Sapphire-Based Fresnel Zone Plate Fabricated by Femtosecond Laser Direct Writing and Wet Etching

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***Abstract*— Here, we report a sapphire-based Fresnel zone plate (FZP), which is fabricated by femtosecond laser direct writing assisted with subsequent wet etching. With this method, we solved the problem of high surface roughness caused by ultrafast femtosecond laser processing. We have obtained ~12-nm average surface roughness smaller than 1/25 of the optical working wavelength. As-formed sapphire FZP also exhibited a well-defined geometry. More importantly, ultraviolet (UV) light focusing and imaging can be easily achieved. Due to the high material hardness, thermal and chemical stabilities of sapphire, such sapphire FZP, may have great potential in UV imaging and focusing under some harsh environments.**

***Index Terms*— Femtosecond laser, sapphire, UV imaging, wet etching.**

I. INTRODUCTION

FOR ITS excellent optical transparency from Mid-IR to UV and high hardness, thermal and chemical stabilities, sapphire is one of the most widely used optical materials. For example, it can be used for never-worn optical window of cameras and watches, and especially harsh-condition-applicable windows of military infrared devices and space optics. However, some advantages and features of sapphire, such as chemical inertness and the largest hardness among oxide, make it difficult to process mechanically or chemically on the other hand. Traditional mechanical polishing process has limitations of high side damage, frequent rupture and tool wearing. As for chemical etching, etching speed is usually slow and changes with crystal lattice orientation, resulting in problems of processing efficiency and controllability. Lithography and nanoimprint could fabricate antireflective sub-wavelength gratings on sapphire for light extraction efficiency enhancement [1]–[4], compared with direct laser writing, they have many drawbacks such as high costs, mask depended and complicated process. Tightly focused femtosecond laser can restrict energy within the minimal scope of both space and time, and therefore have a very small heat effect zone [5]. The highly spatially localized irradiation of femtosecond pulses at the dielectric breakdown conditions creates the amorphous which can be removed in aqueous solution of hydrofluoric acid [6]–[10]. Femtosecond laser ablation of sapphire is emerging as an alternative powerful method for sapphire micro/nano-fabrication. Recently, femtosecond laser processing of sapphire have been reported for various applications such as micro-channel construction for microfluidics [8], [9], crystalline state analysis and polarization response [10]–[13], generation of surface nanostructures and micro-ripples [14]–[16].

However, sapphire is not exploited and utilized for fabricating optical micro-devices by femtosecond laser as widely as other optical material like photoresists, biopolymers, glass and quartz [17]–[25]. That is mainly because femtosecond laser ablation of sapphire is a multi-photon-absorption-induced coulomb micro-explosion process which has a thorny problem of material fracture and the surface roughness cannot satisfy the requirements of optical applications [10]. Here, we adopt near-threshold processing to solve the material fracture problem and use wet etching method to reduce the surface roughness of laser processed areas.

To our knowledge, we are presenting in this letter the first report of femtosecond laser fabrication of micro-optical devices on the surface of sapphire. Femtosecond laser direct writing is a facile, rapid and maskless approach that can realize arbitrary, designable and complicated architectures with a nanometric resolution, which conventional fabrication methods fail to provide [26]–[28]. So we can control the thickness of geometrical profile of fabricated FZP on the surface of sapphire. Furthermore, after wet etching, the surface roughness of as formed FZP decreased conspicuous compared with FZP without etching. The as-formed FZP exhibited not only excellent surface quality but also well-defined geometry. At last, we obtained unique UV imaging and focusing properties.

II. EXPERIMENTS

Samples of a c-plane sapphire (HEFEI KEJING MATERIALS TECHNOLOGY CO., LTD.) for 3D laser processing were polished to 430-um thickness and scanned by tightly focused femtosecond laser pulses through a high numerical aperture (NA = 0.85, 80×) objective lens. Laser source (Spectra-Physics Solstice) was delivering 120-fs pulses of

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800-nm wavelength at repetition rate of 2.5 kHz. We use a BBO crystal to get 400-nm laser light for fabrication, because shorter laser wavelength helps to have a higher machining precision. Pulse energy was measured in front of the objective. To achieve 3D microstructures, a two-galvano-mirror set was used to control the sample's horizontal scanning. Simultaneously, the beam's vertical movements were performed by a piezo stage with 1-nm precision (PI P-622 ZCD). The complicated 3D geometry of microstructures was first designed in C# and then converted to computer processing data for 3D scanning. After femtosecond laser fabrication and wet etching, the as-formed micro-FZPs could be obtained on the surface of sapphire. The scanning electron microscopy (SEM) characterization was carried out using a field emission scanning electron microscope (JSM-7500F; JEOL, JEOL Ltd., Tokyo, Japan.), and the samples were sputter-coated with Au film with a thickness of 10 nm (at a current of 20 mA for 60 s) using an auto fine coater (JFC-1600; JEOL). Here, the optical performance of the FZP in sapphire were evaluated by an ultraviolet microscope imaging system. The UV imaging system's configuration is similar to the optical microscope, but all components in our system are working in ultraviolet band. For example, illumination source uses a deuterium lamp (luminescent spectrum 190nm∼400nm), all of the lens are made of quartz material.

III. RESULTS AND DISCUSSION

The processing parameters have to be carefully optimized because the excellent geometry quality and surface quality are the prerequisites for the optical properties of FZP on the surface of sapphire. In fact, numerous FsLDW parameters, including laser power density, scanning step, and exposure time on a single point, play important roles in determining the quality of the three dimensional (3D) geometry and the quality of the micro structure surface, and, furthermore, the final properties of the FZP in sapphire. First is the scanning line topography with power intensity. The exposure time on a single point was fixed at 1000 μs and the scanning step is 100 nm. When the laser power is 60 μW, phenomenon of laser induced periodic structures emerged, which is disadvantageous for laser fabrication. When the power decreased to 50 μW, one line left but still with some signs of surface fracture. And only when the power was 40 μW, close to the threshold of 38 μW, one line of width ∼100nm was fabricated, showed in Fig. 1(a3). Meanwhile, square was fabricated by line scanning with powers in Fig. 1(a1)∼(a3). Surface roughness was measured respectively, showed in Fig. 1(b1)∼(b3). It decreased with power, ranging from 96.4nm to 69.0nm. Second is the etching method. We found the line surface becomes smooth after etching 6min in a mixture of sulfuric acid and phosphoric acid (3:1) at 300 centigrade, shown in Fig. 1(a4). Especially, the surface roughness got a remarkable change from 69.0nm to 11.9nm after processed with the same etching method, shown in Fig. 1(b4). Actually, we obtained low surface roughness through near threshold processing method and wet etching method. For optical imaging in ultraviolet band (accurate 300nm), surface roughness smaller than 1/25 of optical working wavelength was obtained which paved the way for the next optical applications.

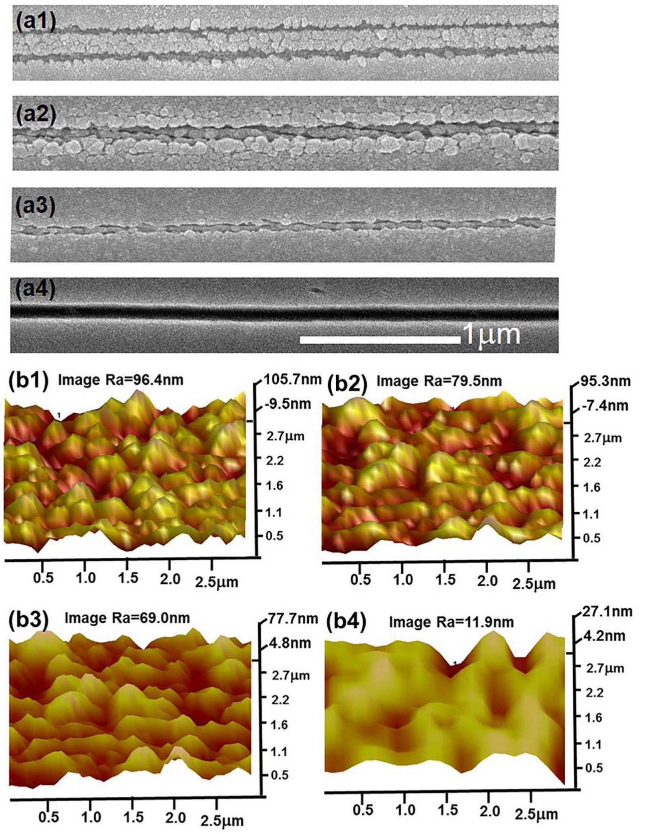

Fig. 1. (a1)-(a3) SEM images showing laser scanning line's topography influenced by average laser power (measured before the objective, 60 μW (a1), 50 μW (a2) and 40 μW (a3) respectively. (a4) SEM images showing laser scanning line's topography after wet etching. (b1)-(b3) AFM images showing laser scanning square area's (3μm × 3μm) surface roughness influenced by average laser power (measured before the objective, 60 μW(b1), 50 μW(b2) and 40 μW(b3) respectively. (b4) AFM images showing laser scanning square area's (3 μm × 3 μm) surface roughness after wet etching. Ra: Roughness average.

The FZP on the surface of sapphire were fabricated by FsLDW and subsequent wet etching use our optimized best laser processing parameters and corrosion conditions. Shown in Fig. 2(a) and Fig. 2(b) are the top view and locally magnified scanning electron microscopic (SEM) images of FZP on the surface of sapphire fabricated by FsLDW (40μW, 2500Hz) without etching. The FZP are composed of five odd and five even zones, and the outer radius r_m of the mth zone (counting from the inside) of the FZP can be determined by the equation

$$r_m^2 + f^2 = (f + m\lambda/N) \tag{1}$$

Where N is the level of FZP, λ is the wavelength of light in vacuum and f is the designed focal length. Here, $N = 2^L$, where L is the number of layers of the FZP. In this work, $L = 1$ and $N = 2$, and the inside radius of FZP was designed at 10μm. Fig. 2(c) and Fig. 2(d) are the top and locally magnified SEM view of FZP on the surface of sapphire with wet etching 6min in a mixture of sulfuric acid and phosphoric acid (volume ratio 3:1) at 300 centigrade corresponding to

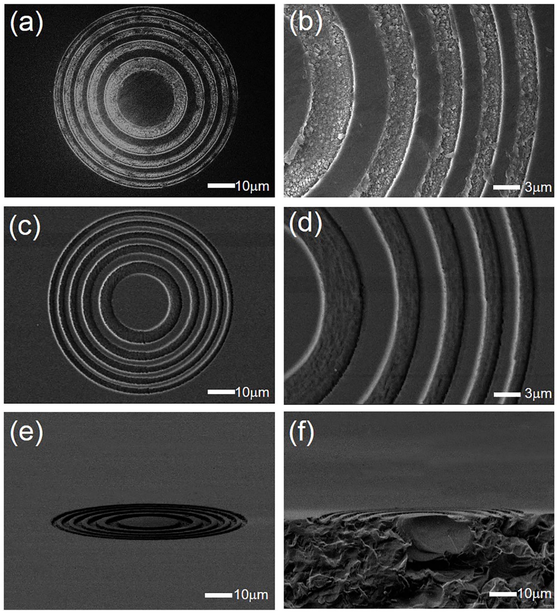

Fig. 2. (a) Top view SEM photograph of FZP without wet etching. (b) Locally magnified SEM view of FZP without wet etching. (c), (d) Top view SEM photograph (c) and locally magnified SEM view (d) of FZP with wet etching 6min in a mixture of sulfuric acid and phosphoric acid (volume ratio 3:1) at 300 centigrade. (e) Side view SEM photograph of FZP with wet etching. (f) Cross-sectional SEM image of the FZP.

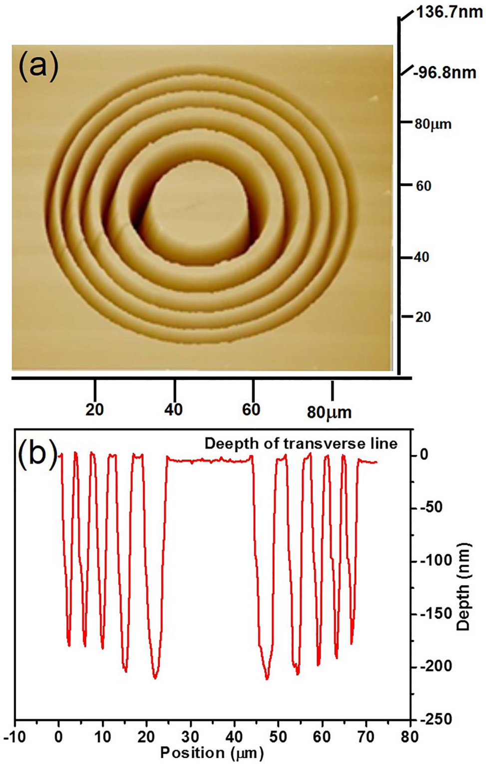

Fig. 3. (a) AFM characterization exhibiting 3D morphology of FZP. (b) The cross section at the central line of the FZP by AFM.

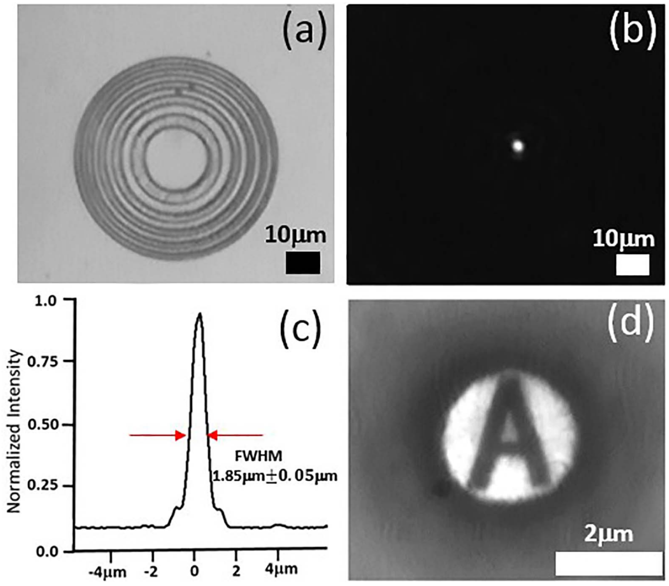

Fig. 4. (a) The UV optical photographs of FZP. (b) UV focusing characteristics of FZP at $\lambda = 300$nm. (c) Intensity cross-section of the focal spot. (d) UV imaging characteristics of FZP on the surface of sapphire.

Fig. 2(a) and Fig. 2(b) respectively. Obviously, the surface roughness of FZP after wet etching reduce conspicuous compared with FZP without etching. Fig. 2(e) and Fig. 2(f) are the side view and cross-sectional SEM image of the FZP with wet etching. Actually, lots of defects should be located just below the laser ablated and wet-etched surface [29]. High optical performance could be obtained by the method of high temperature (1100 °C) annealing to remove the defects.

The depth of the FZP on the surface of sapphire was approximately 190 nm, which was demonstrated by atomic force microscope (AFM), as shown in Fig. 3. Fig. 3(b) shows the cross section at the central line of the FZP shown in Fig. 3(a) by AFM and shows that the 3D controllability of FsLDW is good. For an n-level FZP, the depth is defined by

$$d = \frac{\lambda}{n(n_{sapphire} - 1)} \tag{2}$$

For two-level FZP, the depth is 185nm ($n_{sapphire} = 1.81$ @300nm) for 300nm UV imaging. The error of the experimental thickness with the theoretical thickness is less than 10 nm. Herein, layer-by-layer scanning method was adopted to control the thickness of the FZP. After the upper layer of FZP on sapphire was processed, debris left which will effect further processing. Debris were cleaned by laser (below damage threshold) for further processing. Wet etching also has a certain influence on depth accuracy. When we carry on the theoretical design we have did some preliminary compensation corresponding to the error that corrosion may cause. The as-formed FZP on the surface of sapphire exhibited not only excellent surface quality but also well-defined geometry. Such well-tailored geometry together with smooth surface morphology can ensure high optical performance.

As showed in Fig. 4(a), the UV optical photographs of FZP were obtained use UV camera, the image is not very clear by reasons of some dust spots on the camera lens. The UV light focusing and imaging performance of FZP in sapphire were showed in Fig. 4(b)-(d). The focal spot was shown in Fig. 4(b), and the measured focal length of the FZP on the surface of sapphire is 340.5μm which is comparable to theoretical focal distance (333.3μm). The measured diffractive efficiency, defined as the ratio of the power collected to the primary focal spot to the total incidence, is 37.5% which is a slightly smaller than theoretical diffraction efficiency (40.5%) for two-level FZP. The wave plate produces a clear, well-defined focal spot of $\mathrm{r} = 1.85\mu\mathrm{m} \pm 0.05\mu\mathrm{m}$ (full-width at half maximum, FWHM; Fig. 4(c)). This focal spot size is comparable to the estimation of a focal spot that can be achieved by an ideal Fresnel zone-plate lens, $\mathrm{r}_{\mathrm{FZP}} = 1.22 \times \Delta r \approx 1.98\ \mu\mathrm{m}$, where $\Delta\mathrm{r}$ is the smallest zone width. The slight difference between the predicted and experimentally achieved focal spot width, diffractive efficiency and focal distance probably due to the limited fabrication precision and wet etching tolerance and measurement error. Fig. 4 (d) showed that FZP's clear UV imaging of capital letter A. In short, the sapphire-based FZP exhibits excellent UV imaging and focusing features.

IV. CONCLUSIONS

In summary, we report in this letter the first FZP on the surface of sapphire fabricated by ultrafast laser writing and subsequent wet etching. We applied near threshold processing method assisted with wet etching method to solve material fracture problem and to reduce surface roughness of laser processing area. Low surface roughness smaller than 1/25 of optical working wavelength was obtained. Moreover, we can control the depth of geometrical profile of fabricated FZP in sapphire, the as-formed FZP also exhibited well-defined geometry. At last, we obtained distinctive and ideal optical properties of fabricated FZP including excellent UV imaging and focusing features. Due to the high hardness, thermal and chemical stabilities of sapphire, the long-term stability of the optical profile and surface morphology of FZP on the surface of sapphire can be ensured. All of these merits give the FZP on the surface of sapphire great potential for practical applications as an outstanding UV micro-optics such as the FZP array on sapphire could be used for high efficiency GaN blue UV LED [30].

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