

# Old Dominion University ODU Digital Commons

Chemistry & Biochemistry Faculty Publications

Chemistry & Biochemistry

2003

# Chemical Vapor Deposited Diamond Films for Self-Referencing Fiber Optic Raman Probes

Sacharia Albin Old Dominion University, salbin@odu.edu

Jianli Zheng Old Dominion University

Bing Xiao Old Dominion University, bxiao001@gsa.odu.edu

John B. Cooper Old Dominion University, jcooper@odu.edu

Robert B. Jeffers Old Dominion University, rjeff002@gsa.odu.edu

See next page for additional authors

Follow this and additional works at: https://digitalcommons.odu.edu/chemistry\_fac\_pubs Part of the <u>Materials Chemistry Commons</u>, and the <u>Physical Chemistry Commons</u>

# **Repository Citation**

Albin, Sacharia; Zheng, Jianli; Xiao, Bing; Cooper, John B.; Jeffers, Robert B.; and Antony, Sonia, "Chemical Vapor Deposited Diamond Films for Self-Referencing Fiber Optic Raman Probes" (2003). *Chemistry & Biochemistry Faculty Publications*. 168. https://digitalcommons.odu.edu/chemistry\_fac\_pubs/168

# **Original Publication Citation**

Albin, S., Zheng, J., Xiao, B., Cooper, J. B., Jeffers, R. B., & Antony, S. (2003). Chemical vapor deposited diamond films for self-referencing fiber optic Raman probes. *New Diamond and Frontier Carbon Technology*, 13(6), 341-351.

This Article is brought to you for free and open access by the Chemistry & Biochemistry at ODU Digital Commons. It has been accepted for inclusion in Chemistry & Biochemistry Faculty Publications by an authorized administrator of ODU Digital Commons. For more information, please contact digitalcommons@odu.edu.

# Authors

Sacharia Albin, Jianli Zheng, Bing Xiao, John B. Cooper, Robert B. Jeffers, and Sonia Antony

New Diamond and Frontier Carbon Technology Vol. 13, No. 6 2003 MYU Tokyo NDFCT 438

# Chemical Vapor Deposited Diamond Films for Self-Referencing Fiber Optic Raman Probes

Sacharia Albin<sup>\*</sup>, Jianli Zheng, Bing Xiao John. B. Cooper<sup>1</sup>, Robert B. Jeffers<sup>1</sup> and Sonia Antony<sup>1</sup>

Department of Electrical and Computer Engineering <sup>1</sup>Department of Chemistry and Biochemistry Old Dominion University, Norfolk, Virginia 23529, U.S.A.

*Key words:* diamond, CVD, Raman, probe, remote spectroscopy, fiber optics, internal reference, thin film, quartz

Diamond thin films grown by the microwave plasma enhanced chemical vapor deposition (CVD) process have been investigated as an internal reference in fiber optic remote Raman sensing. The growth parameters have been optimized for diamond thin films on quartz substrates using a gas mixture of methane, carbon dioxide, and hydrogen. The resulting films exhibit essentially no Raman spectral background while exhibiting a strong Raman peak at 1332 cm<sup>-1</sup>. The films are used as an internal reference in the quantitative measurement of chemical concentration using remote fiber optic Raman sensing. Internal referencing is accomplished by normalizing all spectral intensities of the chemical species to the integrated area of the CVD diamond reference peak at 1332 cm<sup>-1</sup> and verified using ethanol/water solutions. It is shown that the measurement is independent of laser power fluctuations.

# 1. Introduction

Recently, we have investigated various fiber optic Raman probe designs incorporating both natural and synthetic bulk diamond to obtain quantitative measurement of analytes.<sup>(1)</sup> Raman spectroscopy is a very powerful tool for quantitative analysis; however, its application has been limited to the laboratory for "off line" analysis, necessitating the test samples to be brought to the laboratory to conduct the analysis. On-line monitoring becomes difficult because of the critical alignment requirement. Fiber optic sampling greatly simplifies

\*Corresponding author: e-mail: salbin@odu.edu

optical alignment and isolates the Raman spectrometer from the harsh environment by transmitting the signal to the centralized control room using long optical fibers. Both excitation light and scattered light can be guided through the flexible fiber, and the Raman spectrum can be easily obtained merely by immersing the fiber optic probe in the sample. Remote monitoring in industrial environments at distances of up to one hundred meters between the instruments and the industrial site can be routinely obtained.<sup>(2)</sup> Multipoint measurement also becomes possible by multiplexing the optical fibers and having the operation of the whole system controlled by microcomputers. Since Raman spectroscopy is a single-beam technique, the intensity of a Raman line is affected by a number of factors, such as incident laser power fluctuation, frequency of the scattered radiation, absorption of the materials involved in the scattering, and the response of the detection system. To eliminate these problems in quantitative analysis, intensity referencing is employed. The widely used referencing technique involves introducing into the sample a small quantity of a presumably inert material that has an easily detectable Raman line as a standard. As the concentration of the standard  $C_{\rm ST}$  is kept constant, the relative intensity  $I_{\rm R}$ , which is the ratio of the Raman line of the analyte  $(I_{SP})$  to the Raman line of the standard  $(I_{ST})$ , depends only on the concentration of the analyte as given  $by^{(1,3)}$ 

$$I_{\rm R} = \frac{I_{\rm SP}}{I_{\rm ST}} = \frac{R(\nu)A(\nu')\nu^4 J(\nu)}{R(\nu')A(\nu){\nu'}^4 J(\nu')C_{\rm ST}} C_{\rm SP}, \tag{1}$$

where C is the concentration, R(v) is the overall spectrometer response, A(v) is the absorption of the medium, v is the frequency of the scattered light, and J(v) and is a molar scattering parameter. All of the terms involving v' correspond to those of the internal standard. At a constant  $C_{\rm ST}$ , all the lead terms on the right-hand side of the equation remain constant. Thus,  $I_{\rm R}$  is proportional to the concentration of the species of interest  $C_{\rm SP}$ :

$$I_{\rm R} = K \cdot C_{\rm SP}.\tag{2}$$

Unfortunately, this invasive method contaminates the test sample, and is usually unacceptable for *in situ* monitoring of industrial processes.

Diamond is an ideal material to serve as a referencing standard. Bulk diamond exhibits a spectrally pure Raman peak at 1332 cm<sup>-1</sup>, with a narrow natural line width (~2 cm<sup>-1</sup>). This is the only active mode corresponding to the triply degenerate first-order phonon with  $F_{2g}$ symmetry. The second-order Raman spectrum is very weak in the 2050–2770 cm<sup>-1</sup> range with a peak at 2458cm<sup>-1</sup>. The first-order peak is nearly 250 times more intense than the latter. Moreover, diamond is transparent in a broad spectral range from ultraviolet to infrared, chemically inert and mechanically robust. These properties make diamond a suitable material for self-referencing in quantitative Raman analysis, posing no interference to most analytes' spectra. In this study, we explore the application of CVD diamond thin film both as a large area reference material and an alternative to the expensive bulk diamond. Diamond film quality is often assessed by its Raman spectrum. The Raman band of CVD diamond usually is broader than that of natural diamond, and the background is not flat due to graphite contamination and other impurities. This may distort the Raman spectrum of the analyte sample.

Microwave plasma enhanced CVD (MPECVD) methods have been used more extensively than any other diamond growth method.<sup>(4-6)</sup> The advantages of the MPECVD method have been well stated by Sato and Kamo<sup>(7)</sup> in a review of different diamond growth methods. The MPECVD method is an electrodeless process, which avoids contamination of the diamond films due to electrode erosion. Microwave discharges at 2.45 GHz produce higher plasma densities than RF discharges, leading to a higher growth rate. Furthermore, the spherical plasma is confined at the center of the chamber, which prevents carbon deposition from occurring on the chamber wall.

Variations in the Raman spectra of CVD diamond, as compared with common types of natural diamond, are caused by the presence of appreciable amounts of  $sp^2$  carbon domains. The quality of CVD diamond depends strongly on the growth conditions, and, most critically, on the gas composition and substrate temperature. When conditions deviate from an optimum range, the occurrence of nondiamond structures increases and can eventually result in the formation of a graphite phase. The optimization of deposition parameters such as temperature, pressure, microwave power, and so forth is very complicated. One of the reasons is that most of the parameters are coupled together, which gives a large space for optimization. An exhaustive determination of the combination of different parameters is almost impossible. As Anthony<sup>(8)</sup> points out, the empirical optimization of all parameters requires millions of growth experiments. To further complicate matters, growth methods reported in the literature are often optimized with different goals in mind. These include optimizing the growth rate, optimizing the optical transparency, optimizing the growth on a particular substrate, optimizing the grain size, optimizing for field emission, and so forth.

The goal is to produce thin film CVD diamond on quartz that can be used as an internal standard for a Raman fiber-optic probe. This will facilitate remote quantitative Raman measurements. In achieving this goal, one of the main considerations is to minimize the Raman spectral background. We have conducted film growth experiments to minimize this background even at the expense of some line broadening of the 1332 cm<sup>-1</sup> peak. We have undertaken an extensive optimization study mainly focused on pressure, substrate temperature, and gas compositions to obtain the desired diamond quality while maintaining a reasonable growth rate. The best first search method, which varies only one parameter in one set of experiments, is used to obtain the optimum result. This approach, although not guaranteed, is however a reasonable approach to obtain the optimized result using a limited number of experiments. The diamond films grown under optimum conditions were used in fiber optic probes to perform quantitative Raman analysis.

#### 2. Experimental Details

#### 2.1 Diamond film growth

In this research, all diamond growth experiments were performed using a commercial MPECVD system (ASTeX) located in the Nanoelectroincs Laboratory at Old Dominion University.<sup>(9)</sup> Fused silica plates were used as substrates. Substrate nucleation is necessary prior to diamond growth. Surface abrasion with hard materials such as diamond,<sup>(10)</sup> cubic born nitride,<sup>(11)</sup> silicon carbide powder<sup>(12)</sup> or stainless steal<sup>(13)</sup> is effective in creating

nucleation sites on the substrate. When diamond powder is used, the enhanced nucleation sites are believed to be due to residual diamond particles left on the surface from the scratching.<sup>(14)</sup> This has also been shown by Iijima *et al.*<sup>(10,15)</sup> with the observation of diamond nucleation on "diamond seeds" left from the scratching process. Nucleation is conducted by placing 0.25  $\mu$ m diamond paste (ENGIS) on ordinary paper, and gently pushing the substrate across the paper. A high nucleation density is easily obtained after 10 passes. For each substrate, half of the substrate area was given a few abrasions (less than 4 times), resulting in a low nucleation density, such that scattered diamond particles would grow during the deposition. Crystal structure and growth rate were examined in this area under the scanning electron microscope (SEM). The other half area of the sample was heavily abraded (more than 10 times), so that a continuous film was grown, and the diamond quality could be roughly estimated by checking the film color visually and via Raman spectroscopy. A process optimization study was conducted by varying pressure, substrate temperature, and gas compositions to obtain diamond films with little Raman spectral background.

#### 2.2 Raman analysis

The experimental setup for Raman spectroscopy is similar to that used for the bulk diamond self-referencing study.<sup>(1)</sup> The 514.5 line of an argon ion laser (Spectra Physics) was used as the excitation source for all Raman experiments. The laser line was filtered with a 514.5 nm band-pass filter (2 nm FWHM, Chroma). A 20x objective was used to focus the laser onto the sample and collect the scattered Raman signal. The Raman light was filtered with a 514.5 nm holographic notch filter (Kaiser Optical) to remove the Rayleigh scattered laser light. The filtered Raman signal was subsequently focused onto the slit (50  $\mu$ m width) of an image-corrected 1/4-m spectrograph (Chromex). The Raman signal was dispered with a 600-groove/mm grating blazed at 0.5  $\mu$ m, and then detected using a CCD detector (ST6-UV Santa Barbara Instruments Group). The CCD detector consists of 750 horizontal pixels and 350 vertical pixels of 12  $\mu$ m pitch. The detector was thermoelectrically cooled to -35°C to reduce thermal noise. The same system was used to conduct self-referencing experiments by interfacing the diamond films with fiber optic probes.

#### 3. **Results and Discussion**

#### 3.1 Growth parameters

Several growth runs were executed with the parameters listed in Table 1. Films were analyzed using SEM and Raman spectroscopy. A well-defined peak at 1332 cm<sup>-1</sup> clearly indicated the existence of diamond while a broad peak centered at 1540 cm<sup>-1</sup>, indicated the presence of graphitic carbon. It has been reported by Tuinstra and Koenig<sup>(16)</sup> that the peak intensity ratio of the 1332 cm<sup>-1</sup> diamond line to 1540 cm<sup>-1</sup> graphite line (D/G) is linearly proportional to the reciprocal of graphite particle size. Thus, a measure of (D/G) can be used as an indication of the diamond quality. For each sample, the (D/G) ratio was measured to study the effect of pressure, substrate temperature and oxygen. The optimum value of each process variable was determined using the (D/G) ratio and the crystalline quality observed under SEM. All process parameters affect the (D/G) ratio; but the ratio is small for the range of pressure and substrate temperature used. Pressure itself does not play a very important Table 1

		di e																		
Growth parameters	Test Run	V	ariable	P	Variable T					Var. CH∉/H₂		Variable CO <sub>2</sub>				Variable CH4/CO2				Optimum
Pressure (Torr)	30	20 40 60			40					40		40				40				40
Temperature* (°C)	750	750			550 600 650 700 750				60	00	600				600				600	
Microwave Power (W)	1000	1000			1000					10	00	1000				1000				1000
Total Flow Rate (sccm)	900	900			900				90	00	900				900				900	
CH4 conc, (mass %)	0.8	0.7			0.7				0,4	0.7	0,8			1.5	3.0	5.0	6.0	. 6		
CO2 conc. (mass %)	. 0 .	· 0· .			0				(	0	0.5	1.0	1.2	1.5	2.0	3.5	5.2	6.0	6	
H <sub>2</sub> conc. (mass %)	99.2		99.3		÷		99,3	1		99.6	99.3	98.7	98.2	98.0	97.7	96.5	93.5	89.8	88.0	88.0
Growth Time (hours)	6	8 .			8					1	6	0.4				4				4
D/G Ratio	0,5	0.5	2	5	24	27 -	23	9	6	43	26	3.6	63	36 :		65	>100	>100	>100	. >100
Growth Rate (µm/hr)	2	1.1	1.7	1.8	1.7	1.5	1.3	1.0	0.7	0.7	1.15	1.7	1.25	0.75	0	1.67	2.5	3.17	3,8	3.8

Growth parameters used during optimization experiments.

\*This temperature is the susceptor temperature measured by a thermocouple. The actual temperature of the sample is higher due to plasma heating. Using an optical pyrometer, we have measured the sample temperatures at 1000 W and 40 Torr and found that they are ~180°C higher than the thermocouple reading.

role in relation to the quality of diamond growth as stated by Clausing.<sup>(17)</sup> However, pressure can change the gas temperature and the plasma composition, and thus changes the growth rate. Pressure determines the recombination length, the lifetime, and the drift distance of atomic hydrogen.<sup>(18)</sup> Substrate temperature plays an important role in both the quality and growth rate of diamond as discussed by many researchers.<sup>(19-24)</sup> The most significant parameter that yields a high (D/G) ratio (>100) is found to be the mass flow ratio of CH4/  $CO_2$  due to the presence of oxygen from  $CO_2$ . The reason for introducing oxygen through carbon dioxide is the safety concerns for the mixing of hydrogen and oxygen. The roles of hydrogen and oxygen are well documented in the etching of  $sp^2$  carbon,<sup>(25-28)</sup> surface reconstruction,<sup>(29-33)</sup> and maintaining the C-H-O phase diagram for diamond growth,<sup>(34,35)</sup> leading to high-quality diamond. This is illustrated in Fig. 1 that shows SEM micrographs of samples of well-defined facets grown using CH<sub>4</sub>/CO<sub>2</sub> variables in Table 1. Note that different magnifications are used for these images as marked on the top of each micrograph. As expected, the growth rate increases when methane and carbon dioxide concentrations increase simultaneously because more carbon species are available. However, the incremental increase in CO<sub>2</sub> is less than that of CH<sub>4</sub>, which means that the selective etching of graphite over diamond by oxygen is very effective. The Raman spectra of these samples are shown in Fig. 2. For all four samples, the 1540 cm<sup>-1</sup> graphite band has almost disappeared, showing the good quality of the diamond. The best result is given by sample (a), which has the highest diamond peak intensity and a high growth rate. This result is in contrast to the corresponding result shown in Fig. 3 for a sample from the test run. The 1332 cm<sup>-1</sup> signal is weak compared to the 1540 cm<sup>-1</sup> graphite band and the latter might interfere with the analytes spectra. Based on the experimental results, the optimized parameters and gas



Fig. 1. The effect of different CH<sub>4</sub> concentrations with optimized CO<sub>2</sub> concentrations: (a) 6% CH<sub>4</sub>, 6% CO<sub>2</sub>, (b) 5% CH<sub>4</sub>, 5.2% CO<sub>2</sub>, (c) 3% CH<sub>4</sub>, 3.5 CO<sub>2</sub>, and (d) 1.5% CH<sub>4</sub>, 2% CO<sub>2</sub>. Note: different scales are used in the SEM as marked on top of each image. Higher growth rate is obtained with higher CH<sub>4</sub> concentration, while the quality can be controlled by CO<sub>2</sub> concentration.





346



Fig. 3. Test run CVD diamond grown on quartz substrate with (a) low nucleation density, (b) high nucleation density, and (c) Raman spectra of the test sample (Growth parameters are given in Table 1).

composition for diamond growth in our system are listed in Table 1, and continuous diamond films were grown on quartz substrate using these parameters for self-referencing experiments.

#### 3.2 Self-referencing Raman probe

Under normal incidence condition, the Fresnel reflection from the interface of two materials is given by

$$R = \left(\frac{n_1 - n_2}{n_1 + n_2}\right)^2,$$

where  $n_1$  and  $n_2$  are the indices of the two materials. For a fiber optic probe coated with diamond film as shown in Fig. 4(a), reflection from the glass/diamond boundary is 6% while it is 17.1% from the diamond/air boundary. Reflection due to the high index of diamond gives rise to a few drawbacks: it returns the glass Raman signal back to the collection fiber and reduces the output of the excitation laser intensity. Moreover, when the probe is inserted into different solutions, the intensity of the reflected glass Raman signal changes with different indices of the solutions, making background subtraction difficult. Alternatively, when the diamond film on a quartz substrate is placed in front of the fiber as seen in Fig. 4(b), these problems are eliminated. For most aqueous or organic solutions,  $n_2$  may vary from 1.33 to 1.5, therefore the reflectivity at the glass  $(n_1=1.46)$ /liquid interface may vary from 0 to 0.21%. This effect is very small; thus the probe design in Fig. 4(b) would not be sensitive to the refractive index of the solution. If the diamond film on a quartz substrate is mounted in front of the fiber at a 45° angle, it will prevent the reflection of the glass Raman signal back to the collection fibers. Diamond film grown on optical fiber using hot filament CVD has been used for quantitative Raman spectral measurement.<sup>(36)</sup> Unfortunately, the optical transmission of the probe was only 14% due to the surface roughness of the diamond film, resulting in weak Raman signals from both the reference and the analytes. Moreover, it is cumbersome to subject the optical fiber to the harsh processing conditions of diamond nucleation and growth.

(3)

New Diamond and Frontier Carbon Technology, Vol. 13, No. 6 (2003)



Fig. 4. (a) A fiber optic probe coated with diamond film. Reflection from the glass/diamond boundary is 6% while it is 17.1% from the diamond/air boundary. (b) A fiber optic probe with the diamond film on quartz substrate that is placed in front of the fiber. For most aqueous or organic solutions, reflectivity at the glass  $(n_1=1.46)$ /liquid interface may vary from 0 to 0.21%.

#### 3.3 Quantitative Raman spectral measurement

The experimental setup for quantitative Raman analysis is shown in Fig. 5. An excitation fiber is placed in the middle of a bundle with six collection fibers surrounding it. The excitation source is the 514.5-nm line of an argon ion laser, which is coupled into the excitation fiber using a  $20\times$  objective lens. The probe is placed in a beaker containing a solution of ethyl alcohol in water. The collection fiber guides the Raman signal from the diamond and alcohol/water solution to the spectrograph through the optical assembly. The laser line is filtered from the Raman signal using a holographic notch filter.

A series of Raman spectra of 60% ethyl alcohol in water was collected by varying excitation laser power from 1.75 to 7 mW. The results are shown in Figs. 6 and 7. Figure 6(a) shows the Raman spectra before normalization. The Raman spectra contain signals from both ethyl alcohol and diamond film. The peak area of the ethyl alcohol Raman line at 883.3 cm<sup>-1</sup> is plotted against laser power, as shown in Fig. 6(b), and as expected, it varies proportionally to the excitation laser power. This peak area is normalized against that of diamond at 1332 cm<sup>-1</sup> for the same range of laser power using the least-mean-square algorithm. The results are shown in Fig. 7. It is clearly seen that the normalized peak area is a constant (within 1.1%) even though we have changed the laser power by a factor of four. Therefore, the concentration of ethyl alcohol calculated using the diamond normalization procedure would give a result independent of laser power.

Raman spectra of ethanol/water solutions at six different ethanol concentrations ranging from 0 to 100% were collected as shown in Fig. 8(a). At constant laser power, the ethanol peaks vary with concentration while the diamond peak remains a constant. The spectra were then normalized to the diamond peak area. A linear regression of the normalized ethanol peak areas at 833 cm<sup>-1</sup> vs the ethanol concentration as shown in Fig. 8(b) gives a linear relationship as expected from Eq. (2). Thus, diamond film can be used for self-referencing in a fiber-optic Raman probe, and quantitative measurements independent of the incident laser power can be performed.



Fig. 5. Schematic diagram of the experimental setup for collecting Raman spectra of liquids using fiber optic probe.



Fig. 6. (a) Raman spectra of 60% ethyl alcohol in water with different excitation laser power. The Raman signals from both ethyl alcohol and diamond film increase with laser power. (b) Peak area of 883.3 cm<sup>-1</sup> band versus excitation laser power, showing linear dependence.



Fig. 7. (a) Normalized Raman spectra of 60% ethyl alcohol in water with different excitation power. (b) Normalized peak area versus laser power. The diamond self-referenced result is independent of excitation power even though the laser power is varied by a factor of four.



Fig. 8. (a) Raman spectra of ethanol/ water solutions of six different concentrations and (b) the normalized peak area as a function of ethanol concentration. A linear dependence of the diamond referenced Raman intensity on the concentration of the analyte is seen as predicted by Eq. (2).

## 4. Conclusions

Using the optimized growth parameters, thin film diamond can be grown on quartz substrates at a reasonable growth rate resulting in films that exhibit essentially no Raman spectral background. Application of the Raman line at 1332 cm<sup>-1</sup> as an internal standard for a fiber optic Raman probe is demonstrated and quantitative measurements independent of the incident laser power are achieved.

# Acknowledgment

This work was supported by the National Science Foundation (NSF-CHE-9982170) and NASA Langley Research Center under NASA-University Photonics Education and Research Consortium (NUPERC).

#### References

- X. Zheng, W. Fu, S. Albin, K. L. Wise, A. Javey and J. B. Cooper: Appl. Spectrosc. 55 (2001) 382.
- 2) N. Q. Dao and M. Jouan: Sensors and Actuators B 11 (1993) 147.
- J. R. Ferraro and K. Nakamoto: Introductory Raman Spectroscopy (Academic Press, Boston 1994).
- 4) Y. Liou, A. Inspector, R. Weimer and R. Messier: Appl. Phys. Lett. 55 (1989) 631.
- 5) W. Zhu, C. A. Randale, R. A. Badzian and R. Messier: J. Vac. Sci. Technol., A 7 (1989) 2315.
- 6) H. Eto, Y. Tamou and N. Kikuchi: *Diamond and Diamondlike and Related Coatings*, Ed. P.K. Bachmann and A. Matthews (Elsevier, Amsterdam, 1992) p. 373.
- 7) Y. Sato and M. Kamo: *The Principles of Natural and Synthetic Diamond*, Ed. J. E. Field (Academic, Orlando, FL 1992).
- R. T. Anthony: Diamond and Diamond-like Films and Coatings, Ed. R. E. Clausing (Plenum, New York, 1991).
- 9) S. Albin, J. Zheng and J. B. Cooper: Diamond Films and Technology 6 (1996) 241.
- 10) S. Iijima, R. Arakawa and K. Baba: Appl. Phys. Lett. 57 (1990) 2646.
- 11) K. Suzuki, A. Sawabe, H. Yasuda and T. Inuzaka: Appl. Phys. Lett. 50 (1987) 728.
- 12) A. Sawabe and T. Inuzaka: Thin Solid Films 137 (1986) 89.
- 13) C. P. Chang, D. L. Flamm, D. E. Ibbotson and J. A. Mucha: J. Appl. Phys. 63 (1988) 1744.
- 14) P. K. Bachmann, W. Drawl, D. Knight, R. Weimer and R. F. Messier: Diamond and Diamond-Like Materials Synthesis, Ed. G. H. Johnson, A. R. Badzian and M. W. Geis (Material Research Society, Pittsburgh, 1988).
- 15) S. Iijima, R. Arakawa and K. Baba: J. Mater. Res. 6 (1991) 1491.
- 16) F. Tuinstra and J. L. Koenig: J. Chem. Phys. 53 (1979) 1126.
- 17) R. E. Clausing, L. Heatherly and E. D. Specht: *Diamond, Diamond and Diamond-Like Films and Coatings*, Ed. R. E. Clausing (Plenum, New York 1991).
- 18) B. V. Spitsyn, L. L. Bouilov and B. V. Derjagin: J. Crystal Growth 52 (1981) 219.
- 19) S. Matsumoto, Y. Sato, M. Kamo and N. Setaka: Jpn. J. Appl. Phys. 21 (1982) L183.
- 20) S. Matsumoto, Y. Sato, M. Tsatsumi and N. Setaka: J. Mater. Sci. 17 (1982) 3106.
- 21) M. Tsuda, M. Nakajima and S. Oikawa: J. Am. Chem. Soc. 108 (1986) 5780.
- 22) D. Huang, M. Frenklach and M. Maroncilli: J. Phys. Chem. 92 (1988) 6379.
- 23) S. J. Harris: Appl. Phys. Lett. 56 (1990) 2298.
- 24) S. J. Harris and M. R. Marata: J. Mater. Res. 5 (1990) 2313.
- 25) J. C. Angus and C. C. Hayman: Science 241 (1988) 913.
- 26) D. V. Fedoseev, V. P. Varnin and B. V. Deryagin: Russ. Chem. Rev. 53 (1984) 435.
- 27) Y. Saito, K. Sato, H. Tanaka, K. Fujita and S. Matsuda: J. Mater. Sci. 23 (1988) 842.
- 28) M. Frenklach and H. Wang: Phys. Rev. B. 43 (1991) 1520.
- 29) K. E. Spear: J. Am. Ceram. Sci. 72 (1989) 171.
- 30) E. S. Machlin: J. Mater. Res. 3 (1988) 958.
- 31) T. Kawato and K. Kondo: Jpn. J. Appl. Phys. 26 (1987) 1429.
- 32) Y. Liou, R. Weimer, D. Knight and R. Messier: Appl. Phys. Lett. 56 (1990) 437.
- 33) T. Kim and T. Kobayashi: Jpn. J. Appl. Phys. 33 (1994) L459.
- 34) M. Marinelli, E. Milani, M. Montuori, A. Paoletti and A. Tebano: J. Appl. Phys. 76 (1994) 5720.
- 35) P. K. Bachman, D. Leers and H. Lydtin: Diamond and Related Materials 1 (1991) 1.
- 36) H. Xiao, S. Dai, J. P. Young, C. S. Feigerle and A. G. Edwards: Appl. Spectrosc. 52 (1998) 626.

## Erratum

New Diamond and Frontier Carbon Technology Vol. 13, No. 6 (2003), pp. 341-351

Chemical Vapor Deposited Diamond Films for Self-Referencing Fiber Optic Raman Probes

by Sacharia Albin, Jianli Zheng, Bing Xiao, John. B. Cooper, Robert B. Jeffers and Sonia Antony

The following information was missing on p. 341: (Received 4 March 2003, accepted 11 April 2003)