# STRAIN AND IMPURITY CONTENT OF SYNTHETIC DIAMOND CRYSTALS

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## ABSTRACT

Samples of diamond crystals produced under various high pressure, high temperature conditions were studied using both micro photoluminescence and Raman spectroscopy. The 0.3 - 0.6 mm sized samples exhibited various levels of inclusion content, impurity content and strain. Photoluminescence studies revealed the presence of nitrogen in three forms. The 1.945 eV, 2.15 eV and 2.46 eV zero phonon lines and their associated sidebands were detected. The ratios between forms of impurities and their integrated intensities varied between samples. Variations in the distribution of the nitrogen forms were seen between regions of high and low strain birefringence patterns.

## INTRODUCTION

The physical properties of diamond have been a constant source of investigations for researchers. The large number and various levels of physical properties between individual crystals makes characterizing these diamonds challenging. Industrial diamonds are used in numerous applications throughout the world. Crystals are classified according to crystal size, shape and bulk crystal strength measurements. It is possible that physical properties such as strain and impurity content should also be used as a classification technique for diamond crystals in industrial applications.

Nitrogen is the primary type of impurity in synthetic type Ib crystals and can be found in many different forms. Davies has compiled a list of known nitrogen forms, structure and methods of detection [1]. Type Ib diamonds are classified by the presence of large amounts of single substitutional nitrogen as opposed to aggregates and platelets detected in type Ia natural diamonds. Photoluminescence has been used as a very sensitive method of detecting impurities of different forms [2]. The method of excitation used here has a limit of ~2.7 eV. Nitrogen impurity zero phonon lines were detected at 1.945 eV, 2.15 eV and 2.46 eV. Variations in the content of each of these forms of impurities were seen when comparing type Ib diamond crystals of different growth processes. Fluctuations in the distribution of impurities between the strained and unstrained regions were also detected.

Strain as well as impurity content can take many different forms. Inhomogeneous strains can be observed as birefringence using crossed polarizers. These types of strains can have many different causes: dislocations, differences in lattice parameters, precipitates and inclusions, fractures and plastic deformation [3]. Although these strains are observable using birefringence they are not quantifiable nor can tensile and compressive strains be distinguished. For large strains Raman spectroscopy has been used to measure and distinguish between compressive and tensile strains [4] however strains due to many of the causes above are not strong enough to be detected through this method. In contrast, the zero phonon lines observed in photoluminescence spectra are very sensitive to strain. In this study the line shape, shift and FWHM of the nitrogen 1.945 eV zero phonon lines have been measured, correlated and compared. A correlation between the peak position and the FWHM was verified and it was determined that samples with higher concentrations of the 2.46 eV (H3 center) exhibited less strain broadening.

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## EXPERIMENT

The research presented here was performed on eight sets of 40/45 mesh synthetic diamonds used in industrial applications. Each set of diamonds varied in inclusion, strain and impurity content. Experiments were performed on both individual crystals and groups of 10-20 crystals.

The individual crystal measurements were performed using a single apparatus for both Raman and photoluminescence. The system consisted of a high resolution spectrometer with an attached Olympus microscope. Magnifications of 10X, 50X and 80X were used to focus the laser excitation, allowing a spot size of <10 μm to be achieved. Spectra were obtained using a argon ion laser operating with 100 mW power at the sample using either the 514.5 or 457.9 nm lines. This light was focused through the microscope. The light was then recollected and dispersed with a U1000 ISA double spectrometer. A photomultiplier was used for detection and a 286 compatible computer was used for collection and analysis of the data. The integrated intensity of the PL was determined using the ratio between the PL intensity and the intensity of the diamond Raman peak. This method allows for comparison between samples of similar growth conditions to the quantity of impurity detected.

Bulk crystal measurements were carried out employing a JANIS CCS-350 closed cycle refrigerator system. The spectra were taken on the samples at a chamber temperature of 8K. The laser was focused to a line image of ~2 mm x 100 μm on the sample. The light was dispersed, detected and collected through the same system described above.

## RESULTS AND DISCUSSION

### Individual Crystal Measurements

Photoluminescence and Raman measurements were conducted on several crystals within each sample set. The laser was focused to a spot void of inclusions on a (111) face of the crystal. Fig. 1 illustrates a typical spectrum for each of the eight samples using the 458.7 nm line of the laser.

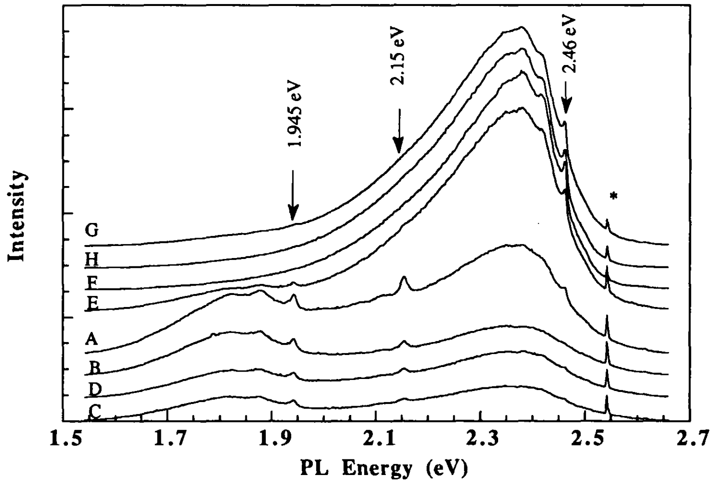

Figure 1 : PL of eight samples taken with the 458.7 nm line of the laser. Nitrogen present in three different forms is observed: 1.945 eV [N-V], 2.15 eV [N-V-V+..], H3, 2.46 eV [N-N-V]. The * indicates the Raman features.

The three observable zero phonon lines and their associated sidebands are indicated in the spectra. Each of these lines is indicative of nitrogen impurities in different forms. The vibronic sidebands, extending to lower energy, are the result of phonon interaction with the defect. The 1.945 eV peak is attributed to a single substitutional nitrogen and an associated vacancy in a nearest neighbor position[5]. The zero phonon line at 2.15 eV is theorized to be a single nitrogen with two or more associated vacancies[2]. The final peak at 2.46 eV is known as the H3 center with a double nitrogen and vacancy structure[2]. The A band is often seen to be convoluted with the H3 center and sideband. It is thought to originate from a donor acceptor transition where the donor is the nitrogen from the A center (two nitrogen) [7]. Fig. 1 illustrates the different distributions of the impurities between the different crystal samples.

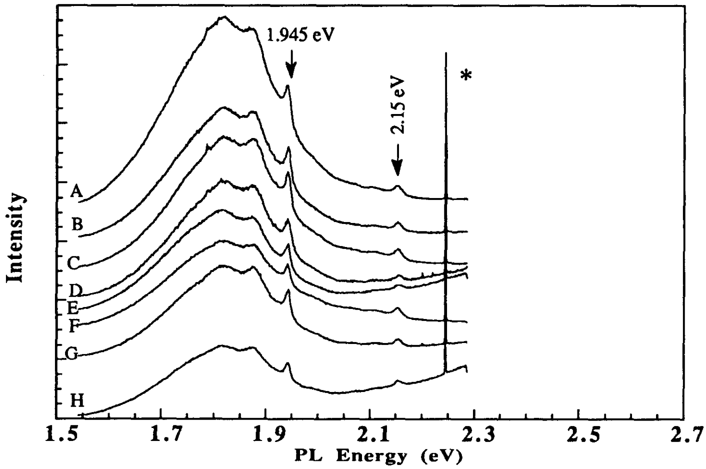

Figure 2: PL using the 514.5 nm line of the laser. Comparative quantities of the 1.945 eV form of nitrogen [N-V] can be seen between the eight samples.

Using the 514.5 nm (2.41 eV) line of the laser the next series of experiments emphasizes the PL from the single substitutional nitrogen at 1.945 eV. Fig. 2 illustrates the spectra from each of the samples included with the Raman peak. The quantity of nitrogen in this form can be compared using this type of ratio. The phonon lines at 1.945 eVand 2.15 eV, and the Raman peak can be seen in each of the spectra. As is evident in Fig. 2 the quantity of nitrogen in this form varies between each of the samples.

Each set of diamond crystals exhibited various levels of strain. Fig. 3 is a photograph of one of these samples. The diamond is viewed through a 10X objective lens and is between crossed polarizers. The strain in a crystal alters the index of refraction, thus allowing the light to pass through the polarizers. To explore the properties of the sample, both light and dark regions of the sample were probed with micro photoluminescence.

Figure 3 : Photograph of ~ 400 μm diameter diamond crystal viewed through crossed polarizers. Strained regions are shown as light areas and extinguished areas are unstrained.

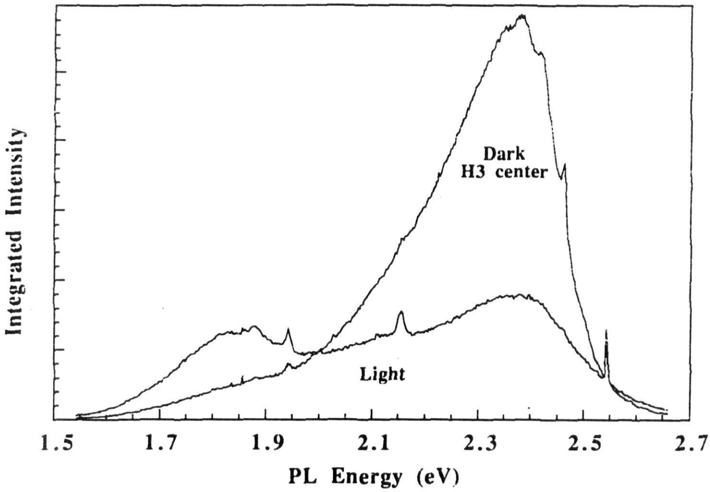

Figure 4 : Spectra from a single diamond crystal with laser focused on the strained (light) and unstrained (dark) areas of the surface.

Fig. 4 illustrates typical spectra resulting from this probe. It was found in most samples that the H3 center was most prominent in the unstrained (dark) regions. Investigations by Collins suggest that the A-band defect, formed from the A center (two nitrogen atoms), gathers around dislocations in diamond[6]. The forming of dislocations in a crystal is often a method of relieving strain. The H3 center is also a product of the A center (A center+V). The result that the H3 center is most prominent in areas outside of and around the areas of strain suggests that this defect also gathers in areas of dislocations.

## Low Temperature Measurements

10 - 20 crystals of each sample were placed in a cryostat chamber, and the temperature was then lowered to 8 K. The lower temperature reduces both the thermal vibrations and the broadening of the zero phonon lines [2]. The resultant broadening is attributed to the inhomogeneous strains within the sample. Measurements of the 1.945 eV zero phonon line were made and both the FWHM and peak position of the samples were compared.

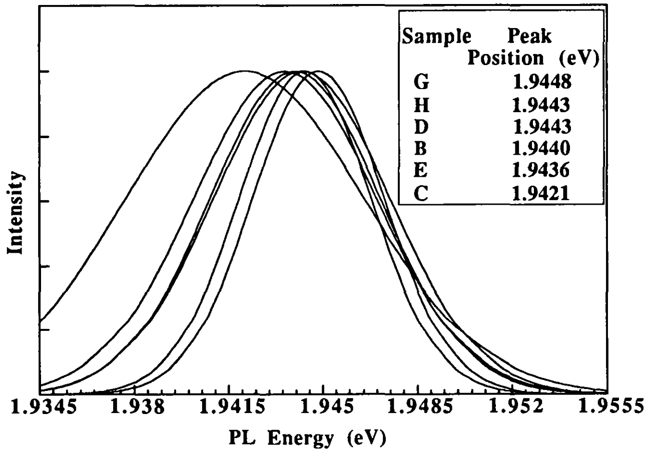

Figure 5 : 1.945 eV zero phonon line of samples with similar physical properties. The peak position of each sample is given in the top right hand corner, in descending order of energy. A broadening of the ZPL is also evident as the peak shifts to lower energy.

Fig. 5 compares the FWHM between samples with similar characterizing features, shape, inclusion content and size. The samples with higher concentrations of the H3 center from Fig.2 (samples G and H) seem to exhibit less strain broadening and peak shifts to higher energy. In the previous experiment described we determined that the H3 center tends to group around areas of relieved strain and dislocations. We suggest here that the high content of H3 centers may indicate higher levels of dislocations and less internal strain. Fig. 6 is a correlation of the FWHM with the peak position. This correlation verifies that the results obtained by Davies for the 2.465 eVphonon line also applies to other zero phonon lines [7].

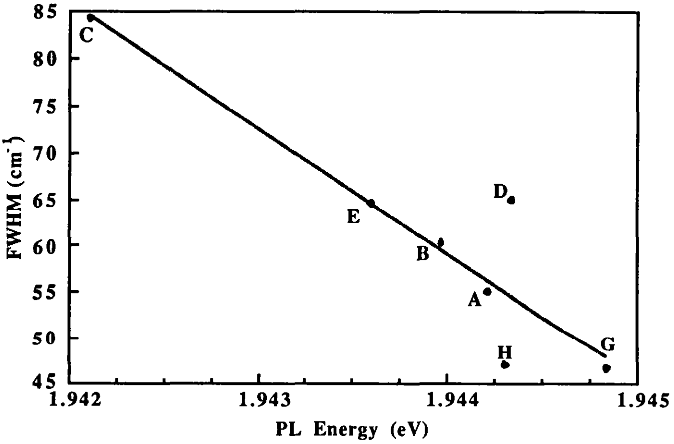

Figure 6 : Correlation between the FWHM of the 1.945 eV zero phonon line and the peak position.

## SUMMARY

In summary we have seen various levels of concentrations of nitrogen impurities in synthetic diamonds grown by different processes. Further investigations reveal variations of nitrogen impurity forms within single crystals. The H3 center seems to form outside of areas of high strain. The samples with higher concentrations of the H3 center also exhibit less inhomogeneous strain broadening of the 1.945 eV zero phonon line. This strain broadening was also seen to correlate well with the peak position of the zero phonon line. The work presented here seems to suggest that the strain and impurity content within a diamond crystal are interrelated. The distribution of the impurities seems to be effected by the strain while the level of internal strain seems to be dependent on the amount and type of nitrogen defect.

## ACKNOWLEDGMENTS

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