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Temperature dependence of optical centers in transmission electron microscope irradiated natural IIa diamond

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ABSTRACT

Diamond, a wide band gap semiconductor material, has been attracting interest in several fields from electrics and optics to biomedicine and quantum computing due to its outstanding properties. These properties of diamond are related to its unique lattice and optically active defect centers. In this paper, we present a detailed study of the temperature-dependent linewidth and energy shift for two zero-phonon lines at 503.5 nm (3H center) and 741 nm (GR1 center). We also discuss the uses and properties of electron-photon coupling and zero-phonon lines. The results show that with the increasing temperature, both centers red-shifted and broadened, and the intrinsic defects of the GR1 center were mainly controlled by the homogeneous broadening mechanism, while the inhomogeneous broadening mechanism of the 3H center was probably caused by local stress.

1. Introduction

Owing to its outstanding properties, such as wide band gap, high thermal conductivity, high breakdown voltage, and high carrier mobility, diamond has attracted much interest in several fields from electrics and optics to biomedicine and quantum computing [1,2]. Most of the extreme properties in diamond are related to its unique lattice and optically active defect centers [3]. The isolated color centers in diamond are single photon sources with potential applications in quantum optics and quantum information processing technology [4]. For the quantum control and ultrasensitive detection of diamond devices, the diamond device's interaction with the environment should be considered. Therefore, the study of the temperature dependence of defects in diamond is an area of active research. Chen et al. in 2011 investigated the temperature dependence of nitrogen-vacancy (NV) defects in diamond by using the optically detected magnetic resonance method [5]. The vibronic properties of N3, ND1, 640 nm, H3, 3.188 eV, 594 nm, and N9 bands were also studied and their temperature dependences were described by the theory and yield effective density of coupling phonon states [6]. In this paper, we present a detailed study of the temperature-dependent linewidth and energy shift for two zero-phonon lines at 503.5 nm and 741 nm in natural IIa diamond. We also discuss the uses and properties of electron-photon coupling and zero-phonon lines.

2. Experimental methods

This work focuses on a cubic, pure, colorless, natural, type IIa diamond, which was provided by the company De Beers. The irradiation was performed by a transmission electron microscope at 800 keV at the Berkeley National Center for Electron Microscopy, California, USA. The irradiated areas were subjected to a uniform intensity of electrons over a circular region of approximately 100 μm in diameter in {1 0 0} sectors of diamond. After irradiation at room temperature, the samples were transferred to a Renishaw micro-Raman spectrometer that was fitted with Oxford Instruments Microstat liquid helium-cooled stages. Photoluminescence examination was mainly performed with an argon-ion laser using an excitation wavelength of 488 nm and recorded as a function of temperature in the 7–300 K range by means of a closed-cycle helium cryogenerator in the cold finger configuration.

3. Results and discussions

Fig. 1. A typical spectrum of the irradiated region obtained at 488 nm excitation and ~7 K.

With the increase in temperature form 7 K to 300 K, a ZPL red-shift was observed, together with intensity quenching and an

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increase in the full width at half-maximum (FWHM), as shown in Fig. 2. In the range from 7 K to 150 K, the position of both 3H and GR1 centers remained constant after which the centers shifted towards lower energies with increasing temperatures up to 300 K.

With regard to the increase in the FWHMs, we should carefully distinguish between inhomogeneous and homogeneous broadening mechanisms and a Voigt function was employed to analytically reconstruct the observed line shape. The Voigt function is defined as a spectral convolution of Gaussian and Lorentzian functions [10]:

$$y = y_0 + A\frac{2\ln 2 W_L}{\pi^{3/2}W_G^2}\int_{-\infty}^{+\infty}\frac{\exp(-t^2)}{\left(\sqrt{\ln 2}\frac{W_L}{W_G}\right)^2+\left(\sqrt{4\ln 2}\frac{x-x_c}{W_G}-t\right)^2}dt \quad (1)$$

where A and x_c are the area and center of the Voigt curve, respectively, while y_0 is the initial value of FWHMs, and W_L and W_G are the Lorentzian width and Gaussian width, respectively. W_L and W_G are proportional to the FWHMs of the pure Gaussian and Lorentzian terms, respectively. In Fig. 3, Voigt curve fitting was performed on the 3H and GR1 centers from 7 K to 300 K and the accuracy was greater than 0.95. At 7 K, both Gaussian and Lorentzian profiles of the 3H luminescence contributed similar weights to the observed linewidth, while the Gaussian contribution dominated the experimental linewidth after 160 K. These results are consistent with the conclusions inferred from the lineshapes and crystal strain field studies of Davies in 1970 [11]. However, the GR1 center showed a higher Gaussian contribution at 7 K and after 200 K, the Lorentzian contribution dominated the linewidth of the GR1 center, which is in agreement with the more efficient electron-photon coupling at higher temperatures [12].

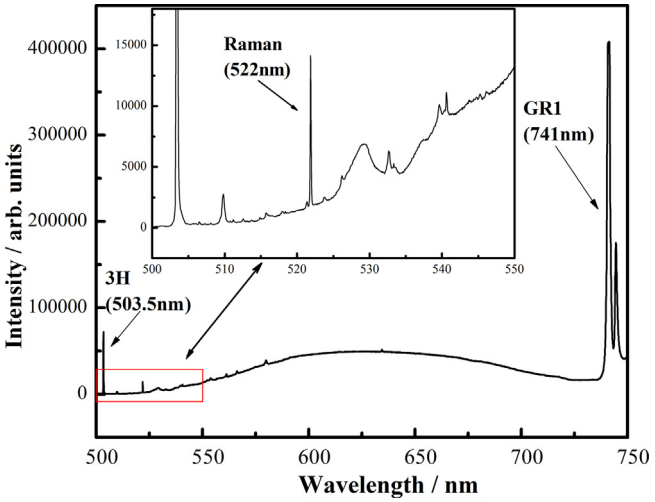

Fig. 1. presents a typical PL spectrum of the IIa diamond obtained at 7 K with 488-nm laser excitation. The zero phonon lines were observed at 503.5 nm and 741 nm, respectively. The 741-nm center was associated with a neutral single vacancy of diamond and was marked as the GR1 center [7]. The 503.5-nm center is commonly observed in IIa diamond, and is referred to as the 3H center and although it is still not well understood, it is generally accepted as being interstitial-related [8]. The magnification of the PL spectrum in the range 500–550 nm is shown in Fig. 1 where a series of peaks are caused by the vibronic coupling of defects [9].

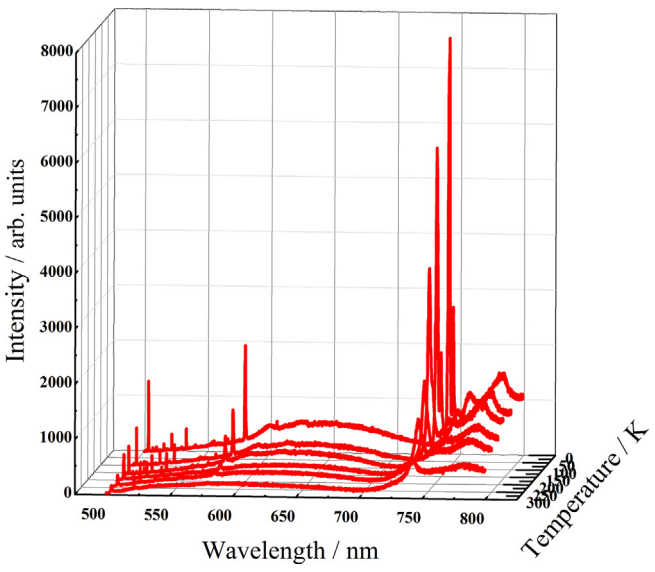

Fig. 2. Full spectra of the irradiated IIa diamond at different temperature.

The almost equal FWHMs of the Gaussian and Lorentzian terms for the 3H center were not related to any physical process but reflected the lower sensitivity of the deconvolution algorithm at low temperature where the actual linewidth was dominated by inhomogeneous broadening [13]. Thus, the actual linewidth (0.15021 cm^{-1}) of 3H should be attributed to the inhomogeneous mechanism alone. The analysis described above was also performed for all temperatures in the 7–300 K range. Fig. 4 shows the FWHM temperature dependence of the Gaussian and Lorentzian components derived from the deconvolution routine for the 3H and GR1 emission. The FWHMs of the 3H and GR1 presented in Fig. 4 were analyzed according to four-order polynomial fitting. The FWHMs of the 3H Lorentzian components were randomly distributed around a mean value of 0.12 cm^{-1} (straight dotted line), thus confirming the temperature independence of the homogeneous broadening. However, the FWHMs of the GR1 Gaussian components were randomly distributed around a mean value of 1.4 cm^{-1}, thus confirming the temperature independence of the homogeneous broadening. However, the FWHMs of the 3H Gaussian components and the FWHMs of the GR1 Lorentzian components increased for temperatures greater than 160 K. For temperatures approaching 0 K, it was considered that the FWHMs of the ZPLs will vanish.

The interaction of the active ions with phonons in crystals at the equivalent sites and the same probability determined a temperature-dependent Lorentzian shape of the emission [14]. This type of line broadening led to the homogeneous broadening, which is one of the consequences of electro-phonon coupling [12]. Inhomogeneous broadening was due to strains and the randomly distributed defects in the crystal host that caused a temperature-independent Gaussian shape [12]. Therefore, the studies of broadening mechanisms imply that the GR1 center was related to the intrinsic defect of the single neutral vacancy but the 3H center was associated with local stress, impurity, or non-symmetrical defects. In our previous works, two close C atoms were associated with the 3H center, and the first evidence of this was the existence of a large number of high-energy local vibrational modes [15]. The most obvious evidence was obtained from the 50% ^{12}C–50% ^{13}C samples in which the highest local mode of the 3H center was split into three peaks corresponding to ^{12}C-^{12}C, ^{12}C-^{13}C, and ^{13}C-^{13}C bonds [15]. Another result [16] was that 3H luminescence became stronger with the increasing nitrogen concentration in diamond, indicating that 3H was related to nitrogen. For the irradiated low-N IIa diamond, the 3H luminescence was weak and—together with the appearance of NV_0 after 750 °C annealing—implying that the 3H center was related to the atomic structure of N-C_i-C_i, which was converted into NV^0 during the migration of intrinsic defects after annealing [17]. However, the ^{15}N-doped diamond did not show the shift for the 3H ZPL [15]. Therefore, it was concluded that the 3H originated from the intrinsic defect of two close interstitials and the inhomogeneous broadening mechanism was probably caused by the local stress.