

Diamond Thin Films: A 21st Century Material. Part 2: A New Hope

Table S1. Some suppliers of diamond gems, HPHT, CVD diamond substrates and nanodiamond powders. Many more Chinese suppliers can be found in Ref. [1].

Supplier	Country	Diamond product	Ref.
Element Six, Ltd	UK, USA	CVD substrates, HPHT	[2]
Audiatec (Augsburg Diamond Technology GmbH)	Germany	Freestanding CVD diamond plates	[3]
DiamFab	France	CVD diamond films	[4]
Ceratonia	Germany	Diamond grit, CVD substrates	[5]
Lightbox	UK	Gems	[6]
Yorkshire Bioscience	UK	Nanodiamond	[7]
Carbodeon	Finland	Nanodiamond	[8]
Diamond Materials	Germany	CVD substrates	[9]
Microdiamant	Switzerland	Nanodiamond	[10]
Nanodiamond.com	Switzerland	Nanodiamond	[11]
Ray Techniques, Ltd	Israel	Nanodiamond	[12]
Advanced Diamond Technologies	USA	UNCD substrates	[13]
Applied Diamond, Inc.	USA	CVD substrates	[14]
CSMH (Compound Semiconductor (Xiamen) Technology Co. Ltd)	China & South Korea	CVD substrates	[15]
Crystallume	USA	CVD substrates	[16]
Diamond Foundry	USA	Gems	[17]
Diam Concept	France	Gems & large mosaic SCD plates. Supply BDD and diamond with NV centres.	[18]
Gemesis	USA	Gems	[19]
SCIO diamond	USA	Gems	[20]
EDP Corporation	Japan	CVD substrates	[21]
NanoCarbon Research Institute, Co., Ltd.	Japan	Nanodiamond	[22]
Crysdiam Technology	China	Gems, CVD substrates and nanodiamond	[23]
Orbray (previously Adamant Namiki Precision Jewel Co., Ltd)	Japan	Large-area CVD substrates	[24]
Pam-Xiamen	China	CVD wafers	[25]
WEC Superabrasives	Taiwan	Gems	[26]
New Diamond Technology	Russia / Hong Kong	Gems, CVD substrates	[27]
2a Technologies	Singapore	Gems, CVD substrates	[28]
Diamond Elements	India	Gems, substrates	[29]
Greenlab	India	Gems	[30]
Hiqute	France	Bespoke SCD substrates, undoped, BDD and NV containing.	[31]
Ningbo Crysdiam Industrial Technology Company, Ltd	China	Gems, SCD substrates	[32]

amorphous sp^2 carbon matrix. It was suggested that with allegedly no H present, a different growth mechanism must be operating, and in the absence of CH_3 , the C_2 radical was the growth species. Indirect evidence was presented for this contentious view in that the plasma was bright green in colour, in contrast to the lilac colour of traditional CH_4/H_2 plasmas. Optical emission spectroscopy (OES) showed that the green colour arose from the bright Swan bands of the C_2 molecule which were dominating the emission in the visible region [43]. Further evidence supporting this claim came in the form of density functional theory (DFT) calculations which showed that C_2 could insert itself into surface dimers [44], providing a plausible route to growth.

However, in the few years following these first reports of 'H-free diamond growth', no research group was able to reproduce the results using the Ar/ C_{60} recipe. In all cases, UNCD films were successfully deposited *only* when trace amounts of H_2 were added to the Ar/ C_{60} gas mixture, or alternatively using Ar/ CH_4 mixtures which produce H atoms upon fragmentation – otherwise the films were graphitic. This suggested that maybe there were trace amounts of H_2 from an unknown source present in the original Ar/ C_{60} experiments. Doubts began to be cast on the veracity of the C_2 mechanism, and evidence to the contrary began to emerge. Cavity ring-down spectroscopy (CRDS) was used to measure the absolute concentration of C_2 in the plasma during UNCD growth, and this was found *not* to correlate with film growth rate [45]. Experimental and modelling findings of the gas-phase concentrations during UNCD growth showed that, although the concentration of C_2 was high in the centre of the plasma (and gave rise to the bright green emission), its concentration fell by many orders of magnitude close to the cooler diamond surface [46] and was insufficient to account for the observed growth rate. Nowadays, the C_2 growth mechanism has largely been discounted as a viable mechanism for UNCD growth – or for the growth of any form of diamond [47] – although it still gets cited in papers! However, the role of C_2 (and the more abundant C_2H) in renucleation and defect formation is still very much a possibility.

1.2 Role of N in growth (extended discussion)

Nitrogen is one of the most abundant impurities found in the diamond lattice [48]. In many of the early diamond CVD studies during the 1990s, problems such as irreproducible growth rates and inconsistent film morphology were eventually tracked down to the variable levels of nitrogen often present in the gas phase due to slight air leaks in the vacuum system or trace impurities in the process gases. The levels of N_2 required to significantly affect the CVD process turned out to be tiny - of the order of only a few parts per million (ppm). In the interests of process control and reproducibility, as well as to maintain crystal purity, diamond researchers are now far more careful to control unwanted N_2 (and other) impurities in the gas mixture, as well as having tighter vacuum controls. It is now common to add high-vacuum turbopumps to CVD reactors to reduce the chamber base pressure to $<10^{-6}$ mbar prior to diamond growth. Such careful control has allowed electronic grade SCD films to be fabricated which contain N concentrations of < 0.1 parts per billion (ppb) [49].

However, sometimes N-containing gases are deliberately added to the gas mixture in known quantities, for purposes such as N-doping (section 8 in the main paper) or NV-centre creation (section 9 in the main paper). Many studies have shown that adding even *trace* amounts of N_2 to the process gas

mixture significantly increases the growth rate from MW-activated CH₄/H₂ gas mixtures, sometimes by a factor of 10 or more [50]. The morphology of the growing diamond surface is also modified by the presence of nitrogen in the gas mixture, which encourages the preferential formation of flat, square {100}-faceted crystals in the case of polycrystalline diamond films. Excess nitrogen in the process gas mixture, however, produces smaller and less well-oriented surface facets. With further increases in gas-phase nitrogen concentration, the films become nanocrystalline or even graphitic [51, 52]. For homoepitaxial growth of single-crystal diamond (SCD), nitrogen in the input gas mixture has been shown to promote macroscopic step-bunching (as shown in Figure 7 in the main paper) and disrupt growth on all but the {100} face of an SCD seed [53].

This so-called 'nitrogen effect' - the addition of tiny amounts of N₂ to the process gas mixture causing dramatic changes to the growth rate and morphology - is still not fully understood. Indeed, nitrogen has sometimes been described as acting as a 'catalyst' in the growth, due to a small concentration causing a large effect, but this term is not strictly correct as the gas-phase nitrogen is not unchanged in the reaction – some small fraction ends up incorporated in the film. So how does the usually inert N₂ molecule cause such huge effects?

To answer this, a combination of experimental studies (such as laser absorption and OES) and computer modelling of MW-activated N₂/H₂ and NH₃/H₂ plasmas revealed that the hot plasma environment could create excited-state N₂ species with high internal energy [54,55]. Some of these excited-state N₂ molecules have sufficient energy that their reactions with other gas-phase species or with the diamond surface break the strong N₂ triple bond. Thus, unreactive N₂ is converted to more reactive N-containing radical species such as N atoms and NH, NH₂, and CN radicals, that can now participate in the diamond CVD process.

Theory suggests that each of the reactive species identified above should be able to insert into a C–C dimer bond on the C(100):H (2 × 1) surface *via* a ring-opening/ring-closing reaction mechanism [56] analogous to that for the case of CH₃ addition. These reactions provide viable routes for N incorporation into substitutional sites in the diamond lattice, but they do not explain the unusually large effect that N has upon growth rates and morphology.

Theoretical calculations have been used to investigate a number of possible mechanisms. The first suggests that adsorbed NH species at different step edges on the C(100):H (2 × 1) surface enhance the binding of gas-phase CH₃/CH₂ groups at these locations [57]. A second suggestion is that the additional electron density provided by a buried near-surface N atom weakens any nearby surface C–H bonds. This enhances the rate of the H-abstraction step that creates the surface radical site necessary for CH₃ radical addition [58].

Other mechanisms explain the apparent 'catalytic' nitrogen effect as a consequence of a growth model in which the rate-limiting step is the nucleation of a new layer. Evidence for this model comes from the observation that the surface of CVD-grown (100) diamond often exhibits a relatively smooth, terraced structure, which is greatly enhanced when N is present in the gas mixture [59]. Such morphologies suggest step-flow growth (layer-by-layer mechanism), in which surface migration of hydrocarbon adsorbates, together with preferential adsorption at step-edges, cause the rapid lateral

growth of the diamond layer. This mechanism also implies that nucleation of a *new* layer, on top of a flat pristine layer with no step-edges, would necessarily be slow. Thus, initiation of a new layer requires the creation of a 'critical nucleus' – an immobile surface feature with a low etch rate, which acts as a starting point for subsequent rapid lateral growth. Indeed, Monte-Carlo models using step-flow growth conditions that include such critical nuclei have demonstrated ten-fold enhanced growth rates [60,61]. The nature of such critical nuclei therefore seems key to understanding the nitrogen effect.

A mechanism proposed by Butler and Oleynik [62] suggests that adsorbed CN might act as just such a critical nucleus because it cannot undergo the β -scission reaction responsible for trimming longer-chained hydrocarbons from the diamond surface, as shown previously in Figure S1. Adsorbed CN cannot participate in a β -scission reaction because the N, which is now in the α -position, is not bonded to any H atoms and so cannot undergo an H abstraction. Thus, the CN group may remain on the surface as a protruding defect for a sufficient length of time that migrating hydrocarbon species will encounter it and attach to it – as they would to a step-edge – thus forming the critical nuclei. Hence, it only takes a single CN adsorbate across an entire surface composed of billions of carbon atoms to initiate a new layer, which explains the apparent 'catalytic' effect.

Following recent DFT calculations, a lone C–C dimer protruding from the flat (100) surface was suggested as a candidate for the critical nucleus [63]. In this model, nucleation of *new* layers occurs through the insertion of C into a C–C surface dimer, leading to a lone protruding C–C dimer. This is a relatively slow process under normal CVD conditions. However, when one of the surface carbons was replaced by N to form a C–N surface dimer, the energy required for C insertion was predicted to be substantially lower. In particular, the rate of the critical dimer ring-opening and closing mechanism was 400 times faster for a C–N dimer compared to that for a C–C dimer. As before, it only takes a single N atom embedded in a (100) surface dimer across an entire surface to act as a 'weak spot', allowing C insertion to occur more easily at this location, creating the lone dimer and thereby initiating the new layer.

1.3 Seeding using Detonation Nanodiamond (extended discussion)

The surface charge (or zeta (ζ)-potential) of the detonation nanodiamond (DND) particles in suspension determines the stability of the suspension at a particular pH. One of the reasons for the success of (DND) seeding is that this ζ -potential can be changed from positive to negative by pre-treatment with hydrogen or oxygen, respectively [64]. DND particles with negative ζ -potential will stick readily to a positively charged surface, and *vice versa*, meaning any kind of substrate can be easily and uniformly seeded this way. Another method that has been used to change the polarity of the DND particles or the substrate is the use of a cationic or anionic polymer as a coating. The substrate is either dipped in the polymer solution, or the polymer is added to the DND suspension, to realise a ζ -potential opposite to that previously [65]. When the DND suspension is applied to the substrate, the opposite charges attract, and a dense near-monolayer of seeds is formed. The hydrocarbon polymer layer is etched away during the first few seconds of CVD growth, leaving only the seeds behind.

DND seeding is particularly useful when the required diamond film is very thin ($< 0.5 \mu\text{m}$) [66], or where the substrate material is prone to etching or damage by the CVD environment. Examples are coating graphitic materials such as carbon-nanotubes [67], carbon fibres [68], or GaN [69]. Here, the dense monolayer of DND seeds protects the surface sufficiently that, during CVD, the seeds can rapidly coalesce to produce an impermeable diamond coating, after which diamond deposition can proceed as normal. In the case of GaN, nanodiamond seeding to prevent substrate etching was combined with microdiamond seeding to produce a good thermal interface, allowing thick diamond films to be deposited onto GaN for heat-spreading applications [70].

2. Distinguishing lab-grown diamonds from natural diamonds.

Lab-grown CVD or HPHT diamond can be distinguished from natural diamonds by a number of identifying markers caused by their growth conditions [71,72]. Some differences can be seen in an optical microscope. HPHT-grown diamonds often contain metallic inclusions (Fe, Ni, Co) as residues from the catalysts, whereas CVD diamonds often contain dark graphite inclusions.

Similarly, if a gemstone is viewed using polarised light microscopy, any internal strain within the stone will be revealed by a random mosaic multi-coloured interference pattern. These patterns are very prominent in natural diamonds, and result from the huge variable pressures imposed on the diamond when deep in the Earth. In contrast, CVD diamonds have more uniform, banded strain patterns due to their more stable, controlled growth environment. HPHT diamonds are grown under conditions with near uniform pressure conditions, and so are not subjected to stress. As such, they show only weak banded strain patterns or no patterns at all [72].

Shining light with a certain wavelength on diamond gemstones causes them to visibly fluoresce at longer wavelengths, and this fluorescence is useful for the identification of a gemstone's origin. Natural diamonds tend to fluoresce more brightly when illuminated with light of longer wavelengths compared to shorter wavelengths. The opposite is true for synthetic diamond, where short-wavelength UV illumination causes brighter fluorescence – often in a characteristic pattern (HPHT tend to show a cross-shaped pattern whereas CVD diamonds show a striped pattern).

The fluorescence pattern can be readily detected using the *DiamondView* imaging instrument developed by de Beers in the mid-1990s [73,74], and by the detection of the SiV defect using photoluminescence (PL) spectroscopy, while Raman spectroscopy is useful for identifying coloured diamonds. More sophisticated analysis techniques, such as X-ray tomography, laser-assisted-inductively coupled plasma-mass spectrometry, and Fourier transform infrared spectroscopy (FTIR), are used in research labs to extract a wealth of information about the gemstone in question. Nowadays, the development of small, portable micro-Raman or hand-held FTIR systems or X-ray fluorescence analysers, along with real-time imaging based on fast charge-coupled device (CCD) detectors, and relatively inexpensive dedicated instruments such as *Diamondview*, have made the near-instant identification of a gemstone's origin possible for jewellers, museums and trade shows [73].

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