Secondary Discharge Induced Nonequilibrium Chemistry in a CVD Diamond DC Arcjet Reactor

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Diamond deposition in an atmospheric pressure direct current arcjet was enhanced through induced nonequilibrium chemistry. A positive potential applied to the growth surface provided targeted energy addition to the free electrons in the plasma, heating them above the bulk gas temperature ($T_e > T_g$). These energetic electrons promote impact dissociation of molecular species, specifically molecular hydrogen, to yield an enhanced flux of radicals important in the diamond growth process to the substrate surface. A factor of 7 increase in growth rate was observed with 4.9 A/cm^2 and 170 V across the secondary discharge as compared with an unbiased (floating) substrate case. Two-dimensional imaging of the plasma jet found a substantial increase in the H_α emission from the boundary layer with a positive potential applied. SEM and Raman spectroscopy analysis indicated that uniform, high quality films were deposited in all cases reported here.

Introduction

Several radical species in the diamond growth environment are thought to contribute to the deposition of the diamond thin-films. Of these, atomic hydrogen is believed to be particularly important [1,2]. Atomic hydrogen makes surface sites available to carbon containing species needed for the diamond growth process by abstraction of surface hydrogen. Atomic hydrogen also acts to incorporate adsorbed hydrocarbon radicals into the diamond lattice. Carbon containing radical fluxes factor directly into the diamond growth rate, as they are the source of carbon for continued diamond growth[2], and are often strongly linked to the available atomic hydrogen concentration.

There are several ways to increase the radical concentration at the growth surface, leading to rapid growth of high-quality diamond. It has been shown[3,4,5] that by increasing the plasma velocity, the boundary layer thickness above the deposition surface is thinned. This effect decreases the time available for recombination of radical species that are created in the freestream and the boundary layer as they approach the substrate. This can lead to higher fluxes of these species to the growth surface and higher growth rates of CVD diamond. A factor of 5 increase in growth rate has been observed when the plasma velocity was increased by an order of magnitude[3]. Additionally, recent analysis of scaling relations for convection-dominated reactors has found that the use of high pressure ($\geq$ 1atm), sonic flow conditions will maximize the H atom concentration delivered to the deposition surface[1]. A different approach to increase radical fluxes to the deposition surface involves actively driving the boundary layer chemistry to a greater degree of nonequilibrium by means of discharge induced plasma chemistry[6,7,8]. Matsumoto, et al.[8,9] applied a positive potential to the deposition surface in a sub-atmospheric dc arcjet and found a twofold increase in diamond growth rate as compared with an unbiased case, although the deposited films had a low degree of uniformity across the deposition surface. They implied that an enhancement in gas phase dissociation near the substrate was the cause for the increased deposition rate[9]. Conversely, negative-biasing of the substrate has been used in low pressure, microwave reactors to enhance and control the nucleation of CVD diamond[10,11] .

This paper addresses the secondary discharge method as a means of augmenting the deposition rate while maintaining a high degree of film quality. By biasing the deposition surface with respect to the plasma, the free electrons gain kinetic energy from the imposed electric field. These energetic electrons can promote super-equilibrium concentrations of radical species in the boundary layer via bond-breaking collisions with the molecular species. In particular these electrons can shift the balance of important dissociation reactions such as

$$H_2 + e^- \Rightarrow H + H + e^- \tag{1}$$

to produce elevated concentrations of atomic hydrogen. Calculations of flowing plasmas[7] with elevated electron temperatures have shown that increased dissociation of hydrogen is possible with moderate discharge currents and voltages. In the case of a recombining plasma approaching a water cooled substrate, energetic electrons can decrease the recombination rate of radical species (specifically atomic hydrogen) which have shown to be important in the diamond CVD process.

Experimental

The experimental facility used to perform this research consisted of an atmospheric pressure Thermal Dynamics Model F-5000 swirl stabilized direct current (DC) arcjet operating at a nominal power of 100 kW. A schematic of the facility can be seen in Figure 1 and discussed in detail elsewhere[12]. The plasma created by the arcjet exits a converging nozzle and impinges upon a molybdenum substrate positioned normal to the flow 4 cm downstream of the nozzle exit. A hot-pressed boron nitride insulator was used on the substrate assembly to confine the discharge current and the deposition area to the 1.25 cm^2 area of the molybdenum rod. The secondary discharge was produced by a bank of four Kepco 100-10M power supplies, each rated at 100 V and 10 A, that were connected together to deliver a biasing voltage of up to +400 V to the deposition surface. The substrate temperature was monitored with a Minolta-Land Cyclops Model 152 infrared optical pyrometer.

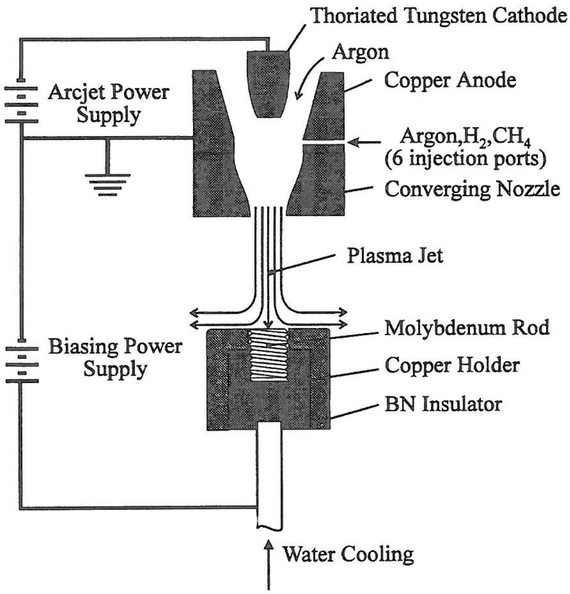

Figure 1 - Schematic illustration of the atmospheric pressure direct-current arcjet and the substrate biasing system.

Results

Diamond deposition experiments were performed over a range of substrate biasing conditions while all other reactor conditions were held nominally constant from case to case. The flow rates of the feed-gases for these experiments were 450 slpm of argon, 4.25% hydrogen in argon, and 2.44% methane in hydrogen. In the cases reported here the substrate temperature was maintained at 1125°C±25°C, and all the deposition times were one hour. Highly uniform films were deposited, covering the full area of the substrate.

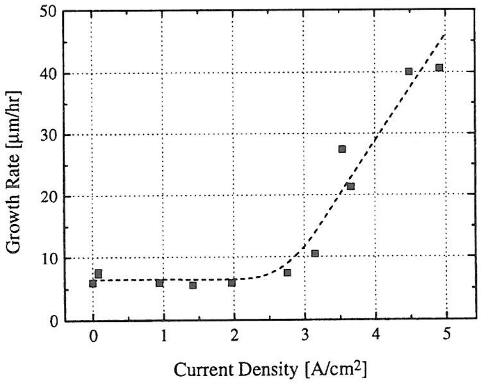

Figure 2 - (◆) Growth rate of CVD diamond as a function of current density in the secondary discharge. (---) Approximate fit to the data.

The deposited films were measured for cross-sectional film thickness using scanning electron microscopy. A summary of growth rate as a function of current density through the secondary discharge can be seen in Figure 2. A factor of seven increase in the growth rate was observed with a significant bias current(4.9 cm^2 at 170 V) compared with the floating substrate case for these conditions. There appears to be a threshold current of ~2.4 A/cm^2 that must be reached in the secondary discharge before an increase in growth rate is observed. This threshold may be related to the energy required to increase the electron temperature to a critical value. At this point electron catalyzed reactions such as the one described in equation 1 may become an important factor in controlling the amount of atomic hydrogen in the boundary layer and at the deposition surface.

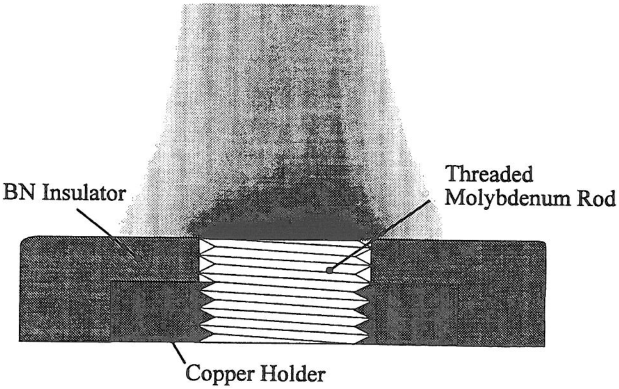

Figure 3 - Two-dimensional image of the increase in the H_α emission due to the secondary discharge(maximum to minimum signal is from black to white).

Optical emission spectroscopy measurements have found that the electron temperature at the substrate is elevated above the freestream electron temperature when a potential is applied to the substrate. This indicates that the secondary discharge can be used to target the energy addition to the highly mobile free electrons in the plasma through joule heating.

Image processing was employed in this study to obtain a two-dimensional map of the emission from the first atomic hydrogen Balmer line (H_α). H_α emission is a result of an H atom decaying from its third to its second electronic energy level. This process emits a photon at a wavelength of 656.3 nm. A charge-coupled device (CCD), a lens system and a narrow band-pass interference filter centered at 656.3 nm were used to obtain images with and without a potential applied to the substrate. A computer analysis package acquired and analyzed the data for different biasing conditions. Figure 3 shows the results of the H_α imaging of the secondary discharge for a typical diamond growth experiment. The biasing conditions for this case were 5.1 A/cm^2 and 140 V across the secondary discharge. This image represents a 40 frame average with the potential applied to the growth surface after subtracting a 40 frame average without the potential applied. There is a large increase in H_α emission, particularly within the boundary layer, with a strong potential applied to the growth surface. The intensity of the H_α emission in this region was much brighter(by a factor of 5) than from the ~5000 K freestream. This may be an indication that the secondary discharge is significantly increasing the atomic hydrogen concentration in the boundary layer and flux to the substrate, leading to the higher growth rates observed here.

Raman analysis of each of the samples indicates very high quality films were deposited over the range of biasing conditions. Each of the spectra consisted of a sharp peak near 1332 cm^{-1} which closely corresponds to the peak at which the *sp*^{3} lattice structure of natural diamond occurs[13]. Little or no amorphous carbon Raman signal was detected in these samples. In all the cases reported here, a full-width half-maximum (FWHM) of no more than 4 cm^{-1} for the diamond peak was measured, indicating high quality films were deposited (natural diamond has a FWHM of 2.0 cm^{-1})[13]. Figure 3 shows the Raman spectra for a diamond film deposited under a highly biased substrate condition(100 V and 2.76 A/cm^2). The inset to Figure 3 displays splitting of the 1332 cm^{-1} diamond line. This phenomena was typical of all the samples grown in this study. The splitting effect has been attributed to high quality, highly oriented films that were stressed perpendicular to the growth direction[14,15] (in-plane stresses). These in-plane stresses can arise in CVD diamond films during the cool-down period after the deposition process, and are caused by the mismatch in the thermal expansion coefficients of CVD diamond and the substrate material. The higher wavenumber peak is attributed to the doublet mode and the lower wavenumber peak to the singlet mode of the Raman diamond line. These modes are normally triply degenerate in the absence of stress[15].

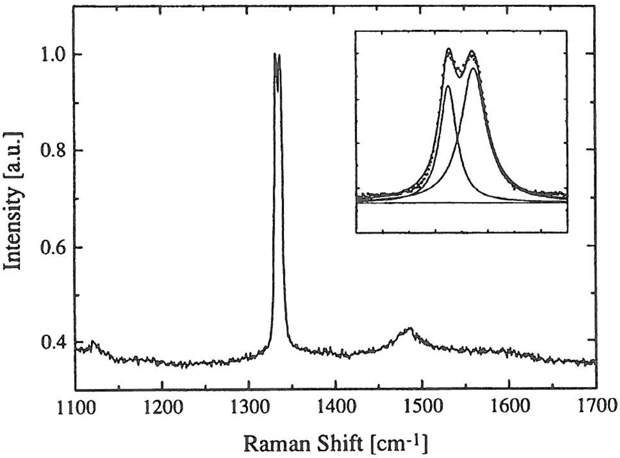

Figure 4 - Raman spectra of the deposited diamond film. Inset shows splitting of the 1332 cm^{-1} diamond peak.

Conclusions

The effects on diamond growth of a nonequilibrium secondary discharge over the substrate have been investigated in an atmospheric pressure dc arcjet. A significant increase in growth rate of CVD diamond was observed with a positive potential applied to the growth surface. The growth rate was found to increase by a factor of 7 when the deposition surface was biased at 170 V and 4.9 A/cm^2 as compared with the floating substrate case. The increased growth rate may be attributed to an increased flux of atomic hydrogen to the growth surface resulting from an elevated electron temperature that increased the dissociation near surface fraction of hydrogen. Imaging of the flow field found a significant increase in the H_α emission signal in the boundary layer over the deposition surface with a positive potential applied. Raman spectroscopy analysis indicated high quality films were deposited in all cases reported here. Splitting of the 1332 cm^{-1} Raman diamond line indicates highly oriented films that have a high degree of in-plane stresses.

Acknowledgments

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