REVIEW of Sp^3 CARBON-BASED DIAMOND DETECTORS: APLICATIONS IN SPECIAL NUCLEAR MATERIALS VERIFICATION

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Abstract

Detectors in nuclear processes can be exposed to very high radiation levels, elevated temperatures, and caustic environments. There are very few materials which can withstand these conditions. The inherent properties of diamond (large band gap, radiation hardness, optical transparency, large saturated carrier velocities, and low atomic number) indicate that it may be an ideal candidate as a neutron detector material for harsh conditions in nuclear processes. Carbon-based detectors and diamond sensor technology, have a lengthy history. However in the past, these devices encountered restricted usage due to technological limitations or poor experimental reproducibility. Recent technological progress on chemical vapor deposition (CVD) synthetic diamond films, detonation nanometer size diamond (DND) particles, electrical and structural modification via dopants have open new doors for ultra-sensitive harsh environment resistance applications such as special nuclear verification on nuclear facilities. Diamond detectors may be applicable to arms control, trans-uranic waste characterization, material safeguards technologies, sensitive nuclear detection, and inspection safeguards tools for the new generation of nuclear reactors. These applications collectively require instruments that can sensitively detect uranium and plutonium isotopes under challenging conditions. This paper reviews the history and recent improvements to diamond detector technology. Experimental data of radiation effects on diamond such as fast neutron and gamma irradiation are presented. Resistance to harsh environment, fast response, and general ruggedness are only a few of the advantages of solid-state, diamond-based detectors

Sp^3 Carbons

Carbon, its allotropes (crystalline properties), and polymorphs (structural and morphological changes) have been intensively studied and regarded as one of the most valuable materials (i.e. diamond) by human kind. Carbon is not only the base of life but has the unique distinction to be the building block for the largest number of structures and compounds in comparison to other elements. Other elements on the fourth column of the periodic table, silicon, germanium, and tin also have similar characteristics. However carbon is unique in the number and variety of its polymorphs; from elemental carbon, organic compounds, and super hard carbon based minerals such as diamond. It is the most exploited element, with no close competitors. The inherent properties of carbon come from its quantum number and electron configuration ($1s^2 2s^2 2p^2$ a total of 4 electrons on the L shell) that allow the formation of hybridized orbital such as strong covalent bonds on sp3 hybridization. It is the element of choice for: highest strength fiber, provides one of the best lubricant, is the strongest natural crystal and hardest material, it is one of the best gas adsorbers, and helium gas barriers. Because of these properties new carbon compounds have been experimentally produced (i.e. fullerenes and hexagonal poly-types) and theoretically postulated (i.e. "super-diamond" and C_{28}). Due to the vast diversity of carbon compounds, its terminology and classification have been a topic of discussion and revision between researchers[i]. Carbon compounds have been classified by their allotropy- and polymorph form. In general the division is breached two main groups Sp2 or graphite nature, and Sp^3 diamond or landslite nature. The main distinction is based on the type of electronic arrangement, which enhances bonds formed with the adjacent atoms. Allotropy refers to crystallographic phenomena in which an element is a solid stated crystalline structure in at least two distinct forms that differ from each other by the spatial arrangement of their atoms[ii]. In the strict sense allotropes refer to the thermodynamic arrangement of the structure. Polymorphism, has in addition, a crystallographic connotation, i.e. deals with structural and morphological changes.

Elemental carbon-atom electronic configuration ($1s^2 2s^2 2p^2$) does not account for the crystalline tetrahedral aliphatic form found on structures such as diamond. In the case of diamond, a carbon atom is bonded to four additional carbon atoms by sharing four outset electrons with it neighboring carbon atoms. In order to make this arrangement possible the electronic configuration of elemental carbon has to be altered to a state of four valence electrons instead of two. Each valence electron needs to a separate orbital with its spin uncoupled from the other electrons. This alteration or hybridization is the result of the modification of the electron on the L shell of the atom. In the case of diamond one of the 2s electrons is raised to a 2p orbital. These new orbital are called hybrids since they combine the 2s and 2p orbitals. They are labeled sp^3 since they are formed from one s orbital and three p orbitals. Carbon atoms are known to exist in three states corresponding to sp^3, sp^2, and sp hybridization of their valence orbital. Sp^3 refer to a spatial (3D) polymer of carbon, sp^2 corresponds to a planar (2D) polymer, and sp-type corresponds to a linear chain like polymer of carbon.

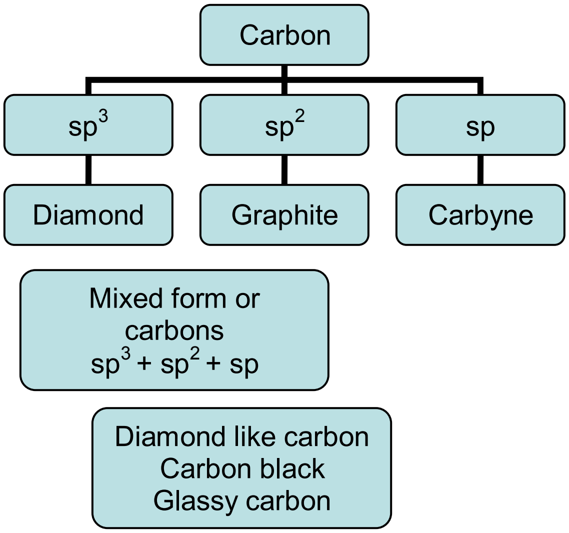


Figure 1. Simplified classification scheme for carbon allotropes.

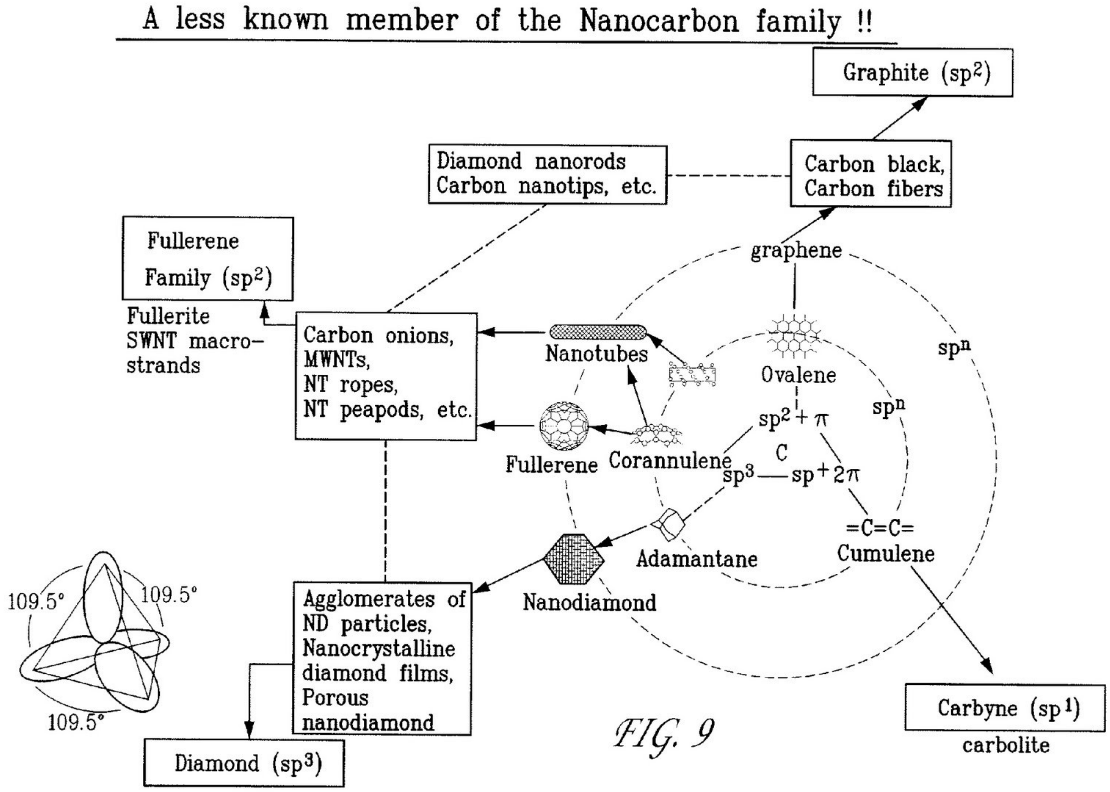


Figure 2. Carbon based allotropes for nano scaled structures

A hybrid sp^3 orbital is covalently bonded with neighboring atoms by sharing a pair of electrons. Since four of the six sp^3 valence electrons of carbon atom form bonds, the resulting structure of small atoms in the crystal has great strength. In the case of diamond, the formed tratrahedron of hybridized carbon atoms combines with four other hybridized atoms to form a three dimensional, entirely covalent, lattice structure shown on figure 2. This structure is the basis for diamond crystal.

Diamond is the densest phase of carbon. The carbon atoms are covalently bonded through sp^3 bonds forming tetrahedral cells (Figure). A rare form of diamond, hexagonal diamond, called lonsdaleite is also possible (Figure). Essentially, the difference in the structures is the type of hybridization, sp^2 or sp^3, or the ratio of sp^2 and sp^3 bonds as well as the structure type[iii]. On the other hand graphite consists of six membered aromatic rings of sp^2 hybridized carbon atoms arranged in layers (Figure). The layers are held together by a weak Van der Waals force while the atoms in the ring are tightly bound with covalent bonds. The layers can slip thus giving graphite excellent lubrication properties.

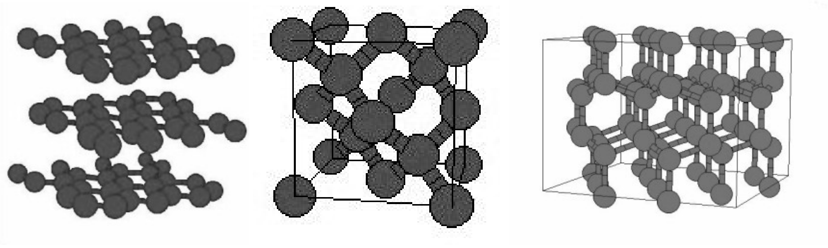


Figure 3. Structure of graphite, diamond and londsdaleite. Adapted from Encyclopedia of Chemical Processing.

Detonation nanodiamond (ND) is produce by high pressure – high temperature (HPHT) during a detonation where a carbon-hydride (i.e. CH_4) is present. The sudden pressure created during the explosion results in a short diamond growth leading to small crystal size – typically on the nanometer scale. The detonation process has been used to synthesis nano phase diamond, zirconium dioxide, and aluminum oxide. Analogues to the impact of meteorite on the earths crust, this process forms ND material by direct synthesis in a detonation wave. The resulting particles have specific surface areas of 270 to 390 m^2/gm with size shapes close to spherical. The size distribution is between 4-6 nm (see Table 1). In addition, the particles have a high porosity, a high degree of chemical inertness, and high sorptive capacity.[iv] Some of the applications include as abrasives for polishing, for the production of composites, and for lubrication. There are other important applications which need to be explored as well which take advantage of the optical, electronic, and magnetic properties of these unique materials

Table 1. Properties of nanophase diamond.

Property	**Value**
Percentage of diamond phase, %	85-91
Original particles size, nm	4-6
Aggregates size, nm	50-1000
Density, g/cm^3	3.10
Specific surface area, m^2/gr	300±60
Carbon percentage, %	85-91
Chemical impurities	O,N,H

Diamond-like carbon (DLC) films contain carbon atoms in a variety of different coordinations. There are the tetragonally coordinated sp3 carbon atoms present in pure diamond as well as the trigonal sp2 coordination as found in graphite. DLC films may contain microcrystalline diamond and graphite as well as a disordered structure containing a mixture of configurations.The amount of sp^2 bonds depends upon the method of deposition and can be as high as 60%. The higher the number of sp^3 bonds the harder the material, the higher the band-gap and the better the overall physical properties of the material. Diamond-like carbon (DLC) films, obtained by chemical vapour deposition, exhibit low friction coefficients, chemical durability and extreme hardness, which makes them excellent candidates for wear-resistant applications. DLC have been studied as both active and passive elements in devices. Their use in an alternating current thin film electro-luminescent device has been reported by Kim and Wager[v]. The emission which occurs during breakdown of the DLC layer is very broad band extending well into the ultraviolet and appears white. Other studied application are use of DLC films as the insulator in metal-insulator-semiconductor (MIS) devices[vi], passive application as a resist for high resolution photolithography of semiconductor surface, and uses DLC as an electrical insulator on copper heat sinks for logic and array chips[vii]. Synthetic diamond has expanded into the markets of electronics, cutting tools, and wear-resistant coatings and have demonstrated other applications in the areas of thermal management, optics, and acoustics. Some of the innovative applications include electrodes for chemical processes and radiation detectors materials Additional applications as cold cathode emitters, as high-temperature sensors, and ultimately as semiconductors are also being developed.

Diamond as an electronic material

Sp^3 carbon (diamond) posses an unique combination of electronic, chemical, optical, and structural properties that make it an ideal candidate in the area of micro-electronics. Furthermore, the large breakdown field, high saturated current velocity, high thermal conductivity and other extreme properties of diamond make it an excellent semiconductor material for active electronic devices[viii]. Diamond's wideband gap (5.46 eV) allow the undoped crystal to be an excellent insulator, if it is doped (i.e. with boron) it becomes a semiconductor material. Diamond as an insulator observes resistivity that exceeds 10^{14} Ω-cm at room temperature[ix] and it can support electric field strengths as high as 10 MV/cm before conduction. The higher band-gap makes it difficult to promote an electron to the conduction band. Modification of the diamond structure by introducing of impurities has been demonstrated to modify the optical and electrical properties of the intrinsic crystal[x]. Although it has a wide band-gap of 5.46 eV, its intrinsic properties of carrier velocity of 2.7×10^7 cm s^{-1} and mobility of 2200 cm^2 V^{-1} s^{-1} for electrons, and dielectric constant of 5.5 give this material a broad advantage over other wide band-gap semiconductors in high power and high frequency applications. Recent doping methods have allowed the increase of concentration of dopants on the crystal and have opened the possibilities to incorporate new impurities (i.e. chromium). As results novel properties of semiconducting diamond are possible. Crystal morphology is an important parameter in determining uncompensated acceptors for different crystal facets as a function of doping concentration. Since conductivity depends on the crystal phase, the combined electromechanical properties can be exploited in sensor applications both for resistive temperature detectors and pressure transducers[xi] . Since electrical conductivity is related linearly with dopant type and concentration, a better controlled process may allow for the development of better semiconductor devices improving crystal quality and operating limits[xii].

Diamond Schottky diodes have large forward resistances 300Ω cm^{-2} that are 10 times the value for Si diodes due to compensated impurities, device geometry and lack of a good ohmic contact. Under uncompensated conditions the forward resistance value for a Schottky diode could range between 0.01 and 0.1Ω cm^{-2} with a breakdown voltage of 10kV[xiii] . A diamond Schottky diode should be a superior device over the Si diode for these parameters. Progress has been made with the formation of p-n junctions in diamond[xiv].

Diamond a wide band-gaps material

A wide band-gap material is a semiconductor that has a band-gap approximately greater than 2 eV. Some of the most prominent wide band-gap materials are GaP (2.26 eV), 3C–SiC (2.36 eV), 6H–SiC (3.0 eV), 4H–SiC (3.23 eV), GaN (3.2 eV), diamond (5.46 eV), AlN (6.2 eV), and BN (6.1–6.4 eV). These materials have applications in high-efficiency optoelectronic devices such as blue and UV light emitting diodes (LEDs) and lasers, as well as high-power, high temperature, and high-frequency electronic devices. Electronic devices formed in wide band-gap materials operate at high temperatures without suffering from intrinsic conduction effects because of the wide energy band-gap. Wide band-gap materials, in general, have a high breakdown voltage, which allows them to withstand a voltage gradient much greater than that of Si or GaAs without undergoing avalanche breakdown. This property makes wide band-gap materials excellent for applications in high resolution and sensitive radiation detectors, very high-voltage, high-power devices such as diodes, as well as high-power microwave devices.

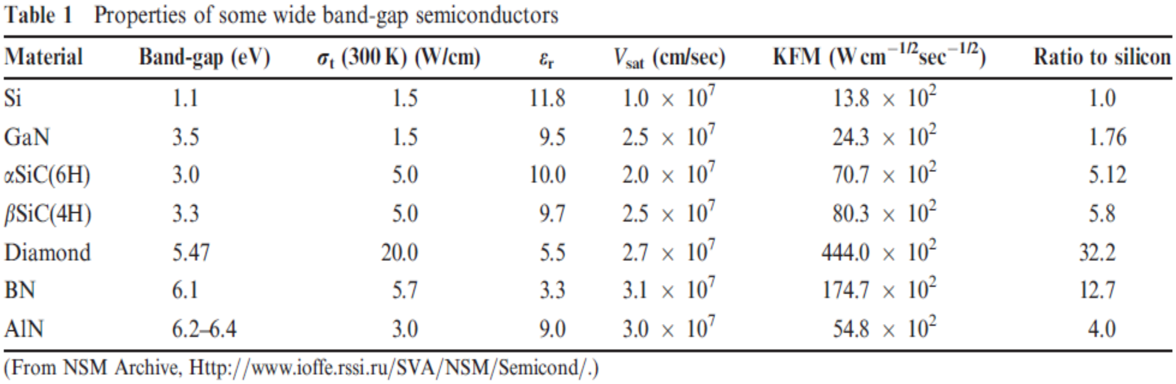


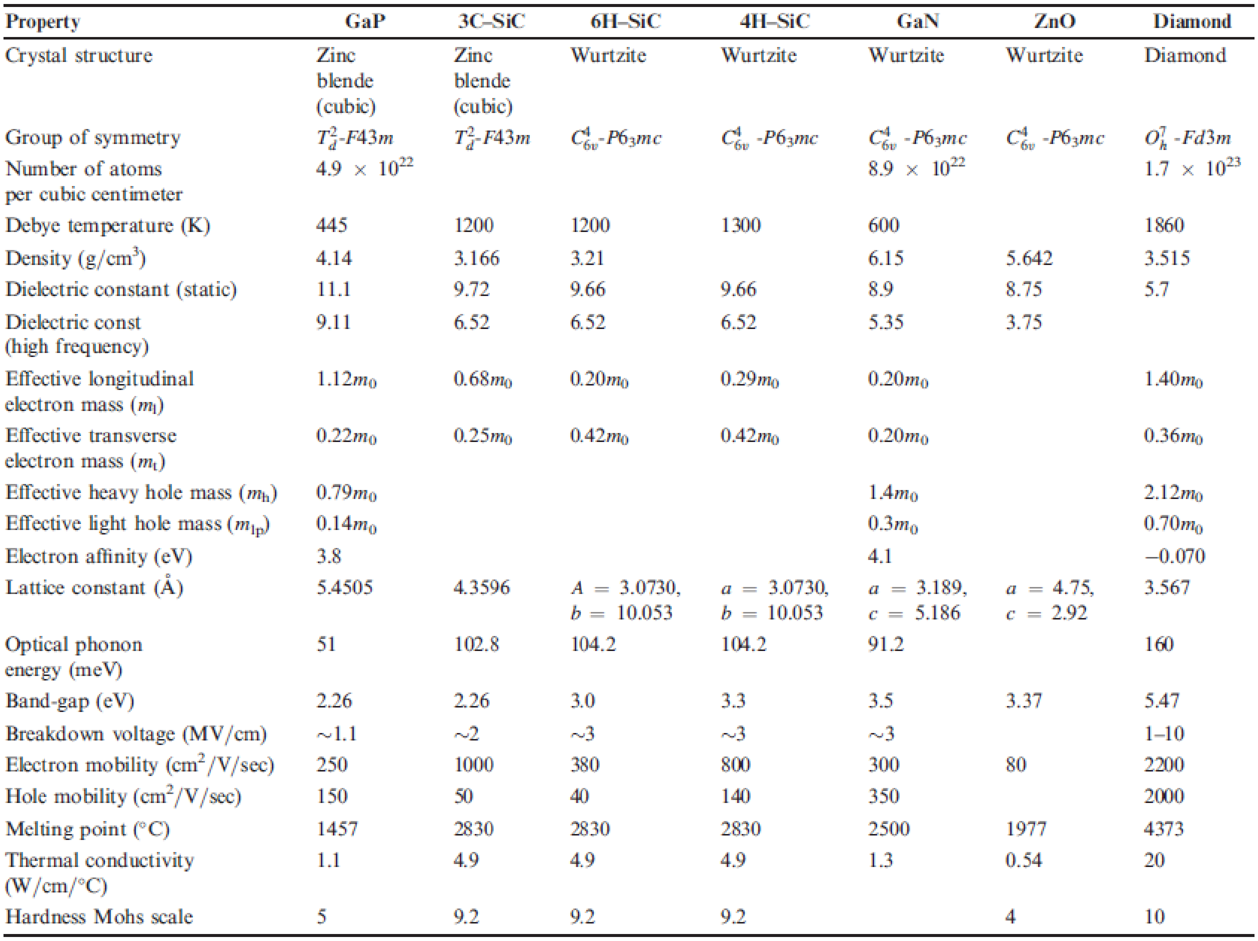
Table 1 Properties of some wide band-gap semiconductors

Material	Band-gap (eV)	σ_t (300 K) (W/cm)	ε_r	V_{sat} (cm/sec)	KFM (W cm$^{-1/2}$sec$^{-1/2}$)	Ratio to silicon
Si	1.1	1.5	11.8	1.0×10^7	13.8×10^2	1.0
GaN	3.5	1.5	9.5	2.5×10^7	24.3×10^2	1.76
αSiC(6H)	3.0	5.0	10.0	2.0×10^7	70.7×10^2	5.12
βSiC(4H)	3.3	5.0	9.7	2.5×10^7	80.3×10^2	5.8
Diamond	5.47	20.0	5.5	2.7×10^7	444.0×10^2	32.2
BN	6.1	5.7	3.3	3.1×10^7	174.7×10^2	12.7
AlN	6.2–6.4	3.0	9.0	3.0×10^7	54.8×10^2	4.0

(From NSM Archive, Http://www.ioffe.rssi.ru/SVA/NSM/Semicond/.)

Table 1 and table 2 show some of the properties of wideband gaps materials. The Keyes figure of merit (KFM) takes into account the power density dissipation for closely packed integrated circuits. High thermal conductivity is an important element for the KFM. The KFM is based on Vsat (electron saturation velocity), st (thermal conductivity), and er (dielectric constant). The relative value of the KFM is related to the speed of the transistor in the material[xv]. The higher the value of KFM, the higher will be the speed of the transistor. A larger band-gap enables the fabrication of diodes with higher breakdown voltages. Diamond has a higher band-gap then SiC, GaN, and Si. However its breakdown voltage is dependent upon impurities in the crystal lattice. To achieve the highest breakdown voltage, high purity diamond is required. Diamond Schottky diodes have large forward resistances 300Ω cm-2 that are 10 times the value for Si diodes due to compensated impurities, device geometry and lack of a good ohmic contact. Under uncompensated conditions the forward resistance value for a Schottky diode could range between 0.01 and 0.1Ω cm-2 with a breakdown voltage of 10kVxvi .

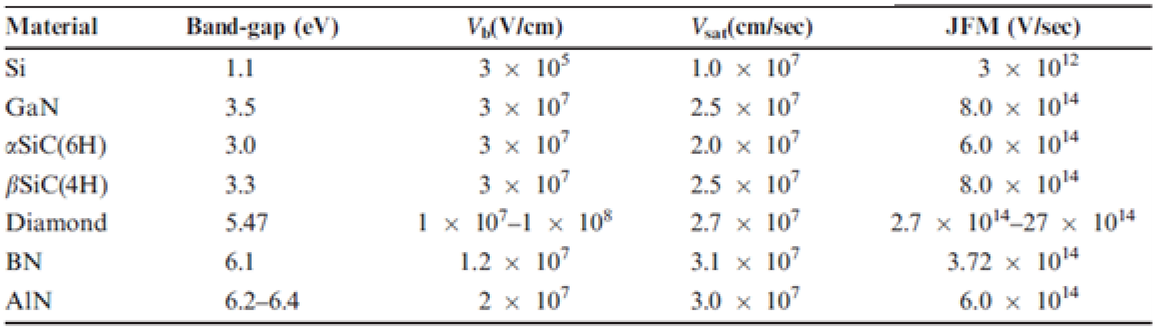
Table 2. Properties of some wide bandgaps materials and its comparison to diamond



Property	GaP	3C–SiC	6H–SiC	4H–SiC	GaN	ZnO	Diamond
Crystal structure	Zinc blende (cubic)	Zinc blende (cubic)	Wurtzite	Wurtzite	Wurtzite	Wurtzite	Diamond
Group of symmetry	T_d^2-$F43m$	T_d^2-$F43m$	C_{6v}^4-$P6_3mc$	C_{6v}^4 -$P6_3mc$	C_{6v}^4 -$P6_3mc$	C_{6v}^4 -$P6_3mc$	O_h^7 -$Fd3m$
Number of atoms per cubic centimeter	4.9×10^{22}				8.9×10^{22}		1.7×10^{23}
Debye temperature (K)	445	1200	1200	1300	600		1860
Density (g/cm^3)	4.14	3.166	3.21		6.15	5.642	3.515
Dielectric constant (static)	11.1	9.72	9.66	9.66	8.9	8.75	5.7
Dielectric const (high frequency)	9.11	6.52	6.52	6.52	5.35	3.75	
Effective longitudinal electron mass (m_l)	$1.12m_0$	$0.68m_0$	$0.20m_0$	$0.29m_0$	$0.20m_0$		$1.40m_0$
Effective transverse electron mass (m_t)	$0.22m_0$	$0.25m_0$	$0.42m_0$	$0.42m_0$	$0.20m_0$		$0.36m_0$
Effective heavy hole mass (m_h)	$0.79m_0$				$1.4m_0$		$2.12m_0$
Effective light hole mass (m_{lp})	$0.14m_0$				$0.3m_0$		$0.70m_0$
Electron affinity (eV)	3.8				4.1		–0.070
Lattice constant (Å)	5.4505	4.3596	$A = 3.0730$, $b = 10.053$	$a = 3.0730$, $b = 10.053$	$a = 3.189$, $c = 5.186$	$a = 4.75$, $c = 2.92$	3.567
Optical phonon energy (meV)	51	102.8	104.2	104.2	91.2		160
Band-gap (eV)	2.26	2.26	3.0	3.3	3.5	3.37	5.47
Breakdown voltage (MV/cm)	~1.1	~2	~3	~3	~3		1–10
Electron mobility (cm^2/V/sec)	250	1000	380	800	300	80	2200
Hole mobility (cm^2/V/sec)	150	50	40	140	350		2000
Melting point (°C)	1457	2830	2830	2830	2500	1977	4373
Thermal conductivity (W/cm/°C)	1.1	4.9	4.9	4.9	1.3	0.54	20
Hardness Mohs scale	5	9.2	9.2	9.2		4	10

A diamond Schottky diode should be a superior device over the Si diode for these parameters. Progress has been made with the formation of p-n junctions in diamond. Wide band-gap materials have such as diamonds are ideals candidates for harsh environment resistance radiation detectors. Diamond wideband gap posses an excellent Johnson figure of merit (JFM) about two orders of magnitude higher than silicon, making it excellent candidates for high-power microwave electronics and radiation detection (Table 2). The Johnson figure of merit (JFM) is used to compare materials for power microwave applications. Larger values indicate superior performance in microwave power.

Table 3. Johnson figure of merit (JFM) of some wide band-gap semiconductors.



Material	Band-gap (eV)	V_b(V/cm)	V_{sat}(cm/sec)	JFM (V/sec)
Si	1.1	3×10^5	1.0×10^7	3×10^{12}
GaN	3.5	3×10^7	2.5×10^7	8.0×10^{14}
αSiC(6H)	3.0	3×10^7	2.0×10^7	6.0×10^{14}
βSiC(4H)	3.3	3×10^7	2.5×10^7	8.0×10^{14}
Diamond	5.47	1×10^7–1×10^8	2.7×10^7	2.7×10^{14}–27×10^{14}
BN	6.1	1.2×10^7	3.1×10^7	3.72×10^{14}
AlN	6.2–6.4	2×10^7	3.0×10^7	6.0×10^{14}

Overall, the properties of wide band-gap materials have many advantages over Si, GaAs, and related semiconductor materials (Table 3). Wide band-gap materials have a much higher breakdown voltage and a higher thermal conductivity than silicon and related semiconductors. In addition when you compare the electron mobility (Si: 1450 cm2=V=sec, GaAs: 8500 cm2=V=sec) and hole mobility (Si: 450 cm2=V=sec, GaAs: 400 cm2=V=sec) of standard semiconductor materials to that of diamond (electron mobility: 2200 cm2=V=sec, hole mobility: 2000 cm2=V=sec), there are some very distinct advantages that come to light. The large band-gap difference makes these materials suitable for high-temperature electronics, power electronics, and radiation- hardened electronics. From the mentioned group of wide band gaps materials Diamond (pure sp^3) is the only one that can resist to a combination of high temperature, high voltage and irradiation simultaneously. Diamond electronic operation temperature can reach up to 800 C on air (twice the temperature of SiC) and up to 1,500 C under an oxygen free environment

CONCLUSION

Sp^3 carbons such as diamond have exceptional properties that can be useful in nuclear field due to its compatibility and the ability to serve as a multifunctional material. Diamond offer exceptional properties desirable in harsh environment and in applications such as diamond based micro- and nano- electronics and radiation sensors for SNM monitoring that can tolerate extreme environments. Wide band gaps material such as diamond are promising for the development of state-of-the-art sensors materials in a broad range of applications including in situ measurements, ultra low level detection. Several applications that include high hardness, low friction coefficient, mechanical and electrical properties can be achieved using impurities containing in diamond crystal. In recent years the exceptional properties of diamond have been exploited since inexpensive synthesis methods for diamond films and diamond nano-particles were developed. Some diamond commercial applications, including radiation detection, are already on the market.

The development of CVD diamond films in large size is progressing rapidly and as result diamond sensors are finding widespread applications in fast and epithermal neutron sensors as well high energy radiation. The radiation resistance is beyond that any actual technology employed for high energy particle detection such as fast neutron. Fast response and radiation tolerance have been reported by several researchers on both CVD and polycrystalline diamond. Advances also have been made in the modification of diamond films and nano-particle by the diffusion of elements such as boron, chromium and erbium. These allow modifying diamond for sensors-specific applications in the area of SNM materials monitoring and detection. Applications areas include arms control, transuranic waste characterization, material safeguards, and facility decontamination and decommissioning. These applications require sensors materials that can sensitively detect SNM under conditions that can be challenging for a variety of different reasons. The large band gap, radiation hardness, optical transparency, large saturated carriers velocity and low atomic number of diamond all make it an unique candidate as a sensor material for harsh environment.

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