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Chapter

Introductory Chapter: Engineering Applications of Diamond

Awadesh Kumar Mallik

1. Introduction

Science is the knowledge of the existing laws and principles, whereas, engineering is the application of such scientific knowledge in building/designing/creating something useful for the humans, and such engineered tools/devices/processes are collectively known as technology. Knowledge about diamond materials is in existence since its early discovery along the river beds or in the mines, as early as from the 4th century BC (**Figure 1**). It was the hardest known stone which were "artfully" cut and polished to shine so beautifully that lured the kings and queens over centuries [1]. The cutting and polishing technology of these rarely found stones was popularly used to make jewellery. The diamond dust particles that are generated during jewellery stone making or the small sized stones from mines which can not be used in jewellery making, are always used as abrasives. Because of its extreme hardness, it was used for engraving other stones or grinding other materials. However, the industrial use of diamond in cutting tools has become possible with the advent of high-pressure high-temperature (HPHT) diamonds in the late 20th Century [2]. The rarity of mined diamonds made them precious and was unaffordable for the average income people. A new process called chemical vapour deposition (CVD) [3] has made it possible now to grow gem quality diamonds for the affordable jewellery application [4]. There is another method where oxygen deficient TNT/RDX

DIAMONDS - TIMELINES

LAB-GROWNS

- 1954 HPHT diamond was discovered by GE, USA
- 1982 Present-day CVD diamond processing was discovered at NIMS, Japan
- 1990s- UHasselt, Belgium CVD diamond research activity initiated
- 2018 De Beers started selling lab-grown CVD diamond jewellery
- March, 2020 celebrated 25th
 Hasselt diamond workshop
 SBDD, just one day befor
 lockdown in Belgium.

FROM MINES

- 9th century BC 18th Century AD: Only India supplied diamond to the world from alluvial river bed deposits and mines
- 15th Century Flemish jeweller Lodewyk van Bercken discovered diamond polishing "scaif" in Antwerp, Belgium
- 1725 Brazil mine discovery
- 1870 South Africa diamond fields started
- 1888 De Beers was founded
- 20th Century De Beers monopoly in mining diamonds
- 21st Century Russia, Botswana, Australia major mining countries

Figure 1.

A brief timeline with respect to the different milestones in diamond material history.

explosive is detonated to create diamond nanoparticles (**Figure 2**). These detonation nanodiamonds (DND) [5] are now extensively used as nucleation seeds for the CVD growth of diamond. However, the detonation process (neither ultrasonic cavitation [6] nor microplasma processing [7]) can not make gemstone quality (**Figure 3**) larger diamond crystals, whereas, HPHT can make gemstones, but they are limited in size [8] and of inferior quality diamond with defects or foreign inclusion [9]. Beauty lies in the eyes of the beholder. For the millennium generation, diamond jewellery is losing its charm and attraction. Other than aesthetic value, because of the stone's other exceptional material properties [10], like thermal conductivity, optical transparency over wide electromagnetic spectrum, velocity of sound waves, tensile strength, doping conductivity etc., diamond can also be used for the greater

DIAMONDS- SOURCES

LAB-GROWNS

CVD or chemical vapor of carbon gas deposition molecules inside vacuum chambers (easy) or bν copying 2. High Pressure Temperature (HPHT) environment extreme diamond forming natural conditions with gigantic in laboratories presses difficult). Detonation nanodiamond (DND) by the explosion graphite of powder with TNT.

FROM MINES

√4. Billions of years ago, under high pressure and temperature, diamond formed from carbon, present 90 mile deep inside earth's surface





Figure 2. Four different sources of diamond. (images are from GIA and Adamas websites).

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DIAMONDS - COMPARISONS



LAB-GROWNS

- ✓ Unlimited source and quantity of diamonds that can be made by scientists in laboratory
- ✓ Sustainable future
- ✓ Environment friendly chemical process
- ✓ Low cost and easy to make
- ✓ Ethical practices
- ✓ Chemically pure Carbon and white
- ✓ Color can also be changed by choosing gas chemistry (N₂-yellow & B-blue)
- Fixed price as carat, clarity, color and cut are controlled by scientific process
- √ Visually IDENTICAL to the mined/natural diamonds

FROM MINES

- Limited source and quantity of diamond from few active mines
- ✓ Diamond mine closes down over time (India)
- ✓ Mining damages environment
- ✓ Expensive and rare to discover
- Unethical business practices conflicts
- ✓ Impurity inclusion creates diamond clarity problems
- ✓ Pure white only 2% of all mined
- √ Variable prices based on 4Cs clarity, color, carat and cut.

Figure 3.

A relative evaluation of the laboratory grown with their mined source of the material.

benefits of the human society [11, 12], like making faster and smaller future electronics, quantum computers, high power lasers, nuclear energy, capturing carbon for reducing its footprint in the environment [13], medical devices for patients [14] or even water purification [15] for a better standard of living (**Table 1**). This chapter lists some of the engineering applications where the scientific knowledge of the diamond material property has been used to build/design/create something useful for the people on earth.

Property	Value	Application
Hardness* [16]	100 GPa	Grinding abrasive, Cutting tool [17, 18], Tribology [19–21], mechanical applications [22]
Young's Modulus*	1100 GPa	
Poisson's ratio	0.1	
Co-efficients of friction	0.1	
Wear resistance*	10 ⁻⁷ mm ³ /N-m	
Thermal conductivity at 300 K*	2000 W/m-K	Heat spreader [23], High temperature application [24, 25
Thermal expansion co-efficient at 300 K	0.8×10^{-6} /K	
Specific heat at 20 °C	0.502 J/g-K	
Debye temperature*	1860 ± 10 K	Acoustic devices [26, 27]
Sound velocity*	17,500 m/s	
Density	3.515 g/cm ³	
Atomic Density*	$1.77 \times 10^{23} \text{cm}^{-3}$	
Bandgap	5.45 eV	Power electronics packaging [28–30]
Electrical resistivity	10^{13} – 10^{16} Ω-cm	
Breakdown Voltage*	10 ⁷ V/m	
Doped [31–33] semiconductor resistivity	10^{-1} - $10^4 \Omega$ -m	Electronic sensors, devices [34–36]
Negative electron affinity	-1.5 eV (H-terminated)	Electron field emitter [37]
IR to UV optical transparency	UV cut off @ 225 nm & absorptions at 2.5–6.5 µm with theoretical 71% transmission	Photonics [38, 39], Power transmission windows [40], Jewellery [41], Quantum computing [42–44]
Absorption co-efficient	$\leq 0.10 \; \text{cm}^{-1} \text{at } 10 \; \mu \text{m}$	
Refractive index	2.38 @ 10 μm, 2.41 @ 500 nm	
Photoluminescence	Nitrogen NV, silicon SiV vacancy centres	
Corrosion resistant	Chemically inert to acids	Electrodes in electro-chemica cells [45]
Biocompatible	Inert to biological cells [46]	Medical devices [14]
Radiation hard	43 eV atomic displacement energy	Nuclear detector [47, 48], instruments [49], Betavoltaics power supply [50]
Nuclear battery	Encapsulation of radio-isotopes	
Extreme conditions	Graphitisation at T > 700 °C in an oxygen containing, and 1500 °C in an inert atmosphere	High pressure cell anvils [51, 5

Table 1.Diamond property and their engineering applications (* highest among all materials).

2. Mechanical engineering

The oldest (engineering) application of diamond has been cutting and polishing. Diamond is the hardest and the strongest materials with highly covalent C-C bonding. It is strong along certain crystallographic planes, in certain directions, due to variable packing density of carbon atoms. Present day scientific knowledge about the diamond crystal structure, chemistry and its other material property was developed much later, than the art of making diamond jewellery was mastered by the ancient craftsmen since the middle ages. Geologists developed the Mohs scale of hardness as shown in **Figure 4** on the basis of the relative hardness between different minerals.

However, much later on when the modern-day science started to develop, scientist found that the indentation hardness values in GPa [53] is the highest for diamond materials. **Figure 5** compares the GPa hardness of different engineering materials. It can be found that hardened steel has only 7 GPa of hardness whereas, diamond has as high as 115 GPa. However, depending on the various factors like, the amount of defects present inside like dislocations, foreign elements, single or polycrystalline diamond, CVD or HPHT grown, crystallographic planes and directions, the hardness values can vary from 25–100 GPa. Due to such high hardness value, it has been used as grinding, lapping and polishing material in the form of slurries, paste, impregnated metallic disc or paper as shown in **Figure 6**.

Diamond carbon atoms are arranged in two inter-penetrating FCC crystal lattice of a diamond cubic structure where the covalent bond length is 0.154 nm with tetrahedral angle of 109.5° between them. The highly covalent nature (deep and symmetric potential well) of the C-C bond makes diamond's Young's modulus tensile strength and the thermal expansion co-efficient, the highest among all the solid materials. The high molecular weight polyethylene polymer which are used for protective armour application has the least tensile strength (about 1 GPa) in the **Figure** 7. The woods (11 GPa) that are used to build houses, or the human teeth enamel (55 GPa) for breaking food and even the structural steel material (200 GPa) have much less stiffness or flexibility i.e. the ability to resist deformation than diamond (>1200 GPa).

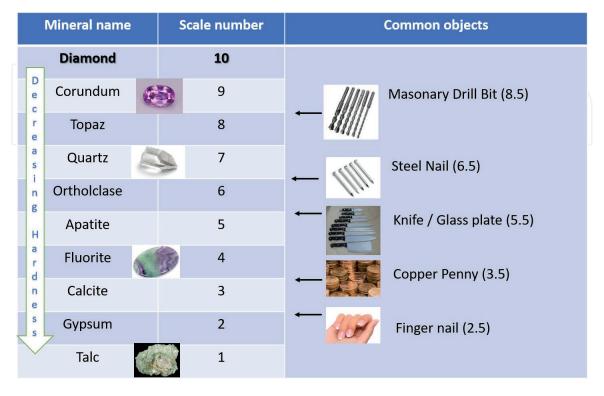


Figure 4. *Mohs scale of hardness of different materials.*

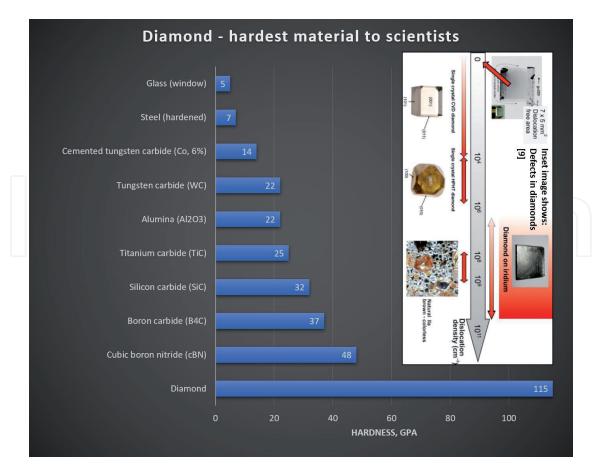


Figure 5. A relative comparison of the hardness of different materials.



Figure 6. *Diamond abrasive application.*

Due to its extreme hardness and strength, it has been traditionally used as cutting tools [54] in machining application as shown in **Figure 8**. Polycrystalline diamond cutting tools of different shapes and sizes are shown. They are used for the processing of natural stones starting from the block extraction in quarries through the intermediate steps of production to the final step of polishing the final product. Diamond tools are extensively used in the construction industry for the cutting and drilling of the concretes, asphalt and other materials. The traditional use of diamond has been for polishing glass, ceramics and the other hard metals, as already described before. Various types of metal bonded or pre-alloyed (cobalt) powders are mixed with synthetic diamond powder by hot pressing or sintering for

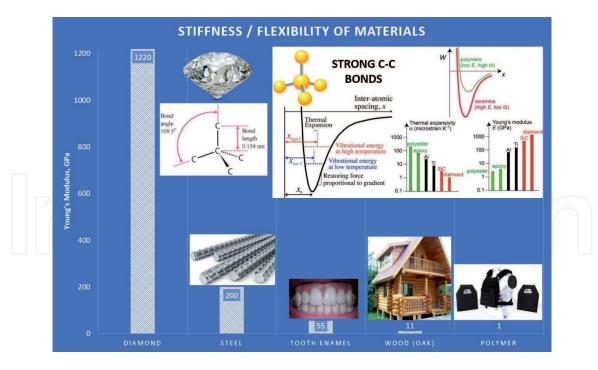
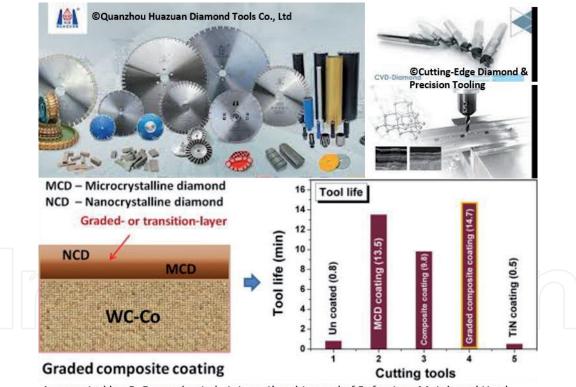


Figure 7. A relative comparison of the strength of different materials.



As reported by, R. Dumpala et al., International Journal of Refractory Metals and Hard Materials, 48, 2015, 24-30, https://doi.org/10.1016/j.ijrmhm.2014.07.023.

Figure 8.Diamond cutting tools application.

the abrasive industry. It has been shown by the researchers (**Figure 8**) that a double-layer diamond coating with micro (MCD) and nanocrystalline diamond (NCD) grains on the top of traditional Co cemented WC cutting tools not only increases the tool life but also it enhances the cutting efficiency. Such coated tools can be recycled time and again after recoating with diamond, once the top coating is worn

out. Diamond is the best protective solution for the coating service industry. Wear is the major cause of economic loss due to the energy that is lost in overcoming the mechanical friction within the moving mechanical assemblies. Diamond tribology [55, 56] is an important engineering application.

3. Electrical engineering

When current passes through electronic circuits, it heats up the devices, which even sometimes lead up to the device failures. Future generation devices will be smaller and faster, therefore there will be more current passing through per unit area of electronic circuits that will heat up the devices enormously. For efficient working of our devices, this heat needs to be thrown out of the electronic circuits, and diamond does this job the best, being the material with highest thermal conductivity (Figure 9). Moore's law earlier predicted that every 2 years the size of the electronics will be reduced by half. Diamond can only keep the pace of the Moore's law with time. Direct contact of diamond with electronic chips will pass the heat away from the circuits and thereby making the current to flow easily within your device for smooth operations (Figure 10). There are commercial suppliers, like Element Six, of such CVD diamond heat spreaders. If we compare the cooling capacity of different coolants, it is observed that diamond is five times more effective than commonly used Cu in electrical engineering. Polycrystalline diamond is alloyed/mixed with Cu/Ag/Ti metal powders and then sintered together for making composites for electronic packaging application [57, 58]. Therefore, engineers are designing future technologies like 5G/7G, radars for space or military communication with the integration of diamond in their electronic circuits. The scanning electron micrograph in Figure 9 shows one such CVD grown polycrystalline diamond plate like microstructure suitable for heat spreading applications.

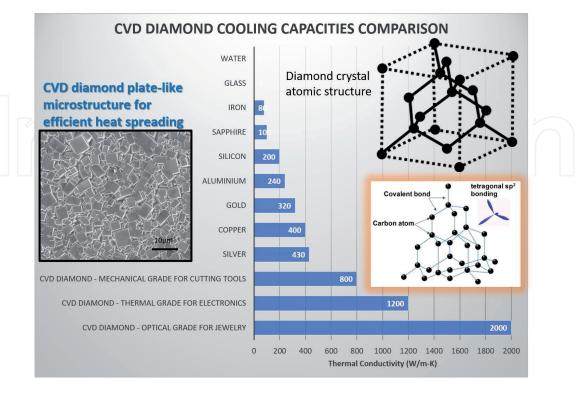


Figure 9.A relative comparison of the thermal conductivity of different materials.

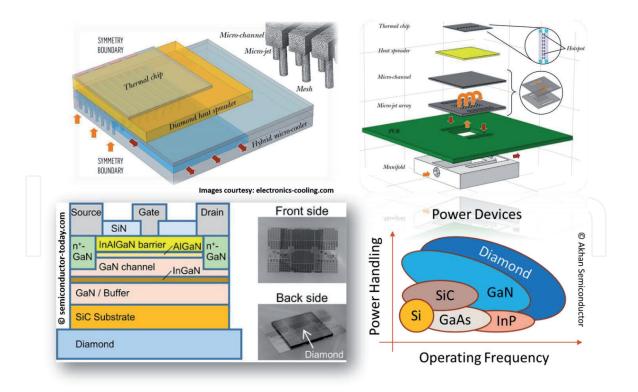


Figure 10.Diamond thermal management application.

4. Energy/power engineering

As we know from our high school physics that the energy level difference between the conduction band and valence band divides materials into a. insulator with large differences, b. semiconductor - with small differences and c. metal - with overlapping of the bands. Materials like GaN (3.44 eV), SiC (2.36 eV) and Diamond (5.45 eV) have large values of band gaps and they are known as wide band gap materials. They are used in high power high temp. high freq. energy engineering applications. In order to keep pace with the Moore's law, Si is running out of gas. It is getting replaced by wide band gap materials for high power density applications (Figure **10**). Compare to other wide band gap materials, diamond is with the highest band gap, also has the best electron-hole mobility (1945 and 2285 cm / V. s), critical breakdown voltage and the best value of the thermal expansion co-efficient. However, it is intrinsically insulator at room temperature and will become semiconductor only by suitable doping. Boron doping has made it possible to produce acceptor levels suitable for room temperature conductivity (metallic to superconductor [59, 60] based on doping concentration and temperature); but phosphorous doped n-type diamond has deep electron donor levels (0.46 eV) which only become active at high temperatures. Nitrogen also could not dope diamond to produce n-type conductivity, rather it produces NV centre defects [38] - suitable for opto-electronic engineering or quantum computer engineering. Absence of suitable n-type dopant atom for diamond, has so far limited the future prospect of diamond based electronic devices. It can only be used as single electrode - but not as transistors.

5. Computer engineering

In a maze puzzle, in order to find out "the only way out of the confinement", one has to explore all the different possible routes, one at a time, in order to look for the "single" viable solution - which is time consuming. Classical computing would take

long time to find a solution by trial and error, on the basis of its binary states of "0" and "1". Quantum mechanics gives wave particle duality i.e., quantum entities or qubits can be present simultaneously at more than one location, therefore, if qubit tries to find the way out of a maze puzzle, due to its entanglement and superposition characteristic of different states at the same time, it will be possible to find/compute the solution of maze puzzle much faster and in efficient manner. In other words, if an electron is asked to find the way out of a maze, due to its quantum nature, it will visit all the routes inside the maze simultaneously and will return with the correct maze path solution within no time! Quantum computing based on qubit has many advantages over classical computing. It can process much bigger amount of data at much less amount of time. In today's world of artificial intelligence and machine learning with increasing amount of data, the classical computing is reaching its limit of computational power. Therefore, there is greater need of increasing the computational power of today's computers. And the solution lies in quantum computers. The search for qubits started in 1980s and there are trapped ions, quantum dots or cryogenic superconductor-based quantum information processing, however, diamond advantageously offers a nitrogen vacancy NV centre based solid state room temperature qubit [61, 62]. First ever continuous-wave (CW) room-temperature solid-state maser using the NV defect in diamond was reported in 2018 [63]. There are numerous large and small start-up companies, supported by national and international government agencies [64], who are devoting research effort in coming up with a viable diamond-based quantum computer in the coming decade or so.

6. Chemical engineering

Boron doped diamond electrodes are used for many electrochemistry-based applications [65] like sensing, environmental, electrosynthesis, electrocatalysis for energy and devices. Chemo-mechanical polishing [66] by diamond slurries uses the combined effect of chemical reaction in addition to the mechanical abrasion of hard surfaces for polishing application.

7. Sonic/acoustic engineering

IDT metallic lines are patterned onto SAW devices. Sound velocity divided by the IDT internal spacing gives the frequency of such devices, which can be used as pressure and temperature sensors under extreme heat and pressure conditions of internal combustion engine for auto-mobile industry. The frequency of SAW devices can be enhanced by the use of diamond substrate material [67] with high sound velocity. Diamond being the material with the highest acoustic wave velocity is ideal for different sonic applications, like tweeter domes [68].

8. Opto-electronics engineering

Nitrogen vacancy (NV) centre [69] defect inside diamond crystal lattice has room temperature quantum spin states which interacts with presence of an external magnetic field. Higher the external magnetic field higher is their interaction. The energy which is required to flip the NV centre spin state would also become higher. This energy of interaction can be probed by electron paramagnetic resonance spectroscopy (EPR) – when input microwave energy/frequency (E = $h\nu$) matches with the interaction energy, input microwave energy flips then NV centre spin state

and thereby the intensity of fluorescence drops which is detected by optical microscope. Thus, the resonance frequency provides a direct and quantitative measurement of the local external magnetic field. NV centre magnetometer has been so far explored for jam-less GPS navigation by interacting with the earth's magnetic field (Lockheed Martin is developing), surface scanning probes to magnetically characterise semiconductors, oxides and other materials, spintronics, nanoscale thermometry, marker for living cells etc.

HPHT or CVD diamond optical lenses [70] are used for wide range of spectrum from infrared to UV windows for their unique optical properties, chemical, mechanical and thermal stability under extreme conditions of high-power optical beams. They can be used as visible intraocular lens, X-ray refractive lens [71] and even for spectrometers.

9. Bioengineering

Artificial retina based on silicon chips was earlier coated with ultra nanocrystalline diamond (UNCD) for eye environment fluid protective application [72]. Nowadays diamond electrode [73] is even tried for electrical stimulation of retinal prosthetic implants [74]. Diamond surfaces have been functionalised [75] for various applications [76, 77] like biomarker, bio-chip using electrochemical reactions. Microwave plasma CVD grown single crystal diamonds [78] is also used as dosimeter detector in radiotherapy treatments for cancer [79].

10. Environmental engineering

Diamond coatings have been developed by many companies to treat industrial waste water and also to disinfect freshwater without use of any chemicals. The boron doped diamond electrodes oxidise the organic pollutant into CO₂ or destroys the dirt and disinfect the germs that are present in the water. Recently a European project titled "DIACAT" has used the same boron doped diamond for direct photocatalytic conversion of CO₂ into fine chemicals and fuels under visible light [80].

11. Nuclear engineering

Diamond has the best mechanical properties alongwith high thermal conductivity [81] and very low dielectric loss tangent [82], which make them the only material that can be used as power transmission windows in the gyrotrons used for fusion reactors [25]. Synthetic diamond detector designed for small field dosimetry is used as a dosimeter for synchrotron microbeam and minibeam radiotherapy to ensure highly localised and precise dose delivery [83]. Betavoltaics are converting the beta particle (high energy electrons) decay of the radioactive material into the electric current of a semiconductor material (electron–hole pair generation by ionisation), that lasts for the half-life time period of the radioactive material itself. Researchers at Bristol, UK, [84] have separated C14 radio-isotope from the nuclear power plant waste material to form diamond out of them, which can be used as a nuclear battery to power low-capacity device application for space, military or medical, like hearing aid in human body for their entire lifetime. But safety is still the main concern for its actual use.

These are some (**Figure 11**), among the many, engineering applications of diamond that are available and/or under testing, for better technologies of the future.

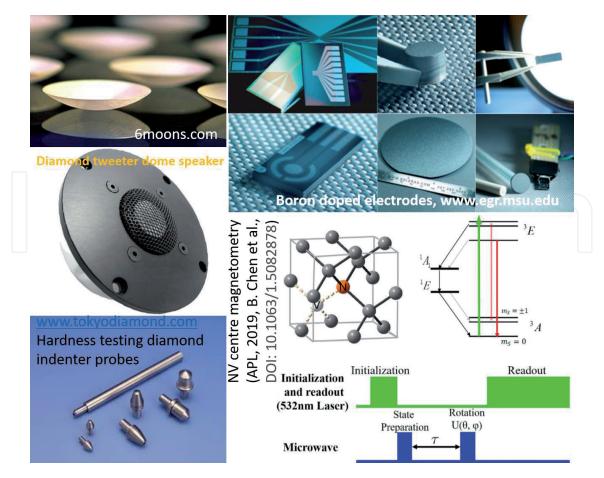


Figure 11. Few important engineering applications of diamond.

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