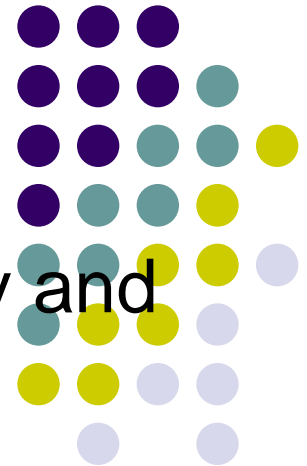


Physics of Materials: Carbon Materials: History and Allotropes

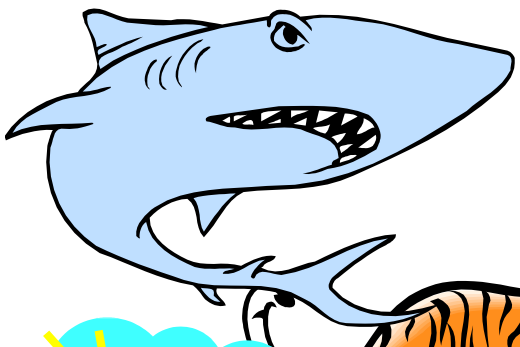
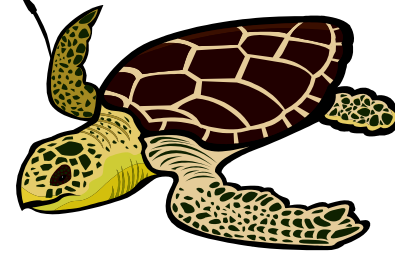
Dr. Anurag Srivastava

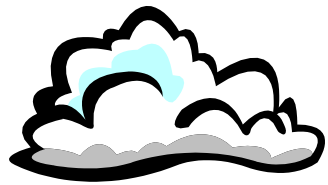
Atal Bihari Vajpayee

Indian Institute of Information Technology and
Management, Gwalior



All living things on Earth contain carbon. But, what is carbon? Why is it important?





Carbon is found all over the Earth.

It is an element. It is in the air, in the ocean, in the Earth's crust.

If carbon is mixed with other elements you get; limestone, chalk, marble, coal, gas, alcohol, sugars, fats, and even medicines. The black stuff in your pencil, graphite, is carbon. Diamonds are 100% pure carbon. Your body even contains carbon, the same stuff from which diamonds are made!

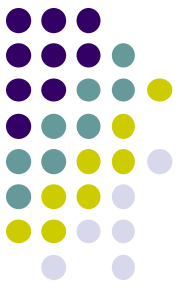
Carbon is inside of us, outside of us, and right now you are breathing out carbon (in the form of a gas: carbon dioxide). Carbon is everywhere.





People and animals all contain carbon. We get our carbon from eating plants or other animals. We breathe in oxygen which mixes with the carbon and then we breathe out carbon dioxide. (CO₂)





Carbon Element

- We have learnt carbon element as the basis of Organic Chemistry.
- Why does carbon can form so many different compounds?
- Carbon is found the second period group IVA of the periodic table.

EXCEPTIONS OF CARBON COMPOUNDS WHICH ARE NOT ORGANIC



- oxides of carbon (CO_2 , CO)
- carbonates, bicarbonates (NaHCO_3 , CaCO_3)
- cyanides (NaCN , etc)

Properties of Carbon Element



- The Lewis structure for carbon shows 4 unpaired valence electrons.
- To fulfill the octet rule, a carbon atom needs 4 more electrons.
- A carbon atom may form 4 covalent bonds and is capable of forming long chains with single, double or triple bonds between carbon atoms.
- These chains may be continuous (straight) or branched.
- The 2 ends of a chain can bond together to form a ring.
- Carbon compounds are divided into classes based on their chemical similarity.

Hydrocarbons



- Hydrocarbons are compounds containing hydrogen and carbon. Hydrocarbons may have different numbers of bonds between carbon atoms.
- The four hydrocarbon classes are:
 - alkane (single bond),
 - alkene, (double bond),
 - alkyne (triple bond),
 - aromatic (benzene ring).
- Alkanes contain only single C-C bonds. They contain as many hydrogen atoms as possible, and are said to be saturated.
- Hydrocarbons containing double or triple bonds are unsaturated.
- A homologous series is series of compounds that differ by a constant increment. Aromatic hydrocarbons include a benzene ring- 6 carbon atoms with all the bonds alternating between a single and a double bond.

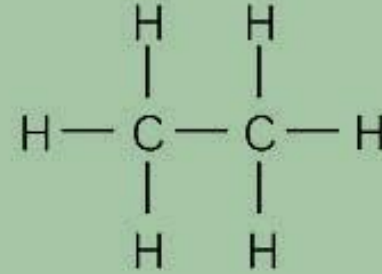
Properties of Carbon Element



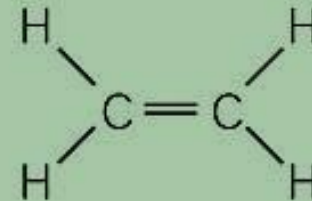
Carbon is unique

- It has 6 electrons in its outer shell arranges $1s^2 2s^2 sp^2$
- It has room for 4 bonds to 4 other atoms.
- Carbon-to-carbon bonds can be single (A),
- double (B), or
- triple (C).

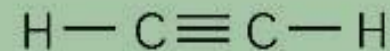
Note: In each example, each carbon atom has four dashes, which represent four bonding pairs of electrons, satisfying the octet rule.



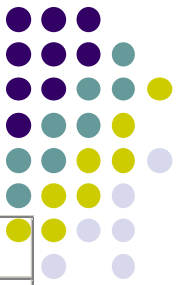
A Ethane



B Ethene



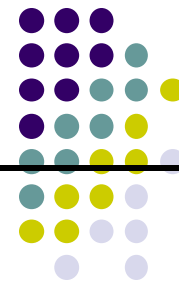
C Ethyne



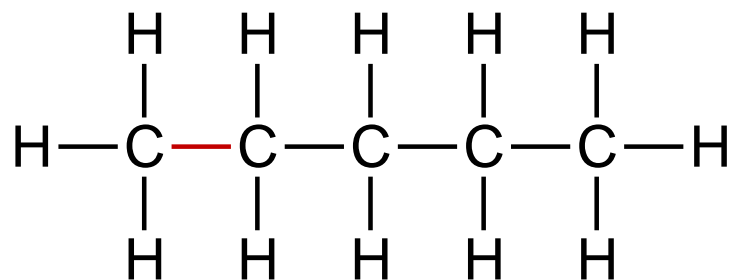
HYDROCARBONS

Alkanes	Alkenes	Alkynes
<p>SATURATED means that each carbon is bonded to four other atoms through single covalent bonds. Hydrogen atoms usually occupy all available bonding positions after the carbons have bonded to each other.</p>	<p>UNSATURATED hydrocarbons contain either double or triple bonds. Since the compound is unsaturated with respect to hydrogen atoms, the extra electrons are shared between 2 carbon atoms forming double or triple bonds.</p>	
<p>PARAFFINS which is derived from a Latin word meaning "little activity", and means that the compounds are very unreactive.</p>	<p>Alkenes are also called OLEFINS because they form oily liquids on reaction with chlorine gas.</p>	<p>Alkynes are also generally known as ACETYLENES from the first compound in the series.</p>

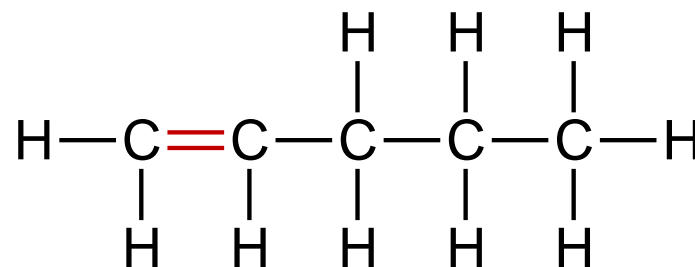
Hydrocarbons



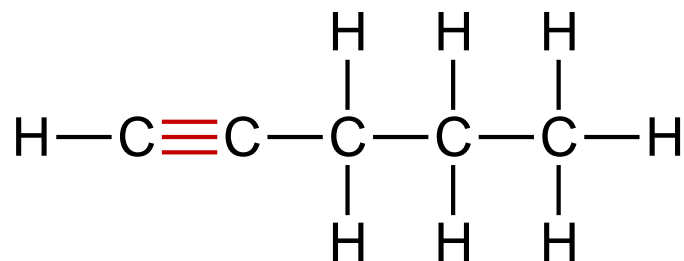
Alkanes C — C



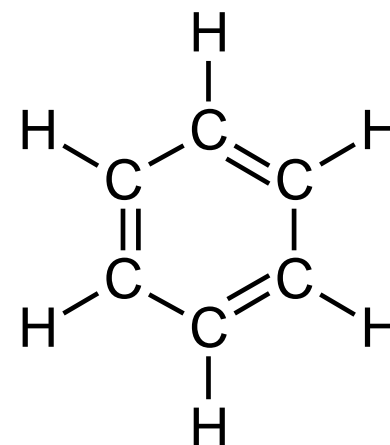
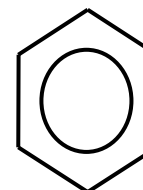
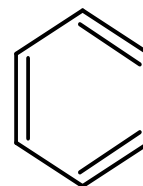
Alkenes C = C



Alkynes C ≡ C



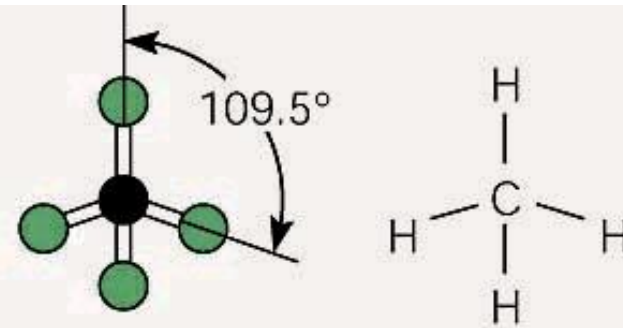
Aromatics



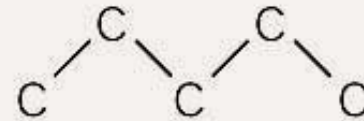


Properties of Carbon Element

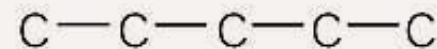
- **A) The carbon atom forms bonds in a tetrahedral structure with a bond angle of 109.5° .**
- **(B) Carbon-to-carbon bond angles are 109.5° , so a chain of carbon atoms makes a zigzag pattern.**
- **(C) The unbranched chain of carbon atoms is usually simplified in a way that looks like a straight chain, but it is actually a zigzag, as shown in (B).**



A Three-dimensional model



B An unbranched chain



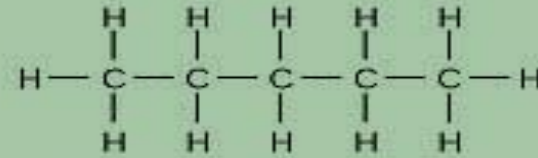
C Simplified unbranched chain



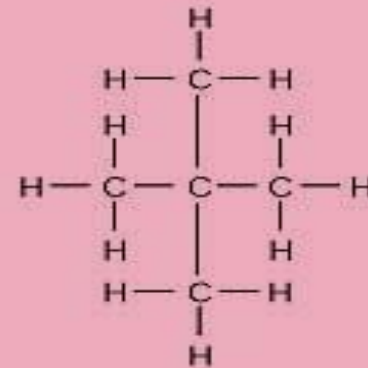
Properties of Carbon Element

Carbon-to-carbon chains can be

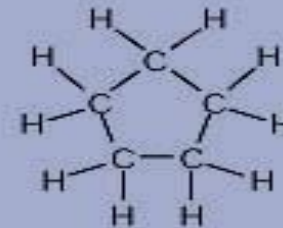
- (A) straight,
 - (B) branched, or
 - (C) in a closed ring.
-
- (Some carbon bonds are drawn longer, but are actually the same length.)



A Straight chain for C_5H_{12}

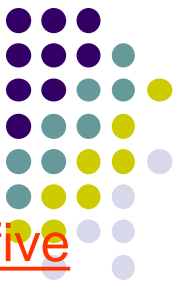


B Branched chain for C_5H_{12}



C Ring chain for C_5H_{10}

Why does carbon can form so many different compounds?



- Carbon's ability to form long carbon-to-carbon chains is the first of five reasons that there can be so many different carbon compounds; a molecule that differs by even one atom is, of course, a molecule of a different compound.
- The second reason for carbon's astounding compound-forming ability is that carbon atoms can bind to each other not only in straight chains, but in complex branchings, like the branches of a tree.
- They can even join "head-to-tail" to make rings of carbon atoms.
- There is practically no limit to the number or complexity of the branches or the number of rings that can be attached to them, and hence no limit to the number of different molecules that can be formed.
- The third reason is that carbon atoms can share not only a single electron with another atom to form a single bond, but it can also share two or three electrons, forming a double or triple bond.
- This makes for a huge number of possible bond combinations at different places, making a huge number of different possible molecules.
- And a molecule that differs by even one atom or one bond position is a molecule of a different compound.



Why does carbon can form so many different compounds

- The **fourth reason** is that the same collection of atoms and bonds, but in a different geometrical arrangement within the molecule, makes a molecule with a different shape and hence different properties.
- These different molecules are called isomers.
- The **fifth reason** is that all of the electrons that are not being used to bond carbon atoms together into chains and rings can be used to form bonds with atoms of several other elements.
- The most common other element is hydrogen, which makes the family of compounds known as hydrocarbons.
- But nitrogen, oxygen, phosphorus, sulfur, halogens, and several other kinds of atoms can also be attached as part of an organic molecule.
- There is a huge number of ways in which they can be attached to the carbon-atom branches, and each variation makes a molecule of a different compound.



The Greater Stability of C-C Bonds

- Since the average bond dissociation energy of C-C is greater than the average bond energies between different atoms.
- Thus the energy released when carbon atom bonds to another carbon atom is greater than the energy released when the other atoms like B,N,O,Si,P and S bonds to each other.
- Thus C-C bond is more stable than the others like B-B,N-N, O-O,Si-Si,P-P and S-S.

Bonding Atoms	Bond Energy (kJ mol⁻¹)
B-B	293
C-C	343
N-N	163
O-O	157
Si-Si	222
P-P	201
S-S	266

Ability to Form Chains Between Their Atoms



- The atoms closer to C in the periodic table are B, N, O, Si, P and S.
- The ability of these atoms to bond each other to form chains is lower than C.
- For example Si can produce chains made of at most 11 atoms of it and N at most three atoms it.
- Although the ability to form chains between their atoms for P and S is greater than Si and N but it is very much smaller compared to C.



Ability to Form Chains Between Their Atoms

The greater ability of carbon to form chains compared to atoms closer to it in the periodic table can be explained by two reasons:

1. The average bond dissociation energies of them is lower than that of carbon.
2. The electronegativity values B,Si and P lower than that of C.atoms.Thus the attraction forces between these atoms are smaller than that of carbon. This is also true when these atoms are bonded to the other atoms like hydrogen or halogens.

Li	Be	B	C	N	O	F
1,0	1,5	2,0	2,5	3,0	3,5	4,0
Na	Mg	Al	Si	P	S	Cl
0,9	1,3	1,6	1,9	2,2	2,5	3,2

Electronegativity values of some elements ording to Pauling's Scale



Electronegativity

- **Electronegativity:**
 - a measure of an atom's attraction for the electrons it shares with another atom in a chemical bond
- **Pauling scale**
 - generally increases left to right in a row
 - generally increases bottom to top in a column





Greater Bonding Capacity of C compared to N and O

The electronegativity values of N and O are greater than that of C. But their bonding capacities are smaller than that of C since they have lower number of unpaired electrons.

I	II	III	IV	V	VI	VII	0
H •							He ••
Li •	•Be •	•B •	•C •	•N •	•O •	•F •	•Ne •
Na •	•Mg •	•Al •	•Si •	•P •	•S •	•Cl •	•Ar •
K •	•Ca •	•Ga •	•Ge •	•As •	•Se •	•Br •	•Kr •
Rb •	•Sr •	•In •	•Sn •	•Sb •	•Te •	•I •	•Xe •
Cs •	•Ba •	•Tl •	•Pb •	•Bi •	•Po •	•At •	•Rn •

Legend: Metal Metalloid Nonmetal

Lewis Dot Diagrams of Selected Elements



Summary...

- Compared to C atom B, Si, P, N and O atoms can not be expected to form greater number of compounds and unbrached and branched chains and cyclic compounds.
- Carbon compounds are more stable than Si_4 , P_4 , O_3 , S_8 and B_4 molecules.

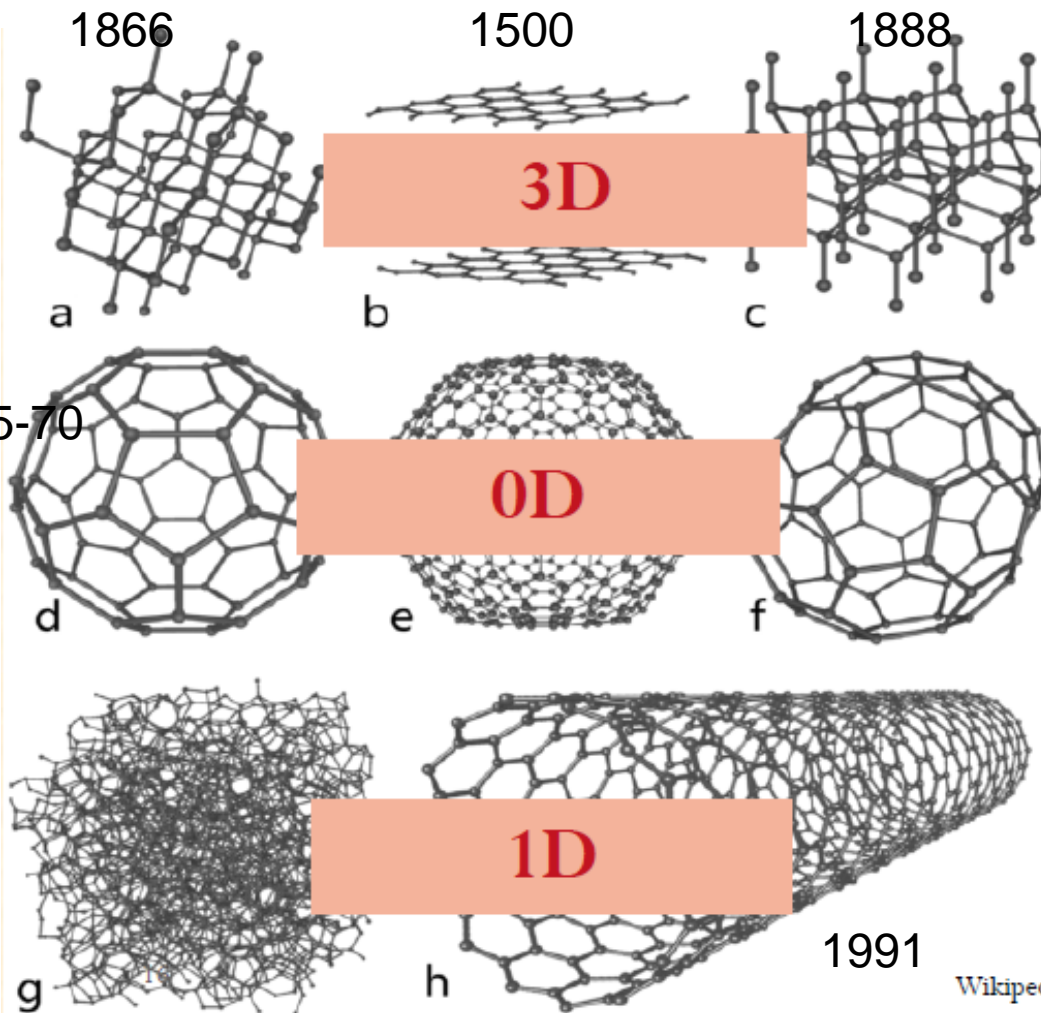
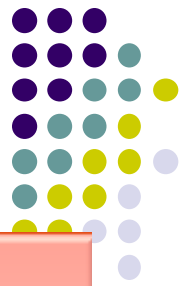
Carbon Allotropes



- Fullerenes
- Carbon nanotubes
- Graphene
- Diamond

Most known Carbon:

From Early 1500 to 1866 - 2010

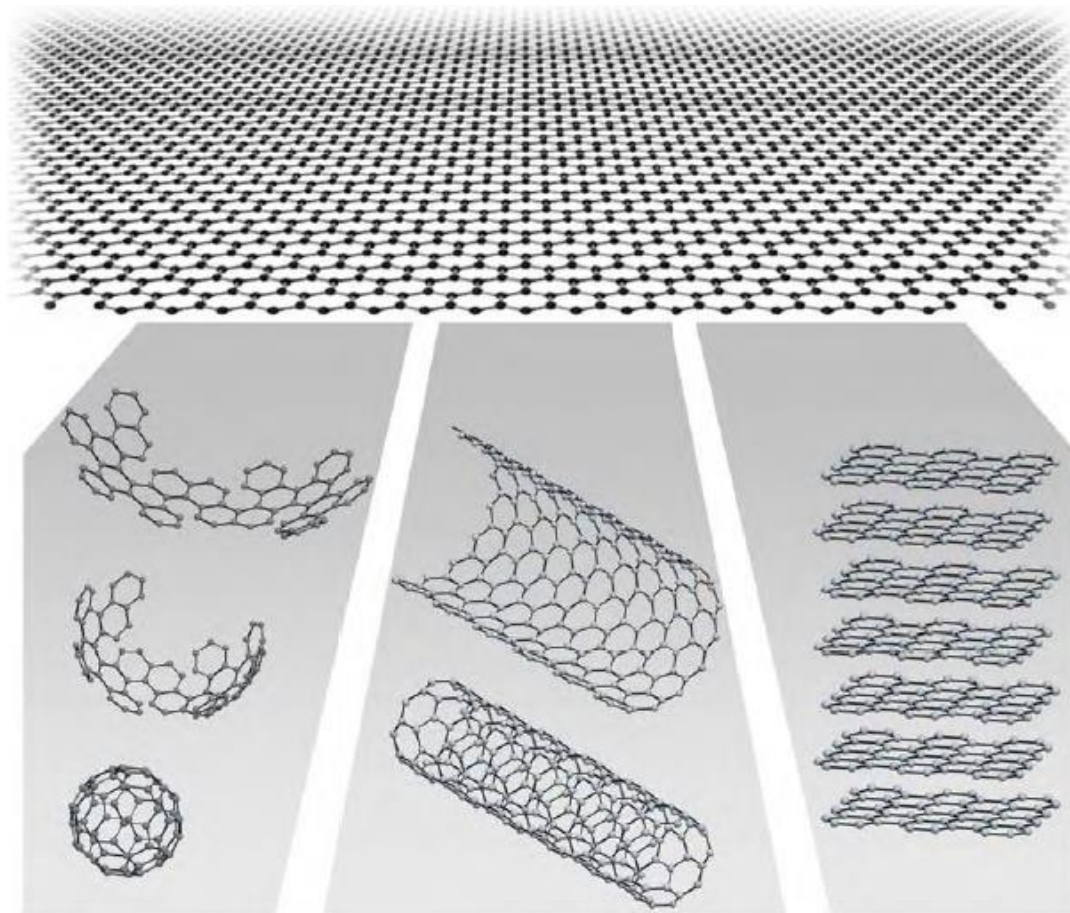


- a) diamond
- b) graphite
- c) lonsdaleite (hexagonal diamond)
- d) - f) fullerenes (C60, C540, C70);
- g) amorphous carbon
- h) carbon nanotube

2D - ???

Wikipedia: 2004, Prof. Andre Geim and Prof. Konstantin Novoselov

Graphene: The mother of all Graphites

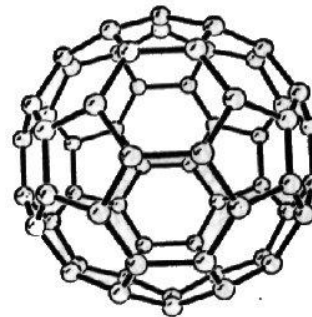


Graphene is a 2D building material for carbon materials of all other dimensionalities. It can be wrapped up into 0D buckyballs, rolled into 1D nanotubes or stacked into 3D graphite.

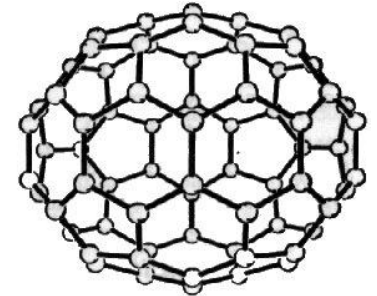
Fullerenes



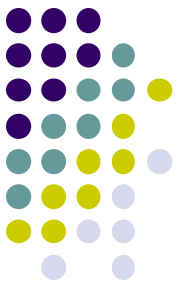
- Discovered in 1985 at Rice Univ. and Univ. Essex
- Includes CNTs, buckyballs, and derivatives
- C_{60} most common, but other forms exists (C_{70} , C_{100} , C_{400})
- The number of carbon atoms (N_c) in molecule can determine its structure (based on molecular orbital theory calculations)
 - N_c odd: linear or ring
 - N_c even: cage-like
- Fulleranes: hydrogenated form of fullerene



C_{60}



C_{70}



Fullerene Properties (C_{60})

- Truncated icosahedron with 32 faces, 90 edges, 60 vertices
 - 20 hexagonal faces
 - 12 pentagonal faces
- Diameter : 7.10 \AA
- Bonds *in* fullerenes: sp^2-sp^3 admixture
- Bonding *between* fullerenes
 - Noncovalent
 - van der Waals
 - $\pi-\pi$ interactions
 - Covalent

Fullerene synthesis



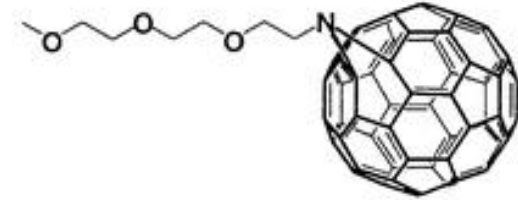
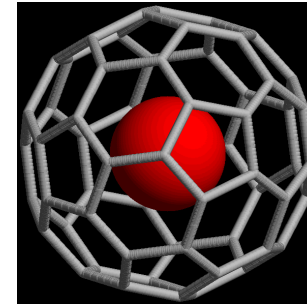
- Arc discharge plasma
 - High current applied between two graphite electrodes in He environment
 - Carbon vaporizes and fullerenes collect on cathode
 - CNTs form if metal catalyst included in graphite
 - Low purity: ~ 15% C₆₀
- Laser ablation
 - Graphite target exposed to extremely high temperatures
 - Produces higher order fullerenes
- Combustion of hydrocarbon fuel under low pressure
 - Requires least amount of energy
 - Produces most pure products

Fullerene modification



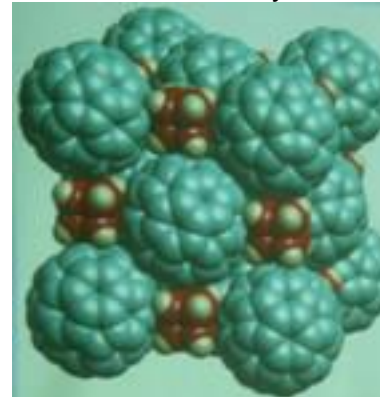
- Endohedral
 - Enclosed chemical species
 - $X@C_{60}$
- Exohedral
 - Functionalization
- Fullerene structures
 - Fullerene crystals
 - fcc structure held together by vdW forces
 - Arrays

Endohedral fullerenes

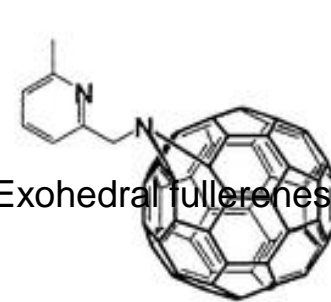


1

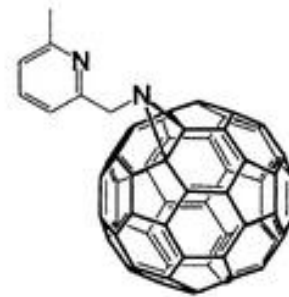
fcc fullerene crystal



Exohedral fullerenes



2



3

Recent Progress - Fullerenes



- Fulleride superconductor: 38 K T_c Cs_3C_{60}
 - Physical Review Letters, v 101, n 13, 26 Sept. 2008, p 136404 (4 pp.)
- Electro spray deposition of C_{60}
 - Journal of Physical Chemistry C, v 112, n 20, 22 May 2008, p 7706-9
- Bottom-contact fullerene C_{60} thin-film transistors with high field-effect mobilities
 - Applied Physics Letters, v 93, n 3, 21 July 2008, p 033313-1-3
- Mechanics of spheroidal fullerenes and carbon nanotubes for drug and gene delivery
 - Quarterly Journal of Mechanics and Applied Mathematics, v 60, pt.2, May 2007, p 231-48
- Applications of fullerene beams in analysis of thin layers
 - Vacuum, v 82, n 10, 3 June 2008, p 1120-3

Carbon Nanotubes (CNTs)



- Single-walled CNTs (SWCNTs)
 - Graphene sheet rolled into a tube
- Forms of SWCNTs
 - Zigzag
 - Armchair
 - Chiral
- Multiwalled CNTs (MWCNTs)
 - Series of concentric SWCNTs

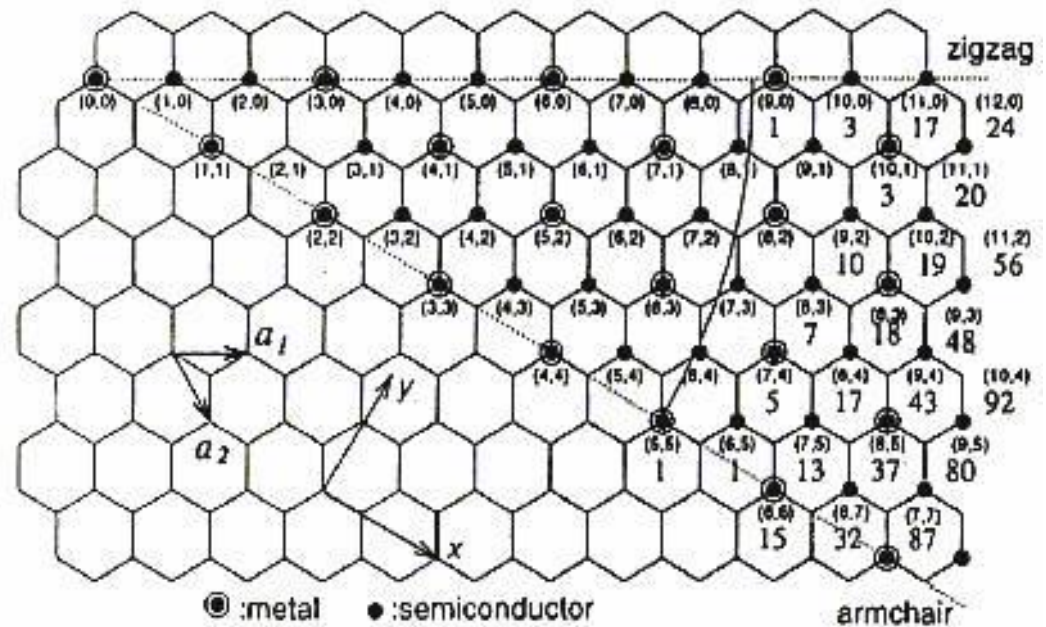
Vector Notation for SWCNTs



Chiral Vector

$$\mathbf{C} = n\mathbf{a}_1 + m\mathbf{a}_2$$

- Description of SWCNTs struct
- \mathbf{a}_1 and \mathbf{a}_2 : unit base cell vector
- $n \geq m$
- $|\mathbf{a}_1| = |\mathbf{a}_2| = 0.246 \text{ nm}$
- Bond length $b = a/\sqrt{3} = 0.142$
- Notation: (n, m)
 - Point $(0,0)$ connected to (n, m)



\mathbf{a}_1 and \mathbf{a}_2 : unit base cell vectors

Diameter

$$d_{SWCNT} = a\sqrt{n^2 + nm + m^2}$$

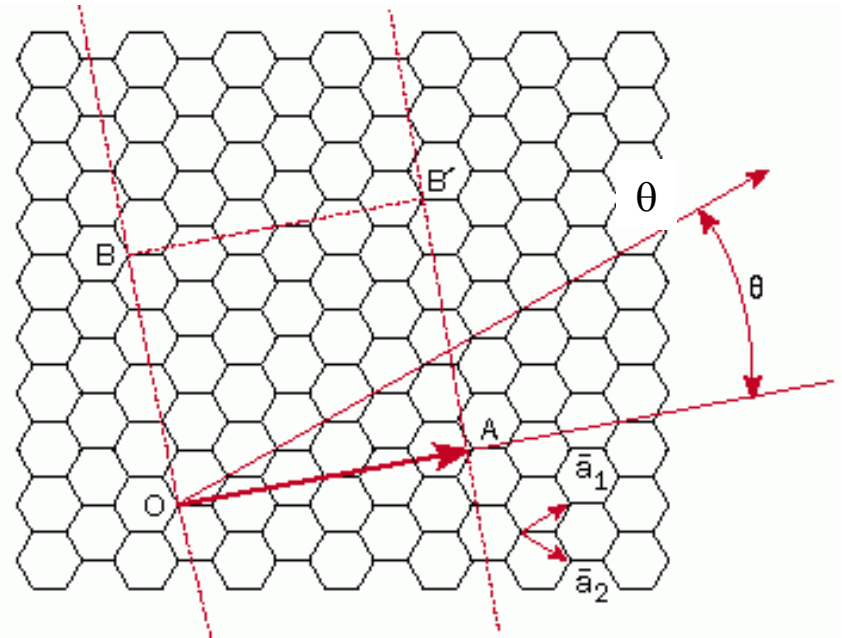


Chiral Angle

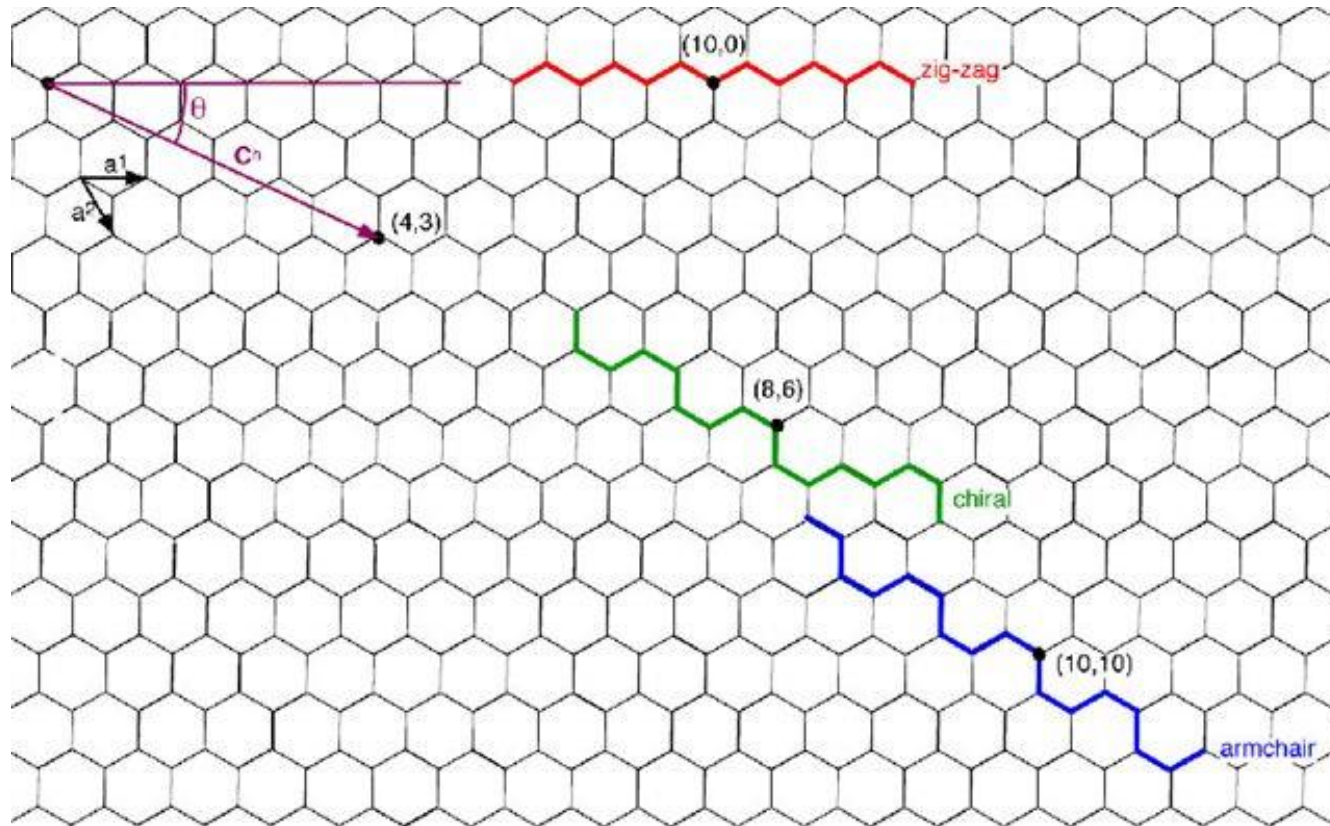
Chiral Angle

$$\cos \theta = \frac{2n + m}{2\sqrt{n^2 + nm + m^2}}$$

- Angle relative to a_1 vector
- Range of chiral angles: $0 \leq \theta \leq 30^\circ$
- Zigzag tubes:
 - $m = 0$
 - $\theta = 0^\circ$
- Armchair tubes
 - $n = m$
 - $\theta = 30^\circ$



Nanotube structure and chiral vector



Electrical Properties



- Metallic SWCNTs
 - Conduction is quantized (m.f.p. of electrons on order of dimensions of tubes)
 - Ballistic transport (no scattering)
 - In theory can carry electrical current density 1000x silver or copper
 - $|(n-m)| = 3q$ where q is an integer
 - Criteria for conduction:
 - All armchair tubes ($n = m$)
 - All zigzag with n multiple of 3
 - Chiral tubes that meet above criteria
- Semiconducting SWCNTs
 - $|(n-m)| \neq 3q$

Other properties of SWCNTs



- Thermal conductivity
 - Thermal conductivity along axis is greater than around circumference
 - ~ 6000 W/m•K along axis (Copper ~ 385 W/m•K) at room T
- Optical
 - Band gap of semiconducting tubes (0.4 to 0.7 eV)

$$E_g \sim 5.4b/d_{SWCNT}$$

b : bond length

d : diameter

Synthesis of CNTs



SWCNTs with chemical vapor deposition

- Regarded as the best method
- Requires little energy ($T \sim 100\text{s } ^\circ\text{C}$)
- Carbon source broken apart in presence of metal catalyst
- Carbon sources for CVD
 - Methane
 - Acetylene
 - Ethylene
 - CO
- Polydisperse products (**bad!**)
 - Diameter
 - Chirality
 - Length
 - Orientation
- No one has been able to synthesize exactly one kind of nanotube at a time
- Synthesis of SWCNT vs. MWCNTs
 - Control deposition conditions (P, T, gas composition, catalyst composition and size)

Growth mechanism of CNTs



- Base-growth
 - Typical of SWCNTs
 - Catalyst remains anchored to substrate (usually alumina)
- Tip growth
 - SWCNTs and MWCNTs
 - Catalyst comes detached from substrate
 - Favored for silica type substrates
- Limitations to growth
 - Increased vdW forces between tube and substrate with tube length
 - Growth terminates when force becomes too great
 - Application of electric field can enhance growth
 - Transport of carbon source to catalyst
 - Diffusion to catalyst from bulk more difficult as tube length increases
 - Diffusion across catalyst surface inhibited by encapsulation

History of Graphene



- Wallace in 1947
 - Created 2D structure to help in the understanding of 3D Graphite
- Single layers of graphite grown epitaxially on metallic substrates in the 1970s
 - Tightly bound to substrate, distorted properties
- Term “graphene” coined in 1987
- 2004, Geim and Novoselov mechanically exfoliated sheets of graphene from graphite
 - Transferred to charge neutral silicon substrate
 - First successful electrical properties measured

Geim, A. K. & MacDonald, A. H. (2007). ["Graphene: Exploring carbon flatland"](#). *Physics Today*.

A Closer Look at Graphene



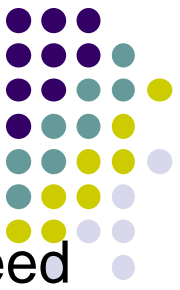
- 2D hexagonal carbon crystal lattice
 - Infinite boundaries
 - Actual 2D structure is debatable
 - Graphene sandwich
 - Thermal effects
- Naturally occurring
 - Multilayer in graphite
 - Nanospecs in soot from exhaust
- Currently one of the most researched materials
 - Unique physical and electrical properties
 - Wide array of potential uses



http://www.nanotechnow.com/images/Art_Gallery/ASgraphene.jpg

Ziegler, K., Robust transport properties in graphene. *Phys. Rev. Lett.*

Graphene Mechanical Properties



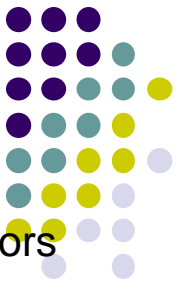
- Breaking strength 200 times greater than steel
- Youngs modulus of ~ 1 tPa
- Incredible rigidity lends themselves to nanoscale pressure sensors
 - Nanoscopic graphene flakes bend with increasing pressure which alters their electrical conductivity which can be related to the pressure
- Thermal properties exceed those of diamond
 - Excellent conductor of heat
 - Phonon dominated although it can be shown that at certain conditions the electrical portion is significant



<http://www.kinectrics.com/images/CableSpan.JPG>

John Scott Bunch. Mechanical and Electrical Properties of Graphene. *Cornell University 2008.*

Graphene Electrical Properties



- Anomalous Quantum Hall Effect
 - Quantization of the Hall effect
- Dirac fermions
 - Carriers have zero effective mass
- Room temperature electron mobility of $15,000 \text{ cm}^2/\text{V}\cdot\text{s}$
 - Theoretically higher conductivity at room temp than silver, but unknown forces are limiting
 - Possible optical phonon scattering from attached substrate

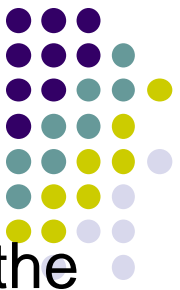


http://www.atwillett.com/lightning_pictures/lightning_bolt_closeup.jpg

- Both P and N-type transistors have been created
- Recent announcement by IBM that graphene transistor was operated at a terahertz frequency
- Tunable band gap from 0 to 0.25 eV
- Excellent conductivity makes graphene ideal for electrical leads in sensors/capacitors or use in touch screens because of its mechanical strength
- Graphene ribbons have tunable electrical conductivity depending on the shape

Charlier, J.-C., Blase, X., & Roche, S. Electronic and transport properties of nanotubes. *Rev. Mod. Phys.*

Electrical Component: Transistor

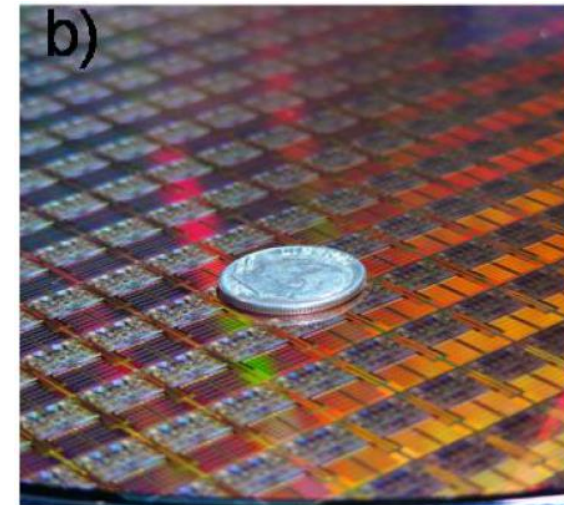
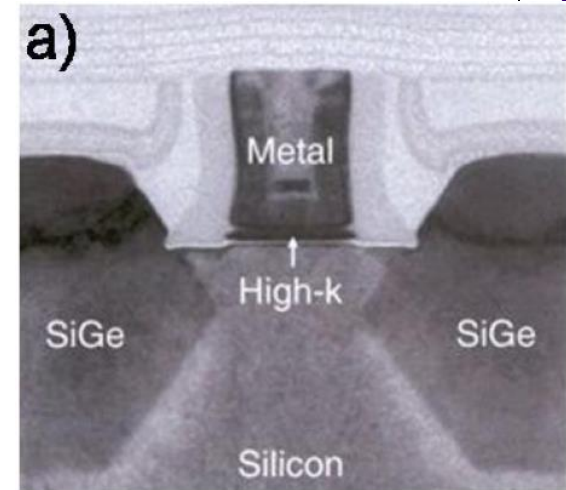


- A transistor's operation speed depends on the size of the device — smaller devices can run faster — and the speed at which electrons travel in it. This size dependence has been one of the major driving forces for making ever smaller silicon transistors.
- The Consortium of International Semiconductor Companies in its *2001 International Technology Roadmap for Semiconductors* projected that transistors have to be smaller than 9 nanometers by 2016 in order to continue the performance trend.

Charlier, J.-C., Blase, X., & Roche, S. Electronic and transport properties of nanotubes. *Rev. Mod. Phys.*

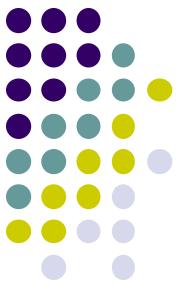
Carbon vs. Silicon

- Figure (a) is Intel's 45 nm silicon transistor which uses a Hafniun based dielectric.
 - Figure (b) is a wafer of the 45 nm transistors photographed with a dime.
- The processors incorporate 410 million transistors for each dual core chip, and 820 million for each quad core chip.



<http://www.intel.com/pressroom/kits/45nm/photos.htm>.

Carbon vs. Silicon



- Graphene could offer a way forward. As well as being extremely thin and a semiconductor, electrons move through graphene at extremely high speeds.



- The cutting edge of silicon-based transistors is at 32 nanometers.

http://mayang.com/textures/Manmade/images/Plastics%20and%20Related/electronic_circuit_board_9131073.JPG

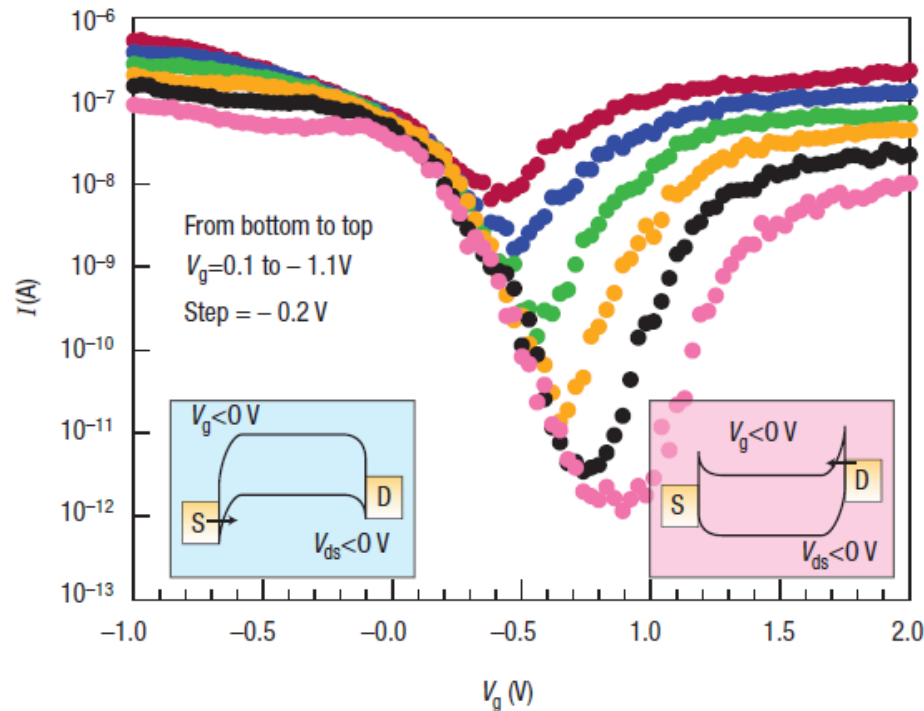
- Graphene has the potential to fabricate transistors only a few atoms across. British researchers have unveiled the world's smallest transistor, which measures one atom thick and ten atoms across. This is in the sub-10 nanometer range

Geim, A. K. & Novoselov, K. S. The rise of graphene. *Nature Mater.*



Performance Characteristics for Carbon-Based Transistor

Ambipolar transfer characteristics [current versus gate voltage]: drain bias increases from -0.1 V to -1.1 V in -0.2 V steps. Red line represents -0.1 V and the pink line is -1.1 V . Step size is -0.2 V

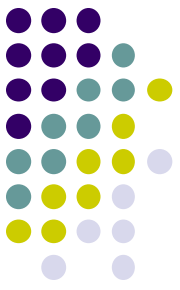


Left Inset: Schematic of the band structure of a Schottky barrier semiconducting carbon nanotube in a field effect transistor under negative gate bias. Holes are injected from the source [S].

Right Inset: Schematic of the band structure of a Schottky barrier semiconducting carbon nanotube in a field effect transistor under positive gate bias. Electrons are injected from the drain [D].

Anantram, M. P. & Leonard, F. Physics of carbon nanotube electronic devices. *Rep. Prog. Phys.*

Two-dimensional nanomaterials



Two of the dimensions are not confined to the nanoscale.

2-D nanomaterials exhibit plate-like shapes.

Two-dimensional nanomaterials include

- nanofilms,
- nanolayers, and
- nanocoatings

2-D nanomaterials can be:

- Amorphous or crystalline
- Made up of various chemical compositions
- Used as a single layer or as multilayer structures
- Deposited on a substrate
- Integrated in a surrounding matrix material
- Metallic, ceramic, or polymeric

2D-Nanostructure

Graphene Sheet (0-Gap semiconductor)

Boron Nitride Sheet (~4.8eV)

Flattened

sp^2



Silicene

Germanene

Phosphorene

Buckled/ Puckered

1) Black Phosphorene : single layer (Direct Band-Gap) (~1.88eV)

On increasing layers it goes upto 0.3eV (2014)

2) Blue Phosphorene (Indirect Band-Gap) (~2eV) 2015

(displacement of some atoms from crystal phosphorene → blue phosphorene)

Arsenene (Theoretically simulated but experimentally not verified)

Antimonene (Theoretically simulated but experimentally not verified)

Borophene (Theoretically simulated but experimentally not verified)

Buckled

sp^3



2 D Materials : 800,000 papers only on Graphene



Silicene and Germanene: A First Principle Study of Electronic Structure and Effect of Hydrogenation-Passivation

Trivedi et al.

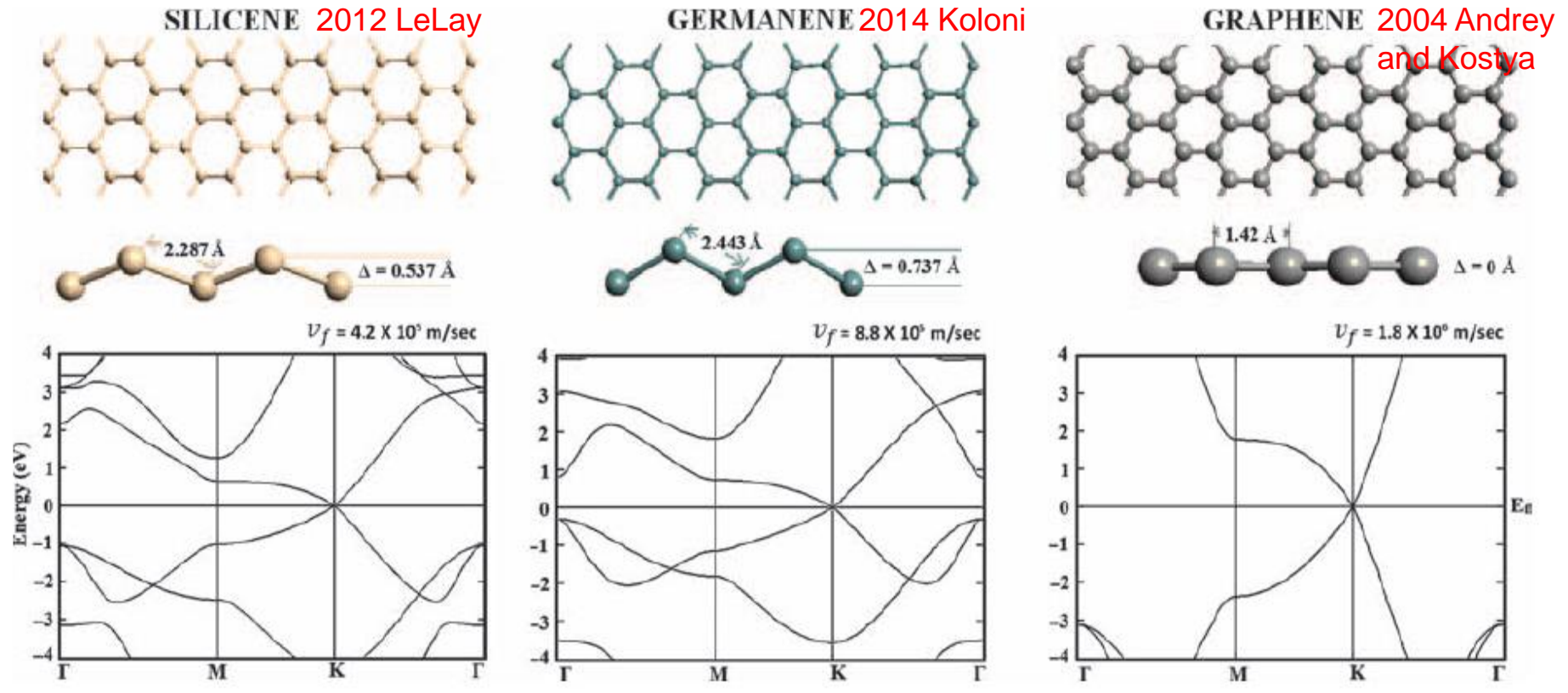
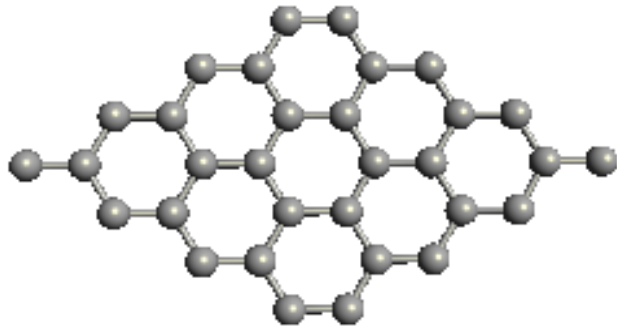
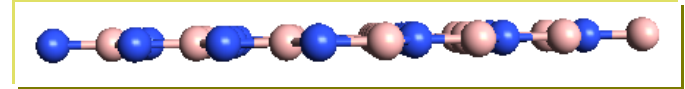
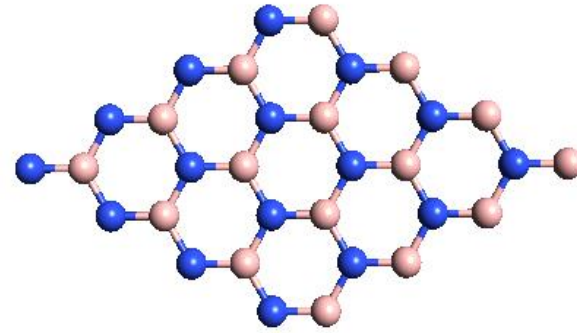


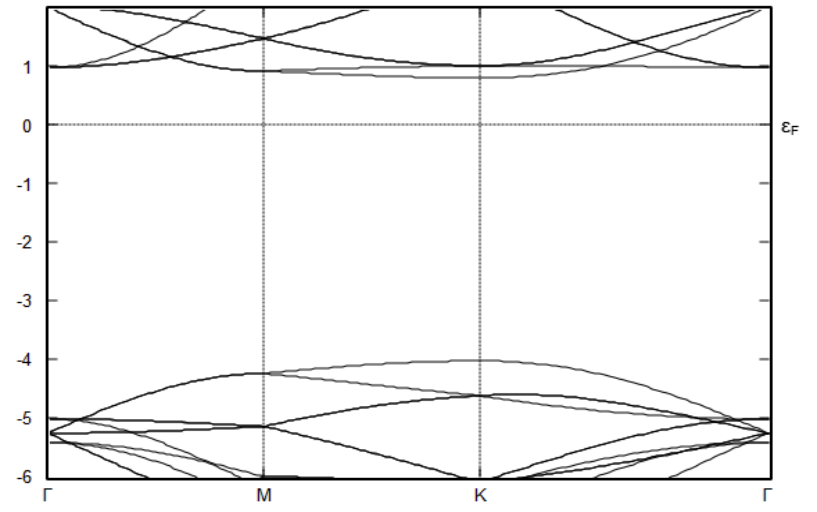
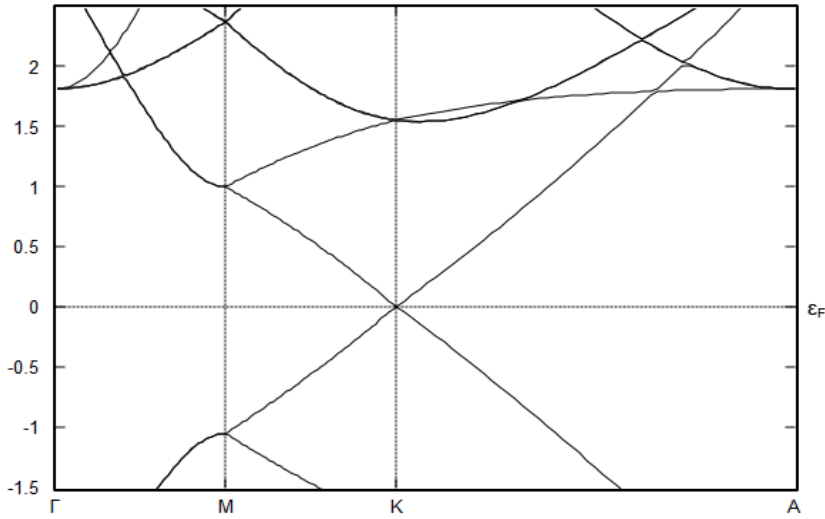
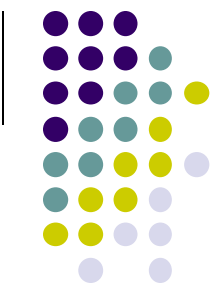
Fig. 2. Structure, bandstructure with Fermi velocities of silicene germanene and graphene. Trivedi and Srivastava, JCTN, 2013



Graphene



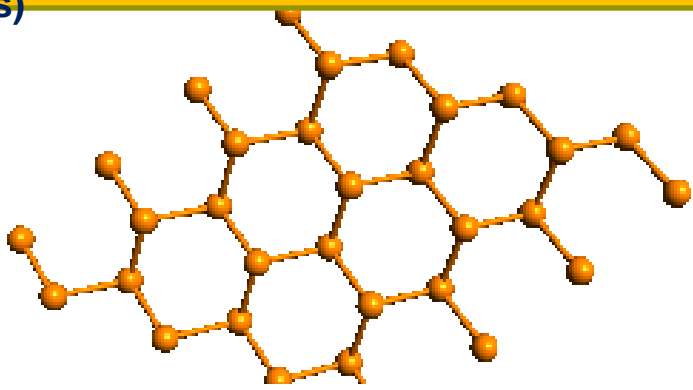
Boron-Nitride



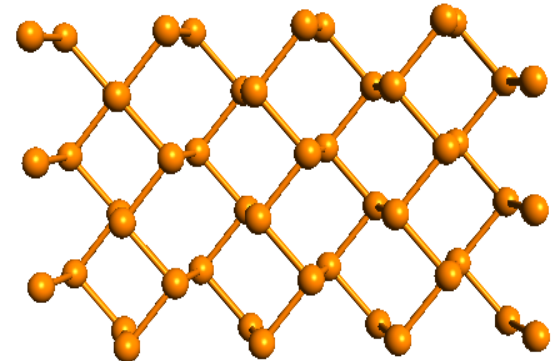
Phosphorene: a new wonder material

(High carrier mobility with bandgap of 0.3eV to 1.88eV depend on thickness)

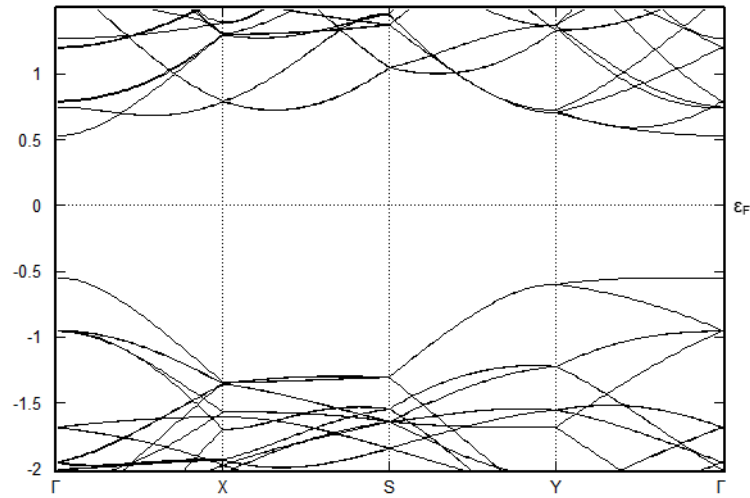
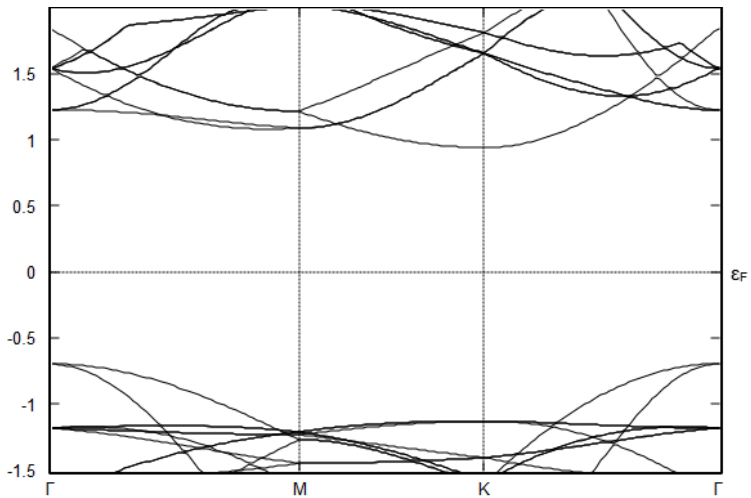
From black phosphorus 1960



Blue-Phosphorene

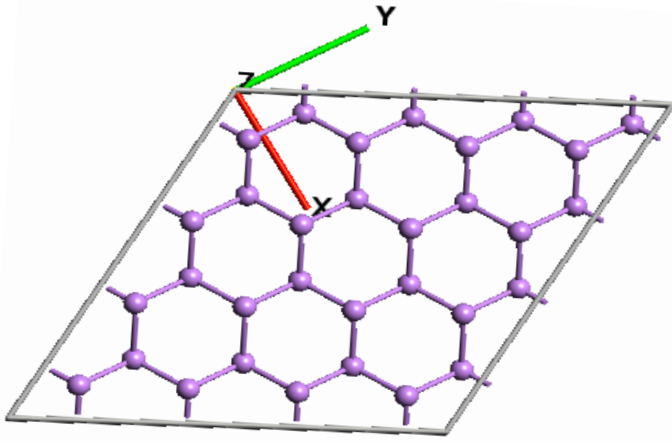


Black-Phosphorene

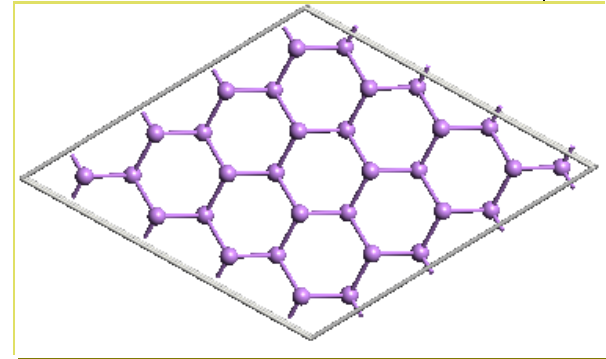


Arsenene and Antimonene

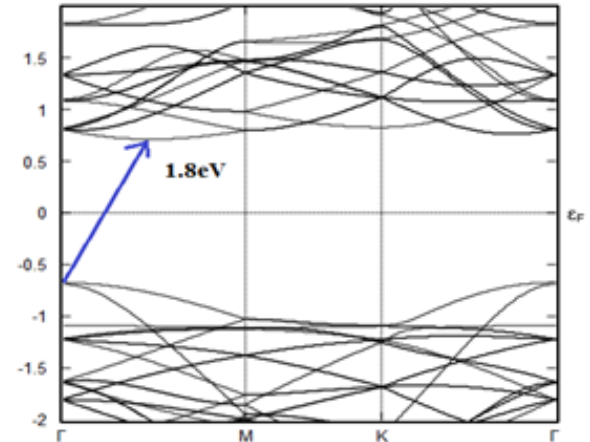
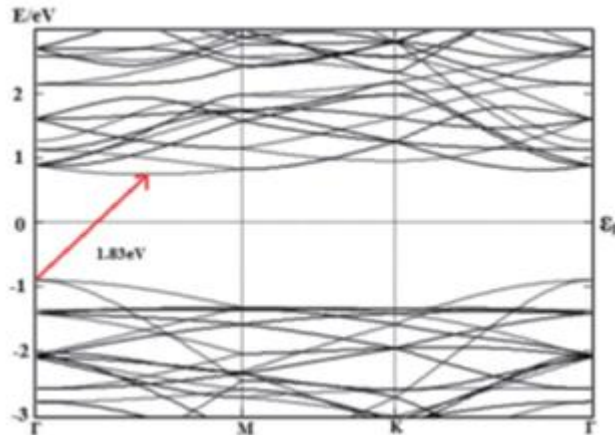
Theoretically proposed



Arsenene



Antimonene



C. Kamal and M. Ezawa, Phys. Rev. B, 91, 085423, 2015

Z. Zhang, J. Xie, D. Yang, Y. Wang, M. Siand ,D. Xue,Appl. Phys. Express, 8, 055201, 2015

