

Efficient generation of nitrogen-vacancy center inside diamond with shortening of laser pulse duration

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(Received 3 September 2018; accepted 4 November 2018; published online 21 November 2018)

We investigated the effect of laser pulse duration on nitrogen-vacancy (NV) center generation inside a single crystal diamond. We compared pulse durations of 40 fs (femtosecond laser) and 1 ps (picosecond laser). We found that in both cases, ensemble NV centers could be generated inside the diamond. However, the maximum photoluminescence intensity of the NV center without graphitization for the 40 fs duration was higher than that for the 1 ps duration. This indicated that the femtosecond laser was harder to graphitize diamond and could generate more NV centers without graphitization. This difference may be due to the difference in the photo-absorption process and the resulting lattice dynamics. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5054730>

Diamond has excellent optical, electrical, and thermal properties; therefore, it has attracted considerable attention for various optical and electronic applications.^{1–3} Diamond is a metastable state of carbon at room temperature and pressure, and high temperature or laser irradiation can induce its phase transition to graphite. Laser induced graphitization of diamond combined with direct laser writing has been utilized as a tool for the fabrication of metallodielectric structures,⁴ three-dimensional (3D) radiation sensors,⁵ and optical waveguides for quantum platforms.⁶ Besides, recently, the generation of nitrogen-vacancy (NV) centers inside⁷ and on the surface⁸ of diamonds using femtosecond laser pulses below the graphitization threshold energy has been demonstrated. The NV center in a diamond has attracted much attention because it acts as a single photon emitter⁹ and its excellent electron spin properties (e.g., long coherence time at room temperature¹⁰) can be utilized for quantum information processing¹¹ and sensing of magnetic fields,¹² electric fields,¹³ or temperatures.¹⁴ In particular, Ref. 7 has demonstrated the generation of a single NV center at the desired location in a diamond with seed defect generation and additional annealing for recombination of diffused vacancies and substitutional nitrogen present as impurities. Compared to conventional electron irradiation or ion implantation methods, this 3D control of color center generation is a unique feature of lasers, because nonlinear photoabsorption can localize material modification only around the focal region.^{15–17} Therefore, laser induced space selective generation of NV centers is an important tool for the fabrication of various NV center related devices. Laser induced material modification depends on various laser parameters; in particular, pulse waveform, e.g., pulse duration, is a crucial parameter.¹⁸ We have confirmed that for the laser induced graphitization of diamond, femtosecond double pulse irradiation is a better option than femtosecond single pulse irradiation.¹⁹ Moreover, we demonstrated

that as the delay between double pulses or the duration of each pulse becomes longer, the graphitized region becomes longer. So far, the effect of the pulse duration on the generation of NV centers has not been clarified. Here, we report the effect of the laser pulse duration on ensemble NV center generation. We show that the laser pulse with shorter durations is hard to graphitize diamond and widens the NV center generation window of pulse energy, thus providing more NV centers.

We used a regeneratively amplified Ti-sapphire laser ($\lambda = 800$ nm, Mira-RegA, Coherent) for internal modification of a diamond sample. The sample was a IIa type single crystal CVD diamond (nitrogen and boron concentration [N] < 1 ppm, [B] < 0.05 ppm; Element Six). To examine the effect of the pulse duration on NV center generation, the pulse duration was controlled by adding a chirp through a liquid crystal pulse shaper (C13880, Hamamatsu Photonics K.K.). We also used the MIIPS method²⁰ to compensate for the high order residual phase of femtosecond laser pulses, which was derived from laser optics and an objective lens. After compensation of the residual phase, we finally obtained a 40 fs laser pulse as the shortest pulse. We used this 40 fs pulse and a chirp controlled 1 ps pulse. The laser pulses were focused through the objective lens (LU Plan Fluor 50 $\times$, NA = 0.8, Nikon), and the focus depth was 50 μ m below the sample surface. The laser irradiation time was 1 s at 250 kHz (250 000 pulses), and the position of the laser spot was fixed during the irradiation. In both cases, the pulse duration was measured just after the objective lens. After laser irradiation, photoluminescence (PL) spectra mapping was performed using a confocal microscope (Nanofinder 30, Tokyo Instruments, Inc.). We obtained the PL spectrum of each measured spot, and for PL mapping, the signals were integrated from 640 nm to 660 nm. Because we could confirm the appearance of the PL spectrum of the NV center even in the pristine region, the PL intensity was normalized based on the intensity of the pristine region.

Figure 1 shows the optical transmission images of the laser modified region along the laser propagation direction.

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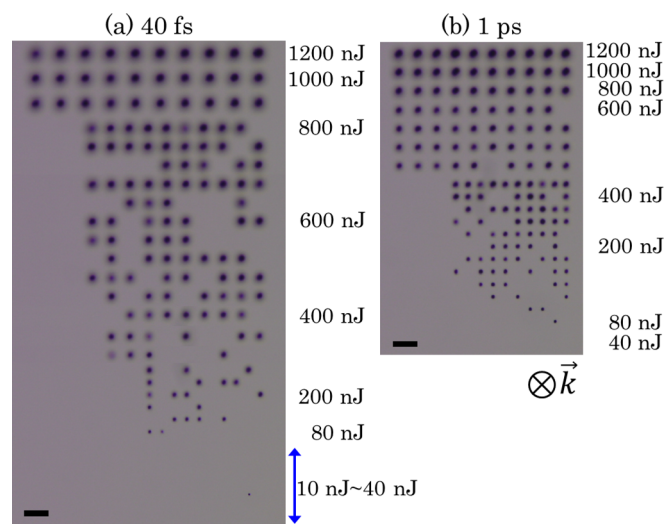


FIG. 1. Optical transmission images of the laser irradiated region: (a) 40 fs and (b) 1 ps. The scale bars in both images indicate $20\ \mu\text{m}$. $\vec{k}$ indicates the laser propagation direction.

In both (a) 40 fs and (b) 1 ps cases, as the pulse energy increased, graphitization started to occur in a somewhat probabilistic manner and any change was not confirmed in the ungraphitized regions. (We refer blackening modification as graphitization.) Though the graphitization was probabilistic, the graphitization probability basically showed an increasing tendency as the pulse energy increased (Fig. 3). The probabilistic behavior may be due to the spatial distribution of impurities, defects, or dislocations in the CVD diamond.²¹

Figure 2 shows the PL spectrum and PL mapping of the laser irradiated and pristine regions. An increase in the PL

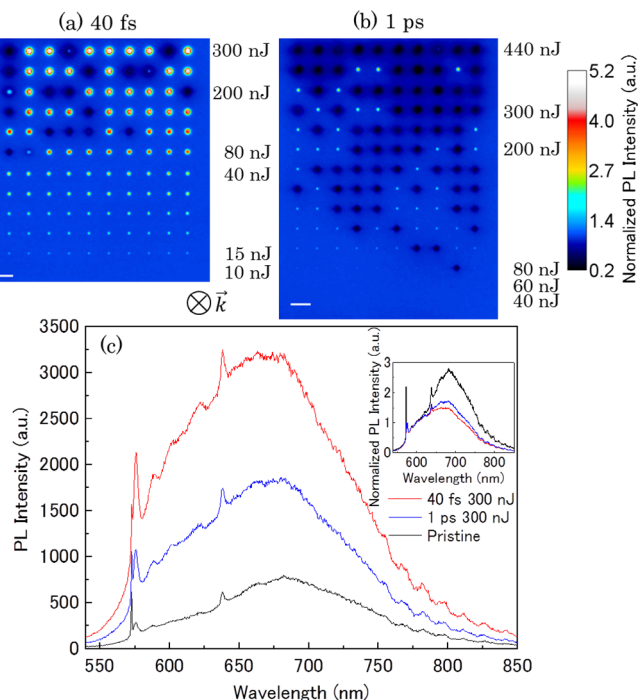


FIG. 2. PL mapping of the laser irradiated region: (a) 40 fs and (b) 1 ps. The pulse energy increases from the bottom part to the top part of the image. The scale bars in both images indicate $10\ \mu\text{m}$. (c) PL spectrum of pristine and laser modified regions. The inset shows the PL spectrum normalized by peak intensity of the zero phonon line of NV^0 ($\sim 576\ \text{nm}$). The peak of the zero phonon line of NV^- is $\sim 638\ \text{nm}$.

intensity was confirmed in the ungraphitized laser irradiated regions at pulse energies above 15 nJ (40 fs) and 80 nJ (1 ps), and the depth of confocal mapping was set in the plane where the maximum PL intensity in the laser irradiated region with the smallest pulse energy was detected [Figs. 2(a) and 2(b)]. From the PL spectrum, we confirmed that the increase in PL intensity was derived from the enhancement of the PL spectrum of the NV center [Fig. 2(c)]. This indicated that NV centers were generated by laser irradiation. The creation of NV centers may be due to photogenerated vacancy diffusion because of laser generated heat and the recombination of substitutional nitrogen and the vacancies.^{6,7}

Figure 3 shows the PL intensity and graphitization probability as a function of pulse energy. We extracted the maximum PL intensity of each ungraphitized laser irradiated region from Figs. 2(a) and 2(b). Note that the PL intensity depended on the position along the laser propagation direction (defined as the z axis). In the case of the 40 fs pulse, the z position showing the maximum PL intensity tended to approach the surface as the pulse energy increased, which may be attributed to the self-focusing effect caused by the strong electric field of the 40 fs pulse, and in the case of the 1 ps pulse, the trend was more moderate. Therefore, in Fig. 3, the PL intensity of the 40 fs pulse may be underestimated compared to that of the 1 ps pulse. For reference, the maximum PL intensity in the PL enhanced region of the highest pulse energy was also plotted (40 fs: 800 nJ, 1 ps: 600 nJ). Nevertheless, although the PL intensity was as high as 3 in the case of the 1 ps pulse, reaching a maximum of 3.7 at 600 nJ, the 40 fs pulse showed a stronger PL intensity in the PL mapping plane (>5), reaching a maximum value of 8.1 at 800 nJ. Moreover, for the 40 fs pulse, the PL intensity reached ~ 3 at 40 nJ and the graphitization probability was

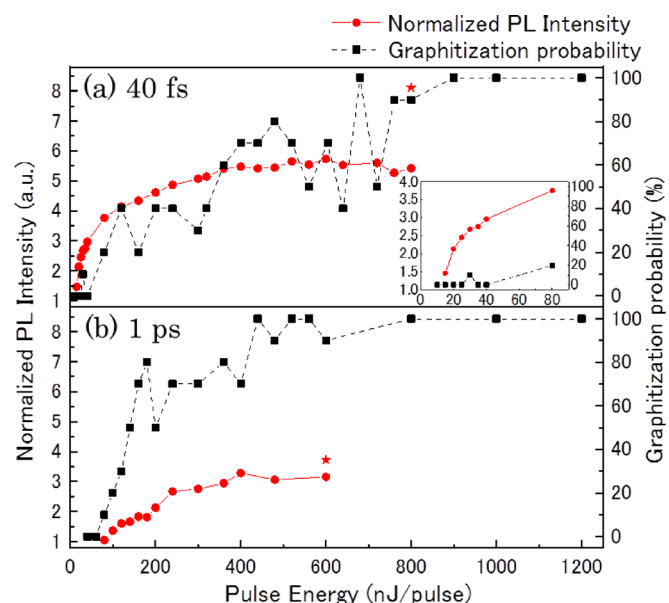


FIG. 3. PL intensity and graphitization probability as a function of pulse energy: (a) 40 fs and (b) 1 ps. Because all of irradiated regions were graphitized at pulse energy higher than 900 nJ (40 fs) and 800 nJ (1 ps), PL intensity is not depicted at the energy higher than its energy. The red star symbols indicate the maximum PL intensity in the modified region of the highest energy (40 fs 800 nJ, 1 ps 600 nJ) extracted from 3D mapping results. The inset shows magnification of the plots from 10 nJ to 80 nJ of the 40 fs case.

almost zero below this energy value; in contrast, for the 1 ps pulse, the graphitization probability steeply increased from the pulse energy just above the value corresponding to the onset of NV center generation. This indicated that the 40 fs laser pulse could generate more NV centers without graphitization than the 1 ps laser pulse. Furthermore, the PL spectra showed that the PL intensity of NV^- relative to that of NV^0 decreased with increasing PL intensity [insets of Fig. 2(c)]. Since the PL intensity was represented by integration of the signals from 640 nm to 660 nm, as the PL intensity increased, the concentration ratio $[\text{NV}^-] / [\text{NV}^0]$ decreased leading to the underestimation of total NV center generation efficiency {total conversion efficiency of substitutional nitrogen to NV center ($[\text{NV}^0] + [\text{NV}^-]$)}. Considering these points, at least 7.1 times of the NV center in the pristine region may be created in the region irradiated with the 40 fs laser pulse (800 nJ).

We will discuss the effect of the pulse duration on the laser modification behavior. First, the threshold pulse energy of NV center generation E_{th}^{NV} is $10 \text{ nJ} < E_{th}^{NV} \leq 15 \text{ nJ}$ for 40 fs pulses and $60 \text{ nJ} < E_{th}^{NV} \leq 80 \text{ nJ}$ for 1 ps pulses. This difference may be due to the difference in the peak intensity because the peak intensity of 40 fs pulses is higher than that of 1 ps pulses with the same pulse energy, and therefore, 40 fs pulses induce multiphoton absorption more easily. As described above, the remarkable difference is that PL intensity did not increase much for 1 ps pulses compared to 40 fs pulses and the graphitization probability steeply increased from the onset of NV center generation and graphitization became dominant modification as the pulse energy increased. From these results, we assume that 1 ps pulses can graphitize diamond more easily than 40 fs pulses do when the same energy is absorbed in a unit volume of diamond. Theoretical studies have shown that laser induced non-equilibrium graphitization within a few hundred femtoseconds is possible.^{22,23} Therefore, to examine the difference in the graphitization process, we focus on the photoabsorption process. Laser irradiation leads to the photoionization of valence band electrons and subsequent free carrier absorption and impact ionization,²⁴ which changes the potential-energy surface and stability of the diamond lattice, finally leading to graphitization. Such non-equilibrium graphitization may depend on the photo-absorption process. For shorter pulses ($\sim$ sub ps or shorter), photoionization may be the dominant process of ionization. On the other hand, for longer pulses (e.g., $\sim$ ps or longer), considering that the photo-generated carrier lifetime of a diamond ranges from tens of picoseconds to hundreds of nanoseconds depending on the photo-generated carrier concentration, temperature, or concentration of impurities,^{25–28} laser absorption by the generated carriers and subsequent impact ionization may become dominant. These differences may affect the time variation of electronic states and hence the force acting on the lattice. In particular, for the 40 fs pulse, the time variation of the electronic state may be more impulsive. This impulsive stimulus seems to induce a collective motion of the lattice and helps maintain the original lattice structure. Thus, the difference in graphitization behavior may be attributed to the difference in the photo-absorption process. Notably, for the internal modification of fused silica using a femtosecond laser, similar results have been reported.²⁹ Laser induced internal modification of

fused silica can be classified into three regimes: (1) smooth refractive index change, (2) nanograting generation, and (3) microvoid generation. In the pulse duration range of 40–600 fs, Ref. 29 reports that the widest window of pulse energy for the smooth refractive index change is obtained at the shortest pulse duration (40 fs) and the window becomes narrow as the pulse duration becomes longer; when the pulse duration is longer than 185 fs, the width of the window tends to zero. These results seem to be similar to those observed for the NV center generation window, which is narrower for the 1 ps pulse. However, the formation mechanism and time scale of defect generation in diamond with the laser are unknown, and the relationship between defect generation and graphitization and relevance to defect generation in other materials are not clear. Further investigations including experiments using other materials or time-resolved experiments are necessary for clarifying the results.

In conclusion, we have shown that a femtosecond laser is hard to graphitize diamond and can generate more NV centers without graphitization compared to a picosecond laser. This indicates that the choice of pulse duration is important, as a shorter pulse duration may be desirable for defect generation without disruptive damages. This result may be adapted for the defect generation of other materials.

We would like to thank Dr. H. Ito from Hamamatsu Photonics K.K. for help with using the pulse shaper.

This work was partially supported by JSPS KAKENHI Grant Nos. JP17H03040 and 16H02088.

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