Diamond chemical vapour deposition

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Diamonds have many commercially useful properties, and finding a quick way of making high quality 'industrial' versions has occupied scientists for many years.

Diamonds (their name is derived from the Greek adamas, meaning 'invincible') receive specific mention in Roman literature dating from as long ago as the first century AD, and have held special appeal both for scientists and the general public since at least that time. As the tetrahedrally (or sp³) coordinated allotrope of carbon, diamond is the hardest known material. It also has the highest thermal conductivity at room temperature, the lowest thermal expansion coefficient, excellent insulating properties, very low friction and broad optical transparency (from the infrared to the deep ultraviolet).

It occurs naturally, crystallising in this form deep in the Earth under conditions of extreme temperature and pressure. Indeed, for centuries this geological route was the only known source of diamond. However, the mid-1950s saw the introduction of the first high pressure high temperature synthetic methods, in which diamond is crystallised out of metal solvated carbon at pressures of about 80kBar and temperatures of around 2000°C. These 'industrial diamonds' have been made commercially in this way for more than three decades.

Using chemical vapour deposition

The discovery (which can be traced back to the pioneering work of John Angus at Case Western Reserve and Boris Spitsyn in Moscow and their respective colleagues) that polycrystalline diamond films can be produced by a variety of chemical vapour deposition techniques using, as process gases, nothing more exotic than a hydrocarbon (for example, methane) and hydrogen, has sparked another huge upsurge of scientific interest in this material. Chemical vapour deposition (CVD), as the name implies, involves gas phase chemistry in the vicinity of a surface, which causes deposition onto that surface. All known CVD processes producing diamond films need some means of activating the gas phase carbon-containing precursor molecules. In a simple laboratory experiment, this may involve nothing more than exposing a mixture of methane in excess H₂ (typical mixing ratio 1:100, and pressures of about 20 Torr) to a hot filament (such as tungsten or tantalum, heated to around 2300°C). The hot metal surface catalyses H₂ decomposition, and the important reactive carbon-containing radical species are formed by subsequent hydrogen atom abstraction reactions. Commercially, plasmas (either microwave or direct current) are the preferred means of activation — power consumption is higher, but so too is the growth rate. Figure 1 shows a 6kW microwave reactor in operation at Heriot-Watt University. The largest of such systems can deposit CVD diamond over areas of up to 300cm², at growth rates approaching 10μm/hr.

The past decade has seen numerous studies of many aspects of the CVD process, as a result of which many (but by no means all) of the subtleties are now recognised. One key requirement is that the substrate itself be hot (700–1100°C). This is quite a serious limitation, since it precludes many important substrate materials (for example, plastics, glasses and aluminium) which could usefully be protected with a hard wear-resistant coating.

The hydrogen atoms are now known to have several other important functions. The CVD process deposits a mixture of both diamond (sp³) and graphitic (sp²) carbon. Atomic hydrogen etches any graphitic carbon much faster than the sp³ bonded carbon atoms, ensuring that the final product is diamond. Hydrogen atoms also terminate 'dangling' bonds on the growing diamond surface, maintaining the necessary tetrahedral coordination and preventing reconstruction to graphitic carbon. At the relevant substrate temperatures hydrogen atoms can also abstract individual surface terminating hydrogen atoms. The resulting deut-
gling bond can either be re-
terminated by another
hydrogen atom incident
from the gas phase (in
effect a null result, and the
most likely outcome) or
bond to a carbon contain-
ing radical — thereby
extending the carbon net-
work.

Clearly, for successful
diamond CVD an optimum
balance between the vari-
ous gas phase and gas-sur-
face addition and abstrac-
tion processes has to be
achieved. This is done
using, as variables, tempe-
ration, gas mixing ratio, pressure, flow rate and power input
(since it affects the extent of reagent dissociation). There is one
other important trick. Like any crystallisation process, diamond
CVD can be enhanced by encouraging the nucleation step. In
the laboratory, this is often achieved simply by pre-abrading the
surface to be coated with, for example, fine diamond grit. More
reproducible methods designed to achieve the same end have
now been developed for most microwave plasma enhanced CVD reactors. These rely on ‘bias enhanced nucleation’ (BEN),
introduced by S Yogo and co-workers in Tokyo,4 and generally
involve a preliminary step in which ions in the plasma are ac-
celerated into the substrate — causing surface damage and/or depo-
sition of a thin interfacial layer before the regular growth step.5

The applicability and impact of CVD diamond as a ‘new mate-
rial’ will largely depend on the continuing efforts of scientists to
find ways of improving growth rates further, preferably at lower
substrate temperatures, without compromising film ‘quality’.

Quality control
Quality, as applied to CVD diamond films, is an important but
rather imprecisely defined concept. One popular diagnostic is

laser Raman spectroscopy. As Figure 2 shows, the Raman spec-
trum of a good quality diamond is dominated by a single sharp
line centred at ca 1332 cm⁻¹, and is very dif-
f erent from that of graphite or other amorphous forms of car-
bon.6 The exact wavenumber of the diamond peak, and its
linewidth, both give an indication of the sign and level of any
residual stress in the sample.

Unfortunately, using Raman spectra to measure the quality of
a CVD diamond film (for example by try and define an sp²/sp³
ratio) is fraught with difficulties. First, it is important to specify
the excitation wavelength used when recording the spectrum,
since the relative Raman cross-sections for the various forms of
carbon show a marked dependence on wavelength. If the exci-
ting laser is polarised, one should also check whether the Raman
spectrum depends on the sample orientation. Second, since
CVD diamond films are polycrystalline, they consist of abutting
crystals of carbon which inevitably must be grain boundaries. This is clear from scanning electron microscope (SEM) images of as-grown CVD diamond films (see Figure 3).

Confocal Raman microscopy (where the exciting laser beam is
focused to a spot size which is small compared with the aver-
age crystallite dimension) shows marked-
ly different Raman spectra depending on
exactly which part of the film is illuminat-
ed. This provides one means of distin-
guishing, and mapping out, regions of
good ‘quality’ diamond in a polycrys-
talline sample. The irradiated area in
more traditional Raman spectroscopy, however, will span many crystallites and
intervening grain boundaries, and the
resulting spectrum may therefore give a
better picture of the average film quality.

Even this result should be treated with
some caution, however, since it will only
be valid for the localised region from
which the spectrum was obtained. The
Raman spectrum from a different region
of the same film will not be the same, as
the deposition conditions (like tempera-
ture and incident gas composition) and
thus the growth rate and, quite possibly,
the resulting film morphology will have
been slightly different.

The SEM images in Figure 3 give an
idea of the range of morphologies achiev-
able by appropriate choice of deposition conditions. Nonetheless, few will argue about ‘quality’ in the case of a CVD diamond film which, after polishing, has the optical transparency of the specimen shown in Figure 4.

Making use of CVD diamond films

The diamond in Figure 4 highlights one obvious application for CVD diamond — as a window material, with particular appeal to those seeking good transmission in the infrared (IR) and X-ray regions. Applications requiring good IR transparency include a wide range of devices (both civilian and military) designed to detect thermal radiation, while X-ray transparency is already proving useful in protecting soft X-ray detectors and in high-resolution X-ray lithography. Given diamond’s hardness and exceptional resistance both to wear and to solvent attack, there is also great interest in using CVD diamond films as thin protective coatings for other (more readily available but softer) IR transmitting window materials like Ge, ZnS, ZnSe and KBr. Note, however, that the free standing film shown in Figure 4 has been polished, after deposition, to give a smooth surface finish. The normal as-grown film has a rough surface (recall Figure 3) which will cause attenuation and scattering of any transmitted IR signal and consequent loss of image resolution. This is just one reason for the continued drive for large area, single crystal diamond films by, for example, heteroepitaxy. Many of the envisaged electronic applications of CVD diamond will also need this sort of material.

Other applications of CVD diamond which are already in the marketplace make use of its exceptional hardness and durability, such as abrasives or as coatings on cutting tool inserts. CVD diamond coated drill bits, reamers and countersinks, for example, are now commercially available for machining non-ferrous metals, plastics and composite materials. Tests to date indicate that these CVD diamond-coated tools have a longer life, cut faster and provide a better finish than conventional tungsten carbide tool bits. The term ‘non-ferrous’ is worth emphasising here, since it is a reminder of one of the biggest outstanding challenges in the application of diamond film technology — whether 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. The exploration of barrier layer materials that might allow iron and steel machine parts to be coated with diamond remains a huge research area.

Diamond is also the stiffest known material, and this property is being exploited in Bristol where we deposit CVD diamond onto the outer surfaces of metal wires or non-metallic fibres (see Figure 5). Such diamond coated fibres have modulus values close to that of diamond, giving them an outstanding stiffness/weight ratio. If growth rates can be increased to economically viable levels, such diamond fibres may find uses as reinforcing agents in metal matrix composites, allowing stiffer and lighter load-bearing structures to be made for use in, say, aerospace applications.

The room temperature thermal conductivity of natural diamond is roughly four times that of copper, and it is an electrical insulator. Hence CVD diamond films are now being used as heat spreaders 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.

The possibility of doping diamond and so changing it from being an insulator into a semiconductor opens up a whole range of potential electrochemical and electronic applications. Note that several major problems need to be overcome if diamond-based electronic circuits are to be achieved. First, CVD diamond films are polycrystalline and hence contain grain boundaries, twins, stacking faults and other defects, all of which 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, corroborated reports of heteroepitaxial growth of device quality diamond on non-diamond substrates remain very rare.

Another problem hindering potential diamond electronics is the difficulty of n-type (electron conducting) doping. P-type (hole conducting) doping of diamond is relatively straightforward; addition of a few parts per million of a boron-containing gas (for example B,H,) to the CVD process gas mixture readily incorporates boron within the lattice. However, the close packing and rigidity of the diamond lattice makes doping with atoms larger than carbon very difficult. This means that the dopants used routinely to n-dope silicon, such as phosphorus or arsenic, cannot easily be used for diamond. Alternative dopants, such as lithium are currently being investigated.

Despite these difficulties, CVD diamond-based devices are beginning to appear, albeit with imperfect characteristics. Piezoelectric effect devices, radiation detectors, and even the first field effect transistors have all been reported recently by groups in the US (for example SI Diamond, Kobe Steel), Japan (such as Sumitomo) and Europe (for example Philips in Aachen, as well as AEA Technology at Harwell and University College, London), with the likelihood that some of the simpler devices will become commercially available in the near future.

Another possible application which is causing much current interest is the idea of using diamond as an electron emitter in flat
SEM of a section through a 125µm diameter tungsten wire that has been coated in diamond using hot filament CVD

Panel displays. When diamond is negatively biased in a vacuum, electrons are ejected from its surface. This process is also common to most metals, but in metals the electrons have to overcome an energy barrier (the work function) to escape from the surface.\textsuperscript{21-23} In diamond this barrier has been measured and found to be very small, maybe even negative.\textsuperscript{24,25} This has led to the term 'negative electron affinity'. In practice, this means that devices based on diamond's electron emission properties could consume very low power levels, making them extremely efficient.

The electrons emitted from the surface are accelerated using a positively biased grid, and then strike a target. The target material determines what type of device is made. If the target is a phosphor screen, light will be emitted where the electrons strike it — the basis for a flat panel display (see Figure 6). Each emitting diamond crystal, or group of crystals, would constitute a 'pixel' on the screen.

Relative to liquid crystal displays — their major competitors — diamond cold cathode emission displays are expected to have a higher brightness, a larger viewing angle, and most importantly, be readily scaled up to large (perhaps m\textsuperscript{2}) sizes. Alternatively, if the target material is a conductor capable of collecting current, the emission device could form the basis of an ultra-fast switch, thus suggesting the possibility of faster computers.

In conclusion, the CVD diamond industry is now beginning to develop quite rapidly. The main products at present are cutting tool inserts, heat-sinks and infra-red windows. Electronic applications are starting to appear, but the dream that a 'diamond age' might supersede the present 'silicon age' in active electronics still seems way off. Outstanding issues at the more fundamental research level include improving growth rates, and achieving uniform deposition over larger surface areas and, preferably, at lower deposition temperatures. The mismatch between diamond's coefficient of thermal expansion and those of all other substrate materials, and its adverse consequences for adhesion, is still a problem; so, too, is the limited number of substrate materials compatible with the process conditions currently required for CVD diamond growth. Single crystal diamond growth remains a huge challenge, as does n-type doping. Everything considered, the prospects for CVD diamond look bright, while outstanding challenges look just that — challenging!

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References

10. Wild, C., et al., ibid., 1993, 2, 158

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