

Femtosecond laser directly writing microholes in $\text{Bi}(\text{Nb}_{0.998}\text{V}_{0.002})\text{O}_4$ ceramic and multi-photon induced large scale nanometer wires array

Jianzhang Shi · Hong Wang · Dongshi Zhang ·
Feng Chen · Xi Yao

Received: 5 October 2009 / Accepted: 26 January 2010 / Published online: 6 February 2010
© Springer Science+Business Media, LLC 2010

Abstract Femtosecond laser pulse directly writing microholes by the matrix microholes ablation technique (MMAT) in a high permittivity microwave ceramic $\text{Bi}(\text{Nb}_{0.998}\text{V}_{0.002})\text{O}_4$ were systematically investigated. The feasible micro-fabricating parameters-output power intensity, writing intervals ΔR and step depth ΔZ , and writing velocity-were discussed and optimized. A large scale crystalline wires array at several hundred nanometers induced by multi-photon absorption was observed and analyzed. The tropism of nanometer array was similar to the epitaxy technique but perpendicular to the writing path. The experiment demonstrated the flexibility and efficiency to micro-fabricated superfine and complex configurations in ceramic materials by femtosecond laser.

1 Introduction

Bismuth based niobate possesses excellent microwave properties with simple phase structures, such as rather high permittivity series ($\epsilon_r \cong 35 \sim 150$), very low dielectric

loss ($\tan\sigma \cong 10^{-4}$), very small temperature coefficient and high quality factor [1–4]. Even at terahertz frequency it still retains good characteristic [5]. In addition, it can be cofired with metal electrode. All these merits bestow it extensive potential applications, such as resonator, filter, dielectric substrate and antenna, even in field effect transistor (FET) and MEMS devices [6–10]. Then the challenges mainly occur on how to integrate it with various practical devices. Fortunately femtosecond laser has powerful capability to machining almost any materials-polymer, metal, glass and various ceramics. Due to its advantages over other machining methods, e.g. the superfine feature size, smooth finishing surface, low energy dissipation, minimum thermal effect, and flexible structuring, even inside materials, femtosecond laser has attracted more and more attentions. At present, femtosecond laser has been successfully applied to machine various polymer, metal, transparent glass and seldom ceramic materials [11–15]. However, there are still some difficulties in directly writing in high permittivity microwave ceramic materials, because the machining results greatly depend upon certain materials and its respective technical parameters.

Herein the authors investigated the femtosecond laser directly writing microholes in a high permittivity microwave ceramic material- $\text{Bi}(\text{Nb}_{0.998}\text{V}_{0.002})\text{O}_4$ for the application purpose of photonic crystals (PCs) and Micro-electromechanical System (MEMS) devices. The matrix microholes ablation technique (MMAT) was introduced based on precise computer numerical control (CNC) motion system. Different micro-fabricating parameters-output power intensity, writing velocity, writing intervals ΔR and step depth ΔZ were discussed and optimized. At certain conditions a large scale crystalline wires array at several hundred nanometers induced by multi-photon absorption was observed and analyzed. The experiments indicated that flexible femtosecond

J. Shi (✉) · H. Wang · X. Yao
Electronic Materials Research Laboratory, Key Laboratory of
Minstry of Education, Xi'an Jiaotong University,
710049 Xi'an, China
e-mail: jzhshi@mail.xidian.edu.cn

H. Wang
e-mail: hwang@mail.xjtu.edu.cn

D. Zhang · F. Chen
Key Laboratory of Photonics Technology for Information,
Xi'an Jiaotong University, 710049 Xi'an, China

J. Shi
School of Technical Physics, XIDIAN University,
710071 Xi'an, China

laser technique was hopeful to apply in practical micro-fabrication of PCs and MEMS devices with $\text{Bi}(\text{Nb}_{0.998}\text{V}_{0.002})\text{O}_4$ microwave ceramic.

2 Experiment

The schematic view of femtosecond laser experimental system was shown in Fig. 1. An amplified Ti: Sapphire system (Femtopower Compact Pro, Austria) with a pulse width of 30 fs at a fundamental wavelength 800 nm, a repetition rate of 1 kHz was employed. The maximum output power was up to 500 mW, and the pulse energy on the sample was adjusted by a neutral density (ND) attenuator. The laser beam was subsequently focused with a 5× microscope objective lens (Numerical Aperture (NA) = 0.15) into the polished $\text{Bi}(\text{Nb}_{0.998}\text{V}_{0.002})\text{O}_4$ ceramic sample which was mounted on a precise computer numerical controlled 3D translation stage, with step resolution of 50 nm and a maximum speed of 1,000 $\mu\text{m}/\text{s}$. All writing process was monitored in situ by computer through a CCD camera with 50× magnifier. And the samples were cleaned by ultrasonic cleaning in water at 40° for 30 min before and after laser processing.

The matrix microholes ablation technique (MMAT) was introduced to write microholes in ceramic sample [16, 17]. The schematic view was shown in Fig. 2. By scanning adjacent circular lines in the transverse plane, one layered microholes were obtained by femtosecond laser. The adjacent circular lines were equally distributed, with the interval ΔR . After then, the Z-axis translation stage moved upward ΔZ to process another layer. By these means, a final microhole came into being. Properly choosing the micro-fabricating parameters, including output power intensity, writing velocity, writing intervals ΔR , and step depth ΔZ , a superfine configuration can be obtained. All the

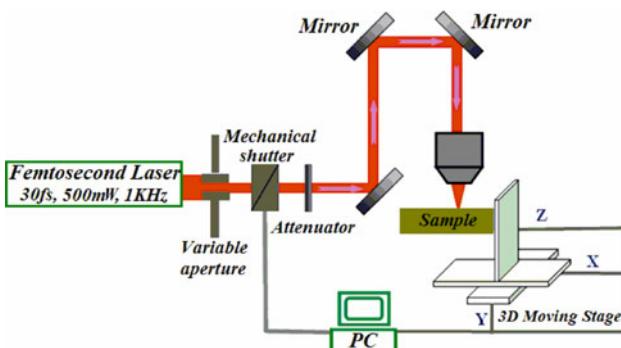


Fig. 1 Schematic view of femtosecond laser setup for directly writing in high permittivity microwave ceramics. All process was monitored in situ by computer through a CCD camera with $\times 50$ magnifier

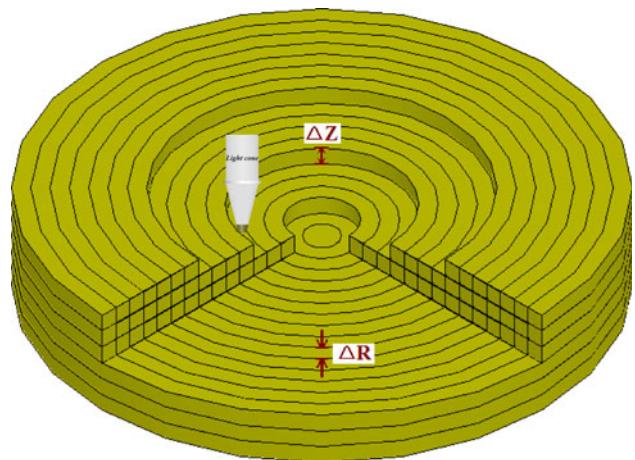


Fig. 2 Illustration of matrix microholes ablation technique (MMAT) for microholes fabrication by femtosecond laser ablation. The femtosecond laser pulse (as the *light gray cone* indicated) scans adjacent circular lines layer by layer. The interval of adjacent circular lines is ΔR . Each step depth of adjacent layers is ΔZ

fabricated samples were studied by X-ray diffraction (XRD, Rigaku D/MAX-2400, Japan), Color 3D Laser Scanning Microscope (Keyence VK-9700, Japan) and scan electron microscope (SEM, JEOL JSM-6360LV, Japan).

3 Results and discussion

The machining results and efficiency greatly depended on the corresponding technical parameters. The first issue was to determine the threshold value of output power of femtosecond laser pulse upon the ceramic sample. Due to the strong electrovalent bond among the atoms in the ceramic, the threshold value here was much larger than that needed in the polymers. Figure 3 showed the pictures machined by different output power intensity, from 30, 45, 60 to 70 mW, with the fixed writing velocity 100 $\mu\text{m}/\text{s}$ and step interval ΔR 8 μm and step depth ΔZ 20 μm . Each output power intensity of femtosecond laser had its characteristic writing depth ΔZ and writing intervals ΔR (as shown in Fig. 4). It was found that if the output power upon the sample was too low, then it was unlikely to ablate the atoms efficiently (as shown in Fig. 3a and b). On the other hand, if the output power was too high, then the peripheries of the holes would suffer from excessive cauterization (shown in Fig. 3d). This process phenomenon was much dissimilar to that in the transparent polymers by femtosecond laser [18–20]. Hence the optimal threshold value of output power from the femtosecond laser was about 60 mW. In this circumstance, the microholes in the ceramic sample could be machined efficiently without much cauterization on the surface and peripheries of the void channels. The relationship between the ablated layered

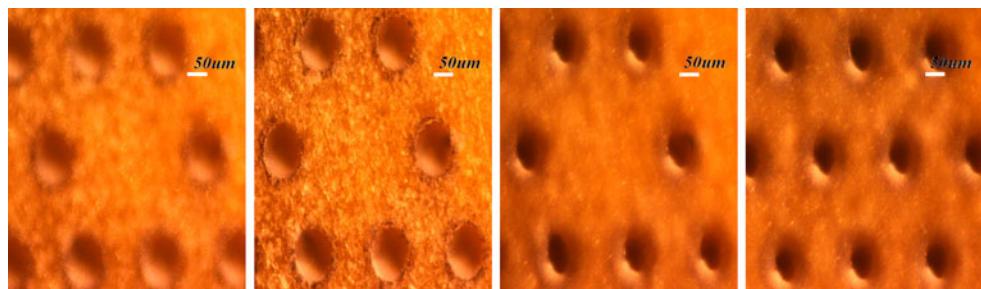


Fig. 3 Pictures of microholes machined by different output power. From left to right: 30, 45, 60, 70 mW. These photos were taken by a CCD camera with $\times 50$ magnifier in situ through the computer

depth ΔZ and single circular line width ΔR with the output power intensity of femtosecond laser was plotted in Fig. 4. Obviously the characteristic writing depth ΔZ and the

circular lines width ΔR increased along with the output power intensity increasing. By optimally adjusting the femtosecond laser pulse intensity, rigorous control of the layered depth and circular line width can be realized.

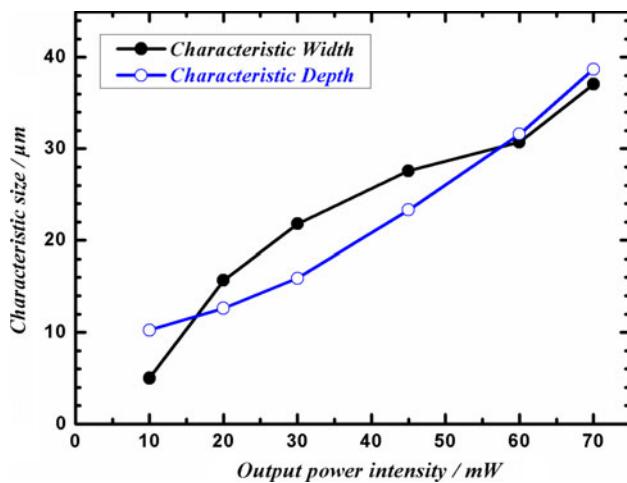


Fig. 4 The characteristic width and depth of the ablated lines with different output laser power intensity at the writing velocity $100 \mu\text{m/s}$

As shown in Fig. 5, other writing technical parameters were also studied here, including the writing interval ΔR , step depth ΔZ and writing velocity. From left to right in Fig. 5a showed the machined microholes with diameter $120 \mu\text{m}$ by MMAT, under the conditions of $\Delta Z 20 \mu\text{m}$ and the writing speed $100 \mu\text{m/s}$, but varying the writing interval ΔR from 2, 4, 8, 16 to $32 \mu\text{m}$ (just equal to the characteristic ablated width at output power intensity 60 mW , see Fig. 4), respectively. When ΔR was more than half of the characteristic ablated width, the depth of the holes was small and irregular, which indicated some materials in the microholes were not ablated completely. This phenomenon should attribute to the laser ablation spot which was indeed the cone conformation, not the cylindrical conformation (see Fig. 2). Hence when ΔR was relatively large, the upper layer materials of the juncture of adjacent circular lines were partly untreated that would hinder the ablation of the

Fig. 5 The effects of different writing parameters on the profiles of microholes in $\text{Bi}(\text{Nb}_{0.998}\text{V}_{0.002})\text{O}_4$ ceramic. The respective writing parameters are as follows: **a** (from left to right) $\Delta R = 2, 4, 8, 16$ and $32 \mu\text{m}$ with $\Delta Z = 20 \mu\text{m}$ and writing velocity of $100 \mu\text{m/s}$. **b** (from left to right) $\Delta Z = 5, 10, 15, 20$ and $25 \mu\text{m}$ with $\Delta R = 8 \mu\text{m}$ and writing velocity of $100 \mu\text{m/s}$. **c** (from left to right) writing velocity was from $100, 200, 400$ to $800 \mu\text{m/s}$, with $\Delta R = 8 \mu\text{m}$ and $\Delta Z = 15 \mu\text{m}$. The experiment was conducted by Color 3D laser scanning microscope

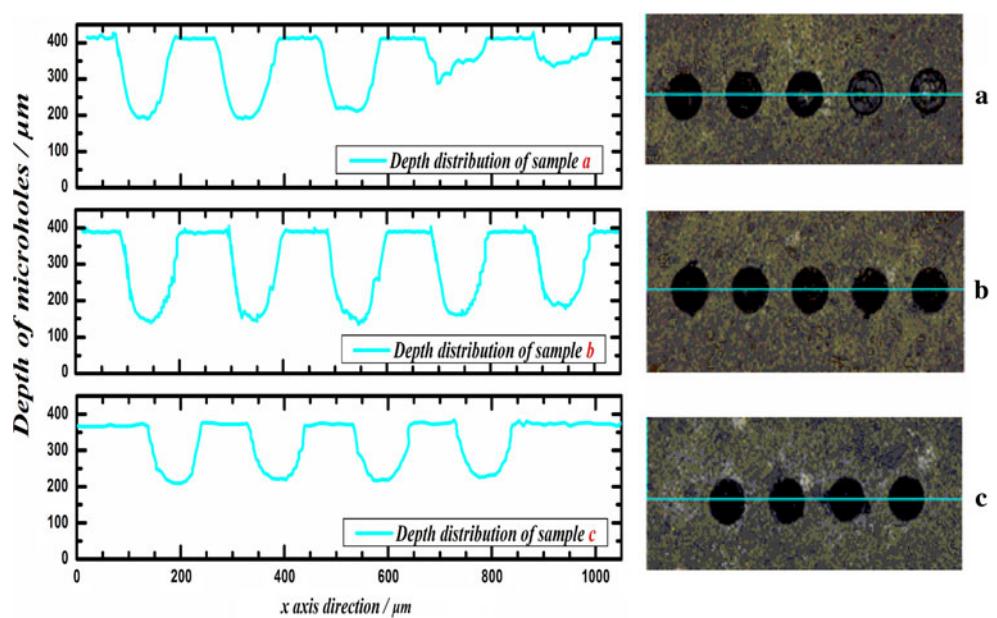
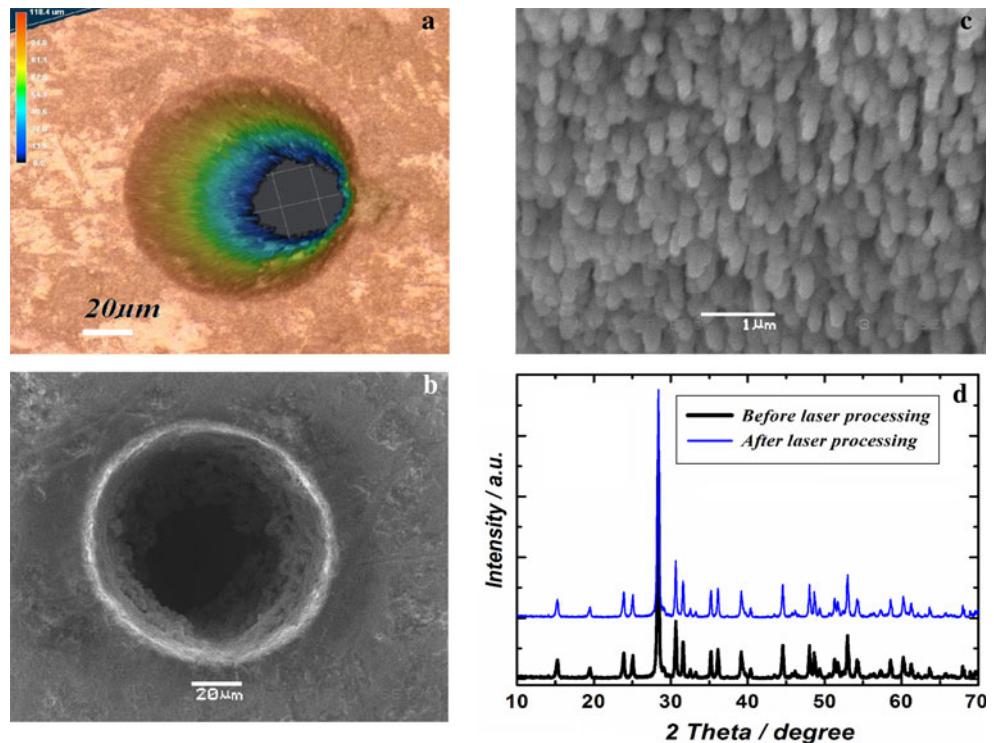


Fig. 6 Properties of machined microhole under the conditions of output power intensity 60 mW, writing interval $\Delta R = 8 \mu\text{m}$, step depth $\Delta Z = 15 \mu\text{m}$, and the writing velocity 400 $\mu\text{m}/\text{s}$. **a** 3D appearance by Color 3D laser scanning microscope; **b** SEM photo of microhole; **c** SEM photo of nanometer wires array on the wall of microhole; **d** the XRD patterns of $\text{Bi}(\text{Nb}_{0.998}\text{V}_{0.002})\text{O}_4$ before and after femtosecond laser writing



next layer. When ΔR got into smaller, the ablation efficiency of the upper layer was very high, thus caused the depth of the holes deeper and regular. However, extremely smaller ΔR was unnecessary, because it severely depressed the machining efficiency. And the depth of the holes would be consistent when ΔR reached certain value.

Similarly in Fig. 5b showed the fabricated microholes with different step depth ΔZ , from 5, 10, 15, 20 to 25 μm , respectively. Here the writing velocity was fixed on 100 $\mu\text{m}/\text{s}$ and the writing interval $\Delta R = 8 \mu\text{m}$. It can be seen when ΔZ became smaller, then the depth of microholes became deeper and regular. However, the depth would settle on a certain point with ΔZ decreasing. The phenomenon was similar to that former situation of varying the writing interval ΔR .

The microholes with fixed $\Delta R = 8 \mu\text{m}$, $\Delta Z = 15 \mu\text{m}$ but different writing velocity were also carried out, from 100, 200, 400 to 800 $\mu\text{m}/\text{s}$, respectively, as shown in Fig. 5c. It indicated that after properly choosing the output power intensity and the writing interval ΔR and step depth ΔZ , the writing velocity has rather small influence on the machined results. It was because the ablation reaction of materials by the femtosecond laser pulse was extraordinarily quick only if other polytechnic parameters were feasible. Hence during the ablation with different writing velocity, the irradiation area had received enough exposure doses to form the designed configuration. So the writing velocity can be fixed on a little higher point to improve the work efficiency in practical processing.

Figure 6 showed the photos of the superfine microhole machined by femtosecond laser pulse under the conditions of $\Delta R = 8 \mu\text{m}$, $\Delta Z = 15 \mu\text{m}$, 400 $\mu\text{m}/\text{s}$ writing velocity, and power intensity 60 mW, which were taken from Color 3D Laser Scanning Microscope and SEM. The diameter of the microhole was 90 μm . The Fig. 6a and b demonstrated that the total depth of the microhole was near 120 μm , and the superficial appearance of the sample almost was smooth, without obvious cauterization. Meanwhile it can be seen that all the wall of microhole were fully covered with numerous weensy overhangs. The amplified SEM photos in Fig. 6c indicated that the overhangs are perpendicular to the wall of microhole. Their height varies from tens nanometers to several hundred nanometers. Because the microhole was fabricated layer by layer by MMAT method, so their tropism was also perpendicular to the writing path. If it was brought about by the fabricating interspaces, then only the lowest layer can preserve the nanometer wires. Hence these large scale nanometer wires array was mainly induced by multi-photon absorption to femtosecond laser pulse, instead of fabricating method itself. The XRD patterns before and after laser writing process (as shown in Fig. 6d) was not considerably transformed. It held the same orthorhombic phase. This interesting phenomenon was very enlightened. If we combine the vertical machining with transversal induced nanometer structures, then complex 3D nanometer configurations with ceramic materials are hopeful to come into being, such as MEMS devices and 3D photonic crystals (PCs) with

microwave ceramic materials, which are very difficult with existing fabricating techniques.

4 Conclusion

In this paper femtosecond laser pulse directly writing microholes in a high permittivity microwave ceramic $\text{Bi}(\text{Nb}_{0.998}\text{V}_{0.002})\text{O}_4$ was presented. Optimal writing polytechnic parameters were determined, i.e. the output power intensity was 60 mW, with writing interval $\Delta R = 8 \mu\text{m}$, step depth $\Delta Z = 15 \mu\text{m}$, and the writing velocity 400 $\mu\text{m}/\text{s}$. A large scale nanometer wires array was discovered and analyzed. The experiment confirmed the flexibility and efficiency to fabricate superfine configuration in ceramic materials by femtosecond laser pulse. More inspiring aspects are its potential applications to micro-fabricating complex 3D nanometer configurations, such as MEMS devices and 3D photonic crystals (PCs) with microwave ceramic materials which are very difficult with existing fabricating techniques.

Acknowledgments The authors gratefully acknowledge the partial financial support for this work provided by the NSFC project of China (under the Grant No. 50572085, 60871044 and 50835007) and 973 project of China (2009CB623302) and National Project of International Science and Technology Collaboration (2009DFA51820).

References

- Q. Wang, H. Wang, X. Yao, Structure, dielectric and optical properties of $\text{Bi}_{1.5}\text{ZnNb}_{1.5-x}\text{Ta}_x\text{O}_7$ cubic pyrochlores. *J. Appl. Phys.* **101**, 104116 (2007)
- D. Zhou, H. Wang, X. Yao et al., Phase transition in BiNbO_4 ceramics. *Appl. Phys. Lett.* **90**, 172910 (2007)
- H. Wang, S. Kamba et al., Microwave dielectric relaxation in cubic bismuth based pyrochlores containing Titanium. *J. Appl. Phys.* **100**, 014105 (2006)
- H. Wang, H. Du, X. Yao, Structural study of $\text{Bi}_2\text{O}_3\text{-ZnO-Nb}_2\text{O}_5$ based pyrochlores. *Mater. Sci. Eng. B* **99**, 20–24 (2003)
- S. Kamba, H. Wang, B. Milan et al., Correlation of infrared and THz dielectric properties of antiferroelectric BiNbO_4 with microwave properties. *J. Eur. Ceram. Soc.* **26**, 2862–2865 (2006)
- W. Fu, H. Wang, L. Cao et al., $\text{Bi}_{1.5}\text{Zn}_{1.0}\text{Nb}_{1.5}\text{O}_7/\text{Mn}$ -doped $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ heterolayered thin films with enhanced tunable performance. *Appl. Phys. Lett.* **92**, 182910 (2008)
- I.D. Kim, M.H. Lim, K.T. Kang et al., Room temperature fabricated ZnO thin film transistor using high-K $\text{Bi}_{1.5}\text{Zn}_{1.0}\text{Nb}_{1.5}\text{O}_7$ gate insulator prepared by sputtering. *Appl. Phys. Lett.* **89**, 022905 (2006)
- I.D. Kim, Y.W. Choi, H.L. Tuller, Low-voltage ZnO thin-film transistors with high-K $\text{Bi}_{1.5}\text{Zn}_{1.0}\text{Nb}_{1.5}\text{O}_7$ gate insulator for transparent and flexible electronics. *Appl. Phys. Lett.* **87**, 043509 (2005)
- L. Cao, W. Fu, S. Wang et al., Effects of film thickness and preferred orientation on the dielectric properties of $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$ films. *J. Phys. D Appl. Phys.* **40**, 2906–2910 (2007)
- L. Cao, W. Fu, S. Wang et al., C-axial oriented $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$ thin film grown on Nb doped SrTiO_3 substrate by pulsed laser deposition. *J. Phys. D Appl. Phys.* **40**, 1460–1463 (2007)
- Y. Wu, W. Jia, C. Wang et al., Micro-hole fabricated inside FOTURAN glass using femtosecond laser writing and chemical etching. *Opt. Quant. Electron.* **39**, 14 (2008)
- Y. Bellouard, A. Said, M. Dugan et al., Fabrication of high-aspect ratio, micro-fluidic channels and tunnels using femtosecond laser pulses and chemical etching. *Opt. Express* **12**(10), 2120–2129 (2004)
- K. Venkatakrishnan, B.K.A. Ngai, P. Stanley et al., Laser writing techniques for photo-mask fabrication using a femtosecond Laser. *Applied Physics* **74**(4), 4932496 (2002)
- M. Deubel, G.V. Freyman, M. Wegener et al., Direct laser writing of three-dimensional photonic crystal templates for telecommunications. *Nature* **3**, 4442447 (2004)
- D.F. Farson, H.W. Choi, C.M. Lu et al., Femtosecond bulk laser micromachining of micro-fluid channels in poly(methylmethacrylate). *J. Laser Appl.* **18**(2), 2102215 (2006)
- P. Moreno, C. Mendez, A. Garcia et al., Femtosecond laser ablation of carbon reinforced polymers. *Appl. Sur. Sci.* **252**(12), 4110–4119 (2006)
- Y. Liao, J. Xu, H. Sun et al., Fabrication of microelectrodes deeply embedded in LiNbO_3 using a femtosecond laser. *Appl. Sur. Sci.* **254**(21), 7018–7021 (2008)
- E.N. Glezer, E. Mazur, Ultrafast-laser driven micro-explosions in transparent materials. *Appl. Phys. Lett.* **71**, 882–884 (1997)
- D. Day, M. Gu, Formation of voids in a doped polymethyl-methacrylate polymer. *Appl. Phys. Lett.* **80**, 2404–2406 (2002)
- M.J. Ventura, C. Bullen, M. Gu, Direct laser writing of three-dimensional photonic crystal lattices within a PbS quantum dot-doped polymer material. *Opt. Express* **15**(4), 1817–1822 (2007)