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Index of refraction from the near-ultraviolet to the near-infrared from a single crystal microwave-assisted CVD diamond

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Abstract: The refractive index of a type IIa CVD-grown single-crystal diamond was measured by ellipsometry from the near ultraviolet to the near infrared region of the spectrum. As a consequence, a one term Sellmeier Equation with coefficients of $B_1 = 4.658$ and $C_1 = 112.5$ for the refractive index of diamond, for the wavelength range from 300 to 1650 nm, was derived that is only as accurate as the input data, ± 0.002 . The experimental results in this paper between 800 and 1650 nm are new, adding to the values available in the literature.

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1. Introduction

Diamond's unique optical properties have been studied for many years and are summarized elsewhere [1,2] and in the references therein. Most of the prior measurements were performed on mined diamonds and little information was provided on the investigated specimens other than qualitative properties such as their color [3–5]. The new measurements presented here support the use of diamond optics with modern lasers operating from the near ultraviolet to as

long a wavelength as 1650 nm. Previously in the spectral range of modern lasers there have been a few discrete measurements and the use of empirical dispersion formulae was required.

In this paper we report measurements of the refractive index of a chemical vapor depositon (CVD) grown, type IIa, single-crystal diamond as obtained by ellipsometry [6], Azzam and Bashara. Measurements were taken from 300 to 1650 nm. Indices above 800 nm are new data for synthetic, type IIa diamond except for discrete values, indicated in Table 1 [2], Zaitsev. The measured indices were used to derive a single term Sellmier Equation for diamond that is an excellent fit to the data and is given with coefficients no more accurate than the data used in the derivation. This is in contrast to the fitting equations previously given for diamond which show either a two-term Sellmeier Equation in [3] or a Herzberger-type Equation in [5,7]. Also in some dispersion formulas in the earlier literature, either the coefficients were knowingly given with precision greater than the data available [5,7] or their precision and accuracy was not discussed [3], Peter. In [8], Draganskii et al used ellipsometry to measure the indices of refraction of pristine and gallium implanted diamond but present the data in such a manner that the precision cannot be determined.

2. Experimental

Details of the growth of a single-crystal diamond can be found elsewhere [9], Webster et al, and in the references therein. The specimen was cut and polished with dimensions of $0.62 \times 0.62 \times 0.2$ cm. Linear absorption results and its analysis performed by spectrophotometry and multi-wavelength calorimetry on this sample and a series of similar samples can be found in [9], Webster et al. A common and precise technique to measure refractive index is the minimum-deviation angle method. This technique requires specimens that are large and thick enough to accommodate the light beam and that can be polished into the shape of a prism. Ellipsometry, based on reflection rather than refraction, can be easily used with thin and flat samples. It provides lateral resolution and, equipped with a spectrophotometer, allows for the rapid measurement over a wide range of wavelengths. The main drawback of ellipsometry is that it is somewhat less accurate than the minimum-deviation technique. In fact, the quantification of the accuracy of ellipsometry measurements is not straightforward. Surface contamination and roughness can introduce inaccuracies that are hard to model, see [6], Azzam and Bashara, for example. Most published values of refractive indexes measured through ellipsometry are reported to the third decimal digit.

Ellipsometry measurements were performed using a Woollam M2000 Ellipsometer that allowed variable angle mapping and spectroscopic data acquisition for determination of refractive index, absorption coefficients and anisotropy in the near-ultraviolet through the near-infrared. Data were acquired with a motorized sample stage to enable automated multi-point measurements or sample mapping. The variable angle option made measurements possible at incident angles of 55, 60, and 65 degrees off-normal.

Between 300 and 1650 nm a total of more than 670 discrete measurements were obtained. Five different locations on the same sample surface were measured. For each location the light was sent at three different azimuth angles. Measurements taken at the same spot but with different angles should return the same results, so their spread can be used as an estimate of the reproducibility of the instrument. On the contrary, different values measured at different locations on the sample could be due either to a real inhomogeneity of the sample refractive index, or be artifacts introduced by different sample surface roughness or contamination. In this sample, surface inhomogeneities should be very small based on our previous study of a similarly prepared diamond [10], Chen et al.

3. Results and discussion

Shown in Fig. 1 are the ellipsometry determined indices of refraction of the single crystal diamond in different regions of the spectrum. Each panel, (a) through (c), in the figure depicts five traces associated with the five different points on the sample where measurements were

taken and each data point is the average of the three different azimuth angles for that position. At all points on the sample and at each wavelength the standard deviation for different angles, depicted as vertical error bars in Fig. 1(a) through (c), is always equal to or less than 0.003, and is less than or equal to 0.002 in most cases, in the 300 to 1400 nm range. Also depicted in Fig. 1 are the measurements from [2–4] which all agree with our values. In the ultraviolet region, Fig. 1(a), some variation of the refractive index of the sample is noticeable, and at all the measured points our results are a bit smaller than [3], Peter's; however, the disagreement is small and is not observed at longer wavelengths.

Figure 1(d) depicts the average of the refractive index as measured at different locations on the sample; the standard deviation was taken as an estimate of the experimental error. In the 300 to 1400 nm range, the standard deviation is equal to or less than 0.003, and equal to or less than 0.002 in most cases, and does not get larger than 0.01 at longer wavelengths. Table 1 also shows some of the values from Fig. 1(d) in the 800 nm to 1650 nm region. These data when combined with the infrared measurements from [5], Edwards and Ochoa, join smoothly with each other. Also, the data from this work seem in agreement with the recent investigation by [8], Draganski et al on refractive index of Type Ib synthetic diamond with gallium-ion surface implantation, as measured with ellipsometry.

Table 1. The refractive index from 300 to 1650 nm as measured in this work (Column 2) and compared with results calculated using Eq. (3) (Column 3) and reported in [2], Zaitsev, (Column 4)

Wavelength [nm]	Refractive index This work Measured	Refractive index Calculated using Equation (3) in this work	Refractive Index from [2]
300	2.531	2.534	2.545 ; 2.5407
350	2.489	2.489	2.490 ; 2.4928
400	2.458	2.461	2.463 ; 2.4641
450	2.443	2.443	2.4454
500	2.429	2.430	2.432 ; 2.4324
550	2.421	2.421	2.4230
600	2.414	2.414	2.415 ; 2.4159
650	2.410	2.409	2.4105
700	2.406	2.404	2.405 ; 2.4062 ; 2.407
750	2.401	2.401	2.4028
800	2.400	2.398	2.400
850	2.397	2.396	
900	2.395	2.394	2.396
950	2.393	2.393	
1000	2.392	2.391	2.394
1050	2.391	2.390	
1100	2.390	2.389	
1150	2.389	2.388	
1200	2.388	2.387	2.390
1250	2.388	2.387	
1300	2.387	2.386	
1350	2.387	2.385	
1400	2.385	2.385	
1450	2.386	2.385	
1500	2.384	2.384	2.386
1550	2.383	2.384	
1600	2.386	2.384	
1650	2.382	2.383	

The index of refraction dispersion of synthetic diamond has been described by [11], Voronkova et al, and [12], Kurdunov et al, as a one-term, Sellmeier Equation [2]:

$$n^2(\lambda) = 1 + \frac{B_1 \lambda^2}{\lambda^2 - C_1^2} \quad (1)$$

For natural diamond, the two-term Sellmeier-type Equation

$$n^2(\lambda) = 1 + \frac{B_1 \lambda^2}{\lambda^2 - C_1^2} + \frac{B_2 \lambda^2}{\lambda^2 - C_2^2} \quad (2)$$

was used by Peter in the 200 to 800 nm range [3].

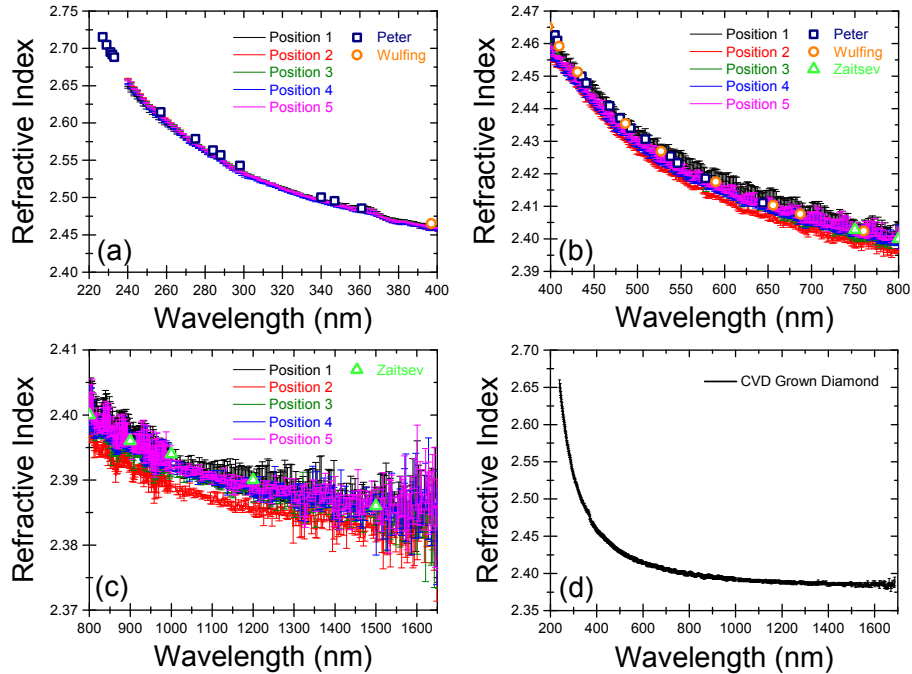


Fig. 1. Refractive index as measured at five different locations on the same sample surface. For each location, the average of three azimuth angles is reported, and the standard deviation is used as the vertical error bars. Values from Peter (squares) [3], Wulffing (circles) [4] and Zaitsev (triangles) [2] are also reported. (d) Refractive index, average of 3 azimuth angles and 5 different locations on the sample surface.

We applied a least-squares fit procedure to the combined data from this work and from [5], Edwards and Ochoa, using Eq. (1) where the B_i and C_i coefficients were left as free fit parameters. The uncertainties of the coefficients were estimated as the 95% confidence interval, under the assumptions of the experimental errors being completely random and normally distributed around a zero mean value. The fitting procedure returned $B_1 = (4.658 \pm 0.001)$ and $C_1 = (112.5 \pm 0.1)$ nm, which differ from those given by [11], Voronkova et al and [12], Kurdunov et al, by less than 2%. The reduced χ^2 parameter is equal to 1.2, and the residuals, defined as the difference between the measured value and the value predicted by Eq. (1), are less than or equal to 0.002 in the 300 nm to 1600 nm range, though they get as large as 0.004 for shorter and longer wavelengths.

Equation (2) can be used to accurately represent the combined data from this work and from [5], Edwards and Ochoa, as the coefficients returned by the fitting procedure also differ from [3], Peter's by less than 2%. However, the generated dispersion curve is no more accurate than that obtained by using Eq. (1), as shown in Fig. 2 where the two curves are

hardly distinguishable. Thus we do not find enough evidence supporting the need for using a two-term rather than a simpler one-term Sellmeier Equation.

If a Herzberger-type Equation (see [7], D.F. Edwards and H.R. Philipp) is used, the dispersion coefficients returned by the fitting procedure strongly depend on the chosen wavelength interval. If the data from this work are combined with those of [5], Edwards and Ochoa, the resulting dispersion curve reproduces the combined data reasonably well. However, the Herzberger Equation requires fitting five coefficients to the data and is only valid in the limited range of wavelengths for which the fitting was performed.

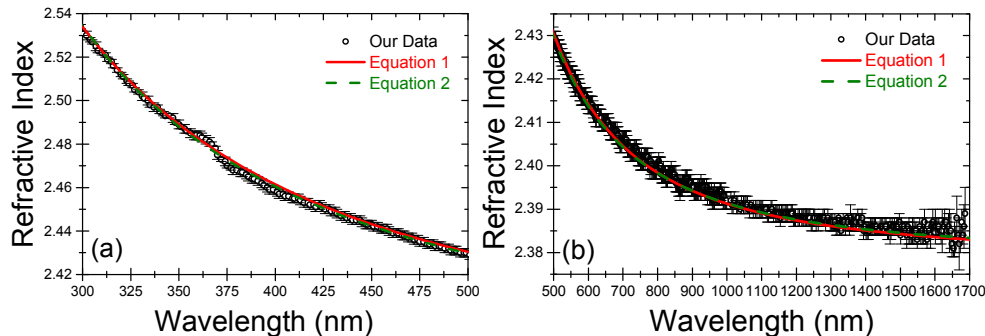


Fig. 2. Refractive index of diamond as measured in this work (circles) and the dispersion curves as generated by Eq. (1) (red full line) and Eq. (2) (green dashed line).

The equation that seems to best describe the index of refraction dispersion of diamond in the ultraviolet to the infrared is:

$$n^2(\lambda) = 1 + \frac{4.658\lambda^2}{\lambda^2 - (112.5 \text{ nm})^2} \quad (3)$$

where λ is expressed in nm. Equation (3) applies both to natural and synthetic diamond, with an accuracy of ± 0.002 in the wavelength range from 300 to 1650 nm.

Equation (3) can be used to determine the index of refraction at wavelengths as long as 25 μm with reasonable accuracy (± 0.004) when compared to the data in [5], Edwards and Ochoa. For example, at 10 μm Eq. (3) predicts the index of refraction would be 2.379 and [5], Edwards and Ochoa, gives it as 2.376, a difference of only 0.003. To obtain more accurate predictions of the index of refraction in the far infrared, a two or even three term Sellmeier Eq. may be needed. Since we do not have data beyond 1650 nm, such extrapolation is suggested only by the fact that both Eq. (3) and the data of [5], Edwards and Ochoa, show little or no dispersion beyond 2.0 μm .

4. Conclusions

We have measured the refractive index of synthetic CVD grown diamond using ellipsometry for more than 680 different wavelengths in the 300 to 1650 nm range. We showed the compatibility of our measurements with previously published results, and we added many new values in the visible and near infrared. Finally, we discussed the previously proposed equations for the dispersion of the index of refraction of diamond and suggested a simple, one-term Sellmeier Equation, Eq. (3), as the better choice and that is no more precise than the data used to obtain it. As a result of studying the Herzberger formula for index of refraction dispersion we find that it can be fit to the data only in some small spectral range. If one tries to apply it to a different spectral range new coefficients must be calculated. Hence, we do not recommend the use of the Herzberger formula but instead recommend the use of the just mentioned one term Sellmeier Equation.