Color Enhancement of Natural Type Ia Diamond Using a Neutron–Irradiation and Annealing Method

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ABSTRACT

      Color in diamonds arises from defects or impurities such as nitrogen, boron or a lattice vacancy. Therefore, suitable types and quantities of defects will assist in creating the most desirable color in a diamond. In this research, ESR spectroscopy was used to find the optimal annealing temperature for color changing in a neutron-irradiated type Ia diamond. It was found that negative vacancies (V^-) became mobile above 600°C and were completely trapped by nitrogen to form color centers at 750°C. Therefore, the optimal temperature for color treatment of irradiated diamonds was 750°C. After annealing, yellow diamond was obtained. The optimal fluence of neutron irradiation to produce green diamond was then determined. This research showed that neutron irradiation could turn brown diamond into green diamond with the shading dependent on the fluence of irradiation. The optimal fluence to obtain green diamond was 1.58×10^{16} n/cm^2, while at higher levels the diamond became opaque. After annealing at approximately 750°C, irradiated diamond turned into yellow diamond. A higher fluence of neutron irradiation provided a relatively dark yellow color after annealing. The pale or dark shade of enhanced yellow diamond seemed to be independent of the annealing time.

Key words: diamond, color enhancement, neutron irradiation, annealing, ESR

INTRODUCTION

      For a long time diamond has been known as the most precious all gemstones. In general, natural diamond is found in several colors ranging from colorless, steel gray, blue, yellow, orange, red, pink, purple, and brown to black. Intense-colored diamonds are also called fancy diamonds (Harris, 1994) and these are rare. Only one out of every ten thousand near–colorless diamonds is a fancy diamond (Fritsch, 1998). This rarity gives them a much higher market value compared to colorless diamonds.

      The color of a diamond is influenced by defects or impurities. The types of impurities can also be used to classify diamonds (Wilks and Wilks, 1991). Nitrogen is the predominant impurity in natural diamond. In type Ia diamond, nitrogen atoms are present either in an aggregated form of nitrogen pairs $[N_s – N_s]^0$ (A center, Type IaA), or in a group of four nitrogen atoms surrounding a vacancy $[4N_s – V]^0$ (B center, type IaB). Type Ia diamond is colorless because the A and B centers can absorb only light with a

wavelength <~300 nm (4 eV). Both A and B centers cannot be observed by ESR spectroscopy, because they are diamagnetic. IR spectroscopy is a suitable tool to observe their absorption band in one phonon region with a maximum peak at 1282 cm^{-1} and 1175 cm^{-1}, respectively.

The majority of natural diamonds are light brown which makes them less attractive. If the unattractive light brown diamond could be changed to a fancy diamond, then the price of that diamond would significantly increase. There are three techniques for enhancing or changing the color of diamonds: irradiation with high–energy particles; the coating or thin film technique; and high temperature and high pressure (HTHP) treatments (Nassau, 1994; Collins, 2001). In this work, neutron irradiation followed by annealing was selected to enhance the color of the natural type Ia diamonds.

The effect of the irradiation is to knock some of the carbon atoms away from their normal lattice sites leaving a vacancy (V). The displaced carbon atoms become interstitial occupying space between carbon atoms. The electronic transition of vacancies gives rise to green or blue green in the diamond, while the interstitial carbon is optically inactive (Clark et al., 1956; Buerki et al., 1999). In addition to vacancy-interstitial pairs, irradiation causes the lattice to be strained which results in an increase in lattice parameters (Levy and Kammerer, 1965). Vacancies can exist in either a neutral (V^0) or a negative (V^-) state. The charge state of the vacancy is controlled by the content of N_s^0 via one-step charge compensation, $N_s^0 + V^0 \rightarrow N_s^+ + V^-$ (Lawson et al., 1998). Theoretically and experimentally, ESR showed that V^0 had S = 0 at ground state and thus no ESR signal was observed (Coulson and Larkins, 1971; Loubser and Wyk, 1978). However, had S = 3/2 for its ground state giving rise to a single isotropic ESR line known as the S1 center (Isoya et al., 1992). A single interstitial (I^0) known as R2 (Hunt et al., 2000) can move during irradiation to form complex defect structures, such as di-interstitials (R1), and tri-interstitials (O3).

In a type Ia diamond, the vacancy can be trapped at either the A or B center to produce optical H3 and H4 centers, respectively (Davies, 1972; Davies et al., 1976; deSa and Davies, 1977; Walker, 1979). The electronic transition of H3 and H4 centers can give rise to yellow, orange or brown color, where the end result depends on the initial color of the diamond before irradiation and the time taken for irradiation and annealing. Both H3 and H4 are diamagnetic at ground state (S=0).

The objective of this work was to study the effect of neutron irradiation and annealing on type Ia white diamond by monitoring the negative vacancies V^- by ESR spectroscopy as a function of temperature. By using a fixed temperature for the disappearance of the V^- ESR signal, the neutron irradiation fluences and annealing times were varied to find suitable conditions for the color enhancement of the natural type Ia brown diamonds.

MATERIALS AND METHODS

Sample characterization

The samples used in this work were white (very light green) and brown diamonds from unidentified locations. A white rough diamond with a cubic shape denoted as Wh was used for the ESR studies. Four samples of round, brilliant, faceted, light brown diamond, denoted as Br1, Br2, Br3, and Br4 each with a diameter of about 3 mm were used for color enhancement.

The type of diamond was classified by infrared and UV-Vis absorption measurements. Infrared absorption spectra were recorded using a Thermo Nicolet Nexus™ 470 FT-IR (ESP) at the Department of Earth Science, Kasetsart University. All IR spectra were measured at room temperature with a range from 500 to 7000 cm^{-1}. Infrared spectra of the rough diamond were recorded by a transflectance technique, whereas those of the

faceted samples were recorded by a diffuse reflectance technique. UV-Vis absorption spectra were measured within the wavelength range of 200-850 nm at room temperature on a Perkin-Elmer Lambda™ 800 UV-Vis spectrophotometer. Transmission spectra converted from absorption spectra were used to calculate the CIE L*a*b* color indices using the color module of the UV-Win Lab software from Perkin-Elmer. The calculations were performed using the CIE 1931 standard colorimetric method with options of an illuminant D65 and an observer at 2° angle.

ESR study

ESR measurements were carried out only on Wh, because ESR measurements need to be performed on samples with a known crystallographic plane. The ESR spectra in the (100) plane were recorded at room temperature using an X-band (~9.8 GHz) Bruker ELEXSYS E500 ESR spectrometer. DPPH (diphenyl picrylhydrazyl) with a g-factor of 2.0036 ± 0.0003 was used as a standard for calibration.

The Wh sample was irradiated for 14 days in a Thai Research reactor at the Office of Atomic Energy for Peace of Thailand, in the CT-2 tube with a neutron flux of about 1.0×10^{13} n/cm^2·sec. For this tube, the Cd ratio was one half. After fluences of 2×10^{18} neutrons/cm^2, each diamond sample was subjected to ESR to determine the defects in the diamond. Then, the sample was annealed for one hour through a temperature range of 100-950°C with an increment of 50°C. After each step, the ESR measurement was recorded. This enabled the monitoring of the effects of annealing on the irradiation-induced centers and the change in color of the diamonds. In this work, the optimum annealing temperature was obtained by observing the ESR signal corresponding to the reduction in the negative vacancy (V$^-$). ESR spectra were analyzed using an EPR-NMR computer program (Mombourquette and Weil, 2002), in which the line positions were calculated using the exact diagonalization of a spin

Hamiltonian matrix.

Color enhancement of type Ia brown diamond

In order to determine the suitable fluence of the neutron irradiation, the faceted diamonds Br1-4 were irradiated at different fluences of 1.58×10^{14}, 1.58×10^{15}, 1.58×10^{16} and 1.07×10^{17} n/cm^2, respectively. They were irradiated in the LZ11 irradiation tube, with a thermal neutron flux of 6.3×10^{11} neutrons/cm^2·sec and an epithermal neutron flux of 0.7×10^{11} neutrons/cm^2·sec. After neutron treatment, all samples were then annealed at the optimum temperature of 750°C determined from ESR studies for 1-3 hours. Photographs of the samples were taken at each step. In addition, color measurements were carried out and CIE indices were calculated to display the effect of neutron irradiation and annealing on the diamond color.

RESULTS AND DISCUSSION

Sample characterization

The concentration of the different forms of nitrogen in the samples was determined using the relationship between the nitrogen concentration and infrared absorption coefficients (Davies, 1999). The concentration of nitrogen and the type of diamond samples are listed in Table 1. All faceted samples are type Ia because they contain A and B centers. Moreover, they are subdivided into IaA and IaB types corresponding to the dominant center. From the IR absorption spectrum of Wh, it is difficult to classify the type due to the saturation resulting from the high content of nitrogen in the one-phonon region. However, the results of the color measurement of untreated diamond in Table 2 show that Wh is type Ia due to its secondary absorption edge of the A center at about 318 nm. All faceted diamonds also exhibited an absorption peak of the amber center I (Massi *et al.*, 2005) at about 4165 cm^{-1}, which was related to plastic deformation.

Table 1 Concentration of nitrogen impurity and type of diamond samples.

Sample	Concentration (ppm)			Type
	A	B	C(P1)	
	(± 6.34%)	(± 12.34%)	(±5%)	
Br1	14.85	133.15	0	IaB
Br2	18.15	100.64	0	IaB
Br3	9.9	170.31	0	IaB
Br4	99	34.06	0	IaA

Table 2 CIE L*a*b* color index of untreated samples.

Sample	Absorption edge (nm)	L*	a*	b*
Wh	318	25.5	-1.94	11.99
Br1	275	46.97	2.06	8.68
Br2	288	41.84	2.19	8.71
Br3	292	38.22	2.51	9.18
Br4	306	36.56	2.39	7.99

ESR study

Figure 1 (a) shows the ESR spectrum of Wh before irradiation with the magnetic field parallel to the [100] direction. The spectrum consists of three lines with equal spacing and intensity. As the hyperfine splitting multiplicity is $2I+1$, this suggests that the spectrum arose from the hyperfine interactions between an unpaired electron ($S=1/2$) and nuclei with nuclear spin $I=1$. Practically, is the only element with this nuclear spin. Thus, the paramagnetic ion of the main lines is nitrogen. The ESR center with $S=1/2$ and $I=1$ can be explained by the spin Hamiltonian (Equation 1):

$$\hat{H} = g\beta\hat{S}\cdot\hat{B} + \hat{I}\cdot\hat{A}\cdot\hat{S} + \hat{I}\cdot\hat{P}\cdot\hat{I} + g_n\beta_n\hat{I}\cdot\hat{B} \quad (1)$$

The first and the last terms on the right hand side represent the electronic and nuclear Zeeman interaction, respectively, the second term represents the hyperfine interaction and the third is a nuclear quadrupole term. This center has a trigonal symmetry and the best fit ESR parameters calculated and optimized by the EPR-NMR program were $g = 2.0023$, $A_{11} = 40.61$ G // [111], $A_\perp = 29.12$ G $\perp$ [111], and $P = -1.5$ G.

The resulting g-factor, hyperfine parameters and their symmetry are typical parameters of a P1 center (single substitutional nitrogen N_s^0). By comparing the area of the absorption spectra of Wh and other diamonds of a specific P1 concentration, the concentration of the P1 center in Wh was evaluated as 0.5 ppm. Due to its low P1 content, it was impossible to observe an absorption band using the UV-Vis and IR techniques. In addition to ^{14}N, ^{13}C and ^{15}N (~2 ppb) were also observed.

The ESR spectra of Wh after irradiation are shown in Figure 1(b). A spectrum is magnified and shown in Figure 2. Figure 2(a) shows that the additional ESR centers observed were negative vacancy (V⁻), single interstitial (R2) and di-interstitials (R1). Their magnetic parameters are summarized in Table 3. Figure 2(b) shows that, after irradiation, the P1 center decreased accompanied by the appearance of V⁻, corresponding to the one-step charged compensation. The mobile paramagnetic electron of the P1 (N_s^0) center was trapped at V^0 to produce V⁻, leaving a P1⁺ (N_s^+) center as ESR-inactive. The details of V⁻, the nearest and next nearest of
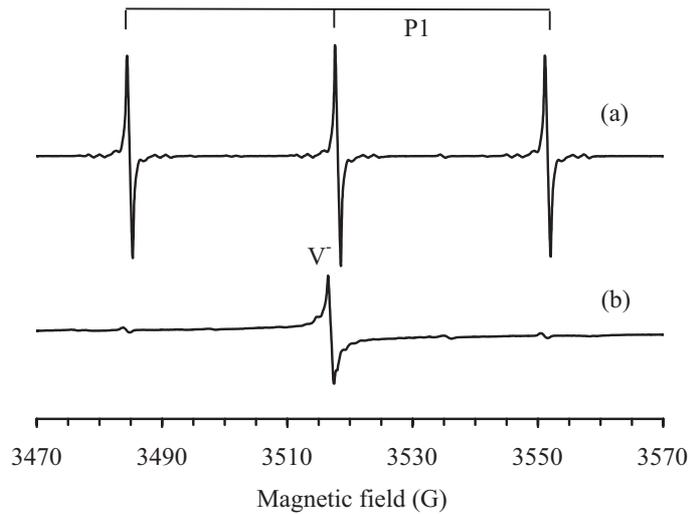
Figure 1 ESR spectrum of Wh (a) before and (b) after 2×10^{18} n/cm^2 irradiation, with the magnetic field // [100] direction.

Table 3 Parameters of ESR centers observed in Wh.

Center	Symmetry	Spin	Parameter[G] and principal axis
P1(N_S^0)	Trigonal	S=1/2	g = 2.0023
		I=1	A_{11} = 40.61 // [111]
			$A_\perp$ = 29.12 $\perp$ [111]
V$^-$	Tetrahedron	S=3/2	g $\approx$ 2.0026
			Nearest ^{13}C
	Trigonal	I=1/2	A_{11} = 50.42 // [111]
			$A_\perp$ = 29.10 $\perp$ [111]
			Next nearest ^{13}C
	Trigonal	I=1/2	A_{11} = 4.87 // [111]
			$A_\perp$ = 3.38 $\perp$ [111]
R2	Tetragonal	S=1	g $\approx$ 2.00
			D_{xx} = 994 // [90,0]
			D_{yy} = -497 // [0,0]
			D_{zz} = -497 // [90,270]
R1	Monoclinic-I	S=1	g $\approx$ 2.00
			D_{xx} = 503 // [45,90]
			D_{yy} = 483 // [102.2,167.5]
			D_{zz} = -986 // [47.56,246.1]
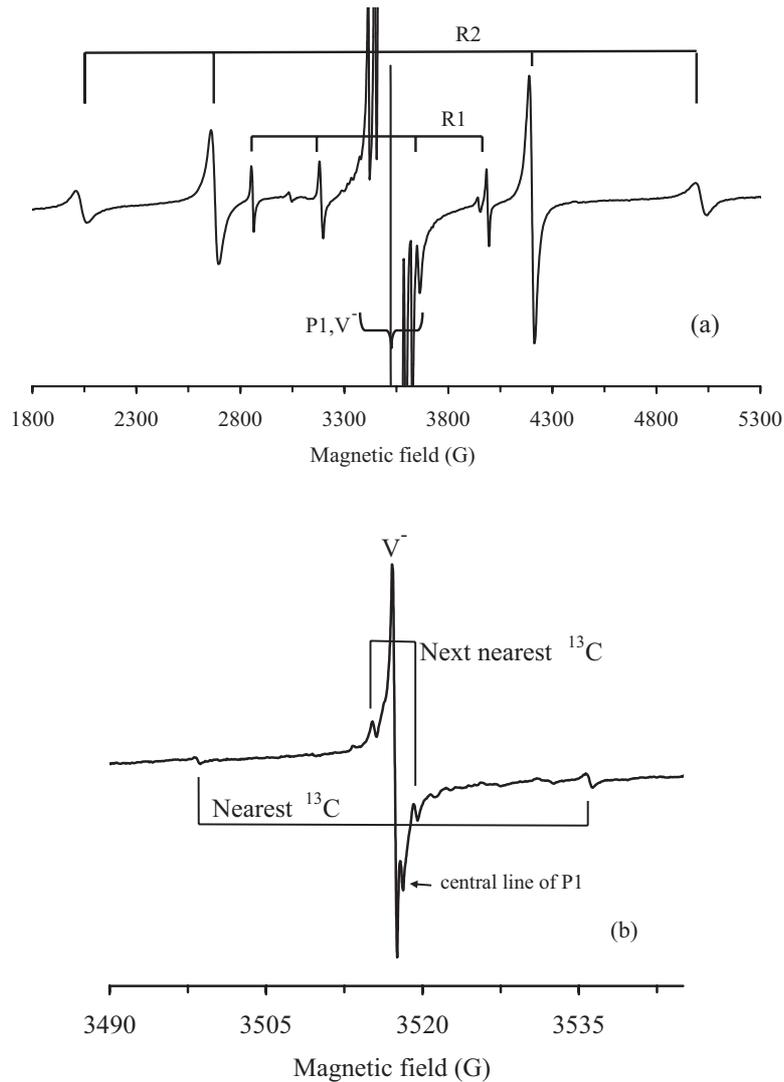
Figure 2 Magnification of ESR spectrum of Wh after 2×10^{18} n/cm^2 with the magnetic field // [100] direction, showing (a) R1, R2 centers and (b) ^{13}C and negative vacancy.

^{13}C, were also observed, which could be explained by a trigonal system of electron spin half interacted with a nuclear spin half of ^{13}C, with the following spin Hamiltonian (Equation 2):

$$\hat{H} = g\beta\hat{S} \cdot \hat{B} + \hat{I} \cdot \hat{A} \cdot \hat{S} + g_n\beta_n\hat{I} \cdot \hat{B} \quad (2)$$

R2 and R1 could be explained by the system with S = 1 and the following spin Hamiltonian (Equation 3):

$$\hat{H} = g\beta\hat{S} \cdot \hat{B} + \hat{S} \cdot \hat{D} \cdot \hat{S} \quad (3)$$

where the second term represents the fine structure interaction (electron spin – electron spin interaction). Roadmaps of the R2 and R1 centers (plots of peak position as a function of rotation angle in a specific plane) are shown in Figures 3(a) and 3(b), indicating monoclinic and tetragonal symmetries, respectively.

To investigate the most suitable annealing temperature, the intensity of V$^-$ was observed as a function of the annealing
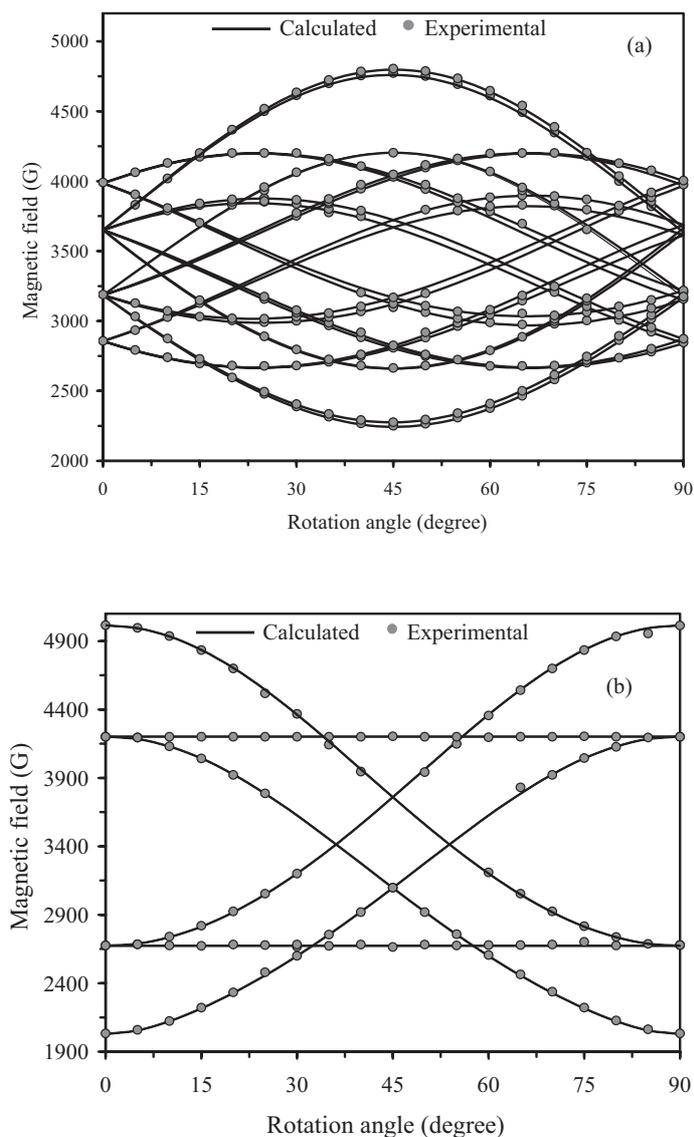
Figure 3 Roadmap of (a) R1 and (b) R2 centers of Wh in the plane close to (001) plane.

temperature. The isochronal annealing curve of V^- in Figure 4 reveals that the suitable temperature for annealing was $750\pm25°C$ above which V^- decreased and then disappeared. At this temperature, the vacancies (V^0 and V^-) could migrate and became completely trapped by the A or B centers while the diamonds turned yellow. This annealing temperature was higher than the previous reported result which was $700\pm25°C$ obtained by identifying the end products which

were H3 and H4 centers using UV-Vis absorption measurements (Davies *et al.*, 1992). The difference was caused by the higher sensitivity of the ESR method compared to the UV-Vis absorption method.

Color enhancement of type Ia brown diamond

CIE L*a*b* color index measurements were carried out for the natural brown Type Ia diamond samples, Br1, Br2, Br3 and Br4 after
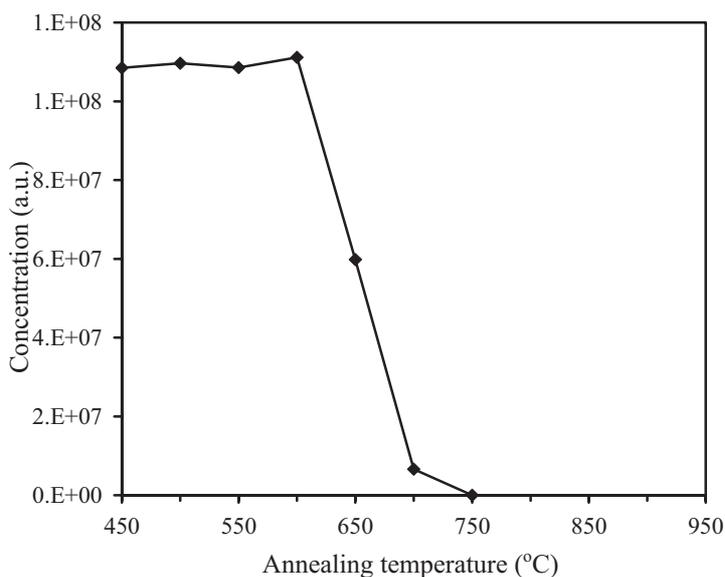
Figure 4 Isochronal annealing curve of V$^-$ in Wh.

irradiation at 1.58×10^{14}, 1.58×10^{15}, 1.58×10^{16} and 1.07×10^{17} n/cm^2, respectively. Color measurements were repeated on the same samples after annealing for 1-3 hours at 750 °C. The effect of fluence of irradiation and annealing time on the color of the diamonds were studied and shown in Figures 5 to 8.

After irradiation, the brown color reduced and eventually turned green, indicated by a negative value of a*. The green color component (-a*) was strongly dependent on the fluence of irradiation. However, the green color was clearly seen only in Br3. In the case of Br4, it turned opaque because of the over-intense irradiation. In the case of Br1 and Br2, irradiation turned the diamond to a light brown color as the value of -a* was small and b* decreased after irradiation, compared with the non-irradiated sample. The lightness of Br1, Br2 and Br3 increased after irradiation, which probably resulted from the effect of the irradiation on the amber center. Therefore, the optimal fluence of irradiation to produce green diamond was 1.58×10^{16} n/cm^2. The lower fluence could be used to reduce the color of brown diamond. The effects of neutron fluence and

annealing time are summarized in Table 4.

After annealing, all samples turned yellow as indicated by the change of sign of a*. This indicated that vacancies migrated and were trapped by the A or B centers to produce H3 or H4, giving rise to a yellow or orange color, respectively. The colors of Br1 and Br2 faded after treatment, as their values of a* and b* were smaller than for the untreated samples. The color of the irradiated Br3 changed from green to light yellow, while the irradiated Br4 turned intense yellow after annealing. Annealing time had a small effect on the color change. There were no significant differences among a*, b* and L* and annealing times of 1, 2 and 3 hours.

CONCLUSIONS

The results are consistent with previous work showing that irradiation produced vacancy-interstitial pairs. The diamonds turned green and the ESR spectra showed the defect centers, such as , R1 and R2, as expected. A suitable annealing temperature for irradiated diamond was 750±25°C obtained by observing the annealing behavior of
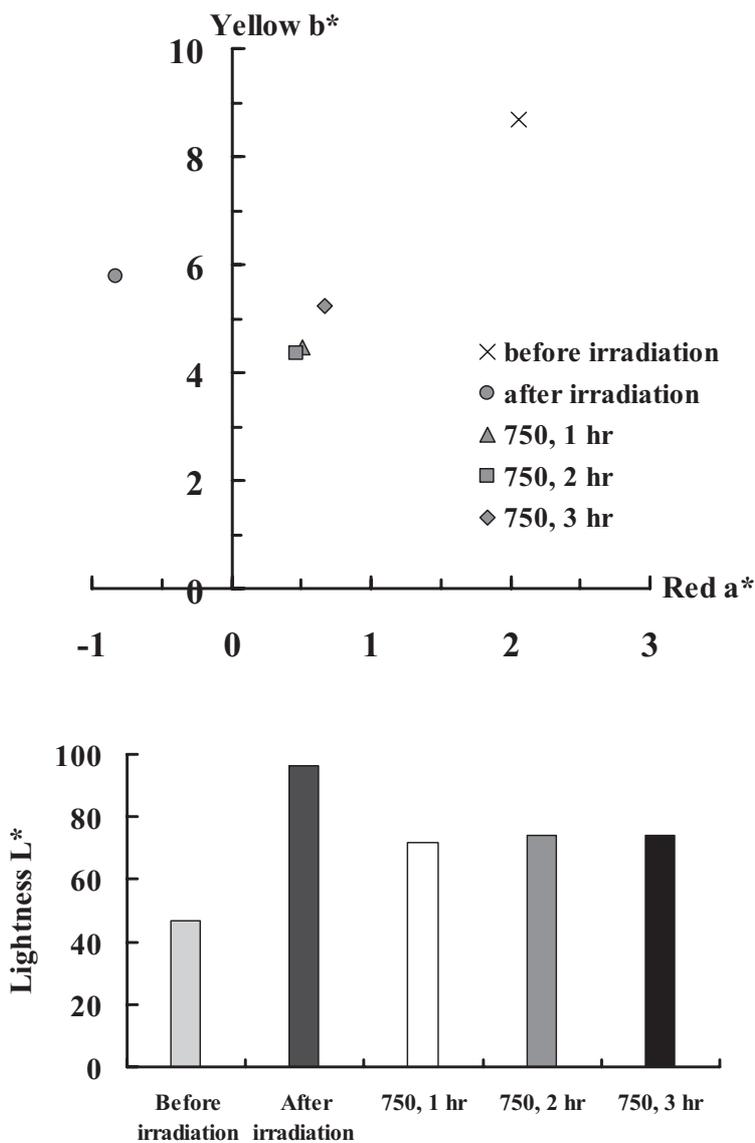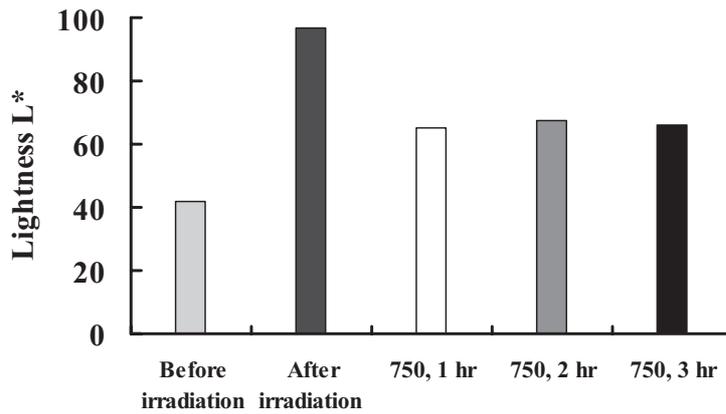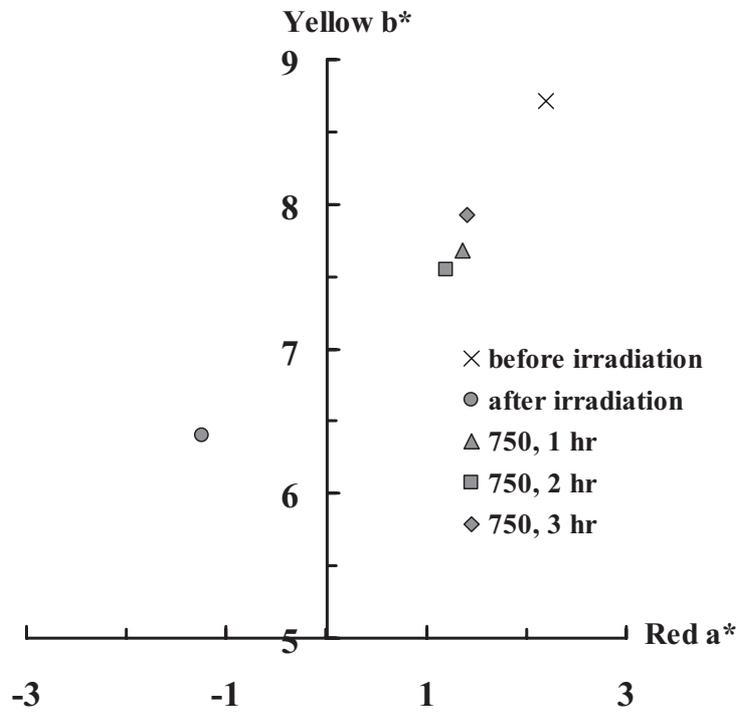
Figure 5 Change in color and lightness of Br1.

V⁻. This temperature was higher than that previously reported which was 700±25°C by UV-Vis measurements because the sensitivity of the ESR method was higher than for the optical absorption method. At the temperature used in this study, the irradiated diamonds turned yellow and vacancies vanished resulting in the formation of nitrogen-vacancy related centers.

From color measurement, neutron irradiation produced a green color with its brightness dependent on the fluenec of irradiation. The optimal fluence for obtaining green diamond was 1.58×10^{16} n/cm^2, with a higher fluence causing the brown diamond to become opaque. After annealing at 750 °C, all type Ia brown diamonds turned yellow. Their resulting color strongly depended on the fluence of irradiation, but not on the annealing time. Intense yellow diamond can be obtained by increasing the fluence of neutron irradiation.
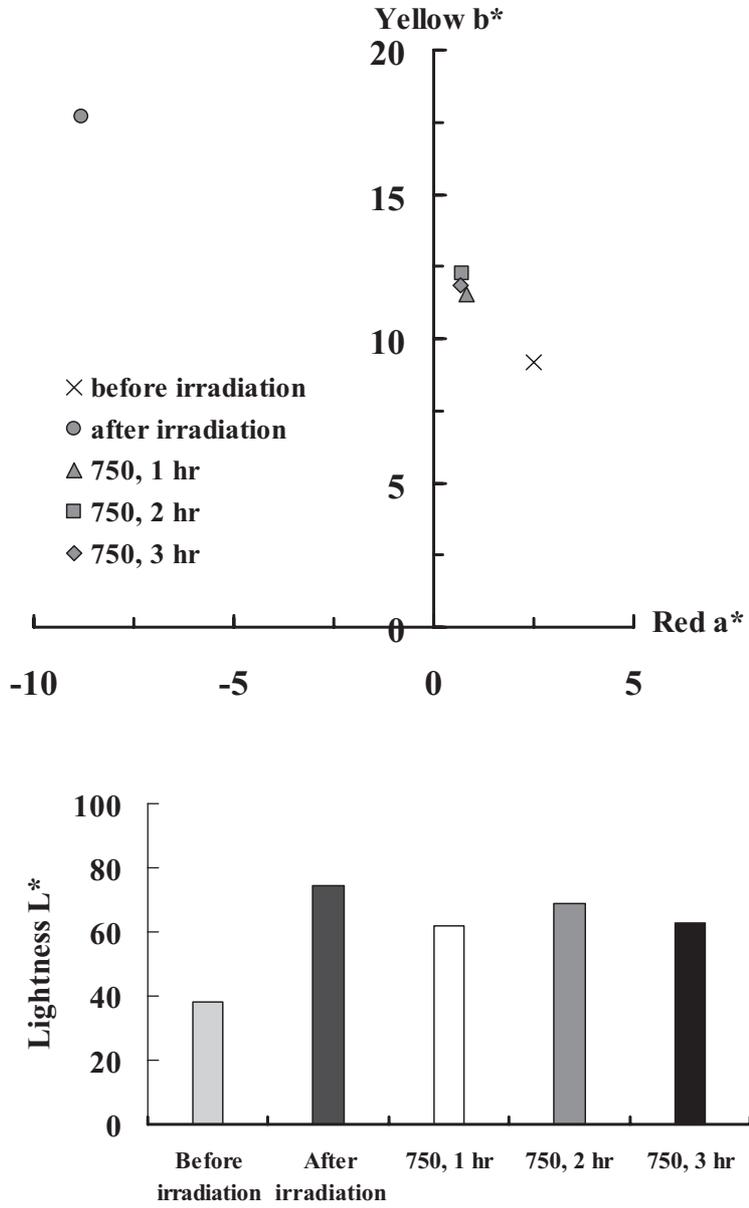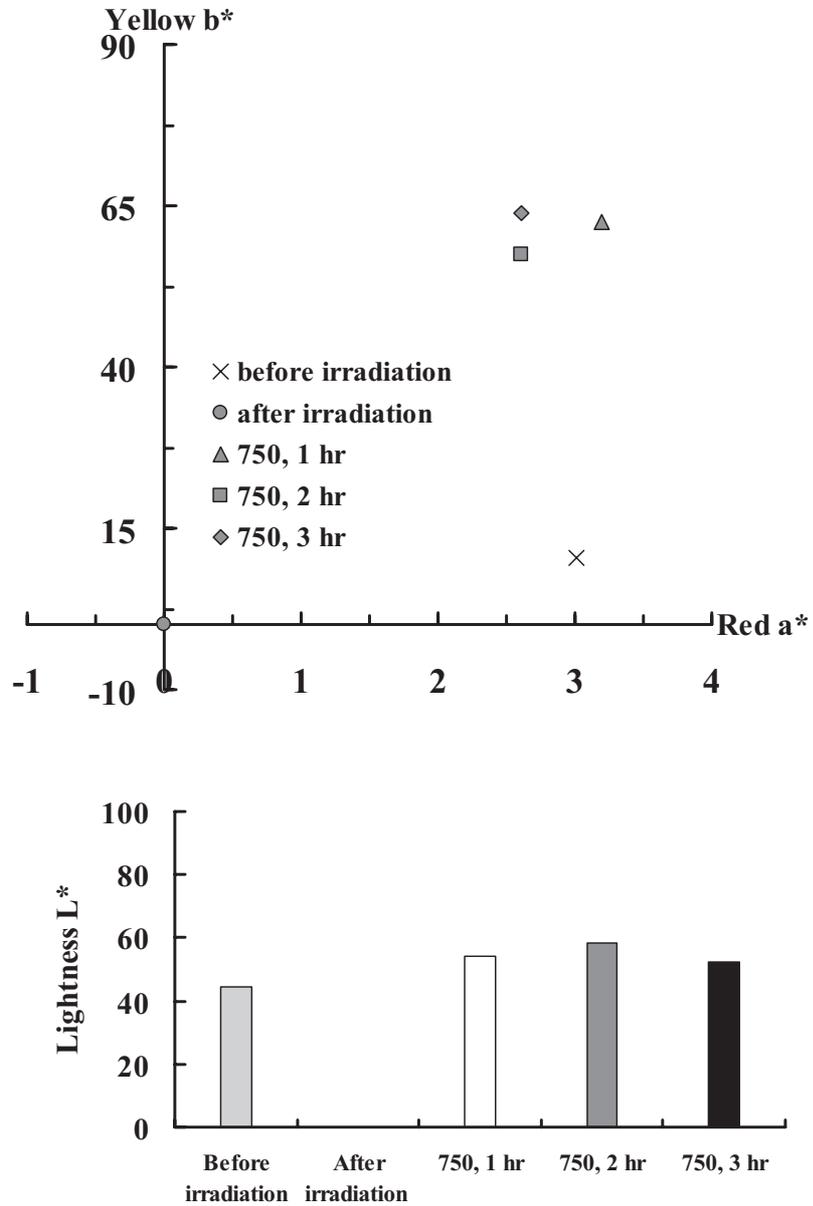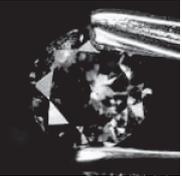
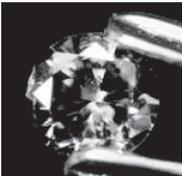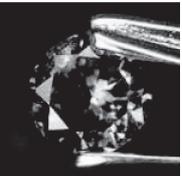**Figure 6** Change in color and lightness of Br2.

Figure 7 Change in color and lightness of Br3.

Figure 8 Change in color and lightness of Br4.

Table 4   Photographs of type Ia brown diamonds before and after treatments.

Sample	Neutron irradiated with fluence	Annealing at 750°C		
		1 hr	2 hr	3 hr
Br1	1.58×10^{14} n/cm^2			
Br2	1.58×10^{15} n/cm^2			
Br3	1.58×10^{16} n/cm^2			
Br4	1.07×10^{17} n/cm^2			

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