

EPR and optical studies on polycrystalline diamond films grown by chemical vapor deposition and annealed between 1100 and 1900 K

D. F. Talbot-Ponsonby, M. E. Newton,* and J. M. Baker

Clarendon Laboratory, Department of Physics, University of Oxford, Parks Road, Oxford OX1 3PU, United Kingdom

G. A. Scarsbrook, R. S. Sussmann, and A. J. Whitehead

De Beers Industrial Diamond Division (UK) Ltd., Charters, Sunninghill, Ascot, United Kingdom

(Received 10 March 1997)

The affect of annealing polycrystalline chemical vapor deposition (CVD) diamond *in vacuo* up to 1900 K has been studied using electron paramagnetic resonance (EPR) and infrared absorption. The concentration of the EPR centers at $g=2.0028$ and the infrared absorption in the CH region are insensitive to annealing below 1500 K. On annealing at 1700 K it was found that (a) some of the hydrogen on internal grain boundaries or in intergranular material became mobile (in samples with strong CH absorption there was a decrease in the peak at 2920 cm^{-1} and an increase in the peak at 2820 cm^{-1}) but was not lost from the sample and (b) the intensity of the EPR absorption at $g=2.0028$ decreased. More than one defect contributes to the EPR absorption at $g=2.0028$ in the samples studied. Annealing at 1900 K (no graphitization of the external surfaces occurred), in all except one case, severely degraded the optical properties of the samples and a different EPR defect at $g=2.0035(2)$ was created. Infrared measurements showed that hydrogen is lost from most CVD diamond samples when annealed to 1900 K for 4 h. [S0163-1829(98)03504-8]

I. INTRODUCTION

The synthesis of free-standing diamond film by chemical vapor deposition (CVD) currently captivates considerable academic and commercial interest. The quality of polycrystalline CVD diamond synthesized by many laboratories is steadily improving, but many questions remain unanswered about the nature and constituents of defects and impurities incorporated into the diamond, the species decorating the grain boundaries, and the material in between the grain boundaries or in voids within the films. The defects, impurities, and nondiamond material may affect the macroscopic properties such as thermal conductivity and optical transparency. In addition their identification may give information about growth mechanisms. The role of hydrogen in CVD diamond growth processes has been the subject of many publications; however, there are fewer publications investigating the location and distribution of hydrogen in polycrystalline films.¹⁻³ Postprocessing of CVD diamond films (e.g., annealing) has attracted even less attention,^{5,6} but may prove useful in fabrication of material for specific applications

Infrared absorption studies on CVD diamond samples have revealed several different CH stretch vibrations in the region $2750\text{--}3300\text{ cm}^{-1}$ arising from carbon-hydrogen bonds in different environments.^{2,3} Infrared absorption spectra in most CVD diamond samples can be fitted using CH stretch signatures of hydrogen bonded to sp^3 -bonded carbon (2850 , 2875 , 2920 , and 2965 cm^{-1}), hydrogen bonded to sp^2 -bonded carbon (2980 and 3025 cm^{-1}), and additional lines at 2820 and 2830 cm^{-1} not seen in hydrogenated amorphous carbon.^{2,3} McNamara *et al.*³ have associated the peaks at 2820 and 2830 cm^{-1} with N-CH₃ and O-CH₃ groups, respectively. However, they could originate from hydrogen adsorbed on a diamond surface.^{2,4}

Studies on samples of widely varying qualities showed a correlation between the total integrated CH infrared absorption and the concentration of paramagnetic centers at $g=2.0028$.⁷ In the study referred to above, the electron paramagnetic resonance (EPR) absorption at $g=2.0028$ was identified as originating from two (or more) different defects.⁷ One of these defects is the H1 center identified from line-shape analysis by Zhou *et al.*^{8,9} as an unpaired electron coupled to a hydrogen atom about 0.19 nm away. Zhou *et al.*^{8,9} proposed that H1 was formed by a hydrogen atom entering a stretched C-C bond at a grain boundary, allowing the carbon to relax back, one bonding to the hydrogen and the other with an unpaired electron localized in its dangling bond. No model was presented for the other defect at $g=2.0028$.⁷ ¹H matrix electron-nuclear double resonance measurements indicated that the H1 and other $g=2.0028$ centers are in an environment with hydrogen atoms $0.2\text{--}1\text{ nm}$ from the defect.⁷ There is now a considerable body of evidence supporting the assertion that the H1 center, and the other defects centered on $g=2.0028$ observed in polycrystalline CVD diamond films are located on grain boundaries or in intergranular material rather than in the bulk diamond.

There has been little work reported on the annealing behavior of the H1 and other $g=2.0028$ centers in polycrystalline CVD diamond. Jia *et al.*⁵ found that the intensity and line shape of the EPR absorption at $g=2.0028$ in hot filament CVD samples did not vary with annealing up to 1400 K , but annealing a sample (which had been ground into a powder) to 1800 K with an oxyacetylene torch for 20 min reduced the overall spin density by a factor of 4.5 and the relative intensity of the satellites increased with respect to the central line. No mention was made in this publication of sample graphitization. In an inert environment (vacuum better than $2 \times 10^{-6}\text{ mbar}$) the conversion of diamond to graph-

TABLE I. N_S^0 and $g=2.0028(1)$ spin concentrations (preannealing) determined by double integration of EPR spectra and comparison with a reference. The relative concentrations of different samples are accurate to $\pm 10\%$, but the errors on the absolute values are $\pm 20\%$. See the text for further details.

Sample No.	N_S^0 concentration (cm^{-3})	$g=2.0028(1)$ concentration (cm^{-3})
1	0.9×10^{17}	0.9×10^{17}
2	0.9×10^{17}	7.2×10^{17}
3	0.6×10^{17}	0.9×10^{17}
4	$< 2 \times 10^{15}$	1.4×10^{17}
5	$< 2 \times 10^{15}$	14×10^{17}

ite is not normally detectable for annealing below 1800 K, but diamond is attacked by oxygen and water vapor at temperatures as low as 900 K.¹⁰

Nitrogen is readily incorporated as a substitutional impurity (N_S^0) into diamond grown at high temperatures and pressures and by CVD. Under the growth conditions reported by Samlenski *et al.*¹¹ 50 parts per 10^6 (ppm) nitrogen in the process gas gave rise to incorporation of between 1 and 10 ppm [$(2-20) \times 10^{17} \text{ cm}^{-3}$] nitrogen in the CVD diamond. In polycrystalline CVD diamond, comparison of the concentration of N_S^0 (measured by EPR) with that of total nitrogen concentrations (from techniques such as combustion analysis) sometimes indicates that considerably more nitrogen can be present in forms other than N_S^0 . The bulk of the extra nitrogen is probably in the intergranular material rather than the diamond. It has been reported that adding nitrogen to the feed gases in various CVD processes can have dramatic effects on the diamond growth, including increased growth rates, textured $\{100\}$ growth, and the suppression of twin formation.¹²⁻¹⁴

The N_S^0 center has been studied extensively:^{15,16} the nitrogen bonds with its four carbon neighbors, the extra electron being localized in an antibonding orbital between the nitrogen and one of the carbon neighbors. This unique N-C bond is estimated to be 20–30% longer than the normal C-C bond¹⁷⁻¹⁹ and forms the principal axis of the defect, which has C_{3v} symmetry. The nitrogen donor level is thought to be about 2 eV below the conduction-band edge.

We report here the results of EPR and infrared studies on ten polycrystalline CVD diamond samples annealed in vacuum at temperatures between 1100 and 1900 K. In five of the samples the N_S^0 concentration was less than $2 \times 10^{15} \text{ cm}^{-3}$ as measured by EPR and in the others it ranged between 2×10^{16} and $4 \times 10^{17} \text{ cm}^{-3}$.

II. EXPERIMENT

The diamond samples used in this work were made by a microwave CVD process under a variety of conditions to obtain a wide range of material qualities. The free-standing polished films were all about 200–500 μm thick and varied from opaque to clear with an optical transparency approaching that of the best natural diamond. All samples showed a strong diamond Raman line at 1332 cm^{-1} with only weak nondiamond features in the Raman spectra. EPR measurements were made at temperatures between 4 and 300 K using a conventional spectrometer and a TE₁₀₄ cavity operating at approximately 9.6 GHz. Double integration of the first-

harmonic EPR signal and comparison with a reference sample allowed bulk spin concentrations to be determined. Infrared absorption measurements were made with the sample at room temperature using a Perkin-Elmer 1710 Fourier transform infrared spectrometer. Several measurements were made on each sample to check for the inhomogeneous distribution of defects. The infrared beam was of similar dimensions to the sample and it was found that the measurements were reproducible without having to position the sample carefully for each measurement.

The samples were annealed at temperatures between 1100 and 1900 K in a silicon carbide vacuum furnace (Severn Furnaces Limited). The sample tube is made from recrystallized alumina and has an internal bore of 50 mm; and the furnace temperature is constant over a region of length 250 mm. The furnace is controlled by a Eurotherm 902-904 controller that allows heating and cooling rates and set points to be maintained automatically. The furnace was evacuated with a diffusion pump, via a cold stage, capable of pumping the furnace down to 5×10^{-7} mbar. Once the samples were loaded, the furnace was purged with oxygen-free argon before pumping and annealing. The initial heating rate was kept low in order to allow the pumping rate to match the furnace outgassing. The furnace was held at the set annealing temperature for 4 h and then cooled at approximately 5 K per minute. During annealing the sample chamber pressure was kept below 5×10^{-6} mbar. The samples being studied were mounted in between pieces of CVD diamond film while being annealed to further reduce the risk of graphitization. Even at the highest annealing temperatures the surface graphitization rate was very low. To remove any surface graphite, the samples were cleaned after annealing in a solution of concentrated H_2SO_4 and KNO_3 held at 550–600 K for 30 min. After this treatment the samples were washed in H_2SO_4 at 550–600 K for a few minutes and then in deionized water. No mass loss was detected for any samples after annealing and cleaning, confirming that the surface graphitization rate was very low.

III. RESULTS

Before annealing, the samples were characterized by EPR (see Table I) and infrared absorption. It is useful to acquire the EPR spectra under a variety of different conditions,²⁰ as is shown for sample 1 in Fig. 1. This figure shows EPR data from the same sample recorded at incident microwave powers of (a) 3 mW and (b) 0.3 nW. At high microwave powers the N_S^0 spectrum [Fig. 1(b)] is strongly saturated such that

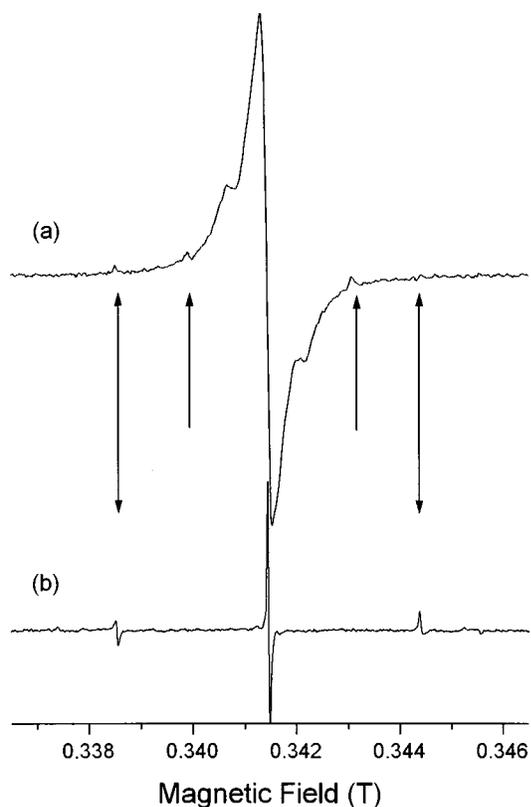


FIG. 1. X-band (9.6 GHz) EPR spectra from sample 1 recorded at 5.0 K with an incident microwave power of (a) 3.0 mW and (b) 0.3 nW. The double ended arrows indicate the $\Delta m_l = \pm 1$ allowed N_S^0 EPR transitions and the single ended lines indicate the $\Delta m_l = \pm 2$ forbidden N_S^0 EPR transitions observed at high microwave powers.

the allowed transitions are very small and the forbidden transitions, marked with the vertical arrows, are observable but weak. Under these conditions of observation the EPR absorption is dominated by the centers at $g=2.0028$, which saturate much less readily [Fig. 1(a)]. Reducing the microwave power by 40 dB diminishes the intensity of the $g=2.0028$ resonance by a factor of 100, but the N_S^0 comes out of saturation and the EPR intensity increases to a maximum before decreasing with further reduction in microwave power. Figure 1(b) is dominated by the N_S^0 EPR spectrum. This is not quite powderlike because preferential growth of specifically oriented crystallites resulted in a slight (110) texturing of the film. The N_S^0 EPR signal has been used to characterize the texturing of polycrystalline CVD diamond films.²¹

The EPR spectrum in Fig. 1(a) is reminiscent of those reported by other workers studying CVD diamond films.^{5,7-9,22-26} The linewidth, resolution, and relative intensity of the satellites are sample dependent, and in the samples we have studied it is not possible to reproduce the EPR spectra with the H1 defect alone. Additional resonances at $g=2.0028$ must be introduced to reproduce the experimental data satisfactorily.⁷

Annealing the CVD samples below 1500 K produced little or no observable change in the intensity or shape of the EPR absorption at $g=2.0028$. However, annealing the samples for 4 h at temperatures above 1500 K produced dra-

matic changes in the EPR intensity and line shape and in some cases the infrared absorption. Not all the samples behaved in the same way. Figure 2 shows results for three of the samples that are representative of those observed for the ten samples studied. Figure 2(a) presents the data from an opaque CVD sample (sample 2; the as-grown defect concentration at $g=2.0028$ was $7.2 \times 10^{17} \text{ cm}^{-3}$ and the single substitutional nitrogen concentration was $0.9 \times 10^{17} \text{ cm}^{-3}$), which shows strong CH infrared absorption. The presence of substitutional nitrogen does not influence the annealing behavior of the resonance at $g=2.0028$. On annealing to 1700 K the resonance at $g=2.0028$ narrows appreciably. The amplitude of the satellites relative to the central peak to peak height decreases and the overall intensity is reduced. The 2820-cm^{-1} infrared absorption peak increases dramatically along with other less pronounced reductions in the infrared absorption at higher energies. Overall, the strength of the CH absorption band does not change appreciably. Further annealing to 1900 K produces a new strong EPR resonance at $g=2.0035(2)$, without apparently reducing the intensity of the $g=2.0028$ resonance further. Annealing at 1900 K dramatically degrades the optical quality of the sample, which becomes much darker. This is not graphitization of the external sample surfaces. The infrared absorption of the overall CH absorption band is reduced with a marked reduction in the 2820-cm^{-1} absorption. Figure 3 shows the behavior of the $g=2.0028$ EPR intensity and the strength of the 2820-cm^{-1} absorption peak as a function of annealing temperature in sample 5, which behaved similarly to sample 2.

Figure 2(b) presents the annealing data for sample 3 (the as-grown defect concentration at $g=2.0028$ was $0.9 \times 10^{17} \text{ cm}^{-3}$ and the single substitutional nitrogen concentration was $0.6 \times 10^{17} \text{ cm}^{-3}$) in which the integrated absorption of the $g=2.0028$ EPR resonance was 8 times less than that of sample 2 [Fig. 2(a)]. The total CH infrared absorption band was also considerably weaker with no resolvable 2820-cm^{-1} peak. This sample was transparent. The satellites on the $g=2.0028$ resonance in sample 3 are less well resolved than in sample 2 and the central peak is slightly broader. On annealing to 1700 K the $g=2.0028$ resonance narrows, the amplitude of the satellites relative to the central peak to peak height decreases, and the overall intensity is reduced. Further annealing to 1900 K produces the new resonance at $g=2.0035(2)$. In this respect samples 2 and 3 behave in the same fashion. However, the infrared absorption spectra for sample 3 do not change appreciably with annealing. With the final annealing at 1900 K the sample, like sample 2, became much darker. Once again this was not graphitization of the external sample surfaces.

Figure 2(c) shows the annealing data for sample 4 (the as-grown defect concentration at $g=2.0028$ was $1.4 \times 10^{17} \text{ cm}^{-3}$ and the single substitutional nitrogen concentration was less than $0.2 \times 10^{15} \text{ cm}^{-3}$). Preannealing the $g=2.0028$ EPR absorption looked similar to sample 3 with poorly resolved satellites. However, the CH infrared absorption band was markedly different with only three broad peaks centered at $2924(5)$, $2850(5)$ (weak), and $2810(5) \text{ cm}^{-1}$. The first two peaks are characteristic of the asymmetric and symmetric stretching of CH_2 groups, respectively, where the carbon is sp^3 bonded. The inequality in the intensities of these two lines has been commented on by others.³

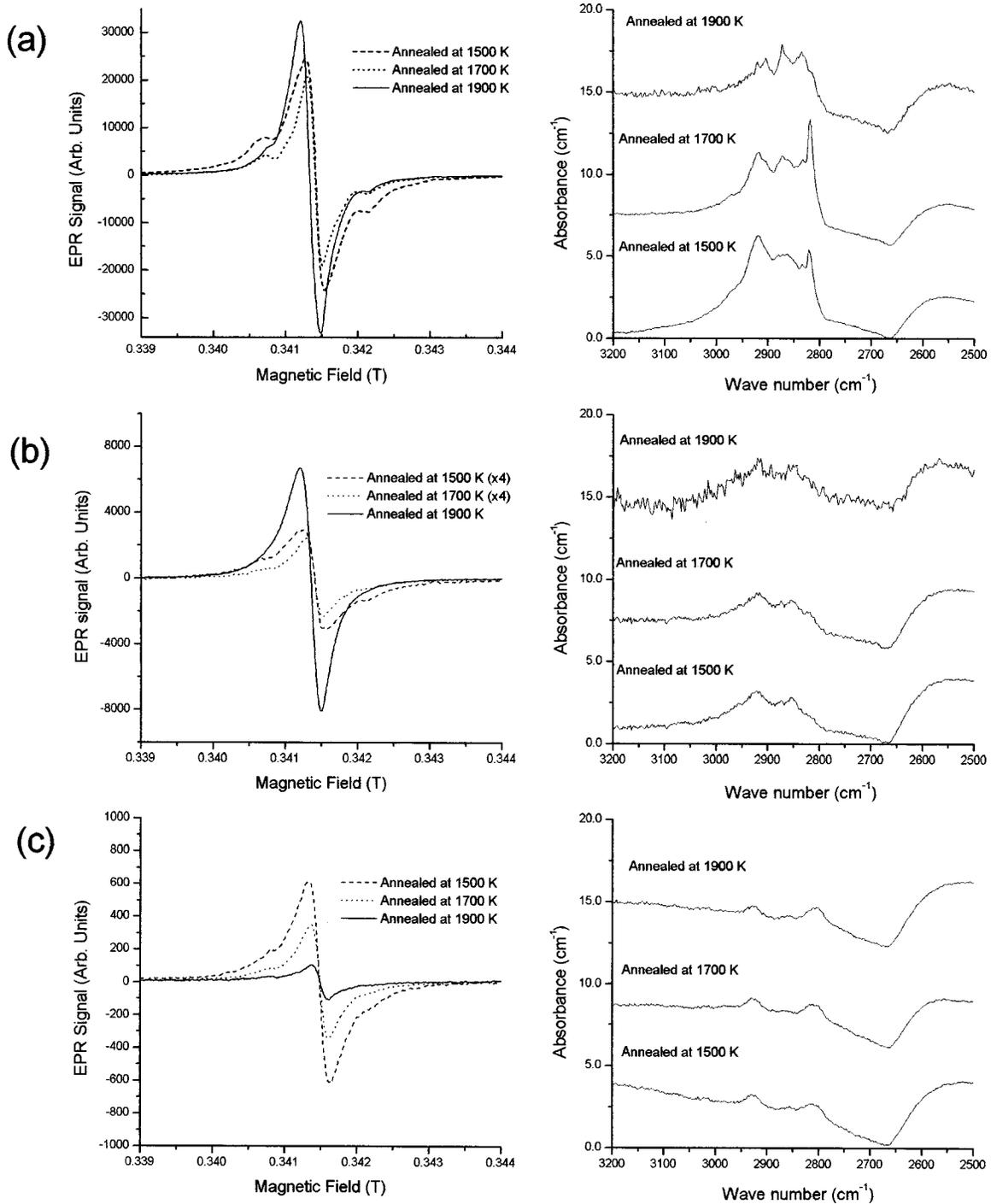


FIG. 2. X-band (9.6 GHz) EPR spectra recorded at 5.0 K and room-temperature infrared absorption spectra in CH region from (a) sample 2, (b) sample 3, and (c) sample 4, taken following annealing *in vacuo* for 4 h at 1500, 1700 (offset 7.5 cm⁻¹), or 1900 K (offset 15 cm⁻¹).

We can find no reference in the literature to the 2810(5)-cm⁻¹ line. Upon annealing, the $g = 2.0028$ EPR absorption diminishes in intensity without significant changes in the line shape, and the $g = 2.0035(2)$ resonance does not appear upon annealing to 1900 K. No changes are observed in the infrared absorption when annealing up to 1900 K and this sample did not show such a marked deterioration in optical quality.

Annealing a CVD sample in stages to a set temperature, holding the temperature for 4 h at each stage, produced the same overall change as annealing a piece of the same as-grown sample directly to the set temperature for four hours.

In five samples the concentration of N_S^0 was monitored between annealings and it was found that annealing up to the maximum temperature used here (1900 K) had no effect on the concentration of this impurity.

IV. DISCUSSION

A. Effect of annealing on N_S^0 concentration

The aggregation of N_S^0 centers to form A centers has been studied by many workers.²⁷⁻³⁰ When annealing type-Ib dia-

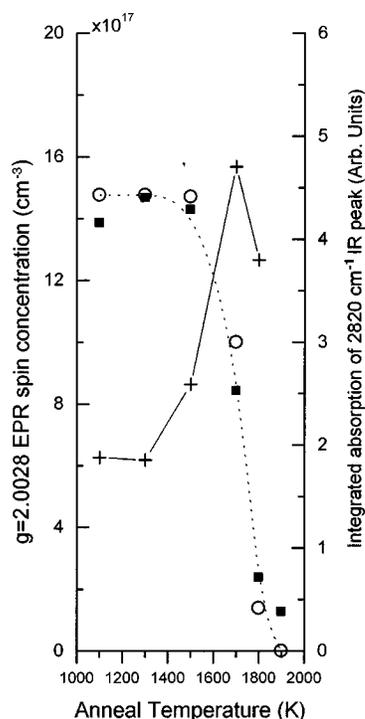


FIG. 3. The $g=2.0028$ EPR spin concentration (solid squares) and the integrated absorption of the 2820-cm^{-1} infrared peak (+) measured in sample 5 plotted as a function of isochronal annealing temperature. The error bars on the EPR and infrared data are approximately $\pm 10\%$. The best fit to the EPR data obtained using first-order kinetics is shown by the open circles; the broken line is drawn as a guide to the eye.

monds, it has been shown that the rate of formation of A centers is proportional to the square of the initial concentration of N_S^0 , showing that the A center consists of two nitrogen atoms.²⁹ It is now accepted that the A center consists of a pair of adjacent substitutional nitrogen atoms.^{17,19,31} The rate of aggregation can be substantially increased if the diamond is subjected to radiation damage.³² In the CVD diamond samples studied the maximum N_S^0 concentration was $4 \times 10^{17} \text{ cm}^{-3}$. With the concentration this low no significant aggregation of N_S^0 was expected in our studies. This is consistent with the N_S^0 concentration being unchanged by annealing. No evidence of thermally or optically activate charge transfer altering the concentration of N_S^0 (N_S^0 donating an electron to a trap or N_S^+ trapping an electron) was detected on annealing. The N_S^0 EPR signal made a useful internal reference for studying the changes in the concentrations of other centers during annealing.

B. Effect of annealing on the concentration of EPR centers at $g=2.0028$ and CH infrared absorption band

In all samples we have studied the intensity of the EPR absorption at $g=2.0028$ reduced on annealing above 1500 K. However, the details of the changes are sample dependent. In most samples on annealing to 1700 K the resonance narrowed and the satellites became better resolved. Neither before nor after annealing could the shape of the $g=2.0028$ EPR signal be successfully simulated with only the H1 EPR resonance. The relative contribution of H1 to the signal at

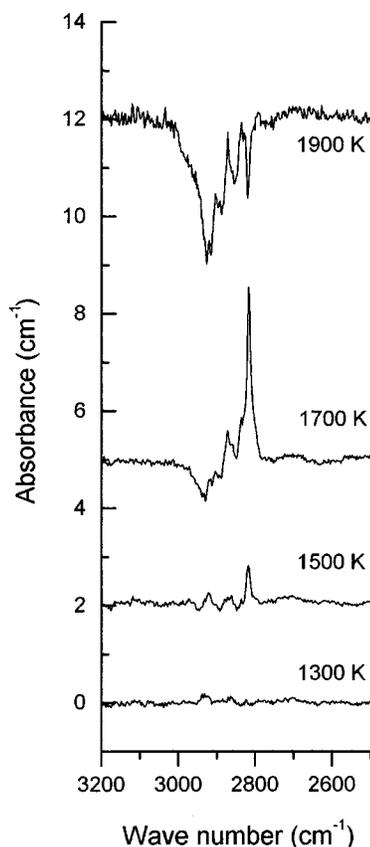


FIG. 4. Room-temperature infrared difference spectra (annealed spectrum minus the as-grown absorption spectrum) for sample 2, offset for clarity of display. See the text for details.

$g=2.0028$ is sample dependent and can change on annealing at 1700 K. This is consistent with other paramagnetic centers contributing to the $g=2.0028$ resonance and these centers annealing at a different rate to H1.

In samples that exhibit strong CH absorption (samples 2 and 5 in this paper), changes in this band can be observed concurrently with changes in the EPR spectra. Figure 3 shows the change in the $g=2.0028$ spin concentration and the change in the 2820-cm^{-1} absorption peak on annealing in such a sample (sample 5). The total change in the CH absorption band in a sample of this type (sample 2) is shown in Fig. 4. Here the as-grown infrared absorption spectrum has been subtracted from the annealed spectrum. The changes in the CH infrared absorption band are not significant below 1500 K, but at 1700 K we find a redistribution of intensity, with some peaks growing and others falling in intensity. There appears to be no overall loss of strength in the band. There is a redistribution of hydrogen amongst different bonding configurations. The reduction in the peak around 2920 cm^{-1} indicates a loss of CH_2 groups (where the carbon is sp^3 bonded). This loss is mirrored by a growth in the intensity of the 2820-cm^{-1} peak, which has been alternately attributed to a N-CH_3 group³ or alternately to hydrogen adsorbed on a diamond surface.^{2,4}

For samples with much lower concentrations of the $g=2.0028$ EPR centers, the EPR signal behaves on annealing to 1700 K in the same fashion as for samples with strong CH absorption, but there are no significant changes in the CH absorption band, presumably because of the low number of

hydrogen atoms redistributing during the annealing. Too many different processes are occurring to correlate the change in the EPR spectra with a specific band in the infrared; however, an increase in the 2820-cm^{-1} absorption peak at 1700 K is always accompanied by a reduction in the $g = 2.0028$ EPR signal strength.

Previous studies have indicated that H1 and the other $g = 2.0028$ defects are probably located on grain boundaries or in hydrogenated intergranular material.^{7-9,26} We have found that the EPR absorption at $g = 2.0028$ reduces at temperatures where some of the hydrogen is mobile, but below 1700 K no hydrogen (as monitored by infrared absorption) is lost from the CVD diamond samples. Annealing to 1900 K produced a new EPR center at $g = 2.0035(2)$ in all samples except one [sample 4, Fig. 2(c)]. The line shape is asymmetric, indicating a small g -matrix anisotropy. No hyperfine structure was observed. We have no reliable model for this defect.

After annealing to 1900 K the overall CH absorption band was reduced in intensity in most samples (e.g., Fig. 3), indicating that hydrogen was either lost from the sample or incorporated in a non-infrared-active form. The first explanation seems to be the most likely. It was not possible to measure the change in some samples due to a significant reduction in infrared transmission following the 1900 K anneal. All samples except sample 4 darkened noticeably during the 1900 K annealing and the visible transmission was reduced significantly. The deterioration of optical quality of the samples was pronounced. It appeared that severe internal degradation of the samples was taking place, but there was no graphitization of the external surfaces. We conclude that the loss and redistribution of hydrogen during the high-temperature annealings destabilizes the internal grain boundaries and diamond is being converted into graphite or hydrogenated amorphous carbon. It is possible that part of the reduction in transmission is due to increased absorption by both electronic band-gap states and vibrational states; however, we believe that the degradation of internal grain boundaries increases the scattering of incident light.

The anomalous behavior of sample 4 is not understood. As can be seen from Fig. 2(c), the $g = 2.0028$ EPR absorption decreases on the 1900 K annealing but no new defects are created. The optical quality and infrared absorption in the CH region did not change on annealing to 1900 K. The CH infrared absorption spectrum for this sample is unusual: We have not seen the broad peak at 2810 cm^{-1} in any other CVD diamond sample. It is possible that the grain boundaries in this material are stabilized by a different, more stable CH species and that the incorporation of intergranular hydrogenated amorphous carbon is much less in this sample. Further work on this sample is planned.

C. Hydrogen termination of diamond surfaces and modeling the kinetics of reduction in the EPR absorption at $g = 2.0028$ on annealing

Quantitative analysis of the isothermal annealing data is difficult because it is possible that many different processes that affect the concentration of H1 and other defects occur simultaneously. It is apparent from the infrared data that CH bonds are being broken on annealing above 1500 K and the

hydrogen released is forming more stable species and is not lost from the sample until the temperature is increased above 1800–1900 K. If the model for the H1 center (hydrogen entering a weak C-C bond at a grain boundary, bonding with one of the carbons and leaving an unpaired electron in the dangling orbital on the other) is correct,^{8,9} it could be destroyed by the evolution of the hydrogen atom on annealing, or by a hydrogen atom (supplied from another surface species, another H1 center, or abstracted by the intergranular material) bonding with the dangling carbon orbital.

It is clear that a redistribution of hydrogen on annealing below 1700 K reduces the concentration of paramagnetic defects. We attempted to fit the reduction in the concentration of H1 centers on annealing using first-order kinetics, which predicts that the concentration after the i th annealing $[H1]_i = [H1]_{i-1} \exp(-k\tau)$, where τ is the time of the annealing at a temperature T . The rate constant is given by $k = A_0 \exp(-E_A/k_B T)$, where A_0 is a constant and E_A the activation energy. We set E_A equal to the energy required to break a CH bond ($E_A \sim 4.3$ eV) and allowed only the constant A_0 to vary. The isothermal annealing data for the EPR concentration at $g = 2.0028$ is reproduced reasonably well using first-order kinetics. The fit obtained to the annealing data from sample 5 ($E_A = 4.3$ eV and $A_0 = 10^8$ Hz) is shown in Fig. 3. If H1 were simply decaying by emission of hydrogen atoms to nonsaturable traps we would expect A_0 to be typical of vibration frequencies ($\sim 10^{13}$ Hz), which is clearly not the case. However, the value of A_0 is consistent with H1 being destroyed by capturing a hydrogen atom, so long as the capture probability is low (i.e., there are many other traps for hydrogen atoms). It is not worth speculating further; because of the complexity of processes that are probably occurring, simple first-order kinetics is likely to be inappropriate. However, the annealing rate of the EPR signal at $g = 2.0028$ is consistent with the requirement of breaking a CH bond in order to destroy the center.

Surface studies have revealed that hydrogen termination of diamond is important in stabilizing the surface structure and hence the bulk diamond against phase transformation. Studies on hydrogen-terminated (external) surfaces indicate that the strongly bound hydrogen is lost on annealing to 1200–1300 K.³³ We do not observe changes until the annealing temperature is raised to 1500 K; therefore, we are not simply dealing with hydrogen on external diamond surfaces. During annealing hydrogen atoms may be exchanged between the diamond surfaces and intergranular hydrogenated material, and the types of CH species present on the surfaces and in intergranular material could be changed. This is consistent with the changes observed in the infrared absorption in some of the samples. Presumable samples that show no change contain only the most stable CH species.

Studies on (111) diamond surfaces show that the chemisorption of hydrogen on a clean surface (2×1 reconstructed) induces a phase transition to a 1×1 structure. The desorption peak occurs around 1300 K, but a few percent of a monolayer on the surface is effective at maintaining the sp^3 1×1 structure.³⁴ An infrared peak at 2830 cm^{-1} has been tentatively assigned to the surface C-H stretching mode.⁴ Studies of hydrogen-induced surface reconstruction on (001) surfaces have also been reported.³⁵ During CVD growth as well as stabilizing the surface atomic hydrogen generates

radical sites at which hydrocarbons can absorb by hydrogen abstraction and assist the incorporation of the hydrocarbons by further hydrogen abstraction.³⁶ Annealing at 1900 K resulted in the breaking of CH bonds, the loss of hydrogen from the sample, and degradation of the optical properties of the sample. New paramagnetic defects were created in the process. It appears that hydrogen stabilizing diamond surfaces were lost and surface reconstruction or internal graphitization took place.

V. CONCLUSION

The infrared absorption and concentration of the EPR centers at $g = 2.0028$ are found to be unaffected by annealing at temperatures below about 1500 K in the CVD diamond samples studied, which is consistent with work previously reported.⁵ However, prolonged annealing at higher temperatures changes both the infrared and EPR absorption. At 1700 K some of the hydrogen on internal grain boundaries or in intergranular material becomes mobile. The intensity of the EPR absorption at $g = 2.0028$ decreases, but the detailed behavior is complicated, indicating the presence of different defects all contributing to the EPR absorption. However, the annealing rate is consistent with the requirement to break a CH bond to reduce the EPR signal at $g = 2.0028$. In samples with strong CH infrared absorption there is a decrease in the peak at 2920 cm^{-1} and an increase in the peak at 2820 cm^{-1} on annealing at 1700 K. The 2820 cm^{-1} peak is strongest in samples with intense CH absorption bands. Its strength does

not correlate with the N_S^0 concentration and the increase in intensity on annealing appears to depend only on the availability of hydrogen. This leads us to believe that the 2820 cm^{-1} peak originates from a hydrogen center on a diamond surface rather than an impurity species.

Annealing for 4 h at 1900 K, in all except one case, severely degraded the optical properties of the sample and a new EPR defect at $g = 2.0035(2)$ was created. Infrared measurements show that hydrogen is lost from most CVD diamond samples on annealing at 1900 K. One sample, with an unusual CH absorption spectrum, did not show the dramatic changes in optical quality and no new EPR centers were created by the 1900 K annealing.

This study has shown that the concentration of paramagnetic defects and the distribution of hydrogen can be altered by high-temperature annealing. A study of the possible correlations of these changes with changes in electrical properties on annealing is planned. The present study has shown that annealing to 1900 K can severely damage the optical quality of polycrystalline films. The processes involved in the degradation are not fully understood but appear to involve loss of hydrogen from the sample.

ACKNOWLEDGMENTS

This work was supported by EPSRC Grant No. GR/K1562.6. D.T.P. thanks EPSRC and De Beers Industrial Diamond Division for financial support. M.E.N. thanks EPSRC for financial support.

*Author to whom correspondence should be addressed.

¹K. M. McNamara, D. H. Levy, K. K. Gleason, and C. J. Robinson, *Appl. Phys. Lett.* **60**, 580 (1992).

²B. Dischler, C. Wild, W. Müller-Sebert, and P. Koidl, *Physica B* **185**, 217 (1993).

³K. McNamara, B. Williams, K. Gleason, and B. E. Scruggs, *J. Appl. Phys.* **76**, 2466 (1994).

⁴R. P. Chin, J. Y. Huang, Y. R. Shen, T. J. Chuang, H. Seki, and M. Buck, *Phys. Rev. B* **45**, 1522 (1992).

⁵H. Jia, J. Shinar, D. P. Lang, and M. Pruski, *Phys. Rev. B* **48**, 17 595 (1993).

⁶S. Mitra and K. K. Gleason, *Diamond Relat. Mater.* **2**, 126 (1993).

⁷D. Talbot-Ponsonby *et al.*, *Phys. Rev. B* (to be published).

⁸X. Zhou, G. Watkins, and K. McNamara-Rutledge, *Mater. Sci. Forum* **196-201**, 825 (1996).

⁹X. Zhou, G. Watkins, K. M. McNamara-Rutledge, R. P. Messmer, and Sanjay Chawla, *Phys. Rev. B* **54**, 7881 (1996).

¹⁰G. Davies and T. Evans, *Proc. R. Soc. London, Ser. A* **277**, 413 (1972).

¹¹R. Samlenski, C. Haug, R. Brenn, C. Wild, and P. Koidl, *Appl. Phys. Lett.* **65**, 2798 (1995).

¹²W. Muller-Seber *et al.*, *Appl. Phys. Lett.* **68**, 759 (1996).

¹³G. Cao *et al.*, *J. Appl. Phys.* **79**, 1357 (1996).

¹⁴S. Jin and T. Moustakas, *Appl. Phys. Lett.* **65**, 403 (1994).

¹⁵W. V. Smith, P. P. Sorokin, I. L. Gelles, and G. J. Lasher, *Phys. Rev.* **115**, 1546 (1959).

¹⁶A. Cox, M. E. Newton, and J. M. Baker, *J. Phys. C* **6**, 551 (1994).

¹⁷P. R. Briddon and R. Jones, *Physica B* **185**, 179 (1993).

¹⁸S. A. Kajihara, A. Antonelli, and J. Bernholc, *Phys. Rev. Lett.* **66**, 2010 (199X).

¹⁹O. D. Tucker, M. E. Newton, and J. M. Baker, *Phys. Rev. B* **50**, 15 586 (1994).

²⁰P. B. Lukins and J. Khachan, *Appl. Phys. Lett.* **65**, 3320 (1994).

²¹C. F. O. Graeff, C. E. Nebel, M. Stutzmann, A. Flöter, and R. Zachai, *J. Appl. Phys.* **81**, 234 (1997).

²²I. Watanabe and K. Sugata, *Jpn. J. Appl. Phys., Part 1* **27**, 1808 (1988).

²³W. Zhang, F. Zhang, Q. Wu, and G. Chen, *Mater. Lett.* **15**, 292 (1992).

²⁴M. Fanciulli and T. D. Moustakas, *Phys. Rev. B* **48**, 14 982 (1993).

²⁵S. L. Holder, L. G. Rowan, and J. J. Krebs, *Appl. Phys. Lett.* **64**, 1091 (1994).

²⁶D. Talbot-Ponsonby *et al.*, *J. Phys.: Condens. Matter* **8**, 837 (1996).

²⁷R. Chrenko, R. Tuft, and H. M. Strong, *Nature (London)* **270**, 141 (1977).

²⁸A. T. Collins, *J. Phys. C* **13**, 2641 (1980).

²⁹T. Evans and Z. Qi, *Proc. R. Soc. London, Ser. A* **381**, 159 (1982).

³⁰T. Evans, in *The Properties of Natural and Synthetic Diamond*, edited by J. Field (Academic, London, 1992), Chap. 6.

³¹G. Davies and M. F. Hamer, *Proc. R. Soc. London, Ser. A* **348**, 285 (1976).

³²A. T. Collins, in *Defects and Radiation Effects in Semiconductors*, edited by R. R. Hasiguti, IOP Conf. Proc. No. 59 (Institute of Physics and Physical Society, London, 1981), p. 247.

- ³³S. Evans, in *The Properties of Growth of Diamond*, edited by G. Davies (Inspec, IEE, London, 1994), pp. 59–69.
- ³⁴Y. Misuda, T. Yamada, T. J. Chuang, and H. Seki, *Surf. Sci.* **257**, L633 (1991).
- ³⁵R. E. Thomas, R. A. Rudder, and R. J. Markunas, *J. Vac. Sci. Technol. A* **10**, 2451 (1992).
- ³⁶J. E. Butler and R. L. Woodin, *Philos. Trans. R. Soc. London, Ser. A* **342**, 209 (1993).