## Chapter 12 CVD Diamond and Nanodiamond: Versatile Materials for Countering a Wide Range of CBRN Threats



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Abstract Fabrication of thin films of diamond by chemical vapour deposition (CVD) has now developed into a mature technology, with high-quality diamond readily available from multiple vendors at relatively low cost. As such, scientists and engineers now have access to the wide range of outstanding mechanical, thermal, optical and electronic properties that diamond has to offer. In this review, we shall discuss a range of applications in which CVD diamond films and nanodiamond particles can help to reduce, remove or mitigate the threats from chemical, biological, radiological and nuclear (CBRN) incidents or attacks. Some of these applications are commercially available today, others may require further research or modification of existing diamond-based devices for the unusual requirements of CBRN events, while others are currently only ideas which have yet to be developed.

**Keywords** Diamond  $\cdot$  Nanodiamond  $\cdot$  CBRN threats  $\cdot$  Water purification  $\cdot$  Chemical reagent detection and analysis  $\cdot$  Antimicrobial surfaces  $\cdot$  Bioimplants  $\cdot$  Radiation detectors  $\cdot$  Radiation dosimeters  $\cdot$  Radiation-hard electronics  $\cdot$  Targeted 'magic bullet' treatments  $\cdot$  Telecommunications  $\cdot$  Reliable power supplies  $\cdot$  Nuclear batteries

## 12.1 Introduction

Diamond has a unique set of extreme properties (Table 12.1) that make it useful for a wide range of thermal, electronic, optical and mechanical applications [1]. However, for much of recent history, diamond was available only in the form of single-crystal natural stones which limited its use to expensive jewellery. The situation began to change in the 1950s, when the high-pressure high-temperature (HPHT) method of synthesising diamond in a laboratory was developed and commercialised by the

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Table 12.1 A selection of some of the outstanding properties of diamond

Extreme mechanical hardness (~90 GPa) and wear resistance		
Highest bulk modulus $(1.2 \times 10^{12} \text{ N m}^{-2})$		
Lowest compressibility (8.3 $\times$ 10 <sup>-13</sup> m <sup>2</sup> N <sup>-1</sup> )		
Highest room temperature thermal conductivity (2 $\times$ 10 <sup>3</sup> W m <sup>-1</sup> K <sup>-1</sup> )		
Very low thermal expansion coefficient at room temperature $(1 \times 10^{-6} \text{ K}^{-1})$		
Optical transparency from the deep ultraviolet to the far infrared		
Highest sound propagation velocity (17.5 km s <sup>-1</sup> )		
Very good electrical insulator (room temperature resistivity is $\sim 10^{13} \Omega$ cm)		
Doped diamond is a semiconductor with a wide bad gap of 5.4 eV		
Very resistant to chemical corrosion		
Biologically compatible		
Some surfaces exhibit very low or 'negative' electron affinity		
The NV centre defect acts as a single-photon source		

General Electric Company. This HPHT process originally produced mm-sized stones which were yellowy-brown in colour due to unwanted nitrogen incorporation, making them unsuitable for gemstones. The ready availability and low cost of these so-called 'industrial diamonds' led to a number of applications that exploited diamond's hardness, such as drilling, sawing or milling, and prompted the beginning of a multi-million-dollar industry which continues to this day [2]. Since ~2015, advances in the HPHT process have allowed colourless gemstone-quality HPHT diamonds to be manufactured which are now good enough for the jewellery market. However, HPHT diamond is only produced in the form of stones or particles, meaning that a large contingent of diamond's exceptional properties still cannot be exploited.

This problem was finally solved with the advent of diamond grown by chemical vapour deposition (CVD) in the 1980s, because this method produces diamond in the form of a thin coating or layer conformally attached to a surface (or as a freestanding diamond plate if removed from the substrate) [3]. Diamond coatings such as these allow almost all of the superlative properties of diamond to be accessed, and as a result, the number of applications for CVD diamond has increased hugely over the past few years. Advances in deposition technology, driven by the burgeoning market in CVD diamond gemstones [4], have allowed thicker diamond films to be deposited at faster rates, and therefore more cheaply. Another factor has been the large increase in the number of companies producing lab-grown diamond (both for gems and as coatings), increasing the availability and supply of diamond material. Nowadays, the previous commonly held perception that diamond is a rare and expensive product only useful for gems or niche applications is rapidly being dispelled, and finally diamond is becoming regarded as a truly useful, affordable, engineering material.

#### 12.2 The CVD Process

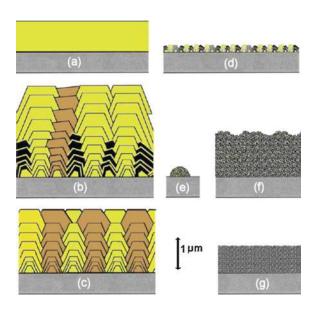
In the CVD process [3], a diamond coating is deposited onto the surface of a suitable substrate, such as a smaller diamond seed in the case of gemstone growth, a Si wafer for electronics, a quartz window for optics, or an engine component for mechanicalwear applications. The substrate is placed onto a heated stage inside a vacuum chamber. The substrate is heated to 700-1000 °C while process gases (a carbon source such as methane diluted to just a few percent input mole fraction in hydrogen) are passed over the substrate at a pressure of 20–200 torr. The gases are typically energised using either a heated metal (W, Ta, or Re) filament placed a few mm above the substrate surface, or by application of a microwave discharge in the form of a stable 'plasma ball' which sits above the substrate surface. In either case, the thermal or electrical energy deposited into the process gases causes the molecules to fragment and form a chemical 'soup' of atoms, radicals, ions and clusters near to the substrate surface. Reactive species (mainly H atoms and CH3 radicals) from this hot gas mixture diffuse to the surface, and if the conditions are optimal, they deposit onto the surface as a continuous layer of diamond [5]. The diamond coating can remain on the surface after growth and be utilised in situ, or the substrate can be removed by a suitable etch process (e.g. conc. nitric acid to dissolve a Si wafer) to create a freestanding diamond 'wafer'.

## 12.3 Types of CVD Diamond

If diamond is grown homoepitaxially [6] onto an existing HPHT or natural diamond seed crystal, then the enlarged single-crystal diamond (SCD) that results can either be cut and polished into a gemstone (which is the basis for the flourishing CVD diamond gemstone market [4]) or laser cut into flat SCD substrates usually a few mm in size, suitable for advanced applications.

In contrast, heteroepitaxial diamond growth on a non-diamond substrate begins from numerous individual, isolated nucleation sites, e.g. from micro- or nanodiamond seed crystals scattered on the surface, or surface defects such as scratches, impurities or dislocations [7]. The individual diamond nuclei grow and fuse with their immediate neighbours to form a coalesced (or closed) two-dimensional film that then continues to grow normal to the surface. The resulting material will usually be polycrystalline, composed of almost pure diamond crystallites (or grains) joined together by grain boundaries that contain varying amounts of impurities and non-diamond carbon. By choosing the appropriate process conditions [8], the morphology and the average crystallite size can be tuned [9], as shown in Fig. 12.1. Diamond films are usually grouped into categories depending upon their crystallite size and morphology.

Fig. 12.1 Schematic representation of various forms of diamond film growth. (a) SCD film grown epitaxially on a SCD substrate. (b) MCD columnar growth from randomly sited nuclei, where the slowest growth face determines the overall film texture, in this case (100). (c) Highly oriented 'textured' MCD obtained following special nucleation procedures. (d) Faceted NCD, which is really just thin MCD with high nucleation density. (e) Cauliflower NCD before it has coalesced into a continuous film. (f) Cauliflower NCD film. (g) UNCD



- Microcrystalline diamond (MCD) films [3] exhibit faceted crystallites of size 0.5 μm to a few 100 μm, with a columnar growth structure that produces anisotropic properties which vary with film thickness.
- Nanocrystalline diamond (NCD) films [10] contain more rounded crystallites (sometimes referred to as 'cauliflower' diamond) ranging in size from ~10–100 nm.
- Ultrananocrystalline diamond (UNCD) films [11, 12] have crystallite sizes
   10 nm embedded in a sp<sup>2</sup> carbon matrix, and although their properties are somewhat degraded compared to MCD and NCD, they have the advantage of being smooth on the nm scale.

## 12.4 Doping

Undoped CVD diamond of any grain size is highly electrically insulating. However, doping by incorporation of a suitable impurity atom, can increase the conductivity of the film in a controllable manner. The dopant atoms are usually added to the input gas mixture in gaseous form, e.g.  $B_2H_6$  for boron,  $NH_3$  or  $N_2$  for nitrogen and  $PH_3$  for phosphorus. Adding boron into diamond at low-to-medium concentrations creates a p-type semiconductor [13], while at high concentrations (>1  $\times$   $10^{20}$  cm $^{-3}$ ) the conductivity becomes near-metallic, and even superconducting at temperatures <10 K [14]. B-doped diamond (BDD) can, therefore, be used in a variety of simple electronic devices, sensors, and especially as

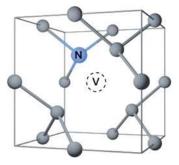
electrochemical electrodes [15] (see Sect. 12.8). In contrast, n-type semiconductivity is much harder to achieve, because most potential n-type dopants (P, As, Li) are too large to easily replace a small C atom in the diamond lattice, and thus have a low solid-state solubility in diamond [16]. Some degree of success has been achieved with phosphorus doping [17], but a reliable n-type dopant with useful electronic properties remains the 'Holy Grail' of diamond semiconductor research.

## 12.5 The NV Centre

Nitrogen atoms, however, are small enough to substitute for carbon [18], however the energy levels of the N donor in diamond are too deep and so the material is electrically useless for most applications. Nevertheless, N in diamond, when situated next to a vacancy, forms the so-called 'NV centre' [19], as shown in Fig. 12.2. This defect is causing a great deal of excitement in the scientific community because NV centres located within a diamond lattice behave as isolated 'chromophores', with a set of energy levels distinct from those of the surrounding diamond. When exposed to a stream of photons from a laser, each NV defect will absorb only *one* photon.

When they subsequently relax, each NV centre will re-emit only a single photon (with reduced energy), and each photon emerges with a specific optically readable spin [20]. The photons can then be individually collected in suitable optical waveguides and transported where required. After a suitable delay, the NV resets, and can absorb and re-emit another photon. Thus, NV centres act as excellent single-photon sources [21], underpinning a host of applications involving quantum computing and quantum information processing [22–24].

**Fig. 12.2** Schematic diagram of the NV defect centre in the diamond lattice



## 12.6 CVD Reactors and Systems

Turning now to the practicalities of deposition, hot filament (HF) CVD reactors can usually only deposit diamond at rates of  $\sim 0.5-1 \, \mu m \, h^{-1}$ , but they can be scaled up to coat large areas (such as 12-inch-diameter wafers) and can coat non-flat shapes such as wires and substrates with complex 3D morphology [3]. In contrast, microwave (MW) plasma CVD reactors can deposit diamond at rates as high as a few 100 μm h<sup>-1</sup> depending on the MW power used, but only over smaller areas (typically 3-inch-diameter samples) and predominantly flat substrates. However, these limitations to growth rates and substrate area are rapidly being overcome, with continuing improvements in reactor technology and more widespread use of CVD diamond in various applications. Currently, there are over 200 research groups worldwide studying growth or applications of CVD diamond, and perhaps 100 commercial companies either making diamond (for gemstone or other applications) or utilising CVD diamond in high-tech devices. As a result, the cost of diamond has fallen rapidly over the past decade; at the time of writing, the typical costs for a freestanding single-crystal diamond sample ( $4 \times 4 \times 0.5$  mm) from a company such as Element Six is  $\sim$ \$1700, while that for a larger (10  $\times$  10  $\times$  0.5 mm) polycrystalline sample is only ~\$50–200 depending on quality, while the number of suppliers has increased accordingly (see Table 12.2).

#### 12.7 Nanodiamond

Together with diamond in the form of single-crystal gemstones or thin films, diamond particles of different sizes are another area of considerable current scientific interest [26]. Here, we shall focus only upon nanodiamond (ND) particles, which typically have sizes 2–10 nm [27]. The most common ND production method is via detonation of explosives (such as TNT and hexogen) in an inert atmosphere or in water/ice, inside a steel chamber [28]. The detonation produces a shockwave which propagates through the reaction mixture at supersonic speeds. In the transient shockwave, the prevailing pressure and temperature can be  $p \sim 10$ –20 GPa and  $T \sim 2000$ –4000 K. Under these conditions diamond is the thermodynamically favoured phase of carbon, while at all other times, the pressure and temperature conditions favour other forms of carbon. Thus, the explosion produces a mixture of diamond particles, soot and other  $sp^2$  carbon material.

The powdery mixture of products from the detonation is cleaned with various acids and reagents to remove unwanted metallic impurities and soot, and the diamond component extracted. The resulting material, often called 'detonation nanodiamond' (DND) is commercially available from many suppliers worldwide (see Table 12.2) as a powder (see Fig. 12.3) or as a suspension in water, and is currently produced at a rate of several tons per year and sold for as little as \$100/kg. Unfortunately, the DND particles tend to fuse into aggregates ~100 nm in size, and

Table 12.2 Selected suppliers of diamond gems, HPHT grit, CVD diamond substrates and nanodiamond powders

Supplier	Diamond product	Country	Refs.
Element Six, Ltd	CVD substrates, HPHT	UK, USA	[36]
DiamFab	CVD diamond films	France	[37]
Ceratonia	Diamond grit, CVD substrates	Germany	[38]
Yorkshire Bioscience	Nanodiamond	UK	[39]
Carbodeon	Nanodiamond	Finland	[40]
Diamond Materials	CVD substrates	Germany	[41]
Microdiamant	Nanodiamond	Switzerland	[42]
Nanodiamond.com	Nanodiamond	Switzerland	[43]
Ray Techniques, Ltd	Nanodiamond	Israel	[44]
Advanced Diamond Technologies	UNCD substrates	USA	[45]
Applied Diamond, Inc.	CVD substrates	USA	[46]
Crystallume	CVD substrates	USA	[47]
Diamond Foundry	Gems	USA	[48]
Gemesis	Gems	USA	[49]
SCIO diamond	Gems	USA	[50]
EDP Corporation	CVD substrates	Japan	[51]
NanoCarbon Research Institute, Co., Ltd.	Nanodiamond	Japan	[52]
Crysdiam Technology	Gems, CVD substrates and nanodiamond	China	[53]
Pam-Xiamen	CVD wafers	China	[54]
WEC Superabrasives	Gems	Taiwan	[55]
New Diamond Technology	Gems, CVD substrates	Russia	[56]
2a Technologies	Gems, CVD substrates	Singapore	[57]
Diamond Elements	Gems, substrates	India	[58]

A more comprehensive and continually updated list of diamond suppliers can be found in Ref. [35]

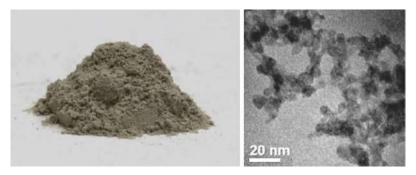


Fig. 12.3 Left: DND powder. Right: transmission electron microscopy image of DND [25]. (Copyright  $^{\circ}$  R. Hamers research group, University of Wisconsin, used with permission)

thus the as-supplied material usually requires de-aggregation before subsequent processing. This can be achieved in many ways, including ball milling, pulverisation, high-power sonication, acid treatments, controlled heating in  $O_2$  or  $H_2$ , or combinations of these methods [29]. The resulting DND particles are best described as having a diamond core surrounded by a (partially) graphitic or fullerene-like shell – and are sometimes described as 'bucky-diamonds' [30].

As a result of the various cleaning processes applied following detonation synthesis, the surfaces of DND particles are usually terminated with oxygen-containing groups like carboxyl, hydroxyl or bridging-ether groups. DND particles are therefore usually hydrophilic, which helps their stability when in aqueous suspensions. This oxygenated surface can be modified by standard chemical methods, replacing the O-groups with H (producing a mildly hydrophobic surface), with F (which is superhydrophobic), or with NH<sub>2</sub>. Both O-terminated and NH<sub>2</sub>-terminated ND are of particular interest because they enable the subsequent binding of a large variety of functional molecules, such as bioactive compounds (proteins, enzymes, antibodies, DNA), catalysts, drug molecules, or polymer building-blocks by amide bond formation or other standard chemical procedures [31].

ND particles containing fluorescent NV centres exhibit bright luminescence, which, combined with a readily modifiable surface and biocompatibility, make them extremely promising for biomedical applications [32], and, in particular, for use as a biomarker to 'tag' biomolecules of interest as they travel around within living organisms [33, 34].

In this short review we shall concentrate on applications of CVD diamond and nanodiamond that may help to mitigate the effects of a chemical, biological, radiological or nuclear (CBRN) threat. The aim is to identify potential applications where CVD diamond is a key component that counter a diverse range of CBRN threats. In some cases, these applications may reduce the likelihood of a particular threat happening, or even prevent it altogether. In others, they may simply help to mitigate the damage following a successful CBRN attack. However, the number of applications involving diamond that could be brought to bear on CBRN issues is huge, so we limit ourselves here to a few examples from each threat type. In some cases, the technology is already being developed, although perhaps only on a small scale; in others it hasn't yet been invented.

#### **12.8** Chemical Threats

Although there are many potential chemical threat scenarios, we shall only consider two here: poisoning of a water supply, such as a reservoir or river, and detection of chemical agents in smuggled items.

## 12.8.1 Poisoning of a Water Supply

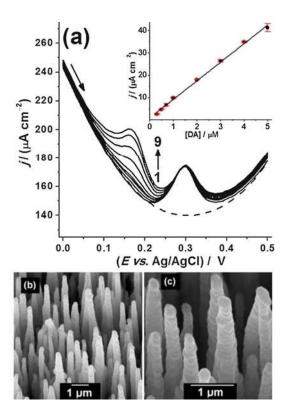
The drinking-water supply to a city or region may become contaminated by toxic chemicals, either accidentally as the result of, say, an industrial leak, or deliberately due to a terrorist attack. In the latter case, there are two scenarios. In the first option, the perpetrator could seek to cause maximum casualties as quickly as possible. In this case, the attack might take the form of dumping a large volume of a highly toxic chemical into a river, reservoir or aquifer, with the aim that by the time it is detected the damage would have already been done. This is quite a challenge, however, because most developed counties have detectors that continuous monitor the water supply, and any sudden spike in toxin concentration would automatically shut down the supply. This strategy might work in less-developed countries without sophisticated monitoring systems, but the perpetrators still have the problems of how to obtain large amounts (perhaps 100 s of litres) of toxic chemicals without alerting the authorities, and then how to transport them undetected to the dump site.

A more subtle approach might be to go for 'little and often'; use much smaller amounts of a toxic substance such that it falls below the detection limit of most current sensors, and add it to the reservoir repeatedly over a long period. A systemic poison like dimethylmercury or thallium, which accumulate in the body, might be piped to a population for many weeks or months, undetected, before the first symptoms of poisoning started to appear – and by then it may be too late.

For the authorities, the challenge here, is in detecting minute concentrations of the toxin, and identifying it unambiguously amongst many other chemicals also present in the water [59]. One possible solution is to use boron-doped diamond (BDD) electrodes to detect the electrochemical oxidation and/or reduction peaks characteristic of known poisons. BDD has a number of advantages over conventional electrodes made from silver, platinum or glassy carbon [15]. It has a wide potential window, from -1 to +1.8 V, allowing detection of redox species that would normally fall outside the operating range of conventional electrodes, including heavy metals (mercury [60], cadmium, lead, nickel [61], arsenic [62]), polycyclic aromatics (PCAs) and pesticides [63], hormones and estrogenic compounds, explosives [64], neurotransmitters such as dopamine [65], drugs (paracetamol, cyanides, narcotics, pharmaceuticals) [66], and water-soluble nerve agents [64]. Within this operating window, the response is flat, so there is no background, making the BDD electrodes highly sensitive. This enables them to detect some compounds at nanomolar (ppb) levels, even in the presence of similar chemical species (see Fig. 12.4a). Furthermore, the BDD electrodes can be nanostructured into needle shapes ('black diamond'), increasing the available surface area by many 100-fold, along with a concomitant increase in sensitivity [65] (see Fig. 12.4b, c). BDD electrodes are robust, have far less tendency to foul than other electrodes, and can be electrochemically cleaned in situ.

Although there are perhaps 50 research groups worldwide studying BDD electrochemistry, there are few, if any, commercially available BDD water monitors on the market, although a number of companies (e.g. Element Six (UK), Windsor

Fig. 12.4 An example of the sensitivity and selectivity of BDD electrodes used for electrochemical trace analysis in water. (a) Differential pulse voltammograms recorded for different dopamine concentrations  $(1-9 = 0.0-5.0 \times 10^{-6} \text{ M})$ in the presence of a chemically similar analyte (uric acid  $3.0 \times 10^{-5} \text{ M}$ ). Inset: Current density j (μA cm<sup>-2</sup>) vs. concentration of dopamine (µM) showing a linear response with concentration. (b) and (c) SEM images of 'black diamond', nanostructured BDD needles on the surface of an electrode. Figures reprinted under CC BY 4.0 licence from Ref. [65]. (Published by The Royal Society of Chemistry)



Scientific (UK), Adamant Technologies (Switzerland), Condias (Germany), Sumitomo (Japan) and sp3 Diamond Technologies (USA)) sell BDD electrode material for use in detectors.

Whether the water-supply was contaminated by accident or deliberately, the next issue would be to clean up the water as quickly and efficiently as possible. One method that would be particularly effective for removal of organic toxins (chemical agents or bacteria/viruses) is electrolytic destruction. This is an electrochemical technique which involves passing a high current (often many tens of amps) through the contaminated water via a series of electrodes. The current fragments any dissolved or suspended molecules, converting the organic components to CO<sub>2</sub> and rendering the toxin harmless. Unfortunately, the high currents sustained for long periods of time cause degradation and erosion of the electrodes, which must be replaced periodically at high cost in money and time. BDD electrodes have proven to be more robust than most alterative materials, allowing higher currents to be used for longer periods between replacements [67].

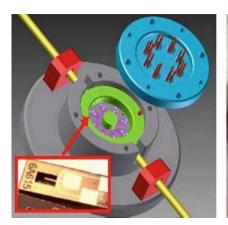
A number of commercial companies offer water purification systems based on BDD electrode technology, such as Proaqua (Austria), CSEM (Switzerland), and WaterDiam (France). These systems may be suitable for household supplies, or perhaps a small factory, but not for emergency rapid clean-up of an entire reservoir following an attack. However, in principle, to do so, this technology just needs to be scaled up and made portable. One might imagine an emergency response team composed of a fleet of trucks, each carrying a BDD water-purification system, that could drive rapidly to the site of a reservoir-poisoning event to begin clean-up within hours.

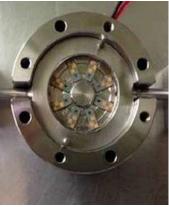
## 12.8.2 Detection of Chemical Reagents

Many chemical reagents, such as nerve agents or poison gases, that might be used in an attack upon a military or civilian population are very difficult to detect, and even tiny amounts can be devastating. The Novichok attack in Salisbury in 2018 used only ~2–10 mL of Novichok A234, smuggled into the UK in a modified perfume bottle [68]. It killed 1 person and severely injured 4 others – but caused an estimated £10–30 M in clean-up costs, plus untold economic damage to this major commercial city, devastating their tourist industry for nearly a year [69]. Most airports use random swab tests to spectroscopically detect chemical residues on the clothes or baggage of travellers. But determined terrorists or government agents can defeat these measures easily. The failure to detect the disguised perfume bottle containing Novichok when it passed through Gatwick Airport border highlights the urgent need to develop new and more sensitive methods to selectively detect these types of reagents at very low levels (ppb).

One solution is a so-called 'electronic nose' (EN), which can 'sniff' out illicit substances. Some airports have these fitted as full body scanners, but they are often large, and create extra queueing time for passengers. A better answer would be an EN that is inexpensive, portable, lightweight, and highly sensitive – but only to the molecules of interest. Many competing gas-sensor technologies are candidates for the next generation of EN [70], including those based on semiconductor-metal-oxides, conducting polymers, surface acoustic waves, QCM, and optical-fibres, but CVD diamond ENs offer a number of advantages. They can use smaller gas volumes, have smaller detection surfaces, and offer shorter detection times.

An example of a diamond-based EN developed by *CEA* (France) is shown in Fig. 12.5 [71]. It uses microelectromechanical systems (MEMS) technology in the form of freestanding diamond cantilevers etched onto a silicon substrate. The cantilevers can be made to resonate using an attached piezo-electric layer. The resonant frequency, *f*, depends upon the dimensions of the cantilever, the material it is made from, and its mass. Because the cantilever is made from diamond, the resonant frequency is very high (20–150 kHz), making it extremely sensitive to





**Fig. 12.5** Left: Three-dimensional drawing of an EN gas sensor showing the 8 MEMS cantilevers inside. Right: Photograph of the sensor. (Figure reproduced from Ref. [71] under CC BY 4.0 licence)

changes in mass. When gas molecules adsorb onto the cantilever, its total mass changes, which lowers the resonant frequency. This frequency change  $\Delta f$  provides an indication of the gas concentration. Selectivity for different gas molecules is achieved by chemically functionalising the diamond electrode surface using a specific binding molecule (protein, antibody, inorganic reagent) which is covalently bonded to the diamond surface. The French group reported successful trials of an 8-cantilever array sensor, each one functionalised to detect a different molecule. Such systems are still in development, but the next stage would be to scale these up to detect simultaneously perhaps 100 different molecules of interest. They could then be deployed at train stations, airports and other critical buildings.

## 12.9 Biological Threats

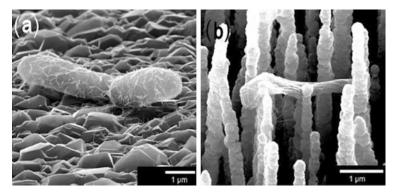
Although there are many types of threats posed by different biological incidents, accidental or otherwise, here we shall concentrate only upon two – the first application is preventative, while the second aims to help victims after the event.

## 12.9.1 Antimicrobial Surfaces

Bioweapons can spread harmful bacteria over large areas; as well as the immediate infection problem and risk of epidemics, the infectious agent may coat the surfaces,

walls, floors, etc. for km around the initial site. These areas may remain infectious until the pathogen finally dies, which maybe days or even weeks. Moreover, surfaces which were clean can become contaminated by contact with people that have been exposed to the bacteria, or via the air. Thus, along with the immediate casualties, a bioweapon attack might also deliver a 'denial of services' effect, because military or emergency services cannot enter the affected areas without special protective clothing and equipment. Furthermore, in an emergency situation, disinfectants or other antibacterial chemical agents might run out or be in short supply, making decontamination even more of a problem.

So, the question is: Can we equip critical equipment (e.g. those used by hospitals, Emergency services, military, etc.) with antimicrobial coatings that kill bacteria mechanically rather than chemically? One possible answer comes from the study of the microstructure of the wings of dragonflies and cicadas [72]. The wings are covered with micropillars a few 100 nm tall, which biologists believe act as a protective antimicrobial surface. A surface with properties similar to these was fabricated using black silicon - a synthetic nanostructured material that contains high-aspect-ratio nanoprotrusions, such as nanospikes or nanoneedles, on its surface produced through plasma etching. Black Si acts as an effective bactericidal surface for both Gram-negative and Gram-positive bacteria [72], but the nanostructured surface is rather delicate and easily damaged or scratched – even a human fingernail dragged across the surface breaks and dislodges the needles. A solution to this is to coat the needles with a conformal layer of diamond, 50-100 nm thick (see Fig. 12.4b, c). The advantage of the diamond coating is that the structures become far more robust and less likely to become damaged. As well as having excellent electrochemical properties (see Sect. 12.4), the diamond-coated spikey surface (called 'black diamond'), generated a mechanical bactericidal effect, killing bacteria efficiently and effectively [65, 73], see Fig. 12.6. When the surfaces of the



**Fig. 12.6** SEM images of *E. coli* bacteria, showing (**a**) healthy, turgid bacterial cells on MCD control samples, but (**b**) deformed and flaccid dead bacteria on a black diamond surface. (Figures reprint from Ref. [74] under CC BY 4.0 licence)

black-diamond needles were fluorinated by exposure to an  $SF_6$  plasma, they became superhydrophobic, further increasing their antimicrobial properties, as well as hindering the growth of biofilm [74].

For applications in the real world, bioresistant surfaces will realistically never be coated with exotic materials, such as black diamond. Instead, similar nanostructured surfaces could be fabricated from more conventional materials like stainless steel, titanium, or polymers such as medical-grade rubber or PTFE. Nevertheless, the general findings from studies such as those on black diamond, optimising biocidal activity in terms of types, shapes and densities of surface morphology and chemical nature, will provide important information for the development of next-generation antibacterial surfaces made from more practical materials.

## 12.9.2 Diamond-Based Bioimplants

One of the long-term after-effects of a CBRN incident may be a large number of civilian and military personnel with chronic medical conditions that might require treatment for years. Neurological conditions and/or nerve damage can be brought about by mechanical trauma, or by exposure to chemicals such as nerve agents, but whatever the cause, there would be a requirement to treat these victims as effectively as possible.

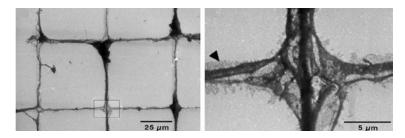
Diamond may again become the material of choice for studying and achieving these treatments [75, 76], mainly because it is bioinert, i.e. it does not provoke an immune response when implanted inside the body. This advantage means that diamond-based implants produce less or even zero inflammation, and can therefore survive and function for years, or even decades, within the body, with no need for the cost and trauma of surgical replacement, probably within the patient's lifetime. Diamond is also corrosion resistant, so is not chemically attacked by the body's fluids. Thus, it can be used to protect non-biologically inert components (such as Si microprocessor circuitry) within hermetically sealed diamond boxes. An example of this is the 'bionic eye' project from Melbourne University [77, 78], that uses an artificial retina chip sealed inside a protective diamond shell, implanted into the eye, to provide some degree of sight for patients with a malfunctioning retina.

Diamond can be heavily doped with boron to increase its electrical conductivity to near-metallic, and this makes it useful as biosensor, allowing signals to be transferred to and from cells. This is especially useful for neurons situated in the brain, the central nervous system, or in the periphery such as arms and legs. There have recently been two major EU-funded research consortia (DREAMS [79] and NEUROCARE [80]) to study the function of diamond-based implants that interface with living human neurons, with the aim of finding treatments for neurological disorders, such as Alzheimer's, Parkinson's, stroke, epilepsy, paralysis due to trauma, and many others. An example is artificial retinas that use a conducting diamond film grown onto a flexible polyimide substrate that can wrap around the back of the eyeball and transfer signals from the retina to the optic nerve [81]. Other

examples currently being researched are diamond sensors embedded into the spinal cord of paraplegic patients, which pick up signals from the brain and transfer them wirelessly to an external computer. Interpretation of these signals using special software may allow robotic legs to be moved at will by the patient. Such treatments for paralysis have already been demonstrated using multiple external sensors placed on the scalp [82], but with a diamond implant, the sensor would be portable and remain *in situ* for perhaps 30 years.

Such two-way communication opens up other possibilities too, such as direct brain-computer interfaces (BCIs) [82]. Here, the diamond sensors would be permanently implanted into the brain, picking up the neural impulses and transferring them wirelessly to an external computer. With suitable software to interpret the signals (a difficult problem in itself), it may, in time, be possible to develop thought-controlled equipment (TVs, cars, drones, etc.), or mind-to-mind communication ('telepathy') to other people with BCI implants linked via the internet. Although this may seem rather far away, the implications of BCI technology for medical applications, military applications, and society as a whole, are huge.

Another approach for using diamond medicinally is as a bioinert culture plate upon which to grow human cells [76]. These cells are then available as in vitro test subjects for determining the efficacy of new drug treatments, or for studying the toxic effects of chemical or neurological agents — without the cost and controversy of using *in vivo* tests or animal experiments. Cells cultured on diamond plates can survive for many months, unlike those on traditional glass or plastic substrates which typically die after a few weeks. This means that long-term testing is possible, as are inheritance tests that require multiple generations of cells. Studies at University College London [83] and Bristol University [84] have demonstrated that human stem cells thrive on diamond culture-plates, and that they can later be transformed into other cell types (kidney, liver, and especially neurons) using suitable chemical treatments. When BDD is used as the substrate, then the cells growing on its surface can be electrically interrogated or stimulated via the conducting substrate. The substrate can be patterned or treated such that areas of the surface are amenable to cell growth, while other areas are not. In this way cells, such as neurons, can be persuaded to grow only in certain areas, allowing two-dimensional neuron networks to be fabricated [85], as shown in Fig. 12.7. These 'brains-on-a-plate' act as models that mimic to some degree the behaviour of a real 3D brain, allowing neuroscientists to study how different types of stimuli propagate through the neural network. Such studies pave the way for future development of organic computers. Diamond is also being used as a scaffold upon which to grow human bone cells or cartilage tissue for subsequent transplant procedures [86, 87].



**Fig. 12.7** Ordered growth of mice neurons on a patterned laminin-coated hydrophilic CVD diamond surface. The neurons only grow along the patterned areas, and then form connections at the crossing points. (Figures reprinted with permission from Ref. [85])

## 12.10 Radiological/Nuclear Threats

## 12.10.1 Radiation Detectors

One way to prevent a CBRN nuclear incident is to detect the presence of nuclear material before it enters the country or crosses a city threshold. Thousands of passive radiation detectors may need to be employed as screening devices at ports, airports, and on highways entering cities, and as air-flow meters in hospitals, or in waste incineration. Such detectors need to be cheap, portable and reliable.

Diamond has a number of advantages compared to competing materials and technologies in relation to detecting and measuring radiation levels [88]. First, diamond radiation detectors can be designed to detect and analyse most forms of ionising and non-ionising radiation, including neutrons, protons, alpha, beta, and gamma radiation, and X-rays, so long as the energies involved are greater than the band gap of diamond (5.4 eV). Diamond-based detectors are very robust and therefore have no need for frequent replacements. They have a high mobility of free charges ( $\sim 4500 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for electrons, 3800 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for holes [89]) which gives a very fast response (<100 ps) and they can be operated at room temperature with no need for cooling. They have a resistivity several orders of magnitude greater than Si-based detectors, with extremely low leakage currents which makes them highly sensitive. Unlike Si detectors, diamond detectors do not require p-type or n-type junctions to connect the detector to the control electronics. Because such junctions are often a point of failure, the diamond detectors are more robust, allowing them to be used in extreme environmental conditions, e.g. high temperature, high humidity, very high radiation, and highly corrosive environments.

These features, combined with the intrinsic properties of diamond, give diamond detectors perhaps their most important advantage over other materials – they are resistant to extremely high radiation levels – values at which most other detectors stop functioning. Indeed, the main Atlas detector used on the Large Hadron Collider at CERN is made from diamond, as no other material could survive the huge radiation levels in the beam (proton fluences of  $1 \times 10^{15}$  cm<sup>-2</sup> and instantaneous

**Fig. 12.8** Photograph of a large area (46 mm diameter by 100 μm thick) diamond radiation detector. (Image reprint under CC BY 3.0 license from Ref. [93])



rates of at least  $1\times10^9~{\rm cm^2~s^{-1}}$  [90]). The intense beams of X-rays from synchrotron sources at ESRF (Grenoble) and the Diamond Light Source (Harwell, UK) are monitored using diamond detectors and focused using diamond compound refractive lenses [91], while the Joint European Torus nuclear fusion facility at Culham (UK) uses diamond detectors for UV and neutron detection.

The diamond research group at CEA Saclay in France have developed a number of different diamond-based radiation detectors [92], and there are several companies worldwide that produce them commercially, including PTW-Freiburg (Germany), St. Gobain/Norton Diamond Film (Northboro, MA, USA), and Element Six, Ltd. (Harwell, UK). An example of such a detector is shown in Fig. 12.8.

#### 12.10.2 Radiation Dosimeters

Similarly, diamond can also be used as a radiation dosimeter, to detect and monitor the total radiation dosage of humans exposed to a radiation incident [94, 95]. Most dosimeters are designed for medical and therapeutic use (X-rays, CAT scans), but these often only work at low radiation levels. Moreover, many existing technologies have limitations: Si dosimeters suffer from radiation damage and low lifetime, whereas ionisation chambers have low spatial resolution and low sensitivity. To overcome these, dosimeters that utilise natural diamond have been developed recently, but these tend to be expensive. Therefore, multiple research groups worldwide are actively developing dosimeters that instead use cheap CVD diamond. Examples include the EU project *MAESTRO* (Methods & Advanced Equipment for Simulation & Treatment in Radiation Oncology) [96] and two projects funded by the Italian National Institute of Nuclear Physics called *CANDIDO* and *CONRAD*, on natural and synthetic diamond-based dosimeters for clinical radiotherapy [97].

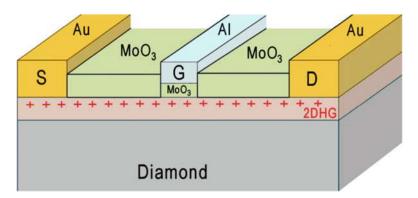
However, in the event of widespread contamination, e.g. following a dirty bomb or nuclear accident (such as those that occurred at Chernobyl and Fukushima), clean-up crews, emergency services and the general population will need to wear portable dosimeters to monitor their radiation exposure. These dosimeters may need to be far more sensitive than standard medical devices, and also be able to withstand far higher radiation dosage than might be expected clinically.

Diamond has a low atomic number (Z=6) while the mean value for soft tissue is  $Z\sim6.5$ –7.5, thus, diamond is described as being 'tissue equivalent'. This means diamond dosimeters have fewer calibration errors or offsets than, say, Si (Z=14) detectors, and do not over-estimate the dosage at lower energies [98]. The CVD diamond detectors that are in development for therapeutic use could easily be adapted to the more extreme conditions of a CBRN incident. Because diamond detectors are highly sensitive, the dosimeters could be made very small, and thus cheap, portable and even disposable. Moreover, they would work at low and high radiation levels, with a long lifetime, and with little/no damage or deterioration of performance over time – which is vital, as clean-up operations following a CBRN incident may take months or even years.

#### 12.10.3 Radiation-Hard Electronics

Ever since the loss of the Telstar 1 satellite in 1962 after a high-altitude nuclear test, scientists have been aware that delicate electronic circuits can be damaged or destroyed by exposure to radiation. Unfortunately, most electronics based on Si, GaAs, GaN or similar semiconductor materials, are not radiation hard [99]. Ionising radiation (alpha and beta) is a particular problem with semiconductor substrates; even a single high-energy particle can create thousands of electron-hole pairs as it passes through the substrate. The resulting large transient currents can disperse through the conducting substrate, damaging circuit components and transistors over a large area, leading to irreversible failure of the device. Some devices can be improved by clever design (e.g. by adding extra error-correcting circuitry) or by using insulating substrates (e.g. silicon-on-sapphire (SoS) and silicon-on-insulator (SoI) wafers). Devices can also be shielded (often by encapsulating the circuitry inside metal boxes), but shielding is large, heavy, and not always viable, for instance, in aerospace applications. Generally, due to the extra cost, complexity and time required for extra testing, radiation-hard devices usually perform poorly compared to standard devices [100].

Diamond can play a vital role, here, too. A variation of SoI technology involves depositing the active semiconductor layer (e.g. Si or GaN) on top of an insulating CVD diamond substrate. Silicon-on-diamond (SoD) [101] or GaN-on-Diamond (GoD) [102] technologies are currently being developed for thermal management in high-power devices (see Sect. 12.11). Studies have shown that SoD devices outperform their SoI equivalents, while being significantly more radiation hard [103].



**Fig. 12.9** Schematic cross-sectional view of a diamond-based MOSFET device utilising the 2DHG conduction channel in H-terminated diamond protected by a MoO<sub>3</sub> capping layer, based on the design proposed in Ref. [104]. S, G, and D refer to source, gate and drain, respectively

One promising new avenue of research involves a new type of field-effect transistor (FET) design based on an unusual property of the diamond surface called 'surface transfer doping' [105]. Hydrogen-terminated diamond exhibits a surface dipole due to the difference in electronegativity between the carbon atoms in the bulk and the H atoms on the surface. Electron-accepting molecules from the ambient air adsorb onto this polar surface and electrons are transferred from the bulk to the adsorbates. As a result, the adsorbates become negatively charged, and a stable two-dimensional hole-gas (2DHG) layer a few nm thick is formed just below the surface [106]. This thin layer is electrically conducting, with both a high hole mobility (100–200 cm²  $V^{-1}$  s<sup>-1</sup>) and high hole concentration ( $10^{12}$ – $10^{13}$  cm<sup>-2</sup>), but the conductivity can be altered or even destroyed simply by changing the atmosphere (pressure, humidity, etc.) above the surface. To stabilise this conductive layer, the diamond can be capped with a protective layer of  $V_2O_3$ , MoO<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub>, which hermetically seals the surface as well as providing additional surface acceptors helping to generate the 2DHG layer.

Many research groups, such as those at Glasgow University [107] and Waseda University (Tokyo) [108], have been exploiting these ideas to produce novel FET devices in which the conduction from source to drain, moderated via a gate electrode as usual, is through this conductive layer, rather than through the semiconducting substrate (see Fig. 12.9). Not only do these 2DHG FETs exhibit excellent device performance, but because they are fabricated directly onto an insulating diamond substrate, they should be considerably radiation more hard compared to standard Si-based devices. If this is proven experimentally, such 2DHG diamond FETs may herald a new paradigm in radiation-hard electronics for space, military, and CBRN applications.

## 12.10.4 Targeted 'Magic Bullet' Treatments

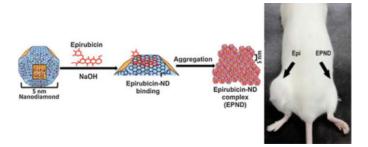
The aftermath of any successful CBRN incident may require hundreds, thousands, or even millions of people requiring medical attention. As well as short-term injures and trauma, there may well be much longer-term treatments required for chronic problems such as different forms of cancer induced by radiation exposure. Moreover, bulk medicines to treat these chronic ailments may be in short supply, or insufficient to treat the potentially large number of patients that require them. One solution is to use targeted treatments that affect only the afflicted part of the body, such as an organ or a tumour. So-called 'magic bullet' treatments require far fewer drugs and have fewer side-effects – but most are still under development.

Targeted treatments use a delivery vehicle, which is usually some sort of nanoparticle, which has had its surface chemically functionalised to allow other molecules to attach to it. Many different nanoparticles have been used for this purpose (metals, carbon nanotubes, lipids, polymers, etc.), but 4–10 nm nanodiamond (see Sect. 12.7) is particularly suitable for this purpose [109] because (a) it is cheap, and readily available as a suspension in water (recall Table 12.2), (b) its surface can be readily functionalised with a wide range of chemical groups, (c) many studies have shown that nanodiamond is bioinert and non-toxic [76], and (d) after its job is done, the nanodiamond will simply be excreted harmlessly from the body.

To make the nanodiamond specific to only the chosen cell type, a molecule (e.g. a reagent, protein, antibody, DNA strand, etc.) known to be a specific binding agent for the chosen cell type is chemically bonded to the ND surface [110]. When the functionalised ND particles are administered into the patient, often intravenously, they travel around the bloodstream until they meet the targeted cell type, at which point they recognise the cell and attach to it.

What happens next depends upon what extra functionalisation the ND has experienced. As mentioned previously, NDs can be treated so that they contain fluorescent NV centres which emit light when illuminated with a laser. These then act as fluorescent biolabels or biotags, revealing the location of the ND along with the cell to which it is attached, thus identifying the regions of interest, such as cancerous cells, within the living organism [32]. Recently, real-time tracking of single florescent ND particles inside a cell has been reported [112]. Such studies are starting to provide valuable insights into the movement of fluids within cells, as well as the mechanisms by which metabolic products are transported around living cells [113].

To convert a ND into a 'magic bullet' requires bonding a second molecule to the ND surface alongside the binding agent. This second molecule interacts with the chosen cell, either killing it in the case of a cancer cell (see Fig. 12.10), or curing/treating it in the case of malfunctioning cells. This drug molecule is usually bound weakly to the ND in such a way that it detaches when activated by an external stimulus such as UV light, or falls off automatically after a few hours to be excreted from the body. Although these sorts of treatments are still under development, they



**Fig. 12.10** Schematic diagram showing 5 nm nanodiamond (ND) being functionalised using the anti-cancer drug epirubicin (Epi) which then aggregate to form an epirubicin-ND complex (EPND). The photo on the right shows a tumour-bearing mouse following treatment with either Epi or EPND. The tumour treated with the EPND was significantly reduced compared to that treated with the Epi control. (Figure reproduced with permission from the ACS, taken from Ref. [111]. Further permissions related to reproducing this figure should be directed to the ACS)

may be a realistic method to treat the mass casualties that may result from a large-scale successful CBRN attack.

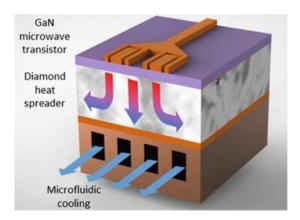
#### 12.11 General Infrastructure

In this section we shall discuss applications that don't counter a specific CBRN threat type, but instead sustain or improve the response of emergency services to a CBRN incident, and in particular maintain the country's power grid, telecommunications network, transport links, and the general infrastructure. We shall focus on two of these aspects: power and telecommunication.

#### 12.11.1 Reliable Fast Communications

In a major CBRN incident the communication networks often fail due to overload, with people frantically trying to use the mobile-phone network to contact family members who may have been caught up in the attack. Failure of these networks due to lack of bandwidth capacity helps to spread fear and panic among the general population. During the 9/11 attacks in New York in 2001 the mobile phone networks in both the US and UK jammed for several hours, while during the London Bridge attacks in June 2017, 'communication issues' between emergency services meant

Fig. 12.11 Concept for a GaN-on-Diamond device. The heat flows from the hot device into the diamond (in this case with no interface layer between them), which then spreads it rapidly into the underlying substrate cooled by microfluidic channels. (Copyright © University of Bristol 2017)



that paramedics did not know which areas were safe and which areas were hot zones, and so were not allowed into these areas to help injured people for up to 1 h [114].

One solution to this problem would be to develop telecom networks that are many times faster than those currently in use (4G & 5G), and which could cope easily with excess demands in an emergency. Current RF power amplifiers and microwave transmitters use GaN as the device material in high electron-mobility transistors (HEMTs). But these devices can only be operated at ~50% max power due to overheating and reduced lifetimes [115]. The next generation transmitters, either HEMTs or monolithic microwave integrated circuits (MMICs), being developed for beyond 5G will be even more power-hungry. In order for these to work effectively, efficient heat extraction is essential. Studies have shown that most of the thermal resistance occurs at the interface between the active GaN device layer and the substrate, which is usually made from Si or SiC [115]. Manufacturers have tried to lower this thermal barrier using thin interface layers, made of materials such as SiC or SiN, between the GaN and substrate, but the results are not ideal.

Diamond has one of the highest thermal conductivity values known (see Table 12.1) and so is ideal for use as a heat spreader. Placing a thin (few μm) layer of CVD diamond between the GaN and Si/SiC substrate should allow the localised heat to be rapidly transported away from the hot device and into the substrate. This heat could then be removed using a suitable heat sink, radiator or microfluidic cooling pipes (see Fig. 12.11). A number of research groups and commercial companies are actively studying this approach, one of the largest of which is a project called *GaN-DAME* [116], a UK six-university consortium based at the University of Bristol funded by a £4.3 M grant in 2017. However, the technical problems are not easy. The CVD conditions for diamond growth (Sect. 12.2) are not compatible with GaN [117], so it is tricky to achieve an adherent diamond coating with good thermal contact. One possible solution is to use a thin 'glue' layer between the diamond and the Si substrate [118]. A promising option for the layer is AlN [119]. Although it has a smaller thermal conductivity (400 W m<sup>-1</sup> K<sup>-1</sup>) than

diamond, so long as the AlN layer is thin (200 nm) the thermal resistance at this interface is acceptable.

Another problem, which is exacerbated with larger wafer sizes, is the mismatch in thermal expansion coefficients between diamond and the Si substrate, which results in the wafers bowing.

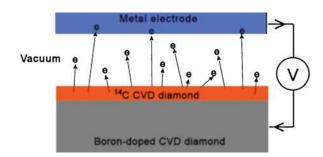
Despite these problems, the ultimate aim is to develop HEMTs with a spectacular >5 times increase in RF power compared to the current commercially available GaN-on-SiC devices. Equally valuably, a dramatic shrinkage in MMIC or power-amplifier size should be possible, delivering an increase in efficiency through the removal of combining networks as well as a reduction in cost. This would be a disruptive change in capability allowing the realisation of new system architectures and thus enabling the bandwidths needed to deliver 5G and beyond. This would deliver a telecom network that works reliably both for day-to-day activities and during emergency situations.

# 12.11.2 Emergency Power for Critical Equipment – Nuclear Batteries

In a CBRN incident the power grid may fail, either locally or city-wide, depending on the type of attack. It is vital that some power is maintained for critical services, e.g. hospitals, police, communications, etc, or for essential equipment, such as radiation detectors, gas sniffers, lighting, and so on. Some of these pieces of equipment are battery operated, but most batteries won't last more than a day or so of continual operation without being recharged. Others may have a generator backup, but these, too, may only work for as long as the fuel lasts, perhaps a few days.

What is required is a power source which does not require charging from the mains supply, and which has a very long lifetime – such as a 'nuclear battery' or 'betavoltaic battery'. In simple terms, a nuclear battery turns radioactivity into electricity. Many different types of nuclear battery exist, developed mainly for powering spacecraft as they travel to distant planets over periods of many years. However, a new type of nuclear battery based on <sup>14</sup>C diamond is currently gaining a lot of interest [120] (see Fig. 12.12). In these proposed devices, radioactive graphite

**Fig. 12.12** Schematic diagram of a concept for a diamond-based nuclear battery



(a waste product from many nuclear power stations) containing <sup>14</sup>C is converted into <sup>14</sup>CH<sub>4</sub> by burning in hydrogen gas. This methane is then used as the carbon source in a CVD reactor, which deposits a layer of <sup>14</sup>C diamond onto a conducting substrate. <sup>14</sup>C is a beta emitter, so it emits high-energy electrons with a half-life of ~8000 years. A second 'collector' electrode is placed a few 100 μm away from the diamond layer, with a vacuum gap between the two. The electrons emitted from the <sup>14</sup>C-diamond layer travel ballistically across the gap and are absorbed by the collector. Thus, the collector gradually becomes more negative while the emitting electrode more positive, and a self-bias develops between the two electrodes. Connecting the two electrodes with a wire allows current to flow back to the emitter, driving an external load, if required. Other designs based on layers of alternating p- or n-doped diamond sandwiched between <sup>14</sup>C diamond emitting layers [121], that utilise <sup>63</sup>Ni or tritium as the radioactive sources [122], or which combine beta radiation and thermionic emission [123], have also been proposed.

Such devices would produce electrical power almost indefinitely (thousands of years), and can be made into small, portable, sealed solid-state packages, with no moving parts and which require zero maintenance. The output power per device would be tiny, perhaps only a few µW, but hundreds or thousands of devices could be joined together in series to produce higher powers if required. Because the battery is always on, it could continuously trickle-charge a capacitor ready for intermittent high-power use, e.g. a burst transmitter on a spacecraft that sends all its data back to Earth in a short high-frequency pulse once a day. As well as spacecraft and satellites, other uses include areas where changing a battery is difficult, costly or impossible, such as military applications (e.g. remote surveillance), aerospace applications (e.g. sensors inside jet engines) or medical applications (perpetual pacemakers). There are numerous commercial applications, such as for domestic use (watches, calculators, mobile phone chargers, etc.), and powering 'smart' devices for the 'Internet of Things' [124]. A great many household devices, from kettles to fridges, may soon be connected to the internet, and these will require a small but continual supply of power. It would be impractical for all these appliances to be mainspowered, whilst normal batteries would need changing continually, but a nuclear battery could supply the small power levels required indefinitely.

In terms of CBRN applications, diamond-based nuclear batteries might provide the power for a maintenance-free network of radiation detectors or biosensors distributed around a city or country. They might also provide a back-up power supply for emergency-service equipment, portable detectors, phones, torches, defibrillators, etc.

## **12.12 Summary**

In this short review, we have attempted to think the unthinkable – if a CBRN attack were to succeed, what might be some of the consequences, and how could advanced materials, and in particular, the new technological applications involving CVD

diamond, be used to mitigate the damage? Although we have covered a rather diverse range of threat scenarios, there are still a multitude of applications for diamond which have been omitted. Examples include: diamond NV centres for quantum computing and quantum information processing (unbreakable codes) [125], spintronics and magnetic field sensing [126], thermionic emission from diamond (cheap solar power) [127], high-power electronics [128], field emission displays (radiation-hard displays) [129], radiation-hard optics (windows, lenses, prisms) and laser windows [130], diamond-fibre reinforced composite materials (lightweight, very stiff materials for aerospace) [131, 132], diamond microplasma arrays (large area UV sources, chemical reactors) [133], secondary electron emission detectors (night-vision goggles, photomultiplier tubes) [134], to name but a few. Although CVD diamond technology is only just over 30 years old, the range of applications made possible by this remarkable material is truly astonishing, many of which may hopefully help to make the world a safer place.

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