Fabrication of large-scale ripples on fluorine-doped tin oxide films by femtosecond laser irradiation*

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The large-scale uniform self-organized ripples are fabricated on fluorine-doped tin oxide (FTO) coated glass by femtosecond laser. They can be smoothly linked in a horizontal line with the moving of *XYZ* stage by setting its velocity and the repetition rate of the laser. The ripple-to-ripple linking can also be realized through line-by-line scanning on a vertical level. The mechanism analysis shows that the seeding effect plays a key role in the linking of ripples.

Keywords: femtosecond laser, ripples, FTO film, seeding effect

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1. Introduction

The fluorine-doped tin oxide (FTO) film as one of transparent conducting oxides (TCO) can be applied to a wide range of devices, including front electrode in thin film solar cells, heat-reflectors, gas sensors, touch screen displays, thin film photovoltaics, electrochromic windows, and other electro-optical equipments. Moreover, the thermal and chemical stability of FTO is highly attractive in dye-sensitized solar cells (DSSCs).[1,2] Wang *et al.* have fabricated periodic nanopillars and nanolines on the FTO by using nanoimprint lithography and reactive ion etching with environmentally friendly gases. The patterned FTO exhibits enhanced light trapping, and the dye sensitized solar cells (DSSCs) fabricated on the patterned FTO exhibited improved performance.[2,3] Generally, the traditional methods to fabricate micro/nano structures on TCO are extremely complicated and time-consuming. The laser direct writing technique, an effective, simple, fast, and low-cost method to process micro/nano structures on a TCO film, is in the center of great concern.[4–6] Therefore, many kinds of structures, such as grooves,[4] ripples,[5] nanodots, and nanolines[6] have been fabricated by laser direct writing on the TCO film. The ripples as a popular structure induced by laser on metal, semiconductors and dielectrics[7–11] could be potentially applied to solar cells,[12] optical memory,[8,9] and polarization micro-optics.[13] However, the fabrication of high-quality and large-scale ripples for their application and the corresponding fabrication mechanism are still the challenges ahead. Therefore, more attention has been paid to the fabrication of uniform large-scale ripples.

In this paper, we report on the ripples induced by femtosecond laser on FTO film coated silica glass. The uniform large-scale ripples can be fabricated on FTO film by laser direct writing. The configurations of the ripples are characterized by scanning electron microscope (SEM) and atom force microscope (AFM). The results show that the coarse ripples with a period of ∼700 nm and the fine ripples with a period of ∼350 nm are fabricated on the FTO film simultaneously. The ripples formed by adjacent scanning lines could be smoothly linked together, and the tooth length increases with widened neighboring line intervals.

2. Experimental

An ultrafast pulse is generated by a Ti: sapphire regenerative amplified laser system (Coherent Inc.), the wavelength, pulse width, and repetition rates of the laser are 800 nm, 120 fs, and 1–1000 Hz, respectively. The laser is focused on the sample by a microscope system (Nikon Inc.), passing through an attenuate and a polarimeter, and the laser power is measured by a power meter (EPM2000, Coherent). The sample, fluorine-doped tin oxide (FTO) film coated silica glass, is mounted on a computer-controlled XYZ translation stage (ProScan II, precision: 100 nm). A charge coupled device (CCD) is used to monitor the experiments in real time. The characterization of morphological changes of the samples after laser irradiation is observed by scanning electronic microscope (SEM, S-4700, Hitachi) and atom force microscope (AFM, Nanoscope IIIa, Digital Instrument). In this paper, all the experiments are performed in the air and under normal pressure. The environment temperature and relevant humidity are ∼22 °C and $< 25\%$, respectively.

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3. Results and discussion

Figure 1 shows the SEM images of structures fabricated by a 5× objective lens (NA = 0.15) on FTO film, with an energy fluence of 1.6 J/cm^2 and a repetition rate of 1000 Hz. The velocity of the translate stage is 200 μm/s (Fig. 1(a)), 500 μm/s (Fig. 1(b)), 1000 μm/s (Fig. 1(c)), 2000 μm/s (Fig. 1(d)), and 3000 μm/s (Fig. 1(e)), respectively. The width of ablation line in a vertical direction is about 10 μm. Obviously, the FTO film can be ablated completely when the velocity of translate stage is 200 μm/s (see Fig. 1(a)), whereas with 500 μm/s, the ablation line becomes more uniform (see Fig. 1(b)). When the velocity increases to 1000 μm/s, ripples with a period of ∼700 nm (called coarse ripples) and a direction perpendicular to the laser polarization, can be observed at the edge of the ablation line (Fig. 1(c)). With the velocity increasing to 2000 μm/s and 3000 μm/s, the ripples spread almost all over the ablation region, which becomes more clear and uniform, as shown in Figs. 1(d) and 1(e). For both, the period still keeps ∼700 nm and the tooth length of the ripples is ∼10 μm. In addition, some fine structures (called fine ripples) can be observed at the edge of the coarse ripples, as shown in the local amplified picture of Fig. 1(e), and some parts of the coarse ripples are removed, as demonstrated in both figures. We try to obtain integral ripples by reducing the energy fluence, and find that when the energy fluence reduces to 1.3 J/cm^2, the coarse ripples can be formed uniformly and integrally, the period still keeps unchanged, yet the tooth length (both coarse and fine ripples) is reduced to ∼8 μm. The results show that the uniform and integral coarse ripples can be formed at 3000 μm/s with the radiation of a 5× objective lens (NA = 0.15) and the laser energy fluence of 1.3 J/cm^2.

In order to fabricate large-scale ripples for application to solar cells or other fields, we try to realize ripple-to-ripple linking through line-by-line scanning at intervals of 6 μm, 7 μm, and 8 μm, respectively. For the experiment, a 5× (NA=0.15) objective lens is chosen, the velocity of the translate stage is set at 3000 μm/s, the energy fluence at 1.3 J/cm^2, and the repetition rate of the laser at 1000 Hz. As shown in Figs. 2(a) and 2(b), longer smooth coarse ripples through ripple-to-ripple linking are formed at ∼12 μm and ∼13 μm in length with a line interval of 6 μm and 7 μm, respectively, with their periods being ∼700 nm. Fine ripples of ∼350 nm can also be observed at the edge. In order to reveal clearer distribution of the ripples spatial frequencies in the Fourier space, the corresponding two-dimensional Fourier transform (2D-FT) of Figs. 2(a) and 2(b) are respectively presented in Figs. 2(d) and 2(e), dominated by symmetric sickles in horizontal direction. For the two pairs of symmetric sickles in Fig. 2(d), their spatial frequencies are ∼1.4 μm^{-1} and ∼29 μm^{-1}, corresponding respectively to a spatial period of ∼700 nm and ∼350 nm which coincides to the period of coarse ripples and fine ones. It is equally true with Fig. 2(e). However, when the line interval increases to 8 μm, ripple-to-ripple links are made only between fine ripples rather than coarse ripples with the tooth length of the ripples (both coarse and fine ripples) increasing to ∼15 μm, as indicated in Fig. 2(c) and the Fourier analysis picture (Fig. 2(f)). However, with the line interval increasing to 10 μm, neither coarse nor fine ripple linking can be observed. That is to say, the ripples formed by two adjacent lines scanning are completely independent at a line interval of 10 μm. The results indicate that the ripple-to-ripple linking of the coarse ripples can be realized, and the tooth length increases at a larger neighboring line interval.

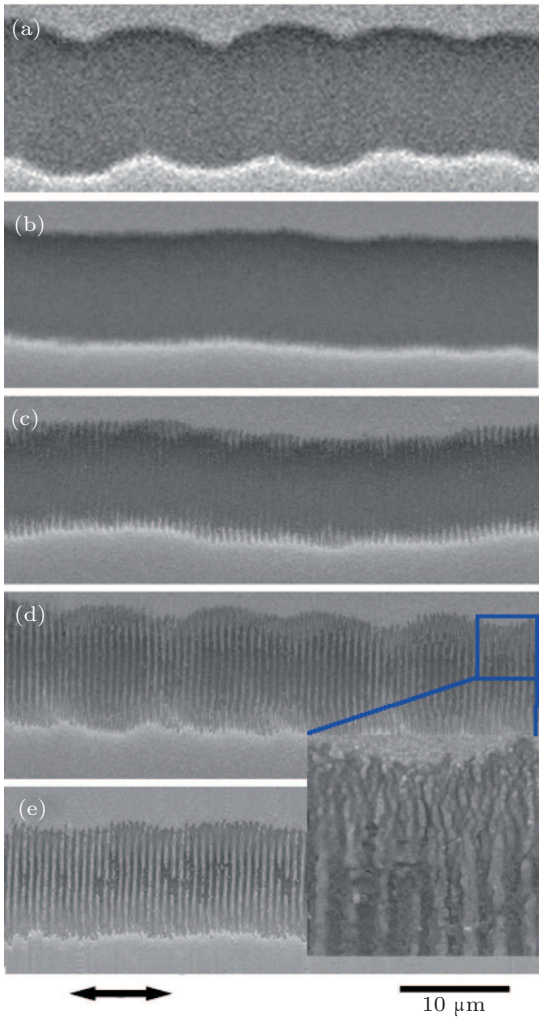


Fig. 1. (color online) Structures irradiated by a 5× objective lens (NA = 0.15) at the energy fluence of 1.6 J/cm^2 with a translate stage velocity of (a) 200 μm/s, (b) 500 μm/s, (c) 1000 μm/s, (d) 2000 μm/s, and (e) 3000 μm/s. Arrow denotes the polarization direction of laser.

Based on above experiments, 5 mm×5 mm coarse ripples were fabricated on FTO film coated glass with a neighboring line interval of 7 μm. The local SEM picture of the as-formed large-scale ripples illustrated in Fig. 3(a) shows coarse ripples are formed on the FTO film uniformly and smoothly by ripple-to-ripple linking. Figure 3(b) is the AFM local amplified picture of Fig. 3(a). Figures 3(c) and 3(d) are the three-dimensional image and the cross-section profile of Fig. 3(b), respectively. From the AFM images we can see that the period and the depth of the as-formed ripples are ∼700 nm and

~100 nm, respectively. The result shows that large-scale and uniform self-organized ripples can be formed on FTO film coated glass smoothly and quickly by single beam femtosecond laser irradiation.

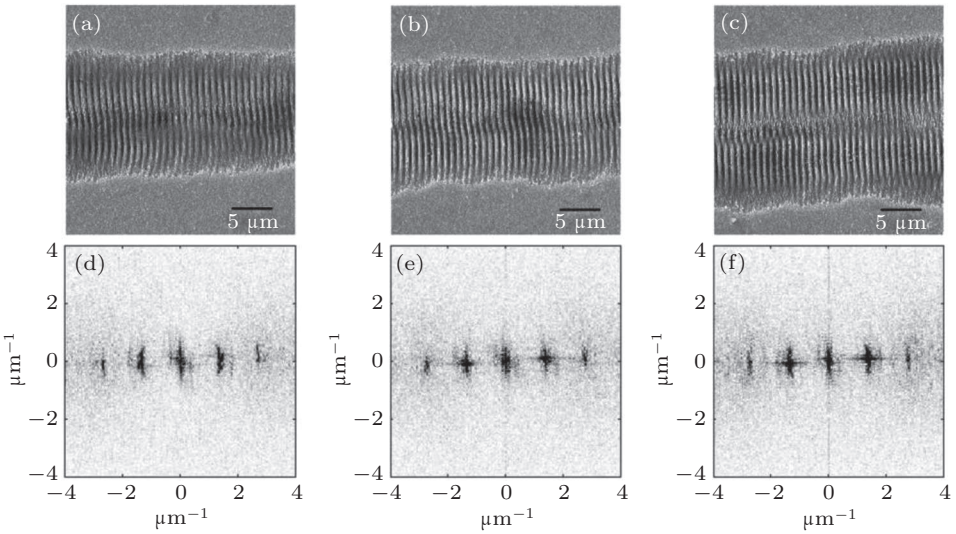


Fig. 2. SEM images and the corresponding 2D-FT images of two linear scanned ripples at a neighboring line interval of (a) 6 μm, (b) 7 μm, and (c) 8 μm.

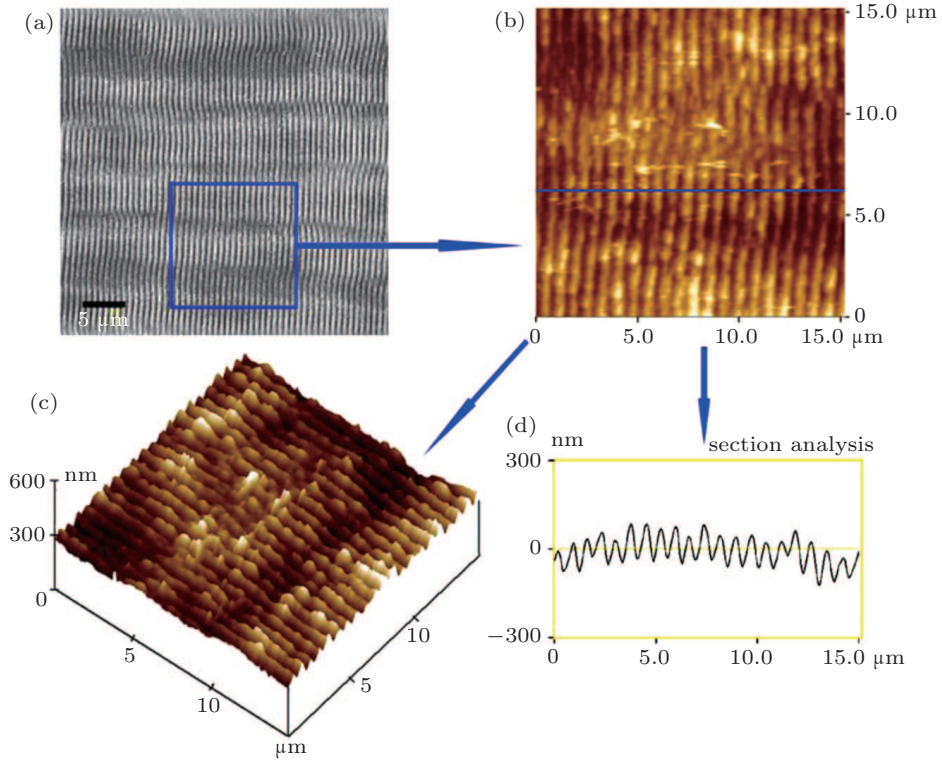


Fig. 3. (color online) (a) Local SEM picture of the as-formed large-scale ripples at a neighboring line interval of 7 μm. (b)–(d) AFM plane-view, three-dimensional, and cross-section images, respectively.

The ripples, as many researchers reported, are usually formed by laser interacting with laser-induced surface plasmas (SPs).[14–16] The period is given by[14]

$$\Lambda = \frac{\lambda}{\lambda/\lambda_{\mathrm{s}} \pm \sin\theta}, \tag{1}$$

where λ and λ_{s} are the wavelength of incident laser and surface plasmas wave respectively, and θ is the incident angle of laser. λ_{s} can be obtained by the dispersion relation on metal/dielectric interface.[14] Therefore, for normal incident ($\theta = 0^{\circ}$) and metal/air interface, the period of the ripples is

$$\Lambda = \lambda_{\mathrm{s}} = \lambda\left(1 + \frac{1}{\varepsilon'}\right), \tag{2}$$

where ε' is the real part of dielectric constant ε for FTO film. Generally, under the irradiation of femtosecond laser, the optical properties of the high-excited surface are determined by abundant hot electrons rather than the intrinsic properties of solid.[14] Thus, the FTO film exhibits metal behavior when exited by femtosecond laser, that is, the dielectric constant fulfills $\varepsilon' < -1$. Therefore, the period of the ripples is smaller than the wavelength of incident laser according to Eq. (2), which is consistent with our previous experimental results.

The evidence has shown that the electron plasma wave can couple with incident light wave only if it propagates in the plane of light polarization.[16] Therefore, the as-formed coarse ripples are perpendicular to the laser polarization. The fine ripples should be formed by the multi-angle diffraction of the multiple incident laser pulses on the intermediate non-sinusoidal surface grating.[17]

As to the linking of ripples with the moving XYZ stage in a horizontal line, we believe that the seeding effect[18] and near field ablation effect[19] play the key roles. The focus spot is divided into two areas (see Fig. 4(a)): Region 1, the higher photon flux area (H) located at the center of the spot, which induces the coarse ripples; and Region 2, the lower photon flux area (L) distributed at the edge of the focus spot, which induces the fine ripples. In our experiments, the laser repetition rate and translate stage velocity are chosen to be 1000 Hz and 3000 μm/s, the moving step length of the stage is ∼100 nm, and the size of the focus spot is ∼10 μm. Obviously, once the coarse ripples and fine ripples are formed in laser irradiated region after several pulses irradiation at one focus spot, the sequent focus spot will overlap with the as-formed ripples, as shown in Figs. 4(b) and 4(c). As previously reported,[20] the ripples in Region B and Region C will be deepened because the laser irradiation on the ripples is a feedback process under the influence of localized static electic fields on the surface (near field ablation effect).[19] The fine ripples in Region D will be melted, forming a thick liquid layer due to the strong thermal effect induced by higher photon flux irradiation, and then the SP-laser interference still forms coarse ripples, that is, the strong thermal effect induces interference rather than near field ablation effect which deepens the grooves.[14] Therefore, the coarse ripples could be growing smoothly in the direction of moving stage. At the edge of focus spot (Region A), the fine ripples, unlike Region D, could not be removed by the lower photon flux irradiation, but as coarse ripples they could also grow smoothly in the direction of moving stage, as shown in Figs. 1(e), and 2(a)–2(c).

As the laser focus spot moves to the next line at an interval of 8 μm, smooth ripple-to-ripple linking between fine ripples can be made (see the sketch map in Figs. 4(d) and 2(c)), that is, the as-formed ripples affect distribution of the surface plasma density wave, so the adjacent-line ripples will be favored only if their orientation reinforces their own growth (seeding effect).[18] When the neighboring line interval reduces to 7 μm and 6 μm, part of the focus spots will overlap with the above line ripples (see Fig. 4(e)). The fine ripples (located at the dashed sash in Fig. 4(d)) will be melted by higher photon flux irradiation, and with SP-laser interference, the coarse ripples are smoothly linked to the above line ripples due to the seeding effect (see Figs. 4(d), 2, and 3). Therefore, uniform large-scale ripples could be fabricated on FTO film coated glass by line-by-line scanning smoothly.

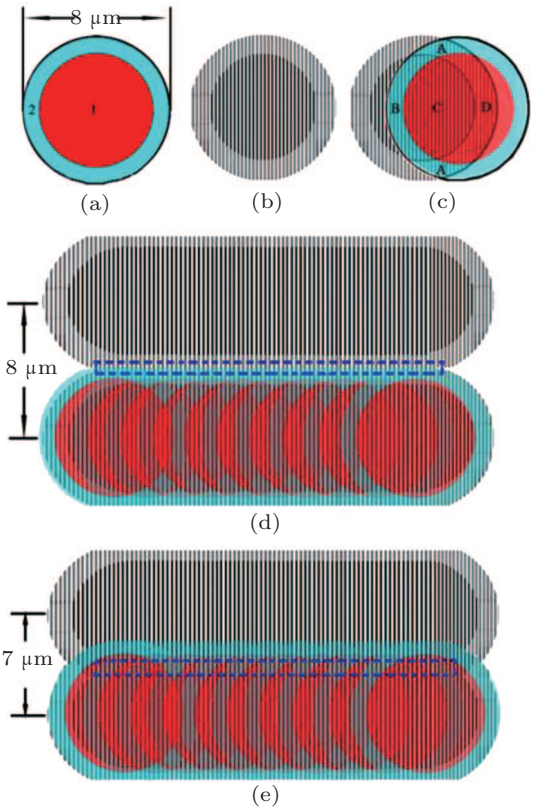


Fig. 4. (color online) Schematic diagram of the linking of coarse ripples and fine ripples with the moving of XYZ stage.

4. Conclusions

In conclusion, we have fabricated uniform large-scale ripples on FTO film coated glass, the coarse ripples with a period of ∼700 nm by the interference of incident laser and surface plasma wave, and fine ripples with a period of ∼350 nm by the multi-angle diffraction of multiple incident laser pulses on the intermediate non-sinusoidal surface gratings. The ripple-to-ripple linking of both coarse ripples and fine ripples are realized by the seeding effect. The findings are expected to be applied to solar cells to improve the light trapping efficiency.

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