

MATERIAL STRUCTURE AND ENGINEERING APPLICATIONS OF CVD DIAMOND

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ABSTRACT

Diamonds possess an extreme range of physical properties, the most outstanding being its mechanical hardness. World interest in diamond has recently increased by the possibility to produce polycrystalline diamond films, or coatings, by a wide variety of chemical vapour deposition (CVD) techniques using, as process gases, such as hydrocarbon gas (methane) in an excess of hydrogen. This CVD diamond can show mechanical, tribological, and even electronic properties comparable to those of natural diamond.

Extension of CVD methods will provide an economically viable alternative to the traditional HPHT methods for producing diamond abrasives and heat sinks, whilst the possibility of coating large surface areas with a continuous film of diamond will open a completely new range of other potential application.

KEYWORDS: Chemical vapour deposition, Polycrystalline diamond, Diamond thin films

1. INTRODUCTION

Diamonds possess a remarkable range of physical properties and a look in any compendium of material data shows that diamond properties are always to the extreme, as presented in Table 1.

Table 1 Some diamond's properties

- extreme mechanical hardness (ca. 90 GPa)
- highest bulk modulus (1.2×10^{12} N/m ²)
- lowest compressibility (8.3×10^{-13} m ² /N)
- highest room temperature thermal conductivity (2×10^3 Wm ⁻¹ K ⁻¹)
- thermal expansion coefficient at room temperature very low (1×10^{-6} K)
- broad optical transparency from the deep ultraviolet to the far infrared
- highest sound propagation velocity (17.5 km/s)
- very good electrical insulator (room temperature resistivity is ca. 10^{13} - 10^{16} Ω cm)
- diamond can be doped, becoming a semiconductor with a wide band gap of 5.4 eV
- very resistant to chemical corrosion
- biologically compatible
-some surfaces exhibit very low or negative electron affinity

Unfortunately, it has proved very difficult to exploit these properties, due both to the cost and scarcity of large natural diamonds, and the fact that diamond was only available in the form of stones or grit.

It had been known for many years that diamond is composed solely of carbon and many attempts were made to artificially synthesise diamond using, as a starting material, another commonly occurring form of carbon, graphite. This proved extremely difficult, mainly because at room temperature and pressure, graphite is the thermodynamically stable form of carbon. Although the standard enthalpies of diamond and graphite only differ by 2.9 kJ mol⁻¹ a large activation barrier separates the two phases preventing interconversion between them at room temperature and pressure. This large energy barrier, which makes diamond so rare, is also responsible for its existence, since diamond, once formed, cannot spontaneously convert to the more stable graphite phase. Consequently, diamond is said to be metastable, that is, kinetically stable but not thermodynamically stable [1]. To overcome these problems, researchers realised that in order to form diamond, conditions are needed where diamond is the more stable phase. The knowledge of the

conditions under which natural diamond is formed deep underground suggested that diamond could be formed by heating carbon under extreme pressure. This process forms the basis of the so-called high-pressure high-temperature (HPHT) growth technique. This method has been used to produce industrial diamond for several decades. In this process, graphite is compressed in a hydraulic press to tens of thousands of atmospheres ($P \sim 50\text{--}100$ kbar), heated to over $2000\text{--}2300$ K in the presence of a suitable metal catalyst, and left until diamond crystallises. The diamond crystals, thus produced, are used for a wide range of industrial processes, which use the hardness and wear resistance properties of diamond, such as cutting and machining mechanical components, and for polishing and grinding of optics. However, the drawback of the HPHT method is that it still produces diamond in the form of single crystals ranging in size from nanometers to millimetres, and this limits the range of applications for which it can be used. What is required is a method to produce diamond in a form that can allow many more of its superlative properties to be exploited, in other words, as a diamond thin film.

2. CHEMICAL VAPOUR DEPOSITION

Chemical vapour deposition, as its name implies, involves a gas-phase chemical reaction occurring above a solid surface, which causes deposition onto that surface. All CVD techniques for producing diamond films require a means of activating gas-phase carbon-containing precursor molecules. This generally involves thermal (e.g. hot filament) or plasma (D.C., R.F., or microwave) activation, or use of a combustion flame (oxyacetylene or plasma torches). Figure 1 and 2 illustrates two of the more popular experimental methods and gives some indication of typical operating conditions. Whilst each method differs in detail, they all share features in common. For example, growth of diamond normally requires that the substrate to be maintained at a temperature in the range $1000\text{--}1400$ K. Beside that, the precursor gas (typical CH_4) have to be diluted in an excess of hydrogen. Whatever the method is used in CVD, this involves much lower pressures than in HPHT and there

would be an obvious advantage in terms of equipment and energy costs.

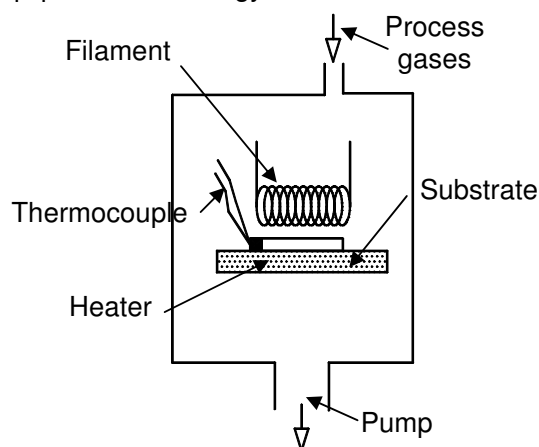


Fig. 1. Hot filament reactor

Hot filament CVD method (HFCVD) (figure 1) uses a vacuum chamber continually pumped using a rotary pump, while process gases are metered in at carefully controlled rates. Throttle valves maintain the pressure in the chamber at typically $20\text{--}30$ Torr, while a substrate heater is used to bring the substrate up to a temperature of $700\text{--}900$ °C. The substrate to be coated sits on the heater, a few millimetres beneath a filament, which is electrically heated to temperatures more than 2200 °C. The filament is made from a metal that will be able to survive these conditions and not react significantly, with the process gas. Metals such as tungsten and tantalum are most often used, although they do eventually react with the carbon-containing gases and carburise, to form the metal carbide. This changes their resistivity and makes them brittle, reducing their lifetime and hence the maximum deposition time that can be performed in one run. The HFCVD method is relatively cheap and easy to operate, producing reasonable quality polycrystalline diamond films at a rate of ca. $1\text{--}10$ $\mu\text{m}/\text{hour}$, depending upon exact deposition conditions. However, it also suffers from a number of major disadvantages. The hot filament is particularly sensitive to oxidising or corrosive gases, and this limits the variety of gas mixtures that can be employed. It is also very difficult to avoid contamination of the diamond film with filament material. For

diamond to be used in mechanical applications, metallic impurities are not an important problem, but it becomes unacceptable for electronic applications. Furthermore, the predominantly thermal nature of the process means that there are very few gas phase ions present, and this reduces the effectiveness of biasing the substrate to improve growth rates or induce oriented growth.

Microwave plasma CVD (MWCVD) reactors (figure 2) use very similar conditions to HF reactors and, despite being more expensive, are now among the most widely used techniques for diamond growth. In a MW reactor, microwave power is coupled into the chamber via a dielectric window (usually quartz) in order to create a discharge. The microwaves couple energy into gas phase electrons, which in turn transfer their energy to the gas through collisions. This leads to heating and dissociation of the gas molecules, the formation of active species. At the end, diamond is deposited onto a substrate, which is immersed in the plasma.

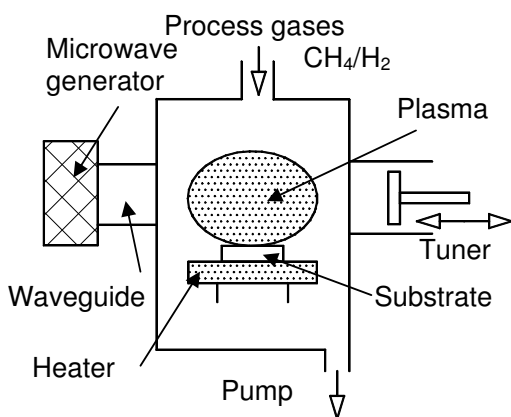


Fig. 2. Microwave plasma enhanced reactor

Thermodynamically, graphite, not diamond, is the stable form of solid carbon at ambient pressures and temperatures. The fact that diamond films can be formed by CVD techniques is inextricably linked to the presence of hydrogen atoms, which are generated as a result of the gas being activated, either thermally or via electron bombardment. These H atoms are believed

to play a number of crucial roles in the CVD process.

They undergo H abstraction reactions with stable gas-phase hydrocarbon molecules, producing highly reactive carbon-containing radical species. This is important, since stable hydrocarbon molecules do not react to cause diamond growth. The reactive radicals, especially methyl, CH₃, can diffuse to the substrate surface and react, forming the C-C bond necessary to propagate the diamond lattice.

Hydrogen atoms terminate the carbon bonds on the growing diamond surface and prevent them from cross-linking, thus reconstructing to a graphite-like surface.

One major problem that is receiving a lot of attention is the mechanism of heteroepitaxial growth, that is, the initial stages by which diamond nucleates upon a non-diamond substrate. Several studies have shown that pre-abrasion of non-diamond substrates reduce the induction time for nucleation and increase the density of nucleation sites. Enhanced growth rates inevitably follow since formation of a continuous diamond film is essentially a process of crystallisation, proceeding via nucleation, followed by three-dimensional growth of the various microcrystallites to the point where they eventually come together.

3. THE SUBSTRATE

Most of the CVD diamond films experiments been grown on single crystal silicon wafers, but this is by no means the only possible substrate material. The substrate must have a melting point (at the process pressure) higher than the temperature window (1000-1400 K) required for diamond growth [1]. This precludes the use of existing CVD techniques to diamond-coat plastics or low melting metals like aluminium. It is also helpful, however not essential, that the substrate be capable of forming a carbide. CVD of diamond on non-diamond substrates will usually involve initial formation of a carbide interfacial layer upon which the diamond then grows. Somewhat, it is difficult to grow on materials with which carbon is too reactive (i.e. many of the transition metals like iron, cobalt, etc) with which carbon exhibits a high solubility. Hence, materials like Si, Mo and W,

which form carbides, are more suitable as a substrate material. The carbide layer can be seen as well as glue and a promoter of CVD diamond growth.

These restrictions regarding materials have ensured the continuing popularity of silicon as a substrate material. It has a sufficiently high melting point (1683 K), it forms a localised carbide layer and it has a comparatively low thermal expansion coefficient. Tungsten and molybdenum display similar virtues and are also widely used as substrate materials. They can also be used as barrier layers - thin coatings deposited on top of certain of the problematic substrate materials to allow subsequent diamond CVD.

4. APPLICATIONS IN MECHANICAL ENGINEERING

CVD diamond has extended the range of suitable superabrasive tool materials. The use of PCD cutting tools and their relative attributes compared with high-speed steel, tungsten carbide or ceramic inserts has been well documented in literature. Like PCD, CVD diamond is also a polycrystalline form of diamond. There are, however, major differences. CVD diamond is almost a pure diamond phase, which does not contain a metallic binder, and is likely to be more temperature stable. The grain structure of CVD diamond, depending on the grade, shows a preferred crystal orientation and a columnar structure [2].

For these reasons, it can be expected that the performance of CVD diamond as a cutting tool may differ from that of PCD.

REFERENCES

- [1] P.W. MAY, *Diamond Thin Films: A 21st Century Material*, The Royal Society, 2000
- [2] R. S. SUSSMANN, J. R. BRANDON, S. E. COE, C. S. J. PICKLES, C. G. SWEENEY, A. WASENCZUK, C. J. H. WORT, C. N. DODGE, *Industrial Diamond Review*, Vol 58, No 578, pp 69 - 77, 1998
- [3] C. PISARCIUC, F. SARBU, *Polycrystalline Diamond Tools In Machining Composites Materials*,

Therefore is important to find the spectrum of machining operations where CVD diamond shows advantages. In its pure form, CVD diamond is an electrical insulator. By introducing suitable dopants during synthesis, it is possible to render CVD diamond electrically conductive. This allows the processing of CVD diamond by Electric Discharge Machining (EDM), the preferred technique used by industry.

An example of where CVD diamond might be used to advantage is in the machining of highly abrasive workpiece materials such as aluminium-based metal matrix composites (MMCs), non-ferrous metals, plastics, chip-board and composite materials. Over the past decade, the machining of MMCs by techniques other than grinding has been made possible using superabrasive tooling such as PCD [3, 4]. CVD diamond offers an interesting alternative. Because of its perceived excellent abrasion resistance and high thermal stability, it should allow increased cutting speeds during dry machining (an increasing requirement of cutting tool materials due to European legislation to minimise effluent streams).

The major disadvantage that diamond has over other tool materials (the same encountered at PCD tools) is that it reacts with iron, and so cannot be used to cut ferrous materials such as steel. Nevertheless, CVD diamond-coated tools have a longer life, cut faster, and provide a better finish than conventional WC tools.

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- [4] C. PISARCIUC, F. SARBU, *Diamond Machining Of Discontinuously Reinforced Composites*, Tehnologii Moderne, Calitate, Restructurare. Vol. 1. Chişinău, UTM, pp 265 – 269, 2003

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