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Diamond Synthesis by High Power Microwave Plasma

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Abstract

Using a high power microwave of $f=915\text{MHz}$, diamond synthesis by the plasma CVD in evacuated and atmospheric pressure environments is studied. The rapid growth of diamond particles at atmospheric pressure is observed with a speed of $20\text{-}50\ \mu\text{m/h}$ depending on the substrate temperature. The plasma density at 100kPa is found to be $10^{14}\text{-}10^{15}\text{cm}^{-3}$, which is lower in two orders of magnitude than the ones by RF- and/or arc-plasma at the same pressure.

KEY WORDS : (Diamond) (Plasma CVD) (Microwave Plasma) (Electron Density) (Thermal Plasma)

1. Introduction

Synthesis of diamond particles and/or films by microwave plasma CVD¹⁾ at a pressure of several kPa have been studied widely by many researchers. The power used is typically below 1kW and the reacting gas is H₂ with an admixture of CH₄. Detailed study on the characterization of the deposits are also progressing. We find, however, that there are quite few studies on the microwave plasma properties correlated with diamond synthesis.

Meanwhile recently the rapid diamond growth by an RF induction plasma²⁾ and an arc plasma jet³⁾ was also found to be successful in atmospheric pressure gas environment.

We consider that study on the diamond synthesis closely relating with plasma properties over the wide range of the gas pressure is very important, whether it is by a microwave-, an RF-, or an arc-plasma.

In this report experimental results on the diamond synthesis using a high power microwave radiation of $f=915\text{MHz}$ are described in evacuated and atmospheric pressure environment.

2. Experimental Procedures

Schematic diagram of the experimental apparatus is shown in Fig. 1. The microwave power from the magnetron can be varied from 0.5 to 20kW in the CW mode with $f=915\text{MHz}$. The matching of the wave with plasma is obtained by the E-H tuner. The plasma is ignited and sustained in a quartz pipe of 40mm in diameter, which is

inserted into the rectangular waveguide. The gas mixture of H₂, Ar and CH₄ is used in the pressure range from 0.5 to 100kPa. Volume percentage of CH₄ to H₂ is varied from 1 to 10%. Heat flow of the plasma was directed upward as shown in the figure.

The substrate material used for the diamond formation is Mo rod and it is supported by a movable SUS holder. Dimension of the substrate is 10mm in diameter and 10mm in length. It is self-heated by the plasma and/or microwave radiation. In the experiment in atmospheric pressure environment, the microwave input higher than 5kW was necessary to sustain a stable plasma flow and the SUS holder was water-cooled to keep the substrate temperature below 900K.

Plasma diagnostics was performed by the optical emission method. The electron density n_e was determined from the Stark broadening of H _{β} line of hydrogen. The plasma temperature T was estimated on the assumption of the LTE (Local Thermodynamic Equilibrium) state.

Before deposition the substrate is polished with the diamond powder of about $1\ \mu\text{m}$ in size. Appearance of the surface after deposition was observed by an optical microscope and its structure was studied with Raman scattering and X-ray diffraction methods.

3. Results and Discussion

First we were interested to examine and compare the diamond synthesis by the 915MHz microwave plasma with the one typically reported by the 2.45GHz one. We obtained several data at a pressure of

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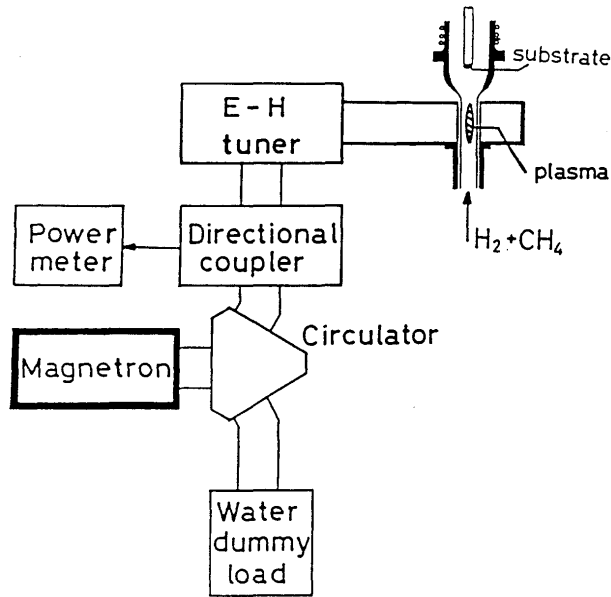


Fig. 1 Schematic diagram of experimental apparatus.

2.7kPa and a power input P_i of 1kW for the two waves. The specimen was inserted into the center of the plasma column without water-cooling. Figure 2 shows an example obtained by 3-hours deposition in the $H_2 + 3\%CH_4$ plasma. The substrate temperature T_s is kept to be 720 and 750 C. As it was measured by an optical pyrometer through the heated quartz tube from the outside, there can be a remarkable error in the estimation of the true emissivity of the substrate during experiment, and we apply each measured value of the temperature only for a relative estimation. We can find similar data in both cases in the particle size and Raman spectra. The Raman data on the right of the figure show typical diamond spectra at $1333cm^{-1}$ and include that of amorphous carbon near $1500cm^{-1}$. The speed of the diamond growth is about $1 \mu m/h$, which is typical in the 2.45GHz microwave plasma deposition.

Figure 3 shows time variation of the synthesis at $p_0 = 2.7kPa$ by the 915MHz radiation. By 1-hour deposition little number of diamond particles are found and at 10-hours' operation many particles with a large size of about $50 \mu m$ are found. But they are nearly spherical in shape and the Raman data has shown a strong peak of carbon spectra as well as diamond.

Next expecting a rapid growth of diamond particles and/or films, synthesis in atmospheric pressure gas environment was performed. We also studied the plasma property by spectroscopic measurement. Figure 4 shows the dependence of the electron density at the center of the plasma on the input power in the case of Ar +

40% H_2 plasma. The data are given for three values of the discharge tube diameter. With a decrease of the diameter the density is raised due to the so-called thermal pinch effect. The absolute value of n_e ranges between 1×10^{14} and $1 \times 10^{15} cm^{-3}$, which is the averaged one over the plasma diameter. In such a range of n_e , we must be careful in applying the Stark broadening for evaluating n_e . First the contribution of the Doppler broadening can be appreciable. At $T = 5000K$, for instance, the Doppler width $\Delta \lambda_D$ in FWHM for the H_β line is 0.25A. While the Stark width $\Delta \lambda_S$ (FWHM) is about 0.4A at $n_e = 1 \times 10^{14} cm^{-3}$ and 1.8A at $1 \times 10^{15} cm^{-3}$. We used the calculated data⁴⁾ based on the VCS (Vidal, Kooper and Smith) theory for the line, where the Doppler profile is convolved with the Stark one. Next in our experiment Ar and CH_4 is mixed into H_2 gas and ion dynamic effect⁵⁾ to the profile might be of problem. This effect gives, strong influence to the central dip of the H_β line profile⁶⁾, but the Stark width $\Delta \lambda_S$ does not change appreciably.

Figure 5 shows the variation of n_e with the flow rate of CH_4 for three different gas pressures. For all cases the density is increased with the flow rate and reaches to a value of $1 \times 10^{15} cm^{-3}$ at $p_0 = 100kPa$. We consider that the formation of various ion species by the dissociation and ionization of CH_4 would cause the increase of n_e with the flow rate of CH_4 .

Figure 6 shows the power dependence of n_e in a gas mixture of Ar, H_2 and CH_4 corresponding to the condition of the diamond synthesis. We again find little variation of n_e as well as in Fig. 4. It is mainly caused by the fact that the incident microwave is absorbed only within a distance of the skin depth from the surface of the plasma column, which was reported by us⁷⁾ for a hydrocarbon plasma with a theoretical calculation. We also note

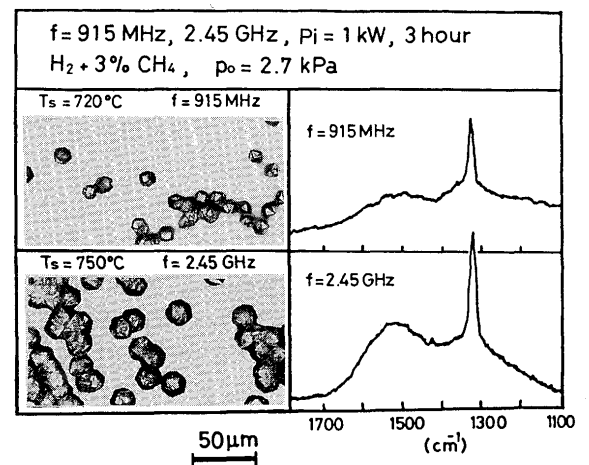


Fig. 2 Diamond synthesis at $p_0 = 2.7kPa$ by the two waves of $f = 915 MHz$ and $2.45GHz$.

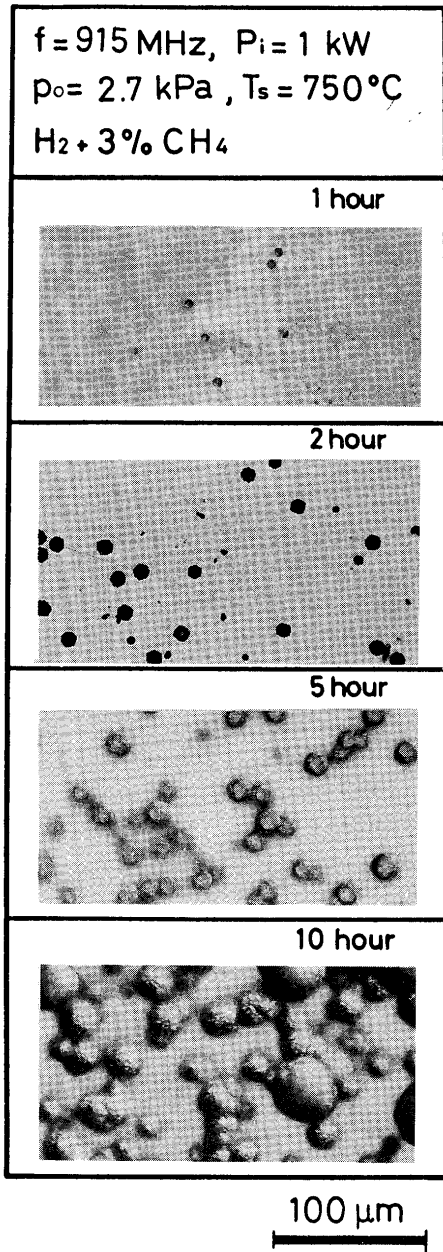


Fig. 3 Time variation of the diamond synthesis at $p_0 = 2.7 \text{ kPa}$.

that the electron density obtained in this microwave plasma at atmospheric pressure is smaller by two orders in comparison with the ones by RF- and/or arc-plasma.

We estimated the plasma temperature T with the assumption of LTE using the experimentally obtained electron density. In the case of $\text{Ar} + \text{H}_2$ plasma it shows a value of $T = 6 \times 10^3 - 7 \times 10^3 \text{ K}$.

In the actual diamond synthesis at atmospheric pressure it was necessary to give an input power higher than 5kW to sustain the plasma steadily, by which it was difficult to set the substrate at the center of the plasma because of its overheating. The substrate was settled at a distance of over 10cm from the center in the axial direc-

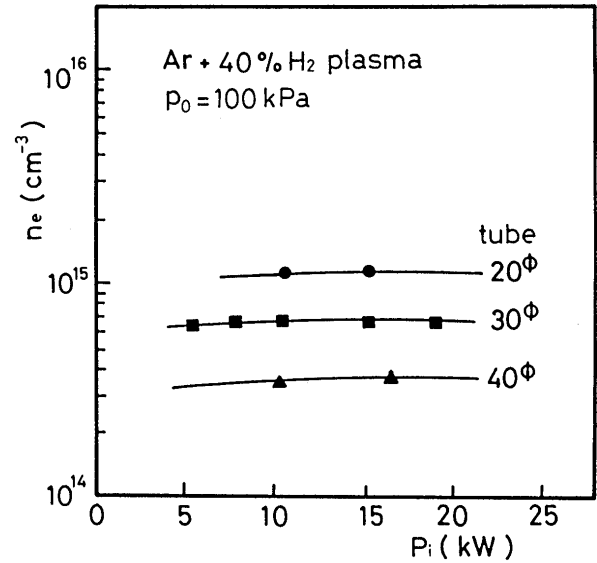


Fig. 4 Dependence of n_e on P_i for different tube diameters in a gas mixture of Ar and H_2 at atmospheric pressure.

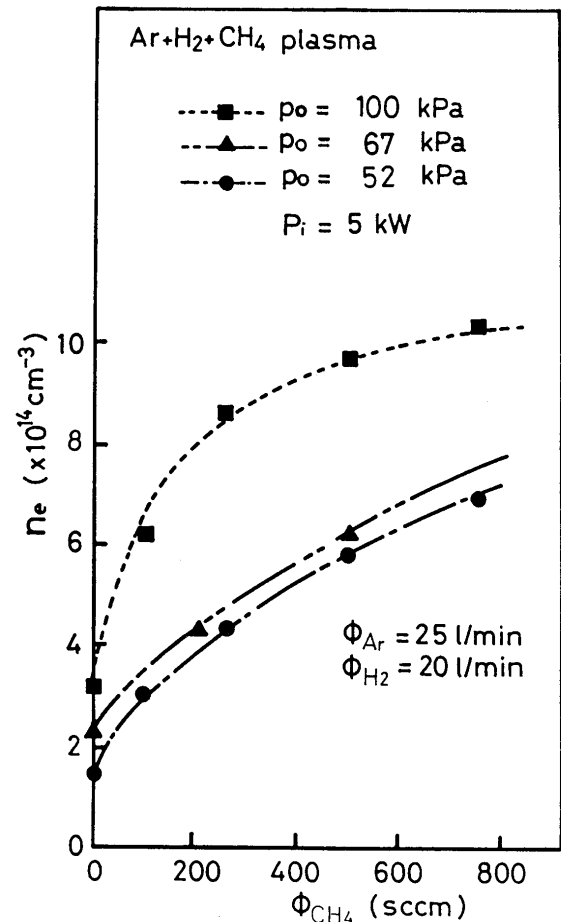


Fig. 5 Variation of n_e with the flow rate of CH_4 in Ar, H_2 and CH_4 gas mixture at 100kPa.

tion, whose schematic diagram is shown in Fig. 1.

Figure 7 shows the diamond formation at atmospheric pressure for various deposition times. At 15 minutes' de-

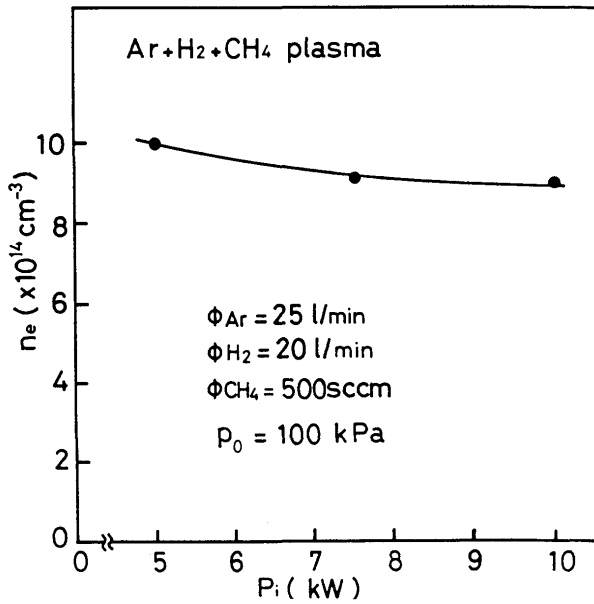


Fig. 6 Power dependence of n_e in Ar, H₂ and CH₄ gas mixture at 100kPa.

position small diamond particles are found along a scratch on the surface. At 30 minutes' deposition the particle size grows to 10-20 μm with a clear crystalline structure of diamond. The speed of the diamond growth was found to be 20-50 $\mu\text{m/h}$ depending on the substrate temperature. Indeed it is higher in order of magnitude than the one at $p_0=2.7\text{kPa}$ in Fig. 3.

By varying the percentage of CH₄/CH₂ we performed an experiment with a deposition time of 30 minutes, whose result is shown in Fig. 8. At 1.8% and 3.5% clear crystalline diamond formation is observed. But at 5% the structure becomes not so simple and carbon is also observed on the surface. In the present study the optimum mixing rate of CH₄ into H₂ was found to be around 3% and it is rather small in comparison with the case of RF- or arc-plasma process at the same pressure²⁻³). We consider this is mainly because the electron density is found to be smaller by about two orders in the microwave plasma, by which number of chemical species related to the diamond forma-

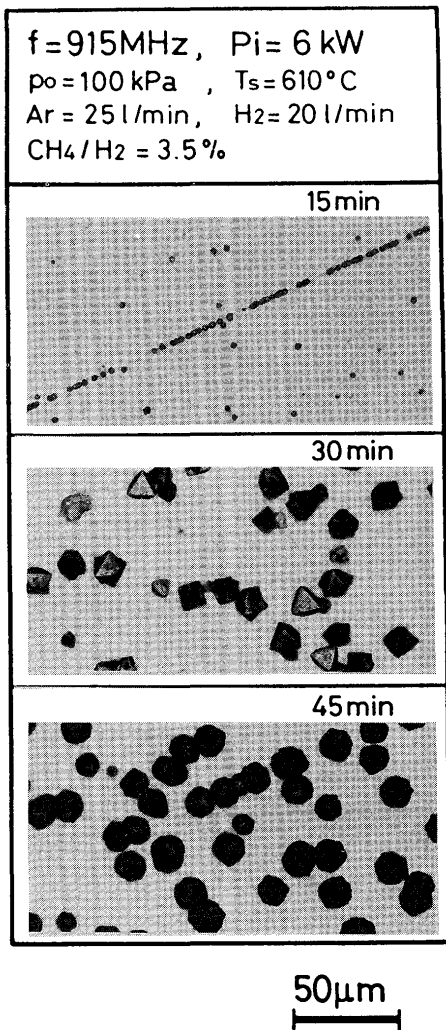


Fig. 7 Time variation of diamond synthesis at $p_0=100\text{kPa}$.

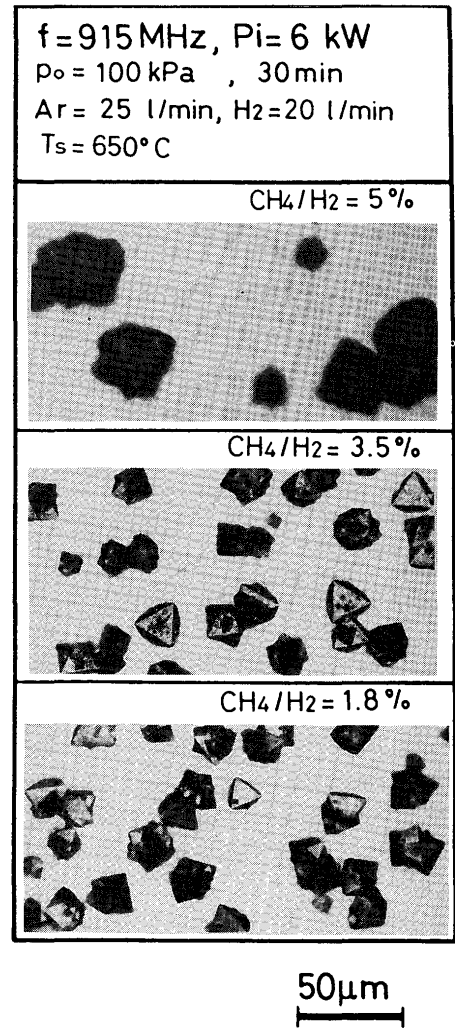


Fig. 8 Variation of diamond synthesis with CH₄ mixing into H₂ at 100kPa.

tion is much lower than the case of RF- and/or arc-plasma.

The data in Figs. 7 and 8 were obtained when the substrate was set at an axial distance of 13cm from the plasma center to avoid its overheating. We have observed the difference of the diamond formation by varying the position h of the substrate from the center. **Figure 9** shows the result in which remarkable difference is found in the particle size even when the distance h is changed a little from 12cm to 14cm. At $h=12$ cm the size is very small but at $h=14$ cm it is large to be about $50\ \mu\text{m}$. We assume that this result comes from the difference in the temperature of the substrate. In this data the flow rate of the cooling water to the substrate was fixed to be constant.

To check this assumption we obtained the data at two values of the input power. **Figure 10** shows the difference in the particle size at $P_i=6\text{kW}$ and 7kW . It was made clear in Fig. 4 or 6 that there was no variation of n_e with the input power. While the particle size at $P_i=7\text{kW}$ is larger in correspondence with a higher T_s . Thus it is important to prepare the well controlled water flow to keep the constant substrate temperature even when the position of the specimen is varied widely.

Figure 11 shows example of the X-ray diffraction data in the case of $T_s=650\text{C}$. The peaks corresponding to the diamond structure with (111) and (220) orientations are found as well as Mo peaks of the base metal. As for the Raman spectra we obtained a similar data as the one in Fig. 2.

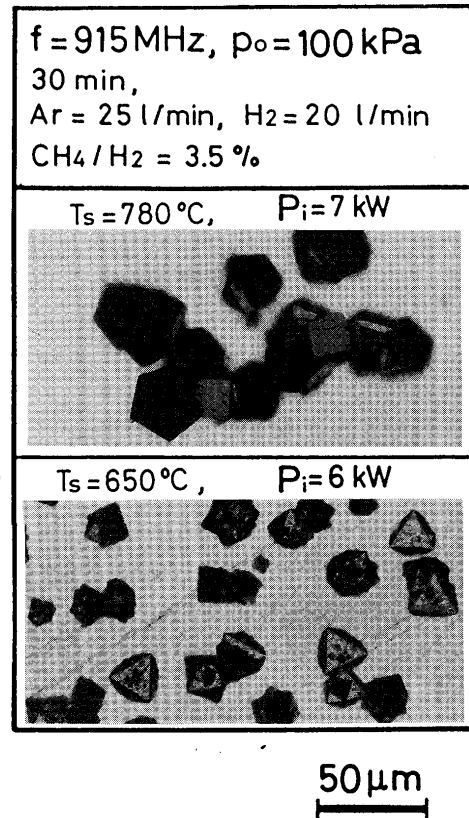


Fig. 10 Diamond deposition at two values of P_i .

$f = 915\text{ MHz}$, $P_i = 6\text{ kW}$
 $p_0 = 100\text{ kPa}$, 30 min
 $\text{Ar} = 25\text{ l/min}$, $\text{H}_2 = 20\text{ l/min}$
 $\text{CH}_4/\text{H}_2 = 3.5\%$, $T_s = 650\text{ °C}$

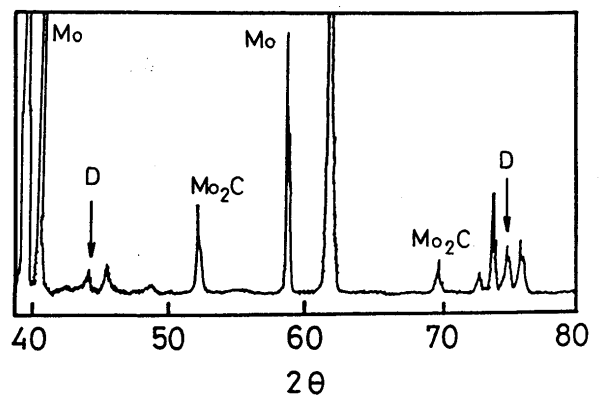


Fig. 11 X-ray diffraction of deposited diamond particles at $p_0 = 100\text{kPa}$ with $P_i = 6\text{kW}$.

In conclusion we demonstrate that we could successfully perform the diamond synthesis by using a high power microwave radiation of $f = 915\text{MHz}$ in atmospheric pressure environment, as well as at a reduced pressure of 2.7kPa . In the pressure of 100kPa rapid diamond growth of $20\text{-}50\ \mu\text{m/h}$ was confirmed in the gas mixture of Ar, H_2 and CH_4 .

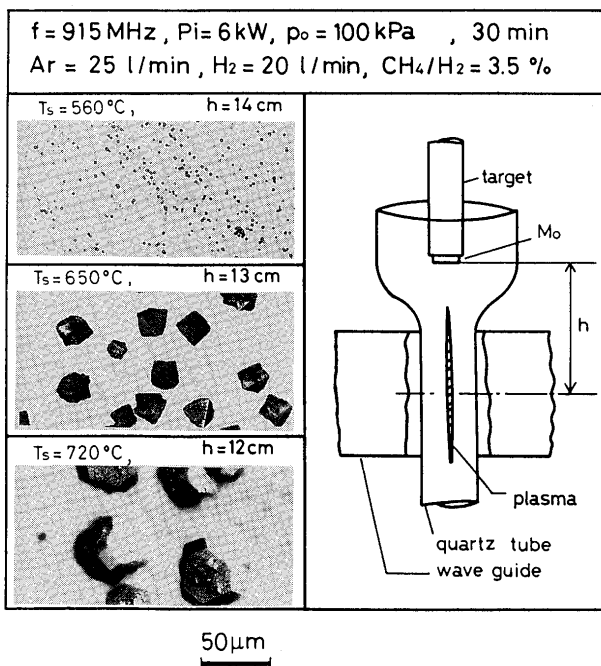


Fig. 9 Deposition of diamond at different positions in the axial direction at 100kPa .

While the plasma density was found to be lower about two orders in comparison with the ones by RF- and arc-plasmas.

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