Carbon nanostructures: background

- Carbon has 3 main kinds of chemical bonding
  - “sp”: linear
    - E.g. acetylene molecule $C_2H_2$
  - “sp$^2$”: 3 bonds in a plane, angles of 120°
    - E.g. ethylene molecule $C_2H_4$
    - Graphite bulk structure
      - Interaction between layers weak
        (no covalent bonding)
    - Single graphene sheet
  - “sp$^3$”: 4 bonds symmetric in 3D
    - E.g. methane molecule $CH_4$
    - Diamond bulk structure

Graphene

- Individual graphene sheets were first isolated as late as in 2004 by Andre Geim et al. at the University of Manchester
  - Andre Geim and Konstantin Novoselov got the Nobel prize for the discovery in 2010!
- Isolation technique in principle very simple
  - Schotch tape and peel off
  - Even an ordinary pencil draw will make a number of isolated graphene sheets
  - But the difficult part was to get large areas, detect and manipulate them in a controlled manner
- Now it can be done routinely
  - A single graphene sheet can be macroscopic and visible to the naked eye!
Graphene properties

- An ideal 2D conducting system
- Very durable mechanically, does not oxidize in air
- Graphene can be grown in various ways – e.g. on Ni and then transferred on Si (C) or on SiC (D)

Graphene paper can be made out of graphene oxide

[Geim, Physics Today 61 (2008), 35–41]

Graphene has incredible strength

The unit hexagonal cell of graphene contains two carbon atoms and has an area of 0.052 nm². We can thus calculate its density as being 0.77 mg/m².

A hypothetical hammock measuring 1 m² made from graphene would thus weigh 0.77 mg.

Strength of graphene

Graphene has a breaking strength of 42 N/m. Steel has a breaking strength in the range of 250-1200 MPa – 0.25-1.2 X 10⁸ N/m². For a hypothetical steel film of the same thickness as graphene (which can be taken to be 3.35 Å – 3.35 x 10⁻¹⁰ m, i.e. the layer thickness in graphite), this would give a 2D breaking strength of 0.004-0.40 N/m. Thus graphene is more than 100 times stronger than the strongest steel.

In our 1 m² hammock tied between two trees you could place a weight of approximately 4 kg before it would break. It should thus be possible to make an almost invisible hammock out of graphene that could hold a cat without breaking. The hammock would weigh less than one mg, corresponding to the weight of one of the cat's whiskers.

Relation of carbon nanostructures

- All of the carbon sp² structures can be conceptually thought of to derive from graphene
  - Real growth is different!

Fullerenes

- The fullerene molecule C₆₀ was found in 1985
  - Kroto, Smalley & co.

- Round carbon molecules
  - Each carbon atom has 3 bonds, and the atoms form rings with 5 or 6 atoms (pentagons and hexagons)
    - Just like in a traditional soccer football!
  - Could be imagined to be formed by strongly bending a graphene sheet to a ball
  - Bond reforming needed to form pentagons, though

- Name got inspiration from the architect
  - Buckminster Fuller who designed similar domes
  - "Fullerene", "Buckyball", "Buckminsterfullerene"
**Different types of fullerenes**

- Even though C\textsubscript{60} is the most common, many other fullerenes do also exist
- At least C\textsubscript{30} – C\textsubscript{720}
- The smallest (N\textsubscript{atoms} < 30) are likely not closed shells, i.e. are not fullerenes
- The largest are no longer round
  - They have more energetically favorable hexagons in flat regions

**Fullerene properties**

- Individual fullerenes are very elastically hard:
  - The C-C bond in graphite is one of the strongest in existence
  - Experimental bulk modulus (capability to resist compression) \( \sim 1000 \) GPa (diamond 442 GPa)
- But the bond between fullerenes is very weak (same as the so called van der Waals/dispersion interaction between graphite shells
  - The bulk modulus of a crystal formed from fullerenes only 14 GPa
  - Melting/boiling point 300 °C
- Interesting new chemistry
  - Already in 1997 over 9000 fullerene compounds was known – now nobody is counting any more
  - It is possible to put atoms or molecules inside fullerenes
    - “Endohedral fullerenes”

**Production**

- Fullerenes can be made in many different ways, but the basic idea of most methods is similar to:
  - Carbon source
  - High voltage or temperature makes the carbon gasify
  - The holder has He gas in a low pressure (e.g. 100 Torr)
  - In the gas or plasma fullerenes are formed
    - Also ordinary soot
  - Fullerenes can be dissolved in e.g. toluene, the soot not

[http://www.sussex.ac.uk/Users/kroto/workshop.html]

**Fullerene properties: superconductivity**

- Maybe the most surprising property of fullerenes is that they can be made electrically superconducting
  - Superconductivity = no electrical resistance
- For instance the K\textsubscript{3}C\textsubscript{60} crystal is superconducting below 18.4 K
  - Rubidium-Thallium-doped fullerenes have a transition temperature as high as 45 K
- Compare this with:
  - Normal metals max. about 20 K
  - Ceramic copper oxide superconductors about 50-100 K
- Fullerene superconductors are their own class of superconducting materials
  - Not understood on a fundamental level!
Carbon nanotubes

- Carbon nanotubes are hollow cylindrical tubes of carbon that have a diameter of only a few nanometers, but may have lengths of microns.
- Like a graphene shell rolled to a tube, all atoms in hexagons.
- The end of the tube can be open or fullerene-like.

Record is 4 cm length for a single tube [Zheng et al, Nature Materials 2004]

Chirality of carbon nanotubes: notation

- The chirality is given by two numbers in the form (A,B), A>B
  - E.g. the cut shown above was (4,2) and the resulting tube becomes:
    - The tube clearly has a helix-shaped “twisted” form, i.e. is chiral
    - Tubes with indices of the form (A,0) and (A,A) are not chiral
      - They are thus called achiral
    - Tubes of the form (A,A) are called armchair tubes
    - Tubes of the form (A,0) are called zigzag tubes
    - All other types are called chiral

Chirality of carbon nanotubes

- A nanotube can conceptually be formed by rolling up a sheet of graphene so that the bonds at the edges match perfectly.
  - A sheet can be rolled up in any way.
  - But a graphene sheet has bonding directions, so all directions are not equivalent.
  - The types of possible cuts can be defined by a single vector OA.
  - This vector can be determined from the bonding directions in graphene, vectors \( a_1 \), \( a_2 \).
  - These can be used to form the vector OA as shown to the right.
  - I.e. 4 and 2 vectors: (4,2)

Nanotube chirality, examples

- (5,5) armchair
- (9,0) zigzag
- (10,5) chiral
**“Armchair” ??**

- Whence the name armchair??
- If you look at the tube from the side, you can imagine seeing the shape of an armchair on it

**Production of the tubes**

- The basic idea of making carbon nanotubes is the same as that of fullerenes
  - Hot gas or plasma of carbon, possibly carrier gases

- Single-walled tubes require metal nanoclusters to grow!
  - Otherwise the end closes quickly and one only gets a fullerene

- Multi-walled tubes can grow spontaneously
  - The different walls interact with each other and prevent closure

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**Single vs. multiwalled nanotubes**

- Nanotubes may have many tubes inside each other
  - Single-walled nanotubes SWNT, multi-walled nanotubes MWNT
    - Special cases of MWNT’s: double-walled: DWNT, triple-walled: TWNT

**Nanotube structures**

- The nanotubes can form a bundle
- And a rope can be formed from the bundles
  - Note the scale!

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*Zhu et al, Science 296 (2002) 884*
Nanotube forest and -paper

- By growing nanotubes from a surface one can form a "forest" out of them
- Paper can be made from the bundles
  - "Paper" in the generalized meaning of a fiber network

[K. Arstila. Accelerator Laboratory]

Properties of a single nanotube

- A single nanotube has incredibly good properties
  - Strength:
    - Young's modulus: 1250 GPa
      - Cf. Fe 211 GPa
    - Tensile strength: in theory 300 GPa, measured 63 GPa
      - Cf. steels 0.5 – 1.5 GPa
  - Electrical conductance
    - The tubes are either metallic or semiconducting depending on chirality:
      - Armchair tubes (A,A) are metals
      - If A-B is divisible by three: small band-gap semiconductor
      - Otherwise: large band gap semiconductor
    - Very large current-carrying capacity:
      - Estimated at 1000 MA/cm²
      - cf. copper 1 MA/cm²

Properties of nanotube agglomerates and composites

- The properties of a single tube are thus outstanding
- But it is important to understand that this is not necessarily the case for macroscopic materials consisting of nanotubes
- The main reason is that between the tubes there is only the weak van der Waals-bonding
  - About 100 times weaker than the covalent bonds inside the tubes
- Big problem especially for the mechanical properties
  - Tubes can easily slide by each other => the excellent strength of a single tube is lost
  - The issue can be improved on chemically or with irradiation – but not up to the full strength of individual tubes, at least yet
  - Also the electrical contact between the tubes is weak
  - But this is not necessarily as problematic as for the mechanical properties
Carbon onions and nanodiamonds

- Carbon also has other interesting nanostructures
- Carbon onions
  - Fullerenes inside each other
- Nanodiamonds
  - Can be made e.g. by irradiating carbon onions: the fullerenes shrink when atoms vanish => high pressure => diamond formation inside
  - Nanodiamonds also exist in nature, due to radioactive decay
  
  
  [F. Banhart, Physikalische Blätter 53, 33-35 (1997)]

Nanoclusters: background

- Ordinary metals have in the solid state 8-12 bonds
- A "metal bond" is not a strongly directional covalent chemical bond, but can be understood to be formed by the attraction between the free conduction electrons and a negative electron gas
- Since there is no directionality, it is energetically favourable for metals to have as many bonds as possible
- FCC- and HCP-structure metals have 12 nearest neighbours, BCC 8
  - FCC and HCP are close-packed spheres
  - Almost all elemental metals have one of these three structures

HCP structure
FCC structure

Nanoclusters: structure

- A nanocluster (nanoparticle): an agglomerate of some 10-100,000 atoms or molecules bonded together, where the local environment of each atom/molecule is similar
  - Nanoparticle = any object in the 1 – 100 nm size range
  - Nanocluster: a 1 – 100 nm agglomerate of identical atoms or molecules
    - A single molecule of complex structure is not a nanocluster
  - Atom cluster ≠ nanocluster
  - Nanocrystal = crystalline or polycrystalline nanocluster
  - Can be formed from any class of materials
    - Metals
    - Semiconductors
    - Carbon: fullerenes!
    - Hydrocarbons, organic molecules
  - In this lecture we focus on 'hard material' i.e. metal or semiconductor clusters

A really large cluster has of course the same shape as the bulk material
  - As if one would cut away a sample of the macroscopic material
  - But smaller (of the order of a few thousand atoms) often exhibit interesting structural effects
  - E.g. Co nanoclusters have mainly the FCC crystal structure, even though bulk Co has the HCP structure!
  - Because a large fraction of the cluster atoms are on the surface, the orientation of the surface affects the energetics of the whole cluster!
  - E.g. for FCC metals the most favorable surface direction is the so-called 111 direction, followed by 100
  - Hence many FCC metals form structures that maximize the number of 111-oriented surfaces
    - Example to the right: a so-called truncated octahedron shape, where all surfaces are the most favorable 111 and 100 oriented ones
Multiply twinned octahedron vs. single crystalline

- Single crystalline
  \[ (111) + (100) = (111) \]

- Twinned (multiply twinned icosahedron)
  \[ \times 20 = (111) \]

[T. T. Järvi et al., EPL 2009]

Nanoclusters: structure

- Due to such effects, nanocrystals tend to have shapes of polygons rather than being spherical
  - This is evidenced by clearly facetted shapes when they are viewed e.g. in an electron microscope


Co nanoclusters on a Cu surface

Nanoclusters: stability

- Nanocluster stability is not a smooth function of the number of atoms \(N\) in the molecule
  - This has at least 2 reasons:
    - Purely geometrical: certain numbers of atoms can maximize the fraction of the most favourable surfaces (e.g. 111 for FCC)
    - Electronic: the electronic structure is energetically more favourable for certain \(N\)

- Plots to the right show the experimental abundance of Na clusters as a function of \(N\) and that it can be explained by electronic structure

For really small clusters, the structure can differ dramatically from that of the bulk phase

- E.g. gold is often considered to be the prototypical FCC metal
  - Hence one could expect that in small clusters gold remains in structures where the fraction of neighbors maximizes
- But e.g:
  - \(\text{Au}_{32}\) has been predicted to be a fullerene!
  - \(\text{Au}\) clusters with less than 13 atoms are fully flat
Nanocluster production

- Nanoclusters can be made in many different ways
- One of these is related to the formation of fullerenes: individual atoms are lead into a gas or plasma where they spontaneously join together
- For metals this is actually a quite simple process
  - Contrary to fullerenes, it is not difficult to find a minimum structure
- Similar clusters can also be formed by chemical reactions in a solution

Example: animation of condensation of Cu in an Ar gas:
- Cu yellow
- Ar red

[Nano-1]


Embedded nanoclusters

- Nanoclusters can also be made inside solid materials
- First a supersaturation of one element is formed inside the material
  - Can be achieved e.g. with irradiation or crystal growth techniques
  - Supersaturation = amount of species above the equilibrium solubility
- Then if by heating the excess atoms become mobile, they may form clusters inside the material

Example: Ge nanoclusters inside SiO₂

[Nano-1]

[M. Backman, F. Djurabekova et al, Phys. Rev. B acceptedish]

Nanocluster properties

- The melting point is lowered
- Interesting optical effects
  - Electronic structure is different from bulk, so also light absorption and emission may differ
- Catalysis properties of nanoclusters are interesting for at least two reasons:
  - Because the fraction of surface of all the material is large in nanoclusters, one can achieve a lot of catalysis effect with a small amount of raw material
    - Due to this e.g. car catalysis is based on about 5 nm Pt/Pd/Rh-nanoclusters
  - But because also the electronic structure of nanoclusters is different from that in the bulk, catalysis may be different
    - E.g. very small Au nanoparticles are very active catalytically, even though bulk Au is in most respects very nonreactive

[Nano-1]

Nanocrystalline thin films

- By depositing or joining nanocrystals together, one can form materials with nanometer-sized basic crystal grains
  - In normal metals the grain size is of the order of 10-100 micrometers, so such a "nanocrystalline" material can be radically different from its bulk counterparts

[Nano-1]
Nanometer-thin films: background

- The concept of a thin film means a layer of one material on top of another bulk (macroscopic) material
  - Thin films are widely used in industry
    - E.g. gilding is a thin film technology
    - The thin film forming process is called coating

- If the thin films have thicknesses in the nm range, and they are made with some novel method, they may be considered nanoscience or nanotechnology

Vacuum thin film techniques

- A large fraction of modern thin film technologies are based on vacuum methods
  - Use of a vacuum ensures good purity in the thin film
  - In these methods a film is formed by placing atoms one by one on a surface
    - Sometimes instead of a single atom, a molecule or a nanocluster
    - This enables making arbitrarily thin foils on top of something, even less than one atomic layer thickness!

Physical deposition techniques

- The deposition techniques are often divided into "physical" and "chemical" ones
- In the physical methods, atoms are deposited on the surface one at a time, and chemical reactions do not have a significant influence on the end result
- Often used general term is "Physical Vapor Deposition (PVD)"
- The PVD methods can be distinguished by how the individual atoms are produced
  - Vaporization: the coating material is heated close to its melting point
  - Sputtering: the coating material is bombarded with energetic ions so that individual atoms are loosened from it
  - Lasers: short intensive light pulses loosen atoms from a material
- If the ions are accelerated to kinetic energies much above normal thermal energies (which are < 1eV), the method is called ion implantation

Chemical deposition techniques

- In the chemical methods atoms or molecules are deposited on a surface, and a chemical reaction plays a role in getting the desired result
- “Chemical Vapor Deposition”, CVD: a group of methods in which the coating molecule breaks up at the surface and some part of it produces the desired coating
Chemical deposition techniques

- "Molecular beam epitaxy", MBE
  - Deposition done by a molecular or atomic beam
  - Surface is at a high temperature, so the atoms find an energetically favorable position
  - Done in ultra-high vacuum (UHV)
  - Enables making of high-quality single crystalline thin films
- "Atomic layer deposition", ALD
  - Sometimes also called "Atomic layer epitaxy", ALE
  - Chemical deposition in two phases done so that when one atom layer A has been deposited, the reaction stops. After that with a different chemical another layer B is deposited, after which the reaction again stops.
  - The desired molecular crystal is thus AB, e.g. SiO₂
  - Possible to control the deposition thickness with 1 atom layer accuracy!

Background: growth modes

- The thin film growth modes are conventionally divided into three categories:
  - Island
  - Layer + Island
  - Layer-by-Layer
  - \( \theta < 1 \text{ML} \)
  - \( 1 < \theta < 2 \)
  - \( \theta > 2 \)

- When ordinary flat thin films are desired, the growth mode of choice is of course Frank-van der Merwe

Growth modes: Stranski-Krastanov

- But with the Volmer-Weber or Stranski-Krastanov growth modes one can obtain nanometer-sized islands on the surface
- Thus one can grow nanoclusters on the surface!
  - For semiconductors or metals a quantum dot
- Using MBE it is possible to grow single-crystalline semiconductor quantum dots
  - Both on the surface and inside the material

Possible properties of thin films

- Thin films may have excellent hardness properties
- Many of the hardest known materials are based on multilayer thin films
- The hardness grows with decreasing thickness
  - Of course effect vanishes at some point, when single atom layer thickness starts to be approached
- Example: hardness of TiN/NbN multilayer thin films

p = \[ \text{HARDNESS (GPa)} \]

\( p = 41 \)
Electrical and optical properties

- Semiconductor lasers are based on multilayer thin films
  - The active layer is a doped semiconductor, often GaAs
  - It forms the “cavity” needed for laser operation
  - The structure is called a quantum well structure and the whole component a quantum well laser

Magnetic properties

- The hard drives of modern computers are based on thin films both in the read/write head and the disk itself
- In the read head, a very good magnetic sensitivity is achieved with very thin metal films
- They have a giant magnetoresistance (MR), i.e. resistivity depends strongly on magnetic field
  - In ordinary materials the MR is almost always below 1%
- In giant magnetoresistance (GMR) and colossal magnetoresistance (CMR)-structures the MR effect may be even hundreds of percents!

Summary

- One can achieve exciting and useful new kinds of materials starting from quite ordinary stone and iron age materials such as carbon, metals and minerals by putting them into a nanostructured form!