PROCESS CHARACTERIZATION OF CVD DIAMOND FROM LIQUID PRECURSORS

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Abstract

It has been observed that extremely high linear diamond growth rates can be achieved (> 1 mm/hr) if liquid precursors are used in the form of an atomized liquid spray. In this investigation, we attempted to ascertain whether the high deposition rate was principally due to the efficient mass transport when liquid droplets are used or the chemistry of the dissociation fragments of the organic molecules. Experiments were conducted in which the atomization behavior of various liquids of interest was characterized. Different liquid feeding arrangements and the corresponding droplet trajectories were investigated using a high speed laser strobe video system. The diamond films obtained with different liquid feeding arrangements and different precursors were characterized and the results were compared. It was observed that acetone resulted in a diamond grain size about five times smaller than that with ethanol, though the two precursors were found to have similar droplet surface mean diameters and evaporation rates. This indicates the important role of chemistry in determining diamond properties.

Introduction

This research has the objective of evaluating the advantages of using liquid precursors as feed stock for diamond deposition. In previous experiments it has been found that very high linear growth rates (>1 mm/hr) and mass deposition rates (>140 mg/hr) can be achieved when some organic liquids are injected from a counterflow arrangement into an argon hydrogen plasma jet [1]. Although it has been clear that the efficient mass transport provided by the liquid droplet spray is beneficial for the deposition rate, we have been unable to explain the differences in deposition rates for different feed stocks. In previous research we performed computer simulation of the liquid injection process, determining the evaporation rates for the different types of droplets when they were exposed to a hot gas stream [2]. It was found that the droplet surface mean diameter of different liquid precursors is a weak function of liquid properties, such as density, viscosity and surface tension. Calculated evaporation rates for the liquid precursors of interest did not show significant differences. The influence of different physical characteristics of the liquids was evaluated during the droplet formation process and during the evaporation of the droplets when they encounter the plasma stream.

The present effort has been directed towards diagnosing the droplet trajectories in the plasma reactor during diamond deposition experiments to determine their influence on growth rate. As part of this effort the total diamond deposition rates for different precursors and for different geometrical arrangements of the liquid injection system have been determined. In the following we describe the experimental approach for the diamond deposition experiments and discuss the results obtained.

Experimental Setup

A dc plasma reactor has been used for the deposition experiments [3]. A summary of the experimental parameters is given in Table 1.

Table 1 Experimental Parameters

Atomizing Gas	Hydrogen	18 L/min.
Torch Gases	Argon	24 L/min.
	Hydrogen	1 - 2 L/min.
Feed stock	Methane	0.25 L/min.
Liquid	Acetone	1 - 3 ml/min.
	Toluene	1.5 - 2 ml/min.
	Ethanol	1.5 ml/min.
	n-Heptane	3.5 ml/min.
	CCl_4	1.7 ml/min.
	Benzene	2 ml/min.
Torch Power	Current x Voltage	6.6 - 11.25 kW
Misc. Parameters	Stand-off Distance	30 mm
	Substrate	Molybdenum
	Side Injection	3 & 13 mm

The jet issues into a cylindrical, water-cooled, stainless steel reactor with several windows for observation. The windows had to be kept small because the main advantage of a counterflow reactor is that the flow field consists of large recirculation zones, keeping the reactants in the hot zone of the reactor. The liquid precursors are injected into the plasma jet using an atomizing probe either through an orifice in the substrate (positioned at a fixed stand-off distance from the torch anode nozzle exit) or from the side (parallel to the substrate surface at different axial locations). The three cases considered are as follows:

(1) Counterflow injection with 30 mm stand-off distance between torch anode nozzle exit and substrate.
(2) Low location side injection, 3 mm above the substrate surface.
(3) High location side injection, 13 mm above the substrate surface.

The observation of the droplet trajectories has been accomplished with a telemicroscope combined with a laser strobe video system. In this system, a 5 ns laser pulse illuminates the droplets while the electronic shutter of a CCD video system is open. Short shutter times of 50 ns to 1 µs result in good signal-to-noise ratios. The video images are captured on tape and processed by a computerized image analysis system. A schematic of the experimental set-up is shown in Figure 1, and specifications of the laser vision system and the telemicroscope are given in Table 2.

Table 2 Diagnostics Equipment

Laser Strobe:			
Shutter Speed	*50 ns*	Framing Rate	*1 - 15 /sec*
Wavelength	*312 nm*	Pulse Duration	*10 ns*
Telemicroscope:			
Focal Length	*6 - 15 inch*	Max. Resolution	*6 μm*

SEM and XRD were used to characterize the diamond films. Diamond mass growth rate and carbon utilization efficiency were evaluated by weighing the substrates before and after experiments using an electronic scale.

Results and Discussion

The results and discussion are arranged to facilitate a comparison between three different liquid precursor feeding arrangements regarding their mass transport processes, process economics, and coating properties.

Mass Transport

Schematic drawings of the images obtained using the laser strobe vision system, based on the computer image processing, are given in Figure 2a-c. It is seen that larger droplets (> 5 μm) appear in the region very close to the substrate (1 mm) for the low location side injection, while for counterflow and high location side injection there is no sign of droplets in a region 2 mm above the substrate surface. It is thought that droplets of this size observed in case #2 are likely to go through the boundary layer and eventually land on the substrate surface.

A direct landing of larger droplets on the substrate surface may mean an efficient mass transport of hydrocarbon species, though it is not clear whether this mass transport mechanism would help diamond growth. It appears that two factors may have contributed to the observed difference in mass transport.

- Less effect of plasma instability (whipping and twisting) on droplet trajectories for case #2.
- Lower evaporation rate because of a lower temperature environment.

Mass Growth Rate

To determine the relative advantages of the liquid feed over methane, the total mass deposition rates were compared for the different cases. It should be noted that these values do not represent the maximum values obtained but rather values obtained under identical conditions. For an optimized process deposition rate of more than 15 mg/kW.hr. has been obtained with this reactor. For example, in the side injection experiments, diamond growth was obtained only in the region where the plasma jet impinged on the substrate surface, indicating that the atomic hydrogen availability may have been the rate limiting step.

It was found that the low location side injection, as compared with the counterflow and the high location side injection, has the highest diamond mass growth rate and carbon utilization efficiency, as shown in Figure 3, both for acetone and ethanol. This may be somehow related to the efficient mass transport associated with the case #2. It will be interesting to find the correlation between the diamond growth and the particular mass transport mechanism observed in the case #2.

CH4 was found to have the highest mass growth rate in the case #1, compared with acetone and ethanol. This is not surprising because one would expect that liquid precursors will lead to high column-growth, which may result in a high linear growth rate but low mass growth rate due to a large number of voids in the diamond films. However, for the two side injection cases, there were no sign of any diamond deposition on the substrate using CH4. This indicates that good mixing between plasma gas and CH4 is critical.

Diamond Grain Size and Morphology

Acetone and ethanol were used to deposit diamond at both low and high side injection locations. It was found that diamond grains from acetone are five times smaller than those from ethanol for both low and high side injection locations (Figure 4).

Considerable change in grain size as a result of different hydrocarbon liquid precursors indicates that a careful choice of liquid hydrocarbon precursors may render a means of control on diamond grain size. A controlled small grain size may help improve diamond adhesion because of an increased contact area between diamond crystals and substrate surface and hence enhance chemical bounding.

SEM photos indicate that the surface morphology of diamond films from acetone and ethanol are similar for low and high side injection locations.

Conclusions

- Droplets from the low location side injection are less affected by the plasma instability, leading to a possible direct landing of larger droplets on the substrate surface.
- Low location side injection has the highest diamond growth rate and carbon utilization efficiency, as compared with counterflow and high location side injection arrangements. This may be attributable to its efficient mass transport.
- For making optimal use of the higher mass transport offered by liquid injection, a reactor has to be designed which will offer an abundance of atomic hydrogen in the deposition region.
- Acetone renders five times smaller diamond grains than ethanol does. A careful choice of liquid precursors will thus provide certain control on diamond grain size, which is critical for improving adhesion.

Acknowledgment

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References

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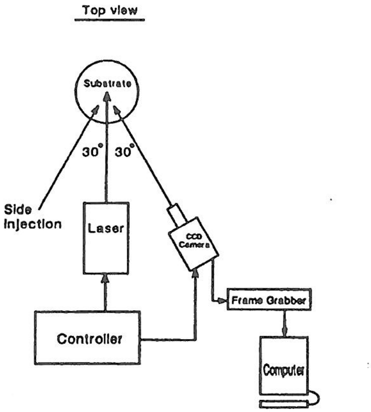


Fig. 1 Schematic of experimental setup with the laser vision system

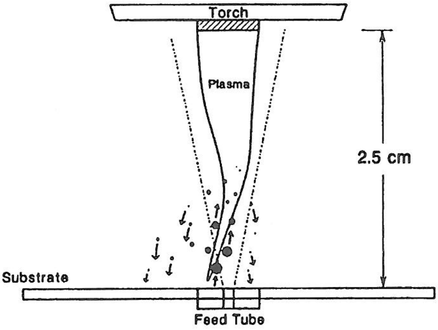


Fig. 2 (a) A schematic of droplet trajectories for counter-flow arrangement
No droplets are seen within 3 mm above the substrate due to the effect of plasma instability and evaporation

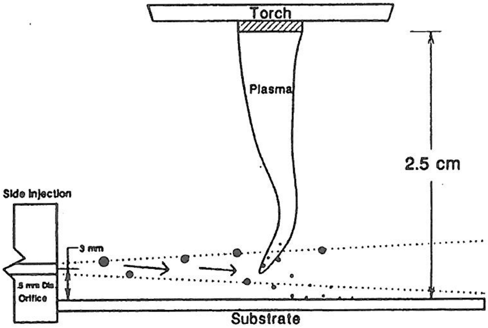


Fig. 2 (b) A schematic of droplet trajectories for lower-location side injection
Droplets are seen at 1 mm above the substrate probably due to less effect of plasma instability and evaporation

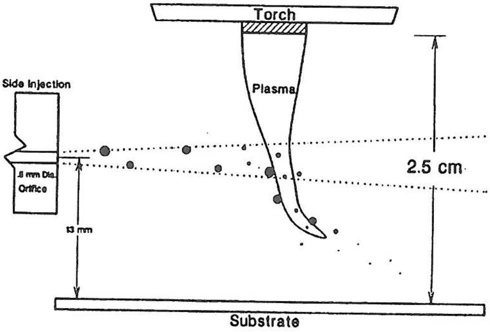


Fig. 2(c) A schematic of droplet trajectories for high-location side injection
There is strong interaction between droplets and plasma plume

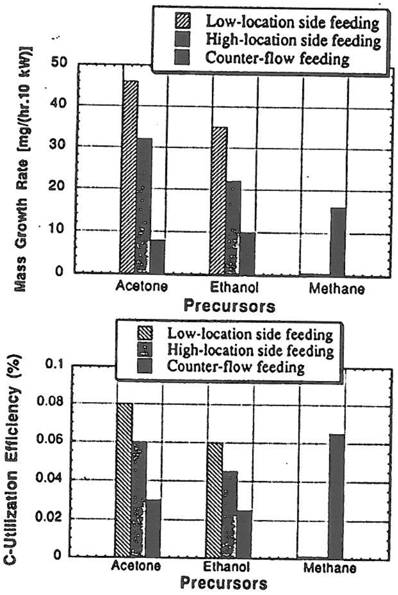
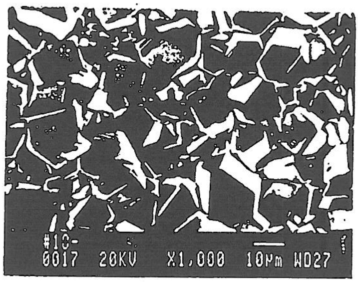
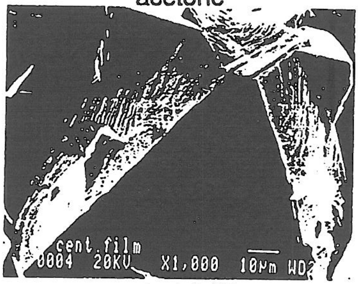


Fig. 3 Diamond mass growth rates vs two different liquid precursors for three feeding arrangements

Note: Mass growth rate for CH4 is available and will be put in later



acetone



ethanol

- Diamond from acetone has a grain size five times smaller than that from ethanol
- Morphology does not appear to change significantly over deposition area

Figure 4