

Diamond films from combustion of methyl acetylene and propadiene

Stephen J. Harris^{a)}

Physical Chemistry Department, General Motors R&D Center, Warren, Michigan 48090-9055

Ho Seon Shin and David G. Goodwin

Division of Engineering and Applied Science, California Institute of Technology, Pasadena, California 91125

(Received 22 August 1994; accepted for publication 3 December 1994)

To date diamond films grown with the combustion technique have used either acetylene or, rarely, ethylene as the fuel. However, there are barriers to large scale commercialization of the combustion technique using either fuel. For example, acetylene is relatively expensive and difficult to handle, while the use of ethylene gives relatively low growth rates. In this letter we propose replacing acetylene with MAPPTM gas, a commercial mixture of methyl acetylene and propadiene in liquefied petroleum gas (primarily propylene). MAPP gas is considerably cheaper, safer, and easier to handle than acetylene. Furthermore, the experiments described here suggest that MAPP gas flames are only slightly less efficient than acetylene flames at converting fuel carbon atoms into diamond. © 1995 American Institute of Physics.

A variety of techniques, including radio-frequency and direct-current plasmas, hot filaments, and arc jets, have been used to activate precursor gases to grow diamond films by chemical vapor deposition (CVD). One rather interesting technology is the combustion technique first demonstrated by Hirose and co-workers.¹ Films grow at very high rates and with excellent quality using atmospheric pressure oxyacetylene torches, although uniform growth occurs only over a small area in most cases.¹⁻³ Low pressure flat (burner stabilized) acetylene flames have been used to grow uniform films over larger areas⁴ but at the cost of lowering the growth rates. It is noteworthy that in almost every case reported, acetylene has been the fuel used for combustion-generated diamond. The reasons for this choice are related to the uniquely high flame speed and radical concentrations found in acetylene flames compared to flames of other hydrocarbons. Since high values for radical concentrations and gas velocity generally lead to high growth rates, diamond films generated from acetylene are expected to grow at much higher rates than films generated from other fuels. This expectation has been verified for ethylene-fueled flames^{5,6} which, although they are faster and have higher radical concentrations than methane or propane flames, generate diamond films at rates considerably lower than acetylene-fueled flames. There are no reports of diamond films having been grown from flames burning methane or other slower-burning fuels, although diamond formation was observed in a hydrogen-oxygen flame to which small quantities of methane were added in the postflame gases.⁷ We note that the hydrogen/oxygen flame has a flame speed even higher than the acetylene/oxygen flame.

In spite of its advantages for generating diamond films, acetylene is, unfortunately, a somewhat expensive and difficult material to handle. For example, acetylene can detonate

even in the absence of oxygen *via* the exothermic reaction



In this letter we demonstrate that another high energy fuel, MAPPTM gas (the name is a trademark of the BOC Group, Inc.), could replace acetylene for growing diamond films. MAPPTM gas is a mixture of about half LPG (mainly propylene) and half C₃H₄. There are two isomers of C₃H₄ contained in MAPPTM gas, methyl acetylene (also called propyne), and propadiene (also called allene). (The concentration of a third isomer, cyclopropene, is very low.) MAPPTM gas flames are nearly as fast and hot as acetylene flames and have radical concentrations that are nearly as high. However, MAPPTM gas is cheaper, safer, and easier to handle than acetylene. We suggest that use of MAPPTM gas could reduce some of the barriers to commercializing combustion-grown diamond.

The experiments were performed using the same facility described previously by Glumac and Goodwin.⁴ Premixed flat MAPPTM/O₂ flames are stabilized on a water-cooled burner. Some experiments were carried out with a 4 cm diam burner and others with a 2 cm diam burner of similar design. The burner face is copper, and the fuel/oxygen mixture emerges through an array of 1 mm diam holes spaced 2.5 mm apart (4 cm diam burner) or 2 mm apart (2 cm diam burner). A molybdenum substrate (5 cm diam, 0.6 cm thick) is placed parallel to the burner face, very near the flame.

The burner is housed in a water-cooled bell jar vacuum chamber, and the pressure is controlled by a valve on the chamber exhaust. The substrate is thermally isolated, such that the heat flux from the flame to the substrate is balanced largely by radiation to the chamber walls. No additional substrate heating or cooling is used in the present work. The substrate temperature is measured by a two-color infrared pyrometer.

Diamond was deposited for pressures ranging from 70 to 180 Torr. Lower pressures were attempted, but the flame was

^{a)}Electronic mail: sharris@gmr.com

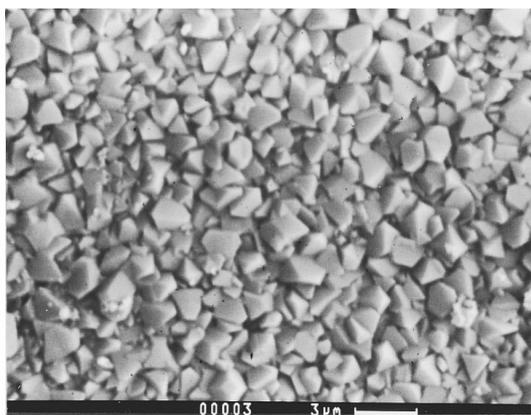


FIG. 1. SEM micrograph of a diamond film grown from a MAPP™ gas flame.

unstable, and no diamond could be grown. As with all flame synthesis methods for diamond, the deposit characteristics depend sensitively on the fuel-to-oxygen ratio. The required ratio depends on pressure, and varied from 0.46 at 180 Torr to 0.51 at 70 Torr. The total flow rate (fuel and oxygen) was typically 0.5–1.9 slm per cm² of burner area.

An SEM micrograph of a typical diamond film is shown in Fig. 1. This film was grown for 2.5 h at 180 Torr. The substrate temperature was 830 °C, and the burner/substrate distance was 3.75 mm. The fuel flow rate was 0.6 slm/cm² and the oxygen flow rate was 1.3 slm/cm². The film growth rate was approximately 1 μm/h. The Raman spectrum for a film grown under these conditions is shown in Fig. 2.

The burner used here was designed for lower-pressure work, where the substrate can be placed farther from the burner. In the present experiments, the small substrate/burner separation (3.75 mm, compared to the hole spacing of 2 or 2.5 mm) resulted in nonuniform films, and some regions of the substrate do not contain diamond. A more suitable burner would result in much more uniform films at these pressures.

Our experiments with filament-assisted diamond growth have shown⁸ that the growth rate of diamond is proportional to the concentration of gas phase methyl radical at the surface. But the factor ultimately limiting the growth rate of

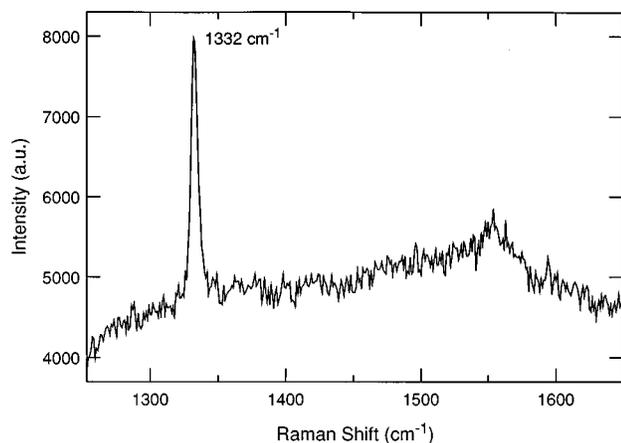


FIG. 2. Raman spectrum of a diamond film grown from a MAPP™ gas flame. Instrumental linewidth is 3 cm⁻¹.

diamond films is the flux of atomic hydrogen impinging on the growing surface. That is, for a given H atom flux, there is a maximum methyl radical flux which can be tolerated consistent with growing a high quality diamond film. High H atom flux is most readily achieved in systems with high radical concentrations (high temperatures) and thin boundary layers (high velocities⁹). Because the acetylene flame is hotter than the flame from any other commercially available hydrocarbon and has the highest flame speed, it can provide an unrivaled flux of H atoms. For comparison, ethylene, with a lower flame temperature and flame speed, provides a lower flux of H, while MAPP™ gas is intermediate.

It is interesting to compare these results to those obtained using acetylene/oxygen flames in the same facility.⁴ With acetylene, the pressure was lower (52 Torr), the fuel/oxygen ratio was significantly higher (0.86), and the fuel flow rate was somewhat lower (0.43 slm/cm²). The film growth rate was 0.6 μm/h. Due to the nonuniformity of the present films, we cannot fairly compare the efficiencies of MAPP™ and acetylene for diamond growth. If we were to simply compare the ratio of linear growth rate to fuel flow rate per unit area, we would conclude that MAPP™ flames are slightly less efficient than acetylene flames at converting fuel carbon atoms into diamond.

Very high quality diamond films have been grown using the oxy-acetylene flame technique. Nevertheless, there are serious safety, handling, and cost considerations involved in using acetylene which could limit the commercial viability of the technique, such as the possibility of detonation mentioned above. MAPP™ gas is also much easier to handle, since its vapor pressure is similar to that of propane, and it liquefies about as readily. Finally, MAPP™ gas costs about half as much per kg as acetylene, even though they have about the same BTU content per kg.

Although C₃H₄ flames have never been studied in the laboratory, detailed chemical kinetics mechanisms exist¹⁰ which could allow fairly accurate species concentrations to be calculated for one-dimensional (flat) MAPP™ gas flames. The present experimental results show that MAPP™ gas has the ability to deliver the high fluxes of atomic H and CH₃ required to support growth rates similar to those found in acetylene flames. Thus, combined with its superior cost, safety, and handling characteristics, MAPP™ gas could replace acetylene as the fuel of choice for combustion-derived CVD diamond films.

Finally, we point out that flame temperature and flame speed can be increased not only by using high energy fuels such as acetylene or MAPP™ gas, but also by using high energy oxidants. For example, flames using N₂O as the oxidant can be hundreds of degrees hotter than flames using oxygen.

One of us (S.J.H.) acknowledges partial support by the Office of Naval Research under Grant No. N00014-92-C-0170. Another author (D.G.G.) acknowledges partial support by the Office of Naval Research under Grant No. N00014-93-K-2020.

¹ Y. Hirose and M. Mitsuzumi, *New Diamond* **4**, 34 (1988).

² K. V. Ravi and A. Joshi, *Appl. Phys. Lett.* **58**, 246 (1991).

- ³L. M. Hanssen, W. A. Carrington, J. E. Butler, and K. A. Snail, *Mater. Lett.* **7**, 289 (1988).
- ⁴N. G. Glumac and D. G. Goodwin, *Mater. Lett.* **18**, 119 (1993).
- ⁵W. A. Carrington, L. M. Hansen, K. A. Snail, D. B. Oakes, and J. E. Butler, *Metall. Trans. A* **20**, 1282 (1989).
- ⁶J. S. Kim and M. A. Capelli, *Appl. Phys. Lett.* **65**, 2786 (1994).
- ⁷N. G. Glumac and D. G. Goodwin, *Appl. Phys. Lett.* **60**, 2695 (1992).
- ⁸S. J. Harris and A. M. Weiner, *J. Appl. Phys.* **70**, 1385 (1991); S. J. Harris and A. M. Weiner, *Thin Solid Films* **212**, 201 (1992).
- ⁹D. G. Goodwin, *J. Appl. Phys.* **74**, 6895 (1993).
- ¹⁰P. Dagaut, M. Cathonnet, and J. Boettner, *Combust. Sci. Technol.* **71**, 111 (1990).