Plasmaphysical and plasmachemical aspects of diamond deposition in low pressure plasmas

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Abstract: Experiments concerning different aspects of plasma influence on low pressure diamond growth in low pressure microwave plasmas are discussed. A planar microwave plasma source is used to perform deposition experiments under well defined afterglow conditions dominated by atomic hydrogen. Experiments with variable atomic hydrogen content indicate that the presence of sufficient amounts of atomic hydrogen is a necessary condition for diamond growth. But further increasing atomic hydrogen content doesn't influence crystal quality remarkably. It is therefore concluded that further improvements in crystal quality can be achieved only achieved with the help of additonal control parameters which exhibit considerable influence on surface energy of the growing nulei. This conclusion is in good correspondence to the investigated plasma effects. Plasmas are best suitable to generate such additional parameters, e.g. plasma induced particle bombardment or external substrate bias. Besides special usefulness for atomic hydrogen generation and low thermal stress of substrates this is a further advantages of low pressure plasma activation.

INTRODUCTION

It is a pecularity of low pressure diamond synthesis that a great variety of deposition technologies exists, including almost all common thermal CVD and plasma CVD methods (1). Nowadays especially low pressure microwave plasma CVD methods dominate the progress towards high performance material.
For the most part the development of low pressure diamond deposition has been proceeded with empirical methods. This is caused by the complexity of the basic microscopic processes both at the growing surfaces and in the volume of the growth medium. But it is widely recognized that atomic hydrogen plays a key role in control of diamond growth. Since atomic hydrogen can be generated in different ways the great variety of deposition techniques evolved. Plasmas offer best conditions for atomic hydrogen generation and so their widespread use is understandable. Additionally low pressure microwave plasmas allow deposition procedures with low thermal stress of the substrates and low contamination of the deposits. The disadvantages of plasmas are complicated correlations between external macroscopic process parameters, microscopic plasma properties and growth. So it is an important to investigate the depositon processes in plasmas in detail. The present paper is related to these problems. It focuses on the investigation of the microwave excited plasmas free of static magnetic fields.

EXPERIMENTAL

Diagnostics of diamond forming low pressure microwave plasmas is rather complicated. So the use of Langmuir probes is restricted to plasmas with pressures not higher than some hundred Pa by the influence of collisions on probe characteristics and by the strong heating of probe surfaces. Due to the large difference in the appearance potentials of methyl radical ions generated from neutral methyl radicals (9.840 eV, (2)) or from methane (14.3 eV, (3)) mass spectrometric plasma monitoring is a good method

for characterization of the kinetics of the methyl radical, which is now most widely accepted to be the main hydrocarbon precursor molecule of diamond growth at low substrate temperatures. But since typical process gases contain hydrocarbons, oxygen and hydrogen a lot of other active neutral species exist which are less simple to analyze. Also optical plasma diagnostic, although better fitted to the problem, has its limitations. These are due to the large number of different species and to inhomogeneous, restricted volume plasmas. The application of parameter separation methods e.g. afterglow experiments would be useful. But the often used classical microwave plasma afterglow extending from discharge tubes inserted into rectangular waveguides is very small. This results in low optical flux densities. In contrast the widespread used microwave bell jar reactors create larger plasmas but with spheric geometry which cannot be neglected.

In general, plasma sources exhibiting homogeneous plasma properties in the plane normal to the afterglow are better fitted to the problem. At least one of the plane dimension should be long extended to enable sensitive optical emission and absorption experiments. Such a plasma device is the planar microwave plasma source. This source is designed to spread microwave power (2.45 GHz) very homogeneously over a large area thus exciting long extended planar plasmas. It is based on the principle of distributed coupling of microwaves propagating along a matched waveguide structure. Adjustable coupling elements and an additonal interface waveguide ensure very homogeneous coupling. The plasmas are strongly decaying in the direction normal to the microwave window. Thus, they are best suited for end-on optical emission investigation of the afterglow. At present, plasma sources with up to 120 cm length have been realized. A detailed description of this type of plasma sources is given in (4).

A test plasma source of this type was used for diamond deposition. The substrates were placed in a flat, long extended molybdenum boat with variable distance to the microwave window. A low heat capacitance and minimized heat dissipation losses enabled calorimetric heat flow measurements. Further, substrate temperature could be controlled by additional heating. For depositions pressures of typically 1.5 kPa to 2 kPa were used. The details of these experiments are reported in (5,6,7). Experiments concerning plasma properties were performed with variable, especially reduced pressures to consider influence of collisions. A powerful equipment was used for optical emission plasma diagnostics, concisting of a 2m grating spectrograph with a resolution of about 0.005 nm and a highly sensitive optical multichannel analyzer (for details see (8)). The optical investigations were completed by spatially resolved Langmuir probe measurements at lower pressures in the decaying plasma region. Also, to contribute to the understanding of basic plasma excitation mechanisms measurements of the energy dependence of electron impact ionization cross sections of typical carbon precursors were performed. For these measurements a special double focusing high resolution mass spectrometer with variable energy range of electrons, from the threshold to 100 eV, was used.

NEUTRAL PARTICLE RELATED PHENOMENA

Based on experiences and technological advantages microwave plasma activation is assumed to have best chances to grow diamond films with perfect crystalline quality and very low impurity levels. As a rule, the first measure taken to achieve high crystalline quality is to use reaction gases consisting of hydrogen with very low admixture of oxygen and carbon precursor gases, e.g. about one percent and less methane or any oxygen containing aliphatic hydrocarbon vapour. To level out this low precursor admixture high microwave power densities of about 10^1 W/cm^2 are used. These conditions are best suited to investigate the influence of atomic hydrogen on the deposition process.

Following this idea, the planar microwave plasma source was used to perform experiments concerning correlation between atomic hydrogen content in plasmas and diamond growth. In Fig. 1 basic plasma source properties relevant for these measurements are summarized. On the abscissa the distance of the substrate, or probe respective, to the microwave window is given. The dotted lines describe the spatial variation of the electron density for different pressures determined from Langmuir probe measurements. The pressure of 400 Pa is at the upper limit for which in the present measuring configuration the influence of collisions on probe characteristics could be neglected. Obviously, an exponential dependence of the electron density on the distance to the microwave window exists. These measurements are compared with experimentally determined total heat flows to the substrate surface. The pressure range of this heat flow data includes typical pressures of deposition experiments and links with its lowest value

to the pressure range of the probe measurements. Q_{total} also exhibts an exponential spatial decay, but with a much longer decay length than electron density. Further, in Fig. 1 the heat flow Q_{ie} due to impact and recombination of charged particles on the substrate surface is given. These values are calculated on the basis of the Langmuir probe data given in the figure. It should be noted, that electron temperature, which is also neccessary for these calculations exhibits an exponential decay too, ranging from about 2 eV at 10 mm distance to about 0.4 eV at 60 mm distance. Very recently these electron temperatures could be confirmed by optical excitation energy measurements. Also, spatial decay constant of excitation energy was the same (9). In connection with measurements concerning neutral gas temperature and relative spatial variation of radical species and hydrogen the results given in Fig. 1 lead to the conclusion, that the difference between heat flows Q_{total} and Q_{ie} is due to atomic hydrogen surface recombination (7). A decisive observation for this conlusion was, that the neutral gas temperature in contrast to substrate temperature decreases with increasing pressure. At typical deposition pressures it is considerably below substrate temperature. This recombination controlled heating offers a good possibility to investigate the influence of atomic hydrogen concentration on deposition.
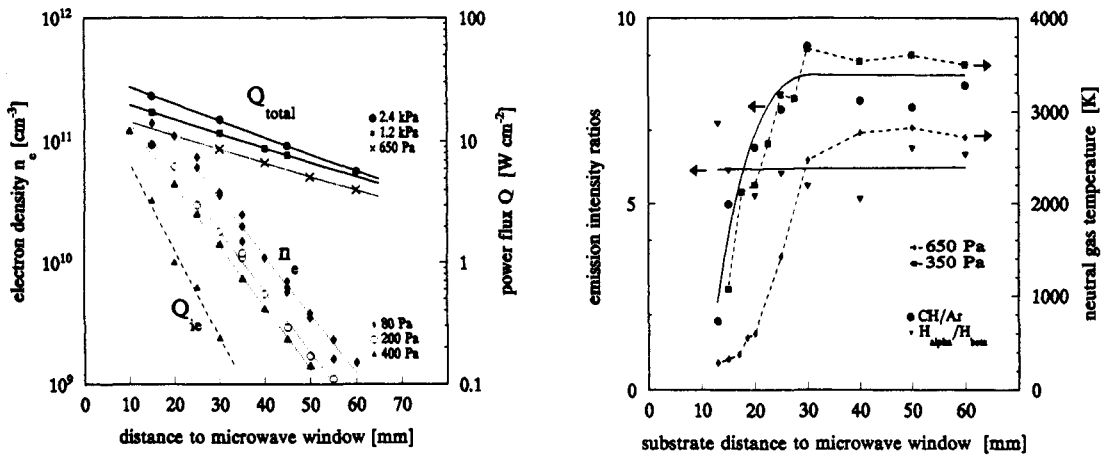

Fig. 1   Spatial distribution of plasma parameters   Fig. 2   Substrates influences on plasma   parameters

The measurements summarized in Fig. 1 characterize the properties of the decaying plasma region only. The microwave power absorbing physically active plasma region is located below 10 mm, adjacent to the window. This was best demonstrated by experiments in which plasma parameters at fixed positions near the window were measured in dependence on the position of the substrate holder. Figure 2 summarizes some of these results. The neutral gas temperature derived from Doppler line broadening at pressures of 350 Pa and 650 Pa (dashed lines), the relative variation of the CH-radical concentration at a pressure of 200 Pa derived from actinometric optical emission measurements (dots) and the ratio of the hydrogen emission lines (triangles) also at 200 Pa are given for a position at 3 mm distance to the microwave window. The H_α to H_β ration is used to look for changes in electron energy. These results can be understood with the help of a discharge model assuming the particle balance of the plasma without substrate holder to be diffusion controlled with losses by surface recombination only at the quartz microwave window, and losses by volume recombination in the decaying plasma region. Particle generation is assumed to occur mainly in the active plasma layer. Obviously, the substrate holder doesn't interact with the active plasma region if it is located outside of a critical distance to the active region.

Following these results it is possible to perform deposition experiments with varying atomic hydrogen concentration in which the influence of simultaneous plasma parameter variations can be neglected. The investigated temperature interval of substrate heating ranges from 500 K to 950 K. At these temperatures it is according to (10) possible to assume a nearly complete coverage of the substrate surface by atomic hydrogen and an approximate proportionality between substrate heating and atomic hydrogen concentration. Therefore in a zero order approximation the substrate temperature change caused by the plasma influence can be assumed to be proportional to atomic hydrogen concentration.

The observed exponential decay of substrate heating, that means, of atomic hydrogen gas phase density, is in good correspondence with the above described discharge model. The dissociation of hydrogen in low

pressure discharges is a well investigated phenomenon (see e.g. (11). It is a reasonable assumption that H atoms are preferentially formed by direct electron impact dissociation of ground and excited vibrational levels of molecular hydrogen

$$e + H_2(^1\Sigma,\nu) \rightarrow e + H_2(b^3\Sigma_u) \rightarrow e + H + H \tag{1}$$

in the active plasma layer. Further dissociation mechanisms like dissociative electron attachment and vibrational energy redistribution are of low propability due to the relative high electron energy, to the close wall contact and to the presence of large molecules in the plasma, which quickly deactivate vibrational excitation. Volume recombination is believed to be effective in the decaying plasma region due to the presence of large hydrocarbon molecules. Numerical investigations of this equation revealed hydrogen atom spatial distributions with a maximum near the active layer followed by an exponential tail. This shape is in good correspondence to results of actinometric concentration measurements given in Figure 3. Based on the heat flow measurements reported in Fig. 1 the degree of hydrogen dissociation was estimated to be about 1 percent (7).
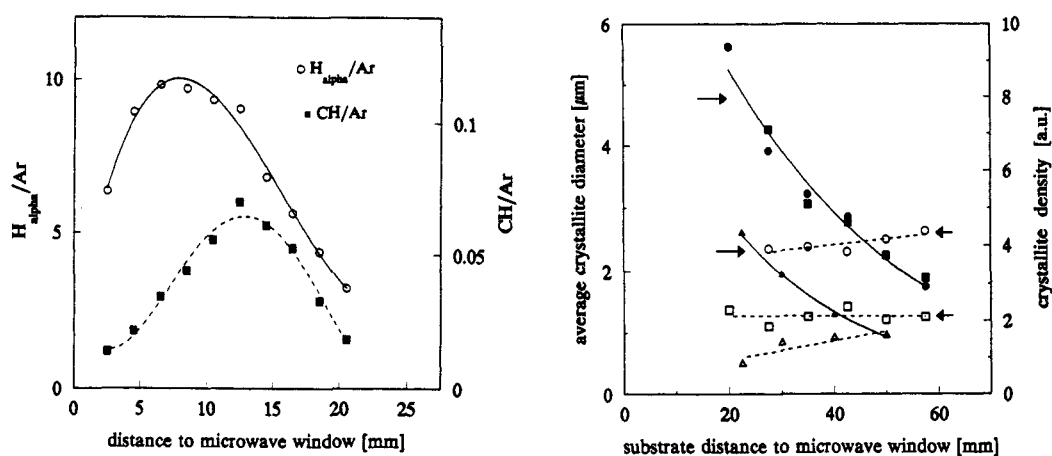

Fig. 3 Spatial decay of emission intensita ratios   Fig. 4 Position dependence of growth

A remaining uncertainty for deposition experiments is the lacking knowledge about carbon precursor spatial distribution. Here are only informations on CH radicals available. They exhibit a similar behaviour like atomic hydrogen (Fig. 3). At charactetristic process temperatures not exceeding 1000 K the methyl radical CH_3 is assumed to be the basic carbon precursor molecule for diamond growth. Of special importance for the methyl radical balance is hydrogen abstraction due to the reaction chain

$$H + CH_4 \rightarrow CH_3 + H_2, \; H + CH_3 \rightarrow CH_2 + H_2, \quad H + CH_2 \rightarrow CH + H_2. \tag{2}$$
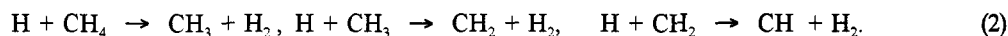
Nevertheless, for plasma activated processes the contribution of electron impact dissociation should be considered. In the present investigations optical actinometry and substrate heating mesurements clearly revealed a reduction of atomic hydrogen density in effect of hydrocarbon addition (7). But the total electron impact ionization cross sections of typical carbon feed gases (see Fig. 6 below) are in the same order of magnitude as for molecular hydrogen (see e.g. (12)). So it is reasonable to assume a similar behaviour for electron impact dissociation. Since the estimated atomic hydrogen concentration is not in large excess to hydrocarbon feed gas concentration only detailed numerical modeling could separate the different dissociation mechanisms.

In Fig. 4 some of the results of deposition experiments within the chemical active region of the planar microwave plasmas are compared. The solid lines and filled symbols show the position dependence of average crystallite diameters, the broken lines and open symbol the position dependence of crystallite densities. Circles and triangles refer to deposition experiments with methyl alcohol CH_3OH, triangles represent depositions with ethyl alcohol C_2H_5OH. Admixtures of 2 percent were used. A constant

temperature regime (750°C) excluded temperature influences. Obviously, the growth rates strongly decrease with the distance to the window, that means also with atomic hydrogen content. The lower growth rates of ethyl alcohol can be explained as a result of the lower oxygen atomic ratio in the gas content. It is known, that best growth results are obtained with oxygen to carbon ratios near one (13). In contrast to the growth rate, the crystallite densities exhibited no clear influence of atomic hydrogen concentration. Only the particle size distributions exhibited a slight variation in form of a narrowing of the peak width and a reduction of the asymmetric peak shape with reduced atomic hydrogen content. According to (14) the asymmetric distribution shape possibly indicates the occurence of intermediate species at the substrate surface during growth. Following this, during growth at higher atomic hydrogen content more nuclei of overcritical size are removed again.

The well defined experimental conditions suggested to perform also experiments with variable substrate temperature for determination of growth activation energy. Here fixed as well as variable plasma cocnditions were used. In these experiments the growth rates varied much more than under constant temperature but variable atomic hydrogen content conditions. Also, large differences in the Raman spectra of the deposits appeared. Interestingly under variable hydrogen but constant temperature conditions nearly no changes in the Raman spectra occured. That means, atomic hydrogen concentration variations didn't influence crystal quality. The growth activation energy determined from an Arrhenius plot of about 50 kJ/mol seems to be typical for very low pressure deposition methods (15).

CHARGED PARTICLE RELATED PHENOMENA

In diamond deposition the addition of oxygen is often used for enhancement of growth rate and improvement of crystal quality. Oxygen addition is performed in different ways, either by addition of molecular oxygen, carbon monoxide CO or by use of oxygen containing aliphatic hydrocarbons like methyl alcohol CH_3OH, ethyl alcohol C_2H_5OH, propyl alcohol C_3H_7OH or Acetone C_2H_6CO. In proportionality to the oxygen to carbon ration equal admixtures of different alcoholes lead to improvements in crystal qualities if oxygen to carbon ratios approach one in the homologous series (13).
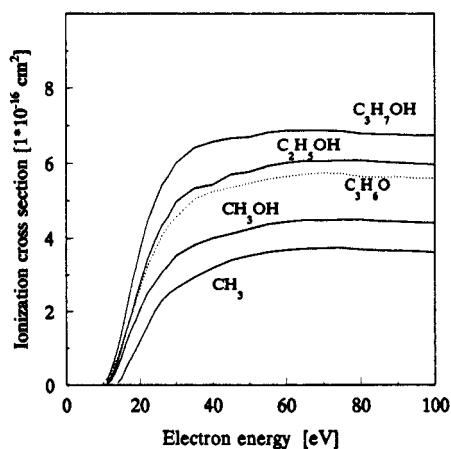
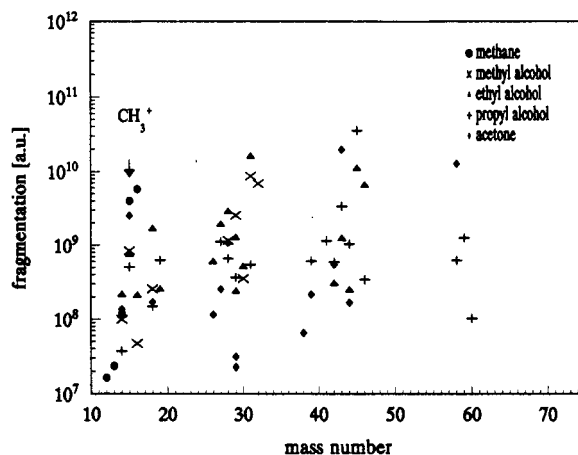Fig.5   Comparison of total electron impact cross sections

Fig. 6   Mass fragmentation schemes at 70 eV electron energy

Concerning plasma specific aspects of diamond deposition it seems interesting to look for excitation specific effects by comparing electron impact effects on these compounds. In Fig. 5 measured energy dependences of total electron impact ionization cross sections of the above mentioned aliphatic hydrocarbons are compared (16). Figure 6 reports the corresponding mass fragmentation schemes at 70 eV electron energy (17). The total electron impact ionization cross sections increase within the homologous series with the size of the molecule. The mass fragmentation scheme exhibits no deep fragmentation of molecules. Interestingly, the abundance of methyl ions is high for all compounds and

decreases for the homologous series of the alcoholes with increasing molecular size. These results are consistent to the experiences of diamond growth. They give no reason to assume electron impact excitation specific effects for plasma processes. Following this, plasmas with electron impact dominated generation of active species, e.g. highly ionized plasmas, are not less useful for diamond synthesis.

Apart from activated neutrals plasmas also contain charged particles and they are sources of uv radiation. Both effects can influence diamond growth. Concerning uv radiation, in (18) a slight but not fundamental alteration of growth activation energy for microwave plasma activation with additional uv irradiation is announced. Concerning the influence of ions different effects are reported. For synthesis of diamond films using magneto microwave plasma activation ions are reported to act in different ways. Many authors report ion bombardment to be detrimental to the formation of diamond. But in (19) positive as well as negative bias were found to improve crystal quality. Very recently it was reported, that negative substrate bias in the initial phase of the non mageto microwave plasma process can be used to enhance in situ nucleation resulting in highly ordered epitaxial growth on silicon substrates (20) and BN substrates (21).
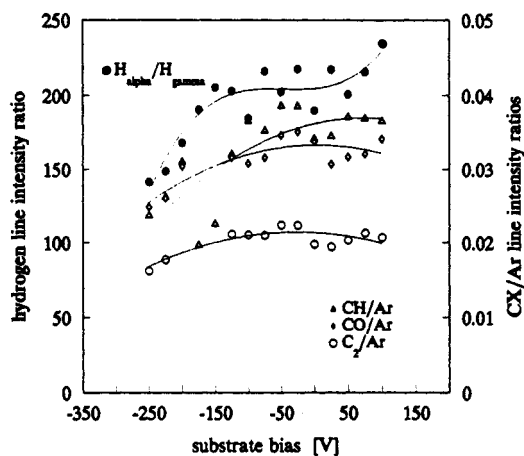

Fig. 7   Influence of substrate bias on plasma properties
          near the substrate surface

With respect to these results the effects of substrate bias on diamond depositing plasmas in the planar microwave plasma source were detailed investigated. Figure 7 reports results of optical emission measurements very near to the surface of substrates located inside of the decaying plasma region. This is indicated by the decrease of the reported intensity ratios. Obviously, negative bias results in an increase of excitation energy. An analysis of these measurements leads to the conclusion, that effects of enhanced ion bombardment of the surface are more likely to improve growth than changes in changes in plasma composition near the substrate (22).

DISCUSSION

In this paper a number of experimental results concerning plasma effects on diamond growth are reported. Obviously, their influence on growth is different. It is the problem to bring an order into these and other, here not discussed effects. For this purpose it is worthwile to discuss growth mechanism in some more detail.

Diamond growth strongly competes with the growth of graphite which is the much more thermodynamically favoured carbon allotrope at low pressures. Best growth conditions have to ensure a dynamic balance between strong suppression of graphite and sufficient support of diamond. Hence, assuming the same gaseous precursors responsible for both growth of diamond and graphite, at least three parameters are necessary to control diamond growth. Besides growth temperature and supersaturation of growth precursor species the balance between graphite and diamond has to be controlled. According to the classical nucleation theory the nucleation rate I for growth of stable nuclei per second from the

vapour phase is expressed as

$$I = q\, A^c (\Delta F^c / kT)\, exp(-\Delta F^c / kT) \tag{3}$$

Here ΔF^c is the free energy change associated with formation of a nucleus of critical size, q is the propability per unit time per unit area of capturing a particle in the nucleus, A^c is the area of the critical nucleus. Using this equation the nucleation intensity ratio of graphite I_g to diamond I_d becomes

$$I_d / I_g = (q_d A^c_d \Delta F^c_d / q_g A^c_g \Delta F^c_g)\, exp\, \{(\Delta F^c_g - \Delta F^c_d)/kT\,\} \tag{4}$$

This equation was discussed in (23) in more detail. The results indicated that especially changes in specific surface energy, which contributes to ΔF, critically affect the relative nucleation intensity since these energies are very similar for diamond and graphite. Following the results reported in the present paper, one then can conclude that all effects which are capable to influence specific surface energy should be most effective to control the dynamic balance and therefore crystalline quality. Surely, the actual microscopic surface kinetics of low pressure diamond growth is a matter of investigation yet. It is known that surface processes of diamond growth must include heterogeneous multistep chemical surface reactions in any case. The actual form of equation 4, especially the preexponential term will be therefore altered. But following basic nucleation theory its general form will be the same. The here reported experiments then indicate that the presence of sufficient amounts of atomic hydrogen is a necessary condition for diamond growth which ensures supersaturation at the surface. Additional atomic hydrogen doesn't influence crystal quality remarkably. Only growth rate is in strong correlation to atomic hydrogen content, due to control of the volume or surface hydrogen abstraction mechanisms. Further improvements in crystal quality depend on additional control parameters which strongly influence surface energy of the growing nulei. Such parameters can be the concentration of additives which much more than atomic hydrogen influence surface, e.g. oxygen or argon. Also changes in plasma energy content can act as sensitive parameters. Especially, substrate bias is a best controllable parameter for this purpose. Besides of the already described advantages this is a further advantage of plasma activation for growth of high qualiy material.

ACKNOWLEDGEMENT

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