

Thin Film Diamond by Chemical Vapour Deposition Methods

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1 Introduction

Diamond, the sp^3 -bonded allotrope of carbon, has long held a special place in the hearts and minds both of scientists and the public at large. For the latter, the word diamond may conjure up images of 57 faceted brilliant gem stones, Amsterdam or mines in South Africa, wealth and special occasions. To the scientist, diamond is impressive because of its wide range of extreme properties. As Table 1 shows, by most measures diamond is 'the biggest and best': It is the hardest known material, has the lowest coefficient of thermal expansion, is chemically inert and wear resistant, offers low friction, has high thermal conductivity, is electrically insulating and optically transparent from the ultra-violet (UV) to the far infrared (IR). Given these many notable properties, it should come as no surprise to learn that diamond already finds use in many diverse applications including, of course, its use as a precious gem, but also as a heat sink, as an abrasive, and as inserts and/or wear-resistant coatings for cutting tools. Obviously, given its many unique properties it is possible to envisage many other potential applications for diamond as an engineering material, but progress in implementing many such ideas has been hampered by the comparative scarcity of natural diamond. Hence the long running quest for routes to synthesize diamond in the laboratory.

At ambient temperatures and pressures *graphite* is the stable form of solid carbon. Its enthalpy of formation is a mere 2.9 kJ mol^{-1} lower than that of diamond, but a large activation barrier rules out simple thermal activation as a means of driving the graphite \rightarrow diamond interconversion. The activation energy for graphitization at the {110} diamond surface has been measured as $728 \pm 50 \text{ kJ mol}^{-1}$,¹ roughly the same as the vaporization

energy of graphite. Diamond is the densest allotrope of carbon ($\rho_{\text{diamond}} = 3513 \text{ kg m}^{-3}$, cf. $\rho_{\text{graphite}} = 2260 \text{ kg m}^{-3}$ at 293 K); thus, at high pressure, *diamond* must be the stable form of solid carbon. This is the scientific basis for the high pressure high temperature (HPHT) techniques (in which diamond is crystallized from metal solvated carbon at $P \sim 50\text{--}100 \text{ kBar}$ and $T \sim 1800\text{--}2300 \text{ K}$) by which diamond has been synthesized commercially for over 30 years.²⁻⁴

Table 1 Some of the outstanding properties of diamond

Extreme mechanical hardness ($\sim 90 \text{ GPa}$)
Strongest known material, highest bulk modulus ($1.2 \times 10^{12} \text{ Nm}^{-2}$), lowest compressibility ($8.3 \times 10^{-13} \text{ m}^2 \text{ N}^{-1}$)
Highest known value of thermal conductivity at room temperature ($2 \times 10^3 \text{ Wm}^{-1} \text{ K}^{-1}$)
Thermal expansion coefficient at room temperature ($0.8 \times 10^{-6} \text{ K}^{-1}$) is comparable with that of invar
Broad optical transparency from the deep UV to the far IR region of the electromagnetic spectrum
Good electrical insulator (room temperature resistivity is $\sim 10^{16} \Omega \text{ cm}$)
Diamond can be doped to change its resistivity over the range $10\text{--}10^6 \Omega \text{ cm}$, so becoming a semiconductor with a wide band gap of 5.4 eV
Very resistant to chemical corrosion
High radiation hardness

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World interest in diamond has been further increased by the much more recent discovery that it is possible to produce polycrystalline diamond films by a wide variety of chemical vapour deposition (CVD) techniques using, as process gases, nothing more exotic than a hydrocarbon gas (typically methane) in an excess of hydrogen.^{5–7} CVD diamond can show mechanical, tribological, and even electronic properties comparable to those of natural diamond. There is currently much optimism that it will prove possible to scale CVD methods to the extent that they 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 up whole new ranges of potential application for the CVD methods.⁸

In this Review we describe some of the various methods for growing CVD diamond, paying particular attention to our current (incomplete) understanding of the underlying chemistry. We also survey some of the more important surface analysis techniques used to characterize thin film diamond, and then consider how the deposition conditions influence the quality and the growth rates of the diamond films produced by the various CVD methods. Attention will then turn to the substrate materials on which the films can be grown. We summarize current thinking regarding what physico-chemical properties of the substrate are important for nucleation, for subsequent film growth, and in determining whether the resulting diamond coating will be strongly adherent. The Review concludes with discussion of a few specific and novel applications (some realized, some in the realms of reasonable expectation) of CVD diamond films.

2 The CVD Process

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. Figure 1 illustrates three of the more popular experimental methods and gives some indication of typical operating conditions. (These and other deposition methods are discussed in greater detail in reference 9.) Whilst each method differs in detail, they all share features in common. For example, growth of *diamond* (rather than deposition of other, less well-defined, forms of carbon) normally requires that the substrate be maintained at a temperature in the range 1000–1400 K, and that the precursor gas be diluted in an excess of hydrogen (typical CH₄ mixing ratio ~ 1–2 vol%). The resulting films are polycrystalline, with a morphology that is sensitive to the precise growth conditions (see later). Growth rates for the various deposition processes vary considerably, and it is usually found that higher growth rates can be achieved only at the expense of a corresponding loss of film quality. 'Quality' here is a subjective concept. It is taken to imply some measure of factors such as the ratio of *sp*³ (diamond) to *sp*² bonded (graphite) carbon in the sample, the composition (*e.g.* C–C versus C–H bond content) and the crystallinity. In general, combustion methods, such as oxyacetylene or plasma torches, deposit diamond at high rates (typically 100 → 1000 μm h⁻¹, respectively), but often only over very small, localized areas and with poor process control leading to poor quality films. In contrast, the hot filament and plasma methods have much slower growth rates (0.1–10 μm h⁻¹), but produce high quality films. However, the filament method often suffers from contamination problems, since metal boiled off the filament can be incorporated into the growing diamond film. One of the great challenges facing researchers in CVD diamond technology is to increase the growth rates to economically viable rates, (hundreds of μm h⁻¹, or even mm h⁻¹) without compromising film quality.

Another major problem that is receiving a lot of attention is

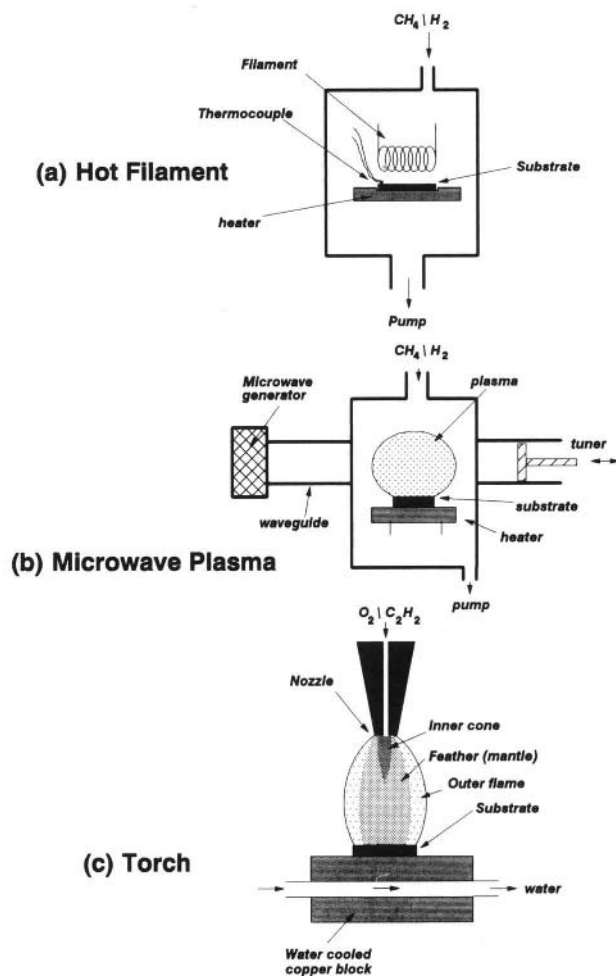


Figure 1 Schematic diagram of three of the most commonly used types of diamond CVD apparatus. (a) Hot Filament reactor, (b) Microwave Plasma Enhanced CVD reactor, and (c) Oxyacetylene Torch.

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 reduces the induction time for nucleation and increases the density of nucleation sites. Enhanced growth rates inevitably follow since formation of a continuous diamond film is essentially a process of crystallization, proceeding *via* nucleation, followed by three-dimensional growth of the various microcrystallites to the point where they eventually coalesce. However the precise manner in which the pre-abrasion enhances surface activity remains a topic of some debate. Suggested mechanisms range from the idea that the initial growth occurs on detritus from the (diamond) abrasive embedded in the substrate surface, to those which maintain that simply the presence of surface defects produced by mechanical damage is sufficient to provide suitable sites for diamond formation *via* a heterogeneous nucleation process. The abrasion process is usually carried out by mechanically polishing the substrate with an abrasive grit, usually diamond powder of 0.1–10 μm particle size, although other materials, such as SiC or sapphire have been used. Better abrasion uniformity (and hence subsequent diamond film uniformity) can be obtained if the substrate is placed into a slurry containing a mixture of the abrasive grit in a hydrocarbon medium, and is then ultrasonically agitated. Whatever the abrasion method, however, the need to damage the surface in such a poorly defined manner prior to deposition may severely inhibit the use of CVD diamond for applications in, say, the electronics industry (see later), where circuit geometries are frequently on a submicron scale. This worry has led to a search for more controllable methods of enhancing nucleation, such as

ion bombardment This is often performed in a microwave deposition reactor, by simply applying a negative bias of a few hundred volts to the substrate and allowing the ions to (i) damage the surface, (ii) implant into the lattice, and (iii) form a carbide interlayer (see later) The exact mechanism by which this process enhances diamond nucleation is still not properly understood but recent evidence¹⁰ shows that biasing the substrate increases both the concentration of H atoms close to the surface and the electron temperature of the plasma

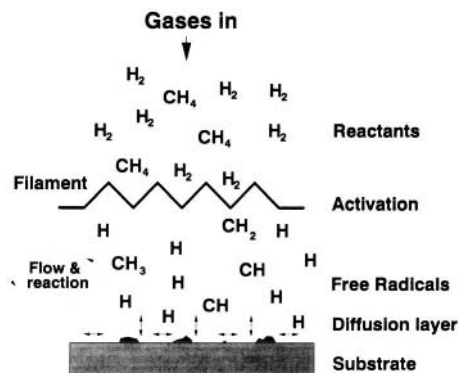


Figure 2 The mechanism of CVD involves dissociation of precursor gases (usually methane and hydrogen) by either electron impact (plasma methods) or, as shown here, thermal energy from a hot filament Atoms and reactive species diffuse to the substrate surface, where they absorb and coalesce to form a carbon film If the deposition conditions are favourable, the film is diamond

Figure 2 provides a schematic of the diamond CVD process Here we assume a CH_4/H_2 source gas mixture, though we note in passing that many other hydrocarbon precursor gases have been investigated^{11, 12} and that extra gases (*e.g.* O_2) are sometimes added with a view to improving the resulting film quality and decreasing deposition temperatures Bachmann *et al.*¹² have shown that successful synthesis of single-phase diamond is only feasible in a localized region of the C/H/O-gas-phase compositional diagram Most of this region straddles the line representing equal C and O atom concentrations, although it is of course also possible to grow diamond films using an oxygen-free gas mixture provided that there is a large excess of H atoms This shows that so long as the deposition conditions are energetic enough to produce complete dissociation of the parent gas molecules, the quality of deposited diamond depends only upon the ratio of carbon-to-hydrogen-to-oxygen within the reactor Activation of the gas, be it thermal or *via* electron bombardment, involves production of H atoms Our schematic shows these causing H-atom abstraction from the methane with the resulting formation of methyl radicals There is now a considerable body of evidence to suggest that methyl radicals are the dominant growth species in many variants of diamond CVD This evidence includes direct *in situ* detection of CH_3 radicals in diamond CVD reactors by a variety of spectroscopic methods (*e.g.* mass spectrometry, resonance enhanced multiphoton ionization (REMPI), and direct infrared absorption spectroscopy), the results of kinetic modelling both of the gas-phase chemistry and of observed film growth rates, and a variety of isotopic labelling studies The methyl radicals, along with other gas-phase species, will be transported towards the substrate by a combination of laminar, convective and/or diffusive flow mechanisms depending on the particular process conditions, whilst the relative species concentrations will continue to evolve as a result of further gas-phase reactions Transport back and forth across the boundary layer over the growing surface will be especially important with the higher pressure (*e.g.* torch) methods, this can be expected to further influence the local gas-phase environment Deposition involves adsorption and desorption at the surface Diffusion *across* the growth surface may well result in nucleation and growth of the diamond film, whilst diffusion

into the bulk substrate is often an alternative, generally undesirable, competitive loss process

We stated earlier that *graphite*, not diamond, was 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 atoms¹³ These are believed to play a number of crucial roles in the CVD process First, as Figure 2 suggests, they are intimately involved in the formation of carbon-containing *radical* species This is important, since stable hydrocarbon *molecules* do not react with diamond to cause diamond growth Secondly, H-atoms terminate the 'dangling' carbon bonds on the growing diamond surface and prevent them from reconstructing to a graphite-like surface However, if these were the only functions of the H atoms, diamond growth would be unlikely to occur This conclusion is reached simply by considering the relative strengths of a C-H and a C-C bond The former is stronger, thus any approaching carbon atom would not be able to displace the surface bonded H-atom Fortunately, the H-H bond in molecular hydrogen is stronger than either Thus abstraction of a surface-bonded H-atom by a gas-phase H-atom leading to formation of a gas-phase hydrogen molecule is an exoergic process, so the H-atoms also 'activate' the growing surface by creating local vacant sites,¹⁴ see Figure 3 Given that the concentration of gas-phase H-atoms generally far exceeds that of any of the carbon-containing radical species, the most likely fate for any vacant site is re-termination by addition of another H-atom Occasionally, however, the colliding species will be a carbon-containing radical (*e.g.* CH_3) A new C-C bond will be formed, thus providing the possibility of extending the diamond lattice Of course this extension of the carbon network need not have the correct diamond structure but, here again, the H-atoms play a helpful role Atomic hydrogen etches both diamond and graphite but, under typical CVD conditions, the rate of diamond growth exceeds its etch rate whilst for other forms of carbon (graphite, for example) the converse is true Thus it is that essentially pure diamond films can be grown

The presence (and importance) of H-atoms has been verified by a number of spectroscopic methods Celii and Butler¹⁵ used three-photon REMPI to probe the spatial distribution of ground state H-atoms in a hot filament CVD reactor and to investigate the way in which the relative H-atom concentration

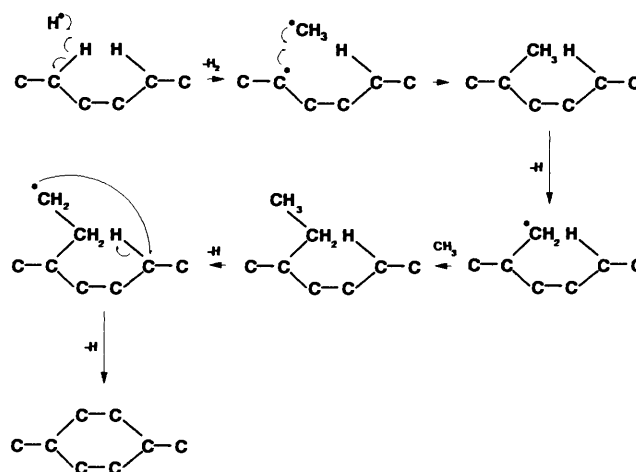


Figure 3 One of the possible reaction schemes for growth of diamond at a {110} trough site Atomic hydrogen abstracts a hydrogen atom from the surface of diamond leaving a surface radical A methyl group then adds to the 'dangling bond', so adding carbon to the lattice A further hydrogen abstraction reaction and methyl addition, followed by an internal hydrogen elimination step closes the ring and propagates the diamond structure All the steps are reversible, but the process is driven to completion by the stability of the contiguous diamond lattice with respect to graphitic structures Similar mechanisms are believed to operate at other lattice sites, using either methyl, ethyl, or acetylene precursors⁶

varied with filament temperature and with CH_4/H_2 mixing ratio. Recent modelling of these data points to the importance of surface-catalysed decomposition of H_2 on the hot filament in establishing the observed H-atom concentrations.¹⁶ Ground state H-atoms have also been monitored *via* their laser-induced fluorescence (LIF) and by *in situ* third harmonic generation.^{6,17}

Plasma-enhanced CVD processes involve different excitation/dissociation mechanisms: electron-molecule collisions play a much more significant role. These tend to yield much higher concentrations of electronically excited species, *e.g.* H-atoms with principal quantum number $n = 3$, which can be detected conveniently through observation of their Balmer- α emission in the red, and simple radical species like CH, OH, and C_2 which can also be detected by their spontaneous optical emission. Following these emissions can conceivably provide some measure of process control, but the information such emissions appear to convey should be treated with circumspection. For example, both C_2 and CH emissions show strongly during growth of CVD diamond using combustion flames and plasma torches, but this does not necessarily imply that these species are important in the diamond growth mechanism. Analysis of the wavelength dispersed emission can provide a measure of the relative populations in the various rovibrational levels of the emitting electronic state. This population distribution often approximates a Boltzmann distribution, characterized by a 'temperature'. However, given the short fluorescent lifetime of the emitting species, collisional thermalization *prior* to emission is unlikely and the 'temperature' deduced is thus more an indicator of the radical production mechanism than any characteristic of the bulk of the discharge. *In situ*, non-intrusive spectroscopic methods capable of probing *ground state* species are more likely to provide realistic measures of the plasma temperature. Examples of such techniques include LIF (though, given their lack of suitable fluorescing excited states this technique is unsuitable for potentially important species like CH_3 radicals or stable molecular species like CH_4 and C_2H_4), REMPI, and, most recently, degenerate four-wave mixing spectroscopy.¹⁸

3 The CVD Diamond Film

Figure 4 shows scanning electron micrographs (SEM) of polycrystalline CVD diamond films grown on a single crystal silicon substrate using two different CH_4/H_2 gas mixtures (CH_4 mixing ratios of 1% and 2.5% respectively) in a hot filament reactor. Such images, in themselves, do not prove whether the films are diamond but monitoring the attendant cathodoluminescence can provide supportive evidence.¹⁹ However, the most widely used technique, both for establishing that a film is indeed diamond and for providing some measure of the film quality, is laser Raman spectroscopy. The Raman spectrum of natural diamond shows a sharp, single peak centred at a wavenumber of $\sim 1332 \text{ cm}^{-1}$. As Figure 5a shows, this feature also dominates the Raman spectra of good quality polycrystalline diamond films grown by CVD methods, though the peak linewidth is usually somewhat greater than for natural diamond and the linecentre is often found to be slightly shifted in wavenumber – both effects generally attributed to compressive stress in the film.^{19,20} By way of contrast, the Raman spectrum of well-crystallized graphite shows a somewhat broader feature centred around 1580 cm^{-1} . When characterizing CVD 'diamond' films, the observation of any broad resonance around this higher wavenumber (such as can be seen, for example, in Figure 5c) is generally taken to indicate the presence of graphite-like non-diamond phases containing sp^2 -bonded carbon atoms.

Raman spectroscopy is just one tool in an armoury of analytic techniques used to characterize CVD diamond films. Other spectroscopies that are useful for distinguishing diamond from alternative forms of carbon include electron energy loss spectroscopy (EELS), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), and X-ray diffraction. Unfortunately, all are *ex*

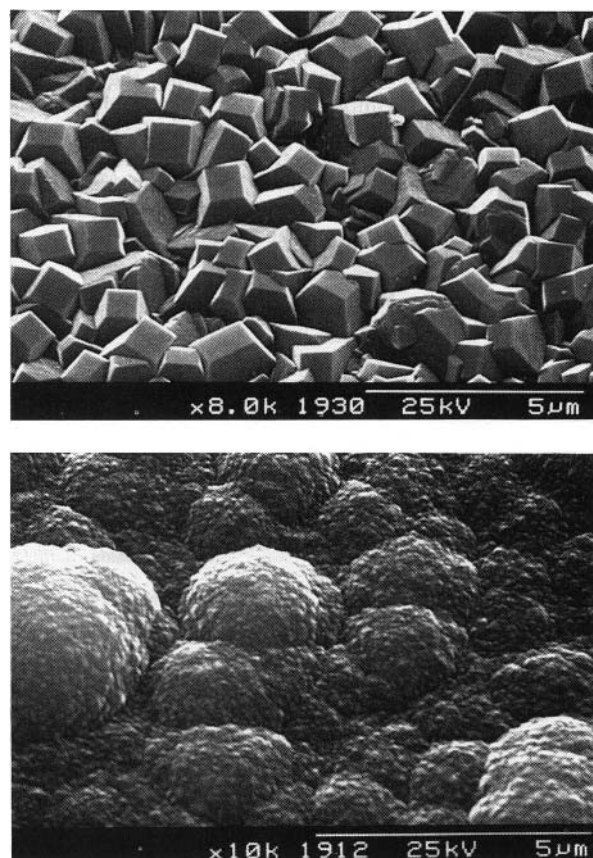


Figure 4 SEM of typical polycrystalline diamond films grown on Si by CVD. (a) was grown using 0.5% methane in hydrogen, which produces sharp angular crystals about $1 \mu\text{m}$ in size.¹¹ (b) was grown using 2.5% methane in hydrogen, which give rise to nanocrystalline diamond particles which aggregate into roughly spherical 'cauliflower' structures.

situ techniques, the implementation of any of which requires cessation of the deposition process, removal of the sample from the reactor and, frequently, some considerable sample preparation and analysis. The same criticisms apply to the use of secondary ionization mass spectrometry (SIMS) and to the technique of transmission electron microscopy (TEM) – arguably the ultimate route to establishing the detailed microstructure of a CVD diamond film. SIMS does not allow one to distinguish between the different forms of carbon, but is ideally suited to mapping out the spatial distribution of different elements residing within a few atomic layers of a surface. Thus it finds particular use as a means of probing the interfacial region when CVD diamond films are grown on non-diamond substrates (after sectioning – see below). Monitoring atomic hydrogen by SIMS is difficult, but not impossible. Given the expectation that hydrogen in CVD diamond films will be concentrated at the surface and in the grain boundaries, the effort involved in such a study might well be very rewarding.

Other measurable properties which give some insight into the quality of CVD diamond films include hardness, coefficient of friction, density, bulk modulus, and thermal conductivity. All have been investigated, as a function of the growth conditions – most notably the CH_4/H_2 mixing ratio. Hardness is traditionally measured by indent testing. Indentation, and scratch testing (a method of measuring friction), both have attendant complications in the case of good quality CVD diamond films, not least because the diamond tip used to make the impression will have a hardness comparable to that of the film under test. Scratch testing is complicated by the fact that the as grown film is rough (recall the microcrystallinity evident in Figure 4), whilst indent measurements on thin films will only be reliable if proper regard is given to the deconvolution of contributions from the underlying

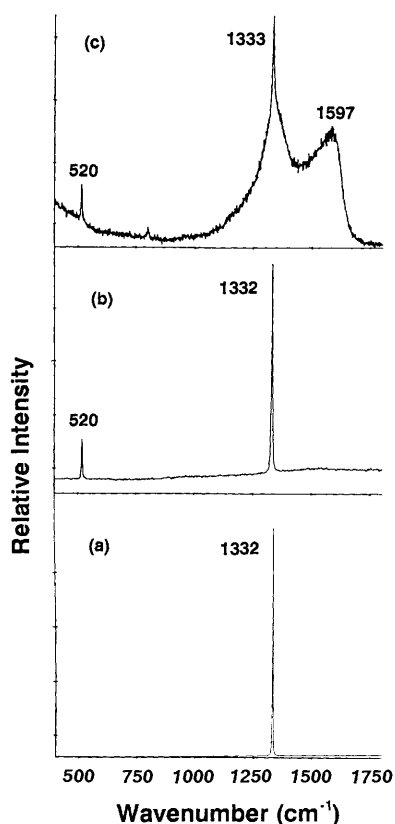


Figure 5 Laser Raman spectra measured by Knight and White.²⁰ (a) Natural diamond showing the characteristic sharp peak at 1332 cm^{-1} . (b) Good quality CVD diamond film grown on Si using 0.5% CH_4 in H_2 gas mixture. The peak at 520 cm^{-1} is due to Si. (c) Poor quality CVD diamond film grown using 1.5% CH_4 in H_2 . The broad hump at $\sim 1597\text{ cm}^{-1}$ is evidence that the film contains non-diamond phases, such as graphite or amorphous carbon. The diamond peak has also broadened considerably.

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ing (almost inevitably softer) substrate. Such measurements have been reported;^{21,22} these show good quality CVD diamond films to have a hardness approaching that of natural diamond.

We have already commented that diamond has a density well in excess of that of graphite or any other form of carbon. Using a sink–float method, Sato and Kamo²³ showed that CVD diamond films grown from lean CH_4/H_2 mixtures (CH_4 mixing ratio $\leq 0.5\%$) have a density that is $> 99.5\%$ of the corresponding value for natural diamond. However, they also found that the film density decreases with increasing partial pressure of CH_4 in the process gas mixture. By attributing this trend solely to progressive contamination of the grown film by disordered graphite, these workers were able to derive a lower limit to the fractional diamond content in films grown with CH_4 mixing ratios as high as 5%. Higher CH_4 mixing ratios have also been shown to have an adverse effect both on the bulk modulus and the thermal conductivity of CVD diamond films.²³

As Figure 4 showed, the surface morphology is another property that is very sensitive to the gas mixing ratio. It also depends on the substrate temperature. Figure 6 provides a qualitative summary of the way both affect the surface morphology. In essence we are here concerned with the way in which the growth rates vary with microcrystallite orientation. Under 'slow' growth conditions – low CH_4 partial pressure, low substrate temperature – triangular $\{111\}$ facets tend to be most evident, with many obvious twin boundaries. $\{100\}$ facets, appearing both as square and rectangular forms, begin to dominate as the relative concentration of CH_4 in the precursor gas mixture, and/or the substrate temperature, is increased. Both types of facet are clearly evident in the scanning electron micrograph shown in Figure 4a. A cross-section through this

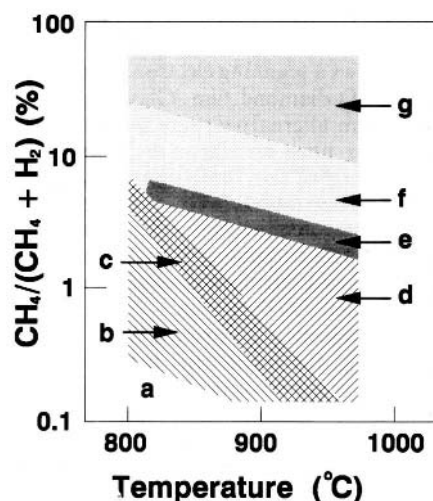


Figure 6 Schematic diagram of film morphology as a function of deposition temperature and methane/hydrogen ratio for CVD between 30–80 Torr (adapted from ref. 23). The regions correspond to different observed morphologies: (a) little or no deposition of either diamond or graphite, (b) $\{111\}$ faces predominate, (c) $\{111\}$ and $\{100\}$ faces appear with comparable frequency, (d) $\{100\}$ faces predominate, (e) $\{100\}$ faces predominate and diamond grains grow preferentially along the $\langle 100 \rangle$ axis, (f) films have a smooth surface composed of nanocrystals of diamond and disordered graphite, (g) film surface is composed of fibrous deposits of soot or disordered graphite growing vertically from the surface.

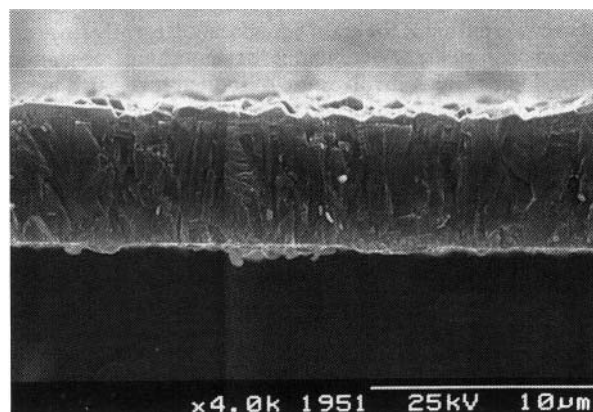


Figure 7 Cross-sectional SEM of a $6.7\text{ }\mu\text{m}$ thick CVD diamond film showing columnar growth.¹¹

film shows the growth to be essentially columnar (Figure 7). At still higher CH_4 partial pressures the crystalline morphology disappears altogether; a film such as that shown in Figure 4b is an aggregate of diamond nanocrystals and disordered graphite.

Obviously, the crystalline morphology of a CVD diamond film is an important consideration when it comes to potential applications. A film like that shown in Figure 4a might find use as a fine abrasive coating, but most of the envisaged uses for diamond films in optics, in thermal management applications, and as possible electronic devices require that the film surfaces be as smooth as possible. One can envisage (at least) two routes to this objective: one has either to identify growth conditions which naturally result in the formation of smooth films, or to optimize ways of 'polishing' away the surface roughness of the film as grown. Both concepts are presently the subject of intense research effort. We have already seen that the film structure and morphology is sensitive to the relative growth rates on the various crystallographic faces. Wild *et al.*²⁴ have demonstrated that, at least in the case of silicon substrates, it is possible to set the deposition parameters in such a way that the CVD process is so biased in favour of growth on the $\{100\}$ facets that the surface

of the resulting film consists entirely of well aligned, coplanar $\{100\}$ facets with the axis of growth normal to the substrate surface. Figure 8 shows a scanning electron micrograph of such a $\{100\}$ textured CVD diamond film. Glass and co-workers²⁵ have demonstrated an alternative route to growing $\{100\}$ textured CVD diamond films on silicon by microwave plasma enhanced CVD. This relied on a three-step 'growth' process, the first two of which (carburization, followed by a negative biasing step at lower substrate temperature, the combined effect of which is believed to be the formation of an epitaxial β -SiC buffer layer) may be viewed as a special pretreatment of the substrate surface prior to 'normal' CVD growth.

We now turn to consider the prospects for post-polishing. Mechanical polishing, the traditional method for preparing diamond gemstones, is one obvious, if uneconomic, possibility. A variant on this theme – chemical–mechanical polishing – relies on the fact that diamond reacts with iron at elevated temperatures. Mechanical polishing on a heated (~ 900 K) iron disc in the presence of atomic hydrogen leads to graphitization of surface diamond and subsequent dissolution of the carbon into the hot iron. The hydrogen serves to remove carbon from the iron and prevents saturation of the iron by carbon. A very recent and exciting extrapolation of this type of process is introduced at the end of this paragraph. Another route to surface smoothing involves use of a high energy pulsed laser (e.g. an excimer or a Nd-YAG laser). The actual polishing mechanism (or mechanisms) remains the subject of some debate: selective ablation of 'high spots' on the rough diamond surface has been suggested but so, too, has local oxidation, particularly in instances where the irradiation was carried out under an oxygen-containing atmosphere. Ion bombardment, and reaction with oxygen atoms, have also been proposed as polishing methods, but both tend to cause pitting at the grain boundaries. Recently Jin *et al.*²⁶ have demonstrated a new technique for smoothing free-standing diamond films which involves use of molten rare-earth metals. The diamond film is sandwiched between layers of the rare-earth metal (e.g. cerium or lanthanum), or a suitable alloy, and held for a few hours under an inert atmosphere of argon at a temperature (~ 1200 K) somewhat above the melting point of the metal. Carbon has high solubility in these metals at such temperatures. After the heat treatment both the residual (unreacted) and the reacted rare-earth metal is removed by acid etching, leaving a greatly smoothed (albeit thinner) diamond film.

4 The Substrate

Most of the CVD diamond films reported to date have been grown on single crystal silicon wafers, but this is by no means the

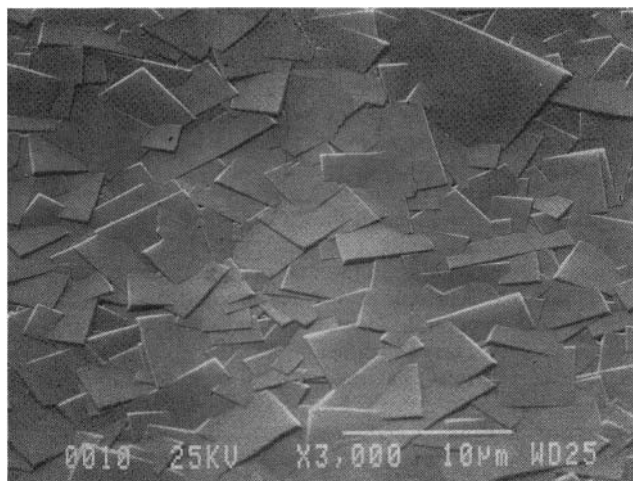


Figure 8 Scanning electron micrograph of a textured $\{100\}$ diamond film.

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only possible substrate material. What are the properties required of a substrate if it is to be suitable for supporting an adherent film of CVD diamond? One requirement is obvious. The substrate must have a melting point (at the process pressure) higher than the temperature window (1000–1400 K) required for diamond growth. This precludes the use of existing CVD techniques to diamond-coat plastics or low melting metals like aluminium. It is also helpful, though 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 paradoxically, it is difficult to grow on materials with which carbon is 'too reactive', i.e. many of the transition metals (e.g. iron, cobalt, etc.) with which carbon exhibits a high mutual solubility. Hence the appeal of substrates like silicon, molybdenum, and tungsten – materials which form carbides, but only as a localized interfacial layer because of their modest mutual solubility with carbon under typical CVD process conditions. The carbide layer can be pictured as the 'glue' which promotes growth of CVD diamond, and aids adhesion by (partial) relief of stresses at the interface.

Turning now to the problem of stress, it is fairly obvious that it is desirable for the substrate material to have a low coefficient of thermal expansion. Diamond has one of the lowest coefficients of thermal expansion of any material (see Figure 9). Since the CVD growth process takes place at elevated temperatures it is almost always the case that upon cooling back to room temperature, the substrate will have contracted more than the diamond film. As a result, the latter will be under compressive stress. This manifests itself in the broadening and shifting of the 1332 cm^{-1} Raman peak mentioned earlier. Clearly, $\Delta\alpha$, the mismatch in the coefficients of thermal expansion for diamond and the substrate material, must be an important factor in determining whether it will be possible to grow an *adherent* CVD diamond film on that particular substrate.

Figures 10 and 11, which show scanning electron micrographs of CVD diamond 'films' that we have grown on quartz and on copper substrates illustrate some of the consequences of a non-zero $\Delta\alpha$. In both cases we have succeeded in growing a CVD diamond film, but the end result is very different. Consider first the case of the quartz (a form of silica). Growth of diamond on quartz proceeds *via* formation of a thin interfacial silicon carbide layer, however the substrate has a coefficient of thermal expansion much greater than that of diamond. Thus it is possible

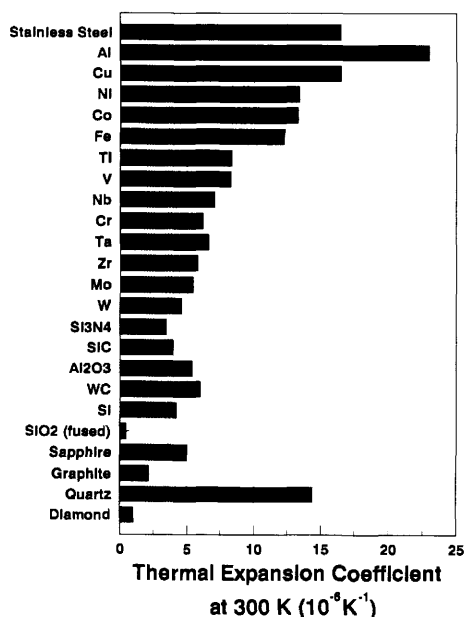


Figure 9 Bar graph showing typical values for the thermal expansion coefficient for a variety of substrate materials at 300 K.

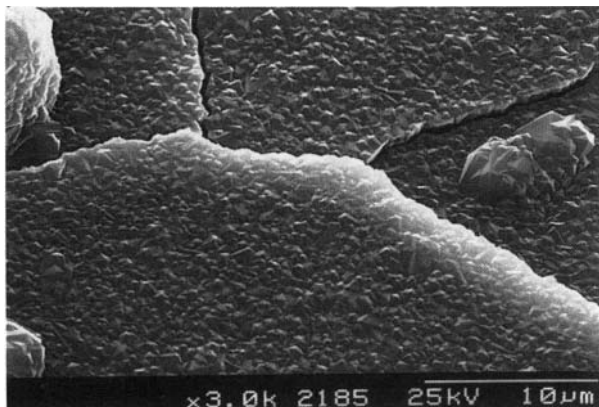


Figure 10 SEM of a CVD diamond film grown on a flat quartz substrate. The film has grown and adhered but, upon cooling, compressive stresses resulting from the contraction of the quartz have caused the diamond film to crack into plates, with the plates riding over one another to relieve the stress. Note that cracking is often transgranular, indicating that grain boundaries are not in themselves an inherent source of weakness in polycrystalline diamond films.

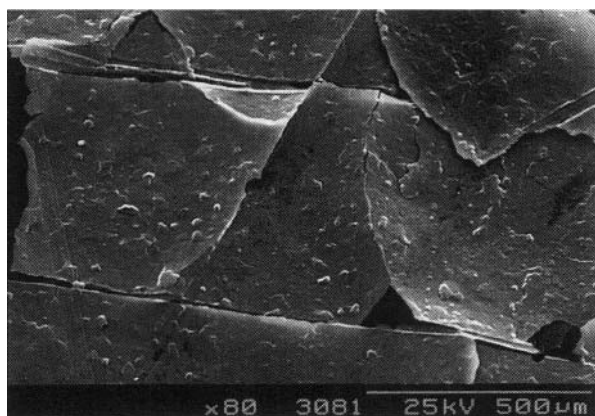


Figure 11 SEM of a CVD diamond film grown on Cu. The film has cracked and crazed into plates, which have partially delaminated.

to grow thin *adherent* films of CVD diamond on pre-abraded quartz, but with increasing film thicknesses and/or areas the internal stresses become too great and the diamond film cracks into a number of 'plates' as shown in Figure 10. In order to alleviate the stress, these plates ride up over one another at their edges; each, however, remains well adhered to the substrate. Contrast this with growth on copper. In this case the substrate does *not* form a carbide and Δa is also very large ($\sim 1.5 \times 10^{-5} \text{ K}^{-1}$). Given these facts, it is perhaps surprising that diamond grows on copper at all. Nonetheless, Figure 11 confirms that it is indeed possible to grow a CVD diamond film on pre-abraded copper but, because there is no carbide layer providing the necessary 'glue' at the interface, it is not an adherent film: it will readily flake off as soon as the substrate is tilted.

If we consider just carbon–substrate interactions, metals, alloys, and pure elements sub-divide into three classes²⁷ exhibiting, respectively:

(a) *Little or no C solubility or reaction.* These include metals such as Cu, Sn, Pb, Ag, and Au as well as non-metals, such as Ge, sapphire, diamond itself, and graphite, although in the latter case etching will occur concurrently with diamond growth.

(b) *C diffusion.* Here, the substrate acts as a carbon sink, whereby deposited carbon dissolves into the metal surface to form a solid solution. This causes large amounts of carbon to be transported into the bulk, leading to a temporary decrease in the surface C concentration, delaying the onset of nucleation.

Metals where this is significant include Pt, Pd, Rh, Fe, Ni, and Ti. For substrates with a very high C diffusion rate, sample thickness becomes a significant parameter influencing the onset of nucleation; thin foils reach their carbon saturation more rapidly than thick plates.²⁸

(c) *Carbide Formation.* These include metals such as Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe, Co, Ni, Y, Al and certain other rare earth metals. In some metals, such as Ti, the carbide layer continues to grow during diamond deposition and can become hundreds of μm thick. Such thick interfacial carbide layers may severely affect the mechanical properties, and hence the utility of CVD diamond coatings on these materials. Non-metals, such as B or Si, and Si-containing compounds such as SiO_2 , quartz, and Si_3N_4 also form carbide layers. Substrates composed of carbide themselves, such as SiC, WC, and TiC are also particularly amenable to diamond deposition.

Such problems with heteroepitaxial growth have ensured the continuing popularity of silicon as a substrate material. It has a sufficiently high melting point (1683 K), it forms a localized 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. Molybdenum, in particular, is finding increasing use, especially as a substrate for CVD diamond films grown by the high growth rate methods (e.g. when using a plasma torch), because of its ability to withstand thermal shock.

A review such as this would not be complete without some mention of current progress towards the growth of single crystal (rather than polycrystalline) diamond films. This remains a major challenge but, given the potential reward, it is an area of great current activity. The need for, and the advantages of, single crystal diamond films are reasonably self-evident. Only the single crystal material will fully exhibit all of the extreme and unique properties we associate with diamond. Most of the potential electronic applications of diamond (see below) demand single crystal material. Devices made from homoepitaxial diamond are actually expected to perform better than comparable gemstone diamond devices with respect to properties such as dielectric breakdown strength and carrier mobility.²⁹ To date, epitaxial growth of diamond films has been reported on diamond^{29,30} and on a single crystal cubic boron nitride substrates³¹ but the quest for heteroepitaxial growth on a cheaper, more readily available substrate material continues. What is required of such a substrate material? Obviously, the various properties discussed earlier but, in addition, one might look for a substrate that had a crystal structure and lattice parameters not dissimilar to that of diamond (cubic, with lattice spacing $a = 356.7 \text{ pm}$). Nickel and copper are two such materials. Both have face-centred cubic structures and similar lattice constants ($a = 352.4$ and 361.5 pm , respectively). Unfortunately both have associated problems when it comes to CVD diamond growth. Diamond grows on copper, but does not adhere (recall Figure 11). Nickel, in contrast, is one of those metals like iron in which carbon has a high solubility. Nonetheless, local epitaxial growth of diamond microcrystals on Ni has been demonstrated,³² though reports of continuous films are rare.

We conclude this section with mention of two alternative strategies which have been shown to yield oriented diamond films, *i.e.* films with a texture and a degree of crystalline order intermediate between that of a typical polycrystalline CVD diamond film and that of a genuine single crystal film. One is the bias-enhanced nucleation technique summarized earlier, by which it has proved possible to grow oriented diamond films, not only on single crystal $\beta\text{-SiC}$ (another scarce substrate material) but also, after an appropriate *in situ* carburization pre-treatment, on single crystal silicon.²⁵ Geis *et al.*³³ have followed a different philosophy. They painstakingly prepare a mosaic of appropriately oriented diamond seed crystals to act as the 'substrate' in their CVD reactor. Subsequent homoepitaxial growth leads to the gradual coalescence of the individual

growing islands and, ultimately, to a highly oriented CVD diamond film.

5 Present Applications and Future Prospects

In this Review we have attempted to provide a snapshot of progress to date in some of the many aspects of research in the area of CVD diamond films. Of course, it is also appropriate to ask how this research effort is feeding through into the market-place. Two areas of application are beginning to show strongly. One comes under the general title of thermal management. Natural diamond has a thermal conductivity roughly four times superior to that of copper, and it is an electrical insulator: it should therefore come as little surprise to learn that CVD diamond is now being marketed as a heat sink for laser diodes and for small microwave integrated circuits. The natural extrapolation of this use in circuit fabrication ought to be higher speed operation, since active devices mounted on diamond can be packed more tightly without overheating. Reliability can be expected to improve also since, for a given device, junction temperatures will be lower when mounted on diamond.

CVD diamond is also finding applications as an abrasive and as cutting tool inserts.^{23,24} In both this and the previous application, CVD diamond is performing a task that could have been fulfilled equally well by natural diamond if economics were not a consideration. However, there are many other applications at, or very close to, the market-place where CVD diamond offers wholly new opportunities. Wear resistant coatings are one such use. CVD diamond-coated drill bits, reamers, countersinks *etc.* are now commercially available for machining non-ferrous metals, plastics, and composite materials. Initial tests indicate that such CVD diamond-coated tools have a longer life, cut faster and provide a better finish than conventional tungsten carbide tool bits.

The phrase 'non-ferrous' is worth emphasizing here since it reminds us of one of the biggest outstanding challenges in the application of diamond film technology – whether as a wear-resistant coating or as a fine abrasive. In any application where friction is important the diamond-coated tool bit will heat up and, in the case of ferrous materials (be it the tool substrate or the workpiece) the diamond coating will ultimately react with the iron and dissolve. Thermal mismatch is another potential problem with diamond-coated tool bits in situations where frictional heating is important. For example, attempts at extending the effective working life of tungsten carbide tool bits by covering them with a wear-resistant film of CVD diamond have met with only limited success. This is not because of growth problems (it is perfectly possible to grow a film of CVD diamond on tungsten carbide substrates with 6% or 10% cobalt binder), but because the diamond film has a tendency to delaminate in order to relieve stresses arising as a result of the very different coefficients of thermal expansion of diamond and tungsten carbide. Hence the current interest in silicon nitride, a hard ceramic material with a smaller coefficient of thermal expansion, as a possible alternative substrate material for CVD diamond-coated cutting tools.

Because of its optical properties, diamond is beginning to find uses in optical components, particularly as protective coatings for IR-optics in harsh environments. Most IR windows currently in use are made from materials such as ZnS, ZnSe, and Ge, which, whilst having excellent IR transmission characteristics, suffer the disadvantage of being brittle and easily damaged. A thin protective barrier of CVD diamond may provide the answer, although it is more likely that future IR windows will be made from free-standing diamond films grown to a thickness of a few mm using improved high growth-rate techniques. However, a major consideration when using polycrystalline CVD diamond films for optics is the flatness of the surface, since roughness causes attenuation and scattering of the transmitted IR signal, with subsequent loss of image resolution. Hence the current interest in techniques for smoothing diamond films we

mentioned earlier. Several reviews considering the potential of CVD diamond in IR optics have appeared.^{35,36}

The possibility of doping diamond and so changing it from being an insulator into a semiconductor opens up a whole range of possible electronic applications.^{37,38} However, there are a number of major problems that need to be overcome if diamond-based electronic circuits are to be achieved. Principal among these is the fact that CVD diamond films are polycrystalline and hence contain grain boundaries, twins, stacking faults, and other defects, which all reduce the lifetime and mobilities of carriers. Active devices have been demonstrated using *homoepitaxially*-grown diamond on natural or synthetic diamond substrates but, to date, there have been no corroborated reports of heteroepitaxial growth of device-quality diamond on non-diamond substrates. This remains a major limiting factor in the development of diamond devices. Nevertheless, the effect of grain boundaries and defects upon electronic carriers in the very best polycrystalline diamond films remains to be ascertained and, clearly, this possible route to active diamond devices cannot yet be ruled out.

Another outstanding problem hindering potential diamond electronics is the inability to produce n-type doping. P-type doping is relatively straightforward, since addition of a few percent of B₂H₆ to the CVD process gas mixture is all that is required to incorporate B into the lattice. However, the close packing and rigidity of the diamond lattice makes doping with atoms larger than C very difficult. This means that the dopants which are routinely used to n-dope Si, such as P or As, cannot easily be used for diamond, and so alternative dopants, such as Li are being investigated.

One further difficulty that must be overcome if diamond devices are to be realized is the ability to pattern the diamond films into the required micron or even submicron geometries. Dry etching using O₂-based plasmas can be used, but etch rates are slow and the masking procedure complex. Alternative patterning methods include laser ablation,³⁹ or selective nucleation.⁴⁰ There are many variants of this latter process, but all involve trying to mask off certain areas of the substrate so allowing diamond to grow only in selected regions. A typical process scheme involves abrading a Si substrate, and then coating it with a thin layer of SiO₂. This oxide layer is then patterned using standard photolithographic and etching techniques to expose areas of Si. CVD diamond is then grown, nucleating preferentially on the abraded Si areas rather than the oxide mask. Subsequent removal of the oxide mask in a chemical bath results in a patterned diamond film on Si, as shown in Figure 12.

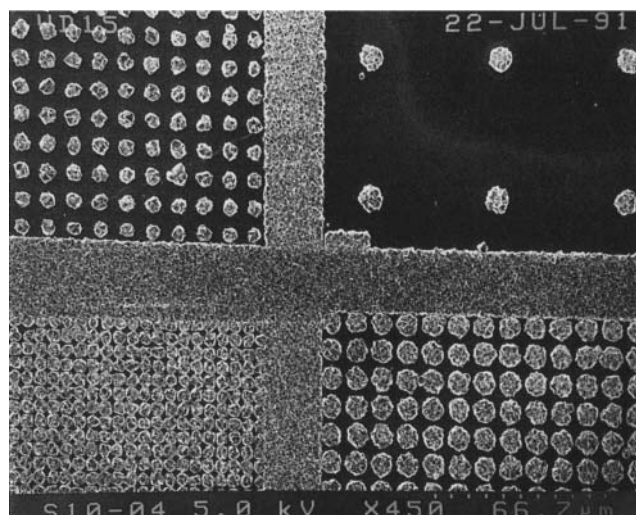


Figure 12 SEM showing patterned CVD diamond growth, using an oxy-acetylene flame, on a silicon substrate which had been pretreated as described in the text.

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Despite these difficulties, CVD diamond-based devices are gradually beginning to appear, albeit with imperfect characteristics. Negative electron affinity cold cathode devices, piezoelectric effect devices, radiation detectors, and even the first field effect transistors have all been reported recently, with the likelihood that some of the simpler devices will become commercially available in the near future.

Another interesting new development in diamond technology⁴¹ is the ability to deposit CVD diamond onto the outer surfaces of metal wires or non-metallic fibres (see Figure 13).

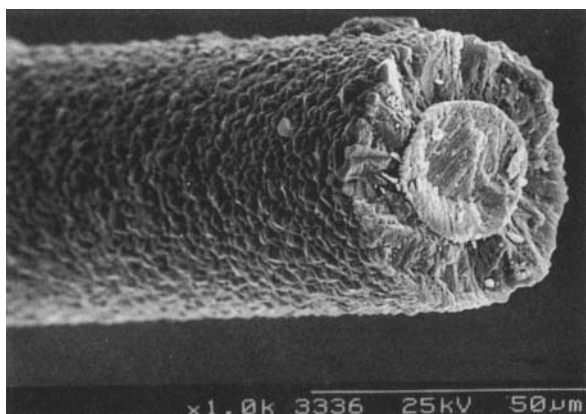


Figure 13 SEM of a section through a 25 μm diameter W wire that has been coated in diamond using hot filament CVD.

Such diamond-coated fibres show increased stiffness and strength over the non-coated fibres, although quantitative measurements of coated fibre properties have yet to be presented. If growth rates can be increased to economically viable levels, such diamond fibres may find uses as reinforcing agents in metal-matrix composites, allowing stronger, stiffer and lighter load-bearing structures to be manufactured for use in, say, aerospace applications.⁴¹ Furthermore, etching out the metal core of the diamond-coated wire using a suitable chemical reagent yields free-standing diamond tubes, or hollow diamond fibres (see Figure 14). These too have potential applications for reinforcing smart composites, since the hollow cores may provide conduits for sealant, coolant, or sensors to be placed into the reinforced structure.

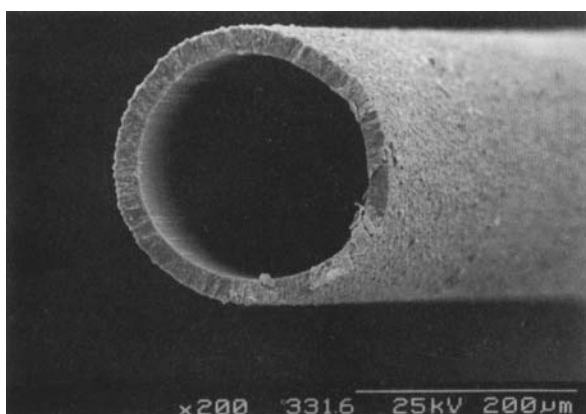


Figure 14 SEM of hollow diamond fibre made by coating a 200 μm diameter W wire with a $\sim 20 \mu\text{m}$ thick film of diamond and then etching away the metal core with hot hydrogen peroxide solution for 1 hour.

6 Summary

Most of the scientific research effort into CVD diamond technology has been concentrated within the past five years yet,

already, some of the more obvious applications, such as cutting tools and heat sinks, have reached the market-place. With the current rapid rate of progress, it should not be too long before this fledgling technology begins to make a significant impact in many areas of modern life. However, several issues need to be addressed before this can happen. Growth rates need to be increased (by one or more orders of magnitude) without loss of film quality. Deposition temperatures need to be reduced by several hundred degrees, allowing low melting point materials to be coated and to increase the number of substrates onto which *adherent* diamond films can be deposited. A better understanding of the nucleation process is required, hopefully leading to an elimination of the poorly controlled pre-abrasion step. Substrate areas need to be scaled up, again without loss of uniformity or film quality. For electronic applications, single crystal diamond films are desperately needed, along with reliable techniques for patterning and controlled n- and p-type doping.

At present, there is a huge amount of work being done throughout the world on solving these issues, and progress is being made seemingly on a daily basis. If this continues, the future for CVD diamond looks bright indeed.

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