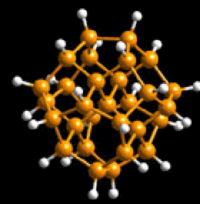
Si nanoparticles: New photonic and electronic material



Dr. Munir H. Nayfeh
Departments of Physics, University of Illinois

NanoSi

Let there be Light

Nature

news feature

Let there be light

A silicon laser would revolutionize telecommunications, electronics and computing. Squeezing light out of silicon is no easy task, but Philip Ball discovers that researchers are becoming more optimistic about its light-emitting abilities.

Tantalizingly, at the Materials Research Society meeting in Boston last December, Nayfeh reported optical gain and stimulated emission from his blue-light-emitting nanocrystals. Others in the field are now waiting for Nayfeh to publish quantitative data so that they can assess these claims.

Dot comms

Using a network of silicon wires is not the only way to make the element glow. The same helpful quantum effects operate if the porous silicon is divided into nanometre-sized particles known as nanocrystals or 'quantum dots'. Last year, Munir Nayfeh of the University of Illinois at Urbana-Champaign and his colleagues used ultrasound to shatter porous silicon into nanocrystals. The smallest of these particles (about 1 nanometre across) emit blue light[5].

From bulk to nanoparticles

What makes silicon Glow?

I) Bulk Silicon (*Emission lifetime ~ ms*) Dull

- Difficult to conserve momentum in transition across bandgap. (Indirect gap)
- Momentum can come from coupling to crystalline phonons. (2nd order process)

II) Si Nanostructure > 3nm (Enhanced *lifetime ~ us*) *Fluorescent*

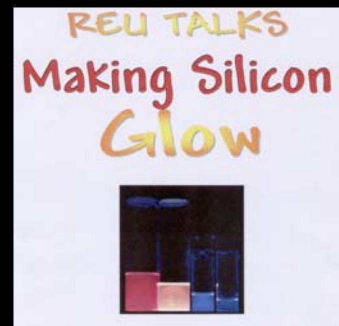
- *Quantum confinement* with bulk-like emission
- Momentum can come from coupling to crystalline phonons
- Additional momentum can come from boundary scattering of electrons (dk dx larger than 1).

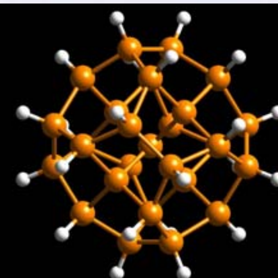
III) Si nanoparticle (1-3nm) (*Enhanced lifetime ~ ns*) Glow

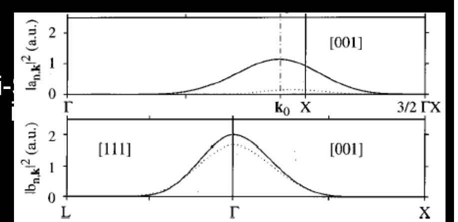
- Trapping of excitons onto atomic intrinsic sites (Si-
example) where the conservation of momentum i
lifted. (direct gap?)

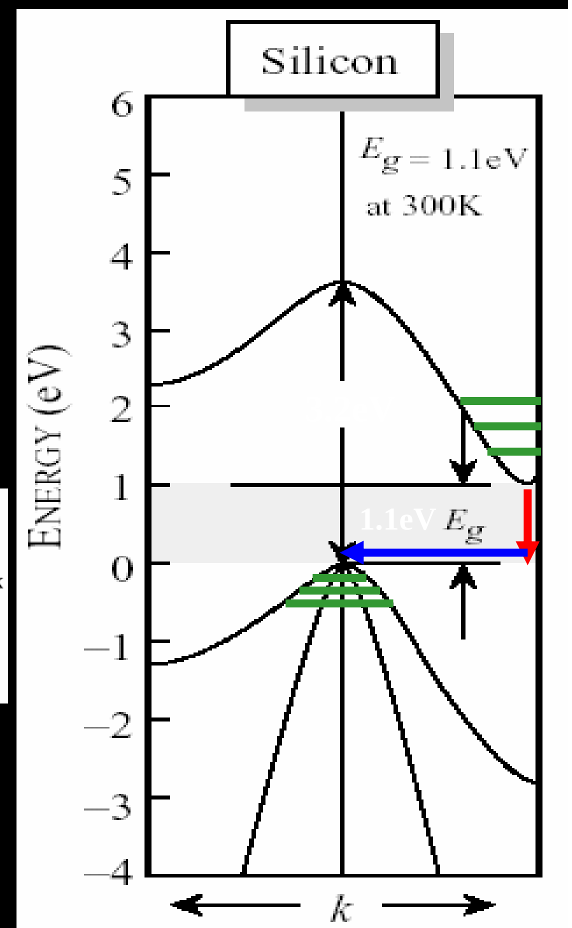
Combination of mechanisms

- *Space confinement*
- *Molecular confinement Self-trapped*
- *Other?*









Process and purification

MRS Bulletin

RESEARCH/RESEARCHERS

Electrochemical Process Makes Ultrasmall Si Nanoparticles

Researchers at the University of Illinois—Urbana-Champaign have developed a process for converting bulk silicon into ultrasmall, nano-sized particles. As reported in the April 3 issue of *Applied Physics Letters*, the nanoparticles—which are about 1 nm in diameter and contain

wafer is then removed from the etchant and immersed briefly in an ultrasound bath." The main contents of the etchant bath are hydrogen fluoride (HF) and hydrogen peroxide (H_2O_2).

Under the ultrasound treatment, the fragile nanostructure network crumbles into individual particles of different size groups, Nayfeh said. The slightly larger, heavier particles precipitate out, while the

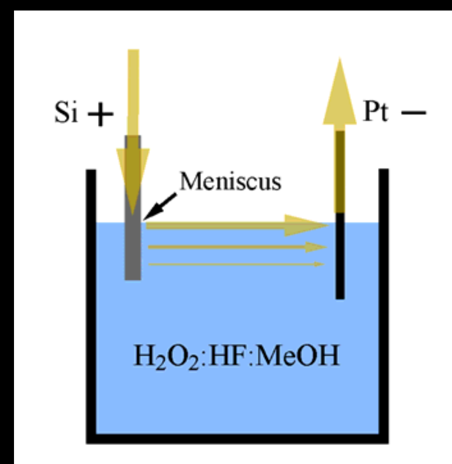
Electrochemical etch of bulk wafers

1-10 ohm-cm p-type <100> Si

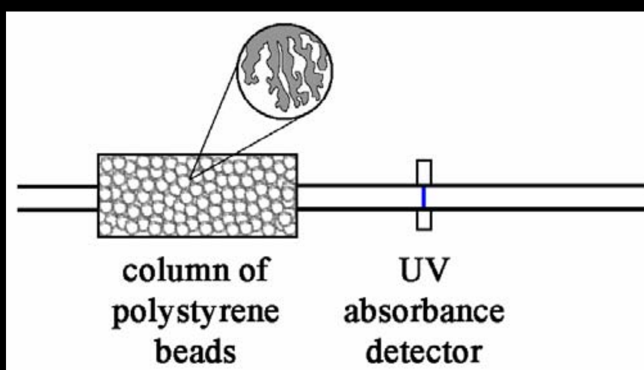
Current concentrates at meniscus (~30mA/cm2)

Particles dispersed in a solvent via sonication

Particles produced are H-passivated.



Particles purified by size via gel permeation chromatography; Fractions exhibit different luminescence spectra

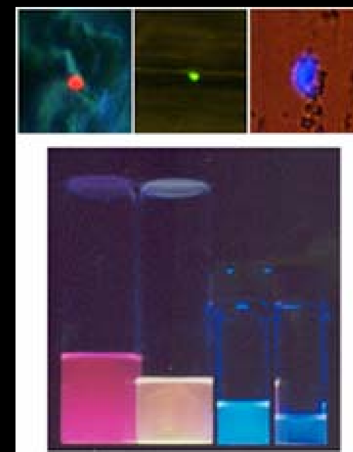


Z. Yamani, H. Thompson, L. AbuHassan, and M. H. Nayfeh , Appl. Phys. Lett. **70**, 3404-3406 (1997)

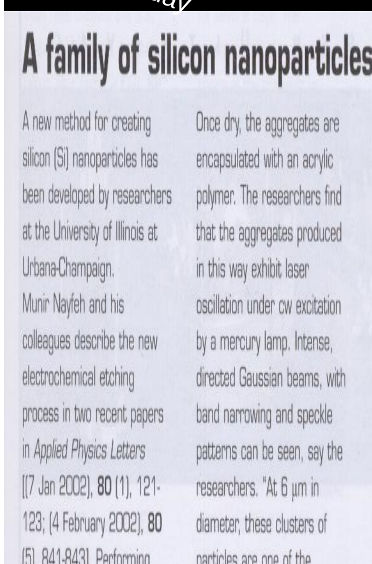
Sweet spots in Si cluster size

A family of magic sizes of hydrogenated Si nanoparticles

No magic sizes > 20 atoms for non-hydrogenated clusters



Materialstoday

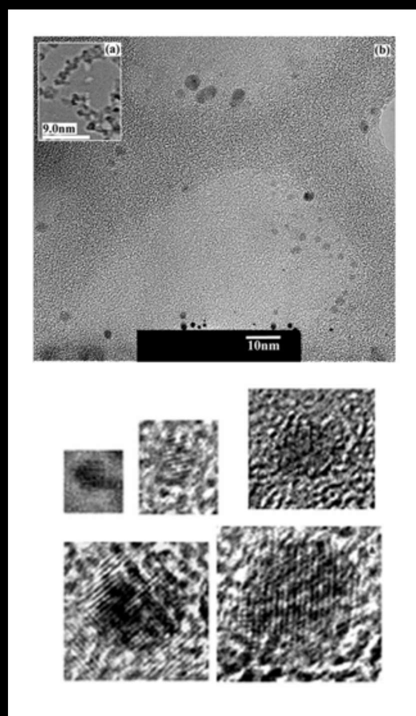


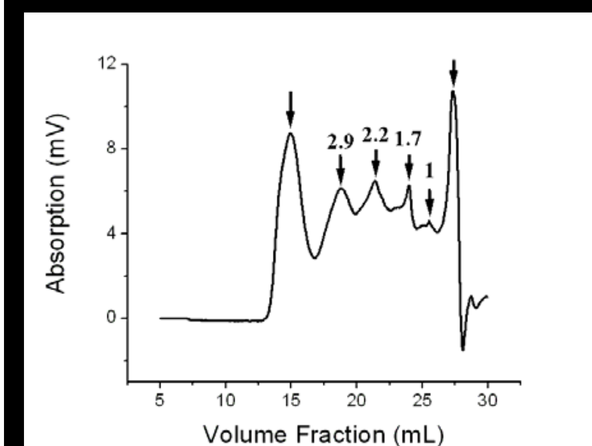
A family of silicon nanoparticles

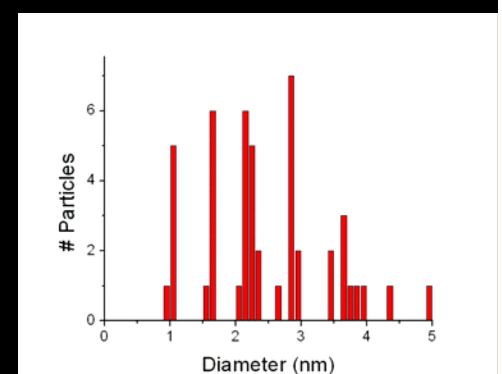
A new method for creating silicon (Si) nanoparticles has been developed by researchers at the University of Illinois at Urbana-Champaign.

Munir Nayfeh and his colleagues describe the new electrochemical etching process in two recent papers in *Applied Physics Letters* [17 Jan 2002], **80** (1), 121-123; [4 February 2002], **80** (5), 841-843]. Performing

Once dry, the aggregates are encapsulated with an acrylic polymer. The researchers find that the aggregates produced in this way exhibit laser oscillation under cw excitation by a mercury lamp. Intense, directed Gaussian beams, with band narrowing and speckle patterns can be seen, say the researchers. "At 6 μm in diameter, these clusters of particles are one of the

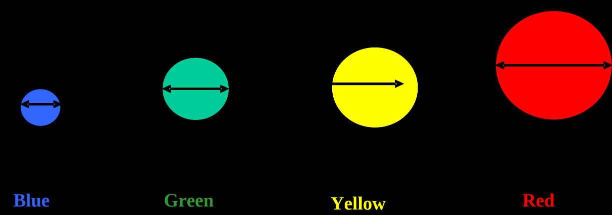






G. Belomoin, J. Therrien, A. Smith, S. Rao, S. Chaieb, M. H. Nayfeh, Appl. Phys. Lett. 80, 841 (2002)

Size-color-bandgap



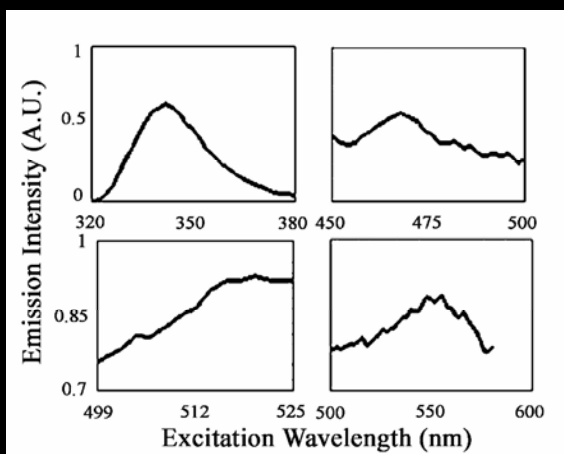
MRS Bulletin

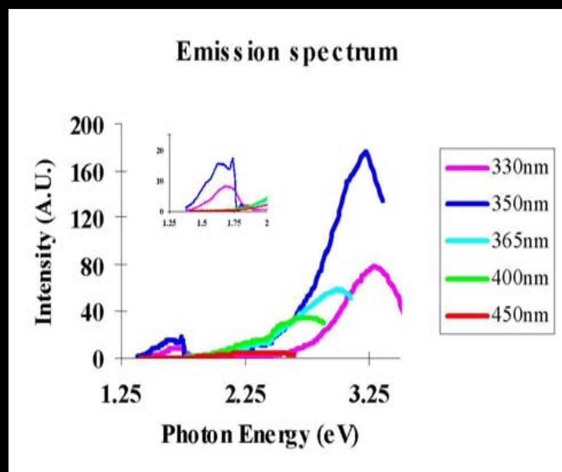
Discretely Sized Si Nanoparticles Fluoresce in RGB Colors

Researchers at the University of Illinois at Urbana-Champaign have demonstrated that their electrochemically etched hydrogen-capped silicon (Si_nH_x) nanoparticles ($n > 20$) come in particular sizes (including diameters of 1 nm, 1.67 nm, 2.15 nm, and 2.9 nm) and fluoresce in blue, green, yellow, and red, respectively, with band peaks at ~410 nm, 540 nm, 570 nm, and 600 nm. To convert bulk silicon into

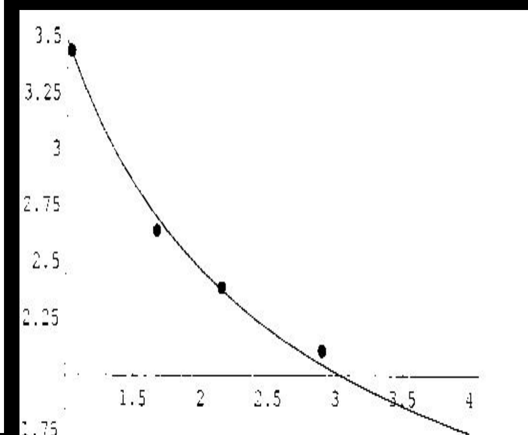
separ… Acco… Carlo… formi… use c… solut… have … that t… etchin… tion c… cally … 4 issu… partic…

Excitation at bandgap





Eg = 3.5 /sqrt d



Z. Yamani, S. Ashhab, A. Nayfeh and M. H. Nayfeh, J. Appl. Phys. **83**, 3929-3931 (1998)

Silicon Nanoparticle prototype

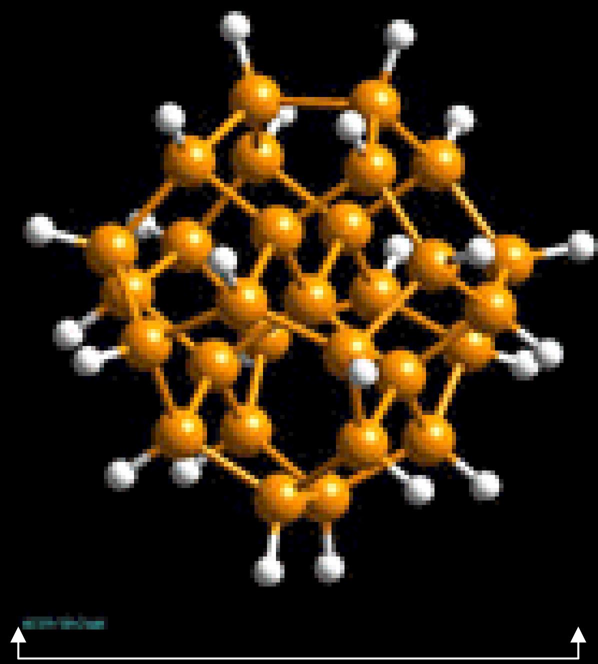
(Quantum Monte Carlo simulation)

I. Ideal bulk-like configuration

(Band gap of 3.6-3.7 eV)

- Filled fullerene configuration
- Tetrahedral Si core (5 atoms)
- 24 hydrogen passivated cage
- Known position of Si and H
- Highly rinckled (puckerred ball)
(pentagons and hexagons)

1 Td atom and 28 atom fullerene cage



1 nanometer

$Si_{29}H_{24}$

29 Silicon (yellow)
24 Hydrogen (white)

L. Mitas, J. Therrien, R. Twesten, G. Belomoin, and M. H. Nayfeh, appl. Phys. Lett. 78, 1918 (2001)

Wide bandgap mateial:

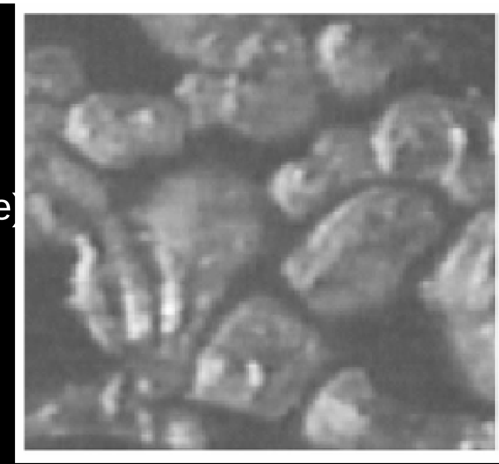
Reconstitution into films and solids

The particles are harvested in a solution. Particles may then be processed into a certain assay using:

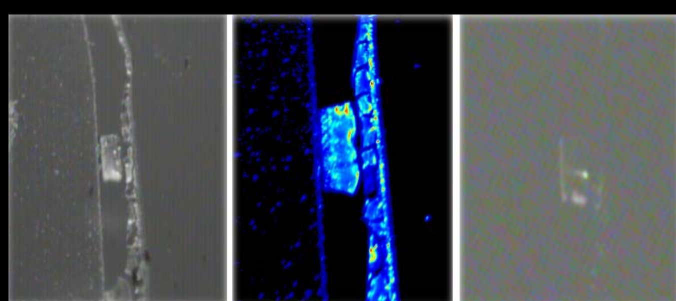
- Drying / evaporation
- Spray
- Jet
- Electrochemical deposition

Produces wide bandgap solids

(from Acetone)



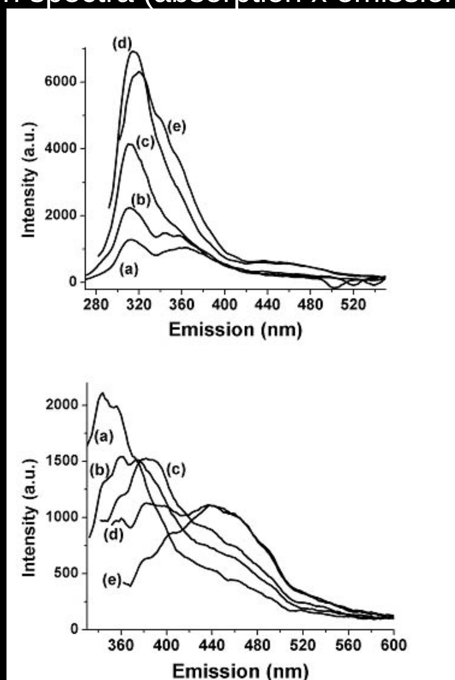
(from water)



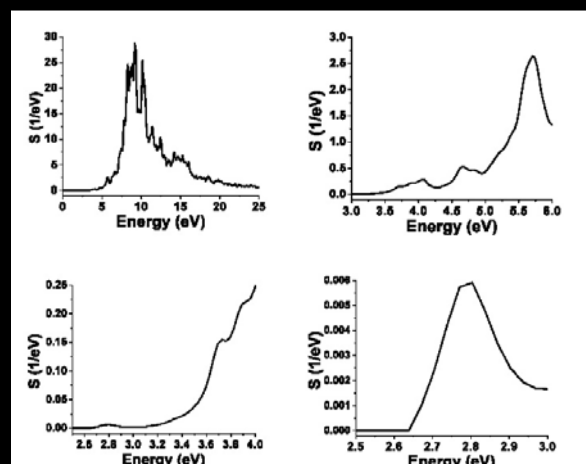
From bulk band structure to molecular bands (Excited states of Si29)

Molecular-like excited state bands --- Richard Martin

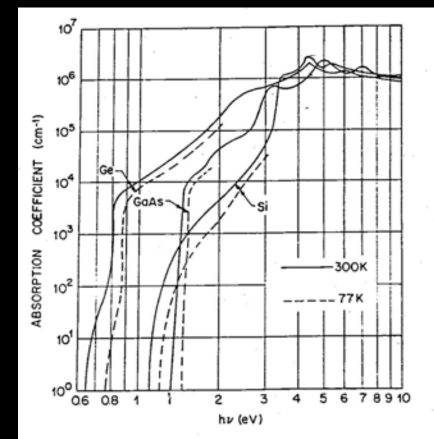
Excitation spectra (absorption x emission)



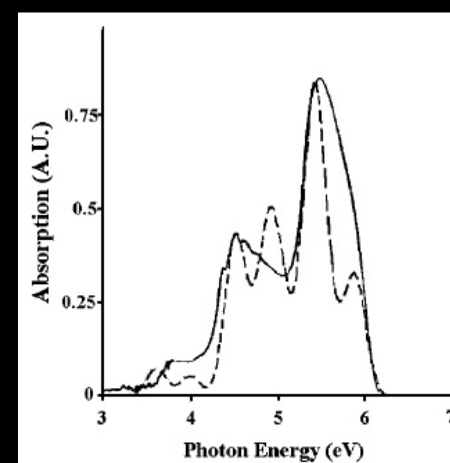
Time dependent LDH theory



Bulk absorption



Particle absorbtion & QMC

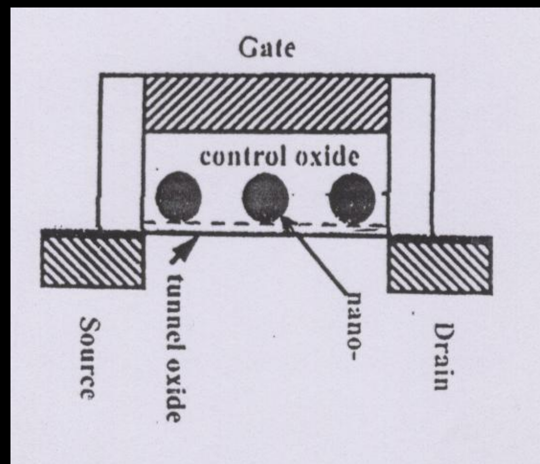


S. Rao, J. Sutin, R. Clegg, E. Gratton, M. Nayfeh, S. Habbal, A. Tsolakidis, R. Martin, Phys. Rev. B (2004)

Single-Electron Transistors and Memory Cells

A **single-electron transis-tor** (SET) is a three-terminal device, with gate, source, and drain.

Memory Nano- cells



Electronic applications (e.g., low-power electronics, nonvolatile floating gate memory): Unlike traditional transistors, silicon nanoparticles can capture/emit a single electron with an energy spacing on the order of 1 electron volt, enabling the manufacture of devices with single-electron operation at room temperature with significantly lower power requirements.

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TECHNOLOGY

Glowing nanoparticles offer memory prospects

By Joanne Aslett
EE Times
February 8, 2002 (11:43 a.m. EST)

PRINT THIS STORY | SEND AS EMAIL

A US research team has discovered a family of discrete-sized ultra-bright nanoparticles in the red, green and blue range that could be useful for biomedical tagging, displays, and flash memories.

Discrete sizes of 1.0 (Si_{29}), 1.67 (Si_{123}), 2.15, 2.9, and 3.7nm diameters were measured. The smallest four

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Technology

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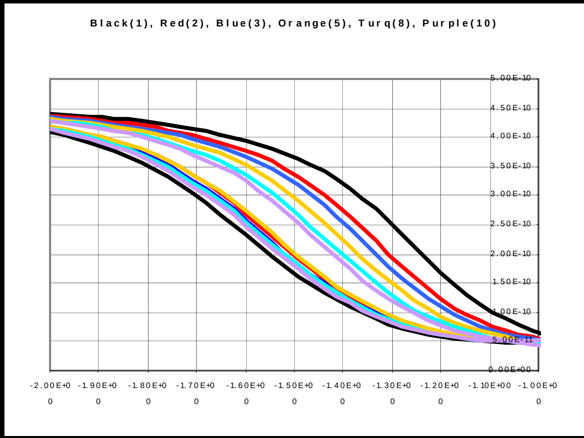
Vendors ramp products for 40-Gbit/s networks

Device to

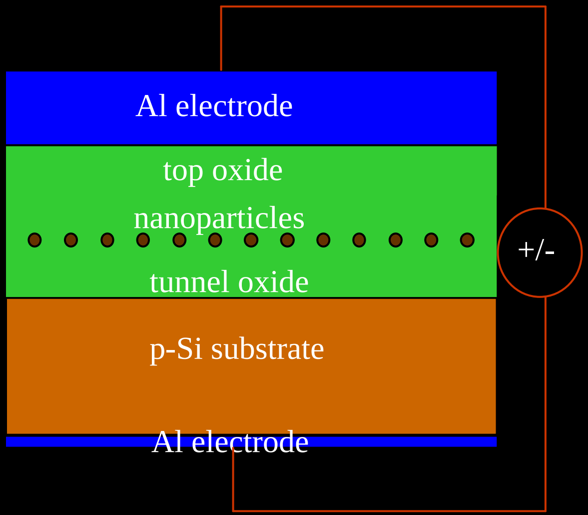
Nano memory on a super chip

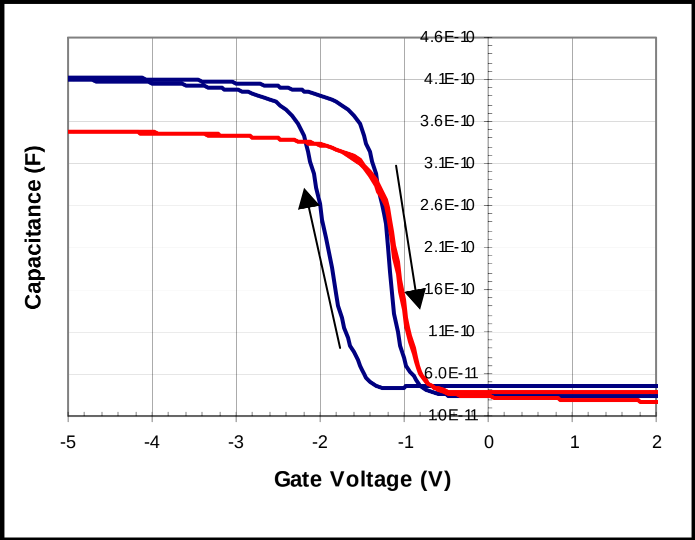


Metal-oxide-silicon (MOS)

Capacitor memory

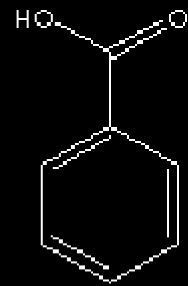
Contain uniform 1 nm silicon nanoparticles



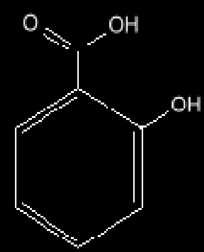


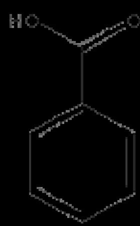
Aromatic bi-linkers

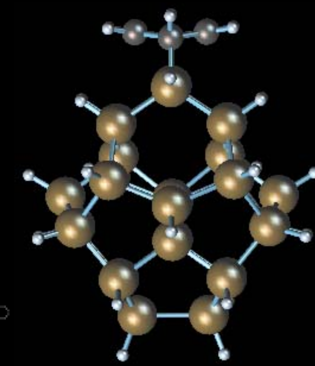
Benzoic Acid, COOH



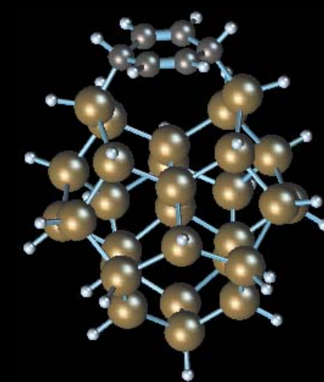
Salicylic Acid, OH and COOH



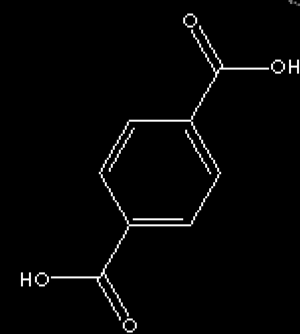




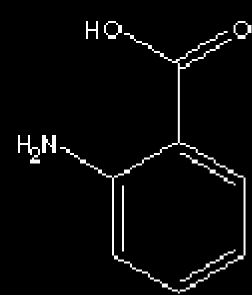
Butterfly conjugation



Terepththalic Acid, COOH and COOH



Anthranilic Acids, COOH and NH2



Simulations:
Structure, Optical properties
Chemical activity
Vibrations