CHEMISTRY IN A SUPERSONIC VACUUM PLASMAJET

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ABSTRACT

We have used optical emission spectroscopy, mass spectrometry and a Pitot tube to analyse the plasma plume of a plasma jet used for diamond synthesis. In the investigated pressure range of 2 to 10 mbar Mach numbers of up to 2 were observed, which decreased with increasing pressure and increasing distance from the nozzle. Experiments with methane injection at the nozzle exit and into the background gas revealed, that with increasing pressure and increasing distance from the nozzle the chemistry is more and more determined by recirculation of hydrocarbons.

INTRODUCTION

Compared to other diamond synthesis techniques the direct-current plasma jet delivers the highest linear growth rate of high quality diamond (up to 1 mm/h) [1,2]. Usually the operating pressure in the deposition chamber amounts to a few hundred mbar. This high pressure however is believed to cause growth rate limiting boundary layer effects in the vicinity of the substrate [3,4]. To overcome the diffusion limitations for the growth rate successful attempts were made to synthesise diamond at low pressures [5-7]. Adiabatic expansion of the working gas into the deposition chamber by means of a laval nozzle is used to match the pressure difference between the arc chamber and the deposition chamber and to generate a super-equilibrium amount of activated species in the gas. Due to the conversion of thermal energy into kinetic energy a supersonically expanding plasma jet is formed. Its wide expansion as a result of the low static pressure is expected to favour larger nozzle to substrate distances and large area deposition. However, growth rates which can be realised seems to decrease significantly [5,6]. According to Goodwin [3,4] the achievable growth rate at a constant film quality (defect density) scales roughly quadratically with $[H]_0$ the atomic hydrogen concentration at the surface of the substrate. $[H]_0$ is simply the product of $X_{H,0}$ the H mole fraction and n_0 the molar gas density at the surface. As $X_{H,0}$ cannot exceed 1, $[H]_0$ has to decrease with decreasing pressure for fully dissociated hydrogen plasmas. Loh and Cappelli [5-7] investigated supersonic vacuum plasma jets at very low pressures (0.2 to 0.5 mbar). However, in respect to growth rate it would be advantageous to operate the plasma jet closer to the edge of the diffusion-limited regime which would be at a few mbar.

EXPERIMENTAL DETAILS

A schematic illustration of the experimental apparatus is shown in Fig. 1. The plasma jet used is a self-made 3 kW water-cooled laboratory type. The main parts are a rod-shaped cathode and a laval nozzle acting as anode. Both electrodes are made of thoriated tungsten to reduce the work function and to withstand high temperatures in a hydrogen environment. The direct-current arc burning between these electrodes is superimposed by a gas flow of a mixture of argon and hydrogen or pure hydrogen. The device is installed on top of a stainless steel vacuum chamber that is evacuated by a roots-blower with an adjustable pumping capacity of up to 650 m^3/h. This allows a minimal working pressure in the deposition chamber of about 1 mbar. The feed gas flow is electronically controlled by mass flow controllers, typical mass flow rates lie in the range of 10 slm. Various nozzles with throat diameters from 0.5 to 1.3 mm and different throat diameter to length ratios were tested.

The electrical set-up consists of a three-phase transformer with a rectifier and an adjustable dc-power supply. Taking into account the dropping V-I characteristics of the arc the power supplies are connected in series with a ballast resistor to set a stable operating point. To ignite the plasma a high frequency, high voltage ignition device of a welding power supply is used because yet no commercially available power supply was found that met the required specification.

Methane serves as carbon source for diamond deposition and is mixed into the plasma plume close to the exit of the laval nozzle. Attempts to inject the hydrocarbon species into the diverging section of the nozzle led to undesirable carbon deposition at the nozzle wall. Injection into the background gas of the deposition chamber is currently under study. Molybdenum and

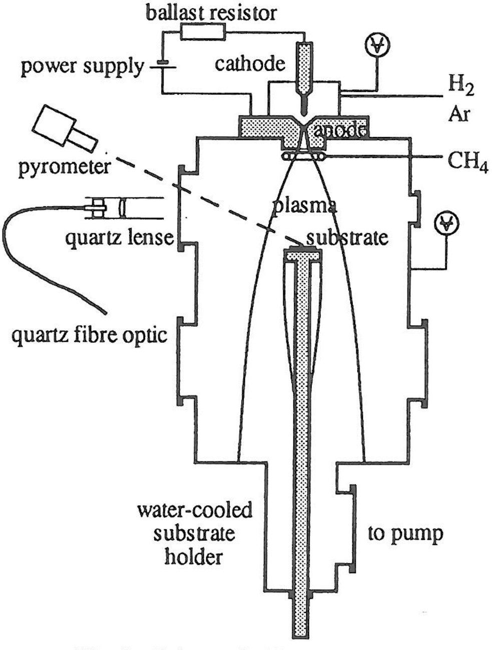

Fig.1: Schematic illustration of experimental set-up.

silicon plates are used as substrates for diamond deposition. Heating up of the substrates, which are mounted on a water cooled, vertical adjustable holder, follows from the heat delivered by the impinging plasma jet, at which the main contribution is made by the recombination of atomic hydrogen at the surface. While the surface temperature of the plates (800 - 1000 °C) is monitored by means of a two-colour infrared pyrometer, the bulk temperature of the molybdenum plates can be measured by a thermocouple. For this purpose the plates with a thickness of 3 mm were equipped with a bore for the thermocouple.

Optical emission measurements were performed using a 0.2 m grating monochromator in the wavelength range of 230 to 850 nm. The light emitted by the plasma plume was collected by a quartz lens and guided to the entrance slit of the monochromator by means of a fibre optic. The lens mounted 10 cm below the nozzle exit was focused at the centreline of the plasma plume.

Stagnation pressure of the gas flow was measured by a diaphragm-type gauge with the help of a water-cooled copper tube (Pitot-tube [8]), which was inserted into the plasma jet instead of the substrate holder.

To analyse gas composition in the deposition chamber gas samples were extracted from the plasma plume as well as from the background gas. Sampling from the plasma plume at different axial positions was made possible by an adjustable water-cooled gas probe. The gas probe is basically a separately pumped tube with an inner diameter of 4 mm. A small fraction of gas is extracted from the sampling-line through a 20 μm diameter orifice into a differentially pumped mass spectrometer (QMS). This bypass allows sampling in the jet environment with its relatively high pressure. A more detailed description is given elsewhere [9].

RESULTS AND DISCUSSION

Optical emission spectroscopy: Operating on a mixture of 70 % argon and 30 % hydrogen the Balmer spectrum is clearly visible, whereas the argon and molecular hydrogen lines are weaker by at least two orders of magnitude. At a pressure of 2 mbar in the deposition chamber the first 15 to 16 Balmer lines are observed. In this situation the H_β-line is by a factor of two larger than the H_α-line that results from a population inversion of the Balmer levels [10]. The situation changes at a pressure around 10 mbar and a more "normal" Balmer spectrum with a predominant H_α-line is observed. This indicates that at least at low pressures the plasma is dominated by 3-body-recombination.

When CH_4 is injected into the expanding plasma, fairly intensive emissions of CH and C_2 occur. The Balmer spectrum is dominated by the H_α-line, which has a much lower intensity as without CH_4. Additionally bands of OH are observed due to impurities. The argon or molecular hydrogen lines have intensities below the detection limit. According to our interpretation this implies that the bands are not excited by electron impact but either by chemiluminescence or recombination. An excitation by electron impact would also excite other species like Ar.

Pitot pressure measurements: Pitot pressure measurements as function of the nozzle distance were performed in order to estimate the velocity of the flow. The resulting Mach numbers ($Ma \approx 2$) are lower than expected which indicates that either the gas velocity is rather low or the gas temperature after the adiabatic expansion is still very high. At a chamber background pressure of 2.7 mbar and a mass flow rate of 12 slm H_2 the transition to subsonic velocity takes place at a nozzle distance of about 10 cm. At a background pressure of 10 mbar however the supersonic flow velocity remains for less than 3 cm.

Gas analysis: Mass spectrometry of gas-samples drawn in from the plasma plume as well as from the chamber background was carried out. To reveal the flow properties in the deposition chamber trace gases were either mixed into the feed gas, injected into the plasma plume at the nozzle exit or added to the background gas. Helium and argon were used because of their inert nature and their difference in molecular weight that made these gases act as substitutes for hydrogen or hydrocarbons, respectively. At a background pressure of a few mbar the trace gas which was injected into the plasma plume at the nozzle exit reached the concentration level of the premixed trace gas within a distance of about 5 cm from the nozzle. Argon which was added to the background gas did approach a constant concentration level, which was slightly below the concentration of the premixed gas, only after 20 cm. Helium with its higher diffusivity reached that concentration level faster. With increasing distance from the nozzle the gas composition of the plasma jet is believed to be more and more determined by the background gas which results from a gas recirculation from the surrounding gas into the jet. The remaining difference between the concentration level of the gas injected at the nozzle exit and the gas added to the background gas was attributed to the fact that a small fraction of the latter one is pumped away directly.

In case of 1% methane injection the development of different hydrocarbon species in the jet was investigated. Because of possible carburization of the arc electrodes methane was only injected at the nozzle exit and added to the background gas. The gas probe we used for this purpose should show a picture equivalent to the situation in the vicinity of the substrate. But we have to consider also the instable species being present at the extraction point, which are transformed into stable ones in the sampling system [6].

In the following only preliminary results will be presented as the evaluation is still in progress. A first result, which is in good agreement with the inert gas results, is that the total carbon content in the plasma jet (sum of all stable C1 and C2 species) decreases much faster with decreasing distance from the nozzle in the case of background injection. The ratio of the total carbon content of both cases of methane injection is shown in Fig. 2b. Contrary to our expectations, the measured relative concentrations of the different hydrocarbons, namely CH_4, C_2H_2, C_2H_4, and C_2H_6 are approximately the same in both cases. Fig. 2a shows the result of nozzle exit injection. As discussed earlier, the relative species concentrations approach background gas composition at a far distance from the nozzle, but how one can explain the development of species concentrations starting from the nozzle. Because of the directed flow of hydrogen and the injection of methane at a defined starting point, measurements of species concentrations with increasing distance from the injection point show the time evolution. However, there is no linear relationship as the measured Mach numbers decreased with increasing nozzle distance. Furthermore, this simple behaviour is superimposed by the recirculation of hydrocarbons and the diffusion to the axis of the plasma plume.

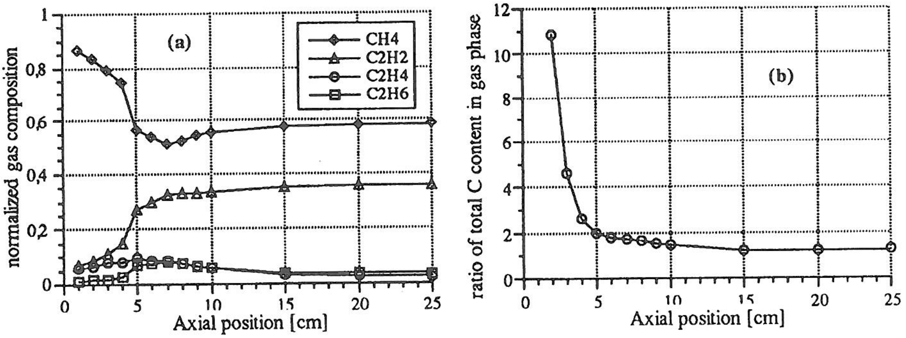

Fig. 2: Mass spectrometric results: (a) Normalized gas composition for 1% methane injection at nozzle exit. (b) Ratio of the total C content in the plasma plume between nozzle exit and backgroung injection.

In the case of nozzle exit injection it looks like as the decomposition of methane is visible, which is followed by the formation of C_2H_2. It would be driven by the high amount of atomic hydrogen one can assume in the vicinity of the nozzle exit. The decomposition of methane is accompanied by the creation of methyl radicals. Preliminary model calculations based on the CHEMKIN code [11] and a mechanism according to ref. 12 at an assumed high degree of dissociation of hydrogen showed a steep increase in CH_3 concentration, which reaches a maximum and levels off later on. At such conditions C_2H_6 is not formed in detectable amounts. Simulations of the reactions of the radicals in the detection system revealed, that most of the CH_3 species recombine with hydrogen to register a methane signal at the mass spectrometer [9]. However, a small fraction recombines to C_2H_6. Therefore one can interpret the measured C_2H_6 signal as an indicator for CH_3. The C_2H_6 signal depends in second order on the CH_3 concentration. From the measured concentration profiles it can be concluded that the maximum CH_3 concentration is reached at a distance of 5 to 10 cm, which is in fair agreement with the flow velocity. The model calculations showed further that the increase in C_2H_2 concentration takes place in a much longer time scale. The steep decrease in CH_4 concentration and the corresponding increase in C_2H_2 concentration can therefore not mainly be caused by the transformation of methane into acetylene in the plasma plume or in the detection system. Fig. 2b shows the true reason.

At a distance of about 5 cm from the nozzle the recirculation of hydrocarbons becomes more and more important. As in the background gas the methane concentration is lower and the acetylene concentration is higher the concentration in the plasma plume is effected in this direction.

In the case of background injection a high fraction of CH_4 next to the nozzle exit was observed, which is actually higher than the assumed background level. An explanation delivered model calculations, as they showed that at a low concentration of hydrocarbons C2 species which are taken in from the background gas are decomposed in the plasma plume into C1 species. After recombination with hydrogen in the detection system they register as methane signal.

CONCLUSION

With the experimental set-up used supersonic gas flows were realised, whereby in the pressure range investigated the gas flow slowed down with increasing distance from the nozzle and reached subsonic conditions. As the measurements showed, recirculation of hydrocarbons becomes more and more important under such conditions. The chemistry in the plasma jet cannot be calculated any more by a simple time evolution. However, full interpretation of mass spectrometric data should be possible after a more detailed model calculation, which is currently under way.

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