CHAPTER 6

Chemical Vapour Deposition – A Route to Microcrystalline, Nanocrystalline, Ultrananocrystalline and Single Crystal Diamond Films

Paul W. May

School of Chemistry, University of Bristol,
Bristol BS8 1TS, United Kingdom

Paul.May@bristol.ac.uk

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1. INTRODUCTION

Apart from their appeal as gemstones [1], diamonds possess a remarkable range of physical properties [2]. Indeed, a glance at any compendium of material data properties will prove that diamond is almost always 'the biggest and best'. Among other properties, diamond is the hardest known material, has the highest thermal conductivity at room temperature, is transparent over a very wide wavelength range, is the stiffest material, the least compressible, and is inert to most chemical reagents. With such a wide range of exceptional properties, it is not surprising that diamond has sometimes been referred to as 'the ultimate engineering material'.

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 200 years that diamond is composed solely of carbon [3], and many attempts were made to synthesize diamond artificially using graphite as a starting material. This proved extremely difficult, mainly because at room temperature and pressure, graphite is the thermodynamically stable allotrope of carbon. Although the standard enthalpies of diamond and graphite only differ by $2.9 \, kJ \, mol^{-1}$ [4], a large activation barrier separates the two phases preventing interconversion between them at room temperature and pressure. Ironically, 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. Thus, diamond is said to be metastable, that is, kinetically stable but not thermodynamically stable.

To overcome these problems, researchers realized 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 idea underpins the so-called *high-pressure high-temperature* (HPHT) growth technique [2], first marketed by General Electric, and which 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, heated to over 2000 K in the presence of a suitable metal catalyst, and left until diamond crystallizes.

The diamond crystals this produces 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. Recently, the process has been improved to such a degree that gemstone quality diamonds have been made [5]. These 'cultured diamonds' are now available in colourless or 'fancy' yellow, and are being sold commercially for the jewellery market (albeit at a much lower price than natural diamonds). However, the drawback of the HPHT method is that it still produces diamond in the form of single crystals ranging in size from nm to mm, 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 - a diamond *thin film*.

Rather than try to duplicate nature's method for creating diamond (as in the HPHT method), the experiments of Eversole [6] in 1958 and Deryagin et al. [7] a decade later, used the thermal decomposition of carbon-containing gases under reduced pressure to grow diamond on the surface of natural diamond crystals heated to 900°C. However, the rate of growth in these early experiments was low, since graphite was co-deposited with the diamond leading to impure mixed phases. The breakthrough came in the late 1960s, when it was discovered that the presence of atomic hydrogen during the deposition process would lead to preferential etching of the graphite, rather than diamond [8,9]. Subsequent Russian work showed that such chemical vapour deposition (CVD) techniques could be used to grow diamond onto *non-diamond* substrates [10,11]. In 1982, Japanese researchers brought all these findings together to build a 'hot filament reactor', which grew good quality diamond films on non-diamond substrates at significant rates ($\sim 1 \ \mu m \ h^{-1}$) [12,13]. The following year the same group reported another method for achieving diamond growth, using a microwave plasma reactor [14,15]. This series of discoveries stimulated worldwide interest in diamond CVD, in both academia and industry, which continues to the present day [16,17,18].

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 activation can involve thermal methods (*e.g.* a hot filament, similar to that found in a light-bulb), electric discharge (*e.g.* DC, RF or microwave), or a combustion flame (such as an oxyacetylene torch). While each method differs in detail, they all share a number of features in common. For example, growth of diamond (rather than graphite) normally requires that the precursor gas (usually CH_4) is diluted in an excess of hydrogen, in a typical mixing ratio of 1%vol. CH_4 at pressures around 10-50 Torr. Also, the temperature of the substrate is usually greater than 700°C to ensure the formation of diamond rather than amorphous carbon. A detailed review of the various methods and apparatus used for fabricating diamond can be found in the book by Dischler and Wild [19].

The various CVD methods allow a range of different diamond morphologies to be deposited, and these can be categorised by the shape and size of the crystallites which comprise the final film. It is common to describe a CVD diamond film by one of four broad categories, based upon the size of the crystallites. At one growth extreme there is *single crystal diamond* (SCD), in which the film is made up of a single-phase, continuous layer of crystalline diamond - effectively one large crystal - usually grown onto a gemstone or HPHT diamond template. At the other extreme is so called *ultrananocrystalline* diamond (UNCD), which is a composite material composed of irregular diamond grains <5 nm in size embedded within a sp^2 carbon matrix. Between these two extremes, there are polycrystalline films with diamond grain sizes of between 10 nm to a few hundred nm, called *nanocrystalline* diamond (NCD), and films with grain sizes of 1 μm to ~ 1 mm, usually

called *microcrystalline* diamond (MCD). In this review, we shall compare the deposition methods, growth chemistry and properties of these different varieties of diamond films, and attempt to provide a coherent picture of the science underlying diamond CVD.

2. MICROCRYSTALLINE DIAMOND FILMS

MCD films were the first type of diamond to be successfully deposited using CVD, and consequently they are the most studied of all the diamond film variants [16].

2.1. GROWTH CHEMISTRY

The complex chemical and physical processes which occur during diamond CVD comprise several different but interrelated features, and are illustrated in Fig.1. The process gases first mix in the chamber before diffusing toward the substrate surface. On the way they pass through an activation region (*e.g.* a hot filament or electric discharge) which causes molecules to fragment into reactive radicals and atoms, frequently creates ions and electrons, and heats the gas up to temperatures approaching a few thousand kelvin. Beyond the activation region, these reactive fragments cool, but continue to mix and undergo a complex set of chemical reactions until they strike the substrate surface. At this point, the species can either adsorb and react with the surface, desorb again back into the gas phase, or diffuse around close to the surface until an appropriate reaction site is found. If a surface reaction occurs, one possible outcome, if all the conditions are suitable, is diamond.
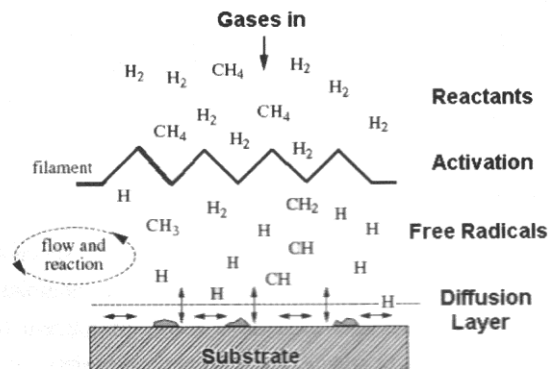
Fig. 1. A schematic diagram illustrating the physical and chemical processes occurring during diamond CVD.

Over the past 20 years, there have been a large number of studies of the gas phase chemistry during growth [20,21], and we are now beginning to obtain a clearer picture of the important principles involved. The first clue was obtained from the 'Bachmann triangle diagram' [22], which is a C–H–O composition diagram based upon over 70 deposition experiments in different reactors and using different process gases. Bachmann found that independent of

deposition system or gas mixture, it was simply the relative ratios of C, H and O which determined if diamond would be deposited. This implied that diamond growth was independent of the nature of the gas phase precursors, and that the gas phase chemistry was so rapid it simply and effectively broke down the constituent gases to smaller, reactive components.

It is now believed that atomic hydrogen is the most critical component in the gas phase mixture, since it drives the whole chemical system. Atomic hydrogen is produced in the hot gas region, either by thermal decomposition of H_2 on a hot filament surface or by electron impact dissociation of H_2 in a plasma system. A high concentration of atomic H is crucial for a number of main processes. Although the bulk of diamond is fully sp^3-bonded, at the surface there is effectively a 'dangling bond', which needs to be terminated in some way in order to prevent cross-linkage, and subsequent reconstruction of the surface to graphite. This surface termination is performed by hydrogen, which keeps the sp^3 diamond lattice stable. During diamond growth, some of these H atoms need to be removed and replaced by carbon-containing species, and the most crucial roles for H are:

(i) Atomic H etches graphitic sp^2 carbon many times faster than diamond-like sp^3 carbon. Thus, the H atoms serve to remove back to the gas phase any graphitic clusters that may form on the surface, while leaving the diamond clusters behind.

(ii) H atoms react with gas phase neutral species such as CH_4 to create reactive radicals, such as CH_3, which can then attach to suitable surface sites.

(iii) Reactive H atoms close to the surface can quickly bond to any excess dangling bonds, so preventing surface graphitization.

(iv) H atoms are efficient scavengers of long-chained hydrocarbons, breaking them up into smaller pieces. This prevents the build-up of polymers or large ring structures in the gas phase, which might ultimately deposit onto the growing surface and inhibit diamond growth.

There have been many suggestions for the diamond growth species, including C, CH, C_2, C_2H, CH_3, C_2H_2, CH_3^+, and even diamondoids, such as adamantane. However, since diamond can be grown in systems which have few ions present (e.g. hot filament CVD reactors), this suggests the growth species must be neutral moiety. A number of studies have been performed to try to identify the growth species [20], and the general consensus is now that the bulk of the evidence supports CH_3 as being the most important radical.
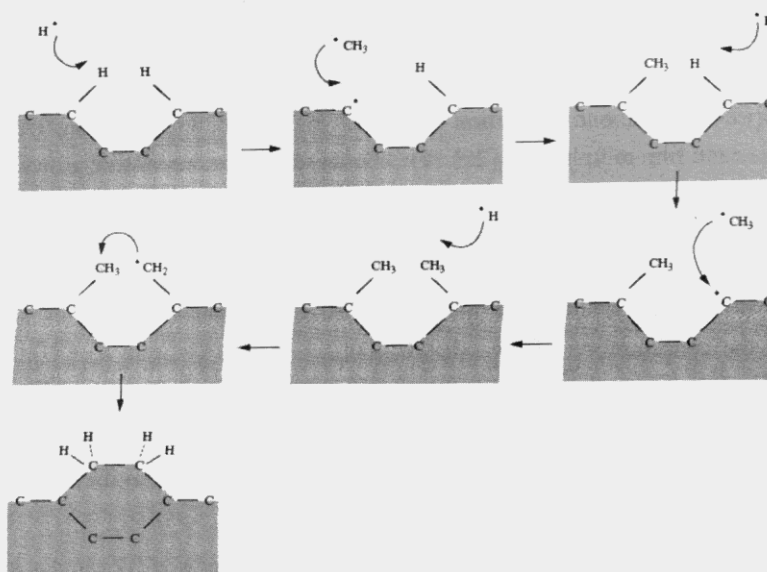
Fig. 2. A schematic diagram of a simplified reaction scheme occurring at the diamond surface leading to stepwise addition of CH₃ species and diamond growth, via a sequence of H atom abstraction reactions.

The overall picture which emerges is that during CVD diamond growth the diamond surface is nearly fully (~90%) saturated with hydrogen. This coverage limits the number of sites where hydrocarbon species may adsorb, and also blocks migration sites once they are adsorbed. A schematic diagram of one of the possible resulting processes is shown in Fig.2. Atomic H abstracts a surface H to form H_2, leaving behind a reactive surface site (or 'dangling bond'). The most likely fate for this surface site is for it to react with another nearby gas phase H atom, returning the surface to its previous stable situation. However, occasionally a gas phase CH_3 radical (or, less often, another CH_x species) can collide and react with the surface site, effectively adding a carbon to the lattice. This process of H abstraction and methyl addition may then occur on a site adjacent to the attached methyl (or elsewhere on the surface and then migrate to this position). A further H abstraction process on one of the chemisorbed groups creates a radical, which attacks the other nearby carbon group to complete the ring structure, locking the two carbons into the diamond lattice. Thus, diamond growth can be considered to be a stepwise addition of carbon atoms to the existing diamond lattice, catalysed by the presence of excess atomic H. In oxygen-containing systems, it is believed that the OH radical plays a similar role to atomic H, except that it is more effective at removing graphitic carbon, leading to higher growth rates and better quality films.

It should be emphasized that the picture outlined above is a very simplified description of diamond CVD growth. The exact mechanism is dependent upon the gas phase chemistry, the reactor used and even the nature of the diamond crystal surface used [20,23,24].

2.2.   CRYSTAL SIZE AND FILM MORPHOLOGY

Recently, a model for diamond growth has been proposed which ties together many of the observed aspects of diamond deposition under varying conditions, including growth rates, crystallite size and film morphology [25]. The model involves competitive growth by all the C_1 radical species that are present in the gas mixture close to the growing diamond surface (*i.e.* C atoms, CH, CH_2 and CH_3). Previous models [20,26] concentrated mainly on CH3 since this is the dominant reactive hydrocarbon radical in standard H2-rich CVD gas mixtures. However, modelling of the gas phase region showed that for some CVD conditions, the concentration of the other C_1 radical species (written as CH_x, $0<x<3$), in particular C atoms, near the growing diamond surface can become a significant fraction (~5%) of that of CH_3, and so may contribute to the growth process.

Different growth behaviour results from addition of CH_3, compared to that from addition of any of the other C_1 species. Considering each group in turn:

(i) CH_3: Since, for most CVD conditions, the concentration of CH_3 is usually much larger than the other growth species, CH_3 will be the dominant growth species, and will add to suitable dangling bonds on the surface. However, since methyl is a relatively large group, only a small percentage of the available dangling bond sites are suitable for direct CH_3 addition due to steric hindrance, and this limits the growth rate. Once attached to the surface, hydrogen abstraction reactions convert these newly-bonded CH3 groups into bridging CH_2 groups, and repetition of this process allows the CH_2 groups to migrate across the surface until they meet a step-edge, at which point they will extend the diamond lattice leading to large regular crystals.

(ii) CH_x, $0<x<3$: As well as CH_3 addition, other CH_x species (especially atomic C) can also be adsorbed on the surface. Due to their smaller size, these species have less steric hindrance than CH_3 and can add to many more of the surface dangling bonds. Thus, even if, as is usually the case, these species are much lower in concentration than CH_3 (*e.g.* $[CH_x]/[CH_3]\sim0.1$), their contribution to the growth rate can become important since they can add to the surface far more frequently. Moreover, when one of these CH_x species adds to a surface dangling bond, the resulting adduct structure would remain reactive since it would still contain (at least one) dangling bond(s) - making this a very high energy site. The most likely fate for such reactive surface sites - considering that they are surrounded by a gas mixture containing a high concentration of H atoms and H2 molecules - is that they are rapidly hydrogenated to CH_2. If so, the subsequent reactions will be indistinguishable from attachment and growth by methyl, and this route would also lead to propagation of the diamond lattice. However, other possible fates for the reactive surface adducts are reaction with other gas-phase hydrocarbon radicals CH_x or restructuring of the surface. This would interrupt the smooth propagation of the diamond structure, and introduce a surface defect, which would not necessarily have the same symmetry as the underlying lattice. In other

words, this would be a site for renucleation, and growth would then continue outwards from this point, but in a different direction to the underlying crystallite.

Thus, depending upon the gas mixture and reaction conditions used, the relative concentrations of each of these species close to the growing diamond surface (*e.g.* [H]/[CH$_3$], [CH$_x$]/[CH$_3$]) together with the absolute concentration of H, determine the probability of a renucleation event occurring, and hence the average crystal size, $<d>$, in the film.

In reactors with *very* high power density, such as those found in DC arc jets or at high MW powers and pressures, the concentration of gas phase C$_1$ species can equal or even exceed that of [CH$_3$]. However, in these cases, the [H] is also extremely large, and so any C$_1$ species that attach to the surface are rapidly hydrogenated to CH$_2$ *before* they have chance to restructure the surface. This allows rapid growth (since *every* C$_1$ species contributes to growth), as well as essentially no renucleation, leading to large crystal sizes – including SCD diamond (see Section 3.2).

For more standard CVD conditions, there will typically be high [CH$_3$] compared to the other C$_1$ species, plus a moderately high [H]. So renucleation will only occur rarely, allowing the films to grow smoothly for many tens of μm and produce a MCD film.

As the ratio of [H]:[CH$_x$] drops, the renucleation rate increases, the crystallite size drops into the nm region, so we get NCD, and ultimately, UNCD (see Fig.3).
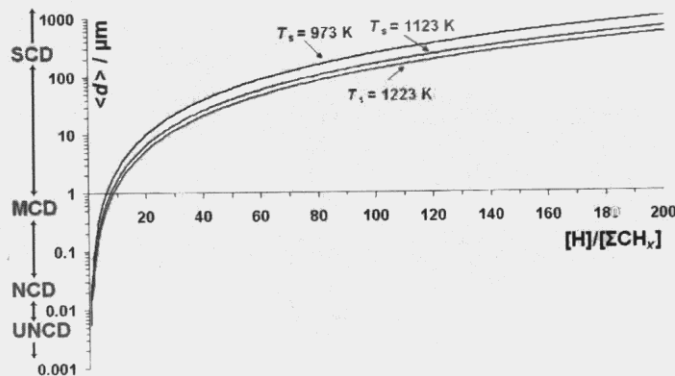

Fig. 3. A plot of average CVD diamond crystal size $<d>$ against the ratio of the concentrations of atomic hydrogen to the sum of those for all the other hydrocarbon radicals ΣCH_x (x<4) close to the growing diamond surface, for three substrate temperatures, T_s, based on the growth model in ref.[25], assuming moderate values of [H]. Note that experimentally it is difficult to vary T_s independently of [H]/[ΣCH$_x$], however this plot serves to illustrate the expected trends. Extrapolation below $<d>$ = 2 nm is unreliable since either [H] becomes so small that diamond growth ceases or [ΣCH$_x$] becomes so large that films become graphitic. Extrapolation vertically will eventually lead to SCD, which will occur at [H]/[ΣCH$_x$] ratios (>100) or at extremely high [H].

2.3.   THE α-PARAMETER

When describing a crystal lattice, it is common to refer to the different faces of the crystal by using an *x,y,z* coordinate system. For diamond, the three most important surfaces for adsorption and growth are the square (100) surface, the triangular (111) surface, and the less well-defined (110) surface. The measured kinetics for microcrystalline diamond growth on each of these three surfaces have growth rates which depend differently upon temperature and gas composition. This feature of the kinetics can be used to control the morphology of the crystals obtained, which is characterized by the ratio of the <100> to the <111> growth rates. The so-called α-parameter is often used to determine the shape of single crystals [27], and is given by

$$\alpha = \sqrt{3}\left(\frac{v_{100}}{v_{111}}\right)$$

where v_{100} and v_{111} are the growth velocities in the <100> and <111> directions, respectively. For single crystals, $\alpha = 1$ for cubes, $\alpha = 3$ for octahedra, and α is a value between 1 and 3 for cubo-octahedra. For microcrystalline films, α controls the film texture, and by carefully controlling α, films can be grown with predominantly triangular (111) facets, square (100) surfaces, or random morphologies (see Fig.4).
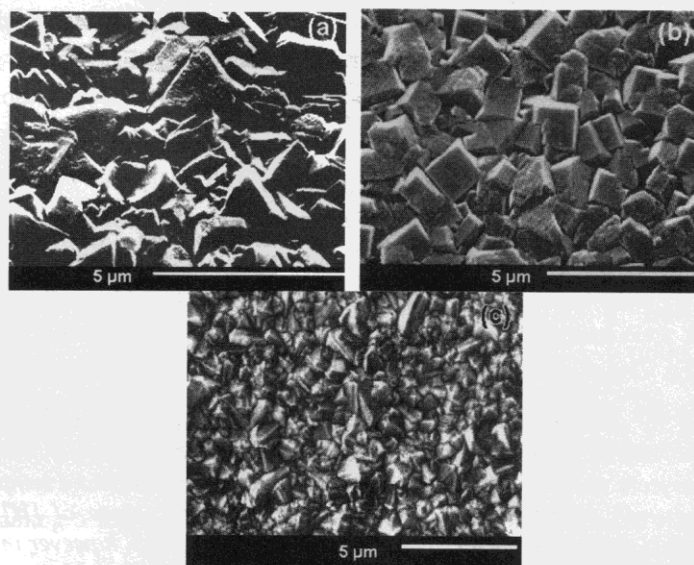

Fig. 4.   Scanning electron micrographs (SEMs) of different MCD film morphologies produced by CVD. (a) triangular (111) facets, (b) square (100) facets, (c) random facets.

2.4.   THE SUBSTRATE MATERIAL

It is possible to grow diamond layers onto existing diamond substrates. Small HPHT samples, or diamond gemstones have been used in an attempt to enlarge these diamonds (see

Section 3), and this is called *homoepitaxial* growth. However, from a technological point of view it is often more desirable to put a diamond coating onto a non-diamond substrate material (*heteroepitaxial* growth). Most of the MCD films deposited by CVD to date have been grown on single-crystal Si wafers, mainly due to the availability, low cost, and favourable properties of Si wafers. Other possible substrate materials must, however, satisfy a number of important criteria. First, the substrate must have a melting point higher than the temperature required for diamond growth (normally greater than 700°C). This precludes the use of existing CVD techniques to coat low-melting-point materials, like plastics, aluminium, some glasses, and electronic materials such as GaAs.

Another criterion resulting from the high growth temperature is that the substrate material should have a thermal expansion coefficient comparable to that of diamond. This is necessary in order to prevent significant compressive stresses from the shrinking substrate upon cooling, which may lead to bowing of the sample, and/or cracking, flaking or even delamination of the entire film.

In order to form *adherent* films, it is a requirement that the substrate material be capable of forming a carbide to a certain extent. This is because diamond CVD on non-diamond substrates usually involves the formation of a thin carbide interfacial layer, upon which the diamond then grows. The carbide layer can be pictured as the 'glue' which promotes growth of diamond and aids its adhesion by (partial) relief of stresses at the interface (caused by lattice mismatch or substrate contraction). If there is no carbide layer (*e.g.* for materials such as Cu, Sn, Pb, Ag and Au, as well as non-metals such as Ge, sapphire, alumina) the diamond layer will simply delaminate upon cooling. In contrast, materials which have too great an affinity for carbon, tend to 'dissolve' any carbon species that adsorb on their surface (at the high deposition temperatures used in CVD), to form a solid carbide layer which increases in thickness as deposition continues. Diamond growth only begins after the substrate is saturated with carbon, and this can dramatically affect the physical properties of the resulting composite. Metals where this is significant include Pt, Pd, Rh, Ni, Ti and Fe. Iron is of particular concern, because this means that, at present, all industrially important ferrous materials (such as iron and stainless steel) cannot be diamond-coated using simple CVD methods. Experiments to lower the deposition temperature using different gas chemistries [28,29], or to protect the substrate surface using barrier layers [30,31], may provide solutions to growing MCD films on these more problematic substrate materials.

2.5.   NUCLEATION

Growth of diamond begins when individual carbon atoms nucleate onto the surface in such a way as to initiate the beginnings of an sp^3 tetrahedral lattice. When using natural diamond substrates, the template for the required tetrahedral structure is already present, and the diamond lattice is just extended atom-by-atom as deposition proceeds. But for non-diamond substrates, there is no such template for the C atoms to follow, and those C atoms that deposit in non-diamond forms are immediately etched back into the gas phase by reaction with atomic H. As a result, the initial induction period before which diamond starts to grow can be prohibitively long (hours or even days).

To combat this problem, the substrate surface often undergoes a pre-treatment prior to deposition in order to reduce the induction time for nucleation and to increase the density of nucleation sites. This pre-treatment can involve a number of different processes. The simplest is abrasion of the substrate surface by mechanical polishing using diamond grit ranging in size from 10 nm to 100 μm. It is believed that such polishing aids nucleation by either (a) creating appropriately-shaped scratches in the surface which act as growth templates, or (b) embedding nm-sized fragments of diamond into the surface which then act as seed crystals, or (c) a combination of both. An example is given in Fig.5, which shows the initial stages of nucleation, with individual diamond crystallites growing in scratches on the surface. Another, better-controlled version of pre-abrasion is to use ultrasonic agitation to polish the substrate while it is immersed in a slurry of diamond grit in a suitable liquid (water, methanol, *etc.*).
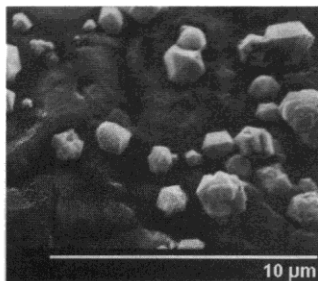

Fig. 5. An SEM showing the initial stages of diamond nucleation on a non-diamond surface (Ni metal), with small randomly oriented crystallites beginning to grow in the cracks on the surface resulting from manual abrasion.

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 diamond for applications in, say, the electronics industry, where circuit geometries are frequently on a submicron scale. Furthermore, such mechanical damage to the surface necessarily results in diamond nucleating in random directions, and so leads to randomly oriented films (see Fig.4(c)).

These worries have led to a search for more controllable methods of enhancing nucleation, such as *bias-enhanced nucleation* (BEN) [32,33], whereby a negative potential (typically 100–200 V) is applied to the substrate for the first few minutes of the deposition process. This is believed to accelerate carbon-containing ions onto the substrate, causing them to sub-plant beneath the surface and create a carbon-rich layer in the topmost few layers of the substrate. This increases the initial nucleation rate, and allows the resulting diamond film to register with the underlying substrate lattice to a much greater extent. If BEN is employed together with growth conditions which favour one particular orientation, highly textured films can be produced which are very closely aligned to the lattice of the underlying substrate (see Fig. 8(e)). This approach can make "quasi-single-crystal" diamond without using a single crystal diamond substrate.

A recent scheme - which aims to make true heteroepitaxial diamond - involves the use of thin buffer layers of iridium sputtered onto various substrates. Iridium has a much closer lattice match to diamond than any other material used to date [34], allowing the diamond nuclei to register with the lattice and grow in the same orientation. However, a complex multi-stage growth process is required, substrate types are limited and can be extremely expensive (as can iridium itself), growth is only possible on a small area, and single crystal films have yet to be achieved.

2.6. DOPING AND DEVICES

The possibility of doping diamond, and so changing it from an electrical insulator to a semiconductor, opens up a whole range of potential electronic applications. However, there are a number of major problems which still need to be overcome if diamond-based devices are to be achieved. First, MCD CVD diamond films contain many grain boundaries, twins, stacking faults and other defects, which all reduce the lifetime and mobilities of carriers. For effective device operation, single-crystal diamond films are required (see Section 3), and this has been the driving force behind the development of the BEN techniques for producing textured films, mentioned earlier. Another problem, which to some extent has recently been solved, is the requirement that the diamond films must be patterned to produce features of similar size to those used in microcircuitry, typically a few microns. Fortunately, diamond can be etched in O_2-based plasmas, provided a suitable non-erodible mask is used. Alternatively, a technique known as selective area deposition can be employed, whereby the diamond is encouraged to grow on only certain parts of the substrate [35]. Whichever patterning technique is used, MCD films suffer from the problem that they cannot be patterned below the size of the individual crystallites within the film, typically ~1 µm. This means that MCD films cannot be used for high resolution nano-structures, and this has been one of incentives for the development of both large area single crystal diamond films (Section 3), as well as much smaller grain sized films, such as NCD and UNCD (Sections 4 and 5).

Unfortunately, the problem of reliably and reproducibly doping diamond has proven much harder to solve. p-type doping is relatively straightforward, since addition of a few ppm of a boron-containing gas, such as B_2H_6, to the CVD process gas mixture is all that is required to incorporate B into the MCD lattice. This gives an activation energy of 0.37 eV, and conductivity can be controlled over many orders of magnitude from extremely insulating to near metallic. As a result, a large number of simple sensors and detectors, as well as electrochemical electrodes have been successfully demonstrated using B-doped MCD [17,19]. However, the close packing and rigidity of the diamond lattice make doping with atoms larger than C very difficult. This means that dopants which are routinely used to n-dope Si, such as P or As, cannot easily be used for diamond [36]. Recent developments in Japan [37,38] have demonstrated that it is possible to dope with P both the (100) and (111) surfaces of homoepitaxial diamond films, although the electrical characteristics are still not adequate for many proposed devices. Unfortunately, to date, there are still no reports of successful n-type doping of polycrystalline MCD films.

An alternative type of p-type "doping" is the "surface conductive" type of diamond. If hydrogen terminated single-crystal, polycrystalline, or NCD films are exposed to air, they develop an extremely thin, p-type conductive layer on the surface or near-surface of the film [39]. The mechanism of this conductivity is still not completely understood, and remains controversial [40,41,42]. It is believed that water vapour and CO_2 from the air adsorb on the diamond surface to form a slightly acidic liquid layer. Due to the very low ionization energy of diamond, electrons move from the diamond into the liquid to form negative ions, leaving an electron-depleted (i.e. holes) conducting region in the region near the diamond surface. Evidence for this mechanism is that this p-type "surface conductivity" disappears upon heating above ~200°C in air (or less in vacuum) as the water vapour is evaporated away, but is recovered on re-exposure to air. Despite the fact that the surface conductivity effect cannot be used at elevated temperatures, in corrosive environments, or when the diamond is functionalised other than with H, some useful devices, such as pH meters and enzyme sensors have been created using it [43].

One recent unexpected finding is that above a doping level of ~10^{20} cm^{-3} B-doped diamond films exhibit superconductivity [44]. The critical temperature is still only around 10 K, so their usefulness is limited. Nevertheless the mechanism for superconductivity in these materials is causing a lot of interest among the low temperature physics community [45].

3.   SINGLE CRYSTAL DIAMOND FILMS

The grain boundaries associated with polycrystalline films are severely detrimental to many of the properties of CVD diamond films. They greatly reduce the film transparency, carrier mobility and thermal conductivity, and act as a region where non-diamond impurities (normally graphite or amorphous carbon) can accumulate. The crystallite size also limits the resolution to which diamond films can be patterned. The elimination of grain boundaries to

make *single crystal* diamond layers at high rates, therefore, has become a major priority for researchers [46,47,48,49]. Another obvious - and potentially lucrative - benefit from such work, is that this might provide a route to high quality diamond gemstones suitable for the jewellery market.

3.1.   THE SUBSTRATE MATERIAL

In order to grow a single crystal diamond layer, the substrate must also be a single crystal diamond – to ensure that growth will be homoepitaxial. Typically, a square (100) HPHT substrate of size around 2-5 mm is used, although a high quality natural diamond can be used as well. In fact, the quality of the starting substrate is crucial, as even the slightest imperfection in the surface of this 'seed crystal' will become amplified as CVD progresses, leading to twinning or dislocation faults, and ultimately a polycrystalline film. Even polishing lines, *e.g.* oriented in the <110> direction, can introduce barriers for the growth leading to step bunching. For the highest quality films, often a large number of potential substrates need to be examined and discarded, before settling on one that is as 'perfect' as possible.

(100) diamond substrates are preferred for high quality single crystal diamond growth, since it is known that homoepitaxial layers grown on (100)-orientated surfaces contain the lowest amount of unwanted defects, allowing nearly perfect layers to be synthesized [50,51]. The substrates also have to be carefully cleaned, usually in a boiling mixture of sulphuric acid and potassium nitrate to remove any organic or metallic contaminants.

3.2.   SCD GROWTH CHEMISTRY

The growth chemistry used for single crystal diamond is thought to be essentially the same as that for MCD films [52], although the exact mechanism is still unclear. This is because, to date, there have only been a handful of reports of successful high rate single crystal diamond deposition, and the process conditions vary slightly between these groups. There are a number of approaches that can be used. One possibility is to reduce the concentration of reactants such that growth of the diamond is limited to a step-flow mechanism, *i.e.* growth occurs *only* at the edges of steps but nowhere else on the surface. This can be achieved using very low CH_4 concentrations (*e.g.* $CH_4:H_2$ <0.05%), which according to Fig.3 would be consistent with very large $<d>$ values. Such conditions have been used to grow thin device grade homoepitaxial diamond films with atomically flat surfaces [53,54]. Unfortunately, the growth rate under these conditions ($<< 1$ μm h^{-1}) is far too low to obtain a useful thickness of diamond films in a reasonable timescale.

Another possibility uses the knowledge of the dependence of the growth parameter, α, on experimental conditions, such as pressure, substrate temperature and methane concentration. In general, an optimal value ($\alpha \sim 3$) for the growth of (100) oriented films can be achieved by using high methane concentrations and low deposition temperatures. Typically, the $CH_4:H_2$ ratio is increased to around 10% (although some groups use values from 2-20%),

which under 'normal' CVD conditions should result in smaller grain sizes and NCD films (see Section 4). However, the process pressure is also increased (from ~20 Torr) to 100-300 Torr to increase the growth rate, and in order to maintain a stable plasma at these higher pressures, higher microwave power must be used - typically 2-10 kW (depending upon the volume of the chamber). This generates a high plasma density (> 20 W cm^{-3}), and the high gas temperatures (>3200 K) this creates greatly increases the dissociation rate of H$_2$, leading to a higher concentration of atomic H at the growing surface (compared with that in the lower power plasmas used for depositing MCD). As mentioned previously, a high ratio of [H]:[CH$_x$] species close to the growth surface is believed to result in growth being dominated by CH$_3$ radicals, facilitating large area, uniform, 'defect-free' deposition (see Fig.3). Thus, single crystal diamond can be grown - even at these high CH$_4$ concentrations - so long as the power density is high enough to maintain a very high [H], and the substrate itself is defect free and cooled efficiently and uniformly to prevent overheating [55]. To decrease further the chances of spontaneous defects (such as unepitaxial crystallites, pyramidal hillocks or penetration micro-twins) appearing in the growing films, O$_2$/H$_2$ plasma pretreatments [46], or additions of N$_2$ to the gas mixture [49] are sometimes used.

Whatever the exact process conditions, the crucial considerations for large area, uniform, thick, defect-free growth, apart from substrate quality, appear to be the purity of the process gases (better than 99.999% is recommended) and the stability of the process conditions. The pressure, gas flows, microwave power and substrate temperature, all need to remain at their constant set values for many hours or even days, with variations of <1% in order to ensure film uniformity. Thus, growth of high quality gemstone diamonds is now really just a question of precise control of the process engineering - plus how much money you are prepared to pay for the best seed substrates, the reactor and associated control systems.

3.3.   SCD FILM PROPERTIES

The growth rates achieved using the high pressure, high power, high methane conditions, described above, can be relatively high, 2-100 μm h^{-1}, and this allows thick diamond films to be fabricated in reasonable timescales. Figure 6 shows a 270 μm-thick single crystal diamond film grown by the group at Hasselt University in Belgium, at 700°C using 10% CH$_4$. The same group have reported epitaxial diamond growth yielding sub-nm smooth surfaces for films with thicknesses up to 730 μm [46,47]. Freestanding diamond films of area 4×4 mm^2 and thickness between 390-690 μm were reported by workers from Element Six [48], and these films had outstanding room temperature electron and hole drift velocities that were significantly higher than those achieved for MCD films. Breakthroughs such as these suggest that single crystal diamond layers could represent a major step toward the realization of viable diamond electronic devices. However, the growth technology still needs to be scaled up to much larger areas (say, 100 mm diameter) and reduced in cost if diamond 'wafers' are to compete with existing Si technology.
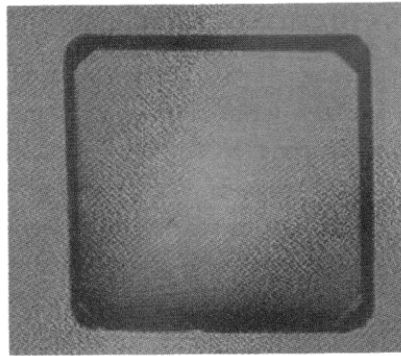
Fig. 6. Normarski contrast optical image of a 2.5×2.5 mm2 270 μm-thick single crystal diamond sample attached to its substrate, grown at Hasselt University. Reproduced with permission from ref. [47].

Recently, a group based at the Carnegie Institute in Washington have grown single crystal diamond up to 4.5 mm in thickness at growth rates as much as two orders of magnitude higher than conventional polycrystalline CVD methods [49,56]. These single crystals can be fashioned into brilliant cut 'gemstones' using standard techniques. Figure 7 shows a photograph of one such CVD single crystal that was grown from a small diamond substrate. Thus, it appears that the era of CVD growth of gemstone quality diamonds is nearly at hand, and there are already companies (*e.g.* Apollo Diamond [57]) beginning to exploit these advances for the commercial gemstone market.
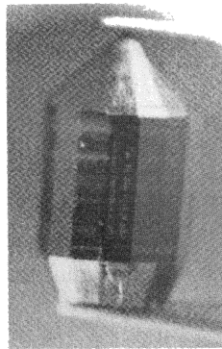

Fig. 7. Five carat CVD single crystal diamond (without seed), 12 mm high and 6.7 mm in diameter, cut from a 10 carat (8×8×12 mm³) block, grown at the Carnegie Institute. Reproduced with permission from ref. [56].

4. NANOCRYSTALLINE DIAMOND FILMS

In contrast to the drive to make single crystal films mentioned above, it may at first sight seem surprisingly that there is also a lot of effort to *decrease* the crystallite size below a micron to make *nanocrystalline* diamond (NCD) films – especially as the very large number of grain boundaries within NCD degrade their electrical and mechanical properties considerably. Nevertheless, for many mechanical applications, the hardness and wear resistance of NCD films are still far superior to competing materials, while the small grain size often allows them to be used in applications for which MCD is too large. For example, micro-electromechanical systems (MEMS), such as freestanding cantilevers for use as accelerometers, require a hard, stiff, robust material, that can be patterned to submicron resolution – and NCD is ideal for this [58]. Coating microelectrodes for electrochemistry, or tips for atomic force microscopy are also applications for NCD films [59,60].

4.1. NCD FILM MORPHOLOGY

Unfortunately, there is no rigorous definition for NCD in the literature, and the only agreed property is that NCD films have grain sizes in the nm range, typically between 10-500 nm, although even the exact range is arguable. In fact, a number of films with quite distinct characteristics all come under the broad umbrella of NCD (see Fig.8). One type of NCD film is the result of deposition using standard growth conditions, but following a very high initial nucleation density (*e.g.* by using nanodiamond grit for abrasion) [61]. These films exhibit columnar growth, just as for MCD, except with nano-sized crystallites (see Figs.8(b) and 9(a)). There is little or no re-nucleation, and the grain size, and hence roughness, increase with film thickness, so above a thickness of around 1 μm, the film becomes microcrystalline. Thus, these NCD films can be considered as just smaller grained, facetted versions of MCD.

However, this description is not appropriate for many other NCD films, which often contain a significant fraction of non-diamond material, and exhibit no faceting or evidence of columnar growth, even at thicknesses of several μm. Some NCD films have a rounded appearance (see Figs.8(c) and 9(b)), and as a result, their morphology is often referred to as 'ballas' (meaning ball-like) or 'cauliflower'-like [62,63]. Other types of NCD films can be grown with essentially flat surfaces with nm smoothness (see Figs.9(c) and (d)), and this allows them to be patterned with much higher resolution than MCD.
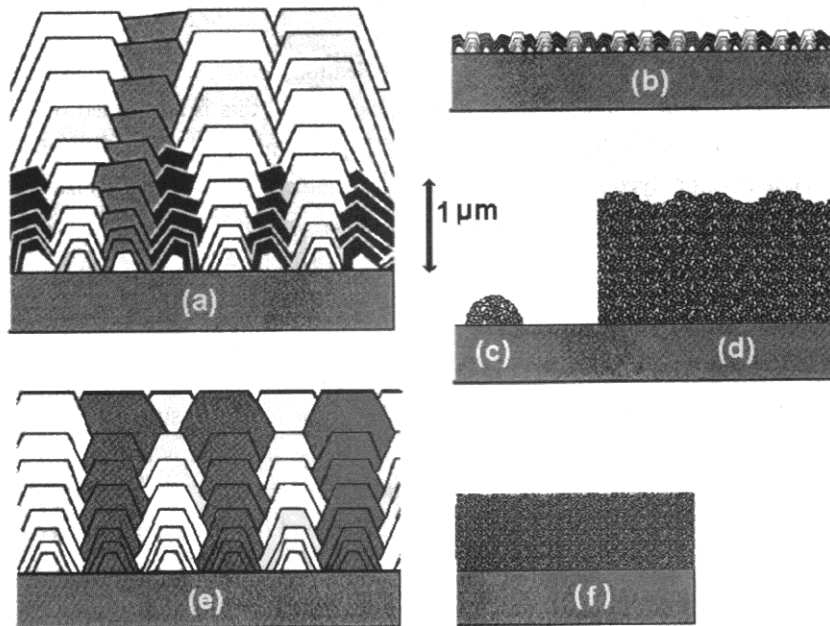
Fig. 8. Schematic diagram illustrating various forms of CVD diamond growth. (a) MCD (adapted with permission from Ref.[64]), (b) facetted NCD, (c) isolated NCD 'cauliflower' islands, (d) NCD cauliflower film, (e) Highly-oriented 'textured' diamond following BEN, and (f) UNCD.
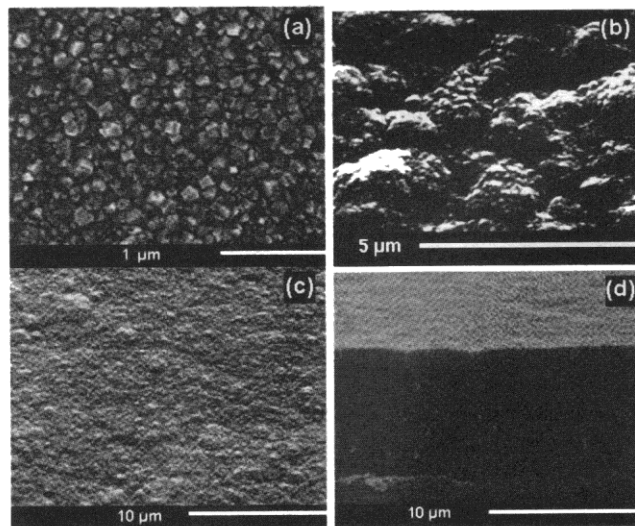

Fig. 9. SEMs from various NCD film morphologies: (a) nano-facetted NCD (reprinted from ref.[61] with permission from Elsevier), (b) 'cauliflower' or 'ballas' morphology, (c) a nm-smooth non-facetted NCD film, and (d) its cross-section.

4.2.   NUCLEATION

Apart from the growth chemistry (Section 4.3), the nucleation density is one of the key factors that determine the type of NCD film that is deposited, and this is controlled by the density of abrasion and size of the diamond grit used. If the abrasion is sparse (as happens if micron-sized diamond is employed for abrasion), then the nanodiamond nucleates as isolated islands which grow upwards and outwards into 'cauliflower' structures (Fig.8(c)), which eventually merge to form a cauliflower film (Figs.8(d) and 9(b)). Denser nucleation can be achieved using sonication of the substrate in a slurry of nanodiamond (5-100 nm diameter) grit. This gives more uniform film growth, leading to smoother films. Even higher nucleation densities can be achieved using a multi-stage nucleation technique developed by Rotter [65]. This starts with a short (~20 min) growth step on the mirror Si surface, which is believed to lay down a thin amorphous carbon layer. Then, the substrate is removed from the deposition chamber and treated in an ultrasonic bath of nanodiamond powder dispersed in ethanol, rinsed, and dried. Finally, the nanocrystalline diamond film is grown using NCD growth conditions (see below).

4.3.   NCD GROWTH CHEMISTRY

A common method to deposit (cauliflower) NCD films is simply to increase the CH_4 concentration within the gas mixture, while keeping the power levels (filament temperature or microwave power) relatively low. This ensures that the $[H]:[CH_3]$ ratio falls, causing the crystallite size to decrease below 1 μm, as predicted by Fig.3. As this happens, the films begin to lose their faceted appearance and become smoother and rounder (Fig.9(b)), while at the same time, the number and thickness of the grain boundaries increases. Since the grain boundaries contain mostly non-diamond carbon, these types of NCD film often contain a significant volume fraction of graphitic and amorphous carbon. NCD films are therefore significantly more conducting than MCD films, since the graphitic boundaries around and between each crystallite provide continuous (if convoluted) electrical pathways through the film. As the $CH_4:H_2$ ratio in the process gas increases further, the grain size continues to shrink, while the grain boundaries enlarge. The film properties progressively worsen, until, effectively, the film becomes an amorphous mixture of sp^2 and sp^3 carbon, at which point it should be considered to be a form of diamondlike carbon (DLC) rather than diamond. This usually occurs when the grain size approaches ~10 nm, so films that can be called predominantly *diamond*, and having grain sizes smaller than 10 nm (*i.e.* UNCD), cannot be made by simply increasing the CH_4 concentration (see Section 4). Note though, as mentioned in Section 3, that the effect of higher CH_4 concentrations can be counteracted by using higher power densities. In this case, even $CH_4:H_2$ ratios approaching 20% can still give MCD or SCD due to the higher H_2 fragmentation rate creating much more atomic H.

Another route to NCD involves applying a voltage bias to the substrate during CVD, in a similar manner to BEN mentioned earlier. The bias accelerates ions from the plasma onto the growing diamond surface, where they impact with sufficient kinetic energy to break

chemical bonds and cause surface reconstruction [66]. The degree of renucleation that results, and hence the crystallite size, can be controlled to some extent by the duration, polarity and voltage of the applied bias. For higher bias values, the crystal size can be reduced to zero, *i.e.* amorphous films can be deposited [67]. Accelerating electrons using a positive bias on the substrate also has a similar effect upon grain sizes [68].

4.4. RAMAN SPECTRA

The change in film composition as the films become more nanocrystalline can be seen in their laser Raman spectra. With red or green excitation, the Raman spectra of NCD films look very similar to those from amorphous carbon or graphite. Subtler details can be seen if blue or better still, ultraviolet laser excitation is used (see Fig.10). MCD films exhibit a single sharp Raman line at 1332 cm^{-1}, but for NCD films the D and G peaks at ~1370 and 1550 cm^{-1}, respectively, from sp^2 carbon become much more pronounced while the diamond peak broadens and becomes less intense. A small feature at 1150-1170 cm^{-1} also appears, and this has been assigned to the presence of long-chained sp^2 carbon molecules (such as *trans*-polyacetylene) that are present at the grain boundaries [69]. This feature is often considered as being a signature for the presence of nano-phase diamond, despite its origin being sp^2 carbon.
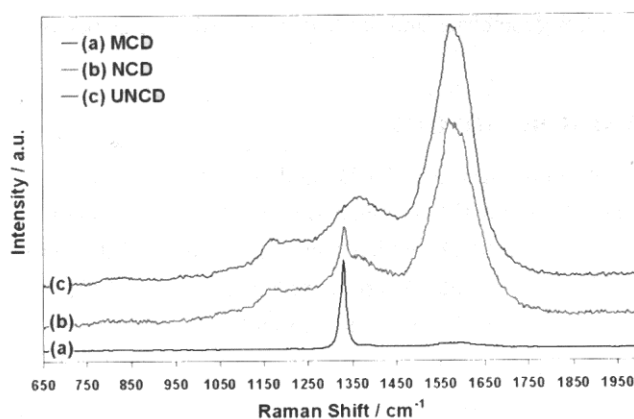

Fig. 10. Laser Raman spectra taken with ultraviolet (325 nm) excitation of (a) an MCD film similar to that shown in Fig.4(c), (b) a cauliflower NCD film (like that in Fig.9(b)), and (c) a UNCD film like that from Fig.11. The spectra have been offset vertically for clarity.

4.5. DOPING

Compared to MCD, far less work has been reported for doping experiments of NCD. Since NCD is just fine-grained diamond, it can be doped with B to make p-type material in the same way as MCD [70]. As expected, the B acts as a conventional substitutional acceptor and produces a level around 0.37 eV above the valence band maximum [71]. There is even

less work published on the effect of B-doping of cauliflower-type NCD. This may be because these films are already somewhat conducting due to the non-diamond carbon present at the grain boundaries. The effect of additional conductivity from substitutional B occurring *through* the grains, as well as *around* the grains, could lead to unusual semiconducting behaviour and a range of new diamond devices [72]. NCD films also exhibit p-type behaviour due to the surface conductivity effect mentioned in Section 2.6. Highly B-doped NCD also exhibits superconductivity [73]. However, just as for MCD, n-type doping of NCD has proved elusive.

5.   ULTRANANOCRYSTALLINE DIAMOND FILMS

Decreasing the diamond crystallite size below 10 nm produces what has come to be known as *ultra-nanocrystalline* diamond (UNCD) films [74]. This material was first developed by Argonne National Labs, using a gas chemistry that at first sight seems very different from the hydrogen-rich mixtures used for MCD or NCD deposition. Most reports of the deposition of these films describe using a microwave plasma CVD reactor and gas mixture of $1\%CH_4$ in Ar, usually with addition of only 1%–$3\%H_2$ to stabilise the 'lively' plasma. Also, process pressures are typically 100-200 Torr, which are $\sim 10\times$ higher than those used for standard MCD growth. UNCD films can also be deposited using $Ar/CH_4/H_2$ gas mixtures in a hot filament reactor [75], although the required gas ratios are somewhat higher in H_2 due to the different geometries and gas activation efficiencies between the two types of reactor.

5.1.   UNCD FILM MORPHOLOGY

UNCD differs from both facetted NCD and cauliflower NCD in two important characteristics. First, the grain size is much smaller, typically 2-5 nm (although anything < 10 nm is often classed as UNCD), which means that $\sim 10\%$ of the carbon is at the grain boundary. Second, the grain boundaries are relatively clean, with little non-diamond carbon present, although some sp^2 carbon must be present at the boundaries, since the Raman spectra of UNCD films show the 1150 cm^{-1} feature (see Fig.10(c)). The films themselves show no microstructure (see Fig.8(f) and Fig.11(a)), although high resolution SEM (Fig.11(b)) and TEM show that they are composed of roughly spherical grains of diamond with abrupt (sometimes even atomically sharp) grain boundaries. There is no evidence of columnar growth and so the surface roughness is independent of film thickness, although there are no reports of UNCD films thicker than a few μm. This may be because the reported growth rate for UNCD is also quite small, typically $10\times$ less than that for MCD.
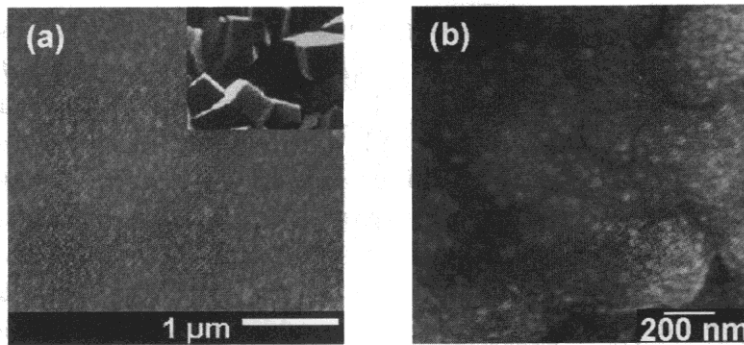
Fig. 11. (a) SEM of a UNCD film, with inset an MCD film on the same scale for comparison. (b) High resolution SEM of a UNCD film.

With such small grain sizes and nm-smoothness, UNCD films can be patterned to high resolution, and so are potential candidates for use in MEMS devices [76], biosensors [77,78], and nanolithography [79]. Furthermore, since the thermal conductivity of argon is much lower than that of hydrogen, and thus the power levels needed for plasma formation are also much less, the heating of the substrate by the plasma is greatly reduced in the $Ar/CH_4/H_2$ mixtures used for UNCD growth. One advantage of this is that it allows UNCD to be deposited at much lower temperatures than other forms of CVD diamond. Indeed, deposition at reasonable rates at temperatures as low as 400°C, have been reported [80], and this may allow UNCD to be readily integrated into Si-based devices.

5.2. UNCD GROWTH CHEMISTRY

Originally, it was suggested [81] that, unlike other forms of diamond, where CH_3 is the major growth species, for UNCD the C_2 radical was playing a more central role. In particular, it was proposed that C_2 could directly insert into the growing diamond lattice, with little or no energy barrier. However, a number of recent reports have cast doubt on the veracity of this C_2 mechanism [25,82,83,84]. The original reports [85] that UNCD could be grown in a completely hydrogen-free gas chemistry have never been substantiated, and now it is generally agreed that for UNCD deposition to occur, hydrogen atoms must be present in the gas mixture in small amounts, either from decomposition of CH_4 or by addition of 1%–2%H_2 [86]. With too little hydrogen present only graphitic films are formed, and with increasing H_2 added, the quality of the diamond improves, and there is a transition from UNCD to NCD, and then to MCD [80,87]. Indeed, MCD and UNCD can be grown simultaneously in a $CH_4/Ar/H_2$ plasma on different parts of the same substrate [88], with tiny, local variations in gas chemistry or substrate temperature altering the morphology accordingly.

The model for diamond growth [25] described in Section 1, above, proposes that UNCD is simply an extension of NCD down to lower crystallite sizes. From Fig.3 we can see that as

the ratio of [H]:[CH$_x$] close to the substrate decreases below about 2, the crystallite size ($<d>$) is predicted to drop below 10 nm. However, this ratio cannot be achieved by simply increasing the CH$_4$ content in conventional CH$_4$:H$_2$ gas mixtures, as the amount of non-diamond carbon that is co-deposited along with the diamond becomes prohibitively large – leading ultimately to amorphous carbon films. It is believed that the required [H]:[CH$_x$] ratio is obtained due to the unique conditions prevailing in these higher pressure Ar-rich gas mixtures. As before, the gas activation serves to create the usual reactive soup of hydrocarbon fragments, and these will undergo many gas phase collisions while diffusing toward the diamond surface. In H$_2$-rich gas mixtures, the majority of these collisions will be with H$_2$ or H atoms, and the resulting reactions will rapidly hydrogenate most hydrocarbon fragments (CH$_x$, $x<3$) back to CH$_3$. Very few CH$_x$ species reach the growing diamond surface - so growth is dominated by CH$_3$. However, when the bulk of the gas is Ar, the collisions between CH$_x$ and inert Ar do not result in any reactions, and so these reactive CH$_x$ species can survive long enough to strike the surface, whereupon they may contribute to diamond growth. The combination of growth by CH$_3$ plus growth from a significant fraction of the other CH$_x$ species, leads to the surface to continually renucleate (or more accurately, restructure) during growth, resulting in very small grain sizes.

5.3. NUCLEATION

UNCD is unusual in that it seems to be able to nucleate automatically upon itself, MCD, SCD, and many non-diamond substrates, such as Si [89]. However, nucleation on non-diamond substrates can be enhanced by ultrasonic abrasion/seeding using nanodiamond slurries [90,91]. Further enhancements can be achieved if a thin layer of tungsten is deposited on top of the substrate [92], or via use of BEN [91] or the 'Rotter' technique [65].

5.4. DOPING

One unusual property of UNCD is that it can be n-doped [93,94], but there are no reports of successful p-doping [95]. This is the opposite of all other types of diamond film mentioned previously, which can be easily p-doped with boron, but for which n-doping is problematic. UNCD does not even show the surface conductivity effect that other forms of diamond exhibit (Section 2.6), probably due to compensation produced by particular defect states in the grain boundaries.

The apparent n-doping of UNCD is a bit misleading, as the dopant (nitrogen in this case), does not substitute for carbon in the lattice, and so this process cannot be considered as true doping in the conventional sense. Instead, the nitrogen atoms aggregate at the grain boundaries, and the more N$_2$ that is added to the Ar/CH$_4$/(H$_2$) gas mixture during deposition, the larger, and also the more electrically conducting, the grain boundaries become [93]. In effect, the nitrogen forces structural changes during the deposition of UNCD, and these lead to enhanced sp^2 bonding which determines the conductivity of the resulting film. Nevertheless, these nitrogen 'doped' films exhibit definite n-type conductivity, and this has

been exploited to enable p-n-junction-like devices to be constructed using n-type UNCD bonded to p-type MCD [96]. Unfortunately, this conductivity mechanism is of little use in more sophisticated active electronic devices, where the formation of depletion regions is crucial to device modulation and rectification. However, conducting UNCD can be very useful where high carrier concentrations are required, such as in electrochemical electrodes, field emission, heterostructures, and in high-temperature stable Ohmic contacts.

6. CONCLUSIONS

This review has described the major varieties of diamond film that are currently being deposited, and shown how their crystallite size, morphology and properties are linked via their growth mechanism. However, there are other forms of diamond which have not been included in this paper, including those grown with nitrogen-based plasmas (*e.g.* CH_4/N_2) [97], the various forms of diamondlike carbon (DLC) and amorphous carbon (a-C) films [98,99], and diamond (nano)particles made from pulsed laser ablation [100], explosion synthesis [101], shock synthesis [102] and HPHT methods [103]. This vast array of different types of diamond, which have only very recently become available with a range of useful and controllable properties, is enabling a whole new set of technologies. These include biosensors, DNA pinning, destruction of chemicals in liquid effluent, radiation detectors, thermal management, high power infrared and x-ray laser windows, electrochemical sensing, scanning microprobes, and new electronic devices. And, of course, large, high quality single crystal CVD diamond can find uses as integrated circuit substrates, diamond anvil cells, and even CVD diamond gemstones that are finally big enough – and clear enough - for use in jewellery and wedding rings!

7. ACKNOWEDGEMENTS

REFERENCES

[1]   F. Ward, "Diamonds", Gem: Bethesda, MD, 1998.

[2]   J.E. Field, "The properties of natural and synthetic diamond", Academic Press: London, 1992.

[3]   S. Tennant, Phil. Trans. R. Soc. Lond., 87, (1797) 123.

[4]   F.P. Bundy, J. Geophys. Res. 85, (1980) 6930.

[5]   http://www.gemesis.com

[6]   W.G. Eversole, US Patent numbers 3030187 and 3030188 (1958).

[7]   B.V. Deryagin, D.V. Fedoseev, V.M. Lukyanovich, B.V. Spitsyn, A.V. Ryanov and A.V. Lavrentyev, J. Cryst. Growth, 2, (1968) 380.

[8]   J.C. Angus, H.C. Will and W.S. Stanko, J. Appl. Phys., 39, (1968) 2915.

[9]   D.J. Poferl, N.C. Gardner and J.C. Angus, J. Appl. Phys., 44, (1973) 1418.

[10]   B.V. Deryagin, B.V. Spitsyn, L.L. Builov, A.A. Klochov, A.E. Gorodetskii and A.V. Smol' yanimov, Dokl. Akad. Nauk. SSSR, 231, (1976) 333.

[11]   B.V. Spitsyn, L.L. Builov and B.V. Deryagin, J. Cryst. Growth, 52, (1981) 219.

[12]   S. Matsumoto, Y. Sato, M. Kamo and N. Setaka, Jpn. J. Appl. Phys. Part 2, 21, (1982) 183.

[13]   S. Matsumoto, Y. Sato, M. Tsutsumi and N. Setaka, J. Mater. Sci., 17, (1982) 3106.

[14]   M. Kamo, Y. Sato, S. Matsumoto and N.J. Setaka, Cryst. Growth, 62, (1983) 642.

[15]   Y. Saito, S. Matsuda and S. Nogita, J. Mater. Sci. Lett., 5, (1986) 565.

[16]   P.W. May, Philos. Trans. R. Soc. London, Ser. A, 358, (2000) 473.

[17]   K.E. Spear and J.P. Dismukes, "Synthetic Diamond, Emerging CVD Science and Technology", Wiley: New York, 1994.

[18]   D.L. Dreifus, A. Collins, T. Humphreys, K. Das and P. Pehrsson, Eds, "Diamond for Electronic Applications", Mater. Res. Soc. Symp. Proc., Vol. 416, 1995.

[19]   B. Dischler and C. Wild, (eds) "Low-pressure synthetic diamond", Springer: Berlin, 1998.

[20]   D.G. Goodwin and J.E. Butler, in "Handbook of industrial diamonds and diamond films", ed. M.A. Prelas, G. Popovici and L.K. Bigelow), ch. 11., Marcel Dekker: New York, 1997.

[21]   M.N.R. Ashfold, P.W. May, J.R. Petherbridge, K.N. Rosser, J.A. Smith, Y.A. Mankelevich and N.V. Suetin, Phys. Chem. Chem. Phys., 3, (2001) 3471.

[22]   P.K. Bachmann, H.-J. Hagemann, H. Lade, D. Leers, F. Picht, D.U. Weichert and H. Wilson, Mater. Res. Soc. Symp. Proc., 339, (1994) 267.

[23]   A. Cheesman, J.N. Harvey and M.N.R. Ashfold, Phys. Chem. Chem. Phys., 7, (2005) 1121.

[24]   M. Frenklach and S. Skokov, J. Phys. Chem. B, 101, (1997) 3025, and refs therein.

[25]   P.W. May, M.N.R. Ashfold, Yu. Mankelevich, J. Appl. Phys., 101, (2007) 053115.

[26]   S.J. Harris, Appl. Phys. Letts., 56, (1990) 2298.

[27]   C. Wild, R. Kohl, N. Herres, W. Müller-Sebert and P. Koidl, Diamond Relat. Maters., 3, (1994) 373.

[28]   M. Asmann, J. Heberlein and E. Pfender, Diamond Relat. Maters., 8, (1999) 1.

[29]   T.P. Mollart and K. L. Lewis, Diamond Relat. Maters., 8, (1999) 236.

[30]   P.S. Weiser, S. Prawer, Diamond Relat. Maters. 4, (1995) 710.

[31]   S. Kadlec, K. Vandierendonck, M. Van Stappen, M. Nesládek, C. Quaeyhaegens, L.M.M Stals, Surf. Coatings Technol., 98, (1998) 1060.

[32]   S. Yugo, T. Kania, T. Kimura, T. Muto, Appl. Phys. Lett., 58, (1991) 1036.

[33]   Y. Lifshitz, Th. Köhler, Th. Frauenheim, I. Guzmann, A. Hoffman, R.Q. Zhang, X.T. Zhou, S.T. Lee, Science, 297, (2002) 1531.

[34]   S. Gsell, T. Bauer, J. Goldfuß, M. Schreck, and B. Stritzker, Appl. Phys. Letts., 84, (2004) 4541.

[35]   P.R. Chalker and C. Johnston, Physica Status Solidi, 154, (1996) 455.

[36]   R. Kalish, Diamond Relat. Maters., 10, (2001) 1749.

[37]   M. Suzuki, S. Koizumi, M. Katagiri, H. Yoshida, N. Sakuma, T. Ono, T. Sakai, Diamond Relat. Maters., 13, (2004) 2037.

[38]   H. Kato, S. Yamasaki and H. Okushi, Diamond Relat. Maters., 14, (2005) 2007.

[39]   M.I. Landstrass and K.V. Ravi, Appl. Phys. Letts. 55, (1989) 1391.

[40]   F. Maier, M. Riedel, B. Mantel, J. Ristein and L. Ley, Phys. Rev. Letts. 85, (2000) 3472.

[41]   F. Maier, M. Riedel, B. Mantel, J. Ristein, and L. Ley, Phys. Rev. Letts. 87, (2001) 209706.

[42]   C.E. Nebel, F. Ertl, C. Sauerer, M. Stutzmann, C.F.O. Graeff, P. Bergonzo, O.A. Williams and R.B. Jackman, Diamond Relat. Maters. 11, (2002) 351.

[43]   K-S Song, M. Degawa, Y. Nakamura, H. Kanazawa, H. Umezawa and H. Kawarada, Jpn. J. Appl. Phys. 43, (2004) L814.

[44]   Y. Takano, M. Nagao, T. Takenouchi, H. Umezawa, I. Sakaguchi, M. Tachiki and H. Kawarada, Diamond Relat. Maters., 14, (2005) 1936.

[45]   E.A. Ekimov, V. A. Sidorov, E.D. Bauer, N.N. Mel'nik, N.J. Curro, J.D. Thompson and S.M. Stishov, Nature, 428, (2004) 542

[46]   G. Bogdan, M. Nesládek, J. D'Haen, J. Maes, V.V. Moshchalkov, K. Haenen and M. D'Olieslaeger, Physica Status Solidi (a), 202, (2005) 2066.

[47]   G. Bogdan, K. De Corte, W. Deferme, K. Haenen, and M. Nesládek, Physica Status Solidi (a), 203, (2006) 3063.

[48]   J. Isberg, J. Hammersberg, E. Johansson, T. Wikström, D.J. Twitchen, A.J. Whitehead, S.E. Coe, G.A. Scarsbrook, Science, 297 (2002) 1670.

[49]   C.-s. Yan, H.-k. Mao, W. Li, J. Qian, Y. Zhao and R.J. Hemley, Physica Status Solidi (a), 201, (2004) R25.

[50]   C. Findeling-Dufour, A. Vignes and A. Gicquel, Diamond Relat. Maters., 4, (1995) 429.

[51]   T. Bauer, M. Schreck, H. Sternschulte and B. Stritzker, Diamond Relat. Maters., 14, (2005) 266.

[52]   J. Achard, F. Silva, A. Tallaire, X. Bonnin, G. Lombardi, K. Hassouni and A. Gicquel, J. Phys. D: Appl. Phys., (2007) in press.

[53]   H. Okushi, Diamond Relat. Maters., 10, (2001) 281.

[54]   H. Watanabe, D. Takeuchi, S. Yamanaka, H. Okushi, K. Kajimura, and T. Sekiguchi, Diamond Relat. Maters., 9, (2000) 231.

[55]   H. Yamada, A. Chayahara, Y. Mokuno, Y. Horino and S. Shikata, Diamond Relat. Maters., 15, (2006) 1738.

[56]   S.S. Ho, C.S. Yan, Z. Liu, H.K. Mao, and R.J. Hemley, Ind. Diamond. Rev., (Jan 2006) 28.

[57]   http://www.apollodiamond.com

[58]   L. Sekaric, J.M. Parpia, H.G. Craighead, T. Feygelson, B.H. Houston and J.E. Butler, Appl. Phys. Letts., 81, (2002) 4455.

[59]   P.S. Siew, K.P. Loh, W.C. Poh and H. Zhang, Diamond Relat. Maters., 14, (2005) 426.

[60]   P. Niedermann, W. Hänni, D. Morel, A. Perret, N. Skinner, P.-F. Indermühle, N.-F. de Rooij, Appl. Phys. A, 66, (1998) S31.

[61]   O.A. Williams, M. Daenen, J. D'Haen, K. Haenen, J. Maes, V.V. Moshchalkov, M. Nesládek and D.M. Gruen, Diamond Relat. Maters., 15, (2006) 654.

[62]   E. Kohn, P. Gluche, M. Adamschik, Diamond Relat. Maters., 8, (1999) 934.

[63]   F.J.H. Guillen, K. Janischowsky, J. Kusterer, W. Ebert, E. Kohn, Diamond Relat. Maters., 14, (2005) 411.

[64] S.K. Han, M.T. McClure, C.A. Wolden, B. Vlahovic, A. Soldi and S. Sitar, Diamond Relat. Maters., 9, (2000) 1008.

[65] S. Rotter, "Applied Diamond Conference/Frontier Carbon Technology (ADC/FCT) Joint Conference", 1999, Tsukuba, Japan, eds. M. Yoshikawa, Y. Koga, Y. Tzeng, C.-P. Klages and K. Miyoshi, p. 25.

[66] V. Grill, J. Shen, C. Evans and R. G. Cooks, Rev. Sci. Instrum., 72, (2001) 3149.

[67] T. Sharda, T. Soga, T. Jimbo and M. Umeno, Diamond Relat. Maters., 10, (2001) 1592.

[68] H.Y. Zhou, R.J. Zhan, X.D. Zhu, X.H. Wen and X. Chen, Nanotechnol., 15, (2004) 1609.

[69] A.C. Ferrari and J. Robertson, Phys. Rev. B., 63, (2001) 121405.

[70] M.W. Geis and J.C. Angus, Scientific American, (October 1992) 64.

[71] O.A. Williams, M. Nesládek, Physica Status Solidi (a), 203, (2006) 3375.

[72] R.B. Jackman, "Synthesis and electronic properties of nanocrystalline diamond", in "Carbon Based Nanomaterials", Eds.: W. Ahmed, N Ali, A. Öchsner, Trans Tech Publications: Switzerland, 2010.

[73] M. Nesládek, D. Tromson, C. Mer and P. Bergonzo, P. Hubik and J.J. Mares, Appl. Phys. Lett., 88, (2006) 232111.

[74] D.M. Gruen, O.A. Shenderova, A.Ya. Vul' (Eds.), "Synthesis, Properties and Applications of Ultrananocrystalline Diamond", Springer: Dordrecht, Holland, 2005 (NATO Science Series part II, vol. 192).

[75] P.W. May, J.A. Smith, Yu. A. Mankelevich, Diamond Relat. Maters., 15, (2006) 345.

[76] A.R. Krauss, O. Auciello, D.M. Gruen, A. Jayatissa, A. Sumant, J. Tucek, D.C. Mancini, N. Moldovan, A. Erdemir, D. Ersoy, M.N. Gardos, H. G. Busmann, E.M. Meyer and M.Q. Ding, Diamond Relat. Maters., 10, (2001) 1952.

[77] W. Yang, O. Auciello, J.E. Butler, W. Cai, J.A. Carlisle, J.E. Gerbi, D.M. Gruen, T. Knickerbocker, T.L. Lasseter, J.N. Russell Jr., L.M. Smith and R.J. Hamers, Nature Materials, 1, (2002) 253.

[78] J. Wang, M.A. Firestone, O. Auciello , J.A. Carlisle, Langmuir, 20, (2004) 11450.

[79] K.-H. Kim, N. Moldovan, C. Ke, H.D. Espinosa, X. Xiao, J.A. Carlisle, O. Auciello, Small, 1, (2005) 866.

[80] D. Zhou, D.M. Gruen, L.C. Qin, T.G. McCauley and A.R. Krauss, J. Appl. Phys., 84, (1998) 1981.

[81]   D. Zhou, T.G. McCauley, L.C. Qin, A.R. Krauss and D. M. Gruen, J. Appl. Phys., 83, (1998) 540.

[82]   J.R. Rabeau, P. John, J.I.B. Wilson and Y. Fan, J. Appl. Phys., 96, (2004) 6724.

[83]   P.W. May, J.N. Harvey, J.A. Smith, Yu. A. Mankelevich, J. Appl. Phys., 99, (2006) 104907.

[84]   P.W. May, Yu. A. Mankelevich, J. Appl. Phys., 100, (2006) 024301.

[85]   D.M. Gruen, S. Liu, A.R. Krauss, J. Luo and X. Pan, Appl. Phys. Letts., 64, (1994) 1502.

[86]   J. Birrell, J.E. Gerbi, O. Auciello and J.A. Carlisle, J. Phys.: Condens. Matter, 18, (2006) S1771.

[87]   J. Birrell, J.E. Gerbi, O. Auciello, J.M. Gibson, J. Johnson and J.A. Carlisle, Diamond Relat. Maters., 14, (2005) 86.

[88]   Y.K. Liu, Y. Tzeng, C. Liu, P. Tso and I. N. Lin, Diamond Relat. Maters., 13, (2004) 1859.

[89]   S. Jiao, A. Sumant, M.A. Kirk, D.M. Gruen, A.R. Krauss and O.A. Auciello, J. Appl. Phys., 90, (2001) 118.

[90]   X. Xiao, J. Birrell, J.E. Gerbi, O. Auciello, J.A. Carlisle, J. Appl. Phys., 96, (2004) 2232.

[91]   Y. Lifshitz, C.H. Lee, Y. Wu, W.J. Zhang, I. Bello and S.T. Lee, Appl. Phys. Letts., 88, (2006) 243114.

[92]   N.N. Naguib, J.W. Elam, J. Birrell, J. Wang, D.S. Grierson, B. Kabius, J.M. Hiller, A.V. Sumant, R.W. Carpick, O. Auciello, J.A. Carlisle, Chem. Phys. Letts., 430, (2006) 345.

[93]   S. Bhattacharyya, O. Auciello, J. Birrell, J.A. Carlisle, L.A. Curtiss, A.N. Goyette, D.M. Gruen, A.R. Krauss, J. Schlueter, A. Sumant and P. Zapol, Appl. Phys. Letts., 79, (2001) 1441.

[94]   O.A. Williams, Semicond. Sci. Technol., 21, (2006) R49.

[95]   P.W. May and M. Hannaway, Mat. Res. Symp. Proc., PV-956, (2006) 0956-J09-31.

[96]   T. Zimmermann, M. Kubovic, A. Denisenko, K. Janischowsky, O.A. Williams, D.M. Gruen and E. Kohn, Diamond Relat. Maters., 14, (2005), 416.

[97]   W. Kulisch and C. Popov, Phys. Stat. Sol. (a), 203, (2006), 203.

[98]   J. Robertson, Mater. Sci. Eng. R., 37, (2002) 129.

[99]   J. Robertson, Diamond Relat. Maters., 3, (1994) 361.

[100] S.R.J. Pearce, S.J. Henley, F. Claeyssens, P.W. May, K.R. Hallam, J.A. Smith, K.N. Rosser, Diamond Relat. Maters., 13, (2004) 661.

[101] N. Greiner, D. Phillips, J. Johnson and F. Volk, Nature, 333, (1988) 440.

[102] J.B. Donnet, E. Fousson, T.K. Wang, M. Samirant, C. Baras, and M.P. Johnson, Diamond Relat. Maters., 9, (2000) 887.

[103] R. Abbaschian, H. Zhu and C. Clarke, Diamond Relat. Maters., 14, (2005) 1916.