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Growth, Characterization and Device Development in Monocrystalline Diamond Films

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13. ABSTRACT *(Maximum 200 words)*

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.

Bias-enhanced diamond nucleation on yttrium aluminum garnet (100) was performed in a microwave plasma chemical vapor deposition reactor. The initial results suggest that this nucleation pretreatment technique enhanced diamond nucleation on this substrate. It is proposed that both the yttrium and aluminum are operative on diamond nucleation. The carbide forming nature of these elements is speculated to be an important attribute of these substrates.

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I. Optical Defects 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.

A. 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. In this paper we investigate the origin of the broadband luminescence in CVD diamond films, exclude the possibility of the broadband PL originating from any vibronic interaction, and posit a different mechanism of origin.

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

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Submitted for presentation at the MRS Spring 1994 Conference 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. 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]. Our experimental data for the 1.681 eV PL band was closely fitted using the Boltzmann activation process for which at the higher temperature range the non-radiative transition competes with the PL intensity. Our data analysis indicates a non-radiative activation energy E_A of ~ 90 meV.

B. Experimental Procedure

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 μm thick (grown 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 μm 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 μm on the sample. In both studies, an ISA U-1000 scanning double monochrometer was used to analyze the signal.

C. 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 Fig. 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. 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.

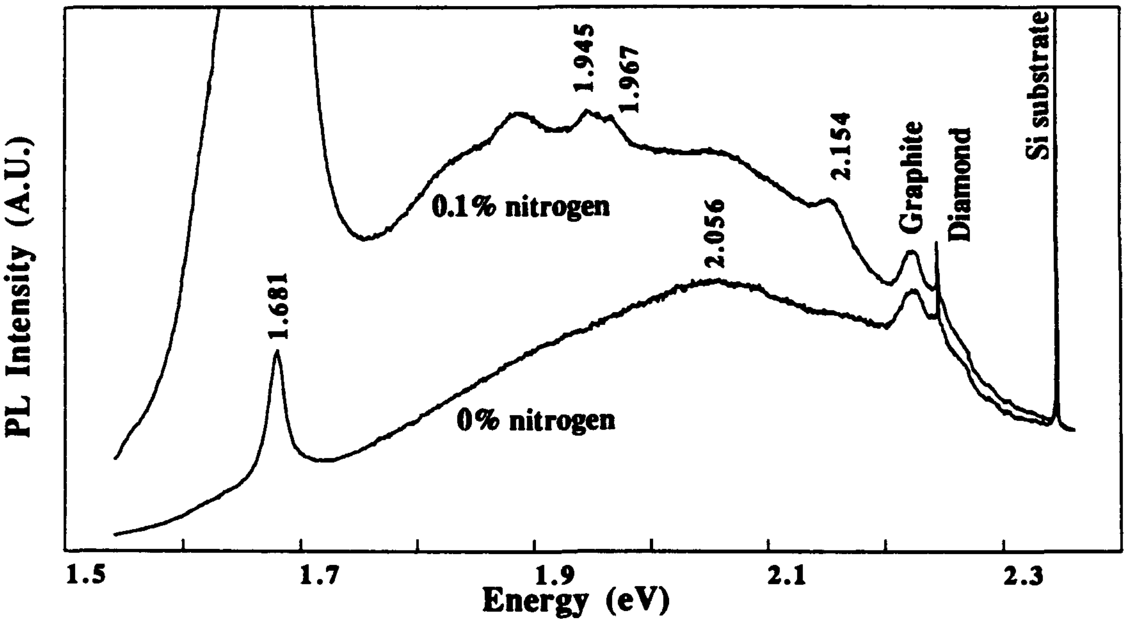

Figure 1. The PL spectra of the diamond films utilizing the 514.5 nm (2.41 eV) laser line.

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, cannot 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. A relatively wide band with line-width ~ 0.3 eV centered at 2.46 eV is also present. Similar wide-band luminescence has been observed in both natural and synthetic diamonds, and is commonly referred to as "band A" luminescence [9]. 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.

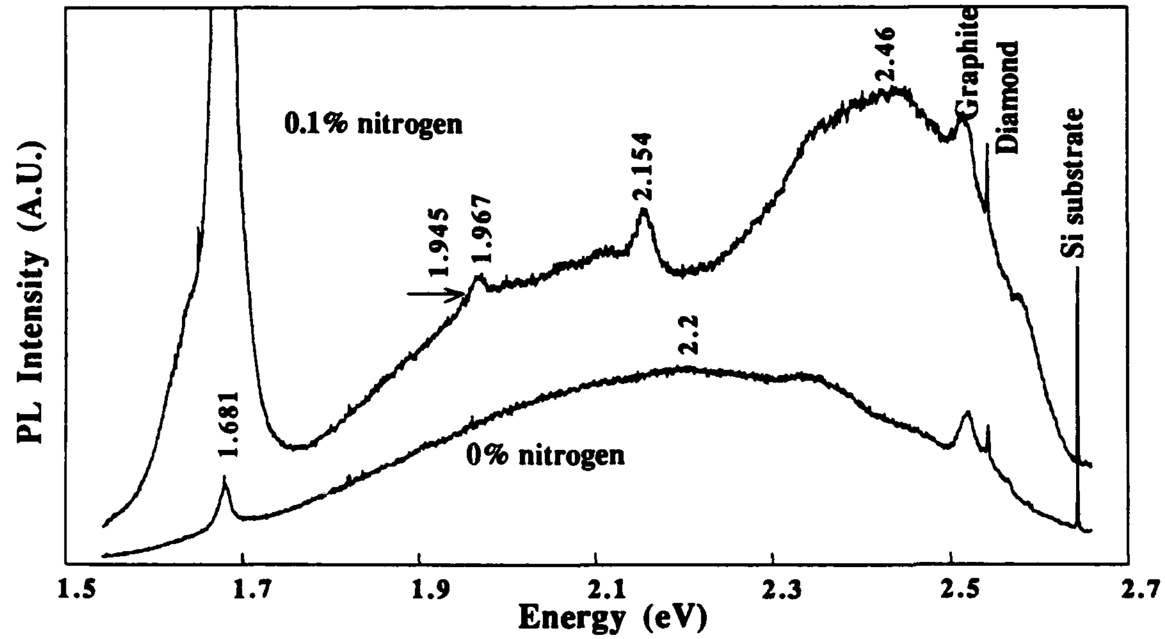

Figure 2. The PL spectra of the diamond films utilizing the 457.9 nm (2.71 eV) laser line.

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 [10], 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 Fig. 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 [5-9]. The temperature dependence we observed is thus not characteristic of a vibronic interaction.

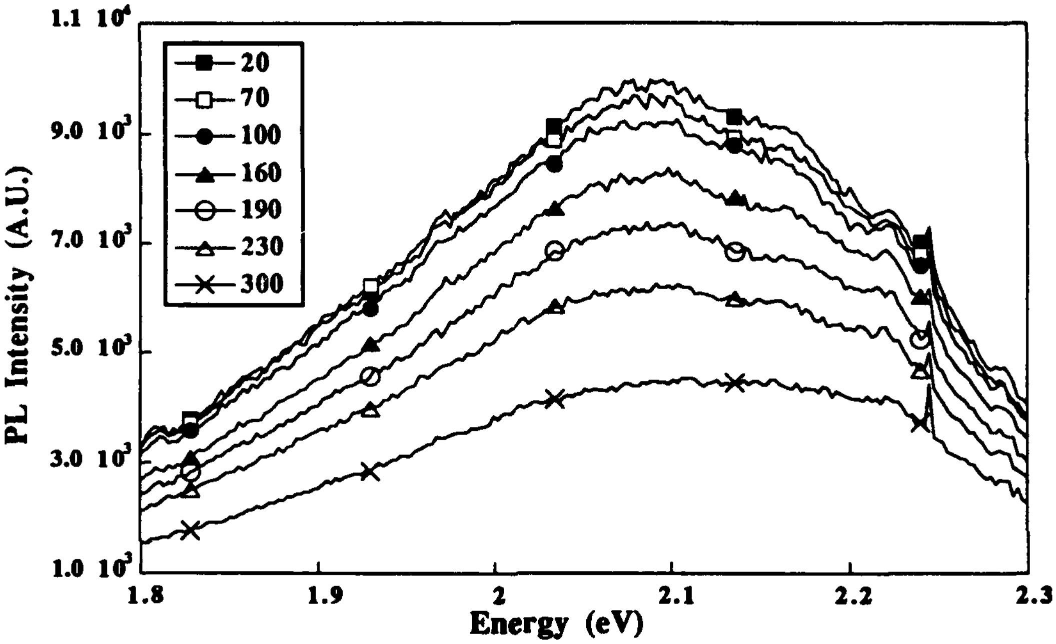

Figure 3. The spectra of the broadband PL of the 20h sample at various temperatures.

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

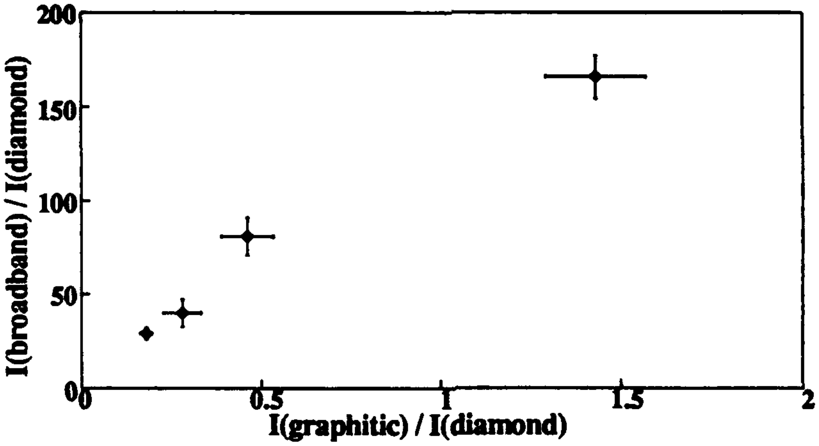

Figure 4. Correlation between the intensities of broadband and the graphitic phase.

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.

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

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

where P_R and P_{NR} are the probabilities for the radiative and the nonradiative recombination respectively [11], I is the PL intensity, and I_0 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

$$P_{NR} / P_R = [I_0 / I(T)] - 1 \sim \exp(- E_A / k_B T) \tag{2}$$

By plotting $\log((I_0 / I(T) - 1))$ vs $1/T$ a straight line should be obtained from which E_A 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 experimental data in the figure indicate the existence of a continuous distribution of activation energies E(T) rather than a single E_A 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

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

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.* [12] 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 [12]. 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 sp^2 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 are responsible for the broadband PL; these bands constitute allowable optical transitions and are in the energy range closest to our laser excitation energy [13].

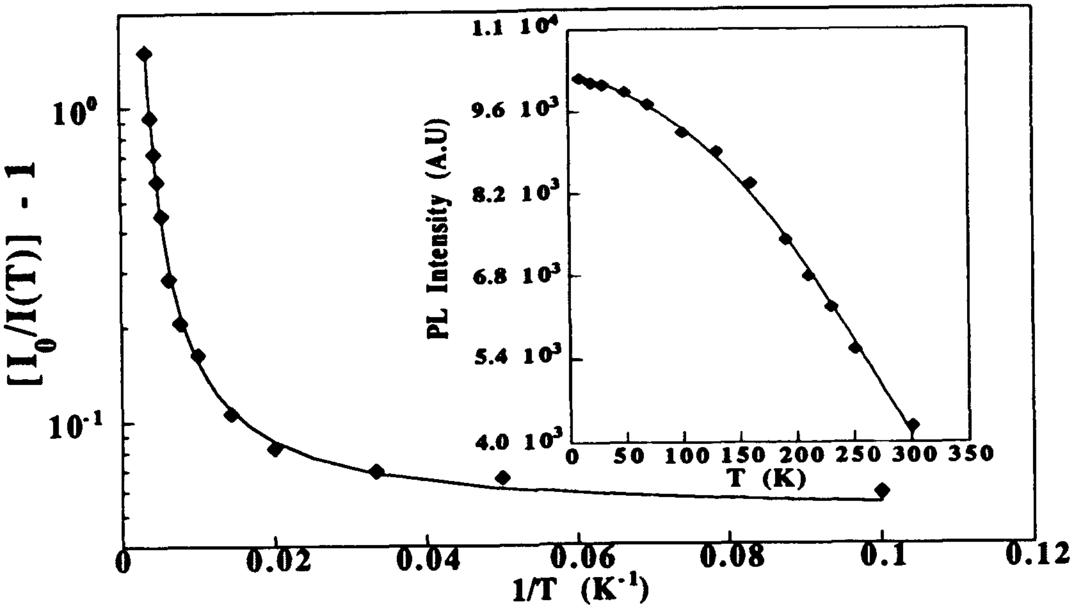

Figure 5. The temperature behavior of the broadband PL obtained from the 20h sample.

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 $E_A = 90$ meV (±10 meV). Thus ~ 90 meV is the energy needed to channel the photo-carriers from the excited state to the nonradiative path.

D. Conclusions

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. Moreover, 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.

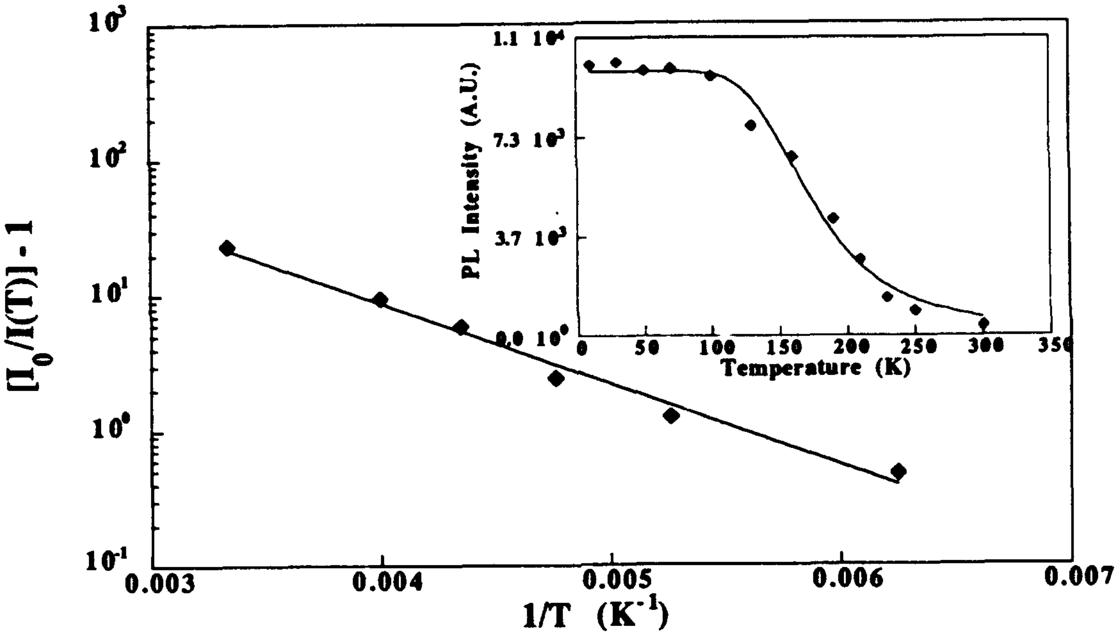

Figure 6. The temperature dependence of the 1.681 eV PL band.

E. References

1. J. A. Freitas, Jr., J. E. Butler, and U. Strom, J. Mater. Res. **5**, 2502 (1990).
2. L.Bergman, B. R. Stoner, K. F. Turner, J. T. Glass, and R. J. Nemanich, J. Appl. Phys. **73**, 3951 (1993).
3. A. T. Collins and S. C. Lawson, J. Phys.: Condens. Matter **1**, 6929 (1989).
4. G. Davies and M. F. Hamer, Proc. R. Soc. Lond. A. **348**, 285 (1976).
5. Maria Estela Pereira, Maria Isabl B. Jorg, and Manuel F. Thomaz, J. Phys. C: Solid State Phys. **19**, 1009 (1986).
6. J. Robertson, Advances In Physics **35**, 317 (1986).
7. R. C. Fang, J. Lumin. **48/49**, 631 (1991).
8. N.F. Mott and E.A. Davis, *Electronic Processes in Non-Crystalline Materials* (Clarendon Press, Oxford, 1979).
9. Gordon Davies, in Chemistry and Physics of Carbon **13**, 2 (1977).
10. Gordon Davies, Rep. Prog. Phys. **44**, 787 (1981).
11. D. Curie, *Luminescence in Crystals* (John Wiley and Sons, 1963).
12. R.A. Street, Advances in Physics **30**, 593 (1981).
13. G.S. Painter and D.E. Ellis, Phys.Rev.B **12**, 4747 (1970).

II. Diamond Deposition on Yttrium Aluminum Garnet via Bias-enhanced Nucleation

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Introduction

The nucleation and growth of heteroepitaxial diamond films is of great interest to the scientific community. Diamond has been epitaxially deposited on both diamond[1] and c-BN[2] which indicates that under appropriate conditions diamond heteroepitaxy is possible. In order to take full advantage of diamond's unique properties, it is necessary to deposit diamond heteroepitaxially. The use of bias-enhanced nucleation (BEN) has proven to enhance diamond nucleation on carbide forming substrates. The negative substrate bias has proven to yield nucleation densities three orders of magnitude higher than those previously recorded using a diamond scratching pretreatment technique. These substrates include silicon[3] and more recently, refractory metals. Copper was investigated to detect the influence of the substrate on diamond nucleation.[4] This study revealed that the substrate is influencing the nucleation of diamond via BEN. In seeking substrates used to the study of diamond deposition, it is helpful to understand how this unique material is formed in nature.

Garnet has been discovered as inclusions in natural diamond. This work by N. V. Sobolev et. al.[5] warrants the investigation of garnet as possible substrates for diamond deposition. The term garnet is used to denote a type of structure rather than a specific material. The garnet structure is found to be $\{X\}_3\ [Y]_2\ (Z)_3\ O_{12}$. The brackets are used to indicate three different types of oxygen ion coordinations. The {X}, [Y], and (Z) cations have 8-fold, 6-fold, and 4-fold coordinations, respectively. Oxygen makes up a large percentage of the structure, while existing in an extended body centered cubic lattice; 45% to 60% of the structure is oxygen. The unit cell is made up of eight formula units of $\{X\}_3\ [Y]_2\ (Z)_3\ O_{12}$. The cations in each of the three variable locations can be altered to obtain various properties. This highly complex structure can be used to form many different garnets with various lattice parameters and interatomic spacings.

This study was performed to investigate the potential use of garnets as diamond deposition substrates. Bias-enhanced nucleation will be used to nucleate diamond and by varying the bias duration the diamond nucleation can be compared to that of other substrates determined in past work. This study should reveal the potential of this material for diamond heteroepitaxy. In addition, it may be determined that other oxide materials may also be used as diamond heteroeptiaxial substrates via this pretreatment.

Experimental

Low pressure diamond deposition was performed using microwave plasma chemical vapor deposition (MPCVD) on yttrium aluminum garnet (100) substrates. The growth chamber and bias-enhanced nucleation apparatus are shown in Figure 1. A further description of this system has been previously documented.[6] As discussed earlier, BEN was used as an in situ pretreatment technique to promote diamond nucleation. In general, a negative substrate potential was applied to the substrate holder with the positive potential applied to ground. The yttrium aluminum garnet (YAG) samples were mirror polished using 600 grit SiC followed by 30μm, 6μm, and then 1μm diamond paste. To insure that the nucleated diamond was formed via negative biasing, care was taken to remove any residual diamond by further polishing with 0.3μm and 0.05μm Al_2O_3. The samples were then solvent cleaned in TCE, acetone, methanol, and propanol, followed by a deionized water rinse prior to insertion into the growth chamber.

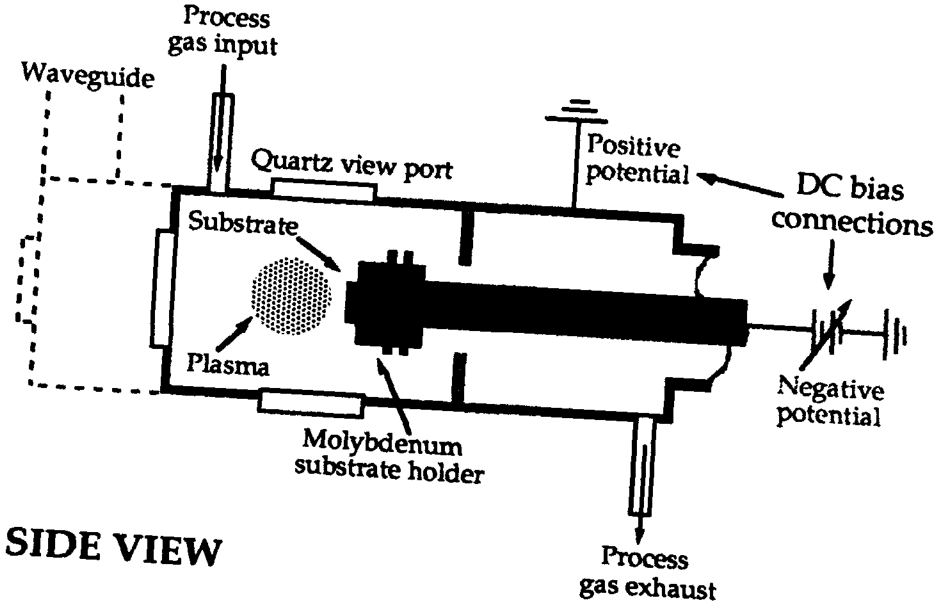

Figure 1. Growth Chamber and Biasing Apparatus

A study of the bias duration was undertaken to note its influence on diamond nucleation. Bias times of 10, 5, and 3 minutes were used for this purpose. The BEN and subsequent growth conditions are listed in Table I. Also, a carburization pretreatment was implemented prior to BEN to observe its influence on diamond nucleation. Previous work on silicon revealed that a carburization pretreatment resulted in the formation of heteroepitaxial diamond.[3] In addition it was also determined that limiting the bias duration had a positive effect on diamond heteroepitaxy. Therefore, with regard to utilizing a carburization pretreatment a short bias duration was used to nucleate diamond. Scanning electron microscopy was used to observe the diamond formed via these pretreatment routines.

Table I. Carborization, Bias, and Growth Conditions

	Carburization	**Bias***	**Growth**
Power	800 Watts	600 Watts	600 Watts
Pressure	25 Torr	15 Torr	25 Torr
Mixture	2 % CH_4	5 %	0.5 %
Approx. Temp.	900° C	750° C	700° C

* Bias voltage is maintained at -250VDC

Results and Discussion

Figure 2 shows the diamond formed on YAG(100) using BEN followed by diamond deposition. Nucleation densities exceeding $1\text{x}\ 10^9\ /\text{cm}^2$ were observed on these substrates. These densities are comparable and in some instances exceed those reported utilizing the classical diamond scratching pretreatment. Thus, diamond nucleation on YAG is affected by the application of a negative substrate bias.

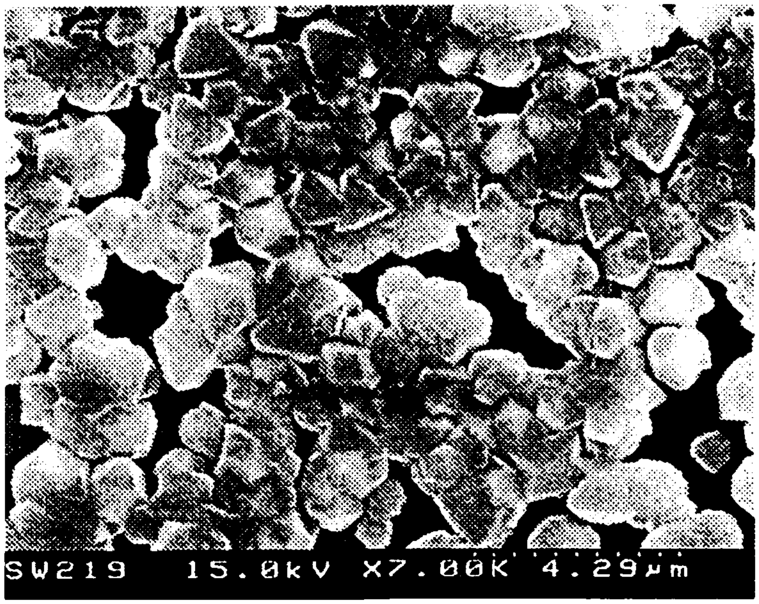

Figure 2. Diamond deposited on YAG(100) by BEN and growth in a MPCVD system.

A number of experiments were performed to observe the influence of the bias and carburization durations on diamond nucleation. It was determined that extending the bias duration led to an increase in the diamond nucleation density. Ultimately, the overall bias duration was reduced from 10 to 3 minutes with no observed preferred orientational relationship with the YAG(100) substrates. Carburization durations of 15 and 60 minutes followed by 3 minutes of BEN were performed to determine their effect on heteroepitaxial diamond formation. Again, there was no distinct preferred orientation observed on the YAG(100) substrates. Figures 3 and 4 denote the influence of a 3 minute BEN pretreatment with and without a carburization pretreatment. These figures revealed that limited nucleation of diamond resulted on the carburized substrates. Table II lists the bias and carburization duration experiments undertaken in this study.

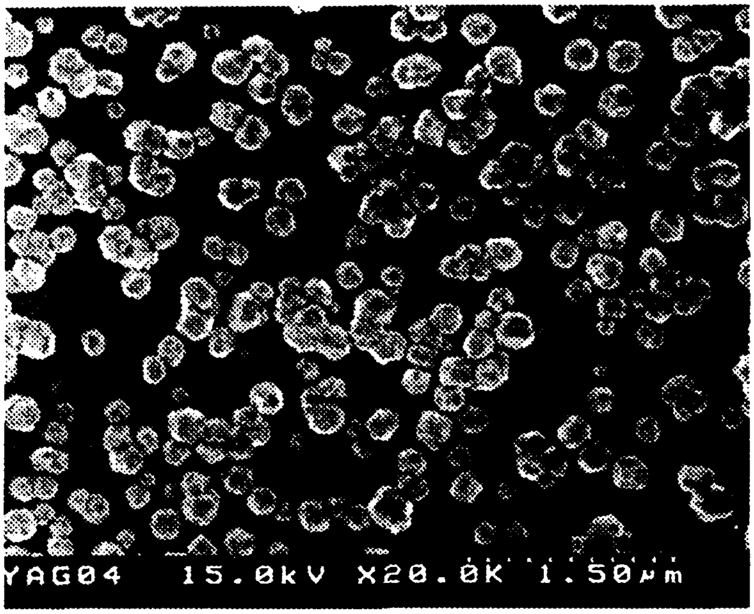

Figure 3. Three minute bias with no carburization on YAG(100).

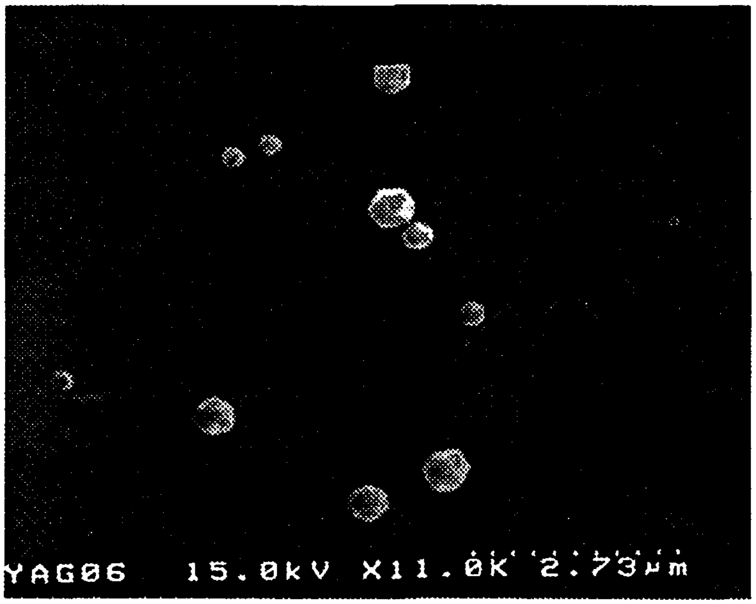

Figure 4. Three minute bias with one hour carburization on YAG(100).

Bias-enhanced nucleation has been reported to be influenced by the substrate material. The carbide forming nature of the substrate has been proposed to be an important attribute for its effectiveness. YAG(100) is composed of yttrium, aluminum, and oxygen and generally exists in the form $Y_3Al_2Al_3O_{12}$. Thus, the carbide forming nature of yttrium and aluminum are speculated to be responsible for diamond nucleation via BEN. A previous study on refractory metal substrates, which are known carbide formers, revealed a correlation to the heat of formation of the metal carbides to that of the nucleation densities at prolonged biasing.[7] Both Al_4C_3 and YC_2 are thermodynamically stable and have carbide heat of formation values of -49.9 kcal/mole and -26.0 kcal/mole, respectively. Figure 5 shows the position of these carbides on a plot of nucleation density[7], which was determined to be $\sim 1\times10^9/cm^2$, versus their respective carbide heat of formation values. This figure was configured for refractory metals subjected to 60 minutes of BEN, whereas in this study the nucleation densities were observed up to 10 minutes in bias duration. It was found that after 60 minutes of biasing no significant increase in the diamond

Table II. Carburization, BEN, and growth times for YAG(100).

SAMPLE	CARB. TIME	BIAS TIME	GROWTH TIME
YAG01	00	10 min.	10 hrs
YAG02	00	05 min.	10 hrs.
YAG04	00	03 min.	10 hrs.
YAG05	15 min.	03 min.	8 hrs.
YAG06	1 hr.	03 min.	10 hrs.

nucleation density was observed. Although an increase in the nucleation density was observed from 3 to 10 minutes of biasing in this study, the increase was not significant. Therefore, any further biasing appears not to substantially increase the nucleation density and may be related to the nucleation density versus carbide heat of formation plot (Figure 5) for the bulk refractory metals. It should be mentioned that this thermodynamic data is reported per metal atom, thus the Al_4C_3 value was adjusted to -37.4 kcal/mole-metal. Since both the yttrium and aluminum are capable of forming carbides, the rule of mixtures was employed to determine their joint effect on diamond nucleation. This value correlates well to the data in this plot considering that relatively short bias durations were studied. The fractional content of aluminum compared to yttrium is 62.5%. Using this fractional relationship Equation (1) was used to determine the fractional influence of the respective carbide heat of formations for aluminum and yttrium.

(1) Combined heats of formation through the law of mixtures;

$$=(-37.4)(.625) + (-26.0)(.375) = -33.1$$

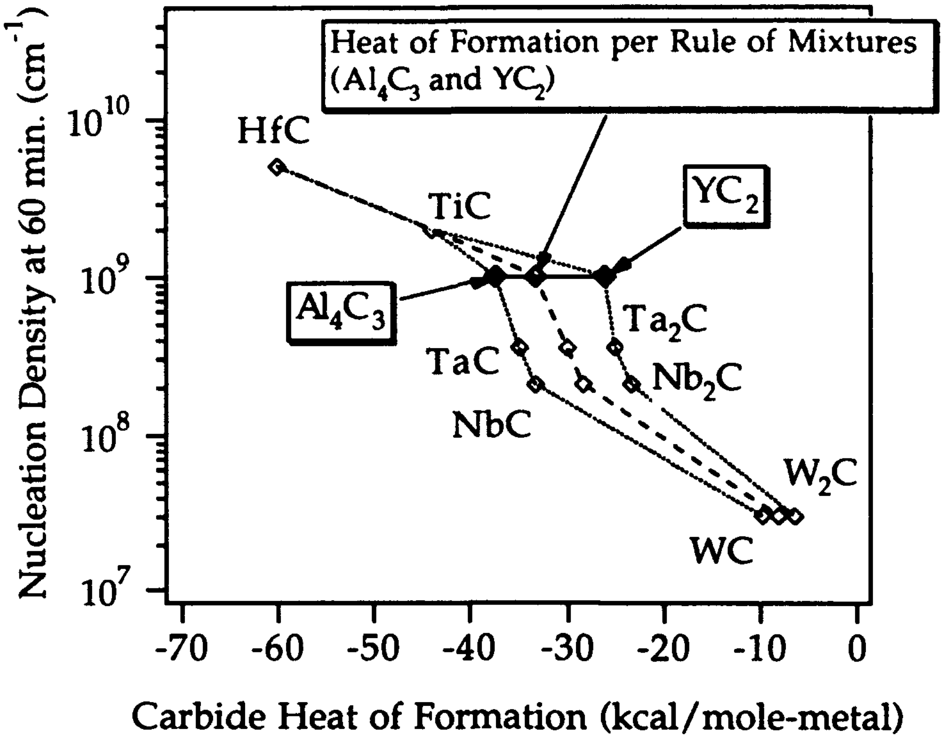

Figure 5. Heat of Formation Vs. Nucleation Density for refractory carbides with Rule of Mixtures formulation of yttrium and aluminum carbides

Conclusions

The successful nucleation of diamond using BEN via MPCVD opens the possibility of garnet as a substrate for heteroepitaxial deposition. It was found that exposing the YAG(100) to a carburization pretreatment deterred the nucleation of diamond. Although no orientation was observed, well-faceted diamond was deposited on YAG(100) with nucleation densities exceeding $1x10^9/cm^2$.

Acknowledgement

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Future Research Plans/Goals

The speculations made above require further work before they can be officially noted. XRD or other similar analysis will have to be utilized to determine if in fact these carbides have formed. Extended bias durations may be used to test the rule of mixtures hypothesis. The use of an in situ hydrogen etch prior to biasing may enhance nucleation. This is assumed since it is speculated that oxygen is possibly being etched from the YAG surface region via BEN, thus forming a yttrium and aluminum-rich surface on which diamond may nucleate. Past work has revealed that chemisorbed oxygen was removed from silicon during BEN. The carburization pretreatment is hypothesized to form a thin surface carbide that hinders oxygen extraction during BEN and results in low nucleation densities. This particular garnet-based material contains no silicon, although many other forms are found to have silicon in the (Z) positions in their structure. Considering the success achieved in the use of silicon as a diamond deposition substrate via BEN[3], these silicon-based garnets will also be tested. Also, due to the complexity of the garnet structure, hemispherical samples will be tested to determine whether an ideal plane exists on which to nucleate and grow heteroepitaxial diamond.

References

1 B.V. Spitsyn, L.L. Bouilov, and B.V. Derjaguin, J. Cryst. Growth, **52** (219), (1981).

2 S. Koizumi, T. Murakami, T. Inuzuka, and K. Suzuki, Appl. Phys. Lett., **57**(6),563 (1990).

3 B.R. Stoner, and J.T. Glass, Appl. Phys. Lett. **60** (6), 1992.

4 S.D. Wolter, B.R. Stoner, and J.T. Glass, Accepted for publication by Diamond and Related Materials, (1994).

5 N.V. Sobolev, and V.S. Shatsky, Nature, **343** 742 (1990).

6 B.R. Stoner, G.-H. M. Ma, S.D. Wolter, and J.T. Glass, Phys. Re. B, **45**(19) 11067 (1992).

7 S.D. Wolter, B.R. Stoner, J.T. Glass, Presented at Spring Meeting of the Materials Research Society, San Francisco, CA, (1994).

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