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Vacancies in polycrystalline diamond films

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Positron-lifetime spectroscopy has been performed in concert with photoluminescence to investigate vacancy-related point defects in polycrystalline diamond films grown by chemical vapor deposition (CVD). Undoped films extensively contain vacancies including monovacancies, divacancies, and vacancy clusters. They are distributed inhomogeneously throughout the films with some crystallites nearly free of vacancies while others contain high concentrations (> 50 ppm). However, boron doping can dramatically reduce the vacancy content in diamond films. The vacancy-related defects are stable up to 1100 °C. The different luminescence peaks can be related to various types of vacancies present in CVD diamond.

I. INTRODUCTION

The nature of vacancies in the diamond lattice is complicated and not well understood. Most of the vacancies are coupled with other defects such as impurities and grain boundaries. Since vacancies are difficult to observe directly, and their formation energy in diamond is high (6–7 eV),[1,2] vacancies have been studied mainly by optical absorption and luminescence following irradiation by energetic particles. Prominent features associated with vacancies are the GR absorption system corresponding to the excitation of neutral vacancies to various excited and charged states, the *ND*1 peak related to negatively charged vacancies, and *H*3, *H*4, and *NV* features from vacancy-nitrogen atom complexes.[3,4] For chemical vapor deposition (CVD) diamond, the incorporation of vacancies can be significant due to the nonequilibrium nature of the growth process and the presence of many other defects such as dislocations, grain boundaries, and planar defects. Previous positron annihilation measurements[5–8] confirmed that the concentrations of vacancies (including monovacancy, divacancies, and vacancy clusters) in undoped CVD diamond films are typically much higher than in natural diamond.

In this paper, positron lifetime spectroscopy was used to investigate vacancy-related defect centers in CVD diamond films. This is a sensitive technique for providing information on the state of vacancies in diamond. When positrons are injected into a material, they can either annihilate in the bulk of the sample, be trapped by vacancy-related defects, or combine with electrons to form positronium (Ps). Each annihilation mechanism produces a characteristic positron lifetime determined by the local electron density in the sample. Positrons trapped by vacancies annihilate more slowly than those not trapped because of the lower electron density in the defect centers. The lifetime is 150 ps for positrons trapped by monovacancies in diamond,[5] compared to 107 ps in the bulk, and the amount of positrons trapped is related to the concentration of the vacancies. Because Ps can be formed in two spin states, two lifetimes arise, one close to 125 ps and the other typically in excess of 1000 ps, and the formation of Ps is promoted by vacancy clusters or by the empty spaces at grain boundaries. By measuring the γ rays emitted from the positron-electron annihilation to determine the lifetimes corresponding to the different annihilation modes and their intensities, information about the type, concentration, and distribution of vacancies can be extracted. These results were then correlated to luminescence features.

II. EXPERIMENTS

Diamond films chosen for the present positron lifetime studies were produced by low-pressure chemical vapor deposition assisted either by microwave plasma or hot filaments. The films exhibit different Raman characteristics and luminescence features, as summarized in Table I. The selection of such a diverse group of diamond films is intended to exemplify the defect properties that CVD diamond films can possibly present. In this work, ^{22}NaCl was used as the positron emitter. A positron was emitted from this source with a maximum energy of 0.5 MeV. Simultaneously, a nuclear γ quantum with an energy of 1.28 MeV was also emitted which was used to detect the time of emission of the positron. The positron entered into the sample and underwent a rapid slowdown to thermal energy before it annihilated with an electron. When this occurred, two annihilation γ quanta were simultaneously emitted with a nominal energy of 0.511 MeV, and one of these quanta was detected. The time span between the 1.28-MeV γ quantum and one of the annihilation quanta was then determined. This time span ranged typically between 0 and 3 ns, which was so short that in practice only one positron was present in the sample at any given instance. Therefore, the annihilations were counted on a one-by-one

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TABLE I. Summary of the characteristics of the four CVD films.

Sample type	Growth method	Film thickness (μm)	Average grain size (μm) [a]	Doping	Raman peak FWHM (cm^{-1})	PL features	Surface morphology [a]	Number of pieces in stack for positron measurement	Percentage of positrons annihilating within the stack (%)
CVD film I	microwave plasma CVD	11	4	boron-doped 10^{20}/cm^3	3.6	none	randomly oriented	1.5 [b]	33
CVD film II	hot filament CVD	30	11	undoped	10.2	broad band centered at 1.72 eV	{111} faceting	4	82
CVD film III	hot filament CVD	12	3	undoped	10.4	sharp peak at 1.68 eV with broad bands at higher energies	randomly oriented	3	54
CVD film IV	hot filament CVD	110	8	undoped	10.7	broad band centered at 1.83 eV	{100} faceting	1	77

[a] From SEM data.
[b] Two pieces on one side of the source, and one piece on the other.

basis. Figure 1 shows raw lifetime spectra for a single crystal bulk diamond and for CVD film IV. This film is heavily defective and exhibits substantial Ps formation, causing a much extended lifetime spectrum.

To measure the positron lifetimes experimentally, the positron source was sandwiched between the thin film samples. Since a total thickness of 300 μm is required to stop 98% of the positrons within the diamond samples, the thin films were stacked upon each other to increase the total sample thickness. But in all cases, the total thickness was much less than 300 μm, for which reason cobalt (or SiO_2) backing plates were placed on both sides of the diamond layers. Each lifetime spectrum therefore contains a contribution from this backing which must be subtracted to obtain the diamond film contribution. The backing contribution was determined experimentally by changing the number of diamond films in each stack and adjusting the backing contribution so that constant results for the diamond layers were obtained. By this method, we experimentally determined the percentage of positrons annihilating inside the stack of diamond films, which ranged from 33% to 82% as listed in Table I, agreeing well with those expected from theoretical calculations. These percentages were determined quite accurately because up to ten parameters (five lifetimes and five intensities) had to agree for a single value of backing contribution, so uncertainties in the lifetime data were dominated by the individual fits. The lifetime spectrometers employed in this work had a time resolution of 190–200 ps (full width at half maximum). The positron source had a strength of 9 μCi, and was encapsulated in 0.8-μm-thin Al foil. Each lifetime spectrum contained 1.2×10^7 counts (6.0×10^6 counts for low-temperature measurements). Data analyses were carried out using the code developed by Kirkegaard *et al.*,[9] in which the backing contribution to the overall lifetime spectra could be subtracted as a "source correction."

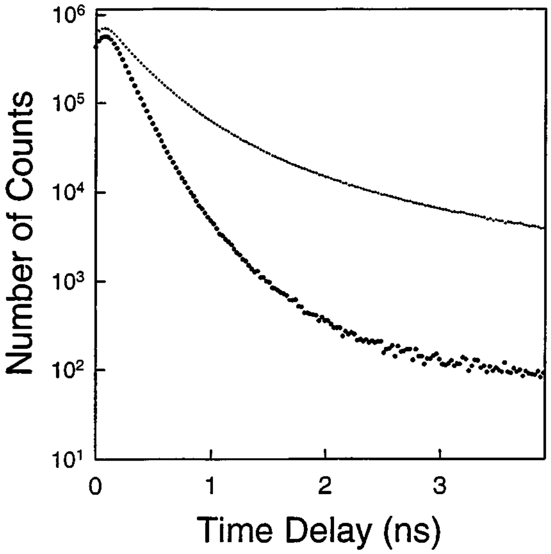

FIG. 1. Positron lifetime spectra for a natural diamond (larger dots) and for CVD film IV.

III. RESULTS AND DISCUSSION

Table II gives the positron lifetime and relative intensity data obtained from CVD diamond films as well as for different types of single-crystal bulk diamonds. All parameters were unconstrained in the analyses. The ability to separate five lifetime components is mainly due to the large numerical differences between the individual lifetimes. The enumeration of the lifetimes and associated intensities follows the practice of designating the shortest lifetime value by τ_1, and the other lifetimes of increasing values by τ_2, τ_3, etc. To

TABLE II. Lifetime and intensity data for three single-crystal diamonds and four CVD films.

Diamond sample	τ_1 (ps)	τ_2 (ps)	τ_3 (ns)	τ_4 (ns)	τ_5 (ns)	I_1 (%)	I_2 (%)	I_3 (%)	I_4 (%)	I_5 (%)
Natural type IaA	112	180	0.40			88	8	4		
Synthetic type Ib	105		0.43			97		3		
Natural type IIa	100		0.38			91.5		8.5		
CVD film I	105		0.45			98		2		
CVD film II	108±2	150±10	0.32±0.01	0.80±0.04	3.1±0.2	59±0.5	6±2	31±1	3.5±0.2	0.5±0.05
CVD film III	78±10	155±15	0.34±0.006	1.0±0.04	4.6±0.1	17±3	20±6	52±3	7.6±0.1	3.4±0.05
CVD film IV	110±10	180±10	0.40±0.01	1.2±0.04	4.7±0.1	6±2	35±3	41±3	13±0.7	5.1±0.05

provide a physical interpretation of these data, it is necessary first to consider the simple trapping model.[10] It states that when positrons are injected into a sample they initially occupy only the bulk state (i.e., are not trapped by vacancies) but can subsequently be trapped with a rate κ (the trapping rate) by defects which is calculable from the experimental data according to

$$\kappa=\frac{I_d}{1-I_d}(\lambda_B-\lambda_d). \tag{1}$$

Here λ_d $(\equiv 1/\tau_d)$ is the annihilation rate for trapped positrons, I_d is this component's relative intensity, and λ_B $(\equiv 1/\tau_B)$ is the bulk annihilation rate. The importance of κ is that this parameter is proportional to the vacancy concentration. It also follows from the trapping model that the τ_1 component which is due to annihilations in the bulk of defect-containing diamonds is given by

$$\tau_1=\tau_B/(1+\kappa\tau_B), \tag{2}$$

and that

$$1/\tau_B=I_1/\tau_1+I_d/\tau_d, \tag{3}$$

where $I_1+I_d=1$.

Thus from Eq. (1) the physically important trapping rate can be calculated from the experimental data, and from Eq. (2) it follows that when κ is nonzero the experimentally determined value of τ_1 is less than τ_B even though this lifetime component arises from positrons annihilating from the bulk state. From Eq. (3), however, τ_B can be calculated from the experimental data even when trapping is occurring. It should be noted that the intensities of the lifetime components do not express the percentage of positrons actually annihilating with the various lifetimes. For example, from the simple trapping model the *fraction* of positrons annihilating from the trapped state (giving rise to τ_d and I_d) is

$$f_d=\frac{\kappa}{\kappa+\lambda_B}=(\tau_d-\tau_B)/(\tau_d/I_d-\tau_B), \tag{4}$$

and the remaining fraction $(1-f_d)$ then annihilates from the bulk state. Generally f_d differs from I_d, but in the case of $I_d=0$ (no trapping), $f_d=0$, $\kappa=0$, and $\tau_1=\tau_B$, while in the case of $I_d=1$, $f_d=1$, $\kappa=\infty$, and $\tau_1=0$ (this later case corresponds to complete trapping).

We will now return to the data in Table II. For the single crystals as well as the boron-doped CVD film, the lifetime spectra are characterized by a dominant component τ_1, with intensities ranging between 88% and 98%. The other lifetime τ_3 (and τ_2 in the case of the type-IaA bulk diamond) is quite large, and must therefore arise from positrons trapped by vacancy clusters. For these samples defect trapping is, therefore, occurring, and τ_1 does not correspond to the bulk lifetime of a perfect diamond crystal, but using Eq. (3) τ_B can be calculated as listed in Table III. These values are quite close to τ_1 due to the small trapping rates κ as calculated from Eq. (1).

It can be seen that the boron-doped film (CVD film I), although polycrystalline, presents very similar positron annihilation data compared to those for the single-crystal bulk diamonds. Thermal annealing of this film up to 1100 °C results in no substantial changes except for a 50% increase in the lifetime component of τ_3 above 800 °C, which indicates growth of the average size of the vacancy clusters. The very small positron response from vacancies in this boron-doped film could be due to the doping in the sense that boron acceptors could render vacancies positively charged so that they would not be detected by the positrons. Alternatively, the high level of boron doping $(10^{20}/\mathrm{cm}^3)$ might reduce the concentration of vacancies, a possibility which is supported by the Raman and photoluminescence data in Fig. 2(a), which show a narrow Raman peak and no photoluminescence (PL).

For the other films the positron data indicate a much more complex defect situation where five individual lifetime components can be resolved. The undoped CVD film II has a large full width at half maximum (FWHM) $(10.2\ \mathrm{cm}^{-1})$ of the diamond Raman peak and a broad luminescence band centered around 1.72 eV [Fig. 2(b)] which suggest a more heavily defective film. The calculation of τ_B by using Eq. (3) as extended to five components (i.e., $1/\tau_B=\Sigma_{i=1}^{5}I_i/\tau_i$ and $\Sigma_{i=1}^{5}I_i=1$) for the CVD film II yields a value of 145 ps, which is clearly too high. However, using only the τ_1 and τ_2 components (where $I_1+I_2=65\%$), a value of 111 ps was obtained. Its numerical proximity to the bulk lifetime of 107 ps in perfect diamond crystals, therefore, suggests that τ_1 arises from positrons annihilating from the bulk state in crystallites which contain vacancies which give rise to τ_2, and that these crystallites comprise a volume fraction of 65% $(=I_1+I_2)$ of all the crystallites present in the film. The remaining fraction (35%) contains a high concentration ($\geqslant 50$ ppm) of vacancies, so that no bulk contribution can be observed, and it is from these crystallites that the τ_3, τ_4, and τ_5 lifetimes originate.

TABLE III. Results extracted from lifetime data. Entry denoted NC stands for not calculable.

Diamond sample	τ_B (ps)	Trapping rate (ns^{-1})	Fraction of crystallites with monovacancies of conc. (ppm)	Fraction of crystallites with divacancies of conc. (ppm)	Fraction of crystallites with large vacancy clusters of conc. (ppm)
Natural type IaA	120	0.3	Not applicable	Not applicable	Not applicable
Synthetic type Ib	107	0.2	Not applicable	Not applicable	Not applicable
Natural type IIa	107	0.6	Not applicable	Not applicable	Not applicable
CVD film I	107	< 0.2	0	0	Not applicable
CVD film II	111[a]	~ 0.2	0.65 ($\sim$0.4 ppm)	0	0.35 ($>$50 ppm)
CVD film III	107[a]	3.4	0.37 (7 ppm)	0	0.63 ($>$ 50 ppm)
CVD film IV	NC	large	0	0.35 ($>$20 ppm)	0.65 ($>$ 50 ppm)

[a] Using only the τ_1 and τ_2 lifetime components from Table II.

CVD film II was also investigated as a function of temperature down to 30 K, but no temperature dependency could be found. This suggests that the vacancies in the less defective crystallites were neutral, since negatively charged vacancies would have exhibited a strong increase in I_2 at low temperatures due to Coulomb attraction with the positively charged positron. For the highly defected crystallites the vacancy charge state cannot be assessed because complete trapping is occurring. The vacancies in the less defective crystallites are dominated by monovacancies because the lifetime τ_2 equals 150 ps, and the concentration of these monovacancies is about 0.4 ppm as determined from the trapping rate. In the heavily defected crystallites the positron lifetime τ_3 of $\sim$0.3 ns suggests the presence of vacancy clusters which have also been found by Yacobi *et al.*[11] and by Fanciulli and Moustakas.[12] The amount of vacancies in these clusters can be estimated by considering results obtained from annealing of electron-irradiated type-IaA natural diamonds. Figure 3 shows that the defect lifetime τ_2 changes from the monovacancy value of 150 ps to about 180 ps in the temperature range in which free monovacancies are known to be mobile.[13] We interpret this lifetime as arising from divacancies. The vacancy cluster lifetime of 0.32 ns therefore indicates at least several vacancies and a linear extrapolation suggests (perhaps fortuitously) a cluster size of $\sim$6 vacancies, a size which is thought to be a particularly stable cluster in the diamond crystal structure.[14] Correlating the positron results for CVD film II with the data presented in Fig. 2(b), suggests that the 1.72 eV photoluminescence peak can be correlated with vacancy clusters.

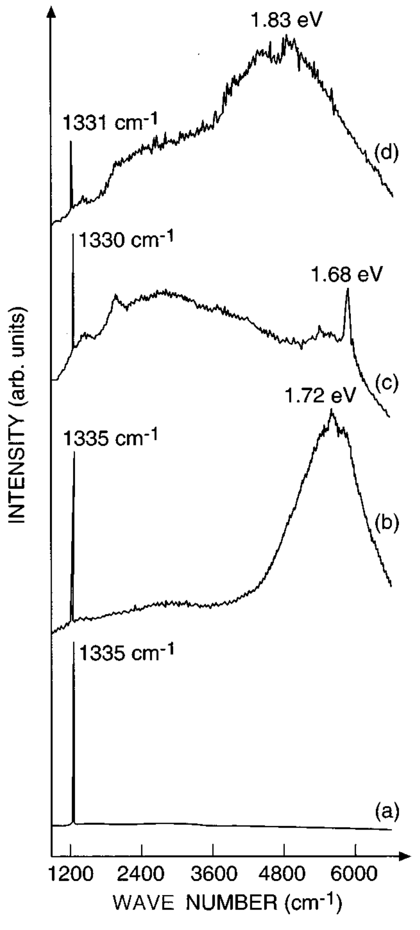

FIG. 2. Photoluminescence spectra for (a) CVD film I, (b) CVD film II, (c) CVD film III, and (d) CVD film IV.

In addition to the three lifetime components (τ_1, τ_2, and τ_3) just discussed, there are two further very long-lived (but weak) lifetime components τ_4 and τ_5 (see Table II). These arise from positronium (Ps) formation, which was verified by Doppler broadening measurements. Ps formation can occur when positrons become trapped by vacancy clusters. Suzuki *et al.*[7] also detected positronium using much thinner films ($\sim 1\,\mu$m) than in this work ($\geqslant 11\,\mu$m), suggesting that the presence of vacancy clusters is independent on film thickness. When Ps formation occurs there will, as mentioned in Sec. I, be present a lifetime of $\simeq$125 ps. This lifetime could not be resolved in free fits and will therefore mix into τ_1 and τ_2. However, because its intensity is small, equal to $(I_4+I_5)/3$, i.e., only 1.3%, this has no effect on the five-term analysis.

For the undoped CVD film III, which is characterized by a sharp luminescence peak at 1.68 eV and a broad back-

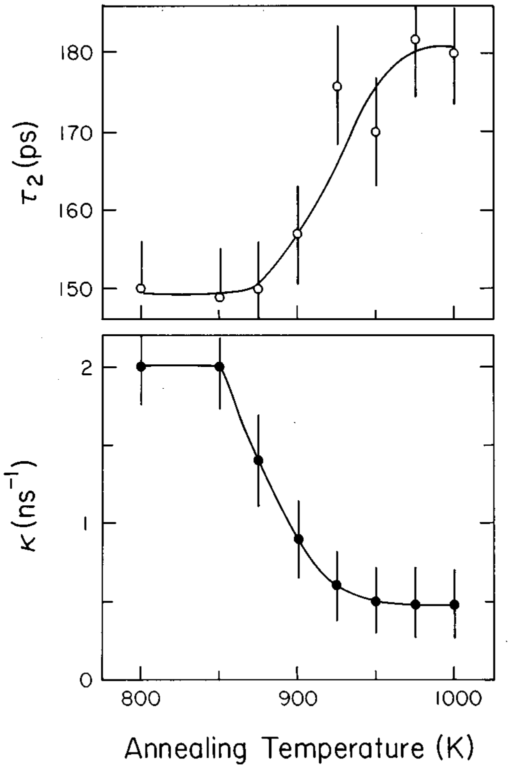

FIG. 3. Isochronal (1 h) annealing data for a type-IaA natural diamond irradiated by 3.5-MeV electrons to a dose of $2.5\times10^{18}e^-/\mathrm{cm}^2$.

ground at higher energies [Fig. 2(c)], the positron data indicate (see Table III) that 37% of the crystallites contain monovacancies at a concentration of 7 ppm. Saleh and Rice-Evans[15] recently found similar defect concentrations based on slow positron experiments and doppler broadening. The occurrence of the sharp 1.68-eV PL line and the "high" monovacancy content suggest that this PL peak is related to an (impurity-trapped) monovacancy, an interpretation which agrees with other PL studies.[16–18] The higher content of crystallites heavily defected with vacancy clusters also appears to correlate with the more intense broad background of the PL spectrum. The higher content of vacancy clusters in CVD film III also enhances the Ps formation, as shown by the higher values of I_4 and I_5. The contribution from the $\simeq$125-ps lifetime component amounts to $(I_4+I_5)/3=4\%$ This is small compared to the combined intensities of τ_1 and τ_2 (37%), and does not affect the calculation of the bulk lifetime as listed in Table III.

CVD film IV has a broad PL spectrum [Fig. 2(d)] centered around 1.83 eV. The positron data (see Table II) show a weak τ_1 component with a value of 110 ps which is, coincidently, close to the bulk lifetime in diamond. It actually arises exclusively from Ps formation which is particularly large for this sample (high values of I_4 and I_5 and verified by Doppler broadening). Therefore, in this sample 35% of the crystallites (corresponding to I_2) contain divacancies which yield a lifetime of 180 ps, and in these crystallites the vacancy concentration is so high that complete trapping occurs. In the remaining crystallites vacancy clusters are present, again causing complete trapping. This film is devoid of monovacancies, which is consistent with the absence of the 1.68-eV PL peak, but contains a substantial amount of divacancies which might be associated with the broadened PL peak at 1.83 eV. No effect from thermal annealing (to 1100 °C) could be found from the positron data, indicating high thermal stability of the grown-in vacancies.

The diamond films investigated in this work showed large variations in vacancy concentrations. This seems symptomatic when considering the results obtained by Uedono *et al.*[8] and Saleh and Rice-Evans,[15] who estimated, respectively, very high ($\approx$400 ppm) and modest ($\approx$5 ppm) concentrations.

It should be noted that positronium formation occurs in solids provided enough "empty" space is available, such as in larger vacancy clusters. However, this is not the only requirement, since in bulk silicon[19] or GaAs (Ref. 20) there is no positronium formation even when large vacancy clusters are present. However, formation of positronium is also very sensitive to the surface "chemistry" of the vacancy clusters, and might be influenced in the present case by hydrogen coverage. The existence of Ps in these diamond films suggests that a "passivation" of the inner surfaces has taken place. Two Ps lifetimes were found in CVD films II–IV. These lifetimes differ significantly (by a factor close to 4; see Table II), which suggests two different environments for Ps. These could be vacancy clusters and open spaces between the crystallites, although this leaves unexplained why no Ps is formed between the crystallites in CVD film I.

IV. CONCLUSIONS

Positron lifetime measurements have shown that vacancies distribute inhomogeneously in CVD diamond films. Some crystallites are essentially vacancy free, while others contain high concentrations ($>$50 ppm). Boron doping dramatically reduces the vacancy content in CVD diamond. For undoped films, a prevalent vacancy cluster configuration appears to be a six-member ring, and the fraction of crystallites containing such vacancy clusters is in the range of 35–65 %. The remaining crystallites contain varying amounts of monovacancies and divacancies. Positronium is formed in the vacancy clusters and possibly also between the crystallites. Correlation of the PL features with the positron results suggest that the broad band situated around 1.72 eV can be related to the presence of vacancy clusters, the 1.68-eV sharp peak can be linked to monovacancies, and the broad band centered at 1.83 eV can be associated with divacancies.

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