Far-Field Nanostructuring in Dielectric Materials Beyond the Diffraction Limit Using Femtosecond Laser

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We review the latest progress in the development of far-field nanostructuring technologies based on femtosecond laser direct writing. The principles for breaking through the diffraction limit in the interaction of a focused ultrafast laser beam with dielectric materials are presented, and applications of the femtosecond laser nanostructuring are discussed.

Key Words: Femtosecond laser, Far field, Nanostructuring, Nanograting, Nanoripple

1. Introduction

One of the dreams in nanoscience and nanotechnology is to create three-dimensional (3D) structures of arbitrary geometries and configurations with nanoscale (< 100 nm) resolutions. Due to the unique characteristics of ultrashort pulse width and extremely high peak intensity, femtosecond lasers have established themselves as excellent tools for high-precision and flexible fabrication of 3D microstructures.12 However, as an optical fabrication approach, femtosecond laser microprocessing inherently suffers from the diffraction-limited fabrication resolution which is at best on the order of the radiation wavelength.35 It should be noted that the diffraction limit reflects the wave nature of light. Therefore, breaking through the diffraction limit has only been achieved either by near-field optics or by nonlinear optical effects.57 Although the near-field fabrication approaches can achieve resolutions on the order of a few tens of nanometers, it’s difficult to create holes or trenches with a high aspect ratio due to the fast decay of the evanescent wave. The nature of evanescent wave restricts the processing only to the material surfaces.59 For 3D nanofabrication, a far-field focusing geometry has to be employed. In addition, for most near-field fabrication technologies, stringent control on the distance between the nanostructures which are used for creating a nanoscale light distribution and the substrate surface is required, which leads to extra complexity and cost. For these reasons, development of far-field nanostructuring techniques is highly in demand as it will benefit a broad range of applications including nanophotonics, nanofluidics, and highly integrated optoelectronics.

In this paper, we present a review of recent progress in the development of femtosecond laser far-field nanostructuring technologies and associated physical mechanisms. First, we will briefly introduce femtosecond laser surface nano-ablation, followed by femtosecond laser induced surface nanoripples and in-bulk nanogratings. Then, we will focus on an innovative technique based on the combination of threshold effect and nanograting/nanoripple formation. Finally, we will discuss the underlying physical mechanism to overcome the diffraction limit by this technique.

2. Nanoablation achieved by threshold effect

The possibility of material nanoprocessing based on femtosecond laser pulse ablation was first demonstrated in 1994.60 By taking advantage of the well-defined ablation threshold as well as the suppressed thermal diffusion, one can beat the diffraction limit by choosing the peak laser fluence slightly above the threshold value. As shown in Fig. 1, the peak intensity exceeds the optical breakdown threshold only in the central area of the focus spot, thus allowing formation of a nanometer-scale hole smaller than focus spot.77 In femtosecond laser ablation, photoionization (including both multiphoton and tunnel ionization), and avalanche ionization are major competing mechanisms for free electron generation.87 It was commonly believed that for nanostructuring of transparent materials multiphoton ionization plays a dominant role in the generation of seed electrons for the avalanche ionization and is responsible for the material-dependent nature of nanostructuring with femtosecond laser.90 Under these circumstances the photoionization rate shows an intensity dependence proportional to $I^2$, where $k$ representing the number of photons required to cross the band gap. However, due to the high nonlinearity of photoionization, the structuring process will become extremely sensitive to the fluctuation of laser intensity, especially when the laser intensity is near the threshold intensity.11 Thus, a compromise has to be made between improving the resolution and maintaining the stability of the fabrication process.

3. Self-organized periodical nanostructures

In the case of multi-pulse irradiation, self-organized periodic nanostructures could be induced both on the surface of materials and in bulk transparent materials. Since the first obser-
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Variation of laser-induced periodic structure on the surface of semiconductors was reported by Birnbaum in 1965; this phenomenon (often referred to as surface ripples) has been observed extensively on various materials (including metals, dielectrics, and polymers) with multifarious irradiation conditions. For the ripples created by nanosecond or longer laser pulses, the ripple period is close to the wavelength of light and perpendicular to the laser polarization, which are generally understood to be formed by the interference of the incident laser light with the scattered light from surface roughness.

However, for the case of femtosecond laser pulses, ripple structures formed at laser fluences near single pulse damage threshold have a period significantly smaller than the laser wavelength (typically 1/10-1/5 of the laser wavelength). Uniquely for the ultrashort laser pulses, self-organized periodical nanostructures can also be formed in the bulk transparent materials (often referred to as nanogratings).

Comprehensive reviews on femtosecond laser induced surface nanoripples and bulk nanogratings can be found elsewhere.

4. A single nanoplane by combination technique

Generally, nanogratings formed in fused silica glass are composed of alternative thin layers with different refractive indexes perpendicular to the laser polarization. Recently, nanogratings were also found in porous glass whereas the gratings are composed of an array of hollow nanoplanes. The porous glass was prepared from phase-separated alkali-boro-silicate glass by removing the borate phase in the hot acid solution. The pores with a mean size of ~10 nm are homogeneously distributed in the glass and occupy 36% in volume of the glass. In particular, the number of the hollow nanoplanes in the grating decreases with laser pulse energy, and a single isolated nanoplane could be induced when the laser pulse energy is close to the damage threshold, as shown in Fig. 2 (a)-(c).

Figures 2 (d)-(f) illustrate the concept to achieve a single nanoplane embedded in a dielectric material by combining the threshold effect and the formation of periodic nanograting. As shown in Fig. 2 (f), when the femtosecond laser intensity is intentionally reduced to a level at which only the intensity in the blue region is higher than the damage threshold, one will be able to select only one nanoplane in the central area of the focal volume. Note that the single nanoplane (green) is much narrower than the above-threshold-intensity region (blue). So there exists a window (a range of laser intensity) for inducing a single nanoplane, which is between the threshold laser intensity of emergence of a single nanoplane and the minimum laser fluence for simultaneously inducing two nanoplanes in porous glass. Therefore, the formation of a single nanoplane is much less sensitive to the fluctuation of the laser intensity by combining the threshold effect and the formation of a periodic nanograting, promising to be a far-field nanostructuring technique with small linewidths and robustness against fluctuations.

The window for fabrication of a single nanoplane can be expanded by optimizing the laser pulse duration. Figure 3 presents the dependence of the threshold power for formation of a single nanoplane and double nanoplanes on the duration.
of laser pulses. The range of laser intensity for producing only a single nanoplane in nanograting formation can be broadened by elongation of the laser pulse duration. However, when the pulse durations are longer than ~300 fs, the roughness of sidewalls in the nanoplanes becomes high probably due to the heat effect which affects the morphology of the formed nanograting. When the femtosecond laser pulses of a duration of ~200 fs are chosen, a sufficiently broad range of laser intensity (~44% of the structuring threshold) for creating a single nanoplane can be achieved, while smooth sidewalls required by nanofluidics applications can still be maintained.

The unique 3D capability of femtosecond laser direct writing allows fabrication of hollow nanoplanes at arbitrary depths inside the glass substrate with a high axial resolution. Moreover, the single isolated nanoplanes can be connected into a continuous structure for construction of 3D nanochannels in glass. In combination with 3D microfluidics previously demonstrated in porous glass, integrated micro-nanofluidic systems with complex 3D geometries and configurations in glass can be achieved in a single continuous step.

Fabrication of nanofluidic channel is achieved by scanning the laser focal spot from a prefabricated microchannel, through which the debris can be driven out from the nanochannel by continuous bubble generation. Figure 4 (a) schematically illustrates an integrated micro-nanofluidic device which contains an array of two-layer nanochannels connected to two microfluidic channels. After direct writing, a postannealing process was performed to collapse all the nanopores in porous glass, integrated micro-nanofluidic devices previously demonstrated in porous glass,26-27 consisting of two microfluidic channels connected by two microfluidic channels. After direct writing, a postannealing process was performed to collapse all the nanopores in porous glass, while the fabricated nanochannels could survive due to their large size. Figures 4 (b)-(d) present the top and cross section views of the 3D nanochannel arrays embedded in consolidated glass. The size of each nanochannel was reduced by ~14% isotropically in all three dimensions after postannealing, resulting in a total channel length of ~40 μm, a width in the range of 30~50 nm, and a height in the range of 1~1.5 μm. To demonstrate the applicability of the fabricated nanochannels, DNA transport in nanochannel arrays was observed. Figure 4 (e) and 4 (f) show that the fluorescently stained λ-DNA molecules can be effectively stretched in the nanochannels with widths of 50 nm and 200 nm, respectively. As shown in these images, the continuous flow and uniform stretching of the DNA molecules in the nanochannel arrays also verify the continuity of the nanochannels and the repeatability of the direct writing process.

This concept mentioned above has also been used for surface nanostructuring. By combining the threshold effect and the surface nanoripple formation, a single isolated nanogroove by laser ablation was demonstrated.28 Figure 5 shows a sub-100-nm-wide groove is achieved on the surface of sapphire by reducing overlap of pulses or increasing the scanning speed. The feature width of nanogroove is only one tenth of the diffraction limit at the employed focusing, and also there is a large processing window for formation of a single nanogroove for the same reason as mentioned above. It is noteworthy that in 2008, Taylor et al. reported fabrication of a single nanoslot with width of ~20 nm on the surface of fused silica by simultaneously operating near the threshold pulse energy for nanograting formation and controlling the focus depth inside the sample so that only the top portion of the focal volume intersects the surface.29 By tilting the sample by 0.2° with respect to the writing direction, one, two, three, or more nanoplanes were made to intercept the sample surface at different locations along the writing direction. However, the major nanogratings still existed below the surface as a result of loose focusing by a low N.A. objective. In addition, extra chemical etching was required to expose these nanoslots due to the laser fluence was well below the ablation threshold.

The surface nanostructuring technology was further used for direct writing of periodic gratings and squares where only one groove was carved in each scanning.30 By controlling the laser fluence and the writing speed, nanogratings and nanosquares with period as small as 150 nm was fabricated on the surface of ZnO immersed in water, as shown in Fig. 6. It was found that the nanoripples formed in water are smoother and more uniform than those formed in air, due to that the water

Fig. 4 (a) Schematic diagram of an array of double-layer nanochannels to bridge two microchannels. (b) Top-view optical micrograph of double-layer nanochannels after postannealing. (c) Cross-sectional SEM micrograph of the nanochannels cleaved along the red dashed line in Fig. 4 (b). (d) Close-up SEM micrograph of cross section of a nanochannel. (e)-(f) Fluorescent images showing the stretching of λ-DNA in two arrays of nanochannels with different widths: (e) 50 nm and (f) 200 nm.

Fig. 5 SEM images of nanoripples fabricated on a sapphire substrate by a scanning at 14 mm/s speed, beam was not blanked during acceleration. (a) 30 μm length line consisting of different number of ripples and extended length of a single ripple. Zoomed-in section (b) show groove width (50–75 nm), (c) transition from 3 to 2 to 1 ripple/groove.

Fig. 6 SEM images of nanosquares with dimensions of (a) 150 × 150 nm², and (b) 150 × 250 nm². Scale bars: 300 nm.
can both carry away the ablated material and mitigate heat effect generated during laser ablation.

5. Formation mechanism of a single nanoplane

Over the recent decade, formation of surface nanoripples and bulk nanogratings by femtosecond laser irradiation has attracted broad attention because of its sub-diffraction-limit nature and its wide potential applications.\(^{19-22}\) However, although great effort has been made on investigating the mechanism behind these phenomena, a clear picture is still lacking until now. The similarities between surface nanoripples and bulk nanogratings provide some important clues for further understanding, including period variation with irradiation conditions,\(^{31-34}\) morphology evolution over the course of multiple laser pulses,\(^{31,32}\) and formation of a single nanoplane as mentioned above. Here, we will discuss the formation mechanism of a single nanoplane responsible for far-field nanostructuring beyond the diffraction limit.

A transient nanoplasmonic model\(^{33,34}\) was proposed to explain the formation of nanoplanes. Initially, a focused ultrashort light pulse ionizes defects and color centers, leading to the formation of inhomogeneous nanoplasma. These hot spots of plasma, after multiple laser pulses, can evolve into spherically shaped nanoplasma. The local field enhancement at the boundary will result in an asymmetric growth of initially spherical nanoplasma in the direction perpendicular to the laser polarization, as shown in Fig. 7.\(^{31}\) However, in this model, the spherical nanoplasmas are randomly distributed which is determined by the spatial distribution of the original defects in glass. Recently, we achieve deterministic nanostructuring by producing a spherical nanoplasma in a porous glass in a controllable manner.\(^{12}\)

Figure 8 presents SEM images of the evolution of formation of a single nanoplane in the porous glass at different writing speeds (i.e., a varying pulse to pulse spatial overlap). At the highest scan velocity, a nanovoid with a diameter of ~300 nm was formed in the central area of focal spot (Fig. 8(a)). With decreasing scanning velocity, the nanovoid becomes smaller, and some defects started to gather along the optical axis of the incident laser in its backward direction. Finally, an isolated nanoplane with a transverse dimension of ~40 nm can be formed with sufficient number of laser pulses, as shown in Fig. 8(e). The nanoplasmonic model can also account for the formation of a single nanogroove on the surface of glass.\(^{31}\) The local field enhancement at the boundary of nanoplasma leading to the formation of a single nanoplane provides a reliable way for far-field nanostructuring by femtosecond laser direct writing.

This direct and high-fidelity observation method can also be used to probe the evolution of nanogratings consisting of an array of nanoplanes, as shown in Fig. 9.\(^{33}\) At the beginning, a well defined laser modified zone can be formed around the focus, in which a large number of randomly distributed defects are formed (Figs. 9(a)-9(d)). It should be stressed that at this stage, there is no any signature of nanograting formation in the laser modified zone. However, in Fig. 9 (d), a boundary between the regions affected and unaffected by the laser irradiation can be clearly seen. The following SEM image in Fig. 9(e) shows that at the interface, some periodically distributed nanovoids have been formed at a scan velocity of 0.5 mm/s. By further reducing the scan velocity to 0.35 mm/s, a few nanovoids develop into nanoplanes whereas the remaining nanovoids are almost unchanged (Fig. 9(f)). At last, at a scan velocity of 0.01 mm/s, all the nanovoids develop into nanoplanes which leads to the formation of a perfect nanograting (Fig. 9(i)). These results establish an important link between the formation of volume nanogratings in glass and surface nanoripples on various substrates observed previously, as the interface created in bulk glass can play the similar role for surface plasma wave excitation.\(^{33,36}\)

6. Conclusions and outlook

We discussed the recent progress in the development of far-field nanostructuring technologies based on femtosecond laser direct writing, including nanoa blation by threshold effect, self-organized periodic nanostructures, and formation of a sin-
ingle nanoplane by combining the threshold effect and nanograting/nanoripple formation. We would like to stress that when exposed to femtosecond pulses, nanoplasmans can be generated in dielectric materials because of the nanostructures formed with previous pulses, and the local field enhancement at the boundary of nanoplasma could lead to the formation of a single nanoplane under the action of many laser shots. This unique mechanism enables reliable nanostructuring not only on the surface but also inside dielectric materials with a reproducible fabrication resolution.

Currently, however, this emerging field is still in its infancy from both fundamental and applied points of view. First of all, the underlying physical mechanisms behind the formation of surface nanoripples and bulk nanogratings are quite complicated and a quantitative understanding is still missing. Secondly, the roughness of nanostructures fabricated by laser direct writing needs to be further improved for nanoptical applications. At last, the cross section of the embedded nanostructures appears highly elliptical and asymmetrical, indicating a relatively low fabrication resolution in the axial resolution. We expect that the future advance in the fundamental understanding of laser-matter interaction will strongly promote the further development and optimization of the technique.

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