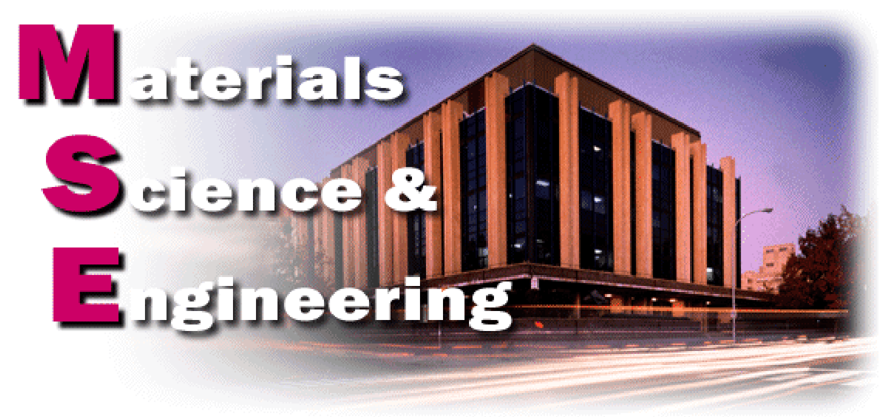
A New Undergraduate Curriculum in Nanoscale Materials Science and Engineering

Peter K. Davies
Dept. Materials Science & Engineering
University of Pennsylvania



• *Background*

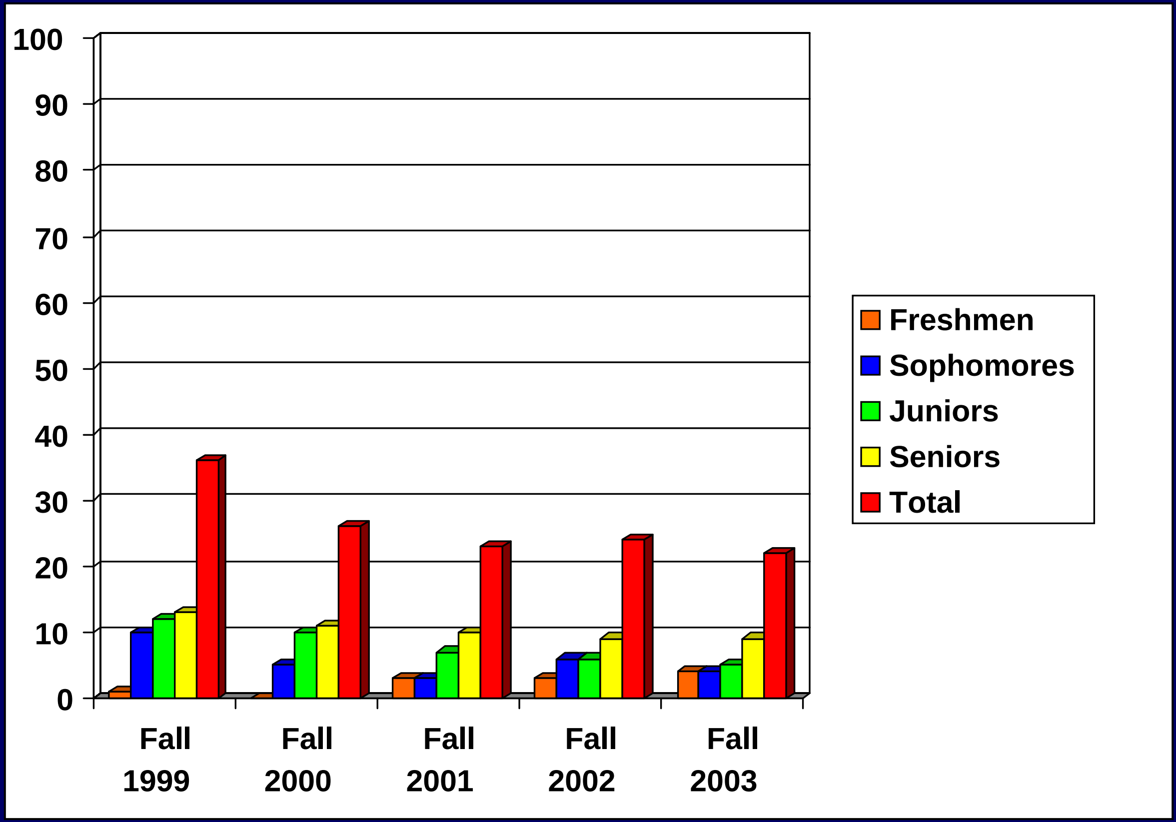
Fall 2002:

- excellent undergrads; program meeting educational goals
  - teaching ratings highest in Engineering.
- Diverse employment fields:
  - common factor: Leadership

PROBLEM: low & decreasing undergrad numbers.

- one of most important quantitative measures for ***survival*** of MSE

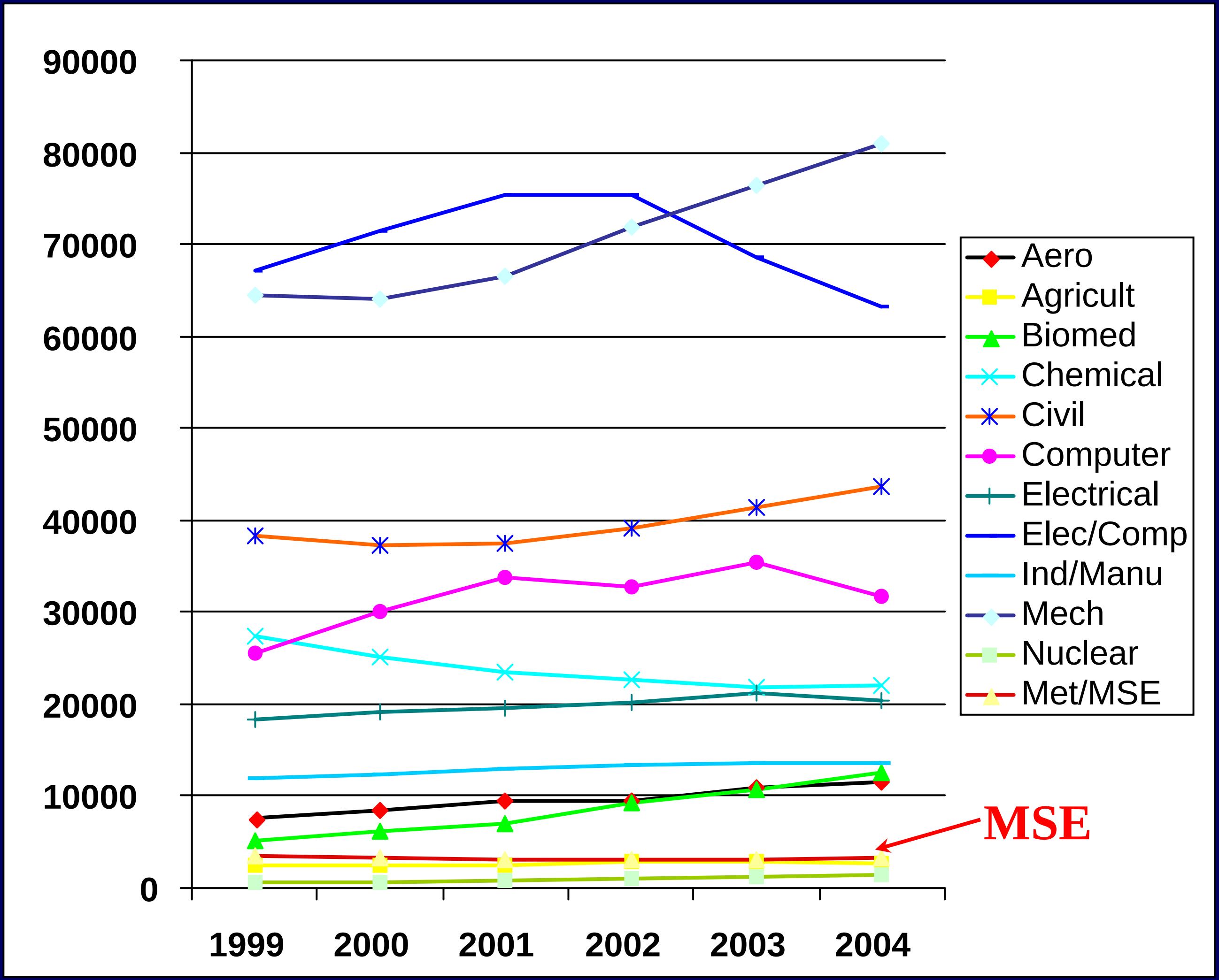
Undergrad Enrollment in MSE at PENN



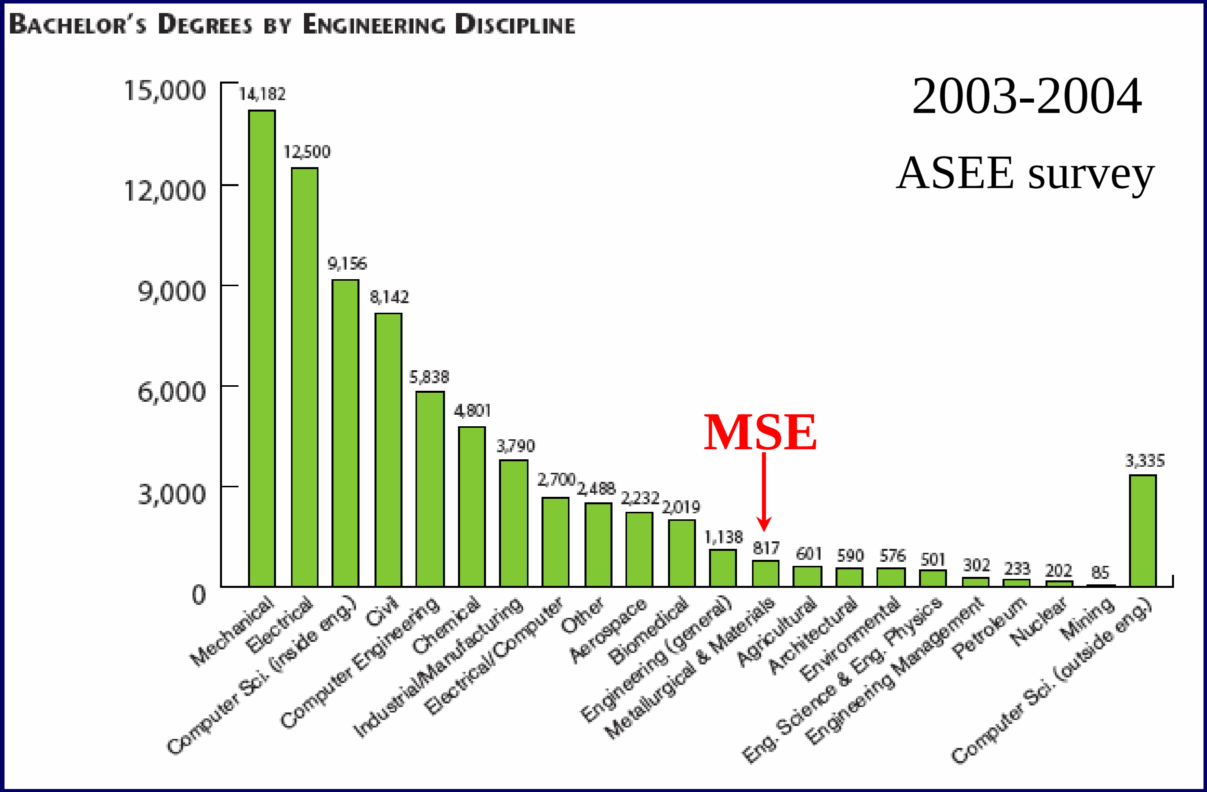
- ~ 3% engineering majors enrolled in MSE

- ***National trends***

Bachelor’s degrees by discipline, 1999-2004 (ASEE)



• *National trends*



BACHELOR'S DEGREES BY ENGINEERING DISCIPLINE

2003-2004

ASEE survey

Almost all MSE enrollments <<5%

• *Why such low enrollments?*

- ***Low visibility of Materials in high schools***

- well known; but this is changing (nano)

- ***Recruiting?***

- countless hours spent on exposing freshmen to MSE; open houses, etc.

- ***Access to freshmen?***

- extensive access of MSE faculty to PENN engineering freshmen
- co-taught freshmen chem (Chem 101 & 102) for 10 years
- Intro to Engineering freshmen course: led by MSE faculty
- taught Materials to BE, MEAM majors

- **Minimal impact on number of MSE majors (though some dual BE)**

IT'S THE CURRICULUM!

• *The need for changes in MSE*

- Over-focused on hard materials and “traditional” applications
- Curricula in MSE departments in danger of becoming “traditional”: irrelevant to students needs, interests and aspirations?
- The ***field*** of Materials Research has changed dramatically
- The ***discipline*** of Materials Science & Engineering must respond.

• *Opportunities*

- *Influences of Bio and Nanoscience*
  - increasing role of Chemistry; completely new building blocks
- *Order of magnitude increase in control of chemistry, structure, morphology*
  - manipulation/management of photons, electrons, macromolecules/biomolecules
  - quantum materials with unique functionalities
- *Increased capability for 3-D "molecular" visualization, (SPM, AFM, STEM)*
- *Nanolithography*
- *Influence of organic based soft materials*
  - plastic electronics, molecular electronics, nano/bio interface, soft forces
- *Computational MSE*

• *Curriculum revision at PENN*

- **Objective:** design and implement a relevant and rigorous new curriculum based on fundamentals that builds on core aspects of MSE and focuses on nanoscale materials and emerging technologies.

- Nano is not just hype, new fundamentals: surface, interface, quantum confinement, soft materials, etc.

- To understand, apply, and engineer at the nanoscale, must understand the “norm” at the macroscale

- Capture excitement and interest of students in nanotechnology: provide a relevant and rigorous curriculum.

- **An Intro. course is not enough**.

- Fundamentals of Nanoscale materials incorporated into all courses

• *Timelines*

- 2003/04: committee to evaluate which core aspects of nano belong in MSE

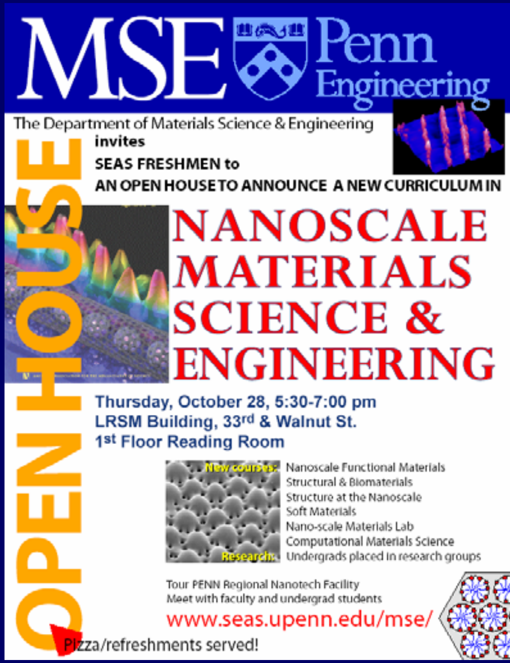
- key fundamentals; key applications; new areas; proposed course layout

- course by course review/evaluation

- **every** faculty meeting& faculty retreat dedicated to course revisions

- New courses:
    - MSE 215 “Nanoscale Functional Materials”
    - MSE 330 “Soft Materials”
    - MSE 460 “Computational Materials Science”
    - new lab experiments
    - Nanoscale phenomena incorporated into every course

- Fall 2004: 1st iteration of curriculum launched



MSE Penn Engineering

The Department of Materials Science & Engineering
invites
SEAS FRESHMEN to
AN OPEN HOUSE TO ANNOUNCE A NEW CURRICULUM IN

OPEN HOUSE

NANOSCALE MATERIALS SCIENCE & ENGINEERING

Thursday, October 28, 5:30-7:00 pm
LRSM Building, 33rd & Walnut St.
1st Floor Reading Room

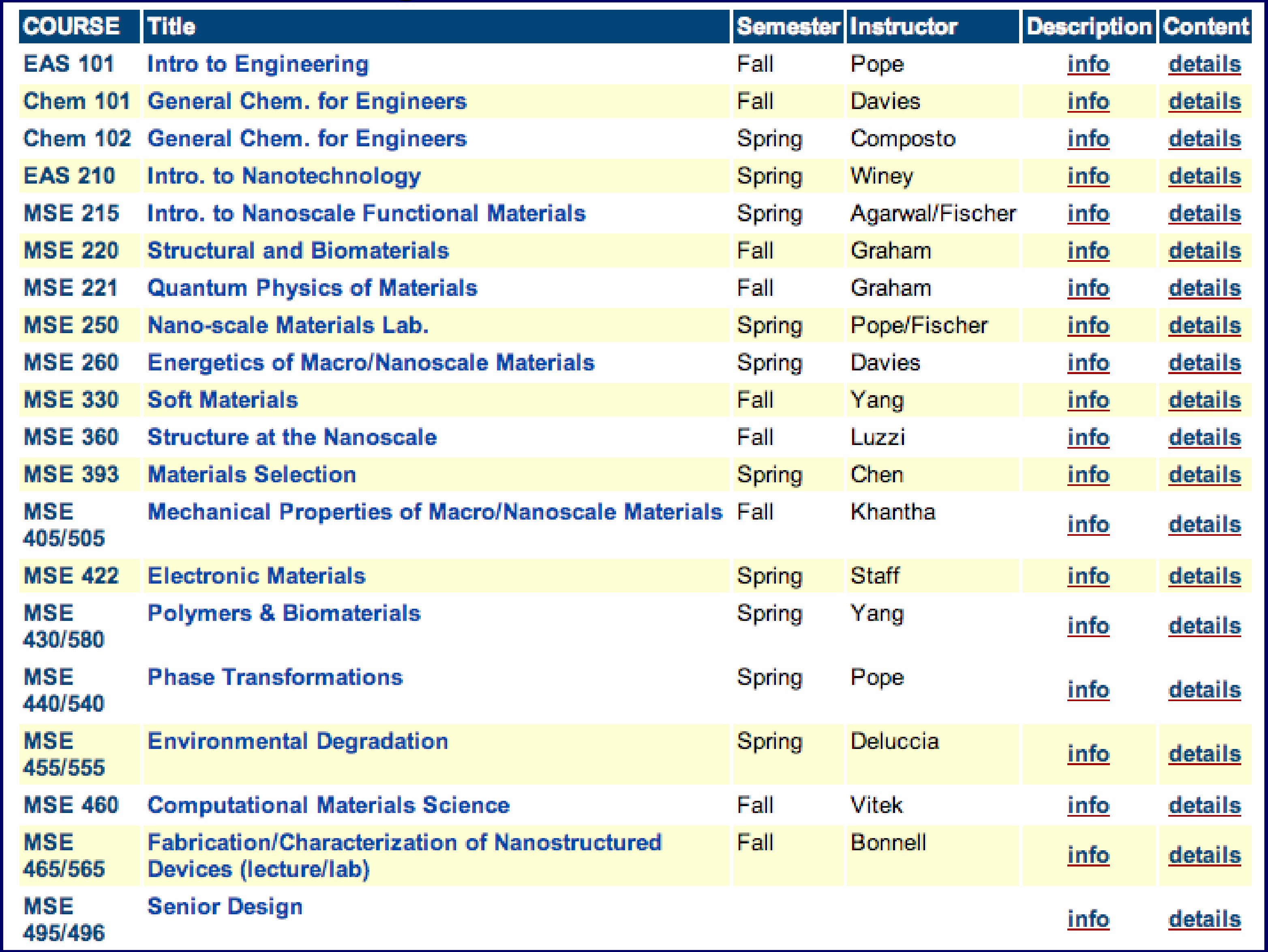
New courses: Nanoscale Functional Materials
Structural & Biomaterials
Structure at the Nanoscale
Soft Materials
Nano-scale Materials Lab
Computational Materials Science
Research: Undergrads placed in research groups

Tour PENN Regional Nanotech Facility
Meet with faculty and undergrad students

www.seas.upenn.edu/mse/

Pizza/refreshments served!

- *New Undergraduate Curriculum*



COURSE	Title	Semester	Instructor	Description	Content
EAS 101	Intro to Engineering	Fall	Pope	info	details
Chem 101	General Chem. for Engineers	Fall	Davies	info	details
Chem 102	General Chem. for Engineers	Spring	Composto	info	details
EAS 210	Intro. to Nanotechnology	Spring	Winey	info	details
MSE 215	Intro. to Nanoscale Functional Materials	Spring	Agarwal/Fischer	info	details
MSE 220	Structural and Biomaterials	Fall	Graham	info	details
MSE 221	Quantum Physics of Materials	Fall	Graham	info	details
MSE 250	Nano-scale Materials Lab.	Spring	Pope/Fischer	info	details
MSE 260	Energetics of Macro/Nanoscale Materials	Spring	Davies	info	details
MSE 330	Soft Materials	Fall	Yang	info	details
MSE 360	Structure at the Nanoscale	Fall	Luzzi	info	details
MSE 393	Materials Selection	Spring	Chen	info	details
MSE 405/505	Mechanical Properties of Macro/Nanoscale Materials	Fall	Khantha	info	details
MSE 422	Electronic Materials	Spring	Staff	info	details
MSE 430/580	Polymers & Biomaterials	Spring	Yang	info	details
MSE 440/540	Phase Transformations	Spring	Pope	info	details
MSE 455/555	Environmental Degradation	Spring	Deluccia	info	details
MSE 460	Computational Materials Science	Fall	Vitek	info	details
MSE 465/565	Fabrication/Characterization of Nanostructured Devices (lecture/lab)	Fall	Bonnell	info	details
MSE 495/496	Senior Design			info	details

• *Course contents*

EAS 210: Intro. to Nanotechnology: overview of field aimed toward all freshmen; “share excitement of Nano” ; also introduce themes of MSE.

MSE 220 Intro. to fundamental concepts of Materials Science through an examination of the structure, property,performance relationship for synthetic and biologic structural materials

MSE 215 Intro. to Nanoscale Functional Materials: key concepts underlying the design, properties, processing, applications of nanoscale functional materials; electronic transport; bands; Hall effect; nano-electronics; molecular electronics; fabrication; nano-photonics.

MSE 250: Lab course: new experiments, greater emphasis on synthesis: e.g. nano and organic electronic materials: quantum dot synthesis; absorption spectroscopy and fluorescence; alkane protected Au nanoparticles; quantum confinement

MSE 260: Energetics: “classical thermodynamics”, but increase focus on surface energy and size-dependent stability; calculate phase diagrams for nanoparticles, Si/Ge superlattice nanowires, contrast to macroscale behavior.

• *Course contents*

MSE 330 Soft Materials: forces, energies, time-scales in soft condensed matter; formation, assembly, phase behavior and molecular ordering; gelation, hydrogels; colloids; amphiphiles, micelles, bi-layers, vesicles, surfactants; soft matter in nature, nucleic acids, proteins, lipids; application of soft materials in nanotechnology, photo-resists, soft lithography, colloidal assembly.

MSE 360: Structure at the Nanoscale: “traditional” crystalline state and 0-D, 1-D, 2-D structures; particulates & colloids; liquid crystals; thin films.

MSE 460: Computational Materials Science: atomic level modeling; atomic interactions, density functional theory, pair potentials, tight-binding; methods of modeling, molecular statics, molecular dynamics, Monte Carlo, lattice dynamics. Applications/interpretation; nano-structures/clusters, point defects, surfaces, grain boundaries/interfaces, dislocations, phonons.

e.g. Thermodynamics (MSE 260)

Nanoparticles and nanowires: size dependent properties and size dependent stabilities.

Semi-conductor Nanowires. InP/InAs heterostructures

(Samuelson, Nanoletters, 2, 87-89,(2002)

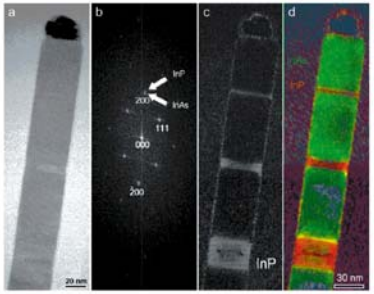


Figure 1. Composition profile of an InAs nanowhisker, containing several InP heterostructures, using reciprocal space analysis of lattice spacings. (a) High-resolution TEM image of a whisker with a diameter of 40 nm. (b) Power spectrum of the image in (a). (c) An inverse Fourier transform using the information closest to the InP part of the split 200 reflection. InP (bright) is located in three bands with approximately 25, 8 and 1.5 nm width, respectively. (d) Superimposed images, using an identical mask over the InP and InAs parts of the 200 reflection, respectively. InAs lattice spacings have been color-coded with green and InP spacings with red.

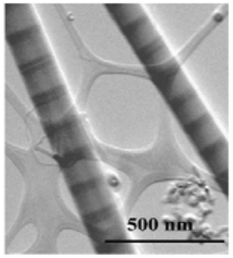


Figure 5 Transmission electron microscopy (TEM) image of two Si/SiGe superlattice nanowires.

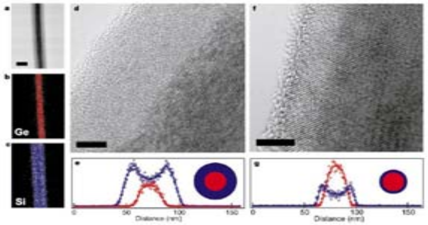


Figure 3 Ge–Si core–shell nanowires. **a**, Bright-field image of an unannealed Ge–Si core–shell nanowire with an amorphous p-Si shell. Scale bar is 50 nm. **b**, **c**, Scanning TEM elemental maps of Ge (red) and Si (blue) concentrations, respectively, in the nanowire of **a**. **d**, High-resolution TEM image of a representative nanowire from the same synthesis as the wire in **a**–**c**. Scale bar is 5 nm. **e**, Elemental mapping cross-section showing the Ge (red circles) and Si (blue circles) concentrations. The solid lines show the theoretical cross-section for a 28-nm-diameter core, 15-nm-thick shell and <1 nm interface according to the model described in the Methods section. **f**, High-resolution TEM image of annealed Ge–Si core–shell nanowire exhibiting a crystalline p-Si shell. Scale bar is 5 nm. **g**, Elemental mapping cross-section gives a 5-nm shell thickness with a sharp interface consistent with the TEM image, suggesting that the Ge and Si do not interdiffuse substantially during the annealing process.

Si/Ge superlattices & heterostructures

Peidong Yang, Ann. Rev. Mater. Res., *Lieber, Nature, 420, 57 (2002)*

CdSe quantum dots

Murray, Bawendi, Science(1995)

Size-dependent fluoresence

Example:

Calculate the melting temperature of gold nanoparticles with a diameter = 10nm.

Data: melting temperature of bulk gold = 1336K;

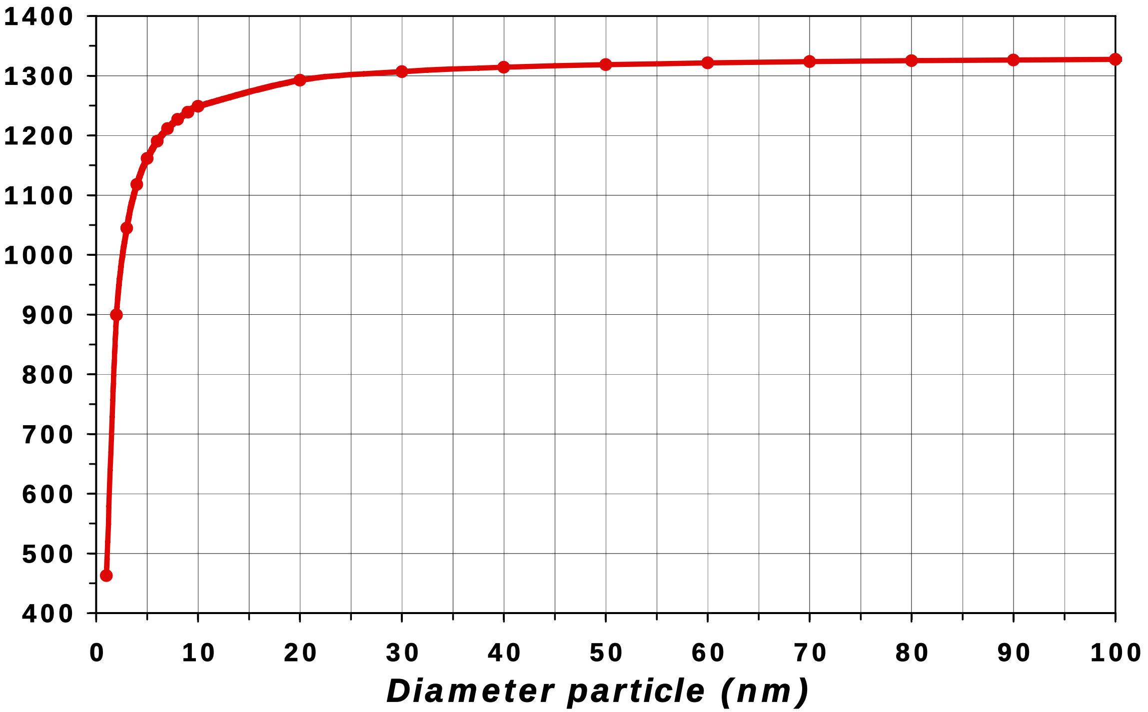
$^{2}\ H_{melt}(Au) = 12{,}360$ J/mol; $V_{molar} = 10.2 \times 10^{-6} m^3/mol$;

$(\gamma_{(s)} - \gamma_{(l)}) = 0.132\ J/m^2$.

$$T = T_{melt,bulk}\{1 - 3V_{molar}(\gamma_{(s)} - \gamma_{(l)})/r^2\ H°_{melt}\}$$

$$T = (1336K)(1 - 3(10.2x10^{-6}m^3/mol)(0.132\ J/m^2)/(5x10^{-9}m.12360J/mol)$$

$$\mathbf{T_{melt,particle} = 1248.7K}$$



Example:

Calculate the melting points of a silicon nanoparticle with d = 10nm and of silicon nano-wires with d = 10nm and aspect ratios of 100:1 and 10,000:1.

Data: Molar volume Si = $12.06 \times 10^{-6}\ m^3/mol$;

Normal melting point = 1687K, $^{2}\ H_{melt}$ = 50.55 kJ/mol.

$\gamma_{(s)} = 1.23\ J/m^2$; $\gamma_{(l)} = 0.78\ J/m^2$.

Nanoparticle:

$$T = T_{melt,bulk}\{1 - 3V_{molar}(\gamma_{(s)} - \gamma_{(l)})/r^2\ H°_{melt}\}$$

$$\mathbf{T_{melt,nanoparticle} = 1578K}$$

Nanowire: 100:1 aspect ratio

$$T = T_{melt,bulk}(1 - (V_{molar}\ /^2\ H°_{melt} r_{wire})[(2+1/x)\gamma_{(s)} - (2.62/x^{1/3})\gamma_{(l)}]$$

$$= 1687K(1 - (12.06x10^{-6}m^3/5x10^{-9}m(50550J/mol)[(2+1/100)(1.23J/m^2) – [(2.62)/(100)^{1/3}](0.78J/m^2)$$

$$\mathbf{T_{melt,100:1nanowire} = 1523K}$$

Nanowire: 10,000:1 aspect ratio

$$T = 1687K(1 - (12.06x10^{-6}m^3/5x10^{-9}m(50550J/mol)[(2+1/10000)(1.23J/m^2) – (2.62)/(10,000)^{1/3}(0.78J/m^2)$$

$$\mathbf{T_{melt,10000:1nanowire} = 1496.6K}$$

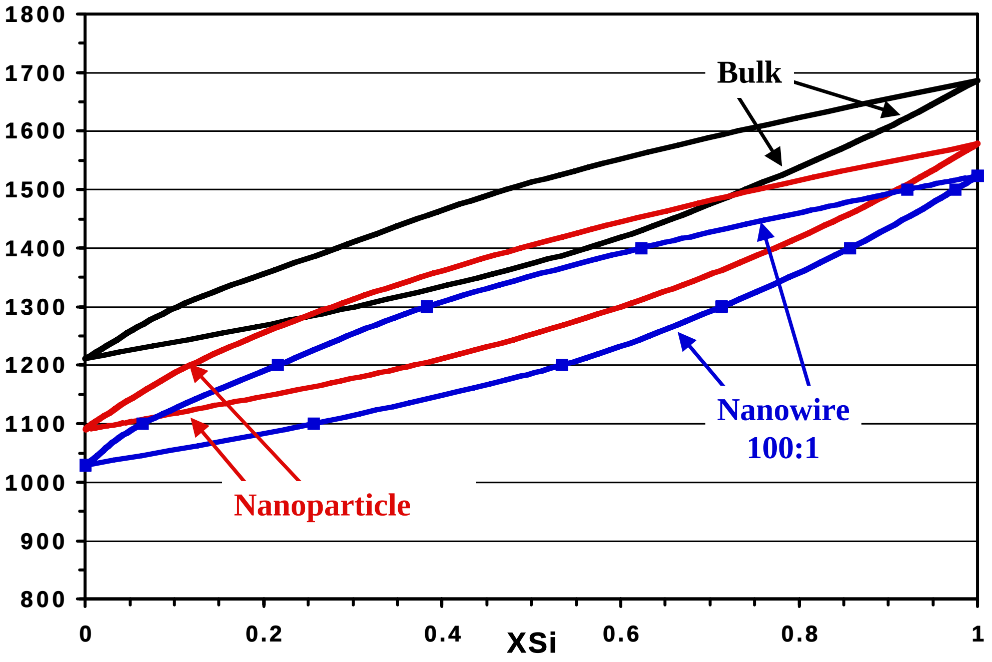
Conclusion: Size and shape matter.

Surface energies and binary phase equilibria.

(1) melting of homogenous solid solution Si/Ge nanospheres;

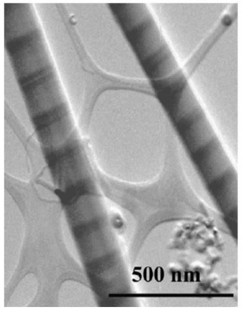
(2) melting of a Si/Ge superlattice nanowires in which the Si and Ge segments remain pure up to the melting point (no mixing in solid state);

Data: Si: $V_{molar} = 12.06 \times 10^{-6}$ m^3/mol;
normal melting point = 1687K, $^2H_{melt}$ = 50.55 kJ/mol;
$\gamma_{(s)} = 1.23$ J/m^2; $\gamma_{(l)} = 0.78$ J/m^2.
Ge: $V_{molar} = 13.63 \times 10^{-6}$ m^3/mol;
normal melting point 1211K, $^2H_{melt}$ = 36,940 J/mol;
assume same surf. energies as Si: $\gamma_{(s)}$=1.23 J/m^2; $\gamma_{(l)}$= 0.78 J/m^2.



Melting of nanowire Si/Ge superlattice.

d =10 nm, aspect ratio =100:1.



(1) Phase separated Si and Ge
(ignore energy of Si/Ge interface)

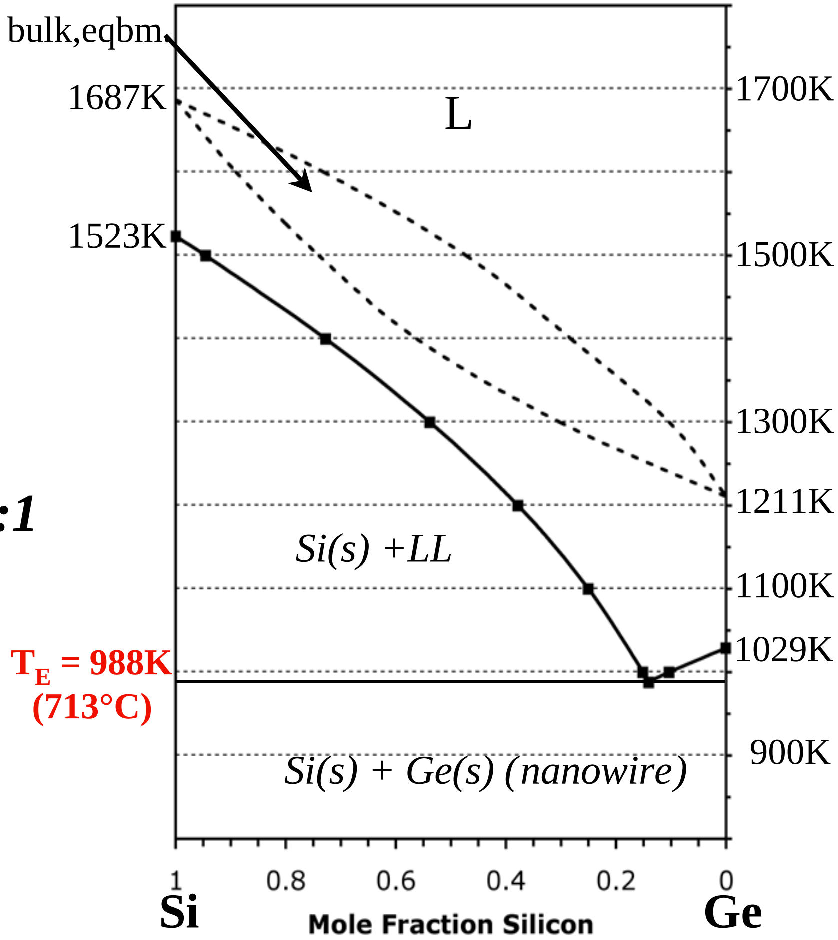
Assume **no** mixing of Si/Ge up to melting pt.

- imposed by artificial structure of modulated wire
- assume ideal mixing in liquid

"Simple eutectic" type system

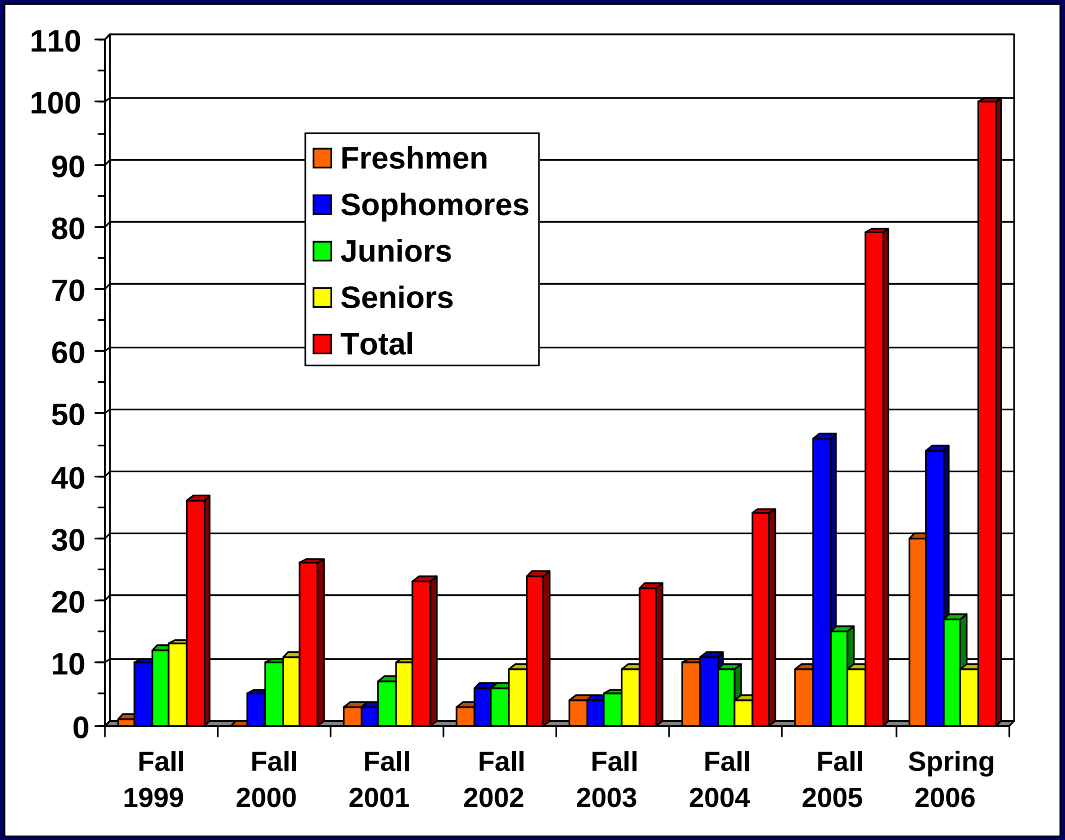
Now: $\mu_{Si(s)} = \mu°_{Si(s)bulk} + \gamma_{Si(s)}A_{Si(s)} + RT\ln a_{Si(s)}$ **; where $a_{Si(s)} = 1$**

Calculated phase diagram for Si-Ge superlattice wires, d = 10nm, aspect ratio 100:1



- **Huge drop in melting temperatures**

• *MSE Undergrad enrollments*



- Record enrollments for Freshmen, Sophomores

- current sophomore class ~ 44 (~13%)
- quality of students has been maintained: av. SAT > 1460

• *Challenges*

- Ensure we meet our objectives and carefully monitor outcomes
- Sustain increases in U/G enrollment but retain quality of teaching & “intimate” atmosphere of MSE department
- Infrastructure/logistics: increased class sizes.

- T.A.’s recitations

- Faculty expertise & time
- Optimize curriculum using expertise of new hires
- Increased diversity of student interest

- entrepreneurial tracks; M&T students

- Employment: career services