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Micro-Character Printing on a Diamond Plate by Femtosecond Infrared Optical Pulses

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Processing of less than 400 nm has been performed on the surface of a diamond plate by means of a femtosecond infrared pulse laser. Various characters with a size of about 1 μm were drawn by the femtosecond pulse laser system in conjunction with a microscope equipped with a precisely controlled piezo-stage. The tightly focused laser light on the flat surface of the diamond made it possible to minimize the light-induced graphitization. The surface of the diamond plate after laser machining was analyzed by micro-Raman measurements to estimate the graphitization effect induced by laser irradiation. The obtained results indicate that graphitization increased with the number of irradiated laser pulses. [DOI: 10.1143/JJAP.42.4613]

KEYWORDS: diamond, laser processing, femtosecond pulse laser, micro-character printing, micromachining, graphitization

The intense Ti:sapphire laser with a femtosecond pulse width is quite an attractive light source for the development of laser processing techniques as well as for the promotion of basic studies on the primary mechanisms of the processing itself. A time duration of 100 fs is compatible with or even faster than the interval for the energy relaxation and/or the thermalization process of photo-injected species in condensed matters. Therefore, femtosecond pulsed laser excitation can be expected to achieve the processing of materials via pure electronic and nonequilibrium excitation, which is free from the heating effect of the injected photon energy. In the conventional laser processing utilizing CW and/or nanosecond pulsed lasers, the light-induced heating process plays a key role, and thus it is often the case that extreme heating on the surface damages the target material itself.

Femtosecond laser processing was demonstrated for the first time by Mann et al. with a KrF eximer laser (248 nm) of 560 fs pulse duration in 1992.[1)] The reported results indicate that the mechanism of ablation in femtosecond laser processing is not a heating process but a multiphoton process. Furthermore, metal surface machining with a size of 300 nm was reported by Pronko *et al.* in 1995 using a Ti:sapphire laser of 200 fs pulse duration.[2)] Since then, intensive studies have been conducted on the ablation of various metals using femtosecond lasers.[3)] In the case of femtosecond laser processing with a near-infrared light, it becomes possible to perform the machining of wide-gap semiconductors and insulators via multi-photon excitation by virtue of the extremely high peak intensity, as demonstrated by several groups.[4–10)] The multi-photon excitation also allows machining with much smaller sizes than the utilized wavelength. This is because the diameter of the photo-excited region via multi-photon excitation, becomes smaller than that of the excitation laser beam. In the case of one-photon excitation, the machining with a smaller size than the utilized wavelength is rather difficult without the help of elaborate micro-optical techniques such as a near-field optical microscope. From this point of view, femtosecond laser processing is one of the important candidates of micro-fabrication techniques.

Diamond is an important target of laser processing, because of the utility in the various applications in terms of hardness, thermal conductivity and high refractive index. A fine machining technique on the surface is a key for the future applications of diamond in the field of microelectronics, micromanufacturing and microoptics. By using a nanosecond laser, the graphitization has occurred on a machined surface as the effect of the thermal process.[11,12)] The femtosecond laser processing is an important candidate to alleviate this disadvantage caused by the thermal process. Recently, micro-[13,14)] and submicromachining[15)] of diamond have been demonstrated by using femtosecond laser. The minimum machining size reported with femtosecond laser processing is 0.65 μm in terms of hole diameter.[15)] The mechanism of the ablation on the surface of a diamond using femtosecond laser has also been reported based on theoretical analyses.[16,17)] The theoretical analysis has predicated the clean machining surface of diamond without graphitization for femtosecond laser processing.[17)] However, the details of graphitization on diamond under femtosecond laser processing have not been investigated experimentally. While an estimation of graphitization was discussed from the existence of Raman peak intensity related to diamond ($1332\,cm^{-1}$),[13)] the details about the existence of graphite could not be concluded.

In this letter, we report micro-machining results on the surface of a diamond plate. The utilized system is constructed using a conventional microscope system and a femtosecond Ti:sapphire laser. We demonstrate the fabrication of holes with a diameter of four hundred nm and alphabet characters with a size of one micron on the diamond surface. With this technique, serial numbers and codes might be inscribed on certain goods. We also discuss the graphitization of diamond in an irradiated area based on a micro-Raman analysis system.

As a light source for femtosecond laser processing, a regeneratively amplified Ti:sapphire laser system (*Hurricane*, Spectra Physics) was used. The utilized light wavelength, pulse width, pulse energy, diameter of the laser beam and repetition rate from the laser system were 800 nm, 120 fs, 0.7 mJ, 6 mm and 1 kHz, respectively. The experi-

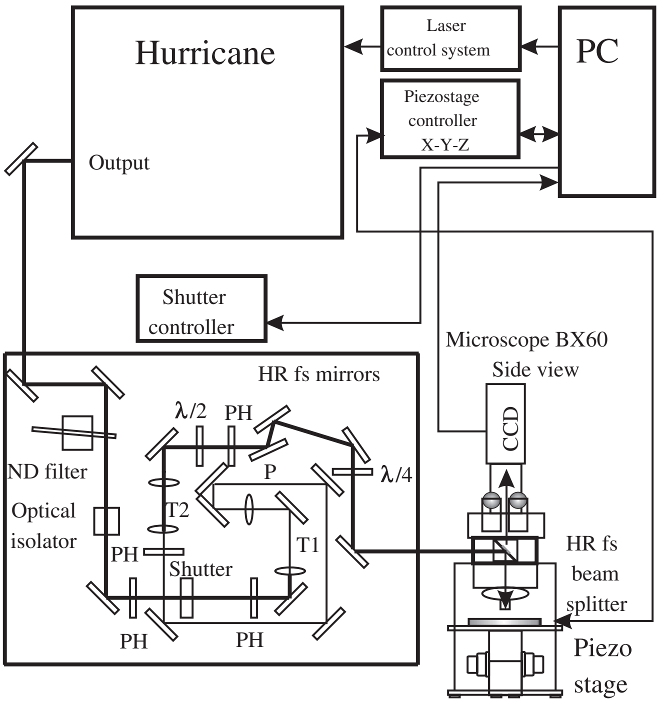

Fig. 1. Experimental setup for micro-machining. PH indicates a pinhole. $\lambda/2$ and $\lambda/4$: $\lambda/2$ and $\lambda/4$ wave plate, respectively. P: polarizer.

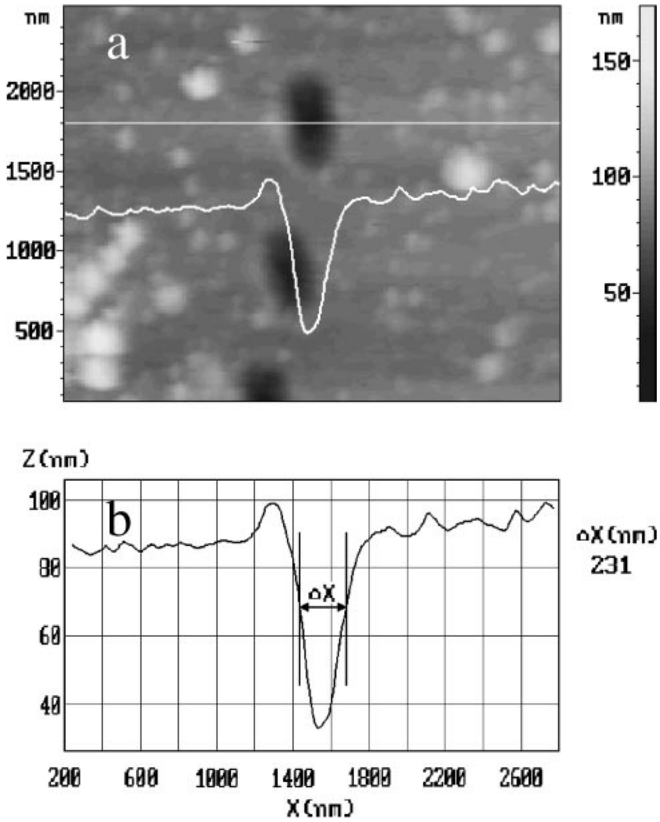

Fig. 2. (a) AFM image of a hole produced with one pulse of 13 nJ energy on the surface of diamond. (b) Cross-sectional profile of the hole.

mental setup is shown in Fig. 1. A high-quality beam of a Gaussian profile with diameter of 6 mm was obtained with a spatial filter including a two-telescope optical system (Fig. 1). The output intensity of the laser light operating with a rather high repetition rate (1 kHz) was precisely controlled electronically. This system enabled us to change the intensity of every laser pulse operating at 1 kHz. The half-wave plate and the polarizer shown in Fig. 1 were used for attenuating the laser light. For homogeneous machining, light pulses were circularly polarized by a $\lambda/4$ wave-plate (Fig. 1).

An objective lens (100^X) with a numerical aperture $NA = 0.95$ (Olympus) was used to focus the laser light for fabricating the holes on the surface of a sample. The sample was mounted on a piezo-electrically driven three-axis stage (Polytec PI, Inc.) to achieve submicrometer spatial control. A polycrystal diamond plate of type IIa was prepared as a sample by the chemical vapor deposition (CVD) method (Sumitomo Electric Industries, Ltd.). The atomic-force microscope (AFM) SMENA (NT-MDT) image in Fig. 2(a) shows an example of a hole drilled on the surface of the diamond plate. The hole was produced with one pulse of 13 nJ energy in air. The width and depth were measured to be 400 nm and 60 nm, respectively [Fig. 2(b)]. The full-width at half depth was 230 nm. It should be noted that the theoretically estimated spot size for 800 nm light based on the present optical microscope is 1.3 μm. The obtained result clearly indicates the merits of the multi-photon absorption effect for the fine machining of materials with wide-gap energy. The hole exhibits sharp edges without heat-affected zones.

The optical microscope image of diamond surface processing with a 100^X objective lens is shown in Fig. 3(a). This image indicates the shot-number dependence of the processing. Blackish parts appear in the case of processing with more than fifty shots, as shown in Fig. 3(a). Raman scattering spectra were observed on the diamond after machining. The characteristic spectrum is shown in Fig. 3(b). The observed micro-Raman scattering spectrum is composed of two Raman lines. The diamond has a single triply degenerate Raman active phonon mode at $1332\,\mathrm{cm}^{-1}$ (diamond line).[18] Graphite has a narrow band around $1575\,\mathrm{cm}^{-1}$ (graphite line),[19] which is a phonon consisting of in-plane C–C stretches with the exact frequency depending upon the type of graphite. However, the observed phonon spectra of the graphite lines are much broader than those reported for graphite.[20] These broad spectra of the graphite lines can be explained by the existence of heterogeneity with glassy and polycrystalline graphitization materials.

The intensity of the graphite line spectrum is related to the graphitization of diamond. Therefore, we could roughly find and estimate the occurrence of graphitization on the surface of diamond as a result of laser irradiation. The mapping image of graphitization on the surface of diamond in the rectangular region of Fig. 3(a) is taken as the intensity of a graphite line from 1565 to $1585\,\mathrm{cm}^{-1}$ using a laser confocal microscope with spectrometer (*Nanofinder*, Tokyo Instruments, Inc.) and shown in Fig. 3(c). An objective lens, $NA = 0.95$ was used for surface scanning. The lateral resolution was about 0.2 μm. The image indicates that graphite exists around the processed surface with fifty shots. On the other hand the amount of graphite is significantly reduced around a hole in the case of machining with fewer than 20 shots Fig. 3(d). However, the graphitization has been observed on the machined surface of diamond even with one shot of laser

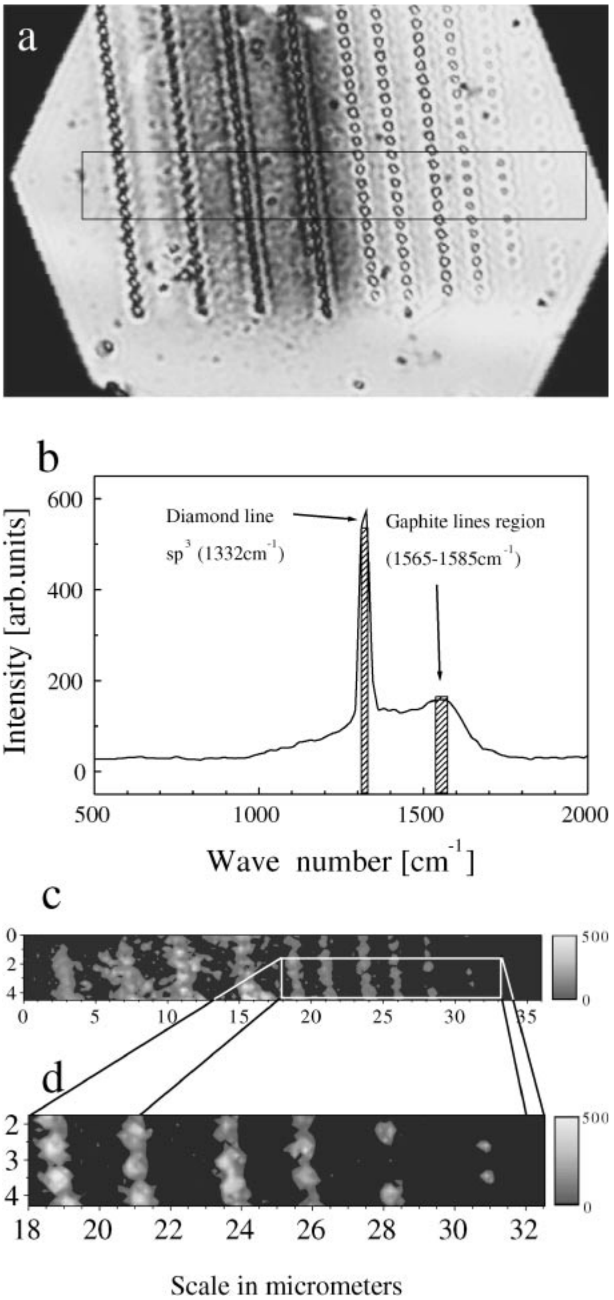

Fig. 3. (a) Microscopic image of the diamond surface after machining. Dot arrays produced with the following number of shots, from left to right, 50, 50, 70, 50, 20, 20, 10, 5, 2, 1. (b) A typical micro-Raman scattering spectrum of diamond on the processing surface. (c) The confocal mapping image of the micro-Raman scattering light intensity in the graphite spectral region from 1565 to 1585 cm^{-1} in the rectangular region of Fig. 3(a). (d) Enlarged mapping of the rectangular region of Fig. 3(c). The dot arrays were produced with the following number of shots, from left to right, 20, 20, 10, 5, 2, 1.

pulse with damage threshold intensity as shown on the right hand side in Fig. 3(c). The graphite produced by laser ablation might be trapped on the surface of diamond in the present experimental condition of abrasion in air. The present result indicates that another elaborate technique is needed for the machining of diamond without graphitization using a femtosecond laser for practical applications.

The characters printed on the surface of diamond with dots as holes using a single pulse per dot are shown in Fig. 4. The space between dots was 0.2 μm, and drawing the

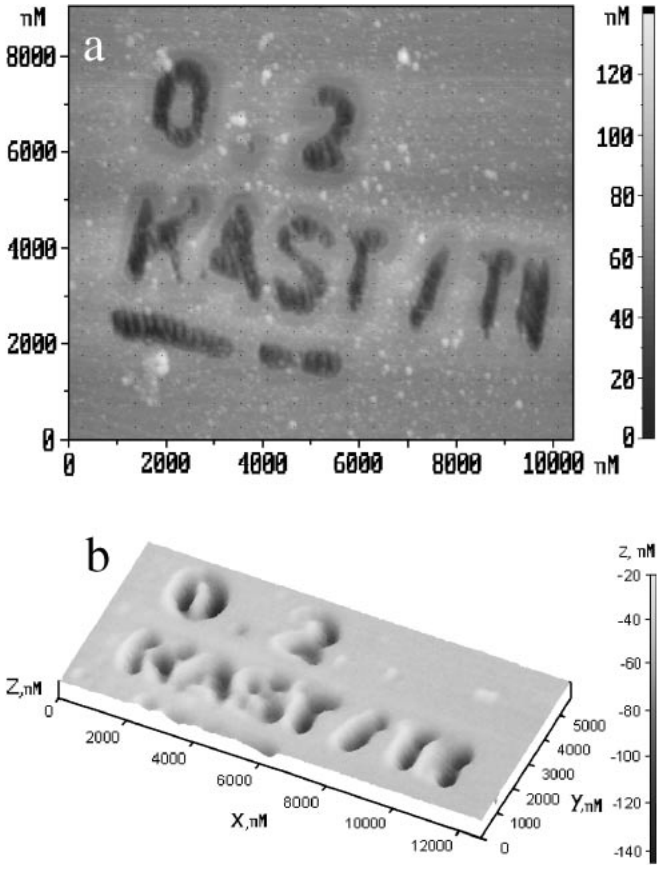

Fig. 4. (a) AFM image of characters fabricated on the surface of diamond with the energy of 17 nJ per pulse and ten shots per dot. (b) Laser scattering light confocal image of the same characters.

characters in Fig. 4 took less than 3 seconds. We consider these results to be the first clear demonstration that femtosecond laser machining is a really powerful tool for the submicron meter scale machining of diamond.

In summary, processing of four hundred nanometers was demonstrated on the surface of a diamond plate by a femtosecond laser. Small characters with a size near 1 μm were written on the surface of a diamond plate by using a femtosecond infrared pulse laser combined with a precisely controlled piezo-stage.

Acknowledgement

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