Photochromism of H2 and H3 centres in synthetic type Ib diamonds

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Abstract. Photochromism has been studied for irradiated type Ib diamonds which are then annealed above 1500 °C. This mainly involves H2 and H3 centres. When the samples are illuminated with light of wavelength shorter than 600 nm, absorption of H2 centres is reduced while that of H3 centres is enhanced. In the dark the process is reversed. Several characteristic features have been examined for various illumination conditions and different samples. On the basis of the results a model is proposed: H2 and H3 centres are the same centre with different charge states and photoionization of H2 may be responsible for the photochromism.

1. Introduction

Several examples of photochromism are known on colour centres in diamonds. Photochromism is defined as a reversible change in the absorption spectrum induced by light illumination, particularly occurring with a relatively long time constant. The study of photochromism gives valuable information on photo-induced change in the state of defects and also on application to optical storage.

Previously Walker (1979) cited in his review article, the old thesis of du Preez that illumination with a mercury lamp produces bleaching of an H2 centre and enhancement of an H3 centre in irradiated and annealed natural type Ia diamonds, and heating in the dark results in the reverse processes. The H3 centre is one of the most studied centres generated in natural type Ia diamonds and their model is generally accepted to be a vacancy trapped at a pair of substitutional nitrogen atoms (Davies *et al* 1976). For the H2 centre, however, no detailed information has been published since the first observation of du Preez. The formation condition and structure are not yet known.

Recently, it has been found that an H2 centre is generated in sufficient density with good reproducibility for synthetic type Ib diamonds, fabricated at Sumitomo Electric Industries Ltd (Nakashima *et al* 1988). Samples are irradiated with a heavy dose and annealed above 1500 °C under 5.5 GPa. Simultaneously an H3 centre is introduced in subsidiary concentrations. The present authors have found the occurrence of photochromism for these samples, which probably gives confirmation of du Preez's old
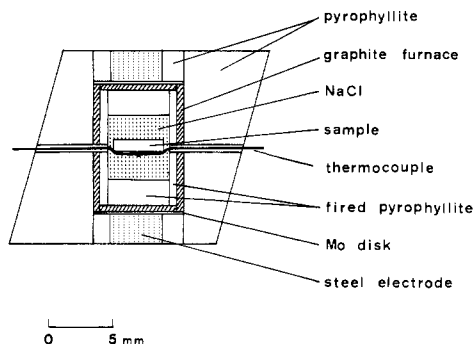
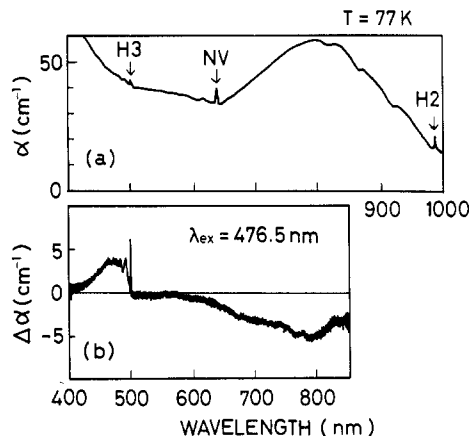**Figure 1.** Sample assembly for annealing at 1500 °C under high pressure, 6 GPa.

Figure 2. Typical absorption spectrum of irradiated and annealed synthetic type Ib diamonds measured at (*a*) 77 K, and (*b*) photochromism induced by illumination of 476.5 nm Ar laser light. Sample 8413H.

result. Furthermore, the present work describes the nature of photochromism in detail and proposes a model for the process.

Other interesting examples of photochromism reported so far are as follows. The best known is of GR1 and ND1 examined by Dyer and du Preez (1965). This photochromism was concluded to arise from conversion between different charge states of the same defect, namely, a single vacancy. On the other hand, Collins and Rafique (1979) found that optical bleach of the vibronic centre with the zero-phonon line at 2.367 eV produces a complementary increase of the 1.979 eV centre, for type Ib diamonds electron-irradiated at low temperature. They inferred that this process is ascribed to a change in the symmetry nature of the same centre, due to lattice distortion induced by photo-illumination. O'Donnell (1980) also reported that photochromism occurred at low temperature for electron-irradiated type IIb diamonds.

2. Samples

The synthetic type Ib diamonds used were supplied from Sumitomo Electric Industries and contain singly isolated nitrogen impurity atoms in densities of around 100 ppm. Samples were irradiated with a $1-6 \times 10^{19}$ cm^{-2} dose of 20 MeV electrons from the Linac at the Institute of Scientific and Industrial Research, Osaka University. Subsequently the samples were annealed at 1500 °C under a pressure of 5.5 GPa, for a half to 15 hours. Table 1 gives a list of samples used. The main results were obtained from sample 8413H and others were used for comparison.

The sample assembly employed for annealing under a high pressure is shown in figure 1. A sample is enclosed with a platinum foil and is surrounded by a pressure media, the nearest being NaCl powder and farthest fired pyrophyllite. All of them are put into a graphite furnace and the furnace is packed in a block of pyrophyllite. This assembly is

mounted into a split-sphere type apparatus (Kawai *et al* 1973) and pressed. The heater current is supplied through steel electrodes.

3. Results

Figure 2(*a*) shows a typical absorption spectrum measured at 77 K. Three zero-phonon peaks at 503, 638 and 987 nm are found, which are assigned to H3, NV and H2 centres, respectively. A broad absorption band extending in the region from 700 to 980 nm is due to the phonon sideband of an H2 centre. An H2 centre is always generated most dominantly after 1500 °C annealing and therefore is characteristic of type Ib diamonds. Since single nitrogen impurities tend to migrate and to aggregate above 1500 °C, the simultaneous formation of H2 and H3 centres seems to be related to this aggregation of nitrogen impurities (Chrenko *et al* 1977, Collins 1980). For the present samples, the infrared measurement indicates the appearance of the major band at 1282 cm^{-1}, which is identified with the formation of nitrogen pairs. Figure 2(*b*) demonstrates photo-chromism, which shows the difference in the absorption coefficient $\Delta\alpha$ between the cases of illumination with 476.5 nm Ar laser light and no illumination. The positive sign of $\Delta\alpha$, means an increase in the absorption coefficient when the light is switched on. This result apparently indicates a bleaching of H2 and enhancement of H3, and occurs at room temperature as well as at 77 K. The magnitude of change in the absorption coefficient is about one tenth the absorption coefficient for H2. Since no remarkable change appears in the sideband absorption of a NV centre, in the range of 500 to 638 nm, a NV centre has no contribution to this effect.

The range of light wavelength responsible for the photochromism is studied, using several laser lines or a combination of optical filters and usual light sources. As a consequence, the photochromism is produced with illumination of light shorter than 600 nm in wavelength. Illumination at the phonon sideband absorption and thus the local excitation of H2 centres has no effect. The shortest wavelength used is 365 nm mercury line, which produces similar effects as the visible light. The range of photon energy for the occurrence of photochromism is thought to coincide with photoionization of H2 centres which triggers the effect, though a direct detection of photo-carriers has not been attempted.

For investigation of temporal change in the absorption coefficients of H2 and H3 centres two probe lights are used at 780 and 480 nm, respectively. The former is generated by a semiconductor laser. In figure 3 the effect of simultaneous illumination of 365 nm and 488 nm is examined by monitoring H2 centres. First when a single light, 488 nm, is applied, the absorption of H2 is reduced and then reaches a steady state, in accordance with figure 2(*b*). Next, the second light, 365 nm, is superimposed on it. An additional change of H2 occurs in the same direction when the 488 nm light intensity is not so strong. However, when the 488 nm light is strong change occurs in the opposite direction, giving a partial increase of H2. This fact indicates the dual nature of ultra-violet (UV) light, which plays two opposite roles to bleach and to enhance H2 centres, depending on the visible light intensity. After the lights are turned off, recovery of H2 centres occurs in several minutes and the recovery curve is not described as a single exponential.

Figure 4 demonstrates a close correlation between H2 and H3 centres. The absorptions of H2 and H3 are simultaneously monitored under illumination of two light beams. In the case of single illumination of 488 nm, H2 is bleached and H3 is enhanced.
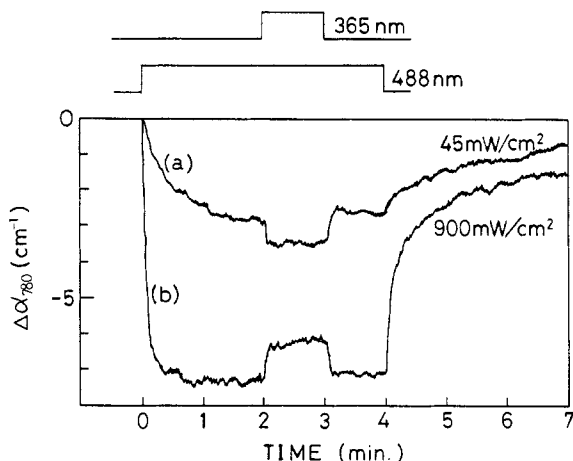
Figure 3. Temporal change in the absorption of H2 monitored at 780 nm with illumination of two lights at 488 and 365 nm. Time sequence of illumination is indicated in the upper part. The intensity of 488 nm is different for curves (*a*) and (*b*). Change induced by 365 nm light occurs oppositely, depending on the 488 nm intensity.
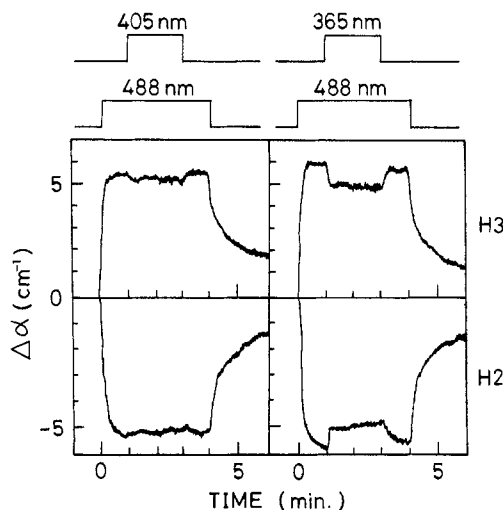

Figure 4. Comparison of temporal changes of H2(lower) and H3(upper). Photochemical processes of H2 and H3 occur simultaneously with the same magnitude but in opposite directions. The time sequence of two-light illumination is shown in the uppermost section. Additional illumination of 405 nm light is less effective in producing the partial reduction of H3 compared with the case of 365 nm light.
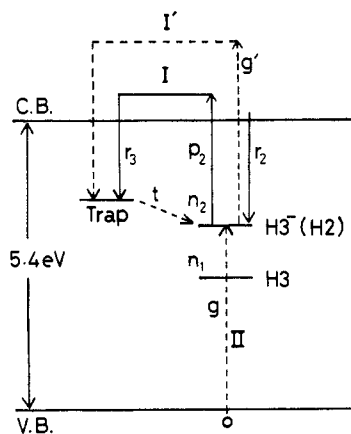
Figure 5. Proposal of a model for photochromism. H2 and H3 centres are assumed to be different charge states of the same centre. The H3 level is about 1.2 eV below the H2(H3$^-$). The trap centre, X, is unknown, probably singly ionized nitrogen, and has a level slightly higher than the H2 level. The visible light induces photoionization of H2 (process I), and the UV produces two photochemical processes labelled I′ and II.

Furthermore, when 365 nm light is additively illuminated, the reverse process is dominant, namely, H2 is partially increased and H3 is decreased. Changes in H2 and H3 are almost the same in magnitude but opposite. In other words, a change of H3 is always

Table 1. Samples used in the measurement.

| Sample | Absorption coefficient (cm^{-1}) | | Ratio $\alpha(H3)/\alpha(H2)$ | Ratio of change $\Delta\alpha(H3)/\Delta\alpha(H2)$ |
	$\alpha(H3)$	$\alpha(H2)$		
8413H	1.02	5.60	0.182	0.723
8604H	0.61	3.25	0.188	0.799
8402H	0.024	1.38	0.017	0.749

accompanied by that of H2 and the change is directly opposite to each other. The recovery rate is quite similar for both changes. These results give evidence for mutual conversion of H2 and H3 centres with each other, and suggest strongly that both are related to different charge states of the same centre. Walker (1979) proposed the same model intuitively in his review.

The UV light yields dual processes as shown in figure 3: photochemical conversion of H2 to H3 as well as the reverse, while the visible light only induces the former. The dual effect of the UV light becomes the more prominent at the shorter wavelength. When the second illumination is at 405 nm, additional change is less appreciable compared with the case of 365 nm, as seen in figure 4. This fact may indicate that the dual nature of the UV light disappears at around 405 nm.

Now, let us consider the difference in photochromism for different samples. Table 1 gives the absorption coefficients at the zero-phonon lines of H2 and H3, α(H2) and α(H3) for three samples, and presents differences in the relative concentration of centres included, which depend on the electron doses and the annealing time and temperature. For all the samples, the major centre is H2. The last column indicates the ratio of the changes in the absorption coefficients of H3 and H2, $\Delta\alpha$(H3)/$\Delta\alpha$(H2), induced by illumination. The noticeable point is that the values of this ratio are almost independent of samples, despite the fact that the densities of centres are quite different. This can be understood as follows. In general, the absorption coefficient α is expressed as a product of the density of centres, n, and the absorption cross section σ, i.e., $\alpha = n\sigma$. Assuming that photochromism arises from a change in the density, Δn, and Δn (H3) $= \Delta n$ (H2), we obtain the relation $\Delta\alpha$ (H3)/$\Delta\alpha$ (H2) $= \sigma$ (H3)/σ (H2). Accordingly the nearly constant value in the last column is interpreted in terms of the ratio of the absorption cross sections of the two centres.

4. Discussion

The discussion is aimed at understanding the observed results of photochromism consistently by a proposed model. We assume H2 and H3 centres to be the same centre with different charge states; H2 is the state of H3 trapping an extra electron, H3$^-$. Furthermore, photochromism is caused by the photoionization process of H2 according to the following reactions;

$$H2 + \hbar\omega \rightarrow H3 + e^- \tag{1}$$

$$e^- + X^+ \rightarrow X. \tag{2}$$

The photoionization is stimulated by light of photon energy greater than 2.1 eV, corresponding to a wavelength of 600 nm. Figure 5 shows the energy level scheme: the band gap of diamond is 5.4 eV, the level of H2 is 2.1 eV below the conduction band and H3 is roughly 1.2 eV below the H2, if it is given by the energy separation of the zero-phonon lines of H2 and H3. Concerning the energy level position of the ground state of H3, another value is deduced based on a recent result of Collins (1983). He reported that the H3 centre in type Ia has a series of higher excited states in the photon range of 3.2 to 3.6 eV, including H13. These absorption lines cannot be observed in samples used in the present experiment, because of a strong absorption band of isolated nitrogen impurities. Assuming that these excited states are shallow, we obtained the ground state of H3 to be at least 3.6 eV below the conduction band, which is compared with the previous one, 3.3 eV. These two values are not largely different and this difference is insignificant in the present discussion.

The electron trapping centre, X^+, is unknown, and it has a level slightly higher than H2. It is probably conceivable that X^+ is the singly ionized nitrogen, N^+, which is formed as a result of compensation of the irradiation defects. If this is the case, the trapping level of X^+ is located at 1.7 eV below the conduction band, which is obtained from photoconductivity measurements (Farrer 1969).

The photochemical reactions of (1) and (2) are indicated by processes I and I' shown in figure 4. The difference between I and I' consists in the difference in the photon energy; the visible and the UV, respectively. When the UV is used for stimulation, another process denoted by II is possible in addition to I'. The process II is described as

$$H3 + \hbar\omega \rightarrow H2 + h^+. \tag{3}$$

An electron is excited from the valence band to the empty H2 level and a remaining hole, h^+, is trapped at a certain unknown centre. Since equation (3) implies the reverse reaction of equation (1), the resultant effect depends on the competition of the two opposite processes and this gives a qualitative explanation for the dual nature of the second illumination of the UV light as mentioned before.

Whether the H2 level is occupied or not is determined by the position of the Fermi level, which depends on several factors; the impurity content of isolated nitrogen, the electron dose and the annealing condition. For as-grown diamonds, the Fermi level exists at the energy level of nitrogen, 1.7 eV below the conduction band (Farrer 1969), and irradiation reduces it due to compensation. Finally the samples used are thought to have a Fermi level around or slightly above the H2 level, because the H2 centre is dominantly formed and H3 less so.

Comparison has been attempted on colour centres in natural type Ia diamonds which contain about 1000 ppm of nitrogen impurities in aggregate forms. In type Ia the absorption spectrum indicates that H3 centres are the major ones and H2 are few. This fact can be explained as a low position of the Fermi level. It seems natural to consider that the electronic level of aggregated nitrogen is deeper, near to the H3 level and the Fermi level is pinning there after irradiation. Consequently only the H3 level is mostly occupied while the H2 remains almost empty. Our preliminary observation does not reveal the present type of photochromism but a different one; a decrease of H3 with illumination of 514.5 nm light. It will be described elsewhere.

Though the IR measurement elucidates that type Ib diamond converts into type Ia by annealing at high temperatures (Chrenko *et al* 1977), colour centres after such an annealing are not the same as those introduced in natural type Ia. Previously, it was

reported that the degree of nitrogen aggregation depends on dose and annealing temperature (Collins 1980), and the luminescent spectrum indicates coexistence of type Ia and Ib. Collins and Stanley (1985) performed optical measurements on type Ib diamonds electron-irradiated after heating at 1700 to 2000 °C, nevertheless they described nothing about the spectral region of H2 absorption. In our samples the ESR measurement shows that an appreciable amount of isolated nitrogen impurities remains even after annealing at 1700 °C for 50 h, whereas they are scarcely detected in natural type Ia. Here, we have discussed the difference in the relative density of H2 centres to H3 centres from the difference in the Fermi level, and have explained the reason why type Ia produces few H2 centres.

In the model of figure 5, it can be explained that single illumination of the visible or UV light takes place with a decrease of H2 and enhancement of H3 through the process I or I′. When the light is switched off, recovery occurs by the process of an electron in a trap returning to the H2 level through thermal ionization into the conduction band and/ or through tunnelling due to the overlapping of the wave functions of the trap state and the H2 state. If the latter is the main process, the recovery curve is expected to be non-exponential due to a random distribution of centres, in accordance with observations. Consequently it is concluded that tunnelling is more probable. Then the question arises of what happens if the observed value of the recovery time is in reasonable agreement with the theory of the electron tunnelling from a nitrogen trap to a H2 centre. We cannot discuss this here, since the spread of the electronic wave functions is unknown. Further study of the temperature dependence of the recovery process is necessary. The charge transfer model also predicts the appearance of a change in the ESR signal, which has been found in our preliminary experiment and is now being studied.

Now we consider the dual nature of the UV light on the basis of rate equations. When the H2 level becomes partly empty by the visible illumination, the UV light induces process II so that the H2 centre is increased, as shown in curve (b) in figure 3. The quantities n_1 and n_2 are the numbers of occupation of levels H3 and H2, respectively. X^0 and X^+ are the number of traps capturing and releasing an electron, respectively, and n_e is the number of free electrons. Optical processes are described by the equations

$$\dot{n}_2 = -\dot{n}_1 = -(p_2 + g')n_2 + r_2 n_e n_1 + g n_1 + t X^0 n_1 \qquad (4)$$

$$\dot{n}_e = (p_2 + g')n_2 - r_2 n_1 n_e - r_3 n_e X^+ \qquad (5)$$

$$\dot{X}^0 = r_3 n_e X^+ - t n_1 X^0. \qquad (6)$$

Here, p_2, g' and g are the rate constants for the optical excitation of processes I, I′ and II, respectively. The letters r_2 and r_3 denote the rate constants for recombination of a photoelectron with an H3 centre and trap, respectively, and t is the tunnelling rate of an electron from the trap to an H3 centre.

In the steady state under illumination, the number of H2 centres occupied, n_2, is

$$n_2 = \frac{(g + tX^0)N}{p_2 + g' + g + tX^0 + r_2 n_e} \qquad (7)$$

where N is the total number of H2 and H3 centres, i.e., $N = n_1 + n_2$. When only the Ar laser light is illuminating, n_2 is written as n_2 (Ar)

$$n_2(\text{Ar}) = N/[1 + (p_2 + r_2 n_e)/tX^0]. \qquad (8)$$

The experimental fact is that the relative change in the absorption coefficient $\Delta\alpha(\text{H2})/\alpha(\text{H2}) \simeq 0.1$ as seen in figure 2, implies $(p_2 + r_2 n_e)/tX^0 \simeq 0.1$ in the present

case. Furthermore when two light beams are illuminating, the value of n_2 is denoted as $n_2(\text{Ar} + \text{UV})$. Then the difference, $\Delta n_2 = n_2(\text{Ar} + \text{UV}) - n_2(\text{Ar})$, is given by

$$\frac{\Delta n_2}{N} = \left[\frac{g}{tX^0} \left(\frac{p_2 + r_2 n_e}{tX^0} \right) - \frac{g'}{tX^0} \right] \Big/ \left[\left(1 + \frac{p_2 + r_2 n_e}{tX^0} \right) \left(1 + \frac{p_2 + r_2 n_e + g + g'}{tX^0} \right) \right]. \quad (9)$$

The above value of $(p_2 + r_2 n_e)/tX^0$ leads to the conclusion that the ratio g'/g is around 0.1, since the change in $\Delta n_2/N$ occurs up and down centred at zero as seen in figure 3. This means, in figure 5, that the probability for the occurrence of process II is an order of magnitude larger than that for process I'.

The Ar laser light intensity is included implicitly in the parameter p_2. When it is weak so that $(p_2 + r_2 n_e)/tX^0 < g'/g$, equation (9) predicts Δn_2 to be negative, which agrees with the behaviour of curve (a) in figure 3. Contrary to this, Δn_2 is positive when $(p_2 + r_2 n_e)/tX^0 > g'/g$ and leads to curve (b). Consequently, it has been shown that the prediction of the rate equations is in qualitative agreement with observation.

In summary, H2 centres are introduced dominantly in type Ib diamonds irradiated and annealed above 1500 °C, and simultaneously H3 centres are generated less dominantly. In these samples, photochromism occurs with light illumination of wavelength shorter than 600 nm at room temperature and 77 K. The H2 absorption is bleached and the H3 is enhanced with the same magnitude and with a similar time constant in temporal change. The observed results can be explained by the proposed model that H2 and H3 are different charge states of the same centre, and photoionization of H2 triggers the photochroimism. In addition to a strong illumination of the 488 nm Ar laser light, the second illumination of 365 nm light partially instigates the reverse process of the above photochromism. This effect may be due to photo-excitation of electrons from the valence band to the vacant H2 level.

Acknowledgments

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