Large area, low temperature nano crystalline diamond coating technology with microwaves: Linear coaxial antenna approach – an alternative to slotted antennas

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Plasma Enhanced Chemical Vapour Deposition of diamond thin films

The growth of diamond films from a carbon containing reactive hydrogen gas phase is a very slow process in terms of common plasma polymerisation involving organic or metal-organic monomers. Carbon or carbon containing molecule fragments produced in a plasma discharge are more likely to form graphitic bonds on suitable substrates than diamond. However, since suitable plasma discharges primarily consists of hydrogen it is the ability of atomic hydrogen to etch back the deposited graphitic carbon but much less carbon atoms which are bonded in the tetrahedral diamond lattice. The diamond films that form on pre-treated substrates usually consist of small crystallites up to several hundred micrometers joined together by so called grain boundaries of amorphous carbon containing material. Depending on the size of the crystallites these films are called poly crystalline or nano crystalline. The growth rate of crystalline material is generally slower than amorphous material since every atom that arrives at the crystalline surface needs sufficient energy and time to migrate on the surface until it finds a void in the lattice of the right energetic state. This process takes time and should be accommodated by a substrate at elevated temperatures. Single crystal silicon substrates suitable for the growth of diamond films are usually heated to 900-1000°C to enable growth rates of circa 1 µm/h which provides optical grade diamond films. Higher growth rates are possible but usually result in a loss of quality in terms of crystalline stacking faults, twinning, voids etc. Most materials of commercial interest, such as glass, have a substantially lower melting point than silicon resulting in lower operation temperatures and therefore show substantial limitations in the maximum growth rate of diamond films. Nevertheless, the plasma needs to be dense and hot to provide fast deposition and subsequent back etch of graphitic carbon. Only a much smaller fraction of the precursor material is deposited as diamond since it resists atomic hydrogen etch due to the strong sp$^3$ hybridized carbon bonds.

The need for a powerful source for atomic hydrogen has established three different approaches each focusing on different requirements of the very different substrates to be coated with diamond thin films.

- Hot Wire Chemical Vapour Deposition (HWCVD)
- Microwave Plasma Enhanced Chemical Vapour Deposition (PECVD)
- DC Arc Chemical Vapour Deposition

Hot Wire CVD is the only technology not based on ionic species of a plasma to activate the precursor material. The hydrogen molecules are dissociated by electrons (H-H bond energy: 4.53 eV) which are emitted by wires made of refractory materials such as tungsten and heated to temperatures well above 2000°C. Hot Wire CVD is very efficiently used for tool coating (drills, inserts etc.) and can also be made into planar arrangements for thin diamond films on planar substrates such as electrodes. Pure thermal gas phase activation demonstrates that no ionic species is necessary to produce good quality diamond crystallites. DC arcs as well as microwave PECVD both depend on plasma discharges to produce atomic hydrogen. DC arcs may be able to produce highest plasma densities and are an extremely efficient source for atomic hydrogen but are bound to columnar shapes which limits their use to the coating of small 3D parts such as cutting tools and similar substrates of small size. Microwave PECVD has initially been used to create ball or disk shaped plasmas for the deposition of diamond on single circular substrates of 4 to 8 inches in diameter usually made from silicon or related crystalline materials. Very dense and hot discharges can only be formed in single or dual wave-mode cavities which were designed to avoid contact between the destructive plasma and adjacent cavity walls. Plasma discharges at several hundred mbar pressure and several kilowatts of microwave power deliver excellent diamond thin films at maximum growth rates but they destroy any solid insulating material like dielectric atmosphere-to-vacuum interfaces they come into contact with. However, enlarging the deposition area turned out to be limited since the design and functionality of wave-mode cavities depend on the wavelength of the respective microwave generators. And the wavelength cannot be chosen arbitrarily but depends on available industrial standards. The most common standard of industrial microwave tubes uses 2.45 GHz with a free space wavelength of slightly more than 12 cm. Cavities designed for this standard are commonly based on the TM$^{01}$ wave-mode (transversal magnetic) which provide acceptable coating uniformity over 4 inch in diameter. Also, commercially available single microwave magnetron tubes at 2.45 GHz are limited to 6 kW of c/w output power.
dual mode cavities can only be enlarged by employing larger wavelength. Powerful magnetron tubes of up to 100 kW c/w power are commercially available for 915 MHz. Since the corresponding free range wavelength is almost three times larger compared to 2.45 GHz the useful maximum substrate size extends to 12 inch, accordingly. However, enlarging the available coating area by reducing the microwave frequency does have a substantial drawback.

\[ \omega_p = \sqrt{\frac{e^2 n_e}{\varepsilon_0 m_e}} \]  

The plasma frequency \( \omega_p \) is the most fundamental plasma parameter. \( e \) is the electron charge, \( n_e \) is the plasma electron density, \( \varepsilon_0 \) the dielectric constant and \( m_e \), the electron mass.

High frequency electromagnetic waves such as microwaves can only propagate and dissipate power to the plasma electrons if they can penetrate the plasma discharge. Electromagnetic waves of a given frequency \( \omega \), however, can only propagate in a plasma of a given plasma electron density \( n_e \) if their frequency \( \omega \) is higher than the plasma frequency \( \omega_p \) as defined in equation (1). Hence, the plasma electron density will not exceed a value that would still allow electromagnetic waves to propagate and subsequently transfer energy to the electrons. The plasma density will decrease quadratically with decreasing high frequency resulting in a drastically lower density of atomic hydrogen at lower frequencies. This is the reason why lower frequencies such as radio frequency (13.56 or 27 MHz) are not commonly used for the deposition of diamond.

Employing microwave power for the deposition of diamond thin films over much larger areas (\( \sim 0.5-1 \, \text{m}^2 \)) requires a different approach. Two fundamental questions such a different approach will bring along is whether there is a feasible non-resonant cavity reactor design which will enable the uniform deposition of diamond films over much larger areas and what kind of surface-to-plasma contact can be accepted, if any. A substantial part of the inner surfaces of a typical plasma reactor is the atmosphere-to-vacuum interface which is necessary to transfer the microwave power from the generator(s) to the plasma discharge. The interface usually consists of a ceramic material (quartz, aluminium oxide, etc.) of a very low dielectric loss tangent. The material should be free of moisture or any other microwave absorbing molecules and therefore absorb as little as possible of the dissipating microwave power. Both shape and size of the interface strongly depends on the individual reactor design but the surface area should be chosen as large as possible to generally enable low power densities on the inner surface area. The total microwave power will cause a certain lateral power density distribution on the inner surface of the interface which is generally low on large interfaces and high on small area interfaces. High power densities naturally result in high thermal plasma loads on the vacuum interface, imposing stress with the possible loss of the interface over time, and also reduces the available power in the vicinity of the substrate. Experience shows that industrial large area diamond coating systems employing microwave PECVD need to allow the plasma to be in contact with the atmosphere-to-vacuum interface in order to produce films of an acceptable thickness uniformity. There is simply no other way to distribute microwave power evenly for sustaining uniform lateral discharges. It is understood that high thermal loads on ceramic interfaces have to be avoided which again means that all coating systems which allow direct plasma-to-interface contact will be substantially slower than single or dual wave mode cavity machines.

**Large area PECVD with microwaves**

The key to depositing uniform diamond thin films from a uniform plasma discharge is the ability of a coating system to evenly distribute microwave power to the plasma discharge. As long as the wavelength of the applied power is larger or comparable to linear dimensions of the plasma processing reactor free range wave propagation is not possible and all wave modes will have to rely on conductive components (waveguide, electrodes, conductive surfaces) inside the reactor. This is both helpful and problematic at the same time. While plasma shaping with metallic surfaces is generally well understood and reliable, the necessity of metal-to-metal electrical contacts is not without risk concerning good electrical conductivity, particularly for moving carrier-based substrates in so-called in-line processes. The wavelengths of industrial microwave frequencies (2.45 GHz, 915 MHz) are usually smaller than the dimensions of large area plasma processing vessels. Here, free range propagation is possible, and microwaves do not have to rely on metallic surfaces for propagation. Hence, the plasma reactor geometry does not have to be part of an electromagnetic resonant circuit which otherwise needs to be kept in resonance to avoid high reflected power levels. While single point power injection is a common way to feed radio frequency (low Megahertz range) into large area plasma reactors this is not possible for microwaves since dense discharges will form near the injection point which will prevent the
waves from propagating further into the reactor chamber. Subsequently, generally more complicated methods of injecting microwave power into plasma discharges have to be used. Amongst them, slotted line antennas [1] [2] with discrete radiating elements, commonly used in radar applications have been tried in the past but are not easy to manage (Fig. 1). The reason is simply that any calculated or predicted performance of such a radiator array is only true for a highly power absorbing environment (i.e. free range radiation) but not really for an unsteady plasma in a metallic container [3]. Once one or more of the radiating elements (slots) experiences a considerable amount of reflected power, the entire intended power distribution of the antenna will be disturbed and and the radiation pattern may change together with the process rates on the substrate. Power reflections may occur from the atmosphere-to-vacuum interfaces if they are small in size resulting in high density plasma discharges close to their vacuum side surfaces. Although slotted lines appear to be suitable to evenly distribute microwave power over the area of interest the problem of high power densities on the atmosphere-to-vacuum still remains since slots are discrete radiating elements.

Fig. 1 Typical layout of an edge shunt slot array (left) as commonly used in navigation radar systems. The slot inclination angle is growing with increasing distance from the point of power generation into the rectangular waveguide to sustain a constant net power output of the all slots. A folded edge shunt slot array in a twin arrangement (centre) and two edge shunt slots with adjacent plasma discharge (right) are shown in the photographs.

The breakthrough on the way to a spatially sustained microwave discharge over areas much larger than the wavelength of the applied microwave power was certainly the both brilliant and simple idea to replace slotted waveguides and their troublesome discrete radiating elements by making the electrically conductive plasma part of a coaxial transmission line. Microwave power is supplied to a vacuum vessel by a coaxial transmission line in the transversal electromagnetic (TEM) wave mode. Inside the vacuum vessel a tube manufactured from a dielectric material acting as an atmosphere-to-vacuum interface replaces the outer conductor of the coaxial line. Since the dielectric material should be heat resistant and have a low dielectric loss tangent either quartz or alumina appears to be the most suitable materials. Microwave power can pass through the tube material and ignite a plasma discharge of high radial symmetry circumjacent the tube surface as indicated in Fig. 2. Experience has shown that contamination of deposited thin films from atmosphere-to-vacuum interface material is not an issue even for plasmas primarily consisting of hydrogen gas.

Fig. 2 The principal layout of the coaxial line plasma source in a semi-remote plasma arrangement. Microwave power is supplied by coaxial lines from both sides to the coaxial line plasma source which simply consists of a metallic inner conductor and a dielectric outer conductor surrounded by the plasma discharge.
Having replaced the metallic outer conductor of the coaxial transmission line by a (electrically conductive) plasma discharge, a surface wave sustained linearly extended discharge is obtained [4] [5] [6]. The microwave power propagating along the “plasma line” experiences a high dissipative attenuation by converting electromagnetic energy into plasma oscillations. Assuming a constant attenuation coefficient per unit length of the plasma line the net amount of power dissipated into the plasma per length unit will decrease with growing distance from the point of power injection to the coaxial line plasma source. This will result in a non-uniform plasma distribution and subsequently in a non-uniform deposition process across a substrate. Measures will have to be introduced to modify the power attenuation of the propagating power, such as a partial outer conductor or the replacement of the straight inner conductor by a helical line. Both methods allow spreading the microwave power more evenly.

Fig. 3 Attenuation of propagating power along the coaxial plasma line is assumed to be constant. Therefore the attenuation needs to increase with growing distance from the power injection point (left side). With the tapered outer coaxial conductor steadily opening up with increasing distance from the power injection point the attenuation of the power by plasma absorption is increasing. The net power transfer to the plasma per unit length should be constant.

Fig. 3 shows a coaxial line plasma source with a tapered outer shielding made from metal resulting in a more even plasma density distribution. The coupling between the coaxial line plasma source and the plasma is increasing with retracting outer conductor thus feeding a higher percentage of the propagating power to the plasma. Although partial shielding is an easy way to control the plasma uniformity it also destroys the radial symmetry of the coaxial plasma source. Maintaining the radial symmetry would be essential if the plasma source was used for bi-directional coating of two substrates simultaneously, minimizing self coating of inner reactor walls and doubling the throughput. This would result in reduced cost of ownership and system footprint. Although being of a more complicated nature, a helical transmission line can be designed so that the length of one turn equals one wavelength of the applied microwaves (operating the device in the T1 “end fire” mode). The electrical field vector of the microwaves across the diameter can rotate around the axis of symmetry. The microwave power will experience circular polarization defined by $\epsilon$, the helicity of the helix. Two opposing helical lines in close proximity sharing the same axis of symmetry can thus be fully decoupled by possessing opposing helicities or act like one long line being of the same helicity. Initial tests with helical structures, however, revealed that some space is required between the outside of the helical turns and the dielectric interface tube. The helix diameter is determined by the wavelength of the microwaves. At 2.45 GHz the necessary diameter of the helix would be quite large and result in large dielectric interface tube diameters causing too much tensile force on the brittle tube walls. However, the diameter of the helix can be reduced substantially by filling the core of the helix with dielectric materials such as quartz or alumina because the wavelength can be reduced according to the dielectric constant of the dielectric material. Also, the dielectric filling helps to concentrate more microwave power in the helical core and therefore strengthen the intended purpose of the helical line.

Fig. 4 The Helix is designed to carry the electromagnetic energy inside of the turns. Therefore, the length of one turn of the helix should be equivalent to one wavelength of the microwaves. To keep the helical line small in diameter the core is filled with dielectric material. The spacing between adjacent turns is widening with increasing distance from the power injection point.
point to allow a stronger coupling between the helix and the adjacent plasma since constant attenuation steadily reduces the propagating power inside the helical line.

Fig. 4 shows a helical line with a dielectric rod. The helical turns are made from a pipe rather than solid material to allow for forced air cooling. The amount of power dissipated to the plasma per unit length can be controlled by adjusting the inclination angle of the helical turns. With increasing distance from the point of power injection the amount of propagating power is decreasing. Subsequently the attenuation of the propagating power needs to increase to make sure equal amount of power is fed to the plasma discharge per unit length. This can be done by increasing the inclination angle between adjacent turns.

Feeding microwave power to the coaxial line plasma source from both ends [7] devices with straight inner conductors of up to 3000 mm in length have been built [8]. Since the inside of the dielectric tube remains on atmospheric pressure, dielectric tube diameters of less than 40 mm are preferable to keep the tensile force on the inner tube walls reasonably small. The inner conductor of the coaxial line plasma source does not necessarily have to consist of a single pipe but can be made of two separate pipes opposing each other. Two separated inner conductors are easier to mount and can also be used for supplying compressed air to cool the inside of the coaxial line plasma source. The heat load from the plasma radiation is the major limitation in the linear extension of this type of plasma source. Large area microwave plasma sources can be built by arranging arrays of parallel coaxial line plasma sources as shown in Fig. 5. Usually not every line source will have its own microwave power generator due to technical and economical restrictions. Depending on the process requirements, costs and availability of suitable power generators, one, two, four or even eight coaxial line plasma sources may be driven with one single generator. Adapted coaxial T-junctions as pointed out in Fig. 5 achieve efficient power splitting. T-junctions are ideal for microwave power splitting since they are quite easy to manufacture and are of compact built but every ordinary T-junction reflects about 1/7 of the incident power. Unacceptable levels of reflected microwave power will have to be anticipated for cascaded T-junctions in particular. But the inherent reflection of a T-junction can be overcome by adequate design modifications employing finite element based computer modeling. Coaxial plasma lines do not reflect incident power and therefore do not require tuning devices like stub tuners or E-H tuners as long as all transmission line elements are impedance matched.

Fig. 5 Coaxial plasma lines in a parallel arrangement to form a planar plasma source. Usually, only an even number of coaxial plasma lines can be supplied with microwave uniformly from one single generator through an impedance matched transmission line.

The merits of pulsed microwave power for the PECVD of diamond films

The deposition of diamond thin films from a hydrogen-methane plasma (other gases like carbon dioxide or nitrogen may also be added to the process) is a considerably slow process and both speed and quality of the deposited material depends on the abundance of atomic hydrogen. Therefore, it is desirable to have powerful and dense plasma discharges. It is common knowledge within the PECVD community that supplying the necessary power during repetitive pulses rather than continuous wave (c/w) generally leads to higher deposition rates, better deposition uniformity and in cases also in a different thin film morphology as well as a
better control over the deposited films. Additionally, there is also an economic advantage of pulsed power over c/w as shown in Fig. 6. The pulsed power regime can be described by pulse shape (usually rectangular), pulse height, duty cycle and repetition frequency. In Fig. 6 only the pulse repetition frequency was changed in steps from 10 Hz to 10 kHz. The light signal from the plasma was taken by a fast photodiode as an indicator of activity in the plasma.

![Figure 6](image.jpg)

**Fig. 6** At very low pulse frequencies the light emitted from a plasma discharge as measured by a photodiode is coherent to the microwave pulse signal taken directly from the waveguide. With increasing pulse frequencies the plasma light signal starts to develop a "tail" and even below 1 kHz the plasma never extinguishes during the break between pulses. At 10 kHz the plasma light signal is basically a flat line.

Activation and decay both take place during the power on time but decay takes place during the pulse break also. Once the pulse ends all excited plasma particles will return to their ground states and ion-electron pairs will recombine. But this takes some time and the plasma still emits light although no external power is supplied. Chemical processes inside the plasma can still continue during the power off time. At 10 kHz pulse frequency the plasma light signal is basically a flat line. Even if power is only supplied to the plasma process 10% of the total process time the process rates show a behavior as if the power was on 100% of the time. This behavior is beneficial in several ways. The costs for utilities can substantially be reduced. This is particularly true for diamond coating systems since the process is mainly producing graphic carbon with subsequent back etching and only a small fraction of the down pouring atoms or molecule fragments is deposited as diamond crystals. One other advantage lies in the reduced thermal load from the plasma on the substrate. This may not be decisive for diamond coatings but it is for other processes like silicon dioxide scratch resistant coatings on plastic surfaces. Any reduction in power would lead to faster processes since the thermal management of the polymer surfaces determine maximum deposition rates and eventually the industrial viability of vacuum based coating processes.

The modulated supply of power to the process opens up a new field of parameter settings since pulse shape, duty cycle and pulse frequency do have strong influences on both plasma electron temperature and density as described in the *Global Model* by Ashida et al. [9]. The validity of this simplified model for non-collisional, homogeneous plasma discharges by electron impact ionisation has been proven experimentally and can be used as a guideline for more complex plasma discharges as well. Generally, the electron temperature shows a steep rise in the beginning of each pulse since only a few charge carriers are available which can absorb an abundance of power and are very unlikely to lose energy on impact with other charge carriers. Shortly after the start-up phase the electron plasma density increases rapidly in an avalanche-like effect and the hot electrons thermalize in the dense plasma discharge and the temperature settles for the c/w value. Fig. 7 indicates that both electron temperature and density remain constant after the initial phase until the pulse comes to an end. The electron temperature decays much faster than the electron density. Fig. 7 also shows that the benefit of pulsed power is not really in elevated electron temperature but in electron density. During the pulses the plasma electron density increases by a factor of four with respect to the c/w value in this particular case.
Generally, the question can be raised under which conditions can a maximum electron density be reached for each particular plasma and what kind of electron density enhancement can be expected? The answer is given by the *Global Model* and it is a rather simple one. As depicted in Fig. 8 (left diagram) the ideal pulse frequency for maximum plasma electron density is purely a function of the electron loss frequency $v_{loss}$ from a given plasma. The higher the electron loss frequency, i.e. the more electrons escape from the plasma per unit time by hitting the wall of the vacuum vessel for instance, the higher the pulse frequency needs to be. Hence, the ideal pulse frequency is dependent on the shape and the size of the plasma both being directly dependent on plasma reactor and vacuum system design. And it is quite clear that larger plasmas require lower ideal pulse frequencies since the volume-to-surface ratio is in favor for larger plasma discharges. However, these considerations are valid for rectangular shaped pulses - "ideal" pulses. If the pulse shape becomes sinusoidal the maximum plasma electron density will be reduced by ca. 50% while the time averaged electron temperature will double.

Fig. 7 At the beginning of a pulse the electron temperature rises very quickly since only a small number of charge carriers is able to pick up electromagnetic power. After a very short time the plasma electron density rises with the onset of an avalanche like effect of electron impact ionisation and the electron temperature quickly settles at the c/w value. Data were taken from 0.7 Pa Argon plasma at 500 W average microwave power input at 1 kHz pulse frequency (30% duty cycle) [9].

Once the ideal pulse frequency has been determined the Global Model devises the duty cycle of the modulation to determine the plasma electron density enhancement factor. Amazingly, Fig. 8 (right diagram) indicates that low duty cycles lead to higher plasma electron densities which is generally true and has been proven on many occasions. Increasing the duty cycle steadily takes the plasma electron density down to the value it would show in continuous wave operation. Of course, steadily reducing the duty cycle to smaller values does not result in an ever increasing plasma electron density since from a certain maximum value on the net power input would be too small to sustain the discharge and the electron density would decay instantaneously.

Fig. 8 In pulsed power operation the attainable mean plasma electron density is generally well above the densities at continuous wave (c/w) mode. According to the GLOBAL MODEL [9] the electron loss frequency $v_{loss}$ from the plasma determines the ideal pulse frequency (at 25% duty cycle) as shown on the left diagram whereas the duty cycle determines the maximum value of the plasma electron density at a constant electron loss frequency (see diagram on the right side).
High plasma electron densities are of outmost importance since they directly result in the dissociation of molecular hydrogen which is the key to high rate deposition of good quality diamond thin films. Gases consisting of molecules rather than atoms are generally much more difficult to activate by a plasma discharge since two energetic steps are necessary to achieve a high plasma electron density. Tab. 1 clearly shows that the energy necessary for the production of hydrogen ions is the combination of dissociation of the hydrogen molecule requiring 4.53 eV of energy plus ionisation energy of 13.59 eV. In comparison it only takes one step of 15.75 eV to produce one argon ion.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Binding Energy [eV]</th>
<th>Atom</th>
<th>Single Ionisation [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-H</td>
<td>4.53</td>
<td>H→H⁺</td>
<td>13.59</td>
</tr>
<tr>
<td>O-O</td>
<td>5.12</td>
<td>O→O⁺</td>
<td>13.61</td>
</tr>
<tr>
<td>N-N</td>
<td>9.79</td>
<td>N→N⁺</td>
<td>14.53</td>
</tr>
<tr>
<td>C-O</td>
<td>11.17</td>
<td>Ar→Ar⁺</td>
<td>15.75</td>
</tr>
</tbody>
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Tab. 1 Energies necessary to dissociate or ionise a selection of molecular and atomic gases which are important for the plasma enhanced chemical vapour deposition of diamond.

It is, for example, even more difficult to "activate" nitrogen. Although the ionisation energy is not much higher compared to hydrogen it takes more than double the energy to dissociate the triple bonded nitrogen molecule compared to hydrogen. Measurements of forward and reflected pulsed microwave power supplied to argon and air (4/5 nitrogen) plasma discharges give evidence of the very different behaviour of plasma discharges of molecular and atomic gases. In Fig. 9 the reflected microwave power signal from an argon plasma (red colour, signal amplified by a factor of 10) is initially very small at the beginning of the pulse at 19.2 kHz meaning that the power is readily picked up by plasma electrons which remain in large quantities at such high pulse frequencies (cycle time is shorter than average time of electron-ion recombination). Power saturation and subsequent reflection occurs some instants later since peak power input is quite high for the size of the plasma. In the case of air/nitrogen the reflected power is highest at the beginning of the pulse and low at the end of the pulse. Even at such a high pulse frequency the microwave power is not easily absorbed at the beginning of each new pulse. Once enough charge carriers are available the provided microwave power is absorbed and reflected power decreases.

Regardless of considerations on the plasma electron density and subsequent atomic hydrogen production it is the quality and growth rate of diamond films that determine the preferable pulse frequency and duty cycle of microwave plasma enhanced chemical vapour deposition systems. Experience shows that the higher the pulse frequency the better the diamond crystal morphology [10].

![Fig. 9](image_url)
Literature