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Defect photoluminescence in polycrystalline diamond films grown by arc-jet chemical-vapor deposition

S. Lal, T. Dallas, S. Yi, S. Gangopadhyay, and M. Holtz
Department of Physics, Texas Tech University, Lubbock, Texas 79409

F. G. Anderson
Department of Physics, University of Vermont, Burlington, Vermont 05405

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We have studied a series of sharp photoluminescence emission lines between 1.65 and 1.80 eV in synthetic diamond films. The series of lines is decomposed into a set of parent lines plus vibrational sidebands spaced 24 meV apart. This energy does not correspond to any phonons with high density of states in the diamond crystal. The relative intensities of the main lines exhibit no temperature dependence (between 20 and 160 K), implying ground-state splitting. The narrow linewidth and temperature-independent emission energy imply only weak interaction with the diamond host. The temperature-dependence of the linewidth is well described by thermal broadening. We attribute the emission to optical centers as a consequence of tungsten incorporation into the diamond film. The tungsten originates from the electrode during deposition. [S0163-1829(96)09044-3]

I. INTRODUCTION

The advent of chemical-vapor deposition (CVD) growth methods of diamond films has accelerated potential application in electronic, optical, and mechanical devices. Improvements in the various CVD techniques have greatly reduced the variety (and enhanced control) of defects. Still, impurities are often inadvertent consequences of the growth process and are undesired. Photoluminescence (PL) methods are capable of achieving low detection limits and give important clues about the roles defects play in recombination processes.

When CVD diamond is excited by visible *sub-band-gap* light, a broadband PL, as well as several sharp features, are generally observed. Sharp bands at 1.945 and 2.155 eV have been extensively studied in natural diamond and are believed to be nitrogen related.[1,2] Emission at 1.681 eV is thought to be related to an optical center containing one or two silicon atoms and nitrogen.[3–7] However, a new series of luminescence bands has been reported in continuous-wave PL (CWPL) near 1.7 eV in hot-filament CVD grown diamonds.[8–11] These have never been seen in natural diamond. In this article, we discuss in detail the nature of these red emission bands, and give a plausible interpretation for their origin. We also discuss the broadband emission underlying these sharp features. We have also performed time-resolved PL (TRPL) studies, and report our findings regarding the sharp lines and the underlying broadband emission.

The remainder of this paper is organized as follows. We first describe our experimental conditions. Next we discuss sharp emission features in the 1.7 eV range, followed by a brief section on the broadband emission. Finally, we summarize our results.

II. EXPERIMENTAL DETAILS

The diamond films were deposited on molybdenum substrates by arc-jet CVD (Norton Diamond Film, Northboro, MA). The samples used in the PL measurements were free standing, approximately 1 cm^2 in area, and 0.225 mm thick. Raman measurements confirmed high crystalline quality.

The CWPL and TRPL studies were carried out with the sample mounted in a closed-cycle helium refrigeration system. Temperature was controlled between 20 K and room temperature. The CWPL was excited primarily with the 2.41-eV green line from an argon-ion laser, but confirmed with other visible lines from the same laser, a helium-neon laser, and a helium-cadmium laser. The spot size on the sample was $\approx$1 mm in diameter. A long-pass filter reduced the intensity of scattered light entering the spectrometer. Light was dispersed by a 0.22-m double monochromator and detected by a cooled InGaAs photomultiplier. All spectra were corrected for the instrumental response.

The TRPL measurements were accomplished using a nitrogen pumped dye laser emitting at 2.48 eV (Coumarin 500 dye cell), which supplied 150-μJ pulses of 500 ps [full width at half maximum (FWHM)] duration with a 10-Hz repetition rate. The same spectrometer was used to analyze the light, which was detected by a two-stage, proximity focused, multichannel plate photomultiplier. The output of the detector was fed into a waveform digitizer (fast analog) and the signal was averaged over multiple pulses. Decay curves were analyzed using an iterative-reconvolution method. Details of the analysis are described elsewhere.[12] This system has shown reliable temporal resolution down to 100 ps.

III. SHARP PHOTOLUMINESCENCE FEATURES

Figure 1 shows CWPL spectra of the CVD diamond film spanning the 1.4–2.20 eV photon energy range. These were taken with the sample at 20 K and room temperature. We see a broad emission which spans the red range in each spectrum. We will return to this in the next section. Additionally, several sharp peaks are seen in the 20 K spectrum, which we divide into two groups. The first group consists of two lines at 1.681 and 2.155 eV. The weak 1.681-eV feature has been

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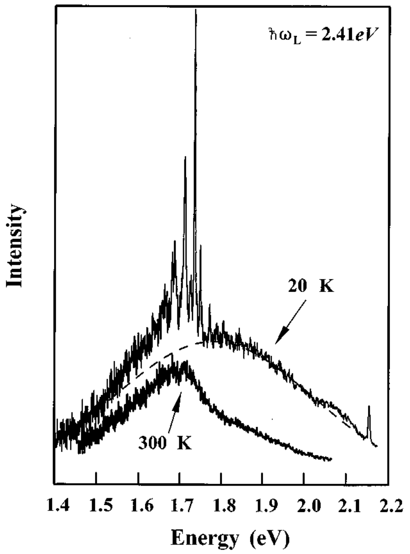

FIG. 1. CWPL spectra of an arc-jet CVD diamond taken at 20 and 300 K. The dashed curve, centered at 1.8 eV, corresponds to the broadband PL discussed in the text.

previously assigned to silicon impurities.[3–7] The line at 2.155 eV has been attributed to a nitrogen-vacancy complex.[13]

The second group of sharp features is composed of lines at 1.663, 1.688, 1.711, 1.723, 1.735, 1.741, 1.750, 1.754, 1.759, and 1.772 eV. These are the main focus of this paper. A detailed spectrum of the 1.60–1.80 eV region is shown in Fig. 2. This spectrum is from a film which showed no 1.681-eV, silicon-related line. Also absent is the 1.772-eV line, which remains unidentified. All but the two highest-energy lines (1.759 and 1.772 eV) were previously reported in hot-filament CVD polycrystalline diamond, grown on silicon substrates with a tungsten-carbide filament, but were not assigned.[8] These lines may also be present in hot-filament CVD films (tungsten filament and nickel substrate) where a very low background is obtained.[14] Since our films were grown on a molybdenum substrate, we conclude that substrate impurities do not play a role in the presence of these sharp lines. We suggest, rather, that they are related to tungsten impurities incorporated into the film due to erosion of the filament.

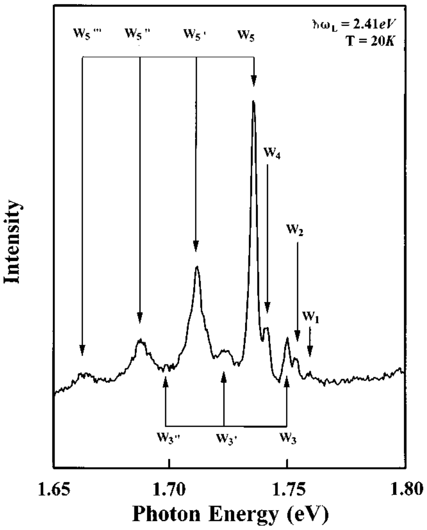

FIG. 2. Detailed spectrum of a CVD diamond film in the region where we observe the sharp series of peaks. The primary lines are labeled W_1 through W_5, with sidebands denoted by successive primes and subscripts corresponding to the parent band.

Upon carefully examining the spectrum in the range of the sharp lines, we observe an interesting pattern. The strongest line at 1.735 eV has one weaker neighbor 6 meV higher in energy. The peak at 1.750 eV has *two* weaker neighbors, one upshifted 4 meV and the second upshifted 9 meV. We denote these bands by W_i (i indexing the five bands) in Fig. 2.

The interpretation of two primary parent bands, with the satellites mentioned, is supported by the following observations. The slightly broader bands below W_5 in this set stem from two series of sidebands incrementally downshifted from the intense W_3 and W_5 parents. For W_5 at 1.735 eV, the sidebands are downshifted by 24, 47, and 72 meV, i.e., a sequence with spacing of ≈24 meV. These are denoted in the figure by successive primes to the W_5 parent. There is evidence for three further bands in this series, confirmed in other spectra, but they are extremely weak. For the 1.750-eV band (W_3), the sidebands are weaker in intensity and mingle with the previous series. This makes them difficult to extract. However, there is clear evidence of the first sideband downshifted by 27 meV, and possibly a second at 51 meV which was confirmed in other spectra. Both series show the same repeat unit, suggesting that they arise from vibrational replicas of the emission process.

The energy of the participating vibrations is 25 meV≈200 cm^{-1}. This is well below the lowest phonon energy of the host lattice which possesses a high density of states [TA(L) at 563 cm^{-1}].[15] This suggests a band resonant mode is involved in the sharp series of PL lines. The replica energy is consistent with vibration of a massive substitutional defect, which we suggest here to be tungsten. The low-temperature linewidth of the W_5 line is ≈2.5 meV. Successive sidebands (corresponding to overtones in vibrational replicas) exhibit increasing linewidth, implying that the vibration participating in the PL process has a linewidth of ≈5 meV. Sidebands to defect PL in diamond have been discussed in Ref. 6, specifically for the 1.681-eV center related to silicon. They note that a common sideband energy for several defect-related PL processes is observed at 42 meV. This is also well below the TA(L) energy. The 42-meV band is significantly broader (25 meV) than the 5 meV we measure. We do not observe any strong feature at 42 meV, although it is conceivable that it is buried beneath our sharper series.

We now turn our attention to the temperature dependence of the ''W'' lines in Fig. 2. The emission energy was found to be constant (to within 1 meV) between 20 and 250 K. In the upper panel of Fig. 3 we show the decrease in intensity of the W_5 line with increasing temperature. The sharp lines diminish more rapidly than the broadband emission as temperature rises. By room temperature, the sharp lines are quenched (Fig. 1). Between 20 and 100 K the CWPL intensity decreases only slightly, indicating dominance by the radiative transitions. Above 100 K, the intensity diminishes exponentially due to competition with nonradiative processes. Analysis yields an activation energy for nonradiative

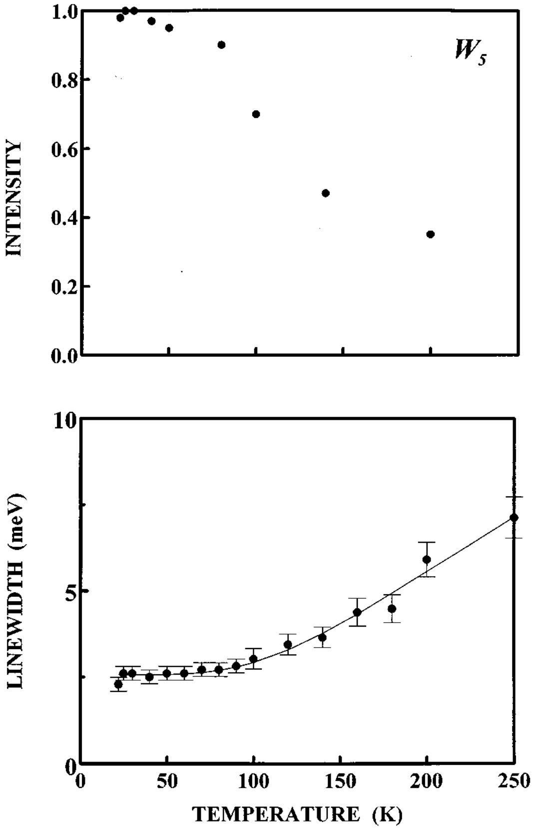

FIG. 3. Temperature dependence of the W_5 line. The upper panel shows the normalized intensity. The lower panel shows the linewidth to increase with temperature. The curve is a fit using Eq. (1). Both panels have the same temperature scale. No temperature dependence is seen to the relative intensities of the main lines.

processes of ≈37 meV. This behavior has been previously seen for the 1.681-eV (silicon related) emission, which exhibits an activation energy of 70 meV.[16]

We also find that the intensity ratios (W_4 to W_5 and W_3 to W_5) are independent of temperature from 20 to 160 K. This is the range for which W_3 and W_4 were sufficiently intense to obtain an accurate measurement. We take this to be consistent with the interpretation that *ground*-state splitting is responsible for the multiple *W* lines observed in the PL process. This could be verified by measuring the temperature dependence of intensities for corresponding lines in the absorption spectrum.

The lower panel of Fig. 3 shows the temperature dependence of the linewidth for the W_5 line, corrected for instrumental resolution. In the low-temperature range, the linewidth is 2.5±0.1 meV and remains constant to ≈80 K. Above this temperature range the linewidth gradually increases until it reaches 7.1±0.5 meV at 250 K. This temperature dependence is not consistent with the configuration-coordinate model,[17] and stays well below kT above 30 K. The temperature dependence of the linewidth is well described by a fit according to

$$\mathrm{FWHM}=\hbar\omega_0+\alpha n_B(\hbar\omega,kT), \tag{1}$$

where n_B is the Bose function and $\hbar\omega=30.6\pm0.8$ meV represents the average vibrational energy causing the broadening. This is acceptably close to the 37 meV from fitting the intensity decrease. The other fit parameters are $\hbar\omega_0=2.55\pm0.04$ meV and $\alpha=14.5\pm0.4$ meV. Results of the fit are shown in the lower panel of Fig. 3. This analysis indicates that the observed broadening is thermal (phonon population).

Incorporation of transition-metal elements into a solid host, as we suggest is the case here of tungsten into diamond, is well described by the Ludwig and Woodbury model.[18] The narrowness of the CWPL lines in our polycrystalline samples suggests that the impurity occupies a high symmetry position within the lattice. A more detailed account of this is in preparation.[19] The line shape is fit adequately by either a Gaussian or a Voigt function. Attempts to fit the data using a Lorentzian line shape were poorer. Higher-resolution spectra at lower temperature would be useful for determining more closely which line shape provides the best description of the *W* lines.

Since our temperature dependence is consistent with splitting of the *W* levels in the ground state, we now discuss two recombination scenarios. The first possibility involves recombination from the conduction-band minimum to the defect levels. This scenario receives some support from the observation that the sharp series emission spectrum is independent of excitation photon energy from 1.96 eV through the near ultraviolet. (We note that better intensity was obtained for lower excitation photon energies.) From this, we can infer that activation of the optical center begins with absorption of a photon by promoting an electron into a continuum (the host conduction band). PL excitation between the 1.735 eV emission energy and 1.96 eV would be necessary to support this scenario. The narrow linewidth and temperature independence of the emission energy argue against this picture.

The second possibility is recombination between levels within the defect. That is, discrete excited state to discrete ground state (which is split into the multiplet). This is supported by the line shape analysis. For the emission energy to remain constant to 250 K, it is possible that the upper and ground states have the same temperature dependence, which we expect to be gradual given the weak interaction between the defect and the host lattice. PL excitation studies would help to confirm or rule out this description.

IV. BROADBAND EMISSION

Figure 1 shows spectra for a CVD diamond film taken at two representative temperatures. We observe quenching of the sharp features and a more gradual decrease of the broadband PL intensity. What is seen in this figure, and is especially clear in the 300-K spectrum, is that the broadband PL is composed of at least two bands. The broadest band appears to be Gaussian and is centered near 1.80 eV (dashed curve in Fig. 1, FWHM≈0.24 eV). This band has been reported in polycrystalline diamond, and was attributed to a disordered carbon phase.[20–22] The other component is not symmetric and exhibits maximum intensity near 1.70 eV. The latter band appears to be present only when tungsten impurities are possible contaminants. This asymmetric band comes from vibronic coupling of the *W* levels to the host lattice.

TRPL decay curves were measured at all sharp peak energies observed in the CWPL spectrum, as well as at several energies where we observe only the broadband emission between 1.55 and 2.07 eV. For all measurements taken at photon energies which did not coincide with a sharp line, only three common lifetimes were observed: 0.58 ± 0.05, 1.6 ± 0.1, and 6.5 ± 1.0 ns. These lifetimes are in good agreement with separate measurements on a hydrogenated amorphous carbon film. Measurements at energies corresponding to the W lines exhibited lifetimes identical to those above. This indicates that we are only measuring the background lifetimes, and those associated with the W emission are below the instrumental limit of 100 ps. Similarly, we see no unique lifetime signature from the asymmetric band we attribute to unresolved vibronic structure associated with the W levels.

V. SUMMARY

We have performed a detailed spectroscopic analysis of sharp emission lines observed near 1.7 eV in polycrystalline CVD diamond films (Figs. 1 and 2). The common denominator for their presence appears to be tungsten, leading us to believe that incorporation of tungsten into the diamond gives rise to the series. The set appears to be composed of five (possibly six) sharp parent lines along with vibrational sidebands at 24 meV spacing. The intensity decrease with rising temperature, as well as the linewidth increase, are well described by thermal broadening (Fig. 3). The relative intensities are not temperature dependent, however, which is consistent with splitting of the parent levels in the ground state. The underlying broadband emission seen in these films (spans the red) is readily split into two broad features. One band is basically symmetric and stems from disordered carbon phases present in the diamond film. The other broadband is asymmetric and comes from unresolved vibronic coupling between the defect levels (tungsten according to our interpretation) and the host lattice.

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