1. Nanocrystalline materials
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3. Bulk nanocrystalline materials
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1. Nanocrystalline materials

- Free nanoclusters in vacuum are scientifically very interesting
  - But it is not exactly easy to think of many practical applications for them
- To obtain practical applications, one has to embed the nanoclusters into something, or form larger materials
- There are at least four obvious ways to do this:
  - A. Nanoclusters deposited on a surface
  - B. Nanoclusters embedded in a solid material
  - C. Nanoclusters inside a liquid
  - D. Materials consisting entirely of nanoclusters
- Case A was discussed on my previous lecture
- This lecture will deal with topics B and D
- Topic C was discussed by C. Johans

2. Formation of embedded nanoclusters

- Embedding nanoclusters isolated from each other into a solid
- There are many possible ways to embed nanoclusters into solids
- The simplest is to just mix metal particles into a liquid and cool the system down
- This technique was already used by the ancient Greeks and Romans
- However, it is difficult to control how much stuff enters and prevent the nanoparticles from sintering (being fused together) with each other
2. Embedded nanoclusters by ion implantation

- Using ion accelerators one can also make nanoclusters inside materials.
- Advantage is that the amount of embedded material and its depth can be very well controlled.

[FIGURE 7.7. Illustration of high-energy ion implantation process to fabricate quantum dots.]

Ventra, ed.: Intro to nanoscale science & techn.
3. Nanocluster formation

- By heating the sample after (or during) the implantation, one can make the ions mobile in the material. They can then (provided the material choice is suitable) join together to form nanoclusters.

4. Ostwald ripening

- Moreover, if the heating temperature is high enough, the clusters start to emit atoms with some probability.
- Emission is more probable the smaller the cluster is (higher curvature => less surface binding energy).
- This so called Ostwald ripening causes the larger clusters to grow at expense of the smaller.

An experimental realization of this looks like follows:

[Image: Diagram of Si wafer and number of clusters before and after Ge irradiation at 1200°C.]

[L. Rebohle et al, FZ Rossendorf]
2. Embedded nanoclusters by ion implantation

- Structure of a Si nanocrystal embedded in Si obtained from molecular dynamics simulations
  - Small clusters easily lose their crystal structure
  - Bigger ones are perfectly crystalline on the inside

3. Bulk nanocrystalline materials

- Background: ordinary metals are almost always polycrystalline, i.e. consist of single crystalline grains which are randomly oriented with respect to each other.
- Typical average grain size: 10-100 µm
  - Smaller grain sizes than ~1 µm practically never obtained in traditional metals processing.
- Obvious nanoscience question: what happens if grain sizes are reduced to nm scale?
- Before this question can be answered, one of course needs to know how one can manufacture such materials.
- Two basic approaches:
  - Start from nanoclusters and press them into a bulk sample.
  - Start from bulk matter and make them into a nanocrystalline powder with ball milling, then press that into a bulk sample.

3.1. Nanoclusters from sources

- The obvious approach to obtain a starting point for making a nanocrystalline material is to use a cluster ion source.
- The cluster beam is directed at some surface which it does not react with and sticks to only weakly.
  - The nanoclusters are then scraped off and lead into a compaction unit where they are compacted into a macroscopic (~mm) pellet suitable for analysis and testing.

[Hahn and Averback, J. Appl. Phys. 67 (1990) 1113]
3.2. Ball milling - basics

- Ball milling is originally a very simple way to grind materials into a fine (down to ~1 µm or even less) powder.
- The original material is put into a milling chamber as some mm-size powder together with cm-size balls of some hard material (e.g., WC).
- The chamber is then rotated and possibly vibrated to put the material and balls into motion.
- When the balls collide, they impart lots of energy to any material which happens to be in between.
- This grinds the material into a fine powder.

3.2. Ball milling – nanoscience relevance

- This seemingly boring business is of nanoscience interest for 3 reasons:
  - The powder made can be in the sub-µm regime.
  - It is possible to make alloys out of normally immiscible elements.
    - New materials
    - Made possible by the high energy transfer.
  - Most importantly, even though the powder is still in the µm regime, the grain size inside the grains may be in the ~10 nm regime!
- The last result is not quite obvious, but can be understood as follows:
  - The high energy imparted to the grains leads to dislocation formation and multiplication in them.
    - Just like most mechanical processing of any metallic material does.
  - When the dislocation density becomes high enough, they divide the grains into smaller subgrains.

3.2. Ball milling - results

- TEM images of ball milled Bi alloys
  - Clearly nm-range particles and even smaller grain sizes
- Ball milling has the advantage it can easily be used to produce very large amounts of material

[Image of TEM images of ball milled Bi alloys]

[Data from Eckert, Abe, Fu, Johnson, "MINIMUM GRAIN SIZE IN NANOCRYSTALLINE METAL POWDERS", MRS Symp. Proc. 272 (1992)]

Minimum grain size that has been achieved in various metals with ball milling:

[Graph showing melting temperature vs. minimum grain size for different metals]

Figure 3.5. Minimum grain sizes for different metallic fcc metals vs. melting temperature. (After Eckert et al.)

[Data from Eckert, Abe, Fu, Johnson, "MINIMUM GRAIN SIZE IN NANOCRYSTALLINE METAL POWDERS", MRS Symp. Proc. 272 (1992).]
3.3 Compactification

- After the nanoclusters have been made (either from a cluster source, by ball milling or in some other way) they have to be pressed into a bulk sample.
- This can in principle be achieved with simple mechanical pressing equipment.
- However, obtaining fully dense material is problematic:
  - It is obvious that just putting the clusters together tends to lead to voids between the cluster/powder particles.
  - This could easily be solved by heating the sample.
  - But heating also leads to grain growth => nanocrystallinity lost!
- Possible solution: repeated processing at low, room or even liquid nitrogen temperatures.

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Example of compactification process conditions [Poole-Owens: Intro to Nanotechnology, ch. 6.1.1]

1. Fe and Cu powders with atom number ratio 85:15 are ball milled for 15 h at 300 K.
2. The resulting material is compacted in a tungsten carbide die at 1 GPa (10 kbar) for 24 h at 300 K.
3. This is then hot compacted at about 870 MPa for 30 min at 400 °C.
- Result: final density 99.2% of the maximum.
- Grain size distribution:
4. Mechanical properties: background

- One of the main (and simplest to understand) possible benefits offered by nanocrystalline materials are their mechanical properties.
- A standard way to characterize the mechanical properties of a material is to consider stress-strain curves:
  - Obtained by pulling out the material in one dimension and measuring the stress (pressure) (force/area) needed to do so.
- Elastic regime: the linear part, reversible.
- Plastic regime: beyond linear, a permanent change in materials properties has occurred:
  - Brittle materials: brief plastic region before break.
  - Ductile materials: long plastic region.

4.1. Elastic properties

- A standard measure of the elastic hardness of a crystal is the Young’s modulus, which is basically the stress/strain.
- The Young’s modulus of a nanocrystalline material is often somewhat smaller than that of the bulk material:
  - Not an improvement!
  - However, effect is fortunately rather small.
4.2 Hall-Petch-relation: background

- The yield strength $\sigma_y$ is a practical measure of how much a sample can be strained before a permanent elongation of appreciable magnitude occurs
  - $\sigma_y \approx$ at what stress has the sample permanently elongated by 0.2%?
  - Value of 0.2% of course just a convention
- The empirical so-called Hall-Petch relation says that the yield strength follows
  $$\sigma_y = \sigma_0 + \frac{K}{\sqrt{d}}$$
  where $\sigma_0$ and $K$ are materials-dependent constants and $d$ is the average grain size of the material
  - cf. regular metals: $d \sim 10-100 \, \mu m$

This is intriguing because the relation is inversely proportional to the square root of the grain size $\Rightarrow$ when the grain size is reduced, the yield strength increases towards infinity!

- Of course this cannot happen in practice
  - Grain size of a single atom $\Rightarrow$ only single crystal left with finite tensile strength
- Law is originally empirical, but has been explained to be due to collective dislocation motion in the grains and the grain boundary impeding that
  - However, in nanosize grains the dislocations can start deforming the entire grain [Louchet et al, Phys. Rev. Lett. 97, 075504 (2006)]
  - So at some nm-grain size the Hall-Petch relation should break down
- The crucial question is of course at what size, and how much the sample has strengthened at that point
4.2 Hall-Petch-relation

The breakdown point has been examined systematically with computer simulations in Cu.

The results is that the breakdown occurs at about 15-20 nm grain size.

Below that a 'reverse' Hall-Petch effect is observed.

But the strength value obtained in the simulations, 2300 MPa, is a huge improvement compared to conventional Cu with 69 MPa.

Achieving the improvement in experiments is not quite trivial, but has been done.

However, samples made by compactification tend to have residual stresses and defects.

This tends to make the samples brittle.

For instance:

- conventional Cu has a good ductility with elongations up to 60% possible.
- nanocrystalline copper often ductility of only 5% or so.
- But in electrodeposited nanocrystalline Cu elongations up to 30% have been achieved.

[K.W. Jacobsen; CSC News 1/2005]

4.2 Hall-Petch-relation

An even more promising recent result:

- Youssef et al report for 23 nm grain size: $\sigma_y = 770$ MPa
- Achieved with compactification and combined 77 K and 300 K processing
- Not as high as in simulations
- But still 10x higher than normal Cu

Moreover, the same authors also report that their samples have good ductility, comparable to ordinary Cu

=> very promising (but to be confirmed)

5.1. Electrical properties of embedded nanoclusters

- Conducting nanoclusters can be used to alter the electrical properties of an otherwise insulating matrix
- To achieve good electrical conductance, the clusters have to be connected electrically
  - If they are touching, electrons can move from one cluster to the next
  - Alternatively they can be connected with conducting organic molecules
- For macroscale electrical conductance (and in the absence of connecting molecules), it is required that the cluster density is high enough that they form a globally connected network
- This is called the percolation threshold and amounts to about 50-60% cluster density
- Just below this threshold the conductivity drops orders of magnitude
5.1. Electrical properties of embedded nanoclusters: example

- Main result: resistivity drops orders of magnitude between $10^{14} - 10^{15}$ ions/cm² dose.
- Explanation is that percolation density is reached at these doses.

![Graph showing resistivity change with dose](image)

5.2 Electrical properties of embedded nanoclusters: non-volatile memory?

- One of the maybe most exciting possible applications of nanoclusters is for non-volatile memories.
- The idea for this was introduced by Tiwari in 1996 [Appl. Phys. Lett 69, 1232].
- Original idea was to use Si nanoclusters in SiO₂, but since then plenty of studies also on metal nanoclusters have been made.

![Diagram of memory structure](image)
5.2 Non-volatile memory: background

- Non-volatile memory means erasable and re-programmable memory which needs no charge to maintain
  - "EEPROM", but better known nowadays as flash memory
- Many (probably most) of today’s nonvolatile memories are based on a so-called ‘floating gate’ structure
  - Instead of a single gate (which steers the operation of a MOSFET transistor) there are two parts
- The floating gate is all surrounded by insulating material
- Hence when it is charged, the charge stays there forever (if there is no leakage)

5.2 Non-volatile memory: nanoclusters

- The idea of Tiwari is to use nanoclusters as the ‘floating gate’
- There are several demonstrated advantages to this:
  - Single-electron charging
  - Quantum confinement: well-defined energy levels
  - Coulomb energy of charged cluster discourages additional charging
  - Strong barrier to surrounding
- Charging and discharging occurs in steps rather than a continuous profile
5.2 Non-volatile memory: nanoclusters

- Already the original paper of Tiwari showed quite good characteristics like:
  - Negligible drain current at low voltages
  - Long charge storage times
  - Lots of write/erase cycles possible
- Since 1996 lots of research attention has been paid to this and similar devices
  - Numerous recent patents
- Situation in 2010: development efforts continue, apparently not yet on market but close


6. Optical properties of embedded nanocrystals

- Recall the Ge nanocrystals embedded in SiO₂:
- These have been demonstrated to enable blue light emission from a Si-based material (which cannot be done with pure Si)!

[L. Rebohle et al, FZ Rossendorf]
6. Optical properties of embedded nanocrystals

- Maybe even more exciting is that it might be possible to use Si nanocrystals in SiO$_2$ to make an Si-based laser
  - L. Pavesi et al showed in 2000 that light amplification can be achieved by this kind of nanocrystals [Nature 408, 440 (2000)]. This is the first step towards making a laser
  - L. Kriachtchev et al (Univ. Helsinki) showed soon afterwards that the amplified pulses can be very short, which is important to achieve fast operation [Appl. Phys. Lett. 79, 1249 (2001)]
  - SiO$_2$ is one of the key materials of conventional Si technology, and ion implantation equipment part of standard beamlines
    - Hence a Si nanocrystal laser would be entirely compatible with standard semiconductor manufacturing technology
    - Si optoelectronics and conventional electronics all integrated on the same chip!
      - That’s the dream anyway…

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6. Optical properties of embedded nanoclusters

- A classic example of nanotechnology is the colouring of glass using metal (most commonly Au) nanoparticles
- This is the technology used by the ancient Greeks and Romans to achieve beautiful effects in glassware
  - The most famous example is the Lucyrgus cup
    - When viewed in reflected light, it appears green
    - However, when viewed in transmitted white light, it appears red!
  - It contains about 40 ppm Au and 300 ppm Ag, which form nanoclusters inside
  - The technique to make glass red by adding gold to it was later rediscovered by Kunckel, a German glassmaker in the 17th century
    [British Museum, Dept. of Scientific Research web pages]
6. Optical properties of embedded nanoclusters

- This effect is shown more systematically here
  - Absorption of glass with 20 and 80 nm Au particles

- When compared with the spectrum of visible light one sees that the middle wavelengths, green and blue, are absorbed well => only red and some violet remains

6. Optical properties of embedded nanoclusters: reasons

- The reasons to this behaviour is not simple
- The free electrons in the metal particles (just as in a bulk metal) can in some respect be considered a plasma
- The electromagnetic wave which is visible light causes a plasma oscillation in the particles, which results in the absorption of light
- A theory by Mie says that the absorption coefficient for small spherical particles is

\[
\alpha = \frac{18\pi N_s V n_0 \varepsilon_2^3 / \lambda}{\left[\varepsilon_1 + 2n_0^2\right]^2 + \varepsilon_2^2}
\]

where \( N_s \) is the number of spheres of volume \( V \), \( \lambda \) is the wavelength of the incident light, the \( \varepsilon \) are the dielectric constants of the cluster material and \( n_0 \) is the refractive index of the glass
- Noteworthy is that the absorbance increases with both \( N_s \) and \( V \)
6. Optical properties of embedded nanoclusters: reasons

- This equation alone does not lead to a maximum in $\lambda$, but one has to bear in mind that also the $\varepsilon$ and $n_0$ depend on wavelength.

- Another feature of interest is that the nanoclusters in glasses exhibit nonlinear optical effects, i.e. the refractive index of the material $n$ depends on the intensity of the light $I$.

- Such a refractive index may be written as

$$n = n_0 + n_2 I$$

- Note that these effects occur independent of quantum confinement in the nanoparticles.

- For particle sizes < 10 nm also the quantum confinement becomes an important additional effect.

7. Nanoporous materials: general

- An interesting special variety of nanostructured materials are the nanoporous ones.

- One may imagine that such a material is like embedded nanoclusters where the ‘nanocluster’ is empty space.

- Below the percolation threshold this is a highly *holey* material (much like Swiss cheese).

- Above the percolation threshold one has a sponge-like material.

- A wide range of materials can be made nanoporous in a wide range of ways:
  - Semiconductors by electrochemical etching
    - Electrochemical etching: an acid and an electric field
  - By nanocluster deposition
  - By prolonged ion irradiation (e.g. Ge but not Si)
  - ….
7. Nanoporous materials: general

- Sample cross-sectional image of porous Si
- The nanoporous materials can also be ordered
  - Combination of lithography and directional etching

7. Nanoporous materials: applications

- Porous materials have a wide range of possible applications:
- Light-weight structural materials
  - Important example: bone
- Optical waveguides
  - Artificial crystals to guide light instead of electrons
- Nanofluidics: storage of fluids in the pores
  - Medical uses...
- Changing the optical or electronic properties of materials
  - By far most promising case: Si

[J. Linnros, KTH Sweden]
One particular case of nanoporous materials which has received immense research attention is nanoporous Si.

Ordinary Si is of course the base of computer technology, but as stated earlier, it is not good for optical applications:
- It has an indirect bandgap => inefficient light emission
- Luminescence (light emission) is in any case poor

But in 1990 it was discovered that electrochemically etched nanoporous Si (PoSi) is luminescent in the near-infrared at room temperature at photon wavelengths which are dependent on the etching time.

This could be of great importance because luminescent Si could easily be adapted to be part of conventional Si chip technology:
- => cheaper components for optoelectronics?
- => cheaper lasers??
- => photonic circuits on Si??

Note that the emission energies of 1.4 – 2.0 eV are well above the band gap of Si (~ 1.1 eV at room T)!

This is not completely surprising, as it is known Si nanoclusters have a much increased band gap of up to 4 eV.
7. Nanoporous Si

- The luminescence can also with various tricks be shifted to be well in the visible light range of 300-700 nm
- The luminescence is also observed to be quite efficient

- The mechanisms behind the effect are not clear at all, though
- Many different explanations have been proposed
  - Oxide impurities, surface defect states, quantum confinement, …
- Early work interpreted the efficient emission to mean that the band gap in PoSi is direct
  - However, later work cast even this into doubt:
    - E.g. Frederiksen, Phys. Rev. B: 58, 8020: "direct or indirect gap has no precise meaning [in nanosystems]"