# Nanostructuring with Femtosecond Laser Pulses on Patterned DLC Surface

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We have studied the origin of nanostructuring on diamond-like carbon (DLC) film in femtosecond laser ablation. Using patterned targets including submicrometer-size stripe arrays on the surface, we found that the nanostructure starts to be formed along the direction perpendicular to the laser polarization on the crest of the stripe. The results obtained demonstrate that the nanometer-size ablation on the DLC surface is initiated and enhanced with a *local field* that is generated by the coherent production of free electrons in a surface area smaller than the laser wavelength.

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## 1. Introduction

Recently several groups have reported observation of periodic nanostructure formed on a surface of several solid-state materials, such as TiN [1,2], CrN [3], diamond-like carbon (DLC) [1,4], SiC [5,6], ZnSe [7], when the target surfaces were irradiated at low fluence of femtosecond (fs) laser pulses. The structure size observed is much smaller than the laser wavelength λ, as small as ~ λ/10 or about 30 nm [1,3,4]. The nanostructuring on solid surfaces with fs laser pulses is attractive as a promising approach to a laser processing at high spatial resolutions less than the diffraction limit of light. Understanding the nanostructure formation process is crucial for further development of nano-processing, since the conventional ripple model [8] can never illustrate the formation of fine structure. Several interaction processes have been proposed so far for the nanostructuring [7,8-11], but the results obtained for the hard thin films such as TiN and DLC [1,3,4] cannot be explained with the existing and/or proposed models.

In our recent studies on DLC films [4,12], we have shown that the nanostructure formation is preceded by the change in bonding structure from DLC to glassy carbon (GC). Based on the results of reflectivity measured as a function of superimposed number of fs pulses, we have suggested that the nanostructure is formed by the ablation induced by a *local field*. Such local fields would be created by the intense laser pulses on a rough or undulating surface through the generation of a non-uniform distribution of free electrons.

In this paper, we report an experimental study to confirm the interaction process proposed in our previous study [12]. For the present ablation experiment we prepared a target of DLC film of which surface is patterned with parallel stripes of sub-micrometer in width. The patterned DLC surface was irradiated with fs laser pulses at different fluences $F$, shot numbers $N$ and different polarizations, and then the surface morphology was carefully observed. The results obtained demonstrate that the nanostructure formation is certainly induced by a *local field* of nanometer size generated in the vicinity of the stripe pattern on the film surface.

## 2. Experimental

We prepared silicon (Si) substrates on which Si stripes were fabricated with electron-beam lithography and liftoff process. Figures 1(a) and (b) show scanning electron microscope (SEM) images of the patterned Si substrate and an array of 36 stripes in the central part, respectively. A single Si stripe is 0.1-μm wide, 50-nm high and 4-μm, and 36 stripes are arranged in an array at four different periods of 200, 400, 800, and 1600 nm, as seen in Fig.1(b). The four arrays are set in a cross shape, as in Fig.1(a), on an area of 50 × 50 μm$^2$, so that the stripes are oriented to both directions parallel and perpendicular to the $E$ field of a linearly

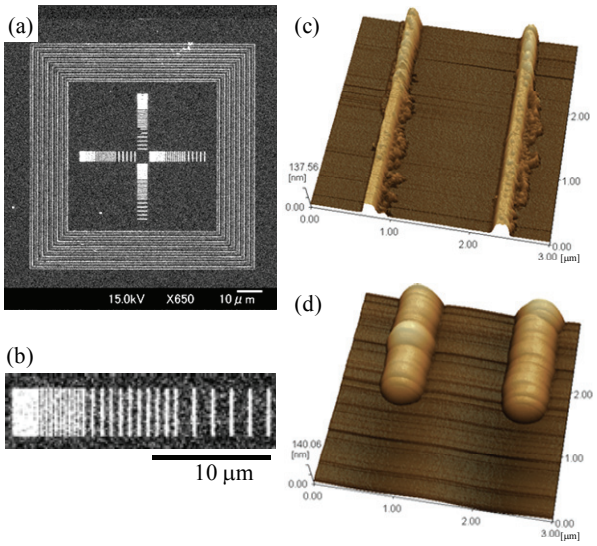


**Fig. 1** SEM images of the patterned Si substrate (a) and an array of stripes on the substrate (b), and SPM images of the Si stripes at 1.6-μm period (c) and the DLC-coated stripes on Si (d).

polarized laser pulse. The eight square box-shape stripes around the crossed arrays are drawn for the sake of detecting and monitoring the focal position onto the patterned area with a CCD camera, while the square stripes work as a grating for the visible light. Figures 1(c) and (d) are the scanning probe microscope (SPM) images of the Si stripe and the stripes coated with DLC, respectively. The DLC film of 900 nm in thickness was deposited on the patterned Si substrate with a plasma-based ion implantation system. The surface roughness was measured to be less than 1 nm with the SPM. The coated DLC stripe was observed to be ~ 500 nm in width and ~ 100 nm in height, as shown in Fig.1(d). The coated stripes were well isolated for the periods of 800 and 1600 nm, whereas those for the 200- and 400-nm periods were partially overlapped with each other to have a reduced height of the DLC stripes.

For the ablation experiment, we used a Ti:sapphire laser system delivering 800 nm, 100 fs pulses at a repetition rate of 10 Hz. The linearly polarized fs pulse was focused in air at normal incidence on the DLC surface with a lens of 1000-mm focal length. The intensity distribution of output beam could be fitted well to the lowest-order Gaussian shape. The focal spot size $w_0$ was 100 μm in radius at $1/e^2$ of the maximum intensity. The focused beam could cover the whole patterned area of 50 × 50 μm$^2$. However, the surface morphology and/or the nanostructuring was observed to be very sensitive to the spatial intensity distribution or the local intensity in the focused beam. In the analysis of the experimental results, therefore, we derived the spatial fluence $F(r)$ at position $r$ in the focused beam, using the Gaussian distribution $F = F_0 \exp(-2 r^2/w_0^2)$, where $F_0$ is the maximum fluence at the beam center. In the present experiment, $F$ was 60 – 150 mJ/cm$^2$. The superimposed number of laser pulses $N$ was in a range of $N$ = 1 – 1000, where $N$ was selected with a mechanical shutter. The surface morphology was observed with the SEM and/or the SPM.

## 3. Results and discussion

Figure 2 shows the SPM images of DLC surface irradiated with $N$ = 0 (a), 100 (b), 200 (c), 300 (d), 500 (e) and 1000 (f) at $F$ = 70 mJ/cm$^2$, which includes the stripes at 800-nm period. Comparing the images in Figs.2(a) and (b), we see that the nanostructure starts to be formed only in a small area on the crest of stripes through the local ablation. The mean spacing $l$ of nanostructures on the stripe is measured to be $l$ ~ 60 nm. The nanostructure is formed perpendicularly to the laser polarization direction. With increasing $N$, the small nanostructure grows up on and along the ridge of stripe, as seen in Fig.2(c), while no structure is created yet on the non-patterned surface outside the stripe arrays, as seen in the lowest part of the image. With a further increase in $N$ to 300, the mean spacing of nanostructure expands to $l$ ~ 110 nm, and then the smaller nanostructure of $l$ ~ 40 nm starts to be formed in the non-patterned surface area, as seen in Fig.2(d). With increasing $N$ up to 500 - 1000, as shown in Figs.2(e) and (f), the nanostructure on the stripe ridge becomes deeper with the increased width of $l$ ~ 180 nm, while the smaller nanostructure of $l$ ~ 90 nm is created in the non-patterned area. It is noted that the nanostructure between the stripes grows up along with that on the flat non-patterned surface outside the stripe arrays.

To see quantitatively the effect of stripes on nano-

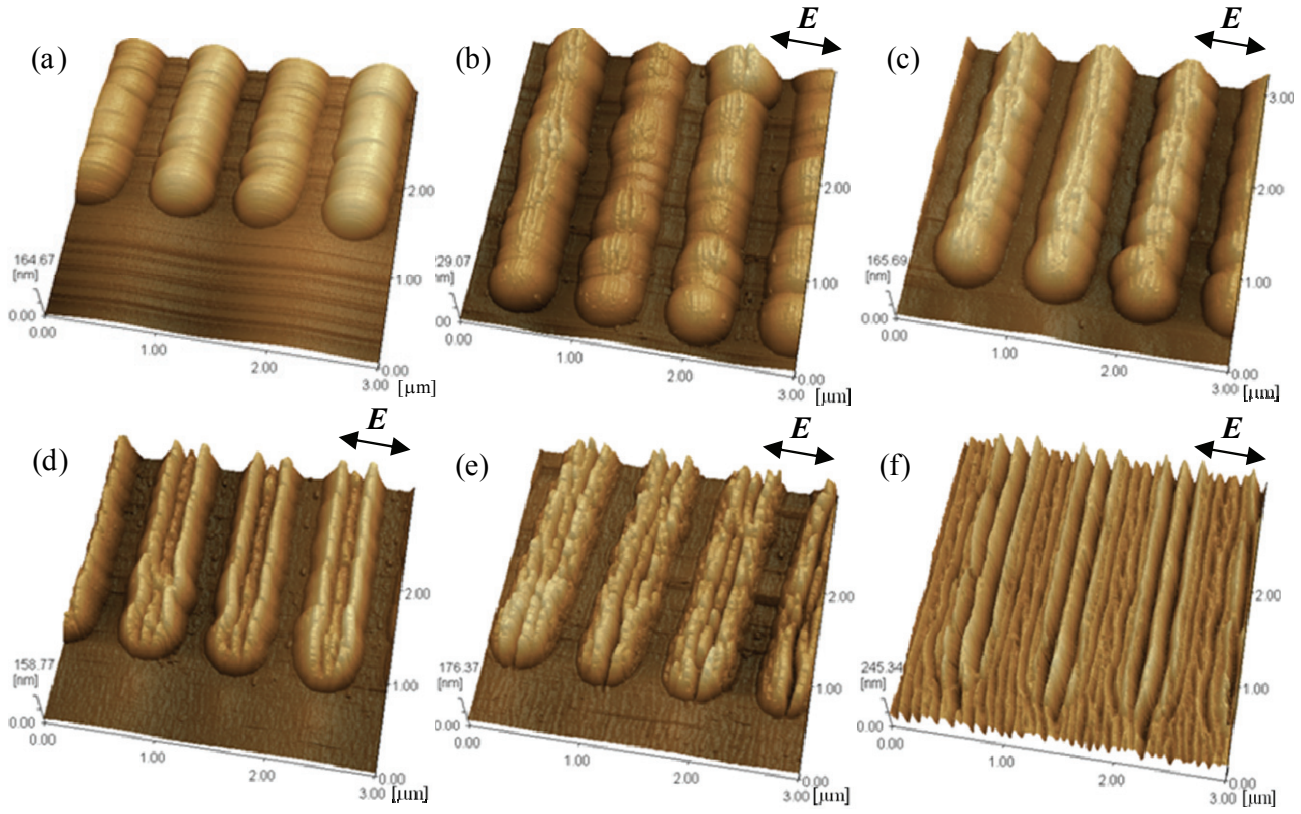


**Fig.2** SPM images of the DLC surfaces on the 800-nm-period stripes irradiated with $N$ = 0 (a), 100 (b), 200 (c), 300 (d), 500 (e) and 1000 (f) at $F$ = 70 mJ/cm$^2$. The arrow denotes the polarization direction.

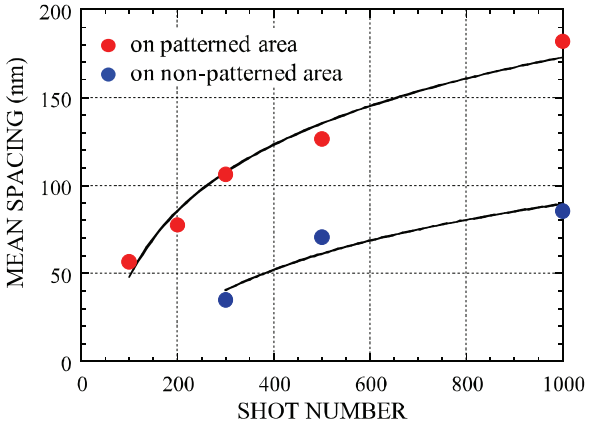


**Fig.3** Mean spacing of periodic nanostructures in the patterned area (red circles) and in the non-patterned area (blue circles) measured with the SEM and/or the SPM as a function of $N$ for the DLC irradiated under the same conditions as in Fig.2.

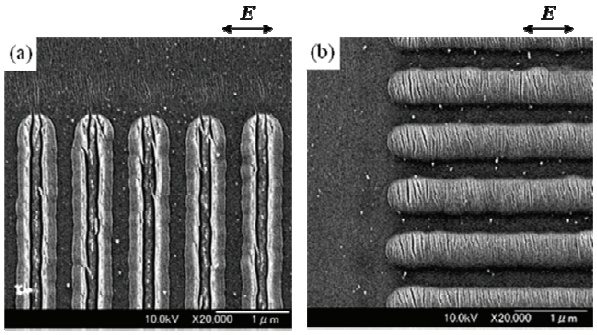


**Fig.4** SEM images of the DLC surfaces on the 800-nm-period stripes irradiated with $N$ = 300 at $F$ = 70 mJ/cm$^2$. The laser polarization direction is perpendicular (a) and parallel (b) to the stripe, as indicated by an arrow.

structuring, we measured the mean spacing $l$ on the stripes 800 and 1600-nm periods and $l$ in the non-patterned area on the surface irradiated at $F$ = 70 mJ/cm$^2$. The results are plotted as a function of $N$ in Fig.3. The spacing $l$ is observed to increase monotonously with an increase in $N$ both on the stripe and non-patterned surfaces. As discussed above, it is clearly seen that the nanostructure is formed much more efficiently on the stripe than on the non-patterned surface. For the surface on the stripe, the shot number $N$ required to create the nanostructure of a spacing $l$ is reduced to about 20 % of $N$ for the non-patterned surface, or the same $N$ at a fixed fluence certainly produces a larger nanostructure on the stripe.

On the stripes at 200- and 400-nm periods, we observed less distinct nanostructure than those at 800- and 1600-nm periods for the same $N$ and/or $F$ as in Fig.3. As mentioned above, this is due to the fact that the stripes at the smaller periods are overlapped to reduce the height or obscure the surface ridge.

These results demonstrate that the sub-micrometer size stripes having the small surface curvature play an essential role in the nanostructuring of DLC film, through the *generation of local fields* to accelerate and enhance the ablation process.

The nanostructure formation on hard thin films has been observed so far to depend on the laser polarization [1,3,4,12]. In the present experiment, we can see this phenomenon in a different point of view of the correlation between the polarization and the stripe direction. The fs laser pulse is focused on the target with the $E$-field direction parallel and perpendicular to the stripes, as described before. Then we can observe the morphology of stripe surfaces irradiated with the different polarizations under an identical condition of $F$ and $N$. Figure 4 shows an example of the pair of SEM images for the stripes irradiated with the perpendicular (a) and parallel (b) polarizations, where $N$ = 300 and $F$ = 70 mJ/cm$^2$ are used. The result shown in Fig.4(a) is the same as in Fig.2(d), where the polarization is perpendicular to the stripe. The nanostructure with $l \sim 110$ nm is formed on the stripe, whereas the much smaller structure with $l \sim 35$ nm is observed in the non-patterned area. On the same DLC surface, the polarization parallel to the stripes is observed to create the shallow nanostructure with the smaller spacing $l \sim 80$ nm, as seen in Fig.4(b), showing that this stripe direction is less effective for nanostructuring. These results indicate that the local field strength to induce the nanoscale ablation strongly depends on the size and shape of the surface undulation or roughness along the laser polarization direction.

The morphological change of the patterned surface would be a fingerprint of the local field generated on the surface, and the generated field strength should depend on $F$, as well as the surface condition. We observed the change in surface morphology in a range of $F$ = 60 – 150 mJ/cm$^2$ and measured the mean spacing $l$ of nanostructure as a function of $F$. For example, with the shot number of $N$ = 100 at $F$ = 60 mJ/cm$^2$, the nanostructure of $l \sim 50$ nm started to be formed on the stripe perpendicular to the $E$-field, while the comparable nanostructure of $l \sim 80$ nm was produced in the non-patterned area at $F$ = 100 mJ/cm$^2$. The result obtained has shown that the nanostructure of comparable size is formed on the stripe at the fluence $F$ smaller by a factor of ~ 0.7 than that on the non-patterned surface.

We made the ablation experiment also for the 500-nm thick DLC films to see the effect of film thickness on the nanostructuring, and the results have shown no fundamental difference from those presented above.

Based on the results obtained, we discuss the detailed interaction process for the nanostructure formation on the DLC surface. In our previous studies [4,12], we have shown that the nanostructure formation is preceded by the change in bonding structure from DLC to GC. The GC layer inevitably swells in volume due to the lower density than the DLC and creates small surface undulation and/or roughness. Then the free-electron density created through the light absorption would be no longer uniform in the area on a nanometer level, while the GC with the smaller bandgap can efficiently produce free electrons in the surface. In the laser field, the free electrons are coherently oscillated and localized along the direction of laser polarization in the surface layer much smaller than the laser wavelength. The localized electron-hole pairs are able to create a *local field*

on the surface of a nanometer size, which is similar to the well-known nearfield created, e.g., on metal surface [13].

In the present experiment, the laser fluence used was less than the ablation threshold for a single pulse. Then the ablation could be initiated when the incident *E*-field on the surface was enhanced with the additional local field to exceed the ablation threshold of the DLC. This has clearly been observed on the crest of the stripe where the field enhancement would be largest due to the high surface curvature along the direction of the incident *E*-field. Thus, the nanometer-size ablation is initiated on the stripe surface at a fluence much lower than that for ablation of the non-patterned surface.

The initial nanoscale ablation produces a small morphological change and resulting higher surface curvature on the film, and then the higher curvature created can further enhance the local field to increase the width and the depth of ablation traces. The successive processes would be developed with increasing *N* and/or *F*. The ablation traces with an increasing width would often be split into two or several ones, depending on the surface curvature and/or the spatial size of local fields.

The present results provide conclusive evidences that the localized nanoscale field plays the essential role in the ultrafast ablation process to form the nanostructure. The nanostructure would certainly be the record of the local filed generation and resulting nano-ablation. A quantitative simulation of nanostructuring on solid surfaces is now in progress to understand the detailed process dominating the structure size and shape, as well as the temporal development of surface structures.

## 4. Conclusions

Using the patterned DLC targets, we have investigated the physical process responsible for nanostructuring on the DLC surface irradiated at low fluence of fs laser pulses. The nanoscale ablation was observed to preferentially develop on the crest of stripe where the local field intensity would be enhanced with the high surface curvature along the laser polarization direction. The experimental results obtained have demonstrated a conclusive picture that the localized nanoscale field creates the nanostructure on the DLC surface.

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