

# Evidence for charged or polar precursors in diamond nucleation

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The nucleation process determines the final properties of thin films significantly. Thus nucleation is important as well from the viewpoint of basic research as from the viewpoint of technical application. Because no comprehensive general theory exists up to now, experimental work has to guide the understanding of the relevant processes. Despite the fact that in the case of diamond nucleation and growth a "common" explanation regarding the methyl radical as growth precursor can be found in the majority of publications, some inconsistent findings remain. These have been worked out and put together with special experiments leading to the suggestion, that charged or polar precursors play a significant role in diamond nucleation.

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## 1. Introduction

### a) History of diamond CVD

Several decades ago it was recognized, that diamond is necessary to drill holes into rocks for petrol exploration, but nearly no resources of natural diamond were present in the industrial nations. Thus significant – and more or less secret – research was started to produce synthetic diamonds. Well known success has been reported in the 1950ies (ASEA, GE) using high pressure/high temperature synthesis (hp/ht) after the basic work of P. W. Bridgeman, who was honored with the Nobel price "for his pioneering work on high pressure physics" in 1946, even if he did not succeed in producing diamonds. Nearly at the same time significant research started to produce diamond at low pressure in the thermodynamic metastable regime. Milestones may be autoepitaxy from CO by Eversole 1953, the use of atomic hydrogen for etching nondiamond phases in a two-step process by Angus 1968, the deposition on nondiamond substrates using a one-step process by Spitsyn and Derjaguin 1981 and last not least the publication of Hot Filament- or Microwave CVD by Matsumoto 1982 and 1983 (for a review of the history see e.g. Angus [1]). It has been proven later on that CVD diamond is formed by nucleation and growth and not by stress induced transformation from graphite [2]. But even if the field of diamond CVD and the number of applications are permanently growing, some aspects of nucleation are not fully understood - despite a lot of practical solutions for nucleation enhancement (see e.g. [3, 4]).

### b) Specific aspects of diamond growth

The first remarkable success in searching for understanding diamond growth was the „Bachmann-diagram“. Bachmann plotted the net chemical composition

of the precursor gases used by different authors for diamond CVD and found that – independent of the specific method and equipment – in a H/C/O phase diagram only a narrow region around the CO-line is usable for diamond growth [5], later on he refined this with own experiments [6], see Fig. 1.

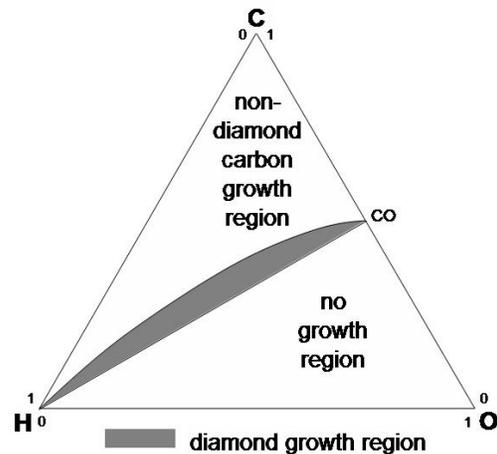


Fig. 1. Bachmann diagram.

Three statements result from his findings:

- There is only a narrow range of chemical composition leading to diamond growth due to a delicate balance between nucleation / growth and etching
- The influence of substrate material (not substrate temperature) is usually only weak
- The plasma chemistry must not be very important (because diamond deposition is following the „Bachmann-diagram“ from hot-filament CVD at  $T_{\text{filament}} = 1500 \text{ K}$  [7] up to plasma jet deposition with  $T_{\text{plasma}} \approx 10000 \text{ K}$  [8, 9].

Despite a lot of work to explain these results (see e.g. [10 – 12], no model exists up to now that explains all experimental findings (e.g. the influence of traces of nitrogen [13] or the dependence of texture from process parameters [14]).

Nevertheless the plasma chemistry has been worked out in great detail (see e.g. [15] and leads to the following reaction chains (after Lang et al. [15]), Fig. 2.

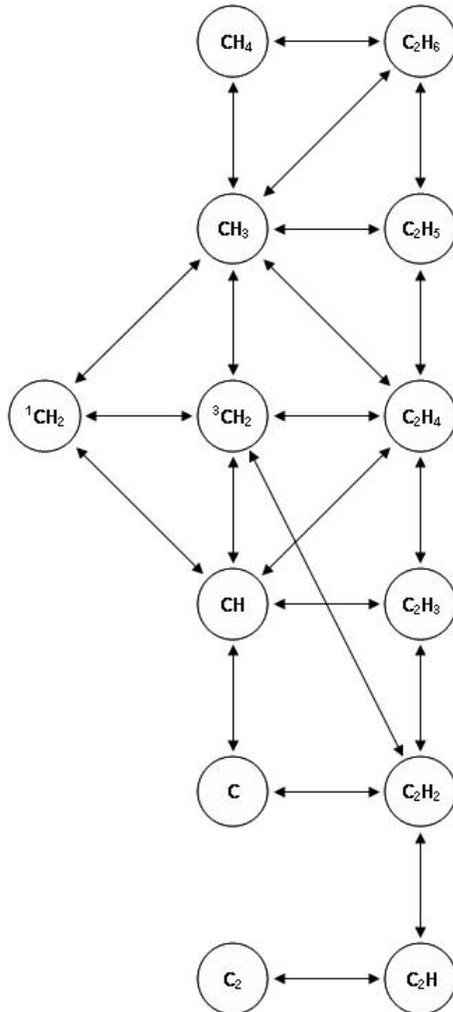


Fig. 2. Chemical reaction chains (after [15]).

To elucidate, if the  $C_1$ - or the  $C_2$ -chain is responsible for diamond growth, a lot of experiments have been carried out (e.g. [16 – 19]) but the detailed investigation of the order of the chemical reaction by Angus [20] shows clearly, that the reaction is of first order and thus (via the  $C_1$ -chain) the methyl radical is the growth precursor; it should be remarked that deviations from first order had been reported, but it could be worked out by Sternschulte [21], that these findings are only due to acetylene production in the plasma and that even in these cases the growth rate is proportional to the methyl concentration in the plasma. Nevertheless all over the time even the  $C_2$ -chain was brought into the discussion again ([22 – 24],

especially with UNCD [25, 26]) and the methyl radical could not be observed in experiments using surface laser spectroscopy [27].

## 2. Results

### a) Nucleation

Usually heterogeneous nucleation of diamond is observed and the nucleation density on usual substrate materials (e.g. Si) is low, Fig. 3.

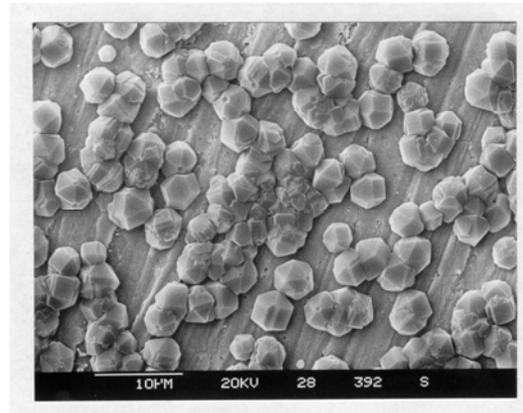


Fig. 3. Heterogeneous nucleation of diamond on Si.

Thus several methods have been developed to enhance the nucleation density leading to the statement: [28] „It is evident from published literature that the technological problems associated with the nucleation of polycrystalline diamond films have been adequately addressed, as demonstrated by the development of the numerous nucleation enhancement methods,....However, the scientific issues integral to diamond nucleation processes remain less well understood...“.

Usually combination of pretreatments [29] and especially mechanical scratching with diamond powder is used for nucleation enhancement (see e.g. [2, 3, 30 – 32]) Fig. 4:

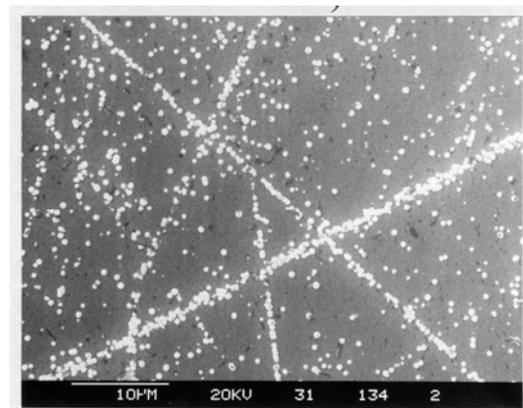
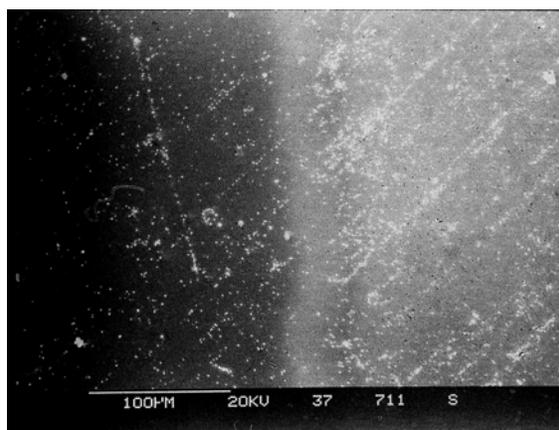


Fig. 4. Enhanced nucleation at scratches.

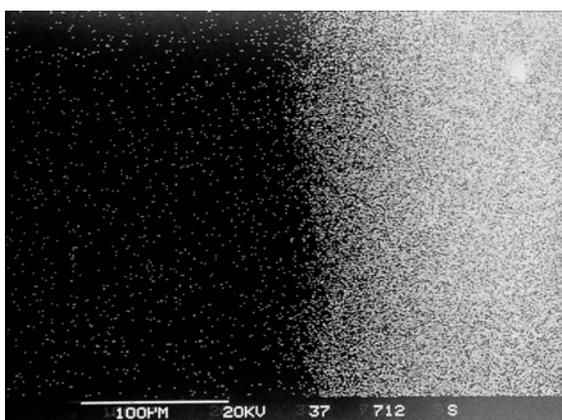
To explain these results, three possibilities exist:

- residues of the diamond powder serve as nuclei for further growth
- lattice defects produced are good nucleation sites
- the morphology of the scratches is the important feature.

To decide between these possibilities, a model experiment has been carried out [33], where one half of a scratched Si-substrate has been covered with a 50 nm thick Cr-layer; this covers as well residues of diamond powder as lattice defects. The results show, that diamond nucleation furthermore occurs at places corresponding to scratches in the substrate (and is even enhanced), Fig. 5.



(a)



(b)

Fig. 5. Nucleation on a scratched Si substrate where the right half is covered with a 50 nm thick Cr layer (a) and Cr-scan (b).

This result excludes the first two possibilities and hints towards a morphological origin. Because it is possible to have an enhancement of electrical fields at the scratch, sharp tips have been prepared (by etching) in a graphite substrate [34]. It can be seen clearly, that nucleation occurs indeed at the top of the tips, Fig. 6:

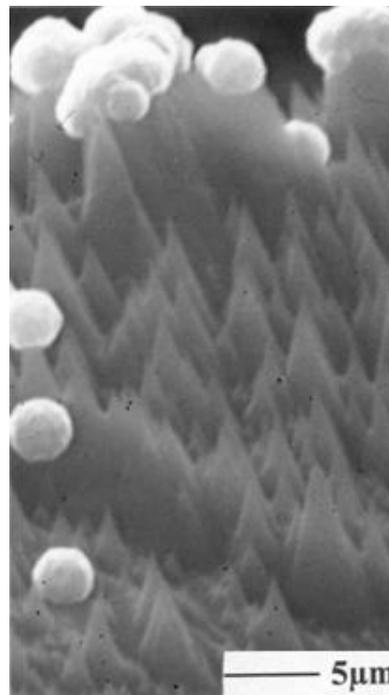


Fig. 6. Nucleation on top of graphite tips.

To further confirm the importance of electrical fields, the field has been produced by a high power laser [35]. Even here the enhancement of nucleation density with laser power comes out clearly, Fig. 7.

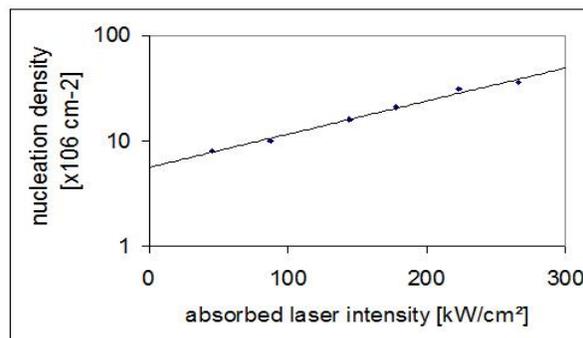


Fig. 7. Enhanced nucleation induced by intense laser radiation.

From these findings it is concluded, that electrical fields or field-gradients are important or even necessary for diamond nucleation. Thus it is suggested, that charged or polar species are involved in diamond nucleation. The existence of charged particles in plasma enhanced CVD is obvious, but even in Hot Filament CVD the existence – and importance – of ions has been already proven [36]. Furthermore charged species have been shown to be important for Silicon Film growth in Hot Wire CVD [37].

### b) Secondary nucleation

Ultra-nanocrystalline diamond films, „UNCD“ result if secondary nucleation dominates (even here an enhancement of primary nucleation is essential to get smooth, continuous films) [38]. Because growth is always more favourable than nucleation, secondary nucleation usually occurs if growth is hindered [39], e.g. by impurities covering the growing surface. The usual method to produce UNCD uses the replacement of hydrogen by argon in the feed gas [40 – 42]. To exclude an influence of the argon, here a recombination of the growth species (or prerequisite of the growth species, as atomic hydrogen) is used for model experiments. For this purpose a special substrate holder has been inserted into a standard hot-filament CVD chamber, possessing a rim for recombination of atomic hydrogen [43], Fig. 8.

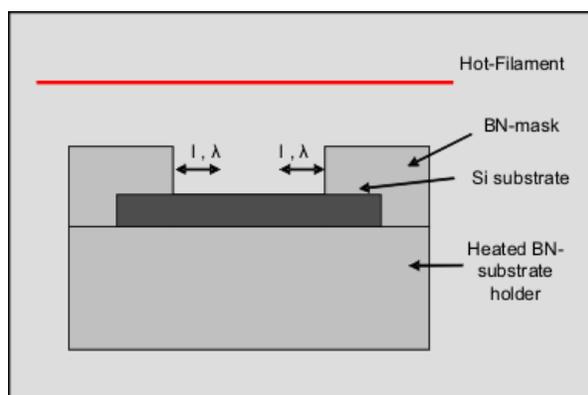


Fig. 8. Substrate holder for model experiments.

Using the substrate holder with the 3 mm thick rim on the silicon substrates (Fig. 8), a peripheral growth zone was discovered, where the morphology of the diamond was significantly changed as can be already seen with the bare eye. Optical microscope pictures give the possibility to distinguish between the rough microcrystalline area on the sample (bright area close to the center) and the nanocrystalline peripheral growth zone (the dark area close to the edge). SEM investigation clearly showed that in the middle of the substrate microcrystalline diamond was growing with typical grain sizes of around 1  $\mu\text{m}$  while nanocrystalline diamond was found in the peripheral zone. Raman spectroscopy supports the results of the SEM investigation, Fig. 9.

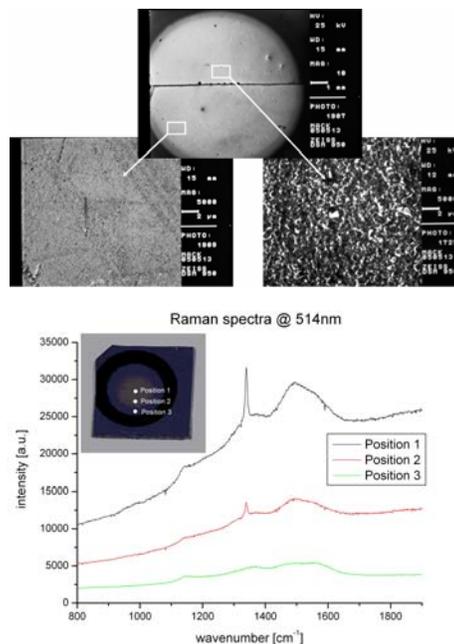


Fig. 9. SEM-pictures (top) and Raman spectra (down) of films grown in peripheral and central zone.

Therefore the observation of different growth zones suggests that a depletion of atomic hydrogen in the process gas in the peripheral zones is happening. A similar change in growth behavior was described by Tzeng and coworkers for microwave plasma [44] where a change in atomic hydrogen concentration close to the substrate was described to be influenced by the distance of the plasma ball from the substrate. This depletion of atomic hydrogen leads to a reduction of the methyl radical density because this radical is usually produced from methane by hydrogen abstraction with atomic hydrogen. But H abstraction by electron collisional impact of methane is still possible, thus diamond growth is not suppressed but only reduced (it is well known that the growth rates for UNCD are lower than for microcrystalline diamond at comparable conditions).

The intense emerald color of the plasma connected with UNCD deposition is due to the  $\text{C}_2$ -Swan band leading to the suggestion that  $\text{C}_2$  could be the growth species in UNCD growth [45, 46], but this model could be excluded [47]. Thus it is concluded here that  $\text{C}_2$  is involved in (secondary) nucleation, that is strongly enhanced in UNCD deposition. Additionally it is known from acetylene plasmas that ions are important for dust formation (i.e. homogeneous nucleation [48]) and that species with even carbon atom number dominate (with long lifetimes of e.g.  $\text{C}_2^-$ ) [49].

### 3. Discussion

From these findings a two step model separating nucleation and growth is derived, Fig. 10:

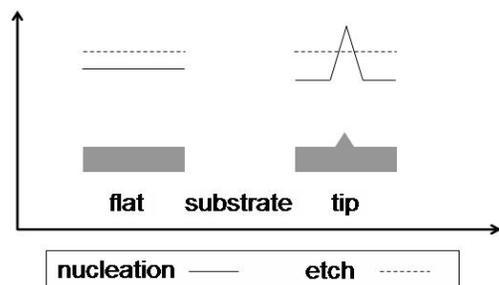


Fig. 10. Nucleation model (full line: nucleation rate, dashed line: etch rate).

- On the flat surface the etch rate of the nucleation species is larger than the nucleation rate, i.e. no nucleation occurs
- At scratches enhanced electrical fields disturb the homogeneous etch/growth balance and attract nucleation species, leading to an enhanced local concentration of nucleation species exceeding the etch rate.
- Nuclei can grow, leading to a positive feedback because diamond nuclei enhance the electrical field above the substrate [50].

Already Tsuda et al. [51, 52] proposed that ions are involved in diamond growth, but the ions are too scarce to explain the deposition rates and thus this argument was abandoned; but here nucleation and growth are treated as two different steps and thus this argument does not hold any more and it can not exclude that charged particles are important for nucleation. The model proposed is furthermore consistent with the observation that diamond can nucleate under conditions under which diamond cannot grow [53]. It explains additionally observations like the enhanced nucleation with slurries consisting of mixture from diamond- and Ti-powder [54] via “metallization” of the tips, the reduced nucleation on substrates like alumina or the promoted secondary nucleation using time modulated methane flow [55] and may also support the observation of modified diffusion as possible nucleation enhancement in bias enhanced nucleation [56].

#### 4. Conclusions

A two step model is proposed that explains nucleation of diamond by charged or polar precursors presumably consisting of species with two carbon atoms as the first step followed by growth via the methyl radical as a second step.

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