

# Raman investigations of diamond films prepared by combustion flames

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(Received 6 December 1989; accepted for publication 8 May 1990)

A detailed Raman analysis has been carried out to establish the mixed nature of carbon bonding in diamond films, deposited at atmospheric pressures in combustion flames. By monitoring the  $sp^3$  bonded  $1334\text{ cm}^{-1}$  Raman signature of diamond and  $sp^2$  bonded  $1350$  and  $1580\text{ cm}^{-1}$  signatures of graphite, it has been established that under optimum conditions of flow rates and substrate temperatures, the primary combustion zone provides an ideal situation for diamond growth. The study points out to an  $a\text{-Si}_{1-x}\text{C}_x$  like interface ( $0.5 \leq x \leq 1$ ) and an amorphous diamondlike precursor phase. These investigations provide insights into the nature of the diamond films prepared by this technique in establishing their potential in various technological applications.

## I. INTRODUCTION

Diamond synthesis at low pressures ( $\leq 1$  atm) and at temperatures less than  $1000^\circ\text{C}$  by various chemical vapor deposition techniques has been a subject of enormous interest, both from the viewpoints of fundamental understanding as well as technological applications.<sup>1-6</sup> Recently, a new synthetic route by which diamond microcrystallites and polycrystalline diamond films can be synthesized at atmospheric pressures in oxyacetylene combustion flames, has been reported originally by Hirose and Kondo<sup>7</sup> and later by other groups.<sup>8-10</sup> At present, experimental details on diamond films deposited by this technique are rather sparse. Though Raman scattering and x-ray (and electron) diffraction techniques are often used in studying the carbon films, the diffraction techniques do not provide sufficient information regarding the nature of chemical bonding of carbon which is very essential to establish the film potential for various applications. This is because, though carbon in diamond is  $sp^3$  hybridized and tetragonally bonded and hence differs from the  $sp^2$  hybridized and trigonally coordinated carbon as in graphite, the interplanar spacings of the cubic diamond and the *c*-axis oriented graphite are located very close to each other.<sup>11</sup> Raman scattering on the other hand, displays vibrational modes which are directly related to atomic (chemical) bonding and hence established by far as the most direct technique to probe the diamond films. In the present investigations we have therefore undertaken a systematic Raman study to establish the nature of carbon bonding, both diamond and nondiamondlike. The role of deposition conditions in obtaining predominantly diamond films has been discussed. This paper reports the results of these investigations.

## II. EXPERIMENTAL DETAILS

The diamond microcrystallites and polycrystalline diamond films were synthesized using a commercially avail-

able oxyacetylene welding torch. Si (100) were used as substrates in the present study. The samples were mounted on a water-cooled copper block and the substrate temperature was monitored by a precalibrated chromel-alumel thermocouple and also by an infrared pyrometer (Micron Instruments Model M 80 HT-2CPH). The substrate temperatures were controlled by adjusting the flow rate of the coolant water. Prior to deposition the substrates were pretreated (scratched) with  $2\mu$  diamond grit to enhance the number of nucleation sites and thereby the diamond nucleation density.<sup>2</sup> The substrates were then thoroughly cleaned ultrasonically in methylalcohol and acetone to ensure that there are no diamond particles remaining on the substrate surface. The oxygen to acetylene ratio was monitored to be around one. The total flow rates were varied from 1.25 to 3 standard liter per minute (SLM). A Spex Ramalog 5 was used to record the Raman spectra at room temperature using  $4880\text{ \AA}$  of argon ion laser (power 60 mW) in the backscattering geometry. A special sample holder facilitated the movement of the substrate so that different zones of the sample can be Raman analyzed.

## III. RESULTS AND DISCUSSION

The present Raman investigations have been addressed to three important parameters. (1) The relative positioning of the substrate with respect to the flame, (2) the flow rates, and (3) the substrate temperature.

### A. Substrate position

Three distinct regions have been identified in the oxyacetylene combustion flame. The luminous mantle of fairly considerable thickness (known as the acetylene feather) is the primary combustion zone in which the primary combustion of acetylene with premixed oxygen occurs.<sup>12</sup> This zone is followed by an intermediate zone and an outer zone. We have carried out depositions (around  $900\text{--}950^\circ\text{C}$ ) in all the three zones and the corresponding Raman features of the films are shown in Fig. 1. Clearly, predominant diamond growth has been observed only on the substrates kept in the

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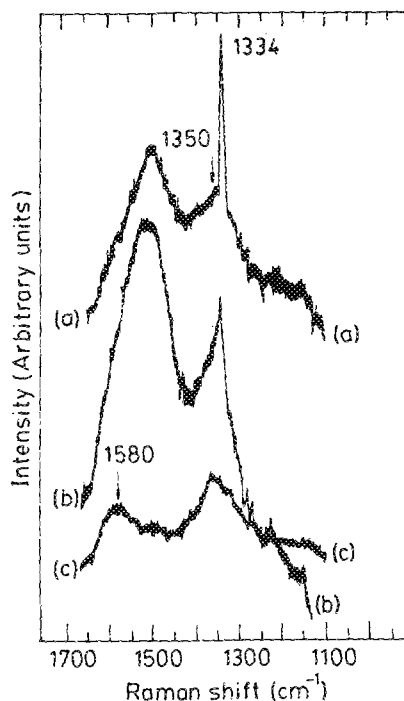


FIG. 1. Raman spectra of carbon films deposited in (a) primary (b) intermediate, and (c) outer zones of oxyacetylene combustion flame.

primary combustion zone (curve, a) as seen by the  $1334 \pm 2 \text{ cm}^{-1}$  Raman signature of the  $sp^3$  bonded carbon. The  $1334 \text{ cm}^{-1}$  peak overrides a low intense broad  $1350 \text{ cm}^{-1}$  peak which is due to traces of microcrystalline graphitic carbon phase in  $sp^2$  bonding. It should be mentioned here that the Raman cross sections for the  $sp^2$  bonded carbon (graphite) is approximately 50 times higher than the  $sp^3$  bonded carbon (diamond).<sup>13</sup> As a result, even small traces of  $sp^2$  bonded carbon features are displayed quite prominently in the Raman spectra and have to be scaled accordingly. The most important observation from Fig. 1, curve a, is that, in spite of such a high Raman scattering cross section, there is no discernible  $1580 \text{ cm}^{-1}$  peak (the G line, representing the first-order zone center mode of graphite) indicating the absence of any predominant graphitic growth. The broad peak centered around  $1480 \text{ cm}^{-1}$  does not correspond to any of the vibrational modes of diamond or graphite and its origin is not clear at present. However, by comparing the Raman spectra of carbon-rich  $\alpha\text{-Si}_x\text{C}_x\text{H}$  alloys produced by plasma chemical vapor deposition, one can speculate that the peak could be due to the formation of  $\alpha\text{-Si}_{1-x}\text{C}_x\text{H}$ : ( $0.5 < x < 1$ ) like phases.<sup>14,16</sup> The assignment of this mode on the lower wave numbers (around  $1480\text{--}1500 \text{ cm}^{-1}$ ) relative to the  $1580 \text{ cm}^{-1}$  mode, to the formation of  $\alpha\text{-Si}_{1-x}\text{C}_x\text{H}$ : ( $0.5 < x < 1$ ) like phases rather than the graphitic phases has been based on the already existing literature,<sup>15-17</sup> and is as follows. The zone center G line of graphite is independent of the orientation of the sample with respect to the incident beam and always appears at  $1580 \text{ cm}^{-1}$ . The frequency shifts observed in some graphitic samples with extremely small crystallite sizes are rather small ( $\sim 10 \text{ cm}^{-1}\text{--}15 \text{ cm}^{-1}$ ) and more importantly they are towards the higher wave numbers.<sup>17</sup> The assignment of the mode at  $1500 \text{ cm}^{-1}$

to microcrystalline graphite, therefore does not appear to be reasonable. This could be due to the amorphous network of four and three fold coordinated carbon or an impurity (such as N and O) carbon amorphous network.<sup>15</sup> This however, does not preclude the possibility of the existence of graphite-like phases in our combustion deposited films. As seen in Fig. 1 (a) (corresponding to the ideal deposition conditions) there is indeed the presence of the mode at  $1350 \text{ cm}^{-1}$  (the D line) attributed to the scattering from a zone boundary phonon activated by the disorder associated with finite crystallite size, pointing out that the films do contain traces of crystalline graphitic fragments. In most of the cases reported in the literature for polycrystalline films however, the G line has been found to be centered at  $1580 \text{ cm}^{-1}$  although shifts towards  $1520\text{--}1535 \text{ cm}^{-1}$  have been reported in certain amorphous carbon films where there is significant bond angle disorder. Based on the above arguments we conclude by suggesting that the assignment of the mode around  $1480\text{--}1500 \text{ cm}^{-1}$  to the graphitic features is unlikely and is more likely due to the formation of carbon-rich  $\alpha\text{-Si}_{1-x}\text{C}_x\text{H}$  alloys. One important point that has to be borne in mind is that, as already mentioned the Raman scattering cross sections for  $sp^2$  bonded graphitic modes is about 50 times higher than that of the  $sp^3$  bonded diamond features. Therefore the graphitic fragments seen through the  $1350 \text{ cm}^{-1}$  mode are not predominant and are present only in the trace amounts. This however does not immediately point out that the films produced here are optically transparent. It only points out that the argon ion laser ( $4880 \text{ \AA}$  line) can sample the film volume much deeper from the surface of the film, more towards the film/substrate interface, owing to the fact that the absorption coefficient of diamond for the  $4880 \text{ \AA}$  line is insignificant. Whether such a phase is interfacial or bulk in origin is yet to be established, though our initial photoemission results point out that it is interfacial in origin. The weak broad band around  $1180 \text{ cm}^{-1}$  needs a special mention, a point to which we shall return later.

It is noteworthy that all the Raman spectra presented here, have been recorded with a laser spot diameter of the order of  $100 \mu\text{m}$ . We have also recorded the spectra with a spot diameter of  $1\text{--}10 \mu\text{m}$ , in which there are however, no graphitic ( $1350$  and  $1580 \text{ cm}^{-1}$ ) features and the feature around  $1180 \text{ cm}^{-1}$  (not shown here). Therefore it is necessary to spatially probe the film surface before any conclusions regarding the "quality" of the film is inferred from the Raman spectra alone. We believe that the subtle spatial variations in the composition and temperature of the flame, even within the primary combustion zone are the primary reasons for such variations in the Raman spectra as seen in the present investigations.

Figure 1, curve b, depicts the Raman spectra of the films deposited in the intermediate zone. As is evident, there is a significant reduction of the diamond fraction as seen by the reduced  $1334 \text{ cm}^{-1}$  line intensity, and a considerable increase in the  $sp^2$  bonded graphitic phase ( $1350 \text{ cm}^{-1}$ ). Further, the broad peak centered around  $1500 \text{ cm}^{-1}$  indicates the presence of amorphous carbon and carbon/silicon alloys. Clearly, the films are multiphase with both diamond and graphitic features. The Raman spectra of the films de-

posited in the outer zone is represented by Fig. 1, curve c and clearly shows features reminiscent only of graphitic fractions; the  $1350\text{ cm}^{-1}$  D line and  $1580\text{ cm}^{-1}$  G line.

From the above observations we summarize that the thermodynamically unequilibrated state of the primary combustion zone<sup>12</sup> with its abundance of C and CH along with atomic O and superequilibrium concentration of atomic H (necessary for the rapid etching of the graphitic and amorphous carbon phases preferentially, thereby promoting the diamond growth kinetically<sup>2</sup>) provides an ideal situation for the diamond growth at atmospheric pressures as monitored by the prominent Raman  $1334\text{ cm}^{-1}$  line. The intermediate zone consists mostly of the above-mentioned species<sup>12</sup> due to their high burning velocities, but their number densities are reduced<sup>12</sup> along with atomic O and H. With less rapid etching of graphitic phases, we are essentially left with a situation in which both graphitic and diamond growth kinetically compete with each other. The corresponding Raman spectra (Fig. 1, curve b) confirm this. The outer zone is essentially reaction free and promotes only the graphitic features (Fig. 1, curve c).

### B. Flow rates

In the present investigations, we have monitored the total flow rates from 1.25 to 3.0 SLM with the oxygen to acetylene ratio ( $\text{C}_2\text{H}_2/\text{O}_2$ ) close to one. Figure 2 (curves a–e) shows the Raman spectra of the films obtained at substrate temperatures  $900\text{--}950\text{ }^\circ\text{C}$  and at various flow rates. The lower flow rates (curves a and b) with respect to the optimum 2 SLM seem to promote Raman features predominantly of graphitic nature as indicated by the  $1350$  and  $1580\text{ cm}^{-1}$

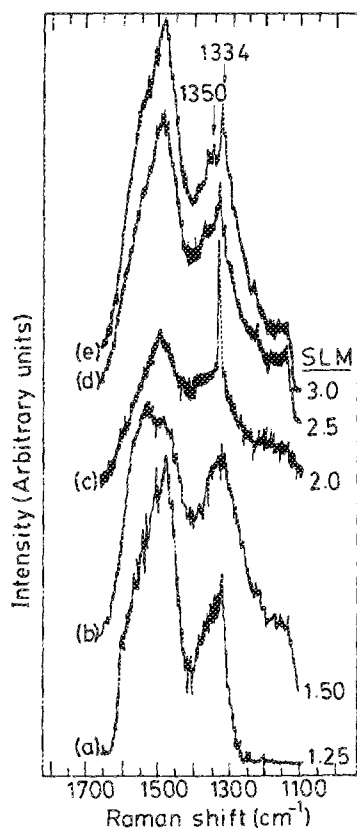


FIG. 2. Raman spectra of diamond films deposited at various flow rates.

features relative to the diamond feature at  $1334\text{ cm}^{-1}$ . At higher flow rates ( $> 2\text{ SLM}$ ) the graphitic fractions seem to be less prominent (curves d and e). However, in all the cases significant intermixing at the Si/C interface seem to have occurred as seen from the broad peak centered around  $1480\text{--}1500\text{ cm}^{-1}$ , though this is yet to be established unambiguously.

It is well known that in combustion flames, the linear gas velocities are highly nonuniform.<sup>12</sup> This, as also cited by Yarbrough *et al.*<sup>10</sup> leads to large variations in the composition and temperature of the flame axially and radially. Our flame emission spectroscopic data (not presented here) also points this out. The Raman features in Fig. 2 suggest that at higher flow rates ( $> 2\text{ SLM}$ ), the nonuniformity in the linear gas velocities and temperatures could be further enhanced, leading to a less favorable condition for the diamond growth. The large thermal gradients reported earlier<sup>10</sup> also seem to impede the uniform diamond growth. We have also observed that as the deposition proceeds, owing to the large thermal conductivity of the diamond film, the temperatures recorded indicate a deviation of as much as  $100\text{--}150\text{ }^\circ\text{C}$ . At the lower flow rates ( $< 2\text{ SLM}$ ) the flame has been found to be unstable, both in composition and temperature, and the corresponding Raman spectra indicate features (curves a and b) more of nondiamondlike carbon ( $1350$  and  $1580\text{ cm}^{-1}$  features).

### C. Substrate temperature

In the present study we have observed that under optimum conditions well-faceted diamond crystallites, predominantly with  $\{111\}$  surfaces grow on the Si (100) substrates as seen from the scanning electron micrographs (not presented here). This indicates that surface mobilities of the adatoms (carbon) on the substrate are large enough for surface reactions to reach equilibrium.<sup>2</sup> We have attempted in this study to understand the role of substrate temperature in affecting the diamond growth process and the Raman spectra obtained for various temperatures (from  $850\text{--}1000\text{ }^\circ\text{C}$ ) are depicted in Fig. 3 (curves a–d). The total gas flow rate is 2 SLM. It is evident from the Raman spectra that the diamond features have a very subtle dependence on the substrate temperature and the best results point out to a substrate temperature of  $900\text{--}950\text{ }^\circ\text{C}$  (curves b and c). At higher (curve d) and lower (curve b) temperatures the graphitic fractions ( $1350$  and  $1580\text{ cm}^{-1}$ ) tend to dominate the spectra. It is to be borne in mind, that we are dealing with a nonuniform situation and hence the temperatures reported here are only experimental. Further, for diamond growth the critical species interactions occurring at the gas-solid interface and the kinetic factors that determine the growth have to be taken into account, not the substrate temperatures alone.

We shall now address ourselves to the relatively weak and broad peak occurring about  $1150\text{--}1180\text{ cm}^{-1}$ . We observe that this has been present in all the films where the  $1334\text{ cm}^{-1}$  Raman signature of diamond is clearly seen and is absent in cases where predominant graphitic features are observed (Fig. 1 curve c and Fig. 2 curve a). Nemanich *et al.*<sup>15</sup> in a recent paper also register a feature at  $1140\text{ cm}^{-1}$  in

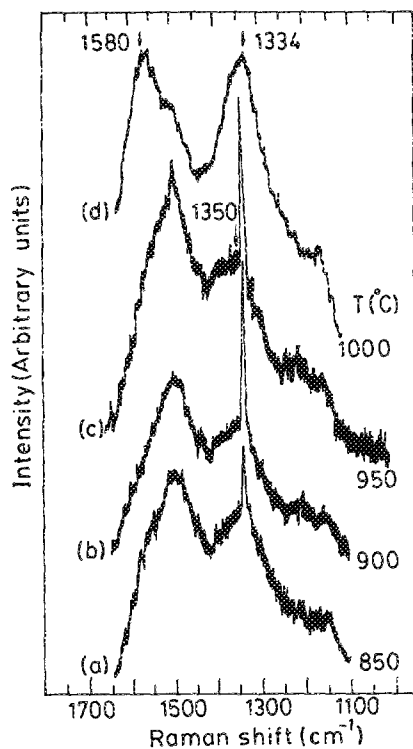


FIG. 3. Raman spectra of diamond films deposited at various substrate temperatures.

their Raman analysis of diamond films obtained by plasma chemical vapor deposition. They suggest that it could be due to amorphous or microcrystalline diamond and by comparison with the frequencies of SiC they deduce a vibrational frequency of the strongest mode to be  $1175\text{ cm}^{-1}$ . The broad peak observed in the present case around  $1150\text{--}1180\text{ cm}^{-1}$  could also be due to a diamondlike precursor phase. Detailed experimental work is however, necessary to establish its origin. In all our present Raman investigations, we have not been able to locate any discernible peak around  $550\text{ cm}^{-1}$  which as reported in a recent paper<sup>18</sup> could be due to a disorder induced mode of amorphous diamond.

#### IV. CONCLUSIONS

A detailed Raman investigation has been carried out to analyze the mixed nature of the carbon bonding in diamond

films synthesized at atmospheric pressures in combustion flames. By monitoring the  $sp^3$  bonded  $1334\text{ cm}^{-1}$  Raman signature of diamond and  $1350$  and  $1580\text{ cm}^{-1}$  signatures of graphite, it has been established that at optimum flow rates and substrate temperatures, the primary combustion zone provides an ideal situation for the diamond growth. The study points out to an  $\alpha\text{-Si}_{1-x}\text{C}_x\text{H}$ : like interface ( $0.5 < x < 1$ ) and an amorphous diamondlike precursor phase. These investigations provide insights into the nature of the diamond films prepared by this technique in establishing their potential in various technological applications.

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