

Two Dimensional Material, Their Properties, Application and Manufacturing

Reading Assignment

Shibu Meher

IIT Bhubaneswar

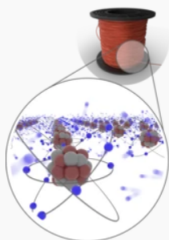
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Outline

- 1 Introduction
- 2 What are 2D materials?
- 3 Why are 2D materials different from bulk materials?
- 4 How to make 2D materials?
- 5 Application of 2D materials

Foundation of Technology

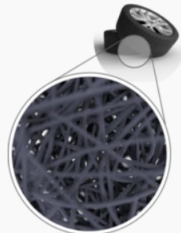
- How well we understand material system
- Material properties depends on what it is made up
- Does the properties depend on size?



Metals conduct electricity because some electrons free themselves from their orbits and can flow through the material.



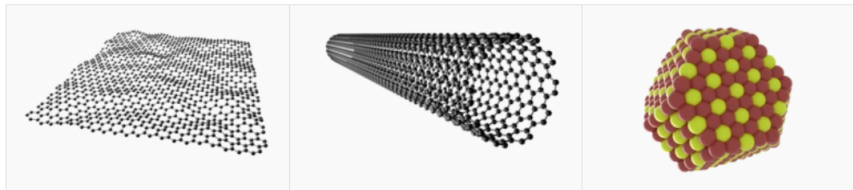
Concrete is strong because cement locks together in-compressible particles of sand and gravel.



Polymer chains give rubber its flexibility. Rigidly locking the chains together increases the durability of the material.

Nanomaterials

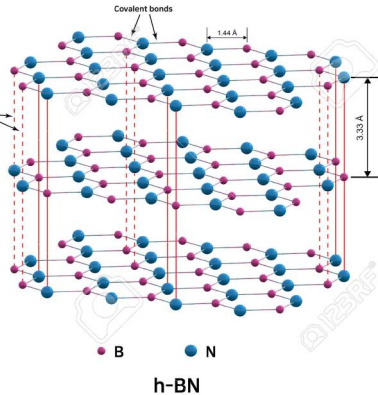
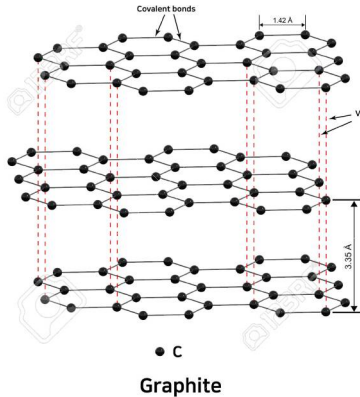
- Having at least one dimension in nano-scale ($< 100nm$)
- Materials -
 - 0D Material - nanoparticle, e.g. quantum dots
 - 1D Material - nanotube/nanowire, e.g. carbon nanotube
 - 2D Material - sheet or film with thickness in nano-scale, e.g. graphene
 - 3D Material or Bulk material - e.g. block of iron.



Properties and example of 2D Material

- Due to nanoscale dimension following properties are affected.
 - Electrical and thermal conductivity
 - Chemical reactivity
 - Mechanical properties
 - Interaction with light and other radiation and beam of particle
 - New phenomenon - Quantum hall effect, Berry phase
- Example - Graphene, Hexagonal Boron Nitride (h-BN), Transition Metal Di-Chalcogenides(TMDCs), Phosphorene, Xenes etc.

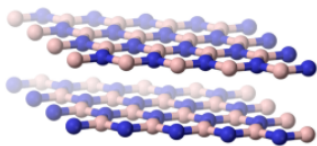
Graphene and h-BN



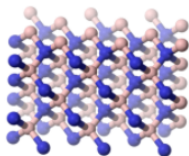
Graphene

- Covalently bonded hexagonal lattice of carbon
- One atom thick - 0.14nm
- Semimetal - Valance and conduction band touch each other
- Unique band structure - Extremely high speed of electron ($\frac{1}{300}$ the speed of light) leading to exceptional thermal conductivity
- Has highest tensile strength
- Fascinating Physical phenomenon - Quantum hall effect, Berry phase

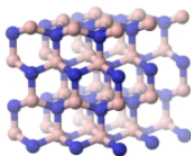
- Has same crystallographic appearance as graphene except that it has B and N atom
- Wide band gap insulator



Hexagonal form (h-BN)
hexagonal analogous to [graphite](#)



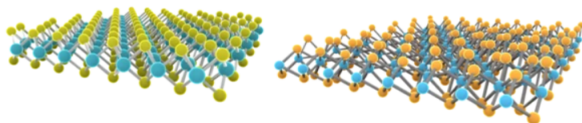
Cubic form (c-BN)
[sphalerite](#) structure
analogous to [diamond](#)



Wurtzite form (w-BN)
[wurtzite](#) structure
analogous to
[lonsdaleite](#)

Transition Metal Dichalcogenides or TMDCs or MX_2

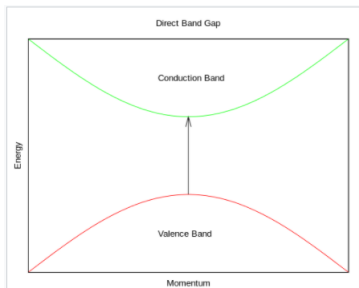
- M - Metal atom, e.g. Mo, W
- X - Chalcogens/oxygen family, e.g. S, Se, Te
- van der Waals material - layer material
- Metal layer is sandwiched between chalcogenide layer
- Two phases - 2H phase (triagonal, semiconductor, e.g. MoS_2 , WS_2 , $MoSe_2$) and 1T phase (hexagonal, metallic, e.g. WTe_2)



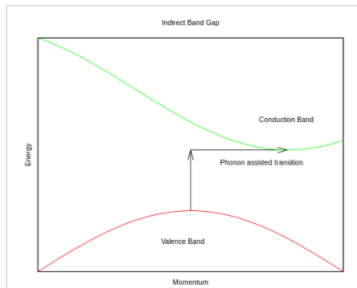
Left: Molybdenum disulphide (MoS_2). Right: Tungsten ditelluride (WTe_2). Both are 2-dimensional transition metal dichalcogenides. MoS_2 is most commonly found in the semiconducting 2H phase, while WTe_2 prefers to adopt the metallic 1T phase.

Direct and Indirect Band gap

- 2H phase - indirect band gap in bulk and direct band gap in monolayer - suitable for optoelectronics
- Direct and Indirect band gap



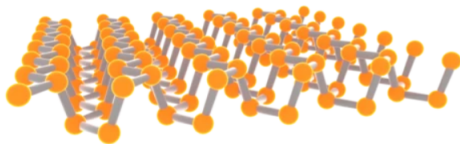
Energy vs. [crystal momentum](#) for a semiconductor with a direct band gap, showing that an electron can shift from the highest-energy state in the valence band (red) to the lowest-energy state in the conduction band (green) without a change in [crystal momentum](#). Depicted is a transition in which a photon excites an electron from the valence band to the conduction band.



Energy vs. [crystal momentum](#) for a semiconductor with an indirect band gap, showing that an electron cannot shift from the highest-energy state in the valence band (red) to the lowest-energy state in the conduction band (green) without a change in momentum. Here, almost all of the energy comes from a [photon](#) (vertical arrow), while almost all of the momentum comes from a [phonon](#) (horizontal arrow).

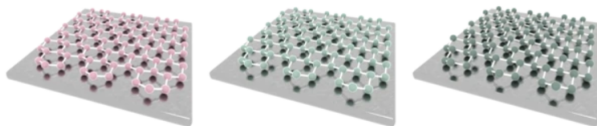
Phosphorene

- Direct band gap semiconductor
- Wrinkled honey comb structure
- Band gap - tunable by stacking layers
- Good charge mobility - about $1000 \frac{cm^2}{Vs}$
- Anisotropic
- Application - Optoelectronics and transistors



Phosphorene (also known as 2D black phosphorus) is a 2D semiconductor that is a promising material for transistors.

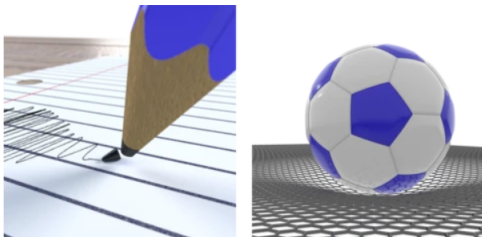
- Monolayer of silicon(silicene), germanium(germanene), tin(stanene)
- Buckled hexagonal structure
- Can not be exfoliated, only grown epitaxially on substrate
- Have strong interaction with the substrate
- Recent - antimonene, bismuthine (magneto-electronics)
- Potential Application - Field Effect Transistors, topological insulator



Silicene (left), germanene (middle) and stanene (right) have buckled hexagonal structure.

Why are 2D material different from bulk materials?

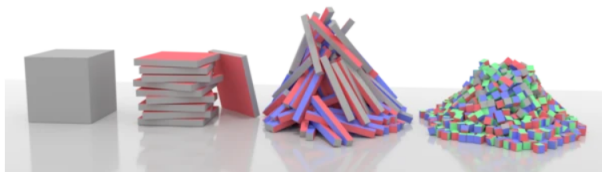
- Removal of van der Waal interaction



Graphite (left) can be easily broken because of its weak interplane Van der Waals forces, while graphene (right) has only covalent bonds and so it extremely strong - a monolayer is strong enough to support a football.

Why are 2D material different from bulk materials?

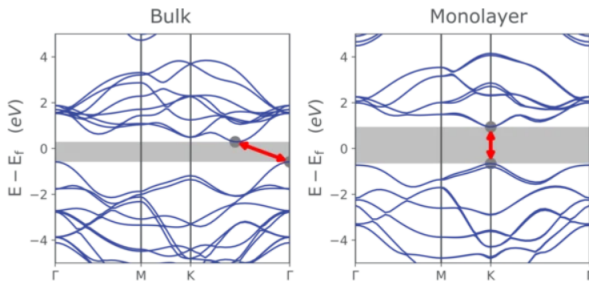
- An increase in ratio of surface area to volume
 - 2D material are more reactive than their bulk counterpart
 - Suitable for sensing application



When an object is divided into smaller components, its total surface area increases. From left to right: a bulk object is divided into 2D sheets - exposing the red surfaces, and the sheets are divided into 1D rods - further exposing the blue surfaces. Finally, the rods are divided into dots - exposing additional green surfaces.

Why are 2D material different from bulk materials?

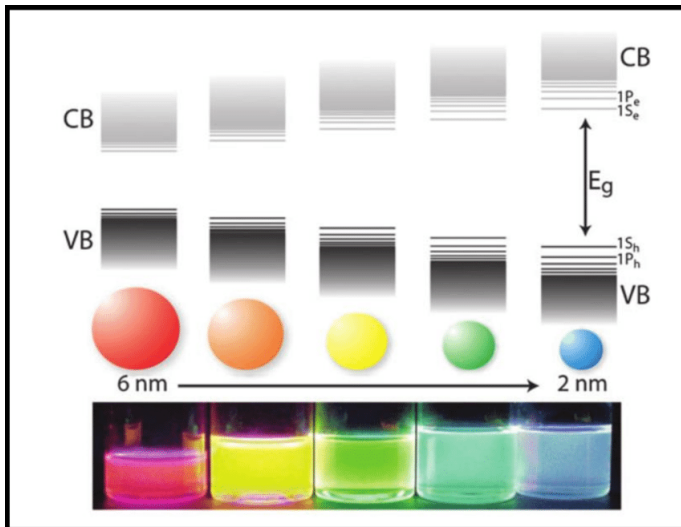
- Confinement of electrons in a plane
 - Change in band structure - Indirect to direct
 - Increase in band gap - Q. Why does the conductivity increases in case of graphene but not in case of h-BN?



Band structure diagram of (left) bulk and (right) monolayer MoS₂ showing the crossover from indirect to direct bandgap accompanied by a widening of the bandgap.

Quantum Confinement

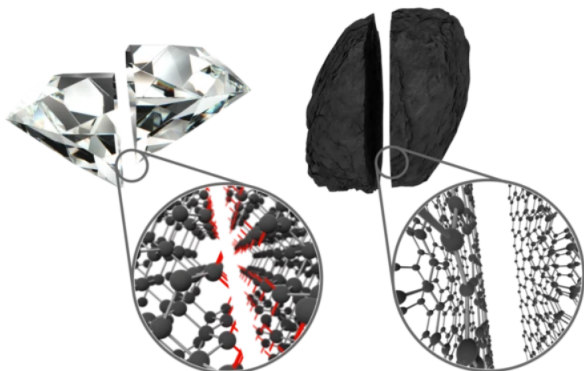
- Increase in band gap
- Bohr radius



Making of 2D Materials

- Graphene - First 2D material, 2004, Scotch-tape mechanical exfoliation
- van der Waals Material - Layered material
- Two approaches
 - Top-down Approach - Start with bulk material make it thinner, e.g. Mechanical exfoliation, Liquid exfoliation
 - Bottom-up Approach - Start with atomic ingredients and assemble them together, e.g. Chemical Vapour Deposition, Solution based chemical synthesis

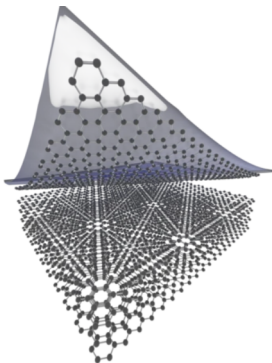
Top-down Approach



Each carbon atom in diamond (left) has bonds extending in 3 dimensions - meaning that when diamond is cut in any orientation, some of these bonds must be broken and are left 'dangling' (shown in red). The atoms in graphite (right) have bonds extending in only 2 dimensions, so when it is cut in an orientation parallel to the bonds, none of them are broken.

Mechanical Exfoliation or Scotch Tap Method

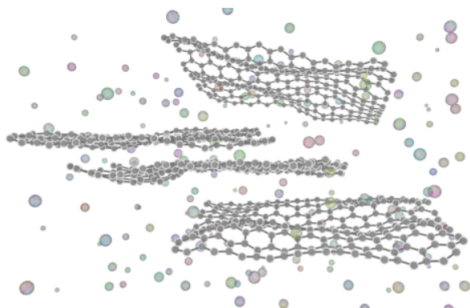
- Monolayer yield is low
- No control of size and shape
- Size - reasonable - few microns to 100 microns
- Quality - excellent
- Popular for van der Waals material and lab based studies



Mechanical exfoliation involves peeling successive layers from a Van der Waals material using a tape.

Liquid Exfoliation

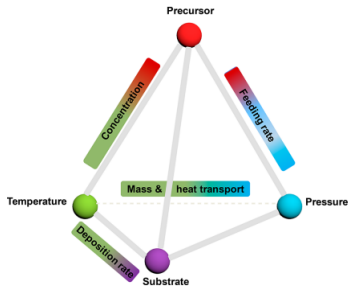
- Use of organic solvent to create force between layer
- Sonication, Use of reactive ions
- Highly scalable
- Low monolayer yield, small flake size ($< 100nm$)
- Not suitable for optoelectronic application - high density of defects, residual solvent



Liquid exfoliation often uses bubbles to force layers apart.

Chemical Vapour Deposition (CVD)

- One or more precursor gases (containing ingredients for the film) are passed through a heated chamber where they react with each other or with the substrate to form thin layer of required material.
- Successfully applied - Graphene, TMDCs
- Complex and expensive
- Highly scalable and quality approaches that of mechanical exfoliation



Application of 2D materials