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Chemical Vapour Deposition of Diamond for Dental Tools and Burs

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Preface

Research and development in the area of machining and cutting tool development is well established in the advanced manufacturing industries. The theories associated with machining traditional materials such as metals, ceramics, polymers, composites, have been developed over the last century to a fairly high level of sophistication. However, the same cannot be said for the development of tools for the medical industry.

The purpose of this Springer 'brief' is to show the embryonic stages of development of highly engineered tools for the medical sector that can equally be applied to all areas of medicine and not just to the development of tools for dentistry. The brief also discusses the merits of applying well-established principles of physical understanding to the problems associated with cutting of biological materials, and is composed of eight chapters that focus on tools, teeth and their environment, the advantage of using coated tools, the synthesis, properties and application of diamond thin films, challenges associated with depositing thin diamond films to flat and curved surfaces, controlling diamond morphology and structure, and the assessment of tool performance using established measures of machinability.

The brief should excite all manner of interested professionals including dentists, orthodontists, surgeons, general practitioners, engineers, physicists, general scientists and students who are actively engaged in studying medicine and biomedical engineering. The authors wish to stimulate the readers' curiosity in order to enable them to conduct their own research, advance their particular frontier in medicine, and innovate and commercialize current and future knowledge generated in this area of medical engineering by experts in the field.

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Contents

1 Diamond Synthesis, Properties and Applications 1
1.1 Diamond 1
1.2 Diamond as an Allotrope of Carbon 2
1.3 Properties and Applications of Diamond 4
1.4 Synthesis of Diamond 5
1.4.1 Historical Perspective of Diamond Synthesis 5
1.4.2 Modern Era of Diamond Growth 7
1.5 Development of CVD Technology 7
1.5.1 Types of Diamond CVD Processes 8
1.5.2 CVD Mechanisms 10
1.5.3 Filament Characteristics 11
1.5.4 Substrates for Growing Diamond 13
1.6 Diamond Nucleation Process 14
1.6.1 Homo-Epitaxial Growth 15
1.6.2 Hetero-Epitaxial Growth 15
1.7 Conclusions 15
References 16

2 Dental Tools, Human Tooth and Environment 19
2.1 Introduction 19
2.2 Dental Burs 20
2.2.1 Dental Bur Construction and Geometry 20
2.3 Bur Materials 22
2.3.1 Stainless Steel Bur 22
2.3.2 Tungsten Carbide WC-Co Bur 22
2.3.3 Sintered Polycrystalline Diamond Dental Bur 23
2.4 Operation Conditions 23
2.4.1 Low Speed Hand Piece 25
2.4.2 High-Speed Hand Piece 25
2.5 Clinical Environment 43
2.6 Machining Materials with Dental Burs 45
2.7 Tooth Materials 46

2.7.1 Human Tooth 46
2.7.2 Artificial Tooth Materials 47
2.8 Conclusions 48
References 48

3 Growth and Application of Diamond Thin Films 51
3.1 Introduction 51
3.2 CVD System 51
3.2.1 Filament Set-Up for Flat substrate (Conventional HFCVD System) 54
3.2.2 Deposition onto Micro Drill and Dental Bur Substrate using the VFCVD System 54
3.3 Experimental Conditions for Diamond Deposition 54
3.4 Substrate Pre-treatments 55
3.4.1 Pre-treatment of Mo/Si Substrates 56
3.4.2 Pre-treatment on WC-Co Dental Bur Substrates 56
3.4.3 Negative Biased Enhanced Nucleation 56
3.5 Machining of Bone with Diamond Coated Tools 57
3.5.1 Micromachining 58
3.5.2 Chip Formation 61
3.5.3 Experimental 65
3.6 Discussion 68
3.7 Conclusions 69
References 81

4 Diamond Deposition onto Flat Substrates 73
4.1 Introduction 73
4.2 Deposition of Diamond onto Flat Substrates by VFCVD System with Horizontal Filament Arrangement 74
4.2.1 Experimental Conditions Relating to Flat Substrates 74
4.2.2 CVD Diamond onto Silicon Substrates 75
4.3 CVD Diamond onto TiN Interlayer 76
4.3.1 Experimental Related to the Deposition of the TiN Interlayer 76
4.3.2 Diamond Deposition onto TiN Interlayer 78
4.4 Conclusions 80
References 81

5 Diamond Deposition onto Wires and Microdrills Using VFCVD 83
5.1 Introduction 83
5.2 Diamond Deposition on Molybdenum Wire Using VFCVD 89
5.3 Diamond Deposition onto Microdrills 89
5.4 Performance of Diamond Coated Micro Drills 91
5.5 Conclusions 95
References 95

6 Diamond Deposition on Tungsten Carbide Burs Using VFCVD 97
6.1 Dental Bur Substrate 97
6.1.1 Grains Effect on WC-Co Substrate 97
6.2 Substrate Pre-treatment 98
6.3 Diamond Deposition Dental Bur Without Substrate Pre-treatment . . . 101
6.4 VFCVD Diamond Deposition 101
References 107

7 Controlling Structure and Morphology 109
7.1 Introduction 109
7.2 Effects of Temperature 110
7.3 Effects of Negative Bias Enhanced Nucleation on the Dental Bur . . . 114
7.4 Influence of Process Parameters on VFCVD Diamond Deposition . . . 117
7.4.1 Effects of Deposition Pressure 118
7.4.2 Effects of Methane Concentration 118
7.5 Conclusions 120
References 120

8 VFCVD Diamond Dental Burs for Improved Performance 123
8.1 Introduction 123
8.2 Experimental 124
8.2.1 Tool Preparation 124
8.2.2 CVD Diamond Deposition onto Dental Burs 124
8.2.3 Dental Bur Machining: Drilling Experiments 125
8.2.4 Dental Bur Machining: Machining Experiments on Human Teeth 127
8.3 Dental Bur Machining: Machining Experiments 128
8.4 Results and Discussion 129
8.4.1 Effects of Substrate Preparation on Diamond Deposition . . . 129
8.5 Performance Experiments 130
8.5.1 Experimental 132
8.5.2 Results and Discussion 133
8.6 Conclusions 139
References 139

Abstract

Chemical vapour deposition (CVD) is a powerful technology for depositing thin films of diamond onto complex substrates such as dental tools and dental burs. The advantages of diamond for these applications are that it is the hardest material known to mankind, has a high thermal conductivity and a high wear resistance. When a diamond coating is applied to dental tools and burs the performance and life are considerably enhanced. This brief book outlines the CVD technologies used, the diamond growth mechanism, film properties and assesses their impact on the performance and life of diamond coated tools compared to uncoated tools and conventional burs.

Chapter 1
Diamond Synthesis, Properties and Applications

Abstract Diamond is an ideal material for numerous applications such as cutting tools such as dental burs and drills due to its unique combination of chemical, mechanical and thermal properties. The most widely used method of growth diamond is chemical vapour deposition (CVD) namely hot filament and microwave plasma processes. The use of vertical filament chemical vapour deposition (VFCVD) process has been developed to uniformly coat complex shaped tools and is described in detail. The growth characteristics and film properties are described for use on dental burs and drills.

Keywords Diamond · Thin films · Chemical vapour deposition · CVD · Growth mechanism · Film properties

1.1 Diamond

For most people diamond is a coveted and famously desired gemstone used for jewellery due to its shiny lustre and attractiveness (May 1995). The word diamond comes from the Greek language and has the meaning "invincible". Its applications are vast arising from its excellent and unique combination of physical, chemical, electrical and optical properties. For example, for cutting tools its extreme hardness, high thermal conductivity and very low coefficient of friction are highly desirable (Angus 1991; Yoder 1994). Its chemical inertness and biocompatibility makes it suitable for biomedical implants such as artificial heart valves, hip and knee prosthesis (Yoder 1994; Field 1992).

Diamond is crystalline and is one of three carbon allotropes along with graphite and fullerenes e.g. (C_{60}). It is the most stable of all of the allotropes with the highest density. Natural diamond, obtained through mining is scare and very expensive, is of limited use hence scientists have been curious to find ways of making high quality synthetic diamond in the laboratory that could be used for a wide range of applications (Field 1992; Anusavice 2012; May 1995). For over a half a

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century a high-pressure high-temperature (HPHT) process has been used. A US patent was granted in 1962 for work on synthetic diamond using chemical vapour deposition (CVD) (Eversole 1962). This powerful technique produces polycrystalline, microcrystalline or nanocrystalline diamond as a thin film, which adheres to a suitable substrate, or as freestanding wafers (May 1995). Free standing may be used for optical windows in space applications because diamond is radiation resistant.

1.2 Diamond as an Allotrope of Carbon

Carbon occurs in different physical forms known as diamond, graphite, fullerene, carbon nanotubes and graphene with various differences in bonding and structure. Graphite and diamond are the most common forms of crystalline carbon whilst graphene has only been discovered recently arousing great curiosity and with new applications being researched for this new wonder material (Geim and Novoselov 2007). The structure and bonding between the carbon atoms determine the properties of these allotropes. For example, graphite is soft and the layers can slide over one another. In contrast, diamond is the hardest natural material. Graphene occurs as a single sheet and potentially numerous applications including solar cells paving the way for an environmentally friendly and sustainable source of energy.

Graphite is thermodynamically stable structure for carbon at standard pressure and temperature (STP), which contains planes of threefold coordinated carbon atoms, bound by strong sp^2 bonds (Trucano and Chen 1975). In this allotrope the *s* orbital mixes with two *p* orbitals forming three new sp^2 hybridised orbital making a planar triangle. The four outer shell electrons are arranged such that three electrons occupy the sp^2 orbitals forming three sigma bonds and one electron stays in the p_z orbital a π bond. The electrons in the π bond are responsible for its good electrical conductivity. A flat sheet of connected carbon atoms is formed. Covalent bonds are present within the layers of graphite and weak van der Waals forces between the layers, each separated by 3.40 Å (Mao et al. 2003). Graphite consists of sheets of hexagonal rings with weak interactions between the sheets. Hence, the layers of carbon rings can slide over each other making graphite a good dry lubricant. This makes it useful for many applications such as bearings in space components.

In diamond, the C–C bonds are of the same length, with equal bond angles at 109.47°. It consists of repeating structural units made of 8 atoms arranged in a cube. Diamond, however, has each carbon bonded to four other carbons in a tetrahedral arrangement (Aleksenskii et al. 1999). Diamond has different properties. It can be cleaved along its planes. However, it cannot flake apart into layers due to the tetrahedral structure of carbon atoms. Diamond has sp^3 configuration of atoms of carbon at 25 °C and 1 atmosphere.

The two most common allotropes diamond and graphite differs in energy by 0.02 eV per atom. In addition, there is a difference in ΔH_f^{θ} values by ~2.9

kJ mol^{-1} (Herman 1952). However, diamond and graphite has a large activation energy barrier at room temperature and pressure. This stops the diamond from converting to graphite and vice versa. However, under aggressive conditions such as at high temperature and ion bombardment the transformation between diamond and graphite occurs at a faster rate.

In 1985 Robert F. Curl, Harold W. Kroto, and Richard Smalley discovered new forms of carbon called fullerenes in which the atoms are arranged in closed shells for which they won the Nobel Prize in Chemistry in 1996 (Kroto et al. 1991). Closed shells with various number of carbon atoms have been found in numerous carbon structures. The most abundant and stable being clusters with 60 atoms known as C_{60} which is a polyhedron consisting of 20 hexagons and 12 pentagons. The structure has been named as "buckminsterfullerene" or the "buckyball" (Kroto 1988).

Recently, there has been considerable research work on new forms of carbon nanostructures called carbon nanotubes (CNTs). These have been observed in the 1950s as filaments of carbon. Iijima in 1991 found them to be hollow tubes of carbon with a diameter of the order of one nanometer and these tubes have been found to be several microns in length (Iijima and Ichihashi 1993). They exist in several forms including single walled CNTs (SWCNT), double walled CNTs (DWCNT) and multi walled CNTs (MWCNT). SWCNT is a layer of graphite one atom thick called graphene. A sheet of graphene can be wrapped into a seamless cylinder with either open or closed ends. DWCNTs consist of two sheets of graphene rolled to form two concentric cylinders. MWCNTs consist of multiple concentric layers of graphene forming tubes of several concentric cylinders. These have numerous potential new applications as novel material (Iijima 2002; Bianco et al. 2005).

In 2010 Geim and Novoselov were awarded the Nobel Prize in physics for their pioneering ground breaking work on graphene, which is a single atomic layer of sp^2 bonded carbon a two-dimensional atomic crystal with a range of unusual properties. It exhibits extraordinary crystal and electronic properties revealing a cornucopia of new physics and numerous potential applications (Geim 2011; Hancock 2011). For example, graphene thermal conductivity and mechanical stiffness may rival the remarkable in-plane values for graphite (~3,000 W m^{-1} K^{-1} and 1,060 GPa, respectively). The fracture toughness could be comparable to carbon nanotubes and with remarkable electronic properties. These properties may be harnessed by homogeneously incorporating graphene into other materials such as polymers to form composite materials and structures (Stankovich et al. 2006). Chemical modification of graphene for use in composite materials could extend the range of its properties and applications. For example, by using chemically modified graphene, polystyrene-graphene composites exhibit percolation threshold of around ~0.1 volume per cents for electrical conductivity at 25 °C which is much lower than the lowest value reported for any carbon based composites except for carbon nanotubes. At 1 % by volume these composites exhibit a conductivity of ~0.1 S m^{-1}, suitable for range of electrical applications. This approach enables a broad new class of graphene-based materials to be used in numerous applications.

Table 1.1 Physical properties of diamond

Property	Value
Hardness (kg mm^{-2})	10,000
Strength, tensile (GPa)	>1.2
Strength, compressive (GPa)	>110
Density (g cm^{-3})	3.52
Young's modulus (GPa)	1.22
Thermal expansion coefficient (K^{-1})	0.0000011
Thermal conductivity (W $cm^{-1}K^{-1}$)	20.0

Table 1.2 Some applications of diamond related to its properties

Properties of diamond	Applications
Hardest known materials	Cutting tools
Chemical inertness	Electrochemical sensors
High thermal conductivity	Heat spreaders
Biological inertness	In vitro applications (coatings/ sensors)
High resistivity (insulator)	Electronic devices, sensors
Semiconducting when doped	Electronic devices, sensors
Negative electron affinity	"Cold cathode" electron sources

1.3 Properties and Applications of Diamond

Diamond has been deposited on various substrates including silicon, which is a semiconductor and metals such as copper and insulators such as SiO_2. They range from single crystals, polycrystalline to amorphous materials. When diamond thin films are grown with CVD methods new technological applications emerge because a variety of substrates can be coated. CVD operates at relatively high temperature compare to PVD. The difference in temperature yields either polycrystalline diamond films in CVD and the softer diamond-like carbon films in the case of PVD. This expands the potential application areas of diamond when compared to natural or HPHT-synthetic diamond. It is anticipated that this technology will have a major economic impact on sectors such automotive, consumer, defence and space applications (Spear and Dismukes 1994).

Diamond, as mentioned earlier, has an extreme combination of properties. These include good electrical insulation, high thermal conductivity, and a low dielectric constant that makes it highly suitable for packaging electronic devices and technologies used in multichip manufacture. Diamond's high hardness value and wide optical band gap renders it suitable for optical applications. Combined with chemical inertness and high wear resistance diamond thin films are suitable protective coatings in cutting tools and metal working industries. Table 1.1 summarises the physical properties of diamond (Field 1992). The electrical, structural, and optical properties of diamond are at the most extreme end of the spectrum. These properties render diamond to be potentially the most useful material across many fields of science and technology. Table 1.2 shows the variety of potential applications of diamond thin films as a function of its extreme properties (Field 1992).

1.4 Synthesis of Diamond

High Pressure High Temperature (HPHT) process and Chemical Vapour Deposition (CVD) are two main methods for synthesising diamond in crystalline and thin film forms respectively. The CVD processes enable the production of diamond coatings of excellent quality on flat or 3-D substrates and also synthesis of freestanding shapes of diamond. Free-standing diamond can be obtained by etching away the substrate using various chemical etching procedures (Anthony and Fleischer 1993; Frey and Simpson 1994; Elmazria et al. 2003). Diamond needs to be formed under conditions that are thermodynamically favourable. From the carbon phase diagram it is evident that heating carbon under pressure can form diamond. Hence, the high-pressure high-temperature technique was developed to produce 'industrial' diamond (Liang et al. 2005). A cell operating at high pressures up to pressures of tens of thousands of atmospheres is used to compress the graphite (G) at >2,000 K with a metal catalyst. This is left until diamond crystals form in the high-pressure cell.

1.4.1 Historical Perspective of Diamond Synthesis

From historical, technological and scientific perspective diamond is fascinating natural material (Angus et al. 2002). Sir Isaac Newton was the first to characterise diamond and determine it to be of organic origin whilst in 1772, the French chemist established that the product of the complete combustion of diamond was limited to carbon dioxide (Hartley 1947). English chemist (Tennant 1797) showed that diamond combustion products were no different than those of coal or graphite and resulted in 'bound air' namely CO_2 (Weeks 1933). Later, the advent of the x-ray diffraction technique enabled scientists Sir William Henry Bragg and his son Sir William Lawrence Bragg to determine the crystalline nature of the carbon allotropes, which were found to be cubic (diamond) and hexagonal (graphite) (Bragg and Bragg 1913). Since diamond is the densest carbon phase, it is feasible that high pressure producing a smaller volume and therefore a higher density, may convert other forms of carbon into diamond. During the 19th and 20th centuries chemical thermodynamics became better understood making it feasible to explore diamond stability in various pressure-temperature regimes (Berman and Simon 1955).

In 1955, these studies led to the development of a high pressure-high temperature (HPHT) process (DeVries 1987). Three problems arose in making HPHT diamond in the laboratory. First, it is difficult to achieve the extreme pressure that is required. Secondly, even when such a high pressure has been achieved, a very high temperature is required to convert graphite to diamond at a reasonable rate. Finally, if diamond is obtained, the grains are very small. In order to achieve large single crystal diamond yet another set of experimental conditions are needed. During that period however, less well known is the development of low-pressure diamond growth. This phase depends on choosing suitable experimental conditions (Butler et al. 1993). The diamond surface converts to graphite spontaneously.

Further nucleation and growth of graphitic species also occurs (Butler and Windischmann 1998).

The most successful process for low-pressure growth of diamond has been chemical vapour deposition from energetically activated hydrocarbon/hydrogen gas mixtures. CVD is a process whereby a thin solid film is synthesised from the gaseous phase via a chemical reaction. The most ancient example of a material deposited by CVD is pyrolytic carbon. Blocher pointed out that incomplete oxidation during the burning of firewood resulted in soot (Blocher 1966). A very early patent was granted for the preparation of carbon black using CVD (Donnet 1993; Bachmann et al. 1991; Bachmann and van Enckevort 1992). Later a patent was also granted for the next major application of CVD, which involved coating fragile filaments made from carbon (Blocher 1966). Several years after this, metal deposition processes for improving lamp filaments were presented (Spear 1989). Prior to late 1930s several techniques were described for refractory metals preparation. Silicon tetrachloride ($SiCl_4$) and hydrogen (H_2) mixture was used to deposit silicon films for microelectronic application (Joffreau et al. 1988).

$$SiCl_4(g) + 2H_2(g) \rightarrow Si(s) + 4HCl(g) \tag{1.1}$$

This led to the development of silicon-based photocells in 1946 as well as rectifiers (Photo-Cell 1946). The electronics industry has driven many of the developments of CVD processes. Consequently, a huge amount of literature on CVD is available. It was the chemical vapour deposition from carbon-containing gases, which enabled Eversole to grow diamond at low pressures (Eversole 1958). In the initial experiments, carbon monoxide was used as a source gas to deposit diamond on a diamond seed crystal. However, in subsequent experiments, methane and other carbon-containing gases were used as well as cyclic growth/etch procedures to grow diamond yet removing co-deposited graphite. In all of his studies, it was necessary to use diamond seeds in order to initiate diamond growth. The deposits were identified as diamond by density measurements, chemical analysis and diffraction techniques. Diamond was also synthesised successfully at high pressure in 1954. However, the important difference was that Eversole grew diamond on pre-existing diamond nuclei (Derjaguin et al. 1975). In 1956 diamond whiskers were grown using a metal-catalysed vapour-liquid-solid process (Spitsyn et al. 1981). A little later, epitaxial growth was the subject of considerable interest. In addition, theoretical studies on the nucleation of diamond and graphite were carried out. Angus and co-workers worked primarily on diamond CVD on diamond seed crystals from hydrocarbons hydrogen mixtures (Angus 1991). The *p*-type diamond was grown from methane/diborane gas mixtures and they studied the rates of diamond and graphite grown from the methane/hydrogen gas mixtures and ethylene. It was suggested that atomic hydrogen increased the rate of graphite etching compared to diamond etch rates. Low energy electron diffraction (LEED) studies (Messier et al. 1987) were done on a (Anusavice)-diamond surface. The hydrogen atoms are believed to be responsible for terminating the dangling bonds normal to the growing surface. Without hydrogen complex surface structures are formed. At high temperatures above 1200 K the carbon atoms move about rapidly on the