

Wavelength-resolved Thermoluminescence of Chemical-vapor-deposited Diamond Thin Film

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Diamond thin films were synthesized by a chemical vapor deposition (CVD). Raman spectrum showed the diamond line at 1332 cm^{-1} and x-ray diffraction pattern exhibited a strong (111) peak of diamond. The scanning electron microscopy analysis showed that the CVD diamond thin film was grown to be unepitaxial crystallites with pyramidal hillocks. A wavelength-resolved thermoluminescence (TL) of the CVD diamond thin film irradiated with X-rays showed one peak at 430 nm around 560 K. The glow curve of the CVD diamond thin film produced one dominant 560-K peak that was caused by first-order kinetics. Its activation energy and the escape frequency were calculated to be $0.92 \sim 1.05\text{ eV}$ and $1.34 \times 10^7\text{ sec}^{-1}$, respectively. The emission spectrum at 560 K was split into 1.63-eV, 2.60-eV, and 3.07-eV emission bands which is known to be attribute to silicon-vacancy center, A center, and H3 center, respectively.

Keyword : Thermoluminescence Dosimetry, CVD Diamond Thin Film

INTRODUCTION

Recently, a diamond has been proved to be a good candidate as a material for dosimetry in clinical application^{1,2)}, because of its chemical inertness, high radiation hardness, and tissue equivalent materials. For the exploitation of the technology for the application, a chemical-vapor deposition (CVD) technique has been developed to improve the quality of the diamond films and to produce them economically. Diamond thin films grown by CVD intrinsically include the formation of crystal defects, such as grain boundaries, twins, bonding defects, and the impurities. Because these impurities and defects affect the electro-optic properties and the sensitivity to radiation dose of

CVD diamond, it is necessary to study their behavior.

Thermoluminescence (TL) can be used to reveal these crystal defects. The defects and the impurities play roles as traps or centers in the bandgap and are reflected in the kinetics of charge trapping and detrapping, which are responsible for TL³⁾. The TL has been used to study trap levels in single diamond crystals. There has been few works related to the TL properties of CVD diamond and its application to dosimetry^{4,5)}. Even in these few works, the TL properties of CVD diamonds have been shown to vary from researcher to researcher⁶⁻⁸⁾. In the present study, to understand the thermoluminescent properties of CVD diamond films, we measured the wavelength-resolved

thermoluminescence over the wavelength range of 300 ~ 800 nm within the temperature range of 300 ~ 650 K.

EXPERIMENTAL

Diamond thin films were deposited on a Si (001) substrate by using microwave-cavity plasma-enhanced chemical-vapor deposition (MWPCVD). The system used in this study was DIAMONDTEK DMS-100. The surfaces of the silicon wafers were treated to make scratches by using a diamond paste, and the substrate was ultrasonically cleaned in acetone and ethanol solution. After chemical cleaning, the substrate was heated to eliminate contaminants from its surface by using a hydrogen plasma. The diamond thin films were synthesized under a substrate temperature of 900 ~ 1000 °C, a working pressure of 48 ~ 58 Torr, a deposition time of 6 ~ 12 hours, a flow of methane gas of 2 ~ 4 sccm, and a flow of hydrogen gas of 400 sccm.

The wavelength-resolved thermoluminescence equipment was composed of a sample holder and a temperature controller, a monochromator, and a current measuring system, all of which were controlled by a computer. In order to deplete trapped charge carriers in traps or centers, we annealed the CVD diamond film at 700 K for 1 hour in air. The excitation was achieved with x-ray units manufactured by Shimadzu company. The TL intensity was measured from 300 K up to 650 K at a linear heating rate of 0.6 K sec⁻¹ in the spectral range of 300 ~ 800 nm.

RESULTS AND DISCUSSION

Various growth conditions of CVD diamond film are summarized in Table 1. The CVD diamond thin film was irradiated with 50 keV x-ray and its TL intensity was measured with linear heating rate of 0.6 K s⁻¹. Figure 1 shows the glow

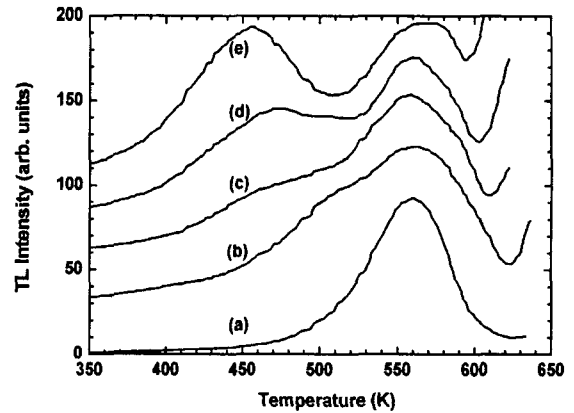


Figure 1. Glow curves of CVD diamond thin films deposited with various growth conditions

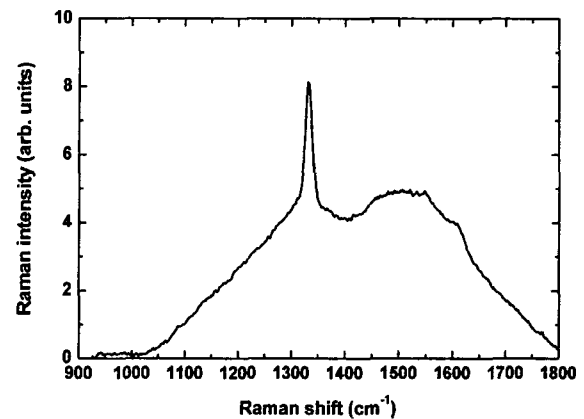


Figure 2. Raman spectrum of synthetic CVD diamond thin film (a)

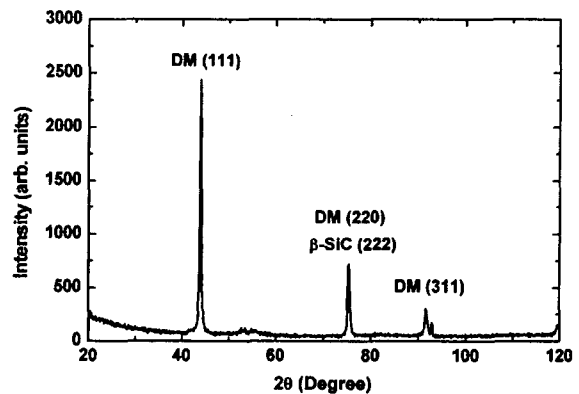


Figure 3. XRD of CVD diamond thin film (a)

Table 1. Various growth conditions of CVD diamond thin film

Diamond film	Substrate Temperature (°C)	Working Pressure (Torr)	Time (hour)	Methane (sccm)	Hydrgen (sccm)
(a)	950	48	6	4	400
(b)	1000	48	6	4	400
(c)	900	48	6	2	400
(d)	900	48	12	4	400
(e)	900	58	6	4	400

curves of CVD diamond thin films deposited with various growth conditions. All five glow curves in the high temperature range show the similarly dominant peak but those in the low temperature range show different shapes. The glow curves of CVD diamond thin films are dependent on the synthetic growth conditions. Borchi et al. reported that the different glow curves in the low temperature range were strongly dependent on the prevailing environmental conditions during the measurement⁶⁾. Even though the band-A emissions attributed to glow curves in CVD diamond films deposited with various growth conditions were systematically investigated, it is hard to control the impurities and defects that contributed to emission due to fluctuation of growth conditions⁹⁾. The relation between the characteristics of glow curves and the growth conditions of CVD diamond films are not yet revealed. The result of Figure 1 obviously shows that the glow curves of CVD diamond films in the low temperature range are closely related to the growth conditions. For these reasons, the present analysis is focused on the glow curve of CVD diamond film (a) in the high temperature range.

Figure 2 of Raman spectrum of synthetic CVD diamond film (a) shows the diamond line at 1332 cm^{-1} and two broad bands around 1350 and 1500 cm^{-1} attributed to disordered sp²-bonded carbon. The bandwidth at half intensity of 8.2 cm^{-1} related to chemical impurities and defects, which

played the role of traps and recombination centers. XRD of CVD diamond thin film (a) shown in Figure 3 exhibits a strong (111) peak and a weak (220) and(311) peaks of diamond besides a (222) peak of β -SiC. And Figure 4 of the scanning electron microscopy (SEM) picture shows that the CVD diamond film (a) is grown to be unepitaxial crystallites with hillocks.

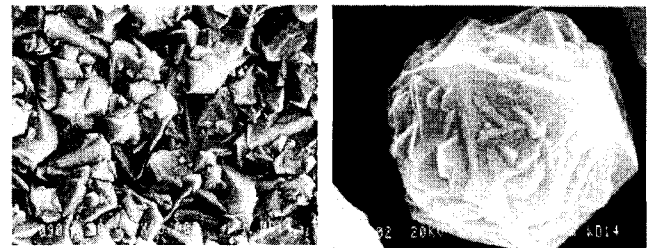


Figure 4. SEM picture of CVD diamond thin film (a)

Figure 5 shows a wavelength-resolved thermoluminescence of a CVD diamond thin film (a) irradiated with 50-keV X-rays for an anode current of 4 mA at room temperature for 5 minutes.

The wavelength-resolved thermoluminescence has one peak around 560 K with 430 nm, which is very broad with a long tail in the low-temperature range, and its emission spectrum at 560 K deviates from a Gaussian contribution with many differences. At high temperature, the emission spectrum caused by the blackbody radiation from the heater embedded in the sample holder is seen in the long-wavelength range. The glow curve of X-ray-irradiated CVD

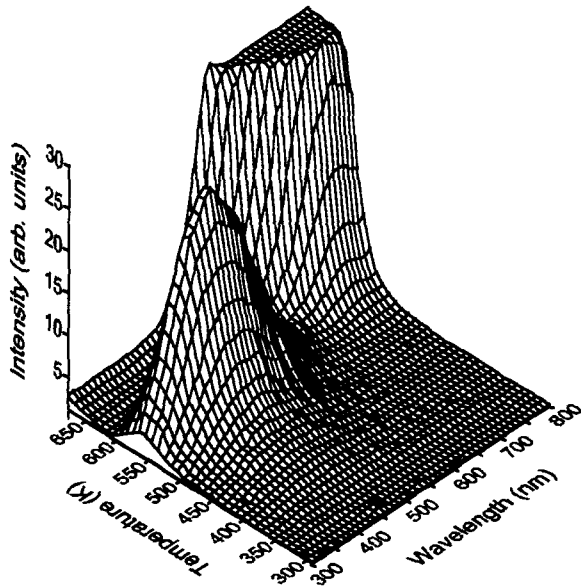


Figure 5. Wavelength-resolved thermoluminescence of a CVD diamond thin film (a)

diamond thin film (a) in Figure 1 shows a monotonously increasing line in the low-temperature region and a dominant peak at 560 K. In the numerical analysis, the activation energy and the kinetics of the 560-K glow curve were fitted to be 1.04 eV and first order, respectively.

The peak shape method can be used to evaluate the kinetics, the activation energy, and the escape frequency factor³⁾. The $\tau = T_m - T_1$, $\delta = T_2 - T_m$, and $\omega = T_2 - T_1$ of the glow curve at 560 K are 34 K, 27 K, and 61 K, respectively, where T_m , T_1 , and T_2 are the maximum intensity temperature and the half intensity temperatures at the low and the high sides of the peak, respectively. The form factor μ_g is calculated to be 0.44, which means that the peak is due to first-order kinetics. The activation energies for τ , δ , and ω are given by

$$E_\tau = 1.51 \frac{k T_m^2}{\tau} - 1.58 (2kT_m) \quad (1)$$

$$E_\delta = 0.976 \frac{k T_m^2}{\delta} \quad (2)$$

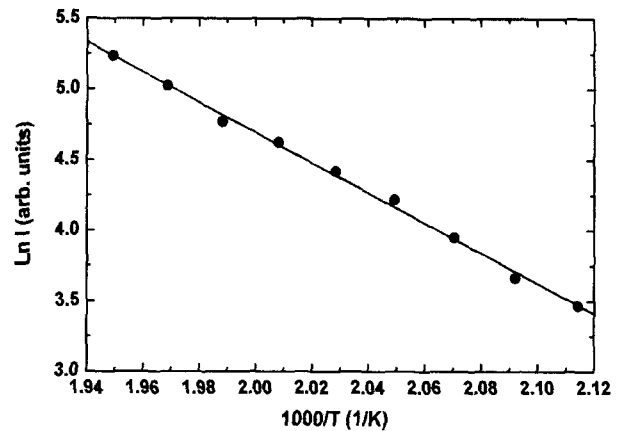


Figure 6. Ln I as a function of 1000/T

$$E_\omega = 2.52 \frac{k T_m^2}{\omega} - 2kT_m \quad (3)$$

respectively. The activation energies for τ , δ , and ω are calculated to be 1.05, 0.98, and 1.02 eV, respectively. The escape frequency factor is defined as

$$s = (0.976 \frac{\beta}{\delta}) \exp(0.976 \frac{T_m}{\delta}) \quad (4)$$

The escape frequency factor is calculated to be $1.34 \times 10^7 \text{ sec}^{-1}$. The intensity for a single-trap TL peak due to first-order kinetics is given by

$$I(T) = n_0 s \exp\left(-\frac{E}{kT}\right) \exp\left[-\left(\frac{s}{\beta}\right) \times \int_{T_0}^T \exp\left(-\frac{E}{kT'}\right) dT'\right] \quad (5)$$

where I is the TL intensity, n the concentration of trapped charge carriers, T the absolute temperature, k the Boltzmann constant, E the activation energy, s the frequency factor, T_0 and n_0 are the initial temperature and the concentration of trapped charge carriers, respectively. As long as T is close to T_0 , the integral value in Eq. (5) is very close to unity. For the initial rise range of $T \approx T_0$, Eq. (5) is transformed into

$$I(T) = n_0 s \exp\left(-\frac{E}{kT}\right) \quad (6)$$

The activation energy can be calculated from the

Table 2. Thermally stimulated characteristics of the main peak observed by various authors.

Authors	Peak Temperature (K)	Measurement	Kinetics	Activation Energy (eV)	Method
Kim et al. (this study)	560	TL	1st order	1.02 0.92 ± 0.02 1.04	Peak shape Initial rise Curve fitting
Borchi et al. [6]	573	TL	1st order	1.00 1.00	Peak shape Curve fitting
Gheeraert et al.[7]	560	TL	1st order	0.97 1.00	Initial rise Chen
Gonon et al. [8]	560	TL	1st order	1.86	Isothermal decay

Arrhenius plot of the glow curve at the initial temperature.

Figure 6 shows $\ln I$ as a function of $1000/T$. The activation energy is calculated to be 0.92 ± 0.02 eV from the line slope.

Table 2 shows the thermally stimulated characteristics of the main peak from CVD diamond thin film (a). Generally, the glow peak of CVD diamond is located at around 560 K and its peak is caused by first-order kinetics. However, the activation energy of the 560-K peak measured with a thermally stimulated current are very different from that measured with TL⁸⁾.

The emission spectrum at the 560-K TL peak of diamond thin film (a) is shown in Figure 7.

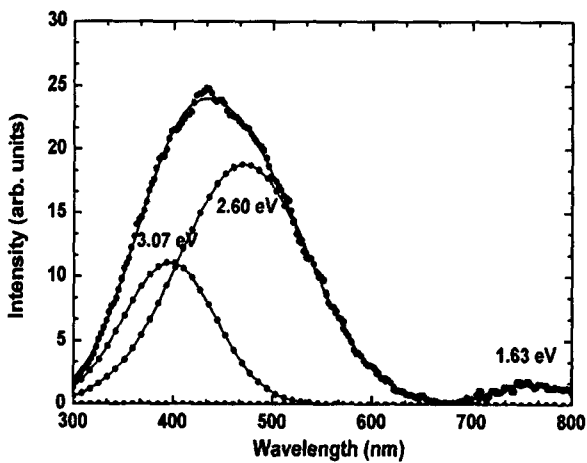


Figure 7. Emission spectrum at the 560-K TL peak of diamond thin film (a)

The overlapping peaks can be resolved into individual peaks by numerical analysis using the least-squares method. The spectrum is split into 1.63-eV, 2.60-eV, and 3.07-eV emission bands. The 3.07-eV emission band is known to be associated with A centers which are related to extended defects and two nearest-neighbor nitrogen atoms on C sites. Manfredotti *et al.* found that the emission band was caused by hole transitions between the valence band and gap states located above the valence band¹⁰⁾. These states acted as recombination centers to capture holes. A nitrogen is the primary impurity with many different defect types in synthetic diamond. Vohra *et al.* reported that unepitaxial crystallites act as preferential site for incorporation of nitrogen-based defects¹¹⁾. Once the A center has trapped the vacancy, the center becomes the H3 center with the vacancy in the near position between nitrogen atoms. The 2.60-eV emission band is found as an H3 center which is associated with a point defect consisting of nitrogen-vacancy (N-V) pairs^{12,13)}.

Also, the peak temperature of the glow curve depends on the capture cross-section of states for charged carriers besides the activation energy, the frequency factor, and the kinetic order. Because the peak temperature of the glow curve for the 2.6-eV emission band is nearly the same as that for the 3.1-eV emission band, the cross section of

the 2.6-eV emission band equals that of the 3.1-eV. Due to the peak intensity of the 2.6-eV emission band being larger than that of the 3.1-eV band, the trap density of the 2.6-eV emission band is larger than that of the 3.1-eV. The 1.63-eV emission band is found to be attributed to an optical center corresponding to a silicon-vacancy (Si-V), where the Si occupies a position in the line joining two adjacent vacancies¹⁴⁾.

CONCLUSIONS

Raman spectrum of synthetic CVD diamond film shows the diamond line at 1332 cm^{-1} and two broad bands around 1350 and 1500 cm^{-1} . XRD exhibits the strong (111) peak and the weak (220) and (311) peaks of diamond besides the (222) peak of β -SiC. From SEM analysis, the CVD diamond film is grown to be unepitaxial crystallites with pyramidal hillocks. The wavelength-resolved TL spectrum of CVD diamond thin film irradiated with X-rays has one peak located at a temperature of 560 K and a wavelength of 430 nm. The glow curve exhibits one dominant 560-K peak. In the numerical analysis, the activation energy and the kinetics of 560-K glow curve are fitted to be 1.04 eV and first order, respectively. The τ , δ , and ω of the glow curve are 34 K, 27 K, and 61 K, respectively. Also, the form factor of the 560-K glow curve is calculated to be 0.44, which means that the peak is due to first-order kinetics. The activation energies for τ , δ , and ω are calculated by using the peak shape method to be 1.05, 0.98, and 1.02 eV, respectively. The escape frequency factor is calculated to be $1.34 \times 10^7\text{ sec}^{-1}$. The activation energy is computed to be $0.92 \pm 0.02\text{ eV}$ by using the initial rise method.

The overlapping emission spectrum at 560 K is split into 1.63-eV, 2.60-eV, and 3.07-eV emission bands. The 3.07-eV emission band is found to be associated with an A center which is related to

extended defects and two nearest-neighbor nitrogen atoms on C sites. The 2.60-eV emission band is found to be an H3 center that is associated with a point defect consisting of nitrogen-vacancy pairs. The 1.63-eV emission band is found to be attributed to an optical center corresponding to a silicon vacancy.

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화학증착된 다이아몬드 박막의 파장 분해된 열자극발광

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다이아몬드는 radiation hardness가 크고, 화학적으로 안정하고, 특히 조직 등과 물질이기 때문에, 선량계 분야에서 각광을 받고 있다. 화학증착법(CVD)에 의해 다이아몬드 박막을 성장시켰고, 선량계로 응용될 수 있는 열자극발광 특성을 조사하였다. 다이아몬드 박막의 라만 스펙트럼은 1332 cm⁻¹에서 peak를 가졌고, x-선 굴절 패턴은 (111) 면을 보였다. 전자주사사진으로부터 다이아몬드 박막은 pyramidal hillock을 가지는 unepitaxial crystallite 로 성장됨을 알았다. X-선 조사된 CVD 다이아몬드 박막의 파장 분해된 열자극발광은 430 nm 및 560 K에서 하나의 봉우리를 가졌다. 560 K에서 주된 봉우리를 가지는 CVD 다이아몬드 박막의 열자극발광 곡선은 1st-order kinetics에 기인한다. 이 봉우리의 활성화 에너지 및 이탈진동수는 각각 0.92 ~ 1.05 eV 및 $1.34 \times 10^7 \text{ sec}^{-1}$ 이다. 560 K에서 방출되는 스펙트럼은 1.63-eV, 2.60-eV 및 3.07-eV 방출 띠로 분해되며, 이들은 각각 silicon-vacancy center, A center 및 H3 center에 기인한다.

중심단어 : 열자극발광 선량계, CVD 다이아몬드 박막