CHARACTERIZATION OF EXCITONIC RECOMBINATION RADIATION FROM HIGH PURITY CVD DIAMONDS

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Free exciton (FE) recombination radiation becomes a dominant emission process in diamonds for the first time. The diamonds are formed at the optimized CO_2 concentration in CO/H_2 system and the appropriate position in microwave plasma. Also the FE emissions are investigated in several types of synthetic diamonds to characterize the crystallinity, the purity, and the internal strain.

1. INTRODUCTION

One of the advantages of chemical vapor deposited (CVD) diamond is its controllabity of impurity [1]. The purest diamonds can be formed from CVD process. To estimate the crystallinity and the purity, cathodo-luminescence (CL) of free exciton (FE) recombination radiation [2] is a suitable diagnostic technique. However, the studies on the edge emissions of CVD diamonds have been limited to date [3-7]. In a nearly-perfect and pure diamond if present, the optical emission should be from only the FE recombination radiation.

The binding energy of FE in diamond is reported to be 80 meV[2]. It is one of the highest in popular semiconductors such as Si, GaAs, ZnSe etc. The edge emission of diamond is due to excitonic recombination even in high temperatures. The high oscillator strength is realized in the FE recombination. This is one of the reason that edge emission is high even for an indirect transition.

In this study, we have investigated the optimum conditions of microwave plasma CVD to form crystals exhibiting dominant FE emissions [6-7] and the variety of FE emissions in several types of synthetic diamonds [8] to characterize the crystallinity and the purity.

2. EXPERIMENTAL

Microwave plasma CVD was used to deposit diamond particles and films. The reaction gas were the mixture of CO and CO_2 diluted with H_2 or CH_4 and O_2 diluted with H_2. The total gas flow rate was normally 0.2 l/min and the pressure was 35 Torr. The substrates were Si or Cu. The substrate temperatures were kept around 800-900°C during deposition. Two typical positions of the substrates in the plasma are the center and the edge of the discharging area of 50 mm in length. The edge part is called 'off-center position' later in this paper.

CL has been observed using a scanning electron microscope (Topcon DS-130 type) equipped with a liquid-nitrogen cooling stage (Oxford C1001), a ellipsoidal mirror, a monochromator fitted with 1200 grooves mm^{-1} grating, and a photomultiplier suitable for 2.0-6.0 eV photon energy region. The

accelerating voltage is 19 kV normally with a probe current of 2 x 10^{-8} - 4 x 10^{-6} A. The emitted photons are collected by the ellipsoidal mirror. Temperature during the observations was varied from 80 to 300 K.

3. DOMINANT FREE EXCITON RECOMBINATION RADIATION

Fig. 1 and Fig. 2 show the overall CL spectra from 2.0 to 6.0 eV of single crystalline particles of the undoped CVD diamonds formed with CO(10%) and CO_2 (0 % -1.5 %) diluted with H_2 at the center and the off-center position respectively [7]. These particles are 10-15 μm in size. The probe current was 5 x10^{-7}A and the temperature

was 80 K. The CL spectra are shown in the samples formed with the concentration of CO_2 varied from 0 to 1.5 %. The intensities have been corrected according to the sensitivity of the optical system. The spectra are composed of sharp edge emissions at mainly 5.27 eV due to free exciton recombination radiation associated with one momentum conserving TO phonon emission (FE_{TO}) and a broad band around 2.9 eV called 'band A emission'. The latter is found to be associated with dislocations or precipitates in bulk diamonds [9]. No other emission was observed in the range of 1.5 - 6.0 eV.

The perfection in diamonds is measured by the peak emission intensity ratio between the FE_{TO} and the band A (F/A ratio) [7].
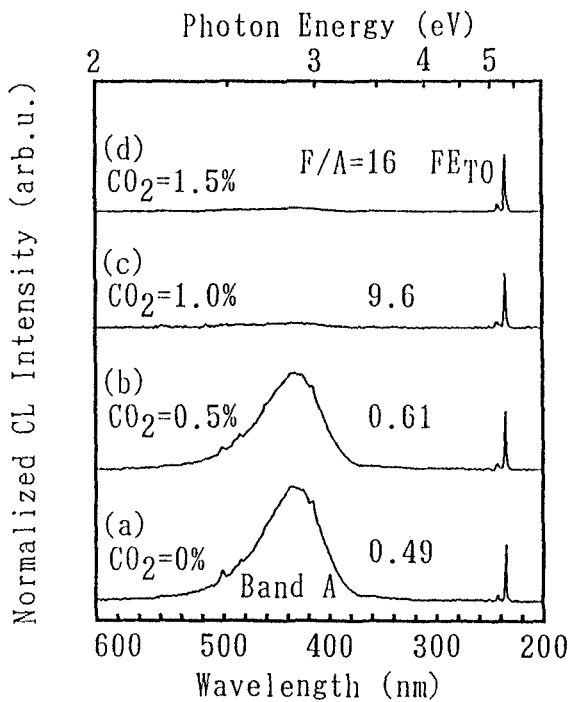

Fig. 1 Overall emissions from the CVD diamond particles formed by microwave plasma using the mixture of CO (10 %) and CO_2 (0%-1.5%) diluted with hydrogen. The substrates are positioned at the center of the discharging areas.
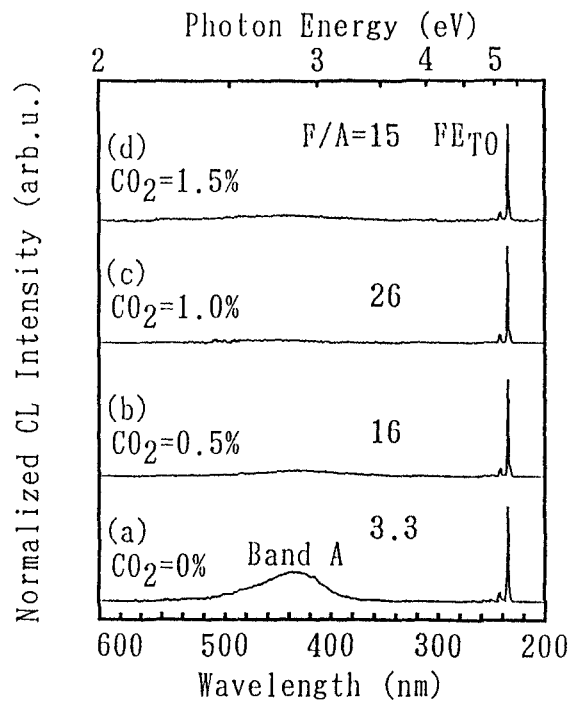

Fig. 2 Overall emissions from the CVD diamond particles formed by microwave plasma using the mixture of CO (10 %) and CO_2(0%-1.5%) diluted with hydrogen. The substrates are positioned at the edge of the discharging area.

The ratio dramatically decreases as the addition of CO_2 to CO/H_2 system as can be observed in Fig.1 and Fig.2. The higher F/A ratio has been observed in the samples formed at the off-center position than the center. The highest one is more than 20. In a high quality natural type IIb diamond the ratio is observed to be 0.12 at the same CL measurement shown in Fig.2. It is almost 100 times lower than those of the spectra in Fig. 2. The F/A values of the CVD diamond formed by CO/H_2 with the addition of CO_2 are the highest ever reported in diamonds. The free exciton recombination is a dominant recombination process in the CVD diamonds if the growth condition is optimized.

In the experiments, there are two main factors which suppress the band A and enhance the edge emission -- the effect of CO_2 and the position of substrate in the plasma. From the experimental results the optimum ratio between C, O, and H are placed around C/O = 1 [10]. Thus, CO/H_2 is thought to be the best reaction gas [11] . The addition of CO_2 in small amount adjust the subtle balance of these three components. In general oxygen is effective in the suppression of non-diamond phases. It is considered that the oxidation of carbon occurs preferentially at pi bonds or imperfect sp^3 bonds. Moreover the effect of oxidation extends to impurities present in the reaction area. Si or other impurities are easier to oxidize than carbon and their oxide cannot be incorporated into the diamond lattice because of the larger molecules. The resulting diamonds are pure as a result.

The distinct reduction of the band A in the off-center position is considered from the point of the balance between the high plasma density and the avoidance of damage from the plasma. The generation rate of useful radicals such as atomic hydrogen is high in the high density plasma. But, the density of harmful species such as high speed atoms or molecules are also increased in the region. If the life times of these species are shorter than those of useful radicals there is a suitable

position for diamond formation away from the center of plasma.

The F/A ratio is almost constant at the probe current between 2×10^{-8} - 4×10^{-6} A as shown in Fig. 3. In usual competing processes between the edge emission and the defect-related one, the ratio of the former increases as the excitation increases, because the latter occurs mainly through deep levels at low excitation and saturated at high excitation. But, Fig. 3 does not show this tendency. It indicates that the emission process of the band A is through the exciton formation which depends chiefly on the excitation density.
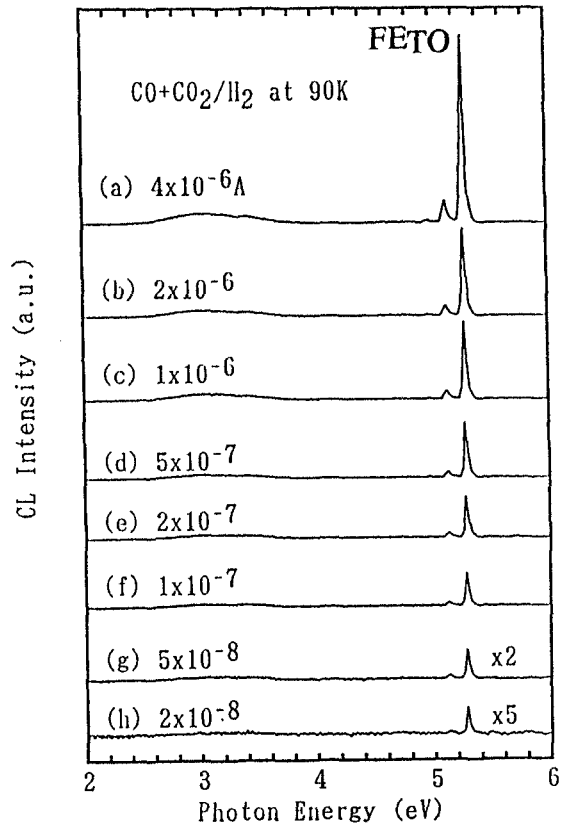
Temperature dependence of FE_{TO} in

Fig. 3 Overall emissions from a CVD diamond particle formed with CO(10%) and $CO_2(1.0\%)$ diluted with hydrogen at different probe currents.

undoped CVD diamond is shown in Fig.4. Below 150 K the intensity of FE_{TO} is saturated because of the large binding energy of 80 meV. Dissociation of the free excitons scarcely occurs below this temperature. Thus, the intensity is expected to be constant until 0 K. Above 170 K the intensity of FE_{TO} abruptly decreases. In general, the probability of nonradiative transitions including the dissociation of excitons, is temperature dependent and that of radiative transition is assumed independent. At room temperature (300 K) the intensity becomes two orders of magnitude lower than at 80 K. However, this decrease is not so large compared with those of excitonic emissions in quantum wells of GaAs or SiGe in the same temperature range.
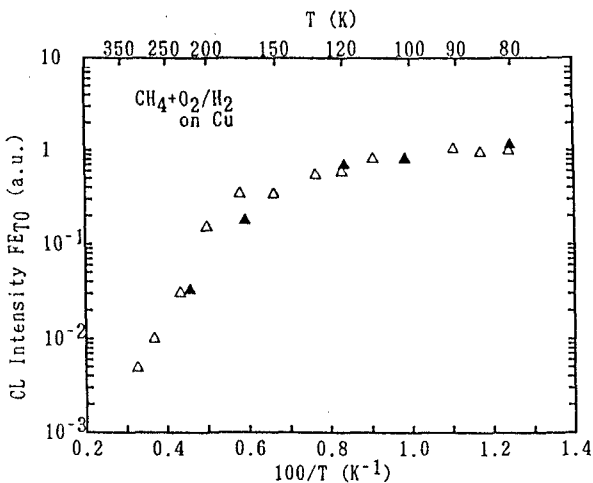

Fig. 4 Emission intensity of FE_{TO} of a CVD diamond particle as a function of temperature. The crystal was formed with CH_4(0.4 %), O_2(0.2 %) and H_2(99.4 %).

4. FE EMISSIONS OF THE DIAMONDS FORMED IN SEVERAL METHODS

Comparative spectra of FE_{TO} in three synthetic diamond crystals are shown in Fig.5 [8]. The impurity especially nitrogen is believed to be harmful for the emission of FE_{TO}, because of the deep electron traps and the absorption band due to nitrogen. The effect of nitrogen is apparent in high pressure synthetic diamonds. In almost all the regions, the FE_{TO} emission has not been observed. However, in small bands less than 50 μm wide, strong FE_{TO} emissions are sometimes observed. One of the examples is shown in Fig. 5 (a). FE_{TO}, FE_{TA}, and BE_{TO} due to boron bound excitons are well resolved in the spectrum. This crystal as a
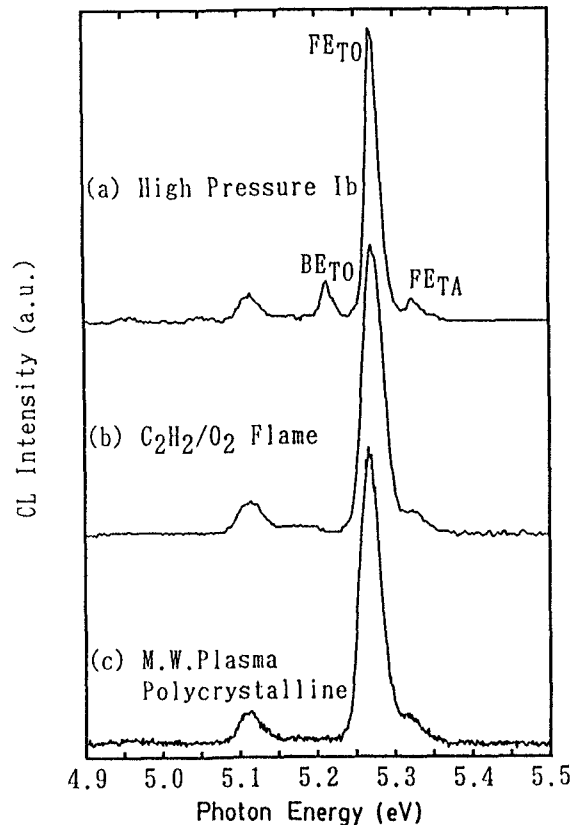

Fig. 5 CL spectra of different diamonds near the energy of the bandgap: (a) a narrow band in a single crystal of high pressure synthetic Ib; (b) a single crystalline particle 10 mm in size formed with combustion flame with C_2H_2/O_2; (c) a polycrystalline film formed by microwave plasma CVD with CO(5%)H_2.

whole is type Ib, but locally type IIb. The luminescent band might be a trace of nitrogen nearly-free condition under high pressure.

The incorporation of nitrogen is expected in the crystals formed by the acetylene-oxygen flame in air. However the single crystalline particle formed in the process exhibits a clear FE$_{TO}$ emission shown in Fig. 5(b). Nitrogen-vacancy related emissions such as the 2.16 eV center are scarcely observed in this sample. Nitrogen incorporation is effectively suppressed in the process.

Figure 5 (c) is the edge emission of a polycrystalline CVD diamond formed by microwave plasma CVD with CO(5%)/H$_2$. This spectrum is not typical for the polycrystalline films formed at the above condition, but one of the best. Usually the FE$_{TO}$ is not observed in polycrystalline films formed with CH$_4$/H$_2$ [4]. The CO/H$_2$ has the advantage in preventing the formation of non-radiative path also in the growth of polycrystalline phase. This kind of variation in crystallinity is not observed in Raman spectra. The local quality of crystal can be characterized by FE$_{TO}$ emission.

5. ISOTOPE EFFECT AND STRAIN EFFECT ON FE$_{TO}$ EMISSION

Natural diamond is 98.9 % ^{12}C and 1.1 % ^{13}C. Even in natural gas this ratio is constant. However, the ^{13}C can be condensed by the difference in boiling point of CH$_4$. Figure 6 shows the two edge emissions of CVD diamond formed by ^{13}C condensed CH$_4$ (96.6 % ^{13}C and 3.4 % ^{12}C) and normal high-purity CH$_4$. The reaction gases were the mixture of CH$_4$(0.4 %) and O$_2$(0.2 %) diluted with H$_2$. The FE$_{TO}$ peak of ^{13}C condensed samples is 5.287 eV and that of normal one is 5.271 eV. The difference is 16 meV. From the point of
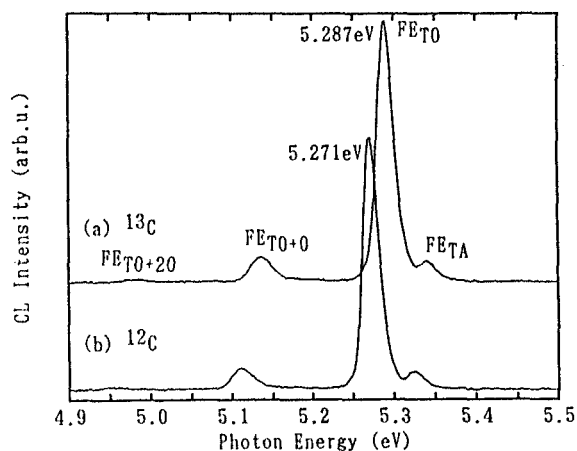

Fig. 6 CL spectra of ^{13}C condensed and normal high purity CVD diamonds near the energy of the bandgap. They are shown as ^{13}C and ^{12}C respectively. The crystals were formed with CH$_4$(0.4 %), O$_2$(0.2 %) and H$_2$(99.4 %).

TO phonon energy difference estimated by the factor $(12/13)^{1/2}$, the peak shift is evaluated to be only 5 meV. The residual shift 11 meV can be explained by the indirect energy gap difference. Collins et al. report that the indirect energy gap is 13.6 meV higher for ^{13}C than for ^{12}C diamond formed by high pressure synthetic process [12]. Our value observed in the CVD diamonds is qualitatively equal to their results.

Figure 7 shows the edge emission of large single-crystal particle 40 μm in size formed with CO(15%)/H$_2$ using microwave plasma CVD. The main peak is composed of 5.27 eV shoulder due to FE$_{TO}$ and an unidentified 5.22 eV peak. The energy of the latter varies in the position of the particles. The possibility of boron bound exciton can be ruled out because the crystals were not intentionally doped and formed in a purified process. From CL imaging, the lower energy emission located in the corners of cubo-octahedral diamond particles. It is expected that the strains are present in the
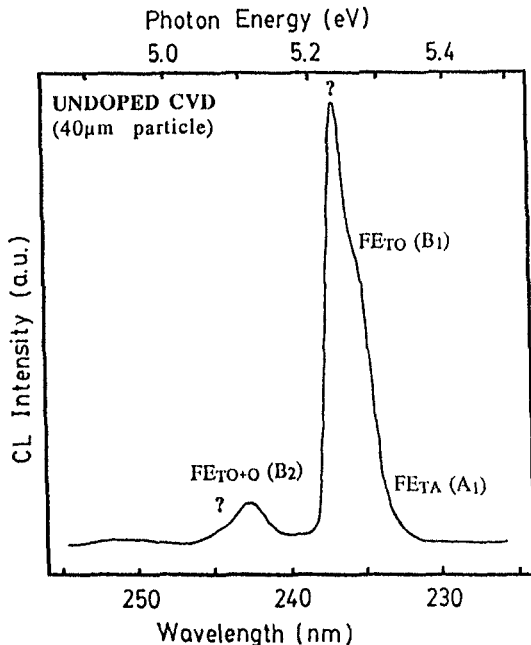
Photon Energy (eV)

Fig. 7 CL spectra of a CVD diamond particle of 40 μm in size near the energy of the bandgap. The particle was formed with CO(15%) diluted with hydrogen and was not intentionally doped.

corners where different growth sectors adjoin. The <001> compressive stress decreases the bandgap energy in the longitudinal stress direction and increases in the transverse direction. The emission occurs in the narrower band gap. Considering that the observed lower energy emission frequently occurs in the particles formed at higher growth rates we speculate that the lower energy emission is caused by internal strains at the interface between different growth sectors.

6. CONCLUSIONS

1) Free exciton recombination radiation becomes a dominant emission process in CVD diamonds formed at the optimized CO_2 concentration in CO/H_2 system and the appropriate position in plasma. The peak emission intensity ratio between the FE_{TO} and the band A is more than 20. The value is the highest ever reported in diamonds.

2) FE_{TO} is a suitable emission process to characterize the crystallinity, the purity, and the internal strain of diamonds.

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