TiO₂ micro-devices fabricated by laser direct writing

Yongsheng Wang,¹,²,³ Junjie Miao,¹,³,⁴ Ye Tian,¹,³ Chuanfei Guo,¹,³ Jianming Zhang,¹,³ Tianling Ren,² and Qian Liu¹,*

¹National Center for Nanoscience and Technology, China, No. 11 Beiyitiao, Zhongguancun, Beijing 100190, China.
²Institute of Microelectronics, Tsinghua University, Beijing 100084, China
³Graduate School of the Chinese Academy of Sciences, Beijing 100190, China
⁴State Key Laboratory on Advanced Optical Communication Systems and Networks, Peking University, Beijing 100871, China

*liuq@nanoctr.cn

Abstract: Constructing micro/nanostructures based on TiO₂ has attracted increasing attention due to the excellent properties of TiO₂. In this study, we report a simple method to directly fabricate TiO₂ micro-devices, including Fresnel lens, gear structures and suspended beams only by laser direct writing and selective-etching processing. This route shows great potential in fabricating TiO₂ structures for micro-electro-mechanical systems, diffractive optical elements and bio-applications, owing to its maskless process, low cost, and flexible dry/wet alternative etching treatment.

©2011 Optical Society of America

OCIS codes: (220.4000) Microstructure fabrication; (220.4610) Optical fabrication; (310.6845) Thin film devices and applications; (350.3390) Laser materials processing.

References and links

1. S. Juodkazis, L. Rosa, S. Bauerdick, L. Peto, R. El-Ganainy, and S. John, “Sculpturing of photonic crystals by ion beam lithography: towards complete photonic bandgap at visible wavelengths,” Opt. Express 19(7), 5802–5810 (2011).
2. W. L. Chang, P. H. Tsao, and P. K. Wei, “Sub-100 nm photolithography using TE-polarized waves in transparent nanostructures,” Opt. Lett. 32(1), 71–73 (2007).
3. B. D. Lucas, J. S. Kim, C. Chin, and L. J. Guo, “Nanoimprint lithography Based Approach for Fabrication of Large-Area, Uniformly Oriented Plasmonic Arrays,” Adv. Mater. 20(6), 1129–1134 (2008).
4. A. Kiani, K. Venkatakrisnan, and B. Tan, “Direct patterning of silicon oxide on Si-substrate induced by femtosecond laser,” Opt. Express 18(3), 1872–1878 (2010).
5. X. Z. Dong, Z. S. Zhao, and X. M. Duan, “Micronanofabrication of assembled three-dimensional microstructures by designable multiple beams multiphoton processing,” Appl. Phys. Lett. 91(12), 124103 (2007).
6. J. Fischer, G. von Freymann, and M. Wegener, “The materials challenge in diffraction-unlimited direct-laser-writing optical lithography,” Adv. Mater. (Deerfield Beach Fla.) 22(32), 3578–3582 (2010).
7. C. M. Chang, C. H. Chu, M. L. Tseng, H. P. Chiang, M. Mansuripur, and D. P. Tsai, “Local electrical characterization of laser-recorded phase-change marks on amorphous Ge:Sb:Te thin films,” Opt. Express 19(10), 9492–9504 (2011).
8. Y. Dai, B. Zhu, J. Qiu, H. Ma, B. Lu, S. Cao, and B. Yu, “Direct writing three-dimensional Ba₂Ti₅O₁₂ crystalline, pattern in glass with ultrashort pulse laser,” Appl. Phys. Lett. 90(18), 181109 (2007).
9. Y. S. Wang, C. F. Guo, S. H. Cao, J. J. Miao, T. L. Ren, and Q. Liu, “Controllable fabrication of super-resolution nanocrater arrays by laser direct writing,” J. Nanosci. Nanotechnol. 10(11), 7134–7137 (2010).
10. C. F. Guo, Z. Zhang, S. H. Cao, and Q. Liu, “Laser direct writing of nanoreliefs in Sn nanofilms,” Opt. Lett. 34(18), 2820–2822 (2009).
11. C. F. Guo, S. Cao, P. Jiang, Y. Fang, J. Zhang, Y. Fan, Y. Wang, X. X. Zhao, and Q. Liu, “Grayscale photomask fabricated by laser direct writing in metallic nano-films,” Opt. Express 17(22), 19981–19987 (2009).
12. F. Sauvage, F. Di Fonzo, A. Li Bassi, C. S. Casari, V. Russo, G. Divitini, C. Ducati, C. E. Bottani, P. Comte, and M. Graetzel, “Hierarchical TiO₂ photoanode for dye-sensitized solar cells,” Nano Lett. 10(7), 2562–2567 (2010).
13. Q. Zheng, B. Zhou, J. Bai, L. Li, Z. Jin, J. Zhang, J. Li, Y. Liu, W. Cai, and X. Zhu, “Self-Organized TiO₂ Nanotube Array Sensor for the Determination of Chemical Oxygen Demand,” Adv. Mater. (Deerfield Beach Fla.) 20(5), 1044–1049 (2008).
14. N. Wu, J. Wang, N. Tafen, H. Wang, J. G. Zheng, J. P. Lewis, X. Liu, S. S. Leonard, and A. Manivannan, “Shape-enhanced photocatalytic activity of single-crystalline anatase TiO₂(101) nanobelts,” J. Am. Chem. Soc. 132(19), 6679–6685 (2010).

#150960 - $15.00 USD
Received 12 Jul 2011; revised 10 Aug 2011; accepted 11 Aug 2011; published 18 Aug 2011
(C) 2011 OSA 29 August 2011 / Vol. 19, No. 18 / OPTICS EXPRESS 17390
1. Introduction

Micro-devices such as diffractive optical elements (DOEs) and micro-electro-mechanical systems (MEMS) have become increasingly attractive in recent years due to their broad applications in photonics, electronics, information technology, bio-sensing etc. Great efforts have been made to fabricate micro-devices with both high performance and low cost. In the past decades, several fabricating techniques have been developed, for example, conventional photolithography, e-beam or ion-beam lithography, nanoimprint, and laser direct writing (LDW). Among the above methods, e-beam and/or ion-beam lithography have the best fabrication precision [1], but their low productivity and high cost have limited their practical applications. Photolithography and nanoimprint techniques are mostly used because of their shorter productive period and large scale manufacturability [2,3]. However, high-cost masks and organic contamination in the two methods are adverse to their applications to some extent. In contrast, as a promising candidate featured with simple process, maskless fabrication and low cost, the LDW method has been used to fabricate various micro/nanostructures in diverse materials [4–8]. Via laser direct writing in thin metal films, we have also demonstrated the fabrications of super-resolution nano-craters [9], novel nanorelief [10], and metal-transparent-metallic-oxides (MTMO) grayscale photomask [11]. It is prospective that LDW method can achieve more interesting results in the fabrication of micro-devices.

As one of the most useful materials for applications in dye-sensitized solar cells [12], electrochemical sensors [13], photocatalysts [14], and biomedical implants [15], TiO$_2$ has attracted more and more attentions. In the fields of DOEs and MEMS, TiO$_2$ has also been employed due to its high refractive index, self-cleaning property, high dielectric constant, biocompatibility and chemical stability. For example, patterned TiO$_2$ structures have been used as etching masks in the fabricating processes of indium doped tin oxides (ITO) and silicon MEMS devices [16], blazed gratings have been also produced in SiO$_2$/TiO$_2$ sol-gel material for realizing multi-level DOEs fabrications [17], and TiO$_2$ film coated on the surface of solid immersion lens has been used to effectively remove organic contaminants based on the self-cleaning effect [18].

In this work, we propose a simple fabricating method of TiO$_2$ micro-devices with only two steps: laser direct writing and selective-etching processing. As a great advantage of this method, both dry and wet etching processes could be carried through, and the two kinds of etching effects were exhibited by constructing micro-devices, for example, a Fresnel lens by dry etching, and a gear and a suspended beam based on wet etching. The results show that our method has great potential in direct building TiO$_2$-based micro-devices.
2. Experiments

Ti films (thickness: 50 nm) were deposited on glass substrates (thickness: 0.17 mm) by electron beam evaporation (BOC Edward FL400). Before the deposition, the substrates were first ultrasonically cleaned for 10 min in turn by immersing in acetone, ethanol and de-ionized (DI) H₂O, and then blown by dry N₂ and baked at 120 °C for 1 hour in a vacuum oven. Then the Ti films were deposited under a work pressure of 1.9 × 10⁻⁴ Pa, with a current of 30 mA, and a depositing speed of 0.2 Å/s, without heating the substrate.

A home-built laser direct writer system adopted a frequency-doubled Nd:YAG 532 nm laser (Spectra Physics, Millenia Pro 2i) was applied to write the Ti films by raster-scan with a typical scan speed of 50 µm·s⁻¹ and a repetition rate of 250 Hz. The sample was placed on an X-Y-Z sample stage, and the focus point (about 350 nm diameter) of object lens in the system could be automatically focused onto the surface of the sample in writing process. The writing path of the laser beam was controlled by a computer, while the writing power and the pulse width could be tuned by an acousto-optic modulator. In the laser writing process, the writing power was changed from 0 mW to 15 mW with a pulse width of 1 ms, corresponding to the laser energy density ranging from 0 to 150 J·mm⁻².

The dry etching process was carried out in a RIE etch lab (SENTECH Etchlab 200) under conditions of 50 Pa pressure, 150 W RF power, 40 sccm CF₄ and 5 sccm O₂ flows. The wet etching process was carried out in a dilute HF solution (the volume concentration: 4.5%) at room temperature, and the sample was promptly transferred and washed into DI H₂O for 5 min, and then blown by high purity N₂.

The morphology of the patterned samples was characterized by optical microscopy (OM, Olympus BX-51 microscope), atomic force microscopy (AFM, Veeco D-3100) and a Hitachi S-4800 field emission scanning electron microscopy (FESEM) at an accelerating voltage of 2 kV. Micro-Raman with a wave number range of 200-1000 cm⁻¹ (Renishaw Micro-Raman Spectroscopy System) was used to analyze the composition of the structures written by laser.

3. Results and discussions

3.1 The morphologies of the laser direct writing patterns

![Fig. 1.](image)

Fig. 1. (a) and (b) OM and SEM images of grating lines fabricated at 3-13 mW with a step of 1 mW, for 1 ms pulse width. The inset in (b) shows that the surface of the grating line (4 mW) is very smooth. (c) AFM image of grating lines fabricated at 3-9 mW with a step of 1 mW, for 1 ms pulse width. (d) The dependence of both line width and line height on laser writing power.

Arbitrary-shaped patterns can be fabricated in Ti film on glass substrate in principle. Here, a grating line array was written on the 50 nm thick Ti films using a laser power from 1 mW to 15 mW (pulse width: 1 ms). No obvious change appears when laser power is lower than 3
mW, while the power increasing from 3 mW to 13 mW, the grating lines are found become transparent gradually as shown in the OM image (Fig. 1(a)). Figures 1(b) and 1(c) are the SEM and AFM images of the patterned structures, showing the unique surface morphologies. From the above images, we speculate that the 50 nm thick Ti film could not be oxidized when the power is lower than 3 mW, which is near the threshold for oxidization under our experimental conditions. In the power range between 3 mW and 13 mW, the dependences of both line width and line height on laser power were investigated, as shown in Fig. 1(d). Grating lines with 400 nm width and 4 nm height were fabricated at the threshold power of 3 mW. An approximately linear relationship between the line width and laser power was found, which is very useful for more exact control of grating line width. In contrast, a saltation of line height happens between 3 mW and 4 mW, probably resulting from the phase change at a laser power rightly around the threshold.

3.2 The oxidation of titanium film investigated by Raman spectra

In order to further understand the mechanism of transparency transformation in Ti film under laser irradiating, Micro-Raman spectra was used to investigate the constituent variation depending on laser power. As shown in Fig. 2, there are two relatively strong bands at 442 and 612 cm$^{-1}$ associated with the rutile TiO$_2$ structure [19]. These peaks emerge when laser power is larger than 3 mW. However, no obvious bands appear when the writing laser power is smaller than 3 mW, and the result is similar to those obtained from the as-deposited Ti films (0 mW). The Raman spectra demonstrates that over the threshold of laser power (~3 mW), oxidation is the main origin of the transparency transformation in Ti film, and this is in accordance with the morphologies shown in Fig. 1.

3.3 Micro-devices fabrication based on our method

Benefiting from the advantages of LDW technique, arbitrary patterns can be easily fabricated in Ti film. In addition, due to the special properties of the rutile TiO$_2$ obtained, both dry and wet etching processes can be used to construct TiO$_2$-based micro-devices.

3.3.1 Micro-devices fabricated by dry etching

In general, fluorine- and/or chlorine-based gas can be employed to etch Ti-based structures [20,21]. Here the dry etching treatment of the patterned samples was achieved by using CF$_4$/O$_2$. The three etching rates: $V_{\text{Ti}} = 36$ nm/min, $V_{\text{glass}} = 9.5$ nm/min, and $V_{\text{TiO}_2} = 1.3$ nm/min can be easily obtained in conditions of 50 Pa pressure, 150 W RF power, 40 sccm CF$_4$ and 5 sccm O$_2$ flows, indicating these TiO$_2$ patterns are good masks due to the high selectivity ratios (Ti:TiO$_2$ = 28:1, and glass:TiO$_2$ = 7:1).
Fig. 3. (a) AFM images of grating lines and (c) concentric rings fabricated at 4 mW with 1 ms pulse width by LDW. (b) and (d) The corresponding AFM images after etching for 4 minutes are shown. The insets of panels (a) and (b) show that the line width and height before and after RIE, respectively.

Utilizing the above dry etching properties, grating lines and concentric rings were fabricated at 4 mW laser power with 1 ms pulse width. The dimensional changes of the grating lines are shown in the insets of Figs. 3(a) and 3(b). Figures 3(a) and 3(c) show the AFM images of samples before RIE treated. After RIE treated for 4 min, the 50 nm thick Ti films were rightly etched out completely, without etching the glass substrate. That means the embossing structures (Fig. 3(b) and 3(d)) obtained are composed of rutile TiO$_2$, which is quite important for further constructing TiO$_2$ micro-devices. The line width was reduced from 503 nm to 498 nm after the dry etching treatment, indicating a low relative error of around 1% .

Fig. 4. Optical microscopy images of Fresnel lens fabricated by LDW at 4 mW with 1 ms pulse width and RIE treated for 4 minutes: (a) morphology image; (b) focusing image; (c) a letter “A” imaged through the lens.

For investigating the practical applications in DOEs of this method, as an example, a Fresnel lens mask was fabricated first in 50 nm thick Ti films by LDW at 4 mW with 1 ms pulse width. Then the sample was etched for 4 minutes by RIE, the Fresnel lens composed of 67 nm thick TiO$_2$ was obtained on glass substrate, as shown in Fig. 4(a). The focusing effect of the lens is shown in Fig. 4(b), indicating good performance of the Fresnel lens. In addition, a letter “A” was successfully imaged through this Fresnel lens (Fig. 4(c)), which further demonstrates the method can make useful optical elements of TiO$_2$.

3.3.2 Micro-devices fabricated by wet etching

Besides the dry etching route, wet etching is also an alternative approach to fabricate micro-devices. Because rutile TiO$_2$ is the most stable phase in the three kinds of TiO$_2$ phases, the reaction between TiO$_2$ and HF at room temperature is the thermodynamically forbidden ($\Delta G = 267.4$ kJ·mol$^{-1}$) [22], and the selective etching of Ti/TiO$_2$ and TiO$_2$/glass should be feasible. The thickness and the morphologies of TiO$_2$ products obtained do not obviously change when the samples are immersed into the dilute HF solution in our experimental conditions, showing
a good accuracy of the fabrication method. The other two etch rates of Ti film and glass substrate can be easily calculated: \( V_{\text{Ti}} = 3.3 \text{ nm/s} \) and \( V_{\text{glass}} = 3.8 \text{ nm/s} \).

To further demonstrate this method, complex patterns were fabricated in 50 nm thick thin films by LDW at 4 mW with 1 ms pulse width. A wet etching treatment was carried out in the following process. The 50 nm thick Ti film surrounding the TiO\(_2\) patterns was completely etched out in about 15 sec, while a gear composed of 67 nm thick TiO\(_2\) patterns was remained. If further etched, the underlayer glass of Ti films can also be isotropic etched. Finally, a gear structure was successfully obtained by etching for about 5 min in HF, as shown in Fig. 5(a) and 5(b). Utilizing the isotropic etching property of glass, completely suspended TiO\(_2\) beam (thickness of 67 nm, length of 8 \( \mu \text{m} \), and width of 1.6 \( \mu \text{m} \)) was also easily fabricated as shown in Fig. 5(c) which may have potential applications in mechanical sensors and micromechanics testing. Because our method is a maskless process, these MEMS structures can be fabricated much simpler than many other methods such as photolithography.

It should be noted that only 3D thin-plane structures can be fabricated by our method although arbitrary plane shapes can be obtained easily. This is because TiO\(_2\) patterns induced by the laser beam are belt-shaped structures in the Ti films. In addition, the thickness of TiO\(_2\) structure can be adjusted by changing the thickness of Ti films and etching conditions to meet different requirements of applications.

4. Conclusion

In conclusion, we proposed a simple two-step method for direct fabricating TiO\(_2\) micro-devices only by LDW and etching treatments. Grating line array was fabricated in titanium films by using gradually-changed laser power. The dependences of line width and line height on laser power have been clarified. Micro-Raman spectra demonstrated that the oxide tracks are composed of the rutile TiO\(_2\), indicating the critical oxidation threshold of a laser power of 3 mW. Some devices such as Fresnel lens, gear structure and suspended beam have also been successfully fabricated by the dry and/or wet etching processing, respectively, exhibiting the huge potential in DOE and MEMS fabrications, especially in specific fields benefiting from the unique optical and electrical properties of TiO\(_2\).

Acknowledgment

This work is supported by NSFC (10974037), NBRPC (2010CB934102), International S&T Cooperation project (2010DFA51970), and Eu-FP7-project (No.247644).