

Many Phases of Carbon

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Introduction

Carbon – the element known from prehistoric time, derives its name from Latin ‘carbo’ meaning charcoal. Carbon is known as the king of elements owing to its versatility and diversity in all fields, which is unquestionable. It is widely distributed in Nature, from molecules of life to matter in outer cosmos. It holds the sixth place in the list of abundance in Universe. The existence of carbon and its role in natural mechanisms are aplenty. The biochemical mechanism responsible for life are very much dependent on the role of carbon either directly or otherwise.

Natural carbon exists in two isotopic forms as C_{12} and C_{13} . The nucleus of the abundant isotope of carbon – C_{12} is composed of six protons and six neutrons. Neutral carbon atom is tetravalent and has totally six electrons with four of them occupying the outer orbit ($2s^2 2p^2$).

In 1772, Antoine Lavoisier realised the allotropic forms of carbon by a famous experiment in which he found that burning a piece of diamond and a charcoal of equal mass yields the same amount of CO_2 which made him conclude that charcoal and diamond are indeed made up of the same element carbon. Presently we know that diamond, graphite, fullerenes, carbon nanotubes and amorphous carbon are also the allotropic forms of carbon. Modified forms of carbon such as diamond-like carbon, glassy carbon and carbon fibres are also present.

Elemental carbon when forming covalent bond exhibits hybridization of orbitals, which is responsible for forming molecules with different structures like methane (CH_4) - tetragonal, ethylene ($CH_2=CH_2$) planar and acetylene ($CH\equiv CH$) linear. The concept of hybridization helps in understanding the structure of the allotropes and their bonding arrangement.

Keywords

Phases of carbon, allotropic forms, crystalline, amorphous.



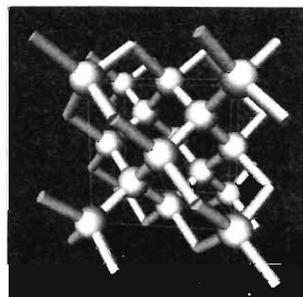
Diamond

Diamond is known to mankind from prehistoric times and has been prized for centuries as a gemstone of exceptional beauty, brilliance and lustre. The word diamond derives its name from the alteration of the Latin word *adamas* meaning 'untamable' or 'unconquerable', referring to its hardness. For over 2000 years, diamonds were found only as eroded crystals in river gravel. Until 1725, India was the major source of diamonds. It is astonishing to note that in the list of world's most famous diamonds, majority find their source originating in India. Diamonds are valued based on the 4C's, they exhibit, namely clarity, colour, carat and cut.

For a scientist diamond, is interesting for its range of exceptional and extreme properties. When compared to almost any other material, diamond almost always comes out on top. It is the hardest known material, also the least compressible, and the stiffest material. It is the best thermal conductor with an extremely low thermal expansion and also chemically inert to most acids and alkalis. Optically diamond is transparent from the deep ultraviolet (UV) through the visible to the far infrared (IR). These impeccable qualities arise from the elemental nature of carbon and its bonding structure. In diamond, each carbon atom is covalently single bonded to four other carbon atoms by strong σ bonds arising out of sp^3 hybridization (Box 1). Carbon when sp^3 hybridized forms four σ bonds with a bond angle 109.5° and is arranged such that they point to the vertices of a tetrahedron. Because of the strong σ bonds and short covalent bond length (C-C $\approx 1.4 \text{ \AA}$) diamond crystal made up of pure sp^3 carbon network has very high hardness. (10 Mohs, the highest hardness of any material) Diamond is dense (3.5 g/cm^3) and also a very hard material due to the compact four-fold coordination of strong σ bonds. Since the bonding is by σ bond there is no delocalisation of electrons and this makes diamond an insulator. Diamond has a band gap of $E_g = 5.5 \text{ eV}$, making it transparent in the IR, visible and UV spectral region.

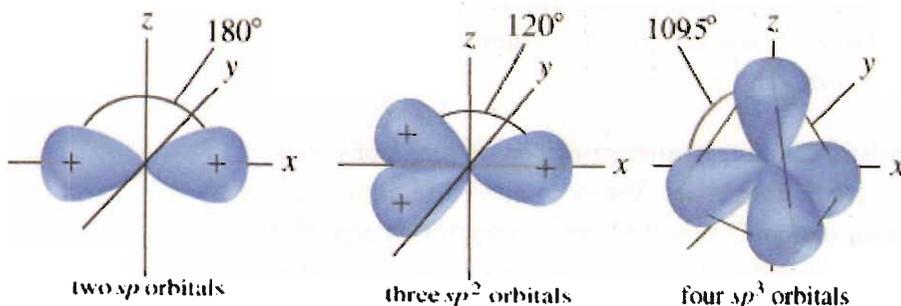
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Figure 1. Crystal structure of diamond.



Box 1. Hybridization

According to the electronic configuration of a neutral carbon atom, there are only two unpaired valence electrons in the $2p$ orbital. This should result in a carbon atom capable of forming two bonds only. However, every neutral carbon atom is tetravalent, and therefore, should have four unpaired electrons from which it can form four bonds. Linus Pauling introduced an interesting concept called hybridization to explain this discrepancy. Hybridization also offers an explanation why carbon-containing molecules can have one of three geometries around each carbon atom in the molecule. In short hybridization is the process of mixing two or more atomic orbitals to create a set of new equivalent hybridized orbitals. In the case of carbon the $2s$ and $2p$ orbital mixing give rise to any one set of sp , sp^2 or sp^3 hybridized orbital, that will fulfill the geometric demands of the system.



The phase diagram of carbon (Figure 2) shows that diamond structure is formed at high temperatures and very high pressures. This means that diamond is crystallised in nature by

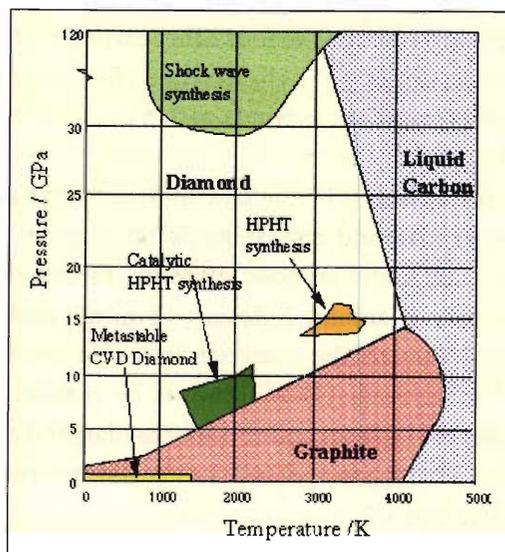


Figure 2. Phase diagram of carbon.

geological processes at great depths below the Earth's surface. These conditions exist generally at more than 150 kilometres down beneath the Earth's crust known as the mantle region. The organic sedimentary material enters the mantle region, where carbon under the prevailing extreme conditions crystallizes into diamond. Diamonds are carried to the Earth's surface by mantle fragments and molten magma, which sprout out through conical pipes called kimberlite during volcanic eruptions. Natural diamond is mainly found in kimberlite pipes of extinct volcanic zones where it is generally mined.

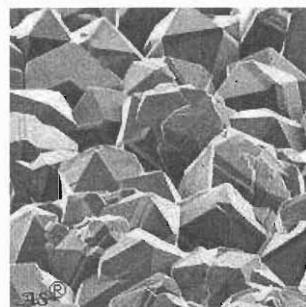


Figure 3. Morphology of synthetic diamond.

Synthetic Diamond

Synthetic diamond (*Figure 3*) is formed much in the same way as natural diamonds. Graphite is heated to temperatures exceeding 1500°C at about 60,000 bar of pressure (60,000 times the atmospheric pressure) in a sophisticated belt apparatus. Diamond crystallizes out of molten phase of carbon. Addition of small amounts of the metallic catalysts like iron or nickel speeds up the reaction and reduces the required pressure and temperature. In diamond formation, the impurity atoms are often trapped in the diamond lattice as it forms. This is the reason why diamonds are coloured.

Apart from the traditional uses of diamond as precious gems and symbol of richness and power we can summarize the industrial uses which dominate the present times. Diamond is used in cutting tools to reduce the wear. Diamond thin films are being used in semiconductor IC's to have better heat dissipation. This helps further shrinking in IC miniaturization.

Graphite

The name for the material graphite comes from the Greek verb *graphain*, 'to write'. Graphite is used as a writing material since mid 15th century. During that time it was thought that graphite contains lead and was called as black lead (plumbago). This is the reason why graphite in pencil, is still called lead. Graphite is present as a natural mineral and mined all over the world. The

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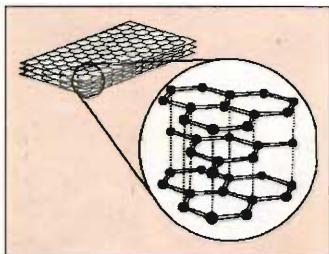


Figure 4. Graphite sheets.

modern uses of graphite are so numerous that it compels and demands the need for synthetic graphite.

Graphite is a layered material (Figure 4) where sheets of hexagonally arranged carbon atoms are stacked and held together. Carbon when sp^2 hybridized contains three strong π bonds which lie in a triangular plane with bond angle of 120° between them and one weakly bonding π bond perpendicular to the plane. Each carbon atom in the plane is covalently bonded to three others in plane with strong σ bonds of the sp^2 hybridization, this network forms a continuous sheet of carbon. These sheets of carbon are stacked together by van der Waal's force, which is weak, causing the sheets to rupture easily.

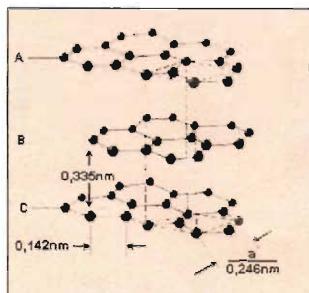
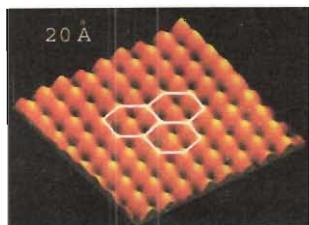


Figure 5. Crystal structure of graphite.

Graphite is a highly anisotropic solid, structurally its interplanar spacing (3.35 \AA) is quite large compared to the in plane interatomic spacing (1.42 \AA) (Figure 5). Physically its stiffness along the plane is quite large because of strong σ bonds and in the perpendicular direction it is weak because of the van der Waal's force. The planes can be cleaved easily making graphite quite a soft material. Also electronically it is anisotropic, because of π and π^* band overlap. This has metallic conductivity along the plane and semiconducting perpendicular to the plane. The anisotropy in conductivity is about 10^3 . The diamagnetic anisotropy exhibited by graphite was first realised and precisely measured by K S Krishnan and N Ganguly in 1939 and is still referred and regarded as a pioneering work in carbon science.

Synthetic Graphite

Figure 6. AFM image of (HOPG) graphite.



The common synthetic graphite is usually manufactured as composites. In this process petroleum coke is mixed into a paste with a coal tar pitch and then heated to around 1200°C - 1400°C . This step drives out all volatile material from the petroleum coke. Further heating this to 2500°C - 3000°C causes an ordering of the carbon atoms to graphitize the mixture into a completely pure graphitic structure (Figure 6).

Natural graphite is mined, processed and used in a variety of

applications such as lubricants, seals, insulation, fillers, refractories and in pencils. The biggest industrial use of synthetic graphite is in massive electrodes used in furnaces in steel and aluminum smelting. Other typical use of synthetic graphite is in battery electrodes, contact brushes, refractories, aerospace applications, nuclear reactors, and as conductive coatings inside picture tubes.

Fullerene

Fullerene (C_{60}) is present in Nature in small amounts. Its recent synthesis in 1985 by Smalley and Kroto threw light on this new allotropic form of carbon. They synthesised C_{60} molecule by laser heating of graphite targets in an argon atmosphere, resulting in carbon soot, mixed with C_{60} . The mass spectral analysis of the product convinced them of the formation of small quantities of C_{60} . C_{60} was separated out and the mass spectrometric and other studies revealed that it is indeed a spherical closed molecular network formed by 60 carbon atoms (*Figure 7*) imitation of the Geodesic Dome designed by the architect Buckminster Fuller. To honor the architect this form of carbon is named as 'Buckminster fullerene' in short as 'fullerene' or nicknamed as 'bucky ball'.

Fullerene is a molecular crystal that contains sixty carbon atoms in a network of sp^2 bonding which forms a spherical structure. Fullerenes are made up of hexagonal and pentagonal rings of carbon arranged exactly as of an Indian football.

This triggered enormous interest among the scientific community. The exploration of this new molecular form of carbon resulted in remarkable progress in the field. Based on fullerenes (C_{60}) presently we find the existence of C_{36} , C_{70} (*Figure 8*), C_{80} , C_{100} and also few members of geometrically allowed fullerene family. These fullerene molecules differ in the number of hexagonal rings present. The shape of this molecule changes as the number of carbon atom differs. The C_{70} looks similar to a rugby ball and C_{120} (*Figure 9*) takes a dumbbell shape.

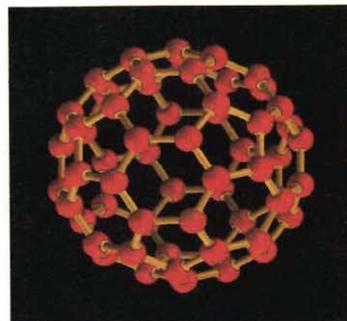


Figure 7. Structure of fullerene (C_{60}).

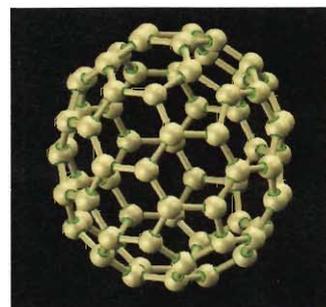
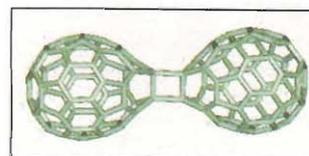


Figure 8. Structure of fullerene (C_{70}).

Figure 9. Structure of C_{120} fullerene.



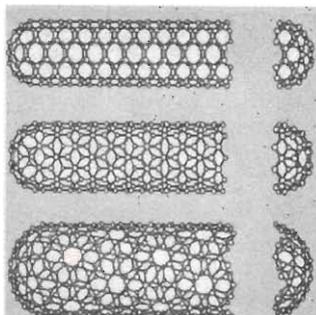


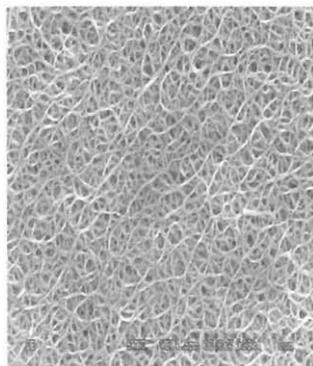
Figure 10. Structure of various CNTs (a) Metallic (b) and (c) Semiconducting.

Presently there are methods to prepare C_{60} molecules in large quantities, so the study of this molecular form of carbon is advancing in all possible arenas. Presently we know that C_{60} doped with alkali metals becomes superconducting with $T_c \sim 50$ K. Fullerene research has got immense scope in nanoscience and technology. To name a few they find use in catalytic chemistry, biomolecular recognition, as molecular sieves, nano reactors, and also as inhibitors to the activity of HIV virus.

Carbon Nanotubes

Similar to discovery of C_{60} , a major breakthrough came in 1991 when Iijima of NEC Japan announced the synthesis of carbon nanotubes (CNTs). In his experiments on the arc discharge between graphite electrodes, along with the collected soot particles there were some fine tube-like structures. This on careful analysis revealed that they are carbon nanotubes (CNTs). These single walled nanotubes are long tubes made entirely out of carbon, they can be thought of as being made from a planar sheet of graphite that is wrapped into a seamless tube, nanometers in diameter and up to few microns in length. The tubes can be either open at their ends or capped at one or both ends with half a spheroidal fullerene. A nanotubes is completely specified by what is referred to as a roll up vector, which identifies its helical nature and diameter. Depending on its roll-up vector, a nanotube can have either metallic or semiconducting properties (Figure 10).

Figure 11. SEM image of CNTs.



There is a sudden surge of interest in this area after realizing their importance in basic and applied research. At present we realize the existence of single, multi-walled nanotubes (MW-NT), in which more than one CNTs are co-axially arranged (Figure 11). Carbon nano-cones have also been observed in recent times.

Semiconducting and metallic nanotubes recently are put into use in field effect transistors (FET) and single electron transistors. The mechanical strength of CNT is amazingly 600 times



tougher than steel, which finds applications in micro electro mechanical systems (MEMS) and in aerospace. The current research targets are many. To give an idea, ultimate interconnects in integrated circuits (IC's) are made of using the nano-wires. Progress has been made in using CNTs as field emission devices for high resolution display systems. Construction of nano-probes and electrodes in biological and other applications are also being aimed.

Amorphous Carbon

Scientific research on amorphous forms of carbon has found importance in recent times owing to its rich underlying physics and tremendous application avenues. The widely known forms of amorphous carbon are carbon black, carbon fibres, porous carbon, glassy carbon, diamond like carbon (DLC) and pyrocarbon. The general structure of disordered forms of carbon contains random network of sp^2 and sp^3 atomic coordination with varying bond lengths and bond angles in presence of dangling bonds and voids (*Figure 12*). The relative presence of sp^2 and sp^3 bonding, the extent of order and consequently the physical properties of the disordered carbon can vary over a wide range.

Glassy carbon is prepared by carbonizing molded products of thermosetting polymers in vacuum or in inert gases. Glassy carbon has isotropic properties, very small porosity and hence it is substantially gas tight. It is as good as platinum in corrosion resistance. Glassy carbon can be used as electrode material and also as cryogenic temperature sensors.

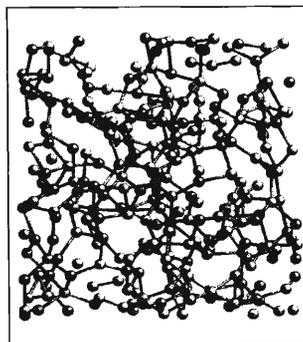
Diamond like carbon (DLC) is a kind of amorphous carbon that contains random network of predominantly sp^3 coordinated carbon atoms. Common method to prepare DLCs is by plasma chemical vapor deposition (CVD) of acetylene/methane in argon atmosphere. DLCs are used as protective coatings for wear, and as heat sinks.

Carbon fibres are high strength materials that are made from

Box 2. Crystalline and Amorphous

In general the term crystalline refers to solids, which contain periodic arrangement of atoms or molecules over the entire material. A more realistic definition would be to describe a crystal to have translational periodicity over very large length scales (long range order) compared to the lattice parameter. On contrast non-crystalline, amorphous and glassy nature is attributed to materials, which lack long range order but possess periodicity on a shorter length scale typically over a few inter-atomic distances (short range order).

Figure 12. Atomic structure of amorphous carbon network.



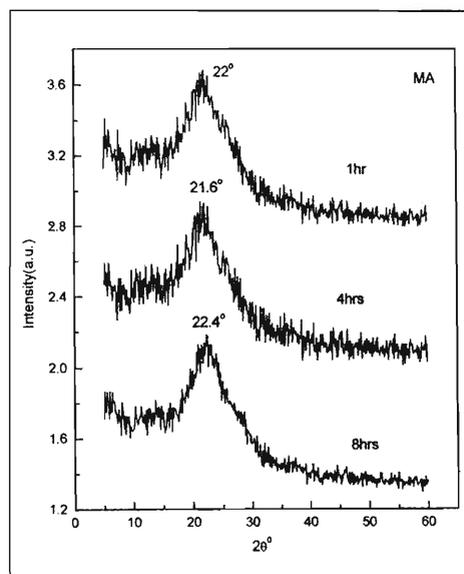
Box 3. Carbon Composites for Public Utility

In an indigenous effort DRDO had implemented the light weight carbon-carbon composite material designed for Agni, to make calipers for the polio affected children. This carbon-carbon composite material (carbon fibre-carbon matrix) reduces the weight of the calipers to 300 grams (original weight of 3 kg). The carbon composites are also used in tennis rackets, golf sticks and even in bicycles. Innovation to harness the power of carbon based advanced materials would make the life of common man better.

organic polymers such as poly-acrylonitrile. The carbon fibre is manufactured by a process in which the polymers are stretched into alignment. Then an oxidation treatment in air at 200 °C-300 °C transforms the polymer into a non-meltable precursor fibres. This precursor fibres is then heated in a nitrogen environment until the volatile products are given off and 92% carbon fibre remains. The temperature used to heat treat the fibres varies between 1000 °C and 2500 °C depending on the desired properties of the carbon fibres.

A special variety of conducting amorphous carbon (a-C) is obtained by the pyrolysis of carbon rich organic anhydrides in inert atmospheres. This variety of a-C has got interesting properties and also distinct applications.

Figure 13. XRD of amorphous conducting carbon.



Conducting amorphous carbon is prepared by pyrolysis assisted chemical vapor deposition (CVD) of chosen organic precursors. The precursors were selected based on the knowledge of thermo-chemistry and possible reaction mechanism. The conducting amorphous carbon film has got few of the general features. The morphology is such that the films are silvery black in colour, shining and has metallic lustre. The elemental composition is typically 99.5 % carbon and 0.5 % hydrogen. The films and powders characterized by X-ray diffraction (XRD), show a broad hump centered around ~22 degrees showing the amorphous nature of the film (*Figure 13*). This amorphous nature is reflected in neutron scattering studies as well.

The transmission electron microscopic (TEM) im-

ages show almost uniform amorphous structure and no trace of any graphitic ribbons or cluster. Samples prepared at different temperature also have similar morphology with no structural ordering in the film. The scanning electron microscopic (SEM) images shows globular structures of 1-2 microns in diameter (Figure 14). The density of these carbon films is around 1.6-1.8 g/cc, which is less than that of graphite.



Figure 14. SEM image of amorphous carbon film.

The electrical conductivity of the films prepared depends on the type of precursor, pyrolysis temperature and annealing time. In general, the material can be tuned to be metallic or insulating with a span of conductivity from 100 S/cm to 1000 S/cm at room temperature. The resistivity vs temperature measurements show that the films are having very weak temperature dependence (temperature co-efficient of resistance – TCR) over a range from 900 K to 1.2 K. These carbon films show an order of magnitude decrease in resistance on application of high pressure. Electrochemical activity analysis suggests that these films are less reactive and superior to platinum electrodes.

These distinct properties of the amorphous conducting carbon invite variety of applications. An inexpensive pyrolysis process is used for coating over various ceramic substrates, like sheets, wafers and flexible mats. These coated materials can be used as miniature, flexible or even large area heaters. The films show a very low TCR, this property is utilised for making the patterned films as standard resistors. The films are inert to acids and alkalis, so this can be used as protective coatings in chemical reactors.

Conclusion

The phases and forms of carbon cover a wide spectrum of properties and applications. Research in carbon unveils the rich science underlying, which facilitates better understanding. Many innovative applications are at the offing and lot of avenues still remain unexplored.

Suggested Reading

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