The origin of the broadband luminescence and the effect of nitrogen doping on the optical properties of diamond films

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The origin of the broadband luminescence and the effect of nitrogen doping on the optical properties of diamond films

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Raman and various photoluminescence (PL) techniques were employed to investigate the role of nitrogen doping on the optical spectra of chemical-vapor-deposited (CVD) diamond films and to determine the origin of the characteristic broadband luminescence which is observed from approximately 1.5 to 2.5 eV and centered at ~2 eV. The PL transitions attributed to the zero-phonon lines (ZPL) of nitrogen centers are observed at 1.945 and 2.154 eV. A new possible nitrogen center at 1.967 eV is also observed as well as the band A luminescence centered at ~2.46 eV. The experimental results preclude the possibility of the broadband PL being due to electron-lattice interaction of the nitrogen ZPL centers. We establish the presence of an in-gap state distribution in CVD diamond films attributed to the sp^2 disordered phase and show that its optical transitions are the likely cause of the broadband luminescence. A model of the in-gap state distribution is presented which is similar to models previously developed for amorphous materials.

I. INTRODUCTION

A broadband luminescence extending from approximately 1.5 to 2.5 eV and centered at ~2 eV has been observed in various photoluminescence (PL) studies of diamond films grown by various chemical-vapor-deposition (CVD) methods.[1-5] In many instances this broadband PL appears as the strongest feature in the spectrum. However, a complete model has yet to be formulated to explain the origin of this broadband PL. Studies utilizing cathodoluminescence (CL) and absorption spectroscopy of crystal diamonds of types Ia and Ib which contain nitrogen have shown that similar broadband luminescence has its origin in the electron-lattice coupling (vibronic interaction) of nitrogen related centers with zero-phonon lines (ZPL) at 1.945 and 2.154 eV.[6,7] These centers, when optically excited, can interact with the lattice vibrations via various mechanisms. One type of electron-lattice interaction is energy transfer from a photoexcited optical center to the phonons which results in a broadband PL spectra. The broadband PL in this case will extend toward lower energy relative to the zero-phonon line. Luminescence studies on natural brown diamonds[8,9] have shown that the brown diamonds luminesce in the yellow and in the red region of the spectrum. The luminescence appears in the optical spectra as wide bands centered at ~2.2 and ~1.8 eV. The spectral width of these luminescence features are again very similar to the one observed in the spectra of the CVD diamond films. The origin of the wide luminescence bands of the brown diamonds has also been determined to be of vibronic nature; this vibronic system has numerous ZPL with the main ones at 2.721 and at 2.145 eV.[9] In this paper we investigate the origin of the broadband luminescence in CVD diamond films, exclude the possibility of the broadband PL originating from any vibronic interaction, and posit a different mechanism of origin.

An alternative mechanism which could give rise to the broadband PL in the CVD diamond films is the amorphic phase of the sp^2-bonded carbon (also called the graphitic phase), the presence of which has been widely confirmed.[10-12] The PL of amorphous carbon films exhibit emission centered at ~1.8-2 eV which is of similar line shape to that observed in the CVD diamond films.[13-17] According to the general model of the state distribution of amorphous materials,[18,19] the distortions of bond angles and of bond lengths which constitute the amorphous phase introduce a continuous state distribution in the optical band gap of the material. The PL of amorphous carbon films has been determined to originate in the optical transitions of an in-gap state distribution related to the disordered forms of the sp^2 carbon bonding. In this paper we establish the presence of an in-gap state distribution in CVD diamond films and suggest that it is the likely cause of the broadband luminescence. It is crucial to electro-optic applications to have knowledge of the properties of this distribution since it can affect and determine the transport and recombination mechanisms of the carriers.

The first part of this paper presents the results of detailed PL studies of nitrogen-doped CVD diamond films. We identify the nitrogen PL centers most likely to be created in the films: the 1.945, 2.154, the band A at ~2.46, and a possible new nitrogen center at 1.967 eV. We show that the broadband PL does not originate from the vibronic interaction of the nitrogen related centers at 2.154 and 1.945 eV. Furthermore, it is shown that the temperature dependence of the broadband PL does not obey the empirical relation expected from electron-lattice interactions. The intensity of a vibronic broadband is expected to increase with increasing temperature since the electron-phonon coupling becomes more probable.[20] We found, however, that the intensity of the broadband PL decreases with increasing temperature. We therefore exclude the possibility of the broadband PL being of vibronic origin.

In the second part of this paper we establish that the broadband PL in the CVD diamond films has characteristics of optical emission originating from a continuous distribution of in-gap states very similar to that found in amorphous

materials. From correlation of the sp^2 amorphous phase present in the diamond film to the PL emission and from the temperature characteristic of the PL, we conclude that the sp^2 amorphous phase introduces an in-gap state distribution which initiates the broadband PL. We also present the results of an initial investigation into the main properties of the state distribution: its profile, density, and width for samples grown in different growth conditions. These parameters are important because the density of states is a measure of the amount of the amorphic phase present in the material, while the width is a measure of how far into the band gap the distribution extends and reflects the magnitude of the fluctuation in the distortion of bond length and angle. Our experimental results are analyzed in terms of the model of in-gap state distribution for amorphous materials developed by Street et al.[19,21,22] The PL experimental data presented here indicate that the profile of the state distribution is of an exponential form and that the specific shape depends on the growth conditions.

Lastly, we present an analysis of the temperature characteristics of the 1.681-eV PL band. The 1.681-eV optical center is commonly accepted to be associated with a Si impurity[10,23–27] introduced into the diamond matrix during growth. Our experimental data for the 1.681-eV PL emission was closely fitted using the Boltzmann activation process for which at the higher temperature range the nonradiative transition probability competes with the PL intensity. Our data analysis indicates a nonradiative activation energy E_A of ~90 meV.

II. EXPERIMENT

In this study diamond samples were grown on Si (100) substrates using an ASTEX microwave plasma CVD system. The plasma power, temperature, and pressure were maintained at 900 W, 850 °C, and 25 Torr, respectively. Three samples involved in the nitrogen study were subjected to $H_2/CH_4/N_2$ flow rates of 500/5/0, 500/5/0.5, and 500/5/10 sccm and will be referred to as the 0%, 0.1%, and 2% nitrogen-doped samples, respectively, according to their gas phase N_2/H_2%. The growth time for these samples was 5 h. We note that the discontinuous island structures of the nitrogen-doped films precluded secondary-ion-mass spectroscopy measurements of the actual nitrogen concentration.

The two undoped diamond samples involved in the density of state distribution investigation were used in our previous study[23] and will be referred to as the 20-h and the 40-h samples, reflecting their respective growth times. Both samples are continuous, with the 20-h sample being about 2 μm thick and the 40-h sample being about 4 μm thick. The plasma for the 20-h and the 40-h samples consisted of 1% CH_4 in H_2 at 1000-sccm total flow. The plasma power, chamber pressure, and substrate temperature were maintained at 800 W, 25 Torr, and 750 °C, respectively. The scanning electron microscope (SEM) micrographs of the above samples are shown in Fig. 1.

The micro-PL and Raman analysis of the 0%, 0.1%, and 2% nitrogen-doped samples was carried out at room temperature employing argon-ion laser excitation (514.5 or 457.9 nm) which was focused on the sample to a spot of ~5
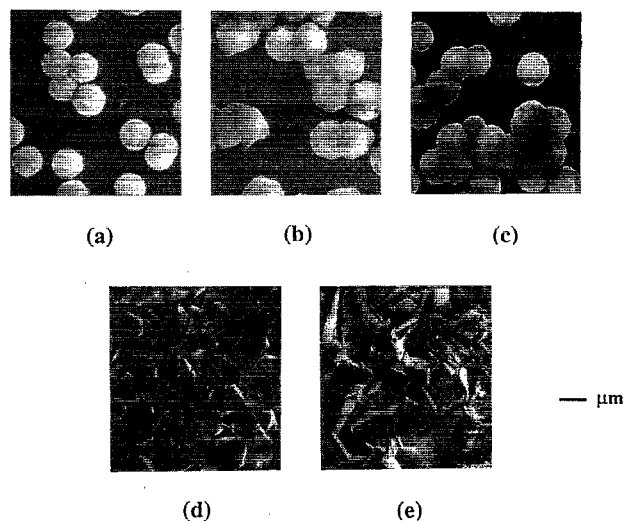

FIG. 1. The SEM micrographs of (a) 0%, (b) 0.1%, and (c) 2% nitrogen-doped samples and of the (d) 20-h and (e) 40-h undoped samples.

μm in diameter. Focusing was facilitated by using an Olympus BH-2 microscope. The macro-PL analysis of the 20-h and the 40-h samples was carried out employing a JANIS CCS-350 closed cycle refrigerator system. The laser was focused to a line of ~2 mm×100 μm on the sample. In both studies, an ISA U-1000 scanning double monochrometer was used to analyze the signal.

III. RESULTS AND DISCUSSION

A. PL and Raman line-shape investigation

The first part of our work focused on obtaining the PL spectra of nitrogen-doped and undoped diamond films, identifying the nitrogen-related PL bands and examining the influence of the nitrogen on the broadband PL. In Fig. 2 the PL spectra of the 0.1% and of the 0% nitrogen-doped diamond films are shown. Both spectra were obtained utilizing the 514.5-nm green line (2.41 eV) of the argon laser. The PL
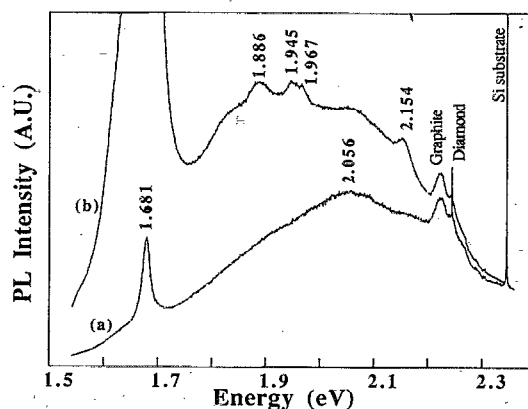

FIG. 2. The PL spectra of (a) 0% nitrogen sample and (b) of 0.1% nitrogen-doped sample employing the 514.5-nm laser line. Raman bands are labeled as to origin and the peak energy of the PL bands are indicated.
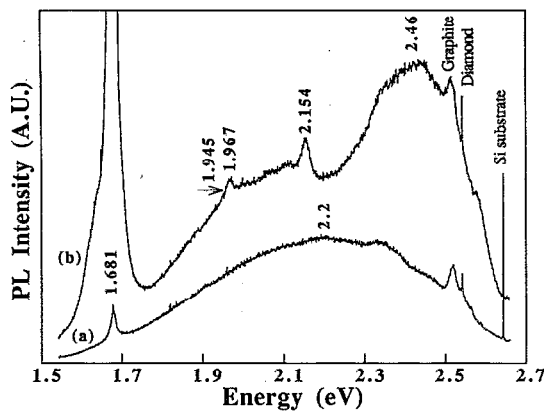
FIG. 3. The PL spectra of (a) 0% nitrogen sample and (b) of 0.1% nitrogen-doped sample employing the 457.9-nm laser line.

FIG. 4. The spectra of the broadband PL of the 20-h sample at various temperatures.

spectra are shown in absolute energy scale. The PL spectra of the undoped diamond film exhibits the fairly smooth broadband line shape centered at ~2.05 eV, and also exhibits the 1.681-eV band which has been attributed to an optical transition in a Si complex center.[10,23–27] However, the spectra of the N-doped film indicates a redshift of the broadband luminescence center as well as a line-shape change. Furthermore, the nitrogen-related bands at 2.154 and 1.945 eV are present. Studies carried out by Davies et al.[7] have suggested that the 1.945-eV band is due to the substitutional nitrogen-vacancy optical center. Collins et al.[6] proposed that the 2.154-eV band is the result of a transition in a center consisting of a single substitutional nitrogen atom with one or more vacancies. Yet another PL band at 1.967 eV is also present in the spectra (barely distinguishable from the 1.945-eV band), which might also be due to a nitrogen-related center. The 1.967-eV band is also CL active, as has been reported by Ruan et al.[26] The possibility that the 1.967-eV band is nitrogen related will be the subject of future investigation.

In order to examine in further detail the line shape of the broadband luminescence, the 457.9-nm blue laser line (2.71 eV) was used for excitation. Figure 3 shows the spectra of the 0% and of the 0.1% nitrogen-doped diamond films for this laser frequency. The broadband luminescence of the undoped diamond film retained its relatively unstructured line shape; however, the maximum intensity is shifted towards higher energy and is centered at ~2.2 eV. The spectra of the nitrogen-doped diamond film exhibits the nitrogen-related band at 2.154 eV, as well as the 1.967-eV band. The 1.945-eV band, which appeared with the 1.967-eV band as a doublet in the spectra obtained using the green laser line, can not be clearly distinguished in the spectra taken using the blue line. This overlapping of the two bands is a resolution artifact of the scaling of the spectra using the blue laser line. A relatively wide band with linewidth ~0.3 eV centered at 2.46 eV is also present. Similar wideband luminescence has been observed in both natural and synthetic diamonds,[28–30] and is commonly referred to as "band A" luminescence. This band has variable peak energy and linewidth depending on the concentration of the nitrogen in the diamond and on the diamond type.[28] The band A luminescence has been sug-
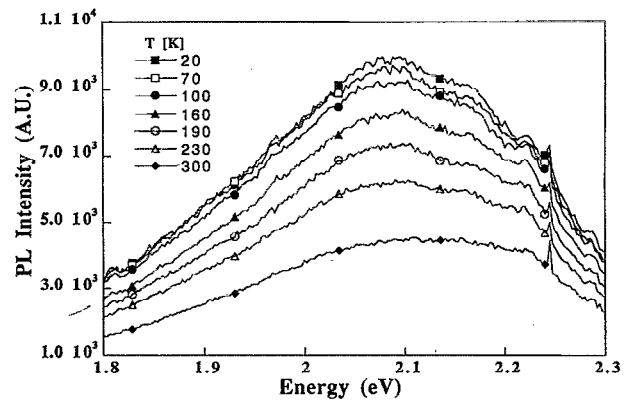
gested to originate from aggregates of nitrogen which consist of a nearest-neighbor pair of nitrogen atoms.[30] The presence of the aggregate form of nitrogen in the CVD diamond films and in diamond grown by the combustion flame method has also been reported for cathodoluminescence measurements.[31–33] It was there shown that the band A centers may be localized at dislocation-type defects in the CVD diamond. Our observation of the three nitrogen-related bands in the spectra may indicate that the paramagnetic (1.945, 2.154 eV) as well as the nonparamagnetic (band A) forms of nitrogen centers can exist simultaneously in the CVD diamond films. It is also evident from the spectra that the incorporation of nitrogen caused a distortion in the line shape of the underlying broadband luminescence. If the broadband PL had been due to the nitrogen-lattice interaction, the line shape would have been invariant, and a change in the intensity would have been anticipated.

A second series of experiments and analysis were conducted to further rule out the possibility of the broadband luminescence being of vibronic origin. According to the theoretical model of the electron-lattice interaction,[20,34] the total band intensity which includes the zero-phonon line and its vibronic sideband is expected to be independent of temperature. As the temperature increases, the zero-phonon line intensity decreases, and the vibronic band intensity is expected to increase as

$$I \sim \coth(\hbar\omega/2k_B T), \qquad (1)$$

so as to keep the total intensity constant with temperature (where the ZPL and sideband intensities are taken relative to the total band intensity).[20] The width of the vibronic band is also expected to increase with temperature as the square root of Eq. (1). In this relation ω is the central frequency of the vibronic band and k_B is the Boltzmann constant. Equation (1) depicts the effect of the interaction between the thermal vibrations of the lattice and the optical centers on the PL vibronic band. According to this formulation, as the temperature increases, more phonons are created in the material and are available to interact with the optical center transitions: this interaction should appear as a vibronic band in the PL spectra. However, as shown in Fig. 4, we found instead that
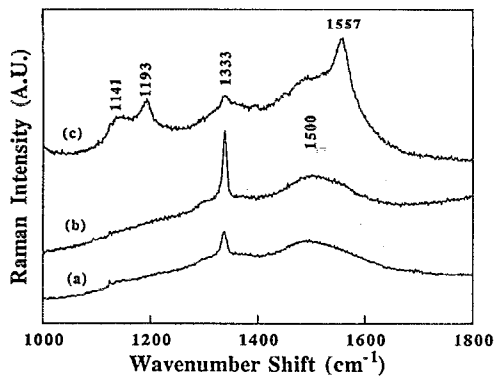
FIG. 5. The Raman spectra of (a) 0%, (b) 0.1%, and (c) 2% nitrogen-doped samples.

FIG. 6. Correlation between the broadband PL intensity and the graphitic Raman intensity.

the broadband PL intensity of the 20-h sample exhibits a ~60% decrease with increasing temperature without any significant change in the bandwidth. Furthermore, no ZPL lines were present at the low-temperature spectra. However, the ZPL responsible for the vibronic band in brown diamonds as well as the ZPL of nitrogen centers are known to be sharp and well pronounced in low-temperature spectra.[9,30] The temperature dependence we observed is thus not characteristic of a vibronic interaction. This will be discussed in further detail in the next section of this paper; it will be shown there that a nonradiative channel attributed to a density of gap states competes with the PL process and quenches the broadband luminescence.

The results of the first and second experiments suggest that the broadband PL in diamond films is not due to the nitrogen-lattice interaction system, nor is it of other vibronic origins. The incorporation of nitrogen instead manifests itself in a change in the PL line shape toward the lower energy side resulting from the electron-phonon coupling in the 2.154- and in the 1.954-eV nitrogen centers.

We now present the preliminary results of the effects of nitrogen doping on the diamond quality. The Raman spectra of the 0%, 0.1%, and 2% nitrogen-doped diamond films are shown in Fig. 5. The spectrum of the 0.1% nitrogen-doped film indicates that this film has the better quality diamond: the graphitic-to-diamond ratio (I_G/I_D) was found to be 4.6, whereas for the 0% nitrogen-doped film the graphitic-to-diamond ratio was 9.3. It is important to note that the Raman cross section from graphite is ~75 times larger than that from diamond,[35] which implies that the diamonds in the research presented here are of good quality. The spectrum of the 2% nitrogen-doped film indicates that a degradation of the diamond structure occurs at that relatively high nitrogen doping. It appears also that the graphitic phase of the 2% nitrogen-doped film exhibits an additional bonding type at 1557 cm^{-1}. Other Raman lines are also present at 1141 and 1193 cm^{-1} which we speculate to be due to bonding between nitrogen and carbon. We also note that the presence of nitrogen in the diamond film enhances significantly the 1.681-eV PL band. More detailed work will be carried out to investigate the nitrogen effect on the quality of the CVD diamond films.
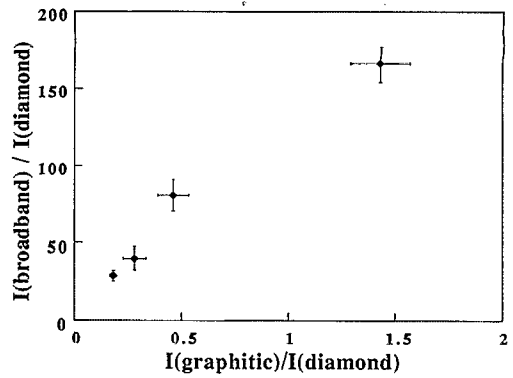
B. Characterization of the broadband PL

Figure 6 shows the correlation between the Raman intensity of the graphitic phase and the intensity of the broadband PL. This correlation was found and described in detail in a previous study.[23] In that study a film was grown in a series of stop growths until it constituted a continuous film 4 μm thick. At regular time intervals the growth sequence was interrupted and the film was characterized. It was found that, as a function of growth time, as the graphitic phase increases so does the intensity of the broadband PL. We have suggested that the amorphic graphitic phase introduces a state distribution in the band gap which provides transition centers for the photoexcited carriers, thus resulting in the broadband PL. We now present the results of a further investigation of the broadband PL obtained from the 20-h and the 40-h undoped diamond films. We establish that it has PL characteristics similar to those found in amorphous materials.

In general the PL process can be expressed by the following equation:[36]

$$\left(\frac{I}{I_0}\right) = \frac{P_R}{(P_R + P_{NR})}, \tag{2}$$

where P_R and P_{NR} are the probabilities for the radiative and the nonradiative recombination, respectively; I is the PL intensity; and I_0 is the PL intensity for the temperature approaching absolute zero. If there exists a single activation energy E_A for P_{NR} for which the thermal quenching of the luminescence is of the form of a Boltzmann activated process: $\exp(-E_A/k_BT)$, and P_R is sensibly independent of temperature, then Eq. (2) becomes

$$\frac{P_{NR}}{P_R} = \frac{I_0}{I(T)} - 1 \sim \exp\left(\frac{-E_A}{k_BT}\right). \tag{3}$$

By plotting $\log\{[I_0/I(T)]-1\}$ versus $1/T$ a straight line should be obtained from which E_A can be evaluated. Figures 7 and 8 show the plots of $\log\{[I_0/I(T)]-1\}$ versus $1/T$ for our experimental data, $I(T)$, for the 20-h and the 40-h samples, respectively. The insets in the figures show $I(T)$ versus the temperature of the samples. The experimental data in these figures indicate the existence of a continuous distribution of activation energies $E(T)$ rather than a single E_A associated with one energy level of a specific defect. Such a
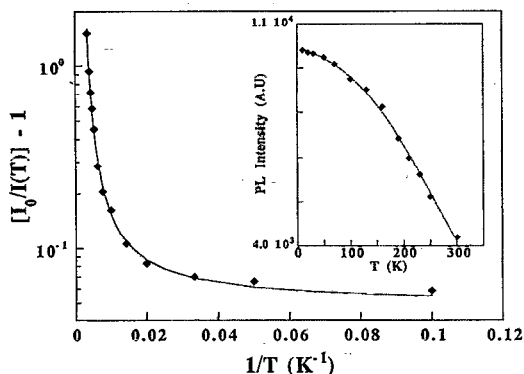
FIG. 7. The functional behavior of the broadband PL vs $1/T$ as obtained from the 20-h sample. The inset shows the PL intensity vs temperature.

FIG. 9. A fit to Eq. (4) of data taken from (a) the 20-h sample and (b) the 40-h sample.

continuous distribution of activation energies $E(T)$ indicates in turn a corresponding distribution of localized energy states in the band gap of the CVD diamond film. $E(T)$ may thus be viewed as corresponding to the binding energies of these localized states. The data in Figs. 7 and 8 can be fitted by the equation

$$\frac{I_0}{I(T)} - 1 \sim \exp\left(\frac{T}{T_0}\right), \qquad (4)$$

for which T_0 is a constant to be determined. Figure 9 shows the plot of $\log\{[I_0/I(T)] - 1\}$ versus T for the same data points used in Figs. 7 and 8. This form of quenching of the PL which we find in our studies has also been observed and its theory developed by Street et al.[19,21,22] in their extensive work on amorphous Si:H. We note that the broadband PL intensity in the diamond films exhibits a much slower decrease with increasing temperature than the PL intensity reported for a-Si:H. A smaller dependence on temperature was also reported for amorphous C:H,[15,16] for which the latter group reported a temperature dependence of the form of Eq. (4) consistent with our findings. We propose that the broadband PL observed in diamond films is due to the presence of amorphous C or C:H structures.
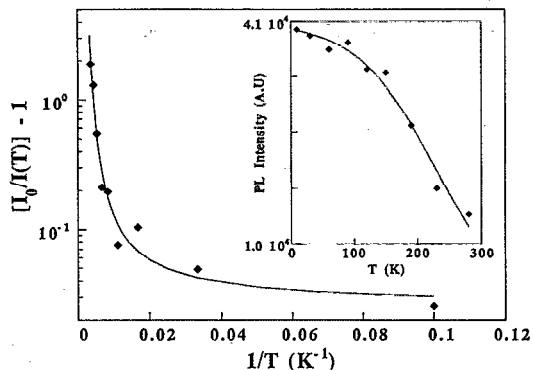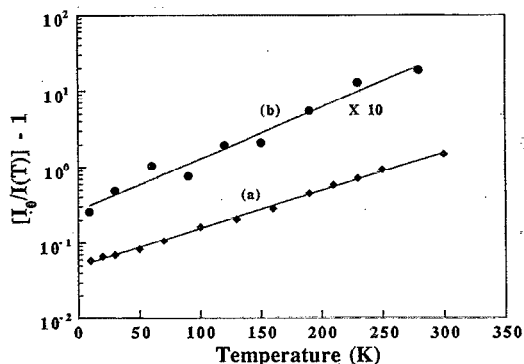
According to the model developed by Street et al. for amorphous materials,[21] there exists an in-gap state distribution $N(E)$ of the form

$$N(E) \sim \exp(-E/E_0), \qquad (5)$$

where the E's are the energies below the conduction band and E_0 is a constant which reflects the degree of randomness in the material. For materials of relatively small bond length or angle distortion, E_0 is small, implying that $N(E)$ is a relatively rapidly decaying function and hence does not extend substantially into the band gap. The same generalized model applies also to an in-gap state distribution extending above the valence band. They concluded that $N(E)$ provides transition centers for the photo-excited carriers for which transitions take place via thermal release from these centers. Based on this model, an equation has been derived to relate the experimental constant T_0 in Eq. (4) and E_0, as follows:[21]

$$E_0 = T_0 k_B \ln(\omega_0 \tau_R), \qquad (6)$$

where ω_0 is the escape frequency of the photoexcited carriers from the state distribution and τ_R is the radiative decay time of the PL. One method of finding $\omega_0 \tau_R$ is from lifetime measurements which at present are beyond our current capabilities. However, by inferring the value of $\omega_0 \tau_R$ (as described in the following paragraph) and determining T_0, the latter which may be found from plots of the type presented in Fig. 9, E_0's for both samples can be estimated and compared.

From the data presented in Fig. 9, we have calculated T_0 to be $\sim 85 \pm 4$ K for the 20-h sample and T_0 to be $\sim 65 \pm 9$ K for the 40-h sample. This is in contrast to $T_0 \sim 23$ K reported for hydrogenated amorphous silicon.[21] Using these values of T_0 we may infer E_0 and the corresponding in-gap state distribution width by the following reasoning. It can be argued that the term $\ln(\omega_0 \tau_R)$ in Eq. (6) has relatively small variation for different samples made of the same material. The escape frequency ω_0 in general depends upon the cross section of the bond types involved in the optical transition. Since for both of our samples the same type of bonding, sp^2, has been assumed to initiate the PL, ω_0 may safely be assumed to have the same value for the 20-h and the 40-h samples. The radiative decay time τ_R, on the other hand, has a larger variation depending on the characteristics of the state distribution.

FIG. 8. The functional behavior of the broadband PL vs $1/T$ as obtained from the 40-h sample. The inset shows the PL intensity vs temperature.
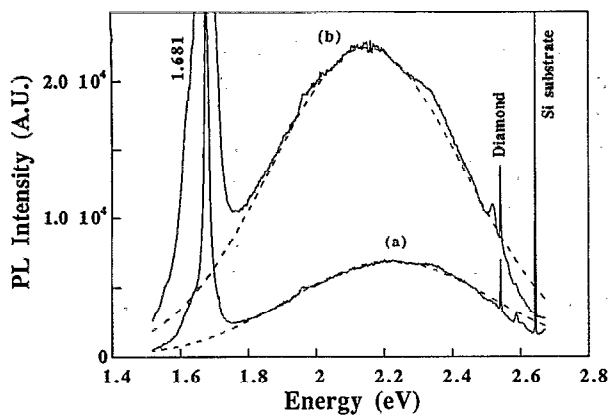
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FIG. 10. The broadband PL of (a) the 20-h sample and (b) the 40-h sample. Data was taken utilizing the 457.9-nm laser line at room temperature. The dashed line represents the Gaussian fit.

FIG. 11. Schematic representation of the in-gap state distribution of (a) the 20-h sample and (b) the 40-h sample.

Since the product $\omega_0 \tau_R$ is the argument of a logarithmic function which is slowly varying, the value of $\ln(\omega_0 \tau_R)$ may assume approximately the same value for both of our samples. In light of the above discussion, we may conclude that the in-gap state distribution of the 20-h sample ($T_0 = 85$ K) extends more widely into the band gap than the state distribution of the 40-h sample ($T_0 = 65$ K). The above finding may imply that the 20-h sample exhibits greater variations in the sp^2 bond length than the 40-h sample.

Further information concerning the density of the state distribution may be obtained from the intensities of the broadband PL. Figures 10(a) and 10(b) show the PL for the 20-h and for the 40-h sample, respectively. Both spectra exhibit a good fit to a Gaussian function with slight asymmetry toward the higher energy range. It can be seen that the PL intensity of the 40-h sample ($I_{PL}/I_D \sim 4.6$) is about three times the intensity of the 20-h sample ($I_{PL}/I_D \sim 1.6$), which is indicative of its higher density of states. We base the latter conclusion on the ability to correlate the PL intensity of the broadband to the sp^2 Raman intensity as was shown previously in Fig. 6. To further support this conclusion, the ratios of the graphitic to the diamond Raman lines I_G/I_D were calculated for both samples. It was found that $I_G/I_D = 0.7$ for the 20-h sample and $I_G/I_D = 1.7$ for the 40-h sample. The higher concentration of the sp^2 phase in the 40-h sample may explain the relatively higher density of states which are manifested in the stronger PL intensity.

More extensive experiments need to be carried out to further quantify and model the state distribution and to determine the bands involved in the optical transitions. In amorphous carbon material, the sp^2 bonding creates sigma bands (σ, σ^*) and pi bands (π, π^*)[13] for which optical transitions can occur. At present we hypothesize that the π-π^* band transitions are responsible for the broadband PL. The basis of this hypothesis lies on the knowledge that the allowable optical transitions in crystalline graphite[37] are the π-π^*, σ-σ^*, and the σ-π^* for which only the π-π^* bands lie in the energy range closest to our laser excitation energy.

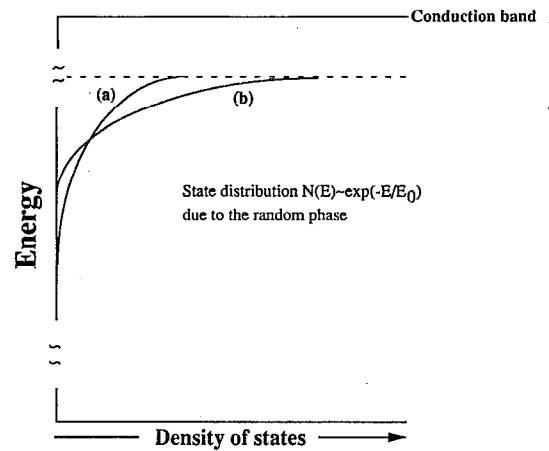Our initial investigation suggests the existence of continuous in-gap state distribution is responsible for the broad-band luminescence in the CVD diamond films. Our ability to determine T_0 by fitting our data to Eq. (4) and the line shape of the luminescence may indicate that the profile of the in-gap distribution is an exponential function. Srikanth et al.[38] have reported an in-gap exponential distribution of defect states of the form shown in Eq. (5). They deduced the existence of an exponential state distribution from conduction measurements in CVD diamond films. A comparative study of PL and electrical conduction would be useful to determine how the state distribution deduced from the PL measurements might affect the electrical transport in the CVD diamond films. The curves in Figs. 11(a) and 11(b) represent schematically the density of the in-gap state distributions for the 20-h and 40-h samples, respectively. The state distribution of the 20-h sample is of lower density than that of the 40-h sample but extends more widely into the band gap of the diamond, implying a higher degree of randomness in this sample.

The last part of this section details the investigation of the temperature behavior of the 1.681-eV PL band for the 20-h and the 40-h samples in the temperature range 10–300 K. The PL spectra of the 1.681-eV optical system is shown in Fig. 12 for various temperatures. The spectra were obtained from the 20-h sample which is ~2 μm thick. The 1.681-eV optical system consists of a zero-phonon line at 1.681 eV and its vibronic sidebands at 1.616 and 1.639 eV, first reported in Ref. 27. Figure 13 shows the PL intensity plotted as a function of temperature. Since the 1.681-eV band is superimposed on the low-energy side of the broadband PL, the values of the intensities in Fig. 13 are compensated by subtracting the temperature-dependent PL background. It can be seen in the figures that the PL intensity in the temperature range 10–100 K is approximately constant, whereas a strong quenching of the PL takes place at $T > 100$ K. The data taken from the 40-h sample (~4 μm thick) was inconclusive due to large scattering of the PL signal. This is consistent with our previous findings[23] that the optical centers responsible for the 1.681-eV PL emission reside mainly next to the interface of the diamond and the Si substrate. The film thickness accompanied by the presence of high density of grain
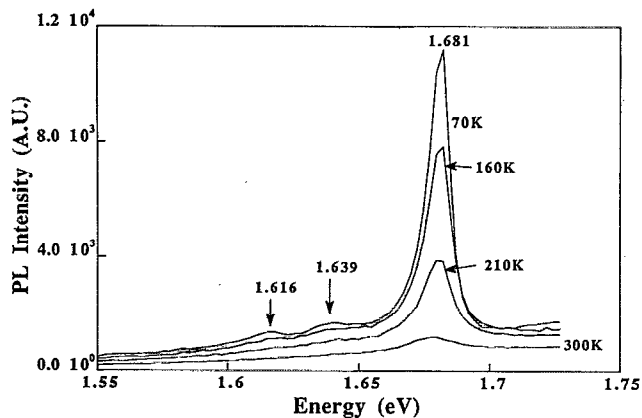
FIG. 12. The 1.681-eV PL band for various temperatures. The data were taken using the 514.5-nm laser line.

boundaries makes the PL signal of the 1.681-eV centers difficult to collect.

The data in Fig. 13 can be fitted by Eq. (3), with an activation energy $E_A = 90$ meV (± 10 meV). Thus ~90 meV is the energy needed to channel the photocarriers from the excited state to the nonradiative path. A similar PL characteristic of the 1.681-eV center has been reported previously,[4,27] for which the latter group found E_A to be ~70 meV. The small difference between their value of activation energy and our finding may be due to experimental error, but we can not exclude the possibility that different activation energies are due to differences in film quality.

IV. CONCLUSIONS

Raman and various photoluminescence techniques were employed in this study to investigate the role of nitrogen doping on the optical spectra of the CVD diamond films and to determine the origin of the broadband luminescence. Our experimental results suggest the following conclusions:

(a) The PL spectra of the 0.1% nitrogen-doped CVD diamond sample indicates that the incorporation of nitrogen into the diamond matrix introduces the optical centers at
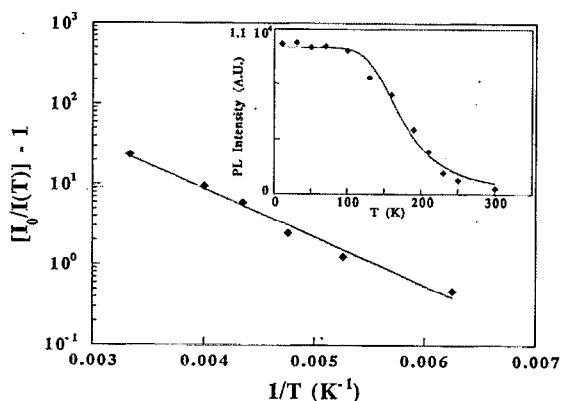

FIG. 13. The functional behavior of the 1.681-eV PL intensity vs $1/T$. The inset shows the PL intensity vs temperature.

2.154 and 1.945 eV, and possibly introduces as well a new nitrogen-related center at 1.967 eV. The band A luminescence was also found in our PL spectra. The spectra of both nitrogen-doped and undoped films exhibit the broadband PL; the nitrogen-doped sample, however, has a line-shape distortion of the underlying broadband PL due to the vibronic interaction of the nitrogen centers.

(b) A higher percentage of nitrogen doping results in a degradation of the diamond quality as indicated by the Raman spectra of the 2% nitrogen-doped sample. Furthermore, new features in the spectra were present and we speculate that they are due to nitrogen-carbon vibrational modes. Future work is in progress to investigate the influence of the percentage of nitrogen doping on diamond quality.

(c) The temperature behavior of the broadband PL indicates that the band does not originate from a vibronic interaction. For the vibronic band, an increase in temperature would result in an increase in intensity and width. However, we found that the broadband PL in the CVD diamond films exhibits rather a decrease in intensity with increasing temperature without any significant change in width. Hence, we exclude the possibility of the broadband PL being due to any vibronic system of an electron-lattice coupling.

(d) The intensity of the broadband PL was found to exhibit a temperature dependence characteristic of optical emission from a continuous distribution of gap states. The temperature dependence of the PL was determined to follow the functional behavior described by Eq. (4), which is characteristic of an amorphous material.[21] In light of the above finding and from the correlation of the PL intensity to the sp^2 amorphous phase determined here and in our previous work,[23] we suggest that the broadband PL in CVD diamond films is due to the optical transitions in an in-gap state distribution, where the in-gap state distribution is introduced by the amorphous phase of the sp^2 hybrid bondings.

(e) Our initial investigation into the characteristics of the in-gap state distribution suggest that it is of an exponential shape. It was found that the width as well as the density of the state distribution varied from sample to sample. These differences in the specifics of the state distribution are attributed to the film quality which in turn depends on the growth conditions.

(f) The 1.681-eV optical center exhibits stronger PL emission for the nitrogen-doped film than for the undoped film. The temperature behavior of the 1.681 PL band has characteristics of the Boltzmann activation process with an activation energy of nonradiative transition $E_A \sim 90$ meV.

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