FAR-INFRARED SPECTROSCOPIC STUDY OF DIAMOND FILMS

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High quality polycrystalline diamond films grown on Si substrates by microwave plasma enhanced chemical vapor deposition were characterized in a far-infrared spectroscopic study. The spectroscopic transmissivity data were used to derive a model for the complex refractive index (n – ik) as a function of wavelength in the 10 to 200 cm^{-1} frequency regime. Similar transmissivity and reflectivity data from samples of varying thickness were used to validate this model. The continuum of measured transmissivity and reflectivity data from 10 to 200 cm^{-1} were shown to be in excellent agreement with the values calculated from the refractive index model. The films were shown to have low loss in this frequency regime.

INTRODUCTION

Recent interest in the growth, production and application of diamond thin films has motivated improvements in growth techniques to produce high quality films for a variety of uses. Diamond films are of interest due to their high mechanical strength, high thermal conductivity, low electrical resistivity and desirable optical properties. At least one important application for diamond films in the 5 to 20 cm^{-1} frequency regime is their use as windows and coatings in gyrotron tubes, a very high power source of millimeter and submillimeter radiation. The excellent thermal conductivity of diamond films along with their anticipated low absorption in the far-infrared makes them a promising candidate for such windows. Diamond coatings may be used for protective and wear coatings and also for anti-reflection (AR) coatings for non-diamond substrates.

FILM PREPARATION AND CHARACTERIZATION

The diamond films were deposited on silicon substrates in a high pressure microwave plasma composed of hydrogen and methane.[1] The Si substrates are positioned in the lower portion of the microwave discharge on an inductively heated, 10 cm diameter, graphite stage. A thermocouple embedded in the graphite stage is used to measure the surface temperature of the stage as a closed-loop temperature control system regulates it from 400-1000 °C. Typical deposition conditions used to grow the diamond films are shown in Table I.

Table I. Deposition Conditions for Deposition of Diamond Films

Base Pressure	50 mTorr
Deposition Pressure	50 Torr
Substrate Temperature	875-950 °C
Hydrogen Flow	250-500 sccm
Methane Flow	2-5 sccm
% Methane	0.8 - 1.0 %
Microwave Power	1500 Watts
Deposition Time	10 - 140 hours

The diamond films have been characterized with scanning electron microscopy (SEM), optical microscopy, Raman Scattering and far-infrared spectroscopy. The SEM micrographs of the film surface provides details of the surface morphology and film uniformity, while micrographs of the film's cross section are useful in determining film thickness and structure. A SEM micrograph of a sample similar to sample "a", cited in this paper, (Figure 1) shows clearly the film's polycrystalline nature with a crystallite size of 1-10 microns. Utilizing optical microscopy, film samples "a" and "b" were observed to have thickness values of 72±3μm and 7.0±0.5μm, respectively. Although a thickness variation inevitably exists in these diamond films, no variation greater than the measurement uncertainty (±7%) was detected in the central region of the sample (2 cm dia.).

Raman Spectroscopy, used extensively to study diamond films, is a sensitive tool for detecting diamond (sp3) and graphitic carbon (sp2) bonds. Figure 2 shows Raman spectroscopy data of sample "a". The spectrum shows a diamond peak at 1332 cm^{-1} and a wide graphitic carbon peak around 1550 cm^{-1}. The spectrum is indicative of a high quality diamond film.[2]

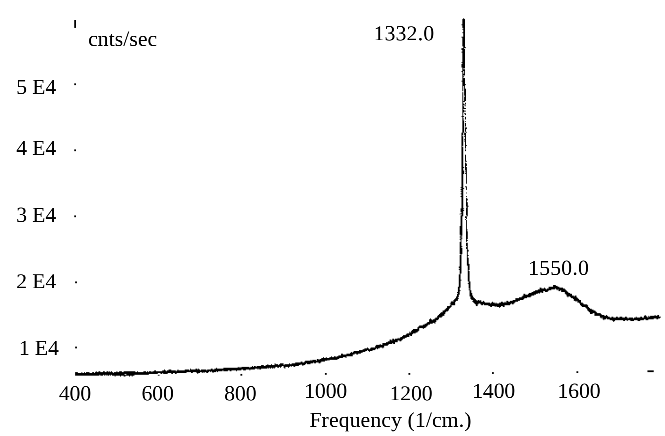

Figure 1 SEM micrograph of diamond film grown under similar conditions as sample "a"

Figure 2. Raman spectroscopy data of sample "a"

INFRARED SPECTROSCOPY

The diamond's far-infrared optical properties were studied using a Digilab FTS-80 Fourier Transform Spectrometer. Transmission and reflection measurements were performed in the 10 to 200 cm^{-1} frequency regime and data is shown in Figures 3 and 4.

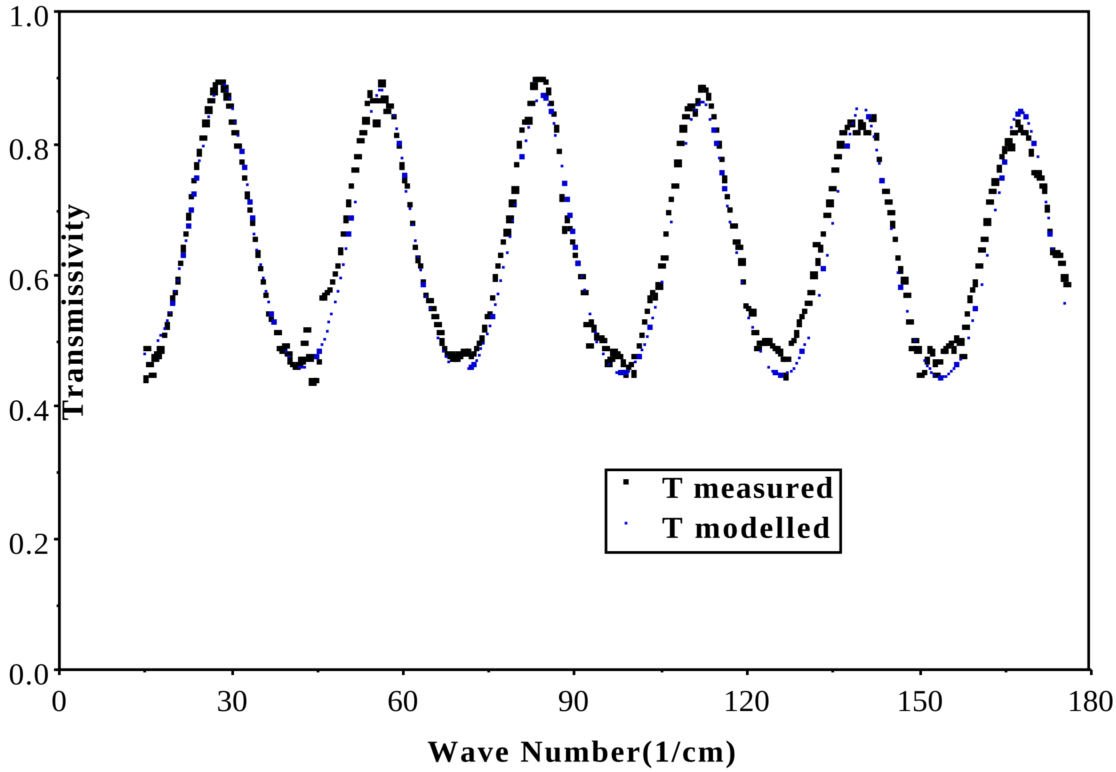

Figure 3. The measured transmissivity as a function of frequency ($1/\lambda$ cm^{-1}) is shown for the 72µm thick diamond film, sample "a", and compared to the model.

To simplify analysis of the far-infrared measurements, the central region of the silicon substrate was etched with a mixture of HF, nitric and acetic acid (3:3:1) leaving a free standing diamond window. The diamond's complex refractive index (n - ik) as a function of wave number ($1/\lambda$) could then be determined using the Fresnel transmission (T) and reflection (R) equations.[3] These equations, when solved for a material of thickness t at normal incidence, have the form:

$$T = \left| \frac{\left(1 - r^2\right) e^{-i\beta}}{1 - r^2 e^{-2i\beta}} \right|^2 \quad \text{and} \quad R = \left| \frac{r\left(1 - e^{-2i\beta}\right)}{1 - r^2 e^{-2i\beta}} \right|^2 \qquad (1)$$

$$\text{where} \qquad r = \frac{(n - ik) - 1}{(n - ik) + 1} \qquad \text{and} \qquad \beta = 2\pi \frac{t}{\lambda}(n - ik)$$

Measured film thickness (t) and the value of transmission (T) at each of the peaks in the spectrum for sample "a" were used to calculate values for n and k. It was then possible to determine algorithms of n and k as a function of wavelength:

$$n = 2.49 - 1.54\,\lambda \qquad (2)$$
$$k = 2.77 \times 10^{-3} + 0.831\,\lambda$$

in the 10 to 200 cm^{-1} frequency regime.

Equations 2 for the complex refractive index, with wavelength (λ) expressed in units of cm, were then utilized to calculate the modelled transmissivity and demonstrate excellent agreement with the measured data at locations of maxima and minima. (See Figure 3) Transmissivity and reflectivity data for sample "b" with a measured thickness of 7.0 ± 0.5µm are shown in Figure 4. Also plotted is the modelled transmissivity and reflectivity which is shown to agree well with the spectroscopic data. Reflectivity and transmissivity data of subsequent diamond samples were used to further validate the modelled refractive index. These spectra were found to agree with their respective models within 5%.

Transmission measurements were also made at a frequency of 19.5 cm^{-1} utilizing a CO_2 optically pumped submillimeter laser. Given the greatly improved signal/noise ratio of the intense monochromatic source over the low intensity broadbanded spectrometer signal, these transmission measurements provided a calibration for the FTS data's intensity scale. The transmittance of sample "a" was measured and determined to have a value of 54.6% which agreed well with the 55.5% spectroscopic value as well as the 54.9% modelled value.

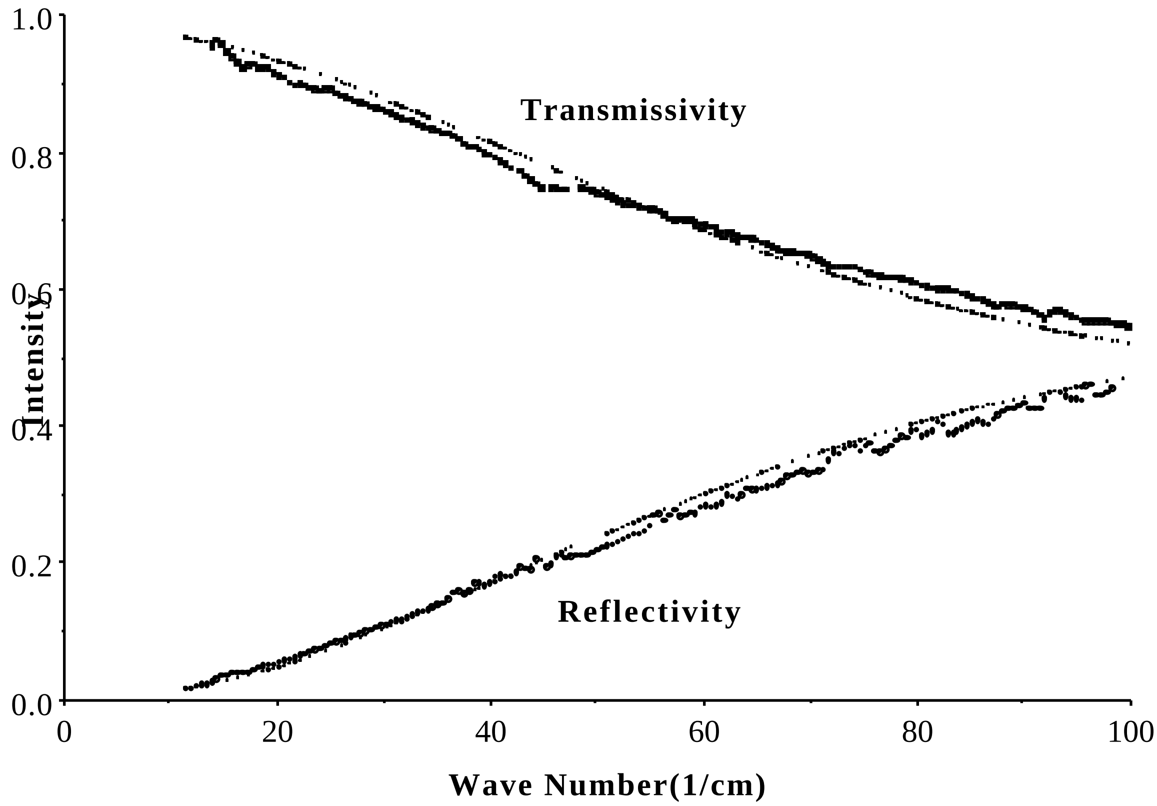

Figure 4. The measured transmissivity and reflectivity as a function of frequency (1/λ cm^{-1}) is shown for the 7µm thick diamond film, sample "b", and compared to the model.

The extinction coefficient, k, is very sensitive to the precision of the transmissivity measurements and therefore the frequency dependence of k modelled by equation 2 is not assured. However, it is instructive to note that the refractive index model does follow a free carrier type dependence on frequency. Through use of Maxwell's equations, this dependency of the complex refractive index on the field's frequency may be expressed as:

$$(n + i\,k)^2 = \mu\left(\xi(\omega) + \frac{4\,\pi\,i\,\sigma(\omega)}{\omega}\right) \qquad (3)$$

where μ is the relative permeability and equal to unity for diamond. In the above expression the frequency dependent dielectric constant, $\xi(\omega)$, describes the oscillation of bound electrons with the electric field while the conductivity, $\sigma(\omega)$, describes this behavior for the free electrons.

When the electric field's frequency is sufficiently low ($\omega << 1/\tau$), the free electrons will oscillate in phase with the field (i.e. $\sigma(\omega)$ is predominately real and constant) and the bound electrons will oscillate out of phase (i.e. $\xi(\omega)$ is also predominately real). The far-infrared measurements and therefore the refractive index model give evidence of this behavior since under these conditions the imaginary component of equation 3 implies:

$$2\,n\,k = \frac{4\,\pi\,\sigma(\omega)}{\omega} \qquad (4)$$

and since n was shown to be roughly constant in this spectral range, we have:

$$\frac{2\,\pi\,\sigma(\omega)}{n} \approx \text{constant}$$

thus $k \approx (\text{constant}) / \omega$

The source of free carriers in these films is unclear.

DISCUSSION

The source of the diamond film's far-infrared loss, and also the model of it's complex refractive index, are still under investigation. The incorporated graphitic carbon in sample "a" shown by the Raman spectrum may explain the free carriers predicted by the material's frequency dependence of k and is one possibility for the far-infrared loss. It should be noted that as concentrations of graphitic carbon detected in diamond films continue to decrease as film quality improves, far-infrared spectroscopy, which is sensitive to the presence of free carriers and may see levels of 1 part in 10^9, could then be employed to detect the free carriers.

The polycrystalline structure of the film produces a small, diffuse scattering component which has not been evaluated. This scattering component could affect the above analysis at the shorter wavelengths where the surface roughness becomes comparable to the wavelength of light. Average crystallite size reaches 10% of that of the wavelength at the high frequency end of the data. Mathematical modelling of this structure and its effect on the refractive index are being considered.

CONCLUSION

High quality polycrystalline diamond films have been successfully grown by a microwave plasma assisted chemical vapor deposition system. Far-infrared spectroscopic transmissivity data in the 10 to 200 cm^{-1} frequency regime allows for the modelling of the material's complex refractive index. This model was shown to demonstrate excellent agreement over the entire range of the spectroscopic data. The data also indicates the films to have low loss in this frequency regime.

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