

## COLOR CENTERS IN SYNTHETIC Ib DIAMONDS AND THEIR APPLICATION TO OPTO-ELECTRONICS

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To search for the possibility of opto-electronics applications of color centers in high-pressure synthetic diamonds, the hole burning effect and the optical gain of nitrogen-vacancy (NV) centers have been studied. Holes can be produced clearly on the zero-phonon line with a weak burning intensity around  $1 \text{ mW/cm}^2$  in the temperature range up to 80K. The temperature dependence of the hole and the burning and filling processes are presented. The generation of photo-products over the whole ZPL range indicates the burning process to be nonphotochemical, which inevitably results in the crosstalk effect of holes. The optical gain measurement demonstrates the occurrence of strong reabsorption from some metastable excited states populated by pumping. The present results elucidate that the application of diamonds is hopeful in hole burning, but not in cw lasers.

In diamonds, the existence of various kinds of color centers is characterized by the optical spectrum,<sup>1)</sup> and is expected to show optically interesting phenomena. Some color centers have a typical vibronic spectrum consisting of a zero phonon line (ZPL) and phonon sidebands. Generally the ZPL shows the hole burning (HB) effect, which may be applied to the optical multiplex memory,<sup>2)</sup> and the strong emission band has possible application in tunable lasers if the optical gain is large. So far, a pulsed laser oscillation has been successful for H3 centers in natural type Ia diamonds.<sup>3)</sup> For HB, it has been reported that NV centers have particularly interesting features.<sup>4)</sup>

Recent development of high-pressure synthetic diamonds has stimulated a systematic study of the optical properties of color centers and their possible applications. The present work aims to investigate the behavior of hole-burning and optical gain for NV centers in synthetic diamonds.

Figure 1 denotes the vibronic spectrum of NV centers and the energy level scheme. The optical spectrum arises from allowed transitions between spin-singlet states  $S_0$  ( $^1A$  in the group-theoretical notation) and  $S_1$  ( $^1E$ ).<sup>5)</sup> The ZPL appears as a sharp

peak at 638 nm and corresponds to the transition between states  $(S_0, v_0)$  and  $(S_1, v_0)$ . Its half-width is  $15.4 \text{ \AA}$  (4.7 meV) and is ascribed to an inhomogeneous broadening due to a distribution of internal strains surrounding an NV center. When the ZPL is illuminated by a narrow laser line, some of the centers excited are removed from the inhomogeneous line and a hole results. The removal is roughly divided into two processes; photochemical (PC) and nonphotochemical (NPC). In the PC process, the centers undergo a photochemical reaction and photo-products are generated in a spectral region far from the original ZPL. In NPC, the optical excitation induces changes in the local field, and photo-products are produced around the hole because of a small shift in transition energy. Therefore the burning processes can be distinguished from the position of photo-products.

In Fig. 1, when excited by the sideband absorption light, the centers make a transition from state  $(S_0, v_0)$  to  $(S_1, v_n)$ , and are relaxed to the lowest excited state  $(S_1, v_0)$  with phonon emission, and fall to the ground state with photon emission. Under strong excitation, a negative population may be realized between states  $(S_1, v_0)$  and  $(S_0, v_n)$ ,

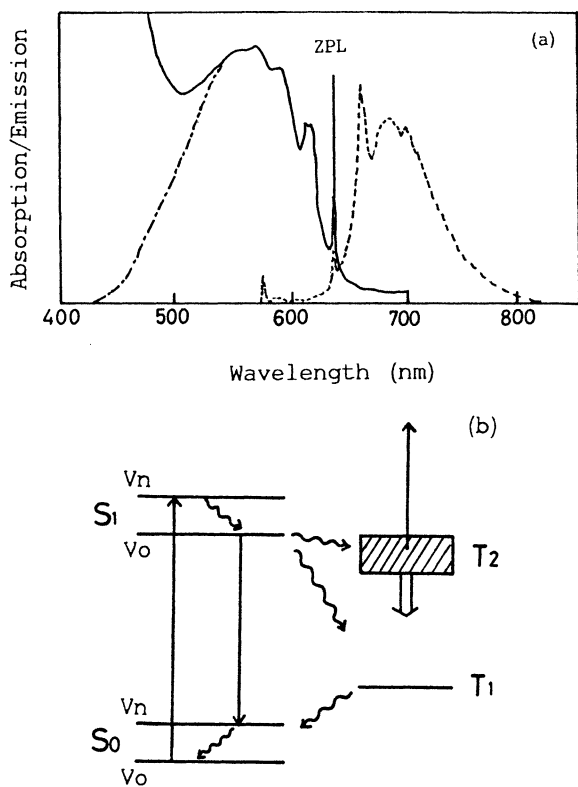


Fig. 1. Vibronic spectra at 77K (a) and energy level scheme (b) of NV centers. (a) Solid line; absorption, broken; emission, and chain; excitation spectrum monitored at 659 nm. (b) S; singlet state, T; triplet state,  $v_0$ ; zero phonon state,  $v_n$ ; vibronic state.

which can be detected by the optical transmission measurement. On the other hand, photo-ESR study has revealed the existence of unknown triplet excited states, e.g.,  $T_1$  and  $T_2$  in Fig. 1(b).<sup>6)</sup> If reabsorption from the triplet overlaps with the emission spectrum, the optical gain is cancelled and laser action becomes impossible.

Samples are synthetic diamonds fabricated at Sumitomo Electric Industries on a commercial basis as heat sinks for semiconductor lasers. These diamonds are type Ib and contain singly substitutional nitrogen atoms around 100 ppm ( $1.76 \times 10^{19}/\text{cm}^3$ ). NV centers were introduced with neutron- or electron-irradiation followed by annealing at 900°C for 2 hours.<sup>7)</sup> In the following, we first describe the HB measurement and next the optical gain.

In the HB experiment, a thin sample with the size of  $3.5 \times 3.5 \times 0.3 \text{ mm}^3$  is mounted in a cryostat and the burning light is supplied from a nitrogen-laser-excited dye laser with a pulse width of 5 ns, a repetition rate of 17 Hz and an average power density of about  $1 \text{ mW}/\text{cm}^2$ . The hole spectrum is measured by monitoring the intensity of very weak broad band light transmitted through the sample with a Spex double monochromator and a photon counting system. The spectral resolution is about  $0.1 \text{ \AA}$ , which is limited by the monochromator and multimode oscillation of the dye laser.

Figure 2(a) denotes the change in the hole spectrum on successive burning at 20K. With increased burning time, the hole-depth is increased with a constant hole-width of  $0.3 \text{ \AA}$ . Figure 2(b) shows that the hole-width increases gradually with increasing temperature below 60K, and remarkably above it. In Fig. 2(c), the hole-depth is decreased with increasing temperature for the same burning energy. Here, the hole-depth is defined as the ratio of the depth of hole to the whole height of the ZPL in transmittance. The present result indicates that the hole is narrow and deep at lower temperatures, while it is broad and shallow at higher temperatures. Roughly speaking, there is a tendency that the product of hole-width and hole-depth is constant for the same burning energy. This means the number of centers removed by burning depends mainly on the burning energy. Physically, hole-width corresponds to the reciprocal of the dephasing time of the wave function of the center due to electron-phonon interaction.<sup>2)</sup> In comparison with previous reports,<sup>4)</sup> the hole-width is consistent with the present result at 20K.

The life of the hole is persistent, on the order of hours, in dark, but is much reduced by light illumination in the ZPL and sideband absorption region. The latter can be used to erase the hole. Figure 3 shows the crosstalk effect of holes and the photochemical burning process. In curve (a), the first hole is produced at the site denoted by the arrow. In curve (b), the second hole is produced at a slightly different site indicated by the arrow. As a result of the second hole, the first hole is partially filled. Without the second hole, the first remains unchanged due to its persistent nature. Furthermore, when the third is formed in curve (c), the

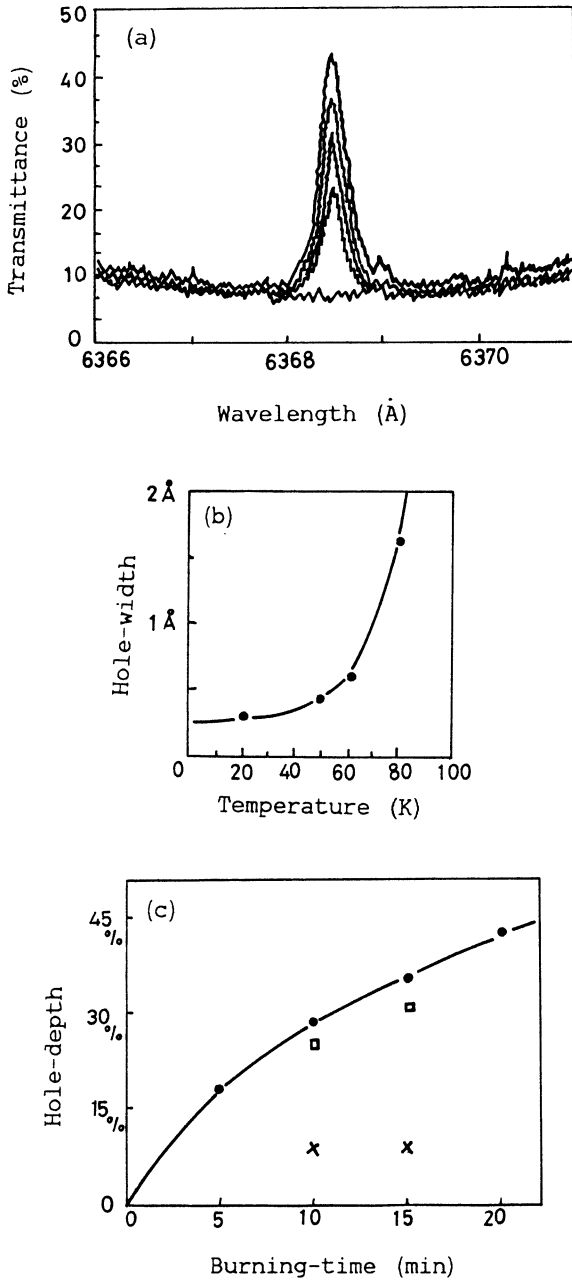


Fig. 2. Hole burning. (a) Hole spectra observed at 20K, before burning, after burning time 5, 10, 15 and 20 min, from the lower to the upper curve. (b) Temperature dependence of the hole width. (c) Relation of the hole depth to the burning time, ●; 20 K, □; 60K, ×; 80K.

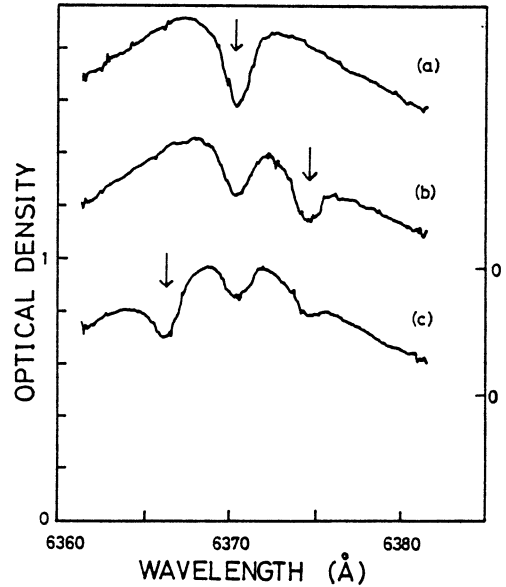


Fig. 3. Crosstalk effect of holes observed at 77K. With the time sequence of (a), (b) and (c), a new hole is produced at the site indicated by the arrow. The previously existing hole is partially filled by the photo-products of the new hole. The burning time is 16 min for curve (a), 30 sec for curves (b) and (c). The zero level of each curve is shifted for clarity.

first and second holes are filled to some extent. This influence of one hole on other holes is called the “hole crosstalk effect”. This fact reveals that photo-products are generated dispersed over the whole region of the ZPL. Consequently, it is concluded that the burning process of NV centers is nonphotochemical. The crosstalk effect is intrinsic to the NPC process and is not desirable from the viewpoint of independence of the optical memory. To improve this disadvantage, it remains to examine the two-step burning or photon-gated process.<sup>2)</sup>

Now, let us discuss the optical gain. Samples are 1.5 mm thick and have the same cross-section as above. The pumping source is more intense, a Xenon-flash lamp-pumped dye laser with a pulse width of 500 ns and a pulse energy of about 100 mJ. The pumping light is focused on a thin surface of the sample through a cylindrical lens and transmission is observed in the direction perpendicular to the pumping. The light used for transmission is at 780 nm from a semiconductor laser with

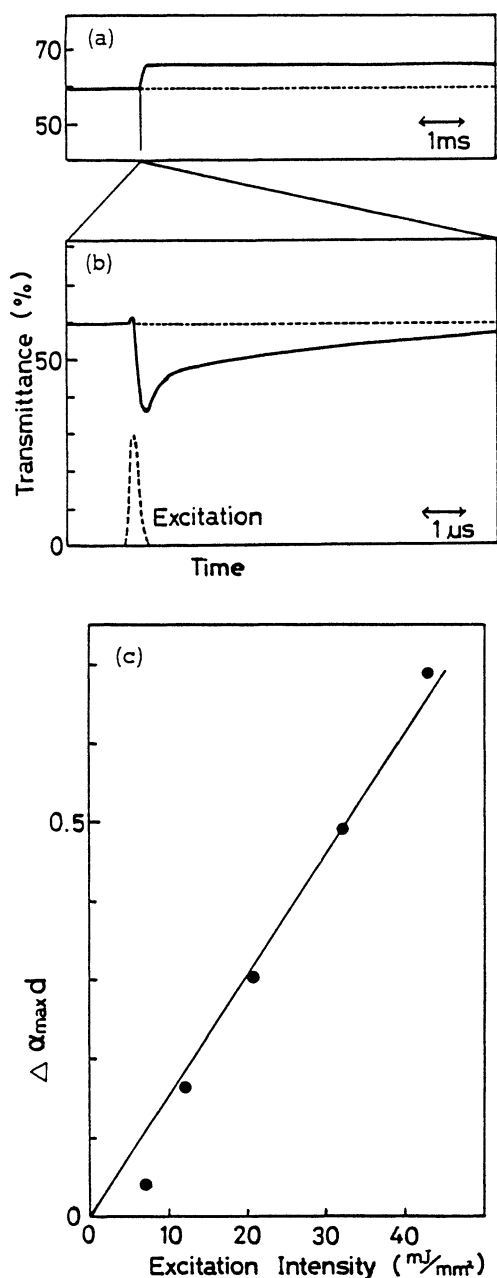


Fig. 4. Temporal change in transmittance at 780 nm with a pumping pulse at 530 nm. Pumping intensity  $20 \text{ mJ}/\text{mm}^2$ , pulse width 500 ns. (a) Time sequence of the transmission light intensity. (b) Expansion of the initial part of curve (a). (c) Difference in the optical density between the minimum transmittance and transmittance before pumping,  $\Delta\alpha_{\max}d$ , vs. the pumping energy, observed at the pumping wavelength 590 nm.  $\Delta\alpha$ ; change in absorption coefficient,  $d=1.5 \text{ mm}$ ; sample thickness.

an output power of 25 mW.

Figures 4(a) and (b) show the temporal change in transmittance when the pumping pulse is applied. This change is divided into three time regions. In the initial region, up to the peak of the pumping pulse, a small enhancement in transmittance is observed. This is thought to arise from the stimulated emission and thus an establishment of the negative population between states  $(S_1, \nu_0)$  and  $(S_0, \nu_n)$  shown in Fig. 1. Next, a sharp decrease in transmittance occurs before the end of the pulse and then recovers with a time constant of the order of  $10 \mu\text{s}$ . This fact indicates that reabsorption takes place from long-life metastable states, probably the triplet states shown in Fig. 1(b). The optical population of the triplet is known from photo-ESR.<sup>6)</sup> In Fig. 4(c), the maximum amplitude of the reabsorption component increases linearly with the pumping energy. Last, transmittance is increased slightly from the initial value, 60 percent, after a sufficiently long time from the pumping. This increase may be due to the decrease of unknown centers showing an absorption around 780 nm by the trapping of photo-carriers.

In summary, the optical gain measurement in the emission region of NV centers reveals strong reabsorption, and consequently NV centers are hopeless for making CW tunable lasers, though a pulsed operation might be possible. It has been found that a hole is produced efficiently with a light intensity of about  $1 \text{ mW}/\text{cm}^2$ , and that the burning process is nonphotochemical.

*Acknowledgements.* Neutron irradiation was done at the Kyoto University Research Reactor, and electron irradiation was done at the Institute of Scientific and Industrial Research, Osaka University. Some aspect of the hole-burning experiment are due to Prof. K. Kushida of Osaka University.

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