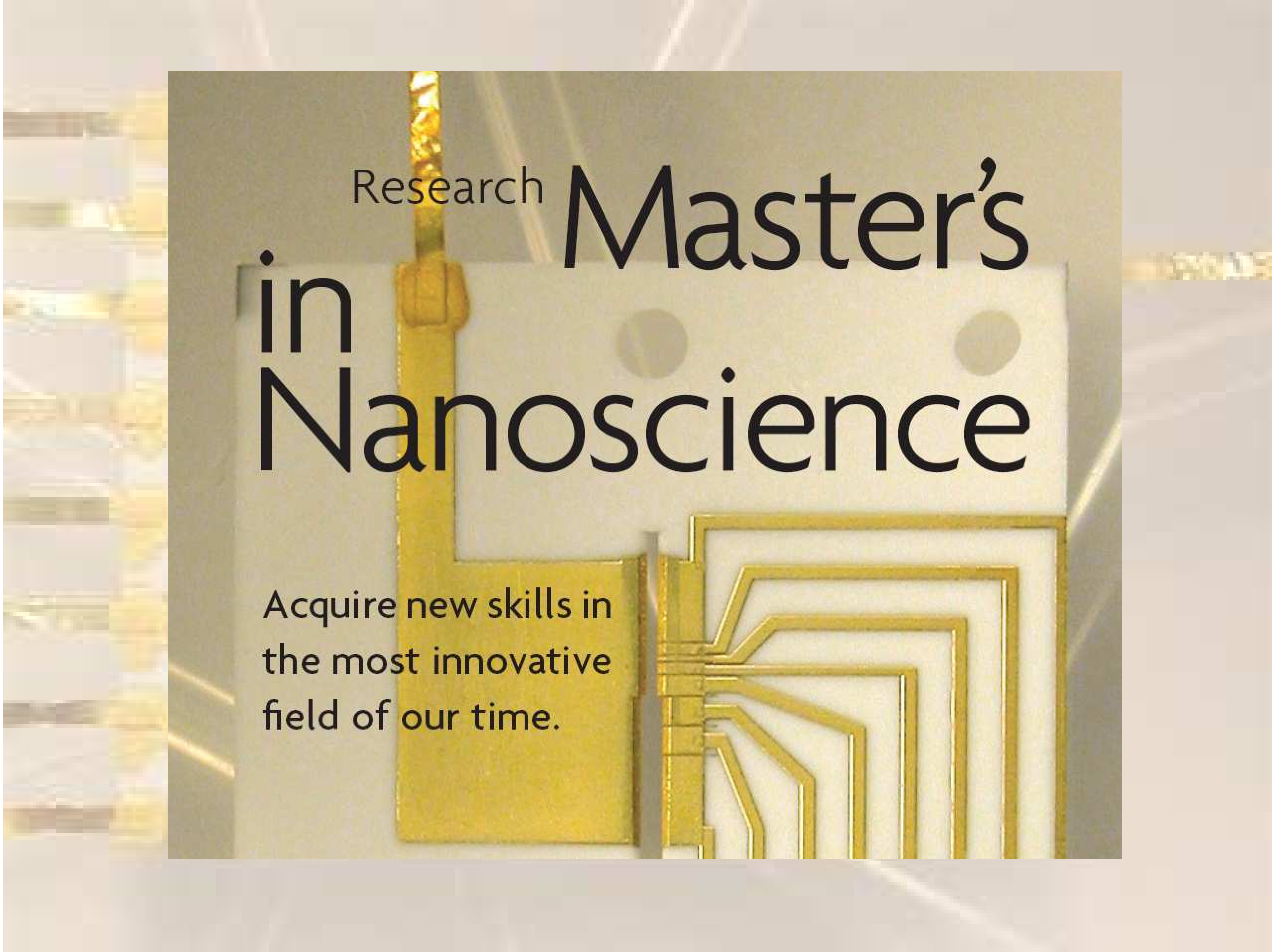
Research Master's in Nanoscience



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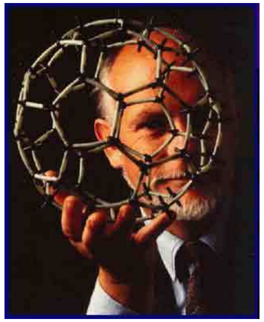
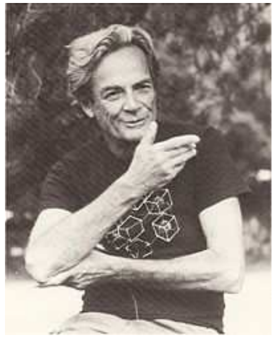


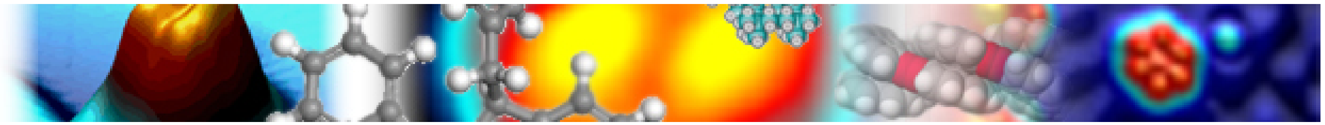


Nanoscience: A historical perspective

R. Díez Muiño and P. M. Echenique

Lecture Notes

Fall 2007



Summarizing… (end of October 3rd Lecture)

Qualitative new step in miniaturization…

- Basic scientific breakthroughs
- New technologies

… with economic consequences
(but always balance the hype)

- Industrial manufacturing: new materials and products
- Medicine: diagnosis and therapies
- Sustainability: environment (solar cells, catalysts, efficient lighting, etc.)
- Nanocomputing: extending Moore's law

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… not only economic, but scientific and social as well!

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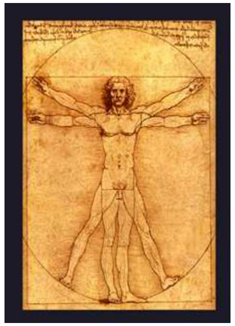
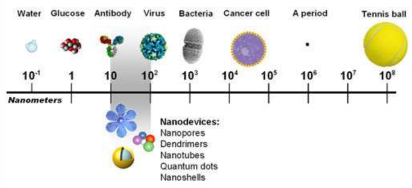
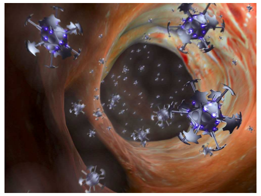
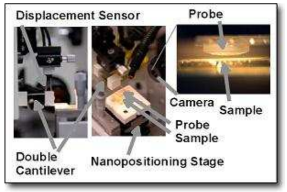
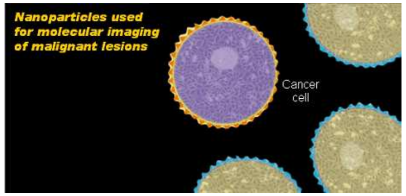


NANOMEDICINE

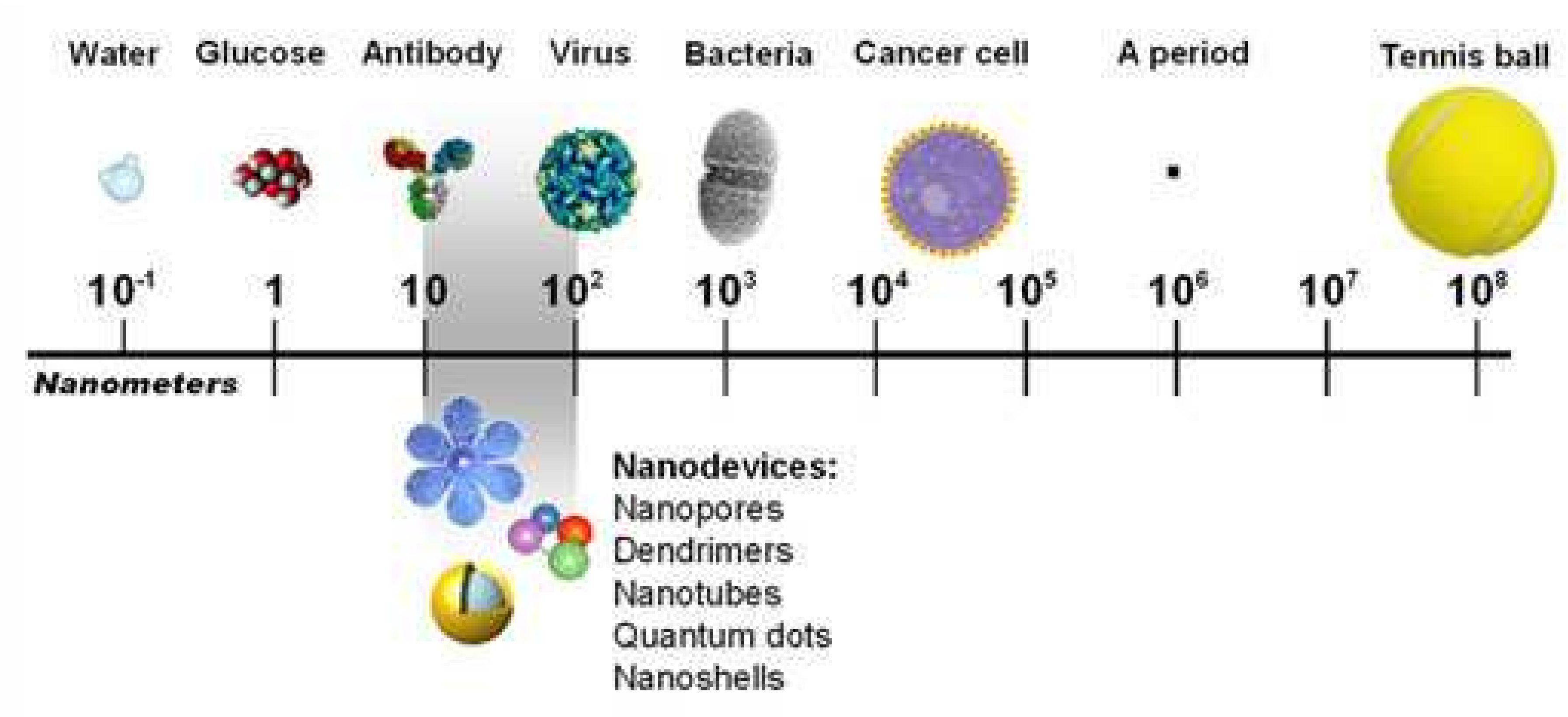




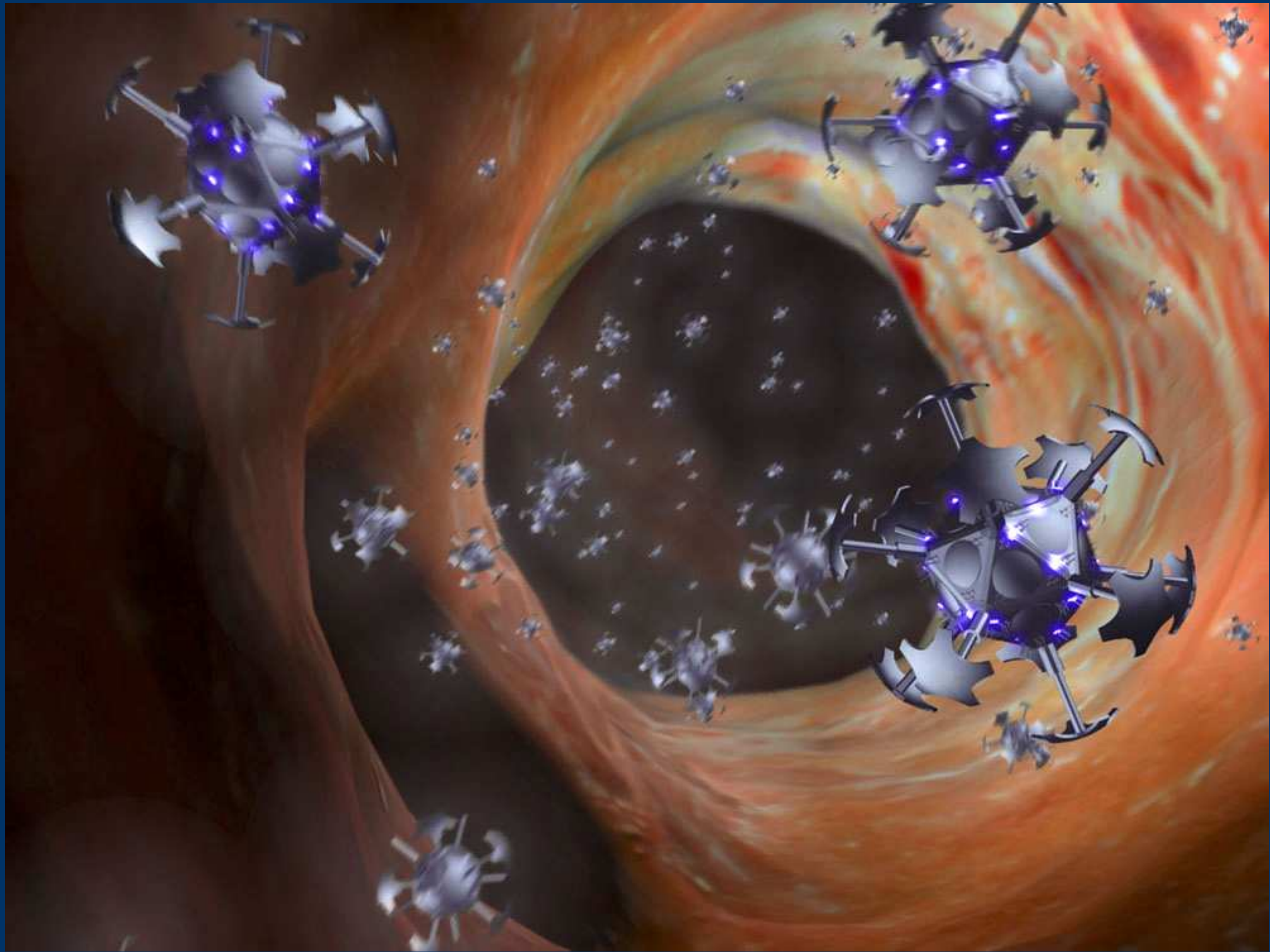




Nanoscience and Medical Research



Source: US NIH



Nano-sized robots in blood stream
Imagine these tiny robots inside your body fixing problems and fighting disease.

Nanoscience and Medical Research

Two different aspects:

- Medical Imaging and Diagnosis

- New Therapeutical Methods

Two different examples of current clinical use:

- Nanotechnology has been used to create new and improved imaging techniques to find small tumors. Researchers have shown that incredibly small iron oxide particles (nanoparticulates) can be used with magnetic resonance imaging (MRI) to accurately detect cancers that have spread to lymph nodes, without requiring surgery.

- Nanoscale drug delivery devices are being developed to deliver anticancer therapeutics specifically to tumors. Liposomes are one such "first generation" nanoscale device. Liposomal doxorubicin is used to treat specific forms of cancer, while liposomal amphotericin B treats fungal infections often associated with aggressive anticancer treatment. Recently, a nanoparticulate formulation of the well-known anticancer compound taxol was submitted as a new treatment for advanced stage breast cancer.

Source: US NIH

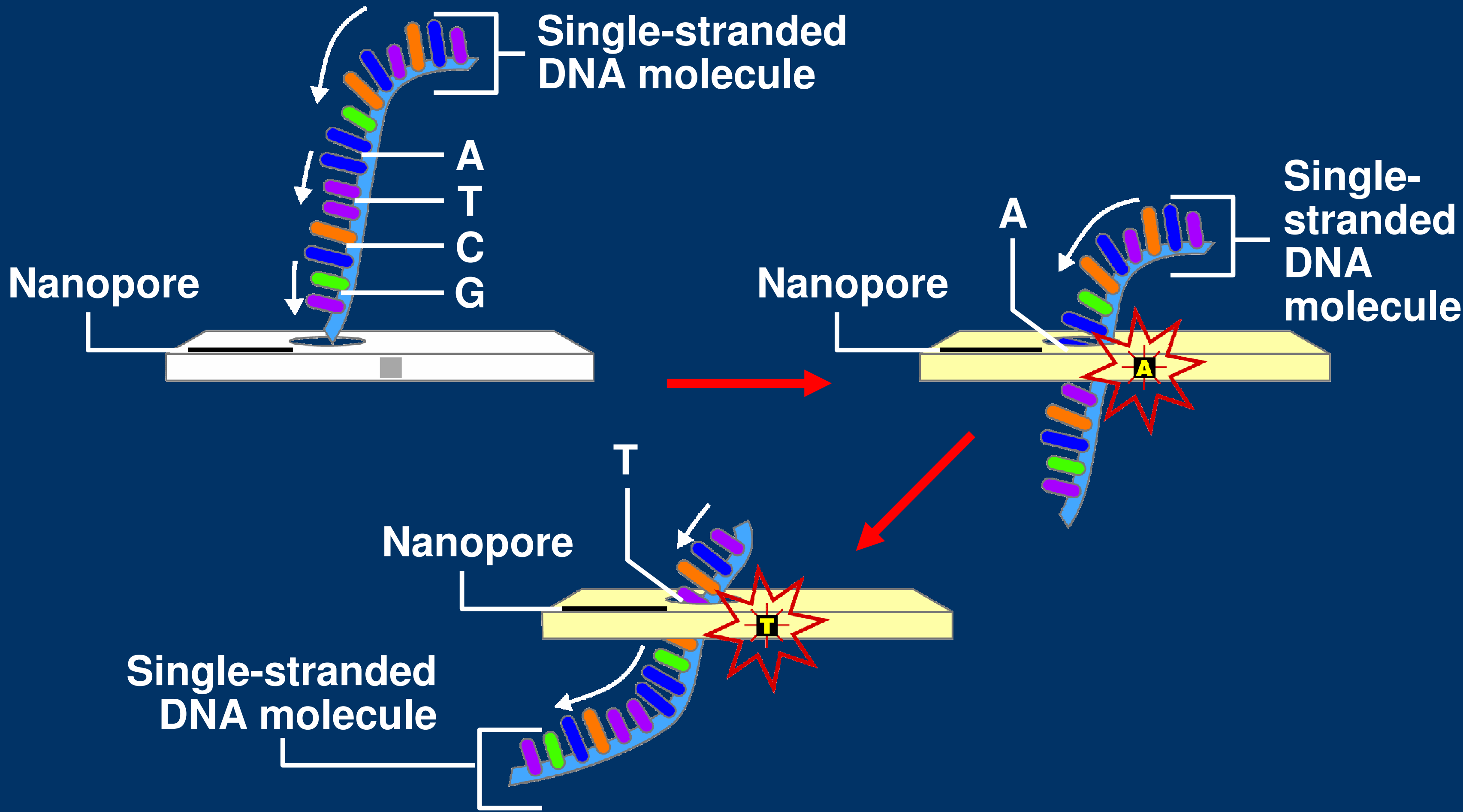
Nanoscience and Medical Research

Nanoscale devices are somewhere from one hundred to ten thousand times smaller than human cells. They are similar in size to large biological molecules ("biomolecules") such as enzymes and receptors. As an example, hemoglobin, the molecule that carries oxygen in red blood cells, is approximately 5 nanometers in diameter. Nanoscale devices smaller than 50 nanometers can easily enter most cells, while those smaller than 20 nanometers can move out of blood vessels as they circulate through the body.

Because of their small size, nanoscale devices can readily interact with biomolecules on both the surface of cells and inside of cells. By gaining access to so many areas of the body, they have the potential to detect disease and deliver treatment in ways unimagined before now. And since biological processes, including events that lead to cancer, occur at the nanoscale at and inside cells, nanotechnology offers a wealth of tools that are providing cancer researchers with new and innovative ways to diagnose and treat cancer.

Source: US National Cancer Institute

Nanopores and genetical information

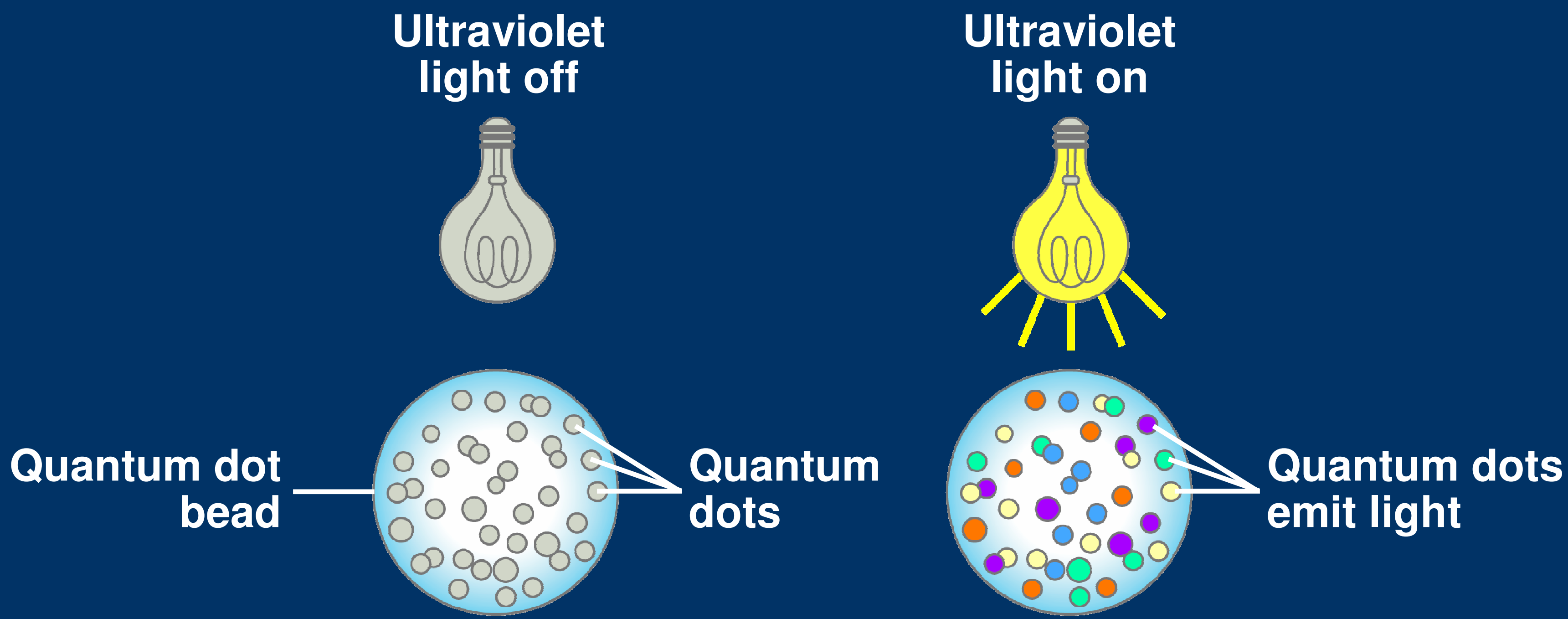


Improved methods of reading the genetic code will help researchers detect errors in genes that may contribute to cancer. Scientists believe nanopores, tiny holes that allow DNA to pass through one strand at a time, will make DNA sequencing more efficient.

As DNA passes through a nanopore, scientists can monitor the shape and electrical properties of each base, or letter, on the strand. Because these properties are unique for each of the four bases that make up the genetic code, scientists can use the passage of DNA through a nanopore to decipher the encoded information, including errors in the code known to be associated with cancer.

Source: US National Cancer Institute

Quantum dots and genetical information

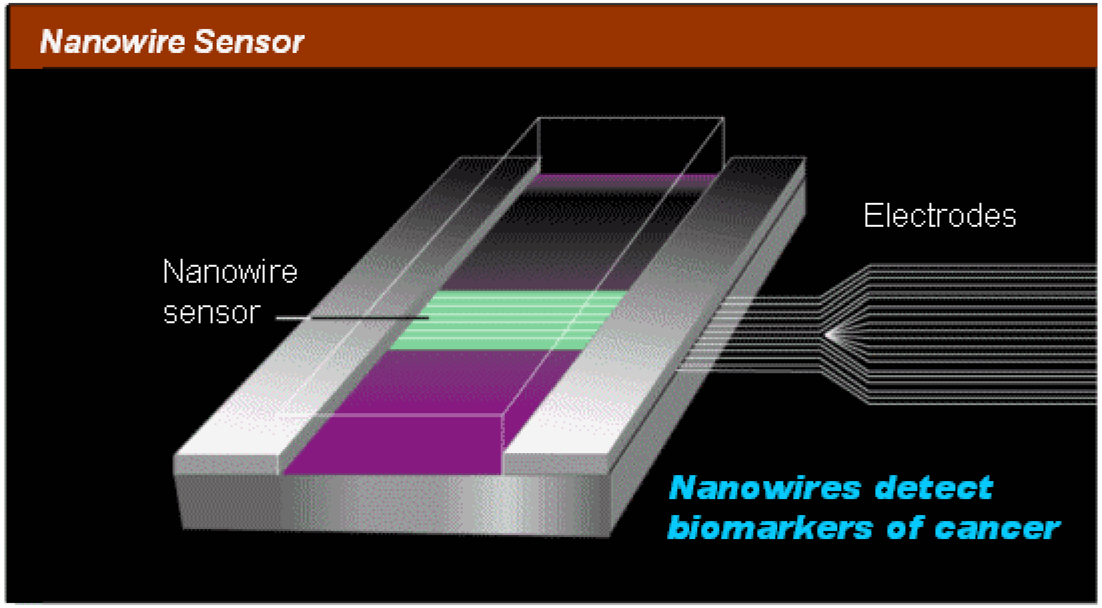


Another minuscule molecule that will be used to detect cancer is a quantum dot. Quantum dots are tiny crystals that glow when they are stimulated by ultraviolet light. The wavelength, or color, of the light depends on the size of the crystal. Latex beads filled with these crystals can be designed to bind to specific DNA sequences.

By combining different sized quantum dots within a single bead, scientists can create probes that release distinct colors and intensities of light. When the crystals are stimulated by UV light, each bead emits light that serves as a sort of spectral bar code, identifying a particular region of DNA.

Source: US National Cancer Institute

Nanowires as biological sensors

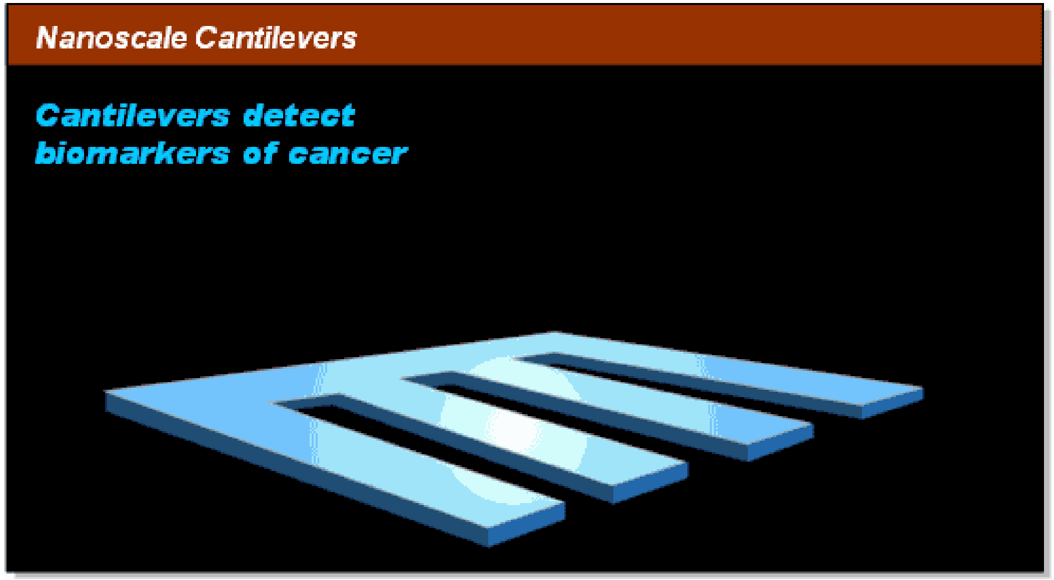


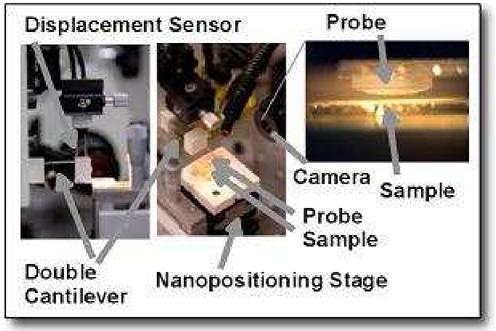
In this diagram, nano sized sensing wires are laid down across a microfluidic channel. These nanowires by nature have incredible properties of selectivity and specificity. As particles flow through the microfluidic channel, the nanowire sensors pick up the molecular signatures of these particles and can immediately relay this information through a connection of electrodes to the outside world.

These nanodevices are man-made constructs made with carbon, silicon and other materials that have the capability to monitor the complexity of biological phenomenon and relay the information, as it is monitored, to the medical care provider. They can detect the presence of altered genes associated with cancer and may help researchers pinpoint the exact location of those changes.

Source: US National Cancer Institute
Reference: Jim Heath, CalTech

Nanoscale - cantilevers



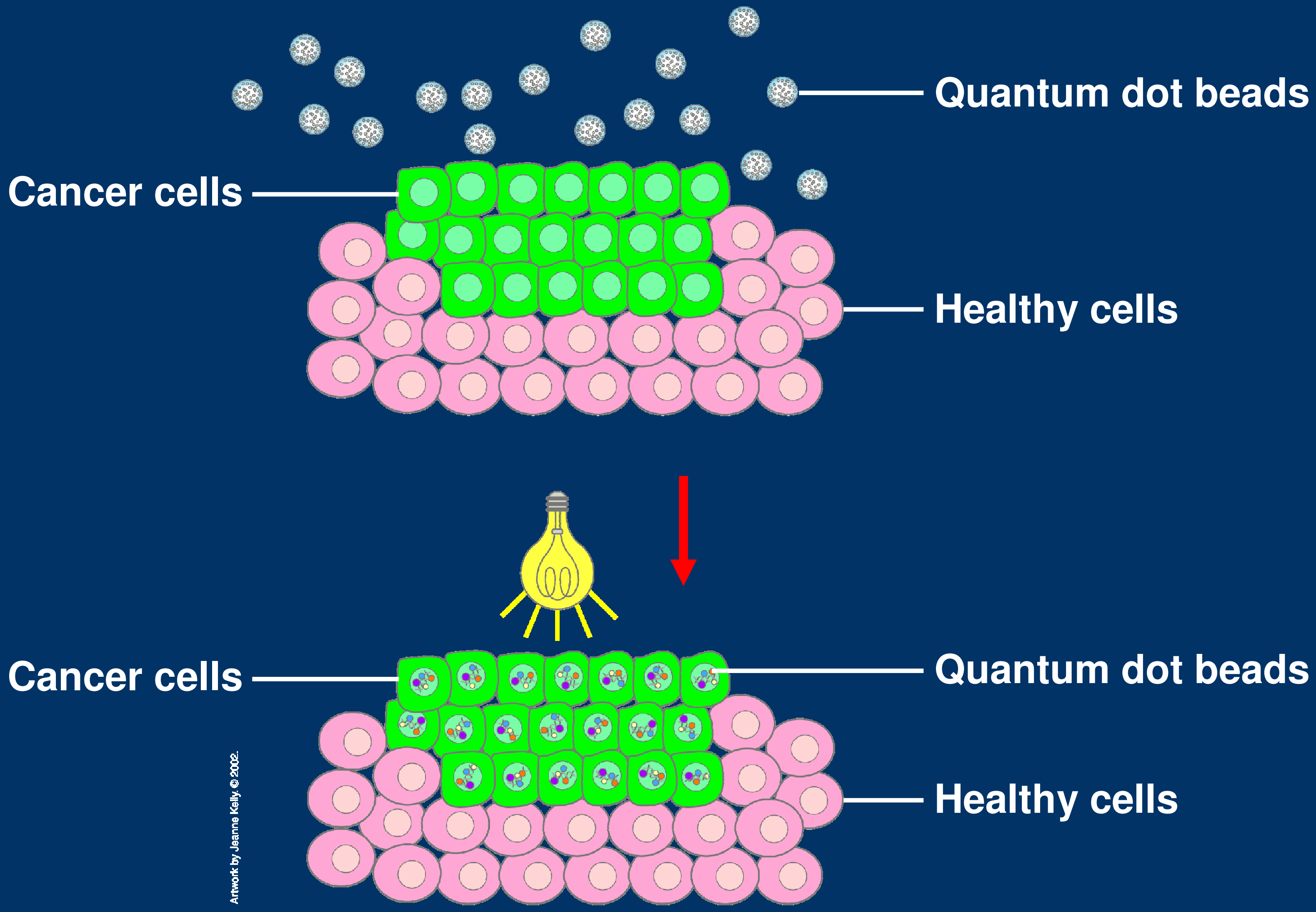


Nanoscale cantilevers - microscopic, flexible beams resembling a row of diving boards - are built using semiconductor lithographic techniques. These can be coated with molecules capable of binding specific substrates-DNA complementary to a specific gene sequence, for example. Such micron-sized devices, comprising many nanometer-sized cantilevers, can detect single molecules of DNA or protein.

As a cancer cell secretes its molecular products, the antibodies coated on the cantilever fingers selectively bind to these secreted proteins. These antibodies have been designed to pick up one or more different, specific molecular expressions from a cancer cell. The physical properties of the cantilevers change as a result of the binding event. Researchers can read this change in real time and provide not only information about the presence and the absence but also the concentration of different molecular expressions. Nanoscale cantilevers, constructed as part of a larger diagnostic device, can provide rapid and sensitive detection of cancer-related molecules.

Source: US National Cancer Institute
Reference: Arun Majumdar, UC Berkeley

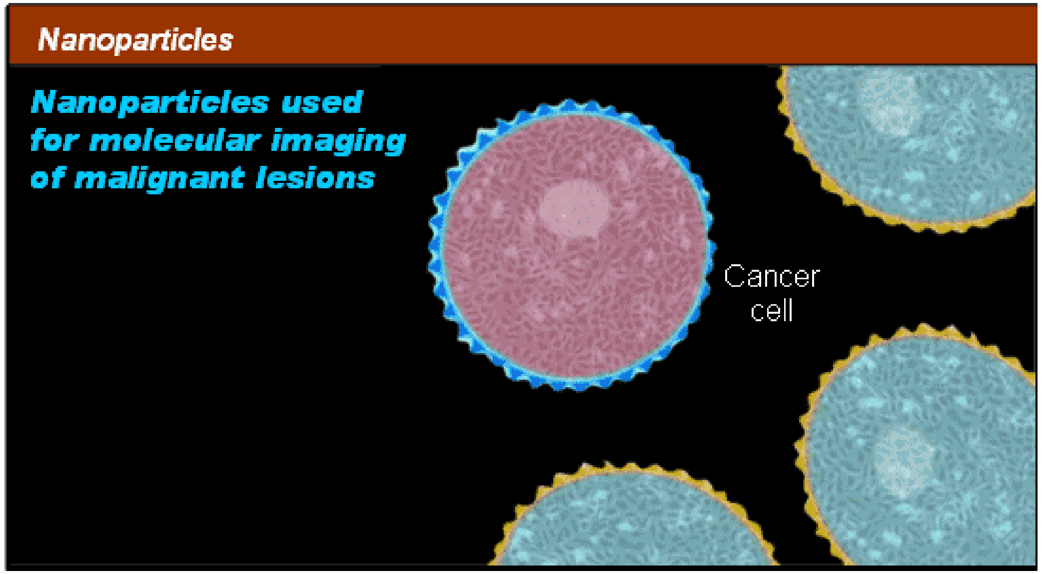
Quantum dots and medical imaging



To detect cancer, scientists can design quantum dots that bind to sequences of DNA that are associated with the disease. When the quantum dots are stimulated with light, they emit their unique bar codes, or labels, making the critical, cancer-associated DNA sequences visible.

Source: US National Cancer Institute

Nanoparticles and medical imaging

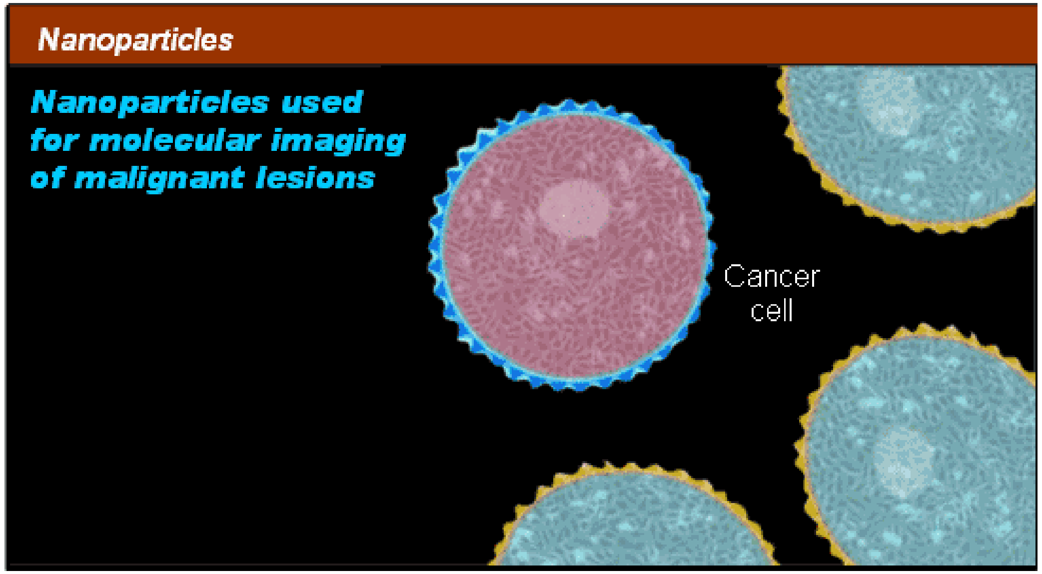


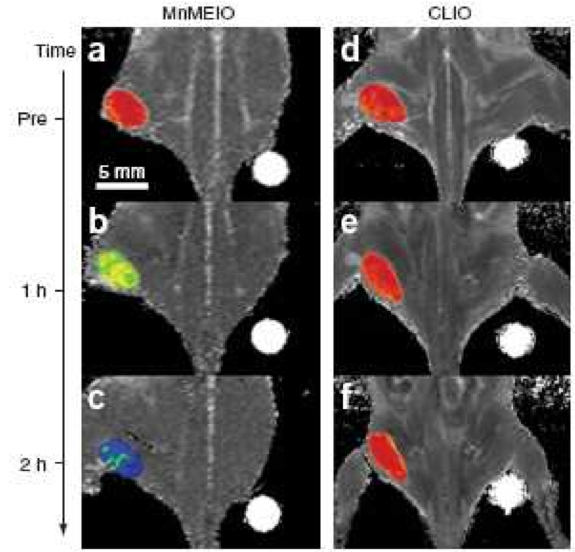
In this example, nanoparticles are targeted to cancer cells for use in the molecular imaging of a malignant lesion. Large numbers of nanoparticles are safely injected into the body and preferentially bind to the cancer cell, defining the anatomical contour of the lesion and making it visible.

These nanoparticles give us the ability to see cells and molecules that we otherwise cannot detect through conventional imaging. The ability to pick up what happens in the cell - to monitor therapeutic intervention and to see when a cancer cell is mortally wounded or is actually activated - is critical to the successful diagnosis and treatment of the disease.

Source: US National Cancer Institute
Reference: Ed Neuwelt, Oregon Health Sciences Univ.

Nanoparticles and medical imaging





In vivo MR detection of cancer using magnetic nanoparticle–Herceptin conjugates. (a–f) Color maps of T2-weighted MR images of a mouse implanted with the cancer cell line NIH3T6.7, at different time points.
Lee *et al.*, Nature Medicine **13**, 95 (2007).

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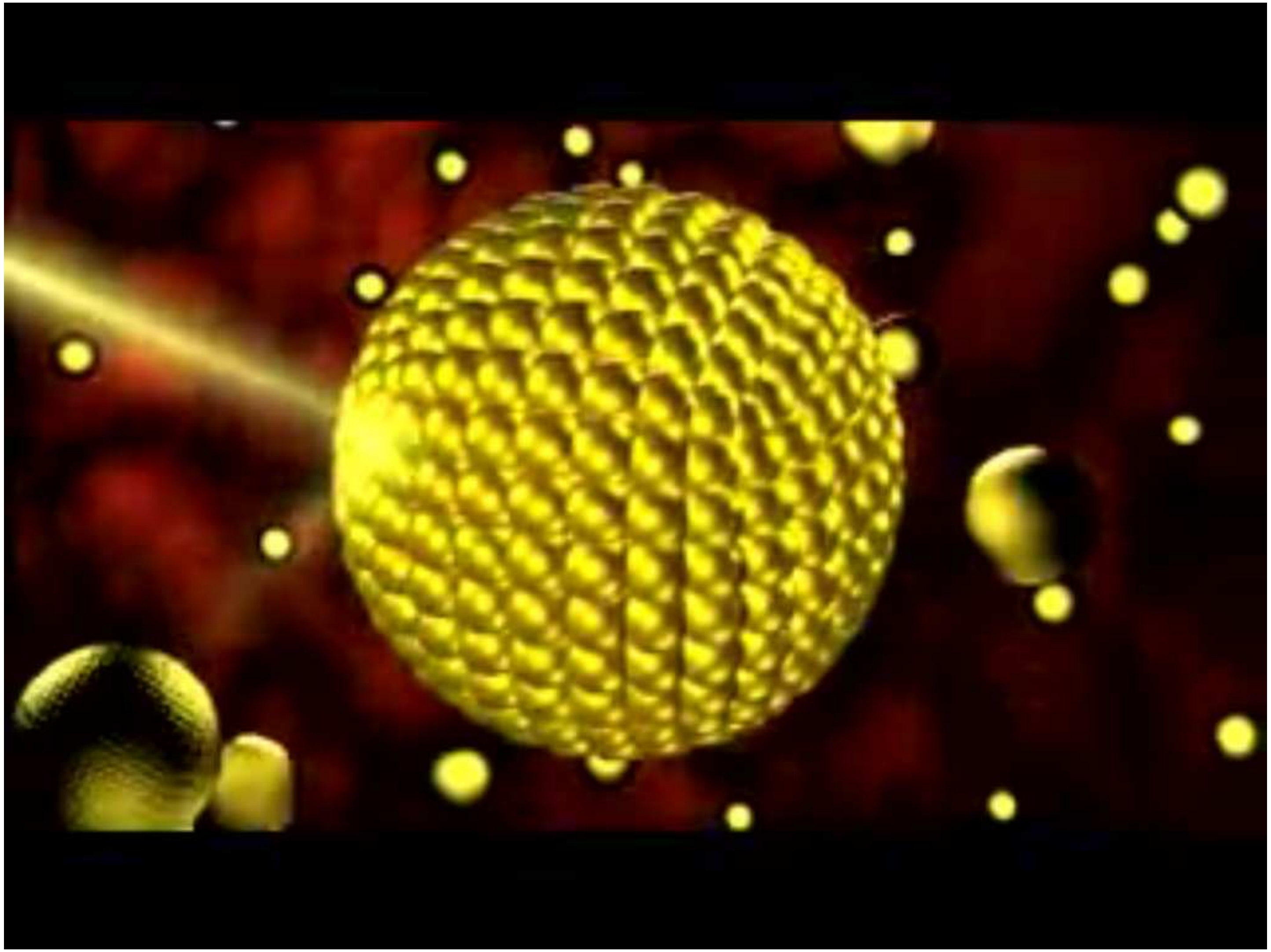
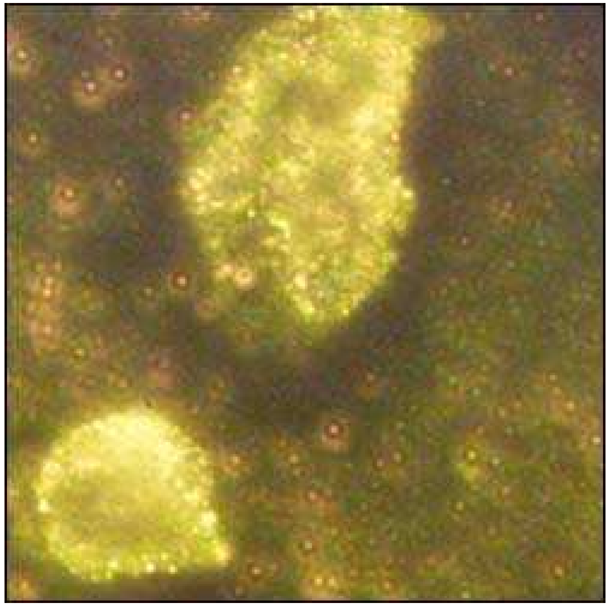
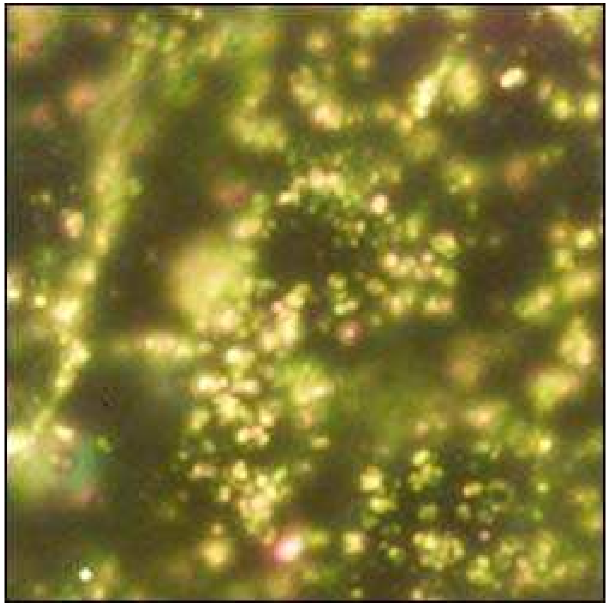
Gold nanoparticles





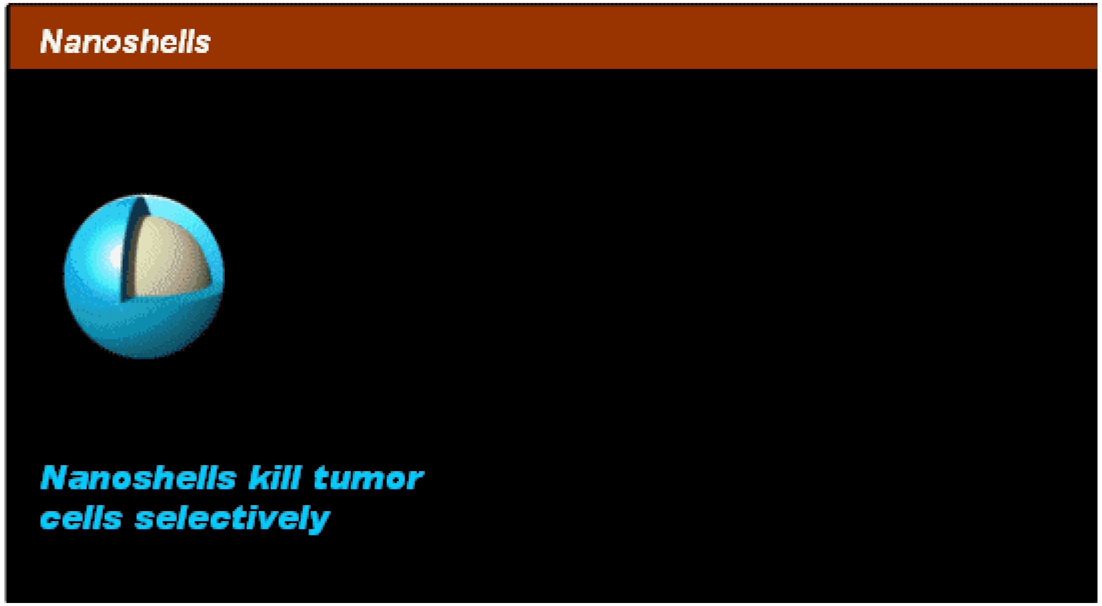
Gold nanoparticles stick to cancer cells and make them shine.



Gold nanoparticles don't stick as well to noncancerous cells. The results can be seen with a simple microscope.

Mostafa El-Sayed, Georgia Tech

Nanoshells and medical therapies



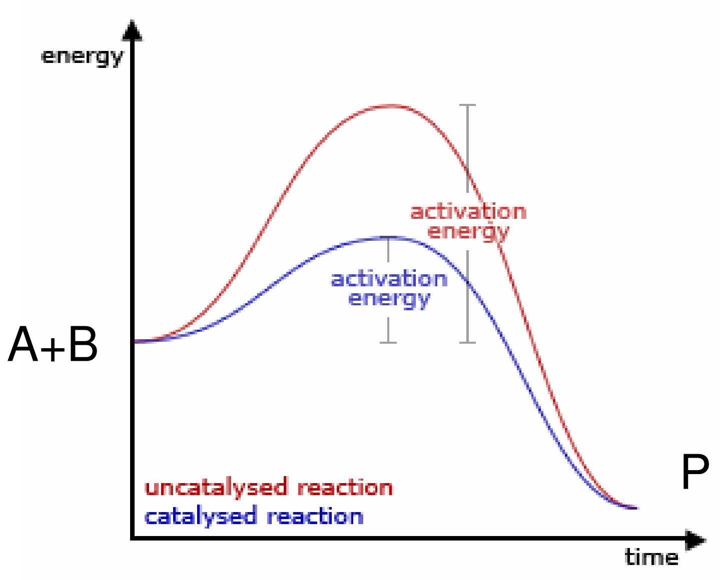
Nanoshells have a core of silica and a metallic outer layer. These nanoshells can be injected safely and will preferentially concentrate in cancer lesion sites. This physical selectivity occurs through a phenomenon called enhanced permeation retention (EPR).

Scientists can further decorate the nanoshells to carry molecular conjugates to the antigens that are expressed on the cancer cells themselves or in the tumor microenvironment. This second degree of specificity preferentially links the nanoshells to the tumor and not to neighboring healthy cells. As shown in this example, scientists can then externally supply energy to these cells. The specific properties associated with nanoshells allow for the absorption of this directed energy, creating an intense heat that selectively kills the tumor cells.

Source: US National Cancer Institute
Reference: Jennifer West, Rice University

NANOCATALYSIS

CATALYSIS:
The effect produced in facilitating a chemical reaction, by the presence of a substance, which itself undergoes no permanent change.
(Oxford english dictionary)

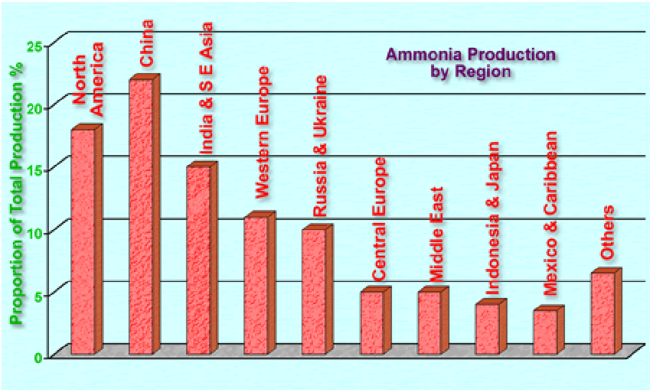


A+B → P direct reaction
A+B+C → P+C catalyzed reaction

A and B are reactants
C is the catalyst
P is the reaction product

HETEROGENEOUS CATALYSIS:
The catalyst is a surface (reactions are made in the nanoscale).
Typically, in order for the reaction to occur, one or more of the reactants must diffuse to the catalyst surface and adsorb onto it. After reaction, the products must desorb from the surface and diffuse away from the solid surface.
The reaction rate is determined by the reaction probability of all processes involved.

Example, synthesis of ammonia:
$3H_2(g) + N_2\,(g) \leftrightarrow 2NH_3(g)$ - catalyzed by Fe surface
World production: 130 million tons (year 2000), ~200US$/ton



Another example, catalysis in car industry:
In car engines, incomplete combustion of the fuel produces CO, which is toxic.
The electric spark and high temperatures also allow oxygen and nitrogen to react and form NO and NO_2, which are responsible for photochemical smog and acid rain.
Catalytic converters reduce such emissions by adsorbing CO and NO onto a catalytic surface, where the gases undergo a redox reaction. CO_2 and N_2 are desorbed from the surface and emitted as relatively harmless gases:

$$2CO + 2NO \quad\quad 2CO_2 + N_2$$

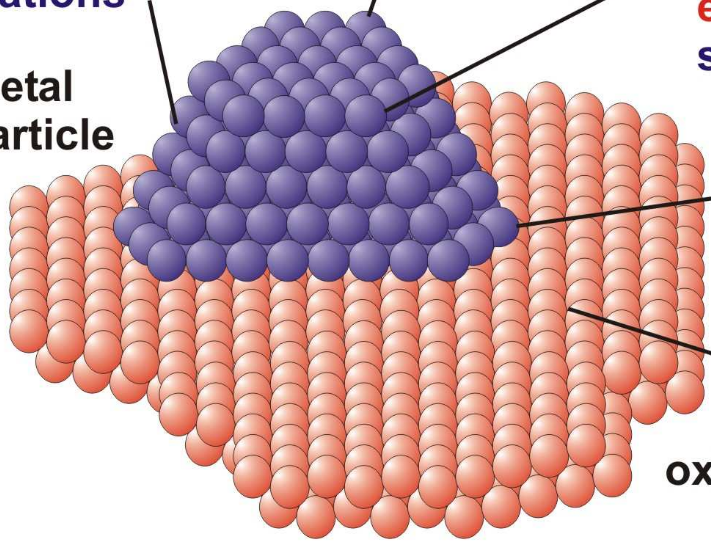
Today's key factors in the development of chemical processes are the concepts of "zero-waste" and "100 % selectivity".

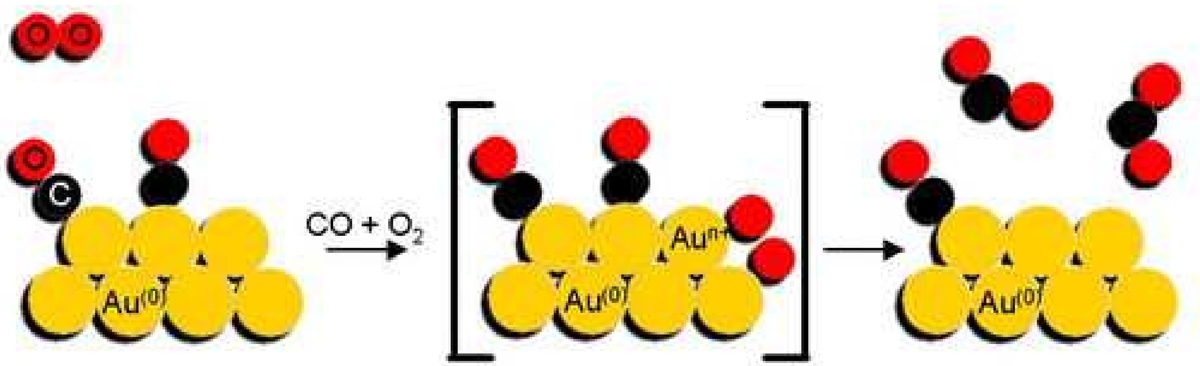
In the field of catalysis, the chemistry at interphases, referred to as heterogeneous catalysis, is promising to achieve both goals.

MB Experiments in Catalysis

Beyond Single Crystal Kinetics

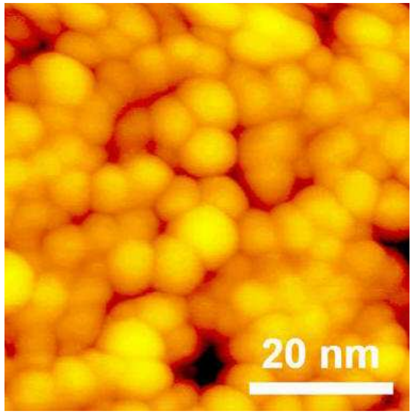
Some Kinetic Effects on Catalyst Surfaces:





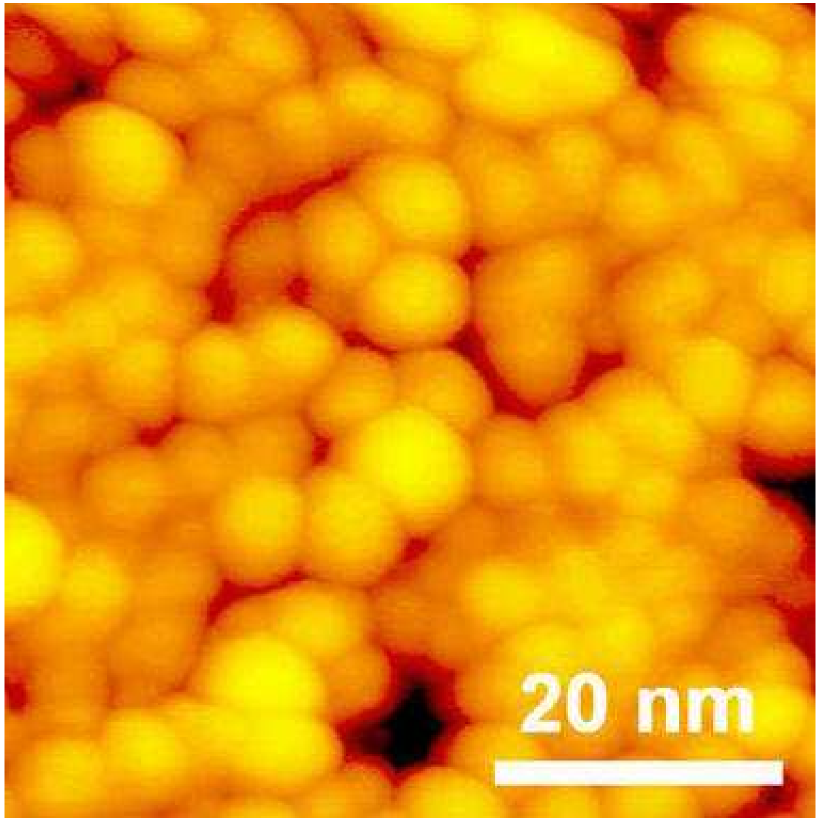
Gold has always been perceived as a precious material: you win a gold medal when you prove to be the best in a competition; you only get a Gold credit card when you are a preferential customer, and the jewelry made of this material is amongst the most valuable. However, gold has also unexpected properties: It can act as a catalyst and transform carbon monoxide (CO) to carbon dioxide (CO_2) when it comes in the form of tiny pieces, called nano-particles.

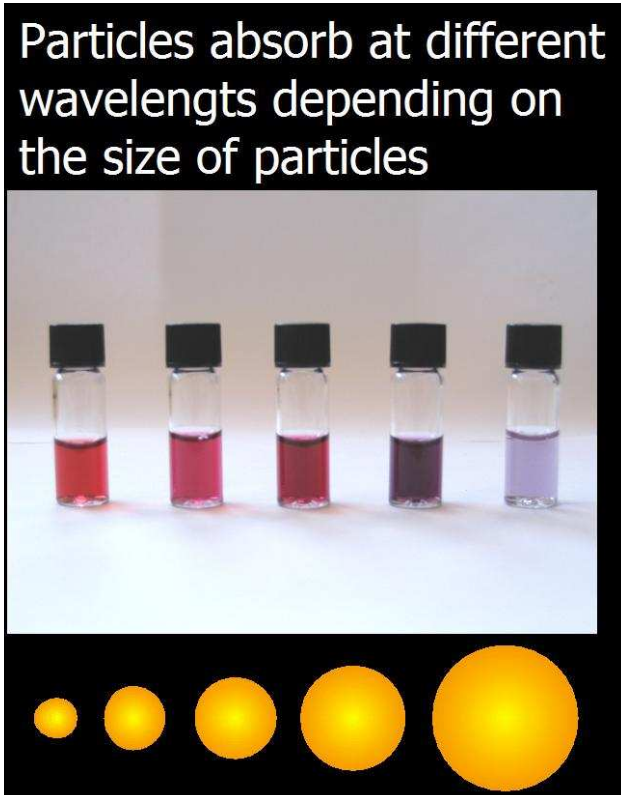
The most inert bulk metal is very reactive when finely dispersed



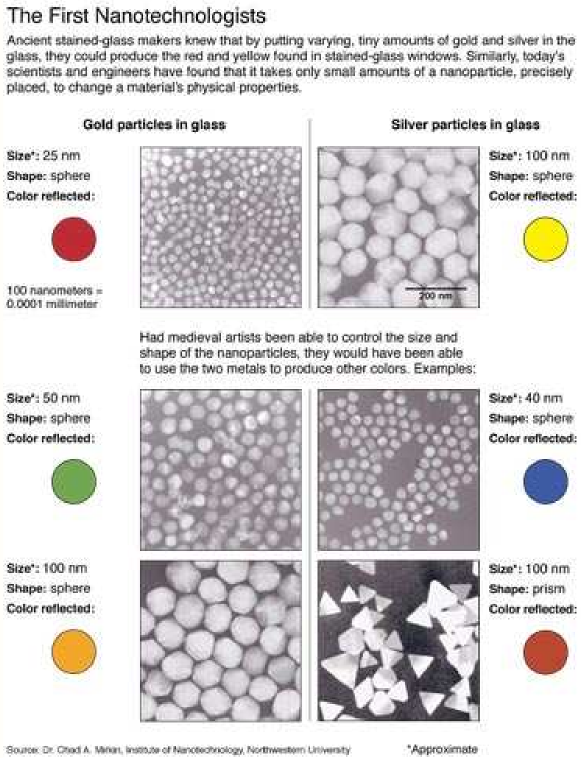
Increased emphasis is being placed on using gold catalysts for selective oxidation. For example, the oxidation of alkanes, alkenes, and alcohols have all been shown to be effective with gold-based catalysts.

Gold Nanoparticles





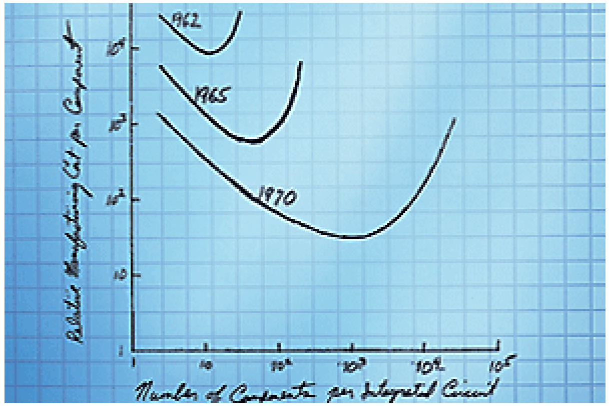
Gold nanoparticles were already used in medieval stained glasses

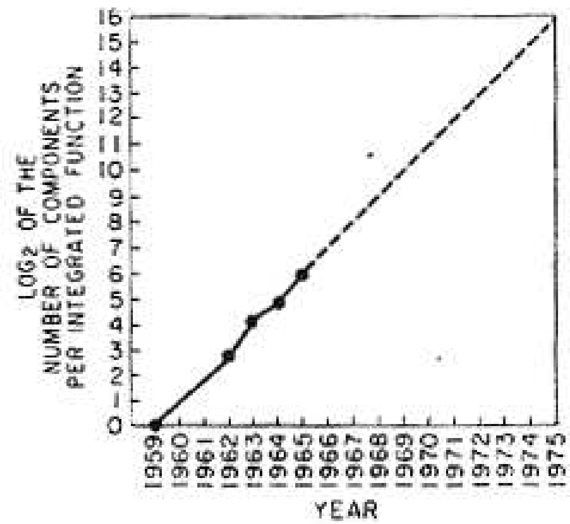


SEMICONDUCTOR INDUSTRY

Moore's Law

Gordon Moore, a physical chemist working in electronics, made a prediction in 1965, that computer processing power, or the number of transistors on an integrated chip, would double every 18 months. While he made that prediction just four years after the first planar integrated circuit was discovered, he proved visionary. "Moore's Law," as it was called by the media, has held firm.





Gordon Moore co-founded Intel Corporation in 1968. Today he is the company's Chairman Emeritus.

The experts look ahead

Cramming more components onto integrated circuits

With unit cost falling as the number of components per circuit rises, by 1975 economics may dictate squeezing as many as 65,000 components on a single silicon chip

By Gordon E. Moore
Director, Research and Development Laboratories, Fairchild Semiconductor division of Fairchild Camera and Instrument Corp.

The future of integrated electronics is the future of electronics itself. The advantages of integration will bring about a proliferation of electronics, pushing this science into many new areas.

Integrated circuits will lead to such wonders as home computers—or at least terminals connected to a central computer—automatic controls for automobiles, and personal portable communications equipment. The electronic wristwatch needs only a display to be feasible today.

But the biggest potential lies in the production of large systems. In telephone communications, integrated circuits in digital filters will separate channels on multiplex equipment. Integrated circuits will also switch telephone circuits and perform data processing.

Computers will be more powerful, and will be organized in completely different ways. For example, memories built of integrated electronics may be distributed throughout the machine instead of being concentrated in a central unit. In addition, the improved reliability made possible by integrated circuits will allow the construction of larger processing units. Machines similar to those in existence today will be built at lower costs and with faster turn-around.

The author

Dr. Gordon E. Moore is one of the new breed of electronic engineers, schooled in the physical sciences rather than in electronics. He earned a B.S. degree in chemistry from the University of California and a Ph.D. degree in physical chemistry from the California Institute of Technology. He was one of the founders of Fairchild Semiconductor and has been director of the research and development laboratories since 1959.

Present and future

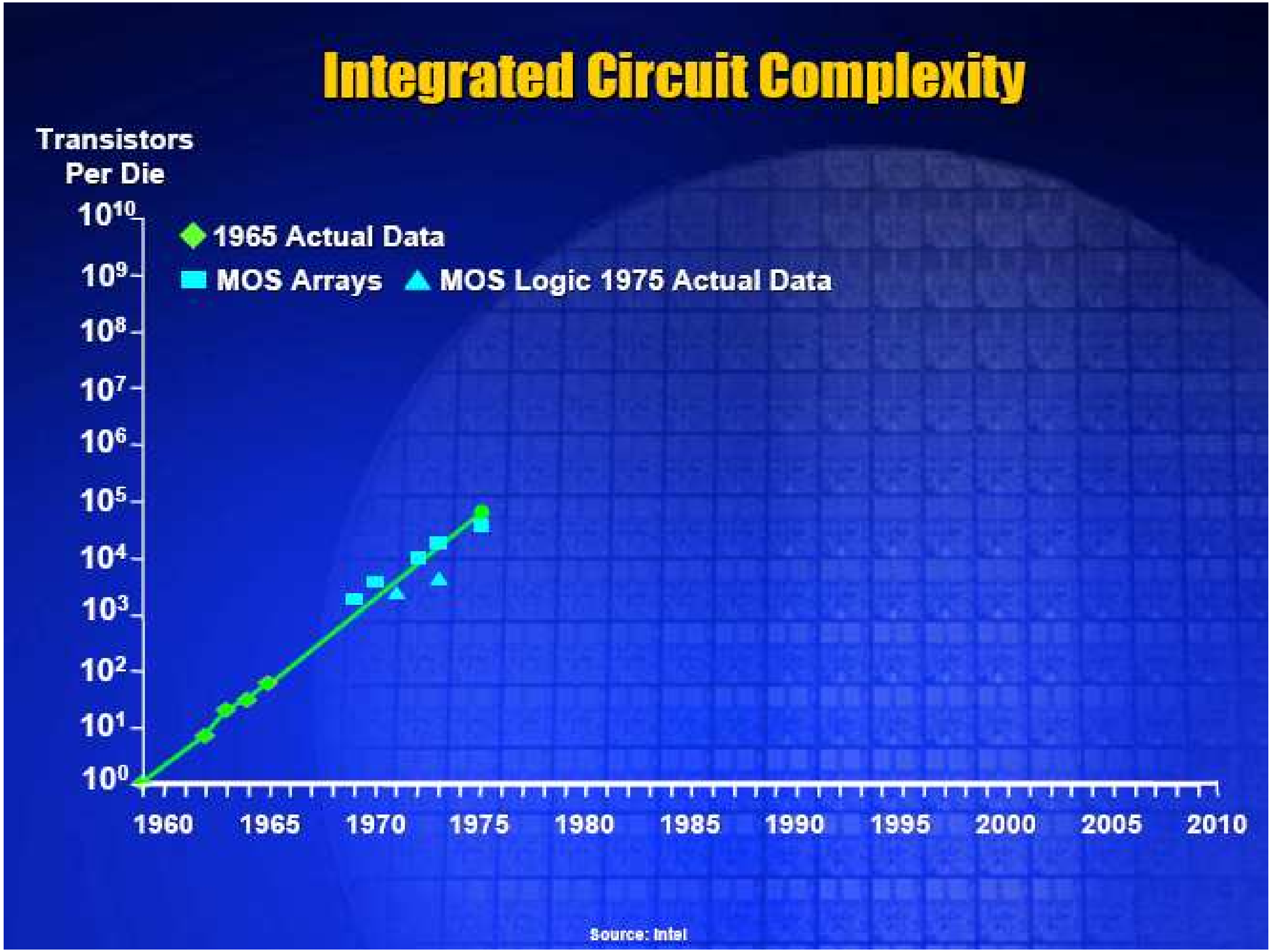
By integrated electronics, I mean all the various technologies which are referred to as microelectronics today as well as any additional ones that result in electronics functions supplied to the user as irreducible units. These technologies were first investigated in the late 1950's. The object was to miniaturize electronics equipment to include increasingly complex electronic functions in limited space with minimum weight. Several approaches evolved, including microassembly techniques for individual components, thin-film structures and semiconductor integrated circuits.

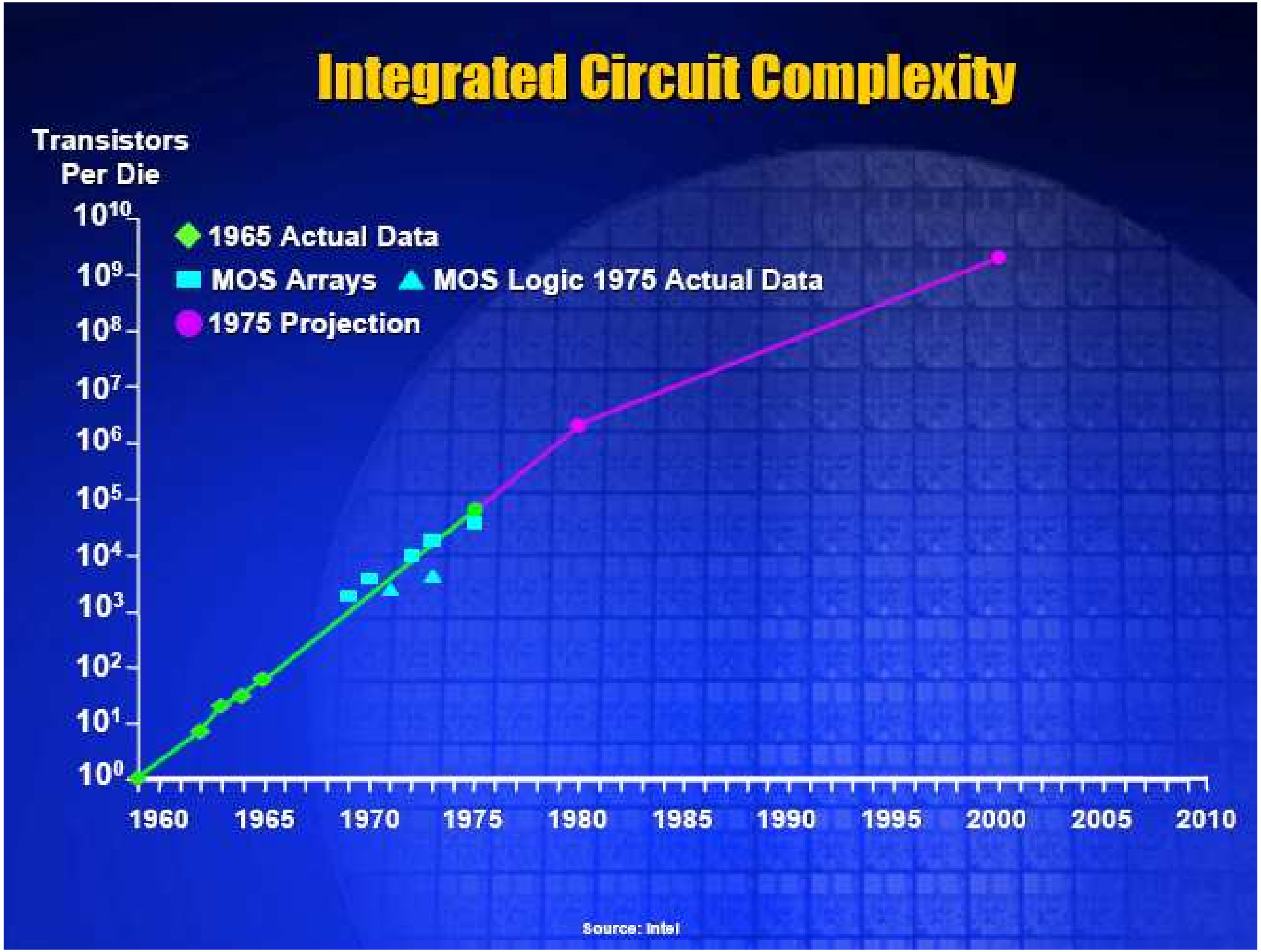
Each approach evolved rapidly and converged so that each borrowed techniques from another. Many researchers believe the way of the future to be a combination of the various approaches.

The advocates of semiconductor integrated circuitry are already using the improved characteristics of thin-film resistors by applying such films directly to an active semiconductor substrate. Those advocating a technology based upon films are developing sophisticated techniques for the attachment of active semiconductor devices to the passive film arrays.

Both approaches have worked well and are being used in equipment today.

Electronics, Volume 38, Number 8, April 19, 1965


Integrated Circuit Complexity
Transistors Per Die
10^10
10^9
10^8
10^7
10^6
10^5
10^4
10^3
10^2
10^1
10^0
1965 Actual Data
MOS Arrays
MOS Logic 1975 Actual Data
1960
1965
1970
1975
1980
1985
1990
1995
2000
2005
2010
Source: Intel


Integrated Circuit Complexity
Transistors Per Die
10^{10}
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1965 Actual Data
MOS Arrays
MOS Logic 1975 Actual Data
1975 Projection
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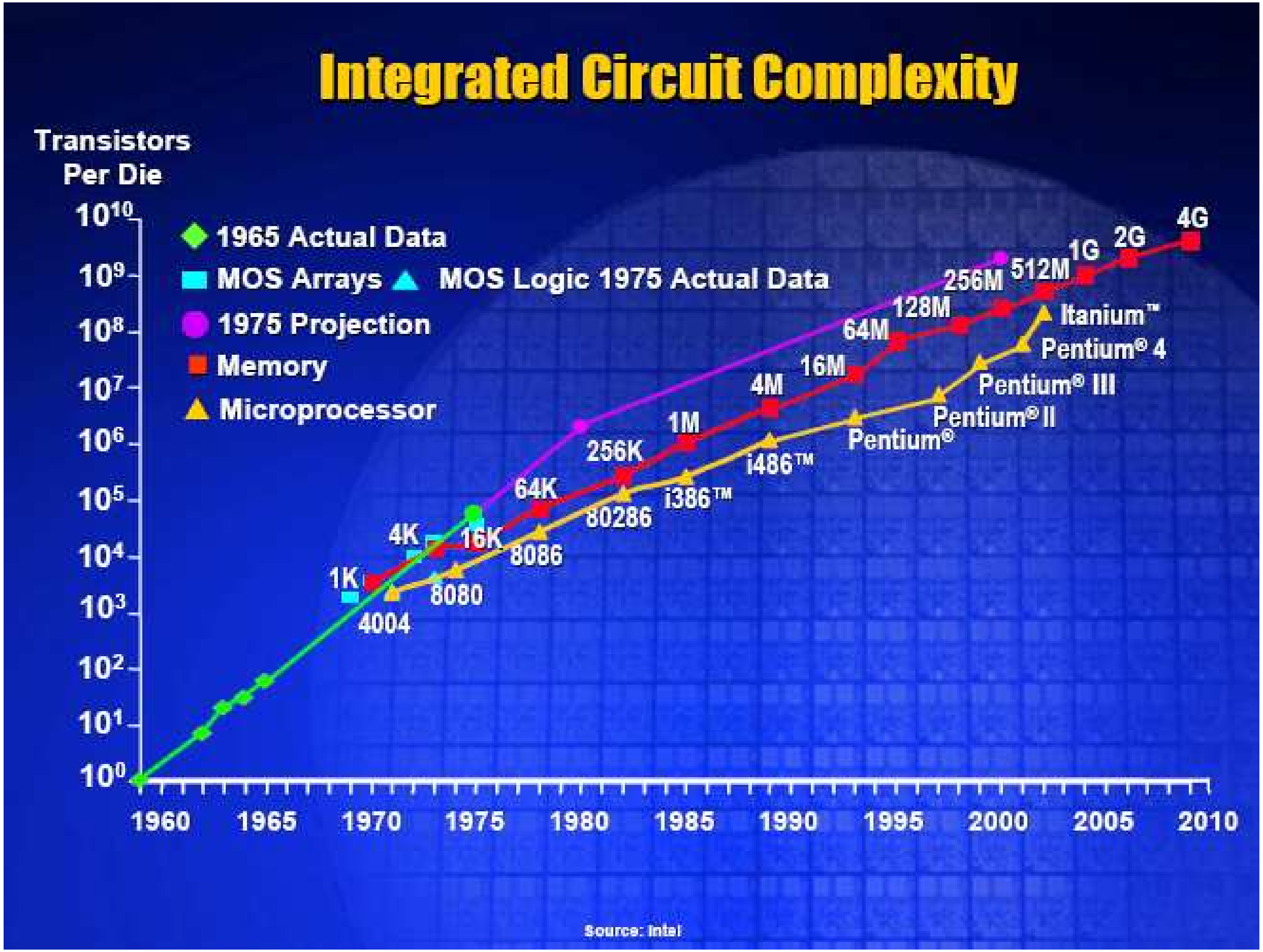
Source: Intel


Integrated Circuit Complexity
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MOS Arrays
MOS Logic 1975 Actual Data
1975 Projection
Memory
Microprocessor
10^{10}
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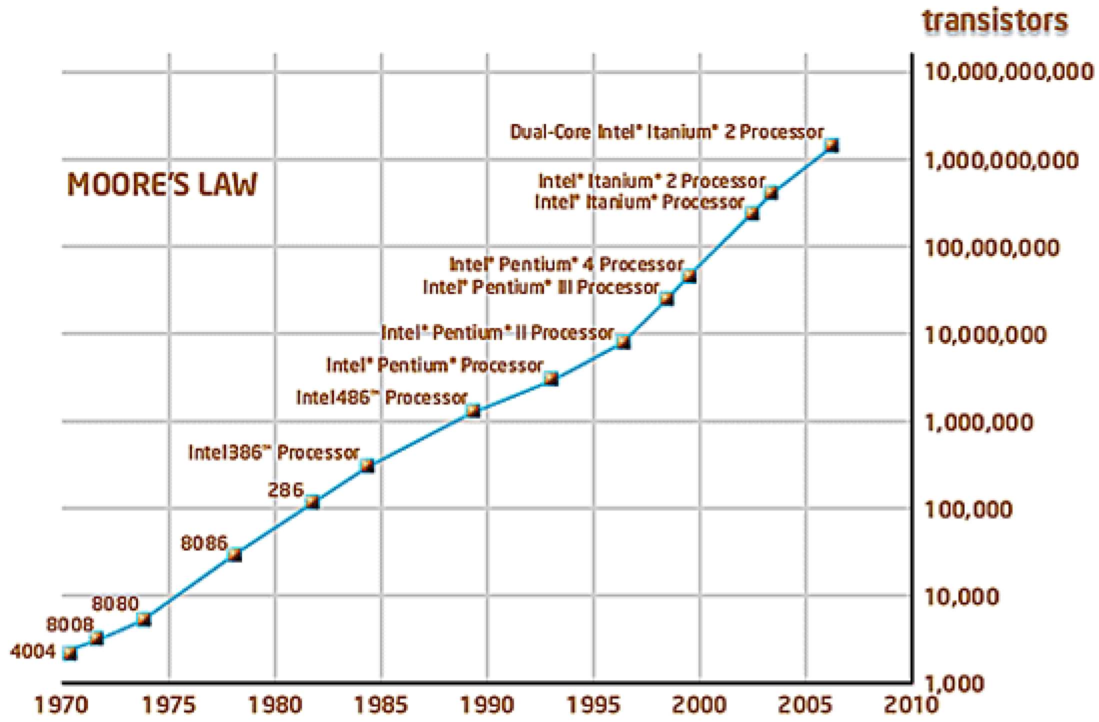
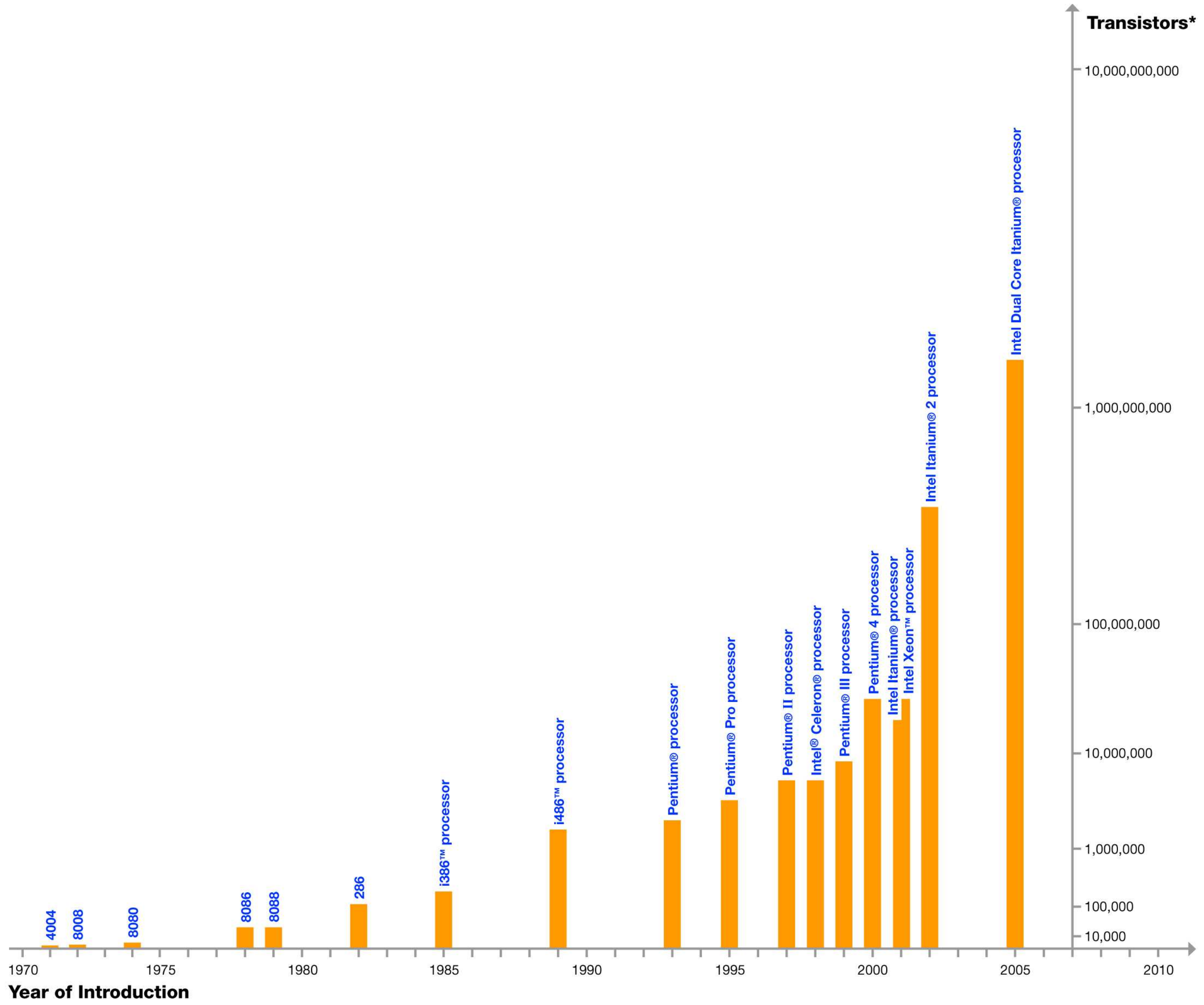
1K
4K
16K
64K
256K
1M
4M
16M
64M
128M
256M
512M
1G
2G
4G
4004
8080
8086
80286
i386™
i486™
Pentium®
Pentium® II
Pentium® III
Pentium® 4
Itanium™
Source: Intel

Moore’s Law (more modern version)



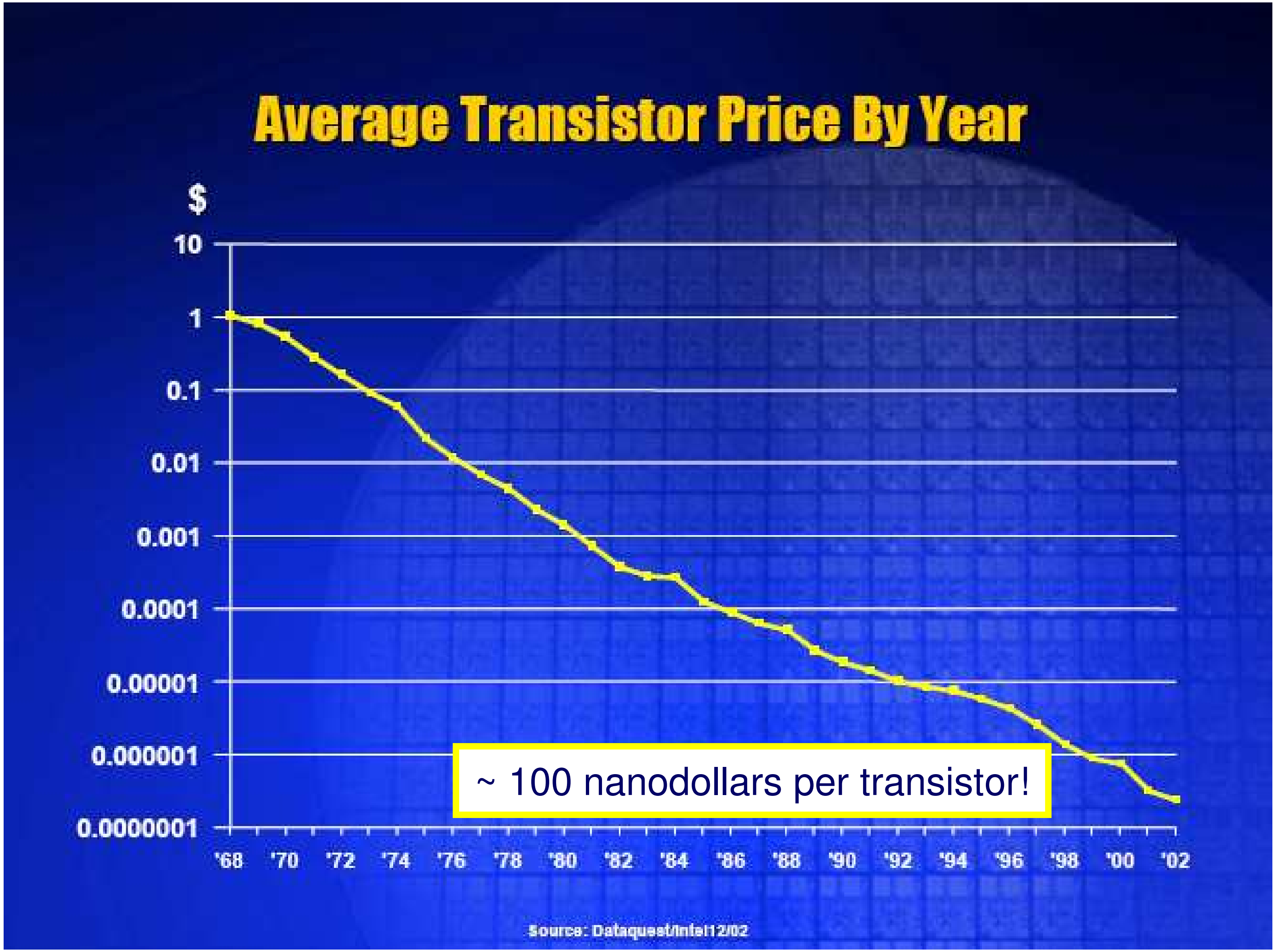
But will Moore’s Law continue to stand? Experts—and Moore himself —believe that technological breakthroughs are needed if this trend is to continue. To sustain Moore's Law, transistors must be scaled down to at least nine nanometers by 2016, according to the Consortium of International Semiconductor Companies.



*Note: Vertical scale of chart not proportional to actual Transistor count.

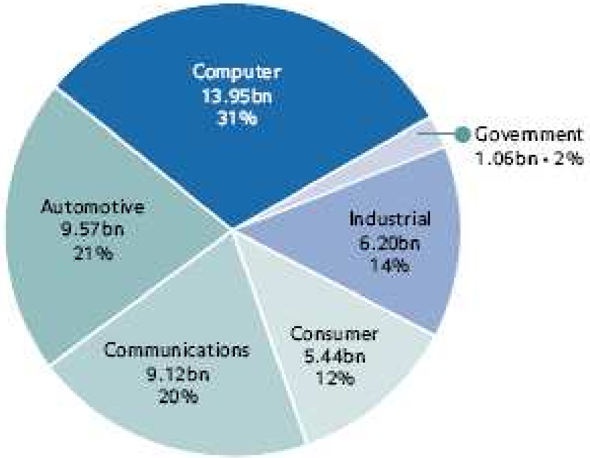
Gordon Moore estimated in 2003 that the number of transistors shipped in a year had reached about 10,000,000,000,000,000,000 (10^{19}). That's about 100 times the number of ants estimated to be in the world.

In 1978, a commercial flight between New York and Paris cost around $900 and took seven hours. If the principles of Moore's Law had been applied to the airline industry the way they have to the semiconductor industry since 1978, that flight would now cost about a penny and take less than one second.

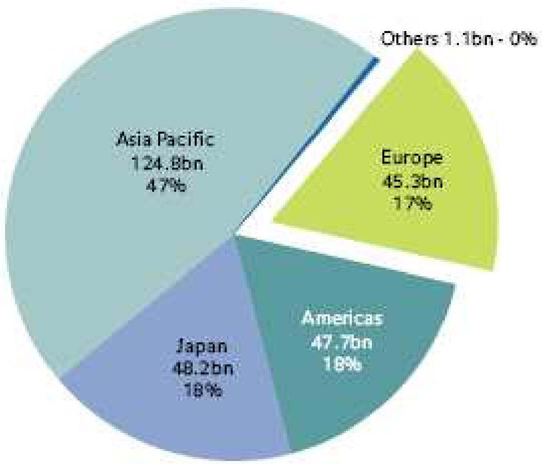

Average Transistor Price By Year
$
10
1
0.1
0.01
0.001
0.0001
0.00001
0.000001
0.0000001
'68
'70
'72
'74
'76
'78
'80
'82
'84
'86
'88
'90
'92
'94
'96
'98
'00
'02
~ 100 nanodollars per transistor!
Source: Dataquest/Intel12/02

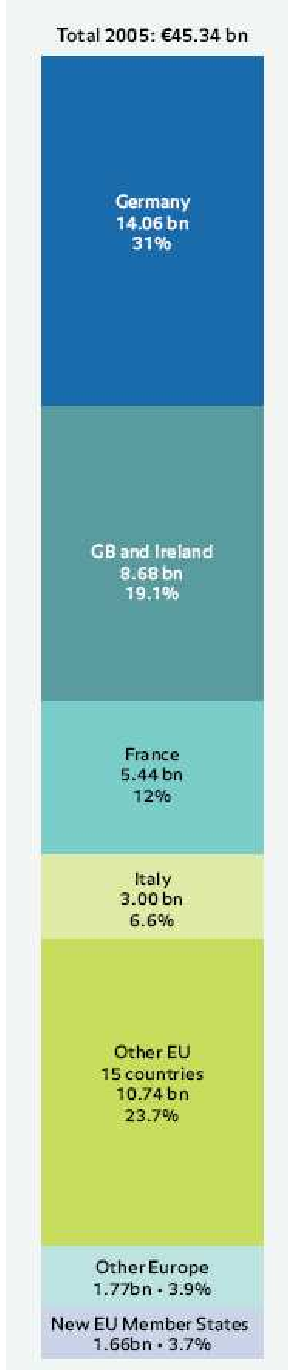

Worldwide Semiconductor Revenues
$B
1000
100
10
1
'68
'70
'72
'74
'76
'78
'80
'82
'84
'86
'88
'90
'92
'94
'96
'98
'00
'02
Source: Intel/WSTS,12/02

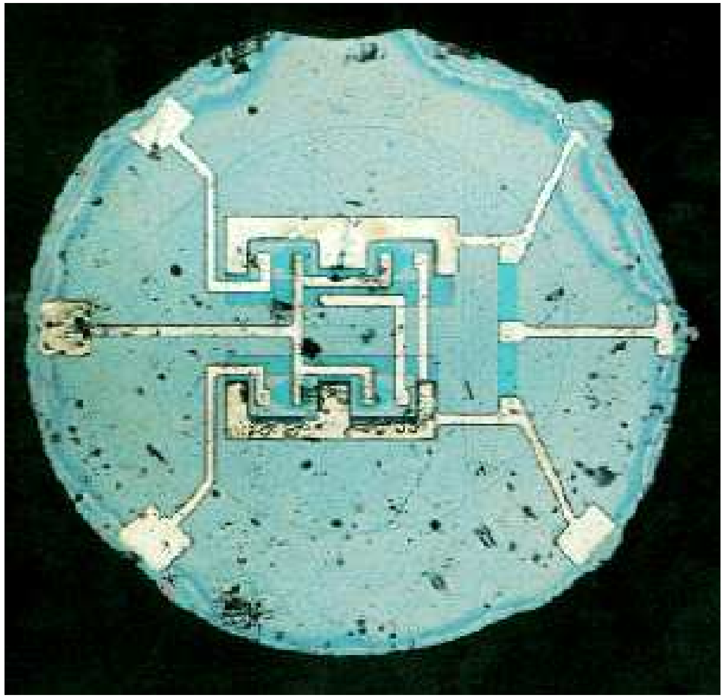
Electronic components markets in Europe – all applications 2005.
Total: €45.3 bn



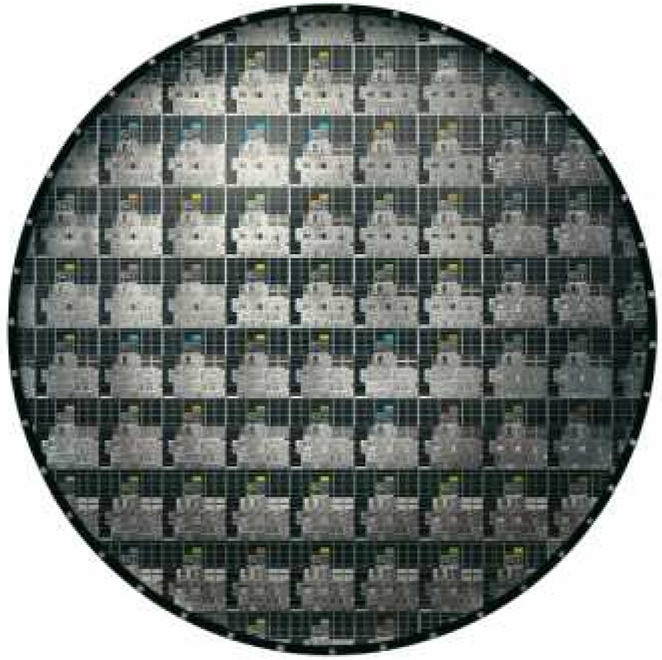
Electronic components worldwide – market size by region 2005.
Total value €267 bn





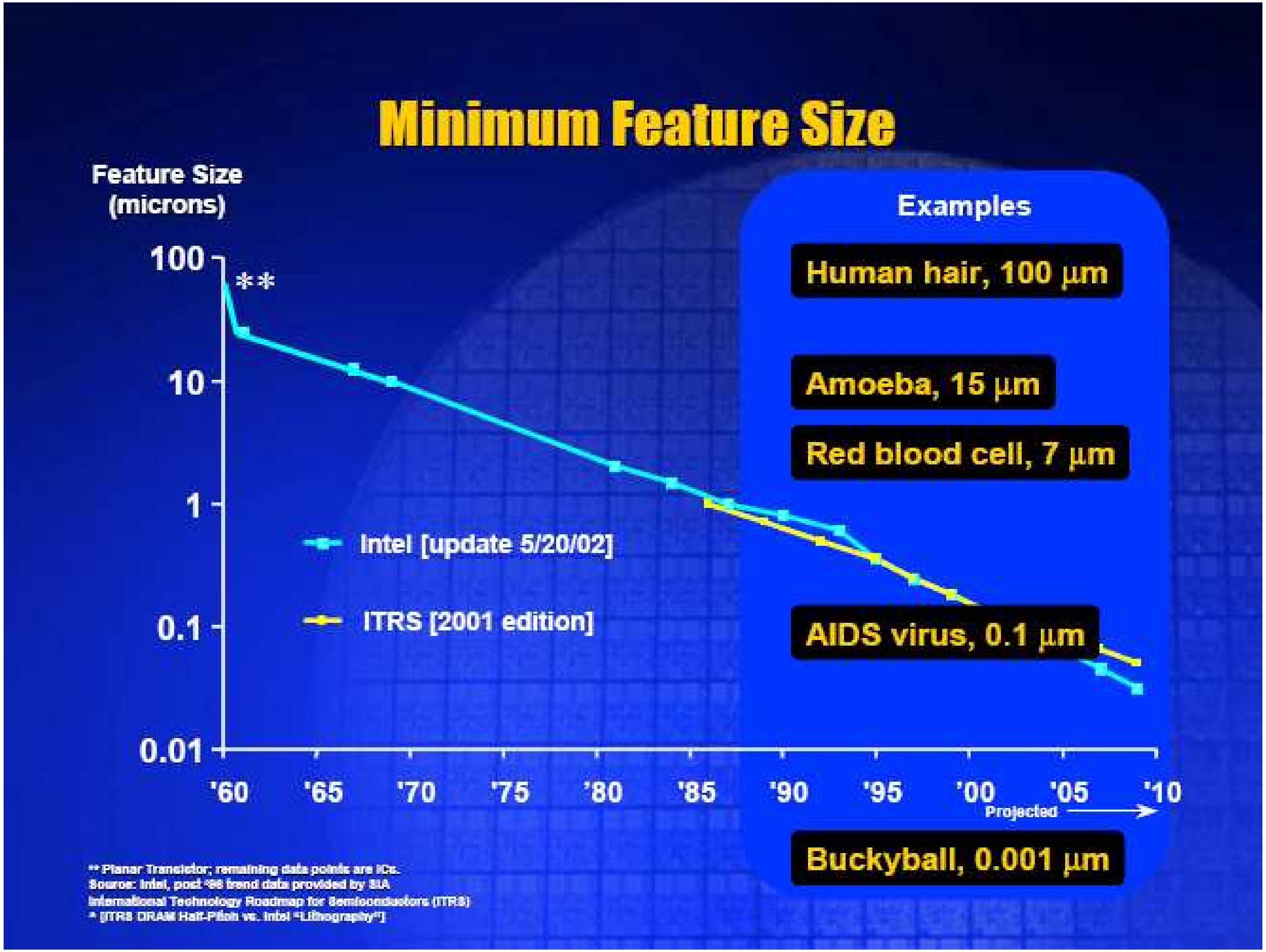


The first planar integrated circuit

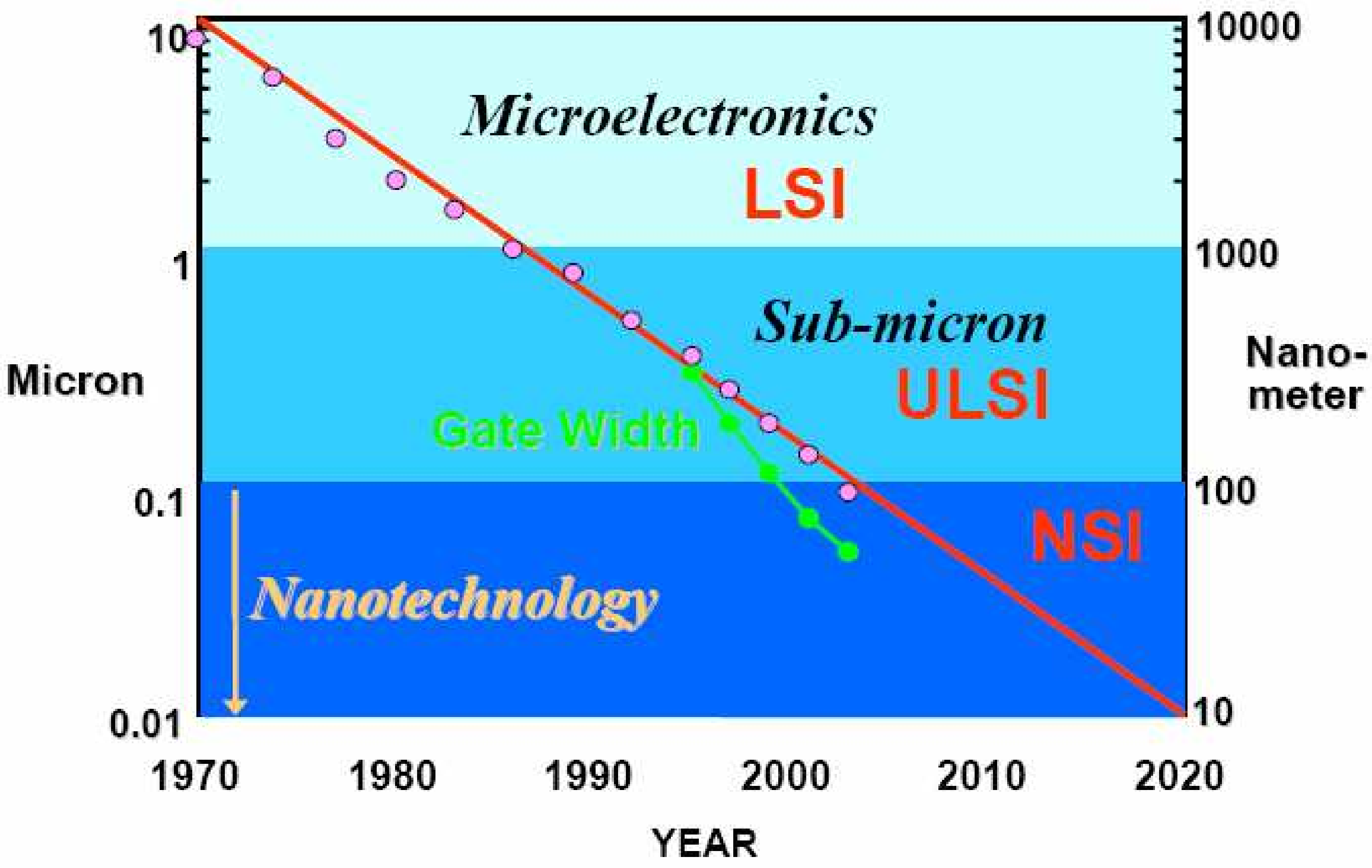


Wafer of Itanium processors

Moore’s words in 2003


Minimum Feature Size
Feature Size (microns)
100
10
1
0.1
0.01
**
'60
'65
'70
'75
'80
'85
'90
'95
'00
'05
'10
Projected
Intel [update 5/20/02]
ITRS [2001 edition]
Examples
Human hair, 100 µm
Amoeba, 15 µm
Red blood cell, 7 µm
AIDS virus, 0.1 µm
Buckyball, 0.001 µm
** Planar Transistor; remaining data points are ICs.
International Technology Roadmap for Semiconductors (ITRS)
* [ITRS DRAM Half-Pitch vs. Intel "Lithography"]

Silicon Nanotechnology is Here!



- Nanoscience = Science at the Nanoscale (10^{-9} - 10^{-7} meters)
- Understanding and control of matter in this scale
- Properties of matter differ from larger scale (solids): quantum mechanics
- Multidisciplinarity and interdisciplinarity