

## DIAMOND SYNTHESIS IN FLAMES

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### INTRODUCTION

The synthesis of diamond in an atmospheric pressure flame was first reported by Hirose and Kondo<sup>1</sup> in March, 1988. The conditions leading to diamond growth were given as an oxygen/acetylene flow ratio of 1.5/2, a substrate temperature of 1000°C, and a Si substrate positioned in the 'inner' or acetylene feather region of the flame. Slower diamond growth was also observed in a hydrogen-methane flame with a filament. More recently, Hirose and Mitsuizumi<sup>2</sup> have reported growing diamond with acetylene, ethylene, methane, propane, methanol and ethanol gases burned in air when mixed with either hydrogen or oxygen. Growth was achieved on Si, SiC, Al<sub>2</sub>O<sub>3</sub>, W, WC, and Mo substrates in an oxygen-acetylene flame, and maximum growth rates of 200 μm/hr for particles<sup>2</sup> and 100-150 μm/hr for films<sup>3</sup> were reported. The effects of varying key parameters on diamond growth were not discussed in these reports.

In the U.S., Hanssen et al.<sup>4</sup> studied the effect of substrate position, fuel/oxidizer gas flow ratio, and substrate temperature on diamond growth in an premixed oxygen-acetylene flame, and observed growth on Si(100), Si(111), BN, Mo(100), Nb(100), TiC(100), Ta and Cu. Carrington et al.<sup>5</sup> reported diamond growth on Si(100) in an oxygen-ethylene flame. Yarbrough<sup>6</sup> confirmed the growth of diamond in an oxygen-acetylene flame at atmospheric pressure. Snail et al.<sup>7</sup> observed diamond growth in an oxygen-ethane flame, studied the uniformity of diamond crystallite growth as a function of position in an oxygen-acetylene flame, and reported that adding hydrogen to an oxygen-acetylene flame increased the ratio of the (diamond / amorphous carbon) Raman peaks. Recently Yarbrough observed diamond growth in a low pressure (25 torr) oxygen-acetylene flame.<sup>8</sup>

The next section of this paper discusses the experimental apparatus used at the Naval Research Laboratory (NRL) to study diamond synthesis in flames. Following that, a partial review of the results obtained at NRL on the flame synthesis of diamond is given. The results of several other studies currently in progress will be presented at the meeting.

### EXPERIMENTAL SETUP

An oxygen-acetylene brazing torch (see Fig. 1) fitted with a .89 mm orifice tip was used to deposit diamond crystallites and films. The torch was mounted on an xyz translation stage and the gas flow rates were adjusted with mass flow controllers. Substrates were mounted on a water cooled copper block and a two color near infrared pyrometer was used to monitor the peak substrate temperature from 650°C to 1200°C. A more detailed description of this setup can be found in Ref. 4.

Most of the depositions reported on in this paper were grown on Si(100) substrates which were prepared by scratching with 5-6 micron diamond paste, and ultrasonic cleaning in acetone and methanol. A typical deposition lasted for 10-15 minutes. During depositions the torch was operated in a fuel rich mode and the substrates were positioned in the first diffusion flame (or 'acetylene feather') beyond the premixed flame front.

The substrate temperature distribution was monitored during depositions with a thermal (8-12  $\mu\text{m}$ ) imaging camera having a spatial resolution on the substrate of  $\sim 1/3$  mm (3 mrad). During several long (2-4 hours) depositions, a zoom microscope (10-70x) with a video camera attachment was used to record the changes in crystallite morphology with time. Square faced (100) diamond crystallites with up to 350 micron sized edges have been grown during these longer depositions, using an oxygen-acetylene flame.

## RESULTS AND DISCUSSION

In the first subsection of this section, the oxygen/acetylene flow ratios and substrate temperatures which lead to the growth of faceted diamond crystallites, micro-crystalline graphite and amorphous carbon (a-C) are reviewed. Adding hydrogen to an oxygen-acetylene flame is then discussed in terms of its effect on the a-C contributions to the crystallite's Raman spectra and the crystallite morphology. Finally, the variation in diamond crystallite growth with position in a premixed oxygen-acetylene flame is analyzed.

### Process parameters - material property relationships

A detailed mapping of the type of material deposited versus the substrate temperature and fuel/oxidizer flow ratio has been performed for an oxygen-acetylene flame. The ( $\text{O}_2/\text{C}_2\text{H}_2$ ) flow ratio, R, was varied from 0.8 to 1.5; this corresponds to a range of equivalence ratios<sup>9</sup> of 3.13 - 1.67, respectively. The total gas flow rate was  $\sim 2.3$  slm and the substrate was positioned 1-2 mm below the inner flame tip. The substrate temperature was varied from 650°C to 1200°C. The deposited material was analyzed with an optical microscope, a field emission scanning electron microscope (SEM), and also by x-ray diffraction (XRD) and Raman spectroscopy. Raman spectra were taken with a 5145 Å laser excitation and  $\sim 30$  mm spot size. The Raman data discussed in the next two subsections were taken with  $\sim 1$  mm spot size using a micro-Raman accessory.

As in the case of the low pressure CVD processes, well faceted crystallite growth occurs when the substrate is near 900°C. For the torch nozzle and total flow rates used, these studies indicate that for flow ratios less than 0.9, ball-like structures (see Fig. 2a, Ref. 4) grow at all substrate temperatures. For values of R between 0.9 and 1.2, well faceted crystallites grow (see Fig 2b, Ref. 4). The temperature range for which crystallite growth occurs expands from near 900°C at R = 0.9 to 650°C - 1050°C at R = 1.2. Above and below this temperature range, ball-like structure growth occurs. For R greater than 1.15, the growth rate decreases rapidly with increasing values of R so that at R = 1.2 the growth rate is very low and at 1.3 and 1.4 growth does not occur.

The variation of material morphology with substrate temperature and oxygen/acetylene ratio encompasses three distinct regions corresponding to the growth of faceted crystallites and ball-like structures, and no growth. The boundary between the ball-like structure and crystallite regions exhibits a gradual transition in particle morphology from faceted crystallites to ball-like particles. For an example of a transitional structure see Fig. 2d of Ref. 4. The diamond Raman peak at 1332  $\text{cm}^{-1}$  is seen in the spectra of some ball-like structures and indicates that the ball-like structures can contain diamond. This suggests that measurements of the growth rates of different materials (diamond, graphite, a-C) versus the substrate temperature and oxygen/acetylene flow ratio are needed. The Raman spectra of both ball-like structures and faceted crystallites grown in an oxygen-ethylene flame also exhibited coexisting peaks due to different forms of carbon<sup>5</sup>.

The ball-like structures grown with R > 0.9 at substrate temperatures above those delineating the ball-crystallite boundary exhibited strong Raman peaks at 1355  $\text{cm}^{-1}$  and 1575  $\text{cm}^{-1}$  associated with micro-crystalline and crystalline graphite, respectively<sup>10</sup>. These peaks were also observed for ball-like structures grown at R < 0.9. Ball-like structures grown with R > 0.9 at substrate temperatures below those delineating the crystallite-ball boundary exhibited a high fluorescence background. This suggests that the region of ball-like growth may have to be further subdivided.

## Hydrogen-oxygen-acetylene flames

The effect on diamond growth of adding hydrogen to an oxygen-acetylene flame was studied for two cases: first, with the  $(\text{O}_2/\text{C}_2\text{H}_2)$  flow ratio fixed at 1.12, and hydrogen added to the flame, and second, with the  $[\text{O}_2/(\text{C}_2\text{H}_2 + \text{H}_2)]$  flow ratio fixed at 1.12, and hydrogen substituted for acetylene. In both cases the oxygen flow rate was fixed at 1.7 slm. The total flow rate for the hydrogen addition study ranged from 3.2 slm to 4.0 slm. In the case where the  $(\text{O}_2/\text{C}_2\text{H}_2)$  flow ratio was fixed, hydrogen was added so that the  $(\text{H}_2/\text{C}_2\text{H}_2)$  flow ratio equalled 0.0-0.50. Most samples had an annular region of heavy crystallite nucleation; Raman spectra were taken at the inner and outer edges of the annuli, and growth center of each sample.

The ratio of the diamond to the amorphous carbon Raman peaks ( $R_{\text{DC}}$ ) of individual crystallites is plotted in Figure 2 versus the  $(\text{H}_2/\text{C}_2\text{H}_2)$  flow ratio for the three different positions on the samples. The  $R_{\text{DC}}$  ratio is essentially constant for crystallites located in the same local region of the sample. These results show a nearly linear increase in  $R_{\text{DC}}$  with increasing hydrogen flow rate, although the diamond growth rate decreased significantly as the  $(\text{H}_2/\text{C}_2\text{H}_2)$  flow ratio exceeded 0.25. For a  $(\text{H}_2/\text{C}_2\text{H}_2)$  flow ratio equal to 0.45, no growth is observed. When the  $[\text{O}_2/(\text{H}_2 + \text{C}_2\text{H}_2)]$  flow ratio is fixed, substituting hydrogen for acetylene leads to an increase in  $R_{\text{DC}}$  for  $(\text{H}_2/\text{C}_2\text{H}_2)$  flow ratios up to 0.02. No diamond growth is observed for  $(\text{H}_2/\text{C}_2\text{H}_2)$  flow ratios equal to or greater than 5/95. This data suggests that oxygen is preferentially burning with acetylene, rather than hydrogen.

## Variation of growth with position in flame

The nucleation density of crystallites deposited in an oxygen-acetylene flame was frequently higher within an annular region, and lower in other regions on the substrate. The causes of this nonuniform growth include both temperature inhomogeneities and species concentration variations. A thermal (8-12  $\mu\text{m}$ ) imaging camera having a spatial resolution on the substrate of  $\sim 1/3$  mm (3 mrad) was used to measure substrate temperature profiles. During a typical deposition on a Si substrate in an oxygen-acetylene flame the substrate temperature profile exhibited large decrease with increasing distance from the center of the growth. For a substrate to flame front distance (D) of 4.5 mm, the temperature decrease observed from the center to edge of the diamond growth region was approximately 250°C.

The variation in diamond growth with position in the acetylene diffusion flame was studied with an oxygen flow rate of 1.7 slm and an acetylene flow rate of 1.5 slm, and is illustrated in Figure 3. When the distance (D) from the substrate to the oxygen-acetylene flame front was 3.0-4.5 ( $\pm 0.5$ ) mm, the resulting nucleation density of diamond crystallites was low directly beneath the flame axis and significantly higher within an annulus centered on the flame axis. The outer edge of this annulus occurred where the edge of the acetylene diffusion flame intersected the substrate. As D was increased to 7.5 mm, the nucleation density increased on the region of the substrate directly under the flame axis and the annular pattern of crystallites disappeared. Growth areal density was estimated by counting crystallites in 3600  $\text{mm}^2$  areas using an 800X optical microscope. A weighting factor was assigned for crystallites less than 50% of the mean size in a region; the typical crystallite size ranged from 1-11 microns.

An SEM and micro-Raman study of the spatial variation of diamond crystallite quality was performed on a sample grown in an oxygen-acetylene-hydrogen flame. For this sample, the  $(\text{O}_2/\text{C}_2\text{H}_2)$  flow ratio was equal to 1.12, the  $(\text{H}_2/\text{C}_2\text{H}_2)$  flow ratio was set at 0.10, and the peak substrate temperature ranged from 910-960°C. The substrate was positioned 4.5 mm below the premixed flame front. Individual crystallites showed a significant decrease in the ratio ( $R_{\text{DC}}$ ) of the 1332  $\text{cm}^{-1}$  diamond Raman peak to the 1510  $\text{cm}^{-1}$  amorphous carbon peak with increasing distance from the growth center. This variation is exhibited in Figure 4. Crystallites outside of the annular region (extending from 0.7-2.7 mm) exhibited a small increase in  $R_{\text{DC}}$  compared to those in the annulus. Electron and optical microscope analyses showed a correlation of the decrease of  $R_{\text{DC}}$  across the annular growth region with the degree of secondary growth observed on the diamond crystallite faces. Significant secondary growth was observed on crystallites in the annular growth region while 'cleaner' better formed crystallites were observed inside and outside of the annulus.

The Raman spectra of all crystallites exhibited a fluorescent background signal level which increased with the wavelength shift up to  $1650\text{ cm}^{-1}$ , which was the limit of the measurements; this background level increased as the crystallites' distance from the growth center increased.

### CONCLUSIONS AND FUTURE DIRECTIONS

These results demonstrate that diamond can be grown at atmospheric pressure in premixed oxygen-hydrocarbon flames on a variety of substrates. Growth in oxygen-acetylene flames occurs throughout the first diffusion flame beyond the premixed flame front, for acetylene rich flames. The type of material grown (diamond, graphite, a-C) in an oxygen-acetylene flame depends on the substrate temperature and oxygen/acetylene flow ratio. The ranges of the parameters found to lead to diamond crystallite growth are: 1) substrate temperatures,  $T = 650$  to  $1050^\circ\text{C}$ , and 2) gas flow ratios,  $R = 0.9$  to  $1.2$  for a total flow rate of  $\sim 2$ - $3$  slm (the appropriate flow rate is strongly dependent on the nozzle used). The "cleanest" crystallites were grown at  $T = 950^\circ\text{C}$ , and  $R = 1.13$ .

The addition of hydrogen to an oxygen-acetylene flame produces significant improvements in the diamond to amorphous carbon Raman peak ratio of the deposited crystallites. For an initial ( $\text{O}_2/\text{C}_2\text{H}_2$ ) flow ratio of 1.12, a significant decrease in crystallite growth rate occurs for ( $\text{H}_2/\text{C}_2\text{H}_2$ ) flow ratios greater than 0.24 when hydrogen is added to the flame, and 0.02 when hydrogen is substituted for acetylene. For flames from a single orifice, the diamond crystallite growth density and quality can vary significantly with the position of the substrate in the flame. These variations are probably caused by variations in chemical species, which are known to vary significantly with position in 2d flames.

Several techniques for controlling and reducing the nonuniformities in the substrate temperature are currently under investigation. These include a mount with both heating and cooling capabilities, and using liquid metals to improve the thermal contact between the substrate and the mount. A microtube flat flame burner is currently being fabricated<sup>11</sup>. This burner is expected to produce flame temperatures that are uniform to  $\pm 50^\circ\text{C}$  over a 1 cm diameter disk. Several other 2d and 1d burner designs are also being studied. The nonuniform flame structure associated with single orifice flames offers an opportunity to identify the chemical species responsible for diamond growth.

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<sup>8</sup>Personal communication with W. Yarbrough, December 1988.

<sup>9</sup>The equivalence ratio is defined as the actual fuel:oxidizer ratio divided by the fuel:oxidizer ratio corresponding to complete combustion to carbon dioxide and water.

<sup>10</sup>F. Tuinstra and J. L. Koenig, J. Chem. Phys. **53**, 1126 (1970).

<sup>11</sup>Research Technologies, P.O. Box 384, Pleasanton, CA. 94566

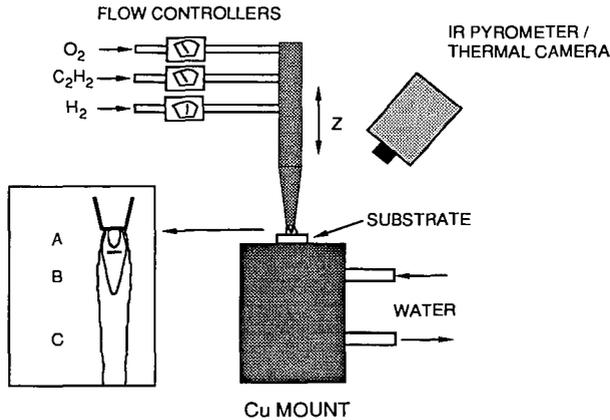


Figure 1: Schematic of the oxy-acetylene torch deposition experiment. The inset is an expanded view of the oxygen-acetylene flame. The three regions described in the text are: A) the inner cone, B) the acetylene feather, and C) the outer flame. For diamond growth, the substrate is positioned inside the acetylene feather region.

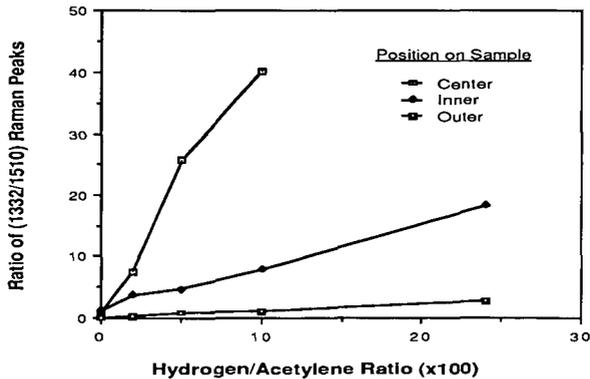


Figure 2: Ratio of the diamond Raman peak ( $1332\text{ cm}^{-1}$ ) to the amorphous carbon peak ( $1510\text{ cm}^{-1}$ ), for different hydrogen flow rates added to an oxygen-acetylene flame with  $R = 1.12$ . Data for the growth center of the sample, and the inner and outer edges of the growth annulus are shown. Note the monotonic increase in crystal quality with increasing hydrogen flow rate.

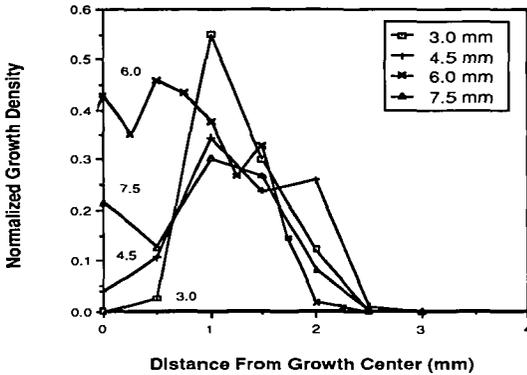


Figure 3: Normalized diamond growth density versus position on the substrate, for different flame-substrate separations (D) and the growth conditions described in the text. Note the transition from annular growth patterns to disk type patterns with increasing D.

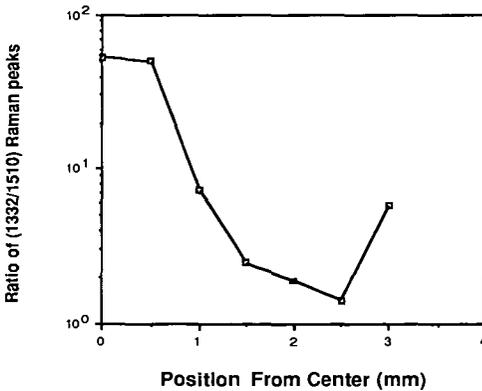


Figure 4. Ratio of the diamond Raman peak ( $1332\text{ cm}^{-1}$ ) to the amorphous carbon peak ( $1510\text{ cm}^{-1}$ ), versus radial distance on the substrate for the conditions described in the text. The increase at large distances is associated with positions outside of the annular growth region. SEM analysis has correlated this increase with a decrease in secondary growth on the crystallite faces.