Creating atomic order in semiconductors quantum dots

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collaborations with
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are kindly acknowledged
Outline

1. Nobel prize for Physics 2000

2. Nanoscience and technology

3. Self-assembled semiconductor quantum dots:

   What are they? How are they made? What structure results from this process? How are they analyzed?

   Might there be atomic order in quantum dots - although the atomic arrangement is originally random? Why can there be atomic order and what needs to be done to create it?

4. Conclusions
1. Nobel prize for Physics 2000

"for his part in the invention of the integrated circuit"

Jack S. Kilby (½): creating first integrated circuit in Ge, September 12<sup>th</sup> 1958, co-inventor of pocket calculator (at HP)

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Today (nm)</th>
<th>2014 (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gate length (L)</td>
<td>120 (≤20%)</td>
<td>22 (≤20%)</td>
</tr>
<tr>
<td>Equivalent gate dielectric thickness (t&lt;sub&gt;ox&lt;/sub&gt;)</td>
<td>1.9-1.5 (≤4%)</td>
<td>0.5-0.6 (≤4%)</td>
</tr>
<tr>
<td>Sidewall spacer length (t&lt;sub&gt;s&lt;/sub&gt;)</td>
<td>72-144 (≤10%)</td>
<td>3.7-7.5 (≤10%)</td>
</tr>
<tr>
<td>Silicide thickness (X&lt;sub&gt;s&lt;/sub&gt;)</td>
<td>55</td>
<td>12</td>
</tr>
<tr>
<td>Contact depth (X&lt;sub&gt;c&lt;/sub&gt;)</td>
<td>75-145</td>
<td>15-35</td>
</tr>
<tr>
<td>Drain extension depth (X&lt;sub&gt;j&lt;/sub&gt;)</td>
<td>42-70</td>
<td>8-13</td>
</tr>
<tr>
<td>Retrograde channel depth (t&lt;sub&gt;rc&lt;/sub&gt;)</td>
<td>21-35</td>
<td>4-8</td>
</tr>
</tbody>
</table>

Gordon Moore 1965: “the numbers of transistors on a Si chip doubles every 18 month”

~ 0.01 diameter of a human hair
"for developing semiconductor heterostructures used in high-speed- and opto-electronics"

Zhores I. Alferov (¼): first (quasi-)cw-lasers on (Ga,Al)As basis without cooling, May 1970, theoretical work on double heterostructures, 1963, creating III-V compound semiconductors (at Ioffe Physicotechnical Institute, Russia)

Herbert Kroemer (¼): theoretical work on double heterostructures, 1963, creating GaP and GaAs heterostructures on Si, “0.61 nm compound semiconductor” heterostructures, i.e. (Ga,In,Al)Sb, InAs (at UCSB)

“I also predict that there will be continued development, as we may be only halfway through the information technology revolution.” Tord Claeson in his Nobel prize presentation speech, 10. 10. 2000
2. Nanoscience and technology

Richard P. Feynman: “Up to now ... we must always accept some atomic arrangement that nature gives us ... when we have some control on the arrangement of things on a small scale we will get an enormously greater range of possible properties the substances can have.”


Neal Lane: “If I were asked for an area of science and engineering that will most likely produce the breakthroughs of tomorrow, I would point to nanoscale science and engineering.”

“There are a variety of nanotechnologies, not just on.” But quantum electronics and growth and characterization of self-assembled compound semiconductor quantum dots are right at the core of it!
3. Self-assembled semiconductor quantum dots: what are they?

Traps for matter waves, artificial pseudo-atoms, entities with discrete energy levels

one-dimensional, time independent Schrödinger’s equation

\[
\frac{d^2 \psi}{dx^2} = -\frac{8 \cdot m \cdot \pi^2}{h^2} [E - U(x)] \cdot \psi
\]

Electron in atom: \( U_0 = 450 \text{ eV}, \ L = 0.1 \text{ nm} \)

Exciton in semiconductor quantum dot: \( ?E \sim 0.1 \text{ eV}, \ L \sim 10 \text{ nm} \)

How are quantum dots made? What structure results from this process?

deposition, surface diffusion, interdiffusion are random events, smaller bandgap semiconductor (alloy) usually larger lattice constant, (one way of self-assembly, resulting in “cake with raisins”)

epitaxially grown quantum dots compressively strained and possess random distribution of atoms? ordinarily strained QDs
**KEY ISSUE**: uniformities of size, shape, chemical composition, strain distribution, crystallographic phase, mutual alignment, …

*How are quantum dots analyzed?*

**Transmission Electron Microscopy**

- *CCD camera* mainly structural characterization
Scanning Transmission Electron Microscopy

EDXS benefiting from high source brightness \(-3 \times 10^8 \text{Am}^2 \text{sr}^{-1}\) factor \(\sim 10\) better than LaB$_6$

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Incident Probe

Annular Detector

Spectrometer

up to \(\sim 0.13\) nm atomic resolution

Z-contrast image

CCD EELS detector, higher dynamic range, more sensitive to light elements

both structural and spectroscopic characterization!
Might there be atomic order in quantum dots - although the atomic arrangement is originally random?

Atomically ordered In(Sb,As) quantum dot in InAs
a) atomic resolution Z-contrast image, [001] plan view; b) Power Spectrum (Fourier transform) showing superlattice spots of projected superlattice cell 3 times larger than matrix cell, ~1.3 nm, anion order

\((110)_{\text{matrix}}\) \(\parallel\) \((210)_{\text{quantum dot}}\)
**Why can there be atomic order and what needs to be done to create it?**

minimization of Gibbs free energy  \[ G = E - T S + p V \]

ordinarily strained quantum dots, subscript \( OS \),  \( p V = B_{OS} \Delta V_{OS} \)

ordinarily strained  \( > \)  atomically ordered (subscript \( AO \)) **negligibly strained**

\[ E_{OS} - T S_{OS} + B_{OS} \Delta V_{OS} > E_{AO} - T S_{AO} \]

\[ T_c = \frac{E_{OS} - E_{AO} + B_{OS} \Delta V_{OS}}{S_{OS} - S_{AO}} \]

\( E_{OS} > E_{AO} \) or \( E_{OS} < E_{AO} \) does not change sigh of \( T_c \)

**larger** \( B_{OS} \Delta V_{OS} \)  \( > \)  **larger** \( T_c \)
What does enhanced $T_c$ mean?

classical theories (Bragg-Williams, Bethe) of atomic ordering as cooperative phenomena

it is possible to design a short thermal treatment at high temperature!

result: more atomic ordering!
--------------------------------------------

What do quenched-in vacancies mean?

$$\frac{n_v}{N} = \exp\left(-\frac{F_v}{kT}\right)$$

if $F_v \sim 1$ eV, fast quench from growth temperature (500 °C) to room temperature

? up to ten order of magnitude higher vacancy concentration

in strain gradients, vacancies move to places of higher compressive strain

more quenched in vacancies, faster atomic ordering!
**Example:** \( \text{In}_{0.75}\text{Ga}_{0.25}\text{P} \) quantum dots embedded in \( \text{Ga}_{0.75}\text{In}_{0.25}\text{P} \) matrix, 3.6% strain, distributed evenly at \( T = 300 \text{ K} \)

\[
E_{\text{OS}} - T S_{\text{OS}} + B_{\text{OS}} \geq V_{\text{OS}} > E_{\text{AO}} - T S_{\text{AO}}
\]

\[-0.66 \text{ eV/atom} + 0.6 \text{ eV/atom} > -0.33 \text{ eV/atom}\]

Lattice mismatch strain destabilizes radon distribution of atom in ordinarily strained quantum dot.

**Prediction:** many different phases, Ostwald ripening

*Atomically ordered \((\text{Cd,Mn,Zn})\text{Se} \) quantum dots in \((\text{Mn,Zn})\text{Se}, <110> \) cross section cation order*
4. Conclusions

atomic order can be created by well designed thermal treatments in self-assembled compound semiconductor quantum dots

Richard P. Feynman 1959:

Up to now ... we must always accept some atomic arrangement that nature gives us. We haven’t got anything, say with a “checkerboard” arrangement, with the impurity atoms exactly arranged 1,000 angstroms apart, or in some other particular pattern.

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Now (2002) we begin creating “checkerboard” arrangements (and other particular patterns) with periodicities of ~ 10 angstroms!

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emerges as a research topic in its own right