RECOMBINATION PROCESSES OF THE BROADBAND AND 1.681 eV OPTICAL CENTERS IN DIAMOND FILMS

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ABSTRACT

Micro- and macro-photoluminescence techniques were employed in this research to investigate the role of nitrogen-doping on the optical spectra of chemical vapor deposited diamond films and to determine whether the origin of the broadband luminescence is due to vibronic interaction of the nitrogen centers. The temperature behavior of the broadband PL and of the 1.681 eV silicon related optical center were analyzed. The intensity of the broadband was found to exhibit a temperature dependence characteristic of optical emission from a continuous distribution of gap states while the temperature dependence of the 1.681 eV band followed the Boltzmann quenching process.

I. INTRODUCTION

This research investigates the broadband, nitrogen-related, and 1.681 eV optical defects in chemical vapor deposited diamond films. 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 [1,2]. 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 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 [3,4]. Luminescence studies on natural brown diamonds [5] 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 eV and at ~ 1.8 eV and is very similar to the one observed in the spectra of the CVD diamond films. The origin of the PL bands of the brown diamonds has also been determined to be of vibronic nature with numerous ZPL the principal ones at 2.721 and at 2.145 eV.

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. 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 [6,7]. According to the general model of the state distribution of amorphous materials [8], 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. We also 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 introduced into the diamond matrix during growth [1,2].

II. EXPERIMENT

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 watts, 850°C

and 25 Torr respectively. Two samples involved in the nitrogen study were subjected to $H_2/CH_4/N_2$ flow rates of 500/5/0 sccm and 500/5/0.5 sccm and will be referred to as the 0% and 0.1% nitrogen-doped samples respectively according to their gas phase N_2/H_2 %. The growth time was 5 hours and the morphology consist of diamond grains. A third undoped diamond continuous sample about 2 μ m thick (described in our previous study [2]) was also used and will be referred to as the 20h sample, reflecting its growth time. The micro-PL analysis of the 0% and the 0.1% 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 μ m in diameter. Focusing was facilitated by using an Olympus BH-2 microscope. The macro PL analysis of the 20h sample was carried out employing a JANIS CCS-350 closed cycle refrigerator system. The laser was focused to a line of ~ 2 mm x 100 μ m on the sample. In both studies, an ISA U-1000 scanning double monochrometer was used to analyze the signal.

III. RESULTS AND DISCUSSION

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 Figure 1 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 of the Argon laser. The PL 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 [9]. However, the spectra of the nitrogen-doped film indicates a red-shift 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. [4] have suggested that the 1.945 eV band is due to the substitutional nitrogen-vacancy optical center. Collins et al. [3] 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 1.945eV band), which might also be due to a nitrogen-related center.



Figure 1. The PL spectra of the diamond films utilizing the 514.5 nm (2.41 eV) laser line.

In order to examine in further detail the line-shape of the broadband PL, the 457.9 nm blue laser line was used for excitation. Figure 2 shows the spectra of the 0% and of the 0.1% nitrogen-doped diamond films for this laser frequency. The broadband PL 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 bands at 2.154 and at 1.967 eV. 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. Α relatively wide band with line-width ~ 0.3 eV centered at 2.46 eV is also present. Similar wideband luminescence has been observed in both natural and synthetic diamonds, and is commonly referred to as "band A" luminescence [10]. This band has variable peak energy and line-width depending on the concentration of the nitrogen in the diamond and on the diamond type. The band A luminescence has been suggested to originate from donor-acceptor recombination process. 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 non-paramagnetic (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.



Figure 2. The PL spectra of the diamond films utilizing the 457.9 nm (2.71 eV) laser line.

A second series of experiments and analysis were conducted to further rule out the possibility of the broadband PL being of vibronic origin. According to the theoretical model of the electron-lattice interaction [11], 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 so as to keep the total intensity constant with temperature (where the ZPL and sideband intensities are taken relative to the total band intensity). The width of the vibronic band is also expected to increase with temperature. However, as shown in Figure 3 we found instead that the broadband PL intensity of the 20h sample exhibits a ~ 60% decrease with increasing temperature without any significant change in the band width. 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 [5,10]. The temperature dependence we observed is thus not characteristic of a vibronic interaction.



Figure 3. The spectra of the broadband PL of the 20h sample at various temperatures.

Figure 4 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 [2]. 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 photo-excited carriers, thus resulting in the broadband PL.



Figure 4. Correlation between the intensities of broadband and the graphitic phase.

We now present the results of a further investigation of the broadband PL obtained from the 20h undoped diamond film. 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

$$I / I_0 = P_R / (P_R + P_{NR})$$
 (1)

where P_R and P_{NR} are the probabilities for the radiative and the nonradiative recombination respectively [12], I is the PL intensity, and I₀ 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 PL is of the form of a Boltzmann activated process then Eq.(1) becomes:

$$P_{NR} / P_{R} = [I_{0} / I(T)] - 1 \sim exp(-E_{A} / k_{B}T)$$
(2)

By plotting $\log((I_0 / I(T) - 1))$ vs 1/T a straight line should be obtained from which EA can be evaluated. Figure 5 shows this plot for our experimental data, I(T), the inset in the figure shows I(T) vs. temperature. The continuous curve of figure 5 indicates the existence of a continuous distribution of activation energies E(T) rather than a single EA associated with one energy level of a specific defect. Such a 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 Figure 5 can be fitted by the equation

$$[I_0 / I(T)] - 1 \sim \exp(T/T_0)$$
(3)

for which T_0 is a constant to be determined. 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. [13] 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 [7] with temperature dependence of the form of Eq.3, consistent with our findings. According to the model developed by Street et al. for amorphous materials T_0 is a measure of the width of an exponential in-gap state distribution from which optical transitions can occur [13]. 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 sp² bonding creates sigma-bands (σ , σ *) and pi-bands (π , π *) for which optical transitions can occur [6]. At present we hypothesize that the π - π * band transitions and are in the energy range closest to our laser excitation energy [14].



Figure 5. The temperature behavior of the broadband PL obtained from the 20h sample.

Figure 6 shows the temperature dependence of the 1.681 eV PL intensity. It can be seen that the PL intensity in the temperature range 10-100K is approximately constant whereas a strong quenching of the PL takes place at T > 100K. The data in Figure 6 can be fitted by Eq.2, with an activation energy EA = 90 meV (\pm 10 meV). Thus ~ 90 meV is the energy needed to channel the photo-carriers from the excited state to the nonradiative path. The substantially different temperature dependence of the broadband PL and the 1.681 eV band, suggests that different non-radiative recombination mechanisms are involved. This may imply that these two optical centers do not directly communicate.



In conclusion, the spectra of both nitrogen-doped and undoped films exhibited the broadband PL; the nitrogen-doped sample, however, had a distortion of the line-shape of the underlying broadband PL due to the vibronic interaction of the nitrogen centers. The nitrogen optical centers at 2.154, 1.945 and at 2.46 eV (band-A) were observed, as well as a new possibly nitrogen-related center at 1.967 eV. The temperature behavior of the broadband PL indicates that the band does not originate from a vibronic interaction. Morever, the intensity of the broadband PL was found to exhibit a temperature dependence characteristic of optical emission from a continuous distribution of gap states. In light of the above findings and from the correlation of the PL intensity to the graphitic phase 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. The temperature-behavior of the 1.681 PL band found to exhibit characteristic of Boltzmann activation process with an activation energy of nonradiative transition $E_A \sim 90$ meV.

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