JTTEE5 1:111-116

Synthesis of Diamond Crystals and Films Using an Oxygen-Acetylene Flame under Atmospheric Pressure

H.-C. Chiao, H.-L. Lin, X.-T. Li, and C.-X. Ding

Diamond growth with rates up to 100 to 140 μm/hr was achieved using an oxygen-acetylene combustion spraying technique in an atmospheric environment. Investigations on the processing indicated that the gas flow ratio, substrate position, substrate temperature, temperature distribution, and substrate pretreatment were the most important factors affecting the growth of diamond crystals. Evaluation by means of X-ray diffraction, Raman spectroscopy, scanning electron microscopy, and electron probe microanalysis showed that the synthesized diamond was nearly perfect in morphology, structure, and purity.

1. Introduction

THE synthesis of diamond films from low-pressure gas phases has been widely studied since the early 1980s.[1] This interest is based on the unique properties and many potential applications of the diamond film.

The principle of diamond synthesis is a chemical vapor deposition (CVD) process in which a hydrogen and hydrocarbon gas mixture (*e.g.*, H_2/CH_4) is activated by a plasma or a hot filament. Diamonds can be grown when the dissociated gaseous species come into contact with a substrate, with typical temperatures ranging from 800 to 1000 °C. Although the mechanism of this metastable diamond growth has not been clarified, the following reasons, based on kinetic considerations, are generally used to explain the growth phenomenon.[2] The graphite phase is more stable than the diamond phase by 0.691 kcal/mol (2.89 kJ/mol) at normal pressure; consequently, the activation barrier for diamond growth in preference to graphite is not large. Additionally, the free energy for carbon in the reactant gaseous state is greater than that for carbon in the solid state, and thus carbon will be deposited. Finally, atomic hydrogen is a more rapid etchant for graphite than for diamond and preferentially removes graphite leaving the diamond phase.

Among various CVD diamond film techniques, hot filament and microwave plasma are the most representative and well studied.[3,4] Relatively large area and uniform diamond films can be prepared by these methods. However, a common feature of all these techniques is the requirement of a low-pressure deposition environment ranging from 1 to 100 torr and very low growth rates of typically 0.1 to 10 μm/hr.[1]

In 1988, Hirose[5] successfully manufactured diamond from an oxygen-acetylene torch under atmospheric conditions with very high growth rates of 100 to 150 μm/hr. Other authors[6-8] have reported experiments and developments with this technique; however, further understanding of this deposition method is necessary before potential applications can be realized.

The purpose of this article is to investigate the role and effect of some key factors on the growth of diamond film, establish deposition parameters with which diamond film could be grown, and present results of diamond films obtained by these methods.

Key Words: gas flow ratio, oxygen-acetylene combustion, synthetic diamond, wear resistant coatings, diamond-like coatings

H.-C. Chiao, H.-L. Lin, X.-T. Li, and **C.-X. Ding,** Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China.

2. Experimental Details

A schematic diagram of the experimental apparatus is shown in Fig. 1. An oxygen-acetylene welding torch of 0.9 to 1.0 mm in diameter was the main deposition tool. Oxygen and acetylene with purities above 98% served as source gases. The gases were mixed in the torch and burned at the nozzle exit after ignition. Two gas flowmeters were used to control the flow rates of the gases and to enable adjustment of the relative ratios.

Silicon and molybdenum substrates about 10 by 10 by 0.6 mm in size were scratched using a fine diamond paste of 6-μm particle size for about 3 min and then ultrasonically cleaned for 20 min prior to deposition. Such pretreatment of the substrate was beneficial for diamond nucleation, as discussed in Section 3.2. The substrates were cooled indirectly by placing them on a

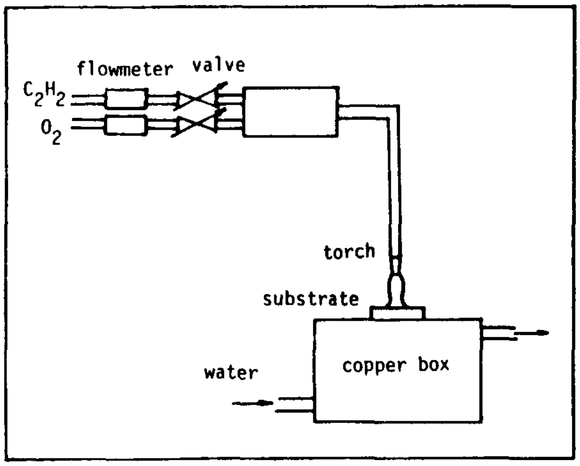

Figure 1 Schematic of the experimental apparatus.

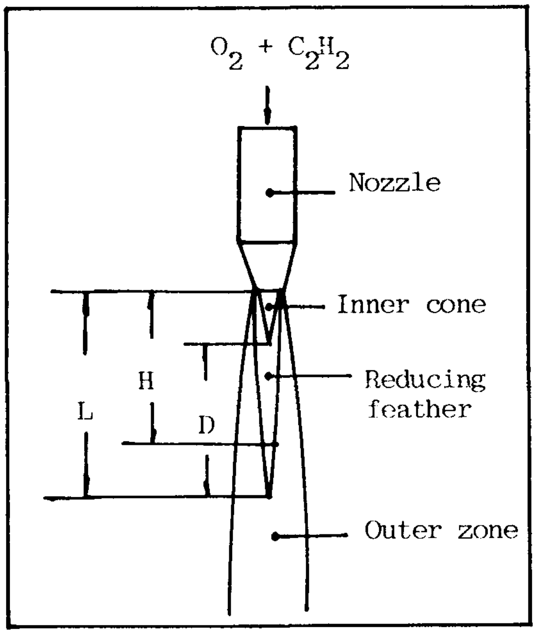

Figure 2 Structure of a C_2H_2-rich oxygen-acetylene flame.

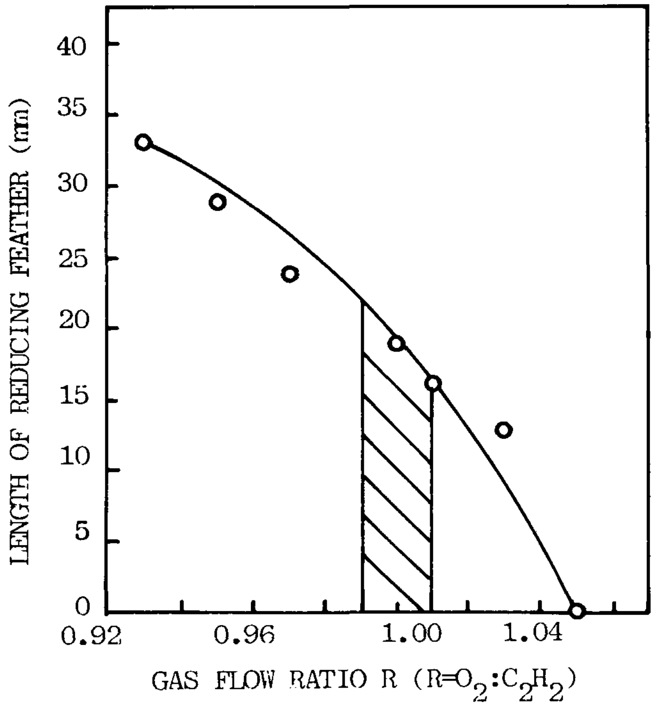

Figure 3 Relationship between the gas flow ratio, R ($R = O_2:C_2H_2$), and the length of the reducing feather. The shaded part is the optimum region for diamond growth.

large water-cooled copper box during deposition. An optical pyrometer was used to estimate the substrate temperature. Diamond deposition was carried out within a time period varying from 20 to 60 min.

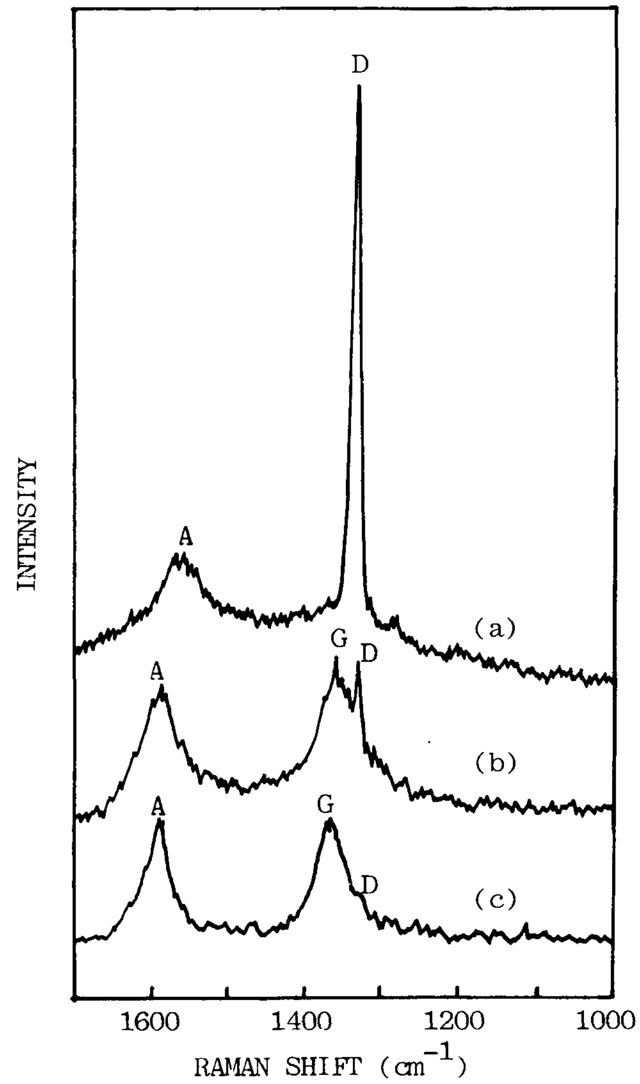

Figure 4 Raman spectra of the films obtained at various gas flow ratios. (**a**) $R = 1.01$, (**b**) $R = 0.98$, and (**c**) $R = 0.97$. A, D, and G denote amorphous carbon, diamond, and graphite, respectively.

3. Results and Discussion

3.1 *Description of Oxygen-Acetylene Flame*

There are three regions in an acetylene-rich oxygen flame, as shown in Fig. 2. The reaction nature of these three regions can be inferred to be different from their different appearances in brightness. The length of the reducing feather, L, decreases significantly with increasing gas flow ratio, R ($R = O_2:C_2H_2$), as illustrated in Fig. 3. Many carbon-containing, oxygen-containing radicals such as C_2, CH, C_2H, and OH and atomic H are detected in the reducing feather.[9] A complete oxidation process to form CO_2 and H_2O should be expected in the outer zone region.

3.2 *Key Factors in Diamond Film Growth*

The gas flow ratio was the most important and sensitive factor in the growth of diamonds. It was found that, if R was less

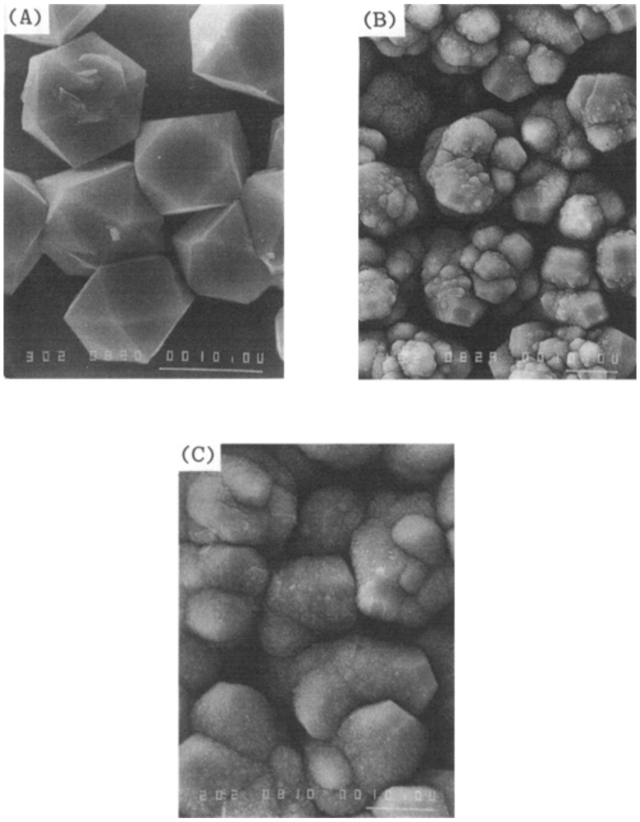

Figure 5 Scanning electron micrograph of diamond crystals obtained at various gas flow ratios. (**a**) $R = 1.01$, (**b**) $R = 0.98$, and (**c**) $R = 0.97$.

than 0.99, then graphite growth was preferred, as demonstrated by the Raman spectroscopy evaluation and scanning electron microscopy (SEM) (see Fig. 4 and 5, respectively). However, with an increase in the R value up to more than 1.01, the length of the reducing feather tended to be either short or nonexistent (see Fig. 3). This would result in a low growth rate or process conditions that are unsuitable for diamond deposition. The optimum gas flow ratio, R, for diamond growth was determined to be from 0.99 to 1.01, with the reducing feather length being from 16 to 21 mm (see the shaded part in Fig. 3).

The substrate position in the flame was directly related to the diamond growth. Diamond crystals could be grown from the entire length of the reducing feather, D (see Fig. 2), but the growth rate and film area decreased with an increase in the deposition distance, H, as described in Fig. 6. When the inner cone of the flame made contact with the substrate, then graphite deposition occurred quickly, whereas no deposit was discovered when a substrate was placed in the outer zone. The latter effect could be explained by complete oxidation of the remaining fuel components within this region.

The substrate temperature and temperature distribution played an important role in the growth of diamond film. It was found that temperatures greater than 1200 °C would promote graphite formation, which appeared dark in color. However, diamond nucleation and growth were observed to be very sluggish

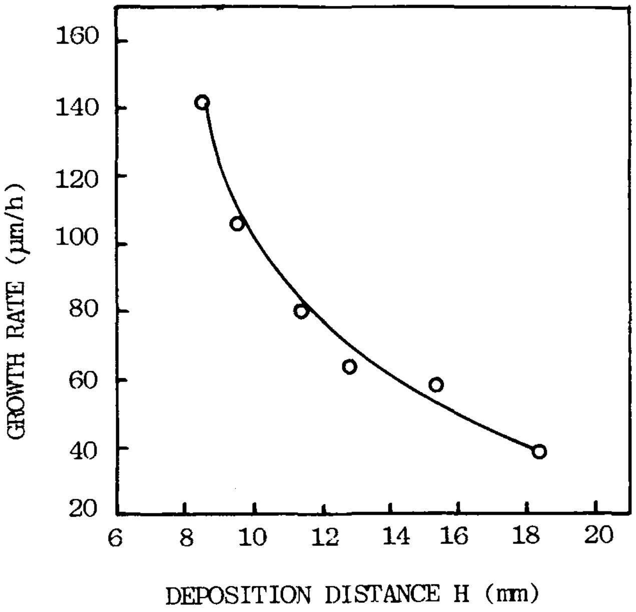

Figure 6 Relationship between diamond growth rate and deposition distance.

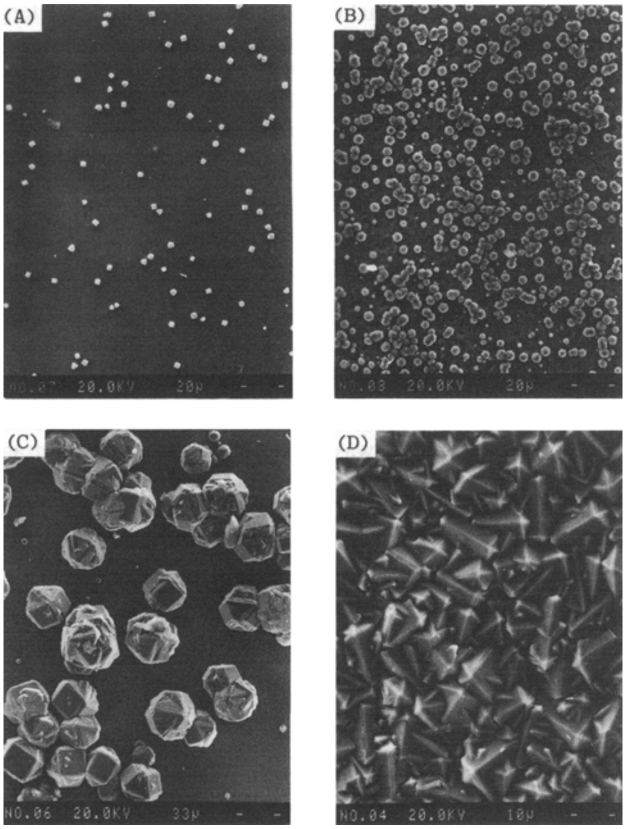

Figure 7 Scanning electron micrograph of diamond nucleation and growth on different pretreated silicon substrates. (**a**) Polished, deposited for 3 min. (**b**) Scratched, deposited for 3 min. (**c**) Polished, deposited for 20 min. (**d**) Scratched, deposited for 20 min.

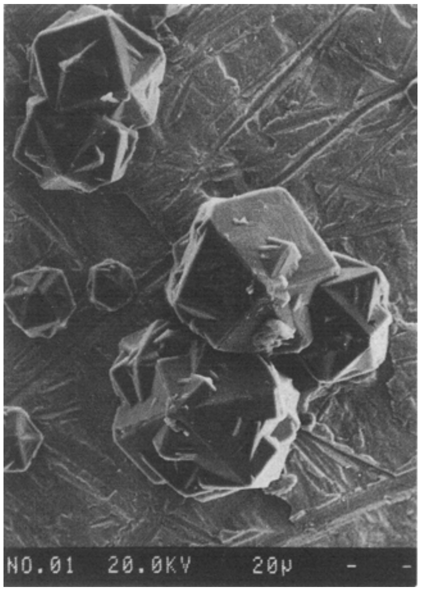

Figure 8 Scanning electron micrograph of diamond crystals grown on a molybdenum substrate.

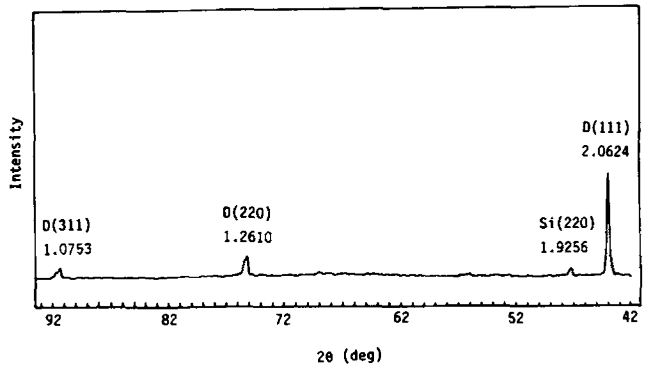

Figure 9 X-ray diffraction pattern of diamond film.

Table 1 Measured and Standard *d* Spacings of Diamond Crystals

h	k	l	Standard	Measured
1	1	1	2.060	2.0624
2	2	0	1.261	1.2610
3	1	1	1.0754	1.0753

at low substrate temperatures of less than 600 °C, and the substrate remained its original color. It was also found that large temperature differences on the substrate caused by imperfect contact with the water-cooled box could result in different growth rates and an inhomogeneous diamond film. Therefore, a uniform temperature distribution was essential for obtaining a uniform diamond film. The reasonable temperature range for diamond growth measured in this experiment was about 800 to 1000 °C, with the substrate color varying from red to bright red.

The substrate surface pretreatment could significantly affect diamond nucleation and the quality of the resulting diamond film. As can be seen from Fig. 7, diamond nucleation was very difficult on a polished silicon substrate, whereas it became quite easy on a scratched one. Moreover, after the same period of deposition, larger, but still isolated, diamond crystals were observed on the polished silicon substrate. However, a dense and continuous diamond film was formed on the scratched substrate. According to our experience, diamond film formation was easier on a silicon substrate than on a molybdenum substrate. The reason for this experimental observation is not known. The bond strength of the diamond film to the silicon substrate was qualitatively appraised as strong, because it could not be removed under rough handling. Figure 8 shows the diamond crystals grown on a molybdenum substrate for 36 min.

3.3 *Characterization of Diamond Film*

Figure 9 shows the X-ray diffraction pattern of the diamond film. Only the characteristic diamond peaks and a silicon peak (from the substrate) were observed, with no peaks from graphite. The interplanar spacings *d* listed in Table 1 show that the measured *d* values agree well with those of the natural cubic diamond.[10]

Raman spectroscopy is a powerful analytical tool used to distinguish various forms of carbon.[1] Figure 4(a) presents the Raman spectrum of the diamond film obtained at the optimum gas flow ratio. A very strong and sharp peak at 1330 cm^{-1}, which is very near 1332.5 cm^{-1} of the intrinsic peak of natural diamond, was characteristic of sp^3 bonded diamond. It also indicated that diamond was the predominant phase in the film. In addition, a small amount of amorphous carbon was detected by the low and broad peak centered at 1551 cm^{-1}.

The morphology of the diamond crystal and film can be seen in Fig. 5(a) and 7(d). The diamond crystals were well faceted, with the (100) and (111) faces clearly distinguished. Dense diamond film was formed within 20 min. The maximum growth rates were calculated to be in the range of 100 to 140 μm/hr.

The diamond film was also characterized by electron probe microanalysis (EPMA) with the aim of identifying the chemical bonding nature of the carbon atoms using the characteristic C Kα X-ray emission spectrum. Figure 10 shows the C Kα X-ray emission spectra of standard diamond, graphite, and synthesized diamond. The spectrum of the flame-synthesized diamond was consistent with that of the standard diamond, and it was different from that of the standard graphite in spectrum wavelength, shape, and intensity. This indicated that the chemical bonding nature of the carbon atoms in the flame-synthesized diamond crystal was the same as that in the standard diamond crystal and proved that the crystals were indeed diamond.[11]

4. Conclusions

The oxygen-acetylene flame technique is a unique and effective way to synthesize diamond crystals and films. The outstanding features of this technique are the low equipment cost, relatively simple processing, and high growth rate (*e.g.*, the thickness rates are 60 to 125 μm/hr). It is suggested that the following consideration should be addressed before routine appli-

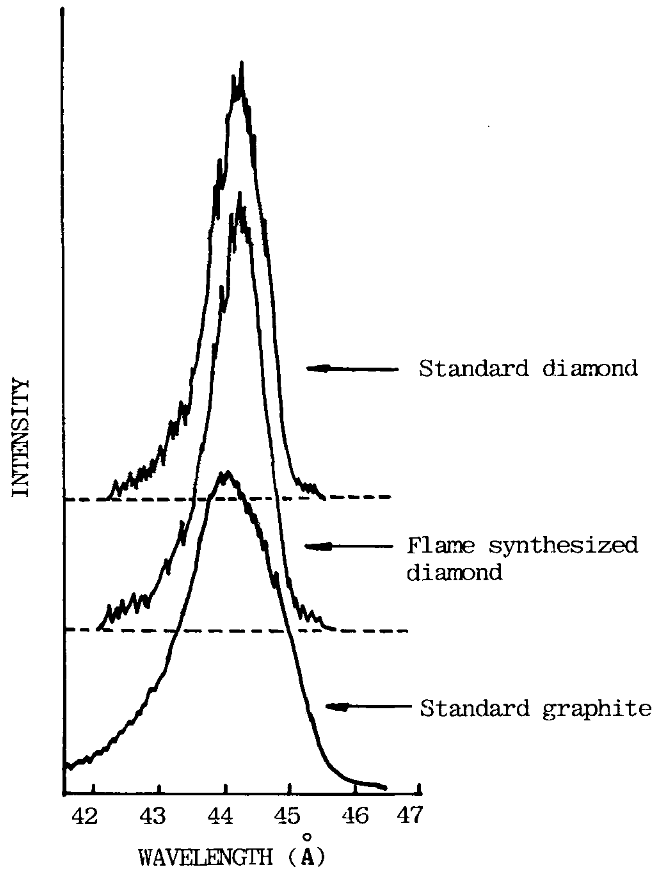

Figure 10 Characteristic C Kα X-ray emission spectra of standard diamond, flame-synthesized diamond, and standard graphite.

cations are explored: (1) the potential of depositing a dense diamond film on substrates rather than silicon (*e.g.*, metal) and technology to overcome the weak bond strength with these substrates; (2) investigate the nonuniform diamond film thickness distribution caused by nonuniform distribution of gaseous species across the lateral direction of the reducing feather, as well as the large surface roughness of the film; and (3) increase the diamond yield to greater than the present 3 to 5 mg/hr to enable the economical manufacture of diamond for applications such as manufacturing grinding materials.

References

1. K.E. Spear, Diamond-Ceramic Coating of the Future, *J. Am. Ceram. Soc.*, *72*(2), 171-191 (1989).
2. P.G. Kosky and D.S. Mcatee, An Experimental and Theoretical Investigation of Flame-Formed Diamonds, *Mater. Lett.*, *8*(9), 369-374 (1989).
3. S.J. Harris, A.M. Weiner, and T.A. Perry, Measurement of Stable Species Present during Filament-Assisted Diamond Growth, *Appl. Phys. Lett.*, *53*, 1605-1608 (1988).
4. Y. Mitsuda, Y. Kojima, T. Yoshida, and K. Akashi, The Growth of Diamond in Microwave Plasma under Low Pressure, *J. Mater. Sci.*, *22*, 1557-1562 (1987).
5. Y. Hirose and M. Mitsuizumi, Diamond Synthesis in Air Using a Flame, *New Diamond*, *4*(3), 34-35 (1988) in Japanese.
6. L.M. Hanssen, W.A. Carrington, J.E. Butler, and K.A. Snail, Diamond Synthesis Using an Oxygen-Acetylene Torch, *Mater. Lett.*, *7*(7/8), 289-292 (1988).
7. K.V. Ravi, C.A. Koch, H.S. Hu, and A. Joshi, The Nucleation and Morphology of Diamond Crystals and Films Synthesized by the Combustion Flame Technique, *J. Mater. Res.*, *5*(11), 2356-2366 (1990).
8. M. Murakawa, S. Takeuchi, and Y. Hirose, An Experiment in Large Area Diamond Coating Using a Combustion Flame Torch in Its Traversing Mode, *Surf. Coat. Technol.*, *43/44*(1/3), 22-29 (1990).
9. Y. Matsui, A. Yuuki, M. Sahara, and Y. Hirose, Flame Structure and Diamond Growth Mechanism of Acetylene Torch, *Jpn. J. Appl. Phys.*, *28*(9), 1718-1724 (1989).
10. Anonymous, Powder Diffraction Data, Inorganic Volume, Card 6-675, Mary E. Mrose et al. Ed., Joint Committee on Powder Diffraction Standards, Swarthmore, Pennsylvania (1976).
11. E.W. White, Microprobe Analysis, in *Application of Soft X-Ray Spectroscopy to Chemical Bonding Studies with the Electron Microprobe*, C.A. Andersen, Ed., John Wiley & Sons, New York, 349-354 (1973).