Femtosecond laser-induced formation of nanometer-width grooves on synthetic single-crystal diamond surfaces

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We form periodic linear grooves in synthetic single-crystal diamond with femtosecond pulses at 800 nm. The grooves are 40 nm wide, 500 nm deep, up to 0.3 mm long, and have an average spacing of 146 ± 7 nm. The grooves are perpendicular to the direction of the laser polarization and are formed below the threshold for ablation throughout the focal volume. The submicrometer periodicity is caused by interference between a laser-induced plasma and the incident laser beam, which locally enhances the field at the surface so the ablation threshold is exceeded. Using Raman spectroscopy we find that the structures retain the original diamond composition. © *2009 American Institute of Physics*.
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I. INTRODUCTION

Because diamond is an ultrahard material, methods for forming submicrometer structures in diamond are limited.[1–5] Synthetic single-crystal diamond recently received much attention because of its outstanding optical, electrical, and mechanical properties.[6–8] The material has found a broad range of applications in deep ultraviolet lasers and photodetectors, field emission displays, high-power semiconductor devices, and surface acoustic wave devices.[2,4,9–11]

Surface processing of diamond has been demonstrated with ultraviolet and near-infrared femtosecond lasers.[1,3,5,12–14] The intensity threshold required to ablate diamond with 800-nm pulses is on the order of 2×10^{16} $\mathrm{W/m^2}$.[13,14] Within the ablated spot, periodic structuring has been observed with a periodicity below the laser wavelength.[3] However, the induced periodic structures are shallow, rough, and confined to the edges of ablation craters or clusters.[1,3] We report on the generation of nanometer-width periodic grooves in synthetic single-crystal diamond using femtosecond laser pulses. In contrast to previously reported structures, the grooves are formed with laser pulses below the ablation threshold, have a large depth-to-width aspect ratio, and can be extended to millimeter length by translating the laser beam over the sample.

II. EXPERIMENT

The experiments described in this paper were carried out on undoped synthetic single-crystal diamond fabricated by chemical vapor deposition (CVD).[8] The diamond samples were 1.2 mm thick oriented along the (100) direction. The real and imaginary parts of the refractive index of diamond at 800 nm are 2.397 and 0, respectively. The optical absorption edge is 235 nm.[11] The diamond surface was polished to optical grade displaying a final mean surface roughness of 0.7 nm, as measured by atomic force microscopy.

To process the diamond we used a 250-kHz, 120-fs, 800-nm amplified femtosecond Ti:sapphire laser. Using neutral density filters, we adjusted the laser pulse energy to be in the range from 50–250 nJ. The laser was incident normal to the diamond surface and focused by a microscope objective with a numerical aperture of 0.45. The laser spot size on the sample was approximately 2 μm. The diamond sample was placed on a scanning stage and translated under computer control during irradiation at a scanning speed of 500 μm/s. The scanning direction was normal to the laser polarization direction. All experiments were carried out in ambient air at atmospheric pressure and room temperature. After irradiation, the diamond sample was rinsed for 30 min with ethanol in an ultrasonic cleaner in order to remove any debris from the ablation process. After cleaning we analyzed the ablated diamond surfaces using a scanning electronic microscope (SEM). No conductive coating was used to avoid blocking the submicrometer structures.

III. RESULTS AND DISCUSSION

Figure 1 shows SEM images of the diamond surfaces after irradiation by femtosecond laser pulses with pulse energies ranging from 72 to 240 nJ; below the energy threshold of 72 nJ we do not observe any surface structures. The dashed arrow in Fig. 1(a) indicates the direction of the laser polarization; the solid arrow shows the direction of sample translation. The grooves always form perpendicularly to the polarization direction. If the laser polarization direction is rotated 90° by inserting a half-wave plate in the optical path, the direction of the grooves also rotates by 90°. Increasing the pulse energy by 10% to 80 nJ leads to ablation throughout the focal volume [Fig. 1(b)]. This observation is consistent with previous reports of the ablation threshold for diamond.[13] As the pulse energy is increased further, more material is removed, but we continue to observe grooves that are perpendicular to the ablated surface [Figs. 1(c) and 1(d)].

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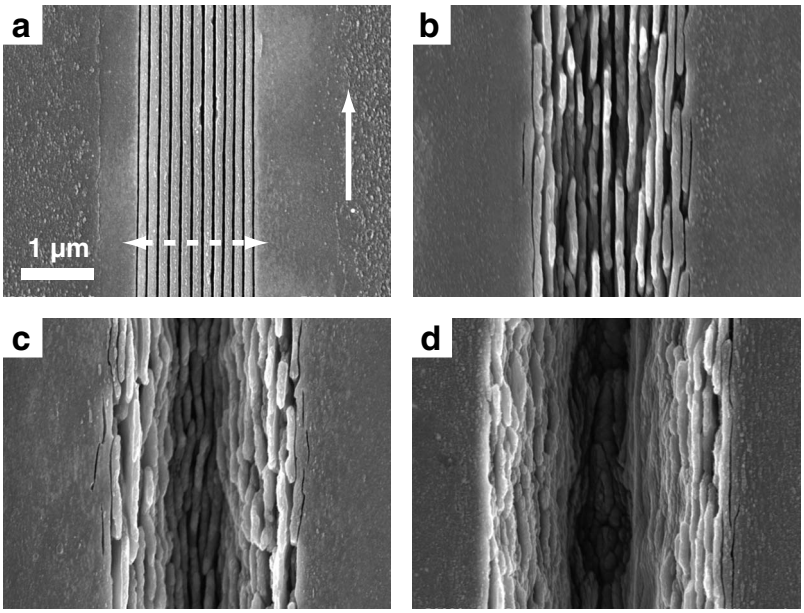

FIG. 1. SEM images of the diamond surface after irradiation with a 1000 pulse train of 120-fs laser pulses at a rate of 250 kHz with a pulse energy of (a) 72, (b) 80, (c) 120, and (d) 240 nJ. The polarization and the scanning directions are indicated by the dotted and solid arrows, respectively.

Figure 2(a) shows an enlarged SEM image of grooves in Fig. 1(a). The average period of the grooves is 146 ± 7 nm, which is about 5.5 times smaller than the free-space wavelength of the laser (2.28 times smaller than the wavelength in diamond). As the laser beam is translated, the periodic grooves continue uninterrupted for hundreds of micrometers [Fig. 2(b)]. The maximum length of the grooves we observed was limited to approximately 300 μm by the translation stage used.

The formation of the grooves is similar to the generation of nanostructures in bulk glass and can be attributed to an interaction between the laser pulse and a laser-induced plasma.[3,15–17] Because the band gap of the diamond (5.47 eV) is much larger than the photon energy (1.55 eV), the incident laser creates a dense electron plasma through multiphoton excitation at the surface of the diamond.[18] The plasma generated by absorption of the front end of the pulse enhances the electric field of the remainder of the pulse and breaks up into a series of planes perpendicular to the electric field with a periodicity close to $\lambda/2n$, where λ is the free-space wavelength of the incident radiation and n the index of refraction.[17,19] As the sample is translated the previously formed periodicity favors nonlinear absorption at an identical spatial distribution, causing the periodicity to be maintained as observed in Fig. 2(b).

The results in Fig. 1 show that the "cleanest" and most uniform grooves occur in a narrow energy range just at the measured ablation threshold. Interestingly, the laser-induced pattern does not reflect the spatial profile of the laser beam, in contrast to the results obtained significantly above threshold. Near the threshold, periodic plasma enhancement of the electric field causes the ablation threshold to be exceeded only at a specific periodicity. Because ablation depends nonlinearly on intensity the resulting grooves are sharp. The periodic grooves are a fingerprint of the plasmonic field enhancement at the surface of diamond and are consistent with previously observed and modeled plasma-induced periodic structures inside the bulk of transparent materials.[16,17]

Figure 3 shows the cross section of the periodic grooves and a close up of the center pillar after removal of the adjacent pillars using focused ion beam etching. Although debris generated by gallium ions from the focused ion beam partially block the grooves, Figs. 3(a) and 3(b) indicate that the shape and period of the grooves are uniform at the nanometer scale. The 40-nm wide grooves have a depth of about 500 nm, giving them an aspect ratio larger than twelve, significantly larger than previously reported period structures on diamond.[1,3] The groove depth can be controlled by varying the repetition rate and scanning speed of the femtosecond laser.

To determine the composition of the irradiated material between the grooves, we performed micro-Raman spectroscopy using a 100× objective lens and a laser wavelength of 532 nm. Figure 4 shows the Raman spectra obtained from irradiated and unirradiated areas on the diamond surface. Both spectra show a unique peak at 1331 cm^{-1}, correspond-

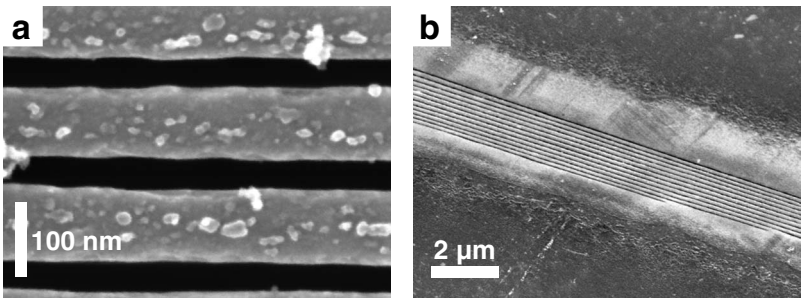

FIG. 2. (a) Enlarged SEM image of the grooves obtained at a pulse energy of 72 nJ. (b) SEM image of grooves of several hundred micrometers length.

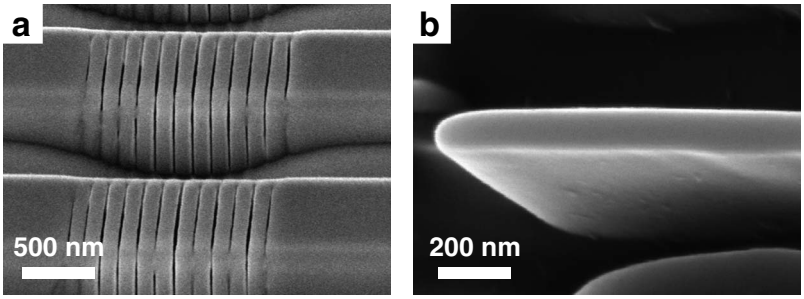

FIG. 3. (a) SEM image of the cross section the periodic surface structure after etching by focused ion beam. (b) SEM image of the center part of a pillar after focused ion beam etching. The SEM images were obtained at an angle of 45° and 30° from the diamond surface, respectively.

ing to the first-order Raman line of a diamond crystal.[20] The reduction in Raman intensity on the irradiated area is due to scattering by the grooves. The micro-Raman spectra indicate that the material between the grooves maintains the original diamond composition after irradiation by the femtosecond laser.

Figure 5 shows how even finer features can be obtained by sequential processing. We irradiated the diamond surface sequentially in two different scanning directions to form parallelepiped-shaped pillar structures with submicrometer dimensions. Although the pulse energy is the same as the one used in Fig. 1(a), the resulting structures are not uniform.

Although all the results presented are for single-crystal CVD-grown diamond, we believe that the same effect would be observed on a natural diamond of sufficient purity. Previous studies with natural diamond (type Ia and IIa) show a significant variation in bulk damage threshold from sample to sample.[21] Defect sites in the form of impurities or point defects are likely to lower the surface ablation threshold, broadening the narrow energy window for periodic structure formation in natural diamond.

IV. CONCLUSION

In summary, we demonstrated the fabrication of long nanometer-width grooves on synthetic single-crystal CVD diamond surfaces by femtosecond laser irradiation. The grooves are formed perpendicular to the laser polarization direction. Their aspect ratio is larger than twelve and their shape is quite uniform at the nanometer scale. We used this technique to fabricate grooves of approximately 300-μm long and parallelepiped-shaped pillar structures with submicrometer dimensions. Raman spectroscopy confirms that the structures maintain the original diamond composition. The average groove spacing of 146 nm corresponds to 1/5.5 of the laser wavelength and can be explained by a plasma enhancement of incident laser electric field at the surface. This process provides a high-speed and low-cost method for fabricating submicrometer devices such as optical gratings or nanoimprint molds in diamond.

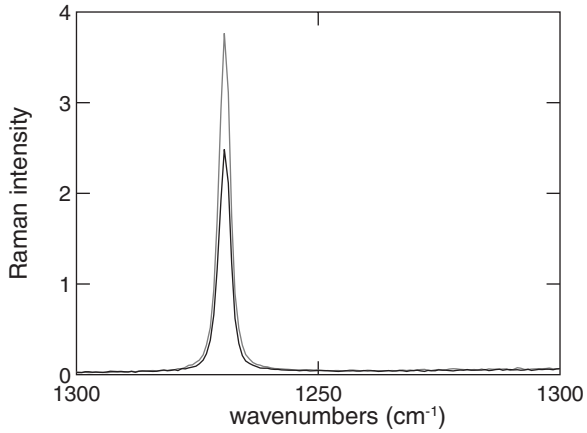

FIG. 4. Micro-Raman spectra of the irradiated (black) and unirradiated (gray) areas a laser-processed diamond sample.

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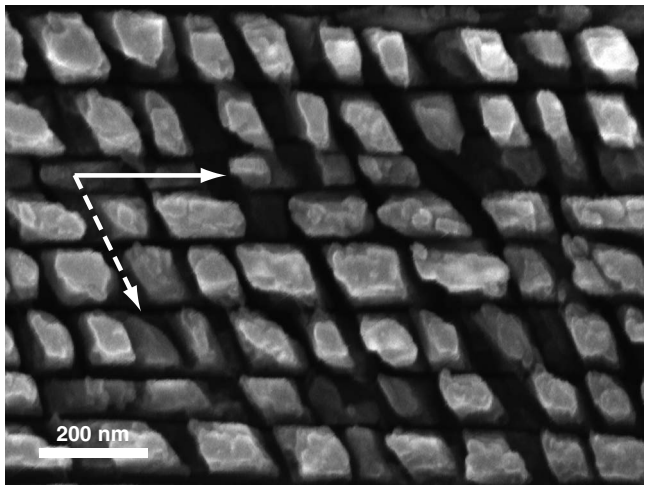

FIG. 5. SEM image of the diamond surface processed sequentially using two scanning directions at 0° (bold arrow) and 300° (dotted arrow).

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