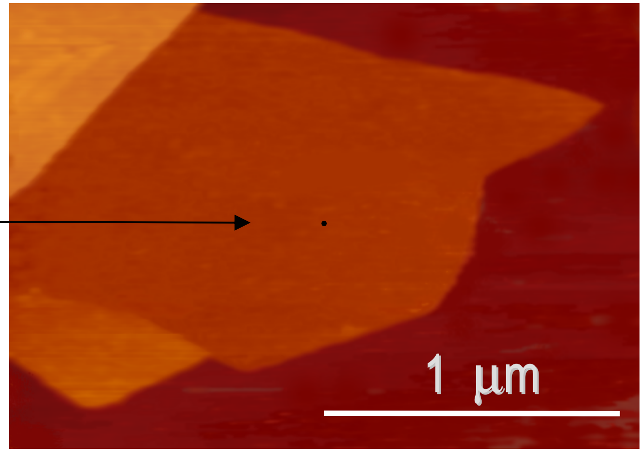


~100 camadas:
Kurtz 91
Chashi 97
Rouff 99

traços de grafite em um substrato de Si oxidado

Quão fino pode ser?

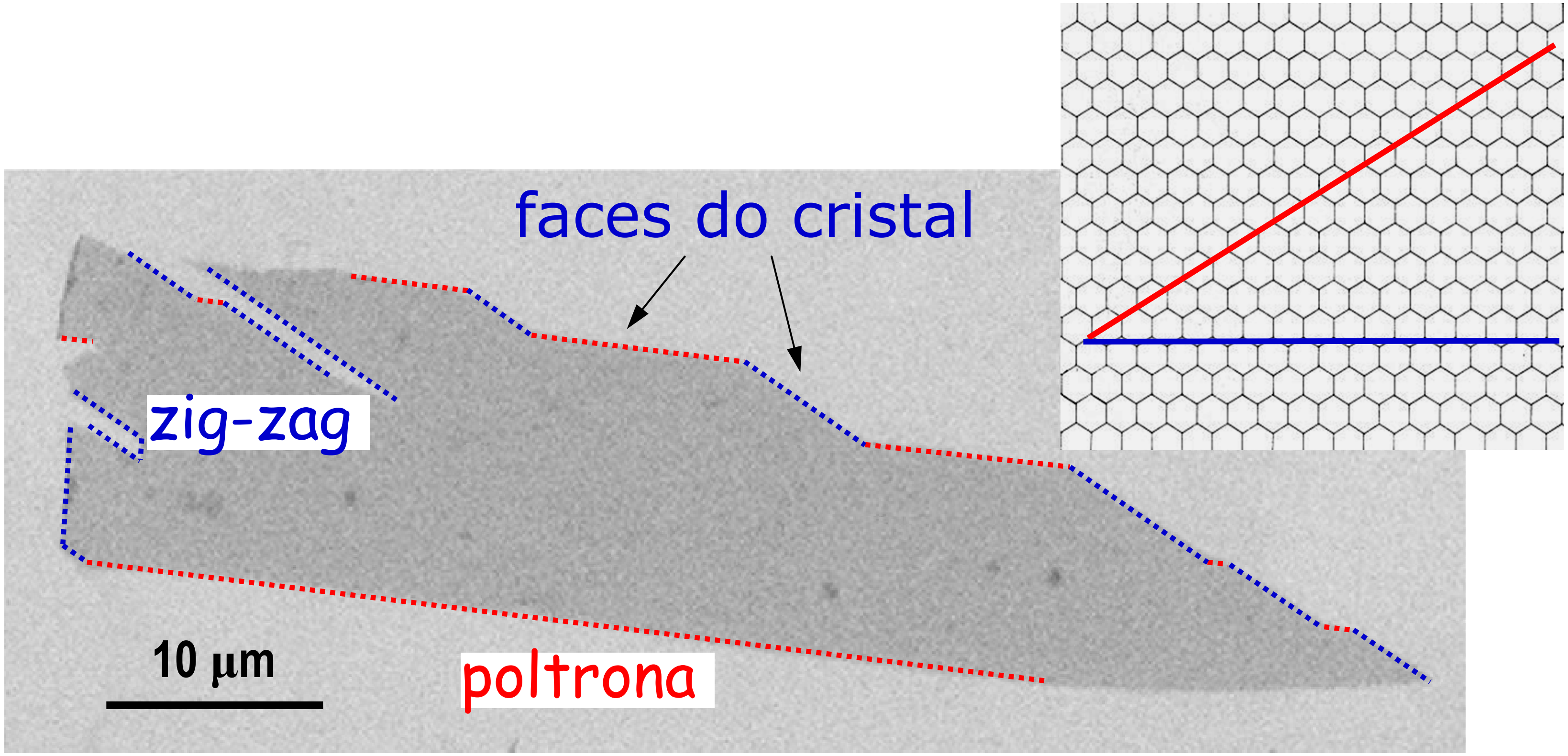




Grafeno – primeiramente demonstrado
Grupo de Manchester, *Science* '04

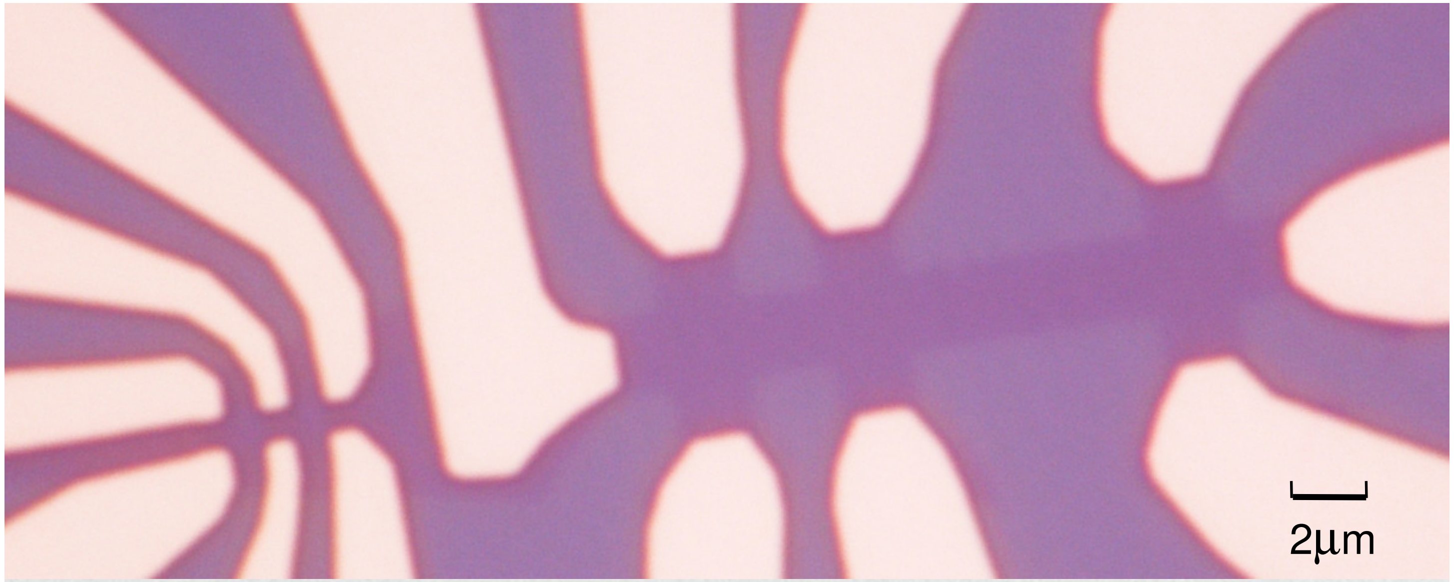
traços de grafite em um substrato de Si oxidado

Estado da arte

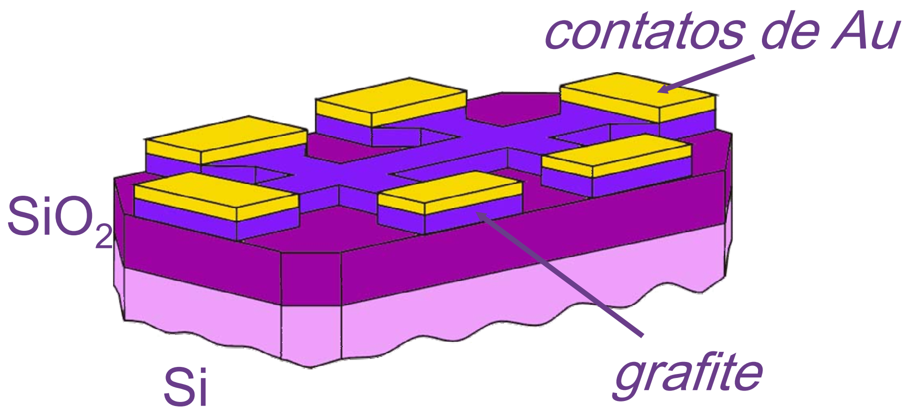


cristais 2D de grafeno

Estado da arte



- imagem ótica
- imagem MEV
- desenho
- contatos e suporte



Grafeno tem a espessura de um átomo e é “mole”

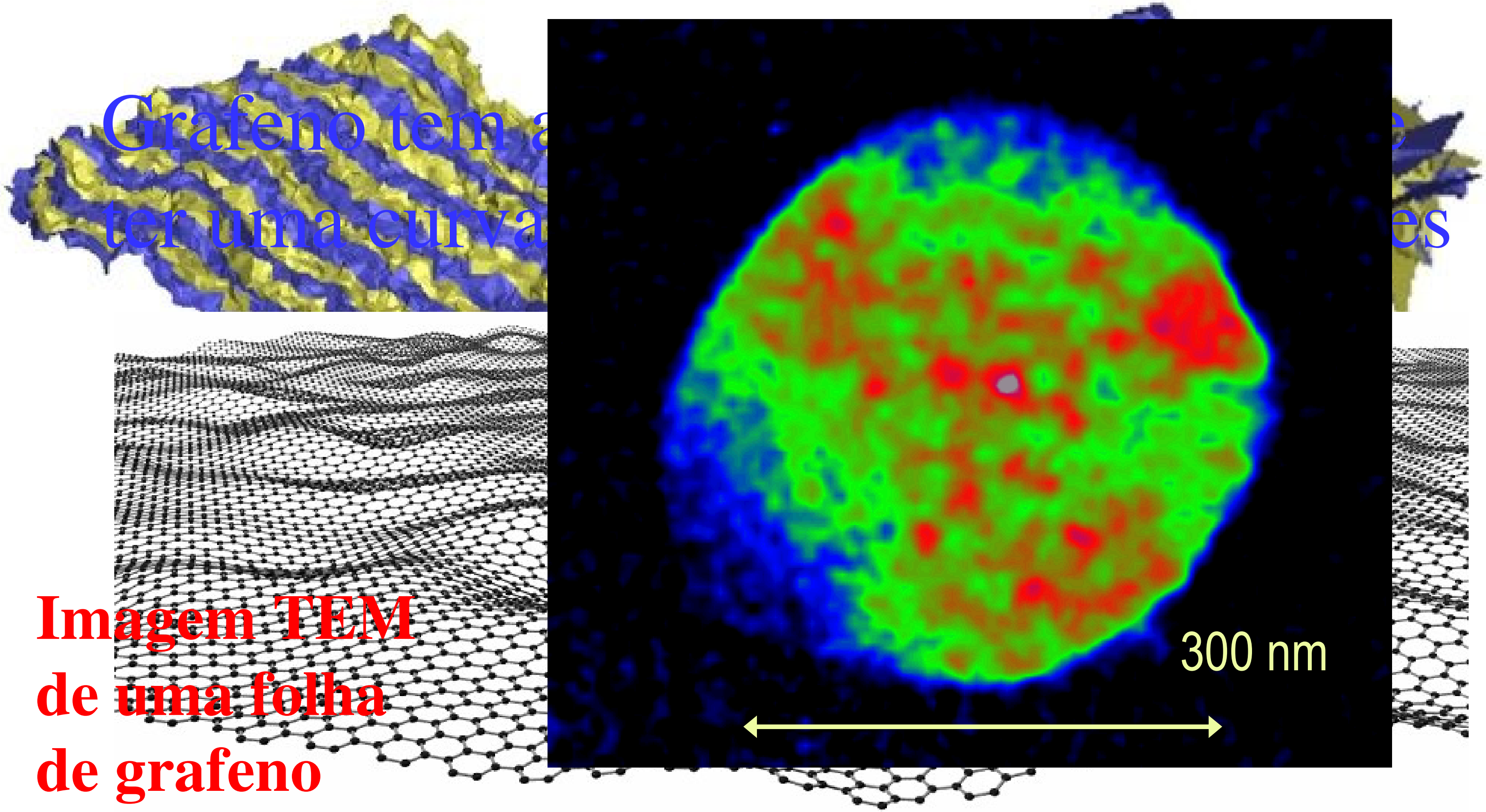
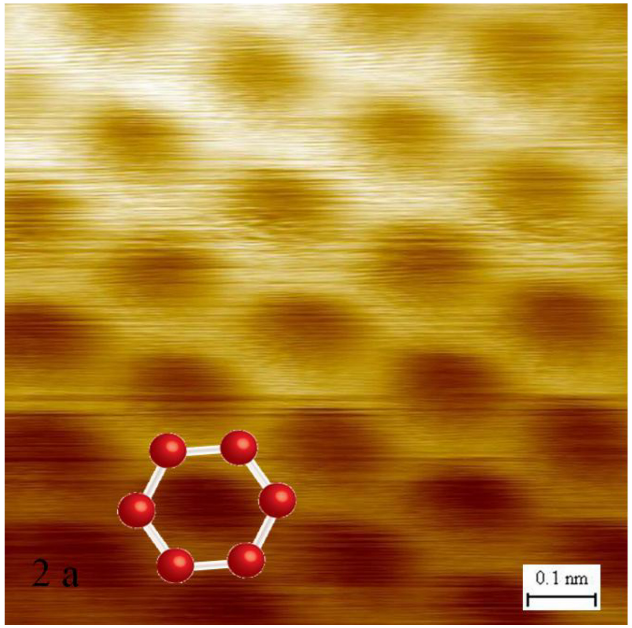


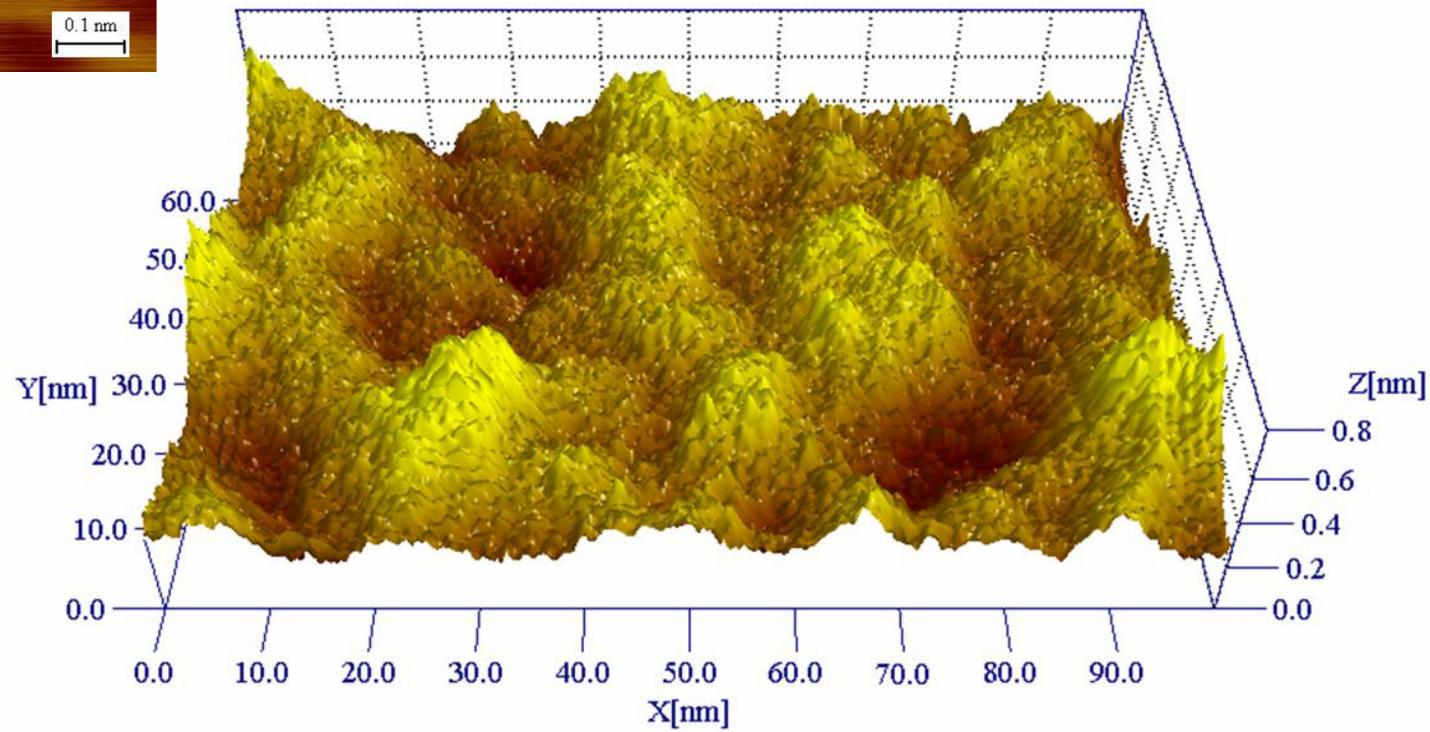
Imagem TEM de uma folha de grafeno

J. C. Meyer *et al.*, Nature **446**, 60 (07)

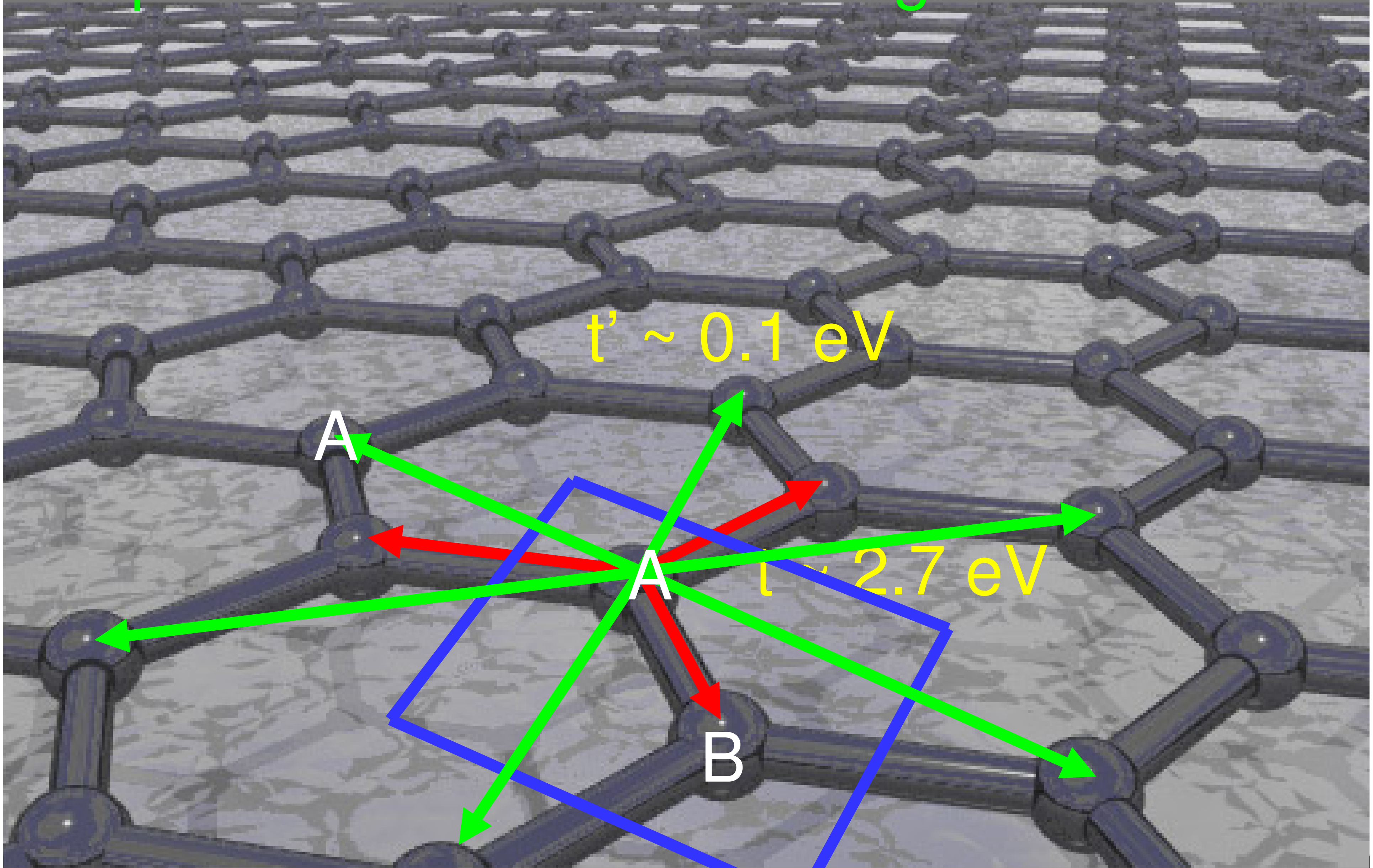
Microscopia de tunelamento



E. Stolyarova et al., PNAS 104, 9209 (2007)
Ishigami et al., Nano Letters (2007)



Propriedades eletrônicas do grafeno

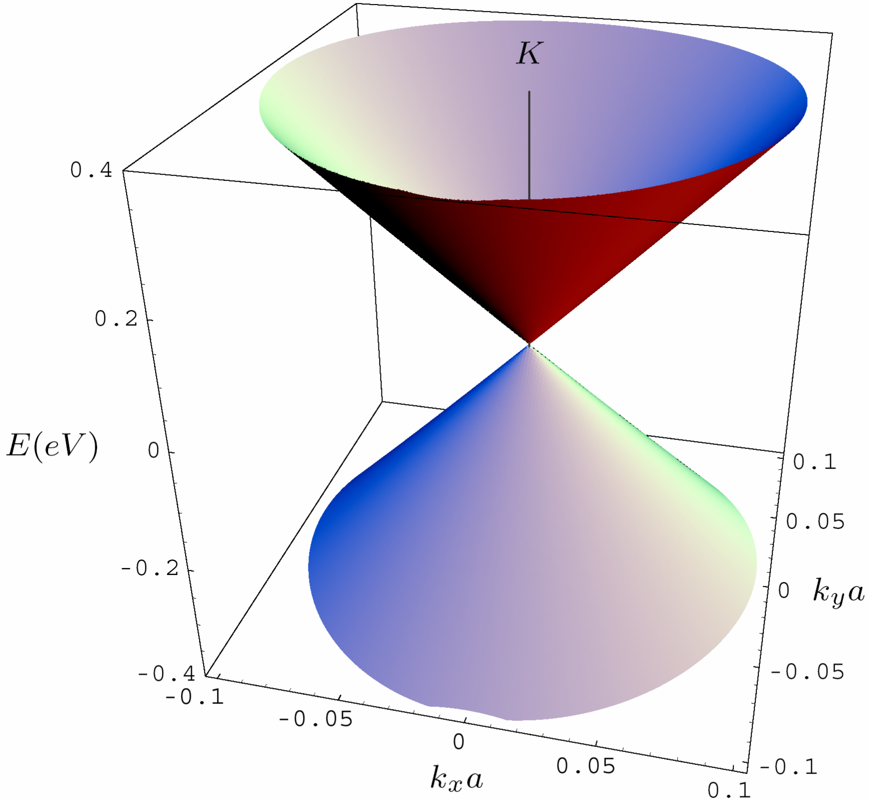


Célula unitária

Segundos vizinhos

Primeiros vizinhos

Espaço de momentos



Cone de Dirac

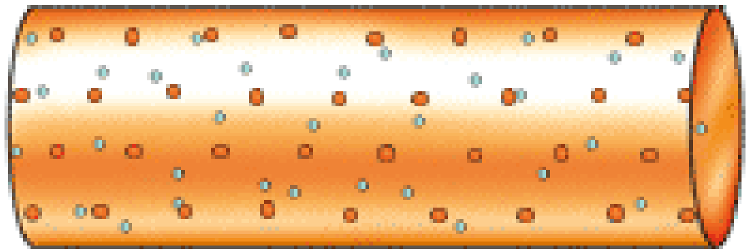
$$E_{\pm}(p) = \pm v_F \sqrt{p_x^2 + p_y^2} = \pm v_F\, p$$

$$E_{\pm}(p,m) = \pm \sqrt{m^2 v_F^4 + v_F^2 p^2} \quad \text{with } m = 0$$

$$v_F = \frac{3ta}{2} \approx c/300$$

Estado sólido "ultra-relativístico" com uma velocidade da luz baixa

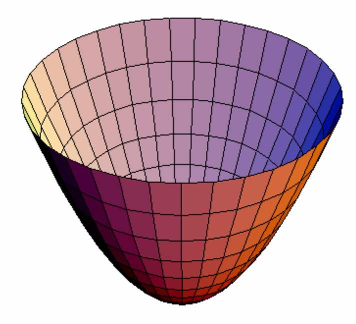
O que é tão especial em grafeno?

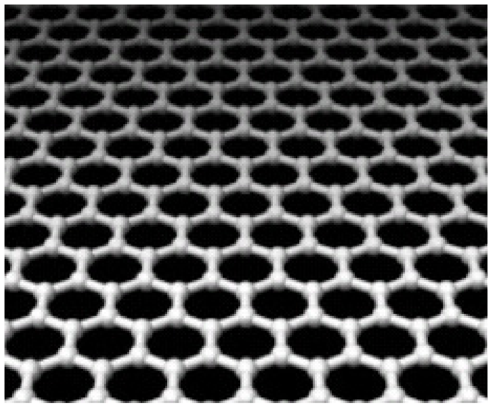


condutor normal

$$E(p) = \frac{p^2}{2m}$$

fermions

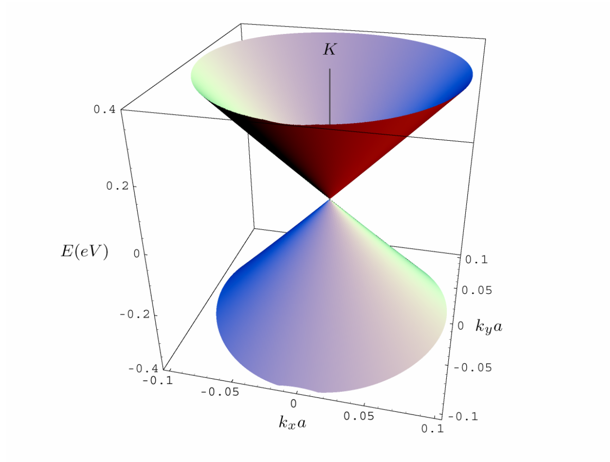




grafeno

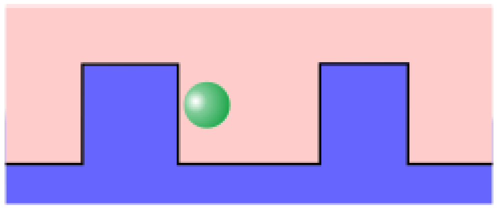
$$E(p) = \pm vp$$

fermions de Dirac



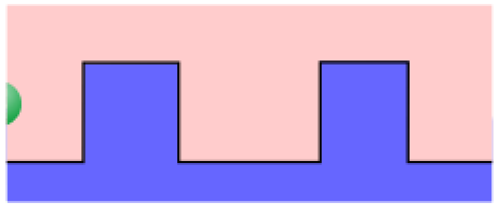
Paradoxo de Klein

partículas massivas em 1D:

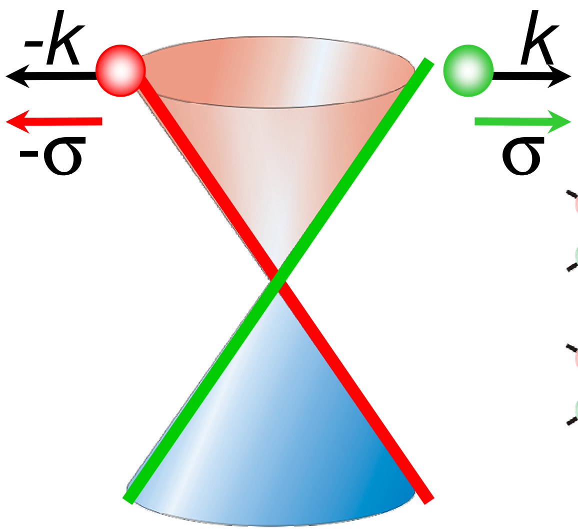


sempre localizadas

partículas sem massa em 1D:

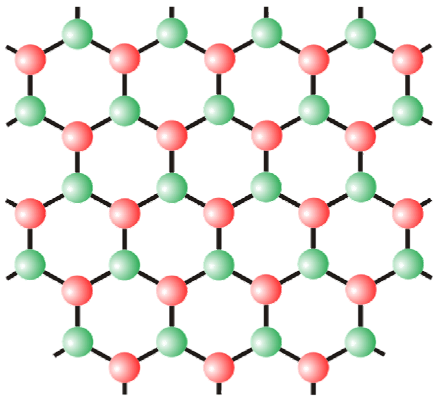


NUNCA LOCALIZADAS



propagação de partícula relativística através de uma barreira

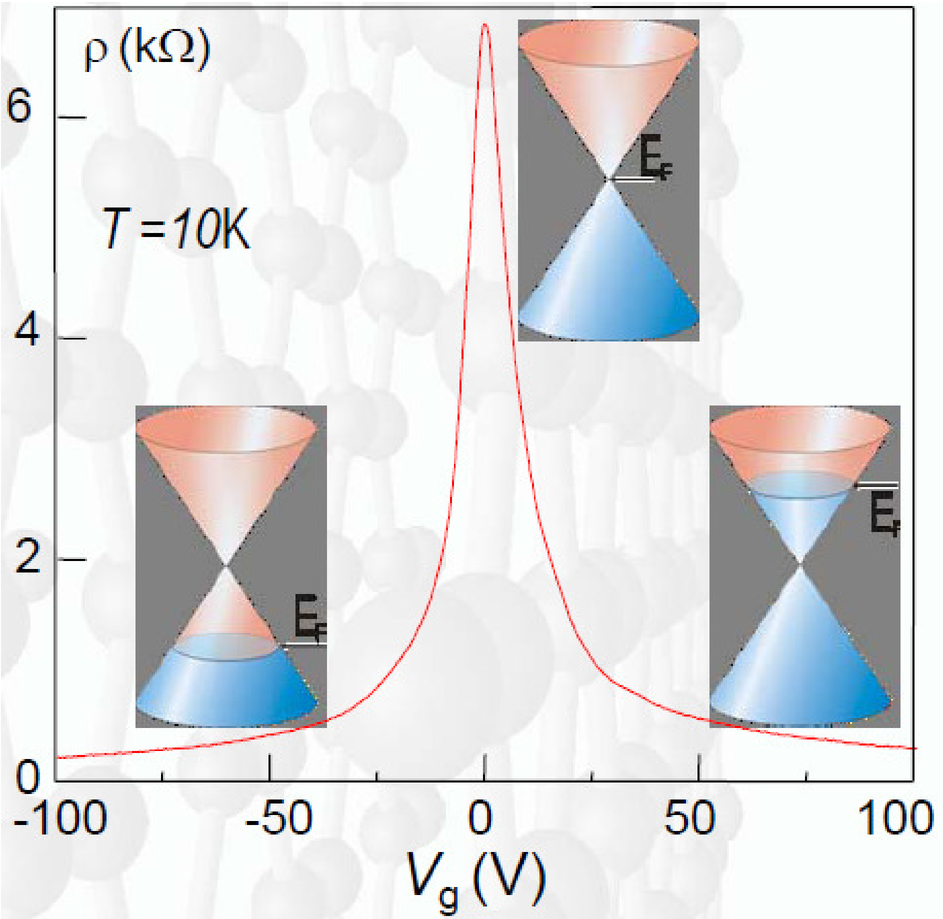
O. Klein, *Z. Phys* **53**,157 (1929); **41**, 407 (1927)



consequência da conservação de pseudo-spin

M.I.Katsnelson *et al*
Nature Physics 2006

Resistividade limitada por efeitos quânticos



Atual mobilidade de portadores até ~15.000cm²/V.s a 300K mesmo com alta dopagem

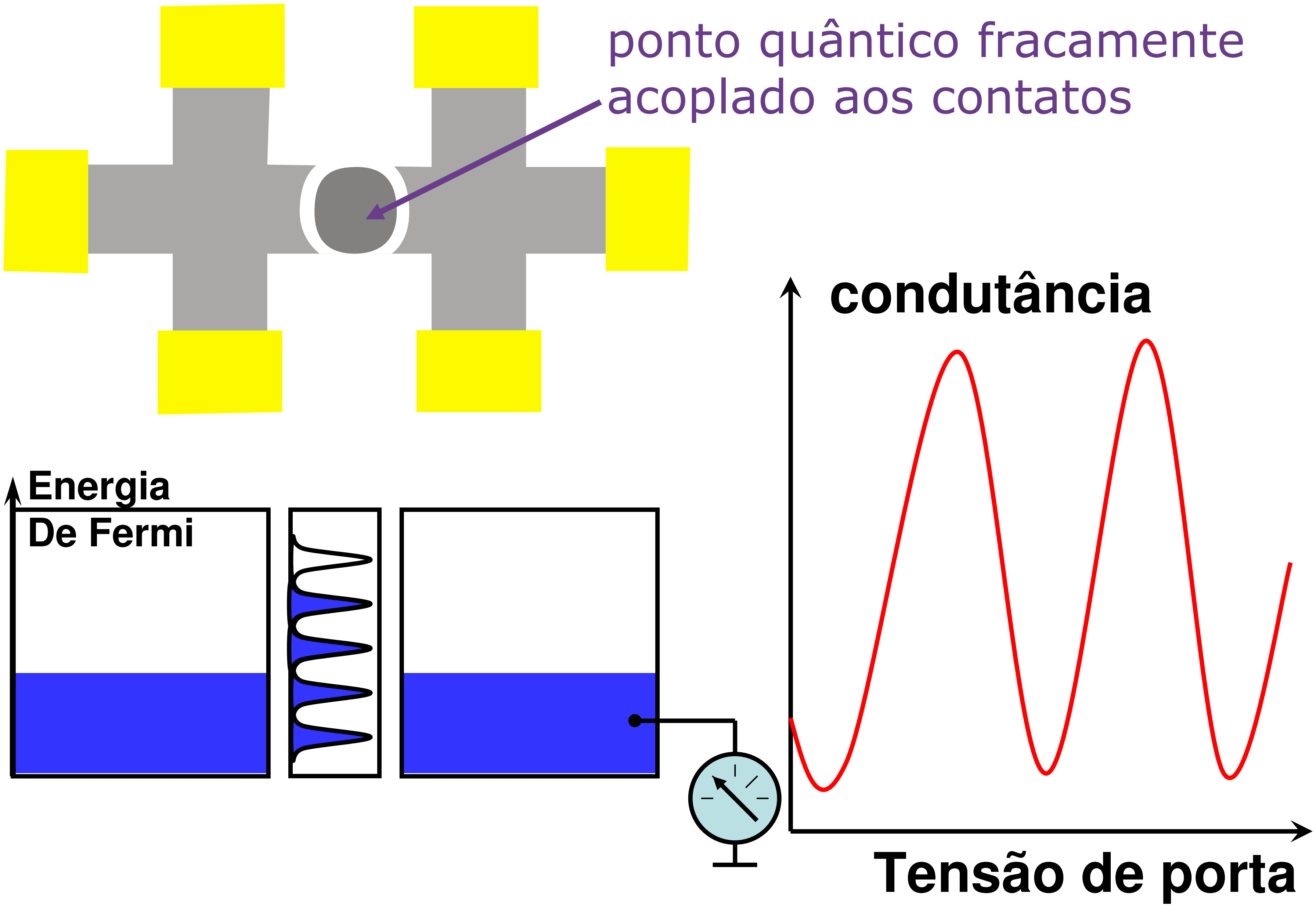
~200.000cm²/V.s a 4K (grupos de Kim e Andrei)

Grafeno suspenso
Intrínseco (limitados por fonons) >200.000cm²/V.s a 300K (maior que qualquer outro material conhecido)

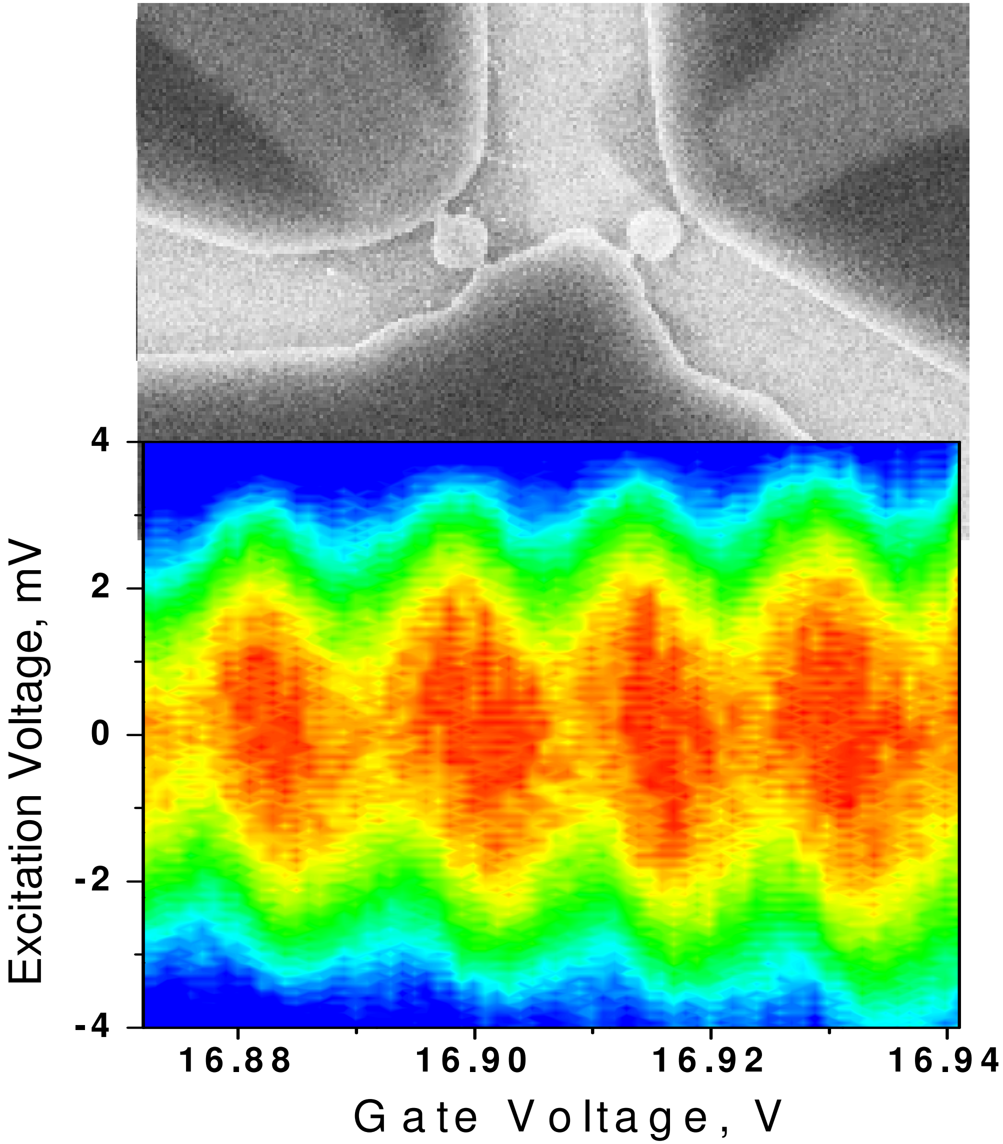
Transporte quase-balístico a condições ambientes?

Qualidade cristalina: poucos defeitos (1 por μm^2)

Ponto quântico de grafeno

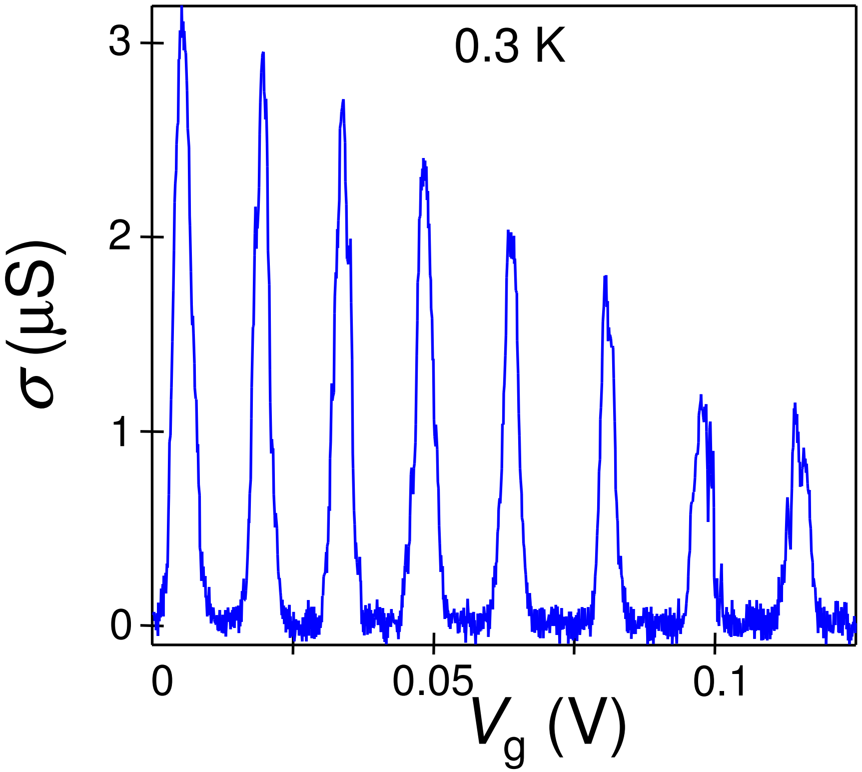


Ponto quântico de grafeno

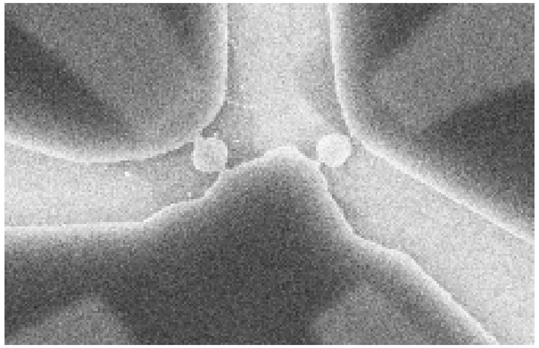


Transistor de um único elétron

Geim *et al*,
Nature Materials 2007



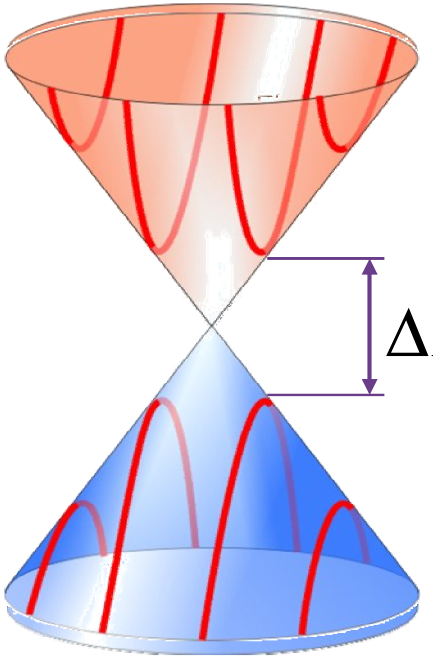
Ponto quântico de grafeno



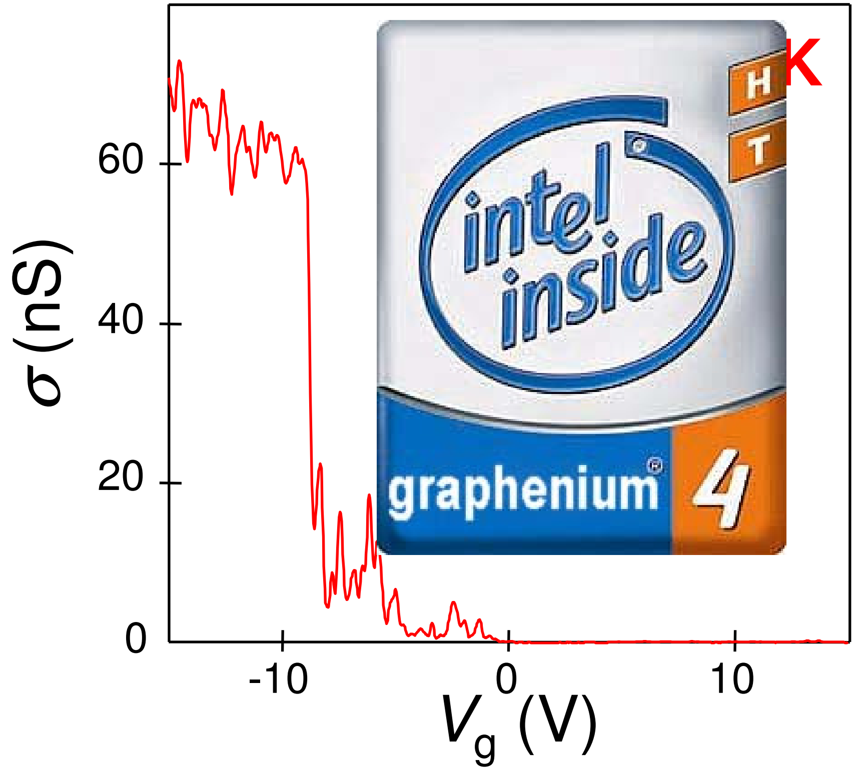
Temperatura ambiente

Transistor de um único elétron

Geim *et al*,
Nature Materials 2007



$$\Delta E = \frac{25.000\,K}{L[nm]}$$

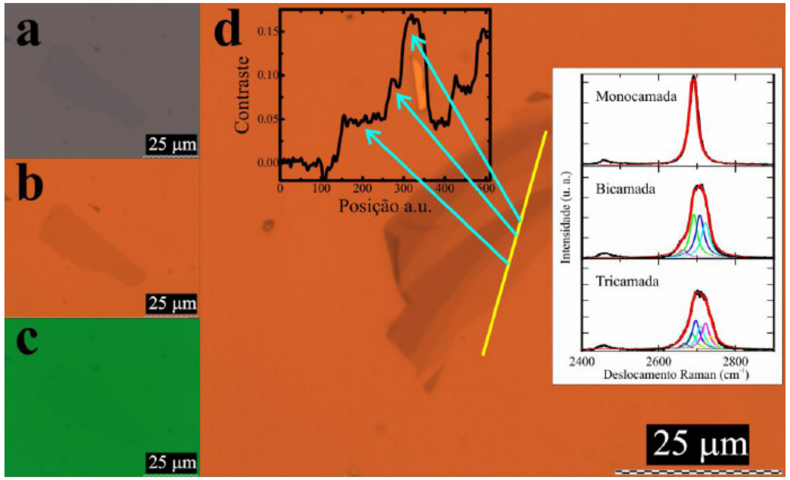


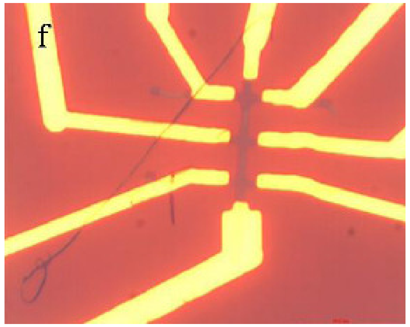
Grafeno no Brasil

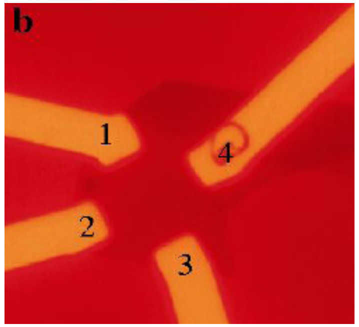
- Grupo da UFMG e colaboradores
- Grupo da USP-SP: transporte eletrônico
- Grupo da Unicamp: compostos grafíticos
- Grupos teóricos (UFRJ,UFF,USP, entre outros)

INCT de Materiais de Carbono

- Síntese:
  - esfoliação mecânica;
  - crescimento epitaxial;
  - síntese química;
  - processamento de amostras
- Caracterização:
  - espectroscopia Raman;
  - microscopia eletrônica;
  - técnicas de luz síncrotron;
  - microscopia de tunelamento
- Modelagem:
  - teoria do funcional da densidade







Cortesia D. Elias

O nascimento do grafeno… e muito mais por vir….