

Commercial CVD diamond films: material properties and their related effects on microwave characteristics

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Abstract

CVD diamond offers significant advantages for thermal management of high-power electronics in military and commercial applications. The use of diamond in high-power, high-frequency transmitters and digital processors are two of the most promising applications. The availability and quality of CVD diamond for such applications are governed by a small number of commercial suppliers. Free-standing CVD diamond films were obtained from three major US manufacturers and characterized using Raman spectroscopy, SIMS, FEM, and microwave cavity measurements. The correlation among the individual test methods is investigated with an emphasis on their relationship to the microwave measurements. A linear relationship between Raman FWHM and microwave dissipation is demonstrated. The primary focus of this research is obtaining accurate and comparable data that can be employed for material selections and quality control in future production applications. Materials were obtained from Crystalline Materials Corp., Diamonex, and Norton Diamond Film. © 1998 Elsevier Science S.A.

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1. Introduction

Thriving government and consumer markets have recently inspired rapid progress in electronics technology resulting in dramatic increases in packaging densities and operating frequencies. This demand is continuing to drive the development of advanced packaging architectures and materials [1]. Increases in packaging densities require higher thermal conductivity materials, whereas increases in operating frequencies demand reduced microwave loss factors. These conditions result in a requirement for a material that not only exhibits high thermal conductivity, but also acts as an efficient microwave dielectric. CVD diamond may offer profound benefits to these and many other applications, but its ultimate success will depend strongly on the ability of the electronics industry both to understand the material and to develop reliable manufacturing processes.

Therefore, the objective of this paper is not only to make comparisons among manufacturers, but also to

validate inclusive characterization techniques and bring them into the context of production programs.

Characterization was performed with the use of: field emission scanning microscopy (FEM), secondary ion mass spectrometry (SIMS), Raman spectroscopy, and evanescent-mode microwave cavity measurements.

Raman spectroscopy was chosen because it has been shown to provide quantitative information on sp^2 (graphite) and sp^3 (diamond) bonded carbon [2], and internal film stress [3]. The presence of electrically conductive graphite is presumed to increase the microwave dissipation factor. High intrinsic stress in the films may increase the incidence of film fracture, which may ultimately relate to the reliability of the electronics system. SIMS was chosen because it provides accurate and quantitative information on the concentration and depth of impurities in the films. Several elements, such as H, N and B, have been shown to reduce the resistivity of diamond films, which would increase the microwave dissipation. FEM was used to determine the grain size of the films. Larger grained films should exhibit a lower microwave dissipation due to fewer grain boundaries, which usually contain a significant concentration of

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graphite and H. Finally, microwave measurements were performed using an evanescent-mode resonant cavity to determine the films' bulk permittivity and dissipation factor at 14 GHz.

Characterization experiments were limited to the following US manufacturers: Crystalline Materials Corporation (CMC), Diamonex, and Norton Diamond Film. A quantity of five coupons were procured from each vendor as "standard" thermal management grade, 1 in. \times 1 in. \times 0.020 in. coupons, with a mirror finish on at least one side. The films were all deep black in color and were deemed the most appropriate grade for the aforementioned applications. The deposition techniques and parameters for the individual manufacturers are shown in Table 1.

2. Experimental details

2.1. Secondary ion mass spectrometry

SIMS measurements were performed using a PHI 6600 quadrupole instrument. Data were obtained by sputtering the samples with a primary ion beam of O₂ and Cs in separate analyses and mass analyzing secondary sputtered ions to give a mass survey of all elements in the material and their relative abundances. The analysis area was approximately 250 μm^2 . Data were obtained both on the surface and a few microns below the surface. Some elements were intentionally left out of the results as they could affect the anonymity of the suppliers.

2.2. Raman spectroscopy

Raman spectra were measured at ambient conditions in the backscattering geometry. The excitation radiation of an argon ion laser with a 5145-Å line was focused to a 100- μm -diameter beam. A power of approximately 0.24 W was measured at the sample. The scattered light was analyzed by a PC-controlled double spectrometer followed by a standard photomultiplier tube detection system. Measurements were performed on both a wide and a narrow energy loss range: from 1000 to 2500 cm^{-1} at 20.0 cm^{-1} resolution, and from 1300 to

1360 cm^{-1} at 4.0 cm^{-1} resolution. The Raman line positions and widths were determined by fitting the measured data to a Gaussian line shape. A natural type II single crystal diamond was measured for comparison. The accuracy of the energy loss measurements was determined to be $\pm 0.6 \text{ cm}^{-1}$.

2.3. EM microwave measurements

Microwave measurements were performed using the "Kent" (evanescent-mode) method [4], which is an alteration of the standard resonant cavity technique. The standard technique uses a closed cylindrical resonant cavity, which is characterized with and without the sample inside, with the difference in the measurements yielding the permittivity and dissipation factor of the sample. The evanescent-mode technique is different in that it is insensitive to the position of the substrate in the gap between waveguide sections, and no intimate contact is required with the sample. The measurement error was calculated to be less than 2% with a repeatability of $\pm 0.5\%$. Measurements were taken at ambient conditions at a nominal frequency of 14 GHz.

3. Results and discussion

3.1. Field emission scanning microscopy

Field emission micrographs were taken with a Jeol JSM-6310F scanning field emission microscope. The grain sizes of the groups were visually approximated and are tabulated in Table 2.

The grain sizes were comparable among all groups; therefore, grain size should not be a significant factor in the microwave measurements.

3.2. Secondary ion mass spectrometry

In Fig. 1 Fig. 2 Fig. 3, an average for the impurities in each group is shown both on the surface and several microns below. For the purposes of this paper, only H, N, and B are discussed in detail. The SIMS results from all groups exhibited a high amount of H (typically 400–4000 ppm), which is common in CVD diamond, as most crystal boundaries are hydrogen-terminated. One coupon in Group A exhibited an abnormally high concentration of H, 28 000 ppm. Groups A and C

Table 1
Summary of manufacturer deposition techniques and characteristics

Parameter	CMC	Diamonex	Norton
Technique	DC arc jet	Hot filament	DC arc jet
Temperature (°C)	800–980	750–900	850–1000
Substrate	Molybdenum	Polysilicon	Not available
Substrate size	> 5 in.	12 in.	Not available
Methane (%)	< 3	< 5	< 5
Pressure (Torr)	< 100	10–100	< 80
Reactor power	80–100 kW	30–60 kW	Not available

Table 2
Summary of coupon grain sizes

Grain size (μm)	Group A	Group B	Group C
Nucleation	5–10	5–15	5–10
Growth	10–60	50–100	40–80

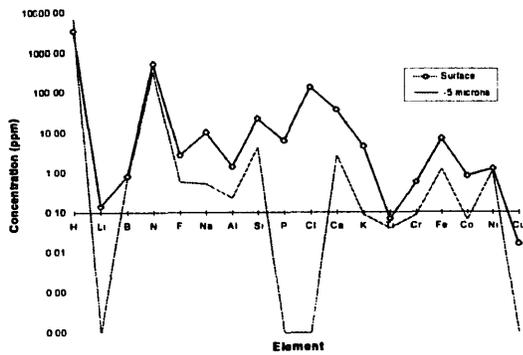


Fig. 1. Group A SIMS analysis of impurity concentrations on the immediate surface and approximately 5 μm below.

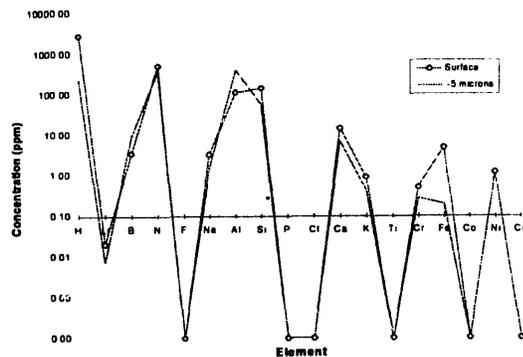


Fig. 2. Group B SIMS analysis of impurity concentrations on the immediate surface and approximately 5 μm below.

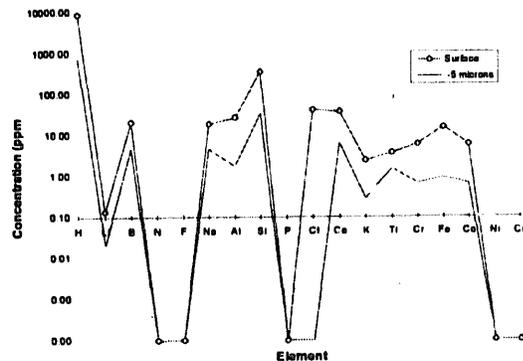


Fig. 3. Group C SIMS analysis of impurity concentrations on the immediate surface and approximately 5 μm below.

exhibited the highest average concentrations of H at ≈ 5000 ppm. The concentrations of B and N in all groups were very low (≈ 460 ppm). Group C had no detectable N.

To obtain a general indication of the films' purity, impurity concentrations for every detectable element in each group were averaged both on the surface and beneath. The average disregarded the concentration of H due to its abundance in all of the samples. Group A reduced from 1064 ppm at the surface to 352 ppm below the surface. Accordingly, group B dropped from 837 to 482 ppm, and group C dropped from 613 to 63 ppm.

Table 3

Raman spectra summary of all coupon groups including a natural diamond specimen for comparison

	Group A average	Group B average	Group C average	Natural diamond
FWHM	6.6	8.4	5.5	4.7
Position	1332.4	1332.7	1332.7	1332.4

3.3. Raman spectroscopy

The Raman spectra results (Table 3) for Group C exhibited the narrowest average FWHM of 5.5 cm^{-1} , with a variation of 13%. Group A followed with an average FWHM of 6.5 cm^{-1} and a variation of 22%. Group B exhibited an average FWHM of 8.5 cm^{-1} and a variation of 16%. The maximum peak shift from 1332.3 cm^{-1} (stress free diamond) was only 1332.9 for the poorest sample; therefore, the maximum intrinsic stress was -0.3 GPa [3]. It is also important to note that the 0.6 cm^{-1} shift is equivalent to the accuracy of the Raman measurements.

Examining the broad band Raman spectra (Fig. 4), it is apparent that groups A and C have additional peaks at $\approx 2060\text{ cm}^{-1}$, which is most likely the photoluminescence background of graphite and amorphous carbon [5]. However, the typical Raman graphite and amorphous carbon peaks at 1581 cm^{-1} and 1352 cm^{-1} do not show up.

3.4. Microwave cavity measurements

The variance in the permittivity and dissipation appear to be related as one would expect due to the change in bulk resistivity. Averaged results are presented in Table 4. An increase in dissipation is related to an increase in dielectric constant. Within the groups, Group A exhibited a variance of 6% in permittivity and 385% in dissipation, Group B exhibited a variance of 2.6% in permittivity and 93% in dissipation, and Group C exhibited a variance of 1.14% in permittivity and 22%

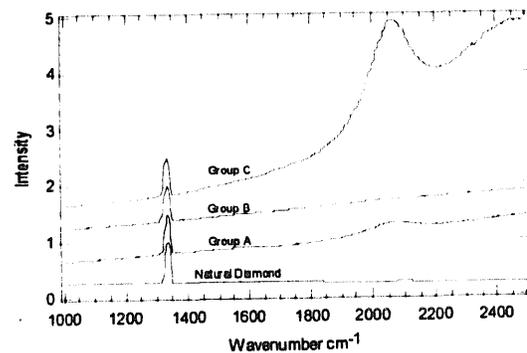


Fig. 4. Representative Raman spectra of each coupon group including a natural diamond specimen for comparison.

Table 4
Summary of the dielectric constant and loss tangent at 14 GHz as measured by an evanescent-mode technique

Parameter	Group A average	Group B average	Group C average
Dielectric constant	5.716	5.867	5.736
Loss tangent	0.005	0.011	0.001

in dissipation. Group C, which had the lowest variance, also had the lowest dissipation. One coupon in Group A (Fig. 5) seemed to have an abnormally large variation in permittivity and dissipation. The average dissipation for Group A was 0.005, whereas this coupon exhibited a dissipation of 0.01. Examining the SIMS results for that coupon revealed an extremely high H concentration of 2.8% as well as abnormally high concentrations of Al, Cl, Na, Si, Ca, and Fe. These results would lead one to conclude that the sample had been contaminated, which was the cause of the excessive dissipation factor.

4. Conclusion

The dependence of the microwave dissipation factor on the Raman FWHM seems to correlate well and follows a linear trend (Fig. 5) relating an increase in Raman FWHM with an increase in microwave loss factor. There is clearly a distinct separation between the CVD diamond manufacturers and a varying amount of scatter within each group. Group A, which exhibited the largest intergroup scatter also had the highest impurity levels. In general, the scatter within the groups was

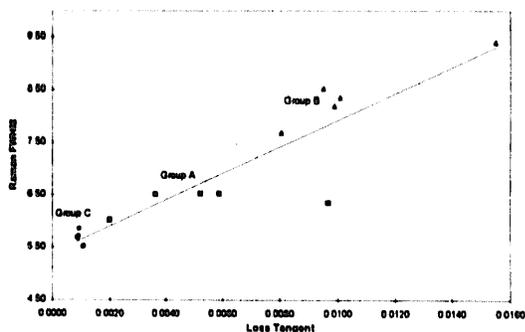


Fig. 5. Raman FWHM plotted against microwave dissipation factor at 14 GHz.

dominated by the microwave loss factor as opposed to the Raman FWHM. In addition, the results of the SIMS surveys suggest that coupon purity and cleanliness play a key role in the microwave loss factor and not in the Raman FWHM.

Currently, Raman measurements have been shown to provide reliable information about the film stress, sp^2 and sp^3 bonded carbon content, loss tangent, and overall quality of the films.

In the future, we hope to demonstrate that Raman FWHM also relates to thermal conductivity. Due to these relationships, Raman spectroscopy will likely serve as a key tool with which a single test will allow electronics companies to easily screen and monitor many important properties of CVD diamond throughout production programs.

5. Future work

Microwave transmission line measurements (1 MHz to 50 GHz) are currently being performed at Georgia Institute of Technology utilizing an advanced NIST technique. Thermal conductivity measurements are also planned pending the results from the latest NIST round-robin.

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